



Modeling and Simulation of BTX Removal Process from Acid Gas

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Abstract:

Whereas usually about 10-15% of BTX compounds in the sour gas are transferred to inlet acid gas feed of the sulfur recovery unit, these components could poison Claus catalyst if they do not decompose in the furnace of the sulfur recovery unit. This phenomenon is caused a decrease about 85% in efficiency of the sulfur recovery and make Claus process expensive due to frequent catalyst replacement. Separation of these components is carried out by the adsorption as the most optimized process. In this paper, theoretical studies were made on the adsorption of toluene, by activated carbon in an isothermal condition. A mathematical model was developed to simulate the adsorption systems. This model has been simulated by MATLAB and then adsorption breakthrough curves of simulations compared at various operation conditions. The breakthrough adsorption indicates that AC, with an appropriate surface area, could be utilized in adsorption BTX from acid gases.

Keywords: Claus process, BTX, adsorption, AC, modeling

Introduction

BTX (Benzene, Toluene, and Xylene) are common contaminants in Claus plant feed gases originated from associated and natural gases. Whereas the temperature in the Claus furnace is too low for effective BTX destruction, these compounds enter directly to the catalyst beds and sit on active sites and deactivate the catalysts. There are several methods such as condensation, absorption, adsorption, thermal oxidation and catalytic oxidation to control BTX content in contaminated gases[1,2,3,4].

Among the alternatives available, adsorption has received wide attention in the past few years. Moreover this method offers some advantages over the others: the possibility of pure product recovery for reuse, high removal efficiency at low inlet concentrations and low fuel/energy costs[5,6].

Adsorbents used in this process must have a reasonably large micropore volume to adsorb BTX, since the molecular size of these hydrocarbons is within the micropore size range [7]. They must also have a well-developed mesopore network to transport the BTX molecules from the air flow into the microporosity rapidly[5].

Carbon adsorption has these properties and is the best method for BTX emission control[8,9].



It is important to understand the thermodynamic equilibrium relations and kinetic characteristics between the adsorbent used and adsorbates to design the adsorption separation processes [8,10].

However, there appears to be relatively little information in the literature concerning adsorption of aromatic hydrocarbons on activated carbon at room temperature and the isothermal adsorption. Cooney et al. studied multicomponent of aromatic compounds in fixed beds. Basmadjian and Wright performed the experimental nonisothermal desorption for a multicomponent system but they did not investigate the modeling of their experiments [10].

In another work, experimental studies were carried out on the adsorption of aromatic solvents such as benzene, toluene and xylene (BTX) vapors and their binary and ternary mixtures, by activated carbon at 303 K [6]. The experimental and predicted breakthrough isotherms for adsorption of benzene, toluene, DMC, and other organic solvents on Y-type zeolites have also been studied [6].

In the present work, a mathematical model is developed to predict the time-dependent concentration profiles of the adsorbing species in the fixed bed of solid adsorbents under isothermal conditions. Among various methods has been proposed to solve the model the finite difference method was chosen. This model has been simulated by MATLAB and adsorption breakthrough curves of simulations compared at various operation conditions.

Mathematical Modelling

The mathematical model of the BTX adsorption process should include both material and energy equations. In most practical applications, the isothermal condition prevails. For the isothermal process, the energy equation may be omitted.

Material Balances of a Conventional adsorption beds

The mathematical model for predicting the breakthrough characteristics (unsteady-state concentrations) of an adsorbed species in the packed fixed bed with adsorbents investigated that constitutes of three equations for concentration balance: (1) in the bulk gas phase in the bed, (2) in the gas phase within the pore volume of the adsorbents, and (3) on the surface of the adsorbents within the pore volume [10].

The following model equations describe the isothermal and operation of the systems in one dimensional [10,11].

$$1) - D_L \frac{\partial^2 C}{\partial Z^2} + \frac{\partial(uC)}{\partial Z} + \frac{\partial C}{\partial t} + \frac{(1 - \epsilon_b)}{\epsilon_b} \frac{\partial \bar{q}}{\partial t} = 0$$

The terms on the left-hand side of Eq. (1) are dispersion, convection, gas phase accumulation and adsorbed phase accumulation, respectively.

Here D_L is the axial dispersion coefficient in the packed bed, u is the gas velocity, ϵ_b is porosity of the bed and \bar{q} is predicting adsorption equilibrium

The simplest and still the most useful isotherm for both physical and chemical adsorption is the Langmuir isotherm, usually written as:

$$q_{ads} = q_{max} \frac{bP_i}{1 + bP_i}$$

where q is the adsorbed quantity and P is the pressure of the adsorbate in the bulk gas phase. Parameters q_{max} and b are respectively the saturation limit and the Langmuir constant.



Average value of adsorption on the spherical adsorbent particles obtained from the following relationship:

$$\bar{q} = \left(\frac{3}{R_p^3} \right) \int_0^{R_p} r^2 q dr$$

an isothermal and plug-flow system were considered, in which pressure drop in the bed is negligible and there is no variation in the fluid velocity along the bed length. The adsorption equilibrium relationship is represented by the extended Langmuir equation because of its simplicity, and the mass-transfer rate inside adsorbent particle is given by linear driving force LDF.

Boundary conditions are as follow:

$$\begin{aligned} c_1(z=0, t) &= c_0 & z &= 0 \\ \frac{dc}{dz}(z=L, t) &= 0 & z &= L \\ c(z, t=0) &= c_1 & t &> 0 \end{aligned}$$

The above model was solved by finite difference method that the diffusion, convection and accumulation terms were assumed as central, backward and forward differences, respectively

A practical case study

The experimental data for a practical case study was borrowed from[11]. The data corresponds to the adsorption of toluene from natural gas using activated carbon as adsorbent. Evidently, toluene is a very appropriate representation of the BTX components. Because, its volatility, adsorbitivity and all other physical properties are midway between benzen and xylene (or ethyl benzene).

Description of system and data tables:

The equilibrium constants of the Langmuir equation were determined at various temperature and constants listed in Table 1[11].

Table 1: Langmuir Parameters for Toluene Adsorption onto Activated Carbon

$T(K)$	$q_{max,L}(mol\ kg^{-1})$	$10^3 b$
298.15	5.54	28.45
318.15	4.66	20.48
333.15	4.39	8.572

Some of the physical properties of the adsorbent used in this work are listed in Table 2 [11,12]. All experimental conditions of adsorption systems are tabulated in Table 3.



Table 2: Adsorbent Parameters

parameter	value
$\rho_b \left(\frac{kg}{m^3} \right)$	720
$a_p \left(\frac{m^2}{m^3} \right)$	1680
$d_p (m)$	0.002
$d_{pore} (A^\circ)$	0.1
ϵ_p	0.67
	30
$S_{BET} \left(\frac{m^2}{kg} \right)$	1.3e6

Table 3: Experimental Condition

parameter	value
$u_s \left(\frac{m}{s} \right)$	2
$L(m)$	1
$D(m)$	0.05
ϵ_b	0.44

Results and Discussion:

The above mathematical model was used to simulate the adsorption of toluene over activated carbon. The simulation was carried out using MATLAB environment. Figure 1,2 illustrates the predictions of the simulation program for the above case study.

Fig 1 describes the effect of inlet concentration of adsorbates on breakthrough time. It was obvious that the breakthrough times decreased with increasing inlet concentration. Moreover, the breakthrough curves became steeper by increasing inlet concentrations. As observed from the figure 1, curve a is breakthrough curve of toluene at 15 mol/m³ inlet concentration that in comparison with curve b that the inlet concentration is 6.650 mol/m³, has rapid slope. For given concentration, the longer breakthrough time indicated greater adsorption capacity.

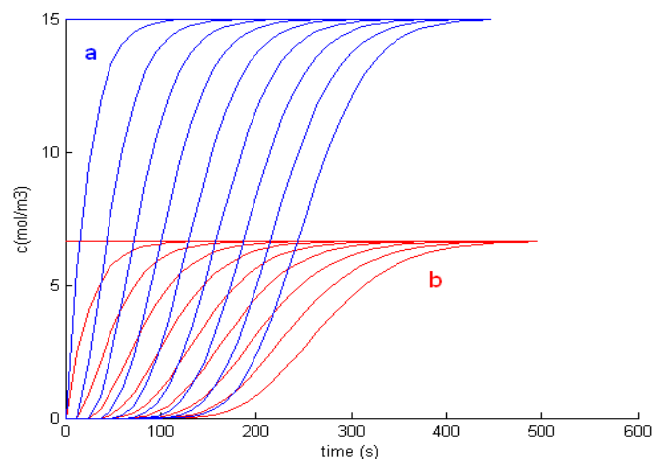


Fig1. Effect of inlet concentration on breakthrough profiles of toluene a=15, b=6.650 mol/m³



The effect of temperature on the breakthrough curve of toluene in activated carbon bed is shown in fig 2. The breakthrough time decreased with increasing bed temperature. This result is ascribed to toluene physical adsorption onto activated carbon. Increasing temperature resulted in decreasing capacity, corresponding to decreasing breakthrough time. As observed from the figure 2 adsorption bed of toluene at 333.15 K saturated near 500s. Whereas saturation time for curve b and c are bigger than 500 s. Curve c has slow slope in comparison with curve b so saturation time for curve c is bigger than curve b.

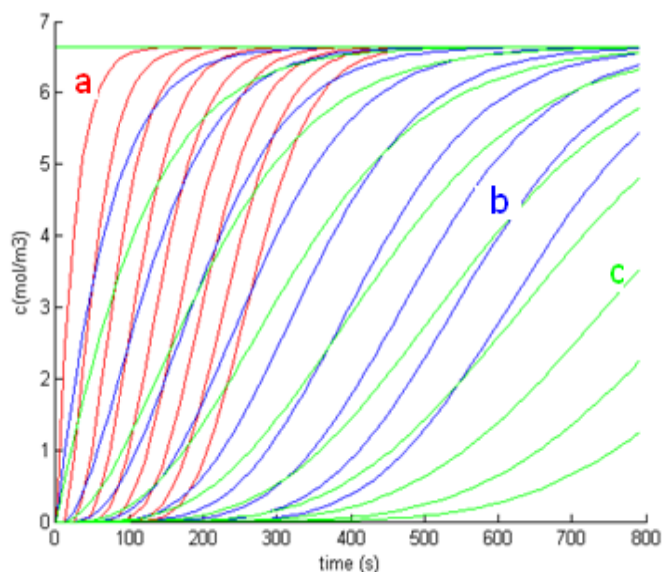


Fig2. Effect of temperature on breakthrough profiles of toluene. a=333.15, b=318.15, c=298.15

Other parameters such as pore size and diffusivity and particle diameter influence on breakthrough profiles. The pore size of the adsorbent is a critical parameter in determining the breakthrough characteristics of an adsorbate.

The smaller the pore size becomes, the larger the diffusion time of adsorbing species within the pores will be due to relatively smaller diffusivity. The large diffusion time causes the adsorption process to be diffusion limited rather than kinetic limited.

In general, the effect of pore diffusivity on adsorption rate is significant at high flow rates; implying adsorption process is limited by pore diffusion. When diameter of pellets is large, the breakthrough time of adsorbing species due to relatively longer diffusion path in the pores is shorter. However, the time of bed-saturation increased due to the large adsorption surface area of the particle [13, 14].

Conclusions

The breakthrough characteristics of toluene in packed beds of AC depended on the adsorption conditions. Higher equilibrium adsorption capacity corresponds to longer breakthrough times at different concentrations. This study shows good agreement between the simulation results and the predicted values for the adsorption of BTX compounds in acid gases.



Notation:

$a_p \left(\frac{m^2}{m^3} \right)$	external surface area per unit volume of the pellet,
$d_p (m)$	diameter of pellets
$\rho_b \left(\frac{kg}{m^3} \right)$	bulk density
$d_{pore} (A^{\circ})$	diameter of pore
ϵ_p	porosity of particle
τ	tortuosity factor
$S_{BET} \left(\frac{m^2}{kg} \right)$	BET area per unit mass of adsorbent,
$v_s \left(\frac{m}{s} \right)$	superficial velocity
$L(m)$	length of bed
$D(m)$	diameter of bed
ϵ_b	porosity of bed

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مدلسازی و شبیه سازی فرایند حذف ترکیبات BTX از گازهای اسیدی

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چکیده

نظر به اینکه معمولا حدود ده تا پانزده درصد ترکیبات BTX موجود در گاز ترش به گاز اسیدی ورودی به واحد بازیافت گوگرد منتقل می شود لذا اینگونه ترکیبات در صورت عدم تجزیه در کوره ی واحد SRU، می توانند باعث مسموم شدن کاتالیزورهای بستر کلاوس شوند. در نتیجه راندمان بازیافت گوگرد را تا حدود ۸۵٪ کاهش می دهد و به دلیل نیاز به تعویض مکرر کاتالیست ها فرایند کلاوس بسیار پر هزینه می شود. جداسازی این ترکیبات با استفاده از فرایند جذب سطحی به عنوان فرایند بهینه صورت می گیرد. مطالعات تئوری برای جذب این ترکیبات با استفاده از کربن اکتیو انجام شده و مدل ریاضی برای شبیه سازی سیستم جذب در شرایط ایزو ترم ارائه می شود. این مدل با روش تفاضل محدود با استفاده از نرم افزار مطلب شبیه سازی می شود و نتایج در شرایط مختلف عملیاتی با هم مقایسه می شوند که نتایج حاصل از شبیه سازی با نتایج پیش بینی شده موافقت دارد.

واژه های کلیدی: فرآیند کلاوس، BTX، جذب سطحی، کربن فعال، مدلسازی

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