Liquid-solid contacting in trickle-bed reactors

by

Arjan van Houwelingen

A dissertation submitted in partial fulfillment of the requirements for the degree

Philosophiae Doctor in Chemical Engineering

in the

Department of Chemical Engineering
Faculty of Engineering, the Built Environment and Information Technology

University of Pretoria
Pretoria

October 30, 2009
Liquid-solid contacting in trickle-bed reactors

Author: Arjan van Houwelingen
Supervisor: W. Nicol
Department: Department of Chemical Engineering
University of Pretoria
Degree: Philosophae Doctor (Chemical Engineering)

Abstract

Several types of reactors are encountered in industry where reagents in a gas and a liquid phase need to be catalysed by a solid catalyst. Common reactors that are used to this end, are trickle-bed reactors, where gas and liquid flow cocurrently down a packed bed of catalyst. Apart from the catalytic process itself, several mass transfer steps can influence the rate and/or selectivity of a solid catalysed gas-liquid reaction. In trickle-bed reactors, flow morphology can have a major effect on these mass transfer steps.

This study investigates the interaction between liquid flow morphology and mass transfer in trickle-bed reactors from three different angles. The primary focus is on liquid-solid mass transfer and internal diffusion as affected by the contacting between the liquid and the catalyst. First, the contacting between the liquid and the solid in trickle-flow, or wetting efficiency, is characterised using colorimetry. Though this investigation is limited to the flow of nitrogen and water over a packed bed at ambient conditions, it provides useful information regarding liquid flow multiplicity behaviour and its influence on the distribution of fractional wetting on a particle scale. The colorimetric study also provides descriptions of the geometry of the liquid-solid contacting on partially wetted particles.

These are used in a second investigation, for the numerical simulation of reaction and diffusion in partially wetted catalysts. This second investigation uses numerical simulations to evaluate and develop simple theoretical depictions of liquid-solid contacting effects on catalyst particle efficiency. Special attention is given to the case where external and intraparticle mass transfer rates of both a volatile and non-volatile reagent affect the overall rate of reaction. Also, since these are not often considered in theoretical studies, some suggestions are made for the evaluation of the particle efficiency of eggshell catalyst.

Finally, liquid-solid contacting is investigated in a high-pressure pilot reactor. Wetting efficiency is measured with a useful technique that does not rely on descriptions of particle kinetics or liquid-solid mass transfer rates. Liquid-solid mass transfer coefficients are also measured and results agree well with the colorimetric investigation, suggesting the existence of different types of flow within in the hydrodynamic multiplicity envelope of trickle-flow.

Since it consists of different investigations of liquid-solid contacting from different
angles, the study highlights several aspects of liquid-solid contacting and how it can be expected to influence trickle-bed reactor performance.

**KEYWORDS:** trickle-bed reactor, trickle flow, wetting efficiency, liquid-solid mass transfer, colorimetry, pellet efficiency factor, finite element method, hydrodynamics, multiplicity
Acknowledgements

Many people have contributed to making this work possible. Thank you all. My supervisor, Prof. Willie Nicol for continued support and guidance. Sasol Technology Research and Development for financial support, as well as the important assistance in the design and construction of the high-pressure experimental set-up described in Chapter 5. In this regards, I particularly want to acknowledge the efforts of Johann Rademan and Randall Hopley. The construction of this set-up was not trivial and would not be possible without their expertise. Also for financial support, the National Research Foundation of South-Africa. The programming skills of Carl Sandrock and the training in finite element methods by Schalk Kok were of extreme importance for the work presented in Chapters 3 and 4. Lastly, to all family and friends as well as the colleague students at the University of Pretoria for guarding my sanity, or insanity, where necessary.
## CONTENTS

1 Introduction 1

2 Literature 4

2.1 Liquid-solid contacting: A short historical overview ....... 6
2.2 Measurement and correlations for solid-liquid contacting .... 8
  2.2.1 Wetting efficiency . 8
  2.2.2 Mass transfer . 11
  2.2.3 Liquid flow morphology and multiplicity .... 13
2.3 Reactor studies and liquid-solid contacting .... 14
2.4 Conclusions . 16

3 Visualisation of wetting morphology 18

3.1 Experimental . 19
  3.1.1 Trickle-flow setup and experimental procedure ........ 19
  3.1.2 Data capturing and processing . 21
3.2 Results and discussion . 25
3.3 Summary . 27

4 Effectiveness factors for partially wetted catalysts 30

4.1 Numerical method .................................... 32
  4.1.1 First-order reaction, \(-r = k_r C\) . 32
  4.1.2 Reactions of the form \(r_A = \alpha r_B = -\alpha k_r C_A C_B\) .... 34
  4.1.3 Meshing . 35
  4.1.4 FEM accuracy . 36
4.2 Monodispersed particles ................................... 38
  4.2.1 Theory . 38
  4.2.2 Verification of existing models . 45
4.2.3 A unified model for \( r_A = \alpha r_B = -\alpha k_r C_A C_B \) ................. 49

4.3 Eggshell particles ........................................... 51

4.4 Summary .......................................................... 56

5 Liquid-solid contacting in a pilot reactor 61

5.1 Finding an applicable reaction system .................................. 62

5.1.1 Theoretical considerations ........................................ 62

5.2 Reaction system characteristics ....................................... 65

5.3 Pilot studies ........................................................ 68

5.3.1 Experimental ..................................................... 68

5.3.2 Results and discussion ........................................... 73

5.3.3 Wetting efficiency ................................................ 77

5.3.4 Liquid-solid mass transfer ....................................... 79

5.4 Conclusions .......................................................... 83

6 Closing remarks ...................................................... 87

A Derivation of equation 4-24 ............................................ 98

B Hydrogenation of linear octene under gas-limited conditions 100
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Mass transfer steps in a trickle-bed reactor.</td>
<td>5</td>
</tr>
<tr>
<td>2.2</td>
<td>Literature correlations for wetting efficiency.</td>
<td>11</td>
</tr>
<tr>
<td>2.3</td>
<td>Literature correlations for liquid-solid mass transfer.</td>
<td>12</td>
</tr>
<tr>
<td>3.1</td>
<td>Colorimetry experimental setup.</td>
<td>20</td>
</tr>
<tr>
<td>3.2</td>
<td>Particle imaging.</td>
<td>22</td>
</tr>
<tr>
<td>3.3</td>
<td>An example of extracted half-particle images.</td>
<td>23</td>
</tr>
<tr>
<td>3.4</td>
<td>The boundary effect as a source of possible experimental error.</td>
<td>23</td>
</tr>
<tr>
<td>3.5</td>
<td>Test for representativeness of 60% PWD’s.</td>
<td>24</td>
</tr>
<tr>
<td>3.6</td>
<td>Test for representativeness in terms of average.</td>
<td>25</td>
</tr>
<tr>
<td>3.7</td>
<td>Test for representativeness in terms of standard deviation.</td>
<td>26</td>
</tr>
<tr>
<td>3.8</td>
<td>Low liquid flow rate particle wetting distributions.</td>
<td>26</td>
</tr>
<tr>
<td>3.9</td>
<td>High liquid flow rate particle wetting distributions.</td>
<td>27</td>
</tr>
<tr>
<td>3.10</td>
<td>Graphic representation of obtained wetting geometry data</td>
<td>27</td>
</tr>
<tr>
<td>4.1</td>
<td>Finite element meshes for the simulation of intraparticle diffusion</td>
<td>36</td>
</tr>
<tr>
<td>4.2</td>
<td>Finite element method stability and accuracy for 1st order reactions.</td>
<td>37</td>
</tr>
<tr>
<td>4.3</td>
<td>Stability and accuracy for reactions of the form $-r_A = k_A C_A C_B$.</td>
<td>39</td>
</tr>
<tr>
<td>4.4</td>
<td>Generalised modulus approach for liquid-limited reactions.</td>
<td>46</td>
</tr>
<tr>
<td>4.5</td>
<td>Accuracy of the weighting model.</td>
<td>47</td>
</tr>
<tr>
<td>4.6</td>
<td>Bischoff modulus approach for reactions of the form $-r_A = \alpha k_C C_A C_B$.</td>
<td>49</td>
</tr>
<tr>
<td>4.7</td>
<td>Performance of the unified model.</td>
<td>52</td>
</tr>
<tr>
<td>4.8</td>
<td>Performance of traditional models over a wide $\gamma$-range.</td>
<td>53</td>
</tr>
<tr>
<td>4.9</td>
<td>Generalised modulus approach for eggshell particles.</td>
<td>54</td>
</tr>
<tr>
<td>4.10</td>
<td>Modified GC model for partially wetted eggshell particles.</td>
<td>55</td>
</tr>
<tr>
<td>4.11</td>
<td>Modified eggshell modulus for liquid-limited reactions.</td>
<td>57</td>
</tr>
<tr>
<td>4.12</td>
<td>Performance of the unified model for eggshell particles.</td>
<td>57</td>
</tr>
</tbody>
</table>
5.1 Estimation of minimum generalised modulus for slower reaction. 63
5.2 Reaction kinetics for grinded catalyst. 67
5.3 Schematic of the trickle-bed facility. 69
5.4 Reactor detail. 70
5.5 Flow map of experimental flow conditions. 71
5.6 Test for feed saturation before entering the catalyst bed. 73
5.7 Test for negligible influence of hydrogen on overall reaction rate. 74
5.8 Typical conversion versus flow rate dataset for an experimental run. 75
5.9 Unrefined upflow conversion data for the hydrogenation of linear octenes. 76
5.10 Catalyst stability checks 77
5.11 Conversion data from experimental runs with stable catalyst. 78
5.12 Measured Wetting efficiencies a function of liquid superficial velocity. 79
5.13 Averaged wetting efficiency as a function of liquid superficial velocity. 80
5.14 Fits of upflow conversion data. 81
5.15 Parity plot for $k_{LSa}f$ and $k_{LSa}$ for upflow operation. 83
5.16 Liquid-solid mass transfer coefficients for trickle flow operation. 84
5.17 Comparison of liquid-solid mass transfer in trickle- and upflow operation. 85

B.1 Overall reaction rate under gas-limited conditions. 101
B.2 Possible overall efficiencies for highest and lowest liquid flow rate. 102
LIST OF TABLES

3.1 Colorimetry experimental flow conditions. .......................... 21
5.1 Approximate requirements for the reaction system. ............... 65
5.2 Liquid reaction mixture properties. .................................... 66
B.1 Hydrogen property estimations ........................................ 101