Polymerization in Multijet Tubular Reactor

Production processes for polymers often involve turbulent flows and rapid reaction kinetics. The sophisticated interplay between fluid dynamics and fast chemical reactions can significantly impact the reactor performance, and thereby affect conversion and yield. Furthermore, the turbulent fluid mixing and its effects on the reaction can influence the average length of polymer chains, the molecular weight distribution, cross-linking, and chain-branching. All these properties are important for the integrity of the final material. This example demonstrates a polyester reactor, with multiple inlets, and includes heat transfer and temperature dependent kinetics. It employs the eddy dissipation concept (EDC), a model for the mean reaction rate in turbulent flows.

Note: This application requires both the Chemical Reaction Engineering Module and the CFD Module.

Model Definition

GEOMETRY

The geometry of the inlet section of a multijet tubular reactor is illustrated in Figure 1.

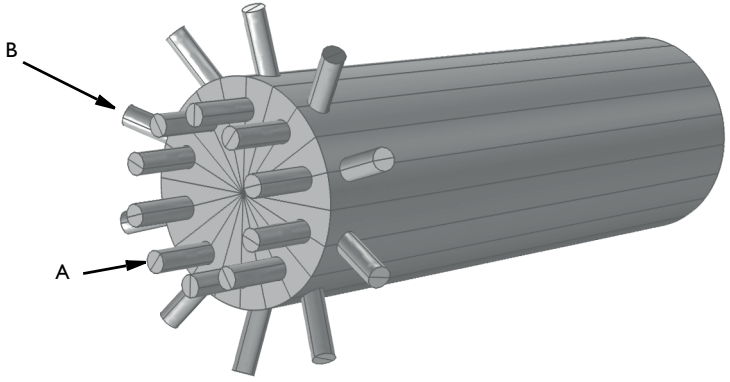


Figure 1: Inlet section of a multijet tubular reactor. Monomer A (diol) enters through the axial inlets while monomer B (diacid) enters through the radial ports.

Two reacting monomers enter through separate inlet ports. Monomer A enters through the axial inlets while monomer B enters through the radial ports.

CHEMISTRY

Condensation reactions are fundamental to the production of many important polymers, such as polyamides, polyesters, polyurethanes, and silicones.

This model simulates a polyester reactor. Condensation polymerization of monomers A (a diol) and B (a diacid), forms the polyester linkage, L (Ref. 1, Ref. 2). The reactions take place in the presence of a solvent catalyst, S.

TABLE 1: SPECIES USED ON THE MODEL

NAME	DESCRIPTION
A	Diol monomer
B	Diacid monomer
L	Polyester linkage (product)
S	Solvent catalyst ($TiCl_3$)
C	Complexating water

The catalytic species, S, is temporarily trapped in an intermediary H_2O complex, S · C, where C represents the complex-forming water in the irreversible reaction

$$2\mathrm{A} + \mathrm{B} + \mathrm{S} \xrightarrow{k_1^f} \mathrm{L} + 2\mathrm{SC} \tag{1}$$

The regeneration of solvent is governed by the reversible reaction

$$\mathrm{A} + \mathrm{SC} \underset{k_2^r}{\overset{k_2^f}{\Leftrightarrow}} \mathrm{S} + \mathrm{AC} \tag{2}$$

The reaction rates for each chemical reaction is determined by the law of mass action and the eddy dissipation concept (EDC) model. The law of mass action gives the rates (mol/(m^3·s))

$$r_1 = k_1^f c_\mathrm{A}^2 c_\mathrm{B} c_\mathrm{S} \tag{3}$$

and

$$r_2 = k_2^f c_\mathrm{A} c_\mathrm{SC} - k_2^r c_\mathrm{S} c_\mathrm{AC} \tag{4}$$

for reactions Equation 1and Equation 2, respectively, where the rate constants are given by the Arrhenius expression

$$k_j = A_j \exp\left(-\frac{E_j}{R_g T}\right) \tag{5}$$

In Equation 5, A_j is the frequency factor and E_j the activation energy (J/mol) for the jth reaction. The table below lists the values of the Arrhenius parameters for the reactions. The rates are adjusted for turbulent conditions according to the EDC model: If the time scale of the turbulent mixing is larger than the reaction kinetics derived by the law of mass action above, the turbulent mixing will be rate determining. For detailed information, see the section Eddy Dissipation Concept in the CFD Module User's Guide.

TRANSPORT

The 3D model geometry is illustrated in Figure 1.

Velocities and Pressure

The velocities at the radial and axial inlets are set to 5 m/s. Furthermore, a constant pressure is set at the outlet and logarithmic wall functions are specified at the solid walls.

Mass Transport

Concentration boundary conditions apply at the inlets:

$$\begin{aligned} c_A &= 1200 \text{ mol/m}^3 \text{ at axial inlets} \\ c_B &= 1000 \text{ mol/m}^3 \text{ at radial inlets} \end{aligned} \tag{6}$$

The catalytic solvent S is set as solvent in the mass transport model.

Energy Transport

The reactor is assumed to be insulated at the walls and all inlet streams are specified to 440 K temperature.

Summary of Input Data

For the rate expressions in Equation 3 and Equation 4 the following data is used (Ref. 1):

TABLE 2: KINETIC DATA

QUANTITY	FREQUENCY FACTOR	ACTIVATION ENERGY	TURBULENT PARAMETERS α AND β
Forward Reaction 1	25.6	61.3[kJ/mol]	4, 0.5
Forward reaction 2	3.9e3	56.8[kJ/mol]	4, 0.5
Reverse reaction 2	4.7e3	102[kJ/mol]	4, 0.5

The material properties and boundary conditions used are (Ref. 1 and Ref. 2).

TABLE 6-1: INPUT DATA

PROPERTY	VALUE
Diffusivity	1e-8[m^2/s]
Density of catalyst solvent	2640[kg/m^3]
Heat capacity of catalyst solvent	2550[J/kg/K]
Inlet velocity	5[m/s]
Inlet temperature	440[K]
Molar mass, monomer A	48[g/mol]

TABLE 6-1: INPUT DATA

PROPERTY	VALUE
Molar mass, monomer B	104[g/mol]
Molar mass, complexating H_2O	18[g/mol]
Molar mass, polymer L	164[g/mol]
Molar mass, catalyst S	154[g/mol]
Molar mass, catalytic species complex SC	172[g/mol]
Molar mass, species complex AC	66[g/mol]
Heat of reaction, Reaction 1	100[kJ/mol]
Heat of reaction, Reaction 2	40[kJ/mol]

Modeling in COMSOL

- For the 3D model, the *Reacting Flow, Turbulent* interface is used for the mass transport, reactions, and fluid flow simulation. The *Heat Transfer in Fluids* interface is used to do the heat transfer simulation including the heat of reactions, coupled with the reacting flow.

STAGED SOLUTION

Since the chemical reactions are strongly depending on the fluid movement, the fully coupled system may be difficult to converge in the first iterations due insufficient start guesses on the velocity field. Therefore the following staged solutions is used. Each study step uses the converged solution from the previous step as a start guess:

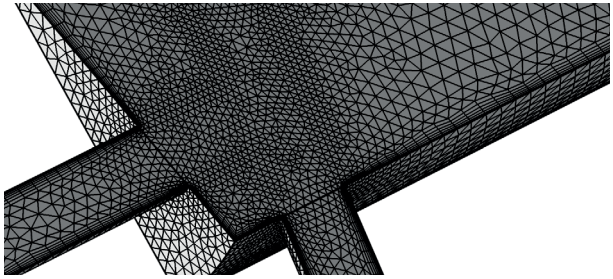
1. Velocity and pressure only.
2. Velocity, pressure, concentrations distribution including reactions. Isothermal.
3. Temperature only, including heat of reaction.
4. All variables.

GEOMETRY

Thanks to symmetry observations, a sector of one 1/20 of the geometry shown in Figure 1 is modeled. The modeling results are rotated to the full geometry by sector datasets.

MESH

The mesh is calibrated to resolve the shear layers that appear near the inlets of the reactor. Further downstream where the flow profile is expected to be more uniform, a simpler extruded mesh is used to save time and memory.



Results

Results of the flow field calculations are presented first. Figure 2 shows the velocity field in the multijet tubular reactor, plotted in two perpendicular planes through the reactor.

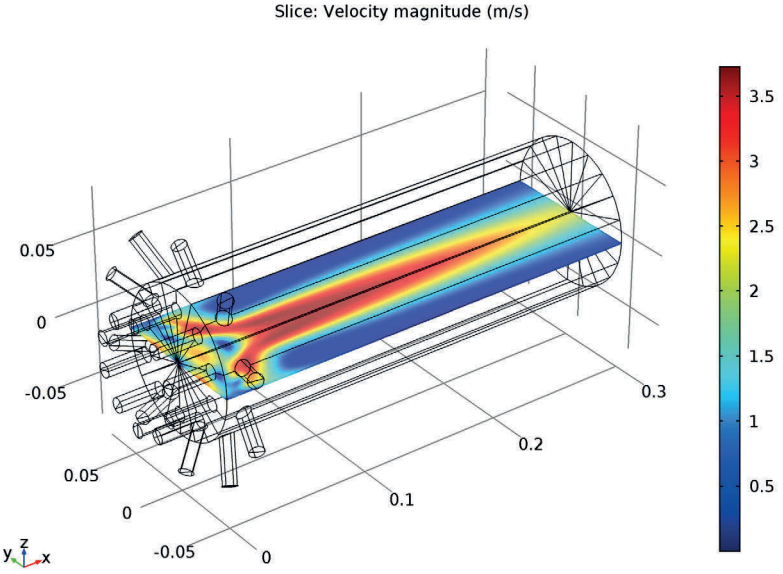


Figure 2: Velocity field (m/s) in the multijet tubular reactor.

The plot illustrates the impinging axial and radial jets.

Plotting the streamlines of the velocity field provides additional information, indicating flow paths. Figure 3 shows such a plot. Closer inspection at the entrance of the reactor reveals several recirculation zones.

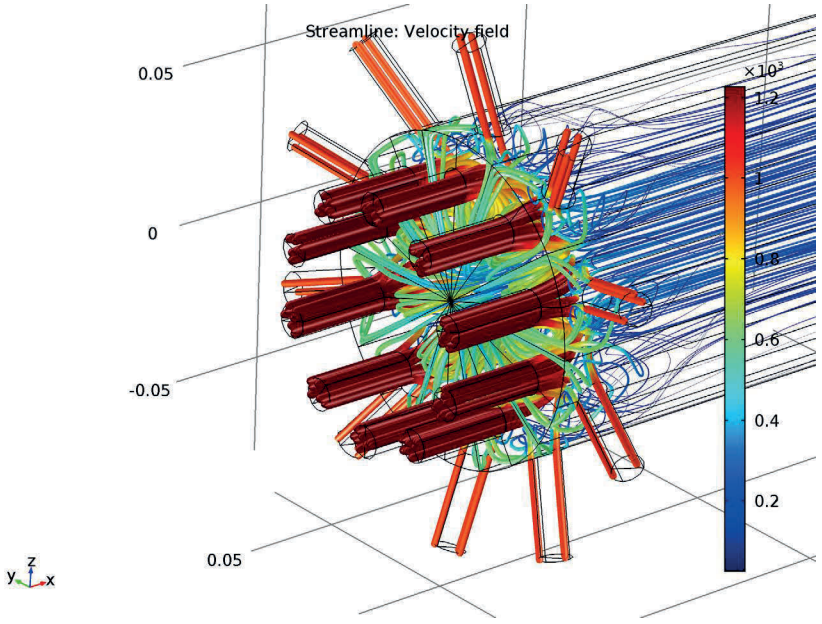


Figure 3: Streamlines of the velocity field shows some recirculation behavior near the inlet orifices. The concentration of reactants decrease rapidly at after the inlet stretch.

Next, mass is transported with the calculated flow field. Once monomer A comes into contact with the radial streams of monomer B, polymerization starts. Figure 4 shows the concentration field of monomer A.

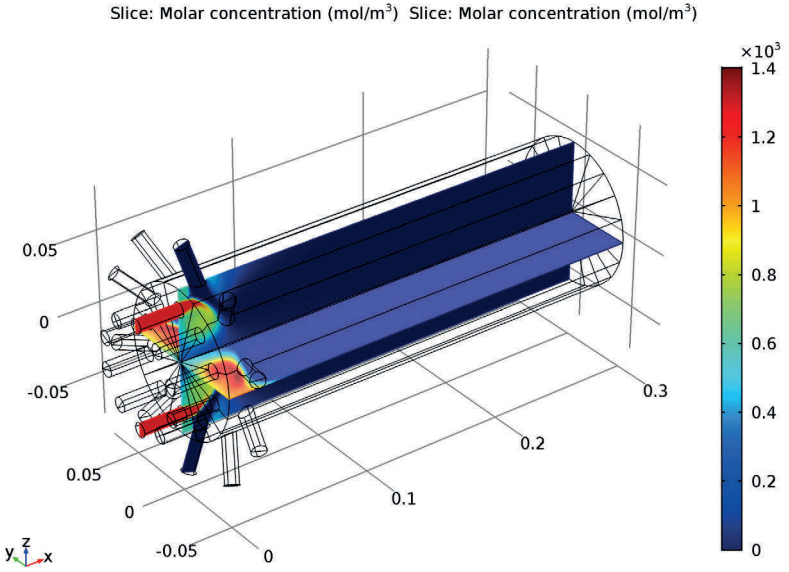


Figure 4: Concentration distribution of monomer A (mol/m^3).

Figure 5 shows isosurfaces for the polymer linkage L concentration. Isolevels at the entrance of the reactor clearly mark the positions of where the inlet streams mix. However, the azimuthal concentration gradients increase quickly with axial position,

indicating that inlet streams are well mixed for reaction to take place approximately 5 cm down the reactor.

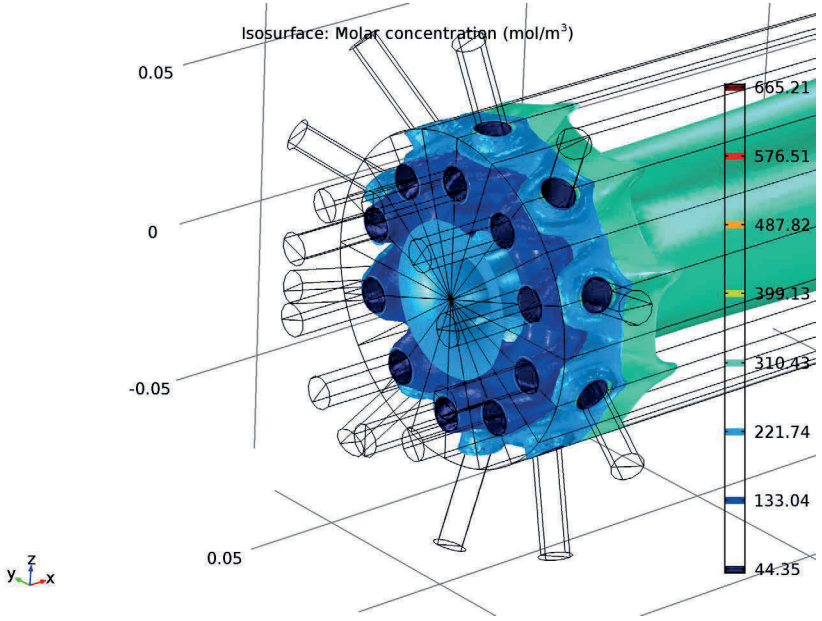


Figure 5: Isosurfaces for the concentration of L (mol/m^3).

As mentioned above, recirculation is evident in the entrance of the reactor. Recirculation will increase the effective residence time of the reactor. Figure 6 shows the concentration of polymer linkage, c_L, with a surface slice plot. The turbulence time scale that is accounted for in the reaction kinetic model according to the EDC concept affects the prediction of reactor turnover.