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DEHYDRATION OF ETHANOL USED AS
A FUEL ADDITIVE

The ecological aspects of utilizing ethanol as fuel additive are discussed. The pressure swing adsorption process used for ethanol dehydration is described. Principles of the modelling of ethanol dehydration by the pressure swing adsorption are presented.

1. INTRODUCTION

Many countries are searching for methods that would help them reduce their dependence on imported fuels, methods which would improve the quality of air by reducing emissions to the atmosphere and increase the production through the utilization of locally produced crops. One solution to meet these aims is the production of ethanol and its use as fuel additive. This has resulted in a substantial increase of the production of ethanol [1].

Fuel with ethanol being added may offer some advantages over fuel without ethanol in reducing particulate and CO emissions and in reducing total hydrocarbon and other (especially benzene) toxic emissions.

For automotive transport, liquid fuels are considered essential, and ethanol derived from starch, cellulose or sugar via hydrolysis and fermentation is one of the most intensively studied renewable alternatives [2]. Although at present the use of pure ethanol as a fuel is less attractive in economic terms, interest in oxygenated organics as substitutes for tetraethyl lead in high octane gasoline is growing, and again ethanol is one of the options.

Ethanol can be used as a blending agent in low-level (e.g., 10%) ethanol-gasoline blends, either directly or indirectly (i.e., in the form of ethyl tetrabutyl ether, ETBE).

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2. ECOLOGICAL ASPECTS OF ETHANOL
AS A FUEL ADDITIVE

The use of biofuels can be considered to be an indirect method for the utilization of solar energy absorbed by plants and used for the photosynthesis process. One of the main advantages of biofuels lies in the fact that the compounds for biofuel production can be synthetized, stored and used when energy is needed regardless of the weather conditions.

Production of fuel ethanol from renewable and waste lignocellulosic materials (bioethanol) offers the possibility of reducing the dependence of the world economy on petroleum. Because of the relatively low toxicity of ethanol (ethanol is fully misci-ble with water and biodegradable), the consequences of large fuel spills would be far less threatening to the environment than those associated with the spills of crude oil or gasoline. Perhaps the most important factor is that using bioethanol, unlike in the case of fossil fuels, actually mitigates the atmospheric accumulation of carbon dioxide or the so-called 'greenhouse' effect. Substituting bioethanol for gasoline as a transporta-tion fuel would substantially reduce net emissions of carbon dioxide because the amount of carbon dioxide released during the production and combustion of fuel etha-nol would be equivalent to the amount of carbon dioxide combined in the replanted biomass.
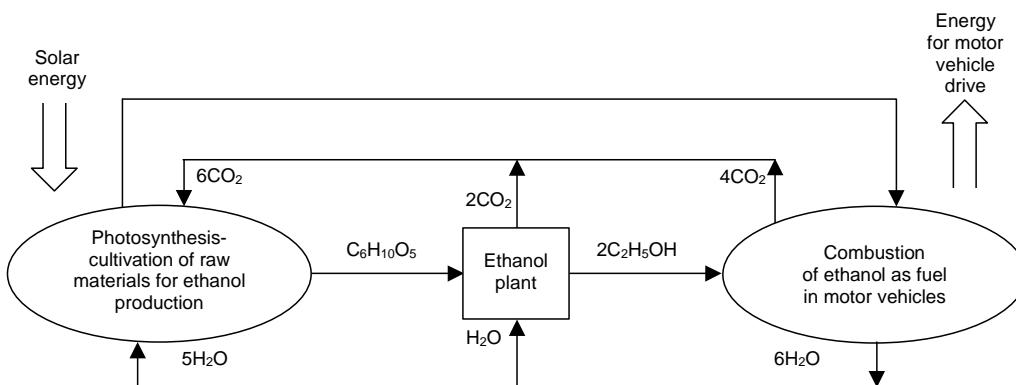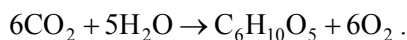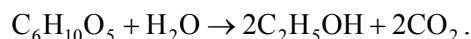

Fig. 1. From circulation of carbon dioxide
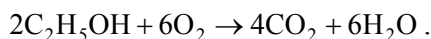in nature to the use of ethanol as fuel additive

The carbon dioxide cycle connected with biofuel (ethanol) production and com-bustion of the biofuel is shown in figure 1. The process of photosynthesis, utilizing solar energy, leads to the production of starch:

$$6CO_2 + 5H_2O \rightarrow C_6H_{10}O_5 + 6O_2 \, .$$

In this process, the energy absorbed by the plants and carbon dioxide, together with water, are transformed into starch which is the main raw material for bioethanol production. The carbohydrates (starch) are first hydrolyzed and the resulting sugar is then fermented. In effect, ethanol and carbon dioxide are produced:

$$C_6H_{10}O_5 + H_2O \rightarrow 2C_2H_5OH + 2CO_2 \,.$$

The reaction taking place in the vehicle engines is:

$$2C_2H_5OH + 6O_2 \rightarrow 4CO_2 + 6H_2O \,.$$

The heat released during this reaction is then transformed into mechanical energy. From the above reactions it is obvious that the carbon dioxide cycle is closed and that the resulting useful energy comes indirectly from solar energy.

3. ETHANOL PRODUCTION

The process of producing ethanol from grain or other biomass can be divided into two separate broad steps. The first step is the fermentation of carbohydrates, saccharified in aqueous suspensions, which yields a broth containing about 10% ethanol. The second step is product recovery, which includes separation of the ethanol from water and then its purification in order to get rid of water and other impurities.

A major problem in obtaining fuel ethanol through fermentation is the high cost of energy used for separating ethanol from a large excess of water. The production of fuel ethanol from the solution requires almost a complete removal of even residual moisture. The cost of separation and purification is one of the major concerns in absolute alcohol production. The conventional process of separation consists in distillation. Because of the formation of an azeotropic mixture with a boiling point minimum, under normal conditions distillation yields only 95 wt. % ethanol. Further dehydration of ethanol is usually carried out by adsorption methods on zeolites 3A.

Earlier systems operated in the liquid phase and used the thermal swing regeneration process, which did not make them very energy efficient. Further development as far as the adsorbent in concerned relied on the introduction of vapour phase applying a pressure swing regeneration system [3]–[5]. This proved to be highly energy-efficient.

4. PRINCIPLE OF THE PSA PROCESS

Pressure swing adsorption is a widely used process for the separation of gases [6]. PSA is attractive because it requires little energy input and operates in cycles of short

duration. Therefore sorbent productivity is high and the process is often capable of producing a very pure product.

In the PSA process, a specific species in the gas mixture is preferentially adsorbed and then desorbed (regenerated) through pressure reduction. Figure 2 illustrates a typical PSA process. At a high pressure, the feed is introduced, and the readily adsorbed species is adsorbed on the adsorbent in the bed. From the bed top, the less adsorbable species is obtained as a raffinate, while the extract drawn from the bottom contains the easily adsorbed species. The process proceeds in two-bed adsorbers: column *A* and column *B*, operating in cycles, in four steps: adsorption, blowdown, purge and pressurization.
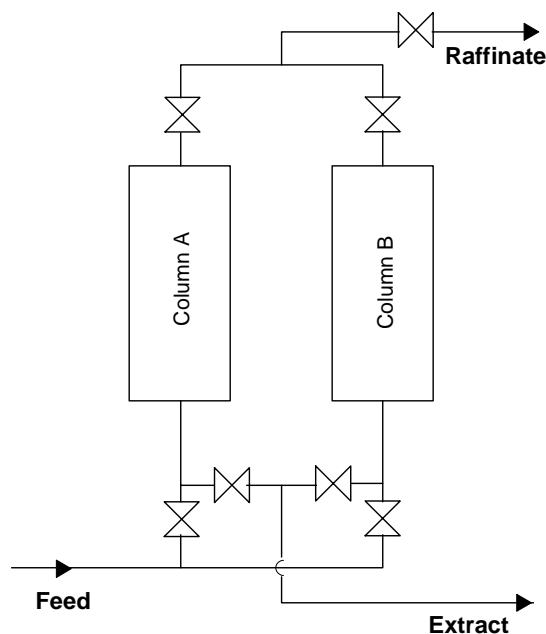

Fig. 2. A two-column PSA process

A typical operating mode of the PSA cycle in column *A* is shown in figure 3. In the first step, a high pressure feed gas is introduced into column *A*, where adsorption of the readily adsorbed gas takes place and less adsorbable gas is removed as the product (raffinate). During this stage, a small portion of the product gas is drawn into column *B*, at a low pressure. In the second step, the pressure in column *A* is reduced to purge pressure level (blowdown). In the third step, a low pressure gas is introduced from column *B* into column *A*, where the desorption of accumulated adsorbate takes place (purge). In the fourth step, column *A* is repressurized with the feed gas (pressurization). In steps 3 and 4, step 1 and step 2 are repeated in column *B* and the roles of the two columns are switched over.
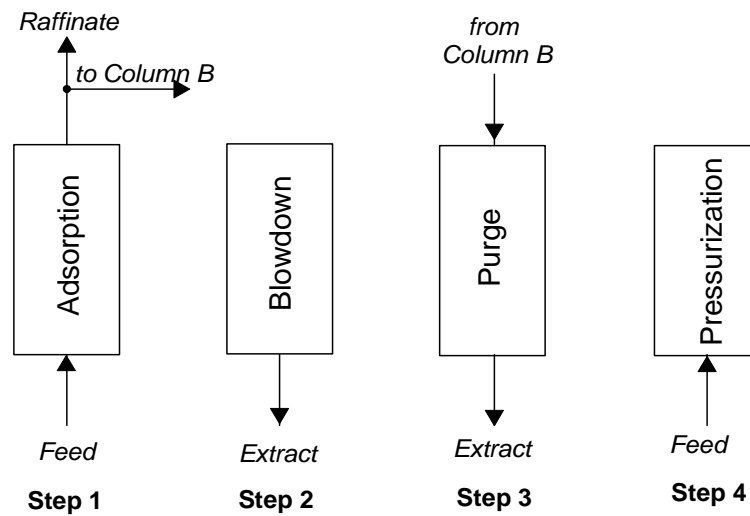
Fig. 3. Operating mode of PSA cycle in column *A*

Many factors influence the PSA process, such as the physical and chemical properties of mixture components, construction of the columns and mode of operation. A detailed analysis based on the principles of chemical engineering allows mathematical models of the process to be developed. Taking advantage of these models, algorithms for the numerical simulation are developed and the resulting software can be used for optimization of the process.

5. MODELLING OF ETHANOL DEHYDRATION BY THE PSA PROCESS

The effects of the process variables in a PSA system are so strongly coupled and the calculations are so rigorous that it is difficult to obtain an optimum design. Since a pilot study of PSA in a plant is costly compared to a computational study, simulation has become a viable alternative to pilot plant experiments. Based on kinetics and equilibrium data as well as parameters of operation, simulation provides a method of predicting outlet concentrations and the dynamic capacity of PSA, without recourse to experimentation.

In the process of ethanol dehydration considered, the separated mixture consists of two components (water and ethanol in vapours). Water is adsorbed, which leads to variations in the velocity of the gas phase. Furthermore, large amounts of heat are released, influencing the adsorption equilibrium and therefore a non-isothermal model is necessary. Since the adsorption–desorption cycles rely on pressure changes, the pressure drop along the adsorbent bed must be taken into account. Therefore, the model consists of the following balance equations:

1. The overall mass balance resulting from variation in the velocity of the gaseous phase.

2. The mass balance of the adsorbed component (water vapour).

3. The heat balance, with the thermal effects of adsorption taken into account.

4. The momentum balance, taking into account pressure changes within the system.

The following assumptions are made to model the PSA process: the ideal gas law is applicable and the effect of dispersion is negligible.

The overall mass balance equation is:

$$\frac{\partial\left(\dfrac{Pu}{T}\right)}{\partial z}+\varepsilon\frac{\partial\left(\dfrac{P}{T}\right)}{\partial t}+\frac{\rho_p(1-\varepsilon)R}{M_w}\cdot\frac{\partial\overline{q}_m}{\partial t}=0,$$

where:

M_w – molecular weight of water,

P – total pressure,

$\overline{q}_m$ – average concentration of the adsorbate in the pellet,

R – gas constant,

t – time,

T – temperature,

u – superficial gas velocity,

z – bed length coordinate,

ε – bed porosity,

ρ_p – density of adsorbent pellets.

Water, mass balance equation:

$$\frac{Pu}{T}\frac{\partial y_{\text{mol}}}{\partial z}+\frac{\varepsilon P}{T}\frac{\partial y_{\text{mol}}}{\partial t}+\frac{\rho_p(1-\varepsilon)R}{M_w}\cdot\frac{\partial\overline{q}_m}{\partial t}(1-y_{\text{mol}})=0,$$

where y_{mol} is a molar fraction of water.

Heat balance:

$$\frac{\partial\left[Pu\left(1-\dfrac{T_0}{T}\right)\right]}{\partial z}+\varepsilon\frac{\partial P}{\partial t}+\frac{c_p\rho_p(1-\varepsilon)R}{C_{\text{mol}}}\cdot\frac{\partial T}{\partial t}$$
$$-\frac{\rho_p(1-\varepsilon)(-\Delta H)R}{C_{\text{mol}}M_w}\cdot\frac{\partial\overline{q}_m}{\partial t}+\frac{4kR}{d_c C_{\text{mol}}}(T-T_f)=0,$$

where:

C_{mol} – molar heat capacity of gas,

c_p – heat capacity of adsorbent,
d_c – column diameter,
$(-\Delta H)$ – molar heat of adsorption,
k – overall heat transfer coefficient,
T_0 – reference temperature,
T_f – ambient temperature.
Momentum balance:

$$-\frac{\partial P}{\partial z} + \frac{\partial P_t}{\partial z} - \frac{M}{RT}\frac{\partial (Pu)}{\partial t} = 0 ,$$

where:

M – molecular weight,
ΔP_t – drop in the friction pressure.

Solution of the balance equations requires knowledge of the state of a column before the startup of the process and at the beginning of each single step. For startup, it has been assumed that bed is clean, which gives the initial conditions as:

$$0 \le z \le L, \quad t = 0; \qquad \overline{q}_m = 0, \quad y_{\mathrm{mol}} = 0, \quad T = T_0 ,$$

where L is the bed length.

At the beginning of each step the concentration profiles in the gaseous and adsorbed phases and the temperature profiles along the bed remain the same as those at the end of the preceding step. Initial conditions for the pressurization step result from the end of the purge step:

$$0 \le z \le L, \quad t = 0; \quad \overline{q}_m = q_m^{\mathrm{purge}}(z, t_{\mathrm{purge}}), \quad y_{\mathrm{mol}} = y_{\mathrm{mol}}^{\mathrm{purge}}(z, t_{\mathrm{purge}}), \quad T = T^{\mathrm{purge}}(z, t_{\mathrm{purge}}) .$$

Boundary conditions for pressurization step are as follows:

$$z = 0, \quad t \ge 0; \qquad y_{\mathrm{mol}} = y_{\mathrm{mol}0}, \quad T = T_0 ,$$

$$z = L, \quad t \ge 0; \quad u = 0 .$$

Initial conditions for adsorption step correspond to those observed at the end of pressurization step:

$$0 \le z \le L, \quad t = 0; \quad \overline{q}_m = q_m^{\mathrm{press}}(z, t_{\mathrm{press}}), \quad y_{\mathrm{mol}} = y_{\mathrm{mol}}^{\mathrm{press}}(z, t_{\mathrm{press}}), \quad T = T^{\mathrm{press}}(z, t_{\mathrm{press}}) .$$

Boundary conditions for adsorption step depend on conditions of feed gas:

$$z = 0, \quad t \ge 0; \qquad y_{\mathrm{mol}} = y_{\mathrm{mol}0}, \quad u = u_0, \quad T = T_0 .$$

Initial conditions for the blowdown step result from the end of adsorption step:

$$0 \leq z \leq L, \quad t = 0; \qquad \overline{q}_m = q_m^{\text{ads}}(z, t_{\text{ads}}), \quad y_{\text{mol}} = y_{\text{mol}}^{\text{ads}}(z, t_{\text{ads}}), \quad T = T^{\text{ads}}(z, t_{\text{ads}}).$$

Boundary conditions for the blowdown step are as follows:

$$z = L, \quad t \geq 0; \qquad \frac{dy_{\text{mol}}}{dz} = 0, \quad u = 0.$$

Initial conditions for the purge step result from the end of the blowdown step:

$$0 \leq z \leq L, \quad t = 0; \quad \overline{q}_m = q_m^{\text{blow}}(z, t_{\text{blow}}), \quad y_{\text{mol}} = y_{\text{mol}}^{\text{blow}}(z, t_{\text{blow}}), \quad T = T^{\text{blow}}(z, t_{\text{blow}}).$$

If the column is fed with the effluent from another column, the temperature and composition of the feed gas are assumed to be the same as those for the effluent. Such a situation occurs during the purge. Therefore the boundary conditions for the purge step are:

$$z = L, \quad t \geq 0; \qquad y_{\text{mol}} = y_{\text{mol}}^{\text{ads}}(L, t), \quad u = G \frac{P_A}{P_D} u^{\text{ads}}(L, t), \quad T = T^{\text{ads}}(L, t),$$

where: G is the purge-to-feed velocity ratio. Indexes *press*, *ads*, *blow* and *purge* refer to the corresponding steps.

The model is completed by the addition of equations for the adsorption equilibrium, adsorption kinetics and the equation for the pressure drop along the adsorbent bed.

6. FINAL REMARKS

1. Bioethanol is a renewable fuel, which when burning causes no net increase in the carbon dioxide concentration in the atmosphere.

2. The production of ethanol is growing and its optimization will exert a substantial influence on the economic aspects of its utilization. The process of ethanol dehydration is an important step in the production of biofuel, and research in this area is needed.

3. The PSA process is widely used in the dehydration of ethanol. A variety of configurations and operational parameters are available and it is desirable to select appropriate methods. Further research (both experimental and theoretical) is justified in terms of the economic, ecological and social significance of using renewable energy sources.

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ODWADNIANIE ETANOLU PALIWOWEGO

Omówiono aspekty ekologiczne dodawania etanolu do paliw. Opisano proces adsorpcji zmiennoci-śnieniowej stosowany do odwadniania etanolu. Przedstawiono zasady modelowania procesu odwadniania etanolu tą metodą.