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Simulation of pressure swing adsorption in fuel ethanol production process

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Abstract

Fermentation derived ethanol is gaining wide popularity as a car fuel additive. A major challenge in the production of ethanol is the high energy cost associated with the separation of ethanol from the large excess of water. Distillation is usually the method of choice; however, water cannot be completely removed due to the presence of the azeotrope. The pressure swing adsorption (PSA) process is attractive for the final separation since it requires little energy input and is capable of producing a very pure product. The goal of this work was to perform a thorough analysis of the PSA process and find process improvements with the aid of mathematical modeling.

A general purpose package for the simulation of a cyclic PSA process was developed. The system of partial differential equations was solved via method of lines using a stiff equation integration package. Parameters for the model are based on the data from an operating plant as well as data from the literature. For the ethanol production technology our model provides a fundamental understanding of the dynamics of the cyclic process and effects of some operating parameters.

Keywords: Pressure swing adsorption; Fuel ethanol; Water adsorption; 3 Å zeolite; Method of lines; Modeling

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1. Introduction

In the past, extractive or azeotropic distillation processes have been used to break the water–ethanol azeotrope (Black, 1980). Since distillation routes are energy intensive and expensive, lower energy separation alternatives such as liquid–liquid extraction, adsorption and membrane processes have been analyzed. The pressure swing adsorption (PSA) process has succeeded on the industrial scale.

Ethanol can be produced by fermentation of practically any starch containing feedstock. Fermented liquor is distilled in a series of distillation columns including a stripping column, rectifying column, and in some processes an added side stripper. To produce anhydrous ethanol, water is removed with an appropriately sized molecular sieve sorbent. A 3 Å zeolite possesses micro-pores, where due to the small size of the pores, the water molecules are adsorbed while the ethanol molecules are not. The rectifying column is used to produce high ethanol content vapor, which is fed to a PSA unit; a 99.5% (by weight) ethanol stream leaves the operation as the final product. The PSA process has proven to be much more energy efficient compared to the classical processes and presently is commercially well established as a separation process for dewatering the mixture of ethanol and water.

The typical PSA cycle includes a production step in which vapor flows into the vessel from the top at a high pressure; water is adsorbed while the ethanol vapor passes through the column and is collected as the high pressure product at the bottom of the bed. After the production step, the bed must be regenerated and prepared for the next cycle. First, the pressure in the bed is reduced while some water is desorbed. This step is referred to as the depressurization step. In the next regeneration step, water is desorbed from the bed under the vacuum. Near the end of the regeneration step, a portion of product gas (99.5% ethanol) is used to purge the vessel to remove the adsorbed water that had been adsorbed during the production step. Then, the vessel is re-pressurized with product ethanol vapor from the operating vessel. The adsorbent bed has then completed its pressure

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Nomenclature

c	fluid phase molar concentration (mol m^{-3})
c_p	isobaric specific heat (J kg^{-1} K^{-1})
c_s	speed of sound (m s^{-1})
d_p	particle diameter (m)
D	bed diameter (m)
D_ax	axial effective dispersion coefficient (m^2 s^{-1})
D_eff	effective diffusion coefficient (m^2 s^{-1})
F	mass flow rate (kg h^{-1})
G	mass velocity (kg m^{-2} s^{-1})
k_ef	axial effective thermal conductivity (W m^{-1} K^{-1})
k_f	external mass transfer coefficient (m s^{-1})
k_LDF	linear driving force mass transfer coefficient (s^{-1})
K	Langmuir isotherm equilibrium constant (Pa^{-1})
M	molar weight (kg mol^{-1})
Mach	Mach number
P	pressure (Pa)
q	molar loading in adsorbed phase (mol kg^{-1})
q^s	saturation loading (mol kg^{-1})
q^*	equilibrium loading (mol kg^{-1})
Q	isosteric heat of adsorption (J mol^{-1})
r_p	adsorbent particle radius (m)
R	universal gas constant (J mol^{-1} K^{-1})
Re	Reynolds number
t	time variable (s)
T	temperature (K)
u	superficial fluid velocity (m s^{-1})
Y	fluid phase molar fraction
z	spatial coordinate (m)

Greek symbols

α	pressure ratio (=$P_\mathrm{F}/P_\mathrm{P}$)
ε	gas void fraction
κ	ratio of isobaric and isochoric specific heats
ρ	density (kg m^{-3})

Subscripts

b	bulk or packed bed
F	feed stream (or high pressure step) conditions
g	gas (fluid) phase
i	adsorbing component (water)
p	particle
P	purge stream (or low pressure step) conditions
s	solid (adsorbed) phase
0	nozzle inlet conditions or reference state for isotherm
1	nozzle exit conditions

swing cycle and is ready to enter a new production step. Numerous PSA cycles have been devised using two or more adsorbent beds; all of them use the steps described above with slight variations.

A precise design of the PSA unit is a difficult task because of many interacting operational parameters characterizing this separation process. Laboratory scale experiments are time consuming and economically demanding. These reasons have lead to the development of mathematical models which are used for initial evaluation of the PSA process. Reliable models enable us to calculate the basic operational characteristics, size the system, and evaluate different scenarios of operation.

2. PSA simulation model

The mathematical model describing the five-step PSA process, involving high-pressure adsorption, depressurization, regeneration with purge and pressurization, has been used in the present study for the simulation of the water–ethanol separation. A non-isothermal non-adiabatic dispersed plug flow model with variation of axial velocity has been used. The model assumes non-linear adsorption equilibrium. The mass transfer rate is described by the linear driving force (LDF) approximation. Based on assumptions of the adsorbing system, PSA bed models can be described by models having different levels of characterization of the system. Several transport effects, including the mechanisms of intra-particle diffusion and external mass transfer need to be considered. In our analysis, the LDF model will be used as a compromise between accuracy and calculation efficiency.

To have a reasonable description of the transient adsorption system following balances and relations should be considered:

1. Mass balance for each component.
2. Energy balance for the gaseous and adsorbed phase and the solid adsorbent matrix.
3. Description of the component transfer rates in the gas and adsorbed phase.
4. Adsorption equilibrium relationship for each component.
5. Equation of state for the gas phase.
6. Momentum balance.

2.1. Mass conservation equations

The conservation equations for mass consider the convection flow term, axial eddy diffusion term, accumulation and source term caused by the adsorption process on the solid matrix. The equations are represented by a set of highly non-linear parabolic partial differential equations. The term representing the axial dispersion is very small compared to the convection term and therefore the equations show the properties of hyperbolic non-linear differential equations of the first order. However, the dispersion term eliminates the shock-like behavior and it is easier to solve these equations compared to those where the dispersion term is eliminated. The spatial discretization must be done carefully to suppress the numerical dispersion.

A material balance for component *i* over a differential volume element yields

$$\frac{\partial c_i}{\partial t} = D_\mathrm{ax}\frac{\partial^2 c_i}{\partial z^2} - \frac{1}{\varepsilon}\frac{\partial}{\partial z}(uc_i) - \frac{(1-\varepsilon)}{\varepsilon}\rho_\mathrm{s}\frac{\partial q_i}{\partial t} \qquad (1)$$