

COMBINED REFORMING AND PARTIAL OXIDATION OF  
CO<sub>2</sub>-CONTAINING NATURAL GAS USING LOW-TEMPERATURE  
GLIDING ARC DISCHARGE: EFFECT OF STAGE NUMBER OF  
PLASMA REACTORS

Wariya Jittiang

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  
The University of Michigan, The University of Oklahoma,  
Case Western Reserve University and Institut Français du Pétrole  
2008

512012

**Thesis Title:** Combined Reforming and Partial Oxidation of CO<sub>2</sub>-Containing Natural Gas Using Low-Temperature Gliding Arc Discharge: Effect of Stage Number of Plasma Reactors

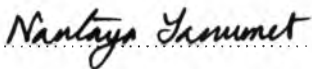
**By:** Wariya Jittiang

**Program:** Petroleum Technology

**Thesis Advisors:** Dr. Thammanoon Sreethawong  
Assoc. Prof. Sumaeth Chavadej


---

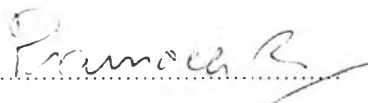
Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.


  
..... College Director  
(Assoc. Prof. Nantaya Yanumet)

**Thesis Committee:**

  
.....  
(Dr. Thammanoon Sreethawong)

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

  
.....  
(Assoc. Prof. Pramoch Rangsunvigit)

  
.....  
(Dr. Korada Supat)

## บทคัดย่อ

วิชา จิตเที่ยง : การรวมกระบวนการเปลี่ยนรูปและการออกซิเดชันบางส่วนของก๊าซธรรมชาติที่มีคาร์บอนไดออกไซด์เป็นองค์ประกอบในระบบพลาสมาประกายไฟฟาร้อนอุณหภูมิต่ำแบบหลายขั้นตอน: ผลกระทบของจำนวนเครื่องปฏิกรณ์ (Combined Reforming and Partial Oxidation of CO<sub>2</sub>-Containing Natural Gas Using Low-Temperature Gliding Arc Discharge: Effect of Stage Number of Plasma Reactors) อ. ที่ปรึกษา : ดร.ธรรมบุญ ศรีทะวงศ์ และ รศ. ดร. สุเมธ ชวเดช, 93 หน้า

ระบบพลาสมาประกายไฟฟาร้อนอุณหภูมิต่ำแบบหลายขั้นตอนได้ถูกนำมาใช้ในการศึกษาผลกระทบของจำนวนเครื่องปฏิกรณ์ต่อการเกิดปฏิกิริยาของระบบการรวมการเปลี่ยนรูปและการออกซิเดชันบางส่วนของก๊าซธรรมชาติจำลองที่มีคาร์บอนไดออกไซด์เป็นองค์ประกอบ โดยมีอัตราส่วนโดยโมลของก๊าซมีเทน, ก๊าซอีเทน, ก๊าซโพรเพน, และก๊าซคาร์บอนไดออกไซด์เป็น 70:5:5:20 ในการศึกษาปฏิกิริยาออกซิเดชันแบบบางส่วน ออกซิเจนบริสุทธิ์และอากาศถูกนำมาใช้เป็นแหล่งของก๊าซออกซิเจน โดยมีอัตราส่วนระหว่างไฮโดรคาร์บอนต่อออกซิเจนเป็น 2/1 จากการศึกษาพบว่าในระบบที่ไม่มีการออกซิเดชันบางส่วนและมีอัตราการใช้ของสารตั้งต้นคงที่ ค่าการเปลี่ยนแปลงของสารตั้งต้นทั้งหมดยกเว้นก๊าซคาร์บอนไดออกไซด์เพิ่มขึ้นเมื่อเพิ่มจำนวนเครื่องปฏิกรณ์เป็น 3 เครื่อง แต่ถ้าเพิ่มจำนวนเครื่องปฏิกรณ์มากกว่า 3 เครื่อง ค่าการเปลี่ยนแปลงของสารตั้งต้นจะไม่เปลี่ยนแปลงต่อไป สำหรับระบบที่มีการควบคุมให้มีเวลาในการเกิดปฏิกิริยา คงที่ มีเฉพาะค่าการเปลี่ยนแปลงของก๊าซโพรเพนเท่านั้นที่เพิ่มขึ้นเล็กน้อย ในขณะที่ค่าการเปลี่ยนแปลงของสารตั้งต้นตัวอื่นๆ ไม่เปลี่ยนแปลงมากนักเมื่อจำนวนของเครื่องปฏิกรณ์เพิ่มขึ้น เมื่อทำการเติมก๊าซออกซิเจนให้แก่ระบบพบว่าช่วยเพิ่มประสิทธิภาพในการเปลี่ยนรูปของก๊าซธรรมชาติเป็นอย่างมาก ซึ่งการใช้อากาศเป็น แหล่งของก๊าซออกซิเจนส่งผลดีต่อประสิทธิภาพของระบบมากกว่าการใช้ออกซิเจนบริสุทธิ์ ทั้งในแง่ของค่าการเปลี่ยนแปลงของสารตั้งต้น ค่าผลได้ และค่าการเลือกเกิดของผลิตภัณฑ์ที่ต้องการ และค่าการใช้พลังงานไฟฟ้า โดยพบว่าค่าการใช้พลังงานไฟฟ้าที่เหมาะสมสำหรับการเปลี่ยนแปลงสารตั้งต้น คือ  $3.21 \times 10^{-18}$  วัตต์ วินาที ต่อโมเลกุลของสารตั้งต้นที่เปลี่ยนแปลงไปและ  $2.57 \times 10^{-18}$  วัตต์ วินาที ต่อโมเลกุลของก๊าซไฮโดรเจนที่ผลิตได้ ซึ่งได้จากระบบที่มีการใช้อากาศเป็นแหล่งของก๊าซออกซิเจนและใช้เครื่องปฏิกรณ์จำนวน 3 เครื่อง โดยควบคุมเวลาของการเกิดปฏิกิริยาให้คงที่ที่ 4.38 วินาที

## ABSTRACT

4973010063: Petroleum Technology Program

Wariya Jittiang: Combined Reforming and Partial Oxidation of CO<sub>2</sub>-Containing Natural Gas Using Low-Temperature Gliding Arc Discharge: Effect of Stage Number of Plasma Reactors.

Thesis Advisors: Dr. Thammanoon Sreethawong and Assoc. Prof. Sumaeth Chavadej, 93 pp.

Keywords: Natural Gas / Reforming/ Partial Oxidation/ Gliding Arc Discharge/ Plasma

The effect of the stage number of a multistage AC gliding arc discharge system on the system performance of the combined reforming and partial oxidation of simulated CO<sub>2</sub>-containing natural gas having a CH<sub>4</sub>:C<sub>2</sub>H<sub>6</sub>:C<sub>3</sub>H<sub>8</sub>:CO<sub>2</sub> molar ratio of 70:5:5:20 was investigated. For the experiments with partial oxidation, either pure oxygen or air was used as an oxygen source, with a hydrocarbons-to-oxygen molar ratio of 2/1. Without partial oxidation at a fixed feed flow rate, all conversions of hydrocarbons, except CO<sub>2</sub>, greatly increased with increasing number of stages from 1 to 3; but beyond 3 stages, the reactant conversions remained almost unchanged. However, for a fixed residence time, only C<sub>3</sub>H<sub>8</sub> conversion gradually increased, whereas the conversions of other reactants remained almost unchanged with increasing number of stages. The addition of oxygen was found to significantly enhance the system performance of natural gas reforming. The utilization of air as an oxygen source showed a superior system performance to pure oxygen in terms of reactant conversions, desired product yields and selectivities, and power consumptions. The optimum power consumptions of  $3.21 \times 10^{-18}$  Ws per molecule of reactant converted and  $2.57 \times 10^{-18}$  Ws per molecule of hydrogen produced were obtained using air as an oxygen source and 3 stages of plasma reactors at a fixed residence time of 4.38 s.

## ACKNOWLEDGEMENTS

This thesis work would have never been possible without the assistance of the following persons and organizations:

First of all, I would like to express my deepest appreciation to Dr. Thammanoon Sreethawong and Assoc. Prof. Sumaeth Chavadej, for all of their excellent guidance, useful recommendations, creative comments, intensive attention, and encouragement throughout the course of my work. They have not only taught me about the theoretical knowledge but also made me realize in myself that this research is very challenging. As well as, they taught me in the better way of working life and working style.

I would like to express my sincere thank to the National Research Council of Thailand (NRCT); the National Excellence Center for Petroleum, Petrochemicals, and Advanced Materials under the Ministry of Education, Thailand; and the Research Unit of Petrochemical and Environmental Catalysis under the Ratchadapisek Somphot Endowment Fund, Chulalongkorn University, Thailand for providing the financial support for this thesis work.

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

Special thanks go to Ms. Nongnuch Rueangjitt for her 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, and encouragement. Also, I am greatly indebted to my parents and my family for their support, love, and understanding.

## TABLE OF CONTENTS

	<b>PAGE</b>
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	x
List of Figures	xi
<b>CHAPTER</b>	
<b>I INTRODUCTION</b>	<b>1</b>
<b>II LITERATURE REVIEW</b>	<b>4</b>
2.1 Natural gas	4
2.2 Physical and Chemical Properties of Methane	5
2.3 Gaseous Plasma for Activating Methane Molecules	6
2.3.1 Fundamental Properties of Plasma	6
2.3.2 Generation of Plasma	7
2.4 Types of Non-Equilibrium Plasma	9
2.4.1 Glow Discharge	9
2.4.2 Corona Discharge	9
2.4.3 Radio Frequency Discharge (RF discharge)	10
2.4.4 Microwave Discharge	10
2.4.5 Dielectric Barrier Discharge	10
2.4.6 Gliding Arc Discharge	10
2.5 Related Research Works	12
<b>III EXPERIMENTAL</b>	<b>19</b>
3.1 Materials	19

<b>CHAPTER</b>	<b>PAGE</b>
3.1.1 Reactant Gases for Reaction Experiments	19
3.1.2 Gases for GC Analysis	19
3.2 Experiment Setup	19
3.2.1 Feed Gases Mixing Section	20
3.2.2 Reaction Section	20
3.2.2.1 Reactor Units	20
3.2.2.2 Power Supply Unit	20
3.2.3 Analytical Section	21
3.3 Experimental Procedure	22
3.4 Studied Conditions	23
3.5 Reaction Performance Evaluation	25
<b>IV RESULTS AND DISCUSSION</b>	<b>27</b>
4.1 Reforming of Natural Gas without Partial Oxidation	30
4.1.1 Effect of Feed Flow Rate at Constant Residence Time	30
4.1.1.1 Effect on reactant conversion and product yield	31
4.1.1.2 Effect on product selectivity	33
4.1.1.3 Effect on power consumption	35
4.1.2 Effect of Residence Time at Constant Feed Flow Rate	36
4.1.2.1 Effect on reactant conversion and product yield	36
4.1.2.2 Effect on product selectivity	38
4.1.2.3 Effect on power consumption	38
4.2 Reforming of Natural Gas with Partial Oxidation	40
4.2.1 Reforming of Natural Gas with Partial Oxidation by Using Pure Oxygen	41

CHAPTER	PAGE
4.2.1.1 Effect of Feed Flow Rate at Constant Residence Time	41
4.2.1.1.1 Effect on reactant conversion and product yield	41
4.2.1.1.2 Effect on product selectivity	43
4.2.1.1.3 Effect on power consumption	44
4.2.1.2 Effect of Residence Time at Constant Feed Flow Rate	45
4.2.1.2.1 Effect on reactant conversion and product yield	45
4.2.1.2.2 Effect on product selectivity	47
4.2.1.2.3 Effect on power consumption	49
4.2.2 Reforming of Natural Gas with Partial Oxidation by Using Air	50
4.2.2.1 Effect of Feed Flow Rate at Constant Residence Time	50
4.2.2.1.1 Effect on reactant conversion and product yield	50
4.2.2.1.2 Effect on product selectivity	52
4.2.2.1.3 Effect on power consumption	53
4.2.2.2 Effect of Residence Time at Constant Feed Flow Rate	54
4.2.2.2.1 Effect on reactant conversion and product yield	54
4.2.2.2.2 Effect on product selectivity	56
4.2.2.2.3 Effect on power consumption	57
4.3 Comparison of Reforming of Natural Gas without and with Partial Oxidation Using either Oxygen or Air	58



<b>CHAPTER</b>		<b>PAGE</b>
<b>V</b>	<b>CONCLUSIONS AND RECOMMENDATIONS</b>	<b>66</b>
	<b>REFERENCES</b>	<b>68</b>
	<b>APPENDICES</b>	<b>72</b>
	<b>Appendix A</b> Experimental Data	<b>72</b>
	<b>Appendix B</b> Comparison of Natural Gas Reforming without/with Partial Oxidation Using either Pure Oxygen or Air Addition	<b>89</b>
	<b>CURRICULUM VITAE</b>	<b>93</b>

**LIST OF TABLES**

<b>TABLE</b>		<b>PAGE</b>
2.1	Average chemical bond energy of some covalent bonds	6
2.2	The first ionization potential of some common gases	6
2.3	Collision mechanisms in the plasma	8
3.1	Experimental conditions that will be used in this study	24

**LIST OF FIGURES**

<b>FIGURE</b>		<b>PAGE</b>
2.1	Phase of gliding arc phenomena: (A) reagent gas break-down; (B) equilibrium heating phase, and (C) non-equilibrium reaction phase	11
3.1	The schematic of the multistage gliding arc discharge system	19
3.2	Schematic of the gliding arc reactor	20
3.3	Schematic diagram of the power supply unit	21
4.1	Effect of stage number of plasma reactor on reactant conversions and product yields for reforming of natural gas without partial oxidation in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	32
4.2	Effect of stage number of plasma reactor on concentrations of outlet gases for reforming of natural gas without partial oxidation in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	32
4.3	Effect of stage number of plasma reactor on product selectivities for reforming of natural gas without partial oxidation in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	34
4.4	Effect of stage number of plasma reactor on product molar ratios for reforming of natural gas without partial oxidation in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	34
4.5	Effect of stage number of plasma reactor on power consumptions for reforming of natural gas without partial oxidation in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	35

FIGURE	PAGE
4.6 Effect of stage number of plasma reactor on reactant conversions and product yields for reforming of natural gas without partial oxidation in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	37
4.7 Effect of stage number of plasma reactor on concentrations of outlet gases for reforming of natural gas without partial oxidation in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	37
4.8 Effect of stage number of plasma reactor on product selectivities for reforming of natural gas without partial oxidation in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	39
4.9 Effect of stage number of plasma reactor on product molar ratios for reforming of natural gas without partial oxidation in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	39
4.10 Effect of stage number of plasma reactor on power consumptions for reforming of natural gas without partial oxidation in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	40
4.11 Effect of stage number of plasma reactor on reactant conversions and product yields for reforming of natural gas with pure O <sub>2</sub> addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	42

<b>FIGURE</b>	<b>PAGE</b>
4.12 Effect of stage number of plasma reactor on concentrations of outlet gases for reforming of natural gas with pure O <sub>2</sub> addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	42
4.13 Effect of stage number of plasma reactor on product selectivities for reforming of natural gas with pure O <sub>2</sub> addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	43
4.14 Effect of stage number of plasma reactor on product molar ratios for reforming of natural gas with pure O <sub>2</sub> addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	44
4.15 Effect of stage number of plasma reactor on power consumptions for reforming of natural gas with pure O <sub>2</sub> addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	45
4.16 Effect of stage number of plasma reactor on reactant conversions and product yields for reforming of natural gas with pure O <sub>2</sub> addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	46
4.17 Effect of stage number of plasma reactor on concentrations of outlet gases for reforming of natural gas with pure O <sub>2</sub> addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	47

<b>FIGURE</b>		<b>PAGE</b>
4.18	Effect of stage number of plasma reactor on product selectivities for reforming of natural gas with pure O <sub>2</sub> addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	48
4.19	Effect of stage number of plasma reactor on product molar ratios for reforming of natural gas with pure O <sub>2</sub> addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	49
4.20	Effect of stage number of plasma reactor on power consumptions for reforming of natural gas with pure O <sub>2</sub> addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	50
4.21	Effect of stage number of plasma reactor on reactant conversions and product yields for reforming of natural gas with air addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	51
4.22	Effect of stage number of plasma reactor on concentrations of outlet gases for reforming of natural gas with air addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	51
4.23	Effect of stage number of plasma reactor on product selectivities for reforming of natural gas with air addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	52

<b>FIGURE</b>		<b>PAGE</b>
4.24	Effect of stage number of plasma reactor on product molar ratios for reforming of natural gas with air addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	53
4.25	Effect of stage number of plasma reactor on power consumptions for reforming of natural gas with air addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	54
4.26	Effect of stage number of plasma reactor on reactant conversions and product yields for reforming of natural gas with air addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	55
4.27	Effect of stage number of plasma reactor on concentrations of outlet gases for reforming of natural gas with air addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	55
4.28	Effect of stage number of plasma reactor on product selectivities for reforming of natural gas with air addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	56
4.29	Effect of stage number of plasma reactor on product molar ratios for reforming of natural gas with air addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	57

<b>FIGURE</b>		<b>PAGE</b>
4.30	Effect of stage number of plasma reactor on power consumptions for reforming of natural gas with air addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm <sup>3</sup> /min)	58
4.31	Comparison of (a) CH <sub>4</sub> , (b) C <sub>2</sub> H <sub>6</sub> , (c) C <sub>3</sub> H <sub>8</sub> , (d) CO <sub>2</sub> , and (e) O <sub>2</sub> conversions for combined reforming and partial oxidation of natural gas in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	60
4.32	Comparison of (a) H <sub>2</sub> and (b) C <sub>2</sub> yields for combined reforming and partial oxidation of natural gas in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	61
4.33	Comparison of (a) H <sub>2</sub> , (b) C <sub>2</sub> H <sub>2</sub> , (c) C <sub>2</sub> H <sub>4</sub> , (d) CO, and (e) C <sub>4</sub> H <sub>10</sub> selectivities for combined reforming and partial oxidation of natural gas in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	63
4.34	Comparison of power consumptions for combined reforming and partial oxidation of natural gas in the case of varying feed flow rate (a) power consumption per molecule converted, (b) power consumption per hydrogen molecule produced) (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s)	64