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Production of Motor Fuel Grade Alcohol by Concentration Swing Adsorption

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Abstract

A new cyclic process concept called "concentration swing adsorption" for separation of bulk binary liquid mixtures is described. The process carries out the primary separation by selective liquid-phase adsorption of one of the components of the feed mixture on an adsorbent. The adsorbed component is then desorbed by a desorbent liquid which is equally or more strongly adsorbed than the selectively adsorbed component of the feed mixture. The desorbent liquid is removed from the adsorbent by displacing it with the less strongly adsorbed component of the feed mixture so that the adsorbent can be reused. The process also includes a complementary step where the adsorbent is rinsed with the more strongly adsorbed component of the feed mixture so that two essentially pure products are produced from the feed mixture with high recoveries of both components. At least one simple distillation is also required by the process which separates the desorbent liquid from the less strongly adsorbed component of the feed mixture. The process can be used to separate liquid mixtures with close boiling components or azeotropic mixtures which require energy intensive distillation. A very efficient separation can be achieved in these cases by spending only a fraction of the distillation energy. An example of such an application, viz., separation of a bulk ethanol–water mixture for motor fuel grade alcohol production, is described. A local equilibrium model of the process is used to evaluate the performance of the process for that separation using an activated carbon as the adsorbent and acetone as the desorbent liquid. Experimentally measured equilibrium adsorption characteristics for ethanol–water, acetone–water, and acetone–ethanol binary liquid mixtures on the carbon as well as adsorption column dynamics for the steps of the process are reported.

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INTRODUCTION

The conventional technology to produce motor fuel grade alcohol (MFGA) containing a 98+ mol% ethanol–water mixture is to distill the effluent of a corn or sugar cane fermenter. The effluent typically contains a 3–5 mol% ethanol–water mixture which is first concentrated to the azeotropic composition of 90 mol% ethanol in a BEER distillation column followed by azeotropic distillation in a multicolumn system in order to produce MFGA. The well-known Katzen cycle is an example of an efficient heat integrated distillation scheme for this purpose (*1*).

This technique is, however, very energy intensive. Figure 1 shows a plot of the relative energy requirement to produce ethanol–water mixtures of various compositions by distillation starting from a feed liquid mixture containing 4.0 mol% ethanol in water. The striking rise in energy requirement to produce an alcohol composition above 80 mol% ethanol is self-evident from the figure. In particular, the energy consumed by the azeotropic distillation portion of the process (≥90% ethanol) is very high.

Numerous ideas have been proposed to reduce the energy of ethanol–water mixture separation for the production of MFGA. Most of them deal with replacing the azeotropic distillation part of the conventional technique by a less energy intensive separation process such as a vapor-phase pressure swing adsorption scheme (*2*), a vapor-phase thermal swing adsorption

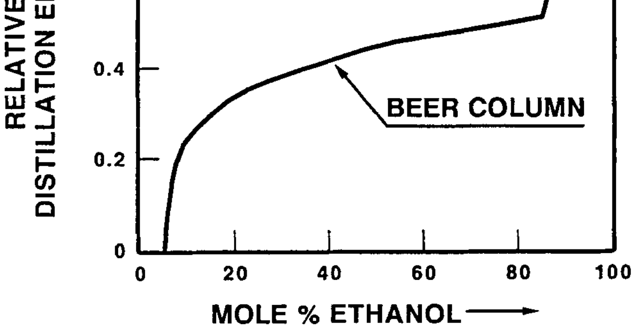

FIG. 1. Relative energy requirement for concentrating a 4.0 mol% ethanol–water mixture to different ethanol composition levels by distillation.

scheme (*3*), or a liquid-phase pervaporation method (*4*). The feed to tnese separation processes typically consists of a superheated vapor-phase azeotropic mixture of ethanol–water or the corresponding liquid–phase azeotropic mixture at ambient temperature.

The purpose of this paper is to describe a novel liquid-phase concentration swing adsorption (CSA) process developed by Air Products and Chemicals, Inc., which has the potential of significantly reducing the energy of separation for MFGA production (*5*).

CONCENTRATION SWING ADSORPTION PROCESS

Figure 2 shows a schematic flow diagram for the new process. The fermenter effluent is fed to a BEER distillation column as in the conventional process but only a part (lower) of the BEER column is used to produce an overhead liquid mixture containing a 10–30 mol% ethanol–water mixture. A stream of water containing the heavier but dilute impurities of the fermenter effluent as well as the suspended solid matters are withdrawn through the bottom of the BEER still. The overhead product is then fed to a four-column liquid adsorption system. The columns are packed with an adsorbent which selectively adsorbs ethanol from water. Each column of the system undergoes the following sequence of adsorption, desorption,

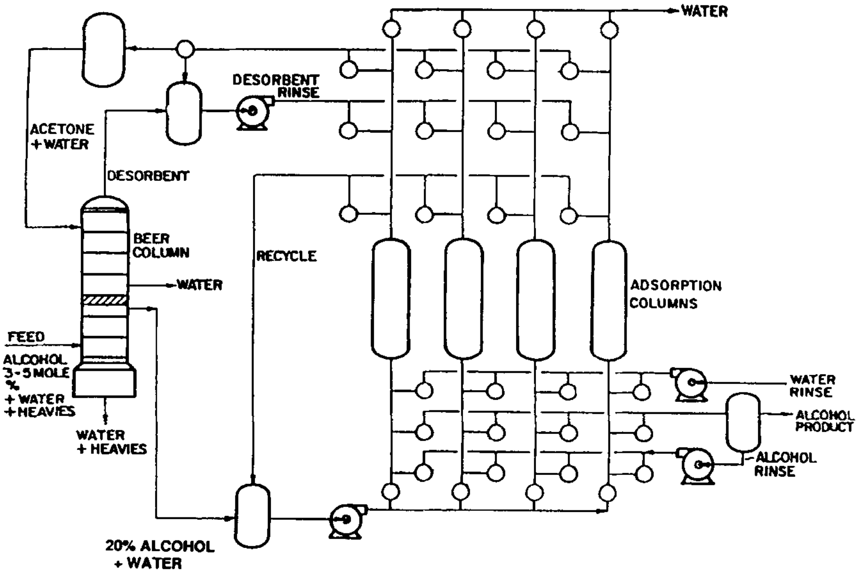

FIG. 2. Schematic flow diagram of the concentration swing adsorption process for the production of MFGA.

and other complementary steps in order to produce a high purity alcohol product with high ethanol recovery.

(a) *Adsorption Step.* The feed liquid mixture containing 10–30 mol% ethanol in water is passed through the column which has been previously saturated with water. A mass transfer zone (MTZ) is formed at the feed end of the column which moves through the column as more feed liquid is introduced. The section of the column ahead of the MTZ contains essentially pure water and the section behind the MTZ is essentially saturated with the feed liquid mixture. This is continued until the leading edge of the MTZ reaches the column effluent end. The effluent from the column during this entire step is essentially pure water.

(b) *Ethanol Rinse Step.* The column is essentially saturated with the feed liquid mixture at the end of Step (a). A stream of pure ethanol is then passed through the column in the same direction (cocurrent) as in Step (a). Another MTZ is formed at the feed end which moves toward the effluent end as more alcohol is passed. The section of the column ahead of the MTZ is now saturated with the feed mixture while the section behind the MTZ is now saturated with ethanol. The step is continued until the MTZ completely exits the column and the column is saturated with ethanol at the end of this step. The effluent during this step has a feedlike composition which is recycled to another column undergoing Step (a) by mixing it with fresh feed.

(c) *Desorbent Rinse Step.* The column is rinsed with an extraneous desorbent liquid (D) at the end of Step (b) by introducing the desorbent through the effluent end (countercurrent). The desorbent is chosen in such a way that it adsorbs more strongly (or equally strongly) than ethanol on the adsorbent and it does not form an azeotrope with either ethanol or water. Another MTZ is formed at the effluent end of the column which moves toward the feed end as more liquid D is passed through the column. The section of the column ahead of the MTZ, in this case, is saturated with ethanol and the section behind the MTZ is saturated with liquid D. The step is continued until the column is completely saturated with D. The effluent during this step (exiting through the feed end) is pure ethanol which is partly withdrawn as the MFGA product and partly used to supply the ethanol for another column undergoing Step (b).

If the MTZ for this step is not sharp, then the effluent near the end part of this step will contain a mixture of ethanol and the desorbent liquid which must be separated by distillation. The ethanol and the liquid D products can be recycled as feeds to Steps (b) and (c), respectively.

(d) *Water Rinse Step.* The column is finally rinsed with pure water countercurrently until it is saturated with water and ready to begin a new cycle starting from Step (a). The effluent during this step is initially pure liquid D which is recycled to another column undergoing Step (c). The latter part of the effluent contains a gradually increasing concentration of water changing between pure D and pure water. This is caused by the less strongly adsorbed component (water) displacing the more strongly adsorbed component (D) for which a diffused MTZ is formed within the column. The water–D mixture is separated by distillation, and the D fraction is recycled as feed for Step (c) to another column.

According to the scheme of Fig. 2, distillation of the water–desorbent liquid mixture is carried out using the upper part of the BEER column, and the two sections of the BEER column are heat integrated for energy savings.

Four adsorption columns are required to run this four-step CSA process cycle in a continuous manner. However, fewer columns can be employed by using surge tanks to hold the feed and effluent liquid mixtures from the various steps. Figure 2 shows the necessary switch valves, pipelines, surge tanks, and liquid pumps required for this process.

The process is run at ambient temperature. The columns remain nearly isothermal during each step of the process due to high heat capacity of liquids which quench any temperature fluctuations in the columns resulting from evolution (consumption) of the heat of ad(de)sorption.

In principle, the CSA process described above replaces most of the energy intensive separation of the ethanol–water mixture by distillation (including azeotropic distillation) used in the conventional technique for MFGA production by a combination of a liquid-phase adsorptive alcohol–water separation scheme and distillation of easy-to-separate mixtures (desorbent–water or desorbent–alcohol). This provides a very energy efficient method for production of MFGA because the energy required to run the CSA process is very small (only the energy of pumping liquids through the columns) and the energy required to separate desorbent–water or desorbent–ethanol mixtures can be minimized by appropriate selection of the desorbent liquid. At the same time, the CSA process is designed to produce a high purity ethanol (98+%) product with high recovery of ethanol (99+%) from the fermenter effluent. The product may, however, contain a trace amount of the desorbent liquid.

SELECTION OF ADSORBENT AND DESORBENT LIQUID

Any adsorbent that adsorbs ethanol from water with high selectivity and capacity and which provides sharp mass transfer zones for Steps (a) and (c) of this process can be used. We evaluated a large pore activated carbon (OL-carbon) manufactured by the Calgon Corp. (*6*) for the separation. The carbon had a total pore volume of 0.88 cm^3/g and a bulk density of 0.48 g/cm^3. More than 90% of the pores of the carbon had pore diameters greater than 1 nm.

Acetone was chosen as an example of the desorbent liquid (D) for the process because acetone–water and acetone–alcohol mixtures are very easy to separate by simple distillation due to the large relative volatilities of these mixtures. The energy consumed for these separations are also small. Figure 3 shows isobaric binary vapor–liquid equilibrium data for the three binaries of interest for this process (*7*). y_i is the mole fraction of Component i in the vapor phase in equilibrium with a liquid phase mole fraction x_i of

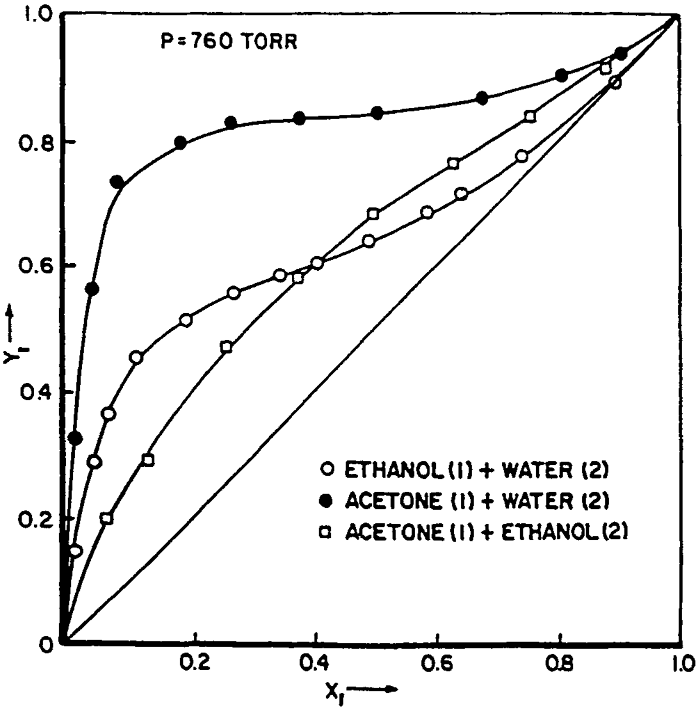

FIG. 3. Vapor–liquid equilibria for ethanol–water, acetone–water, and acetone–ethanol binary mixtures at atmospheric pressure.

that component. It will be shown in the next section that acetone is adsorbed on the OL carbon as strongly as ethanol, which is another criteria for the selection of the desorbent liquid for the present CSA process.

ADSORPTION EQUILIBRIA

The liquid-phase surface excess isotherms for adsorption of (a) ethanol (1) + water (2), (b) acetone (1) + water (2), and (c) acetone (1) + ethanol (2) binary mixtures were measured on the OL carbon at 30°C using the conventional method (*8*). A gas chromatograph was used to analyze the compositions of the bulk liquid mixtures before and after contact with the adsorbent. Figures 4(a), (b), and (c) show the measured surface excess isotherms. n_i^e is the surface excess of adsorption for Component *i* in equilibrium with a bulk liquid phase mole fraction x_i of that component.

It may be seen from Fig. 4(a) that the surface excess isotherm for the ethanol–water mixture is U-shaped with a very large initial slope ($x_1 \to 0$) and a prolonged linear section at higher concentrations of ethanol. This indicates that ethanol is very selectively adsorbed from water on the OL carbon (*9*). The large cacpacity for ethanol adsorption on the carbon is indicated by the large surface excess (4.7 mol/kg) at the maximum of the isotherm.

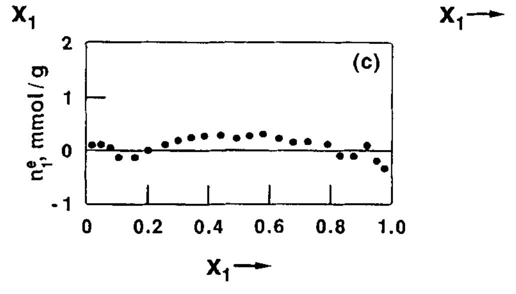

FIG. 4. Surface excess isotherms for adsorption of (a) ethanol (1) + water (2), (b) acetone (1) + water (2), and (c) acetone (1) + ethanol (2) binary mixtures on Calgon OL carbon at 30°C.

Figure 4(b) shows that acetone is also very selectively adsorbed from water on the carbon. In fact, acetone and ethanol are adsorbed from water on the carbon with comparable selectivity. This is demonstrated by Fig. 4(c) which shows that the surface excess isotherm for the acetone–ethanol mixture is nearly zero at all compositions, indicating no preference for adsorption of one component over the other (*9*).

ADSORPTIVE MASS TRANSFER

A major practical problem in carrying out bulk liquid-phase separation by adsorption in a fixed adsorbent column is the relatively low ad(de)sorptive mass transfer coefficients for the adsorbates caused by their slow counterdiffusion through liquid-filled pores of the adsorbent. This can significantly elongate the mass transfer zones in the column which makes the separation inefficient. For the present case, we need to have the sharpest possible MTZ for Steps (a)–(c) of the process which are adsorption or displacement steps. A more strongly adsorbed component is displacing a weakly adsorbed component (Steps a, b) or an equally strongly adsorbed component (Step c) in these steps.

This was achieved by using very small adsorbent particles (diameter d_p = 0.4 mm) in the column which reduces the dominating macropore diffusional resistance for the ad(de)sorption process (*10*). Use of small particles increases pressure drop through the column during the steps of the CSA process, but the energy penalty for compressing the liquid mixtures is negligible since the liquids are incompressible fluids.

We measured the characteristics of the mass transfer zones for Steps (a) and (d) of the process in a column apparatus using a column (diameter = 0.05 m, length = 4.3 m) packed with small diameter OL-carbon particles. The tests essentially consisted of saturating the column with a pure liquid (water for Step a, acetone for Step d) and then displacing it with another pure liquid (water for Step d) or a liquid mixture (22.0 mol% ethanol–water for Step a). The feed was introduced into the column at a constant flow rate at a pressure of 300–500 kPa, and the effluent liquid composition and quantity were monitored as a function of time. An automated gas chromatograph and a mass flow counter were used to analyze the effluent composition and quantities, respectively.

Figures 5 and 6 show the experimentally measured (circles) breakthrough curves for Steps (a) and (d), respectively. A dimensionless column effluent concentration α [$= (x_1 - x_1^S)/(x_1^F - x_1^S)$] is plotted against a dimensionless column effluent quantity β [$= Q/Qm$] in these figures. x_1^F and x_1^S are, respectively, the mole fractions of Component 1 in the feed liquid mixture and the initial saturating liquid mixture during the test. x_1 is the mole

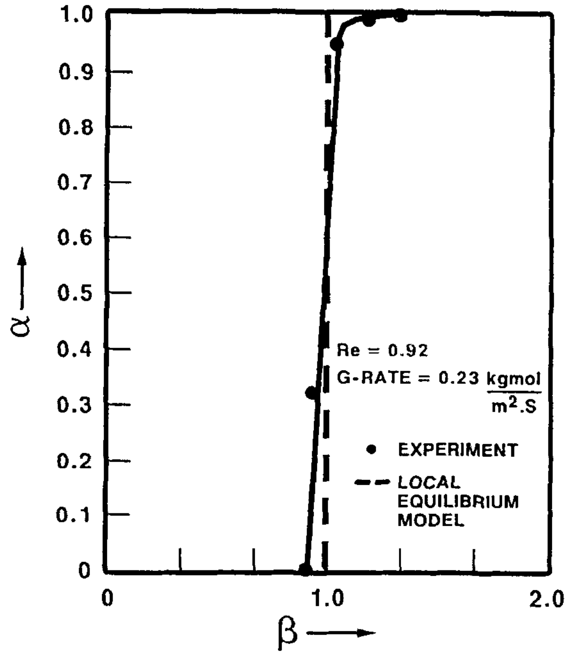

FIG. 5. Breakthrough curve for 22.0 mol% ethanol–water mixture displacing pure water in a Calgon OL carbon column.

fraction of Component 1 in the effluent liquid when the effluent quantity is Q (mol/kg). Qm (mol/kg) is the stoichiometric effluent quantity for the breakthrough curves (first moment). The figures also show the mass flow rates G (kgmol/m^2·s) and the particle Reynolds number ($\mathrm{Re} = d_pG/\mu$) for the feed liquid at the column entrance. μ is the viscosity of the feed liquid.

In the absence of dispersive forces in the column (mass transfer resistances, axial dispersion, channeling, fingering, etc.), the breakthrough curve of Fig. 5 should be a vertical line (α changing from zero to unity) at $\beta = 1.0$. The experimental data in Fig. 5 show that a nearly vertical breakthrough curve (symmetric around $\beta = 1.0$) could be obtained at the process conditions of the test. This indicates that Step (a) of the process can be run at near local equilibrium conditions. Qm for this step is equal to 121.0 mol/kg.

Figure 6, on the other hand, shows that the breakthrough curve for Step (d) of the process is very asymmetric around $\beta = 1.0$. α rises sharply from zero to 0.8 at $\beta = 0.83$ and then it slowly approaches unity (pure water)

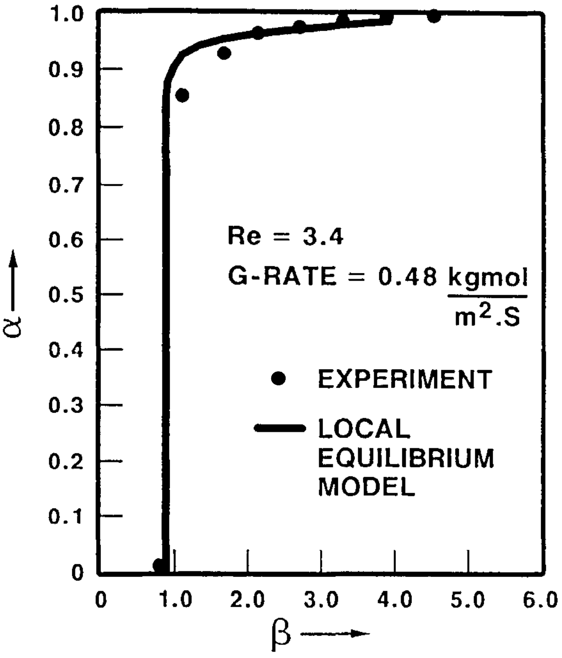

FIG. 6. Breakthrough curve for pure water displacing pure acetone in a Calgon OL carbon column.

at a β value of 4.8. *Qm* for this step is equal to 23.0 mol/kg. Consequently, the effluent liquid from the column during this step is pure acetone until β = 0.83 (total effluent = 19.0 mol/kg), followed by an effluent consisting of an acetone–water mixture of varying composition. The total quantity of mixed effluent is 91.0 mol/kg, and the mixed composition of that stream is 4.8 mol% acetone.

The diffused breakthrough curve of Step (d) is exhibited because a weakly adsorbed component (water) is displacing (desorbing) a strongly adsorbed component (acetone) in this step. This behavior can be explained even when local equilibrium conditions prevail (*11*). In fact, desorption under local equilibrium conditions can adequately describe the breakthrough curve of Fig. 6 as indicated by the solid line. The details of this calculation are given elsewhere (*11*).

LOCAL EQUILIBRIUM MODEL FOR CSA PROCESS

Assuming that the steps of the proposed CSA process can be run at near local equilibrium conditions, we calculated the sizes of the adsorbers as well as the feed and effluent streams for each step of the process by using a local equilibrium process model and the equilibrium data of Fig. 4. The model is described in Ref. *11*. Only the key design equations are reproduced here.

For adsorption Steps (a)–(c) of the process, the specific amount (mol/kg) of feed to the column (composition x_1^F) per cycle (F) is given by

$$F = \left[\left(\frac{n_1^{eF} - n_1^{eS}}{x_1^F - x_1^S}\right) + \bar{n}^F\right] \tag{1}$$

and the total specific amount of effluent from the column (composition x_1^S) per cycle (E) is given by

$$E = \left[\left(\frac{n_1^{eF} - n_1^{eS}}{x_1^F - x_1^S}\right) + \bar{n}^S\right] \tag{2}$$

where n_1^e is the surface excess of the more strongly adsorbed Component 1 in the system in equilibrium with its bulk liquid phase mole fraction of x_1. The superscripts F and S represent, respectively, the column feed and the initial saturating condition of the column during any step. $\bar{n}$ represents the specific total saturation capacity (mol/kg) of the packed column for a liquid mixture of composition x_1. $\bar{n}$ can be independently measured by filling a clean packed column with a liquid mixture of composition x_1 until the effluent liquid composition is x_1 and measuring the total amount of liquid introduced and removed from the column during the process.

For the desorption Step (d) of the process, we used actual column dynamic data (Fig. 6) for calculation of the column feed and the column effluent quantities.

Table 1 summarizes the calculated process performance results for separating an ethanol–water mixture containing 20.0 mol% alcohol. The $\bar{n}$ values for saturating a packed column of OL carbon with pure water, pure ethanol, pure acetone, and the 20.0 mol% ethanol–water mixture were measured to be 96.5, 33.1, 24.8, and 69.8 mol/kg, respectively.

It may be seen from Table 1 that the calculated effluent quantity (118 mol/kg) for Step (a) of the process compares very well with the experimental value of 121.0 mol/kg. Also, the calculated acetone feed quantity of 24.8 mol/kg for Step (c) compares well with the total acetone effluent of 23.7 mol/kg measured experimentally for Step (d).

Furthermore, Table 1 shows that the net specific amount of feed ethanol–water mixture (Feed in Step a − Effluent of Step b) which can be handled by the CSA process is 26.8 mol/kg and the net amount of alcohol produced

TABLE 1
Local Equilibrium Model Calculations of the Performance of the CSA Process for MFGA Production

	Feed		Effluent	
Step	Quantity/cycle (mol/kg)	Composition (mol%)	Quantity/cycle (mol/kg)	Composition (mol%)
(a) Adsorption	91.3	20.0% Ethanol + 80.0% water	118.0[a]	100.0% Water
(b) Ethanol rinse	27.7	100.0% Ethanol	64.4	20.0% Ethanol + 80.0% water
(c) Acetone rinse	24.8	100.0% Acetone	33.1	100.0% Ethanol
(d) Water rinse[b]	184.2	100.0% Water	19.0[c]	100.0% Acetone
			91.0[c]	4.8% Acetone + 95.2% water

[a] First moment of experimental breakthrough curve = 121.0 mol/kg.

[b] Step (d) performance was obtained from actual column dynamics data.

[c] Total acetone out during step = 23.7 mol/kg.

by the process is 5.3 mol/kg. The molar amount of acetone–water mixture (4.8 mol% acetone) to be distilled per unit molar amount of alcohol produced is 17.0.

The energy requirement for separating a 4.8 mol% acetone–water mixture to pure acetone and water products by simple distillation was estimated to be 2.6×10^4 kcal/kg mol acetone by using a standard distillation design program. This information was used in conjunction with the distillation energy to produce a 20.0 mol% ethanol–water mixture from the fermenter effluent containing 4.0 mol% ethanol in order to estimate the total energy required by the CSA process to make MFGA. It was found that even without heat integration, the CSA process consumes only 60.0% of the energy needed to produce MFGA by the distillation route.

The adsorber sizes for the CSA process using the OL carbon were also found to be very reasonable. For example, using a 30-min cycle time for each step of the CSA process, it was calculated that the adsorbers would contain 8000 kg adsorbent per column for producing 38,000 m^3/yr MFGA per year.

The above calculations are based on an idealized local equilibrium model of the CSA process but they show the potential advantages of this process for MFGA production.

CONCLUSIONS

The CSA process provides an energy efficient means to produce MFGA from a fermenter effluent. It avoids the conventional azeotropic distillation route of making high purity alcohol by using selective liquid-phase adsorption of alcohol from water and thus reduces the energy requirement for the ethanol–water separation. The process can also be used to separate other azeotropic mixtures or liquid mixtures having close-boiling components by appropriate selection of the adsorbent and the desorbent liquid.

REFERENCES

1. R. Katzen, J. D. Kumana, and G. D. Moon, "Distillation System for Motor Fuel Grade Anhydrous Alcohol," U.S. Patent 4,217,178 (1980).
2. W. F. Ginder, "Method of Removing Water from Ethanol," U.S. Patent 4,407,662 (1982).
3. D. R. Garg and C. M. Yon, "Adsorptive Heat Recovery Drying System," *Chem. Eng. Prog.*, *82*, 54 (1986).
4. R. A. Tidball and G. F. Tusel, "Advantages of Combining Distillation and Pervaporation in Power Ethanol Production," in *Proceedings of First International Conference on Pervaporation Processes* (R. Bakish, ed.), Bakish Materials Corporation, Englewood, New Jersey, 1986, p. 142.
5. S. Sircar, "Process for Preparing Motor Fuel Grade Alcohol," U.S. Patent 5,030,775 (1991).
6. Calgon Corporation Data Sheet 23-102d, Pittsburgh, Pennsylvania.
7. J. Gmehling et al. (ed.), *Vapor–Liquid Equilibrium Data Collection*, DECHEMA, Frankfurt, Germany, 1981.
8. S. Sircar and A. L. Myers, *AIChE J.*, *17*, 186 (1971).
9. S. Sircar, *J. Chem. Soc., Faraday Trans. I*, *82*, 831 (1986).
10. M. B. Rao, S. Sircar, and T. C. Golden, in *Extended Abstracts, 20th Biennial Conference on Carbon*, 1991, p. 54.
11. S. Sircar and M. B. Rao, "Kinetics and Column Dynamics for Adsorption of Bulk Liquid Mixtures," *AIChE J.*, *38*, 811 (1992).