


การจำลองแบบสองมิติของการขยายตัวอย่างรวดเร็วของ
คาร์บอนไดออกไซด์เหนือวิกฤต



นางสาว กนกวรรณ กรรณ

ศูนย์วิทยทรัพยากร

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต

สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี

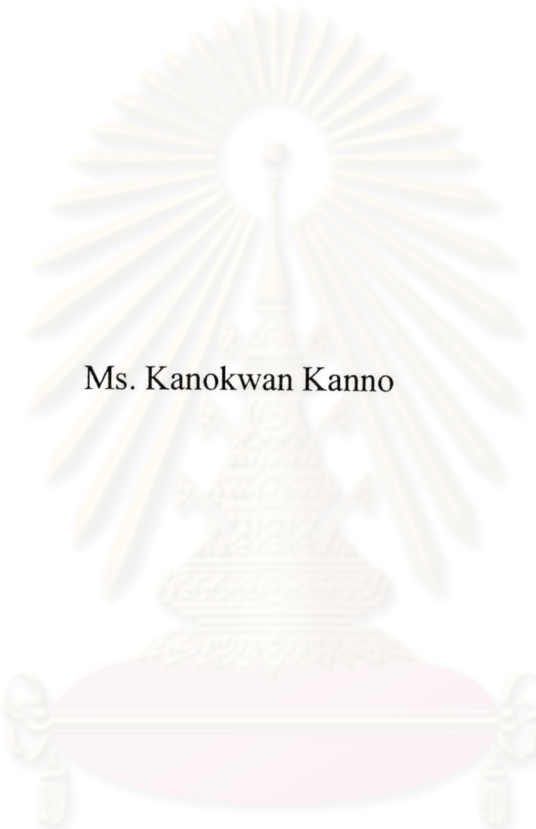
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2546

ISBN 974-17-4497-8

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

TWO DIMENSIONAL SIMULATION OF RAPID EXPANSION OF
SUPERCRITICAL CARBON DIOXIDE



Ms. Kanokwan Kanno

ศูนย์วิทยทรัพยากร
A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering

Department of Chemical Engineering

Faculty of Engineering

Chulalongkorn University

Academic Year 2003

ISBN 974-17-4497-8

กนกวรรณ กรรณโณ: การจำลองแบบสองมิติของการขยายตัวอย่างรวดเร็วของคาร์บอนไดออกไซด์เหนือ
วิกฤต(TWO DIMENSIONAL SIMULATION OF RAPID EXPANSION OF SUPERCRITICAL CARBON
DIOXIDE) อ.ที่ปรึกษาวิทยานิพนธ์: รศ. ดร. ธวัชชัย ชรินพานิชกุล 148 หน้า ISBN 974-17-4497-8

การขยายตัวของของไหลเหนือวิกฤตผ่านหัวฉีดเป็นกระบวนการที่สามารถนำมาประยุกต์ใช้ในการผลิต
อนุภาคนาขนาดเล็กมากๆ โดยอาศัยการเปลี่ยนแปลงค่าความหนาแน่นสารละลายของของไหลที่เกิดจากการขยายตัว
ของของไหลจากสภาวะเหนือวิกฤตไปสู่สภาวะก๊าซ การจำลองปรากฏการณ์การขยายตัวอย่างรวดเร็วของ
คาร์บอนไดออกไซด์เหนือวิกฤตโดยอาศัยแบบจำลองทางคณิตศาสตร์ ต้องคำนึงถึงการประมวลผลชุดสมการที่นำมา
ใช้ในการพิจารณากลไกการไหลของของไหล รวมถึงชุดสมการสภาวะที่ใช้ในการประมาณค่าคุณสมบัติของ
คาร์บอนไดออกไซด์ด้วย

จากการทดสอบพบว่าสมการสภาวะ Soave-Redlich-Kwong EOS ที่ใช้ค่า compressibility of CO₂ เป็น
ชุดสมการสภาวะที่เหมาะสมสำหรับการประมาณค่าคุณสมบัติของคาร์บอนไดออกไซด์

สำหรับเทคนิคที่นำมาใช้ในการพิจารณากลไกการไหลของคาร์บอนไดออกไซด์ที่เลือกใช้ในงานวิจัยนี้มี 2
เทคนิคคือวิธีผลต่างสี่แบบเอ็กซ์พลลิสิทและแบบอิมพลลิสิท พบว่าผลที่ได้ให้ค่าที่สอดคล้องกับงานวิจัยที่ผ่านมา จาก
การศึกษาค้นคว้าที่มีผลกระทบต่อกรขยายตัวของคาร์บอนไดออกไซด์เหนือวิกฤตผ่านหัวฉีด พบว่าอุณหภูมิและความ
ดันของคาร์บอนไดออกไซด์ก่อนออกจากหัวฉีดมีผลกระทบต่อกระบวนการค่อนข้างมาก ส่วนความเร็วของ
คาร์บอนไดออกไซด์ที่ถูกฉีดออกจากหัวฉีดพบว่ามีผลกระทบต่อกรขยายตัวน้อยมาก

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

ภาควิชา.....วิศวกรรมเคมี.....ลายมือชื่อนิสิต.....กนกวรรณ กรรณโณ.....
สาขาวิชา.....วิศวกรรมเคมี.....ลายมือชื่ออาจารย์ที่ปรึกษา.....
ปีการศึกษา.....2546.....ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

4370203021 : MAJOR CHEMICAL ENGINEERING

KEY WORD: RESS / COMPRESSIBLE FLOW / CFD / CARBON DIOXIDE

KANOKWAN KANNO: TWO DIMENSIONAL SIMULATION OF RAPID EXPANSION OF SUPERCRITICAL CARBON DIOXIDE. THESIS ADVISOR : ASSOCIATE

PROFESSOR TAWATCHAI CHARINPANITKUL, D. ENG, 148 pp. ISBN 974-17-4497-8

The expansion of supercritical fluid solution through a nozzle is a key step for producing fine particles. It makes use of the density change of a fluid from its supercritical state to its gaseous state due to expansion to a lower pressure environment. Simulation of rapid expansion of supercritical carbon dioxide requires a set of basic equations of fluid flow field and thermodynamic properties of carbon dioxide from suitable equation of state (EOS).

From investigation, it was found that Soave-Redlich-Kwong EOS incorporated with the compressibility factor of carbon dioxide is suitable for estimating of the carbon dioxide thermodynamic properties. The explicit finite-difference and implicit finite-different methods are employed to solve two-dimensional Euler equations for fluid flow field. The calculation results shown that the inlet temperature and inlet pressure gave impact effects on the predicted temperature of flowing fluid passed through the nozzle and for inlet velocity, it could be seen that it rarely gave effect on the predicted temperature of fluid.

ศูนย์วิจัยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Department..... Chemical Engineering..... Student's signature..... *K. Kanno*.....

Field of study..... Chemical Engineering..... Advisor's signature..... *T. Charinpanitkul*.....

Academic year..... 2003..... Co-advisor's signature..... *Minat Tanthapanichaloon*.....

ACKNOWLEDGEMENT

I wish to sincerely express my gratitude to my advisor, Associate Professor Tawatchai Charinpanitkul, for his immense support and encouragement. This also extends to my thesis co-advisor, Professor Wiwut Tanthapanichakoon, who advises me with useful and comments suggestions. In addition to them, Dr. Somprasong Srichai is another one that I am very grateful for his kindness of guiding me through various difficult situations.

I also would like to gratefully acknowledge my thesis committee, for their kind evaluation of my work and valuable suggestions that could be beneficially used to improve my working behavior.

Special thanks to members of the Particle Technology and Material Processing (PTMP) Laboratory, we share our thoughts, ideas, and suggestions together. They provide me many good experiences, and good friends. It 's a memorable period of time in my life.

Thanks are due the Graduate School, Chulalongkorn University and Matching Fund (Senior Research Project of Associate Professor Tawatchai Charinpanitkul) for their research assistantship and their financial support, respectively.

Most importantly, my parents and my family are the greatest who supported me not only financially but also with their love, care, understanding and morale support.

จุฬาลงกรณ์มหาวิทยาลัย

CONTENTS

| | Page |
|--|------|
| ABSTRACT (IN THAI) | iv |
| ABSTRACT (IN ENGLISH)..... | v |
| ACKNOWLEDGEMENTS | vi |
| CONTENTS..... | vii |
| LIST OF FIGURE..... | ix |
| LIST OF TABLES | xiii |
| NOMENCLATURE..... | xiv |
| | |
| CHAPTER | |
| 1. INTRODUCTION | |
| 1.1 Background | 1 |
| 1.2 Objectives of the thesis | 2 |
| 1.3 Scope of the thesis..... | 2 |
| 1.4 Obtained benefits | 3 |
| 2. LITERATURE REVIEW | 4 |
| 3. THEORETICAL CONSIDERATIONS | |
| 3.1 Rapid expansion of supercritical solution..... | 7 |
| 3.2 Compressible Flow | 9 |
| 3.3 Equation of State..... | 10 |
| 4. MATHEMATICAL MODELING AND SIMULATION OF RAPID EXPANSION OF SUPERCRITICAL SOLUTION (RESS) IN FLUIDIZED BED | |
| 4.1 CFD modeling..... | 13 |
| 4.2 Governing Equation..... | 14 |
| 4.3 Numerical Approach | 15 |
| 4.3.1 Explicit and Implicit Approach : Definitions and Contrasts..... | 15 |

CONTENTS (continue)

| | Page |
|---|------------|
| 4.3.2 Explicit Finite Difference Method | 16 |
| 4.3.2.1 The numerical method..... | 17 |
| 4.3.2.2 Assumptions used in the explicit model | 18 |
| 4.3.2.3 Algorithm of the explicit model..... | 19 |
| 4.3.2 Implicit Finite Difference Method..... | 26 |
| 4.3.2.1 The numerical method..... | 26 |
| 4.3.2.2 Assumptions used in the explicit model | 37 |
| 4.3.2.3 Algorithm of the explicit model..... | 37 |
| 5. MODEL VERIFICATION | |
| 5.1 Comparison between Peng-Robinson EOS and Soave Redlich-Kwong EOS..... | 42 |
| 5.2 Verification of the developed simulation model incorporated with the investigated EOS | 47 |
| 6. SENSITIVITY ANALYSIS | |
| 6.1 Identification of significant factors for the model..... | 59 |
| 6.2 Effects of significant factors..... | 60 |
| 6.2.1 Effect of inlet temperature..... | 62 |
| 6.2.2 Effect of inlet velocity | 66 |
| 6.2.3 Effect of inlet pressure..... | 70 |
| 7. CONCLUSION AND RECOMMENDATIONS..... | 80 |
| REFERENCES | 82 |
| APPENDICES | 84 |
| APPENDIX A | 85 |
| APPENDIX B | 106 |
| APPENDIX C | 139 |
| APPENDIX D | 143 |
| APPENDIX E | 146 |
| VITA | 148 |

LIST OF FIGURES

| | | Page |
|-------------|---|------|
| Figure 3.1 | Experimental system of RESS process | 8 |
| Figure 3.2 | Compressible system | 9 |
| Figure 4.1 | Schematic Diagram for Predictor and Corrector steps | 17 |
| Figure 4.2 | Block diagram of computation viscosity by using Prandtl number | 22 |
| Figure 4.3 | Block diagram simulation of RESS process by explicit finite difference technique | 23 |
| Figure 4.4 | Block diagram of computation viscosity by using Sutherland's law | 24 |
| Figure 4.5 | Block diagram of Equation of State | 24 |
| Figure 4.6 | Block diagram of MacCormack's technique | 25 |
| Figure 4.7 | Control volume for scalar variables | 26 |
| Figure 4.8 | Control volume for continuity equation | 27 |
| Figure 4.9 | Control volume for momentum equations | 28 |
| Figure 4.10 | velocity for Upwind scheme | 29 |
| Figure 4.11 | Control volume for energy equations | 32 |
| Figure 4.12 | Block diagram simulation of RESS process by implicit finite difference technique | 40 |
| Figure 4.13 | Block diagram of Fluid loop in implicit finite difference technique | 41 |
| Figure 5.1 | The relation between the pressure and the density of carbon dioxide calculated from Peng-Robinson Equation of State and Soave-Redlich-Kwong Equation of State and the density measured in experiment by Hewlett Packard Co. (Wilmington, DE), 1993 at temperature 313 K | 44 |

LIST OF FIGURES (continue)

| | | Page |
|-------------|---|------|
| Figure 5.2 | The relation between the pressure and the density of carbon dioxide calculated from Peng-Robinson Equation of State and Soave-Redlich-Kwong Equation of State and the density measured in experiment by Hewlett Packard Co. (Wilmington, DE), 1993 at temperature 333 K | 44 |
| Figure 5.3 | The relation between the pressure and the density of carbon dioxide calculated from Peng-Robinson Equation of State and Soave-Redlich-Kwong Equation of State and the density measured in experiment by Hewlett Packard Co. (Wilmington, DE), 1993 at temperature 353 K | 45 |
| Figure 5.4 | The relation between the pressure and the density of carbon dioxide calculated from Peng-Robinson Equation of State and Soave-Redlich-Kwong Equation of State and the density measured in experiment by Hewlett Packard Co. (Wilmington, DE), 1993 at temperature 373 K | 45 |
| Figure 5.5 | Temperature dependence of relative difference of CO ₂ density predicted by Soave Redlich-Kwong EOS with Zc of CO ₂ | 46 |
| Figure 5.6 | Simplified scheme of the expansion nozzle | 48 |
| Figure 5.7 | Relative graph of temperature and distance from nozzle at inlet pressure 200 bar and inlet temperature 333 K | 51 |
| Figure 5.8 | Relative graph of temperature and distance from nozzle at inlet pressure 200 bar and inlet temperature 353 K | 52 |
| Figure 5.9 | Relative graph of temperature and distance from nozzle at inlet pressure 260 bar and inlet temperature 373 K | 53 |
| Figure 5.10 | Relative graph of temperature and distance from nozzle at inlet pressure 260 bar and inlet temperature 333 K | 54 |

LIST OF FIGURES (continue)

| | | Page |
|-------------|--|------|
| Figure 5.11 | Relative graph of temperature and distance from nozzle at inlet pressure 260 bar and inlet temperature 353 K | 55 |
| Figure 5.12 | Relative graph of temperature and distance from nozzle at inlet pressure 260 bar and inlet temperature 373 K | 56 |
| Figure 6.1 | Relative graph of temperature and distance from nozzle, Inlet pressure 80 bar and Inlet velocity 0.0 m/s | 63 |
| Figure 6.2 | Relative graph of temperature and distance from nozzle, Inlet pressure 80 bar and Inlet velocity 10.0 m/s | 64 |
| Figure 6.3 | Relative graph of temperature and distance from nozzle, Inlet pressure 80 bar and Inlet velocity 100.0 m/s | 65 |
| Figure 6.4 | Relative graph of temperature and distance from nozzle, Inlet pressure 80 bar and Inlet temperature 300 K | 67 |
| Figure 6.5 | Relative graph of temperature and distance from nozzle, Inlet pressure 80 bar and Inlet temperature 340 K | 68 |
| Figure 6.6 | Relative graph of temperature and distance from nozzle, Inlet pressure 80 bar and Inlet temperature 380 K | 69 |
| Figure 6.7 | PT diagram of the throttling process | 70 |
| Figure 6.8 | Relative graph of temperature and distance from nozzle, Inlet velocity 0.0 m/s and Inlet temperature 300 K | 71 |
| Figure 6.9 | Relative graph of temperature and distance from nozzle, Inlet velocity 0.0 m/s and Inlet temperature 340 K | 72 |
| Figure 6.10 | Relative graph of temperature and distance from nozzle, Inlet velocity 0.0 m/s and Inlet temperature 380 K | 73 |
| Figure 6.11 | Relative graph of temperature and distance from nozzle, Inlet velocity 10.0 m/s and Inlet temperature 300 K | 74 |
| Figure 6.12 | Relative graph of temperature and distance from nozzle, Inlet velocity 10.0 m/s and Inlet temperature 340 K | 75 |

LIST OF FIGURES (continue)

| | page | |
|-------------|---|----|
| Figure 6.13 | Relative graph of temperature and distance from nozzle, Inlet velocity 10.0 m/s and Inlet temperature 380 K | 76 |
| Figure 6.14 | Relative graph of temperature and distance from nozzle, Inlet velocity 100.0 m/s and Inlet temperature 300 K | 77 |
| Figure 6.15 | Relative graph of temperature and distance from nozzle, Inlet velocity 100.0 m/s and Inlet temperature 340 K | 78 |
| Figure 6.16 | Relative graph of temperature and distance from nozzle, Inlet velocity 100.0 m/s and Inlet temperature 380 K | 79 |

LIST OF TABLES

| | Page |
|---|------|
| Table 5.1 Parameters for analytical solution and simulation in this study | 43 |
| Table 5.2 Calculation conditions of employed in Reverchon and Pallado's work. | 48 |
| Table 5.3 Simulation conditions used in the explicit finite difference simulations | 49 |
| Table 5.4 Simulation conditions used in the implicit finite difference simulations | 50 |
| Table 5.5 Calculated Percent Relative difference | 57 |
| Table 6.1 Ranges of the significant factors | 59 |
| Table 6.2 Simulation conditions used in the simulations to find out the significant factors | 59 |
| Table 6.3 The simulation conditions for all cases | 60 |
| Table A.1 Objective of Subroutines | 86 |
| Table A.2 Description of Parameters | 87 |
| Table B.1 Objective of Subroutines | 107 |
| Table B.2 Description of Parameters | 108 |

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

NOMENCLATURE

| | |
|------------|---|
| p | = pressure (Pa) |
| t | = time (sec) |
| T_{ref} | = Ref. Temperature |
| E_t | = sum of kinetic and internal energy per unit volume |
| k | = thermal conductivity |
| C_p | = heat capacity for constant pressure |
| C_v | = heat capacity for constant volume |
| Pr | = Prandtl number |
| V | = fluid velocity in y direction (horizontal direction) |
| W | = fluid velocity in z direction (vertical upward direction) |
| Δt | = Step size of integration, sec |
| e | = internal energy per unit volume |
| q_y | = heat flux vector in y direction |
| q_z | = heat flux vector in z direction |

Greek symbol

| | |
|-------------|---|
| ρ | = fluid density (kg/m^3) |
| μ_{ref} | = ref. fluid viscosity ($\text{g/cm} \cdot \text{s}$) |
| μ | = fluid viscosity ($\text{g/cm} \cdot \text{s}$) |