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# Focusing in Liquid Thermal Adsorption Systems

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**Abstract.** Focusing can be obtained in liquid thermal cycling zone adsorption by significantly increasing the temperature of the hot feed. To prevent boiling column pressure is raised. This method for concentrating dilute fluids was studied using the simulation package ADSIM. The systems studied were ethanol-water on silicalite and toluene-*n*-heptane on silica gel. Substantial concentration of dilute feeds while producing a pure solvent product were obtained. This research highlights the need for equilibrium data for liquid adsorption systems at elevated temperatures and pressures.

**Keywords:** adsorption, cycling zone adsorption, focusing

## 1. Introduction

The use of cyclic sorption of a solute as a means of separation has been studied for some time but has received renewed attention recently as the needs of the marketplace have called for higher purity products and specialty separations. Cyclic adsorption techniques work by varying a thermodynamic variable that affects the adsorption equilibrium in order to obtain the separation. The two variables most commonly manipulated are the pressure and the temperature, though the manipulation of solution pH has also been investigated.

The original cyclic liquid thermal swing adsorption (TSA) processes were parametric pumping (Wilhelm et al., 1966; Rolke and Wilhelm, 1969) and cycling zone adsorption (CZA) (Pigford et al., 1969; Baker and Pigford, 1971). This research is reviewed by Wankat (1986). The CZA method was first developed for removing and concentrating all solutes from a feed that is fed continuously to an adsorption column. It can be operated by externally heating or cooling the adsorption column (direct mode) or by heating and cooling with hot and cold fluid (traveling wave mode, see Fig. 1).

CZA is a co-current process that operates by alternating between cold and hot feed solutions to concentrate the solute. Since feed is always processed, productivity is high. The inherent disadvantage of CZA is that in many situations it is impossible to obtain almost pure solvent product. However, under favorable conditions, a phenomenon called focusing occurs which results in large increases in concentration of the concentrated product and very pure solvent product. Unfortunately, focusing is common only in thermal gas adsorption (Natarajan and Wankat, 2003).

The goal of this paper is to develop a method for focusing a thermal adsorption with liquids. The commercial adsorption simulation package, ADSIM™ is used to simulate the separations.

## 2. Theory

The local equilibrium model is a method for performing calculations on adsorption systems using simplified forms of the mass and energy balances to enable analytical calculations. This model, developed in detail by Baker and Pigford (1971) and discussed by Wankat

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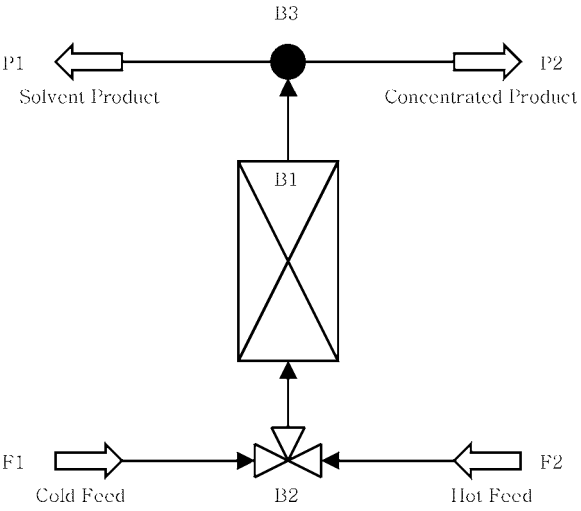


*Figure 1.* ADSIM flowsheet for co-current liquid simulation of traveling wave mode of CZA.

(1986, 1990), will be used to explain the separation. The solid and fluid are assumed to be locally in equilibrium. The mass and energy balances for non-isothermal fixed bed adsorption can be derived by writing differential balances around the solid and fluid phases. If one assumes that radial gradients are negligible, no chemical reactions take place, mass transfer is extremely rapid and there is no axial dispersion, the mass balances can be solved for the solute wave velocity.

$$u_s = \frac{v}{1 + \left(\frac{1-\varepsilon}{\varepsilon}\right)\rho_p \frac{\partial q}{\partial c}} \tag{1}$$

If the isotherm follows a Langmuir shape and a concentrated fluid pushes out dilute fluid, one needs to replace $\partial q/\partial c$ in Eq. (1) with $\Delta q/\Delta c$ and $u_s$ becomes the shock velocity $u_{sh}$.

$$u_{sh} = \frac{v}{1 + \left[\left(\frac{1-\varepsilon}{\varepsilon}\right)\rho_p \frac{(q_2 - q_1)}{(c_2 - c_1)}\right]} \tag{2}$$

In order to calculate the velocity from Eqs. (1) or (2), an equilibrium expression is required. The most commonly used form is the Langmuir isotherm.

$$q = \frac{A(T)c}{1 + B(T)c} \tag{3}$$

where $A(T)$ and $B(T)$ are both isotherm parameters, which often follow an Arrhenius form.

In the CZA process, temperature changes force the separation. The velocity at which temperature moves in the column can be obtained from the energy balance. If one assumes the heats of adsorption and mixing are negligible, the column is adiabatic, heat transfer is very rapid, and thermal axial dispersion is negligible, the average velocity of the thermal wave is

$$u_{th} = \frac{v}{1 + \left[\frac{(1-\varepsilon)C_{p,s}\rho_p}{\varepsilon\rho_f C_{p,f}}\right]} \tag{4}$$

In a typical liquid system,

$$u_{th} > u_s(T_h, c_F) > u_s(T_c, c_F) \tag{5}$$

If the thermal wave velocity moves at a velocity in between the solute wave velocities,

$$u_s(T_h, c_F) > u_{th} > u_s(T_c, c_F) \tag{6}$$

then focusing occurs. The result is a large increase in concentration, which forms a shock wave which moves ahead of the thermal wave (e.g., see Wankat, 1990). By raising the pressure to prevent boiling, one will often be able to increase the temperature sufficiently to satisfy Eq. (6) and thus ensure focusing will occur. The regeneration temperature at which focusing occurs is determined as the characteristic temperature (Basmadjian et al., 1975),

$$\left.\frac{\partial q}{\partial y}\right|_{y=0} = \frac{C_{p,s}}{C_{p,f}} \tag{7}$$

Unfortunately, since we were unable to find any data for liquid adsorption isotherms at the elevated pressures and temperatures that satisfy Eq. (7) without boiling, we had to extrapolate to do calculations.

## 3. Simulation

To obtain more accurate predictions than the results of the local equilibrium model, the processes were modeled and simulated using ADSIM™ v.10.2 adsorption software by Aspen Technology Inc. ADSIM directly solves the complete mass and energy balances numerically. Figure 1 is a schematic of the process that was simulated. Brief details of the simulation are given by Natarajan and Wankat (2003) and extensive details are given by Natarajan (2002).

*Table 1.* Langmuir isotherm constants.

| Isotherm constants | Toluene-*n*-heptane system | Ethanol-water system |
|---|---|---|
| $A_1$ | 4.2966E-7 | 1.2060E-5 |
| $A_2$ | 3012.9789 | 2271.2258 |
| $B_1$ | 3.0892E-3 | 4.7200E-3 |
| $B_2$ | 3309.3490 | 2313.8391 |

The flow is modeled as convection with constant dispersion and pressure drop is calculated using the Carman-Kozeny equation. The velocity is allowed to vary with the material balance. The kinetic model assumption is set as linear lumped resistance. The bed is assumed to be adiabatic. The expressions for the enthalpy, density, component molecular weights, average molecular weight of the solutions, heat capacity, viscosity (Yaws, 1999) and the necessary transport parameters for both system are supplied using FORTRAN code. Also, an adsorption equilibrium relation is needed in order to use ADSIM. The isotherm parameter values for the high temperatures were estimated by extrapolating the experimental data reported for toluene-*n*-heptane with silica gel (Matz and Knaebel, 1991) and ethanol-water systems with silicalite (Bui et al., 1985). The equilibrium data used in this research were correlated with the Langmuir isotherm. Both isotherm parameters followed a pseudo-Arrhenius temperature

*Table 2.* Simulation conditions.

Toluene-*n*-heptane system

Flow rate: 0.00024 $m^3$/min

Initial feed composition of toluene:

$C_F = 0.00134$ kgmol/$m^3 = 0.020$ wt%

$C_F = 0.00434$ kgmol/$m^3 = 0.064$ wt%

$C_F = 0.00834$ kgmol/$m^3 = 0.123$ wt%

Cold feed temperature: 298.15 K

Hot feed temperature: 420.15 K

Pressure: 10 atm

Column length: 0.61 m

Column diameter: 0.051 m

Ethanol-water system

Flow rate: 0.01257 $m^3$/min

Initial feed composition of ethanol:

$C_F = 0.00134$ kgmol/$m^3 = 0.007$ wt%

$C_F = 0.00434$ kgmol/$m^3 = 0.021$ wt%

$C_F = 0.00834$ kgmol/$m^3 = 0.041$ wt%

Cold feed temperature: 298.15 K

Hot feed temperature: 490.15 K

Pressure: 17 atm

Column length: 1 m

Column diameter: 0.4 m

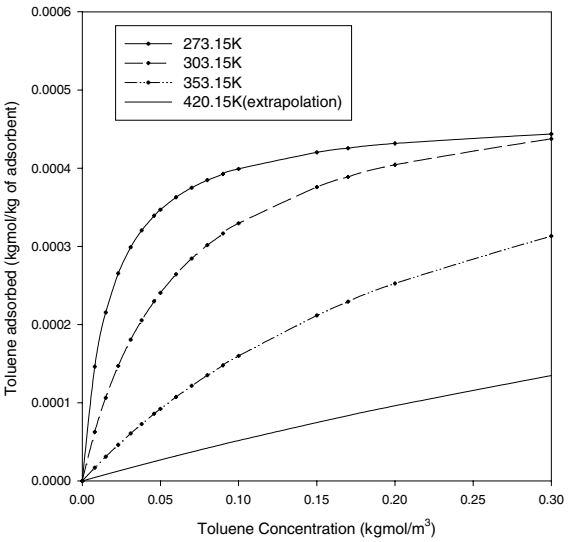


*Figure 2.* Adsorption isotherms of toluene-*n*-heptane system. Data at 273.15, 303.15 and 353.15 K is experimental results by Matz and Knaebel (1991).

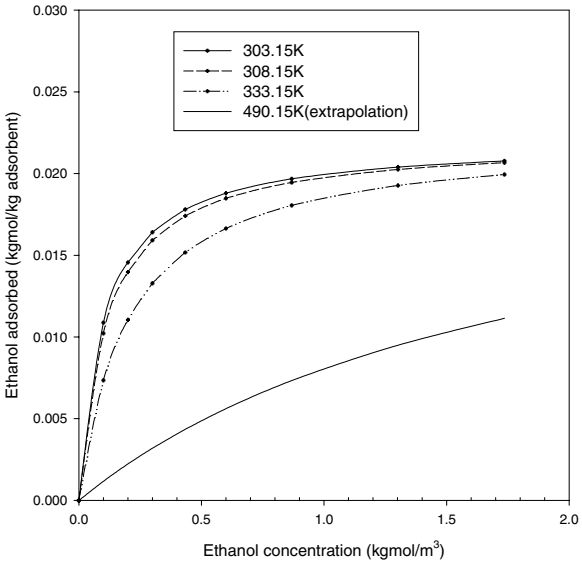


*Figure 3.* Adsorption isotherms of ethanol-water system. Data at 303.15, 308.15 and 333.15 K is experimental results by Bui et al. (1985).

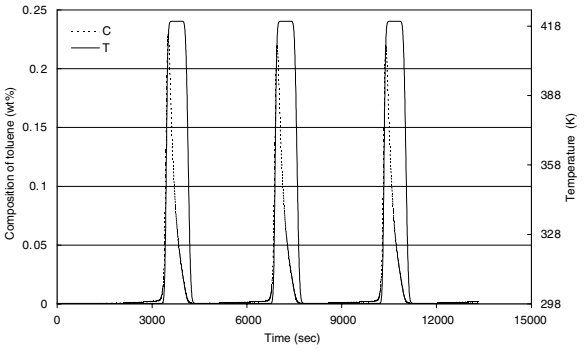


*Figure 4*. Outlet composition of toluene and temperature profiles for toluene-*n*-heptane system. Feed composition = 0.00134 kgmol/m$^3$ = 0.02 wt%. P1 does not include the lag time.

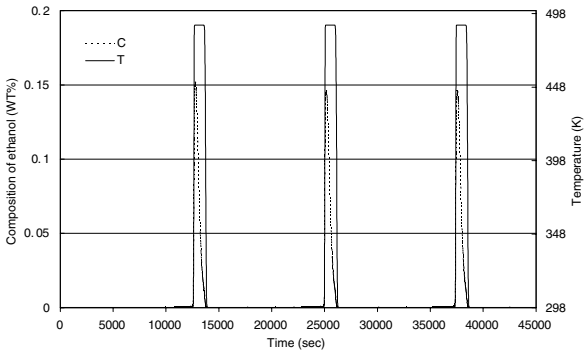


*Figure 5*. Outlet composition of ethanol and temperature profiles for ethanol-water system. Feed composition = 0.00134 kgmol/m$^3$ = 0.007 wt%. P1 does not include the lag time.

dependence.

$$A(T) = A_1 \cdot e^{\frac{A_2}{T}} \tag{8}$$

$$B(T) = B_1 \cdot e^{\frac{B_2}{T}} \tag{9}$$

The isotherm parameters are shown in Table 1 and the resulting isotherms are shown in Figs. 2 and 3, respectively.

The simulation was performed for two operating models. After the bed is filled with pure cold solvent,

*Table 3*. Cyclic times for the two operating modes.

| Toluene-*n*-heptane system (Fig. 4) | |
|---|---|
| Condition: $C_F$ = 0.00134 kgmol/m$^3$ = 0.02 wt% | $T_{cold}$ = 298.15 K, $T_{hot}$ = 420.15 K |
| 1. No lag time | 2. With lag time |
| 1. Cold feed for 2988 sec. to P1 | 1. Cold feed for 2988 sec. to P1 |
| 2. Hot feed for 690 sec. to P2 | 2. Hot feed for 440 sec. to P1 |
| 3. Cold feed for 475 sec. to P2 | 3. Hot feed for 250 sec. to P2 |
| 4. Cold feed for 2279 sec. to P1 | 4. Cold feed for 475 sec. to P2 |
| 5. Hot feed for 690 sec. to P2 | 5. Cold feed for 2279 sec. to P1 |
| 6. Cold feed for 475 sec. to P2 | 6. Hot feed for 440 sec. to P1 |
| | 7. Hot feed for 250 sec. to P2 |
| | 8. Cold feed for 475 sec. to P2 |
| **Ethanol-water system (Fig. 5)** | |
| Condition: $C_F$ = 0.00134 kgmol/m$^3$ = 0.007 wt% | $T_{cold}$ = 298.15 K, $T_{hot}$ = 490.15 K |
| 1. No lag time | 2. With lag time |
| 1. Cold feed for 11824 sec. to P1 | 1. Cold feed for 11824 sec. to P1 |
| 2. Hot feed for 1114 sec. to P2 | 2. Hot feed for 714 sec. to P1 |
| 3. Cold feed for 849 sec. to P2 | 3. Hot feed for 400 sec. to P2 |
| 4. Cold feed for 10423 sec. to P1 | 4. Cold feed for 849 sec. to P2 |
| 5. Hot feed for 1114 sec. to P2 | 5. Cold feed for 10423 sec. to P1 |
| 6. Cold feed for 849 sec. to P2 | 6. Hot feed for 714 sec. to P1 |
| | 7. Hot feed for 400 sec. to P2 |
| | 8. Cold feed for 849 sec. to P2 |
| Steps 4–6 and 5–8 are then repeated to obtain cyclic steady state. | |

*Table 4*. Simulation results for toluene-*n*-heptane system (P1 does not include the lag time).

| $C_F$ (kgmol/m$^3$) | $C_F$ (wt%) | $C_{avg}$ (wt%) | $C_{max}$ (wt%) | $C_{pure}$ (wt%) | $C_{avg}/C_F$ | $C_{max}/C_F$ | $C_{pure}/C_F$ |
|---|---|---|---|---|---|---|---|
| 0.00134 | 0.020 | 0.056 | 0.220 | 0.0009 | 2.800 | 11.00 | 0.045 |
| 0.00434 | 0.064 | 0.178 | 0.625 | 0.0031 | 2.781 | 9.77 | 0.048 |
| 0.00834 | 0.123 | 0.330 | 1.034 | 0.0061 | 2.683 | 8.41 | 0.050 |

*Table 5*. Simulation results for toluene-*n*-heptane system (P1 includes the lag time).

| $C_F$ (kgmol/m$^3$) | $C_F$ (wt%) | $C_{avg}$ (wt%) | $C_{max}$ (wt%) | $C_{pure}$ (wt%) | $C_{avg}/C_F$ | $C_{max}/C_F$ | $C_{pure}/C_F$ |
|---|---|---|---|---|---|---|---|
| 0.00134 | 0.020 | 0.083 | 0.220 | 0.0027 | 4.150 | 11.00 | 0.135 |
| 0.00434 | 0.064 | 0.255 | 0.625 | 0.0110 | 3.984 | 9.77 | 0.172 |
| 0.00834 | 0.123 | 0.450 | 1.034 | 0.0270 | 3.659 | 8.41 | 0.220 |

*Table 6*. Simulation results for ethanol-water system (P1 does not include the lag time).

| $C_F$ (kgmol/m$^3$) | $C_F$ (wt%) | $C_{avg}$ (wt%) | $C_{max}$ (wt%) | $C_{pure}$ (wt%) | $C_{avg}/C_F$ | $C_{max}/C_F$ | $C_{pure}/C_F$ |
|---|---|---|---|---|---|---|---|
| 0.00134 | 0.007 | 0.040 | 0.146 | 0.0003 | 5.714 | 20.87 | 0.043 |
| 0.00434 | 0.021 | 0.128 | 0.501 | 0.0009 | 6.105 | 23.86 | 0.043 |
| 0.00834 | 0.041 | 0.242 | 1.044 | 0.0016 | 5.895 | 25.46 | 0.039 |

*Table 7*. Simulation results for ethanol-water system (P1 includes the lag time).

| $C_F$ (kgmol/m$^3$) | $C_F$ (wt%) | $C_{avg}$ (wt%) | $C_{max}$ (wt%) | $C_{pure}$ (wt%) | $C_{avg}/C_F$ | $C_{max}/C_F$ | $C_{pure}/C_F$ |
|---|---|---|---|---|---|---|---|
| 0.00134 | 0.007 | 0.063 | 0.146 | 0.0003 | 8.914 | 20.87 | 0.043 |
| 0.00434 | 0.021 | 0.201 | 0.501 | 0.0010 | 9.517 | 23.86 | 0.048 |
| 0.00834 | 0.041 | 0.376 | 1.044 | 0.0020 | 9.171 | 25.46 | 0.049 |

the simulation is started by feeding the cold dilute solution to the bed. In procedure 1, when the oulet concentration reaches 10% of the feed value (the break point), the outlet destination is changed from P1 to P2 and the feed is switched from the cold stream to the hot stream. The product port switching times are determined based on the column outlet results. In procedure 2, the feed is switched from the cold stream to the hot stream when the outlet concentration again reaches 10% of the feed value. After a lagtime, which is the time required for breakthrough of the shock wave ($L/u_{sh} \sim L/u_{th}$), the outlet destination is switched from P1 to P2. After the hot step, the column input is switched back to the cold feed solution, which is the start of the next cycle. The hot feed step ends at the moment the shoulder starts to form in outlet concentration profile.

## 4. Simulation Results

Simulation conditions are summarized in Table 2 and the cycle times are given in Table 3. The concentration and temperature profiles obtained from simulations are shown in Figs. 4 and 5 and are summarized in Tables 4 through 7. As expected, Figs. 4 and 5 look like typical results for focusing systems. The concentration suddenly jumps upon the introduction of the thermal wave. Since the first peak is a start-up peak, only the results after the first peak are of interest. All simulations reached cyclic steady state after two cycles. The results for the operation with lag times are not shown because they look very similar to Figs. 4 and 5. Differences in the operations are clear from comparision of Tables 4 and 5, and of 6 and 7.

If the goal is to obtain a more concentrated product (P2), the lag time is very important because the low composition solute in the column during this lag greatly reduces this concentration. Consequently, the operations with proper lag time (Tables 5 and 7) show significantly higher average compositions of the concentrated products. However, the average composition of solvent product, $C_{\text{pure}}$, aiso increases. The lag time does not change the maximum composition.

## 5. Discussion and Conclusions

By increasing pressure sufficiently that hotter feeds do not boil, a method of obtaining focusing with liquid thermal adsorption system was developed. Since the very dilute solutions show the highest concentration factor and the highest dilution of the pure solvent product, this method works best for very dilute solutions. The CZA cycle can be tuned to produce very pure solvent product or more concentrated solute. Energy requirements for CZA are very low compared to evaporation without heat recovery (Natarajan and Wankat, 2003). Since more than half of the solvent is removed, CZA is a very low energy process for preliminary concentration of dilute solutions. These simulations show that CZA with focusing can be used to concentrate liquid systems. As long as the liquid system and the adsorbent are thermally stable, this approach should be applicable to a large variety of systems.

Since the isotherm data was extrapolated, there is uncertainty in the results of our simulations. The toluene, *n*-heptane simulations are probably more accurate since much less extrapolation was required. We hope that this research will encourage experimentalists to measure isotherm data for liquid systems at temperatures above the normal boiling points of the liquids.

## Nomenclature

| | |
|---|---|
| $A(T)$ | Isotherm parameter |
| $B(T)$ | Isotherm parameter |
| $c$ | Component concentration, kgmol/m$^3$ |
| $c_{\text{avg}}$ | Average concentration, kgmol/m$^3$ |
| $c_F$ | Feed concentration, kgmol/m$^3$ |
| $c_{\text{pure}}$ | Sovent product composition, kgmol/m$^3$ |
| $C_{p,f}$ | Fluid heat capacity, J/kg/K |
| $C_{p,s}$ | Solid heat capacity, J/kg/K |
| $q$ | Amount of solute adsorbed, kgmol/kg adsorbent |
| $T$ | Temperature, K |
| $T_c$ | Cold feed temperature, K |
| $T_h$ | Hot feed temperature, K |
| $u_s$ | Average velocity of the solute, m/s |
| $u_{sh}$ | Shock wave velocity, m/s |
| $v$ | Interstitial velocity, m/s |

*Greek Symbols*

| | |
|---|---|
| $\varepsilon$ | Porosity |
| $\rho_f$ | Fluid density, kg/m$^3$ |
| $\rho_p$ | Particle density, kg/m$^3$ |

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