

**PARTIAL OXIDATION OF METHANE IN A MULTI-STAGE
GLIDING ARC SYSTEM**

Ms. Piyaphon Thakonpatthanakun

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science
The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with
Case Western Reserve University, The University of Michigan,
The University of Oklahoma, and Institut Français du Pétrole

2004

ISBN 974-9651-38-3

721619050

Thesis Title: Partial Oxidation of Methane in a Multi-stage Gliding Arc System
By: Ms. Piyaphon Thakonpatthanakun
Program: Petrochemical Technology
Thesis Advisors: Assoc. Prof. Sumaeth Chavadej
Prof. Lance L. Lobban

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

K. Bunyakiat.
..... College Director
(Assoc. Prof. Kunchana Bunyakiat)

Thesis Committee:

Sumaeth Chavadej
.....
(Assoc. Prof. Sumaeth Chavadej)

Pramoch R.
.....
(Asst. Prof. Pramoch Rangsunvigit)

Lance Lobban
.....
(Prof. Lance L. Lobban)

Thirasak R.
.....
(Assoc. Prof. Thirasak Rirksomboon)

ABSTRACT

4571019063: PETROCHEMICAL TECHNOLOGY

Piyaphon Thakonpatthanakun: Partial Oxidation of Methane in a Multi-stage Gliding Arc System.

Thesis Advisors: Assoc. Prof. Sumaeth Chavadej and

Prof. Lance L. Lobban, 77 pp. ISBN 974-9651-38-3

Keywords: Gliding Arc Discharge / Partial Oxidation of Methane / Synthesis Gas Production

Natural gas, with methane as the main component is regarded as a very desirable fuel and chemical feedstock. Conventional processes of methane conversion to produce H₂, methanol, and synthesis gas require high temperature and high pressure over catalysts. Nonthermal plasma is considered to be a promising technology for methane conversion since it can be operated in ambient conditions. A multi-stage gliding arc discharge system was employed in this study to investigate the effects of CH₄/O₂ feed molar ratio, total flowrate, frequency, voltage, and gap width on methane conversion and product distribution. Air was used instead of pure O₂ in the feed gas since it can reduce investment and operating cost. A four-stage plasma system in series was set up to determine the effect of stage number on the conversion of methane. The results showed that increasing stage number, residence time, applied voltage or gap distance enhanced both CH₄ and O₂ conversion in contrast with the negative effects of CH₄/O₂ feed molar ratio, total feed flowrate and frequency. The optimum condition was found at a CH₄/O₂ feed molar ratio of 3/1, a feed flowrate of 150 cm³/min and a frequency of 300 Hz for the maximum CH₄ and O₂ conversion and high synthesis gas selectivity. The energy consumption of the gliding arc system was found to be very low about 15.3-18.5 eV/molecule of methane converted as compared to 21 eV/molecule of methane converted obtained from the corona discharge system with pin and plate electrodes.

บทคัดย่อ

ปิยาภรณ์ ถกพัฒนกุล: การออกซิเดชันบางส่วนของก๊าซมีเทนในระบบประกายไฟฟ้า ร้อนแบบหลายขั้นตอน (Partial Oxidation of Methane in Multi-stage Gliding Arc System) อ. ที่ปรึกษา: รศ. ดร. สุเมธ ชวเดช และ ศ. ดร. แลนซ์ แอล ลอบเบน 77 หน้า ISBN 974-9651-38-3

ก๊าซมีเทนเป็นองค์ประกอบส่วนใหญ่ที่พบในก๊าซธรรมชาติ วิธีดั้งเดิมที่ใช้ในการเปลี่ยนก๊าซมีเทนเป็นก๊าซไฮโดรเจน, เมทานอล และก๊าซสังเคราะห์ เป็นกระบวนการที่ต้องควบคุมการทำงานที่อุณหภูมิและความดันสูงบนตัวเร่งปฏิกิริยาเคมี การใช้ประกายไฟฟ้าร้อนที่อุณหภูมิต่ำเป็นอีกทางเลือกหนึ่งของการเปลี่ยนก๊าซมีเทน เนื่องจากสามารถดำเนินการได้ที่สภาวะบรรยากาศ ระบบประกายไฟฟ้าร้อนแบบ 4 ขั้นตอนถูกสร้างขึ้นเพื่อศึกษาการออกซิเดชันบางส่วนของก๊าซมีเทน อากาศถูกใช้แทนการใช้ออกซิเจนบริสุทธิ์เพื่อลดค่าใช้จ่ายในการลงทุนและการดำเนินการ วัตถุประสงค์หลักของงานวิจัยนี้คือ ศึกษาผลกระทบที่เกิดจากอัตราส่วนระหว่างก๊าซมีเทนต่อก๊าซออกซิเจนในก๊าซขาเข้า, อัตราการไหลเข้าของก๊าซ, ความถี่, ความต่างศักย์ไฟฟ้าและระยะห่างระหว่างอิเล็กโทรดต่อประสิทธิภาพการเปลี่ยนแปลงของก๊าซมีเทนและก๊าซออกซิเจนรวมทั้งผลิตภัณฑ์ที่เกิดขึ้นโดยใช้ระบบประกายไฟฟ้าร้อนแบบ 4 ขั้นตอน จากการศึกษาพบว่าจำนวนขั้นตอนของเครื่องปฏิกรณ์ประกายไฟฟ้าร้อนช่วยเพิ่มค่าการเปลี่ยนรูปของทั้งก๊าซมีเทนและก๊าซออกซิเจนเมื่อความต่างศักย์ไฟฟ้าและระยะห่างระหว่างอิเล็กโทรดเพิ่มขึ้น ประสิทธิภาพการเปลี่ยนรูปของทั้งก๊าซมีเทนและก๊าซออกซิเจนเพิ่มขึ้น ซึ่งแตกต่างจากผลกระทบที่เกิดขึ้นจากการเพิ่มอัตราส่วนระหว่างก๊าซมีเทนต่อก๊าซออกซิเจนในก๊าซขาเข้า, อัตราการไหลเข้าของก๊าซและ ความถี่ ผลการทดลองแสดงประสิทธิภาพสูงสุดของการเปลี่ยนรูปของก๊าซมีเทนและก๊าซออกซิเจน รวมทั้งการเลือกสรรของการเกิดก๊าซสังเคราะห์ที่อัตราส่วนระหว่างก๊าซมีเทนต่อก๊าซออกซิเจนในก๊าซขาเข้าเท่ากับ 3/1, อัตราการไหลเข้าของก๊าซ 150 ลูกบาศก์เซนติเมตรต่อนาที และความถี่ 300 เฮิรซ์ โดยพบว่าพลังงานที่ใช้ในระบบประกายไฟฟ้าร้อนต่ำเพียง 15.3-18.5 อิเล็กตรอนโวลต์/โมเลกุลมีเทนที่เปลี่ยนไป ซึ่งเทียบกับ 21 อิเล็กตรอนโวลต์/โมเลกุลมีเทนที่เปลี่ยนไปของระบบโครโนที่ใช้ขั้วไฟฟ้าแบบปลายแหลมและแผ่น

ACKNOWLEDGEMENTS

This work would not have been possible without the assistance of the following individuals and organization.

First of all, I deeply indebted to Assoc. Prof. Sumaeth Chavadej and Professor Lance L. Lobban, who provided useful recommendations, creative comments, and encouragement throughout the course of my work. Assoc. Prof. Sumaeth Chavadej, my Thai advisor, has not only taught to me about theoretical knowledge but also made me realize that research work is very challenging.

This thesis work is partially funded by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium).

I deeply appreciate C.P.O. Poon Arjpru, who assisted me to design and set up a new experimental instrument and electrical parts. I would like to thank the Petroleum and Petrochemical College's staff for their help in many aspects.

Special thanks go to Ms. Korada Supat, Ms. Kanokwan saktrakool and Mr. Siriphong Roatluechai for their valuable suggestions throughout this research work.

Finally, I would like to take this opportunity to thank all of my PPC friends for their friendly assistance, cheerfulness, creative suggestions, and encouragement. I had the most enjoyable time working with all of them. Also, I am greatly indebted to my parents and my family for their support, love and understanding.

TABLE OF CONTENTS

| | PAGE |
|--|-------------|
| Title Page | i |
| Abstract (in English) | iii |
| Abstract (in Thai) | iv |
| Acknowledgements | v |
| Table of Contents | vi |
| List of Tables | viii |
| List of Figures | ix |
| | |
| CHAPTER | |
| I | |
| INTRODUCTION | 1 |
| | |
| II | |
| BACKGROUND AND LITERATURE SURVEY | 3 |
| 2.1 Physicals and Chemical Properties of Methane | 3 |
| 2.2 Gaseous Plasmas for Activating Methane Molecules | 4 |
| 2.2.1 Fundamental Properties of Plasma | 5 |
| 2.2.2 Generation of Plasma | 5 |
| 2.3 Types of Non-Equilibrium Plasmas | 7 |
| 2.3.1 Radio Frequency Discharge | 7 |
| 2.3.2 Microwave Discharge | 8 |
| 2.3.3 Glow Discharge | 8 |
| 2.3.4 Corona Discharge | 8 |
| 2.3.5 Dielectric-Barrier Discharge | 9 |
| 2.3.6 Gliding Arc Discharge | 9 |
| 2.4 Related Research Works | 10 |
| | |
| III | |
| EXPERTIMENTAL | 17 |
| 3.1 Materials | 17 |
| 3.1.1 Reactant Gases | 17 |
| 3.2 Experimental Setup | 17 |

| CHAPTER | PAGE |
|---|-------------|
| 3.2.1 Feed Gases Mixing Section | 17 |
| 3.2.2 Reaction Section | 17 |
| 3.2.2.1 Reactor Unit | 17 |
| 3.2.2.2 Power Supply Unit | 19 |
| 3.2.3 Analytical Section | 20 |
| 3.3 Studied Conditions | 21 |
| IV RESULTS AND DISCUSSION | 22 |
| 4.1 Effect of Molar Ratio | 22 |
| 4.2 Effect of Feed Flowrate | 28 |
| 4.3 Effect of Residence Time | 34 |
| 4.4 Effect of Frequency | 39 |
| 4.5 Effect of Applied Voltage | 45 |
| 4.6 Effect of Gap Distance | 52 |
| V CONCLUSIONS AND RECOMMENDATIONS | 59 |
| REFERENCES | 61 |
| APPENDICES | 64 |
| Appendix A Assumptions, definitions and calculations | 64 |
| Appendix B Experimental data | 66 |
| CURRICULUM VITAE | 77 |

LIST OF TABLES

| TABLE | | PAGE |
|--------------|---|-------------|
| 2.1 | Average chemical bond energy of some covalent bond | 3 |
| 2.2 | The first ionization potential of some common gases | 4 |
| 2.3 | Collision mechanisms in the plasma | 6 |
| 3.1 | Experimental conditions | 21 |

LIST OF FIGURES

| FIGURE | PAGE |
|--|-------------|
| 2.1 Phase of gliding arc phenomena | 10 |
| 3.1 The schematic diagram of the gliding arc discharge system | 18 |
| 3.2 Schematic diagram of the reactor | 19 |
| 3.3 Schematic diagram of the power supply unit. | 20 |
| 4.1 Effect of molar ratio on CH ₄ conversion at different stage numbers of the plasma system | 22 |
| 4.2 Effect of molar ratio on O ₂ conversion at different stage numbers of the plasma system | 23 |
| 4.3 Effect of molar ratio on CO selectivity at different stage numbers of the plasma system | 24 |
| 4.4 Effect of molar ratio on H ₂ selectivity at different stage numbers of the plasma system | 24 |
| 4.5 Effect of molar ratio on CO ₂ selectivity at different stage numbers of the plasma system | 25 |
| 4.6 Effect of molar ratio on C ₂ H ₂ selectivity at different stage numbers of the plasma system | 25 |
| 4.7 Effect of molar ratio on C ₂ H ₄ selectivity at different stage numbers of the plasma system | 26 |
| 4.8 Effect of molar ratio on C ₂ H ₆ selectivity at different stage numbers of the plasma system | 26 |
| 4.9 Effect of molar ratio on power consumption at different stage numbers of the plasma system | 27 |
| 4.10 Effect of feed flowrate on CH ₄ conversion at different stage numbers of the plasma system | 28 |
| 4.11 Effect of feed flowrate on O ₂ conversion at different stage numbers of the plasma system | 29 |

| FIGURE | PAGE |
|--|-------------|
| 4.12 Effect of feed flowrate on CO selectivity at different stage numbers of the plasma system | 30 |
| 4.13 Effect of feed flowrate on H ₂ selectivity at different stage numbers of the plasma system | 30 |
| 4.14 Effect of feed flowrate on CO ₂ selectivity at different stage numbers of the plasma system | 31 |
| 4.15 Effect of feed flowrate on C ₂ H ₂ selectivity at different stage numbers of the plasma system | 31 |
| 4.16 Effect of feed flowrate on C ₂ H ₄ selectivity at different stage numbers of the plasma system | 32 |
| 4.17 Effect of feed flowrate on C ₂ H ₆ selectivity at different stage numbers of the plasma system | 32 |
| 4.18 Effect of feed flowrate on power consumption at different stage numbers of the plasma system | 33 |
| 4.19 Effect of residence time on CH ₄ conversion at different stage numbers of the plasma system | 34 |
| 4.20 Effect of residence time on O ₂ conversion at different stage numbers of the plasma system | 35 |
| 4.21 Effect of residence time on CO selectivity at different stage numbers of the plasma system | 36 |
| 4.22 Effect of residence time on H ₂ selectivity at different stage numbers of the plasma system | 36 |
| 4.23 Effect of residence time on CO ₂ selectivity at different stage numbers of the plasma system | 37 |
| 4.24 Effect of residence time on C ₂ H ₂ selectivity at different stage numbers of the plasma system | 37 |
| 4.25 Effect of residence time on C ₂ H ₄ selectivity at different stage numbers of the plasma system | 38 |
| 4.26 Effect of residence time on C ₂ H ₆ selectivity at different stage numbers of the plasma system | 38 |

| FIGURE | PAGE |
|---|-------------|
| 4.27 Effect of frequency on CH ₄ conversion at different stage numbers of the plasma system | 39 |
| 4.28 Effect of frequency on O ₂ conversion at different stage numbers of the plasma system | 40 |
| 4.29 Effect of frequency on current at different stage numbers of the plasma system | 40 |
| 4.30 Effect of frequency on CO selectivity at different stage numbers of the plasma system | 41 |
| 4.31 Effect of frequency on H ₂ selectivity at different stage numbers of the plasma system | 42 |
| 4.32 Effect of frequency on CO ₂ selectivity at different stage numbers of the plasma system | 42 |
| 4.33 Effect of frequency on C ₂ H ₂ selectivity at different stage numbers of the plasma system | 43 |
| 4.34 Effect of frequency on C ₂ H ₄ selectivity at different stage numbers of the plasma system | 43 |
| 4.35 Effect of frequency on C ₂ H ₆ selectivity at different stage numbers of the plasma system | 44 |
| 4.36 Effect of frequency on power consumption at different stage numbers of the plasma system | 45 |
| 4.37 Effect of applied voltage on CH ₄ conversion at different stage numbers of the plasma system | 46 |
| 4.38 Effect of applied voltage on O ₂ conversion at different stage numbers of the plasma system | 46 |
| 4.39 Effect of applied voltage on current at different stage numbers of the plasma system | 47 |
| 4.40 Effect of applied voltage on CO selectivity at different stage numbers of the plasma system | 48 |
| 4.41 Effect of applied voltage on the selectivity of H ₂ at difference stage number of the plasma system | 48 |

| FIGURE | PAGE |
|---|-------------|
| 4.42 Effect of applied voltage on CO ₂ selectivity at different stage numbers of the plasma system | 49 |
| 4.43 Effect of applied voltage on C ₂ H ₂ selectivity at different stage numbers of the plasma system | 49 |
| 4.44 Effect of applied voltage on C ₂ H ₄ selectivity at different stage numbers of the plasma system | 50 |
| 4.45 Effect of applied voltage on C ₂ H ₆ selectivity at different stage numbers of the plasma system | 50 |
| 4.46 Effect of applied voltage on power consumption at different stage numbers of the plasma system | 51 |
| 4.47 Effect of gap distance on CH ₄ conversion at different stage numbers of the plasma system | 52 |
| 4.48 Effect of gap distance on O ₂ conversion at different stage numbers of the plasma system | 53 |
| 4.49 Effect of gap distance on CO selectivity at different stage numbers of the plasma system | 54 |
| 4.50 Effect of gap distance on H ₂ selectivity at different stage numbers of the plasma system | 54 |
| 4.51 Effect of gap distance on CO ₂ selectivity at different stage numbers of the plasma system | 55 |
| 4.52 Effect of gap distance on C ₂ H ₂ selectivity at different stage numbers of the plasma system | 55 |
| 4.53 Effect of gap distance on C ₂ H ₄ selectivity at different stage numbers of the plasma system | 56 |
| 4.54 Effect of gap distance on C ₂ H ₆ selectivity at different stage numbers of the plasma system | 56 |
| 4.55 Effect of gap distance on power consumption at different stage numbers of the plasma system | 57 |
| 4.56 Effect of stage number on power consumption at different gap distance | 58 |