Modeling Flow through a Fixed Bed Packed Reactor

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Abstract

A fixed-bed flow reactor packed with activated carbon has been modeled using COMSOL Multiphysics. Fixed beds are used to test the performance of adsorbents for sulfur removal from liquid transportation fuels for fuel cell applications. Assuming a uniform velocity profile across the bed implies that Darcy's Law expressions can be used to model the pressure drop across the reactor. Carmen-Kozeny equations were used to determine the permeability of the packed bed. The permeability results were used in subsequent modeling scenarios and hand calculations. For the given system, the solutions obtained using COMSOL agreed with validation calculations of Darcy's Law. Finally, a parametric study demonstrated the effect of smaller particle sizes and higher liquid fuel flow rates on pressure drop in the reactor. This model can be used and built upon to evaluate a number of different materials, conditions, and reactions.

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Introduction

The removal of sulfur from liquid transportation fuels has become an important topic due to the growing demand for more environmentally friendly liquid transportation fuels and the interest in fuel cell technology for stationary and portable fuel cell applications[1-3]. Adsorptive desulfurization processes can be achieved at ambient temperatures and pressures, thus, less energy is required[4]. Moreover, adsorptive desulfurization is a means to remove sulfur without hydrogen, which is expensive and impractical for portable fuel cell applications where fossil fuel reforming processes will be the source of hydrogen. Since sulfur poisons the fuel processing and reforming catalysts and also the fuel cell electrode catalysts, the hydrocarbon feed should have essentially zero sulfur[5].

For these reasons, research on materials for adsorptive desulfurization is an important topic. Several materials have been developed and studied by the Clean Fuels and Catalysis Research Group at the Penn State EMS Energy Institute. In order to investigate the sulfur removal potential of these materials, batch and flow tests are conducted to test the thermodynamics and kinetics, respectively. Flow tests are carried out in a small, 2.49 ml stainless steel column packed with the adsorbent material, as described in Figure 1.

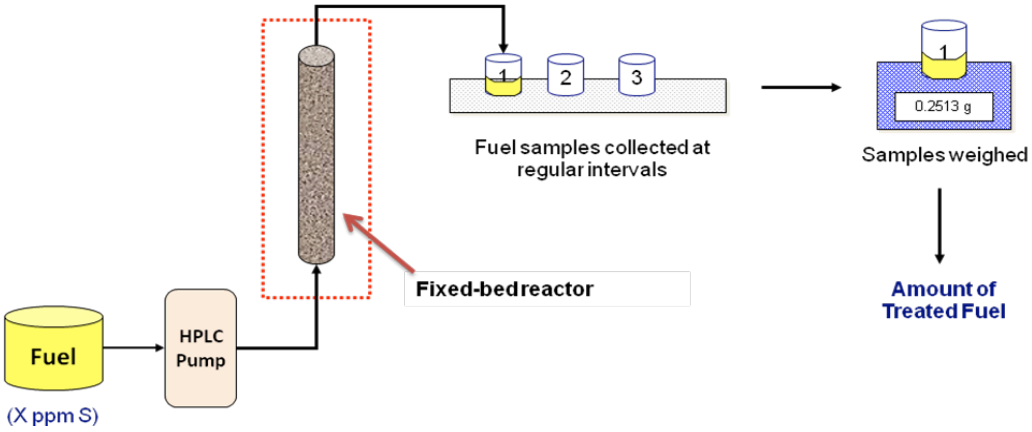


Figure 1. Schematic of fixed-bed flow system experiment

During the experiments, fuels are fed at various temperatures and low flow rates (as liquid hourly space velocities) through columns packed with materials that can vary greatly in physical properties such as particle size and surface area. For packed beds, high surface area materials are desired to provide a larger area for the reaction to occur[6]. Thus, an ideal reactor design will allow maximum contact between liquid and solid adsorbent. One engineering issue that should be considered for these flow tests is aspect ratio, which is the ratio of the dimensions of the column to the size of the particles inside[7]. The overall, axial, and radial aspect ratios should be considered, so that minimum values are achieved in order to avoid diffusion and mass transfer problems[7].

Granular activated carbon (GAC) is a porous material that is useful for many environmental separation processes, including desulfurization of transportation fuels, due to its high surface area and large pore volumes. Sulfur compounds in diesel fuel can be selectively adsorbed due to the polarity of the refractory sulfur compounds and particularly the 4,6-dimethyldibenzothiophene (4,6-DMDBT), which is especially difficult to remove by hydrodesulfurization (HDS) and other conventional desulfurization approaches[8, 9]. This study will focus on the engineering aspects of liquid diesel fuel flow through a column packed with activated carbon.

Governing Equations

The two basic equations that govern the flow of liquid fuels through a bed of packed, solid particles are the Diffusion equation (1) and the Navier-Stokes equation for an incompressible fluid. The Navier-Stokes equation is an expression of conservation of momentum as is presented as Equation (2).

$$(1)\quad \frac{\partial ci}{\partial t} + \nabla \cdot \left(-D_i \nabla c_i\right) = R_i$$

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

As the ratio of the column geometry to the particle geometry exceeds a minimum value, plug flow and a uniform velocity distribution across the column can be assumed. This velocity is expressed by Darcy's Law, which describes the velocity field through a porous medium by using average flow variables over a unit volume.

$$(3)\quad q = -\frac{\kappa}{\mu} \nabla p$$

In this expression, q is the Darcy velocity, κ is the hydraulic permeability of the porous material, and μ is the dynamic viscosity.

In COMSOL, the Chemical Engineering Module combines Darcy's Law and the Continuity equation as Equation 4, where ρ is the density of the fluid and ε is the porosity:

$$(4)\quad \frac{\partial}{\partial t}(\rho \varepsilon) + \nabla \cdot (\rho q) = 0$$

Results

Boundary Conditions

In order to model the flow of liquid through a packed bed reactor, a 2D element with axial symmetry was drawn, as shown in Figure 2.

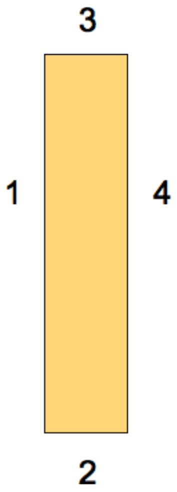
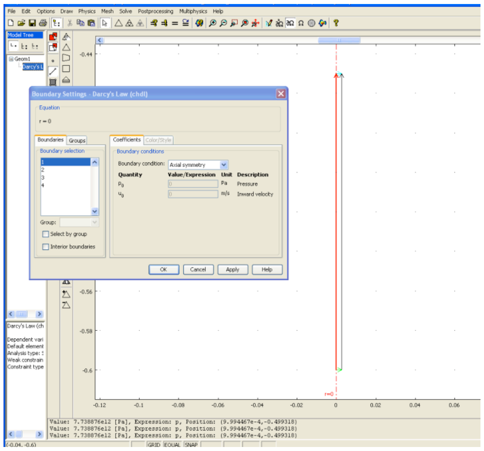


Figure 2. Schematic diagram of stainless steel column.



Boundary Settings - Darcy's Law (chdl)

Equation

r = 0

Boundaries | Groups

Boundary selection: 1, 2, 3, 4 (1 selected)

Group:

☐ Select by group

☐ Interior boundaries

Coefficients | Color/Style

Boundary conditions

Boundary condition: Axial symmetry

Quantity	Value/Expression	Unit	Description
p_0	0	Pa	Pressure
u_0	0	m/s	Inward velocity

Darcy's Law (ch

Dependent vari
Default element
Analysis type: S
Weak constrain
Constraint type

```
Value: 7.738876e12 [Pa], Expression: p, Position: (9.994467e-4,-0.499318)
Value: 7.738876e12 [Pa], Expression: p, Position: (9.994467e-4,-0.499318)
Value: 7.738876e12 [Pa], Expression: p, Position: (9.994467e-4,-0.499318)
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Figure 3. Model setup of stainless steel packed column.

Darcy’s Law can be modeled using the Chemical Engineering Module for COMSOL Multiphysics. The reactor is drawn using 2-Dimensional axial symmetry around side #1, with inflow and outflow velocity at sides #2 and #3 at 0.0005 m/s. The outer edge (#4) is an insulation/symmetry boundary. The boundary conditions and subdomain settings, which describe the fluid and material properties and sources and sinks, are detailed in Tables 1 and 2.

Table 1. Boundary Conditions for Darcy’s Law

Boundary Conditions	
1	Axial symmetry
2	Inflow = 0.005 m/s
3	Outflow = -0.005 m/s
4	Insulation/symmetry

Table 2. Subdomain Settings for Darcy’s Law.

Subdomain Settings			
ρ	Density	0.8	kg/m^3
κ	Permeability	1.88x10^{-11}	m^2
μ	Dynamic Viscosity	.0024	Pa·s
F	Source Term	0	kg/(m^3·s)

Assuming a column volume of 2.49 mL and a length of 0.15 m, the inlet liquid flow rate of 0.05 mL/min was converted to a velocity of 0.0005 m/s.

Table 3. Void Data. Experimental data for packing density of stainless steel columns packed with activated carbon.

	Test 1	**Test 2**	**Average**
AC (g)	0.8128	0.8069	0.8098
Fuel (g)	0.5627	0.4937	0.5282

The activated carbon was a commercial material called MaxZorb. The average particle size (d_p) is about 50 microns ($50x10^{-6}$ m). The calculations assume the density of activated carbon and the liquid fuel are about equal, at 800 kg/m3, or 0.8 g/mL. Experiments show that one 2.49 column can be packed with 0.81 grams of activated carbon, so the volume occupied by the material is 1 mL. Therefore, the void volume is 1.49 ml, or $\varepsilon = 1.49/2.49 = 0.60$.

If the fluid density is 0.8 kg/m^3 and the kinematic viscosity is 3 cSt ($3x10^{-6}$ m^2/s), the absolute viscosity is 0.0024 Pa·s.

Laminar flow is assumed, since the Reynolds' number is 0.008, which is much less than 1. The Reynolds' number was calculated using Equation 5:

$$(5)\quad \mathrm{Re} = \frac{d_p u_o \rho}{\mu}$$

$$\mathrm{Re} = \frac{\left(50x10^{-6}m\right)\left(.0005\frac{m}{s}\right)\left(.8\frac{kg}{m^3}\right)}{\left(2.4x10^{-6}\frac{kg}{m\cdot s}\right)} = .0008 < 1$$

For Reynolds' numbers less than 1, the permeability of the porous media and the pressure drop across the bed can be calculated using the Carman-Kozeny equation and Darcy's Law[6]:

$$(6)\quad \frac{\Delta p}{L} = 5\frac{(1-\varepsilon)^2}{\varepsilon^3}\mu v\left(\frac{6}{d_p}\right)^2$$

$$\frac{\Delta p}{L} = 5\frac{(1-.6)^2}{0.6^3}\left(.0024\frac{kg}{m\cdot s}\right)\left(0.0005\frac{m}{s}\right)\left(\frac{6}{\left(50x10^{-6}m\right)}\right)^2 = 64000\frac{kg}{m^2\cdot s^2}$$

For a bed length of 0.15 m, the pressure drop can be calculated as follows:

$$\Delta p = \left(64000\frac{kg}{m^2\cdot s^2}\right)(0.15m) = 9600\frac{kg}{m\cdot s^2} = 9600\ Pa = 0.095\ atm$$

The permeability input value for COMSOL was calculated using Equation 7, the Carman-Kozeny equation, where K is the Kozeny constant, which is 5 for fixed beds[6].

$$(7)\quad k = \frac{\varepsilon^3}{K(1-\varepsilon)^2\left(\frac{6}{d_p}\right)^2}$$

$$k = \frac{.6^3}{5(1-.6)^2\left(\frac{6}{50x10^{-6}}\right)^2} = 1.88x10^{-11}m^2$$

Table 4. Packed bed modeling conditions.

	Property	**Value**	**Unit**
d_p	Particle size	$50x10^{-6}$	m
u	Inlet velocity	.0005	m/s
V	Column volume	2.49	ml
ε	Void fraction	0.60	
ρ	Liquid density	0.8	kg/m^3
μ	Dynamic viscosity	.024	g/cm·s
μ	Dynamic viscosity	.0024	Pa·s
v	Kinematic viscosity	3.0	cSt
v	Kinematic viscosity	$3x10^{-6}$	m^2/s
k	Permeability	$1.88x10^{-11}$	m^2

Solution & Validation

Modeling results indicate that the pressure drop across the bed will vary from 1.069 atm at the inlet to 0.974 atm at the outlet. Therefore, the pressure drop across the bed is 0.095 atm. This is the same as the calculated value for the pressure drop across a bed length of 0.15 m using the Carmen-Kozeny equation and Darcy's Law.

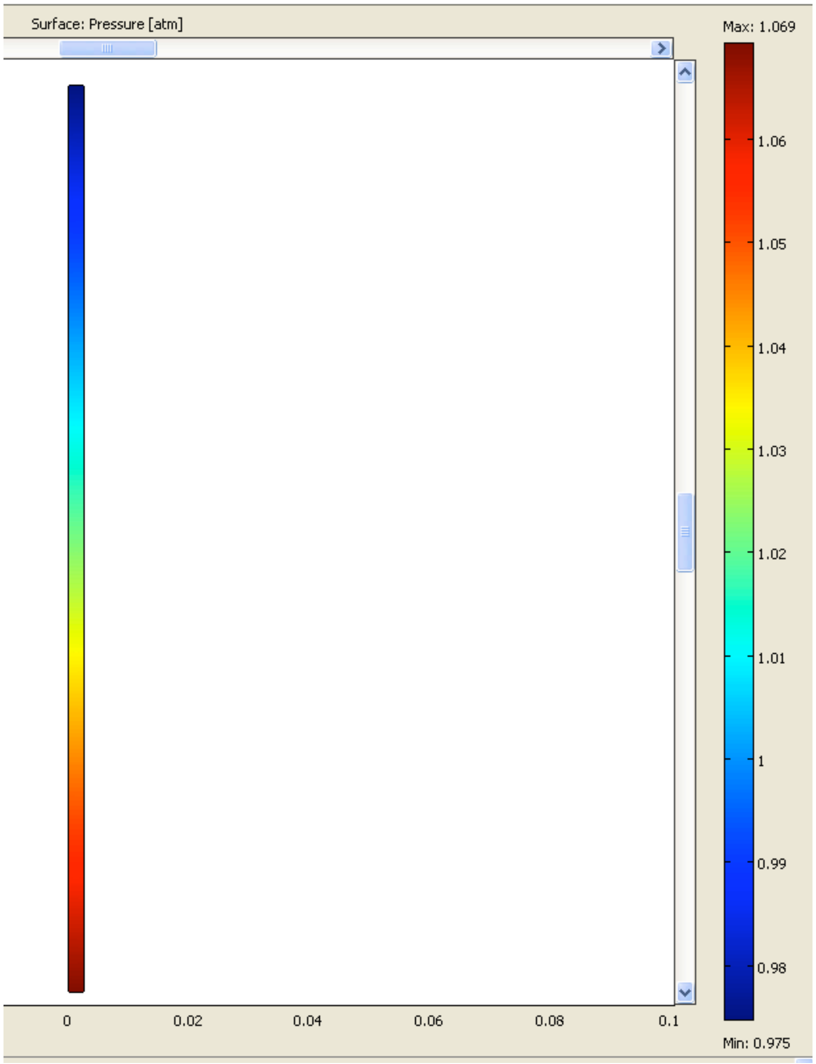

Figure 4. COMSOL model of pressure across reactor. *For the given conditions, the minimum and maximum pressure are 0.974 atm and 1.069 atm, respectively.*

Parametric Study

The goal of the parametric study is to determine how input variables affect the pressure drop across the packed bed. This information is useful in determining how pressure will change when scaling up reactors for industrial applications. Furthermore, these models can be used to show how changing physical properties of the adsorbent, such as density and particle size, will affect reactions in the lab. For this reason, the parametric study focuses on varying the particle size and liquid fuel flow velocity to determine the pressure drop across the bed. For our group research lab at the Energy Institute, typical feed flow rates can range from 0.05 ml/min to 1.0 ml/min and above. Currently, 0.05 and 0.20 ml/min flow rates are used, but the flow can easily be increased to 1.0 or 2.0 ml/min. Also, particle sizes can range greatly by an order of magnitude or more. Since the flow was not a problem at the particle size chosen for this study, the parametric study examines if/how smaller particle sizes affect the pressure drop.

Variations in particle size and flow velocity affect the permeability calculation and the input velocity. A table of the scenarios and calculated input parameters is shown below. Minimum and maximum pressures at the outlet and inlet, respectively, were extracted and tabulated in order to determine the pressure drop for each scenario.

Table 5. Scenarios and parametric study results for pressure drop across packed bed.

Case #	Flow Rate (ml/min)	Velocity (m/s)	Particle Size (m)	Permeability (m^2)	Max (atm)	Min (atm)	Pressure Drop (atm)
1	0.05	0.0005	5E-05	1.875E-11	1.069	0.974	0.095
2	0.20	0.002	5E-05	1.875E-11	1.278	0.9	0.378
3	1.00	0.04	5E-05	1.875E-11	6.56	-0.999	7.559
4	0.05	0.0005	5E-06	1.875E-13	8.095	-1.34	9.435
5	0.20	0.002	5E-06	1.875E-13	29	-8.4	37.4
6	1.00	0.04	5E-06	1.875E-13	569	-187	756
7	0.05	0.0005	5E-07	1.875E-15	770	-174	944
8	0.20	0.002	5E-07	1.875E-15	2736	-1042	3778
9	1.00	0.04	5E-07	1.875E-15	5470	-20890	26360

Conclusions

Results indicate that COMSOL can be a useful tool to model adsorbents packed in a small, fixed bed reactor for adsorptive desulfurization of liquid transportation fuels. The solutions obtained for pressure drop across the fixed bed are consistent with hand-calculations for Darcy's Law. In order to model the pressure drop, the following adsorbent properties should be known: void space, density, and porosity. Required fuel properties include liquid density and fuel flow rate.

Now that the tools and template have been developed, further studies and development of the model can be performed. It may be useful to model the behavior of flow on a larger scale to see how the materials in our lab will behave on an industrial scale. Additionally, it would be very interesting and useful in incorporate surface reactions and sulfur adsorption within the reactor systems.

A parametric study showed that both the particle size and fuel flow rate begin to strongly affect the pressure drop across the bed, even for only slightly higher flow rates and for smaller particle sizes. Therefore, the aspect ratio, an engineering parameter determined by the particle size and also the bed dimensions, will indeed affect the pressure drop or Darcy velocity of the system. The system is more strongly affected by the particle size than the fuel flow rate.

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