Top Questions About Polymer Process Modeling in Aspen Plus®

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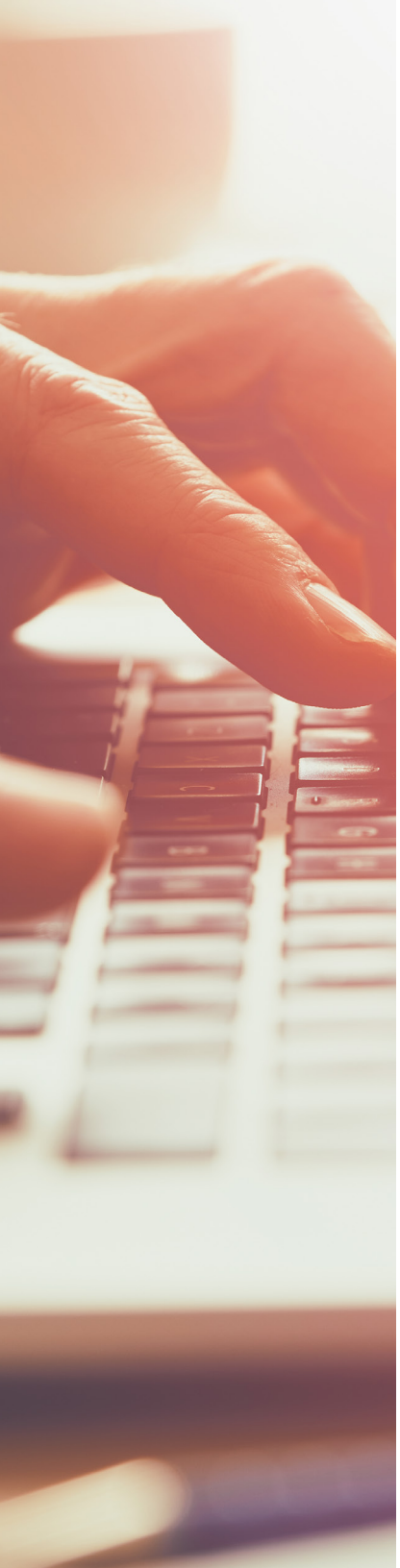


During a recent webinar "**Accelerate Innovation and Improve Sustainability Through Polymer Process Modeling**," several technical questions were asked that could be relevant to you and your own usage of Aspen Plus. AspenTech experts have provided detailed, insightful answers below to help you get the most value from your process simulation tools including tips and tricks that you can use immediately to reduce batch cycle times and improve overall product quality.

Q: After simulating a polymer reactor, how do you get the MI and density of produced polymer in Aspen Plus?

A: "Melt Index," also known as "Melt Flow Index," "Melt Flow Rate," "MI," and "MFI" is a measure of the ease with which polymer flows through a narrow channel under well-defined conditions defined by standards such as ASTM D1238 and ISO 1113. It is measured in terms of grams/10-minute interval. The Melt Index is influenced by the viscosity of the polymer, which in turn depends on the weight-average molecular weight, polydispersity, copolymer composition and long- and short-chain branching content. Since polymer viscosity is also a function of the force applied, the MFI test specifies specific capillary diameter, length and applied force (see: **http://www.campoly.com/blog/correlating-melt-flow-index-molecular-weight/** for a simple description of the procedure to measure MI). There is no universal equation for MI.

Instead, the MI is typically related to fundamental properties through empirical correlations. For homopolymers like HDPE or PP, the MI can be calculated from a power-law function such as:

$$MI = aM_w^b \times PDI_c \times FLCB_d$$

Where:

MI = Melt Index
Mw = Weight-Average molecular weight
PDI = Polydispersity Index
FLCB = Long-chain branching frequency (long-chain branch/1000 repeat units)
Parameters "a", "b", "c" and "d" are empirically fit against data for various grades

The author has applied this equation form to various grades of LDPE achieving 95% correlation coefficient from the first term alone. The additional terms improve the correlation to 98% correlation coefficient, indicating the weight-average molecular weight is by far the dominate feature influencing the melt index.

Sinclair (1983) suggests using $a = 3.354 \times 10^{16}$, $b = -3.472$ for HDPE from Chromium catalyst. The Polypropylene Handbook (2005) suggests the following correlation for homopolymer grade PP:

$$MFR = \left(\frac{10(5.7243 - \log_{10}(M_w)}{0.2773} \right)$$

Polymer density is a function of polymer structure, composition and temperature. Aspen Polymers includes calculation methods to evaluate the density of crystalline, amorphous, semi-crystalline or melt polymers.

The built-in methods account for copolymer composition, temperature and crystallinity, but the crystalline fraction must be specified by the user through property parameter POLCRY (weight fraction crystallinity). When used as a key performance indicator, the polymer density usually refers to the density of polymer pellets at 25 deg C and atmospheric pressure. In this case, the most important contributing factors to density are the copolymer composition (segment fractions) and the branching content (especially short-chain branching). These properties influence the crystallinity by making the molecular structure of the polymer less regular (crystallinity, and hence the density, is expected to decrease with higher copolymer content and higher branching). Further, the nature of the copolymer content is also important– blocky copolymers exhibit higher density than random copolymers with the same average copolymer content. These observations imply that product density can be correlated against dyad fractions (which in turn can be directly predicted by Aspen Polymers). Typically, in our consulting projects we have used simple linear correlations such as:

$$density = a(1 + b \times wx + c \times FSCB)$$

Where

x = weight fraction of comonomer "x,"
FSCB = short chain branching frequency,
and "a," "b," and "c" are empirical parameters fit against data.

Aspen Polymers directly predicts the number and weight-average molecular weight, polydispersity, long and short-chain branching frequencies, and dyad concentrations. These predictions are stored as component attributes of the polymer component. These primary properties can be accessed in calculator blocks, sensitivity blocks, etc. through the "COMP-ATTR" variables in the DEFINE forms. The component attribute array is also part of the stream structure of Aspen Plus and is available in the context of any of the user models which reference streams.

There are two common ways to include these types of empirical correlations inside Aspen Plus models:

1. Use DEFINE statements to reference primary properties of a stream, and then enter the correlation to calculate empirical end-use properties in the context of CALCULATOR blocks (or DESIGN-SPEC, SENSIVITITY, or other features that use DEFINE forms;

2. Use the "User Prop-Set Property" feature of Aspen Plus to add these correlations to Aspen Plus as property sets.

Option (2) is preferred as a it allows users to reference KPIs such as melt flow index in the context of unit operation reports, stream reports and as PROP-SET variables in any DEFINE statement. However, this option requires a supported FORTRAN compiler to compile and link any user routines you develop.

Aspen Plus includes user prop-set property subroutine examples for HDPE and PP. The HDPE examples can be found here: C:\Program Files (x86)\AspenTech \Aspen Plus V10.0\GUI\Examples \Polymers\Polyethylene\USRPRP.F

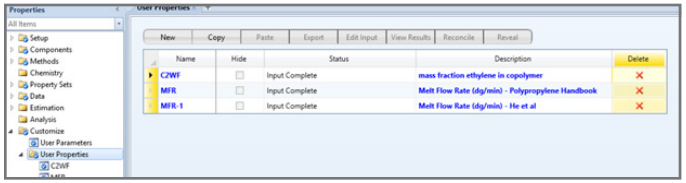
C:\Program Files\AspenTech\Aspen Plus V11.0\GUI\Examples\Polymers \Polyethylene\USRPRP.F

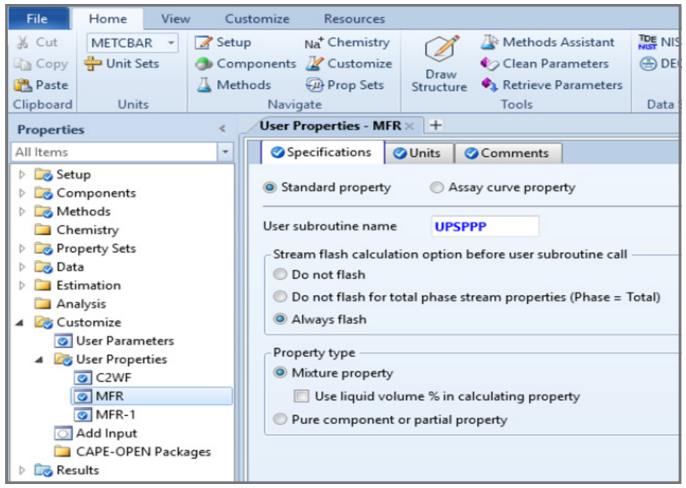
The PP user properties are referenced in the Spheripol example model, and can be found here: C:\Program Files (x86)\AspenTech \Aspen Plus V11.0\GUI\Examples \Polymers\Polypropylene\USRPRP.F

C:\Program Files\AspenTech\Aspen Plus V11.0\GUI\Examples\Polymers \Polypropylene\USRPRP.F

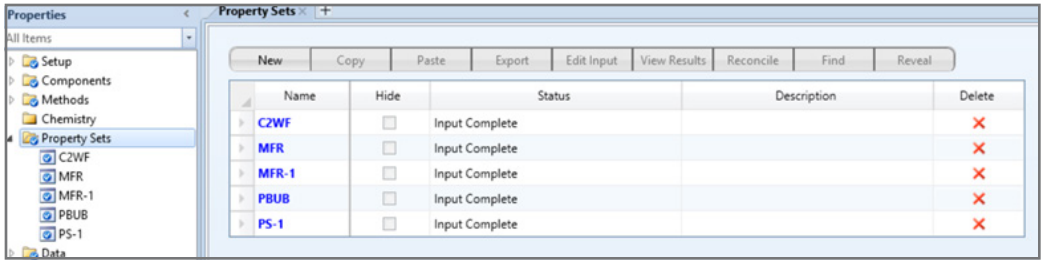
User prop-set properties are declared in the physical property environment, under "Customize," "User Properties" as shown below. The first form shows the User Properties Object Manager. Use this form to create a new user prop-set property (assign a unique name with up to eight characters to each prop-set property).

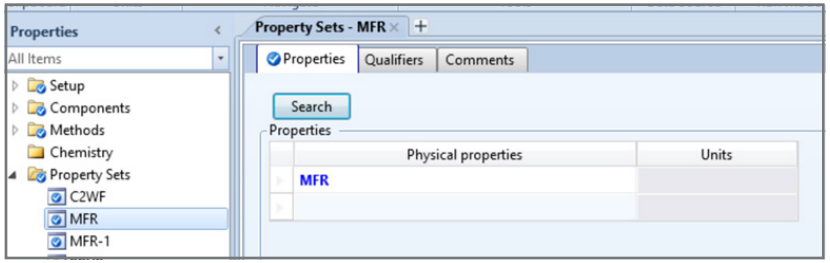
The second form shows how to reference the name of the subroutine used to calculate the user property set.





You need to create a Property Set corresponding to each user property, as shown below. As a best practice, use consistent naming between user properties and property sets, and avoid names of built-in properties such as "density." The Property Set declaration allows you to define additional qualifiers such as phase type and component. These declarations will control how the properties are displayed in the stream report. As with the User Property definition, there is an Object Manager to create and manage property sets, in addition to the Property Set form used to set up qualifiers.





For more information, refer to Aspen Plus help and the Aspen Plus User Models Manual, posted on the customer support site at:

https://esupport.aspentech.com/S_Article?id=000072570 (v10)

https://esupport.aspentech.com/S_Article?id=000057444 (v11)

References:

1 N. Pasquini, Editor. Polypropylene Handbook, 2005 (ISBN 9781569903858).

2 Sinclair, K. B. (1983). Characteristics of Linear LPPE and Description of UCC Gas Phase Process, Process Economics Report. Menlo Park, CA: SRI International. Sinclair, K. B. (1983). Characteristics of Linear LPPE and Description of UCC Gas Phase Process, Process Economics Report. Menlo Park, CA: SRI International.

Q: I'm interested in using Aspen Plus to build a simulation to optimize transitions in a gas phase reactor. Have you had similar experiences in other plants?

A: Aspen Plus includes an application example for high-impact polypropylene via the Spheripol PP process, which involves two loop reactors in series followed by a gas-phase (fluidized bed) reactor to produce the impact polymer. This model is delivered with Aspen Plus—you can access it by opening Aspen Plus and navigating to the "Resources" ribbon, clicking the "Examples" button, and then going to the Polymers\Polypropylene folder.

The Spheripol polypropylene model treats the fluid-bed reactor and each loop reactor as an ideal CSTR, which is reasonable given the high circulation rate in these types of systems. A second example involving an LLDPE / HDPE swing reactor is posted on our support site here: **https://esupport.aspentech.com/S_Article?id=000096819**.

Aspen Polymers models are fully supported in Aspen Dynamics. From Aspen Plus, go to the "Dynamics" ribbon and select the "Dynamic Mode" button to expose additional input forms in Aspen Plus to specify equipment geometry. After filling in the additional required data, you can export the model as a flow-driven or pressure-driven dynamic simulation. The pressure-driven option is more rigorous, but it requires addition of pressure-control elements such as valves and pumps. The resulting dynamic model will be translated to Aspen Plus Dynamics, which provides additional features to specify and configure the control system. Aspen Plus Dynamics also provides a "task" feature to define time-dependent process recipes, which can be used to emulate the sequence of events used to make a rate or grade transition.

Q: Can you share the pyrolysis process model which was shown during the webinar?

A: During the presentation we showed a published SBR pyrolysis model: Wojtwicz and Serio, "Pyrolysis of waste tires: A modeling and parameter estimation study using Aspen Plus,®" Waste Management V 60, February 2017, Pages 482-493.

We also presented some modeling results from a simple HDPE gasification model, which is published in our knowledgebase here: **https://esupport.aspentech.com/S_Article?id=000083520.**

Q: What is the accuracy level of Aspen Polymers with plant data in a case study?

A: All models need to be calibrated against plant data, especially models that involve rate-limited reaction kinetics. Based on personal experience modeling high-temperature thermal decomposition processes such as pyrolysis and gasification, the accuracy can vary widely depending on the consistency of the feed stream compositions and on the degree of conversion to simple molecules.

Pyrolysis processes typically produce complex mixtures of solids, liquids and gasses. The PYGAS composition is the easiest to predict since the composition is relatively simple and because the lower molecular weight products are very well characterized (for example, heat capacity and Gibbs energy of formation of methane and other light gases is very well established, so equilibrium constants estimated from these thermodynamic properties tend to be quite accurate). PYGAS composition of +/- 5% would be reasonable given uncertainty in plant measurements.

Determination of the composition of the pyrolysis oil and char is much more difficult, especially if the feed material is a blend of polymers which may be inconsistent over time. With this type of process, one poses an assumed reaction network, then tunes the individual reaction rate parameters against data. The more data you have, the better and more reliable your model can be. Aspen Plus provides features such as "Data-Fit" to help automate the calibration of complex models against multiple sets of data, but before going there you need to do some calibrations manually (for example using sensitivity studies) to rough-tune the model kinetics. Achieving an accuracy of PYOIL compositions better than +/- 10% would be exceptional, accuracy of +/- 20% is more likely without extensive sets of data.

Char formation depends on the type of polymer in the feed (for example, extend of cross-linking). Char formation may also depend on reactor geometry and the nature of mixing within the reactor. First principle simulation cannot capture all these effects alone. Hybrid approaches combining machine learning or advanced correlation techniques with first-principle physical/chemical simulation may offer the best chance of prediction char quantities and particle size distributions. Given the PSD, Aspen Plus models can predict separation efficiencies in gas/solid separators such as cyclones.

Q: What recommendation do you have for modeling the PET with the actual recycling glycolysis technologies (Twin Screw extruder/glycolysis reactors etc.)?

A: AspenTech has a fully developed set of polyester polymerization models which we make available to customers on request. The PET models include extensions of the built-in reactor models to account for mass-transfer limits related to the high viscosity of polymer in the finishing stages. These models use the standard plug-flow reactor model as a calculation engine, but the reaction models are modified to take mass-transfer limits into account. These techniques can be applied to depolymerization reactions occurring in batch autoclaves (represented using RBATCH or the new BATCHOP model) or continuous reactors such as extruders (using RPLUG to represent the extruder).

Contact one of our **AspenTech experts** directly for more detailed information.

Q: Will AspenTech provide additional hands-on training for polymer modeling anytime soon?

A: AspenTech has recently posted e-learning materials covering polymer physical properties, phase equilibrium and simulation of free-radical reactions. Please contact **our customer care team** for more details.

In addition, we offer virtual training—a three-day, hands-on polymer course. **Click here** for details. Refer to the training catalog for additional information on available training: **https://www.aspentech.com/en/knowledge/classroom-learning**.

Live classroom and in-person on-site training are suspended in some regions due to COVID19 restrictions.

Please keep in touch with your services and sales representatives and check our support site for ongoing updates. We expect to restart live, in-person training as appropriate subject to local conditions and regulations and of course the safety of our customers and employees.

Q: Have you modeled any industrial biopolymer processes using Aspen Polymers? If so, are there any open source examples available? Were there any issues in defining and modeling the thermodynamic properties since most property parameters may not be available in Aspen databases?

A: Aspen Polymers has been applied to several bio-based polymers including polylactide (PLA), poly(triethylene gycol) (PTT) and other polymers with at least one monomer produced through fermentation.

In addition, customers have used Aspen Polymers to simulate production of starches, to characterize biodiesel components, cellular biomass (proteins) and woody plant biomass to simulate modification of natural fibers. Our involvement in this area has been in the context of customer support and paid consulting, so at this time we have not published any specific models addressing these processes.

We have published some rudimentary examples related to biodegradable polymers. These can be found on our support knowledgebase at: **https://esupport.aspentech.com/S_Article?id=000086001**.

Q:Where can I find the HDPE example presented during the webinar?

A: The HDPE gasification model is posted in our support website:
https://esupport.aspentech.com/S_Article?id=000083520

View the On-Demand Webinar!

If you missed the live presentation of "Accelerate Innovation and Improve Sustainability Through Polymer Process Modeling" or want to view it again, **Click here**.

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