



<http://researchspace.auckland.ac.nz>

### *ResearchSpace@Auckland*

#### **Copyright Statement**

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage.

<http://researchspace.auckland.ac.nz/feedback>

#### **General copyright and disclaimer**

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the Library Thesis Consent Form.

ASPECTS OF FERMENTATION  
AND DISTILLATION  
IN  
ETHANOL PRODUCTION

Thesis submitted for the degree  
of Doctor of Philosophy

at the

School of Engineering,  
The University of Auckland,  
New Zealand

by

M. G. WEEKS

December, 1983

### Corrections

<u>Page</u>	<u>Line</u>	<u>Replace</u>	<u>With</u>
4	22		insert (Othmer, 1981)
10	10	10 %	10 v/v %
11	11	operation	operating
20	2	insoluble	soluble
24	21	pthalate	phthalate
35	equation 1.19	$\frac{dy_i}{dy}$	$\frac{dy_j}{dy}$
42	16	directionally	directly
64	Figure 2.1	fermenter	fermentor
69	9	calibrated	graduated
70	21	$\pm 0.1^{\circ}\text{C}$	$\pm 0.125^{\circ}\text{C}$
80	Figure 3.2	Iron Sand Concentration	Iron Sand Concentration (as received)
81	Table 3.1, for stainless steel	0.26 mm/s 0.19 mm/s	2.6 mm/s 1.9 mm/s
84	Figure 3.4,ln 2	initial	nominal initial
91	Figure 3.8,ln 2	0.2 g/l ..... 0.5 g/l	0.5 g/l ..... 0.2 g/l
184	12	Reynolds Number	length Reynolds Number

i

## ABSTRACT

The fermentation of sugars from biomass to produce liquid fuels is receiving widespread attention as a renewable source of energy. For such processes to become competitive with current alternatives, technology must be improved to increase the efficiency and productivity of the operation. Using ethanol fermentation by *Saccharomyces cerevisiae* yeast as a model system, two aspects of the process were considered in detail.

The first aspect concerned the use of cell recycle in a continuous fermentation. A new technique was developed for the rapid settling of yeast cells in the fermentation medium and involved the addition of dense, inert particles to a yeast suspension at pH 4.5, followed by a rapid change in pH to 8.0 - 9.0. Large flocs formed immediately and settled rapidly, leaving a clear supernatant. Separations of 99.9% were possible, even at yeast concentrations of 50 g/l (dry weight) and increases in settling rate of up to 1600 fold were observed. When the pH was returned to 4.5, the flocs were destroyed.

Seeded settling at constant pH was possible although the flocs were smaller, the settling rates were lower and significantly more seed was required. Flocculation was also found to be influenced to a greater extent by certain components in solution.

Nickel powder was used extensively in these experiments although several other materials were tested, with ground iron sand showing potential for application on a larger scale.

The pH switching technique for seeded settling was used to recycle

yeast cells in a semi-continuous fermentation. Application of the technique to this and similar systems is discussed.

The factors affecting yeast/inert powder flocculation is discussed and a model is proposed to explain the observed experimental behaviour for flocculation, both at constant pH and with rapid pH switching.

The second aspect of ethanol production considered in this thesis was the distillation stage. Equipment and techniques were developed to obtain basic mass transfer information in binary or multi-component systems. A new design of evaporation cell was used to measure the evaporation of ethanol and water mixtures into an air stream in a wind tunnel. This enabled the effect of liquid concentration on evaporation rate to be studied dynamically from batch tests. Radiochemical labelling was used to measure liquid concentrations and proved to be a relatively simple, rapid and precise analytical technique. Coupled with the direct measurement of liquid displacement, precise information on the evaporation loss of both ethanol and water components was obtained.

The pure component evaporation data agreed well with literature correlations and, for the binary liquid mixtures, good agreement was found between the experimentally determined mass transfer flux ratios and those predicted from Gilliland's solution to the multi-component gas diffusion equations.

The velocity dependence of the overall mass transfer coefficients enabled estimates to be made of the distribution of diffusional resistance between the gas and liquid phases.

For the ethanol-water system diffusion was gas film controlled and the overall mass transfer driving forces could best be represented in terms of vapour concentration.

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr P.A. Munro, for his guidance, advice and continued encouragement throughout all aspects of this investigation. I would also like to thank my co-supervisor, Associate-Professor P.L. Spedding, and Associate-Professor D.J. Spedding for their advice and assistance.

The financial support of a University Grants Committee Post-Graduate Scholarship is gratefully acknowledged.

I would also like to thank:

The technical staff of the Chemical and Materials Engineering Department for their willing and able assistance, in particular Mr T.N. Gray, Mr J.P. Batt and Mr T.A. Snape;

Mrs Anne Marie McGlashan for her excellent typing and her patience and skill in deciphering the script;

My fellow graduates for providing a congenial atmosphere in which to work; Mark Jablonka for his computer software, Pare Keiha for help in proof-reading, and Mark Taylor for his 'helpful' comments;

Last, but not least, my parents for their support and encouragement throughout the course of this work.

TABLE OF CONTENTS

	<u>PAGE</u>
ABSTRACT	i
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
LIST OF FIGURES	ix
LIST OF TABLES	xiii
<u>SECTION 1. INTRODUCTION</u>	1
1.1 Liquid Fuel Production	1
1.1.1 The Global Energy Crisis	1
1.1.2 Liquid Fuels from Biomass	2
1.1.3 Energy Farming	5
1.1.4 Choice of Areas for Experimentation	7
1.2 Ethanol Fermentation	9
1.2.1 Current Ethanol Fermentation Technology	9
1.2.2 Continuous Fermentation Concepts	11
1.2.3 Techniques for Retaining or Recycling Micro-Organisms	14
1.2.4 The Concept of Cell Flocculation with an Inert Seed	19
1.3 Ethanol-Water Separation	21
1.3.1 Current Ethanol-Water Distillation Technology	21
1.3.2 Alternatives to Distillation for Ethanol-Water Separation	23
1.3.3 The Relevance of Fundamental Mass Transfer Research	26
1.3.4 Mass Transfer Theory	29
1.3.4.1 General	29
1.3.4.2 Fick's law of diffusion	30
1.3.4.3 Multi-component diffusion in gases	35
1.3.4.4 Mass transfer across the gas-liquid phase boundary	39
1.3.4.5 The mass transfer coefficient	43



	<u>PAGE</u>
1.3.5 Fundamental Research on Gas-Liquid Mass Transfer	45
1.3.5.1 Gas-liquid mass transfer in ducts	45
1.3.5.2 Mass transfer correlations	51
1.3.5.3 The wetted wall column for research into gas-liquid transfer	54
1.3.5.4 Scope for further gas-liquid mass transfer research	57
<u>SECTION 2. EXPERIMENTAL</u>	59
2.1 Yeast Settling Experiments	59
2.1.1 Seed Material Characteristics	59
2.1.2 Seeded Yeast Settling at Constant pH	60
2.1.3 Seeded Yeast Settling with pH Switching	61
2.1.4 Microscopic Analysis of Floccs	62
2.1.5 Seeded Settling with Bacteria	62
2.2 Ethanol Fermentation	62
2.2.1 Batch Fermentation	62
2.2.2 Semi-Continuous Fermentation	63
2.2.3 Assay Techniques	67
2.3 Wind Tunnel Evaporation of Ethanol and Water	67
2.3.1 General Description	67
2.3.2 Air Velocity Measurement	72
2.3.3 Ethanol Concentration Measurement	74
2.3.4 Procedure for Evaporation Runs	76
<u>SECTION 3. NOVEL METHODS OF YEAST RECYCLE</u>	78
3.1 Selection of Seed Materials	78
3.2 Seeded Settling with Nickel	85

	<u>PAGE</u>
3.3 Batch Fermentation	96
3.4 Factors Influencing Yeast Separation	98
3.5 Preliminary Investigation of a pH Switching Technique	102
3.6 Seeded Settling with pH Switching	108
3.7 Semi-Continuous Fermentation	116
3.8 Settler Design	122
3.9 Determination of Flocculation Mechanism	125
3.10 Acid and Base Requirements for pH Switching	128
3.11 Seeded Settling with Bacteria	129
3.12 A Proposed Mechanism for Seeded Settling	130
3.13 The Potential for Industrial Application of Seeded Settling	140
3.14 Conclusions	144
<u>SECTION 4. ETHANOL-WATER MASS TRANSFER</u>	147
4.1 Velocity and Temperature Calibration	147
4.2 Preliminary Experiments	147
4.3 Mass Transfer Results	150
4.3.1 Evaporation of the Pure Components	150
4.3.2 Evaporation of Ethanol-Water Mixture	154
4.4 Data Analysis Using Multi-Component Diffusion Equations	162
4.5 Selection of the Overall Mass Transfer Driving Force	163
4.5.1 Liquid Concentration as the Driving Force	164
4.5.2 Vapour Concentration as the Driving Force	171
4.5.3 Summation	182
4.6 The Effect of Air Velocity on the Overall Mass Transfer Coefficient	182
4.6.1 The Pure Component Mass Transfer Coefficients	182

	<u>PAGE</u>
4.6.2 The Mass Transfer Coefficients for Ethanol-Water Mixtures	187
4.7 The Phase Distribution of the Mass Transfer Resistance	189
4.8 Theoretical Prediction of the Mass Transfer Flux	195
4.8.1 The Ternary Diffusion Equations	195
4.8.2 Comparison of Theory with Experiment	196
4.9 Conclusions	201
<u>SECTION 5. RECOMMENDATIONS</u>	203
5.1 Yeast Recycle	203
5.2 Ethanol-Water Mass Transfer	204
<u>SECTION 6. APPENDICES</u>	205
6.1 Raw Data for Ethanol-Water Evaporation	205
6.2 Effect of Sampling on Evaporation Data	230
6.3 Determination of the Gas Phase Diffusion Coefficients	236
6.4 Vapour-Liquid Equilibrium Data for Ethanol-Water	238
Notation	239
References	242
Publications	247

LIST OF FIGURES

<u>FIGURE</u>		<u>PAGE</u>
1.1	Concentration Profile at a Gas-Liquid Phase Boundary	40
2.1	Semi-Continuous Fermentation Equipment	64
2.2	The Fermentor and Cell Separator in Operation	65
2.3	Schematic Diagram of Wind Tunnel	68
2.4	Overall View of Wind Tunnel	69
2.5	A Cross-Sectional View of the Evaporation Cell	71
2.6	The Evaporation Cell	72
3.1	Initial Settling Rate versus Seed Concentration	79
3.2	Initial Settling Rate versus Iron Sand Concentration	80
3.3	Supernatant Yeast Concentration versus added Seed Concentration for nominally 20 g/l (dry weight) yeast suspensions in distilled water	83
3.4	Supernatant Yeast Concentration versus Iron Sand Concentration	84
3.5	Supernatant Yeast Concentration (log scale) versus added Nickel Concentration for a range of initial yeast concentrations	87
3.6	Batch Settling Curves for various concentrations of yeast seeded with nickel	88
3.7	Initial Settling Velocity versus Yeast Concentration for yeast seeded with sufficient nickel to give very low supernatant yeast concentrations	89
3.8	Nickel Concentration required to give Supernatant Yeast Concentrations of 0.2 g/l and 0.5 g/l for various Initial Yeast Concentrations	91
3.9	Concentration Profiles in Batch Fermentation using 20 g/l yeast at 35 <sup>o</sup> C	97
3.10	Yeast Supernatant Concentration versus added Nickel Concentration in distilled water and in the presence of various fermentation medium components	99

<u>FIGURE</u>		<u>PAGE</u>
3.11	Effect of Salt Concentration on Supernatant Yeast Concentration after seeded settling	101
3.12	Supernatant Yeast Concentration after switching the pH from acidic to basic conditions	103
3.13	Yeast and Nickel Floccs formed after pH Switching	105
3.14	A 20 g/l Yeast Suspension before and after pH Switching with Nickel Seed	106
3.15	Scanning Electron Micrograph of Yeast/Nickel Floccs formed at Constant pH	107
3.16	Scanning Electron Micrograph of Yeast/Nickel Floccs formed by pH Switching	107
3.17	Supernatant Yeast Concentration (log scale) versus Nickel Concentration after pH switching from 4.5 to 9.0 in distilled water, followed by gravity settling	109
3.18	Batch Settling Curves for various yeast concentrations seeded with nickel using pH switching from about 4.5 to 9.0	111
3.19	Initial Settling Velocity versus Yeast Concentration for yeast seeded with sufficient nickel to give a low supernatant yeast concentration and with pH switching from about 4.5 to 9.0	112
3.20	Nickel Concentration required to give a Supernatant Yeast Concentration of 0.2 g/l (after pH switching from about 4.5 to 9.0) for various Initial Yeast Concentrations	115
3.21	Settler in Operation with Yeast and Nickel Suspended in Distilled Water	117
3.22	Glucose Concentration and Ethanol Concentration in the settler overflow and Total Fermentor Output versus Time, for operation of the semi-continuous fermentation equipment	118
3.23	Settler in Operation during a Semi-Continuous Fermentation	119
3.24	Settling Curve for Yeast/Nickel Floccs produced by switching the pH of the fermentor outflow from 4.5 to 8.0 after a fermentation time of 49 hours	121
3.25	Solids Sedimentation Flux Curve obtained from batch settling of 50 g/l yeast and 200 g/l nickel	124

<u>FIGURE</u>		<u>PAGE</u>
3.26	Schematic Representation of Flocculation Processes	136
4.1	Vertical Velocity Profiles at the centre of the Wind Tunnel	148
4.2	A Cross-Sectional Velocity Profile at a bulk velocity of 4.05 m/s	148
4.3	The Evaporation of Pure Ethanol versus Time at air velocities of 4.05 m/s, 4.91 m/s, 5.64 m/s and 6.47 m/s	152
4.4	The Evaporation of Pure Water versus Time at air velocities of 4.05 m/s, 4.91 m/s, 5.64 m/s and 6.47 m/s	153
4.5	Evaporation with Time of an aqueous ethanol solution (initially 0.2 v/v %) at an air velocity of 4.91 m/s	156
4.6	Evaporation with Time of an aqueous ethanol solution (initially 5 v/v %) at an air velocity of 4.91 m/s	157
4.7	Evaporation with Time of an aqueous ethanol solution (initially 25 v/v %) at an air velocity of 4.91 m/s	158
4.8	Evaporation with Time of an aqueous ethanol solution (initially 50 v/v %) at an air velocity of 4.91 m/s	159
4.9	Ethanol Evaporative Flux versus Liquid Concentration at four air velocities	165
4.10	Ethanol Evaporative Flux versus Liquid Concentration at an air velocity of 4.05 m/s	166
4.11	Ethanol Evaporative Flux versus Liquid Concentration, corrected to a temperature of 17°C for air velocities of 4.05 m/s and 5.64 m/s	169
4.12	Ethanol Evaporative Flux versus Liquid Concentration, corrected to a temperature of 17°C for air velocities of 4.91 m/s and 6.47 m/s	170
4.13	Evaporative Flux versus Vapour Mole Fraction Driving Force for the ethanol component at an air velocity of 4.05 m/s	172
4.14	Evaporative Flux versus Vapour Mole Fraction Driving Force for the ethanol component at air velocities of 4.05 m/s and 5.64 m/s	174
4.15	Evaporative Flux versus Vapour Mole Fraction Driving Force for the ethanol component at air velocities of 4.91 m/s and 6.47 m/s	175

<u>FIGURE</u>		<u>PAGE</u>
4.16	The Evaporative Flux versus Vapour Mole Fraction Driving Force for the water component at an air velocity of 4.05 m/s	177
4.17	Evaporative Flux versus Vapour Mole Fraction Driving Force for the water component at an air velocity of 4.91 m/s	178
4.18	Evaporative Flux versus Vapour Mole Fraction Driving Force for the water component at an air velocity of 5.64 m/s	179
4.19	Evaporative Flux versus Vapour Mole Fraction Driving Force for the water component at an air velocity of 6.47 m/s	180
4.20	The Effect of Air Velocity on the Pure Component Mass Transfer Coefficient for ethanol and water	183
4.21	$J_D$ versus $Re_x$ for the pure components of this study and for the $x_D$ data of Wade (1942)	186
4.22	The Effect of Air Velocity on the Overall Mass Transfer Coefficients for both the ethanol and water components	188
4.23	A Comparison between Theory and Experiment of the Molar Flux Ratio of Water to Ethanol in a mixture initially 5 % ethanol	197
4.24	A Comparison between Theory and Experiment of the Molar Flux Ratio of Water to Ethanol in a mixture initially 25% ethanol	198
4.25	A Comparison between Theory and Experiment of the Molar Flux Ratio of Water to Ethanol in a mixture initially 50% ethanol	199
6.1	Liquid Volume versus Time	231
6.2	Liquid Volume versus Time	232
6.3	Ethanol and Water Vapour Pressures versus Liquid Concentration at 20°C and 1 atm	238

LIST OF TABLES

<u>TABLE</u>		<u>PAGE</u>
3.1	Properties of Seed Materials	81
3.2	Comparison of Seed Materials in Settling a 20 g/l Yeast Suspension	82
3.3	Characteristics of Yeast/Nickel Floccs	93
3.4	Effect of Seed Addition Method	95
3.5	Characteristics of Yeast/ Nickel Floccs (pH Switching)	114
4.1	Sample Data for 50 v/v % Ethanol at 6.5 m/s	154
4.2	Correction Factor for Equation 1.25	162
6.1-24	Raw Data for Ethanol and Water Evaporation	206-229
6.25	Effect of Sampling	234