

This column addresses aspects of lifelong learning for current students, alumni, and faculty. Examples of student and faculty activities that involve industrial practice and engagement as well as continuing education are welcome. These topics may not always lend themselves to the traditional scholarly format with formal assessment and extensive literature review but may be more editorial in nature. Please submit manuscripts to Professor Lisa Bullard at lisa_bullard@ncsu.edu. A previous incarnation of the column, Learning in Industry, was edited by Professor William Koros, who oversaw the contribution below.

BATCH REACTOR KINETIC AND HEAT TRANSFER MODELING OF THE METHOCEL™ PRODUCTION PROCESS

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METHOCEL™ is a water-soluble polymer derived from cellulose with a variety of applications in many industries. A well-established product for The Dow Chemical Company (“Dow”), METHOCEL has been produced for more than 75 years and is used in manufacturing of food and pharmaceuticals, among many other areas.^[1] Production of the versatile polymers occurs at Dow locations in North America and Europe.

The polymeric backbone of cellulose reacts with reagents such as methyl chloride (MeCl) and propylene oxide (PO) to form METHOCEL variants with a vast range of properties. For example, viscosity levels can range from 3 to 200,000 mPa·s.^[1] The properties of the materials are adjusted based on the side chain properties of the cellulose polymer. Methyl cellulose is formed when MeCl reacts with the hydroxyl groups on a given glucose unit. Three hydroxyl groups are available per glucose, and the degree of substitution (DS) for a METHOCEL product is defined as the average number of hydroxyl groups that react with MeCl per glucose molecule.

The reaction of hydroxyl groups with PO can provide even more variety to the cellulosic polymers, forming five other categories of Dow products and a plethora of specific recipes. The extent to which cellulose reacts with PO is described by the molar substitution (MS), or the number of moles of hydroxypropyl groups per mole of anhydroglucose in the chain.

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Alan Murley is technology associate in the Dow Pharma & Food Solutions Technology Center at The Dow Chemical Company. Since joining Dow in 1982, he has worked on many capital projects and process optimizations for several manufacturing processes. He holds a Bachelor's degree in chemical engineering from Michigan Technological University.

Anja Puettmann is senior Process R&D engineer in Dow's Food & Pharma division with broad background in solids processing and reactor simulation. She completed her Ph.D. at the University of Technology, Hamburg-Harburg (Germany) in 2010. She developed unit operation models and applied them in the flowsheet simulation framework “SolidSim” to optimize the energy and material balance of complex fluidized-bed systems. In her current Process R&D role at Dow Chemical, Anja is involved in plant optimization and capacity creep projects and is acting as subject matter expert in several projects for the development and simulation of new solid processing units.

Dan Hickman is a fellow in the Reaction Engineering group in Core R&D at The Dow Chemical Company. Dan has been a subject matter expert and technical leader in reaction engineering and process development for numerous reaction systems across a variety of Dow businesses and technologies. In addition to holding 11 patents, Dan's contributions at Dow include designing reactors for three commercial processes, two currently in operation and a third under construction.

Paul M. Witt is the senior technical leader of the Reaction Engineering group in Core R&D at The Dow Chemical Company. Through various roles, he has supported numerous undergraduate and graduate internships supporting reaction engineering and process optimization. He also benefited from two multi-year internships while an undergraduate student at Iowa State University.

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While the reaction of MeCl with a hydroxyl group effectively caps the side chain, preventing further reactions, multiple reactions with PO can occur on the same side chain. Figure 1 shows the types of METHOCEL products and the sites for reaction.

Producing METHOCEL with the desired DS and MS is heavily dependent on the feed rates, reaction time, and temperature profile of a reactor system. As a well-established process in Dow, working METHOCEL recipes exist that meet consumer requirements. However, there is recognized potential for process and product optimization in this area utilizing modeling techniques in established software such as Aspen Custom Modeler® (ACM). A model with accessible data input through Microsoft Excel® that accurately predicts DS and MS (molar substitution) would provide ample opportunity to improve product properties, reduce cycle time, optimize feed inputs, improve process economics, and safely test new METHOCEL recipes. The scope of this internship project begins with the conversion of existing kinetic models into ACM. After integrating this model with Microsoft Excel, kinetics and heat transfer predictions will be validated with plant data and the potential for optimization is demonstrated with a specific METHOCEL recipe.

The internship was presented to the student as an opportunity to incorporate a variety of chemical engineering concepts into one centralized project. Reaction kinetics, dynamic simulation, control principles, optimization, economic analysis, and statistics would all be required to properly implement and analyze a METHOCEL production model. Beyond this, a high level of comfort with a variety of chemical engineering software types would be necessary; the student had never used Aspen Custom Modeler before the internship, and the student was required to quickly adapt to the software. Exposure to controls simulation software, reactor modeling with POLYMATH, and Aspen Plus at Michigan State University (MSU) prepared the student for a smooth, swift adjustment to the new software tools available at Dow.

ASPEN CUSTOM MODELER AND MICROSOFT EXCEL INTEGRATION

Aspen Custom Modeler is a valuable modeling tool in the AspenTech suite of process simulation software. With the ability to execute dynamic simulations using equation-

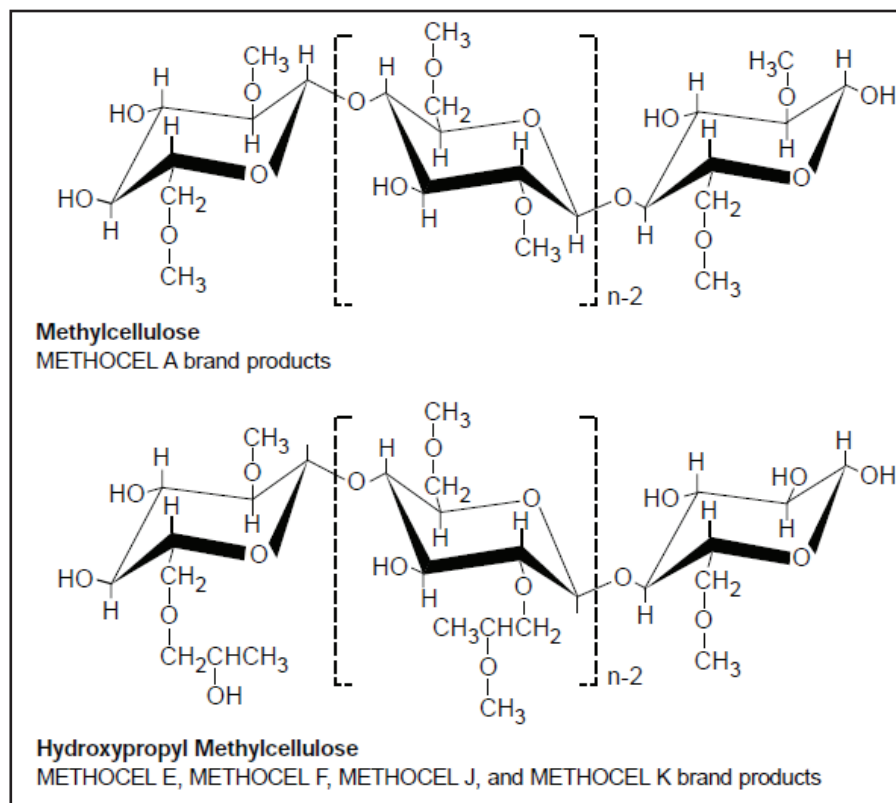


Figure 1. Chemical structures of methylcellulose and hydroxypropyl methylcellulose.

oriented modeling, ACM provided the platform for simulating a METHOCEL batch reactor. Kinetic data from Dow internal research was previously placed into ACM, and the program was designed such that a temperature profile and two feed stages for five reagents were available for user input. Initially, a user-programmed control scheme was also implemented.

During the project, the ACM model functionality was expanded to allow the input of four feed stages, a variety of cellulose loads and reactor properties such as volume, heat transfer coefficients, cooling water rates, etc. The final ACM flowsheet for the METHOCEL model is shown in Figure 2. Five feed streams, each representing one major feedstock component, enter the batch reactor. The times and flow rates of the feeds, provided by the user, are used to switch the streams on and off. The previously programmed control scheme was updated with a built-in ACM PID controller to simulate temperature control around the desired profile.

To make the model more accessible for those who are not familiar with ACM, a user interface was developed in Microsoft Excel to execute the model. Thus, a user can input data in a familiar environment, and execute the model with instantaneous feedback involving temperature, pressure, and product DS/MS. Upon completion of the simulation, all relevant data are also automatically extracted into the spreadsheet

to provide plots of reactor performance. Excel VBA Macros were utilized to input the data, execute the desired ACM model, and retrieve results. The basics for linking ACM

with Microsoft Excel are found in AspenTech's user guides for ACM. A screenshot of this Microsoft Excel interface is shown in Figure 3.

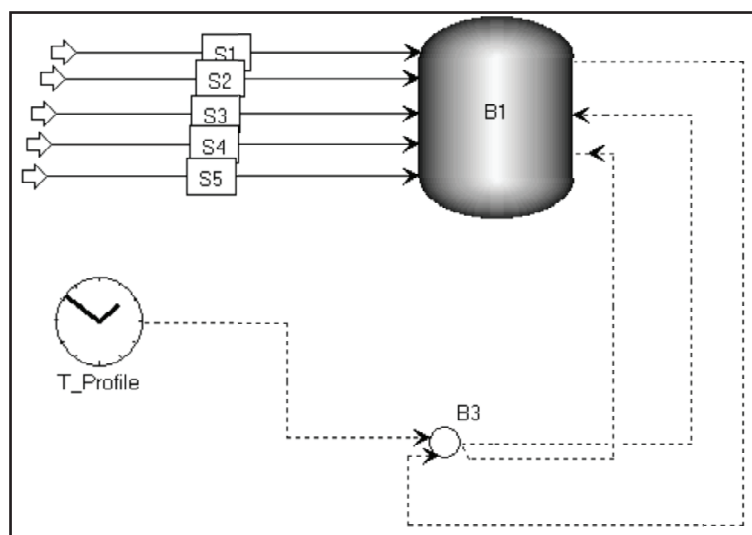


Figure 2. ACM flowsheet of METHOCEL batch reactor.

The linking of the Microsoft Excel spreadsheet with ACM was a unique part of the internship and added immense utility to the tool but would not have been possible for the student in a three-month internship without a variety of factors. First, the student had been able to take computer science courses outside of his major at MSU, developing a skillset that is becoming increasingly useful and important for chemical engineers, especially those with interest in computational research. Such skills are often undervalued or underdeveloped inside the chemical engineering major. Beyond this, the student had access to multiple subject matter experts inside of Dow who had utilized similar VBA functionalities and who were well-acquainted with the Aspen suite of software. By the end of the internship, the student was even included in monthly seminars inside of Dow for those working with Aspen on a regular basis, a unique opportunity that many undergraduates will never receive.

Feed		S1	S2	S3	S4	S5
Step 1	Start Time, min	X	X	X	X	X
	End Time, min	X	X	X	X	X
Feed Basis Flow	Mass Load Ratio (kg / kg °C)	X	X	X	X	X
	Molar Load Ratio (mol / mol °C)	X	X	X	X	X
	Flow, kg/s	X	X	X	X	X
	T, °C	X	X	X	X	X
Step 2	Start Time, min	X	X	X	X	X
	End Time, min	X	X	X	X	X
Feed Basis Mass Load Ratio	Mass Load Ratio (kg / kg °C)	X	X	X	X	X
	Molar Load Ratio (mol / mol °C)	X	X	X	X	X
	Flow, kg/s	X	X	X	X	X
		X	X	X	X	X
Step 3	Start Time, min	X	X	X	X	X
	End Time, min	X	X	X	X	X
Feed Basis Mass Load Ratio	Mass Load Ratio (kg / kg °C)	X	X	X	X	X
	Molar Load Ratio (mol / mol °C)	X	X	X	X	X
	Flow, kg/s	X	X	X	X	X
		X	X	X	X	X
Step 4	Start Time, min	X	X	X	X	X
	End Time, min	X	X	X	X	X
Feed Basis Mass Load Ratio	Mass Load Ratio (kg / kg °C)	X	X	X	X	X
	Molar Load Ratio (mol / mol °C)	X	X	X	X	X
	Flow, kg/s	X	X	X	X	X

Figure 3. Microsoft Excel user interface for ACM-based METHOCEL model (user enters desired values to replace "x" entries).

MASS BALANCE

For the mass balance, the ordinary differential equation for the change in moles of each component due to reactions and the inlet streams was calculated as follows, assuming a well-mixed reactor with no concentration gradients:

$$\frac{dM(i)}{dt} = \sum_j \frac{F_{in,j}}{MW_j} X_{m,j,i} + V_{liq} \sum_j v_{i,j} r_j \quad (1)$$

$dM(i)/dt$ = change per time in moles component i , kmol/s

$F_{in,j}$ = mass flow into the reactor of stream j , kg/s

MW_j = molecular weight of stream j , kg/kmol

$X_{m,j,i}$ = liquid mole fraction of component i in feed stream j

$v_{i,j}$ = stoichiometric coefficient of component i in reaction j

V_{liq} = liquid volume calculated from total moles and density, m^3

r_j = reaction rate, $kmol/m^3/s$

Below is a sample rate expression:

$$r_i = r_{emp,i} k c_i^\alpha \quad (2)$$

$r_{emp,i}$ = empirical reaction rate function, $kmol/m^3/s$

k = reaction rate constant

c_i = concentration of component i in the liquid volume, $kmol/m^3$

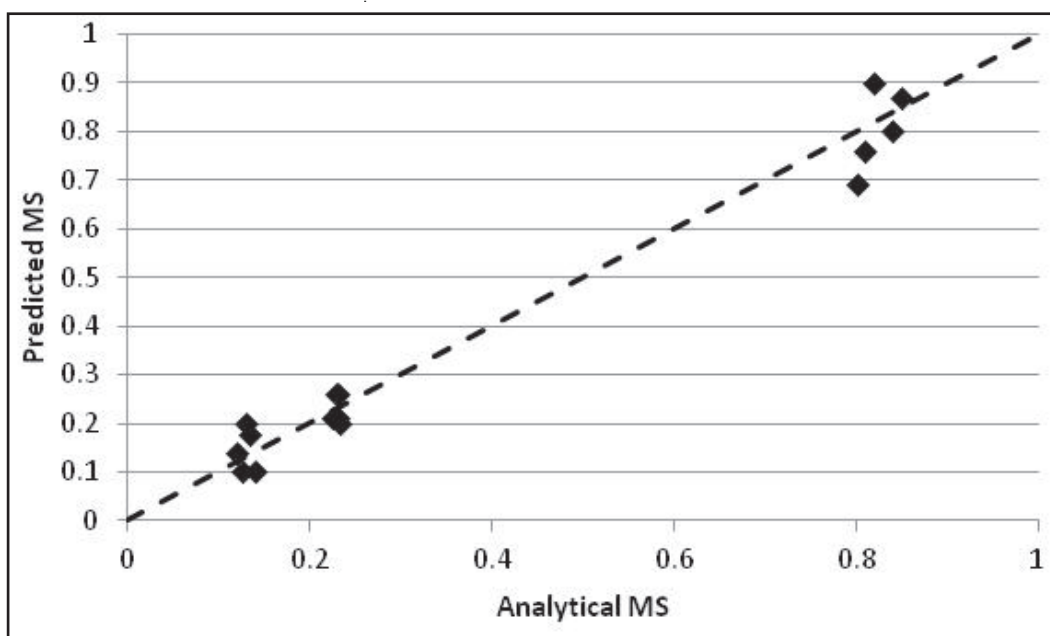
α = reaction component order

KINETIC MODELING

The final METHOCEL™ model constructed in ACM contained more than 30 possible reactions. The kinetics of each reaction were implemented utilizing an Arrhenius equation approach following Eq. (3).

$$k = A e^{-\frac{E_a}{RT}} \quad (3)$$

Figure 4. Hypothetical plot of predicted molar substitution values from the ACM model against the actual molar substitution values from plant trials in Midland, MI. The diamonds representing plant validation trial should theoretically fall on the dashed $y=x$ line if the model was predicting MS concentration with perfect accuracy.



Values for the pre-exponential factor A , and activation energy E_a were calculated experimentally through previous analysis of a pilot plant METHOCEL process.^[2] Utilizing the known stoichiometries of METHOCEL reactions and the reaction rates provided from Eq. (3), the kinetics were fully implemented in the model for the plant reactor.

Multiple recipes of METHOCEL from three different product brands were used to validate the empirical kinetic model. Plant data were extracted from the Midland, MI, plant, including the temperature profile of the reactor, the initial loads and feed stages of reactants, and general reactor characteristics. Using this plant data, predictions of the DS and MS for each batch were calculated in ACM and exported into Microsoft Excel.

The results immediately indicated that the DS is accurately predicted within a reasonable percent error for each METHOCEL product and recipe tested. Thus, the kinetic parameters used for reactions involving MeCl reacting with cellulose did not require any updating from the previous batch trial data. However, the results from the plant validations required improvement in batches that required MS predictions, indicating an invalid kinetic parameter for a PO reaction.

Plotting the values of predicted MS from the model and calculated MS from analytical chemistry should theoretically yield a profile falling on $y=x$. An example of such a plot is demonstrated in Figure 4, with hypothetical data representing how batch validation trials could appear. In reality, unlike in Figure 4, a systematic under-estimation of MS for PO-based METHOCEL recipes was discovered based on the plant trials. By reviewing the reactions included in the model, a specific pre-exponential factor for a PO reaction with cellulose was identified that had a key influence on the predicted MS of the product with minimal impact on the final DS values.

A sensitivity analysis was conducted on the value of the pre-exponential factor to identify if changing this value could universally improve the accuracy of the model for all batches that involve PO reactions. The goal of the sensitivity analysis is to minimize the total residuals from the predicted and calculated MS values so that the model can be utilized across all METHOCEL product types and recipes. The analysis initially analyzed 25 different plant batches from five different recipes and three product types in order to find an ideal value of the pre-exponential factor. After this initial analysis, the new pre-exponential factor was tested again with 25 new batch trials. The sensitivity analysis yielded an improved kinetic model that predicted MS and DS within an acceptable percent error range across all recipes.

HEAT TRANSFER MODEL

In the model, the energy balance (shown as a conceptual diagram in Figure 5) is calculated as follows:

$$dU_{\text{tot}} = \sum F_{\text{in},j} + Q_r + Q + Q_s \quad (4)$$

dU_{tot} = change in total energy in the system, kW

$F_{\text{in},j}$ = mass flow into the reactor, kg/s

$H_{\text{in},j}$ = specific enthalpy of feed stream j , kJ/kg

Q_r = heat released by all reactions, kW

Q = heat transfer, kW

Q_s = heat added by agitator shaft work, kW

The reaction heat is calculated as follows, assuming a well-mixed reactor with no temperature gradient in the reaction mixture:

$$Q_r = V_{\text{liq}} \sum \Delta H_{r,j} r_j \quad (5)$$

$\Delta H_{r,j}$ = heat of reaction j , kJ/mol

r_j = reaction rate, mol/m³/s

V_{liq} = liquid volume calculated from total moles and density, m³

The reactor is heated or cooled via the reactor jacket and cooled via a heat exchanger:

$$Q = Q_{\text{jacket}} + Q_{\text{cond}} \quad (6)$$

Q_{jacket} = heat transfer from jacket, kW

Q_{cond} = heat loss from heat exchanger, kW

The energy removed via the jacket is calculated using the following relationship:

$$Q_{\text{jacket}} = k_{\text{jr}} A_{\text{jacket}} (T_{\text{jacket}} - T_{\text{out}}) \quad (7)$$

k_{jr} = heat transfer coefficient of liquid to jacket, kW/m²K

A_{jacket} = jacket area, m²

T_{jacket} = temperature of jacket, °C

T_{out} = temperature inside the reactor, °C

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The energy accumulated in the jacket is the difference between the energy removed from the jacket by heat transfer to the cooling water and the energy transferred from the reactor:

$$c_{\text{p,jacket}} m_{\text{jacket}} \Delta T_{\text{jacket}} = k_{\text{cwj}} A_{\text{jacket}} (T_{\text{kwj}} - T_{\text{jacket}}) - Q_{\text{jacket}} \quad (8)$$

$c_{\text{p,jacket}}$ = heat capacity of jacket, kJ/kg/K

m_{jacket} = mass of jacket, kg

k_{cwj} = heat transfer coefficient of jacket, kW/m²K

T_{kwj} = jacket controller temperature, °C

The energy that is transferred from the jacket equals the energy change in the cooling water:

$$k_{\text{cwj}} A_{\text{jacket}} (T_{\text{jacket}} - T_{\text{kwj}}) = F_{\text{jacket}} c_{\text{pcw}} (T_{\text{jout}} - T_{\text{kwj}}) \quad (9)$$

T_{jout} = jacket cooling outlet water temperature, °C

c_{pcw} = cooling water heat capacity, kJ/kg/K

A heat transfer model with reasonable accuracy is useful for investigating the safety and feasibility of new recipe implementation in plant settings. The METHOCEL reactor modeled in ACM utilizes cooling water in order to maintain the desired temperature profile. Cooling water and steam flow rates to the reactor are regulated by a control scheme, although various control methodologies are implemented based on Dow location. Thus, the model was designed with “if-then” blocks of code to execute different heat transfer models based on the user’s preferred control scheme.

The heats of reaction for the METHOCEL recipes were implemented from previous experimental data, and were used to calculate the adiabatic temperature rise in the reactor along with the amount of cooling water necessary. The dynamic nature of the batch reactor and control scheme prevented the use of a basic log-mean temperature difference expression of heat transfer to a jacket. Thus, the heat transfer was modeled using a heat transfer balance on the reactor wall and cooling water jacket. This required the approximation of either film heat transfer coefficients and thermal conductivities or an overall heat transfer coefficient. This choice was presented to the user in the Excel interface. Implementation of the heat transfer model enabled reasonable matching to plant data.

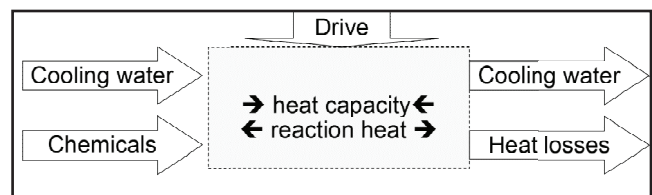


Figure 5. Heat transfer model taking into account all inlet and outlet streams (including steam and cooling water), heat losses to the environment, phase changes, the agitator’s dissipated energy, and temperature changes in the reactor mass.

STUDENT INTERACTIONS FOR MODEL VALIDATION

The implementation and validation of the METHOCEL model required close collaboration with a variety of subject matter experts within Dow. Multiple perspectives were required due to the number of production locations and the variety of METHOCEL products. To ensure the student was meeting expectations regarding model development, biweekly conference calls were scheduled with representatives from North American and European plants. The student was able to summarize results and gain feedback on the model developments, demonstrating the clear need for written and verbal communication skills to be developed during undergraduate educations. This was reiterated during his two internal Dow seminars to subject matter experts in the METHOCEL community and in the Reaction Engineering group of Core R&D.

As the model was directly validated with data in Midland, MI, the student interacted directly with a plant operator as well as a METHOCEL engineer to acquire the data and to understand the systems in place in Midland. In particular, these interactions gave valuable insights into why the model deviated at times from plant operation, specifically in terms of the heat transfer expectations. As some curriculums move away from requiring a course on control principles for chemical engineers, these concepts were crucial for the student's understanding of the control scheme for the METHOCEL reactor and for choosing the control scheme in ACM.

The validation of the model highlights the importance of process simulation instruction in chemical engineering education. The model simply could not be constructed without tools such as Aspen or Microsoft Excel, and the student's experience with this software was crucial for the overall internship. Importantly, instruction should be careful to emphasize what is really occurring beneath the user interface for chemical engineering software; if Aspen or similar software is presented as simply a black box simulation, students will be lacking in their ability to troubleshoot real models or solve problems effectively with these tools. For this particular internship, without a fundamental understanding of reaction kinetics, heat transfer, and control systems, the student would not have been able to accurately represent the METHOCEL process.

His background with computer science and with Aspen was extremely helpful, but the chemical engineering principles should remain at the center of effective modeling instruction.

BATCH OPTIMIZATION CASE STUDY

The true utility of the METHOCEL ACM model exists in the potential to optimize the cycle times and product yields of the METHOCEL process. This was demonstrated with a case study involving a specific METHOCEL product recipe. The specific recipe tested required a two-stage feeding process, with two separate temperature ramps during the process and a

considerable time of cooling between each stage. The process had not previously been optimized before the creation of the ACM model and Excel interface.

Many possible parameters could be considered for an objective function in the optimization of a METHOCEL recipe, including the reduction of cycle time or the maximization of product yield. Beyond this, many factors can be considered during the optimization, ranging from the temperature profile to product feed rates. For this specific case study, the temperature profile of the recipe was analyzed to minimize the cycle time of the reactor. The optimization was constrained with the required values of molar substitution and degree of substitution, to ensure that product characteristics would not change. The cooling water and heats of reaction for the process were also key factors in determining feasibility of new recipes.

A generic temperature profile for the recipe was constructed by averaging the temperature profiles for multiple batch trials from the Midland plant. This profile was used as a base case for the optimization process, and initial values of the DS and MS were then calculated as a comparison for all further runs. The ACM model was then utilized to test profiles with shorter cooling times in between stages, along with faster temperature ramping in the stages.

Optimization of the process demonstrated that the cycle time of a batch could be reduced considerably simply by changing the temperature profile sent to the controller of the reactor, with minimal change in the final DS and MS of the product. The results also demonstrated that this cycle time reduction could be tested in a sequence of steps in the plant; that is, acceptable temperature profiles that would eliminate 10 minutes, 20 minutes, etc., were provided. This would allow plant trials to occur in such a way as to ensure product quality was not hampered by changes in temperature profile. If the fully optimized recipe is realized in plant operation, the optimization would noticeably improve the net present value of the METHOCEL process.

The optimization case study performed during this evaluation was a very simple, "hand-optimization" case in which the user of the model made intuitive changes in the temperature profile that would lead to a reduction of cycle time. The Excel interface and ACM model provide opportunities for such optimization across all METHOCEL recipes and batch types. However, a more robust and impactful optimization process could be conducted if a similar model was developed in software such as GAMS. Future work in this area should certainly involve investigation of this potential.

CONCLUSIONS

This summer internship project at Dow provided useful experience in equation-oriented modeling while demonstrating the technical feasibility and benefits of simulating plant processes. The investigation required knowledge from a variety of core

chemical engineering principles, involving reaction kinetics, transport, and process control. METHOCEL production was accurately modeled using Aspen Custom Modeler and linked with Microsoft Excel to provide users with the ability to easily input run specifications. Empirically derived kinetics and heat transfer models were validated using real plant data within reasonable levels of accuracy. The utility of the model was then demonstrated through batch optimization trials, demonstrating clear value from plant economics analysis. The work resulted in two internal seminars and an internal publication for the student.

ACKNOWLEDGMENTS

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