Modeling of Fluidized-Bed Reactors: Generalization of the Weather Model

by

Saud Hasan Batran

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

August, 1992
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Modeling of fluidized-bed reactors: Generalization of the Werther model

Batran, Saud Hasan, M.S.
King Fahd University of Petroleum and Minerals (Saudi Arabia), 1992
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GENERALIZATION OF THE WERTHER MODEL

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I wish to express my deep appreciation, gratitude and indebtedness to my Thesis Advisor Dr. Abdulla A. Shaikh. Without his continuous encouragement, advice and guidance, this work wouldn't be possible. I am really impressed by his kindness, understanding, endless patience and humbleness. I also wish to thank the other members of my Thesis Committee: Dr. Mohammad A. Al-Saleh and Dr. Hussein K. Abdel-Aal for their useful comments and valuable suggestions.

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<table>
<thead>
<tr>
<th>TABLE OF CONTENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
</tr>
<tr>
<td>LIST OF ILLUSTRATIONS</td>
</tr>
<tr>
<td>ABSTRACT</td>
</tr>
<tr>
<td>ABSTRACT (ARABIC)</td>
</tr>
<tr>
<td>CHAPTER 1 INTRODUCTION</td>
</tr>
<tr>
<td>1.1 Background</td>
</tr>
<tr>
<td>1.2 Objectives of the Proposed Work</td>
</tr>
<tr>
<td>CHAPTER 2 LITERATURE REVIEW</td>
</tr>
<tr>
<td>2.1 Origin of the Werther Model</td>
</tr>
<tr>
<td>2.2 Development of the Model</td>
</tr>
<tr>
<td>2.3 Application to Complex Reactions</td>
</tr>
</tbody>
</table>
2.4 Improvements to the Model ......................................................... 8

2.4.1 Improving the Estimation of the Bubble-to-Emulsion Mass-Transfer Coefficient $k_c$ ................................................................. 9

2.4.2 Improving the Estimation of Bubble Gas Hold-up and Interfacial Area. ....................................................................................... 10

2.5 Influence of the Change in the Number of Moles ......................... 11

2.6 Contribution of the Grid-Zone and the Freeboard ......................... 12

CHAPTER 3 FUNDAMENTALS OF FLUIDIZATION .............................. 13

3.1 Basic Concepts ............................................................................. 13

3.1.1 Fluidization Modes ................................................................. 13

3.1.2 A Typical Fluidized-Bed Reactor .............................................. 16

3.1.3 The Types of Solids and Their Influence on the Hydrodynamics .... 19

3.1.4 Entrainment and Elutriation .................................................... 21

3.2 Basic Correlations and expressions ............................................... 22

3.2.1 Overview .................................................................................. 22
3.2.2 The Minimum Fluidization Velocity ........................................... 23

3.2.3 The Mass Transfer Coefficients .................................................. 24
    3.2.3.1 Bubble to Emulsion Mass-Transfer Coefficient .................... 24
    3.2.3.2 Gas-Side Mass-Transfer Coefficient .................................. 25

3.2.4 The Bubble Diameter ............................................................... 25

3.2.5 The Bubble Gas Hold-Up and Interfacial Area ............................ 28
    3.3 The Werther Model ................................................................. 29

3.3.1 Overview .................................................................................. 29

3.3.2 Model Equations ........................................................................ 30

CHAPTER 4 GENERALIZATION OF THE WERTHER MODEL TO CASES
IN VOLVING TRANSPORT LIMITATIONS AND CHANGES IN THE NUMBER
OF MOLES ............................................................................................. 35

4.1 Gas-Side Mass-Transfer Resistance ............................................. 35

4.1.1 Introduction .............................................................................. 35

4.1.2 Mathematical Model ................................................................. 35
CHAPTER 5 APPLICATION OF THE WERTHER MODEL TO COMPLEX REACTIONS

5.1 Introduction ................................................................. 60

5.2 Denbigh Reaction Network ............................................ 60

5.2.1 Model Equations ....................................................... 61

5.2.2 Solution of the Problem ............................................. 61

5.2.3 Simulation ............................................................... 61

5.2.4 Comparison with Experimental Data .......................... 66

5.3 A General Reversible Reaction ..................................... 69

5.3.1 Model Equations ....................................................... 69

5.3.2 Solution of the Problem ............................................. 73

5.3.3 Simulation ............................................................... 76

5.4 A General Consecutive-Parallel Reaction ..................... 80

5.4.1 Mathematical Model Equations ................................ 80
5.4.2 The Performance Equations .................................................. 83

5.4.3 Application to an Industrial Reactor .......................................... 83

CHAPTER 6 COMPARISON BETWEEN THE WERTHER MODEL AND THE KUNII-LEVENSPIEL MODEL .................................................. 89

6.1 Introduction ................................................................................. 89

6.2 What is the Kunii-Levenspiel Model ? ........................................... 90

6.3 Comparison for the Simple Case A→B .......................................... 92

6.4 Effect of the Change in the Number of Moles ................................. 95

6.5 Application to Complex Reactions .............................................. 96

6.6 Comparison with Kunii-Levenspiel and Other Models on the Basis of Industrial Reactor Data ......................................................... 97

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS ....................... 102

7.1 Introduction ................................................................................. 102

7.2 Conclusions ................................................................................ 103

7.2.1 Effect of Gas-Side Resistance .................................................. 103
7.2.2 Effect of the Change in the Number of Moles ......................... 103

7.2.3 Application to Complex Reactions ........................................... 104

7.2.4 Comparison with the Kunii-Levenspiel and Other Models ......... 104

7.3 Recommendations........................................................................ 105

LIST OF SYMBOLS ........................................................................... 107

REFERENCES ....................................................................................... 111

APPENDIX A DERIVATION OF THE MODIFICATIONS OF $u$ AND $d_b$ IN A
FLUIDIZED-BED WHEN THE NUMBER OF MOLES IS CHANGING ............. 116

A.1 Modification of the Gas Superficial Velocity $u$ .......................... 117

A.2 Modification of the Bubble Diameter $d_b$ .................................... 120

APPENDIX B CALCULATION PROCEDURE FOR EQUATIONS 6.14 AND
6.15 ..................................................................................................... 122

APPENDIX C Mathematica PROGRAM USED IN THE GENERATION OF
EQUATIONS 6.16 AND 6.17 ................................................................... 126
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1. Some Applications of Fluidized-Bed Reactors</td>
<td>2</td>
</tr>
<tr>
<td>Table 2. Parameters for the Werther Model</td>
<td>34</td>
</tr>
<tr>
<td>Table 3. Modified Model Equations</td>
<td>38</td>
</tr>
<tr>
<td>Table 4. Modified Model Equations in Dimensionless Form</td>
<td>39</td>
</tr>
<tr>
<td>Table 5. Reactions Involving a Change in the Number of Moles</td>
<td>50</td>
</tr>
<tr>
<td>Table 6. Dimensional Model Equations</td>
<td>53</td>
</tr>
<tr>
<td>Table 7. Dimensionless Model Equations and Groups</td>
<td>54</td>
</tr>
<tr>
<td>Table 8. Degenerate Subcases From Denbigh Network</td>
<td>62</td>
</tr>
<tr>
<td>Table 9. Material Balance Equations for Denbigh Network</td>
<td>63</td>
</tr>
<tr>
<td>Table 10. Dimensionless Model Equations for Denbigh Network</td>
<td>64</td>
</tr>
<tr>
<td>Table 11. Concentration Profiles for Denbigh Network</td>
<td>65</td>
</tr>
<tr>
<td>Table 12. Degenerate Subcases for the Reversible Reaction</td>
<td>70</td>
</tr>
<tr>
<td>Table 13. Material Balance Equations for the Reversible Consecutive Reaction</td>
<td>71</td>
</tr>
</tbody>
</table>
Table 14. Dimensionless Model Equations for the Reversible Consecutive Reaction.................................................................72

Table 15. Parameters for Equations 5.45 and 5.46.................................74

Table 16. Material Balance Equations for the Consecutive-Parallel Reaction.................................................................................81

Table 17. Dimensionless Model Equations for the Consecutive-Parallel Reaction........................................................................82

Table 18. Concentration Profiles for the Consecutive-Parallel Reaction84

Table 19. Measured and Calculated Parameters for the Phthalic Anhydride Reactor..................................................................86

Table 20. Comparison Between the Assumptions of the Werther Model and the Kunii-Levenspiel Model........................................91

Table 21. Parameters for the Kunii-Levenspiel Model..........................93

Table 22. Simulation Parameters for Figure 21 and Figure 22, (reaction constants are based on the volume of solids)........................98

Table 23. Comparison of the Werther Model and the Three Models Studied by Johnsson et al with Data from Industrial Unit............101
## LIST OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1. Schematic diagram of the phase regions</td>
<td>14</td>
</tr>
<tr>
<td>Figure 2. Fluidization modes</td>
<td>15</td>
</tr>
<tr>
<td>Figure 3. Typical bubbling fluidized-bed reactor</td>
<td>17</td>
</tr>
<tr>
<td>Figure 4. Geldart particle classification</td>
<td>20</td>
</tr>
<tr>
<td>Figure 5. Werther fluidized-bed model</td>
<td>31</td>
</tr>
<tr>
<td>Figure 6. Effect of transport limitations in the gas-side</td>
<td>36</td>
</tr>
<tr>
<td>Figure 7. The influence of $Ha$ on the ratio of conversions</td>
<td>41</td>
</tr>
<tr>
<td>Figure 8. The influence of $\Phi$ on the ratio of conversions</td>
<td>42</td>
</tr>
<tr>
<td>Figure 9. The influence of $NTU$ on the ratio of conversions</td>
<td>43</td>
</tr>
<tr>
<td>Figure 10. Effect of gas-side resistance on the catalytic decomposition of nitrous oxide at $T=672$ °C and $H_{mf}=1.09$ m, data of Shen and Johnstone [43]</td>
<td>47</td>
</tr>
<tr>
<td>Figure 11. Effect of gas-side resistance on the catalytic oxidation of ammonia at $T=250$ °C and $H_{mf}=0.58$ m, data of Massimilla and Johnstone [43]</td>
<td>48</td>
</tr>
</tbody>
</table>
Figure 12. Model basis with the convectional flux shown..........................52

Figure 13. Influence of the stoichiometric coefficient on the conversion
along bed height.................................................................................57

Figure 14. Influence of the feed inerts' ratio on the exit conversion......58

Figure 15. Concentration profiles along the bed height for a Denbigh
reaction.................................................................................................67

Figure 16. Comparison of model predictions and experiment, maleic
anhydride production at T=460 °C and u/u_m=10.8, data from [32]......68

Figure 17. The general shapes of concentration curves for the reversible
consecutive reaction and subcases.........................................................77

Figure 18. The general shapes of concentration curves for the reversible
parallel reaction and subcases..............................................................78

Figure 19. Comparison between a reversible and a non-reversible
consecutive reactions.........................................................................79

Figure 20. Concentration profiles along the phthalic anhydride reactor88

Figure 21. Ratio of conversions from Kunii-Levenspiel and Werther
models for the first-order reaction  A → B............................................94

Figure 22. Comparison between Kunii-Levenspiel and Werther models
on the basis of a complex reversible reaction.....................................99
ABSTRACT

NAME OF THE STUDENT: Saud Hasan Batran
TITLE OF STUDY: Modeling of Fluidized-Bed Reactors: Generalization of the Werther Model
MAJOR FIELD: Chemical Engineering
DATE OF DEGREE: August, 1992

The recent Werther model for fluidized-bed reactors is generalized and expanded in this study. First, the model is generalized to account for possible mass transfer resistance in the bubble-side. The model is also generalized to include reactions that involve a change in the number of moles.

The model has been further generalized to complex reaction networks. It has been applied to several complex reaction networks that cover a wide range of industrially important reactions.

The generalized solutions for the simple and complex reactions were compared to some available experimental and industrial data in the literature, and good agreements were found.

Finally, the Werther model was compared to the Kunii-Levenspiel model in the cases of simple and complex reactions. Our solution to a complex reaction network was compared to a published comparison of Kunii-Levenspiel and other models, on the basis of industrial reactor data. The predictions of the different models are in general similar with the Werther model being the best to predict the low feed breakthrough.

MASTER OF SCIENCE DEGREE
KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
Dhahran, Saudi Arabia
August, 1992
خلاصة الرسالة

اسم الطالب الكامل: سعود حسن بدران

عنوان الدراسة: نمذجة مفاعلات المُهج المُمِضعة: تعميم نموذج ورشُر الرياضي

الخاصة: هندسة كيميائية

تاريخ الشهادة: أغسطس 1992

لقد تم في هذه الرسالة تعميم وتطوير نموذج ورشُر الرياضي الخاص بوصف أداء مفاعلات المُهج المُمِضعة. شمل هذا النموذج أولاً إضافة وتحليل تأثير مقاومة إنتقال المادة من حبّية تقاطعات الغاز على أداء هذه المفاعلات. كما أن هذا النموذج طُور باشتقاق معايير رياضية جديدة لتعزيزه على التفاعلات التي يحدث خلالها تغيير في عدد الأجزاء الغازية. كما تم في هذه البحث تعميم نموذج ورشُر الرياضي باشتقاق معاييره في حالات التفاعلات المعقدة (أي متعددة المراحل). وبصورة محددة، طبق هذا النموذج في حالات تفاعلات معقدة ذات أهمية صناعية.

لقد تم كذلك مقارنة النماذج والحلول المطردة في بعض هذا، للتفاعلات الزيتية والتفاعلات المعقدة، مع بيانات ونتائج تحليلية وصناعية من نشرها. وقد دلت هذه المقارنة على أن هناك توازناً جيداً بين النماذج والحلول الجديدة وبين البيانات التحليلية والصناعية.

وفي نهاية البحث الحالي تم مقارنة نموذج ورشُر مع نموذج كوني-ليفينشيب، في حالات التفاعلات الزيتية والمعقدة. كما تم مقارنة الحلول الجديدة المشتركة هنا لتفحص معقد مع حلول المماثلة المشتركة باعتماد نموذج كوني-ليفينشيب واعتماد نماذج أخرى، واحتماء مباشتر بين هذه النماذج المختلفة باستخدام بيانات نشرت حديثاً عن مجال صناعي. لقد بنيت هذه المقارنة على أن توقعات النماذج الرياضية المختلفة متقاربة بشكل عام، إلا أن نموذج ورشُر هو أفضل النماذج من ناحية توفر القصة المنخفضة للتحول النهائى للمادة المفصلة.

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران، المملكة العربية السعودية

أغسطس 1992

xv
CHAPTER 1
INTRODUCTION

1.1 Background

The fluidized-bed is a vessel containing a mass of powder lifted by the flow of a fluid, forming an emulsion of solids and fluid behaving very much like a fluid. Fluidized-beds are used in industry as reactors, dryers, mixers, and heat transfer units. The most important—and challenging—of these, is the use of fluidized-beds as catalytic and non-catalytic chemical reactors.

Fluidized-bed reactors have been used on a commercial scale in the 1920s for coal gasification, but it was not before the 1940s when the fluidized catalytic cracking (FCC) process was developed and the importance of fluidization was recognized. Since then, numerous applications were found suitable for fluidized-bed reactors. Some of the most important applications are listed in Table 1 [13].

Compared to the other types of chemical reactors, fluidized-bed reactors possess many advantages:

1. They are particularly useful for those applications that suffer from rapid catalyst deactivation. It is simple in fluidized-bed reactors to take the catalyst in and out of the reactor, for regeneration for example. This particular advantage made the fluidized-bed the most
Table 1. Some Applications of Fluidized-Bed Reactors [13]

<table>
<thead>
<tr>
<th>Catalytic gas phase reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon cracking</td>
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<td>Catalytic reforming</td>
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<tr>
<td>Phthalic anhydride manufacture</td>
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<tr>
<td>Acrylonitrile manufacture</td>
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<td>Aniline production</td>
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<tr>
<td>Synthesis of high-density and low-density polyethylene</td>
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<td>Fischer-Tropsch synthesis</td>
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<td>Chlorination or bromination of hydrocarbons</td>
</tr>
<tr>
<td>Oxidations of SO₂ to SO₃</td>
</tr>
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<td>Methanol to gasoline process</td>
</tr>
</tbody>
</table>

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<tr>
<th>Non-catalytic gas phase reactions</th>
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<tbody>
<tr>
<td>Hydrogenation of ethylene</td>
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<tr>
<td>Thermal cracking e.g. to give ethylene or for fluid coking</td>
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<th>Gas-solid reactions</th>
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<tr>
<td>Roasting of sulphide and sulphate ores</td>
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<tr>
<td>Calcination of limestone, phosphates etc.</td>
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<tr>
<td>Incineration of water liquors and solids refuse</td>
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<tr>
<td>Combustion of coal, coke, peat, biomass</td>
</tr>
<tr>
<td>Gasification of coal, peat, wood wastes</td>
</tr>
<tr>
<td>Pyrolysis of coal, silane</td>
</tr>
<tr>
<td>Catalyst regeneration</td>
</tr>
<tr>
<td>Fluorination of UO₂ pellets</td>
</tr>
<tr>
<td>Chlorination of rutile, ilmenite</td>
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</table>
suitable reactor to carry out petroleum cracking, where severe coking occurs.

2. Fluidized-beds operate isothermally. This is an important feature in several cases. One such a case is when selectivity is sensitive to temperature variations. Another case is when the catalyst is liable to damage and sintering at the hot spots in the reactor.

3. The fluidized-bed is an excellent choice for the highly exothermic reactions, because of the high rates of heat transfer between the bed and the immersed heat transfer tubes.

4. Fluidized bed reactors utilize the active surface area of the catalyst more efficiently, due to the small sizes of the particles, and hence less amounts of the catalyst are needed than in the other reactors.

Alongside with these advantages, fluidized-bed reactors suffer from some disadvantages:

1. At high gas superficial velocities, erosion of reactor internals is a problem, specially at the grid-zone.

2. The particles are ground to very fine sizes and consequently could be carried over by the gas. This is vitally important when the solid is an expensive catalyst.

3. The conversion in the fluidized-bed reactor is sometimes lower than that of the other types of reactors. The main reasons for this are the solid bypassing by the gas through the bubbles and by the mixing in the emulsion-phase

4. Fluidized-beds are hydrodynamically more complex which makes scale-up more difficult and less certain.
Following the outstanding success of the FCC process, several fluidized-bed reactors were built to carry out other applications in the 1940s and 1950s. Although some of them were successful, "others were not and never operated to their full design specifications" [48]. There are certainly some reasons that make the scale-up more difficult for some applications. This dilemma forced researchers worldwide to study the phenomenon more carefully and to pay attention to the special characteristics of fluidized-beds. A large number of fluidized-bed models have accumulated over the past thirty years as a result of the continuous research in the field. The different models have been recently discussed by Yates [48] and Doraiswamy and Sharma [9] and authoritatively reviewed by Wen [38] and more recently by Grace [13].

Despite the large number of models, only few of them are suitable for design and scale-up purposes. Of these is the relatively recent model of Werther [42]. This model has been described by Pell [31] in his recent book as "the best model for commercial systems that the author is aware of." The model of Werther is believed to be the most suitable for reaction modeling in fluidized-beds for the following reasons:

(i) The model is free from any adjustable parameters.
(ii) The influence of bed diameter on the hydrodynamics is described.
(iii) The influence of the different types of solids and the existence of a maximum bubble diameter are recognized.
(iv) The model is physically simple to visualize and mathematically tractable in a relative sense.
(v) A complete set of expressions, necessary to describe the model is available and is continuously improved.

Furthermore, the model has already been applied to experimental data (see for example [43]) and remarkable agreements were found. These reasons give the Werther model an advantage over the other models and this encouraged us to do this work.

1.2 Objectives of the Proposed Work

The objectives of the research work in this thesis are:

(a) Review of existing models for the fluidized-bed reactor to verify the strengths and weaknesses of the Werther model. Review of the recent literature to find if the model has been applied to complex reactions, which are representative of industrial systems.

(b) Generalization of the Werther model to cases involving gas-side mass-transfer limitations.

(c) Application of the Werther model to first-order reactions, $A \rightarrow mB$, in order to study the effect of change in the number of moles on reactor performance. A similar study [16] was done on the well-known Kunii-Levenspiel model, so results can be compared with that work. Another similar study on transport-line reactors was recently done by Shaikh and Carberry [33].

(d) Application of the Werther model to the following complex linear reaction networks:
1. *Denbigh Reaction Network*

\[ A \xrightarrow{k_1} R \xrightarrow{k_3} S \]
\[ \quad \xrightarrow{k_2} T \quad \xrightarrow{k_4} U \]

2. *General Series Reactions*

\[ A \xrightarrow{k_1} R \xrightarrow{k_3} S \]
\[ \quad \xrightarrow{k_2} k_4 \]

3. *General Parallel Reactions*

\[ A \xrightarrow{k_1} R \]
\[ \quad \xrightarrow{k_2} A \]
\[ \quad \xrightarrow{k_3} S \]

4. *Series-Parallel Reactions*

\[ A \xrightarrow{k_1} R \xrightarrow{k_3} S \xrightarrow{k_4} T \]
\[ \quad \xrightarrow{k_2} \]

Specifically, the objective here is to derive *analytic* expressions for conversion and yield of all product species without any assumption. This should provide a reasonable coverage of complex reactions of practical importance.

(e) Once objective (d) is accomplished, yield predictions from the Werther model can be compared to those from the Kunii-Levenspiel and/or other models. Such comparisons are useful and necessary to discriminate among rival fluidized-bed models.
CHAPTER 2
LITERATURE REVIEW

2.1 Origin of the Werther Model

The Werther model is based on the two-phase theory, first proposed by Toomey and Johnstone in 1952 [35]. The two-phase theory says that the reactor contains two phases—an emulsion phase consisting of the solid fines and part of the gas at minimum fluidization velocity, and a bubble phase formed entirely of the rest of the gas in excess to that needed for fluidization.

The origin of the Werther model may be traced back to 1959 when May [28] proposed a two-phase model with plug flow in the bubble phase and back-mixing in the emulsion phase. The interaction between the two phases is represented by a cross-flow parameter. The model was further developed and refined by van Deemter [36] and van Swaaij and Zuiderweg [37]. It was shown that in view of practical applications, the dispersion term can be dropped and the gas flow in the emulsion is insignificant compared to gas flow in the bubble-phase.

2.2 Development of the Model

In 1978, Werther [42] showed that the May model is good only for slow reactions, where the mass transfer coefficient is not significantly affected by the reaction. To incorporate the effect of the reaction on the mass-transfer
coefficient, Werther proposed a model that views the fluidized-bed as an analog to gas-liquid systems where the mass transfer across the phases can be described by the film theory.

The mass balance equations and the conversion predicted by the model for a first-order reaction are presented in Chapter 3. After that, Werther [43] applied the model to some available experimental data from the literature and the agreement was remarkably good.

2.3 Application to Complex Reactions

The model has been applied to few complex reactions. In 1980, Werther and Hegner [47] extended the model to the consecutive first-order reaction $A \rightarrow B \rightarrow C$ and got a closed form solution.

Bauer and Werther, in 1982, [2] applied the model to two parallel consecutive reactions representing the synthesis of maleic anhydride. The equations were solved numerically.

Subsequently, in 1984, Perrier et al [32] applied the model to a triangular reaction scheme. The analytical solution was tested against experimental data, and good agreements were found.

2.4 Improvements to the Model

The model has been improved by improving and refining the methods and correlations used to estimate the hydrodynamic parameters of the model. The basic hydrodynamic parameters are the bubble-to-emulsion mass-transfer coefficient $k_c$, the bubble diameter $d_b$, the bubble rise velocity $u_b$, and
the visible bubble flow rate $V_b$. In the following sections, a literature survey on the development of the forgoing parameters is presented. The recommended updated expressions are presented in the next chapter.

2.4.1 Improving the Estimation of the Bubble-to-Emulsion Mass-Transfer Coefficient $k_c$

In 1978, Werther [41] offered two correlations for the bubble diameter growth and for the height of a mass-transfer unit from which the mass-transfer coefficient $k_c$ can be deduced. These correlations are based on his work in fluidized-beds with diameters between 10 and 100 cm and the work of other investigators in fluidized-beds with diameters ranging from 5 to 300 cm and bed heights up to 10 meters.

Direct RTD measurements by Bauer, Werther and Emig in 1981 [3] showed that $k_c$ is not sensitive to many parameters in the fluidized-bed. It hardly changed with changing gas velocity, bed height, and type of gas distributor. On the other hand, $k_c$ is strongly influenced by the type of particles used in the bed. A value of 0.0088 $m/s$ is typical for sand-like materials and 0.0159 $m/s$ for the fine particles such as the FCC catalyst [45].

The measured values of $k_c$ are in good agreement with an expression given by Sit and Grace in 1981 [34]. This expression, however, is good only in the absence of adsorption effects. A theoretical expression for the ratio of the mass transfer coefficient with adsorption effects to that without adsorption effects was given by Chiba and Kobayashi (1970) [6]. Kunii and Levenspiel (1991) [25] studied the effect of adsorption on the interchange coefficient
from a different point of view. However, their expression contains some
difficult to estimate parameters.

2.4.2 Improving the Estimation of Bubble Gas Hold-up and
Interfacial Area.

The interchange surface area $a$ and the gas bubble hold-up $e_g$ are
calculated from the bubble diameter $d_b$, bubble rise velocity $u_b$ and the bubble
visible flow rate $V_b$. Therefore, it is important to have adequately reliable
expressions to calculate these hydrodynamic parameters.

When the Werther model was developed, the correlations available were
based on experimental results usually gathered from sand fluidized-beds. It
became apparent later that the hydrodynamic behavior is different for
fluidized-beds with different types of solids.

A new set of correlations for bubble diameter, bubble rise velocity, and
the visible bubble flow rate was given by Hilligardt and Werther in 1986
[14]. This set of correlations identifies the differences between the types of
solids.

In 1987, the same authors [15] developed theoretical differential
equations for the bubble growth and coalescence. They showed that the
equations reflect the effect of temperature and pressure on the bubble
diameter. The maximum bubble size is predicted by these equations.
Unfortunately, the equations are implicit and need to be solved by numerical
techniques.
The initial size of the bubbles is influenced by the gas distributor. A procedure is given by Werther [40] to account for the effect of some practically important gas distributors on the bubble diameter. Another way to account for distributor effect is via the initial conditions of the differential equations, proposed by Hilligardt and Werther. Bauer et al [3] studied the effect of distributor designs on the reactant conversions and found that it is very important in shallow beds.

2.5 Influence of the Change in the Number of Moles

Despite the importance of the subject, that many commercial reactions involve a change in the number of moles, the work done in this area in the literature is scarce. Regarding the model of Werther, as far as we know, no attempt has been done to investigate the ability of the model to model reactions with the number of moles changing.

In 1980, Irani et al [16] proposed a model based on the well-known Kunii-Levenspiel model that accounts for the change in the number of moles. The model, however, does not account for the convectional flux between bubble and emulsion, induced by the increase or decrease in the number of moles. Furthermore, the change in gas superficial velocity is neglected.

Another model, based on the simple two-phase theory, was proposed by Kai and Furusaki in 1983 [20]. The model is limited to the case where no inerts are present in the feed and the number of moles decreases upon reaction.
A similar study on the transport line reactor has been done by Shaikh and Carberry [33] in 1984.

2.6 Contribution of the Grid-Zone and the Freeboard

The Werther model is designed for the main part of the bubbling fluidized-bed reactor excluding the grid-zone and the freeboard. As it is discussed in the next chapter, the grid-zone and the freeboard could be very important and a way to add their effect on reactant conversion is needed. Regarding the grid-zone, Werther suggested accounting for it by adding the volume and surface area of the jets to that of the bubbles.

In 1990, Pell [31] suggested dividing the fluidized-bed reactor to three parts in series: the grid-zone, the main bed and the freeboard. He offered shortcut methods to estimate the number of reaction and mass transfer units in the grid-zone and the freeboard. By using the simple May-van Deemter model [28,36], the conversions are calculated in those two parts. He recommended using the model of Werther to find the conversion in the main bed. The overall conversion is calculated from the three separate conversions.
CHAPTER 3

FUNDAMENTALS OF FLUIDIZATION

3.1 BASIC CONCEPTS

When the superficial velocity of a gas flowing upward through a bed of fine particles—carried on a plate (gas distributor) in a vessel—reaches a velocity called the minimum fluidization velocity \( u_{mf} \), the system of the gas-particles (emulsion) behaves as if it were a fluid. It can be stirred, poured and transferred in pipes. The other fluid characteristics are observed in the emulsion such as viscosity, pressure gradients—increasing from the top to the bottom—and the propagation of shock waves.

The emulsion may expand upon increasing the gas velocity until the bubbles begin to appear and travel through the emulsion. The velocity marking the appearance of bubbles is known as the minimum bubbling velocity \( u_{mb} \) and it may be greater than or equal to \( u_{mf} \). The bubbles are nearly spherical in shape with the bottom indented and they are surrounded by a cloud and followed by a wake of particles as shown in Figure 1.

3.1.1 Fluidization Modes

The fluidized-beds operate in different fluidization modes (regimes) depending mainly on the gas superficial velocity and the type of particles in the bed as shown in Figure 2. Every mode has its own special hydrodynamic
Figure 1. Schematic diagram of the phase regions
Figure 2. Fluidization modes
characteristics. Therefore, it is a prerequisite for modeling and design to know enough information about the mode of operation.

The minimum bubbling velocity specifies the beginning of the bubbling fluidization regime. Most of the of the fluidized-bed models, found in the literature, are set to describe the behavior of bubbling fluidized-bed reactors. The models of Werther and Kunii-Levenspiel are examples of bubbling fluidized-bed models.

As the gas superficial velocity increases, the fluidized-bed shifts at some point to the turbulent mode. This mode is characterized by a high degree of contact between the gas and the solid resulting from the vigorous movements in the bed. The gas is believed to move through the bed in the form of streams of irregular-shape bubbles that are in continuous break-up and coalescence.

Increasing the gas velocity further, leads to the fast fluidized-beds and finally to the pneumatic conveyers (i.e., transport line mode) where the whole bed is carried by the gas. The exact conditions at which the different fluidization modes begin are still undetermined.

3.1.2 A Typical Fluidized-Bed Reactor

The typical bubbling fluidized-bed reactor consists of three main parts as shown in Figure 3. These are:
Figure 3. Typical bubbling fluidized-bed reactor
The Grid-Zone: It begins at the gas distributor and ends at the point where bubbles can be seen. Its height is the length of the jets for perforated gas distributors and the height of the cap for bubble cap distributors. The grid-zone is important in design because internal pipes and baffles are exposed to severe erosion if placed within the reach of high velocity gas jets. It is also important when the reactor is used to carry out a fast reaction.

The Bubbling Bed: The bubbling bed is the main part of the reactor. In practical applications, the bubbling bed could have a height of several meters. Most of the reaction takes place in this part of the reactor except in the case of very fast reactions.

The Freeboard: It is the region above the surface of the bed. It contains some particles coming from the eruptions of bubbles as they reach the surface of the bed. The freeboard is designed with enough height for the heavier particles to settle down. The lighter particles that have terminal velocities less than that of the gas are returned by cyclones. Because of the low density of particles in the freeboard, its contribution to the overall conversion is negligible unless the bed is shallow and the reaction is somewhat slow where large amounts of the reactants leave the bed unreacted.
3.1.3 The Types of Solids and Their Influence on the Hydrodynamics

The useful work of Geldart in 1973 [10] divided the solids into four main groups depending mainly on their average particle diameter and density as shown in Figure 4. These groups are:

*Group C*: Cohesive particles having mean diameters less than 20 μm. Due to their irregular shapes and because of the presence of the interparticle forces, group C particles are difficult to fluidize. Bubbles do not appear; instead, the gas breaks through the bed by making irregular cracks and channels. At high enough gas velocities these fines are lifted in the bed in the form of slugs of solids. Cement and flour are examples of group C.

*Group A*: Aeratable fine particles with mean particle diameters ranging from 30 μm to 100 μm. Group A particles fluidize at a low velocity but the bed expands considerably on increasing the inlet gas velocity until the minimum bubbling $u_{mb}$ velocity is reached where the first bubbles appear. The gas velocity $u_{mb}$ could be several times greater than $u_{mf}$.

The bubbles grow by coalescence as they rise through the bed until they reach a maximum bubble size—resulting from the dynamic equilibrium between bubbles breaking apart and rejoining. The maximum bubble diameter in group A is usually small (few centimeters) leading to high interchange surface area. The mixing in a fluidized-bed of type A particles is high and the mass transfer rate is excellent due to the vigorous motion and the continuous process of bubbles breaking apart and coalescence. An example of group A is the FCC catalyst.
Figure 4. Geldart particle classification
Group B: Sand-like particles that show no difference between $u_{mf}$ and $u_{mb}$.

Their diameters usually range from 200 μm to 500 μm.

The hydrodynamic behavior of the bubbles in type B particles is different from that of group A in some aspects. The process of breaking apart is not appreciable for the bubbles in type B solids. Coalescence is more important. As a result, the bubbles grow to large sizes and no limiting bubble diameter is observed in tubes of practical diameters. Slugging is more likely to occur in deep beds as the bubble diameter grows approaching the diameter of the fluidized-bed. This is prevented by inserting baffles and other internals inside the bed. Mixing and mass transfer rates are not as good as in group A.

Group D: Large particles such as coffee beans and crushed limestone.

Bubbles, slower than the interstitial gas, are observed. However, most of the gas flows through the dense phase using the slow bubbles as short cuts. As a result, fluidization quality (mixing) and mass interchange are poor. It is more practical to let the gas flow in the form of spouts not bubbles; a method that greatly improves mixing and mass transfer rates.

3.1.4 Entrainment and Elutriation

As the bubbles reach the surface of the bed, they erupt blowing chunks of particles into the freeboard. The particles move up with the help of the flowing gas to various distances. This phenomenon is called entrainment. After some heights in the freeboard, the heavier particles begin to fall back.
The particles whose terminal velocities are smaller than the velocity of the gas are elutriated—separated and carried out of the reactor. A gradient of particles concentration, decreasing upward, occurs in the freeboard and the height where the solid particles concentration becomes constant is known as the TDH (Transport Disengagement Height).

It is necessary to design the height of the freeboard of no less than TDH to give the heavy particles a chance to settle and to reduce the rate of elutriation. The rate of elutriation is important, since it is the way the small particles escape. Enough information about elutriation is essential in the design of cyclones—the equipment that returns back the escaping particles.

3.2 BASIC CORRELATIONS AND EXPRESSIONS

3.2.1 Overview

The accuracy of the predictions of the Werther model or any other model is dependent on the accuracy of the correlations and methods used to estimate the physical, chemical and hydrodynamic parameters. Although the Werther model recognized the influence of solid properties on the hydrodynamics since its appearance in 1978 (in German), the important role that solids play is getting more obvious and new correlations and concepts have already been established. Therefore, it is useful to create a set of updated correlations for use with the model. Most of the time, the correlations and expressions recommended or set by the original author of the model are preferred.
3.2.2 The Minimum Fluidization Velocity

The minimum fluidization velocity $u_{mf}$ can be estimated from the well-known correlation of Wen and Yu [39]:

$$Re_{mf} = \left(33.7^2 + 0.0408 \frac{Ga}{\eta} \right)^{1/2} - 33.7$$  \hspace{1cm} 3.1

where

$$Re_{mf} = \frac{u_{mf} d_f \rho_f}{\eta}$$

$$Ga = d_f^2 \rho_f \left( \frac{\rho_s - \rho_f}{\rho_s} \right) g / \eta^2$$  \hspace{1cm} 3.2

If the value of the minimum velocity of fluidization is known at the ambient conditions where it is usually easy to measure, then the following procedure, suggested by Werther [44], is shown to be very accurate for extrapolation to other values of temperature and pressure. Equating the fixed-bed pressure drop to the fluidized-bed pressure drop leads to:

$$u_{mf} = 7.19 (1 - \varepsilon_{mf}) \nu S_v \left\{ \frac{1 + 0.067 \varepsilon_{mf}^3 (\rho_s - \rho_f) g}{\left(1 - \varepsilon_{mf}\right)^2 \rho_f \nu^2} \frac{1}{S_v - 1} \right\}$$  \hspace{1cm} 3.3

The parameters of this equations can be adequately estimated or measured except for $S_v$—the ratio of surface area of all particles to their volume—which should be back calculated from the known $u_{mf}$ at the ambient conditions. Note that $\nu$ is the kinematic viscosity of the gas.
3.2.3 The Mass Transfer Coefficients

3.2.3.1 Bubble to Emulsion Mass-Transfer Coefficient

The experiments of Bauer et al in 1981 [3] showed that the bubble to emulsion mass transfer coefficient is a strong function of the type of solid. The influence of gas velocity, fixed-bed height and the type of gas distributor was insignificant. The values recommended by Werther [45] are:

\[ k_c = 0.0159 \text{ m/s, type A Solids} \]
\[ k_c = 0.0088 \text{ m/s, type B Solids} \]

The numbers of Werther are adequately predicted by the expression given by Sit and Grace [34]:

\[ k_c = \frac{u_{mf}}{3} + \sqrt{\frac{4D\varepsilon_{mf}u_b}{\pi d_b}} \tag{3.4} \]

This expression accounts for the effect of coalescence in freely bubbling beds. Since the expression explicitly reflects the effect of temperature and pressure, through \( u_{mf} \) and \( D \), it should be used in the calculation of \( k_c \).

If gas adsorption is significant, the correction proposed by Chiba and Kobayashi [6] is needed. It is given as the ratio of the mass transfer coefficient with adsorption to that without adsorption:

\[ \frac{k_{c}^{*}}{k_c} = \left[ 1 + \frac{2}{3} M \left( \frac{1 - \varepsilon_{mf}}{\varepsilon_{mf}} \right) \left( \frac{1}{2} + \frac{\alpha}{\alpha + 1} \right) \right]^{1/2} \tag{3.5} \]
where

\[ M: \text{adsorption equilibrium constant defined as the ratio of gas} \]
\[ \text{concentration on the surface of the bubble to that in the gas phase.} \]

\[ \alpha = \frac{u_c \varepsilon_{mf}}{u_{mf}} \]

\[ u_b: \text{bubble rise velocity} \]

3.2.3.2 Gas-Side Mass-Transfer Coefficient

No expressions are found in the literature for the gas-side mass transfer coefficient \( k_g \) in fluidized-bed reactors. However, \( k_g \) may be evaluated by analogy with gas-liquid systems. This parameter is going to be estimated from the expression of Newman [30] which was derived for gas bubbles in a liquid, and is given by:

\[ k_g = 6.58 \frac{D}{d_b} \frac{P}{P_i} \]

3.6

where

\[ P: \text{total pressure} \]
\[ p_i: \text{partial pressure of the inerts} \]

3.2.4 The Bubble Diameter

When we talk about the bubble diameter we mean the equivalent bubble diameter, defined as the diameter of a sphere having the same volume as the bubble. There are many correlations in the literature for the bubble
diameter as a function of bed height. The recent correlation of Hilligardt and Werther [14] clearly reflects the effect of solid type on initial bubble diameter and is given by:

\[ d_o = d_o \left[ 1 + 27(u - u_{mf}) \right]^{1/3} (1 + 6.84h)^{1/2} \] (3.7)

where \( d_o \) is found to be:

\[ d_o = \begin{cases} 
0.0061 & \text{for A type solids} \\
0.0085 & \text{for B type solids} 
\end{cases} \]

This relationship is designed for fluidized-beds with porous plate gas distributors. For different types of distributors, \( h \) in equation 3.7 should be replaced by \( h + h_o - \hat{h} \) [40]. The parameter \( \hat{h} \) is found by equating equation 3.7 to equation 3.10 (the technical distributor) and solving the resulting equation for \( h \), where \( \hat{h} = h \). The other parameter \( h_o \) is the jet length for perforated plates, the height of the cap for bubble cap distributors, and the height of the nozzle for nozzle plates.

The jet length \( l_j \) for the perforated gas distributors may be calculated from the correlation of Merry [29]:

\[ l_j / d_{or} = 5.2 \left( \frac{\rho_j d_{or}}{\rho_p d_p} \right)^{0.3} \left[ 1.3 \left( \frac{u_{o}}{g d_{or}} \right)^{0.2} - 1 \right] \] (3.8)

where:

\( d_{or} \): diameter of an orifice
\( v_o: \) gas velocity inside one orifice

A maximum bubble diameter exists for type A solids. Therefore, Equation 3.7 should be applied only in the region where the bubbles grow. In many cases, the bubbles in type A solids grow to the maximum equilibrium size in a short distance. Moreover, the bubbles in such fine powders may emanate from the practical-type distributors in sizes larger than the equilibrium ones. These bubbles then break up to more stable sizes.

The maximum bubble diameter can be calculated from the analytical expression of Hilligardt and Werther [15]:

\[
d_{b \ max} = 3\lambda v_o \left( \frac{2\varepsilon_b}{9\pi} \right)^{1/3} \tag{3.9}
\]

where \( \lambda \) is the average duration of life of a bubble between two splitting events and is given by:

\[
\lambda = 280 \frac{u_{mf}}{g}
\]

The initial size of bubbles in solids of types A and B is given by [15,46]:

\[
d_{b0} = \begin{cases} 
0.008 \varepsilon_b^{1/3} & \text{porous plate} \\
1.3 \left( \frac{v_o^2}{g} \right)^{1/3} & \text{technical gas distributor}
\end{cases} \tag{3.10}
\]

where \( v_o \) is the velocity inside one hole in the distributor.
Equation 3.7 is to be used to calculate the bubble size for type B solids. For type A solids, equation 3.10 is used to find the initial bubble size and then equation 3.7 is used if the maximum bubble diameter predicted by equation 3.9 is larger than the initial size from 3.10. It should be noted that equation 3.9 is not explicit in \( d_{b,\max} \), and the equation needs to be solved numerically.

3.2.5 The Bubble Gas Hold-Up and Interfacial Area

The local bubble gas hold-up \( \varepsilon_b \) and interfacial area \( a \), assuming the bubbles are spherical, can be calculated from:

\[
\varepsilon_b(h) = \frac{V_b}{u_b} \tag{3.11}
\]

\[
a(h) = \frac{6 \varepsilon_b(h)}{d_b} \tag{3.12}
\]

where \( V_b \) is the visible bubble flow rate and \( u_b \) is the rise velocity of bubbles in a freely bubbling bed and are given by [15, 46]:

\[
V_b = 0.8(u - u_{mf}) \tag{3.13}
\]

\[
u_b = V_b + 0.719 \sqrt{g d_b} \tag{3.14}
\]

where the parameter \( \mathcal{G} \) is given by:

\[
\mathcal{G} = \begin{cases} 
3.2d_i^{1/3}, & 0.05 \leq d_i \leq 1.0 \text{ m} \\
2.0d_i^{1/2}, & 0.10 \leq d_i \leq 1.0 \text{ m}
\end{cases} \tag{3.15}
\]

for type A solids

for type B solids
and outside the range of diameter $d_i$ given, the parameter $\vartheta$ may be taken as constant.

The average bubble gas hold-up and interfacial area are determined by integrating equations 2.11 and 2.12 over the whole bed height, $H$:

$$\varepsilon_i = \frac{1}{H} \int_{0}^{H} \frac{V_i}{u_b} dh$$

$$\sigma = \frac{1}{H} \int_{0}^{H} \frac{6\varepsilon_b(h)}{u_b} dh$$

3.3 THE WERTHER MODEL

3.3.1 Overview

The Werther model [42,43] is a relatively recent model that belongs to the group of models known as the two-phase models. What makes the Werther model exceptional among the other models is the intelligent idea of visualizing the interaction between the bubbles and emulsion in the fluidized-bed reactor as an analog of the interaction between bubbles and a liquid in gas-liquid systems. Hence, the mass transport between the phases occurs by the absorption of the reactants from the gas phase followed by a pseudo-homogeneous reaction in the dense-phase which can be described by the film-theory. According to the film theory, the resistance lies in a film of thickness $\delta$. 
where $\delta = \frac{D}{k_e}$

It is known from gas-liquid systems that the mass-transfer is enhanced when the reaction rate increases. This effect has long been neglected in fluidized-bed modeling. Treating the bubble-emulsion system like gas-liquid systems brings a way of incorporating that enhancement which manifests itself through the Hatta number $Ha$. Hatta number is interpreted as the ratio of the reaction rate to the mass-transfer rate in the dense-phase.

3.3.2 Model Equations

In accordance with the two-phase theory, the inlet gas splits into two streams; one goes through the emulsion at the minimum fluidization velocity $u_{mf}$ and the other stream rises in the form of segregated bubbles as shown in Figure 5. The Werther model is based on this concept and the following assumptions:

(i) Compared to the gas flow rate in the bubble phase, the flow rate of the gas in the emulsion is neglected; i.e. $u \gg u_{mf}$.

(ii) The gas-phase is in plug flow

The plug flow material balance for the reactor is given by:

$$-(u - u_{mf}) \frac{dC_{Ab}}{dh} = -\alpha D \frac{dC_{Ab}}{dy} \bigg|_{y=0}$$

3.18

i. c. $h=0$, $C_{Ab}=C_{A0}$
Figure 5. Werther fluidized-bed model
and the bubble-emulsion material balance equations for the first-order reaction $A \rightarrow B$ are:

$$D \frac{d^2 C_{Ad}}{d \gamma^2} = k C_{Ad}$$  \hspace{1cm} (3.19)

$\gamma=0, \quad C_{Ad}=C_{Ab}$

$\gamma=\delta, \quad -a D \frac{d C_{Ad}}{d \gamma} \left|_{\gamma=\delta} \right. = k C_{Ad} \left[ (1 - \varepsilon_b) - a \delta \right]$

Integrating equations 3.18 and 3.19 gives the reactant conversion:

$$X_A = 1 - \exp \left[ -\frac{(\Phi^{-1} - 1) Ha + \tanh Ha}{1 + (\Phi^{-1} - 1) Ha \tanh Ha} \right] H_a NTU$$  \hspace{1cm} (3.20)

where

$$H_a = \frac{\sqrt{kD}}{h_e}, \quad \text{Hatta number}$$

$$\Phi = \frac{a \delta}{1 - \varepsilon_b}, \quad \text{ratio of film volume to emulsion volume}$$

$$NTU = \frac{h_e a H}{u - u_{mf}}, \quad \text{number of transfer units}$$
The expressions needed to calculate the preceding parameters are summarized in Table 2 [45]. These expressions are prepared from hydrodynamic relationships similar to the ones given in the previous section.

In Table 2, \( h^* \) is the bed height at which bubble growth ceases. The method of estimating \( h^* \) consists of solving equation 2.9 for \( d_{b\,\text{max}} \) and substituting it in equation 2.7 to get

\[
h^* = 0.203 \left[ \frac{d_{b\,\text{max}}}{d_0} (1 + 27(u - u_{m_l}))^{-1/3} - 1 \right]^{0.83}
\]  

3.21
Table 2. Parameters for the Werther Model

\[
\begin{align*}
\alpha &= \begin{cases} 
4190(u - u_{umf}) \left[ \phi_A F_1 F_2 \right]^{-1} & \text{group A powders} \\
2270(u - u_{umf}) \left[ \phi_B F_1 F_2 \right]^{-1} & \text{group B powders}
\end{cases} \quad 3.22 \\
\varepsilon_b &= \begin{cases} 
\alpha_A (u - u_{umf}) \frac{F_2}{\phi_A F_2^{1/3}} & \text{group A powders} \\
\alpha_B (u - u_{umf}) \frac{F_5}{\phi_B F_2^{1/3}} & \text{group B powders}
\end{cases} \quad 3.23 \\
k_r &= \begin{cases} 
0.0159 \text{ m/s} & \text{group A powders} \\
0.0088 \text{ m/s} & \text{group B powders}
\end{cases} \quad 3.24 \\
F_1 &= \begin{cases} 
H & \text{if } H \leq h^* \\
H / \left[ 0.18 \left( 1 - (1 + 6.84H)^{-0.815} \right) \right] & \text{if } H > h^*
\end{cases} \quad 3.25 \\
F_2 &= \sqrt{1 + 27.2(u - u_{mf})} \quad 3.26 \\
F_5 &= \begin{cases} 
0.37 \left( 1 + 6.84H \right)^{0.4} - 1 \bigg/ H & \text{if } H \leq h^* \\
0.37 \left( 1 + 6.84h^* \right)^{0.4} - 1 \bigg/ H + \left( 1 + 6.84h^* \right)^{-0.3} \left( H - h^* \right) \bigg/ H & \text{if } H > h^*
\end{cases} \quad 3.27 \\
\phi_A &= \begin{cases} 
1.0 & d_i \leq 0.1m \\
2.5d_i^{0.4} & 0.1 \leq d_i \leq 0.1m \\
2.5 & d_i \geq 1.0m
\end{cases} \quad 3.28 \\
\phi_B &= \begin{cases} 
0.64 & d_i \leq 0.1m \\
1.60d_i^{0.4} & 0.1 \leq d_i \leq 0.1m \\
1.60 & d_i \geq 1.0m
\end{cases} \quad 3.29 \\
\alpha_A &= 3.27 \quad 3.30 \\
\alpha_B &= 2.47
CHAPTER 4

GENERALIZATION OF THE WERTHER MODEL TO CASES INVOLVING TRANSPORT LIMITATIONS AND CHANGES IN THE NUMBER OF MOLES

4.1 GAS-SIDE MASS-TRANSFER RESISTANCE

4.1.1 Introduction

An implicit assumption in the Werther model is that there is no concentration gradient for the reactant inside the bubble-phase—and hence no mass transport resistance; an assumption that may be justified only in the case of a high reactant concentration in the bubbles and a slow reaction. Practically, the reactant is usually diluted by some kind of inert and the assumption of negligible transport resistance in the gas-phase becomes questionable. Therefore, it is reasonable to assume a resistance in the gas-side and test its influence on the process.

4.1.2 Mathematical Model

The resistance to mass transfer in the gas-side is assumed to lie in a film of a thickness $\delta_g$ defined by the film theory as $D/k_g$ as shown in Figure 6, while the resistance in the emulsion-side occurs in the film $\delta$, defined in the original Werther model. The chemical reaction occurs in the film $\delta$ and emulsion-phase. The basic assumptions made by Werther are retained; namely: the gas-phase is in plug flow and the gas flow-rate in the emulsion-
Figure 6. Effect of transport limitations in the gas-side
phase is neglected. Based on the stated concepts and assumptions, the
material balance equations in Table 3 may be derived for the first-order
reaction $A \rightarrow B$. These equations are cast into dimensionless form and shown
on Table 4.

The extent of reactant conversion is found by solving the equations in
Table 4, and is given by:

$$X_A = 1 - \exp \left[ -\frac{(\Phi^{-1} - 1) \frac{Ha + \tanh Ha}{1 + (\Phi^{-1} - 1) \frac{Ha \tanh Ha}{Bi}}}{1 + \frac{Ha (\Phi^{-1} - 1) \frac{Ha + \tanh Ha}{1 + (\Phi^{-1} - 1) \frac{Ha \tanh Ha}{Bi}}}{1 + (\Phi^{-1} - 1) \frac{Ha \tanh Ha}{Bi}}} \right]$$

4.1

The parameters of equation 4.1 are the same as the ones appearing in
the original Werther model and described under equation 3.20, except for the
new parameter $Bi$—Biot number. This parameter reflects the effect of the
transport resistance in the gas-side and is defined by:

$$Bi \equiv \frac{k_e}{k_c} = \frac{1/k_c}{1/k_e} = \frac{\text{mass transfer resistance in the emulsion phase}}{\text{mass transfer resistance in the bubble phase}}$$

4.2

For a high value of $Bi$—negligible resistance in the gas-side—equation
4.1 reduces to equation 3.20 of the original Werther model.
Table 3. Modified Model Equations

**Reactor Balance:**

\[ -(u - u_m) \frac{dC_{Ab}}{dh} = a k_e (C_{Ab} - C_{Ad} \mid y=0) \]  \hspace{1cm} 4.3

\textit{i.e.:} \hspace{0.5cm} h=0, \hspace{0.5cm} C_{Ab} = C_{Ad}

**Bubble-Emulsion Balance:**

\[ D \frac{d^2 C_{Ad}}{dy^2} = k C_{Ad} \]  \hspace{1cm} 4.4

**Boundary Conditions:**

\[ y=0, \hspace{0.5cm} k_e (C_{Ab} - C_{Ad}) = -D \frac{dC_{Ad}}{dy} \bigg|_{y=0} \]  \hspace{1cm} 4.5

\[ y=\delta, \hspace{0.5cm} -a D \frac{dC_{Ad}}{dy} \bigg|_{y=\delta} = k C_{Ad} \left[ (1 - \varepsilon_k) - a \delta \right] \]  \hspace{1cm} 4.6
Table 4. Modified Model Equations in Dimensionless Form

\[
\frac{dX_A}{dL} = Bi \ NTU \ (1 - X_A) \left[1 - \overline{C} \right]_{Y=0} \tag{4.7}
\]

\[L=0, \quad X_A=0 \]

\[
\frac{\partial \overline{C}}{\partial Y} = Ha^{-2} \overline{C} \tag{4.8}
\]

\[Y=0, \quad \frac{d\overline{C}}{dY} = -Bi (1 - \overline{C}) \tag{4.9}
\]

\[Y=1, \quad \frac{d\overline{C}}{dY} = -Ha^{-2} (\Phi^{-1} - 1)\overline{C} \tag{4.10}
\]

**Dimensionless Groups**

\[X_A = 1 - \frac{C_{ab}}{C_{A0}} \quad L = \frac{h}{H} \quad NTU = \frac{k_c a H}{u - u_{mf}} \]

\[\overline{C} = \frac{C_{\text{ad}}}{C_{\text{ab}}} \quad Y = \frac{y}{\delta} \quad Ha = \frac{\sqrt{kd}}{k_c} \]

\[Bi = \frac{k_e}{k_c} \quad \Phi = \frac{aD}{k_c (1 - \epsilon_b)} \]
The parameter $Bi$ can be estimated from the correlations developed to predict the mass-transfer coefficients. More specifically, equations 3.6 and 3.24 are combined to give:

$$Bi = \begin{cases} 
414 \frac{D}{d_b} \frac{P}{P_i} & \text{group A powders} \\
748 \frac{D}{d_b} \frac{P}{P_i} & \text{group B powders}
\end{cases}$$

where:

$P$: total pressure

$p_i$: partial pressure of inerts

4.1.3 Parametric Study

In order to study the importance of the parameter $Bi$ in equation 4.1 at the various conditions, the following parametric study is performed. In particular, the influence of $Bi$ on the ratio of the exit conversion in the presence of gas-side resistance to that without gas-side resistance is investigated at various values of $Ha$, $\Phi$, and $NTU$.

Figure 7 shows the effect of $Ha$ on the ratio of conversions at fixed values of $\Phi$ and $NTU$, while the effects of $\Phi$ and $NTU$ are displayed in Figure 8 and Figure 9, respectively. The range of parameters in Figure 7, Figure 8 and Figure 9 is typical of that encountered in practice. In fact, the clear cut between the behavior of the two groups of solids commonly used in industry, group A and group B, allows us to define an active area for each group, as
Figure 7. The influence of $Ha$ on the ratio of conversions
Figure 8. The influence of $\Phi$ on the ratio of conversions
Figure 9. The influence of NTU on the ratio of conversions

\[ \Phi = 0.02 \\
H_a = 0.20 \]

\( NTU \)

- [1] 20.0
- [2] 10.0
- [3] 5.00
- [4] 1.00
shown in Figure 9. This is achieved with the aid of the correlations in Chapter 3 and the defined ranges in Geldart chart in addition to the common operating conditions for bubbling fluidized-bed reactors (cf. Grace [12]).

4.1.4 Discussion of the Results

4.1.4.1 Effect of *Ha*

Hatta number is a measure of reactivity; the faster the reaction, the higher *Ha* is. It is obvious from Figure 7 that the effect of Bi is higher when the reaction is fast. The achievable conversion is only about 40% of that without gas-side resistance when Bi=0.2 and Ha∈(0.1-1.0).

The relative magnitudes of the reaction rate to the gas-side mass-transfer rate play an important role. When the reaction rate is slower, the gas-side resistance is overshadowed by the kinetics and no transport limitations appear. On the other side, when the reaction rate is faster, the effect of the gas-side resistance appears and the reaction becomes limited, to some degree, by the transport in the gas-side.

4.1.4.2 Effect of Φ

This parameter is interpreted as the ratio of film volume to emulsion volume. The most important parameter that affects Φ is the bubbles' interfacial area *a*. The other parameters that define Φ change within limited ranges. Figure 8 shows that an increase in the value of Φ increases the ratio of conversions. The parameter Φ is larger when *a* is large, and this is a direct result from the smaller bubble diameters. The smaller bubble diameters have another effect; they increase the gas-side mass-transfer coefficient *k*ₚ as can
be seen from equation 3.6. and hence, the gas-side mass-transfer resistance decreases. This is why the conversions of the modified model and the original Werther model get closer when $\Phi$ increases.

### 4.1.4.3 Effect of $NTU$

The number of transfer units $NTU$ is a function of the operating conditions and scale of the reactor. A quick look at Figure 9 shows that the ratio of conversions decreases as $NTU$ decreases. The reason is that a low value of $NTU$ indicates that the gas residence time is short and/or the mass transfer in the emulsion is poor and consequently, the reaction is not able to compensate for the transport limitations in the gas-side.

### 4.1.4.4 Effect of Particles Mean Size

As indicated earlier, the clear difference in the behavior of group A and group B powders allows us to draw general conclusions about them. As it is apparent from Figure 9, a fluidized-bed with group A powders is affected the least. This is attributed mainly to the smaller bubble size $d_b$. This leads to a higher values of $Bi$, $\Phi$ and $NTU$, thus reducing the effect of the gas-side mass-transfer resistance.

### 4.1.5 Comparison with Experimental Data

The model of Werther has been used to fit experimental data for several first-order reactions, found in the literature [43]. Applying our modified model to fit the same data, shows some improvement, specially in the region where the gas velocity is not high—low $NTU$, as shown in Figure 10 and Figure 11. The values of $Bi$ are also plotted on the same figures. $Bi$ decreases
with gas velocity, as result from the increase in bubble diameter with gas velocity. It should be noted that comparing the ability to fit experimental data by the two models does not reveal the importance of the gas-side resistance, because the parametric values of the two models change by fitting.
Figure 10. Effect of gas-side resistance on the catalytic decomposition of nitrous oxide at T=672 °C and $H_m=1.09$ m, data of Shen and Johnstone [43]
Figure 11. Effect of gas-side resistance on the catalytic oxidation of ammonia at T=250 °C and $H_{mf}=0.58$ m, data of Massimilla and Johnstone [43]
4.2 EFFECT OF THE CHANGE IN THE NUMBER OF MOLES

4.2.1 Introduction

A large number of industrial reactions involve a change in the number of moles. Some of the typical examples are listed in Table 5. Few models have been extended or modified to account for gas volume changes that result from a change in the number of moles (see Chapter 2 for a discussion of these models and Chapter 6 for some comments about the work of Irani et al [16]).

In this study, a modification of the Werther model is proposed to analyze the effect of the change in the number of moles for the first-order reaction \( A \rightarrow mB \). The serious limitations and assumptions of the models of Irani et al [16] and Kai and Furusaki [20] are avoided. In other words, the model will account for:

1. the presence of inerts; a limitation of Kai-Furusaki model [20].
2. the bulk flow, induced by the change in the number of moles; not accounted for by Irani et al [16].
3. the change in gas superficial velocity; not accounted for by Irani et al.

4.2.2 Model Equations

The molar flux across the bubble-emulsion interface for the reaction \( A \rightarrow mB \) is described by the relationship:

\[
N_{A'} = -CD \frac{dy_{Ad}}{dy} + y_{Ad} (N_{Ad} + N_{B'})
\] 4.12
Table 5. Reactions Involving a Change in the Number of Moles \([16,20]\)

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dehydration of alcohol</td>
</tr>
<tr>
<td>2</td>
<td>Catalytic cracking</td>
</tr>
<tr>
<td>3</td>
<td>Oxidation of hydrocarbons</td>
</tr>
<tr>
<td>4</td>
<td>Ammoxidation of nitrobenzene</td>
</tr>
<tr>
<td>5</td>
<td>Manufacture of high density polyethylene</td>
</tr>
<tr>
<td>6</td>
<td>Absorption of sulfur dioxide in lime</td>
</tr>
<tr>
<td>7</td>
<td>Hydrogenation of nitrobenzene</td>
</tr>
<tr>
<td>8</td>
<td>Oxychlorination of ethylene</td>
</tr>
<tr>
<td>9</td>
<td>Methanation of carbon monoxide</td>
</tr>
<tr>
<td>10</td>
<td>Fischer-Tropsch syntheses</td>
</tr>
</tbody>
</table>
where

\[ y_{Ad} \]: mole fraction of species A in the dense-phase

\[ N_{Ad} \]: flux of species A

\[ N_{Bd} \]: flux of species B, and equals \((-mN_{Aa})\)

The first term is the concentration gradient contribution, while the second term is the bulk flow contribution as depicted in Figure 11. The second term becomes zero when there is no change in the number of moles (i.e., when \(m=1\)).

Using equation 4.12 and the basic assumptions of the Werther model, the material balance equations are developed for the system and summarized in Table 6.

A material balance on the inerts leads to the relationship:

\[
\frac{u - u_{mf}}{u_0 - u_{mf}} = \frac{y_i|_{h=0}}{y_i}
\]  

4.13

where \(y_i\) is the mole fraction of inerts.

With the aid of this relationship, the balance equations are transformed into a dimensionless form and summarized in Table 7, along with the new resulting dimensionless groups. The other dimensionless groups are the same as those defined in Table 4.
Figure 12. Model basis with the convectional flux shown
Table 6. Dimensional Model Equations

Reactor Balance:

\[
\frac{d}{dh} \left[ (u - u_m) \gamma_{Ab} \right] = \frac{a D \frac{dy_{Ad}}{dy}}{1 - (1 - m) \gamma_{Ad}} \bigg|_{y=0} \tag{4.14}
\]

\(i.c. \quad h=0, \quad \gamma_{Ad} = \gamma_{A0}\)

Bubble-Emulsion Balance:

\[
\frac{d}{dy} \left[ \frac{D \frac{dy_{Ad}}{dy}}{1 - (1 - m) \gamma_{Ad}} \right] = k \gamma_{Ad} \tag{4.15}
\]

with the boundary conditions:

\(y=0, \quad \gamma_{Ad} = \gamma_{Ab}\)

\[
\frac{-a D \frac{dy_{Ad}}{dy}}{1 - (1 - m) \gamma_{Ad}} = k \gamma_{Ad} (1 - \varepsilon_b - \alpha \delta) \tag{4.16}
\]

\(\gamma_{Ab}^i: \) mole fraction of species A in the bubble-phase

\(\gamma_{Ad}^i: \) mole fraction of species A in the dense-phase
Table 7. Dimensionless Model Equations and Groups

**Reactor Balance:**

\[
\frac{d\bar{y}_{AB}}{dL} = \frac{R + 1}{R + m} NTU_0 \bar{y}_{AB} \left[ 1 - (1 - m)\bar{y}_{AB} \right] \frac{d\bar{y}_A}{dY} \bigg|_{\bar{y}=0}
\]

i.e. \( L = 0, \quad \bar{y}_{AB} = \bar{y}_{A0} \)

**Bubble-Emulsion Balance:**

\[
\frac{d}{dY} \left[ \frac{d\bar{y}_A}{dY} \frac{1 - (1 - m)\bar{y}_{AB}}{\bar{y}_A} \right] = Ha^2 \bar{y}_A
\]

with the boundary conditions:

\[
\bar{y}_A = 1 \quad Y = 0
\]

\[
\frac{-d\bar{y}_A}{dY} = Ha^2 \left( \Phi^{-1} - 1 \right) \bar{y}_A \left[ 1 - (1 - m)\bar{y}_{AB} \bar{y}_A \right]
\]

**New Dimensionless Groups**

\[
R = \frac{y_i}{y_{A0}} \quad NTU_0 = \frac{k_c A H}{u_0 - u_m}
\]

\[
\bar{y}_A = \frac{y_{Ad}}{y_{AB}} \quad m: \text{Stoichiometric Coefficient}
\]
The system of equations shown in Table 7 reduces to the original Werther model in two cases. The first case is when \( m=1 \) where no change in the number of moles occurs. The other case is when \( R \to \infty \), which means that the reactant species is present in a very dilute form and thereby any change in its volume goes unnoticeable by the system.

**4.2.2.1 Solution of the Model**

The system of differential equations presented in Table 7 is not linear because of the interdependence of the various parameters. Therefore, the system is to be solved numerically. The bubble gas hold-up and interfacial area are calculated from equation 3.11 and equation 3.12, respectively. Those equations are functions of bed height and gas superficial velocity. When the number of moles changes, there arise two additional problems:

1- The gas superficial velocity is not constant and is calculated from the relationship:

\[
\frac{u - u_{mf}}{u_0 - u_{mf}} = 1 + \frac{m - 1}{R + 1} X_A
\]

where:

\[
X_A = 1 - \frac{(m + R) y_{A,b}}{1 - (1 - m) y_{A,b}}
\]

and \( y_{A,b} \) is the mole fraction of species A in the bubble-phase. The derivation of these relations is described in detail in Appendix A.
2- In their analysis of this problem, Irani et al [16] assumed that the new gas which is generated by reaction, forms new bubbles. In light of the new findings in fluidization technology, that bubbles in group B powders grow with negligible break-up while bubbles in group A powders quickly reach a maximum size, we propose the following:

i- For group B particles, the diameters calculated from an equation such as equation 3.7 should be modified by:

$$d_b|_{\text{modeled}} = d_b \sqrt{1 + \frac{m - 1}{R + 1} X_A}$$

This equation is derived assuming the ideal gas law, and details of the derivation are given in Appendix A.

ii- For group A powders, the preceding expression is applicable in the region where $h < h^*$.  

4.2.3 Parametric Study  

The influence of the stoichiometric coefficient $m$ and the inert to reactant ratio $R$ are shown on Figure 13 and Figure 14, respectively. Figure 13 shows the influence of the stoichiometric coefficient on the conversion inside the reactor, while Figure 14 shows the influence of the presence of inerts in the feed on the exit conversion. Simulation parameters are: $u=0.3$ m/s, $u_m=0.03$ m/s, $d_f=1.0$ m, $H=1.0$ m, $k=10$ s$^{-1}$, $D=2 \times 10^{-5}$ m$^2$/s, and the solid is Geldart type B.
Figure 13. Influence of the stoichiometric coefficient on the conversion along bed height
Figure 14. Influence of the feed inerts' ratio on the exit conversion
4.2.4 Discussion of the Results

4.2.4.1 Effect of the Stoichiometric Coefficient $m$

Figure 13 shows that the predicted conversion, when the number of moles decreases, is always greater than that if $m$ is taken as 1. On the other hand, the predicted conversion decreases when the number of moles increases. This effect is attributed to the fact that an increase in the number of moles dilutes the reactant species.

4.2.4.2 Effect of the Presence of Inerts in the Feed

As it is apparent from Figure 14, the influence of the stoichiometric coefficient becomes less important as the fraction of inerts in the feed increases. The reason is that the presence of inerts dilutes the reactant species. Therefore, a change in the number of moles has less influence on the overall volume of the gas in the reactor. Note that the curves meet at the point where $m=1$, which means that whatever the amount of inerts in the feed, it will not affect the exit conversion when there is no change in the number of moles.
CHAPTER 5
APPLICATION OF THE WERTHER MODEL TO COMPLEX REACTIONS

5.1 Introduction

While the simple reaction $A \rightarrow B$ is useful for learning purposes, most of the industrial reactions, we are aware of, are actually complex reactions. Because of this fact, and because the strengths of a model and model discrimination are revealed by its application to yield-sensitive complex reactions, we analyze in this chapter three general complex reaction schemes. These reaction schemes degenerate to many subcases, covering a wide range of reactions of practical importance.

The objective is to determine the performance equations that give the reactant conversion and yields for all of the other species.

5.2 DENBIGH REACTION NETWORK

The Denbigh reaction [8] is considered first. It is the general first-order reaction network given by:

$$
A \xrightarrow{\text{$k_1$}} R \xrightarrow{\text{$k_2$}} S
$$

\[\text{T} \xrightarrow{\text{$k_2$}} \text{U} \xrightarrow{\text{$k_4$}} \]
This network degenerates to seven distinct subcases as shown in Table 8, by setting the appropriate conditions. These subcases include all the subcases previously studied by Werther and coworkers [2,47] and Perrier et al [32].

5.2.1 Model Equations

The governing differential equations that result from material balances for each species are shown in Table 9. The derivation is generalized by assigning a different diffusivity coefficient for each species. Note that this is a more realistic generalization that was not used in [2] and [32]. The equations of Table 9 are normalized and summarized in Table 10 and the resulting dimensionless groups are listed in Table 11.

5.2.2 Solution of the Problem

The system of differential equations shown in Table 10 is linear and therefore an analytical solution is possible. In order to find the reactant conversion and yields for the other species, we need to solve a total of eight differential equations—four from the bubble-emulsion balance and four from the reactor balance. The remaining species is calculated by difference. After simplification, we arrive at the conversion and yield equations presented in Table 11.

5.2.3 Simulation

The analytical solution presented in Table 11 is better illustrated by a numerical example. The parametric values used exemplify a fluidized-bed
Table 8. Degenerate Subcases From Denbigh Network

<table>
<thead>
<tr>
<th>Condition</th>
<th>Subcase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (k_2=k_3=k_4=0)</td>
<td>A→R</td>
</tr>
<tr>
<td>2 (k_2=k_4=0)</td>
<td>A (k_1) → R (k_3) → S</td>
</tr>
<tr>
<td>3 (k_2=k_4=0)</td>
<td>A (k_1) → R (k_2) → T</td>
</tr>
<tr>
<td>4 (k_4=0)</td>
<td>A (k_1) → R (k_3) → S (k_2) → T</td>
</tr>
<tr>
<td>5 (k_2=0)</td>
<td>A (k_1) → R (k_3) → S (k_4) → U</td>
</tr>
<tr>
<td>6 (k_2=0)</td>
<td>A (k_1) → R (k_2) → P</td>
</tr>
<tr>
<td>(C_P=C_S+C_T)</td>
<td></td>
</tr>
<tr>
<td>7 (C_P=C_T+C_U)</td>
<td>A (k_1) → R (k_3) → S (k_2) → P</td>
</tr>
</tbody>
</table>
Table 9. Material Balance Equations for Denbigh Network

**Reactor Balance:**

\[(u - u_{mf}) \frac{dC_{jk}}{dh} = a D_j \frac{dC_{jd}}{dy} \bigg|_{r=0} \]

i.e. \( h=0, \ C_{yj} = C_{j0} \quad j=A,R,T,U \)

**Bubble-Emulsion Balance:**

\[D_A \frac{d^2 C_{Ad}}{dy^2} = (k_1 + k_2) C_{Ad} \]

\[D_T \frac{d^2 C_{Td}}{dy^2} = -k_2 C_{Ad} \]

\[D_R \frac{d^2 C_{Rd}}{dy^2} = (k_3 + k_4) C_{Rd} - k_1 C_{Ad} \]

\[D_U \frac{d^2 C_{Ud}}{dy^2} = -k_4 C_{Rd} \]

**Boundary Conditions:**

\( y=0, \ C_{yj} = C_{j0} \quad j=A,R,T,U \)

\( y=\delta, \)

\[-a D_A \frac{dC_{Ad}}{dy} = (k_1 + k_2) C_{Ad} (1 - \varepsilon_b - a\delta) \]

\[-a D_T \frac{dC_{Td}}{dy} = -k_2 C_{Ad} (1 - \varepsilon_b - a\delta) \]

\[-a D_R \frac{dC_{Rd}}{dy} = [(k_3 + k_4) C_{Rd} - k_1 C_{Ad}] (1 - \varepsilon_b - a\delta) \]

\[-a D_U \frac{dC_{Ud}}{dy} = -k_4 C_{Rd} (1 - \varepsilon_b - a\delta) \]
### Table 10. Dimensionless Model Equations for Denbigh Network

#### Reactor Balance:

\[
\frac{d\theta_j}{dL} = NTU \left. \theta_j \frac{d\overline{C}_j}{dY} \right|_{y=0} \quad \text{5.10}
\]

i.e. \( L=0, \quad \theta_A=1, \quad \theta_{j, j=1 \text{or} j=0} = \theta_{j, j=1 \text{or} j=0} \) \( j=A,R,T,U \)

#### Bubble-Emulsion Balance:

\[
\frac{d^2\overline{C}_A}{dY^2} = Ha_{12}^2 \overline{C}_A \quad \text{5.11}
\]

\[
\frac{d^2\overline{C}_T}{dY^2} = -r_T Ha_{12}^2 \overline{C}_A \frac{\theta_A}{\theta_T} \quad \text{5.12}
\]

\[
\frac{d^2\overline{C}_R}{dY^2} = r_R Ha_{12}^2 \overline{C}_A - r_R Ha_{12}^2 \overline{C}_A \frac{\theta_A}{\theta_R} \quad \text{5.13}
\]

\[
\frac{d^2\overline{C}_U}{dY^2} = -r_U Ha_{12}^2 \overline{C}_A \frac{\theta_R}{\theta_U} \quad \text{5.14}
\]

#### Boundary Conditions:

\( Y=0, \quad \overline{C}_j = 1, \quad j=A,R,T,U \)

\( Y=1, \)

\[
-\frac{d\overline{C}_A}{dY} = Ha_{12}^2 \overline{C}_A (\Phi^{-1} - 1) \quad \text{5.15}
\]

\[
-\frac{d\overline{C}_T}{dY} = -r_T Ha_{12}^2 \overline{C}_A \frac{\theta_A}{\theta_T} (\Phi^{-1} - 1) \quad \text{5.16}
\]

\[
-\frac{d\overline{C}_R}{dY} = \left( r_R Ha_{12}^2 \overline{C}_R - r_R Ha_{12}^2 \overline{C}_A \frac{\theta_A}{\theta_R} \right) (\Phi^{-1} - 1) \quad \text{5.17}
\]

\[
-\frac{d\overline{C}_U}{dY} = -r_U Ha_{12}^2 \overline{C}_R \frac{\theta_R}{\theta_U} (\Phi^{-1} - 1) \quad \text{5.18}
\]
Table 11. Concentration Profiles for Denbigh Network

\[ \theta_A = \exp(-NTU \, Ha_{12} \, a_{12} L) \]  \hspace{1cm} 5.19

\[ \theta_T = \theta_{R0} + \frac{r_T Ha_{12}^2}{Ha_{12}^2} (1 - \theta_A) \]  \hspace{1cm} 5.20

\[ \theta_R = \left[ \frac{r_R Ha_{12}^2}{Ha_{12}^2 - r_R Ha_{24}^2} + \theta_{R0} \right] \exp(-NTU \, r_R^{12} Ha_{24} \, a_{24} L) - \frac{r_R Ha_{12}^2}{Ha_{12}^2 - r_R Ha_{24}^2} \theta_A \]  \hspace{1cm} 5.21

\[ \theta_U = \theta_{U0} + \frac{r_U Ha_{24}^2}{r_R Ha_{24}^2} (\theta_{R0} - \theta_R) + \frac{r_U Ha_{12}^2}{Ha_{12}^2} \frac{Ha_{24}^2}{Ha_{34}^2} (1 - \theta_A) \]  \hspace{1cm} 5.22

\[ \theta_S = 1 + \theta_{R0} + \theta_{T0} + \theta_{U0} + \theta_{S0} - \theta_A - \theta_R - \theta_T - \theta_U \]  \hspace{1cm} 5.23

**Parameters**

\[ \Phi = \frac{a D_A}{(1 - \varepsilon_b) k_c} \]  \hspace{1cm} 5.24

\[ NTU = \frac{k_c a H}{u - u_{nf}} \]  \hspace{1cm} 5.25

\[ Ha_{l}^2 = \frac{k_c D_A}{k_c^2}, \quad l = 1, 12, 2, 34, 4 \]  \hspace{1cm} 5.26

\[ a_l^j = \frac{(\Phi^{-1} - 1) r_{j}^{12} Ha_l + \tanh r_{j}^{12} Ha_l}{1 + (\Phi^{-1} - 1) r_{j}^{12} Ha_l \tanh r_{j}^{12} Ha_l}, \quad l = 12, 34, \quad j = A, R \]  \hspace{1cm} 5.27

\[ k_{mn} = k_m + k_n, \quad m, n = 1, 2, 3, 4 \]  \hspace{1cm} 5.28

\[ r_j = \frac{D_A}{D_j}, \quad j = A, R, T, U \]  \hspace{1cm} 5.29

\[ \theta_j = \frac{C_{j_d}}{C_{A0}} \quad j = A, R, S, T, U \]  \hspace{1cm} 5.30

\[ L = h / H \]  \hspace{1cm} 5.31
reactor with Geldart type A solids. The concentration curves are displayed in Figure 15.

Note that the intermediate species R reaches a maximum value at some point above the distributor. This point marks the optimum height if R is the desirable product.

5.2.4 Comparison with Experimental Data

The production of maleic anhydride from benzene oxidation was studied experimentally by Jaffres et al [18] in a small fluidized-bed reactor. Perrier et al [32] applied the Werther model to predict the performance of that reactor and compared the prediction with the experimental data of Jaffres et al. The reaction is described by the triangular subcase shown in Table 8 (subcase number 6):

\[
\text{Benzene} \rightarrow \text{Maleic Anhydride} \\
\text{CO}_2 + \text{H}_2\text{O}
\]

Some of the data studied by Perrier et al are replotted on Figure 16 and compared versus our solution, using the new hydrodynamic expressions of Chapter 3, and a good agreement is found. It looks, however, that the improvement by using the new hydrodynamic parameters is not significant for that small reactor. It should be noted that the catalyst they used falls into group B on Geldart chart and the average species diffusivity, at the temperature T=460 °C, is estimated to be $3.0 \times 10^{-5}$ m/s. The other parametric values may be found in the article of Perrier et al.
Figure 15. Concentration profiles along the bed height for a Denbigh reaction
Figure 16. Comparison of model predictions and experiment, maleic anhydride production at T=460 °C and \( u/u_{mf} = 10.8 \), data from [32]
5.3 A GENERAL REVERSIBLE REACTION

The next reaction to consider is the general reversible first-order reaction:

\[
\begin{align*}
A & \xrightleftharpoons[k_2]{k_1} R \xrightleftharpoons[k_4]{k_3} S \\
A & \xrightleftharpoons[k_1]{k_2} R \xrightarrow[k_3]{k_4} S
\end{align*}
\]

As in the case of Denbigh network this reaction degenerates to the new four distinct subcases listed in Table 12, given the appropriate conditions.

5.3.1 Model Equations

This three species system is defined mathematically by four initial and boundary value differential equations, in addition to two overall species balances in bubble and emulsion phases. These equations are shown in Table 13 and in dimensionless form in Table 14. The derivation is made general by considering the possibility of the presence of any species in the feed. The balance equations and the subsequent solution are valid for both the reversible consecutive reaction as written above and for the reversible parallel reaction:

\[
\begin{align*}
A & \xrightleftharpoons[k_2]{k_1} R \\
A & \xrightleftharpoons[k_3]{k_4} S
\end{align*}
\]

by making the following three transformations:

\[C_A \leftrightarrow C_R\]
Table 12. Degenerate Subcases for the Reversible Reaction

<table>
<thead>
<tr>
<th>Condition</th>
<th>Subcase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>The Consecutive Reaction</strong></td>
</tr>
<tr>
<td>1 ( k_1 = k_2 = 0 )</td>
<td>[ \text{A} \xrightarrow{k_1} \text{R} ]</td>
</tr>
<tr>
<td>2 ( k_1 = 0 )</td>
<td>[ \text{A} \xrightarrow{k_2} \text{R} \xrightarrow{k_3} \text{S} ]</td>
</tr>
<tr>
<td>3 ( k_2 = 0 )</td>
<td>[ \text{A} \xrightarrow{k_1} \text{R} \xrightarrow{k_3} \text{S} ]</td>
</tr>
<tr>
<td></td>
<td><strong>The Parallel Reaction</strong></td>
</tr>
<tr>
<td>4 ( k_2 = 0 )</td>
<td>[ \text{R} \xrightarrow{k_1} \text{A} \xrightarrow{k_2} \text{S} ]</td>
</tr>
</tbody>
</table>
Table 13. Material Balance Equations for the Reversible Consecutive Reaction

**Reactor Balance:**

\[
(u - u_{mf}) \frac{dC_{jb}}{dh} = a \frac{dC_{jd}}{dy} \bigg|_{y=0}
\]

i.e. \( h=0, \ C_{jb}=C_{jp}, \ j=A,R \)

**Bubble-Emulsion Balance:**

\[
D_A \frac{d^2C_{Ad}}{dy^2} = k_1C_{Ad} - k_2C_{Rd}
\]

\[
D_R \frac{d^2C_{Rd}}{dy^2} = (k_2 + k_3)C_{Rd} - k_1C_{Ad} - k_4C_{Sd}
\]

**Boundary Conditions:**

\( y=0, \ C_{jd}=C_{jp}, \ j=A,R \)

\( y=\delta, \)

\[
-\alpha D_A \frac{dC_{Ad}}{dy} = [k_1C_{Ad} - k_2C_{Rd}] (1 - \epsilon_b - \alpha \delta)
\]

\[
-\alpha D_R \frac{dC_{Rd}}{dy} = [(k_2 + k_3)C_{Rd} - k_1C_{Ad} - k_4C_{Sd}] (1 - \epsilon_b - \alpha \delta)
\]

**Overall Species Balance**

\[
\sum C_{jb} = \sum C_{jd} = \sum C_{j0}, \quad j = A,R,S
\]
Table 14. Dimensionless Model Equations for the Reversible Consecutive Reaction

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{d\theta_i}{dL} = NTU \theta_i \frac{d\overline{C}_j}{dY} \Big</td>
<td>_{Y=0} )</td>
</tr>
<tr>
<td>( \frac{d^2\overline{C}_A}{dY^2} = Ha_1^2 \overline{C}_A - Ha_2^2 \overline{C}_R \frac{\theta_R}{\theta_A} )</td>
<td>5.39</td>
</tr>
<tr>
<td>( \frac{d^2\overline{C}<em>R}{dY^2} = Ha</em>{23}^2 \overline{C}_R - Ha_1^2 \overline{C}_A \frac{\theta_A}{\theta_R} - Ha_3^2 \overline{C}_S \frac{\theta_S}{\theta_R} )</td>
<td>5.40</td>
</tr>
<tr>
<td><strong>Boundary Conditions:</strong></td>
<td></td>
</tr>
<tr>
<td>( Y=0, \quad \overline{C}_j = 1, \quad j=A,R )</td>
<td></td>
</tr>
<tr>
<td>( Y=1, )</td>
<td></td>
</tr>
<tr>
<td>( -\frac{d\overline{C}_A}{dY} = \left[ Ha_1^2 \overline{C}_A - Ha_2^2 \overline{C}_R \frac{\theta_R}{\theta_A} \right] (\Phi^{-1} - 1) )</td>
<td>5.41</td>
</tr>
<tr>
<td>( -\frac{d\overline{C}<em>R}{dY} = \left[ Ha</em>{23}^2 \overline{C}_R - Ha_1^2 \overline{C}_A \frac{\theta_A}{\theta_R} - Ha_3^2 \overline{C}_S \frac{\theta_S}{\theta_R} \right] (\Phi^{-1} - 1) )</td>
<td>5.42</td>
</tr>
<tr>
<td><strong>Overall Species Balance</strong></td>
<td></td>
</tr>
<tr>
<td>( \theta_S = 1 + \theta_{R0} + \theta_{S0} - \theta_A - \theta_R )</td>
<td>5.43</td>
</tr>
<tr>
<td>( \theta_S \overline{C}<em>S = 1 + \theta</em>{R0} + \theta_{S0} - \theta_A \overline{C}_A - \theta_R \overline{C}_R )</td>
<td>5.44</td>
</tr>
</tbody>
</table>
\[ C_{A0} \leftrightarrow C_{R0} \]

\[ k_1 \leftrightarrow k_2 \]

where the elements around the symbol \( \leftrightarrow \) replace each other.

### 5.3.2 Solution of the Problem

The preceding equations, although linear, are highly interlinked. The problem is attacked first by simultaneously solving the two second-order boundary-value differential equations that describe the bubble-emulsion interactions. Then, the resulting expressions are integrated into the other two first-order differential equations, which are solved simultaneously, as well. The resulting solution is algebraically very complex. Upon extensive simplification and rearrangement, we arrive at the following expressions for the concentrations:

\[
C_A = C_1 \exp(NTU \alpha_1 L) + C_2 \exp(NTU \alpha_2 L) + P_2 \quad \text{(5.45)}
\]

\[
C_R = C_1 \gamma_1 \exp(NTU \alpha_1 L) + C_2 \gamma_2 \exp(NTU \alpha_2 L) + P_1 \quad \text{(5.46)}
\]

\[
C_s = C_{A0} + C_{R0} + C_{S0} - C_A - C_R \quad \text{(5.47)}
\]

where the parameters in these expressions \( (C_1, C_2, \alpha_1, \alpha_2, \gamma_1, \gamma_2, P_1, P_2) \) are defined in Table 15.

Despite its complexity, the solution presented above is explicit and is valid for both the consecutive case and the parallel case after making the required transformations as described earlier.
Table 15. Parameters for Equations 5.45 and 5.46

\[
\begin{align*}
\alpha &= Ha_4^2 + Ha_1^2 + Ha_4^2 \\
\bar{\alpha} &= -Ha_4^2 + Ha_1^2 - Ha_4^2 \\
\beta &= \bar{\alpha}^2 - 4Ha_2^2[Ha_4^2 - Ha_1^2] \\
A_1 &= \sqrt{\frac{1}{2}(\alpha - \sqrt{\beta})} \\
A_2 &= \sqrt{\frac{1}{2}(\alpha + \sqrt{\beta})} \\
B_1 &= \frac{\frac{1}{2}(\bar{\alpha} - \sqrt{\beta})}{Ha_4^2 - Ha_1^2} \\
B_2 &= \frac{\frac{1}{2}(\bar{\alpha} + \sqrt{\beta})}{Ha_4^2 - Ha_1^2} \\
\psi_1 &= \frac{A_1(\Phi^{-1}-1) + \tanh A_1 + A_1A_2(\Phi^{-1}-1)^2 \tanh A_2 + A_2(\Phi^{-1}-1)\tanh A_1 \tanh A_2}{1 + A_1(\Phi^{-1}-1)\tanh A_1 + A_2(\Phi^{-1}-1)\tanh A_2 + A_1A_2(\Phi^{-1}-1)^2 \tanh A_1 \tanh A_2} \\
\psi_2 &= \frac{A_2(\Phi^{-1}-1) + \tanh A_2 + A_2A_1(\Phi^{-1}-1)^2 \tanh A_1 + A_1(\Phi^{-1}-1)\tanh A_2 + A_1A_2(\Phi^{-1}-1)^2 \tanh A_1 \tanh A_2}{1 + A_1(\Phi^{-1}-1)\tanh A_1 + A_2(\Phi^{-1}-1)\tanh A_2 + A_1A_2(\Phi^{-1}-1)^2 \tanh A_1 \tanh A_2} \\
\hat{A}_1 &= -\frac{1}{2} \left( \frac{\bar{\alpha}}{\sqrt{\beta}} + 1 \right) \psi_1 \\
\hat{A}_2 &= \frac{1}{2} \left( \frac{\bar{\alpha}}{\sqrt{\beta}} - 1 \right) \psi_2 \\
\hat{B}_1 &= \frac{Ha_4^2 - Ha_1^2}{\sqrt{\beta}} \psi_1
\end{align*}
\]

Continues on the next page ...
\[ B_2 = - \frac{Ha_1^2 - Ha_2^2}{\sqrt{\beta}} \varphi_2 \]  
5.60

\[ G_1 = A_1 A_1 + A_2 A_2 \]  
5.61

\[ G_2 = A_1 \hat{B}_1 + A_2 \hat{B}_2 \]  
5.62

\[ H_1 = A_1 \hat{A}_1 B_1 + A_2 \hat{A}_2 B_2 \]  
5.63

\[ H_2 = A_1 B_1 \hat{B}_1 + A_2 B_2 \hat{B}_2 \]  
5.64

\[ \alpha_1 = \frac{1}{2} \left( G_1 + H_2 - \sqrt{(G_1 - H_2)^2 + 4G_2 H_1} \right) \]  
5.65

\[ \alpha_2 = \frac{1}{2} \left( G_1 + H_2 + \sqrt{(G_1 - H_2)^2 + 4G_2 H_1} \right) \]  
5.66

\[ \gamma_1 = \frac{1}{2H_1} \left( G_1 - H_2 - \sqrt{(G_1 - H_2)^2 + 4G_2 H_1} \right) \]  
5.67

\[ \gamma_2 = \frac{1}{2H_1} \left( G_1 - H_2 + \sqrt{(G_1 - H_2)^2 + 4G_2 H_1} \right) \]  
5.68

\[ P_1 = \frac{Ha_1^2 Ha_2^2}{A_1^2 A_2^2} \]  
5.69

\[ P_1 = \frac{Ha_2^2 Ha_1^2}{A_1^2 A_2^2} \]  
5.70

\[ C_0 = C_{A0} + C_{R0} + C_{S0} \]  
5.71

\[ C_1 = \frac{-C_{R0} + P_1 C_0 - \gamma_2 (P_2 C_0 - C_{A0})}{\gamma_2 - \gamma_1} \]  
5.72

\[ C_2 = \frac{C_{R0} - P_1 C_0 + \gamma_1 (P_2 C_0 - C_{A0})}{\gamma_2 - \gamma_1} \]  
5.73
5.3.3 Simulation

The general shapes of the concentration curves of the consecutive and parallel reactions and their degenerate subcases are displayed in Figure 17 and Figure 18. The behavior of these curves is very similar to what has been observed in batch and plug flow reactors [26]. One of the similarities is that an intermediate in a reversible consecutive reaction does not need to pass through a maximum, while a product in a reversible parallel reaction may show a maximum; a behavior known for intermediates.

A comparison between a reversible and a non-reversible consecutive reactions at the same operating conditions is shown in Figure 19. The reactions compared are:

\[ A \xrightleftharpoons{10}{1} R \xrightleftharpoons{1}{0.1} S \]

\[ A \xrightarrow{10} R \xrightarrow{1} S \]

where the numbers above the arrows represent the values of the corresponding rate constants.

Note that although the forward reaction constant is 10 folds greater than the backward reaction constant, the result is different and can not be ignored.
Figure 17. The general shapes of concentration curves for the reversible consecutive reaction and subcases
Figure 18. The general shapes of concentration curves for the reversible parallel reaction and subcases.
Figure 19. Comparison between a reversible and a non-reversible consecutive reactions
5.4 A GENERAL CONSECUTIVE-PARALLEL REACTION

An important complex reaction is considered here. It is the first-order consecutive-parallel reaction given by:

\[ A \xrightarrow{k_1} R \xrightarrow{k_3} S \xrightarrow{k_4} T \]

with the new degenerate subcase:

\[ A \xrightarrow{k_1} R \xrightarrow{k_3} S \xrightarrow{k_4} T \]

The other possible subcases have already been covered by the previous reaction schemes.

An example of the industrially important reactions that can be described by this scheme is the phthalic anhydride production from naphthalene. This reaction is considered below and in Chapter 6.

5.4.1 Mathematical Model Equations

A total number of six initial and boundary value differential equations, in addition to the overall composition balance, are needed to model this system. The differential equations and their initial and boundary conditions are given in Table 16 and in dimensionless form in Table 17. As was done in the analysis of the Denbigh reaction network, the derivation is generalized by accounting for the presence of any product in the feed and by assigning a deferent diffusivity coefficient to each species.
Table 16. Material Balance Equations for the Consecutive-Parallel Reaction

**Reactor Balance:**

\[
(u - u_{ni}) \frac{dC_{jh}}{dh} = \alpha D_j \frac{dC_{j\delta}}{dy} \bigg|_{\gamma=0}
\]

i.c. \( h=0, \quad C_{\delta}=C_{\bar{\delta}}, \quad j=A,R,S \)

**Bubble-Emulsion Balance:**

\[
D_A \frac{d^2C_{Ad}}{dy^2} = (k_1 - k_2) C_{Ad}
\]

5.75

\[
D_R \frac{d^2C_{Rd}}{dy^2} = k_2 C_{Rd} - k_1 C_{Ad}
\]

5.76

\[
D_S \frac{d^2C_{Sd}}{dy^2} = k_3 C_{Sd} - k_2 C_{Rd} - k_2 C_{Ad}
\]

5.77

**Boundary Conditions:**

\( \gamma=0, \quad C_{\delta}=C_{\bar{\delta}}, \quad j=A,R,S \)

\( \gamma=\delta, \quad \)

\[-\alpha D_A \frac{dC_{Ad}}{dy} = (k_1 + k_2) C_{Ad} (1 - \varepsilon_b - \alpha \delta) \]

5.78

\[-\alpha D_S \frac{dC_{Sd}}{dy} = [k_4 C_{Sd} - k_2 C_{Rd} - k_2 C_{Ad}] (1 - \varepsilon_b - \alpha \delta) \]

5.79
Table 17. Dimensionless Model Equations for the Consecutive-Parallel Reaction

**Reactor Balance:**

\[
\frac{d\theta_j}{dL} = NTU \theta_j \frac{d\overline{C}_j}{dY}
\]

\[\text{i.c. } L=0, \quad \theta_A=1, \quad \theta_j, \theta_\phi = \theta_j, \quad j=A,R,S\]

**Bubble-Emulsion Balance:**

\[
\frac{d^2 \overline{C}_A}{dY^2} = Ha_{12}^A \overline{C}_A
\]

\[
\frac{d^2 \overline{C}_R}{dY^2} = r_R Ha_3^R \overline{C}_R - r_R Ha_1^C \overline{C}_A \frac{\theta_A}{\theta_R}
\]

\[
\frac{d^2 \overline{C}_S}{dY^2} = r_S Ha_2^S \overline{C}_S - r_S Ha_2^C \overline{C}_R \frac{\theta_R}{\theta_S} - r_S Ha_2^C \overline{C}_A \frac{\theta_A}{\theta_S}
\]

**Boundary Conditions:**

\[Y=0, \quad \overline{C}_j = 1, \quad j=A,R,S\]

\[Y=1,\]

\[-\frac{d\overline{C}_A}{dY} = Ha_{12}^A \overline{C}_A (\Phi^{-1} - 1)\]

\[-\frac{d\overline{C}_R}{dY} = \left(r_R Ha_3^C \overline{C}_R - r_R Ha_1^C \overline{C}_A \frac{\theta_A}{\theta_R}\right)(\Phi^{-1} - 1)\]

\[-\frac{d\overline{C}_S}{dY} = \left(r_S Ha_2^C \overline{C}_S - r_S Ha_2^C \overline{C}_R \frac{\theta_R}{\theta_S} - r_S Ha_2^C \overline{C}_A \frac{\theta_A}{\theta_S}\right)(\Phi^{-1} - 1)\]
5.4.2 The Performance Equations

The above system is analytically solvable because of its linearity. The solution of the system is presented in the form of dimensionless concentrations in Table 18. The dimensionless groups are defined in the same way as in Denbigh reaction (Table 11), only the indices are slightly different. The parameters may be calculated from the expressions in Table 2 or the other correlations in Chapter 3.

5.4.3 Application to an Industrial Reactor

It is rare to find industrial reactor data in the open literature. However, recently, Johnsson, Grace, and Graham [19] studied an industrial fluidized-bed reactor (2.13 m diameter and 7.9 m expanded bed height). The reactor produces phthalic anhydride by catalytic oxidation of naphthalene and the reaction may be represented by the consecutive-parallel scheme under study:

\[ \text{Naphthalene } + \text{O}_2 \rightarrow \text{Naphthoquinone } \rightarrow \text{Phthalic Anhydride } \rightarrow \text{Oxidation Products} \]

\[ \text{Maleic Anhydride } \]

\[ + \text{H}_2\text{O} + \text{CO}_2 + \text{CO} \]

Therefore, the performance equations for this system, according to the Werther model, are the ones shown in Table 18.

The reactor operates at a gas superficial velocity of 0.43 m/s with a catalyst of 53 µm mean diameter and 1200 kg/m³ particle density (Geldart type A) and a temperature and pressure of 636 K and 266 KPa, respectively.
Table 18. Concentration Profiles for the Consecutive-Parallel Reaction

\[
\theta_A = \exp\left(-NTU \, Ha_{12} \, a_{12}^A L\right)
\]

\[\theta_R = \left[ \frac{r_p Ha_1^2}{Ha_{12}^2 - r_p Ha_3^2} + \theta_{R0} \right] \exp\left(-NTU \, r_p^{\text{th}} Ha_{90} \, a_{90}^R L\right) - \frac{r_p^2 Ha_1^2}{Ha_{12}^2 - r_p Ha_3^2} \theta_A \]

\[
\theta_S = \left[ \frac{r_p Ha_1^2}{Ha_{12}^2 - r_2 Ha_4^2} \frac{r_2 Ha_3^2}{r_p Ha_3^2 - r_2 Ha_4^2} + \frac{r_5 Ha_2^2}{Ha_{12}^2 - r_5 Ha_4^2} + \frac{r_5 Ha_3^2}{r_p Ha_3^2 - r_5 Ha_4^2} \theta_{R0} + \theta_{S0} \right] \times 
\exp\left(-NTU \, r_p^{\text{th}} Ha_{90} \, a_{90}^S L\right) - \frac{r_5 Ha_3^2}{r_p Ha_3^2 - r_5 Ha_4^2} \theta_R - 
\left[ \frac{r_5 Ha_1^2}{Ha_{12}^2 - r_5 Ha_4^2} \frac{r_5 Ha_3^2}{r_p Ha_3^2 - r_5 Ha_4^2} + \frac{r_5 Ha_2^2}{Ha_{12}^2 - r_5 Ha_4^2} \right] \theta_A \]

\[\theta_T = 1 + \theta_{R0} + \theta_{S0} + \theta_{T0} - \theta_A - \theta_R - \theta_S \]
The reaction parameters used by Johnsson et al [19] are those of De Maria et al [7]. Using their methods, Johnsson et al derived a set of hydrodynamic parameters for the system. The kinetic parameters of the reaction in addition to the calculated and measured parameters are listed in Table 19. The reaction constants $K_r$ are based on the volume of solids and are related to those of Werther model. $k_i$ by:

$$k_i = (1 - \varepsilon_a)K_r, \quad i = 1,2,3,4$$  \hspace{1cm} (5.91)

Direct measurements of gaseous molar flow rates at the inlet and outlet of the reactor showed that there were no change in the number of moles. For this reactor, $u \gg u_{m}$ as shown in Table 19, which means that gas flow rate in the emulsion is negligible.

Johnsson et al [19] tested the predictions of three models versus the actually measured values from the reactor. The predictions of the Werther model, using the performance equations listed in Table 18, are compared to the predictions of these models in Chapter 6.

Johnsson et al, also, performed a sensitivity analysis to estimate the effect of possible variations in the values of the different parameters. They found that model predictions are sensitive to changes in the values of the reaction constants and bubble size. Variations in the values of most of the other parameters such as molecular diffusivity of the organic species and the fraction of solids in the bubbles are less important.
Table 19. Measured and Calculated Parameters for the Phthalic Anhydride Reactor [19]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{r,f}$</td>
<td>1.8 s&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>$K_{r,s}$</td>
<td>1.8 s&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>$K_{r,2}$</td>
<td>4.6 s&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>$K_{r,3}$</td>
<td>0.023 s&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>$\varepsilon_i$</td>
<td>0.39</td>
</tr>
<tr>
<td>$\varepsilon_d$</td>
<td>0.52</td>
</tr>
<tr>
<td>$d_i$</td>
<td>0.09 m</td>
</tr>
<tr>
<td>$D$</td>
<td>1.06 x 10&lt;sup&gt;-5&lt;/sup&gt; m&lt;sup&gt;2&lt;/sup&gt;/s</td>
</tr>
<tr>
<td>$u$</td>
<td>0.43 m/s</td>
</tr>
<tr>
<td>$u_m$</td>
<td>7.7 x 10&lt;sup&gt;-4&lt;/sup&gt; m/s</td>
</tr>
<tr>
<td>$H$</td>
<td>7.9 m</td>
</tr>
<tr>
<td>$d_i$</td>
<td>2.13 m</td>
</tr>
</tbody>
</table>
The effect of the grid-zone and the freeboard were also investigated in the study of Johnsson et al, on the basis of the phthalic anhydride reactor. Their analysis showed that the contribution of the grid-zone and the freeboard are minor for this reactor.

The concentration curves, predicted by the Werther model, for the phthalic anhydride reactor are displayed in Figure 20. The reactor concentrations are given only at the exit. However, the agreement at that point is remarkably excellent, which is another indication of the success of the model.
Figure 20. Concentration profiles along the phthalic anhydride reactor
CHAPTER 6

COMPARISON BETWEEN THE WERTHER MODEL AND THE KUNII-
LEVENSPIEL MODEL

6.1 Introduction

There is a large number of fluidized-bed models in the literature. They are usually based on different physical principles. Each model highlights certain aspects of the fluidized-bed phenomena that are considered important and disregards the parts that are believed unimportant. The result is that every model comes with a different set of equations that are thought to describe these phenomena.

Comparison of models on the basis of experimental or industrial data is essential to evaluate the models against each other and to prove or disprove the inherent principles of the models. In spite of the large number of models offered in the literature, the studies on model comparison are scarce. To be mentioned, are the recent work of Johnsson, Grace, and Graham [19], the work of Jaffres et al [18], and the work of Yates and Gregoire [49]. Johnsson et al compared the predictions of the models of Kunii-Levenspiel [23], Kato-Wen [21], and Grace [11] on the basis of industrially measured data. This comparison is extended here to the Werther model and is presented at the end of this chapter.
In the next sections, the results of our work is compared to the well-known model of Kunii and Levenspiel [23]. This model has been the subject of several works in the last decade. It has been applied to cases involving a change in the number of moles and it was extended to complex reactions.

6.2 What is the Kunii-Levenspiel Model?

It is a bubbling-bed model that treats each bubble as a separate batch reactor carrying its gas from the gas distributor to the surface of the bed. The bubbles are assumed to have a single effective diameter and each bubble has a cloud around it and a wake at the bottom (see Figure 1). The mass transfer occurs from the bubble to the cloud and from the cloud to the emulsion. A comparison between the assumptions of the Kunii-Levenspiel model and the Werther model is summarized in Table 20.

The model first appeared in 1968 [22] and is described in detail in [23]. An updated version of the model appeared in 1990 [24]. In this analysis, the part of the updated version that is restricted to fine-particle bubbling beds is adopted. In fact, the main difference between this part and the old model of 1968 is an expression for the bubble rise velocity \( u_b \), proposed on the basis of the measurements made by Werther and Hilligardt [24].

The conversion for the first-order reaction \( A \rightarrow B \), in a fluidized-bed of fine particles is given by:

\[
1 - X_A = \frac{C_A}{C_{A0}} = \exp\left( -K_r \frac{H}{u_b} \right)
\]  

6.1
Table 20. Comparison Between the Assumptions of the Werther Model and the Kunii-Levenspiel Model

<table>
<thead>
<tr>
<th>Assumption</th>
<th>Werther model</th>
<th>K-L model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Division of gas between phase</td>
<td>two-phase theory</td>
<td>all gas in bubbles</td>
</tr>
<tr>
<td>Flow in the gas-phase</td>
<td>plug flow</td>
<td>plug flow</td>
</tr>
<tr>
<td>Flow in the emulsion-phase</td>
<td>negligible</td>
<td>stagnant</td>
</tr>
<tr>
<td>Solids in bubbles</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Mass transfer</td>
<td>correlations</td>
<td>correlations</td>
</tr>
<tr>
<td>Cloud and wake</td>
<td>no, uses film theory</td>
<td>yes</td>
</tr>
<tr>
<td>Bubble size</td>
<td>increases with height</td>
<td>single bubble diameter</td>
</tr>
<tr>
<td>Fitting parameter</td>
<td>no</td>
<td>yes, bubble diameter</td>
</tr>
</tbody>
</table>
where $H$ is the expanded bed height and the other parameters of equation 6.1 are defined in Table 21 [24]. Note that this model contains one adjustable parameter, namely, $d_b$.

6.3 Comparison for the Simple Case A→B

Equation 6.1 is the equivalent to equation 3.20 from the Werther model, which may be rewritten in the form:

$$1 - X_A = \frac{C_A}{C_{A0}} = \exp\left[-K_w \frac{H}{u - u_m}\right]$$

where:

$$K_w = \frac{\left(\Phi^{-1} - 1\right)Ha + \text{tanh} Ha}{1 + \left(\Phi^{-1} - 1\right)Ha \text{tanh} Ha} \times a \times k_c \times Ha$$

and the other parameters are defined as in Chapter 3.

The two equations, although based on different principles, are very similar in form, indeed. One way of comparing the two models is by examining the ratio of the conversions predicted by equations 6.1 and 6.2. Since the most obvious difference between the two models is the inclusion of reaction-transport interaction in the Werther model, the ratio of conversions is plotted in Figure 21 against the reaction constant $k$. The simulation parameters are those in Table 22, except for the bed height $H$ which is set to be 2.0 $m$ in order to compare conversions before they reach completion for the range of reaction constants used. It should be noted that the reaction
Table 21. Parameters for the Kunii-Levenspiel Model

\[
K_f = \left[ \gamma_b K_r + \frac{1}{K_{bc}} + \frac{1}{\gamma_c K_r + \frac{1}{K_{cr} + \frac{1}{\gamma_c K_r}}} \right]
\]

\[
K_{bc} = 4.5 \frac{\mu_{mf}}{d_b} + 5.85 \frac{D_{\text{eff}}^{1/2} g^{3/4}}{d_b^{5/4}}
\]

\[
K_{cr} = 6.77 \sqrt{\frac{D_{\text{eff}} \mu_{br}}{d_b^3}}
\]

\[
\gamma_b \approx 0.005
\]

\[
\gamma_c = \left(1 - \varepsilon_{mf}\right) \left[ \frac{1}{u_{br} \varepsilon_{mf}} - f_w \right]
\]

\[
\gamma_e = \frac{(1 - \varepsilon_{mf})(1 - \varepsilon_b)}{\varepsilon_b} - \gamma_b - \gamma_c
\]

\[
\varepsilon_b = u / u_b
\]

\[
u_b = 1.55 \left((u - u_{mf}) + 14.1(d_b + 0.005)\right) d_b^{0.33} + u_{br}, \quad \text{group A powder}
\]

\[
u_{br} = 0.711 \sqrt{gd_b}
\]

\(d_b\) is fitted or estimated

\(f_w\) is the wake fraction, evaluated from a figure in [24]
Figure 21. Ratio of conversions from Kunii-Levenspiel and Werther models for the first-order reaction $A \to B$. 
constant $K$, for Kunii-Levenspiel model is based on the volume of the solids, while it is based on volume of emulsion in the Werther model. The two constants are related by equation 5.91, where $\varepsilon_d$ is taken as $\varepsilon_{mf}$ in the simulation.

The figure shows that the Kunii-Levenspiel model always predicts less conversion than the Werther model. The predictions of the two models are closer when the reaction is slow. This is not surprising, because the Werther model accounts for reaction enhancements on the mass transfer. As seen from the figure, the ratio of conversions decreases with $k$ but it rises up again at the higher values of $k$. This increase occurred merely because the two models predicted the completion of reaction ($X_\rightarrow 1$) under the range of the parameters used in the simulation.

6.4 Effect of the Change in the Number of Moles

Irani et al [16] were able to get an analytical solution based on the Kunii-Levenspiel model for the first-order reaction $A \rightarrow mB$, where the volume changes because of reaction. It was possible for them to get an analytical solution because they, implicitly, assumed that the gas superficial velocity is constant along the bed height at the inlet value $u_o$. This assumption contradicts with the meaning of volume change and can not be used in our analysis. However, the general shapes of the curves of Irani et al are similar to those in our analysis.
6.5 Application to Complex Reactions

The Kunii-Levenspiel model also has been applied to some complex reaction schemes by Kunii and Levenspiel [23] and Carberry [5]. Levenspiel et al [27] subsequently applied the model to the Denbigh reaction considered in Chapter 5. The reversible reaction and the consecutive-parallel reaction were later studied by Irani et al [17], using this model. The performance equations, based on the Kunii-Levenspiel model, are similar in their general form to those in our analysis.

To get some feeling of the similarities and differences between the two models, in the area of complex reactions, their predictions for the reversible consecutive reaction:

\[ A \xrightleftharpoons[k_2]{k_1} R \xrightleftharpoons[k_4]{k_3} S \]

are displayed graphically in Figure 22. The performance equations that are used in the simulation are:

1. Kunii-Levenspiel model:
   \[ \theta_A = 0.0909 + 0.909 \exp(-3.01L) \]  \hspace{1cm} 6.12
   \[ \theta_R = 0.112 + 0.459 \exp(-1.59L) - 0.572 \exp(-3.01L) \]  \hspace{1cm} 6.13

2. Werther model:
   \[ \theta_A = 0.00901 + 0.892 \exp(-4.59L) + 0.099 \exp(-2.72L) \]  \hspace{1cm} 6.14
\[ \theta_R = 0.0901 - 0.981 \exp(-4.59L) + 0.099 \exp(-2.72L) \]

Reactor data used in the simulation are listed in Table 22. The calculation procedure for the Kunii-Levenspiel model is similar to the one in [17] and is summarized in Appendix B. The performance equations from the Werther model were symbolically evaluated by loading the list of expressions in Appendix C into Mathematica Program.

The two sets of equations are quite similar in form. However, it looks from Figure 22 that the Kunii-Levenspiel model predicts lower conversion than the Werther model. Based on industrial data from the phthalic anhydride reactor, discussed in the next section, the Kunii-Levenspiel model actually underpredicted the reactant conversion of naphthalene. The prediction of the Werther model is, on the other hand, very close to the measured conversion.

6.6 Comparison with Kunii-Levenspiel and Other Models on the Basis of Industrial Reactor Data

As discussed in Chapter 5, Johnsson et al [19] studied an industrial phthalic anhydride fluidized-bed reactor. They used the actual data to test the predictions from the models of Kunii and Levenspiel [23], Kato and Wen [21], and Grace [11].

In Chapter 6, the Werther model was applied to this reaction. The exit concentrations from the Werther model are compared to the calculations of Johnsson et al for the other models and the actual data in Table 23.
Table 22. Simulation Parameters for Figure 21 and Figure 22, (reaction constants are based on the volume of solids)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{r_1}$</td>
<td>10 s$^{-1}$</td>
</tr>
<tr>
<td>$K_{r_2}$</td>
<td>1.0 s$^{-1}$</td>
</tr>
<tr>
<td>$K_{r_3}$</td>
<td>1.0 s$^{-1}$</td>
</tr>
<tr>
<td>$K_{r_4}$</td>
<td>0.1 s$^{-1}$</td>
</tr>
<tr>
<td>$\varepsilon_m$</td>
<td>0.5</td>
</tr>
<tr>
<td>$f_w$</td>
<td>0.3</td>
</tr>
<tr>
<td>$d_o$</td>
<td>0.05 m</td>
</tr>
<tr>
<td>$D$</td>
<td>$2.0 \times 10^{-5}$ m$^3$/s</td>
</tr>
<tr>
<td>$u$</td>
<td>0.3 m/s</td>
</tr>
<tr>
<td>$u_m$</td>
<td>0.005 m/s</td>
</tr>
<tr>
<td>$H$</td>
<td>5.0 m</td>
</tr>
<tr>
<td>$d_i$</td>
<td>1.0 m</td>
</tr>
</tbody>
</table>
Figure 22. Comparison between Kunii-Levenspiel and Werther models on the basis of a complex reversible reaction.
The predictions of the different models are quite similar only for the phthalic anhydride and the oxidation products concentrations, with the Werther model being the best to predict the very low feed breakthrough; a crucial point in the operation of the reactor as discussed by Bolthrunis [4] who commented "If 2% of the feed passed through the reactor unconverted, not only would it be detected, it would cause a major problem—it would condense, be collected with the phthalic anhydride, and cause purification problems." In practice, none of these symptoms appear, as indicated by Bolthrunis [4].

The predictions of the models, however, are dependent on parameters that are subject to many uncertainties. For example, the kinetic parameters used in the analysis were calculated by De Maria et al [7] in 1961 for a similar catalyst under conditions which are not clearly defined, where it should have been determined from the same catalyst of the reactor under the actual operating conditions of the reactor.
Table 23. Comparison of the Werther Model and the Three Models Studied by Johnson et al with Data from Industrial Unit

Dimensionless concentrations $C_j/C_{Ao} \times 100$

<table>
<thead>
<tr>
<th>Model</th>
<th>$j$</th>
<th>A</th>
<th>R</th>
<th>S</th>
<th>T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kunii-Levenspiel [23]</td>
<td></td>
<td>2.13</td>
<td>0.95</td>
<td>86.2</td>
<td>10.7</td>
</tr>
<tr>
<td>Kato-Wen [21]</td>
<td></td>
<td>0.14</td>
<td>0.11</td>
<td>88.8</td>
<td>10.9</td>
</tr>
<tr>
<td>Grace [11]</td>
<td></td>
<td>1.28</td>
<td>0.55</td>
<td>87.5</td>
<td>10.7</td>
</tr>
<tr>
<td>Werther (present work)</td>
<td></td>
<td>0.03</td>
<td>.03</td>
<td>89.2</td>
<td>10.8</td>
</tr>
<tr>
<td>Measured industrial data</td>
<td></td>
<td>0.0</td>
<td>1.31</td>
<td>88.9</td>
<td>9.8</td>
</tr>
</tbody>
</table>

A: naphthalene  
R: naphthoquinone  
S: phthalic anhydride  
T: oxidation products
CHAPTER 7
CONCLUSIONS AND RECOMMENDATIONS

7.1 Introduction

In this research work, the Werther model has been generalized to account for the gas-side resistance. It has also been generalized to account for the change in the number of moles for the reaction A → mB. The effect of the different influential parameters in these cases has been studied.

The model is then extended to several complex reaction schemes of general nature. These schemes degenerate to many subcases, thus covering a wide range of industrially important reactions.

Finally, some of the results of this work has been compared to the corresponding results that have been obtained by using the well-known Kunii-Levenspiel model.

Accomplishing the results mentioned above, we end up with some conclusions about each part of this work, and finally we propose some recommendations for further research.
7.2 Conclusions

7.2.1 Effect of Gas-Side Resistance

By analyzing the equations and figures, related to this subject in Chapter 4, we find that gas-side resistance is important in the cases when:

- the reactant is diluted,
- the reaction rate is not slow,
- the number of transfer units is low,
- the fluidized powder belongs to group B.

7.2.2 Effect of the Change in the Number of Moles

When the number of moles changes as the reaction proceeds, gas density changes with bed height and subsequently, gas superficial velocity, reaction rate, and mass transfer rate between phases are affected. From this study, we conclude the following about this effect:

- The effect of the change in the number of moles is important and can not be neglected. Large deviations can occur in the predictions obtained from models that neglect the effect of such changes.
- The exit conversion increases when the stoichiometric coefficient decreases and vice versa.
- The effect of the change in the number of moles decreases as the mole fraction of inerts in the feed increases.
• The effect of the change in the number of moles can be neglected when the reactant is very diluted, which greatly simplifies the model.

7.2.3 Application to Complex Reactions

In this part of this work:

• The Werther model has been extended to several general complex reaction schemes. These schemes degenerate to many subcases covering a wide range of industrially important reactions.

• Generalized explicit expressions for conversion and yields for these complex reaction schemes have been developed, based on the Werther model.

• The applicability of the developed expressions has been confirmed by experimental and industrial data.

7.2.4 Comparison with the Kunii-Levenspiel and Other Models

The problem of the change in the number of moles has also been studied by Irani et al [16], using the Kunii-Levenspiel model. The same model has also been extended to the complex reaction schemes, studied in Chapter 5, by Levenspiel et al [27] and Irani et al [17]. Comparing the results from [16], [17], and [27] to the results of this work, we end up with several conclusions:

• With respect to the work of Irani et al [16] on the change in the number of moles, we have found that the general conclusions are the same, although direct comparison can not be made, because the model of Irani et al rests on some assumptions that we feel
unrealistic, specially the assumption of constant gas superficial velocity in the bed.

- Comparing the results of this work to those obtained in [17] and [27], we found that the Kunii-Levenspiel model predicts, generally, less conversion and yields than the Werther model. This behavior is also observed for the case of the simple first order reaction A → B.

- Based on industrial unit data (phthalic anhydride reactor):

  (a) All models, including the Werther model, predicted somewhat close results, despite their different assumptions.

  (b) The Kunii-Levenspiel model underpredicted the actual conversion of the reactant (naphthalene) and the yield of the desired product (phthalic anhydride).

  (c) The Werther model is the best to predict the low feed breakthrough. At the same time, the Werther model underpredicted the yield of the intermediate naphthoquinone.

7.3 Recommendations

At the end of this work, we propose several recommendations for further research, in the area of this work. Most of the proposed recommendations are to test the inherent assumptions of the Werther model. These recommendations are:
• Account for bubble surface curvature in the bubble-emulsion balance by using the spherical coordinates and compare the results with the analytical solution derived by using the linear coordinates.

• The Werther model uses the film theory. However, the penetration theory seems to be advantageous in the case where the number of moles changes. Try this theory and compare the results obtained by using the film theory.

• Account for the flow in the emulsion, and study its importance, in view of practical applications.

• Include dispersion coefficients in the gas and emulsion phases and study their effect. Dispersion coefficients are difficult to estimate. Some values may be found in Pell [31].

• Apply the model to complex reactions of the Langmuir-Hinshelwood form to study the effect of concentrations and particle size on the reaction rate coefficients, and to study the applicability of the Werther model in these cases. An example of a reaction of this type may found in [20].

• From the shapes of the bubbles, try to determine a shape factor that relates the surface area of a bubble to that of a sphere having the same volume. This parameter is important for the Werther model in determining the interfacial area of bubbles.
LIST OF SYMBOLS

\( a \)  bubble interfacial surface area / reactor volume, \( m^{-1} \)

\( Bi \)  Biot number, defined by equation 4.2

\( C \)  total concentration, \( mol/m^3 \)

\( C_{jb} \)  concentration of species \( j \) in the bubble-phase, \( mol/m^3 \)

\( C_{js} \)  concentration of species \( j \) in the dense-phase, \( mol/m^3 \)

\( \overline{C} \)  dimensionless concentration defined in Table 4

\( d_b \)  equivalent bubble diameter, \( m \)

\( d_p \)  mean particle diameter, \( m \)

\( d_i \)  bed diameter, \( m \)

\( D \)  average species diffusivity, \( m^2/s \)

\( D_j \)  diffusivity of species \( j \), \( m^2/s \)

\( f_w \)  wake fraction

\( g \)  gravitational acceleration, \( m/s^2 \)

\( h \)  height above distributor plate, \( m \)

\( h_0 \)  grid-zone height, \( m \)

\( h^* \)  height above gas-distributor at which bubble growth ceases, \( m \)

\( H \)  expanded bed height, \( m \)

\( Ha \)  Hatta number defined under equation 3.20

\( H_{mf} \)  Height of bed at minimum fluidization, \( m \)

\( k \)  reaction rate constant, based on emulsion volume, \( s^{-1} \)

\( k_e \)  bubble to emulsion mass transfer coefficient, \( m/s \)
$k_g$  gas-side mass transfer coefficient, $m/s$

$K_{bc}$  bubble to cloud mass transfer coefficient, $s^{-1}$

$K_{ce}$  cloud to emulsion mass transfer coefficient, $s^{-1}$

$K_i$  a parameter in the Kunii-Levenspiel model, defined in Table 20

$K_r$  reaction rate constant, based on solids volume, $s^{-1}$

$l_j$  jet length, $m$

$L$  dimensionless bed height

$m$  Stoichiometric coefficient

$M$  adsorption equilibrium constant in equation 3.5

$n$  number of moles

$N_j$  flux of species $j$, $mol/m^2s$

$NTU$  number of transfer units, defined under equation 3.20

$NTU_o$  number of transfer units based on the inlet gas velocity

$P$  total pressure, $atm$

$p_i$  partial pressure of inerts, $atm$

$r$  diffusivity ratio, defined in Table 11

$R$  ratio of inerts to reactant mole fractions in the feed, defined in Table 7

$S_v$  ratio of surface area of all particles to their volume, $m^{-1}$

$u$  gas superficial velocity, $m/s$

$u_b$  bubble rise velocity, $m/s$

$u_{br}$  rise velocity of a bubble with respect to the emulsion flow, $m/s$

$u_{mf}$  minimum fluidization velocity, $m/s$

$u_{mb}$  minimum bubbling velocity, $m/s$

$u_o$  velocity inside one orifice hole in the gas distributor, $m/s$
$V_b$ visible bubble flow, $m/s$
$X_A$ reactant conversion
$y$ distance inside emulsion phase
$Y$ dimensionless distance inside emulsion phase
$y_j$ mole fraction of species $j$

Greek Symbols

$\delta$ film thickness, $m$
$\varepsilon_b$ bubble gas hold-up
$\varepsilon_d$ overall bed voidage
$\varepsilon_{mf}$ void fraction at minimum fluidization
$\Phi$ film volume / emulsion volume, defined under equation 3.20
$\mu$ gas viscosity, $Pa\ s$
$\nu$ kinematic viscosity
$\theta_j$ dimensionless concentration of species $j$
$\rho$ density, $kg/m^3$

Subscripts and Superscripts

$A$ species A
$b$ bubble-phase
dense-phase
$f$ fluid
$g$ gas-side
$i$ inerts
or orifice
$p$ solid particles
$R$ species R
$s$ solids
$S$ species S
$T$ species T
$U$ species U
0 at $h=0$
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APPENDIX A

DERIVATION OF THE MODIFICATIONS OF $u$ AND $d_b$ IN A FLUIDIZED-BED WHEN THE NUMBER OF MOLES IS CHANGING
A.1 Modification of the Gas Superficial Velocity \( u \)

Material balance on the inerts side in the bubble-phase gives

\[
Q_0 C_{i0} = QC_i \tag{A.1}
\]

where \( Q \) is the gas flow rate in the bubble-phase given by:

\[
Q = A_i (u - u_{mf}) \tag{A.2}
\]

and \( A_i \) is the cross-sectional area of the bed.

\[
\therefore (u_0 - u_{mf}) C_{i0} = (u - u_{mf}) C_i \tag{A.3}
\]

\[
(u_0 - u_{mf}) \gamma_{i0} C_0 = (u - u_{mf}) \gamma_1 C \tag{A.4}
\]

where \( C \) is the total concentration. Since bed temperature and pressure are almost constant, \( C_0 = C = \text{constant} \).

\[
\therefore \frac{(u - u_{mf})}{(u_0 - u_{mf})} = \frac{\gamma_{i0}}{\gamma_i} \tag{A.5}
\]

The right hand side is evaluated as follows:

\[
\frac{\gamma_{i0}}{\gamma_i} = \frac{n_i/(n_i + n_{A_0})}{n_i/(n_i + n_A + n_B)} = \frac{n_i + n_A + n_B}{n_i + n_{A0}}
\]
\[
\frac{n_i + n_A + m(n_{A0} - n_A)}{n_i + n_{A0}} = \frac{n_i + (1 - m)n_A + mn_{A0}}{n_i + n_{A0}}
\]

\[
\frac{n_i / n_{A0} + (1 - m)n_A / n_{A0} + mn_{A0} / n_{A0}}{n_i / n_{A0} + n_{A0} / n_{A0}}
\]

where \( n_j \) denotes the number of moles of species \( j \).

By using the definition:

\[
R = \frac{n_i}{n_{A0}} = \frac{\gamma_{i0}}{\gamma_{A0}}
\]

and the reactant conversion definition:

\[
X_A = 1 - \frac{n_A}{n_{A0}}
\]

equation A.6 becomes, upon simplification:

\[
\frac{\gamma_{i0}}{\gamma_i} = 1 + \frac{m - 1}{R + 1} X_A
\]

Combining equations A.5 and A.9 yields:

\[
\frac{u - u_{mf}}{u_0 - u_{mf}} = 1 + \frac{m - 1}{R + 1} X_A
\]
This equation is the same as equation 4.21. The right hand side becomes 1 in three cases: when $m = 1$, $R \to \infty$, and when $X_A \to 0$, as expected.

Note that $X_A$ is related to reactant mole fraction in the bubble-phase $y_{Ab}$ as follows. The reactant mole fraction is defined as:

$$
y_{Ab} = \frac{n_A}{n_A + n_B + n_i} = \frac{n_A}{n_A + m(n_A - n_A) + n_i}
$$

$$
= \frac{n_A / n_{A0}}{n_A / n_{A0}(1 - m) + m + n_i / n_{A0}} \tag{A.11}
$$

Equation A.11 can be rearranged to:

$$
\frac{n_A}{n_{A0}} = \frac{y_{Ab}(m + R)}{1 - (1 - m)y_{Ab}} \tag{A.12}
$$

Now, equation A.12 can be combined with equation A.8 to give:

$$
X_A = 1 - \frac{y_{Ab}(m + R)}{1 - (1 - m)y_{Ab}} \tag{A.13}
$$
A.2 Modification of the Bubble Diameter $d_b$

Consider Figure B, where bubble 1 grows by coalescence to bubble 2, in the absence of any change in the number of moles (i.e. $m=1$). For $m>1$, the bubble at the location $h$ would be larger than bubble 2, say bubble 3, and the opposite is true when $m<1$.

![Figure B](image)

The relationship between bubble 2 and bubble 3 may be governed by an equation of state such as the ideal gas law where,

$$\frac{V_3}{V_2} = \frac{n_3}{n_2} \quad \text{A.14}$$

and $V_2$ and $V_3$ are the volumes of bubble 2 and bubble 3, respectively.

Because there is no change in the number of moles of bubble 2, $n_2 = n_{A_0} + n_i = \text{constant}$, and hence,

$$\frac{V_3}{V_2} = \frac{n_3}{n_{A_0} + n_i} = \frac{n_A + n_B + n_i}{n_{A_0} + n_i} \quad \text{A.15}$$

The right hand side of equation A.15 is the same as that of A.6 and A.9,

$$\frac{V_3}{V_2} = 1 + \frac{m-1}{R+1} \chi_A \quad \text{A.16}$$
where

\[ \frac{V_3}{V_2} = \left( \frac{d_{v_3}}{d_{v_2}} \right)^3 \]  

From equation A.16 and equation A.17 we get:

\[ d_{b_3} = \frac{d_{v_2}}{\left(1 + \frac{m-1}{R+1}X_A\right)^{1/3}} \]  

where \( d_{b_3} \) is bubble diameter predicted by correlations such as equation 3.7.

Although equation A.18 is derived for \( m>1 \), it is general (i.e. valid for \( m>1 \) and \( m<1 \)), because the argument is the same for both cases. The cubic root term in equation A.18 becomes 1 when \( m=1, R \to \infty \), and \( X_A \to 0 \). Moreover, this term is greater than 1 when \( m>1 \) and less than 1 when \( m<1 \).

When the bubble reaches its equilibrium size, it may not grow further or shrink because of the change in the number of mole, simply because it will break apart or join with other bubbles to retain the equilibrium size. As a result equation A.18 will have no effect in this case, and hence, it should be used only in the region where the bubbles are below the equilibrium size, (i.e. when \( h < h^* \)).
APPENDIX B

CALCULATION PROCEDURE FOR EQUATIONS 6.14 AND 6.15
The problem of the reversible consecutive reaction:

\[ \text{A} \xrightleftharpoons[k_2]{k_1} \text{R} \xrightleftharpoons[k_4]{k_3} \text{S} \]

has also been solved by Irani et al [17], using the Kunii-Levenspiel model. In their article, Irani et al presented an example and a calculation procedure for that example which is going to be used here, with few modifications in the model parameters. Specifically, the two parameters \( u_e \) and \( K_{\alpha e} \) are going to be calculated using the new expressions given by Kunii and Levenspiel [24] and shown in Table 21.

The parameters used in simulation are listed in Table A. The reaction constants in the table are based on the volume of solids and are related to those of the Werther model by equation 5.91.

<table>
<thead>
<tr>
<th>( K_{r_t} ) 10 s(^{-1})</th>
<th>( K_{r_s} ) 1.0 s(^{-1})</th>
<th>( K_{r_d} ) 1.0 s(^{-1})</th>
<th>( K_{r_d} ) 0.1 s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D = 2 \times 10^{-5} \text{ m}^2/\text{s} )</td>
<td>( u = 0.3 \text{ m/s} )</td>
<td>( u_m = 0.003 \text{ m/s} )</td>
<td>( f_w = 0.3 )</td>
</tr>
<tr>
<td>( \varepsilon_m = 0.5 )</td>
<td>( d_b = 0.05 \text{ m} )</td>
<td>( d_i = 1.0 \text{ m} )</td>
<td>( H = 5.0 \text{ m} )</td>
</tr>
</tbody>
</table>

| Solid type: A |

Using the notation of Irani et al [17] (except for the reaction rate constant where the lower case \( k_j \) is reserved for the Werther model) and
following their procedure, bearing into mind that model parameters are going
to be calculated from the expressions of Table 21 we get:

\[ \hat{C}_A = \frac{K_9}{K_1 + K_2} = 0.0909 \]

\[ \hat{C}_R = \frac{K_4}{K_3 + K_4} = 0.0909 \]

\[ u_{br} = 0.711 \sqrt{9.8 \times 0.05} = 0.498 \text{ m/s} \]

\[ u_b = 1.55[0.297 + 14.1 \times 0.055] + 0.498 = 2.16 \text{ m/s} \]

\[ \delta = \frac{u}{u_b} = \frac{0.3}{2.16} = 0.139 = \{\varepsilon_\theta \text{ in the Werther model}\} \]

\[ K_{bc} = 4.5 \left( \frac{0.003}{0.05} \right) + 5.85 \left( \frac{\sqrt{2 \times 10^{-5} \times 9.8^{1/2}}}{0.05^{5/4}} \right) = 2.23 \text{ s}^{-1} \]

\[ K_{cr} = 6.77 \left( \frac{2 \times 10^{-5} \times 0.5 \times 0.498}{0.05^3} \right)^{1/2} = 1.35 \text{ s}^{-1} \]

\[ \gamma_c = (1 - 0.5) \left[ \frac{3}{0.498 \times 0.5 / 0.003 - 1} + 0.3 \right] = 0.337 \]

\[ \gamma_c = (1 - 0.5)(1 - 0.139) / 0.139 - 0.005 - 0.337 = 2.76 \]

Using these values and the expressions in [17], we get the
parameters listed in Table B.
Table B.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_i=1.51$ s$^{-1}$</td>
<td>$K_j=0.798$ s$^{-1}$</td>
<td>$\psi_j=1.33$</td>
<td>$K_j'=1.51$ s$^{-1}$</td>
</tr>
<tr>
<td>$\phi_e=21.75$ s$^{-1}$</td>
<td>$\phi_j=23.0$ s$^{-1}$</td>
<td>$\phi_j'=0.258$ s$^{-1}$</td>
<td>$K_{jj}=0.419$ s$^{-1}$</td>
</tr>
<tr>
<td>$K_{ij}=0.124$ s$^{-1}$</td>
<td>$K_{ji}=0.222$ s$^{-1}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Inserting these values into equations 17 and 18 in [17], we get:

\[
C_{ab} = 0.0909 - 0.909 \exp(-0.419 \tau)
\]

\[
C_{ab} = 0.112 - 0.459 \exp(-0.222 \tau) - 0.572 \exp(-0.419 \tau)
\]

where $\tau$ is the gas residence time, defined in [17] and is related to gas superficial velocity and height above gas distributor by:

\[
\tau = \left(1 - \delta\right)\left(1 - \varepsilon_m\right) \frac{h}{u} = 1.435h = 1.175L
\]

where $L$ is the dimensionless height above distributor defined in Table 4.
APPENDIX C

*Mathematica* PROGRAM USED IN THE GENERATION OF EQUATIONS 6.16 AND 6.17
The following program is written in Mathematica format. It can be loaded into Mathematica as follows:

After starting Mathematica type:

```mathematica
<< filename
```

where `filename` is the name of the file that contains the expressions below. The expressions for \( C_A \) and \( C_R \) can be viewed simply by typing: CA and CR.

This program, with the parameters given below was used in the generation of equations 6.16 and 6.17. The program was also used in the generation of figures 17 and 19 using different parameters.

```
CR0=0.0
CA0=1.0
CS0=0.0
De=2.*10^-5
kc=0.0159
k1=5.
k2=0.5
k3=0.5
k4=0.05
db=0.05
H=5.0
u=0.3
umf=0.003
vb=vb+0.71*3.2*Sqrt[9.8*db]
Eb=vb/ub
a=6*Eb/db
phi=a*De/(kc*(1-Eb))
f=1/phi-1
NTU=kc*a*H/(u-umf)
Ha1=Sqrt[De kl]/kc
Ha2=Sqrt[De (k2+k3)]/kc
Ha3=Sqrt[De k2]/kc
Ha4=Sqrt[De k4]/kc
C0=CR0+CA0+CS0
```

Continues on the next page
\[\begin{align*}
&\alpha_1= H^3 + H^1 + H^2 \\
&\alpha_2=-H^3 + H^1 - H^2 \\
&\beta=t=\alpha_2 - 4H^2 (H^4 - H^1) \\
&\alpha=(\alpha_1-(\beta)^{(1/2)})/2,\quad a=(\alpha_1+(\beta)^{(1/2)})/2 \\
&b_1=(1/2) (\alpha_2-(\beta)^{(1/2)})/(H^4-H^1) \\
&b_2=(1/2) (\alpha_2+(\beta)^{(1/2)})/(H^4-H^1) \\
&\text{term} = (a_1f + \text{Tanh}[a_1] + a_1a_2f^2 \text{Tanh}[a_2] + a_2f^2 \text{Tanh}[a_1]*\text{Tanh}[a_2])/(1 + a_1f^2 \text{Tanh}[a_1] + a_2f^2 \text{Tanh}[a_2] + a_1a_2f^2 \text{Tanh}[a_1]*\text{Tanh}[a_2]) \\
&\text{term}2 = (a_2f + a_1a_2f^2 \text{Tanh}[a_1] + \text{Tanh}[a_2] + a_1f^2 \text{Tanh}[a_1]*\text{Tanh}[a_2])/(1 + a_1f^2 \text{Tanh}[a_1] + a_2f^2 \text{Tanh}[a_2] + a_1a_2f^2 \text{Tanh}[a_1]*\text{Tanh}[a_2]) \\
&\alpha_0=-(\alpha_2+\sqrt{\beta})/(2 \sqrt[4]{\beta}) \times \text{term} \\
&\alpha_2=(\alpha_4^2 - \alpha_1^2)/\sqrt[4]{\beta} \times \text{term} \\
&\beta_0=-(\alpha_2-\sqrt{\beta})/(2 \sqrt[4]{\beta}) \times \text{term2} \\
&\beta_2=-(\alpha_4^2 - \alpha_1^2)/\sqrt[4]{\beta} \times \text{term2} \\
&G_1= a_1^0a_2 + a_2^0b_0 \\
&G_2= a_1^0a_2 + a_2^0b_2 \\
&H_1= a_1a_2^0b_1 + a_2^0b_2 \\
&H_2= a_1^0a_2^0b_1 + a_2^0b_2 \\
&\alpha_1=(G_1 + H^2 - (G_1^2 + 4G_2^2H_1^2 - 2G_1^2H_2 + H_2^2)/(1/2))/2 \\
&\alpha_2=(G_1 + H^2 + (G_1^2 + 4G_2^2H_1^2 - 2G_1^2H_2 + H_2^2)/(1/2))/2 \\
&\gamma_1=(G_1 - H^2 - (G_1^2 + 4G_2^2H_1^2 - 2G_1^2H_2 + H_2^2)/(1/2))/(2H_1) \\
&\gamma_2=(G_1 - H^2 + (G_1^2 + 4G_2^2H_1^2 - 2G_1^2H_2 + H_2^2)/(1/2))/(2H_1) \\
&\beta_1=(H_1^2+H_4^2)/(a_1^2+a_2^2) \\
&\beta_2=(H_2^2+H_4^2)/(a_1^2+a_2^2) \\
&c_1= -(\text{CR} + \beta_1^2 \text{CO} - \gamma_2^2(\beta_2^2 \text{C}^2 - \text{CA}^2))/(\gamma_1^2 + \gamma_2^2) \\
&c_2= (\text{CR} - \beta_1^2 \text{CO} + \gamma_1^2(\beta_2^2 \text{C}^2 - \text{CA}^2))/(\gamma_1^2 + \gamma_2^2) \\
&\text{CR}=c_1^2(\text{gamma}^1 \text{Exp}[\text{NTU} \alpha^1 L]^1 + c_2^2 \text{gamma}^2 \text{Exp}[\text{NTU} \alpha^2 L] + \beta_1 \\
&\text{CA}=c_1^2(\text{Exp}[\text{NTU} \alpha^1 L]^1 + c_2^2 \text{Exp}[\text{NTU} \alpha^2 L] + \beta_2 \\
&\text{CS}=\text{CO} - \text{CR} - \text{CA}