Adsorptive Desulfurization of Liquid Hydrocarbons: Langmuir Adsorption Modeling Using COMSOL

Abstract:

In this paper, adsorption modeling based on Langmuir adsorption isotherm using COMSOL is discussed. The solution to the model was built starting from a simple one component adsorption with a pulse feed to a two component adsorption with continuous feed in 2 D model. Modeling was to represent adsorption removal of sulfur compounds from a fuel containing other aromatic compounds. Fuel being a mixture of numerous components the model was simplified to a two component system representing sulfur and an aromatic compound. Breakthrough profiles were obtained for adsorption in the 2 D model and were compared with the data available in literature. Because basic studies done with regards to Langmuir adsorption are not plenty, validation was done by comparing the breakthrough profiles obtained. Also the effect of varying the surface area of the adsorbent was also studied. The model seem to represent closely the breakthrough profiles of aromatic and sulfur compound but more systematic study needs to be done experimentally in order to determine the parameters involved with the Langmuir adsorption. Nevertheless, the model helps one to simulate experiments on computer rather than repeating experiments where lot of time and money will be involved. But for obtaining a more realistic model, one needs to eliminate a few of the assumptions that were considered in the model like treating of the adsorbent as an unstructured homogenous medium, equilibrium between the adsorbent and the adsorbate is immediate. With all these assumptions, comparable breakthrough profile with literature was obtained.

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1. Introduction:

Adsorption is and is also emerging in a few areas as one of the desired unit operation because of its simplicity, lower energy consumption and also to meet the stringent environmental legislations [1, 2]. Few examples include softening of water using zeolite based material, adsorption of CO_2 and H_2S by suitable adsorbents, demetallization of waste streams from the industries, adsorbents for pre-treatment of fuels for fuel cell applications [4-15].

Research on adsorption desulfurization of liquid fuels has gained much of importance over the past decade. This is partly due to the strict environmental legislations that are been implemented by EPA for SO_x emission which are the precursors for acid rain and also the limitations of the current refinery process "Hydro-desulfurization of diesel fuels (HDS)" for sulfur removal. This process is a high pressure and high temperature process which utilizes hydrogen to remove the S (sulfur) compounds present in the fuel. The EPA regulation for S limit in diesel fuel in the year 2002 was 500 ppm. But the regulations in the year of 2005 and 2006 were 30 and 15 ppm each. The last few ppm S compounds in diesel fuel are not catalytically active in the process and attempts are made to vary the reactor configuration, increasing H_2 pressure etc [18]. To overcome the issue involved with HDS, researchers have been working on adsorption desulfurization of S compounds with various adsorbents [1, 2, 15, and 16]. But selectivity of the process towards sulfur compounds is a big issue. S to be removed is in ppm levels where as aromatics present are in the range of 25-35% in middle distillates. There are many adsorbents that have been developed for adsorption of desulfurization on a lab scale but have not been commercialized on an industrial level [16, 17]. Although, adsorption is not energy intensive as the HDS process, it still has the selectivity issues that have not been discussed in research articles clearly [17].

So the objective of this project is to come up with a physical description of the adsorption behavior of sulfur and aromatic compound in paraffin. An adsorbent that is not highly selective towards sulfur compounds (activated carbon) will be considered. Equal - molar concentration of sulfur and aromatic compounds will be considered to begin with. It will be assumed, that the law of conservation of mass will be conserved since the amount of the solvent which will be paraffin in this case is much larger that the solute which is to be adsorbed is present. It will be assumed that the column will be homogeneous, isothermal with respect to conditions etc. Also few of the experimental data like adsorption equilibrium and mass transfer coefficient might not be available readily from literature, so related realistic assumption might be applied here also for example dispersion coefficient might not be available in literature.

The objective of the work is not to criticize the work that has been going on in the area of adsorption desulfurization but it is to realize the issues that are associated with the process such as selectivity and model fuel that are been considered by researchers. It is hoped with the help of COMSOL and other related equations, this objective can be projected, from a perspective of hydrodynamics. The basic idea is to obtain the amount of S compounds that will be adsorbed from the paraffin against the aromatics by giving a physical picture.

2. Governing equations

The solid adsorbent considered in the adsorption modeling was assumed to be a homogeneous medium leading to an assumption that the adsorbent is packed uniformly through the reactor. To make the simulation simpler, differential mass balance in the liquid phase was considered with immediate equilibrium assumption which means that the equilibrium for the component between the adsorbent (solid phase) and the solvent (liquid phase) is immediate. Also the viscous force around the adsorbent due to the flow of the feed was neglected. This allows one to have a combination of equation comprising of the solid and liquid phase concerning equations. The mass balance in the liquid phase is given by

$$\frac{\partial c_i}{\partial t} + S.\rho \frac{1-\varepsilon}{\varepsilon} \frac{\partial q_i}{\partial t} + \frac{\partial}{\partial x}(-D_x \frac{\partial c_i}{\partial x}) + \frac{\partial}{\partial y}(-D_y \frac{\partial c_i}{\partial y}) = \frac{D_y}{y} \frac{\partial c_i}{\partial y} - \frac{u}{\varepsilon} \frac{\partial c_i}{\partial x} - \frac{v}{\varepsilon} \frac{\partial c_i}{\partial y}$$

Equilibrium between the solid and liquid phase is given by

$$\frac{\partial q_i}{\partial t} = \left(\frac{dn}{dc}\right).\frac{\partial c_i}{\partial t}$$

Thus the mass balance in the liquid phase becomes

$$\frac{\partial c_i}{\partial t} + S.\rho \frac{1-\varepsilon}{\varepsilon} \left(\frac{dn}{dc}\right).\frac{\partial c_i}{\partial t} + \frac{\partial}{\partial x}(-D_x \frac{\partial c_i}{\partial x}) + \frac{\partial}{\partial y}(-D_y \frac{\partial c_i}{\partial y}) = \frac{D_y}{y} \frac{\partial c_i}{\partial y} - \frac{u}{\varepsilon} \frac{\partial c_i}{\partial x} - \frac{v}{\varepsilon} \frac{\partial c_i}{\partial y}$$

The dispersion coefficient in the equation can be determined by using the theoretical plate equivalent for the column and with velocity of the feed through the column.

Dispersion coefficient is give by $Hv/2$

It was assumed that both the components assume Langmuir adsorption isotherm, according to which the relationship between the concentration of the component in solvent and that of the monolayer capacity of the column is given by [21]

$$q_i = \frac{q_{oi} K_i c_i}{1 + K_i c_i}$$

And

$$\frac{\partial q_i}{\partial c_i} = \frac{n_{oi} K c_i}{(1 + K_i c_i)^2}$$

Input to the column was pulse and continuous in some cases which are given by

$$0 < t \le t_{pulse}, c_1 = c_{1o}; c_2 = c_{2o}$$

$$t > t_{pulse}, c_1 = c_2 = 0 \text{ For the pulse input}$$

And

$$0 < t \le t_{reactiontime}, c_1 = c_{1o}; c_2 = c_{2o}$$

c_i	Concentration of the components in the fluid phase
q_i	Concentration of the components in the solid phase
q_{0i}	Monolayer capacity of the adsorbent for the component
D_x, D_y	Axial and Radial Diffusion Coefficient
u, v	Horizontal & Vertical fractions of velocity
t	Time
K_i	Adsorption equilibrium coefficients of the components
k_i	Mass transfer coefficient of the components
x, y	Horizontal & Vertical co-ordinates
P	Pressure
ε	Bed voidage

Thus the Navier Stokes equation which was supposed to be included in the simulation was dropped assuming that change in concentration is same throughout the column at one point radially. This assumption sounds reasonable as the variation in breakthrough profile at the wall and at the center of the reactor was less when Navier Stokes equation was considered in the linear adsorption isotherm project done last year.

3. Formulation:

A reactor with L/D ratio of 300 was considered which was a fixed bed reactor with uniform packing of the adsorbent. The inlet of the reactor was set to a continuous supply of the feed which was set with the help of the boundary conditions. In the case of pulse feed, concentration at the entrance of the reactor at $t > t_{pulse}$ was set to zero. The walls of the reactor was insulated which implies that there was no concentration gradient at the walls. The reactor is assumed to be isothermal through the process. The outlet of the reactor was set to convective flux. With the above constraints, the convection and diffusion model in the chemical engineering module under mass balance seem to be the best fit. This is an application mode with flux, insulation and concentration boundary conditions. The reactor schematic looks like the one as shown in the figure below.
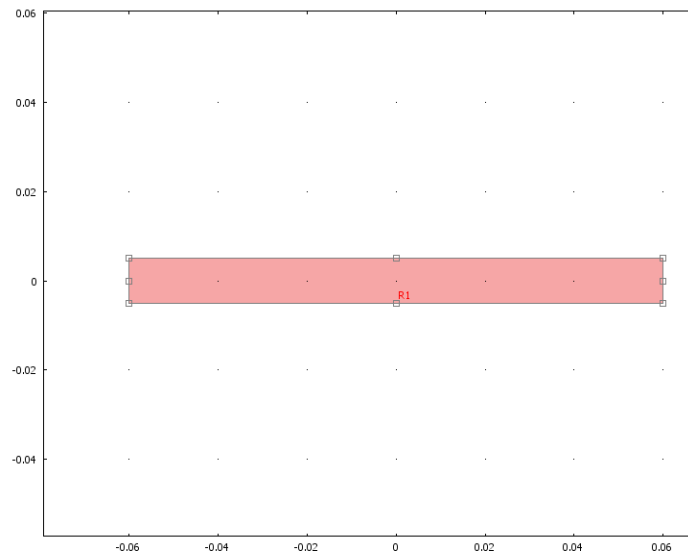

Figure 1 Geometry obtained from COMSOL representing an adsorption column

The top and bottom walls of the reactor represent the walls that are insulated. The components to be adsorbed and the adsorbent that was used were represented by their physical properties. These physical properties are built in the mass balance equation which was discussed in the governing equations section.

The Langmuir adsorption equation was fitted in to the scalar expressions available in the option menu under expression as a first derivative of moles with respect to concentration which is represented by

$$\frac{\partial q_i}{\partial c_i} = \frac{n_{oi} K c_i}{(1 + K_i c_i)^2}$$

Then the boundary conditions stated above were fitted in. The adsorption mechanism considered here was physical and the reaction rate was assumed to be zero in all cases. The diffusion coefficient and the velocity in the x and y direction were defined in the constant section. The time scaling coefficient

$$1 + S.\rho \frac{1-\varepsilon}{\varepsilon} \left(\frac{dn}{dc} \right)$$

which is available in the sub domain settings. This represents the coefficient of the time dependent term in the mass balance equation.

The initial conditions for concentration are represented by a normal distribution equation. The total solving time for the simulation was 600 sec and this was adjusted in the solver parameter section.

A basis was considered from which parameters were changed for a parametric study or for some other cases where it was required.

All the units are represented in SI units.

Quantity	Expression
$S.\rho \dfrac{1-\varepsilon}{\varepsilon}$	1.5E8
u	2.2E-3
v	1.1E-3
D_x	1E-6
D_y	1E-3
c_{o1}	1
c_{o2}	1
n_{o1}	1E-6
n_{o2}	1E-6
K_1	.04
K_2	.01

Table 1 Values of parameters used in the simulation

4. Solution using COMSOL:

The above values were the basis which was assumed and various other parametric studies were compared with the output obtained from the simulation with the above values. For the simplified model with only one component, convective flux was obtained along the length of the reactor for different time interval; this is shown in figure below
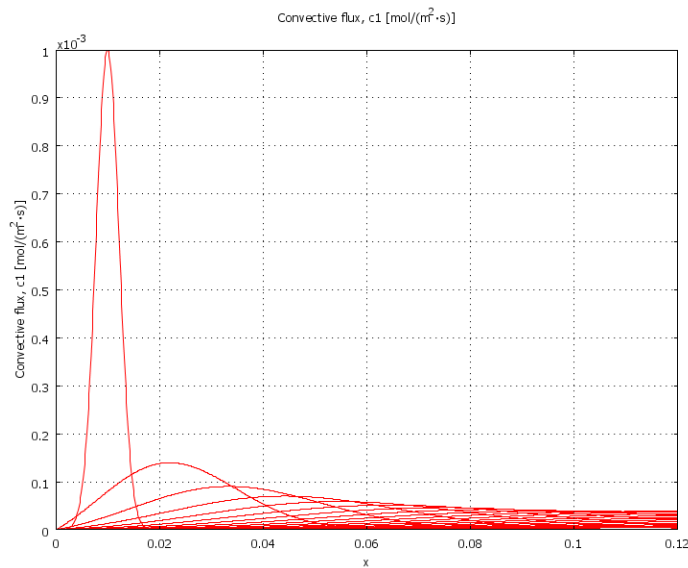

Figure 2 Convective Flux of for different time frames along the length of the reactor for a pulse mode inlet

This was the simplified model with a very large ratio of L/D; here the dispersion along the y direction was neglected. As seen from the figure, the concentration of the component decreases along the reactor with time.

Then the reactor L/D ratio was decreased and the dispersion along the Y axis was also considered. First a one component adsorption was considered followed by a two component adsorption. Then parametric studies were done for different cases. Figure below shows the breakthrough profile for a single component adsorption
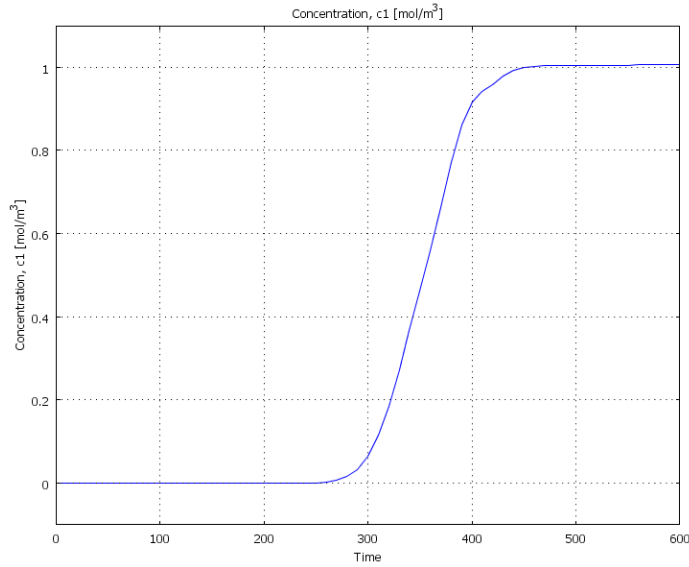
Figure 3 Breakthrough profile for a single component adsorption

As seen from the figure, the component to be adsorbed reaches the break through point at time equal to 270 sec of the reaction time. Then the component gradually reaches its saturation value which is 1 mol/m3 in this case. Also as seen from figure, the concentrations along the length of the reactor at different time intervals are plotted. After the breakthrough point is reached, the concentration of the component at the inlet and outlet of the reactor is the same as the component has reached saturation.
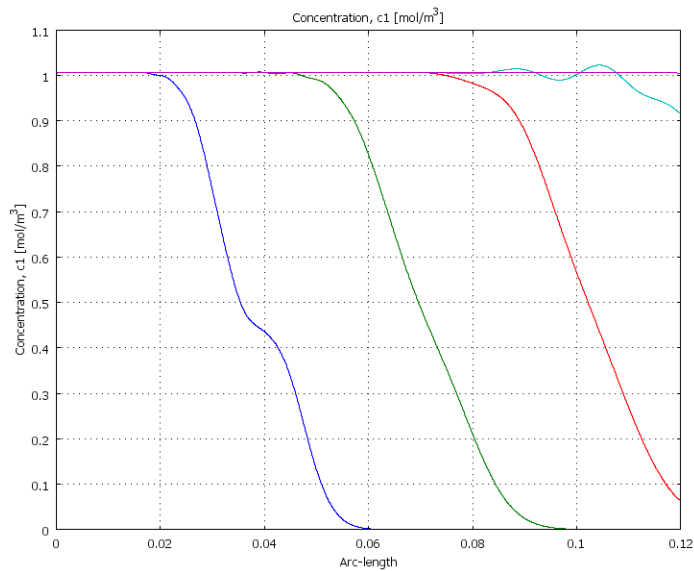

Figure 4 Variation of concentration along the length of the reactor for different times

Then a two component adsorption was considered. The adsorption coefficient of one of the component was 4 times less than the other component to be adsorbed. The break through profile for the two components are shown in figure
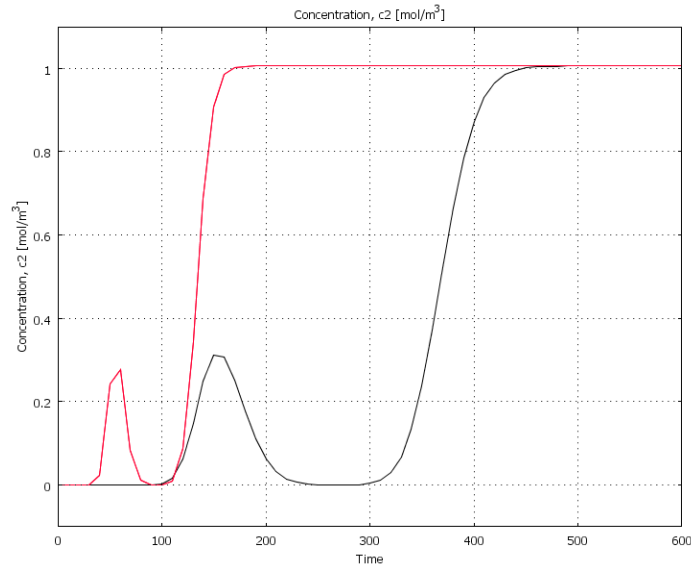

Figure 5 Breakthrough profile for a 2 component adsorption

The line in red represents the second component which is weakly adsorbed because of the lower value of adsorption coefficient. Also during the adsorption, there seems to be some desorption of the both the components followed by adsorption again before they reach saturation. This might be due to the competitive adsorption involved in this case as the both the components scramble for the active sites on the adsorbent. As seen from the figure both the components are adsorbed in the initial stages of the reaction but since component 1 is more selective towards the adsorbent than 2, part of the 2nd component adsorbed is desorbed which can be seen from the first peak in the figure, then adsorption of 2 starts again with elution of component 1. After component 2 has reached saturation, component 1 adsorbs for a longer time and reaches the break through point at somewhere around 300 sec. This implies that component 1 is adsorbed preferentially in comparison with component 2. This preferential adsorption depends upon the values of the Langmuir adsorption parameters which are defined by the chemical interaction between the adsorbent and the adsorbate and also on the physical properties of the adsorbent.

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5. Validation using COMSOL:

The figure above represents the breakthrough profile of 2 components. Ideally it is preferred that component 1 be a sulfur compound and 2 be aromatic compound in a fuel which allows one to adsorb more of sulfur compound from the fuel mixture with less of aromatic or fuel loss. The breakthrough profile obtained represents a typical Langmuir adsorption isotherm curve which can be seen from the reference obtained from literature. The figure below consists of many components that were adsorbed. Due to the time limitation, more than 2 components were not tried as the simulation time will be much larger for many compounds to be adsorbed.
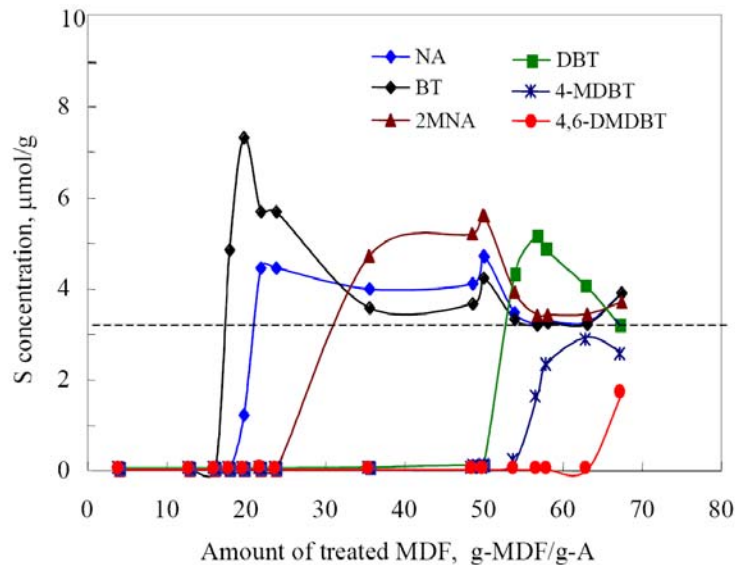

Figure 6 Breakthrough profiles for different components from a model diesel fuel [22]

The above figure represents the breakthrough profile of different components that were considered in a model diesel fuel. As seen from the figure, some of the components elute early than others. Also the breakthrough profile looks similar to the 2 component adsorption seen in figure obtained by COMSOL. With more reliable parameters involved with Langmuir adsorption isotherm which requires experimental data, adsorption experiments can be done with COMSOL instead of carrying out experiments. But it involved tuning of different parameters like the concentration of the components, reactor size etc. But it can be seen from the breakthrough profiles from COMSOL and literature that both the Langmuir adsorption seems to be the best fit in this case.

6. Parametric Study:

Then a parametric study was done by varying the values of adsorption coefficient, the surface area of the adsorbent and also the concentration of the components.

6.1 Varying the adsorption coefficient (K):

The values of the adsorption coefficient for single component adsorption was changed by a value of 4 and the breakthrough profile were compared. This can be seen in the figure below.
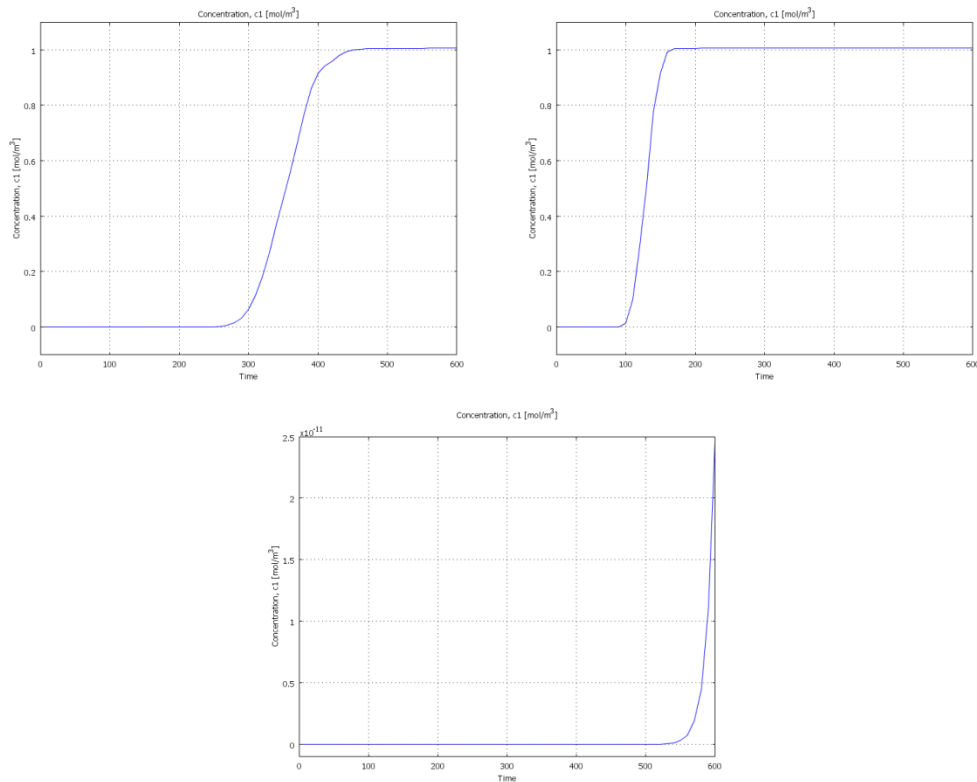

Figure 7 Variation in breakthrough profiles for different values of K

Figure on the top left shows the basis and other two figure represent different values of K. With value of K decreased by 4 times, the breakthrough point is much earlier, this is because of the low adsorption coefficient of the component. The breakthrough point is at 90 seconds when compared with the basis of 270 seconds. Whereas when the value of K is increased by 4 times, breakthrough point increases to 550 seconds as the number of molecules adsorbed increases with increasing value of K as it represent the ratio between adsorbed and desorbed molecules at equilibrium.

6.2 Varying the surface area of the adsorbent:

The initial surface area of the adsorbent considered in the simulation was 100m2/g. The surface area was changed to 10 and 100 m2/g to check the change in adsorption capacity of the adsorbent in terms of breakthrough profile.
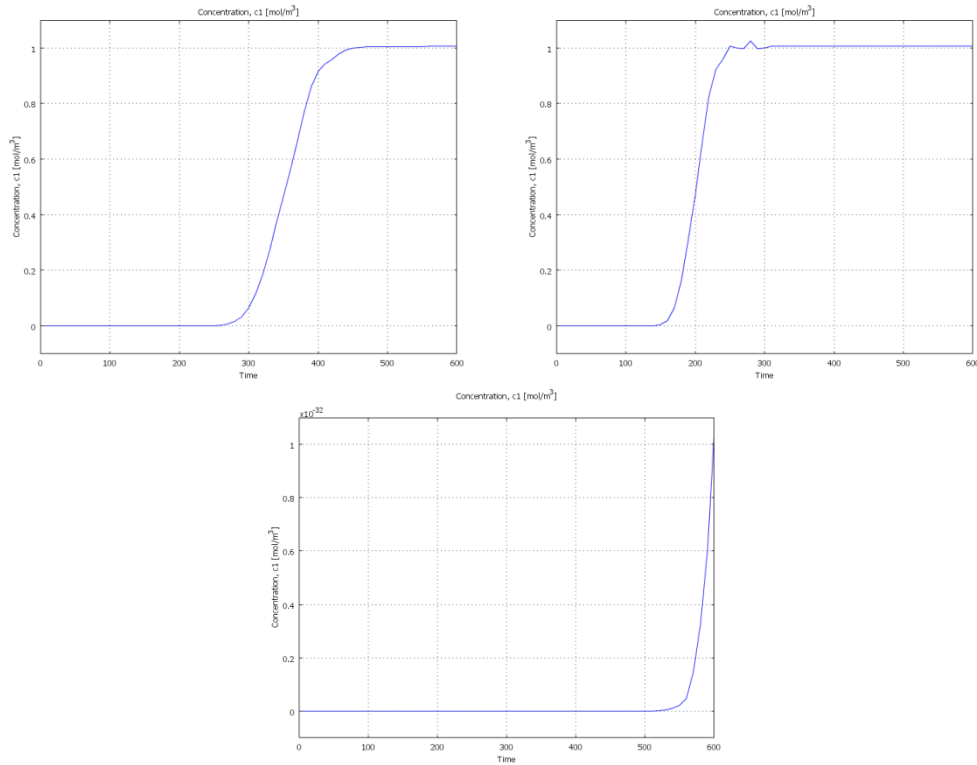

Figure 8 Variation in breakthrough profiles for different values of surface area

By decreasing the surface area of the adsorbent the capacity of the adsorbent for the adsorbate decreases as seen from the decrease and increase in the breakthrough profile as seen from the figure.

6.3 Varying the concentration of the component:

The concentrations of the two components to be adsorbed were kept the same with different adsorption parameters so as to compare the selectivity for adsorption for the two components. The concentration of weakly adsorbed component was increased by 10 times so as to see whether the breakthrough point was influenced by the change in concentration of the compound. This change also enables one to represent the weakly adsorbed compound as a mimic to the aromatics in fuel as these compounds are present in larger proportion when compared with that of the sulfur compounds in fuel.
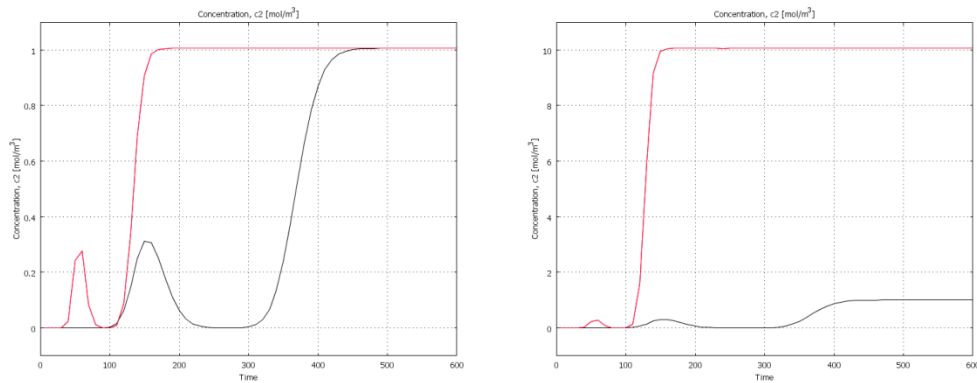

Figure 9 Breakthrough profiles for different values of inlet concentration

As seen from the figure above, variation in breakthrough point was minimal or zero when concentration of one of the component was increased by 10 times. This is interesting because as the concentration of one of the components was increased, there was no change in time it elutes but probably there was an effect on the adsorption capacity of the adsorbent for the component.

7. Conclusion:

COMSOL seem to provide a reasonable breakthrough profile for adsorption behavior. The model was assumed to follow a Langmuir adsorption isotherm pattern. Comparable profiles in terms of breakthrough were obtained using the adsorption isotherm. There were a few assumptions that were considered for the model, like only 2 component adsorption with one having a better selectivity than the other, a homogeneous mixture of adsorbent, the equilibrium between the adsorbate and the adsorbent is immediate. Since a good fundamental study on the adsorption parameters are not readily available, values were to be assumed to get a breakthrough profile. Although the project was carried out with many assumptions, it does show that COMSOL with the help of adsorption parameters can allow one to obtain the variation in concentration in terms of time and also with other parameters which allows one to save both time and money as development of pilot scale plant would involve lot of money. But increasing the size of the reactor and having more constraints in modeling will require a need for a fast processor and also time.

8. References:

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