Chemical Engineering Journal 241 (2014) 485–494

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Heat and mass transfer in adsorption–desorption cyclic process for ethanol dehydration

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HIGHLIGHTS

- The profiles of water content in adsorbent bed after purging step have been determined.
- The temporal courses of bed temperatures at different levels have been determined.
- A consistence between experimental and calculation values has been obtained.
- The maximum bed temperature has been determined numerically.

ARTICLE INFO

Article history:
Received 8 August 2013
Received in revised form 9 October 2013
Accepted 15 October 2013
Available online 24 October 2013

Keywords:
Ethanol dehydration
Pressure swing adsorption–desorption process

ABSTRACT

A process of water removal from ethanol, based on pressure swing adsorption–desorption cycles was investigated in a laboratory scale installation. The regeneration of zeolitic adsorbent was performed under lowered pressure by purging unhydrated ethanol through the bed. For the adsorption step the breakthrough curves and temporal variations in temperature at different bed heights were carried out whereas for the purge (regeneration) step the final water concentration profiles in the bed were determined. Two mathematical models of the process were developed. It is shown that the mathematical models adequately describe the process. Simulation calculations were also carried out for the conditions of industrial dehydration process. The calculations were designed to evaluate the maximum temperature values that can occur in the bed.

1. Introduction

One way of solar energy utilization is its bioconversion. As a result of this process one can obtain, inter alia, the (bio) liquid fuels such as fatty acid esters or ethanol. The recently observed increase of interest in biofuels results from the awareness of unavoidable restrictions on exploitation of traditional fuels, especially crude oil. Ethanol is one of the most commonly used organic substances. About 3/4 its production volume is utilized as a fuel.

The application of biofuels can be considered as an indirect method for the utilization of solar energy absorbed by plants and used in the photosynthesis process. One of the main advantages of biofuels as compared to other methods for solar energy utilization comes from the fact that biofuels can be stored and used when the energy is needed regardless of the weather conditions.

Bioethanol produced from food products such as potatoes, corn, sugar cane, is a first-generation bioethanol. Its production is associated with high costs, resulting primarily from food prices and may result in adverse social impact. For this reason, the current research focuses on the technology of production of second-generation bioethanol from lignocellulosic raw materials coming from agricultural activities and forestry production, involving energy crops and vegetable wastes [1,2]. In the near future, this trend could allow a significant increase in world production of ethanol.

The major problem with using ethanol obtained fermentatively is a high cost associated with the separation of ethanol from large amount of water. The production of fuel ethanol requires almost the complete removal of water. The cost of this separation and purification is an essential position in the production of fuel ethanol. Ethanol–water solutions are conventionally separated by distillation. However, the distillation allows to obtain a solution containing only 95 mass% ethanol solution. Further dehydration can be carried out by extractive, adsorption or membrane methods [3]. For water removal from ethanol solutions, which usually are enriched by distillation, the adsorption methods are mostly applied. Recently, some research on direct obtainment of ethanol from liquid solutions, coming into existence in fermentation process, by adsorption method is carried out [4–6].

The most common are adsorption methods using zeolite adsorbents. A research on comparison of various types of zeolite adsorbents were carried out by Sowerby and Crittenden [7]. In most

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http://dx.doi.org/10.1016/j.cej.2013.10.043

Nomenclature

b	constant in D–R equation
C_{mol}	molar specific heat of gas phase
c_p	specific heat of adsorbent pellet
d_c	column diameter
d_p	diameter of adsorbent pellet
k	number of subsequent cycle
$k_s a$	mass transfer coefficient in solid phase
L	bed length
M	molar mass
m_p	mass of the adsorbent pellets
m_w	mass of water
$\dot{m}_{ads}$	feedstock mass flow rate
$\dot{m}_{pur}$	mass flow rate of purge agent
P	total pressure
P_{sat}	saturation pressure
$\bar{q}_m$	water content in pellet (averaged)
q_m^*	water content in pellet in equilibrium with water concentration in gas phase
q_{m0}	water content in the pellet in equilibrium with water concentration in feedstock
q_{ms}	constant in D–R equation
Q_{st}	isosteric heat of adsorption
R	gas constant (=8.314 J/(mol K))
t	time
T	temperature
t_{st}	stoichiometric time of breakthrough of bed
T_a	ambient temperature
u	superficial gas velocity
U	overall heat transfer coefficient
x (=z/L)	dimensionless coordinate of bed length
y, y_{mol}	mass fraction and molar fraction of water in gas phase
z	coordinate of bed length
ε	bed porosity
μ_g	gas viscosity
ρ_p	pellet density
ρ_g	gas density

Indices

ads	adsorption
et	ethanol
H	high value
i	initial
L	low value
max	maximum
pur	purge
w	water
0	inlet in adsorption step
1	inlet in purge step

cases for water adsorption zeolites 3A are used. Adsorption of ethanol on these zeolites is minimal so they adsorb water selectively. Simo et al. [8] confirmed that the diameter of micropores in the zeolite 3A virtually eliminates the possibility of adsorption of ethanol molecules, which allows to treat the adsorptive dehydration process as a one component adsorption (water) from a binary mixture. The adsorbent regeneration is carried out by lowering the pressure (PSA process). Particularly effective is a reduction of the total pressure in combination with purging the bed by an inert agent (purging). This process leads to an effective desorption of previously adsorbed component, needed to realize a next cycle.

Ethanol dehydration process can be also realized on natural adsorbents [9–15] as well as in the liquid phase [16–17].

Adsorptive dehydration of ethanol by PSA method has been a subject of many works. An empirical model of the process presented Carmo and Gubulin [18]. Jain et al. [19] analyzed numerically effects of various process parameters on the product purity. A model based on electrical analogue for analysis of results of measurements was applied in [20] while the Monte Carlo methods in [21]. The effect of proces parameters on the results of dehydration in small scale was investigated in [22] whereas the results obtained in pilot scale at various configurations of PSA process were presented in [23].

In [24] an adsorption–desorption process consisting of three steps i.e. adsorption and two-stage vacuum regeneration: initially without an inert gas blowdown then purge with an inert gas was investigated. The model profiles of concentrations, pressures and velocities of gas flow in function of the duration time of the various stages of adsorption–desorption cycles were also presented. In [25] the impact of pressure drop of gas in the vacuum purging step of the bed was considered.

The formation of hot spots in the zeolite bed was described by Simo and co-workers [26]. The adsorption process of water from vapor mixtures with ethanol was considered. The carried out numerical calculations show that the bed temperature can reach values of about 300 °C. These hot zones disappear when moving towards the outlet of the bed.

A major problem for processes in which the heat is produced is a maximum temperature that can occur in the bed during the process. The problem occurs during the start-up of installation containing a fresh load of adsorbent lacking in the adsorbed component. Under such conditions, the adsorbate is adsorbed significantly more intensively than during the operation under the cyclic steady state conditions. In a steady cyclic operation the adsorbate is adsorbed by the incompletely regenerated bed which results in moderate amount of adsorbed component per time unit. For this reason, the amount of generated heat is limited and the temperature increment of the bed is relatively small. Nevertheless, during the start-up the adsorbancy of pure adsorbent is high, which may cause extreme temperature increments. In case of application of zeolite adsorbent, high temperatures may lead to the irreversible destruction of its structure. However, in case of using carbonaceous adsorbents there is a risk of their ignition.

The study presents the results of experimental research involving the adsorptive dehydration of ethanol solutions on zeolites in the laboratory scale. There were two types of studies conducted. The first involved the pressure swing adsorption–desorption cycle consisting of two steps: adsorption under atmospheric pressure and purge under reduced pressure. In these studies, the breakthrough curves in the adsorption step as well as the water content profiles in the adsorbent bed after purging step (regeneration) of the bed with a dehydrated ethanol were determined. Variable parameters were: flow rate of feedstock, duration time of various steps and water concentration in the feedstock subjected to dehydration.

The second type of research concerned the temporal temperature courses at different heights of bed in the adsorption step. In these experiments, an influence of water concentration in feedstock and initial water content in pellet on thermal effects was determined.

The aim in the both types of studies was to compare the experimental results with the results obtained from the mathematical model of the process. The successfully verified mathematical model can be a base for simulation and optimization calculations. The