Adhesion and agglomeration of catalyst particles in three phase reactors

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The impact of hydrophobic activated carbon particles on the hydrodynamics of aqueous slurry bubble columns*

Abstract

The hydrodynamics of three phase bubble columns is affected by the presence of particles in the liquid phase. This is commonly attributed to a change in the apparent viscosity and density of the slurry phase. Besides these commonly known effects, the column hydrodynamics may also be affected by adhesion of particles to the gas bubbles. As shown by Vinke, et al. (1991) and in Chapter 2, activated carbon particles may easily adhere to gas bubbles in aqueous slurries. The impact of adhesion on the hydrodynamics may be attributable to an effect on the bubble coalescence. The adhesion behaviour depends on the hydrophobicity of the solid particles and consequently the impact on the bubble coalescence is related to this parameter as well. A possible explanation for the impact of hydrophobicity is that hydrophobic particles will penetrate into the bubble-liquid interface resulting in an easier rupture of the liquid film between two gas bubbles, causing an easier coalescence between bubbles.

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5.1 Introduction

Slurry bubble columns are widely used in chemical industry. Nevertheless, the impact of catalyst particles present in the liquid phase on the overall hydrodynamics is not well understood. This matter has been subject of research by, for instance Bukur et al. (1990), Gavroy et al. (1995), Ghandhi et al. (1999), Krishna et al. (1997), Saxena et al. (1992), Tsutsumi et al. (1999), and Yasunishi et al. (1986). The research described in their articles is performed using glass, sand, or silica particles as solid phase. The impact of solid particles on the gas holdup and the bubble size distribution is generally attributed to parameters like the apparent viscosity or apparent density of the slurry. According to theory the gas holdup should decrease with an increasing solid concentration due to the resulting higher apparent viscosity and density. However, in contrast to this theory, the results reported by Tsutsumi et al. (1999) shows no effect. Furthermore, a literature review, presented by Banisi et al. (1995), shows that an increase of the gas holdup with increasing catalyst concentration can be found if very low concentrations (< 0.6 v/v%) and very small particles (< 10 μm), or very large particles (> 2000 μm) and high concentrations (> 10 v/v%) are used.

The impact of solid segregation, as apparent in particle agglomeration and particle to bubble adhesion is generally neglected in the literature. Exception to this is the study of Banisi et al. (1995). These authors used both silica (hydrophilic) and carbon (hydrophobic) particles for their investigations. It was demonstrated that the nature of the solids affects the gas holdup: the holdup in presence of 15 v/v% carbon is lower than in presence of 15% silica. The difference can obviously not be attributed to differences in the apparent viscosity or apparent density. This suggests that another phenomenon is to be held responsible for the changed hydrodynamics in a slurry bubble column, like adhesion of particles to the gas bubbles. For hydrophobic activated carbon particles in water, earlier work of described in Chapter 2 and published by Vinke (1991) revealed that such particles may indeed easily adhere to bubbles. This adhesion behaviour is affected by the hydrophobicity of the particles.

It is generally accepted that bubble coalescence occurs in three steps (Chaudari and Hofmann, 1994)). Initially a film between two bubbles is formed. Secondly thinning
of this film occurs and thirdly the film may rupture at a critical thickness. The last step may be affected by the presence of particles in the film layer.

As will be demonstrated, the impact of adhering particles on the slurry-bubble-column hydrodynamics may be substantial. In this study, the impact of the hydrophobicity of activated carbon on the gas holdup, as a measure for the hydrodynamics in a three phase reactor, is investigated. Two types of carbon are used, differing in hydrophobicity.

5.2 Experimental

5.2.1 Materials and Preparation

A steam activated peat based carbon, SX1G, supplied by Norit NV (Amersfoort, The Netherlands) is used for the experiments. The SX1G carbon is oxidised with nitric acid to obtain a more hydrophilic activated carbon. For this treatment the carbon is refluxed for 45 minutes in 200 ml 65 % nitric acid. Subsequently it is filtered and washed six times with water and dried at 80 °C over night. This carbon will be denoted as SX1G-HNO₃.

5.2.2 Characterisation

The results presented in Chapter 4 and results presented by Heinen et al. (2000) showed that the amount of carboxylic sites on the surface is a measure for the hydrophobicity of activated carbons. Therefore, FTIR is used to characterise the activated carbons. In this way a signal for the carboxylic groups (at 1700 cm⁻¹) and a signal for the bulk aromatic groups (1580 cm⁻¹) is obtained (Vinke, et al., (1994)). The ratio between the areas of both signals, so A₁₇₀₀/A₁₅₈₀ is a measure for the concentration of acidic groups, and thus a measure for the hydrophobicity. The infrared spectra were recorded with a Biorad FTS 45A spectrometer. FTIR is carried out by dispersing the activated carbon particles in pentane and subsequently brushed on a KBr-tablet. The obtained spectra are based on 256 scans and are corrected using a curved baseline.
SEM analysis is used to investigate the macroscopic structure of the activated carbon particles. The equipment used is a Philips XL30 FEG.

5.2.3. Holdup measurements

Holdup experiments are performed in a cylindrical bubble (3-D) column of 0.15 m diameter and a height of 4 m and in a two dimensional (2-D) slit-column, with a width of 0.3 m, a depth of 0.005 m and a height of 2 m. All experiments are carried out at room temperature and atmospheric pressure. The gas (air) inlet in both columns consists of a P00 glass filter. The superficial gas velocity \( v_{sg} \) is varied between 0 and 0.1 m s\(^{-1}\). After changing the gas flow, a wait time of 10 minutes is required before steady state is reached. In the 3-D bubble column, the pressure at different heights (0.6 and 1 m) is used to calculate the holdup. The gas holdup can be calculated from the time average pressure difference. In the 2-D slit-column the holdup was determined by measuring the liquid height with and without gas flowing through the column. In both columns, experiments are performed using activated carbon loadings varying between 0 and 6 v/v\% in water.

5.3.4 Bubble size distribution measurements

The average bubble size distribution is obtained by high speed video recording of the hydrodynamic behaviour in the 2-D slit-column as described by de Swart \textit{et al.} (1996). The camera is placed at a column height of 0.75 m. The image analysis is performed using SCIL-image, a commercial image analysis software program. To measure bubble size distributions in absence of carbon, it is important to obtain contrast between the bubbles and liquid. Therefore, 0.25 v/v\% activated carbon was added to the water. This resulted in a grey coloured liquid. It was verified that the addition of 0.25 v/v\% had no influence on the column hydrodynamics compared to water.

5.3 Theory

A Two Bubble Class hydrodynamic model was introduced by Shetty \textit{et al.} (1992). These authors assume that small bubbles follow the flow regime of the liquid in the column, where as large bubbles are transported in a plug flow through the column. The
small bubbles together with the liquid phase are denoted as the dense phase, while the large bubbles are called the dilute phase. Krishna and Ellenberger (1996) proposed equation (5.1) to describe the dilute phase gas holdup $\varepsilon_b$ for gas liquid bubble columns as a function of superficial gas velocity $v_{sg}$, the dense phase gas velocity $v_{df}$, and the column diameter $D_T$. The parameters $\alpha_2 (-)$, $N (-)$, and $b (-)$ are empirical constants.

$$\varepsilon_b = \alpha_2 \frac{1}{D_T^N} \left( \frac{1}{v_{sg} - v_{df}} \right)^{b} \left( v_{sg} - v_{df} \right)^{A}$$  \hspace{1cm} (5.1)

Krishna and Ellenberger (1996) showed that

1) the dense phase gas velocity is equal to the gas velocity at which the transition from homogeneous to heterogeneous flow takes place ($v_{df} = v_{trans}$).
2) the gas holdup in the dense phase is equal to the gas holdup at the transition point ($\varepsilon_{df} = \varepsilon_{trans}$).

Furthermore, they validated that the equations of Reilly et al. (1994) describe the gas velocity and the gas holdup at the transition point best.

$$v_{trans} = U_{small,0} \varepsilon_{trans} \left( 1 - \varepsilon_{trans} \right)$$  \hspace{1cm} (5.2)

$$\varepsilon_{trans} = 0.59 B^{1.5} \sqrt[3]{\frac{\rho_g^{0.96}}{\rho_l}} \sigma^{0.12}$$  \hspace{1cm} (5.3)

$$U_{small,0} = \frac{1}{A} \frac{1}{\rho_g^{0.04}} \sigma^{0.12}$$  \hspace{1cm} (5.4)

$U_{small,0}$ is the rise velocity of the small bubbles in liquid. A and B are constants. The value of these constants are: $A = 2.84$ and $B = 3.85$ (Krishna and Ellenberger (1996)) if the gas and liquid densities $\rho$ are given in kg m$^{-3}$ and the surface tension $\sigma$ in N m$^{-1}$. The total gas holdup $\varepsilon$ can be calculated by the following equation:
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\[ \varepsilon = (1 - \varepsilon_{df}) \varepsilon_h + \varepsilon_{df} \]  

(5.5)

The presence of particles can influence the gas holdup in a bubble column significantly. This may be due to either a change in the apparent viscosity of the slurry, or a change in the apparent density, or to adhesion of particles.

Krishna et al. (1997) showed that equations (5.1-5.5) may be used for gas-liquid-solid bubble columns as well, provided that additional equations for the rise velocity of the small bubbles, and of the dense phase gas holdup as a function of the particle concentration are used (equations (5.6) and (5.7)). These latter equations describe the contribution of the apparent viscosity and apparent density.

\[ U_{small} = U_{small,0} \left(1 + \frac{0.8}{V_{small,0}} \varepsilon_s \right) \]  

(5.6)

\[ \varepsilon_{df} = \varepsilon_{df,0} \left(1 - \frac{0.7}{\varepsilon_{df,0}} \varepsilon_s \right) \]  

(5.7)

For the derivation of these equations, Krishna et al. used non-adhering silica particle, the impact of adhesion is not well accounted for.

5.4 Results

5.4.1 Gas holdup experiments

Holdup experiments are carried out using two activated carbons (SX1G and SX1G-HNO₃). The carbons differ notably in hydrophobicity (Table 5.1 and Figure 5.1) as indicated by FTIR analysis.
Table 5.1. Physical properties of the activated carbon particles.

<table>
<thead>
<tr>
<th></th>
<th>(&lt;d_\text{p}&gt;) (µm)</th>
<th>(S_{\text{BET}}) (m(^2\text{g}^{-1}))</th>
<th>(\rho_{\text{pg}}) (kg m(^{-3}))</th>
<th>(A_{1700}/A_{1580})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SX1G</td>
<td>20</td>
<td>999</td>
<td>824</td>
<td>0.404</td>
</tr>
<tr>
<td>SX1G-HNO(_3)</td>
<td>18</td>
<td>918</td>
<td>807</td>
<td>0.518</td>
</tr>
</tbody>
</table>

Figure 5.1. FTIR spectra of SX1G (—) and SX1G-HNO\(_3\) (—) activated carbon particles.

The FTIR band intensities at 1700 cm\(^{-1}\) and 1580 cm\(^{-1}\) are used to characterise the carbon hydrophobicity. The \(A_{1700}/A_{1580}\) ratio of the SX1G-HNO\(_3\) is higher than the ratio for SX1G, indicating that the nitric acid treatment decreases the hydrophobicity of the activated carbon, while the other properties are not changed significantly.

Many authors (Banisi et al. (1995), Krishna et al. (1997), Yasunishi et al. (1986)) report that in a three phase bubble column the gas holdup decreases with increasing concentrations of particles.
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Figure 5.2. The total air holdup as a function of the superficial gas velocity $v_{sg}$ in the 3-D column for activated carbon concentrations in water.

- $\bullet$: 0 v/v%, $\Delta$: 3 v/v%, $\blacksquare$: 4 v/v%, $\star$: 5 v/v% -: 6 v/v%.

Closed bullets (left): SX1G, Open bullets (right): SX1G-HNO₃.

The decrease of gas holdup with increasing particle concentration is found for both types of activated carbon particles as can be seen in Figure 5.2. Up to a carbon concentration of 1 v/v% no significant effect of the activated carbon particles is observed, in accordance with data from Gavroy et al. (1995).

Figure 5.3 shows the holdup results for both the 3-D column and the 2-D slit-column using water, 6 v/v% SX1G, and 6 v/v% SX1G-HNO₃ respectively. It clearly demonstrates that, in both columns, a significant difference exists between the gas holdup of SX1G and SX1G-HNO₃ particles. In spite of the qualitative difference, Fig 5.3 shows that the 2-D slit-column is quantitatively representative for the 3-D column. Figure 5.3 also demonstrate the theoretical predictions, based on equations (5.1-5.7), for the gas holdup in case of an air-water system and an air-water-6 v/v% particles system.
A significant difference between the measured gas holdup in presence of activated carbon and the gas holdup predicted by the model presented by Krishna et al. (1997) is found (Figure 5.3). The difference between model and experimental result implies that adhesion of particles is an important parameters for hydrodynamics in a bubble column. This means that equations (5.6) and (5.7) can not be used to describe the hydrodynamics in a column if adhering particles are present.

5.4.2 Bubble coalescence

Experiments in a 2-D slit-column were used to assess the bubble size distributions, using high-speed video imaging. The results for various catalyst concentrations are given in Figures 5.4, 5.5, and 5.6, showing a large decrease in the amount of small bubbles with increasing catalyst concentration. Because of the large fraction of small bubbles (< 5 mm) found for air-water systems, only the bubbles larger than 5 mm are analysed.
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Figure 5.4. Six successive frames in time of air bubbles in 0.25 v/v% SX1G in water recorded with 40 ms interval. The frame width is 0.3 m, $v_{sg} = 0.1$ m/s.

Figure 5.5. Six successive frames in time of air bubbles in 3 v/v% SX1G in water recorded with 40 ms interval. The frame width is 0.3 m, $v_{sg} = 0.1$ m/s.
Figures 5.4, 5.5 and 5.6 also demonstrate the coalescence behaviour of the bubbles. As illustrated in Figure 5.4 (water-air system) a liquid layer between interacting bubbles is present at low activated carbon concentrations. This layer remains stable until the coalescence of the bubbles occurs. In presence of 3 v/v% activated carbon (Figure 5.5), film rupture occurs faster compared to the pure water-air system. The liquid layer between interacting bubbles disappears quicker for higher solids concentration (6 v/v% SX1G) (See Figure 5.6). This indicates that particles do indeed affect the film rupture. With increasing catalyst concentration the film thinning is faster, or the critical film thickness increases. Both phenomena would result in an easier coalescence between two bubbles.
Figure 5.7. Contribution of specific bubble size classes to the total air holdup of bubbles with a diameter exceeding 5 mm at $v_{s g} = 0.1 \text{ m s}^{-1}$.

Figure 5.7 gives the results of image analysis of the video frames and shows that for increasing particle concentration the contribution of the smallest analysed bubbles (5-10 mm) decreases and the contribution of the largest analysed bubbles (> 40 mm) to the gas holdup increases. This is also qualitatively observable from the frame sequences given Figures 5.4, 5.5, and 5.6.

By comparing the results obtained with 6 v/v% SX1G (Figure 5.6) and 6 v/v% SX1G-HNO$_3$ (Figure 5.8), it can be concluded that more small bubbles and a more stable liquid film are found in presence of less hydrophobic SX1G-HNO$_3$ particles. This corresponds with the results presented in Figure 5.3: the gas holdup in the 3-D column for 6 v/v% SX1G is significantly smaller than the gas holdup for 6 v/v% SX1G-HNO$_3$. Because of the small amount of bubbles smaller than 5 mm, all bubbles are counted using SCIL-image.
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Figure 5.8. Six successive frames in time with of air bubbles in 6 v/v% SX1G-HNO₃ in water recorded with 40 ms interval. The frame width is 0.3 m, $v_{sg} = 0.1 \text{ m/s}$.

The difference in bubble size distribution for the SX1G and SX1G-HNO₃, based on image analysis, are shown in Figure 5.9. As can be observed in this figure, the contribution of small bubbles in presence SX1G particles is smaller compared to the contribution of small bubbles in presence of SX1G-HNO₃. The opposite holds for the contribution of large bubbles. As demonstrated in Figure 5.10, the difference in bubble size distribution is mainly caused by a larger absolute amount of smaller bubbles for SX1G-HNO₃ ($< 5 \text{ mm}$) and an about equal amount of visible parts of larger bubbles ($> 10 \text{ mm}$).
Figure 5.9. The contribution of different bubble size classes to the total air holdup at $v_{sg} = 0.1 \text{ m s}^{-1}$. , 6 v/v% SX1G in water, , 6 v/v% SX1G-HNO$_3$ in water.

Figure 5.10. Gas holdup for different bubble size classes at $v_{sg} = 0.1 \text{ m s}^{-1}$. Bubbles smaller than 5 mm: left picture ($d_b$ class 0.1 mm around x value). Bubbles larger than 25 mm right picture ($d_b$ class 5 mm around x value). ●, 6 v/v% SX1G in water, , 6 v/v% SX1G-HNO$_3$ in water.

When the video frames of the movies of 6 v/v% SX1G and SX1G-HNO$_3$ are examined in more detail, adhesion of activated carbon particles on the bubbles is observable (Figure 5.11). Especially for SX1G-carbon a large part of the bubbles are covered with carbon particles. The covered parts of the bubbles are not detectable using SCIL-image analysis, resulting in underestimation of the bubble size. The bubble coverage of the
larger bubbles is higher. Because the coverage of the bubbles by particles is more pronounced in presence of SX1G than for SX1G-HNO₃, the underestimation of large bubbles in the air-water SX1G system is largest. This means that the difference in bubble size distribution as shown in Figure 5.9 is even larger.

As demonstrated by Figures 5.6, 5.8, 5.9, 5.10, and 5.11, a treatment of activated carbon with nitric acid leads to an increase in the gas holdup, as compared to the untreated carbon. This is caused by an influence on the bubble coalescence: in presence of SX1G particles the liquid layer is less stable than in presence of SX1G-HNO₃ particles. An effect of adhering particles on the bubble coalescence can either be caused by the roughness of the macroscopic surface of the particles, or by the hydrophobicity of the particles. For rough particles, the bubble surface is easily ruptured, causing coalescence. Accordingly, surface roughness may affect the coalescence behaviour. If the particles are hydrophobic, they will penetrate into bubble surface. The penetration depth is a function of the three phase contact angle. Penetration of the particles can either affect the film thinning velocity or the rupture of the film. If the particles are less hydrophobic, the three phase contact angle is lower, as compared to more hydrophobic particles, consequently a lower penetration depth of the hydrophobic particles into the gas phase will be found (Figure 5.12).
As a result of the decreased penetration depth, a more stable layer between two bubbles can exist. In addition, agglomeration of adhering particles can influence the coalescence behaviour. More hydrophobic particles have a stronger tendency to form agglomerates, resulting in an increase of the effective particle diameter. If such agglomerates are present in the film, the film will be easier ruptured.

SEM pictures of the carbon particles are shown in Figure 5.13, demonstrating that nitric acid treatment does not really change the macroscopic roughness of particles. Therefore, the difference in bubble coalescence is not easily explained by a difference
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in particle roughness. The impact of acid treatment on the hydrophobic nature of carbon forms an alternative, more plausible, explanation for its impact on penetration depth, and thereby on the coalescence behaviour.

5.5 Conclusions

It is well known that the presence of particles has an impact on the hydrodynamics in a slurry bubble column by changing the apparent viscosity and density of the slurry phase. This work shows that the hydrophobicity of the particles also appears to be important. The results presented demonstrate that the presence of hydrophobic particles results in a decrease of the gas holdup compared to a gas-liquid system. This is contributed to the influence of the particles on the coalescence behaviour of the bubbles. When the expected gas holdup is corrected for the impact of the presence of carbon particles on the apparent slurry density and viscosity using the equations of Krishna et al. (1997), still a net effect remains. The net effect is attributed to the hydrophobic nature of the activated carbon particles, leading to adhesion of the particles on the gas-liquid interface. The adhesion of particles in turn results in enhanced bubble coalescence, and significantly changes in the total gas holdup in the slurry bubble column may arise.

A plausible explanation for the change in coalescence behaviour in presence of adhering particles might be the impact on the film rupture. The liquid film between to gas bubbles is ruptured earlier in a gas-liquid-adhering particle system compared to the gas-liquid-non adhering particles system. This is caused by the fact that in case of more hydrophobic particles the three phase contact angle, θ, is larger, resulting in a deeper penetration into the bubble. A deeper penetration accelerates the rupture of the film. Alternatively, more hydrophobic particles form larger agglomerates, which still may adhere to the bubbles. Larger particles in the gas-liquid film may also accelerate film rupture. This might explain the impact of hydrophobicity on the holdup, and thereby, on the hydrodynamics of a three phase reactor.
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5.6 Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Equation</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>constant in equation (5.4), not dimensionless</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>constant in equation (5.1), -</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>constant in equation (5.3), not dimensionless</td>
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<td>(d_b)</td>
<td>bubble diameter, m</td>
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<td>(d_{pen})</td>
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<td>(D_T)</td>
<td>column diameter, m</td>
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<td>(F_a)</td>
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<td>(F_b)</td>
<td>buoyancy force, N</td>
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<td>gravity force, N</td>
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<td>(F_\sigma)</td>
<td>capillary pressure, N</td>
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<tr>
<td>N</td>
<td>constant in equation (5.1), -</td>
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</tr>
<tr>
<td>(v_{sg})</td>
<td>overall superficial gas velocity, m s(^{-1})</td>
<td></td>
</tr>
<tr>
<td>(v_{df})</td>
<td>superficial gas velocity of gas through the dense phase, m s(^{-1})</td>
<td></td>
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<td>(v_{trans})</td>
<td>superficial gas velocity at the regime transition, m s(^{-1})</td>
<td></td>
</tr>
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<td>(U_{small})</td>
<td>rise velocity of small bubbles, m s(^{-1})</td>
<td></td>
</tr>
<tr>
<td>(U_{small,0})</td>
<td>rise velocity of small bubbles at zero solids concentrations, m s(^{-1})</td>
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Greek symbols

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<td>(\epsilon)</td>
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<td></td>
</tr>
<tr>
<td>(\epsilon_b)</td>
<td>gas holdup of the dilute phase, -</td>
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<tr>
<td>(\epsilon_{df})</td>
<td>holdup of gas in dense phase, -</td>
<td></td>
</tr>
<tr>
<td>(\epsilon_{df,0})</td>
<td>holdup of gas in dense phase in two phase system (G-L), -</td>
<td></td>
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<tr>
<td>(\epsilon_i)</td>
<td>holdup of gas of bubble size class i, -</td>
<td></td>
</tr>
<tr>
<td>(\epsilon_{large})</td>
<td>holdup of bubbles larger than 5 mm, obtained by image analysis, -</td>
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<td>(\epsilon_s)</td>
<td>solids holdup, -</td>
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<td>(\epsilon_{trans})</td>
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</tr>
<tr>
<td>(\theta)</td>
<td>three phase contact angle, rad</td>
<td></td>
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</table>
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\( \rho_g \)  
density of the gas phase, kg m\(^{-3}\)

\( \rho_l \)  
density of the liquid phase, kg m\(^{-3}\)

\( \sigma \)  
surface tension of the liquid phase, N m\(^{-1}\)
5.7 References


