MODEL FOR FLAME-RETARDANT POLYURETHANE FOAM
MANUFACTURING

By

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Model for Flame-Retardant Polyurethane Foam Manufacturing

Abstract

By

CODY S POWELL

Polyurethane foam has required flame-retardants for safe use in household furniture for some time. Many have negative health effects and are either banned or expected to be. Brannum and Wnek have developed a silica based flame-retardant that is much safer. To manufacture foam with this flame-retardant will require scale up. A model was created to simulate a manufacturing process for the foam. The modeling software chosen uses differential equations for governing transport processes was used to build the model. Appropriate processes and equations were chosen, properties of the necessary materials were found, and boundary conditions were applied as befitted the manufacturing process to be simulated. Results will show a model that confirms what was expected and the outcome of the proposed manufacturing process. Future work has been suggested in order to find a process of making the foam that would work in an industrial sized plant.
**Introduction**
Polyurethane foam has been a great material with which to make furniture. However, it is also susceptible to fire and when aflame will drip burning hot enough to burn through the floor of a home. This drip is very hot and spreads a fire much quicker than if the material were to stay as a whole piece. Naturally, this makes polyurethane foam use in household furniture dangerous. In the 1970’s states, and even countries, began to require that manufacturers of polyurethane foam for the use in homes make their foam flame-retardant. Brominated compounds have been the flame retardant of choice since then as they are very effective. They are also very dangerous. Polybrominated diphenyl ethers, PBDE’s, have been found in greater concentrations in both people and the environment. Some have linked them to thyroid hormone disruption, neurodevelopmental deficits, and even cancer\(^1\). In addition, several investigators have found evidence of PBDE’s in breast milk\(^2\)-\(^6\) and blood\(^7\).

Since this information has come to light, legislators are enacting laws to ban brominated flame retardants. In 2003, a bill was passed in California detailing the ban of polybrominated diphenyl ethers\(^8\). This is pushing the industry toward safer, more environmentally stable compounds. The new choices are mainly phosphorous compounds. These also come with health and environmental problems however. Van der Veen and de Boer\(^9\) have listed some of the many different phosphorus based compounds and outlined the various mechanisms and health and environmental effects. There are some types that are toxic to both people and animals and others that cause cancer. Some have been found toxic to dogs\(^10\).
Brannum and Wnek have developed a new flame-retardant solution that uses silica\(^{11}\). Silica has no negative environmental effects, as it is simply quartz in the natural environment. In addition, it has no health effects aside from crystalline silica inhalation which has been known to cause various lung conditions including lung cancer\(^{12}\) and lupus\(^{13}\). There have also been found to be negative health effects due to nanoparticles\(^{14,15}\). The overall effect of this polyurethane foam is believed to be a net positive when looking at the effectiveness, little to no environmental harm, and similar human harm to the currently lawful and used phosphorous compounds.

This thesis will discuss the flame-retardant to be used on the foam, the modeling software chosen, how that software will operate, the model parameters such as material properties and how they were gathered, and finally the building of the model itself and interpretations of the results.
Chapter 1: Mechanism Description

Using the Stöber process, the silica particles developed within the foam are bound structurally to the open cell pores of the foam. It is thought that the silica has an effect on the reaction kinetics of the burning foam.

\[
(CH_2O)_n + nO_2 \rightarrow nCO_2 + nH_2O
\]

\[
(CH_2O)_n \rightarrow nC + nH_2O
\]

The first reaction is the typical burning of cellulose, which is a good analogue for the foam. This reaction releases carbon dioxide which can burn and release more heat. The second reaction, however, produces carbon and creates a char layer. As time moves forward, more char is created, indicating the second reaction may dominate. Eventually the fire goes out as the foam is covered in the char layer and no longer burns.

This ensures that the flame drip described above does not occur. Polyurethane foam without silica is completely burnt and leaves nothing behind. When the solution has been added, 50% of the foam is still intact after the flame goes out. This solution is effective and less harmful than the flame-retardant compounds that have come before it.
Chapter 2: Goals for model
Currently, this foam is simply soaked in the flame-retardant solution for 30 minutes, removed, and finally washed. While this works for a bench scale experiment, this process needs to be improved and scaled up for a manufacturer to be able to implement it, as submerging large pieces of foam in solution for long periods of time is not a good manufacturing process. This model is the first step for a scale up of an effective flame-retardant foam manufacturing process. The final result is a model that is an accurate picture of the reaction kinetics and solute transport of the process. The model uses a 2D geometry to simulate a long piece of foam rolling along a conveyor with the solution falling on the foam as a waterfall.

Upon completion, if a future researcher wishes to see what might happen with a change of a certain parameter, the parameter may easily be adjusted to see the resulting process. In addition, they may also be able to change the geometry to test new methods of adding the solution to the foam. This will allow future researchers to see what might or might not be possible before having to spend the time and money on experiments.
Chapter 3: Modeling software

COMSOL Multiphysics is a useful simulation tool to model many transport processes including different types of fluid or heat flow, reaction chemistry, electrical process, and much more. I have used the Computational Fluid Dynamics module, specifically the Reacting Flow in Porous Media physics, to simulate our solution flow through the polyurethane foam. This model is helpful in finding how the solution will need to be mixed and dispensed onto the readymade polyurethane foam for good silica propagation throughout.

COMSOL uses governing differential equations to solve for fluid profiles, heat and mass transfer, and chemical reactions. These equations are picked according to the physics chosen. Once picked, certain parameters must be entered that will allow COMSOL to solve the differential equations. The Reacting Flow in Porous Media physics uses a combination of differential equations including the Navier-Stokes equations for free fluid flow, the Brinkman equations for flow through porous media, and the continuity equation for mass flow. In addition, the transport of chemical species is governed by transport equations for convection and diffusion. Once COMSOL knows what equations to use and all necessary variables have been stated, such as viscosity and density, the boundary and initial conditions must be set. This is how COMSOL explicitly solves for solutions instead of giving generic ones. These conditions are simple. For example, to model the fluid flow in a pipe the velocity must be set to a value at the entrance of the pipe.
Chapter 3.1: Navier-stokes equation

The general Navier-Stokes equation is shown below. This applies only to a Newtonian fluid with constant density and viscosity.

\[
\rho \frac{Dv}{Dt} = -\nabla p + \mu \nabla^2 v + \rho g
\]  

Each group of variables represent a contribution from different forces. The left side of the equation is the contribution from inertial forces, the first variable set on the right side are the pressure forces, the middle variables the viscous forces, and the far right variables the external forces.

Adding in the rectangular coordinate system we get the governing equations shown here. These are for the various velocities in the x, y, and z directions. Which direction the equation describes corresponds to which subscript the velocity variables carry.

\[
\rho \left( \frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \right)
= -\frac{\partial p}{\partial x} + \mu \left[ \frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} \right] + \rho g_x
\]

\[
\rho \left( \frac{\partial v_y}{\partial t} + v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} + v_z \frac{\partial v_y}{\partial z} \right)
= -\frac{\partial p}{\partial y} + \mu \left[ \frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} + \frac{\partial^2 v_y}{\partial z^2} \right] + \rho g_y
\]

\[
\rho \left( \frac{\partial v_z}{\partial t} + v_x \frac{\partial v_z}{\partial x} + v_y \frac{\partial v_z}{\partial y} + v_z \frac{\partial v_z}{\partial z} \right)
= -\frac{\partial p}{\partial z} + \mu \left[ \frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} + \frac{\partial^2 v_z}{\partial z^2} \right] + \rho g_z
\]
Specifically $\rho$ is the density of the fluid, $v_x$, $v_y$, and $v_z$ are the velocities in the x, y and z directions, $\frac{\partial v}{\partial t}$ is the change in velocity with time, $\frac{\partial v_x}{\partial x}$, $\frac{\partial v_x}{\partial y}$, and $\frac{\partial v_x}{\partial z}$ are the changes in velocity in the x direction with respect to the x, y, and z directions, $\frac{\partial p}{\partial x}$, $\frac{\partial p}{\partial y}$, and $\frac{\partial p}{\partial z}$ are the changes in pressure with respect to the x, y, and z directions, $\mu$ is the viscosity of the fluid and combined with $\frac{\partial^2 v_x}{\partial x^2}$, $\frac{\partial^2 v_x}{\partial y^2}$, and $\frac{\partial^2 v_x}{\partial z^2}$ represent the viscous stresses, and $\rho g$ is the force per volume due to gravity, $g$.

In addition to the Navier-Stokes equations, the continuity equation is also useful in determining fluid profiles. Generally, the equation is as follows for Newtonian, incompressible fluids.

$$(\nabla \cdot \mathbf{v}) = 0 \quad (5)$$

When the Cartesian coordinate system is applied the following is derived.

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0 \quad (6)$$

**Chapter 3.2: Brinkman equation**

Henry Darcy, in 1856, published "Les fontaines publiques de la ville de Dijon: exposition et application" in which he described experimentally an equation for fluid flow through porous media now called Darcy’s Law$^{17}$.

$$Q = -\frac{kA\Delta p}{\mu L} \quad (7)$$

Here $Q$ is the volumetric flow, $k$ is the media permeability, $A$ is the cross sectional area of the media, $\Delta p$ is the pressure difference, $p_b - p_a$, where b is the end of
the channel and $a$ is the start, $\mu$ is the viscosity, and $L$ the length the fluid has to travel through the media.

Darcy’s Law works well for porous media, but cannot satisfy the necessary boundary conditions for the transition between free flow and porous media flow, continuity of fluid velocity, and shear stress. Brinkman\textsuperscript{18} created a modification to Darcy’s Law in order to attain consistent boundary conditions for solving the equations. Brinkman describes Darcy’s Law as written below.

$$v = -\frac{k}{\mu} \nabla p$$ \hspace{1cm} (8)

Where $v$ is the rate of flow per unit surface area and all other variables are the same as described above from Darcy’s Law. Brinkman describes fluid flow in porous though equation 8 and equation 5, while free flow in empty space is described by equation 5 and the Navier-Stokes equation, neglecting inertial terms. The Navier-Stokes equation in this form is shown below.

$$\nabla p = \mu \nabla^2 v$$ \hspace{1cm} (9)

Equations 8 and 9 are now differential equations of different orders which makes it tough to make rational boundary conditions for the interface. The change in flow characteristics from free to porous media flow, cause difficulty in rationalizing velocity and pressure between the flow areas. Brinkman suggests setting up an equation for a force balance on a volume element of fluid describing the pressure gradient, viscous stress, and damping force of the porous media. Below is equation 8 with Brinkman’s suggested modification.

$$\nabla p = -\frac{\mu}{k} v + \mu' \nabla^2 v$$ \hspace{1cm} (10)
Here $p$ is the pressure force, $v$ is the rate of fluid flow through a surface element of unit area and is the average velocity through the porous media just as in equation 8, $\mu$ is the fluid viscosity, $k$ is the media permeability, and $\mu'$ is an effective viscosity parameter. Brinkman proposed defining the effective viscosity using the Einstein formula.

$$\mu' = \mu (1 + 2.5(1 - \varepsilon)) \quad (11)$$

This makes sense as at high porosities the effective viscosity is close to the actual viscosity, and at low porosities the effective viscosity is as much as 3.5 times higher than the actual viscosity. This allows for boundary conditions at the interface to be appropriately defined. For instance, the shear stress boundary condition at the interface can be define as shown.

$$\mu \frac{dv_x}{dy} (y = 0^+) = \mu' \frac{dv_x}{dy} (y = 0^-) \quad (12)$$

Here $y = 0$ is the interface of the foam and where the governing equation changes from the Navier-Stokes to the Brinkman. The superscripts for the zero dictate whether the fluid is in the free flow region, $0^+$, or the porous flow region, $0^-$. The equation used by COMSOL is different than the equation Brinkman originally proposed. This equation is displayed below.

$$\frac{\rho}{\varepsilon} \left( \frac{\partial v}{\partial t} + (v \cdot \nabla) \frac{v}{\varepsilon} \right) = -\nabla p + \frac{\mu}{\varepsilon} \nabla^2 v - \frac{\mu}{k} v \quad (13)$$

COMSOL had the inertial terms on the left with the pressure forces, the added viscous term, and the rest of Darcy’s law on the right. While Brinkman originally uses an effective viscosity term, $\mu'$, defined in equation 11 above, COMSOL
divides viscosity by the input porosity. The velocities are all the same velocities Brinkman described in equation 10. COMSOL has an option to disable the inertial forces on the left hand side, though it was not used in this model.

**Chapter 3.3: Chemical species transport**

Chemical species transport is governed by convection and diffusion. This uses a derived form of the continuity equation. Below is the continuity equation for a species $A$ on a per mole basis in terms of $x_A$ for constant molar density, $c$, and diffusion, $\delta_A$. Chemical reactions are represented through $r_A$ on a mole per volume per time basis.

$$\frac{c}{D} \frac{Dx_A}{Dt} = c\delta_A \nabla^2 x_A + r_A$$  \hspace{1cm} (14)

For Cartesian coordinates this equation becomes:

$$c \left( \frac{\partial x_A}{\partial t} + v_x \frac{\partial x_A}{\partial x} + v_y \frac{\partial x_A}{\partial y} + v_z \frac{\partial x_A}{\partial z} \right) = c\delta_A \left[ \frac{\partial^2 x_A}{\partial x^2} + \frac{\partial^2 x_A}{\partial y^2} + \frac{\partial^2 x_A}{\partial z^2} \right] + r_A$$  \hspace{1cm} (15)
Chapter 4: Chemistry
Chapter 4.1: Basic Chemistry
The Stöber process is used to develop crystalline silica particles within the foam.

This involves using a solution of water, alcohol, and a silica precursor\(^\text{16}\). This involves a hydration and subsequent condensation reaction. This condensation can be either aqueous or alcoholic.

The first step, hydrolysis:

\[
\text{RO-Si-OR} + \text{H}_2\text{O} \rightleftharpoons \text{RO-Si-OH} + \text{ROH}
\]

*Figure 1 - Hydrolysis reaction, Alongi et al.\(^\text{19}\)*

The possible second steps, aqueous condensation:

\[
\text{RO-Si-OH} + \text{HO-Si-OR} \rightleftharpoons \text{RO-Si-O-Si-OR} + \text{H}_2\text{O}
\]

*Figure 2 - Aqueous condensation, Alongi et al.\(^\text{19}\)*

And alcoholic condensation:

\[
\text{RO-Si-OH} + \text{RO-Si-OR} \rightleftharpoons \text{RO-Si-O-Si-OR} + \text{ROH}
\]

*Figure 3 - Alcoholic reaction, Alongi et al.\(^\text{19}\)*
Typically, tetraethyl orthosilicate, \( TEOS \), is used as the source for the silica particles.

![TEOS structure](image)

**Chapter 4.2: Kinetics**

Chen et al.\(^{21}\) determined the reaction kinetics of the hydrolysis and condensation reactions shown in Figures 1-3. \( TEOS \) was used as the silica precursor resulting in the general reaction steps of \( TEOS \) to \( Si(OH)_4 \) to \( SiO_2 \). Using gas chromatography and a conductivity meter the concentrations were measured throughout the course of the reactions. They found the hydrolysis reaction to be first order with \( TEOS \) and the condensation reaction to be first order with \( Si(OH)_4 \).

In addition, they were able to find the effects of temperature, \( NH_3 \) concentration, and \( H_2O \) concentration. Assuming the rates of hydrolysis, \( K_h \), and condensation, \( K_c \), are dependent on the variables described previously they found a general rate equation equal to be

\[
K = K_0 \exp\left(-\frac{E_A}{RT}\right)[H_2O]^\alpha [NH_3]^\beta
\]  

(16)
While $NH_3$ does not participate in the reactions show in Figures 1-3, it is a catalyst that affects the rate of reaction. It was observed by Chen et al.\textsuperscript{21} that an increase in $NH_3$ concentration corresponded to an increase in reaction speed. After collecting and analyzing data they found the rate constants to be

$$K_h = 74.36 \exp\left(-\frac{E_a}{RT}\right)[H_2O]^{1.267}[NH_3]^{0.971}, \quad E_a = 25.2 \frac{kJ}{mol} \quad (17)$$

$$K_c = 19408 \exp\left(-\frac{E_a}{RT}\right)[H_2O]^{1.196}[NH_3]^{0.7854}, \quad E_a = 33.2 \frac{kJ}{mol} \quad (18)$$

The rate constants are in units of $min^{-1}$. Next, Chen et al.\textsuperscript{21} found the growth rate of the silica nanoparticles. They assumed the reaction intermediates were mostly made up of silicic acid, and so, ignored the other possible products. This leads to a general reaction shown below:

$$TEOS \xrightarrow{K_h} Si(OH)_4 \xrightarrow{K_c} SiO_2 \text{ particles}$$

Chen et al.\textsuperscript{21}, citing Bogush\textsuperscript{22}, argue that as the equilibrium concentration of $Si(OH)_4$ in alcohol solutions is low, about $10^{-4}M$, compared to in this reaction, $10^{-2}M$, the condensation of $Si(OH)_4$ is estimated to be irreversible, allowing the ability to ignore the loss of silica nanoparticles back into silicic acid. Knowing this, they have defined the kinetic equations as follows below.

The change in concentration of $TEOS$ with time:

$$\frac{d[TEOS]}{dt} = -K_h[TEOS] \quad (19)$$

The change in the silicic acid, $Si(OH)_4$ concentration with time:

$$\frac{d[Si(OH)_4]}{dt} = K_h[TEOS] - K_c[Si(OH)_4] \quad (20)$$
The silicic acid production is driven by the TEOS reaction, equation 15, and the reaction of silicic acid is driven by the condensation reaction to produce silica oxide.

And finally, the rate at which silica nanoparticles are produced:

\[
\frac{d[SiO_2]}{dt} = K_c[Si(OH)_4] \tag{21}
\]

Chen et al.\textsuperscript{21} have experimentally determined the rate of seeded \(SiO_2\) growth with time. Using this data in conjunction with the equations described above, they determined also

\[
\frac{d[SiO_2]}{dt} = \frac{(TEOS)_0 \, dL_t^3}{L_{\infty}^3 - L_0^3} = K_c[Si(OH)_4] \tag{22}
\]

Solving these equations results in an expression for the change in silica particles diameter with time.

\[
L(t) = \left\{ L_0^3 + \left[ 1 - \frac{K_c}{K_c - K_h} \exp(-K_h t) + \frac{K_h}{K_c - K_h} \exp(-K_c t) \right] \left( L_{\infty}^3 - L_0^3 \right) \right\}^{1/3} \tag{23}
\]

Here \(L_0\) is the initial seed diameter, \(L_{\infty}\) is the final diameter, and \(L_t\) the growing diameter \(t\) minutes after the reaction. Here the time is explicitly stated in the equation. This means that whenever the simulation is running the reaction time variable needs to be specified as this equation is built in as a separate entity and used within the chemical reaction. After determining the time necessary to solve for a time dependent solution, the reaction time needs to be specified to correlate
with the time stated for the time dependent solver. This will be expanded upon in a later section.

To describe the silica particle concentration in time

\[ [Si(OH)_4] = [TEOS]_0 \frac{K_h}{K_c - K_n} [\exp(-K_h t) - \exp(-K_c t)] \]  

(24)

The consumed concentration of TEOS, \([TEOS]_R\), is

\[ [TEOS]_R = [TEOS]_0 \left[ 1 - \exp(-K_h t) \right] \]  

(25)

Combining equation 17 and 20 yields:

\[ [SiO_2] = [TEOS]_0 \frac{L_t^3 - L_0^3}{L_\infty^3 - L_0^3} \]  

(26)

These equations are based on seeding silica particles with a starting particle diameter. The Stöber process does not use the seeding of silica, so Chen et al. sets \( L_0 \) equal to zero:

\[ [SiO_2] = [TEOS]_0 \left( \frac{L_t}{L_\infty} \right)^3 \]  

(27)

Equations 13, 14, 19, and 23 were added to the model to calculate the silica concentration over time.

Chen et al. used multiple methods for data collection. TEOS concentration was found through gas chromatography, and silicic acid concentration was found through a conductometer. Using the relationship between molal conductivity and concentration, they developed an equation to simulate reaction conductivity.

They compared the expected results from calculation with results found experimentally. These results were all plotted together.
Silica particle diameter was determined in experiment by Chen et al. by transmission electron microscope. The results were plotted with those calculated through equation 23 above.
Chapter 4.3: Kinetic Parameters

Below is the list of explicit values used for the variables for the reaction equations.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H₂O]</td>
<td>5.98 M</td>
<td>Chen et al.\textsuperscript{21}</td>
</tr>
<tr>
<td>[NH₃]</td>
<td>0.996 M</td>
<td>Chen et al.\textsuperscript{21}</td>
</tr>
<tr>
<td>[TEOS]</td>
<td>0.212 M</td>
<td>Chen et al.\textsuperscript{21}</td>
</tr>
<tr>
<td>[SiO₂]</td>
<td>0 M</td>
<td>No seeding</td>
</tr>
<tr>
<td>D_{TEOS}</td>
<td>3.74 × 10^{-10} \text{ m}^2 \text{ s}^{-1}</td>
<td>Calculation described below</td>
</tr>
<tr>
<td>D_{SiO2}</td>
<td>1 × 10^{-25} \text{ m}^2 \text{ s}^{-1}</td>
<td>Effectively zero</td>
</tr>
<tr>
<td>Lf</td>
<td>50 nm</td>
<td>Chen et al.\textsuperscript{21}</td>
</tr>
</tbody>
</table>

Table 1 - Kinetic parameters

The values for the concentration of water, ammonia, and TEOS and the final silica diameter were all taken from experimental data from Chen et al.\textsuperscript{21} The concentrations were values used during one of the experiments, and the final diameter was the observed diameter as a result of that particular experiment. The diffusivity of silica particles, D_{SiO2}, is effectively zero. Unfortunately, COMSOL cannot handle a zero value for this parameter as it will not converge; so it is set to be so small as to be zero. The diffusivity of silica is zero as the particles are bound to the structure of the polyurethane foam. Once they are created within the foam, they no longer move nor release from the foam. This is demonstrated through lab experiments in which the foam is washed post solution.
addition and it still retains the flame-retardant properties. To calculate the diffusion of $TEOS$, the Stokes-Einstein relation$^{23}$ was used.

\[
D = \frac{k_B T}{6\pi \mu r}
\]  

(28)

Here $D$ is the calculated diffusion, $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, $\mu$ is the viscosity, and $r$ is the particle radius. The particle radius was calculated through finding the particle volume. The calculations are described below.

\[
V_{\text{molar}} = \frac{M}{\rho} = \frac{208.329 \text{ g mol}^{-1}}{0.933 \text{ g cm}^{-3}} = 223.3 \text{ cm}^3 \text{ mol}^{-1}
\]  

(29)

\[
V_{\text{molecule}} = \frac{V_{\text{molar}}}{N_A} = \frac{223.3 \text{ cm}^3 \text{ mol}^{-1}}{6.0221409 \times 10^{23} \text{ mol}^{-1}} = 3.71 \times 10^{-22} \text{ cm}^3
\]  

(30)

\[
V_{\text{sphere}} = \frac{4}{3} \pi r^3
\]

(31)

\[
r = \sqrt[3]{\frac{3}{4} \pi V_{\text{molecule}}} = \sqrt[3]{\frac{3}{4} \pi (3.71 \times 10^{-22}) \text{ cm}^3} = 9.56 \times 10^{-8} \text{ cm}
\]  

(32)

Inserting this calculated radius into the equation 24 the diffusion is calculated:

\[
D = \frac{1.38064852 \times 10^{-23} \text{ m}^2 \text{ kg} \text{ s}^{-1} \text{ K}^{-1}}{6\pi (0.0006 \text{ Pa} \cdot \text{s})(9.56 \times 10^{-10} \text{ m})} = 3.74 \times 10^{-10} \frac{\text{m}^2}{\text{s}}
\]  

(33)
Chapter 5: Model Parameters

Chapter 5.1: Needed Parameters

COMSOL needs both the porosity and permeability of the porous media as well as the transport properties of the fluid, namely density and viscosity. Descriptions of how these parameters were obtained follows.

Chapter 5.2: Transport Properties

The solution is half propanol and half water so an of average their two values was calculated. This should be accurate enough to serve for the model. The properties and the resultant solution properties are given in the table below.

Sources have been added for the properties of water and propanol.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Density $[\text{kg/m}^3]$</th>
<th>Viscosity $[\text{Pa} \cdot \text{s}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>$1000^{24}$</td>
<td>$0.0008949^{24}$</td>
</tr>
<tr>
<td>Iso-propanol</td>
<td>$803^{25}$</td>
<td>$0.002256^{25}$</td>
</tr>
<tr>
<td>Averaged</td>
<td>$901.5$</td>
<td>$0.001727$</td>
</tr>
</tbody>
</table>

*Table 2 - Liquid transport properties*

Chapter 5.3: Porosity

The porosity of a material, $\varepsilon$, is the ratio of empty pore volume to the total volume of the material.

$$
\varepsilon = \frac{V_{pore}}{V_{total}}
$$

(34)
The total foam volume, $V_{\text{total}}$, was found by measuring the geometry of a block of foam.

<table>
<thead>
<tr>
<th>Measure</th>
<th>Value [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>99</td>
</tr>
<tr>
<td>Width</td>
<td>127</td>
</tr>
<tr>
<td>Height</td>
<td>50</td>
</tr>
<tr>
<td><strong>Total Volume</strong></td>
<td><strong>628650 mm$^3$</strong></td>
</tr>
</tbody>
</table>

*Table 3 - Foam dimensions for porosity measurement*

*Figure 7 - Foam in container for porosity measurement*
The foam block was put into a box with similar dimensions so that the foam was snug without being compressed. Water was slowly added from above the foam onto the top until the foam became saturated. The foam was compressed to allow the water to fill it entirely and eliminate any air pockets that may have been trapped in the foam. There was a noticeable color change from the light green of the foam to a darker green once the foam contained a significant amount of water. The difference in weight from unsaturated to saturated foam is the total water weight added. Using the density of water, $1 \frac{g}{cm^3}$, the pore volume was found, $V_{pore} = 371.7 mL$.

The porosity of the foam was calculated.
\[
\varepsilon = \frac{V_{\text{pore}}}{V_{\text{total}}} = \frac{371.7}{628.65} = 0.59
\] (35)

It is likely that not all of the pores are open cells. This means that this porosity is not in fact the total porosity of the foam but the effective porosity that any fluid or species may actually flow into. This is ok as when the flame-retardant solution is dumped onto the foam, it will only be able to flow into these open cells characterized through this effective porosity.

**Chapter 5.4: Permeability**
Using an apparatus made by Dr. Wainright’s group and the assistance of postdoc Dr. Yufeng Zhu, the permeability was experimentally found. Based on the principal of Darcy’s Law, equation 1 above, and using the known liquid viscosity (water), length of porous media to be traveled, \( L = 0.7 \text{ cm} \), and cross sectional area of media, \( A = 0.0005 \text{ m}^2 \), the permeability may be calculated.

\[
k = -\frac{Q\mu L}{A\Delta p}
\] (36)

The foam was cut in a cylinder, soaked in water to avoid expansion during testing, and two gaskets covered on each side of it.
This was placed in between two flanges and tightened. This left the edges tight to prevent leakage (as that would've ruined the measurement) and the area in the middle exposed for the water to flow. The configuration can be seen in Figure 10 below.
The water inlet is the reservoir that contains the water for the experiment, and the water outlet is the exit for the water after passing through the foam slice. It was attached to a tube that runs along a ruler. This measured the distance traveled by the fluid. When that distance is timed the flow rate, $Q$, can be calculated. In addition, there is a pressure valve and gauge that will read in inches of water. This experiment was done at a pressure of 3 inches of water. The chambers before and after the foam were filled with deionized water to ensure consistent pressure and velocity. A hose connected to the pressure valve
was put into the chamber before the foam, the pressure was dialed to 3 inches of water, and then connected to a tube that ran the length of a measuring stick. The water was timed as it moved down the tube and gave a distance \( d = 90 \text{ cm} \) in the time \( t = 6.57 \text{ s} \). With a tube cross sectional area of \( 1 \text{ mm}^2 \) the volumetric flow was calculated to be \( Q = 140 \frac{\text{mm}^3}{s} \). Solving for permeability:

\[
k = \left( 1.4e^{-7} \frac{\text{m}^3}{\text{s}} \right) \left( 0.0008949 \frac{\text{Pa} \times \text{s}}{\text{m}} \right) \left( 0.007 \text{ m} \right) = 2.3 \times 10^{-12} \text{ m}^2
\]

The model did not converge when a value this small was used. The smallest value that would enable the model to converge was \( 2.3 \times 10^{-10} \text{ m}^2 \). While this is two orders of magnitude higher than the experimentally determined value, the model should not be terribly inaccurate due to this. After a permeability of \( 2 \times 10^{-8} \text{ m}^2 \) the model changes dramatically, but after this there are little to no change only due to the permeability. This change can be seen in the velocity plots below.

*Figure 11 – Permeability $1 \times 10^{-7} \text{ m}^2$*
The model shows a dramatic shift in the flow through the foam at this permeability change; however, outside of this shift, the model does not change much due to a permeability lower than $1 \times 10^{-7} \, \text{m}^2$ or higher than $1 \times 10^{-8} \, \text{m}^2$. This seems to be a permeability issue; however, COMSOL does not account for the wettability of the foam. According to Darcy’s Law, the permeability is the ability of a fluid to flow through a porous media (see Equation 30). Wettability is also a concern that should be evaluated.

**Chapter 5.5: Wetting**
Wetting is the ability of a liquid to keep in contact with a solid surface. Wettability is the degree of wetting, and it is determined through the cohesive and adhesive forces. Strong cohesive forces will cause the liquid to bead on the solid and not soak into it. Strong adhesive forces between the liquid and solid will cause the liquid to spread across the solid. The contact angle, $\theta_c$, is the angle the liquid meets the solid-liquid interface. This helps to characterize the wettability.
<table>
<thead>
<tr>
<th>Contact Angle</th>
<th>Wettability</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_c = 0$</td>
<td>Perfect wetting</td>
</tr>
<tr>
<td>$0 &lt; \theta_c &lt; 90^\circ$</td>
<td>High wettability</td>
</tr>
<tr>
<td>$90^\circ \leq \theta_c &lt; 180^\circ$</td>
<td>Low wettability</td>
</tr>
<tr>
<td>$\theta_c = 180^\circ$</td>
<td>Perfectly non-wetting</td>
</tr>
</tbody>
</table>

*Table 4 - Contact angle and wettability*

It is possible that the reason there is such a dramatic shift in the results of the model (Figures 11 and 12) is due to the wettability rather than the permeability, as COMSOL would suggest. An attempt to study the free flow-porous media interface in COMSOL will be discussed in a later section.
Chapter 6: Model Development
Chapter 6.1: Building the geometry
The model is a 2D configuration of a block of foam with a surrounding flow channel. The channel is wide enough so as to ignore edge effects. The picture below shows a narrower flow area than was finally used. A block just above the foam has been added to designate the flow inlet. The foam is 1-meter by 1-meter. The flow channel extends a meter on either sides. In the final geometry, the flow area extends 2 meters on either side of the foam. The flow inlet is 25 centimeters above the top of the foam. This will simulate a waterfall of the flame-retardant solution falling onto what would be a long piece of foam.

Figure 13 - Model geometry

A spray geometry was also made, but COMSOL could not converge on a solution even using the largest mesh. This may be something a future researcher could work on.
Chapter 6.2: Materials node
The model contains a material to simulate the water-propanol mixture used. The properties were detailed in the above section Transport Properties. The density is $\rho = 901.5 \frac{kg}{m^3}$ and the viscosity is $\mu = 0.001727 \ Pa \cdot s$.

Chapter 6.3: Physics and governing equations
The Reacting Flow in Porous Media was chosen to model this system. The equation specifics described above in the Intro to COMSOL chapter will be lightly reiterated here. Fluid flow in the open regions are governed by the Navier-Stokes equations, equations 2, 3, and 4 above.
\[ \rho \left( \frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \right) \]
\[ = -\frac{\partial p}{\partial x} + \mu \left[ \frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} \right] + \rho g \]  
(2)

\[ \rho \left( \frac{\partial v_y}{\partial t} + v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} + v_z \frac{\partial v_y}{\partial z} \right) \]
\[ = -\frac{\partial p}{\partial y} + \mu \left[ \frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} + \frac{\partial^2 v_y}{\partial z^2} \right] + \rho g \]  
(3)

\[ \rho \left( \frac{\partial v_z}{\partial t} + v_x \frac{\partial v_z}{\partial x} + v_y \frac{\partial v_z}{\partial y} + v_z \frac{\partial v_z}{\partial z} \right) \]
\[ = -\frac{\partial p}{\partial z} + \mu \left[ \frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} + \frac{\partial^2 v_z}{\partial z^2} \right] + \rho g \]  
(4)

In the porous media, transport is governed by the Brinkman equation, equation 13 above.

\[ \frac{\rho}{\varepsilon} \left( \frac{\partial v}{\partial t} + (v \cdot \nabla) \frac{v}{\varepsilon} \right) = -\nabla p + \frac{\mu}{\varepsilon} \nabla^2 v - \frac{\mu}{k} v \]  
(10)

And species transport is governed by the continuity equation.

\[ c \left( \frac{\partial x_A}{\partial t} + v_x \frac{\partial x_A}{\partial x} + v_y \frac{\partial x_A}{\partial y} + v_z \frac{\partial x_A}{\partial z} \right) = c \delta_A \left[ \frac{\partial^2 x_A}{\partial x^2} + \frac{\partial^2 x_A}{\partial y^2} + \frac{\partial^2 x_A}{\partial z^2} \right] + r_A \]  
(15)
Chapter 6.4: Boundary conditions
Boundary conditions must be set to solve the above equations. Below, each number is next to a line that represents a possible boundary where a boundary condition may be applied. Boundaries 1, 3, 12, and 13 are specified walls and no flux zones. This means that no flux will be allowed through them and a no-slip condition has been applied. The no-slip condition is why the flow channel edges are extended so far past the foam. The condition will not affect the results closest to the foam. Boundaries 2, 5, and 10 are specified as outlets for both the fluid and any species. Whenever there is an inlet there must also be an outlet to satisfy the conservation of mass. Boundary 8 is designated as the inlet for the fluid and $TEOS$. The fluid is specified to enter the geometry at $\frac{1\, m}{s}$ and the $TEOS$ concentration has been designated above as $[TEOS] = 0.212\, M$.

Figure 15 - Possible boundaries within geometry
Chapter 6.5: Mesh
The geometry employed is not complicated and does not require anything greater than a normal mesh. The foam has been specified as a separate body within the flow channel and the mesh conforms accordingly.

Chapter 6.6: Study
Time-dependent studies were done for various time profiles. This allows for the reaction time and boundary conditions to be adjusted while the simulation is being computed. The study was split into two separate steps. Step 1 was shorter, generally a second or less, and contained the boundary condition that allowed fluid and reactant flow. This simulates the waterfall of solution being turned on over a piece of foam, or in the case of a conveyor with a long piece of foam, the riding on the conveyor under a continuous waterfall. The second step is longer,
generally around 9 seconds, and the boundary conditions allowing fluid and reactant flow were disabled. This simulates the waterfall being turned off or the foam riding on a conveyor leaving the waterfall. For both steps the reaction time was the same as the time allowed for the steps.
Chapter 7: Results
The model resulted in velocity, pressure, and TEOS and SiO₂ concentration plots.

Chapter 7.1: Velocity
Below are velocity plots at various times. This study was ran as described above: flow conditions on for one second, turned off, and ran for another nine seconds. The time step was 0.01 seconds. These plots were taken at 0.5, 1, 1.5, and 5 seconds into the simulation.

\[ \text{Figure 17 - Velocity from left to right at simulation times } t=0.5, 1, 1.5, \text{ and } 5 \text{ seconds} \]

The scale bar on the right indicates the velocity, in meters per second, with color. The scale is different for each plot. The solution falling on top of the foam does not penetrate into it. According to COMSOL, this is an issue of permeability (seen in Figures 9 and 10). It is possible that this is an issue of wettability instead. This will be discussed in a later appendix. Though there is an outlet boundary specified at the bottom of the model, it is there for reasons of mass conservation. With the inflow boundary condition turned off, there is no outflow of fluid so it continues to stay and oscillate around the flow area.
With a no-slip condition boundary applied to the sides, there is no flux through those boundaries. This means, that while the model is set to run past the time the flow is turned off, the velocity plots are not entirely accurate. Further research into other possible boundary conditions or how to perfect this should be done.

Chapter 7.2: Pressure
Below are various pressure contour plots for the same time selections as above.

Here the plots show the pressure contours during the simulation with units of Pascals. Once again, the color scale is different for each plot. At 0.5 seconds there is a low, even slightly negative pressures as the fluid is just starting to flow into the flow channel. At 1 second the pressures are now much larger except for the negative area just below where the fluid was entering. At this time the flow was turned off, resulting in the negative pressure in that area. At 1.5 seconds, immediately after the flow change, there is a low pressure area in the areas where the fluid is oscillating. This is apparent in the above velocity plot at the
same simulation time. The pressure become more uniform as the simulation continues, which is expected as there in no more inlet flow.

**Chapter 7.3: Concentration**
The \( \text{TEOS} \) is flowing into the model flow channel through the top, with the fluid. Below are plots showing the concentration with position at various times, in units of moles per cubic meter.

![Figure 19 - TEOS concentration from left to right at simulation times t=0.5, 1, 1.5, and 5 seconds](image)

Each color scale has different magnitudes for the concentration. The first and second plots make sense as \( \text{TEOS} \) is flowing in with the carrying fluid. It penetrates slightly into the foam, though not much. After time 1 second the flow is turned off. In plot \( t=1.5 \) seconds, there is some \( \text{TEOS} \) left within the flow channel and a significant amount left above the foam, where the inlet was. This isn’t entirely accurate. In a legitimate manufacturing process, the remaining \( \text{TEOS} \) in plots \( t=1.5 \) and 5 seconds would be washed away in the carrying fluid as the
foam is surrounded by air. The problem mentioned earlier about the velocity plots, in that no more mass is leaving since there is no more mass entering the model, is the cause of this discrepancy.

There is no silica, \( SiO_2 \), in the model to start with. Below are plots describing the silica propagation with position in units of moles per cubic meter. They have been taken at the same times as the previous plots. The scales are different for every plot.

At time 0.5 seconds there is little silica in the model from the small amount of \( TEOS \) that has entered. At time 1 second there is more silica, as well as a layer of silica forming on the top of the foam. The plot for time 1.5 seconds is very similar to the \( TEOS \) concentration plot. There continues to be more silica being produced in the model, especially above the foam where there is a large amount of \( TEOS \) collecting and now reacting. Time 5 seconds shows most of the \( TEOS \) being converted into silica. Unfortunately, there has been little penetration of the \( TEOS \) into the foam, and therefore, little silica production within it.

\[ Figure\ 20 -\ Silica\ concentrations\ from\ left\ to\ right\ at\ simulation\ times\ \( t=0.5,\ 1,\ 1.5,\ and\ 5\ seconds \]
The method of using a waterfall of solution to produce silica within the foam for flame-retardancy does not seem to work, according to this model. Due to the extremely low permeability of the foam, very little solution can penetrate into it, despite the high porosity. Little to no silica can be produced inside the foam because of this.
Conclusions
The model is a good representation of dousing a piece of polyurethane foam in the proposed flame retardant solution. The geometry was created to have a block of polyurethane foam with a surrounding flow channel. The properties for the fluid and foam were determined analytically and by experiment. The chemical reactions for silica production through hydrolysis and condensation reactions were taken from Chen et al.$^{21}$ as were the reactions properties. Boundary conditions for the velocity and reactants were included at the solution inlet in the top of the model. During the time-dependent study, these boundary conditions were changed during the simulation to simulate the foam on a conveyor passing under a waterfall of the flame-retardant solution. The solution penetrates very little into the foam. The model suggests this is due to permeability, especially after viewing Figures 11 and 12; however, it does not account for wettability. Investigation into the interface of the foam and free flow region was attempted through building a small scale model, simulating a 1 cm by 1 cm block of foam. After numerous attempts, the model still will not converge. It is potentially a helpful model for determining the limiting factor(s) in flame-retardant foam manufacturing of this type and should be completed in the future.

Future work
In the future, work on this model should focus on finding a solution for the issue of retaining solution in the model. While this can be ignored and effectively thought around, the model would be more accurate if the fluid did not stay within the flow channel, wherein reality it would continue to flow out. In addition, a new method for delivery of the solution should be sought out and attempted. This will
involve building a new geometry and setting new boundary conditions that conform to that geometry. The spray geometry proposed might be a good method to try if it can be converged. Simply soaking the foam for a set amount of time may also work, if it can be reconciled with manufacturing needs.

Once again, the small scale model could be helpful in determining the effect of wettability, as it was not accounted for in the large scale model. A future researcher may be able to succeed in the completion of this model. It is described more in Appendix 1.
Appendix 1: Small scale model for interface investigation

According to the above Figures 11 and 12, the reason there is little solution penetration into the foam is due to the low permeability of the foam. This can again be seen in Figures 17, 19, and 20. This effect may instead be attributed to a low wettability of the foam or low contact time, rather than low permeability. A small scale model was created to further investigate the interface between the foam and the free flowing fluid.

A geometry consisting of a 1 cm block of foam with a 1 cm flow area directly above it. A different type of physics was used instead of the Reacting Flow in Porous Media that was used in the previous model. The small scale attempted to use Two Phase Fluid Flow to show how the solution may penetrate the foam when full of air.

First, a simple model was made that contained no foam to verify the ability of the model to determine a liquid/gas interface. Below are selected time plots showing the volume fraction of water.
Seen here, is a water/air system. From left to right, these plots represent the same 2 cm square at time t = 0, 0.3, 0.5, and 0.7 seconds. Red is completely water, white is anything with a water volume fraction less than 0.5, and the rainbow is anything in between. This shows distinctly the water and air phases as well as the interface between them. This type of model can be helpful in finding more about the interface between the 2 fluids.

Figure 21 - Volume fraction of water in water/air system
After this the model for the foam was built. The geometry is shown below.

![Figure 22 - Small scale model geometry](image)

The lower block is the foam while the top is the open channel. Unfortunately, once porous media is added the solution no longer converges. This could be a crucial simulation into understanding the interface from free flow into the foam, and should be looked into further by a future researcher.
Appendix: 2 Intro to COMSOL for new users

COMSOL Multiphysics is a platform for modeling a multitude of processes. With COMSOL you can determine fluid flow profiles, heat fluxes through a microchip, or simulate reactions on a catalyst. It is an incredibly powerful piece of software. This appendix will walk through the basic steps of setting up a simulation and some of the things possible with COMSOL.

How COMSOL works

COMSOL works by solving differential equations to characterize phenomena. When told set what physics to simulate, COMSOL finds the differential equations needed to solve for those physics. Setting geometries, properties, and boundary conditions tells COMSOL what variables are known. COMSOL solves for the remaining variables and will give flow profiles, heat flux rates, or species concentrations.

Model Wizard

The model wizard will assist in beginning a new model from scratch. For an example, this appendix will build a simulation for the fluid flow through a vertical channel using the Laminar Flow physics. First, the dimensions to simulate in must be chosen. The example will use 2D. While 3D would give more information, it will also take much longer to simulate. Symmetric dimensions might also be chosen if the model will be symmetric. This will help to eliminate excess time for calculation.

Selecting next will bring up a new screen to pick the physics to be simulated. There are many available. If the one needed is not here it may be found in another module available from the COMSOL parent company. Selecting a
physics will provide a short summary of what is simulated to the right. Multiple physics can be joined together if there are multiple process needed. This example will use the Laminar Flow physics.

Next will be the study selection. There are many available with stationary and time-dependent being the most utilized. This example will choose the stationary study to find what happens at steady-state. This will eliminate the time variable from the necessary differential equations. Clicking done will bring up the model home page.

**Model Home**
Below is the model page. Designated are the model builder, settings window, and graphics window. The model builder houses the nodes that will are the road map for the model. Nodes will contain the physical geometries, boundary conditions, materials details, and more. The settings window is where the specific pieces are modified. A rectangle from the geometry is defined or properties for a material are expressed. The graphics window shows the model, the geometry, or simulation results.
Adding variables
It is good practice to add variables that will be needed in multiple parts of the model to the Global Definition node. Right clicking the node and selecting variables will allow for adding the variable name, value and units, and a description of that variable. Below is a small example.
Equations or explicit values can be entered into the Expression field. Units must be included using brackets.

**The Geometry Node**

The geometry node is used to build the physical pieces of the model. Right clicking the node will bring up a menu of items that can be built. This changes
according to what dimension is being used. A circle in two dimensions is a sphere in three.

Figure 25 - Selecting geometry

Selecting an object will open the settings window for that object. Here the size and location of the object can be changed. Selecting build selected will show this piece in the graphics window on the right.
Figure 26 - Geometry settings

Multiple objects can be built, but the “Build All Objects” button must be used in order to build everything together. There are more advanced building options like merging two blocks together, adding filets, points for measurements, and a parts library of pre-built objects that might be helpful.

Materials
COMSOL needs material properties to solve the given equations. In the laminar flow example, the fluid density and viscosity are necessary to solve the Navier-Stokes equations. Adding a material that has the properties is a good way to do this. Right clicking the materials node and selecting add material will open a menu of preprogrammed materials. This example will use water.
If the desired material is not available, then right click the material node and selecting “Blank Material”.

*Figure 27 - Adding materials*
Figure 28 - Adding blank materials

A settings window will appear where different properties can be entered in for the material.
COMSOL has already determined what properties are needed for the model to run. As mentioned, density and viscosity are required for the laminar flow physics. Using the material properties dropdown, more properties can be added, though for this model they would be superfluous.

If there are multiple geometries used in the model, different materials can be assigned for different parts. Be sure that the right materials are linked to the right part of the geometry. Here that is not an issue as there is only one part and only one material.
The physics node
The physics chosen previously will be displayed below the materials node. In this example, that is the laminar flow node. This node is where boundary conditions will be applied. There are some predetermined boundary conditions, but more will likely need to be added. In this example, an inlet and outlet condition will need to be applied.

Figure 30 - Adding boundary conditions

There are many boundaries that can be used. For the laminar flow physics, these boundaries have to deal with the Navier-Stokes equations. Once a boundary condition has been chosen and the value determined, that condition must be applied to the model. Looking at the graphic window, the user can select what interface or domain the condition should be applied to. Here, the top of the
column will become the inlet with a velocity magnitude of \( \frac{3 \text{ m}}{\text{s}} \). The bottom has been set as an outlet.

In this condition, a predefined variable, \( U = \frac{3 \text{ m}}{\text{s}} \), was used to defined the velocity boundary condition. The blue line indicates where this was applied. This can also be seen in the boundary selection list in the settings window. The boundary is listed as number 3.

**Mesh**

The mesh tells COMSOL how many different places to calculate the given equations. Each new mesh piece is new geometrical information to enter. This means that a course mesh with few pieces will take less time to calculate but will also be less accurate. On the other hand, a finer mesh will take more time to calculate.
calculate but will be more accurate. If the geometry being simulated is complicated, then a finer mesh will be needed to calculate the intricacies involved. If the geometry is relatively simple, then a normal or even course mesh will be fine. Selecting the mesh node will bring up the settings window. There is a dropdown here the indicates the various element sizes: extremely fine, extra fine, finer, fine, normal, course, courser, extra course, and extremely course. Selecting one of these and clicking “Build All” will build the desired mesh. This example uses a normal mesh as it is a simple geometry.

![Mesh diagram](image)

*Figure 32 - Mesh diagram*
The study type determines how to solve the equations. A stationary study will set the time variable to zero and solve explicitly for the remaining variables. Below is equation 2, the Navier-Stokes equation with this time variable circled.

\[
\rho \left( \frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} + v_z \frac{\partial v_x}{\partial z} \right) = -\frac{\partial p}{\partial x} + \mu \left[ \frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} \right] + \rho g_x
\]

If a time-dependent study was selected, then this variable needs to have set values for solving the equations.

**Figure 33 - Time-dependent setting range**
Shown above, the range must be selected for the time parameter. This tells COMSOL how what time to start the simulation, what time step to take, and at what time to end it. In the example above, the simulation will start at time zero, use 0.1 second time steps, and end at time one second.

Using a time-dependent study will also allow for changing boundary conditions during the simulation. For this there needs to be another step added to the time-dependent study. Find the study tab in the ribbon at the top, selecting study steps, and selecting time-dependent will add this step.

Clicking Step 2 will open the settings window. Open the dependent variables, changing the settings to “User Controlled”, changing Method to “Solution”, and Study to “Study 2 Time Dependent” will accomplish this.

*Figure 34 - Adding time dependent step*
Now the two steps can be set at separate time intervals for when the boundary conditions will change. Changing the initial values for the second step will force the step to pick up where the last step stopped. To change the boundary conditions between steps simply select the step and check the box labeled “Modify physics tree and variables for study step”. This allows for enabling or disabling boundary conditions and variables. For instance, the inlet velocity may be disabled for the second step. This will, after the duration of the first step, turn off the condition allowing flow through the pipe.

**Results**

After the model has finished calculating the results, the user can add new plots and make animations to represent the results. In the continued example of laminar fluid flow, the default plot is a velocity surface plot. Using a color scale, this shows the magnitude and gradient of the velocity profile.

![Example velocity plot](image)

*Figure 35 - Example velocity plot*
The picture has been zoomed in to show that since the wall has a no-slip condition applied, there is in fact no fluid flowing along the wall; however, in the middle of the channel the velocity is $3 \, \frac{m}{s}$.

Right clicking the Velocity node shows the other available plot types. Selecting the arrow surface plot will add arrows to the surface plot showing the direction of fluid flow.

![Example arrow plot](image)

**Figure 36 - Example arrow plot**

Shown above is the menu of different available plots as well as a portion of an arrow plot.

If a time-dependent study was selected, then there will be a plot for every time step. These can be put into a single animation to show how the flow profile changes. Selecting animation to player from the ribbon will put together the animation.
The settings can be changed in the settings window. The amount of frames available to use is equal to the amount of time steps used in the calculation. The default amount of frames is 25, but this can be changed to use more, less, or all of the time steps. In addition, it is possible to select exactly what time steps are to be animated.
Figure 38 - Animation settings
Bibliography
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