Residual Monomer Reduction in Polymer Latex Products by Extraction with Supercritical Carbon Dioxide

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Summary: Extraction of residual monomer from a latex product with supercritical carbon dioxide ((sc)CO_2) in a column was studied. Operating conditions were chosen at 35 °C and 100 bar. For reducing the residual styrene level in a polystyrene latex from 10^4 ppm to 100 ppm and from 10^4 ppm to 10 ppm, a countercurrent bubble column with latex as continuous and (sc)CO_2 as dispersed phase is suggested. Monomer partitioning was demonstrated to be a key parameter in the equipment design. Monomer transport was found to be governed by the shuttle effect, caused by Brownian motion of the latex to and from the H_2O/CO_2 interface. The drift-flux approach was followed to determine the column flooding conditions. Small column volumes are obtained. (sc)CO_2 is a promising extraction medium for residual monomer reduction in latex products. Performance towards steam stripping is better as the final residual monomer level becomes lower.

Keywords: extraction; latex; partitioning; residual monomer; shuttle effect; supercritical carbon dioxide

Introduction

Emulsion polymerization is widely used in industry for production of paints, coatings, adhesives and rubbers.[1] The resulting latex is a dispersion of submicron (~100 nm) polymer particles in water (H_2O). The polymerization reaction does not proceed to completion due to e. g. diffusion limitations of the monomer molecules in the polymer particles. As a consequence, the polymer product contains a significant amount of residual monomer inside the particles, generally in the range of thousand parts per million (ppm). Legislation on the residual monomer level in polymer products is becoming increasingly strickt. Reducing the residual monomer level is therefore a major incentive for the polymer producing industry. In practice, techniques as steam stripping or a post polymerization temperature increase to reduce the residual monomer level are both energy intensive, time consuming and unable to meet future requirements.[2] A novel method to reduce residual monomer in the latex particles based on high pressure or supercritical carbon dioxide ((sc)CO_2) extraction is being developed. The fugacity of the monomer tremendously increases with the volume fraction of low molecular weight species in the polymer particles on addition of carbon dioxide. Moreover, high pressure CO_2 is an excellent extraction medium for various monomers as monomers have a relatively high solubility in CO_2, while very little water and practically no polymer dissolves in CO_2. Solubility and diffusivity of the monomer in (sc)CO_2 can easily be tuned by small changes in pressure and temperature. Due to the plasticizing effect the diffusion coefficient of the monomer in the polymer particles increases from$D_m^P = 10^{-15}\,\frac{m^2}{s}$ to $D_m^P = 10^{-12}\,\frac{m^2}{s}$ or even higher.[3]

In this study a process design for (sc)CO_2 extraction of residual monomer from

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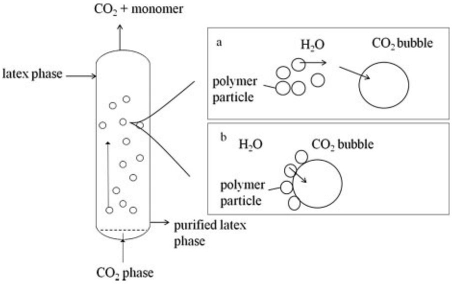

Figure 1.
Equipment for extraction of residual monomer from latex with (sc)CO_2. a) resistance in series mass transport; b) shuttle effect.[4]

polystyrene latex in a bubble column is made with latex as the continuous and the (sc)CO_2 bubbles as the dispersed phase. Figure 1 schematically pictures the extraction equipment.

Calculations are conducted based on experimentally determined parameters for a reduction of residual monomer from 10000 ppm to 100 and 10 ppm.

Partitioning

The key parameter for equipment design is partitioning of the monomer between the latex and the (sc)CO_2 phase. Partitioning is expressed in the partition coefficient:

$$K_m = \frac{C_m^{CO_2}}{C_m^P}\left[\frac{\text{kg polymer}}{\text{kg } CO_2}\right] \quad (1)$$

In equation (1) $C_m^{CO_2}$ and C_m^P are the equilibrium concentrations of the monomer in the CO_2 and the polymer phase. Note that the partition coefficient depends in general on concentrations.

The partition coefficient governs the amount of (sc)CO_2 needed for extraction, as indicated by the mass balance over one stage of a countercurrent extraction column, equation 2, see Figure 2.

$$\phi_{CO_2} = \phi_P * \frac{C_{m,n-1}^P - C_{m,n}^P}{C_{m,n}^{CO_2} - C_{m,n+1}^{CO_2}}\left[\frac{m^3}{hr}\right] \quad (2)$$
$$\text{with } C_{m,n}^{CO_2} = K_m * C_{m,n}^P$$

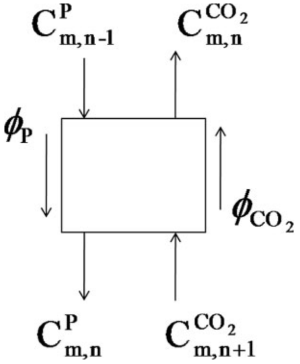

Figure 2.
Flowrates and concentrations through a theoretical stage in extraction equipment.

where ϕ_{CO_2} and ϕ_P are the volumetric flowrates of CO_2 and latex per hour.[5]

On swelling the particles with (sc)CO_2 the volume fraction of polymer in the polymer phase (*i. e.* the polymer particles) decreases and remains in the reduced state as long as there is (sc)CO_2 present in the column. Consequently, the monomer partition coefficient does not change from stage to stage, but can be assumed to be a constant.

Monomer Transport

Two mechanisms for transfer of monomer from latex particles to (sc)CO_2 can operate in parallel. The classical, resistance in series, solid-to-liquid-to-gas (SLG) mass transfer model and a direct solid-to-gas (SG) mass transfer model, also referred to as the shuttle effect.[4,6]

In the resistance in series approach, the monomer diffuses out of the polymer particles through the H_2O phase into the (sc)CO_2 phase. The main resistance against mass transfer is located in the H_2O phase (low monomer solubility[7]), Figure 3.

The partial mass transfer coefficient of the monomer in the polymer, H_2O and (sc)CO_2 phase follows from the film theory, equation 3.

$$k_m^i = \frac{D_m^i}{\delta_i}\left[\frac{m}{s}\right] \quad (3)$$

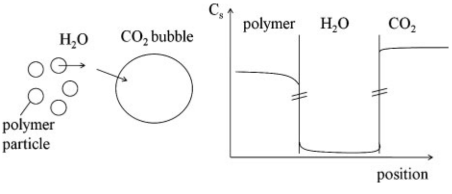

Figure 3.
The resistance in series mass transport approach.

where D_m^i is the diffusion coefficient of the monomer in phase i, δ_i is the boundary layer thickness of phase i.

In the SG mass transfer approach, the monomer diffuses out of the polymer particles directly into the (sc)CO_2 phase, see Figure 4.

The polymer particles are small enough to follow Brownian motion and consequently can reside, or adsorb, for some time at the (sc)CO_2/H_2O interface.[8] At the (sc)CO_2/H_2O interface the polymer particle is in direct contact with the (sc)CO_2 phase allowing direct diffusional transport of the monomer from the polymer particles to the (sc)CO_2 phase. Alper et al.[9] use the boundary layer model to describe mass transfer by the shuttle mechanism. However, in case of a system with particles with a limited adsorption capacity, stationary models cannot be applied. After a certain contact time the particles near the interface are depleted of monomer. Dumont[10] emphasized that in many situations the contact time between particle and fluid is so short that the steady-state concentration gradient of the film theory does not have time to develop. Therefore, only unsteady-state models can be used to estimate the mass transfer coefficient.

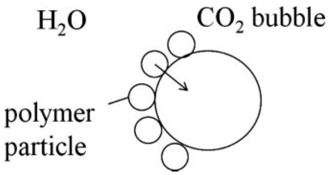

Figure 4.
The shuttle mechanism.

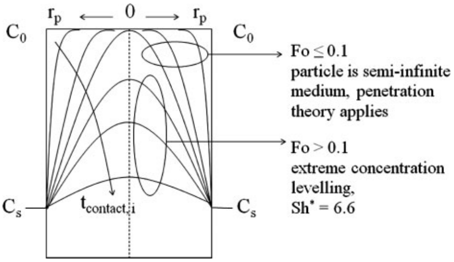

Figure 5.
Concentration levelling of the monomer in the polymer phase. r_p is the polymer particle radius, C_o the monomer concentration in the center of the particle, C_S the monomer concentration at the surface of the particle.

Concentration levelling of the monomer in the polymer phase is related to time or the Fourier number, see equation 4 and Figure 5.

$$\mathrm{Fo} = \frac{D_m^P * t_{\mathrm{contact,P}}}{d_{\mathrm{particle}}^2} \tag{4}$$

where $t_{\mathrm{contact,P}}$ is the time the polymer particles reside at the (sc)CO_2/H_2O interface (*i. e.* the contact time), d_{particle} is the polymer particle diameter (~100 nm).

$$*\mathrm{Sh} = \frac{k_m^i * d_i}{D_m^i}$$

Chon et al.[11] suggested that the residence time of polymer particles at the (sc)CO_2/H_2O interface can be regarded in terms of Brownian motion of the polymer particles in the H_2O phase, equation 5. Chon et al. used Al_2O_3 nanoparticles to increase the heat conductivity of water and validated that Brownian motion of the nanoparticles is the key mechanism for thermal conductivity enhancement. Comparable observations are reported by other authors.[12]

$$t_{\mathrm{contact,P}} = \frac{\Delta s}{v_{\mathrm{Br}}} \tag{5}$$

where Δs is the distance a particle travels in the interfacial region. The lenghtscale of the interfacial region is assumed to be 10 μm;[13] Δs is of the same order of magnitude. v_{Br} is the velocity of the polymer particles due to Brownian motion, see equation 6.

$$v_{Br} = \frac{k_b * T}{3 * \pi * \eta * d_{particle} * l_{BF}} \tag{6}$$

where k_b is the Boltzmann constant, T the absolute temperature, η the viscosity of water, l_{BF} the mean free path of the particle in water (*i. e.* $l_{BF} = 0.17\,nm$).[12]

For $Fo \leq 0.1$, the mass transport in the particles can be regarded to be in a semi-infinite medium. Then the penetration model applies for mass transport, see equation 7.

$$k_m^P = 2 * \sqrt{\frac{D_m^P}{\pi * t_{contact,P}}} \tag{7}$$

For $Fo > 0.1$, intraparticle mass transport can be described with equation 8, see Figure 5.

$$Sh = \frac{k_m^P * d_{particle}}{D_m^P} = 6.6 \tag{8}$$

Based on intrinsic properties of latex and (sc)CO_2, one can assume that the (sc)CO_2 bubbles can be regarded to behave as rigid spheres.[14] The monomer mass transfer coefficient in (sc)CO_2 is then dependent on the contact time between the polymer particle and the rising (sc)CO_2 bubble (~1 mm, specified by sieve plate in the column).

$$Fo = \frac{D_m^{CO_2} * t_{contact,CO_2}}{d_{CO_2}^2} \tag{9}$$

In a certain stage of the column, at the entrance of the (sc)CO_2 bubbles, the bubble needs a time $t_{contact,CO_2}$ for the monomer concentration at the center of the bubble and the monomer concentration at the surface of the bubble C_s to become equal; i.e. $Fo = 0.1$, see also Figure 5. In the neighboring stage, the bubble contacts polymer particles with a higher concentration of monomer. Again, the bubble needs a time $t_{contact,CO_2}$ to reach $Fo = 0.1$. This cycle repeats itself till the exit of the column. Note that the concentration levelling of monomer in the (sc)CO_2 bubble can only develop when the (sc)CO_2 and the latex phase are ideally mixed after every theoretical stage. Van den Akker[15] reported that bubbles in an empty bubble column, *i. e.* no packing is included, endure an overall circulation inside the column. The overall circulation the bubbles describe can be regarded as mixing the latex and (sc)CO_2 phase. The mass transport coefficient of monomer in the (sc)CO_2 phase is then approximated according to equation 10.

$$k_m^{CO_2} = 2 * \sqrt{\frac{D_m^{CO_2}}{\pi * t_{contact,CO_2}}} \tag{10}$$

The mass transfer resistance depends on the specific area of the (sc)CO_2/H_2O interface. Joly-Vuillemin et al.[16] suggested the polymer particles partially cover the (sc)CO_2/H_2O interface. The effective specific mass transfer area is then defined as

$$a_{eff} = a * \theta \text{ for the shuttle effect} \tag{12}$$

$$a_{eff} = a * (1 - \theta) \text{ for the SLG approach} \tag{13}$$

where a is the total (sc)CO_2/H_2O specific interfacial area $\left(\frac{m^2_{CO_2}}{m^3_{CO_2}}\right)$, θ is the fraction of the interfacial area covered by polymer particles; Note that θ_{max} is 0.91, *i.e.* the maximum bubble surface coverage by spherical particles in a two dimensional closest packing.[17]

The SLG model is diffusion limited due to the low solubility of the monomer in water.[7] In comparison with the SG mass transfer model, equilibrium cannot be reached within a short time. The shuttle effect is therefore dominating monomer mass transfer. The mass transfer-in-series contribution is assumed to be negligible.

Equipment Design

For extraction of residual monomer from a polystyrene (PS) latex by (sc)CO_2 an empty bubble column is chosen. Latex (containing 45% solids) enters the column at the top with a throughput of 6000 kg/hr; the continuous latex flow is comparable to stripping a batch of 30 ton latex with steam in about 5 hours. Countercurrently 1 mm (sc)CO_2 bubbles (specified by the sieve plate in the column) are dispersed into the latex. Both the latex and the (sc)CO_2 flow are considered to move through the column with negligible axial dispersion and perfect radial mixing, *i. e.* plug flow. Considering energy consumption and apparatus costs, the operating conditions of the bubble column are chosen; operating pressure of 100 bar and an operating temperature of 35 °C. The partition coefficient of styrene between the PS latex and (sc)CO_2 at the operating conditions mentioned is 0.4 $\frac{\text{kg polymer}}{\text{kg CO}_2}$. The lowest (sc)$CO_2$ flowrate, *i. e.* when the incoming latex and the outgoing (sc)CO_2 are at phase equilibrium,[5] to reduce the residual styrene level in the PS latex to 100 and 10 ppm, is approximately 15000 kg/hr. Note that for reducing the residual methyl methacrylate (MMA) level in a polymethyl methacrylate (PMMA) latex the lowest (sc)CO_2 flowrate is just about 3000 kg/hr. Less (sc)CO_2 is required to extract a similar amount of residual monomer from the PMMA latex in comparison to the PS latex due to the higher partition coefficient of MMA between PMMA latex and (sc)CO_2, *i. e.* $K_{MMA} = 2 \frac{\text{kg polymer}}{\text{kg CO}_2}$at 100 bar and 35 °C.

The drift-flux model reported by Wallis et al.[18] has been applied to describe the flow characteristics in the latex-(sc)CO_2 two-phase system. The drift-flux model is most importantly used to predict the flooding point, *i. e.* the limit of operation in countercurrent bubble flow.[19] The drift flux is proportional to the slip velocity. For solid (rigid spheres)-liquid systems, Richardson and Zaki[20] experimentally determined the relationship between the slip velocity, v_s, and the single sphere terminal settling/rising velocity, v_∞, equation 14. Note that the slip velocity is also a function of the volume fraction of the dispersed phase in the column, ε_d.

$$v_s = v_\infty * (1 - \varepsilon_d)^{n-1} \tag{14}$$

In equation 14, n is a function of the Reynolds number (Re) for the rigid spheres.

The terminal rising velocity of one bubble is primarily controlled by buoyancy forces and the fluid drag, also a function of Re, equation 15.

$$v_\infty = \sqrt{\frac{4 * \Delta\rho * g * d_{bubble}}{3 * \rho * C_D}} \tag{15}$$

For low Reynolds numbers (*i. e.* creep flow) the drag coefficient is $C_D = \frac{24}{Re_{bubble}}$.[21]

Evaluating the drift-flux model for the latex-(sc)CO_2 system described above, the flooding point is assigned to a volume fraction of (sc)CO_2 in the column of 0.55. It is recommended that the actual value of the slip velocity should be taken at no more than 70% of the estimated slip velocity at the flooding point;[22] in other words, the (sc)CO_2 hold up in the column is 0.35.

In Table 1 the results of the calculations for design of the bubble column are collected. The values reported are column volumes for both a residual monomer reduction from 10^4 ppm to 100 as well as from 10^4 ppm to 10 ppm at some values of θ. The column diameter is taken 1 m, the (sc)CO_2 or dispersed phase hold up is 0.35. To analyse the effect of the transport constant of styrene in the polymer phase,

Table 1.

The column volume for a residual monomer reduction from 10^4 ppm to 100 ppm and from 10^4 ppm to 10 ppm in function of the fraction of the H_2O/CO_2 interface covered with polymer particles (θ).*

θ [-]	$D_m^P = 10^{-12}\,\frac{m^2}{s}$		$D_m^P = 10^{-11}\,\frac{m^2}{s}$	
	V_{100} [m^3]	V_{10} [m^3]	V_{100} [m^3]	V_{10} [m^3]
0.9	10	20	8	18
0.3	28	60	25	53

*operating conditions: 100 bar, 35 °C, $K_s = 0.4$, $\varepsilon_{CO_2} =$ 0.35, column diameter $D_c = 1$ m

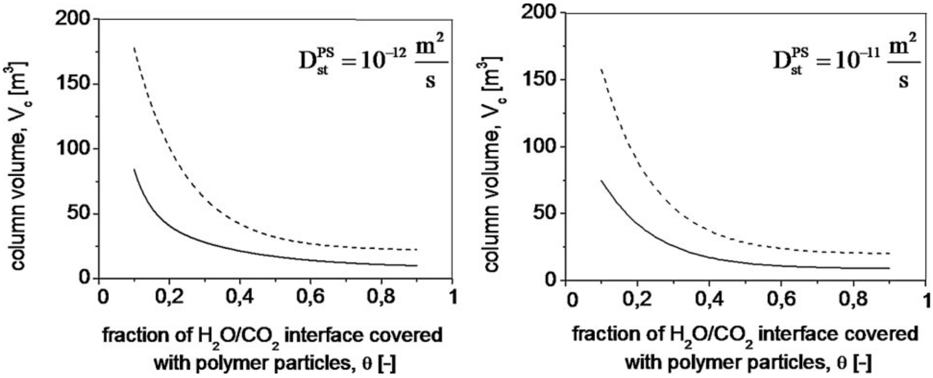

Figure 6.
Bubble column volume for high pressure extraction of styrene from PS latex in function of the fraction of the H_2O/CO_2 interface covered with polymer particles at 100 bar and 35 °C. $K_{st} = 0.4 \frac{\text{kg polymer}}{\text{kg } CO_2}$; $\varepsilon_{CO_2} = 0.35$; $D_c = 1$ m; —100 ppm, ----10 ppm residual monomer.

two values of the diffusion coefficient of monomer in polymer are chosen, *i. e.* $D_m^P = 10^{-12} \frac{m^2}{s}$ and $D_m^P = 10^{-11} \frac{m^2}{s}$.

Figure 6 represents column volumes as a function of θ.

Figure 6 shows that the fraction of the H_2O/CO_2 interface covered with polymer particles affects the column volume tremendously. Note that in Figure 6 the horizontal axis has a range of $0.1 < \theta < 0.91$. The upper limit is $\theta_{max} = 0.91$;[17] the lower limit follows from the assumption that mass transport of monomer from polymer particles into the (sc)CO_2 phase is dominated by the shuttle effect. How many polymer particles actually adsorb to the H_2O/CO_2 interface depends on interfacial surface tensions between H_2O(with surfactant)/polymer, polymer/CO_2 and H_2O(with surfactant)/CO_2[23] and on the frequency the polymer particles arrive at and move from the H_2O/CO_2 interface.

Although the monomer transport constant in the polymer particles decreases, *i. e.* increasing diffusion coefficient, column volumes are in the same order of magnitude, compare Figure 6 left to 6 right. This indicates that resistance against mass transport is not located inside the polymer particles. Resistance against mass transport is completely governed by the Brownian motion of the polymer particles to and from the surface of the (sc)CO_2 bubble, for $D_{st}^{PS} = 10^{-13} \frac{m^2}{s} \leq D_{st}^{PS} \leq D_{st}^{PS} = 10^{-10} \frac{m^2}{s}$.

Note that for a latex not swollen with (sc)CO_2 the monomer transport coefficient is very low due to the low diffusion coefficient of the monomer in the polymer particles, $D_{st}^{PS} = 10^{-15} \frac{m^2}{s}$.[3] Resistance against mass transport is then located inside the polymer particles.

In case of residual monomer reduction in a PMMA latex even smaller column volumes apply. The smaller column volume is a result of the higher partition coefficient, indicating that much less (sc)CO_2 is required to perform the extraction from 10^4 ppm to 100 and from 10^4 ppm to 10 ppm residual monomer, as mentioned above. Note that in this case the latex flowrate is higher than the (sc)CO_2 flowrate. It is then recommended to choose a spray tower instead of a bubble column.

Conclusion

Small column volumes apply for design of extraction equipment to reduce the residual monomer level in latex from 10^4 ppm to 100 and from 10^4 ppm to 10 ppm. Herein the monomer partition coefficient over the particles and the (sc)CO_2 phase is a key parameter, as the partition coefficient governs the amount of (sc)CO_2 needed for extraction. Monomer transport from the submicron polymer particles into the (sc)CO_2 phase is dominated by the shuttle effect. The fraction of the H_2O/CO_2 interface covered with polymer particles has a big impact on the column volume. Due to the plasticizing effect the diffusion coefficient of monomer in the polymer particles tremendously increases. As a consequence the Brownian motion of the polymer particles completely governs resistance against mass transfer.

Reducing the residual monomer level from a 6000 kg PS latex from 10^4 ppm to 100 ppm with (sc)CO_2 at 35 °C and 100 bar, bubble column volumes of 8-84 m^3 apply ($0.91 > \theta > 0.1$). When $\theta > 0.3$, θ affects the column volume less, *i. e.* column volumes less than 25 m^3 apply.

Reducing the residual monomer level from a 6000 kg PS latex from 10^4 ppm to 10 ppm at the same operating conditions, bubble column volumes of 18-178 m^3 apply ($0.91 > \theta > 0.1$). When $\theta > 0.3$, column volumes less than 55 m^3 are sufficient to perform the extraction.

Comparing the (sc)CO_2 extraction of residual monomer from a latex product with steam stripping, (sc)CO_2 is a promising extraction medium. For a reduction of residual monomer from 10^4 ppm to 100 ppm, both methods are comparable in efficiency and column volume[2]. Reducing the residual monomer from 10^4 ppm to 10 ppm by steam stripping is not achieved without high energy consumption due to thermodynamic and transport limitations. (sc)CO_2 is not only able to reduce the residual monomer level from 10^4 ppm to 10 ppm, (sc)CO_2 extraction columns of less than 55 m^3 apply.

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