ผลกระทบของการใช้สารช่วยกระจายตัวต่อสารพอลิไซคลิกอะโรมาติก ไฮโดรคาร์บอนในไอเสียจากเครื่องยนต์แกโซลีน

นายกานต์ วัชระกิติพงศ์



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต สหสาขาวิชาปิโตรเคมี-โพลิเมอร์

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2539

ISBN 974-636-654-8

ลิบสิทธิ์บองบัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

THE EFFECT OF DISPERSANT ON POLYCYCLIC AROMATIC HYDROCARBONS IN GASOLINE ENGINE EXHAUST

Mr. Kant Wacharakitiphong

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science
Multidisciplinary of Petrochemistry and Polymer
Graduate School
Chulalongkorn University
Academic Year 1996
ISBN 974-636-654-8

Thesis Title THE EFFECT OF DISPERSANT ON POLYCYCLIC AROMATIC HYDROCARBONS IN GASOLINE **ENGINE EXHAUST** Mr.Kant Wacharakitiphong By Petrochemistry **Program** Associate Professor Sophon Roengsumran, Ph.D. Thesis Advisor Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Masters's Degree. Sayan Dean of Graduate School (Professor Supawat Chutivongse, M.D.) Thesis Committee Chairman

(Associate Professor Supawan Tantayanon, Ph.D.) (Associate Professor Sophon Roengsumran, Ph.D.) Member (Assistant Professor Amorn Petsom, Ph.D.) Somel' Rengpre de Member (Assistant Professor Somchai Pengpreecha, Ph.D.)

(Assistant Professor Prapaipit Chamsuksai Ternai, Ph.D.)

P. Tesnai Member

พิมพ์ต้นฉบับบทคัดย่อวิทยานิพนธ์ภายในกรอบสีเขียวนี้เพียงแผ่นเดียว

กานต์ วัชระกิติพงศ์ : ผลกระทบของการใช้สารช่วยกระจายตัวต่อสารพอลิไซคลิกอะโรมาติก ไฮโครคาร์บอนในไอเสียจากเครื่องยนต์แกโซลีน (THE EFFECT OF DISPERSANT ON POLYCYCLIC AROMATIC HYDROCARBONS IN GASOLINE ENGINE EXHAUST) อ. ที่ปรึกษา : รศ. คร. โสภณ เริงสำราญ , 107 หน้า. ISBN 974-636-654-8.

การวิจัยนี้เป็นการศึกษาผลกระทบของการใช้สารเติมแต่งประเภทสารช่วยกระจายตัว (Dispersant) และความเร็วรอบเครื่องยนต์ (Speed) ที่มีต่อสารพอลิไซคลิกอะโรมาติกไฮโดรคาร์บอน (Polycyclic Aromatic Hydrocarbons; PAHs) ในใอเสียจากเครื่องยนต์แกโซลีน การวิจัยใช้เครื่องยนต์ขนาด 4 สุบ ความจุกระบอกสูบรวม 1,500 ลูกบาศก์เซนติเมตร อนุภาคขนาดเล็ก (Particulates) และสารกึ่งระเหย (Semivolatile gases) จากไอเสียถูกเก็บรวบรวมด้วยแผ่นกรองใยแก้ว (Glass microfibre) และโฟมโพลิยูรีเทน ตามลำคับ ตัวอย่างถูกนำมาสกัดแยกด้วยเครื่องสกัดแยกแบบ Soxhlet โดยใช้ใชโคลเฮกเซน เข้มข้นขึ้นก่อนนำไปวิเคราะห์ด้วยเครื่องแก๊สโครมาโตกราฟ-แมสสเปกโทรมิเตอร์ สารพอลิไซคลิก อะโรมาติกไฮโครคาร์บอนที่พบในใอเสียจากเครื่องยนต์ทคสอบคือ naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene และ pyrene ผลการศึกษาแสดงให้เห็นว่าความเร็วรอบของ เครื่องยนต์มีผลต่อปริมาณสารพอลิใชคลิกอะโรมาติกไฮโครคาร์บอนในไอเสีย ความเร็วรอบที่เหมาะสมซึ่ง ทำให้มีปริมาณสารพอลิไซคลิกอะโรมาติกไฮโครคาร์บอนในไอเสียต่ำที่สุดคือ 1,500 รอบต่อนาที ปริมาณ สารพอลิไซคลิกอะโรมาติกไฮโครคาร์บอนในไอเสียถูกพบมากขึ้นเมื่อความเร็วรอบสูงขึ้น อะโรมาติกไฮโครคาร์บอนในใอเสียยังขึ้นอยู่กับสารช่วยกระจายตัวในน้ำมันแกโซลีน กระจายตัวที่ให้ประสิทธิภาพสูงที่สุดในการลดปริมาณสารพอลิไซคลิกอะโรมาติกไฮโดรคาร์บอนในไอเสีย คือ 400 ส่วนู่ในล้านส่วน (โคยปริมาตร)

| ภาควิชา | สหสาขาวิชาปีโตรเคมี-โพถิเมอร์ |
|---------|-------------------------------|
| | ปิโตรเคมี |
| | .2539 |

พิมพ์ต้นฉบับบทคัดย่อวิทยานิพนธ์ภายในกรอบสีเขียวนี้เพียงแผ่นเดียว

C785076 : MAJOR PETROCHEMISTRY

KEY WORD: POLYCYCLIC AROMATIC HYDROCARBONS / PAHs / EXHAUST EMISSION /

GASOLINE ENGINE COMBUSTION / DISPERSANT / GASOLINE ADDITIVE

KANT WACHARAKITIPHONG : THE EFFECT OF DISPERSANT ON

POLYCYCLIC AROMATIC HYDROCARBONS IN GASOLINE ENGINE EXHAUST.

THESIS ADVISOR : ASSO. PROF. SOPHON ROENGSUMRAN, Ph.D. 107 pp.

ISBN 974-636-654-8.

The effects of dispersant gasoline additive and engine speeds on polycyclic aromatic hydrocarbons (PAHs) emitted in the exhaust emission of a gasoline engine were studied. The test was performed by employing the four-cylinder engine with displacement volume of 1,500 cm³. The particulates and semivolatile gases from exhaust emission were collected by glass microfibre filters and polyurethane foams, respectively. The samples were then subjected to the Soxhlet extraction with cyclohexane and concentrated before analysis by GC/MS. PAHs recovered from the test engine exhaust emission were naphthalene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene. The results show that the engine speed influences the amount of total PAHs. The optimum engine speed at which the emission of PAHs is lowest is 1,500 rpm. The higher amount of PAHs was recovered when the engine speed increases. PAHs in exhaust emission were also influenced by the dispersant in gasoline fuel. The effective quantity of dispersant for decreasing PAHs in exhaust emission is 400 ppm (v/v).

| ภาควิชาสหสาขาวิชาปีโตรเคมี-โพลิเมอร์ | ลายมือชื่อนิสิต 🏻 🖟 |
|--------------------------------------|--------------------------------|
| สาขาวิชา ปีโตรเคมี | ลายมือชื่ออาจารย์ที่ปรึกษา |
| ปีการศึกษา ²⁵³⁹ | ลายมือชื่ออาจารย์ที่ปรึกษาร่วม |



ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude to his advisor, Associate Professor Sophon Roengsumran for his helpful advice, and encouragement throughout the research. Especial gratitude is offered to Assistant Professor Amorn Petsom for his valuable guidance, helpfulness, and advice. He is also greateful to Associate Professor Supawan Tantayanon, Assistant Professor Somchai Pengprecha, and Assistant Professor Prapaipit Chamsuksai Ternai for their valuable suggestions and comments.

He wishes to express his appreciation to the Petroleum Authority of Thailand (PTT) and the Metallurgy and Materials Science Research Institute for their kindness in allowing him to use the instruments. Thanks are extended to Miss Wanwiwa Namtip, Miss Jirathiti Tangsuwan, Mr.Opart Septum, Mr.Banjong Marksoong, and everyone who has contributed suggestions, and support during the research.

Finally, he would like to express his greatest appreciation to his family for understanding, heartening, and support during his studies.

CONTENTS

| Page |
|--|
| ABSTRACT (in Thai) |
| ABSTRACT (in English) v |
| ACKNOWLEDGEMENT vi |
| CONTENTSvii |
| LIST OF TABLESx |
| LIST OF FIGURES xi |
| LIST OF ABBREVIATIONSxv |
| |
| CHAPTER I INTRODUCTION |
| 1.1 Objectives and Scope of the Research |
| 1.1.1 Objectives |
| 1.1.2 Scope of the Research |
| T |
| CHAPTER II THEORY AND LITERATURE REVIEW |
| 2.1 Polycyclic Aromatic Hydrocarbons (PAHs) 5 |
| 2.1.1 Atmospheric Forms of PAHs |
| 2.1.2 Health Hazard of PAHs9 |
| 2.2 Gasoline Engine and Gasoline Fuel |
| 2.2.1 Fundametal Principles of Gasoline Engine Operation |
| 2.2.2 Fuel Metering Systems of Gasoline Engine |
| 2.2.3 Effect of Operating Variables on Gasoline Engine Exhaust Emission 17 |

CONTENTS (continued)

| Page |
|--|
| 2.3 Gasoline Fuel |
| 2.4 Dispersant Gasoline Additive |
| 2.5 PAHs in Exhaust Emissions |
| 2.5.1 Exhaust Sampling Systems |
| 2.5.2 Analytical Methods |
| 2.6 Literature Review |
| |
| CHAPTER III EXPERIMENTAL |
| 3.1 Instruments and Apparatus |
| 3.2 Chemicals and Materials |
| 3.3 Test Engine |
| 3.4 Test Fuels |
| 3.5 Exhaust Sampling System |
| 3.6 Exhaust Emission Test Procedure |
| 3.6.1 Sample Collection |
| 3.6.2 Sample Extraction and Concentration |
| 3.6.3 Analysis |
| 3.7 Standard and Calibration Curve Preparation |
| 3.8 Calculation of PAHs in Exhaust Samples |
| 3.8.1 Calculation of the Exhaust Volume |
| 3.8.2 Calculation of PAH Quantity in Exhaust Sample 44 |

CONTENTS (continued)

| | Page |
|--|------|
| CHAPTER IV RESULTS AND DISCUSSION | |
| 4.1 Effect of Engine Speeds on Emission of PAHs | 51 |
| 4.2 Effect of Dispersant on Emission of PAHs | 52 |
| | |
| CHAPTER V CONCLUSIONS AND SUGGESTIONS FOR FUTURE WOR | RΚ |
| 5.1 Conclusions | . 54 |
| 5.2 Suggestions for Future Work | . 54 |
| | |
| REFERENCES | 55 |
| APPENDIX A | |
| APPENDIX B | |
| APPENDIX C | |
| APPENDIX D | |
| APPENDIX E | |
| APPENDIX F | |
| | 03 |
| VITA | 07 |

LIST OF TABLES

| TA | BLE | age |
|-----|---|-----|
| 1.1 | Air Quality of Bangkok in 1996 | _ |
| | Vehicle Population in Bangkok in 1995 | |
| | Vehicle Emission in Bangkok in 1995 | |
| | Test Engine Specification | |
| | GC-MS Conditions for PAHs Analysis | |
| | List of Selected PAHs in Standard Mixture of PAHs according to EPA 610 including Retention Times and Detection Limits | |
| D1 | PAHs in Blank Glass Microfiber Filter (GF) and Blank Polyurethane Foams (PUF) | |
| D2 | Repeatability of the Analytical Method | |
| | Recovery of the Extraction Method | |
| | Concentration of PAHs in Gasoline Test Engine Exhaust Emission 10 | |

LIST OF FIGURES

| FIG | FURES | Œέ |
|------|---|----|
| 2.1 | Mechanism of Benzo(a)pyrene Formation | |
| | Formation of PAHs in Pyrolysis Tyre Oil | |
| | Chemical Structures of Selected PAHs in EPA 610 | |
| | The Four-Stroke Spark-Ignition (SI) Cycle | |
| | Elements of a Simple Updraft Carburator | |
| | Carbureted Gasoline Metering System | |
| | Electronic Fuel Injector System of a Gasoline Engine | |
| 2.8 | Typical Concentration of Unburned Hydrocarbons, CO, and NO _x as a Function of Air-Fuel Ratio at 60 mph | |
| | Effect of Engine Speed on Exhaust Gas Hydrocarbon Concentration at 12:1, 14:1, and 16:1 Air-Fuel Ratio | |
| 2.10 | Effect of Spark Advance on Exhaust Gas Hydrocarbon Concentration; Constant Load at Engine Speed of 1,500 rpm | |
| 2.11 | Effect of Spark Timing on Exhaust Hydrocarbon Emission and Fuel Economy at 30 mph and Road Load | |
| 2.12 | Effect of Spark Advance on Exhaust Carbon Monoxide Emission for Fixed Throttle with Constant Load at 1,500 rpm | |
| 2.13 | Stylized Dispersant | |
| | Sludge Dispersion | |
| | Polymeric Dispersant Gasoline Additives | |
| | Schematic of Exhaust Gas Dilution Tunnel | |
| 2.17 | | |

LIST OF FIGURES (continued)

| FIC | GURE Page |
|-----|---|
| 3.1 | Schematic of Exhaust Sampling System39 |
| | Schematic of Sampling Device for Particulates and Semivolatile Gases Collecting |
| 4.1 | GC Chromatogram of Standard PAHs Mixture according to EPA 61048 |
| | GC Chromatogram of Extract form Gasoline Test Engine Exhaust at 1,000 rpm Powered by Gasoline Base Fuel |
| 4.3 | Effect of Engine Speeds and Total PAHs in Gasoline Test Engine Exhaust Emissions |
| 4.4 | Effect of Dispersant on Total PAHs in Exhaust Emissions53 |
| | Calibration Curve of Naphthalene60 |
| | Calibration Curve of Acenaphthylene61 |
| | Calibration Curve of Fluorene |
| | Calibration Curve of Phenanthrene |
| | Calibration Curve of Anthracene |
| A6 | Calibration Curve of Fluoranthene |
| | Calibration Curve of Pyrene63 |
| | Performance Curve of Vacuum Pump65 |
| C1 | Gas Chromatogram of Standard PAHs Mixture according to EPA 61067 |
| C2 | Mass Spectrum of Standard Naphthalene and its NIST Library Searching Result |
| C3 | Mass Spectrum of Standard Acenaphthylene and its NIST Library Searching Result |
| C4 | Mass Spectrum of Standard Acenaphthene and its NIST Library Searching Result |

LIST OF FIGURES (continued)

| FIC | BURE Pa | ge |
|------|--|----|
| C5 | Mass Spectrum of Standard Fluorene and its NIST Library Searching Result | |
| C6 | Mass Spectrum of Standard Phenanthrene and its NIST Library Searching Result | |
| C7 | Mass Spectrum of Standard Anthracene and its NIST Library Searching Result | |
| C8 | Mass Spectrum of Standard Fluoranthene and its NIST Library Searching Result | |
| C9 | Mass Spectrum of Standard Pyrene and its NIST Library Searching Result | |
| C10 | | |
| C11 | Mass Spectrum of Standard Chrycene and its NIST Library Searching Result | 7 |
| C12 | | |
| C13 | Mass Spectrum of Standard Benzo(k)fluoranthene and its NIST Library Searching Result |) |
| C14 | | |
| C15 | • | |
| C16 | | |
| C17 | | |
| E1 7 | Fotal Ion Chromatogram of Gasoline Test Engine Exhaust Emission88 | |

LIST OF FIGURES (continued)

| FIC | FURE | Page |
|-----|---|-------|
| E2 | (a) Total Ion Chromatogram of Naphthalene Fraction (b) Selected Ion Chromatogram of Naphthalene at m/z = 128 (c) Mass Spectrum of Naphthalene Fraction and its NIST Library Searching Result | 89 |
| E3 | (a) Total Ion Chromatogram of Acenaphthylene Fraction (b) Selected Ion Chromatogram of Acenaphthylene at m/z = 1 (c) Mass Spectrum of Acenaphthylene Fraction and its NIST Library Searching Result | 15291 |
| E4 | (a) Total Ion Chromatogram of Fluorene Fraction (b) Selected Ion Chromatogram of Fluorene at m/z = 166 (c) Mass Spectrum of Fluorene Fraction and its NIST Library Searching Result | 93 |
| E5 | (a) Total Ion Chromatogram of Phenanthrene Fraction (b) Selected Ion Chromatogram of Phenanthrene at m/z = 178 (c) Mass Spectrum of Phenanthrene Fraction and its NIST Library Searching Result | 95 |
| E6 | (a) Total Ion Chromatogram of Anthracene Fraction (b) Selected Ion Chromatogram of Anthracene at m/z = 178 (c) Mass Spectrum of Phenanthrene Fraction and its NIST Library Searching Result | 97 |
| E7 | (a) Total Ion Chromatogram of Fluoranthene Fraction (b) Selected Ion Chromatogram of Fluoranthene at m/z = 202 (c) Mass Spectrum of Fluoranthene Fraction and its NIST Library Searching Result | 99 |
| E8 | (a) Total Ion Chromatogram of Pyrene Fraction (b) Selected Ion Chromatogram of Pyrene at m/z = 202 (c) Mass Spectrum of Pyrene Fraction and its NIST Library Searching Result | 101 |

LIST OF ABBREVIATIONS

A/F = Air-fuel ratio

amu = Atomic mass unit

BaA = Benz(a)anthracene

BaP = Benzo(a)pyrene

CFR = Cooperative Fuels Research

CVS = Constant Volume Sampler

DHHS = The Department of Health and Human Services

EI⁺ = Electron Impact Ionization

EPA = The Environmental Protection Agency of United States

GC = Gas Chromatography

GC-FID = Gas Chromatography - Flame Ionization Detection

GC-MS = Gas chromatography - Mass spectrometry

HC = Hydrocarbon

HPLC = High Performance Liquid Chromatography

i.d. = Internal diameter

in = Inch

LPG = Liquefied Petroleum Gas

M.W. = Molecular Weight

m/z = Mass to Charge Ratio

MDL = Minimal Detection Limit

MON = Motor Octane Number

mph = Miles per hour

MS = Mass Spectrometry

NIST = Nation Bureau of Standard Library

 NO_x = Oxides of Nitrogen

PAH = Polycyclic Aromatic Hydrocarbon

PAHs = Polycyclic Aromatic Hydrocarbons

ppm = Parts per million

RON = Research Octane Number

rpm = Revolution per minute

SIM = Selected Ion Monitoring

SOF = Soluble Organic Fraction

TESSA = Total Exhaust Solvent Scrubbing Apparatus

TLC = Thin Layer Chromatography

UV = Ultraviolet Spectrometer