

ผลของดีบุกอินทรีย์ในแก๊สลิ้นต่อไอเสียรถยนต์



นางสาว สุพัตรา มิตรภานนท์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

สาขาวิชา ปิโตรเคมี

บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

พ.ศ. 2538

ISBN 974-632-198-6

ลิขสิทธิ์ของบัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย

**EFFECT OF ORGANOTINS IN GASOLINE ON EXHAUST EMISSION
FROM CAR**

MISS SUPATTA MIDPANON

A Thesis Submitted in Partial Fulfillment of the Requirements

for the Degree of Master of Science

Graduate School

Chulalongkorn University


1995

ISBN 974-632-198-6

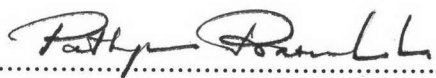
Copyright of the Graduate School, Chulalongkorn University

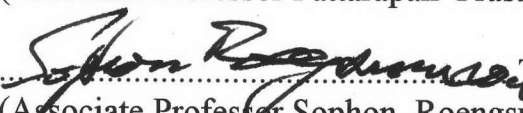
Thesis Title EFFECT OF ORGANOTINS IN GASOLINE ON
EXHAUST EMISSION FROM CAR
By Miss Supatta Midpanon
Department Petrochemistry
Thesis Advisor Associate Professor Sophon Roengsumran, Ph. D.
Thesis Co-advisor Mrs. Ratanavalee Inochanon

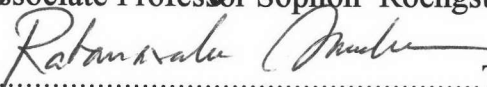
Accepted by the Graduate School, Chulalongkorn University in Partial
Fulfillment of the Requirements for Master's Degree

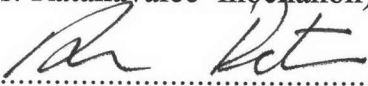

.....Dean of Graduate School
(Associate Professor Santi Thoongsuwan, Ph.D.)


Thesis Committee


.....Chairman
(Associate Professor Pattrapan Prasassarakich, Ph. D.)


.....Thesis Advisor
(Associate Professor Sophon Roengsumran, Ph. D.)


.....Thesis Co-advisor
(Mrs. Ratanavalee Inochanon)


.....Member
(Assistant Professor Amorn Petsom, Ph.D.)


.....Member
(Assistant Professor Somchai Pengprecha, Ph.D.)

พิมพ์ต้นฉบับบทความวิจัยวิทยานิพนธ์ภายในกรอบสี่เหลี่ยมนี้เพียงแผ่นเดียว

สุพัตรา มิตรภานนท์ : ผลของดีบุกอินทรีย์ในแกโซลีนต่อไอเสียรถยนต์
(EFFECT OF ORGANOTINS IN GASOLINE ON EXHAUST EMISSION FROM CAR)

อ.ที่ปรึกษา : รศ. ดร. โสภณ เรืองสำราญ อ.ที่ปรึกษาร่วม : นาง รัตนาวลี อินโชนานนท์,
113 หน้า. ISBN 974-632-198-6

การวิจัยนี้เป็นการศึกษาผลของการผสมเมธิลเทอร์เชียรีบิวทิลอีเธอร์ ไอโซโพรพานอล และเตตรา-
บิวทิลทิน หรือเตตราเฮกซิลทิน กับแกโซลีนเพื่อใช้เป็นน้ำมันเชื้อเพลิงรถยนต์ เครื่องยนต์ที่ใช้ในการทดลอง
เป็นเครื่องยนต์โตโยต้า 4 สูบ ซึ่งทำการทดลองที่ห้องสุญญากาศและความเร็วรอบต่างๆกัน ผลของการวิจัย
แสดงให้เห็นว่าการมีเมธิลเทอร์เชียรีบิวทิลอีเธอร์ ไอโซโพรพานอล และสารดีบุกอินทรีย์ (เตตราบิวทิลทินหรือ
เตตราเฮกซิลทิน) จะช่วยลดความเข้มข้นของคาร์บอนมอนอกไซด์ในไอเสียรถยนต์อย่างเห็นได้ชัด (ประมาณ 30-
40 % เมื่อเปรียบเทียบกับน้ำมันพื้นฐาน) ซึ่งเตตราบิวทิลทินจะมีผลช่วยลดปริมาณคาร์บอนมอนอกไซด์ได้ดีกว่า
เตตราเฮกซิลทินเล็กน้อย นอกจากนี้ยังมีผลในการช่วยลดปริมาณสารประกอบไฮโดรคาร์บอนอีกเล็กน้อย

ภาควิชา..... สหสาขาวิชา โอลิมปิก - โพลีเมอร์.....
สาขาวิชา..... โอลิมปิก.....
ปีการศึกษา..... 2537.....

ลายมือชื่อนิสิต..... สุพัตรา มิตรภานนท์.....
ลายมือชื่ออาจารย์ที่ปรึกษา.....
ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.....

C485100 : MAJOR PETROCHEMISTRY

KEY WORD: AIR POLLUTION / GASOLINE ADDITIVES / ORGANOTINS / EXHAUST GAS / EMISSION
SUPATTA MIDPANON : EFFECT OF ORGANOTINS IN GASOLINE ON EXHAUST
EMISSION FROM CAR. THESIS ADVISOR : ASSO. PROF. SOPHON ROENGSUMRAN,
Ph.D., THESIS CO-ADVISOR : MRS. RATANAVALLEE INOCHANON 113 pp.
ISBN 974-632-198-6

The effect on exhaust gas emissions of carbon monoxide, CO, and hydrocarbons, HC, resulting from mixing methyl tert-butyl ether (MTBE), isopropanol (IPA), and tetrabutyltin or tetrahexyltin with gasoline for automotive fuels has been studied experimentally. Tests were conducted on a Toyota four-cylinder engine running at different conditions of spark timing and engine speed. Results of this investigation indicate that the presence of the MTBE, IPA, and organotins (tetrabutyltin or tetrahexyltin) in the fuel blend significantly reduce the concentration of carbon monoxide in the exhaust emissions (up to 30-40 percent compared to base fuel), with tetrabutyltin slightly more effective than tetrahexyltin. Hydrocarbon emissions were only slightly decreased in this experiment.

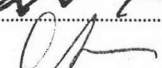
ภาควิชา..... ส่วนสาขาปิโตรเคมี - โพลีเมอร์

สาขาวิชา..... ปิโตรเคมี

ปีการศึกษา..... ๒๕๓๗

ลายมือชื่อนิสิต..... สุพัฒน์ มิตรภานนท์

ลายมือชื่ออาจารย์ที่ปรึกษา..... 

ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..... 



ACKNOWLEDGEMENT

The author would like to express her sincere thanks to advisor, Associate Professor Dr. Sophon Roengsumran for his encouraging guidance, supervision and helpful suggestions throughout this research. She is grateful to her co-advisor, Mrs. Ratanavalee Inochanon for her guidance and understanding and Assistant Professor Dr. Amorn Petsom for his unfailing guidance and help throughout this research. In addition, she is also grateful to Associate Professor Dr. Pattarapan Prasassarakich and Assistant Professor Dr. Somchai Pengprecha, serving as chairman and members of her thesis committee, respectively, for their valuable comments.

Special thanks are due to the Petroleum Authority of Thailand for their help in determining quality of the blended gasolines and permitting use of some equipment in the experiments.

Finally, she owes very deep thanks to her family for their love, support and encouragement.

CONTENT

	PAGE
ABSTRACT (in Thai).....	iv
ABSTRACT (in English).....	v
ACKNOWLEDGEMENT.....	vi
CONTENTS.....	vii
LIST OF TABLES.....	xii
LIST OF FIGURES.....	xiii

CHAPTER I INTRODUCTION

Air Pollution from Vehicles.....	3
1. Engine.....	3
2. Fuel.....	4
Objective and Scope of the Research.....	5
1. Objective.....	5
2. Scope of the Research.....	5

CHAPTER II THEORY AND LITERATURE REVIEW

Fundamental Principles of Engine Operation.....	6
1. The Four-Stroke Cycle Engine.....	7
Combustion.....	10
Polullants from Engine.....	12
1. Carbon Monoxide.....	14
2. Hydrocarbons.....	17
3. Oxides of Nitrogen.....	21

	PAGE
4. Particulates.....	21
5. Odor.....	22
Effect of Operating Variables on Gasoline Engine	
Exhaust Emissions.....	23
1. Air-fuel Ratio.....	23
2. Engine Speed.....	24
3. Spark Timing.....	26
Gasoline.....	30
1. General Characteristics.....	30
2. Performance Requirements.....	31
2.1 Antiknock Quality.....	31
2.2 Surface Ignition.....	33
2.3 Volatility.....	34
2.4 Starting.....	34
2.5 Vapor Lock.....	34
2.6 Oxidation Stability.....	35
2.7 Odor and Color.....	35
3. Gasoline Additives.....	35
3.1 Antiknock Compound.....	36
3.2 Deposit Modifier Additive.....	37
3.3 Antioxidants.....	37
3.4 Metal Deactivators.....	37
3.5 Anti-rust Agent.....	38
3.6 Anti-icing Agent.....	38
3.7 Carburetor Detergent.....	39
3.8 Dyes.....	39
3.9 Upper-Cylinder Lubricants.....	39

	PAGE
Combustion and Theory of Knock.....	40
1. Normal Combustion.....	40
2. Abnormal Combustion.....	41
3. Characteristics of Knock.....	43
The Use of Oxygenated Compounds in Motor Gasolines.....	45
1. Manufacture of Oxygenates.....	47
1.1 Methanol.....	47
1.2 Ethanol.....	48
1.3 Tertiary Butyl Alcohol.....	48
1.4 Mixed Alcohol.....	49
1.5 Methyl tertiary-Butyl Ether.....	49
1.6 Tertiary Amyl Methyl Ether.....	50
1.7 Mixed Ether.....	51
2. Materials Compatibility.....	52
3. Distribution of Fuels Containing Oxygenates.....	53
4. Vehicle Performance with Fuels Containing Oxygenates.....	54
4.1 Exhaust Emissions.....	54
4.2 Fuel Economy.....	56
5. Oxidation of Methyl tertiary-Butyl Ether.....	57
Tin Chemicals.....	59
1. Tin (IV) Chloride.....	60
2. Tin (IV) Oxide.....	61
3. Organotin Compounds.....	62
4. Tetraorganotin Compounds.....	62
Basic Methods of Preparation of Organotin Compounds.....	63
1. Grignard Reaction.....	64
2. Wurtz Reaction.....	65
3. Organoaluminums.....	67

	PAGE
4. Direct Reaction.....	68
4.1 Rochow Method.....	68
4.2 Sisido Method.....	69
4.3 Matsuda-Matsuda Method.....	70
5. Redistribution Reaction (Kocheskov Reaction).....	70

CHAPTER III EXPERIMENTAL

Apparatus and Instrumentations.....	71
Reagents and their Purification.....	72
Synthesis of Tetrahexyltin by Grignard Reaction.....	73
Engine Description.....	79
Test Fuel.....	79
Exhaust Emissions Testing Procedures.....	81
1. Sample Collection.....	81
2. Chromatographic Conditions.....	82
3. Compound Identification.....	82
4. Standard Preparation.....	83
5. Calculation of Hydrocarbons Concentrations.....	83

CHAPTER IV RESULTS AND DISCUSSION

Synthesis of Tetrahexyltin.....	84
Test Properties of Blended Fuels.....	86
Effect of Engine Parameters.....	88
1. Effect of Spark Timing.....	89
2. Effect of Engine Speed.....	92
Effect of Fuel on Exhaust Emissions.....	96
Compositions and Concentrations of Hydrocarbons in Exhaust Gases of Fuel1.....	100

	PAGE
CHAPTER V CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK	
5.1 Conclusions.....	104
5.2 Suggestions for Future Work.....	105
REFERENCES.....	106
APPENDIX.....	111
VITA.....	113

LIST OF TABLES

TABLE	PAGE
1.1 Volume of air pollution of Thailand in 1982.....	1
2.1 Relative emission rates for various engine-operating modes.....	25
2.2 Effect of design and operating variables on exhaust emissions and engine air flow.....	29
2.3 Operating conditions for Research and Motor methods.....	32
2.4 Engine variables which affect knock.....	43
2.5 Oxygenate supply/demand balance.....	46
3.1 Description of the test engine.....	79
3.2 Composition of gasoline test fuel.....	80
3.3 Chromatographic condition of individual hydrocarbons analysis.....	82
3.4 Dilution for preparation of standards.....	83
4.1 Properties of blended fuels.....	87
4.2 Octane number of blended fuels and commercial gasolines.....	88
4.3 Carbon monoxide and hydrocarbons in exhaust gases at 800 rpm and various spark timing advances.....	89
4.4 Carbon monoxide and hydrocarbons in exhaust gases at various operating speeds.....	92
4.5 Carbon monoxide and hydrocarbons in exhaust gases at 800 rpm and 7°BTDC.....	96
4.6 Compositions and concentrations of hydrocarbon emissions produced by Fuel1 at spark timing 7°BTDC and speeds of 800 and 1500 rpm.....	100

LIST OF FIGURES

FIGURES	PAGE
1.1 Sources of air pollution in Thailand.....	2
2.1 The four-stroke spark-ignition (SI) cycle.....	8
2.2 Pressure-volume diagram for a four-stroke cycle engine.....	9
2.3 Valve-timing diagram.....	9
2.4 Pressure-time diagram.....	10
2.5 Sources of pollution from automobiles.....	13
2.6 Pollutants and their harmful effects.....	13
2.7 Carbon monoxide concentration as a function of time following combustion.....	15
2.8 Carbon monoxide concentration as a function of air-fuel ratio.....	16
2.9 Toxicity of carbon monoxide.....	16
2.10 The quench zone in the piston-cylinder engine, (a) and (b).....	17
2.11 Variation of hydrocarbon emissions with air-fuel ratio.....	18
2.12 Sources of atmospheric benzene (West Germany).....	20
2.13 Mass rate balance for lead for an individual.....	22
2.14 Typical concentrations of unburned hydrocarbons, carbon monoxide, and nitrogen oxides as a function of air-fuel ratios at 60 mph.....	24
2.15 Effect of engine speed on exhaust gas hydrocarbon concentrations at 12:1, 14:1, and 16:1 air fuel ratios.....	25
2.16 Effect to spark advance on exhaust gas hydrocarbon concentrations at constant load-engine speed 1500 rpm.	27
2.17 Effect of spark timing on exhaust hydrocarbon emissions and fuel economy in car at 30 mph road load.....	27

FIGURE	PAGE
2.18 Effect of spark advance on exhaust gas carbon monoxide concentration for fixed throttle versus constant load at 1500 rpm.....	28
2.19 Schematic of normal combustion process.....	40
2.20 Abnormal combustion characteristics.....	42
2.21 US oxygenate supply / demand MTBE equivalents.....	47
2.22 Oxygen in gasoline reduces emissions	55
2.23 Volumetric fuel consumption (average of five vehicles).....	56
2.24 Fuel energy consumption (average of five vehicles).....	57
3.1 FTIR spectrum of tetrahexyltin.....	75
3.2 ¹ H-NMR spectrum of tetrahexyltin.....	76
3.3 ¹³ C-NMR spectrum of tetrahexyltin.....	77
3.4 Mass-spectrum of tetrahexyltin.....	78
3.5 Schematic of sample collection for analysis by GC.....	81
4.1 Effect of spark timing on carbon monoxide concentration in exhaust emissions.....	90
4.2 Effect of spark timing on hydrocarbon concentration in exhaust emissions.....	91
4.3 Effect of engine speed on carbon monoxide concentration in exhaust emissions.....	94
4.4 Effect of engine speed on hydrocarbon concentration in exhaust emissions.....	95
4.5 Effect of fuel composition on carbon monoxide concentration in exhaust gases at 800 rpm and 7°BTDC.....	98
4.6 Effect of fuel composition on hydrocarbon concentration in exhaust gases at 800 rpm and 7°BTDC.....	99
4.7 GC analysis of exhaust emissions sample from Fuel1.....	101

FIGURE	PAGE
4.8 Hydrocarbon emission concentrations in exhaust emissions from Fuel1 at 800 rpm and 1500 rpm.....	102