Optimization of Polymerization Reactor

Objective: To maximize polymer molecular weight by optimizing reactor operation

In this example, we optimize the operating variables of a batch polymerization reactor. In particular, we will analyze the impact of the pressure profile and the ratio of alcohol to acid monomer on the growth of the polymer chain. You may download the rex zipped file to follow this example. We will use the kinetic model developed in this previous example for the optimization case studies.

Features Illustrated
- Simulations in Optimization Mode
- Enabling Control Profiles in Optimization mode
- Setting a profile for Pressure Controller Setpoint

Model Description and Analysis

In this example for condensation polymerization, the reaction takes place in the liquid phase of a liquid-gas batch reactor. Acid and Alcohol monomers react to create an ester polymer whose molecular weight increases with time. (Please see the previous example on the kinetic estimation of this system to get a better understanding of the chemistry.)

The esterification releases water as byproduct. As the water is formed, part of it goes to the gas phase, thus increasing pressure. The pressure is then controlled by opening a gas outflow valve that removes water. Removal of water helps to reduce the hydrolysis reactions which break the polymer chain into smaller fragments.

Reducing the pressure setpoint opens the outflow more facilitating water removal and thus promoting esterification (chain growth) and reducing reverse hydrolysis (chain scission). Ideally, one would want to run at the lowest pressure setpoint to evacuate water and grow the polymer chain. However, in reality, the monomer alcohol is also volatile. Monomer concentration is highest at the beginning, so if we reduce the pressure too early in the batch reactor, we may lose some of the alcohol monomer along with water, which is undesirable. If we wait for monomer alcohol to be consumed and then reduce the pressure, monomer loss may be mitigated. The question then becomes: How long should we wait to reduce the pressure? In the example below, we consider different pressure profiles and evaluate their impact on the molecular weight growth.

The second question is: What is the optimal alcohol excess? For a single phase system where the objective is to get the largest polymer chain, the optimal alcohol to acid ratio would be 1:1. This allows every acid functional group to find a pairing alcohol group to join with and grow the chain. However, in the case where the alcohol is volatile, some alcohol is lost in the gas phase and therefore excess alcohol must be provided in order to consume the terminal acid functional groups in the liquid phase. We would like to determine this optimal excess in this project.
Working in Optimization Mode

In order to answer the questions above, we need to know the reaction kinetics which were determined from experimental data as shown in this example. We start with this example and change the project from Estimation to Optimization mode, so that we can optimize the operating conditions to maximize a chosen objective. The Optimization mode can be enabled in either the main Projects node or by right clicking on the Project Name node and then selecting Mode → Change to Optimization.

We would like to enforce a time dependent profile for variables like Temperature and Pressure Setpoint. To enable this feature, we right click on the Optimization node and select the Enable Control Profiles option. The REX zipped file provided here already has everything set up, so you don't need to execute the above actions. The project has the same specifications in the Reactor node that the estimation example: multiphase liquid gas reactor with pressure controlled with an outflow stream. The same Pseudo-compounds and Derived quantities are defined to allow the average molecular weight calculation.

We simulate different operating conditions to see the impact on the average molecular weight of polymer. We set the objective function to be $M_n$, the average molecular weight of polymer. Note that since we are only doing simulations, we do not actually need to define an objective function, which is needed only for running optimization cases. The only advantage here is that REX will report the $M_n$ value for every simulation. In the Objective node, we set the objective function weight for $M_n$ to be one, keeping all other weights to the default zero value:

In the Case Design node, we define the cases to be run. We will first explore two cases, namely C1-T2-P1-Fast and C1-T2-P1 which denote the fast pressure reduction and slow pressure reduction cases respectively. The reactor variables and initial load are specified in Design Values node:
Initial charge of alcohol monomer HO-B-OH is 0.6 gmol, so the initial alcohol hydroxyl (-OH) available is 1.2 gmol. T-A-COOH (1.2 gmol in the above picture) represents the acid groups. At the initial point, it corresponds to -COOH moles in the acid monomer. Thus, we have equal amount of acid and alcohol.

We enforce profiles for Temperature and Pressure along the reaction time. That is done by selecting Specify Profile for those variables in the Case Design→Control Profiles node:
Bounds and values defined in Design Values are overridden for the variables selected in the Control Profiles node.

In both Cases, we will have temperature starting at 180°C and increasing linearly to 220°C in half an hour and then remaining constant. Regarding pressure, we will start at 1 atm and end at 0.05 atm in both cases, but the pressure profile will be different as shown below:

In the first case indicated in red in the above chart, the pressure setpoint is set to decrease from the start of reaction. In the second, pressure is kept constant for one hour and then starts decreasing; the profile is similar to the first case but delayed by one hour.

Now we set those profiles in the Control Profile tree. You may enter as many datapoints as needed for each case:
Finally, in Run→Solution Options node we select Design Values = Simulate Only to enable the simulation of cases.

Results and Further Analysis
After running the project, the results of the simulation are available in the Optimization→Results tree. In the Results→Profiles node we can chart the model variables. The molecular weight and pressure for the two cases studied are shown below:

The molecular weight trends are interesting. $M_n$ grows faster with faster pressure reduction, because more water is removed. However, that operating procedure causes the loss of alcohol monomer that ultimately results in an imbalance between acid and alcohol terminal groups in the polymer. After about 3.5 hours, there are several terminal acid groups in the reaction mixture that cannot react with alcohol because of the loss of alcohol in the outflow due to aggressive pressure reduction. With delayed pressure reduction, the monomer alcohol has a chance to react to create non-volatile oligomer. When pressure reduction is done after 1 hour, there is less monomer and therefore loss of monomer alcohol to the gas outflow is reduced. The terminal acids in the reaction mixture still have
pairing terminal alcohols to react and grow the chain. At the operation endtime, molecular weight is 1866, 15% higher for the operation with deferred pressure decrease. One can therefore choose the optimal pressure profile depending on constraints on the residence time and the other reaction variables.

The second question we look at is the optimal alcohol to acid ratio. If we increase the initial alcohol-to-acid monomer ratio, we can compensate for the alcohol lost in the gas outflow. In this study, we simulate the reactor operation with the delayed pressure profile but with different reactant feed ratio. To do this, please go back to the Case Design node, un INCLUDE the first case and INCLUDE all the others. The alcohol to acid ratio is changed by perturbing the initial load of acid (T-A-COOH) in the Initial Charge tab of the Design Values Node:

After running the model, we can see the final molecular weights in the Optimization → Results Node. Shown below is a plot of the average molecular weight at end time vs alcohol to acid ratio at the start of the reaction:
Maximum polymer molecular weight of 2083 is achieved at alcohol-to-acid load ratio of 1.09. Higher ratios than 1.09 reduces molecular weight as there is more alcohol terminal groups that cannot grow because of lack of corresponding acid. Similarly, lower alcohol to acid ratios produce an excess of terminal acid groups that cannot grow due to lack of alcohol. If the alcohol monomer were non volatile, the optimal load ratio would always be one.

Further Analysis
You can verify that the optimal alcohol to acid ratio is 1 when alcohol is not volatile. You must assign HO-B-OH to be only available in liquid phase in the Phase Distribution node, and then rerun the cases. You may also change the project from simulation to automated optimization and find the optimal alcohol to acid ratio under different conditions by setting bounds on the HO-B-OH initial moles and fixing the initial acid load. To enable automated optimization, go to the Run→Solution Options node and select Design Values = Optimize and provide appropriate bounds for the design variables you wish to optimize.