INFORMATION TO USERS

STUDY OF OCTANE ENHANCERS FOR GASOLINE IN THE KINGDOM OF SAUDI ARABIA

BY

FARHAN MOHAMMAD AL-SHAHRANI

A Thesis Presented to the

DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

JANUARY, 2003

UMI Number: 1412287

UMI®
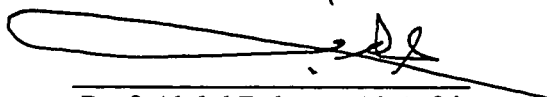
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN 31261, SAUDI ARABIA

DEANSHIP OF GREADUATE STUDIES

This thesis, written by **FARHAN MOHAMMAD AL-SHAHRANI,** under the direction

of his thesis advisor and approved by his thesis committee, has been presented to and

accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for

the degree of **MASTER OF SCIENCE IN CHEMISTRY.**

<u>**Thesis Committee**</u>

Prof. Abdul Rahman Al-Arfaj
Thesis Advisor

Dr. Gary Martinie
Member

Dr. Sami Barri
Member

Dr. Assad A. Al-Thukair
Department Chairman

Prof. Osama A. Jannadi
Dean, College of Graduate Studies

15/02/2003
Date

Dedicated to

My Parents,

Brothers,

Sisters,

Wife

And

My Two Kids

ACKNOWLEDGMENT

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

THESIS ABSTRACT

NAME: **Farhan M. Al-Shahrani**

TITLE: **Study of Octane Enhancers for Gasoline in the Kingdom of Saudi Arabia**

MAJOR FIELD: **Chemistry**

DATE: **January 2003**

The main objective of this project was to study the efficiency, synergism, advantages, economics, environmental, and mechanical impact of metallane combustion and octane improvers in combination with oxygenates on Saudi Arabian fuels. Various fuel streams was investigated including reformate, light straight run naphtha, butanes, pentanes, hydrocracker naphtha, FCC [Fluid Catalytic Cracking] Gasoline, and Natural Gasoline. Used additives were Tetra-Ethyl Lead [TEL] (1), Methyl-Cyclopentadienyl Manganese Tricarbonyl [MMT] (2), Dicyclopentadienyl Iron [DCI] (3), and Iron pentacarbonyl [IPC] (4). The effect of these additives along with MTBE [Methyl Tertiary Butyl Ether] and Ethanol on gasoline octane number and their different specifications was included in this study.

As a result of the economical and environmental evaluation, DCI and MMT can be used as a gasoline octane number enhancer in the Kingdom of Saudi Arabia.

MASTER OF SCIENCE DEGREE
KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
DHAHRAN - SAUDI ARABIA

ملخص الرسالة

الاسم: فرحان محمد الشهراني

عنوان الدراسة: دراسة محسنات الاوكتان في البنزين المنتج في المملكة العربية السعودية

التخصص: كيمياء

التاريخ: يناير 2003م

الهدف الرئيس من هذه الرسالة كان لدراسة تأثير و كفاءة استخدام محسنات مختلفة على رقم الأوكتان في البنزين المنتج في المملكة العربية السعودية, و كذلك دراسة مدى تأيره على البيئة و جدواه الإقتصادية.

إعتمد استخدام أنواع مختلفة من أجزاء الوقود المكونة للبنزين المنتجة في مصافي ينبع , جدة , الرياض و كذلك رأس تنورة.

المضافات المستخدمة في هذه الدراسة شملت أربعة أنواع هي [TEL] Tetra-Ethyl Lead , -Methyl Cyclopentadienyl Manganese Tricarbonyl [MMT] , Dicyclopentadienyl Iron [DCI] و Iron Pentacarbonyl [IPC].

نتائج الدراسات الإقتصادية و البيئية تشير إلى أن DCI و MMT قد تستخدم لتحسين رقم الأوكتان في البنزين في المملكة العربية السعودية.

درجة الماجستير في العلوم
جامعة الملك فهد للبترول والمعادن
الظهران-المملكة العربية السعودية

CHAPTER 1

INTRODUCTION

With the elimination of lead from the gasoline pool worldwide, refiners now rely on oxygenates like Methyl Tertiary Butyl Ether [MTBE] , Ethyl Tertiary Butyl Ether [ETBE], Tetra Amyl Methyl Ether [TAME], Di Iso Propyl Ether [DIPE], Di Methyl Ether [DME], and Methanol, to increase octane of the reformate, naphtha, and FCC gasoline blends, to achieve acceptable octane levels. New metallane additives are now being introduced, such as Iron Penta Carbonyl [IPC] , Di Cyclo Pentadienyl Iron [DCI], and Methylcyclopentadienyl Manganese Tricarbonyl [MMT], which will be blended with Tertiary Ethyl Lead [TEL] , oxygenates, and hydrocarbons.   Carriers, antioxidants, detergents, dyes, and deposit control additives are also present in gasoline.

The objective of this study is to develop data and record observations of the efficacy, synergism, advantages, economics, environmental, and mechanical impact of metallane combustion and octane improvers in combination with oxygenates like MTBE on Saudi Arabian fuels.   Various fuel streams to be studied include reformate, light straight run naphtha, butanes, pentanes, hydrocracker naphtha, FCC Gasoline, Pyrolysis Gasoline, and Natural Gasoline.   These additives include Tetra-Ethyl Lead [TEL] (1), Methyl-Cyclopentadienyl Manganese Tricarbonyl [MMT] (2), Dicyclopentadienyl Iron [DCI] (3), and Iron pentacarbonyl [IPC] (4). The affect of different additives and oxygenates on different gasoline specifications will be included to ensure the production of clean and efficient gasoline.

1

1.1   GASOLINE CHEMISTRY

Gasoline is composed of hydrocarbons mainly ranging from C_5 to C_{10}. including paraffins, isoparaffins, naphthenes, olefins, and aromatics. The distillation range is 180-380 °F. From the time of the first Drake well till the time of the automobile gasoline had no value and was usually discarded. Automobiles required a very significant increase in gasoline production. Since crude oil contains only 10-40 % gasoline, the cracking process was developed. Combination of smaller molecules into gasoline was also practiced, through polymerization and alkylation. Combined cracking and polymerization allowed production of as much as 70 % gasoline per barrel of crude. [1] Later, more complex processes were developed, such as cyclization of paraffins to naphthenes, and dehydrogenation of naphthenes to aromatics. [2]

Reforming hydrocarbon molecules is vital to developing high octane gasoline without the use of additives such as TEL and MTBE. When gasoline was first used in a spark ignition engine, it was observed that the initial explosion in the cylinder was followed by secondary explosions that caused the engine to knock badly. Since the cause of the knock was not understood, chemists tried the approach of using every conceivable chemical added to gasoline in hopes of reducing knock. The ultimate anti-knock compound, tetraethyl lead, was found which could eliminate knock by adding 1-3 ml to a gallon of gasoline. [3]

At the same time, individual hydrocarbons were being tested as fuel. It was found that isooctane caused the least knock so it was given a rating of 100. N-Heptane caused the most knock, so it was given a rating of zero. The knock characteristics of all hydrocarbons were rated relative to the isooctane-heptane scale. As time went on, it was

observed that structural groups which retarded oxidation had the least knock. The ring compounds and branched paraffins would not oxidize until temperatures were high enough for complete combustion [4]. Long chain paraffin would start oxidation at a lower temperature, and later combustion would cause knock . [5]

A comparison of standard oxidation temperature with octane number is shown in Table 1. The increase in oxidation temperature and octane number with increased branching is apparent.

Table 1. Comparison of Knock Resistance and Oxidation Temperature

Hydrocarbon	Oxidation Temperature [°C]	Research Octane Number
Normal Octane	265	-19
Normal Heptane	275	0
3-Methyl Heptane	295	27
2,4-Dimethyl Hexane	320	65
2,2,4-Trimethyl Pentane	465	100

As a straight hydrocarbon chain becomes branched, the octane rating increases. The naphthenes and aromatics generally have higher octane numbers than paraffins, because their rings are basically compact. Adding long chains to rings will lower their octane number. Cyclopentanes have increasing octane numbers as the side chains are shortened. Symmetrical molecules, such as 1,3,5-trimethyl benzene, has a higher octane value than 1,2,4-trimethyl benzene. [6]

1.2 GASOLINE COMBUSTION

Combustion of hydrocarbon fuels in the reciprocating internal combustion spark ignition engine is quite different from the relatively simple continuous combustion that takes place in engines such as the gas turbine. It is intermittent and occurs under complex and continuously changing conditions of temperature and pressure. Combustion efficiency under such conditions is very sensitive to fuel quality and the fuel quality requirement of the gas turbine is strongly dependant on operating conditions.

The amount of air required to combust a fuel can readily be calculated from the Carbon-Hydrogen content of the fuel. Gasoline requires about 14.5 parts by weight of air for complete combustion, depending on the fuel composition. Generally speaking, if the air fuel ratio is less than 7:1, it will be too rich to ignite, and if it is more than 20:1 in a conventional engine, it will be too lean to ignite. When a fuel is mixed with oxygen, so-called preflame conditions will commence, even before the mixture has reached the combustion chamber, and will continue after ignition until all the fuel has been consumed by the advancing flame front. The extent of these reactions will depend on a number of factors including the fuel composition, and the temperature and pressure of the mix. The nature of the reactions will determine if the fuel will burn in a smooth efficient manner, or will give rise to some abnormal condition such as knock or pre-ignition.

Normal combustion occurs when a flame front moves smoothly, if somewhat irregularly across the combustion chamber after being initiated by the spark, until combustion is complete. The irregular movement is caused by turbulence and incomplete mixing. The pressure changes within the cylinder are large, they increase as the mixture

4

is compressed, then rise rapidly after ignition due to temperature increase and formation of combustion gasses.

Even with normal combustion, all spark ignition engines show variation in maximum cylinder pressure and rate of pressure rise from cycle to cycle [cyclic dispersion] in spite of close control of the operating conditions. This dispersion is believed to be a result of variations in turbulence between cycles, causing differences in flame speeds across the combustion chamber. If reduction in cyclic dispersion could be achieved, there would be significant benefits in terms of improved fuel consumption and lower octane requirements for spark ignition engines. [7]

Spark knock is one of the most important forms of abnormal combustion, as it determines to some extent the thermal efficiency that can be achieved in an engine. The higher the compression ratio, the better the thermal efficiency, but also the greater the tendency for spark knocks to occur, and the higher the octane quality required. By retarding the ignition timing, the tendency for knock will decrease, and conversely. Going beyond a certain limit will adversely effect the engine power output, however. This sensitivity to ignition timing distinguishes knock from other forms of abnormal combustion such as pre-ignition or run-on.

The sequence of events in the combustion chamber when knock occurs is well known as shown in Fig. 1-4. As the flame propagates from the spark plug, the temperature and pressure of the unburned gasses ahead of the flame front are raised due to the heat from the flame itself, and the pressure of the expanding gasses. Because of this temperature increase, preflame reactions take place at an increasing rate and may eventually reach a point when the mixture will self-ignite. In normal combustion this

5

stage is never reached because there is insufficient time for this to occur. As engine speed is increased, the time for preflame ignition to take place is reduced, so the tendency to knock decreases, although normally engine timing is advanced as engine speed increases.

Figure 1: Induction stroke in the combustion chamber of a gasoline engine

Figure 1: INDUCTION STROKE

Intake Valve

Cylinder

Air & Fuel

Piston

1. Induction
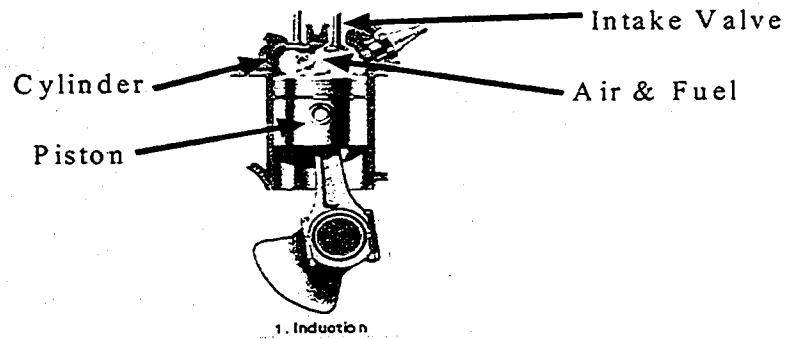
Figure 2: Compression stroke in the combustion chamber of a gasoline engine

Figure 2: COMPRESSION STROKE

Compressed air fuel mixture to 1/10 of original volume

2. Compression
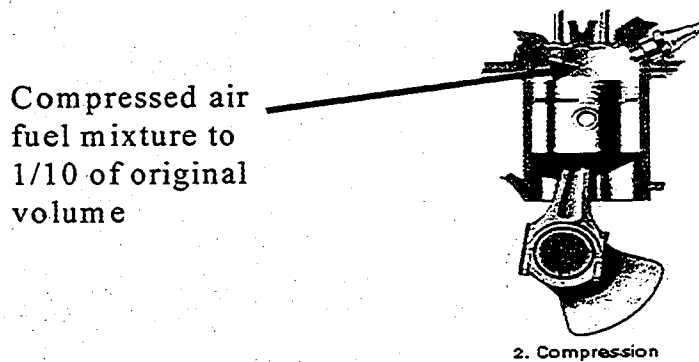
Figure 3: Expansion stroke in the combustion chamber of a gasoline engine

Figure 3: EXPANSION STROKE

Spark Plug

3. Expansion or power
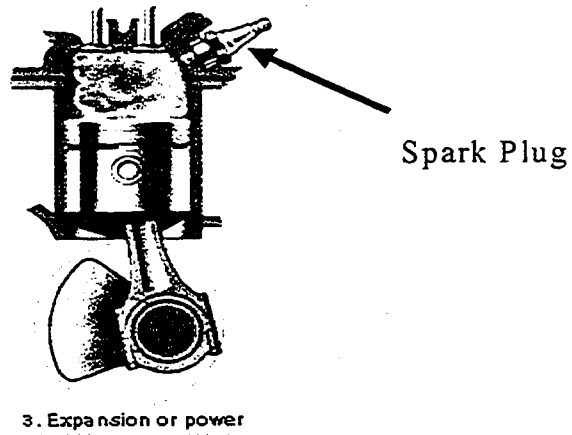
Figure 4: Exhaust stroke in the combustion chamber of a gasoline engine

Figure 4: EXHAUST STROKE

4. Exhaust
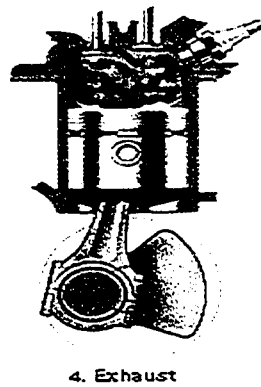
The auto-ignition of the end gasses causes a rapid increase in pressure, setting up a pressure wave, which resonates in the combustion chamber at a frequency of 5000 to 8000 Hz, depending on the chamber geometry. This produces the characteristic pinking sound associated with knock. Knock during acceleration at wide open throttle from a low engine speed is of such short duration, that it does not normally cause damage, and unless it is severe, will not cause loss of power. High constant-speed knock, however, can cause loss of power and severe damage usually to the cylinder head gasket, the spark plug electrodes, and the piston head. In extreme cases, knock can lead to preignition and runaway knock where the knock intensity gets progressively higher until catastrophic engine damage occurs. [8]

CHAPTER 2

SPARK IGNITION ENGINE KNOCK AND ENGINE OCTANE

Since 1912 the spark ignition internal combustion engine's compression ratio had been constrained by the unwanted "knock" that could rapidly destroy engines. "Knocking" is a very good description of the sound heard from an engine using fuel of too low octane. The engineers had blamed the "knock" on the battery ignition system that was added to cars along with the electric self-starter. The engine developers knew that they could improve power and efficiency if knock could be overcome.

Kettering assigned Thomas Midgley, Jr. to the task of finding the exact cause of knock. They used a Dobbie-McInnes manograph to demonstrate that the knock did not arise from pre-ignition, as was commonly supposed, but arose from a violent pressure rise *after* ignition. The manograph was not suitable for further research, so Midgley and Boyd developed a high-speed camera to see what was happening. They also developed a "bouncing pin" indicator that measured the amount of knock. Ricardo had developed an alternative concept of HUCF [Highest Useful Compression Ratio] using a variable-compression engine. His numbers were not absolute, as there were many variables, such as ignition timing, cleanliness, spark plug position, engine temperature.

In 1927 Graham Edgar suggested using two hydrocarbons that could be produced in sufficient purity and quantity. These were "normal heptane", that was already obtainable in sufficient purity from the distillation of Jeffrey pine oil, and " an octane, named 2,4,4-trimethyl pentane " that he first synthesized. Today we call it " iso-octane " or 2,2,4-trimethyl pentane. The octane had a high antiknock value, and he suggested

using the ratio of the two as a reference fuel number. He demonstrated that all the commercially-available Gasoline could be bracketed between 60:40 and 40:60 parts by volume heptane:isooctane. The properties of n-heptane and isooctane are shown in Table2

The reason for using normal heptane and isooctane was because they both have similar volatility properties, specifically boiling point, thus the varying ratios 0:100 to 100:0 should not exhibit large differences in volatility that could affect the rating test.

Table 2. Properties of Normal Heptane and Isooctane

Property	Melting Point	Boiling Point	Density	Heat of Vaporization
Units	°C	°C	g/ml	MJ/kg
Normal Heptane	-90.7	98.4	0.684	0.365 @ 25 °C
Isooctane	-107.45	99.3	0.6919	0.308 @ 25 °C

Having decided on standard reference fuels, a whole range of engines and test conditions appeared, but today the most common are the Research Octane Number [RON], and the Motor Octane Number [MON].

To obtain the maximum energy from the gasoline, the compressed fuel-air mixture inside the combustion chamber needs to burn evenly, propagating out from the spark plug until all the fuel is consumed. This would deliver an optimum power stroke. In real life, a series of pre-flame reactions will occur in the un-burnt "end gases" in the combustion chamber before the flame front arrives. If these reactions form molecules or species that can auto-ignite before the flame front arrives, knock will occur. [11]

Simply put, the octane rating of the fuel reflects the ability of the sunburn end gases to resist spontaneous auto-ignition under the engine test conditions used. If auto-ignition occurs, it results in an extremely rapid pressure rise, as both the desired spark-initiated flame front, and the undesired auto-ignited end gas flames are expanding. The combined pressure peak arrives slightly ahead of the normal operating pressure peak, leading to a loss of power and eventual overheating. The end gas pressure waves are superimposed on the main pressure wave, leading to a saw-tooth pattern of pressure oscillations that create the "knocking" sound. [8]

The combination of intense pressure waves and overheating can induce piston failure in a few minutes. Knock and pre-ignition are both favored by high temperatures, so one may lead to the other. Under high-speed conditions knock can lead to pre-ignition, which then accelerates engine destruction.

The fuel property the octane ratings measure is the ability of the un-burnt end gases to spontaneously ignite under the specified test conditions. Within the chemical structure of the fuel is the ability to withstand pre-flame conditions without decomposing into species that will autoignite before the flame-front arrives. Different reaction mechanisms, occurring at various stages of the pre-flame compression stroke, are responsible for the undesirable, easily-autoignitable, end gases.

During the oxidation of a hydrocarbon fuel, the hydrogen atoms are removed one at a time from the molecule by reactions with small radical species [such as OH and HO_2], and O and H atoms. The strength of carbon-hydrogen bonds depends on what the carbon is connected to. Straight chain Hydrocarbons such as normal heptane have

12

secondary C-H bonds that are significantly weaker than the primary C-H bonds present in branched chain hydrocarbons like isooctane. [12]

The octane rating of hydrocarbons is determined by the structure of the molecule, with long, straight hydrocarbon chains producing large amounts of easily-autoignitable pre-flame decomposition species, while branched and aromatic hydrocarbons are more resistant. This also explains why the octane ratings of paraffins consistently decrease with carbon number. In real life, the unburnt "end gases" ahead of the flame front encounter temperatures up to about 700 °C due to compression and radiant and conductive heating, and commence a series of pre-flame reactions. These reactions occur at different thermal stages, with the initial stage [below 400 °C] commencing with the addition of molecular oxygen to alkyl radicals, followed by the internal transfer of hydrogen atoms within the new radical to form an unsaturated, oxygen-containing species. These new species are susceptible to chain branching involving the HO_2 radical during the intermediate temperature stage [400-600 °C], mainly through the production of OH radicals. Above 600 °C, the most important reaction that produces chain branching is the reaction of one hydrogen atom radical with molecular oxygen to form O and OH radicals.

The addition of additives such as alkyl lead and oxygenates can significantly affect the pre-flame reaction pathways. Antiknock additives work by interfering at different points in the pre-flame reactions, with the oxygenates retarding undesirable low temperature reactions, and the alkyl lead compounds react in the intermediate temperature region to deactivate the major undesirable chain branching sequence. [11]

The antiknock ability is related to the "auto-ignition temperature" of the hydrocarbons. Antiknock ability is not substantially related to: The energy content of fuel

[this should be obvious, as oxygenates have lower energy contents, but high octanes], or the flame speed of the conventionally ignited mixture [this should be evident from the similarities of the two reference hydrocarbons]. Although flame speed does play a minor part, there are many other factors that are far more important [such as compression ratio, stochiometry, combustion chamber shape, chemical structure of the fuel, presence of antiknock additives, number and position of spark plugs, turbulence etc.] Flame speed does not correlate with octane. [9]

2.1 OCTANE AND KNOCK MEASUREMENT

The correct name for the [RON+MON]/2 formula is the *"antiknock index"*, and it remains the most important quality criteria for motorists. The initial knock measurement methods developed in the 1920s resulted in a diverse range of engine test methods and conditions, many of which have been summarized by Campbell and Boyd. In 1928 the Co-operative Fuel Research Committee formed a sub-committee to develop a uniform knock-testing apparatus and procedure. They settled on a single-cylinder, valve-in-head, water-cooled, variable compression engine of 3.5"bore and 4.5" stroke. The knock indicator was the bouncing-pin type. They selected operating conditions for evaluation that most closely match the current Research Method, however correlation trials with road octanes in the early 1930s exhibited such large discrepancies that conditions were changed [higher engine speed, hot mixture temperature, and defined spark advance profiles], and a new tentative ASTM Octane rating method was produced. This method is similar to the operating conditions of the current Motor Octane procedure. Over several decades, a large number of alternative octane test methods appeared. These

14

were variations to either the engine design, or the specified operating conditions. During the 1950-1960s attempts were made to internationally standardize and reduce the number of Octane Rating test procedures. [8]

During the late 1940s - mid 1960s, the Research method became the important rating because it more closely represented the octane requirements of the motorist using the fuels/vehicles/roads then available. In the late 1960s German auto-makers discovered their engines were destroying themselves on long Autobahn runs, even though the Research Octane was within specification. They discovered that either the MON or the Sensitivity [the numerical difference between the RON and MON numbers] also had to be specified. Today it is accepted that no one octane rating covers all use. In fact, during 1994, there have been increasing concerns in Europe about the high Sensitivity of some commercially-available unleaded fuels. [12]

The design of the engine and vehicle significantly affect the fuel octane requirement for both RON and MON. In the 1930s, most vehicles would have been sensitive to the Research Octane of the fuel, almost regardless of the Motor Octane, whereas most 1990s engines have a 'severity" of one, which means the engine is unlikely to knock if a changes of one RON is matched by an equal and opposite change of MON. It should be noted that the Research method was only formally approved in 1947, but used unofficially from 1942. [10]

2.1.1 Octane Number Sensitivity:

RON - MON = Sensitivity.

Because the two test methods use different conditions, especially the intake mixture temperatures and engine speeds, then a fuel that is sensitive to changes in

operating conditions will have a larger difference between the two rating methods. Modern fuels typically have sensitivities around 10. The US 87 [RON+MON]/2 unleaded gasoline is recommended to have a 82+ MON, thus preventing very high sensitivity fuels. Recent changes in European Gasoline has caused concern, as high sensitivity unleaded fuels have been found that fail to meet the 85 MON requirement of the EN228 European gasoline specification. [8]

2.1.2 Octane Engine

Automotive octane ratings are determined in a special single-cylinder engine with a variable compression ratio (CR 4:1 to 18:1) known as a Cooperative Fuels Research (CFR) engine. The cylinder bore is 82.5 mm, the stroke is 114.3mm, giving a displacement of 612 cm^3. The piston has four compression rings, and one oil control ring. The intake valve is shrouded. The head and cylinder are one piece, and can be moved up and down to obtain the desired compression ratio. The engines have a special four-bowl carburetor that can adjust individual bowl air-fuel ratios. This facilitates rapid switching between reference fuels and samples. A magneto-restrictive detonation sensor in the combustion chamber measures the rapid changes in combustion chamber pressure caused by knock, and the amplified signal is measured on a "knock-meter" with a 0-100 scale. A complete Octane Rating engine system costs about $200,000 with all the services installed. Only one company manufactures these engines, the Waukesha Engine Division of Dresser Industries, Waukesha. WI 53186. (8)

The conditions of the Motor method represent severe, sustained high speed, high load driving. For most hydrocarbon fuels, including those with either lead or oxygenates,

16

the motor octane number (MON) will be lower than the research octane number (RON). The motor Octane Number and Research Octane Number conditions are listed consequently in Tables 3 and 4.

Table 3. Motor Octane Number Test Conditions

Test Engine Conditions	Motor Octane
Test Method	ASTM D2700-92 [104]
Engine	Cooperative Fuels Research (CFR)
Engine RPM	900 RPM
Intake Air Temperature	38 °C
Intake Air Humidity	3.56 - 7.12 g H2O / kg dry air
Intake Mixture Temperature	149 °C
Coolant Temperature	100 °C
Oil Temperature	57 °C

Table 4. Research Octane Number Test Conditions

Test Engine Conditions	Research Octane
Test Method	ASTM D269992 [105]
Engine	Cooperative Fuels Research [CFR]
Engine RPM	600 RPM
Intake Air Temperature	Varies With Barometric Pressure [88kPa=19.4 °C, 101.6kPa=52.2 °C]
Intake Air Humidity	3.56 - 7.12 g H2O / kg dry air
Intake Mixture Temperature	Not Specified
Coolant Temperature	100 °C
Oil Temperature	57 °C

To rate a fuel, the engine is set to an appropriate compression ratio that will produce a knock of about 50 on the knock-meter for the sample when the air-fuel ratio is adjusted on the carburetor bowl to obtain maximum knock. Normal heptane and iso-octane are known as primary reference fuels. Two blends of these are made, one that is one octane number above the expected rating, and another that is one octane number below the expected rating. These are placed in different bowls, and are also rated with each air-fuel ratio being adjusted for maximum knock. The higher-octane reference fuel should produce a reading around 30-40, and the lower reference fuel should produce a reading of 60-70. The sample is again tested, and if it does not fit between the reference fuels, further reference fuels are prepared, and the engine readjusted to obtain the required knock. The actual fuel rating is interpolated from the knock-meter readings. [8]

CHAPTER 3

FUEL PROPERTIES

The combination of vehicle and engine can result in specific requirements for octane that depend on the fuel. If the octane is distributed differently throughout the boiling range of a fuel, then engines can knock on one brand of 87 [RON+MON]/2, but not on another brand. This "octane distribution" is especially important when sudden changes in load occur, such as high load, full throttle, and acceleration. The fuel can segregate in the manifold, with the very volatile fraction reaching the combustion chamber first and, if that fraction is deficient in octane, then knock will occur until the less volatile, higher- octane fractions arrive.

Some fuel specifications include delta RONs, to ensure octane distribution throughout the fuel boiling range was consistent. Octane distribution was seldom a problem with the alkyl lead compounds, as the tetra methyl lead and tetra ethyl lead octane volatility profiles were well characterized, but it can be a major problem for the new, reformulated, low aromatic Gasoline, as MTBE boils at 55 °C, whereas ethanol boils at 78 °C. Drivers have discovered that an 87 [RON+MON]/2 from one brand has to be substituted with an 89 [RON+MON]/2 of another, and that is because of the combination of their driving style, engine design, vehicle mass, fuel octane distribution, fuel volatility, and the octane-enhancers used. [12]

To obtain an indication of behavior of a gasoline during any manifold segregation, an octane rating procedure called the Distribution Octane Number was used. The rating engine had a special manifold that allowed the heavier fractions to be

separated before they reached the combustion chamber. That method has been replaced by the "delta" RON procedure.

The fuel is carefully distilled to obtain a distillate fraction that boils to the specified temperature, which is usually 100C. Both the parent fuel and the distillate fraction are rated on the octane engine using the Research Octane method. The difference between these is the delta RON[100C], usually just called the delta RON. The delta RON ratings are not particularly relevant to engines with injectors, and are not used in the US.

Several other properties affect knock. The most significant determinant of octane is the chemical structure of the hydrocarbons and their response to the addition of octane enhancing additives. [9] Other factors include:

3.1   FRONT END VOLATILITY:

Paraffins are the major component in gasoline, and the octane number decreases with increasing chain length or ring size, but increases with chain branching. Overall, the effect is a significant reduction in octane if front-end volatility is lost, as can happen with improper or long term storage. Fuel economy on short trips can be improved by using a more volatile fuel, at the risk of carburetor icing and increased evaporative emissions.

3.2   FINAL BOILING POINT:

Decreases in the final boiling point increase fuel octane. Aviation Gasoline have much lower final boiling points than automotive Gasoline. Note that final boiling points are being reduced because the higher boiling fractions are responsible for disproportionate quantities of pollutants and toxins.

On modern engines with sophisticated engine management systems, the engine can operate efficiently on fuels of a wider range of octane rating, but there remains an optimum octane for the engine under specific driving conditions. Older cars without such systems are more restricted in their choice of fuel, as the engine can not automatically adjust to accommodate lower octane fuel. Because knock is so destructive, owners of older cars must use fuel that will not knock under the most demanding conditions they encounter, and must continue to use that fuel, even if they only occasionally require the octane. [11]

If the proper octane fuel is being used, it will not be possible to obtain more power from higher-octane fuels. The engine will be already operating at optimum settings, and a higher octane should have no effect on the management system. Your drivability and fuel economy will remain the same. The higher-octane fuel costs more, so you are just throwing money away. If you are already using a fuel with an octane rating slightly below the optimum, then using a higher octane fuel will cause the engine management system to move to the optimum settings, possibly resulting in both increased power and improved fuel economy. You may be able to change octanes between seasons [reduce octane in winter] to obtain the most cost-effective fuel without loss of drivability.

3.3   OCTANE REQUIREMENTS

Once the fuel that keeps the engine at optimum settings has been supplied, there is no advantage in moving to an even higher-octane fuel. The manufacturer's recommendation is conservative, so you may be able to carefully reduce the fuel octane.

The penalty for getting it badly wrong, and not realizing that you have, could be expensive engine damage.

If the octane requirement is not met, the engine will rapidly suffer major damage due to knock. You must not use fuels that produce sustained audible knock, as engine damage will occur. If the octane is just sufficient, the engine management system will move settings to a less optimal position, and the only major penalty will be increased costs due to poor fuel economy. Whenever possible, engines should be operated at the optimum position for long-term reliability. Engine wear is mainly related to design, manufacturing, and maintenance and lubrication factors. Once the octane and run-on requirements of the engine are satisfied, increased octane will have no beneficial effect on the engine. Run-on is the tendency of an engine to continue running after the ignition has been switched off. The quality of gasoline, and the additive package used, would be more likely to affect the rate of engine wear, rather than the octane rating. [11]

Attempts to mix leaded high octane to unleaded high octane to obtain higher octane are useless for most commercial gasoline. The lead response of the unleaded fuel does not overcome the dilution effect, thus 50:50 of 96 leaded and 91 unleaded will give 94. Some blends of oxygenated fuels with ordinary gasoline can result in undesirable increases in volatility due to volatile azeotropes, and some oxygenates can have negative lead responses. The octane requirement of some engines is determined by the need to avoid run-on, not to avoid knock.

3.3.1 Octane Number Requirements

The actual octane requirement of a vehicle is called the **Octane Number Requirement [ONR]**, and is determined by using series of standard octane fuels that can be blends of iso-octane and normal heptane [primary reference], or commercial Gasoline [full-boiling reference]. In Europe, delta RON [100C] fuels are also used, but seldom in the USA. The vehicle is tested under a wide range of conditions and loads, using decreasing octane fuels from each series until trace knock is detected. The conditions that require maximum octane are not consistent, but often are full-throttle acceleration from low starting speeds using the highest gear available. They can even be at constant speed conditions, which are usually performed on chassis dynamometers. Engine management systems that adjust the octane requirement may also reduce the power output on low octane fuel, resulting in increased fuel consumption, and adaptive learning systems have to be preconditioned prior to testing. The maximum ONR is of most interest, as that usually defines the recommended fuel, however it is recognized that the general public seldom drive as severely as the testers, and so may be satisfied by a lower octane fuel. [7]
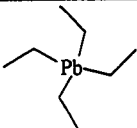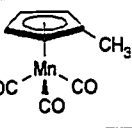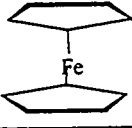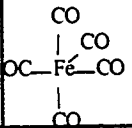
CHAPTER 4

FUEL ALTERNATIVES AND GASOLINE OCTANE IMPROVERS

Most refiners have been inspired to re-examine some alternative gasoline additives such as the metallanes: methylcyclopentadienyl manganese tricarbonyl [MMT], iron pentacarbonyl [IPC], and di-cyclopentadienyl iron [DCI]. The acceptance of these alternative octane improvers is not yet widespread, and most refiners are seeking more information on their performance, toxicity, and impact on engine maintenance. While Ethyl, Octel, and Novaktan continue with their evaluation and development of these additives, individual fuel providers are now undertaking their own studies, to discern the octane response, stabilities, compatibilities, synergies, and usable ranges. The limitation on usage of iron and manganese to levels of around 30 mg/liter is due primarily to engine and converter deposits. This is unfortunate, since we have been able to demonstrate up to 10 octane points gain from using iron in combination with an oxygenate carrier. We have already identified an excellent scavenger for ferrous oxides on aluminum surfaces, however, and will be working with additive developers to try to develop a way to use this additive to alleviate engine deposits. The evolution of gasoline continues as environmental issues and government regulations continue to pressure the fuel industry. Controversial decreasing targets for sulfur levels remain a challenge to process developers and refiners, and the debate continues to resonate in North America, Europe, and Asia. Recent bans on MTBE will abruptly deny a valuable blending component, and diminish our efforts to combat air pollution. The increasing content of unstable cracked stock from pyrolysis, FCC, and hydrocrackers require additional stabilizers and

antioxidants. Sulfur regulations and fuel instability are stimulating the development of selective catalysts for pyrolysis and FCC gasoline sulfur and gum reduction. The elimination of lead from the last few regions still using it, requires refinery upgrades and alternative octane improvers. Used additives in this study are shown in Table 5

Table 5: Comparison between candidate gasoline additives

	__TEL__	__MMT__	__DCI__	__IPC__
Chemical Name	Tetraethyl Lead	Methylcycyclopentadienyl Manganese Tricarbonyl	Dicyclopentadienyl Iron	Iron Pentacarbonyl
Structure				
Manufacturer	Associate Octel	Ethyl Corp.	Octel-Novaktan	Alcor-Novaktan
Location	UK	USA	UK-FRG	FRG
Concentration	112 g Pb/liter	4 g Mn/liter		10 g Fe/liter
Carrier	Toluene / Heptane	Toluene	Xylenes	Ethanol
Typical Level	250 mg/liter	30 mg/liter	30 mg/liter	30 mg/liter

Alternatives are needed to replace current octane [anti-knock] enhancers in gasoline, to oxygenate [add oxygen to] gasoline for pollution reduction, and to extend dwindling supplies of light crude petroleum used to produce transportation fuels.

4.1 GASOLINE ADDITIVES AND ENVIRONMENT

All gasoline additives are considered to be toxic, except for perhaps alkylate. Nevertheless, refiners must continue to provide higher octane fuels with tightening economics, tighter environmental controls, and lower quality feedstocks. As there are many commercial octane enhancers available, the relative merits of these additives need to be compared. This study is to perform an evaluation of the effect of using octane improving additives in fuel from four Saudi Arabian Refineries on gasoline produced in the Kingdom. These additives such as iron and manganese alkyls, unlike lead, have no reported adverse effects on the environment, and manganese additives have a proven performance record with respect to engine performance, automobile maintenance, and octane improvement. Aromatics including benzene are considered toxic and carcinogenic. Tetraethyl and tetramethyl lead are highly toxic. Iron pentacarbonyl is toxic, water soluble, and spontaneously combustible, and thermally unstable. Methylcyclopentadienyl tricarbonyl is considered by many to be a health and environmental hazard. Dicyclopentadienyl Iron or Ferrocene is considered to be non-toxic and harmless. MTBE is suspected of causing liver ailments and other health problems, and because of it's water solubility, has invaded the California water supply, and may be subject to restriction or an outright ban in some states.

Environmentalists don't want any additives in gasoline, and don't even like us to use gasoline. Auto manufacturers don't like any gasoline additives except lead, and they certainly don't like catalytic converters or emission controls. Nevertheless, refiners must continue to provide higher octane fuels with tightening economics, tighter environmental controls, and lower quality feedstock.

The 1990 Clean Air Act Amendments set stringent rules governing the quality and characteristics of gasoline used in the United States. These regulations have caused oxygenates such as MTBE and ethyl alcohol to play a significant role as gasoline octane improvers. Overall U.S. oxygenate demand in MTBE equivalents amounted to nearly 12 million metric tons in 1993, with MTBE accounting for nearly half. Total U.S. oxygenate demand will amount to nearly 19 million metric tons of MTBE equivalents in 1997, with MTBE accounting for over half. The extent of ethyl alcohol's role in reformulated gasoline is uncertain until the EPA makes a final ruling.

Evaluation of the environmental impact of a new fuel additive is a massive project, typically involving the close scrutiny of large fleets of controlled study automobiles over the course of several years. This is beyond the scope of our investigation. Our preliminary efforts will include literature review of the known and projected toxicological and environmental effects of the additive chemical package ingredients, and their known or identifiable oxidation products.

4.2 OXYGENATES

Oxygenates are compounds such as alcohols and ethers which contain oxygen in their molecular structure. Oxygenates improve combustion efficiency, thereby reducing polluting emissions. Many oxygenates also serve as excellent octane enhancers when blended with gasoline. ARCO Chemical is a pioneer in the development of gasoline additives based on the TBA molecule. Since the 1970's, these additives have been incorporated into gasoline to help meet increasing standards for cleaner burning fuels. Other oxygenates such as tertiary-amyl methyl ether [TAME], ethyl tertiary-butyl ether

28

[ETBE], and di-isopropyl ether [DIPE] may be manufactured by modification of MTBE units. In order to meet the increasing oxygenate needs of refiners, ARCO Chemical developed TBA, MTBE, TAME and ETBE as fuel additives, volume extenders, octane improvers, and oxygen carriers. Physical and Chemical properties of oxygenates appear in Table 6. All of these oxygenates will suffer the same objections to health and environmental concerns that MTBE has encountered. [13]

Table 6. Properties of Oxygenated Fuel Blending Components

Name	Methanol	Ethanol	i-Propanol	t-Butanol	MTBE	ETBE	TAME	Gasoline
Formula	CH_3OH	C_2H_5OH	$[CH_3]_2OH$	C_4H_9OH	$C_4H_9OCH_3$	$C_4H_9OC_2H_5$	$C_5H_{11}OCH_3$	C_4 to C_{12}
Mol. Wt.	32.04	46.07	60.09	74.12	88.15	102.18	102.18	100-105
Composition Weight %								
Carbon	37.5	52.2	60.0	64.8	68.1	70.5	70.5	85-88
Hydrogen	12.6	13.1	13.4	13.6	13.7	13.8	13.8	12-15
Oxygen	49.9	34.7	26.6	21.6	18.2	15.7	15.7	0
Spec. gravity 60 °F/60 °F	0.796	0.794	0.789	0.791	0.744	0.742	0.770	0.72-0.78

Contd.

30

Density lb/gal 60°F	6.63	6.61	6.57	6.59	6.19	6.25	6.41	6.0-6.5
Boiling Temp Temperature °F	149	172	180	181	131	164	187	80-437
Reid Vapor Pressure psi	4.6	2.3	1.8	1.8	7.8	4.4	1.5	8-15

Contd.

31

Water								
Solubility @ 70								
°F	100	100	100	100	4.3	--	--	Neg.
Fuel / Water	100	100	100	100	1.4	--	0.6	Neg.
Vol%								
Water / Fuel								
Vol %								
Viscocity								
@ 68 °F	0.59	1.19	2.38	4.2	0.35	--	--	0.37-0.44
@ -4 °F	1.15	2.84	9.41	Solid	0.6	--	--	0.60-0.77

Contd.

32

Auto-ignition Temperature °F	867	793	750	892	815	--	--	495
Flammability Limits								
Vol. %								
Lower	7.3	4.3	2.0	2.4	1.6	--	--	1.4
Upper	36.0	19.0	12.0	8.0	8.4	--	--	7.6
Heating Value								
Lower BTU/gal								
@ 60 °F	8570	11500	13300	14280	15100	--	15690	18500
BTU/lb @60 °F	56800	76000	87400	94100	93500	--	100600	114000
Blending RON	127-136	120-135	--	104-110	115-123	110-119	111-116	89-101
Blending MON	99-104	100-106	--	90-98	98-104	95-104	98-103	82-97

33

4.2.1 Methyl Tertiary Butyl Ether [MTBE]:

MTBE is an oxygenate which has been used in recent years in the U.S. and Canada as an octane-enhancer for gasoline. It is currently manufactured from methanol [derived from natural gas] and isobutylene [an oil refinery product]. In the mid-1970's, ARCO Chemical developed MTBE, a derivative of TBA, as a high octane gasoline component which not only replaced octane lost in the phasing out of lead, but also added oxygen to gasoline. This results in cleaner burning gasoline and helps refiners meet the specifications of the Clean Air Act of 1990. ARCO Chemical's Channelview, Texas plant was the world's largest MTBE production facility, until overtaken by Saudi Arabia's Sabic Complex in Al-Jubail. [15]

Worldwide MTBE annual capacity amounted to nearly 14 million metric tons in 1992 and is projected to increase to over 24 million metric tons by 1997. Based on this capacity projection, the operating rate would increase to about 85% worldwide in 1997, up from 70% in 1992. North America is by far the largest market, accounting for over 50% of world capacity. Western Europe, the Middle East and Asia together accounted for another 40% of world capacity. Most of the capacity additions are expected in the Middle East, South America and the United States. Western Europe does not have mandated oxygenate requirements. However, as the consumption of lead alkyls has decreased rapidly, the consumption of MTBE for octane enhancement has increased significantly. The availability of C_4 streams at an acceptable price is expected to be a significant limiting factor to the increasing use of MTBE in Western Europe. [14] Other gasoline improvers have only secondary importance in Europe; however, ETBE and TAME could gain more importance. MTBE demand is projected to increase from 2.8 million metric

tons in 1992 to 3.9 million metric tons in 1997. In Japan, practically no lead alkyls and very small amounts of oxygenated blending agents are currently used as gasoline octane improvers due to the fact that many Japanese automotive engine designs do not require as high an octane-rated gasoline. However, in November 1991, the Ministry of International Trade and Industry approved the use of MTBE as an octane improver in premium gasoline, allowing a blend of 7 volume percent of MTBE. Ethanol, methanol, TBA and TAME are not currently used as gasoline additives in Japan. Japanese consumption of MTBE is projected to increase from 35 thousand metric tons in 1992 to 200 thousand metric tons in 1997, mainly as a result of a projected increase in premium gasoline demand. [15]

4.2.2   Ethyl Tertiary Butyl Ether [ETBE]

ETBE is another gasoline additive produced from TBA. This material is produced from isobutylene and ethanol and has superior RVP and octane properties to MTBE, although more expensive than MTBE, has the technical superiority [slightly higher octane and lower energy content] to promote its use in the future. ETBE is manufactured from ethanol and isobutylene. The lower volatility of ETBE, relative to other oxygenates, would help reduce the evaporative emissions, but could cause problems with respect to cold starting and driveability. TAEE [tertiary amyl ethyl ether], the ethanol-based counterpart of TAME, is also being evaluated as an oxygenate. [15]

4.2.3 Di-isopropyl Ether [DIPE]

DIPE is another new ether oxygenate. It is manufactured by reaction of two molecules of propylene with one molecule of water. As far as raw materials go, it is much cheaper than the methanol ethers. The process is offered by UOP, and only a few facilities have been built. [16]

4.2.4 Tertiary Butyl Alcohol [TBA]

Initially, TBA was blended into gasoline as a high octane component to replace tetraethyl lead. After over 25 years of use by refiners in the U.S. and Europe, ARCO Chemical's original blending component, TBA, is still a cost-effective oxygenated octane enhancer. Because it behaves more like an ether rather than alcohol, gasoline with TBA can be transported via pipeline and intermixed with ether blends. [17]

4.2.5 Ethanol

It is a non-corrosive and relatively non-toxic alcohol made from renewable biological feedstocks. It is used directly as fuel [most commonly in Brazil], or as an octane-enhancing gasoline additive [throughout the United States, Canada and Europe]. Approximately 8-9% of all U.S. gasoline contains ethanol at a blending percentage of 10%. In Canada, blends containing 5-10% ethanol in gasoline are being marketed by several companies [throughout Ontario, Quebec, the western provinces and the Yukon]. Blends of 10% ethanol with gasoline can be used in all gasoline-powered automobiles, without engine or carburetor modification. [17]

4.2.6 Methanol:

It is an alcohol made from natural gas, biomass or coal. It can be used directly as an automobile fuel [the automobile engine needs modification for this purpose], or as a gasoline-blending compound. When methanol is blended with gasoline, a co-solvent such as ethanol is required. Methanol is quite corrosive and poisonous. Methanol is produced primarily, as a derivative of natural gas. [17]

Several other compounds have been investigated as octane improvers. These include amines, sulfur compounds, selenium compounds, tin, mercury, germanium, and boron compounds. Although some of these show promise, all were found to have some drawback, such as toxicity, reactivity, or harmful effects to the engine and mechanical system. [18]

CHAPTER 5

OCTANE ENHANCERS

5.1 HYDROCARBONS

5.1.1 Aromatic Hydrocarbons

These are petroleum-derived compounds including benzene, xylene and toluene characterized by the "benzene" ring in their molecular structure. They are being used increasingly in recent years as octane enhancers, even though some of them are carcinogenic [e.g., benzene], or form highly toxic compounds during combustion. [3,4]

5.1.2 Propane and Natural Gas

Both of these fuels are based on fossil hydrocarbons and, therefore, their combustion contributes to increased levels of atmospheric carbon dioxide. As well, modifications to vehicles are required to use these fuels. In Canada, federal and provincial governments have provided fuel tax reductions or exemptions, as well as grants for vehicle conversion, to encourage the use of these "alternative" fuels. [6]

5.2 OCTANE ENHANCERS METALLIC COMPOUNDS

Metallanes include many different types of organometallic compounds in which the carbon atoms are bonded directly to the metals. [19] Of course the most well known of these is tetraethyl lead, and the other lead alkyls. Many of the metallanes are toxic,

often due to the toxicity of the metal itself, or the toxicity of the ligand group, as is true of all the metal carbonyls. [20,21]. The chemical and physical properties of used metallanes are listed in Table 7. Their safety limits are shown in Table 8.

Table 7. Properties of Metallance Antiknocks

	TEL	MMT	DCI	IPC
Chemical Name	Tetraethyl Lead	Methylcyclopentadienyl Manganese Tricarbonyl	Dicyclopentadienyl Iron	Iron Pentacarbonyl
Formula	$Fe[CO]_5$	$[C_5H_5]_2Fe$	$Pb[C_2H_5]_4$	$C_9H_7MnO_3$
Formula mass	195.9	186.03	323.45	218.1
Melting pt. [°C]	-20	173	-136.8	2.2
Boiling pt. [°C]	103	249	200 [decomposes]	231.7
Specific gravity	1.49		1.7	1.39
Solubility in water	Insoluble	Insoluble	0.02 mg/100ml	Insoluble
Flash point [°C]	-15		77	110

40

Table 8. Safety Limits for Metallanes

Property	TEL	MMT	DCI	IPC
Hazards	The vapor is heavier than air. Decomposes on heating above 110 C and under influence of light producing toxic fumes: carbon monoxide, lead. Reacts violently with strong oxidizers, acids, halogens, oils and fats causing fire and explosion hazard. Attacks rubber and some plastics and coatings.	On combustion, forms toxic or irritating fumes including manganese oxides and carbon monoxide. Decomposes under influence of light. Class IIIB Combustible Liquid.	Ammonium perchlorate, tetranitromethane, mercury[II] nitrate. Combustible Solid.	The vapor is more dense than air. It may travel along the ground and be ignited at a distant location. May explode on heating. The substance may spontaneously ignite on contact with air. Decomposes on heating, on burning or under influence of light producing toxic gases including iron oxides and carbon monoxide. The substance is a strong reducing agent and reacts violently with oxidizers. Class IB Flammable Liquid. marine pollutant.

5.2.1 Methylcyclopentadienyl Manganese Tricarbonyl [MMT]:

MMT is widely used in Canada as an octane enhancer in lead-free gasoline. In the U.S., the Environmental Protection Agency [EPA] banned MMT usage in lead-free gasoline for many years. This ban was over-turned as the result of a 1995 court challenge. [31] However, MMT usage in U.S. gasoline remains very small. Automobile manufacturers are opposed to the use of MMT-blended gasoline in vehicles equipped with catalytic converters because MMT tends to plug the converters and oxygen sensors. All MMT used in Canada is imported from the United States. The Canadian government has introduced legislation to ban the importation of MMT for environmental reasons. [32,33] If MMT is removed from Canadian gasoline, ethanol would be an excellent replacement as an octane enhancer. MMT is a very valuable additive [octane booster] for unleaded gasoline that also provides numerous environmental benefits. [34,35]

Being a true antiknock additive [ppm treat rates], it gives refiners a lot of flexibility in gasoline blending. [36-41] Unlike TEL, the concentration of MMT in unleaded gasoline is only a few ppm. For example, for unleaded gasoline manufactured for catalyst-equipped automobiles, manufacturers recommend a maximum dosage of 18 mg Mn/liter as MMT. [42] Elimination of lead from gasoline, leaves many automobiles without catalysts and with engines that have soft exhaust valve seats, then they recommend a maximum concentration of 36 mg Mn/liter. [43] This concentration of manganese will protect engines from valve seat recession problems. The octane response of MMT at 18 mg Mn/liter in typical gasoline will provide an RON increase of 1.5 to 3.5 numbers depending on the octane level and the components of the blend. MMT will

respond best in saturated components, then olefinic, and lastly aromatics. [44] Also MMT responds better to RON than MON and to lower octane gasoline than higher octane gasoline. So, for example in the components listed, MMT will respond better to light naphtha and natural gasoline and not so well in high octane CCR reformate. Some limited octane work with MMT and oxygenates has been done, and the study confirmed that MMT works well with all of them. There is not any octane response synergy between MMT and any of the oxygenates nor is any negative response discernable when they appeared in tandem. That is, the octane response of the combination of MMT and oxygenate approximated the octane response of the sum of the MMT response alone and the oxygenate response alone. [45]

The auto industry criticizes it, the petroleum industry is avoiding it, the U.S. government was forced to legalize it, and animal studies suggest that its key ingredient can damage health. Yet MMT, a fuel additive that increases octane and reduces oxide emissions, is marketed worldwide as safe, effective and efficient. Its manufacturer, Ethyl Corporation, based in Richmond, Va., is so sure of MMT that it is now suing the Canadian government, which in April 1997 banned for health concerns the import and inter-province trade of MMT, after 20 years of use. [46]

Air-quality studies around Toronto reveal no risk of high-level exposure of MMT. But there have been no examinations of chronic, low-level exposure in humans, mainly because those types of experiments are tough to design. Jerry Pfeifer, a biochemist at Ethyl, points out that MMT is not the only source of airborne manganese. Commuting via the subway, he suggests, where the steel tracks are 12 percent manganese, has a much greater impact than MMT usage does. "Therefore, it is virtually impossible to design a

meaningful experiment to determine the long-term effects to low-level manganese from MMT because humans are already exposed to significant and variable amounts of manganese throughout their lives in air, food, water and soil," he said in a statement. [48]

Without human studies, no one can agree on a safe level. The U.S. Environmental Protection Agency set the reference concentration at 0.05 microgram of manganese per cubic meter, and the agency may increase it. In any case, the amount of manganese in air is well below this limit. Only one drop is added to a gallon of gasoline, and both Ethyl and the EPA concur that only 10 to 15 percent of the manganese in MMT becomes airborne. Such a small amount, Ethyl argues, poses no real threat.

The provinces of Alberta, British Columbia, Quebec, Saskatchewan and Nova Scotia apparently agree. Along with Ethyl, they have filed suit against the Canadian government's action against MMT, which is sold under the brand name HiTEC 3000. They argue that the transport ban violates the North American Free Trade Agreement. The case mirrors the controversy over another fuel additive: tetraethyl lead. Like MMT, it was known to be harmless at low doses when it was approved 75 years ago under pressure from its maker, also Ethyl. As it turned out, the increased use of lead in gasoline, combined with the use of lead in paints, was associated with severe neurological disorders, particularly in children. [49]

After the debacle of leaded gasoline, the EPA has been reluctant to legalize MMT, or methylcyclopentadienyl manganese tricarbonyl. Several times since 1978 Ethyl presented emissions studies to comply with the Clean Air Act, and each time the agency denied Ethyl's request for legalization, asking for more data. In 1995 Ethyl took the EPA

to federal court, which decided there was no basis for making MMT illegal. So the additive entered the U.S. bulk market. [50]

Right now the chances of coming across the additive at a U.S. gas station are slim. None of the major oil refineries currently use MMT. According to Ethyl, MMT's unpopularity does not stem from concern over adverse health effects. Jack Graham, an Ethyl spokesperson until this past March, suggests the large refineries have yet to adopt MMT simply because they have other options. "They can afford to make higher-octane gasoline and purchase other fuel additives, such as ethanol," he says. "The fact that they aren't buying it is just part of the ebb and flow of business." [51]

Oil companies may also be avoiding MMT because of pressure from auto makers. Mark Nantais of the Canadian Motor Vehicles Manufacturers Association states that "80 percent of the manganese in MMT stays in the vehicle and clogs the system," coating spark plugs, clogging hoses and impairing emissions-control devices. For those reasons, Ford, General Motors, Chrysler and Toyota discourage MMT use. Ethyl contests the charges, citing its own studies that dispute the auto industry's claims. [52]

5.2.2   Di-cyclopentadienyl Iron [DCI] or Ferrocene:

Geoffry Wilkenson won the Nobel Prize for the discovery of ferrocene, and other metallocenes. [23] Ferrocene has been used for over 50 years since World War II, in Germany it was utilized as an octane improver and combustion aid. Today it is used in many countries, such as Europe, South Africa, China, Australia. It has been introduced in the Philippines by Petron, the Saudi Aramco affiliate. Ferrocene has been reassessed as an antiknock more recently, at low concentrations [15-30 ppm] and it raises octane

values by 1-3 octane units. Drawbacks appear to be engine wear, combustion chamber deposits, and sparkplug fouling. It is manufactured by Associated Octel and Novaktan. Exhaust Emission Toxicological Data: DCI is classified in the EU as "Harmful if swallowed"the lowest class of toxicity for chemicals. And it's occupational exposure limit [TLV 8h TWA] is 10 mg/m$_3$ relative to 0.8 mg/m$_3$ for MMT. Testing at Motortestcenter in Sweden in 1993 met Swedish EPA requirements and demonstrated that DCI in gasoline presents no additional hazard over conventional gasoline. [26] Testing at Fraunhofer Institute in Germany completed in 1996 showed no differences in the toxic effects of exhausts derived from fuel with and without Ferrocene. [27] Based on the Fraunhofer study waiver from the German lead law [which from 1976 has banned the use of any metal in gasoline] was achieved from the BAW following recommendation by the UBA. Testing by Technik Themische Maschinen completed in 2000 does not effect controlled pollutants or fine particulates from catalyst vehicles. [28]

All trials and studies have shown excellent additive performance and no increases in engine deposits or wear. Selected vehicles have been returned to their OEM manufacturers and engines rated as normal after extended operation on DCI treated fuel. Octel has also coordinated a OEM 400hr engine durability tests confirm the absence of wear or deposits from DCI use. Reduced combustion chamber deposits have been linked to use of DCI treated fuel and linked to reduced octane requirement of vehicles. Testing using standard deposit test procedures such as CEC -PF-005 M102E Inlet Valve Cleanliness test show no increase in inlet valve or combustion chamber deposits from DCI use. [30]

5.2.3 Iron Pentacarbonyl [IPC]:

Iron pentacarbonyl has been used in both the US and Europe since the 1930s. It is manufactured in Germany by Alcor Chemie and Novaktan. It is typically formulated in ethanol at 1 percent concentration. IPC demonstrates many of the characteristics of Ferrocene, although it is very toxic and less stable. [22] It is often formulated with a diketone stabilizer, which may also function as a scavenger and deposit control additive. [23,24]

It is highly flammable, oily, and colourless to yellow liquid. The Agency proposed, and the final rule establishes, permissible exposure limits of 0.1 ppm In studies of rats, iron pentacarbonyl has been reported to have approximately one-third the acute toxicity of nickel carbonyl.

In 1970, Gage found that a 5.5-hour exposure at 33 ppm caused fatalities in three of eight rats; four of eight animals died after two 5.5-hour exposures at 18 ppm. At 7 ppm, no ill effects were observed in rats exposed 18 times in 5.5 hours. There are no reports of long-term dose-response exposure studies in laboratory animals, and no evidence exists that iron pentacarbonyl is carcinogenic in either humans or animals

Immediate symptoms of acute exposure to high concentrations of iron pentacarbonyl include headache and dizziness, followed in 12 to 36 hours by fever, cyanosis, cough, and shortness of breath. Another clinical effect of overexposure to this substance is lung injury, and degenerative changes in the central nervous system have also been reported

In the final rule, OSHA establishes a permissible exposure limit of 0.1 ppm. The Agency concludes that these limits will protect workers from the significant risks of

material health impairment in the form of headache, dizziness, fever, dyspnea, cyanosis, pulmonary injury, and central nervous system effects, which are potentially associated with exposures at levels above the new limits. Note references indicated above are:

NIOSH: National Institute for Occupational Safety and Health

ACGIH: American Conference of Government Industrial Hygienists

OSHA: Occupational Safety and Health Agency

CHAPTER 6

EXPERIMENTAL PROCEDURES

6.1 GASOLINE BLENDING

Gasoline blends were prepared for this project from authentic refinery blending streams obtained from Riyadh, Jeddah, Yanbu, and Ras Tanura Refineries. Streams include light straight run naphtha, heavy naphtha, Platformate, CCR reformate, hydrocracker naphtha, FCC gasoline, unleaded gasoline, mixed pentanes, mixed butanes, ethanol, and methyl t-butyl ether.

Handling of large quantities of these flammable fuel streams is hazardous, and all fuels were received in 1-gallon metal cans and stored in a flammables cabinet. All blending and handling was done in a well-ventilated laboratory, with a properly working hood. The lab was equipped with an eye-wash station and a safety shower, and fire extinguishers were kept close at hand. Gasoline metallane additives used in this study include:

- o Tetraethyl Lead [TEL] Associated Octel

- o Methylcyclopentadienyl Manganese Tricarbonyl [MMT] Ethyl Corporation

- o Dicyclopentadienyl Iron [Ferrocene] [DCI] Associated Octel

- o Iron Pentacarbonyl [IPC] Alcor Novaktan

Three of these fuel additives are very toxic, [TEL, MMT, IPC] and all work with the concentrated additives was done in a well-ventilated room with a properly working hood. Rubber gloves were worn for handling all of the additive solutions and glassware. When

49

working with MMT, the solutions were pipetted with actinic glass pipettes, or with clear glass pipettes in a darkened room. Used pipettes were immediately rinsed inside and out with reagent grade acetone before storing in a drying rack.

In order to measure butane volumes blended, the butane was discharged to a 1-liter graduated cylinder in a hood, to the volume required. Then the cold butane was diluted to one liter with light naphtha, in order to prevent the butane from evaporating while pouring. Fuels were blended in 8-liter batches, using polyethylene containers. After the required amount of fuel was blended, usually 24 liters, then the polyethylene containers were blended with each other by pouring half of each into empty 8-liter containers. These half-full containers were then filled with fuel from a different container. After final mixing, 1-liter samples were prepared by pumping 900 ml of the standard fuel into a 1-liter graduated cylinder, then pipetting the appropriate amount of the fuel additive formulation into the 900 ml in the cylinder. The cylinder was then topped to 1-liter with the blank fuel blend, and transferred to a 1-liter fuel can, which was then capped and properly labelled. Fuel blends with additives were then transported to Ras Tanura Refinery, where the Research Octane Value was measured in their engine laboratory.

6.2 OCTANE MEASUREMENTS

6.2.1 Research Octane Number [RON] Engine:

Automotive Research Octane Number [RON] was determined in a special single-cylinder engine [Fig. 1] with a variable compression ratio [CR 4:1 to 18:1] known as a

50

Cooperative Fuels Research [CFR] engine. The cylinder bore is 82.5 mm, the stroke is 114.3mm, giving a displacement of 612 cm^3. The piston has four compression rings, and one oil control ring. The intake valve is shrouded. The head and cylinder are one piece, and can be moved up and down to obtain the desired compression ratio. The engines have a special four-bowl carburetor that can adjust individual bowl air-fuel ratios. This facilitates rapid switching between reference fuels and samples. A magnetorestrictive detonation sensor in the combustion chamber measures the rapid changes in combustion chamber pressure caused by knock, and the amplified signal is measured on a "knockmeter" with a 0-100 scale [104,105]. A complete Octane Rating engine system costs about $200,000 with all the services installed. Only one company manufactures these engines, the Waukesha Engine Division of Dresser Industries, Waukesha. WI 53186.

Fig. 5: Waukesha Single Cylinder Engine for Octane Number Measurements

To rate a fuel, the engine is set to an appropriate compression ratio that will produce a knock of about 50 on the knockmeter for the sample when the air-fuel ratio is adjusted on the carburetor bowl to obtain maximum knock. Normal heptane and iso-octane are known as primary reference fuels. Two blends of these are made, one that is one octane number above the expected rating, and another that is one octane number below the expected rating. These are placed in different bowls, and are also rated with each air-fuel ratio being adjusted for maximum knock. The higher-octane reference fuel should produce a reading around 30-40, and the lower reference fuel should produce a reading of 60-70. The sample is again tested, and if it does not fit between the reference fuels, further reference fuels are prepared, and the engine readjusted to obtain the required knock. The actual fuel rating is interpolated from the knockmeter readings.

6.2.2   Interference in the Octane Engine

Certain gases and fumes that can be present in the area where the octane engine is located may have a measurable effect on the Research Octane Number test results. Halogenated refrigenator fluids used in air conditioning and refrigeration equipment can promote knock. Halogenated solvents can have the same effect. If vapors from theses materials enter the combustion chamber of the octane engine, the Research Octane obtained for sample fuels cab be depreciated. Electrical power subject to transient voltage or frequency surges or distortion can alter the octane engine operating conditions or knock measuring instrumentation performance and thus affect the Research Octane Number obtained for sample fuels.

6.2.3 Precision of the Octane Engine

The precision of samples having an octane number between 90 and 100 based on the statistical data of different laboratories is as the following:

Repeatability:

The difference between two test results, obtained by the same operator with the same engine under constant operating conditions on identical test samples within the same day would, in the long run, in the normal and correct operation of the test method, exceed 0.2 O.N. in only one case in twenty.

Reproducibility:

The difference between two single and independent results obtained by different operators in different laboratories on identical test samples would, in the long run, in the normal and correct operation of the test method, exceed 0.7 O.N only in one case in twenty.

CHAPTER 7

EXPERIMENTAL DATA

7.1   FIRST PHASE

In the first phase of this study, we prepared fuel blends from Riyadh, Yanbu, and Jeddah Refineries, and added TEL, MMT, IPC, Ethanol, and MTBE.   Base fuel formulations were obtained from the Manufacturing Planning Unit of each refinery, and additives were used according to manufacturers and refineries recommendations.

7.1.1   Jeddah Refinery

Jeddah is a rather small refinery, with a platformer and an FCC unit.   It blends a rather large amount of gasoline however, by utilizing unleaded gasoline from the SAMREF refinery in Yanbu.   This unleaded gasoline contains MTBE as well as reformate, and may at times also contain FCC gasoline, so great care must be exercised in fuel formulation to ensure compositions are known.   The base fuel formulation appears in Table 9 and is represented in Figure 6.

Table 9. Jeddah Base Gasoline Formulation

COMPONENT	OCTANE	LV %	EXPECTED RON
FCC GASOLINE	89.6	44.0	39.42
PLATFORMATE	95.0	15.0	14.25
BUTANE	95.0	2.0	1.90
SAMREF REF	93.5	39.0	36.47
FINAL BLEND			92.04

FIGURE 6 JEDDAH REFINERY BLENDING LV %
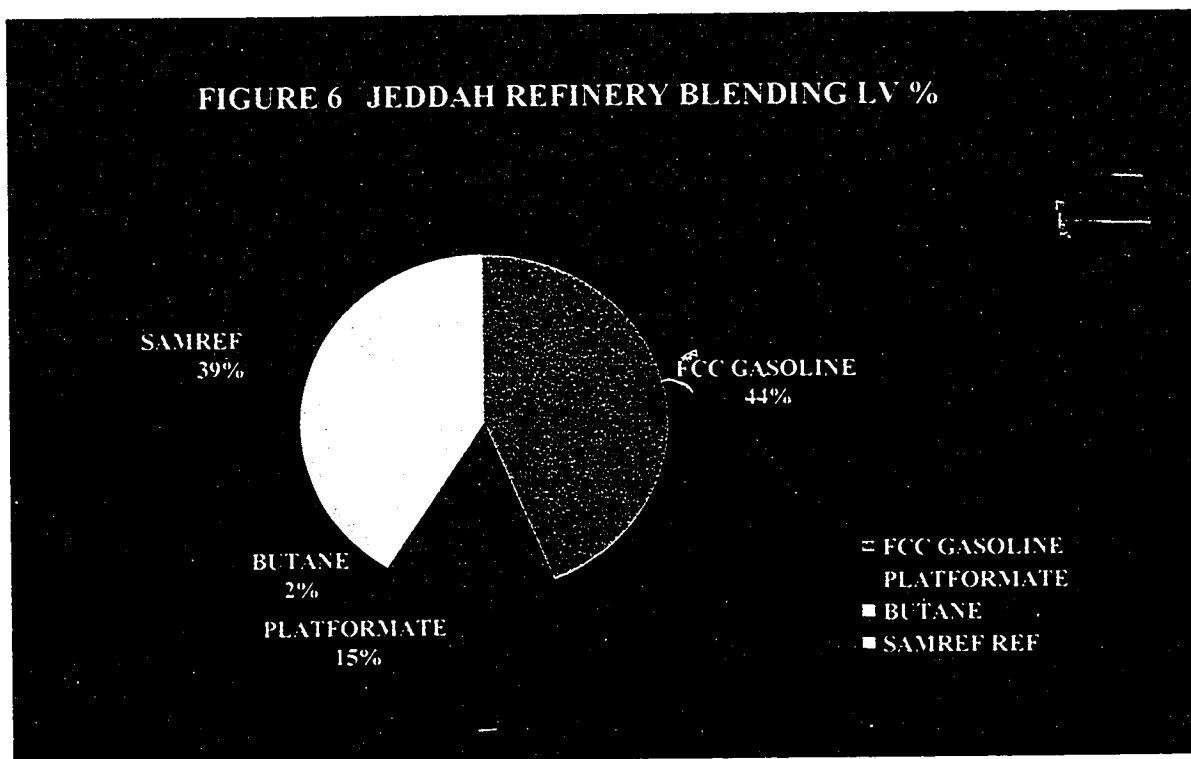
The base fuel From Jeddah Refinery had an octane value of 91.5 RON. It was blended with TEL, MMT, MTBE, Ethanol, and Alcor 116 which is a formulation of 1.00 % iron pentacarbonyl in ethanol. Octane value results for metallanes appear in Tables 10 and Figure 7. Values for oxygenates appear in Table 11 and in Figure 8.

Table 10. Octane Response for Metallanes in Jeddah Gasoline

ML Additive/Liter Fuel	TEL	MMT
0.0	91.5	91.5
2.5	95.9	93.3
5.0	97.4	93.9
7.5	98.1	94.7

FIGURE 7. JEDDAH REFINERY METALLANE RESPONSE
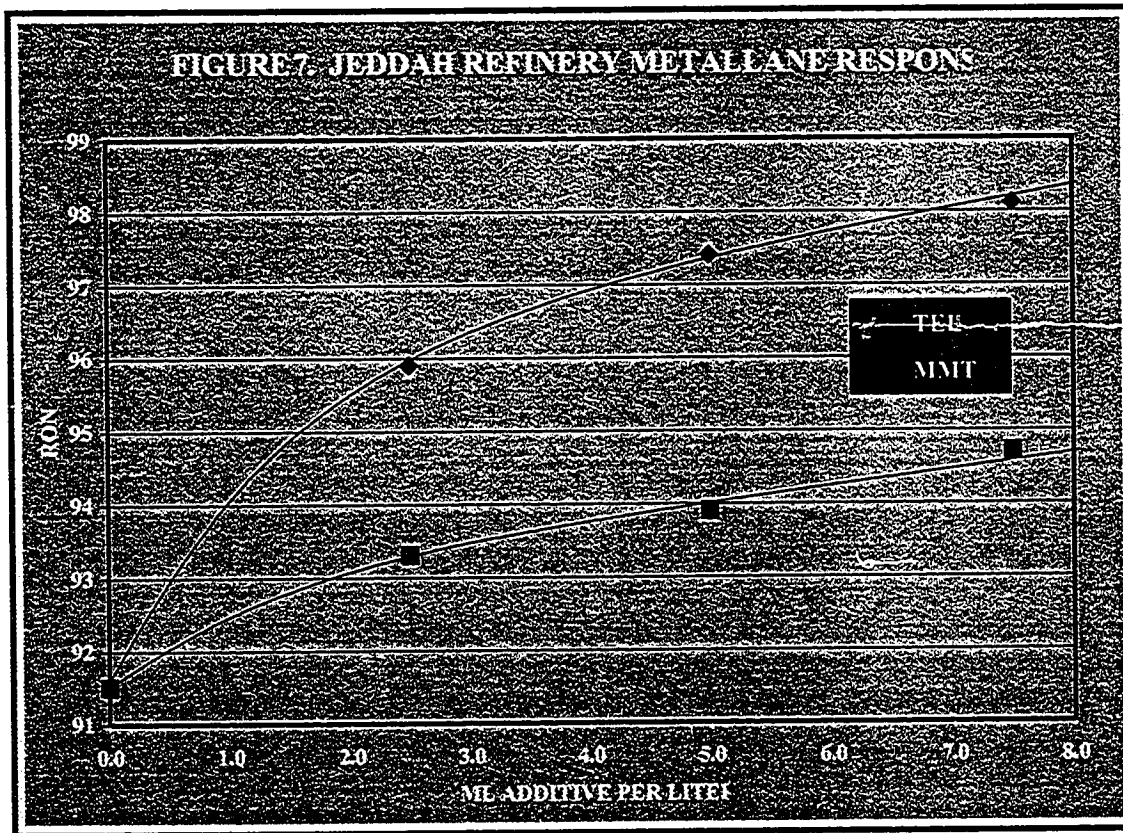
Table 11. Octane Response for Oxygenates in Jeddah Gasoline

Ml Additive/Liter Fuel	MTBE	ETHANOL	ALCOR 116
0.0	91.5	91.5	91.5
30.0	92.0	92.2	95.8
60.0	92.9	92.8	98
100.0	93.8	93.7	100.0

FIGURE 8. JEDDAH REFINERY OXYGENATES RESPONSE
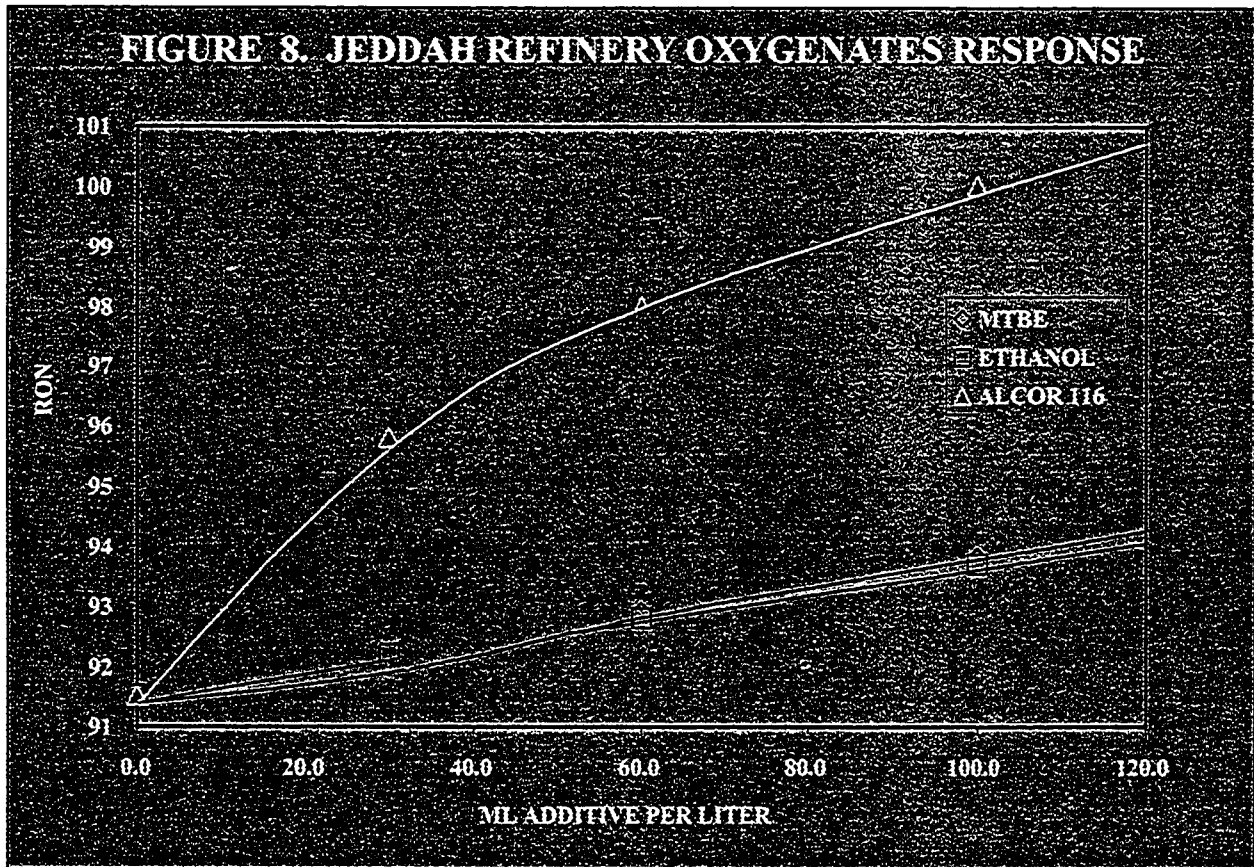
7.1.2 Yanbu Refinery

Yanbu is a larger refinery, which produces 100 MBPD of gasoline, including a small amount of MTBE purchased from SAMREF. It has neither a hydrocracker nor a FCC unit. The base fuel formulation appears in Table 12 and is represented in Figure 9.

Table 12. Yanbu Refinery Gasoline Formulation

COMPONENT	OCTANE	LV %	EXPECTED RON
NAPHTHA	65.0	26.2	17.03
PLATFORMATE	94.6	62.8	59.41
BUTANE	95.3	4.3	4.10
MTBE	110.5	6.7	7.40
FINAL BLEND			87.94

FIGURE 9. YANBU REFINERY BLENDING LV %
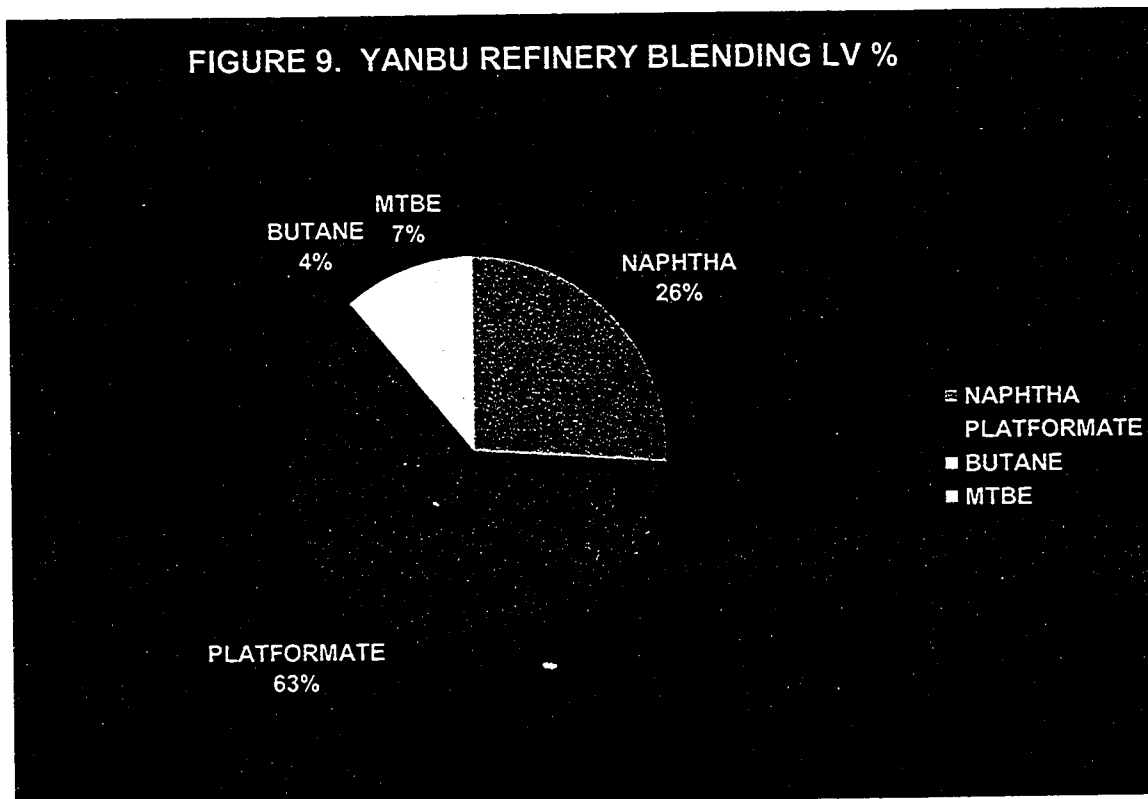
The base fuel From Yanbu Refinery had a RON value of 87.7. It was blended with TEL, MMT, MTBE, Ethanol, and Alcor 116 which is a formulation of 1.00 % iron pentacarbonyl in ethanol. Octane value results for metallanes appear in Table 13 and Figure 10. Octane values for oxygenates are in Table 14 and in Figure 11.

Table 13. Octane Response for metallanes Added to Yanbu Gasoline

Ml Metallane/Liter Fuel	TEL	MMT
0.0	87.7	87.7
2.5	93.8	89.5
5.0	96.3	90.2
7.5	97.5	90.6

FIGURE 10. YANBU REFINERY METALLANE RESPONSE
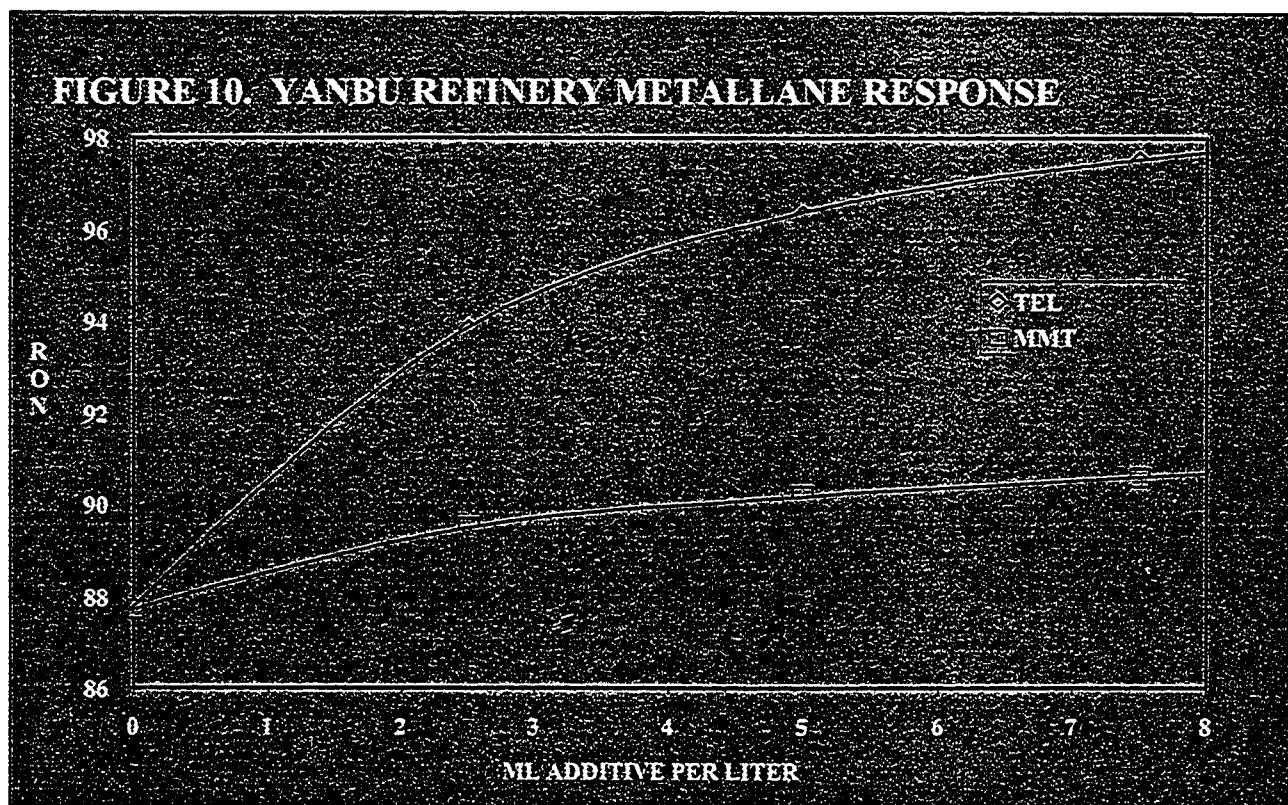
Table 14. Octane Response for Oxygenates Added to Yanbu Gasoline

Ml Oxygenate/Liter Fuel	MTBE	ETHANOL	ALCOR 116
0.0	87.7	87.7	87.7
30.0	88.4	88.7	93.0
60.0	89.0	90.3	95.7
100.0	90.4	92.4	98.5

FIGURE 11. YANBU REFINERY OXYGENATES RESPONSE
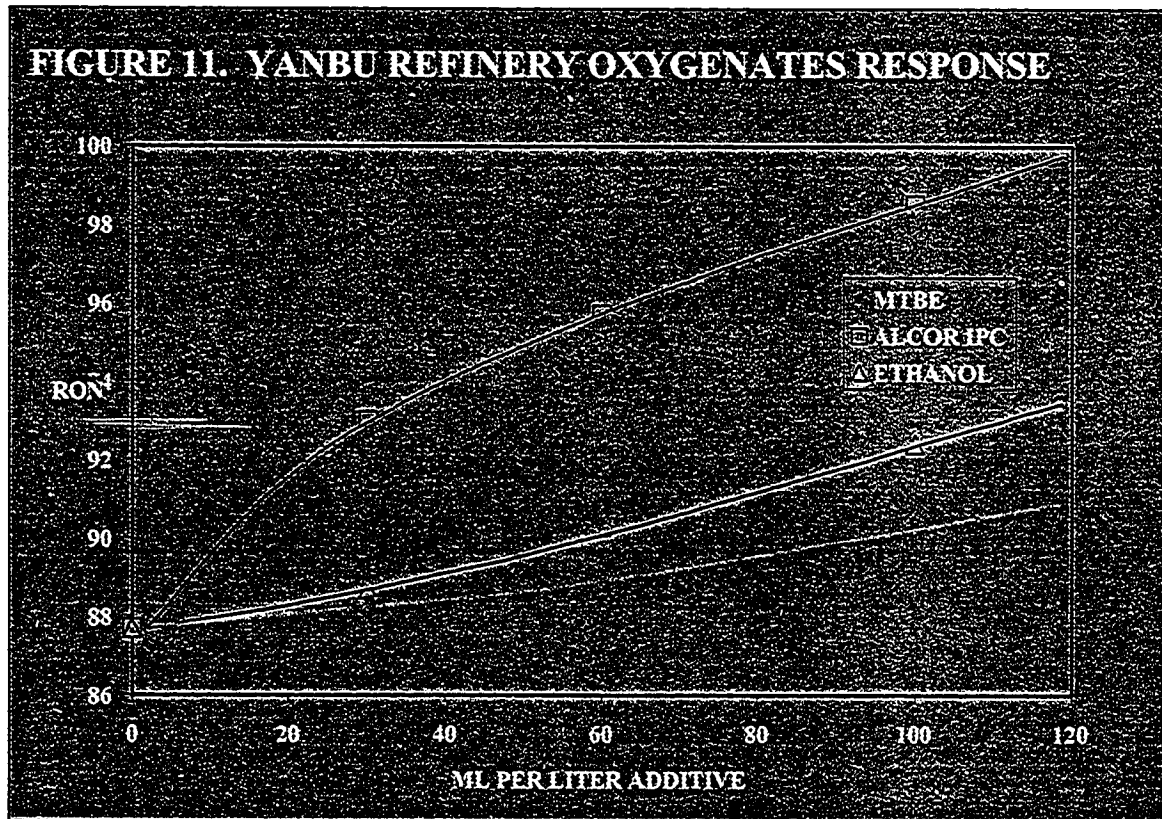
7.1.3 `Riyadh Refinery

Riyadh is a mid size refinery producing 50 MBPD of gasoline from it's platformer blend. It has a platformer and a hydrocracker which produces naphtha, which is feed to reforming and is also used for blending. The base fuel formulation appears in Table 15 and is represented in Figure 12.

Table 15. Riyadh Refinery Gasoline Formulation

COMPONENT	OCTANE	LV %	EXPECTED RON
REFORMATE	96.2	64.0	61.57
LSRN	65.0	18.0	11.70
ISOMAX	80.0	14.0	11.20
BUTANE	95.0	4.0	3.80
FINAL BLEND			88.27

FIGURE 12. RIYADH REFINERY BLENDING LV %
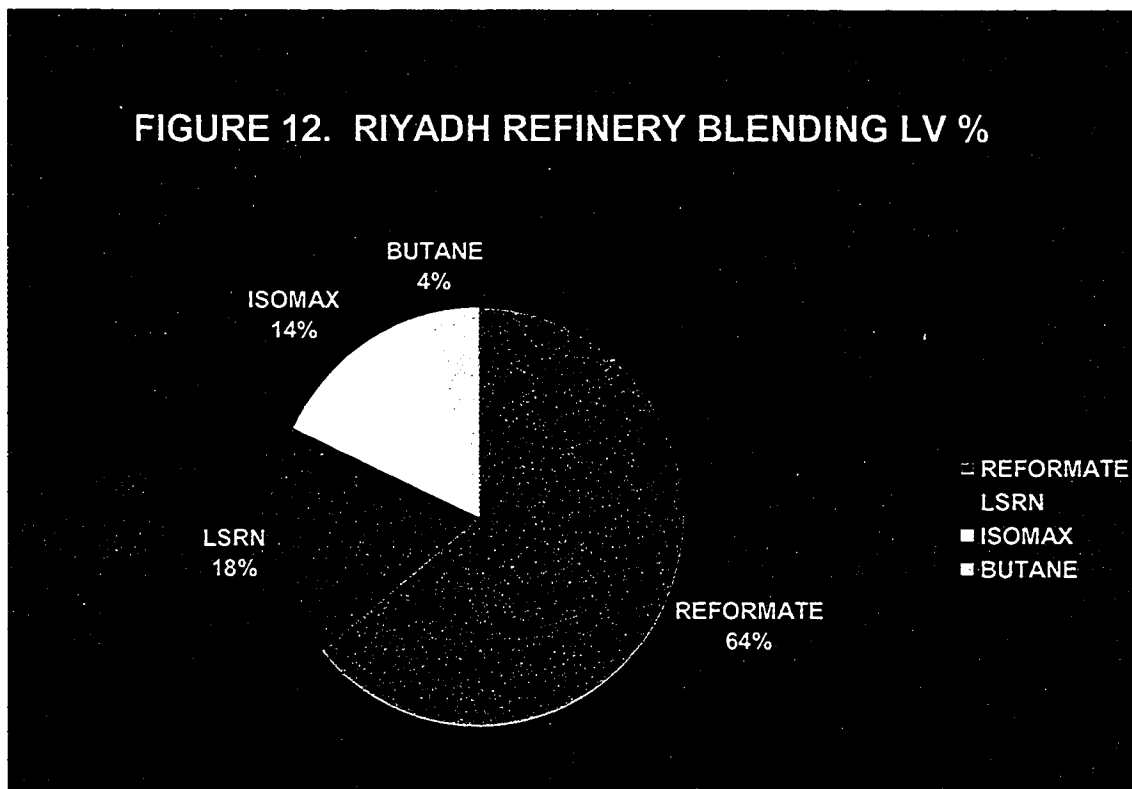
The base fuel From Riyadh Refinery had a RON value of 87.9. It was blended with TEL, MMT, MTBE, Ethanol, and Alcor 116 which is a formulation of 1.00 % iron. Octane values for metallanes appear in Table 16 and Figure 13. Octane values for oxygenates follow in Table 17 and in Figure 14.

Table 16. Octane Response for Metallanes Added to Riyadh Gasoline

Ml Metallane Added/Liter Fuel	TEL	MMT
0.0	87.9	87.9
2.5	95.2	89.7
5.0	97.5	90.6
7.5	98.9	91.7

FIGURE 13. RIYADH REFINERY METALLANE RESPONSE
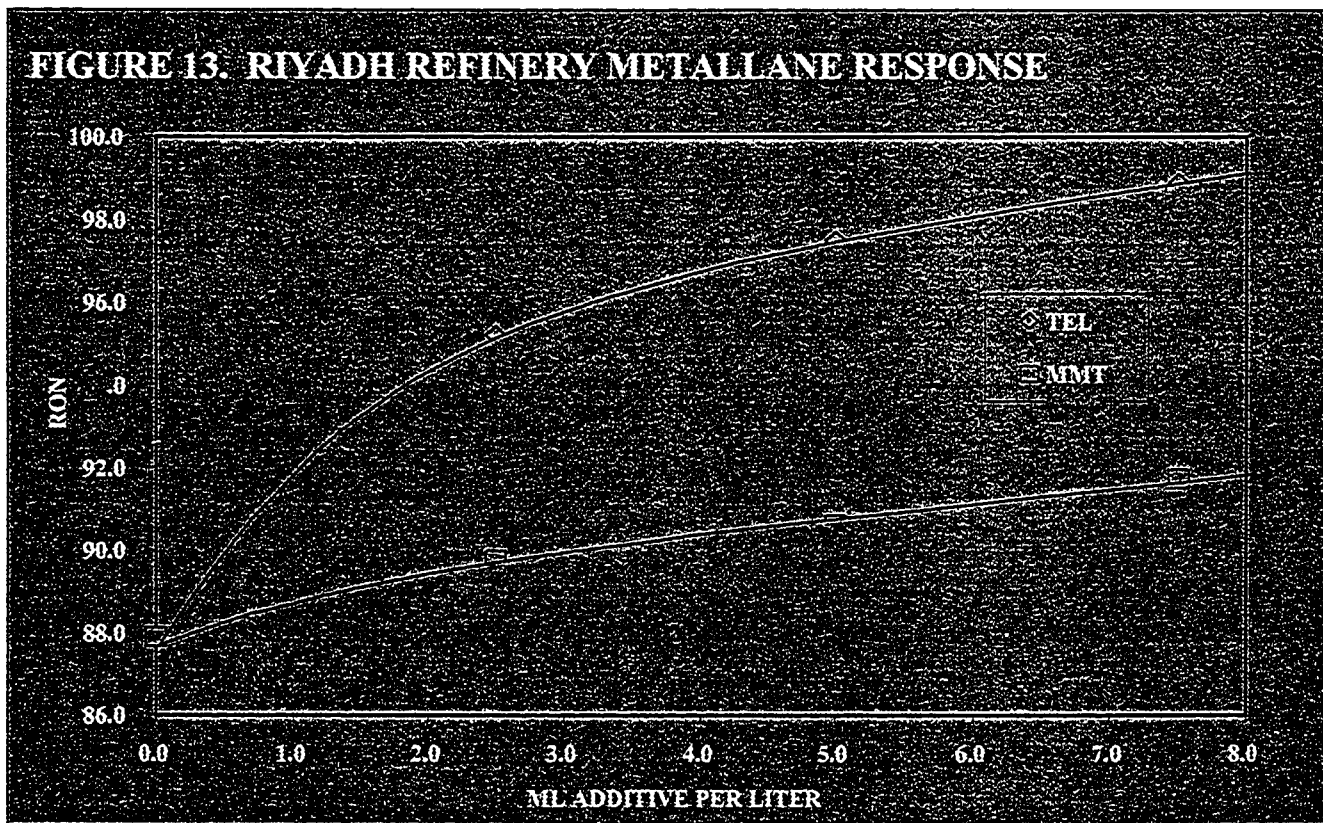
Table 17. Octane Response for Oxygenates Added to Riyadh Gasoline

Ml Oxygenate/Liter Fuel	MTBE	ETHANOL	ALCOR 116
0.0	87.9	87.9	87.9
30.0	88.2	89.4	91.8
60.0	89.4	90.9	95.2
100.0	91.2	92.8	98.7

FIGURE 14. RIYADH REFINERY OXYGENATES RESPONSE
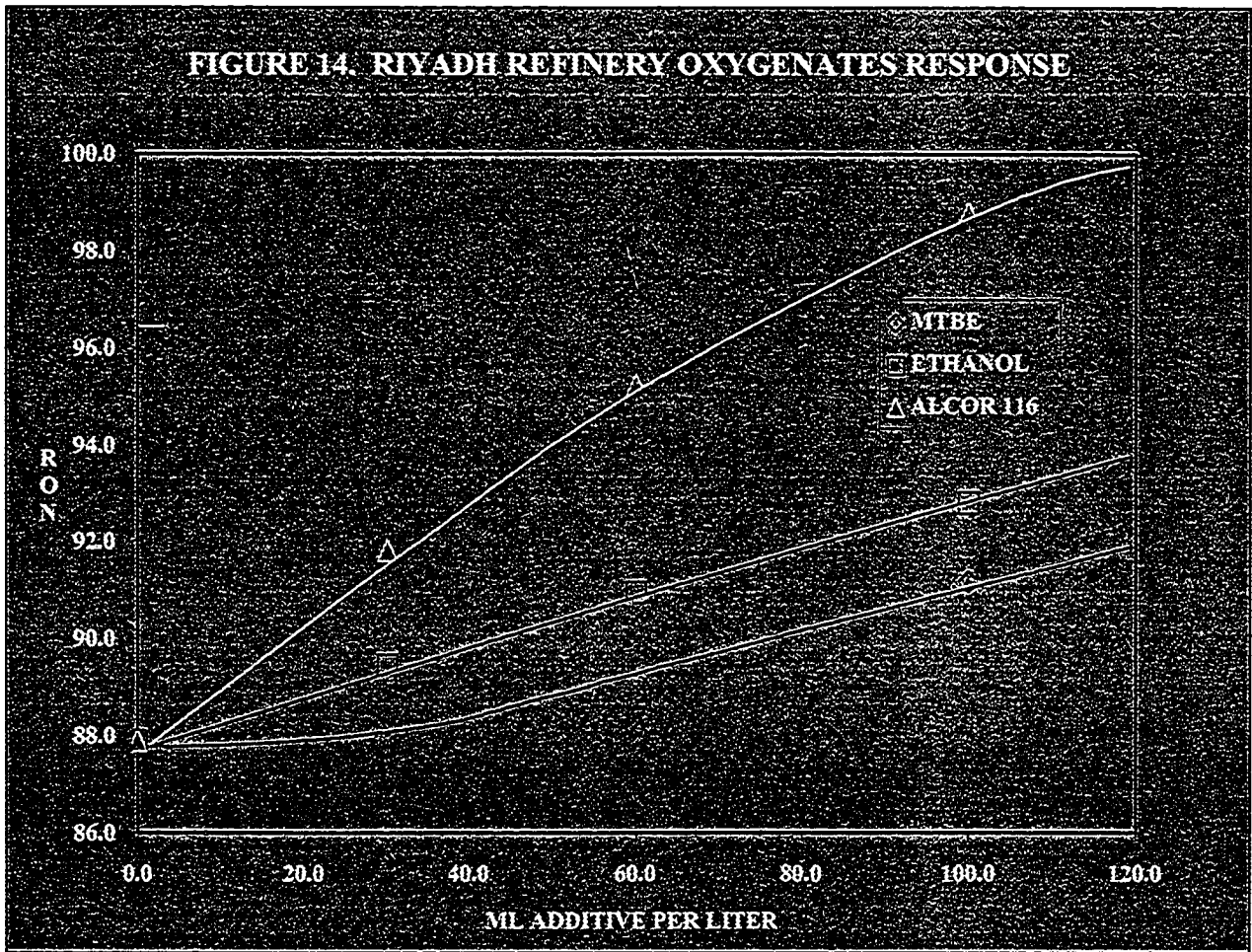
7.2   RESULTS AND DISCUSSION

Octane response for metallanes in fuel from the three refineries was very similar as shown in Table 18. Jeddah base fuel was 91.5 RON. At 7.5 ml TEL per liter of gasoline [equivalent to 836 mg Pb per liter], Jeddah refinery fuel gave an octane increase of 6.6 RON for TEL. With 7.5 ml of MMT [equivalent to 30 mg Mn per liter], Jeddah fuel gave a 3.2 RON increase. Jeddah fuel gave a 2.3 RON increase with 10 volume % MTBE, 2.2 RON increase with 10 volume % ethanol, and 8.5 RON increase with 10 volume % Alcor 116 [equivalent to 1000 mg/liter iron].

Yanbu base fuel was 87.7 RON. At 7.5 ml TEL per liter of gasoline [equivalent to 836 mg Pb per liter], Yanbu refinery fuel gave an octane increase of 9.8 RON for TEL. With 7.5 ml of MMT [equivalent to 30 mg Mn per liter], Yanbu fuel gave a 2.9 RON increase.

Yanbu fuel gave a 2.7 RON increase with 10 volume % MTBE, 4.7 RON increase with 10 volume % ethanol, and 10.8 RON increase with 10 volume % Alcor 116 [equivalent to 1000 mg/liter iron].

Riyadh base fuel was 87.9 RON. At 7.5 ml TEL per liter of gasoline [equivalent to 836 mg Pb per liter], Riyadh refinery fuel gave an octane increase of 11.0 RON for TEL. With 7.5 ml of MMT [equivalent to 30 mg Mn per liter], Riyadh fuel gave a 3.8 RON increase. Riyadh fuel gave a 3.3 RON increase with 10 volume % MTBE, 4.9 RON increase with 10 volume % ethanol, and 10.8 RON increase with 10 volume % Alcor 116 [equivalent to 1000 mg/liter iron].

Table 18. Comparison of Octane Sensitivity for Metallanes and Oxygenates in Jeddah, Yanbu, and Riyadh Gasoline Formulations

ADDITIVE	ACTIVE LEVEL	JEDDAH	YANBU	RIYADH
TEL	836 mg/liter Pb	6.6	9.8	11.0
MMT	30 mg/liter Fe	3.2	2.9	3.8
MTBE	100 ml/liter	2.3	2.7	3.3
Ethanol	100 ml/liter	2.2	4.7	4.9
Alcor 116	1000 mg/liter Fe	8.5	10.8	10.8

All metallane octane responses were found to be quadratic in the three fuels, that is, they increased linearly with the square root of the amount of metallane added. Riyadh fuel showed the greatest sensitivity to both metallanes, probably because it is more paraffinic. Jeddah gasoline showed the lowest sensitivity to lead, and the median sensitivity to manganese, perhaps due to it's high olefin content. Yanbu gasoline showed the lowest sensitivity for manganese, and the median sensitivity to lead. Of course it also already contains 4.6 volume % MTBE.

Oxygenate responses from the three refineries were more complex, with variation between almost linear, to quadratic. Jeddah gave the lowest sensitivity to ethanol, MTBE, and Alcor 116. This may be due to the higher olefins content in Jeddah gasoline. Riyadh refinery fuel gave the highest sensitivity to the oxygenates, and this may be due to the larger paraffin content of Riyadh gasoline. Yanbu gasoline had the median sensitivity to oxygenates, but was much closer to Riyadh than Jeddah.

7.3   SECOND PHASE

7.3.1   Study of MMT and DCI in Ras Tanura Refinery

This phase of the project was intended to focus on the comparison of octane improvement from Dicyclopentadienyl Iron [DCI] and Methylcycopentadienyl Maganese Tricarbonyl [MMT] in Ras Tanura gasoline blends with MTBE. The study involved blending with Ras Tanura Gasoline, to determine the octane response of gasoline containing 0-10 % MTBE, to levels of DCI and MMT, as well as to measure any synergism between these two additives. Four Gasoline were prepared from blends of Light Straight Run Naphtha [LSRN], Hydrotreated Light Naphtha [HTLN], Hydrocracked Naphtha [HKN], CCR Reformate, Pentanes, and Rheniformer Reformate.

We targeted 93 RON for the four synthetic gasoline blends, but they actually varied from 93.9 to 94.5 RON before addition of metallane additives. MTBE levels were 0, 3.0, 6.0, and 10.0 volume % MTBE. DCI was formulated at 4.0 grams/liter in toluene carrier, with a 1.0 % concentration of β-diketone to be a combustion improver, deposit modifier and iron scavenger. MMT was formulated at 4.0 grams/liter in mixed xylenes carrier. We then prepared a mixture of the two metallanes in aromatic solvent and added this mixture at the same level, in order to see if there was in positive or negative advantage to the mixture. The mixed metallane additive [MIX] was formulated at 2.0 grams iron and 2.0 grams manganese per liter. Thus the addition of 2.5 ml of additive formulation resulted in 10 mg/liter metal added to gasoline. DCI, MMT, and MIX were added at 0, 10, 20, and 30 mg/liter of iron or manganese. Details of the blending are in Table 19-22.

Table 19: Gasoline Blend A without MTBE

BLEND A [MTBE-FREE]				
STREAM	OCTANE NUMBER	VOL%	OCTANE CONTENT	LITERS
CCR	100	40	40	4.0
REF	95	40	38	4.0
LSRN	65	4	2.6	0.4
HTLN	70	4	2.8	0.4
PENTANE	80	12	9.6	1.2
MTBE	110.5	0	0	0.0
TOTAL		100	93	10.0

Table 20: Gasoline Blend B with 3% MTBE

BLEND B [3% MTBE]				
STREAM	OCTANE NUMBER	VOL%	OCTANE CONTENT	LITERS
CCR	100	38	38	3.8
REF	95	38	36.1	3.8
LSRN	65	4	2.6	0.4
HTLN	70	6	4.2	0.6
PENTANE	80	11	8.8	1.1
MTBE	110.5	3	3.3	0.3
TOTAL		100	93.02	10.0

Table 21: Gasoline Blend C with 6% MTBE

STREAM	OCTANE NUMBER	VOL%	OCTANE CONTENT	LITERS
BLEND C [6% MTBE]				
CCR	100	36	36	3.6
REF	95	36	34.2	3.6
LSRN	65	4	2.6	0.4
HTLN	70	8	5.6	0.8
PENTANE	80	10	8	1.0
MTBE	110.5	6	6.6	0.6
TOTAL		100	93.03	10.0

Table 22: Gasoline Blend D with 10% MTBE

STREAM	OCTANE NUMBER	VOL%	OCTANE CONTENT	LITERS
BLEND D [10% MTBE]				
CCR	100	33	33	3.3
REF	95	33	31.4	3.3
LSRN	65	4	2.6	0.4
HTLN	70	10	7	1.0
PENTANE	80	10	8	1.0
MTBE	110.5	10	11.1	1.0
TOTAL		100	93.03	10.0

7.4 RESULTS AND DISCUSSION

Research Octane Numbers [RON] for all of the fuels was measured at the Ras Tanura Engine Laboratory. The results appear in Table 23-26 and Figures 15-18. Octane improvement for the two additives and their mixture, are almost the same. Octane improvement for all three metallane formulations ranged from 1.9 to 2.6 RON points at 30 mg/liter metallane. Octane improvement was greater with no MTBE present, then decreased as MTBE dosages increased to 10.0 %. At low levels of MTBE, MMT seems to be slightly better than DCI as an octane improver, while at higher levels of MTBE, DCI appears to be a better octane improver. The MIX metallane additive appears to be between MMT and DFCI in effectiveness. With experimental error of octane measurement at +/_ 0.2 RON, and with other expected measurement and blending errors, it is difficult to discern any real differences among the octane performance of the three additives, all were essentially of the same effectiveness.

Table 23: Research Octane Number of Blend A

Concentration [mg/Liter]	Mn	Fe	Mn & Fe
0	91.4	91.4	91.4
10	93.2	92.7	92.7
20	93.7	93.4	93.5
30	94	93.8	93.9

Fig. 15: RON of Blend A
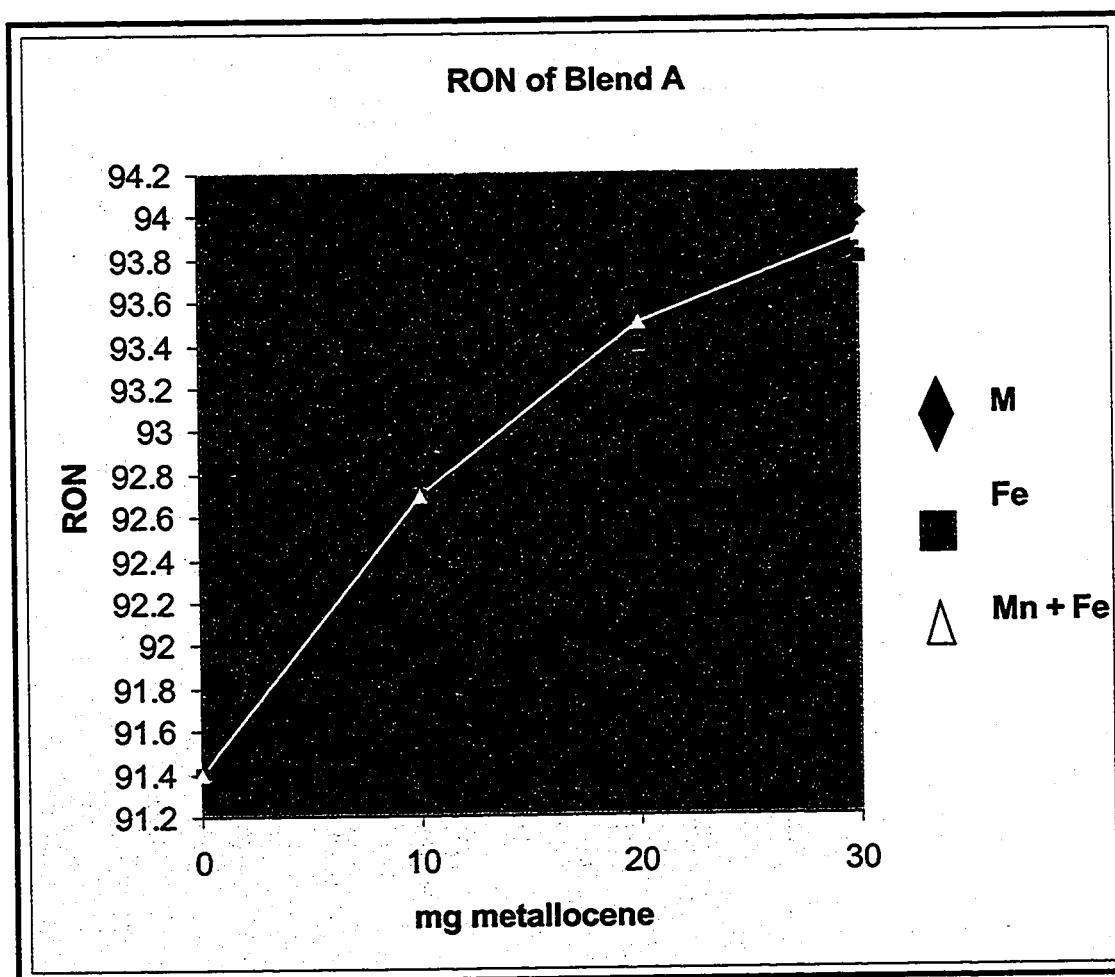
Table 24: Research Octane Number of Blend B

Concentration [mg/Liter]	Mn	Fe	Mn & Fe
0	91.8	91.8	91.8
10	93.3	92.8	93
20	93.8	93.4	93.5
30	94.3	93.9	94

Fig. 16: RON of Blend B
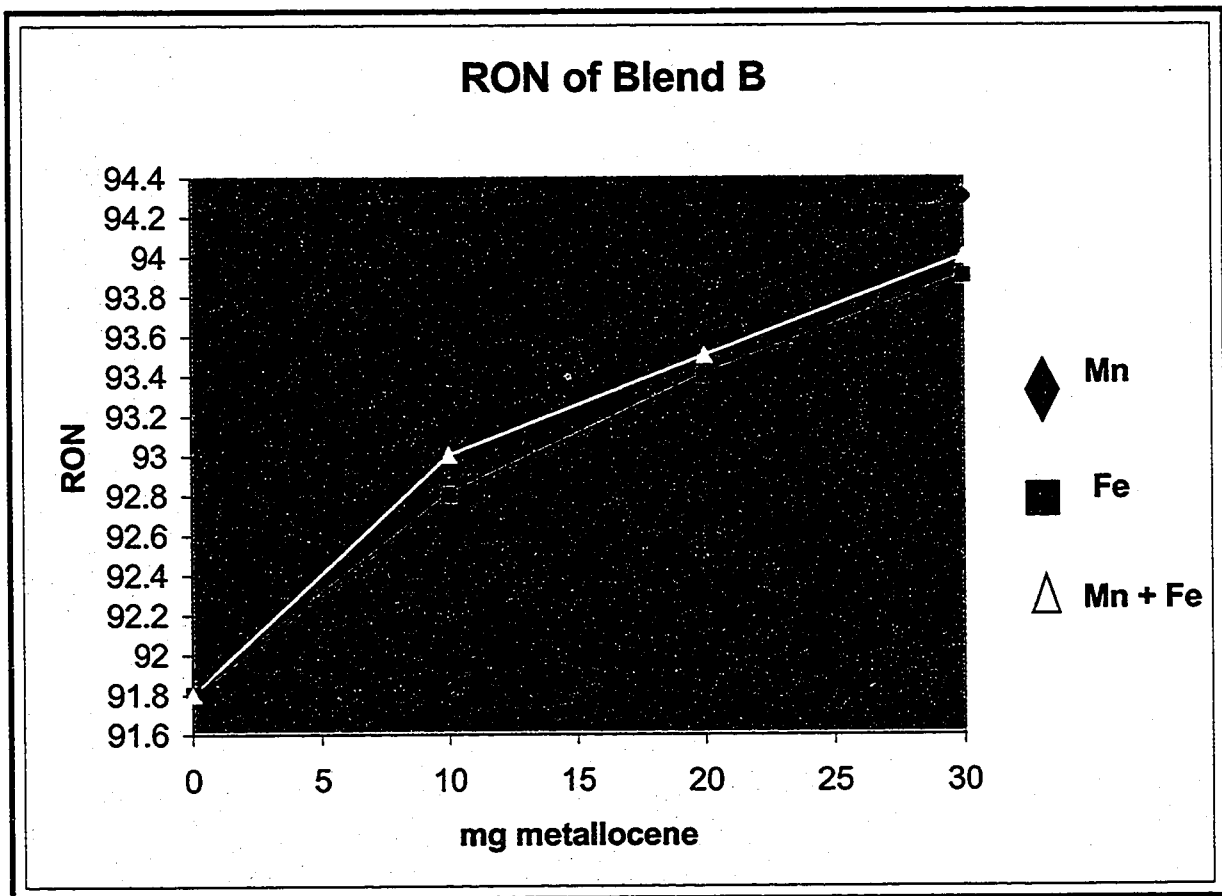
RON of Blend B

Table 25: Research Octane Number of Blend C

Concentration [mg/Liter]	Mn	Fe	Mn & Fe
0	92.2	92.2	92.2
10	93.3	93.4	93.2
20	94	93.9	94.2
30	94.4	94.4	94.5

Fig. 17: RON of Blend C
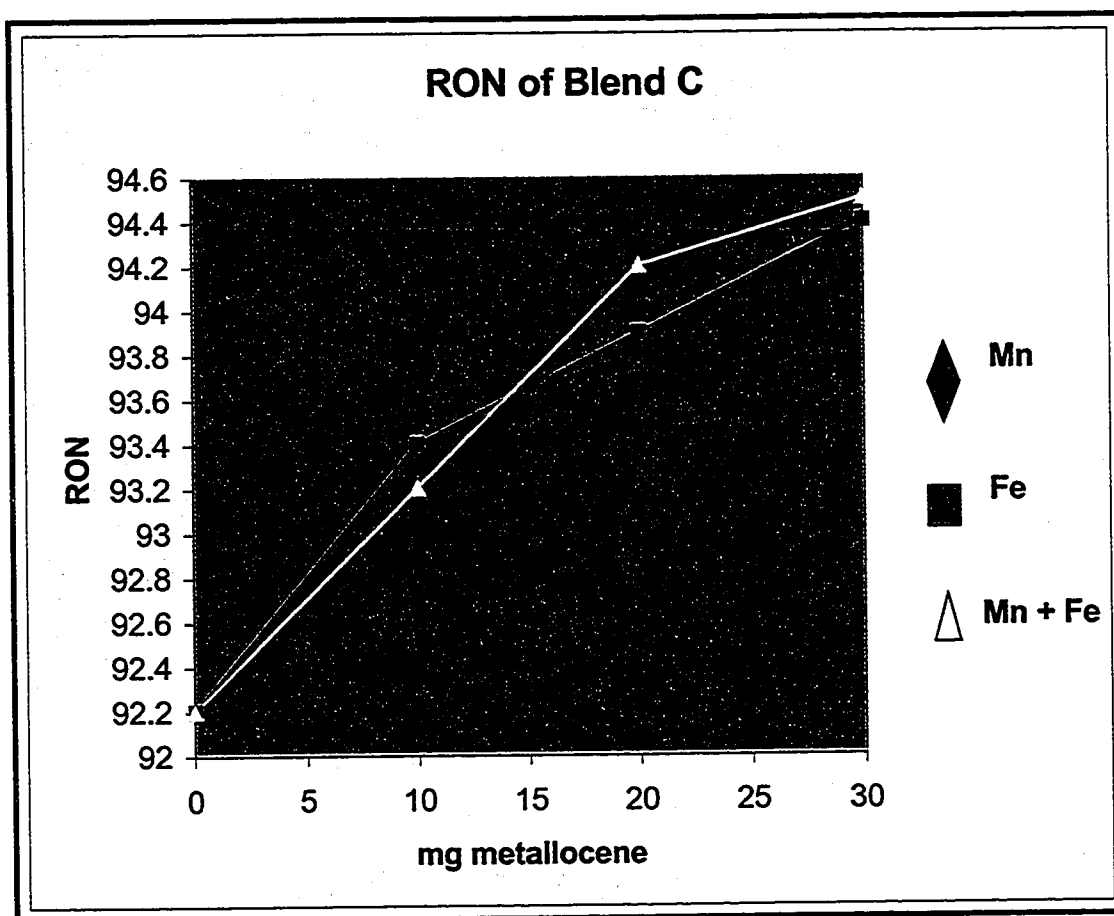
Table 26: Research Octane Number of Blend D

Concentration [mg/Liter]	Mn	Fe	Mn & Fe
0	92.6	92.6	92.6
10	93.9	93.7	93.8
20	94.5	94.3	94.4
30	94.8	94.7	94.7

Fig. 18: RON of Blend D
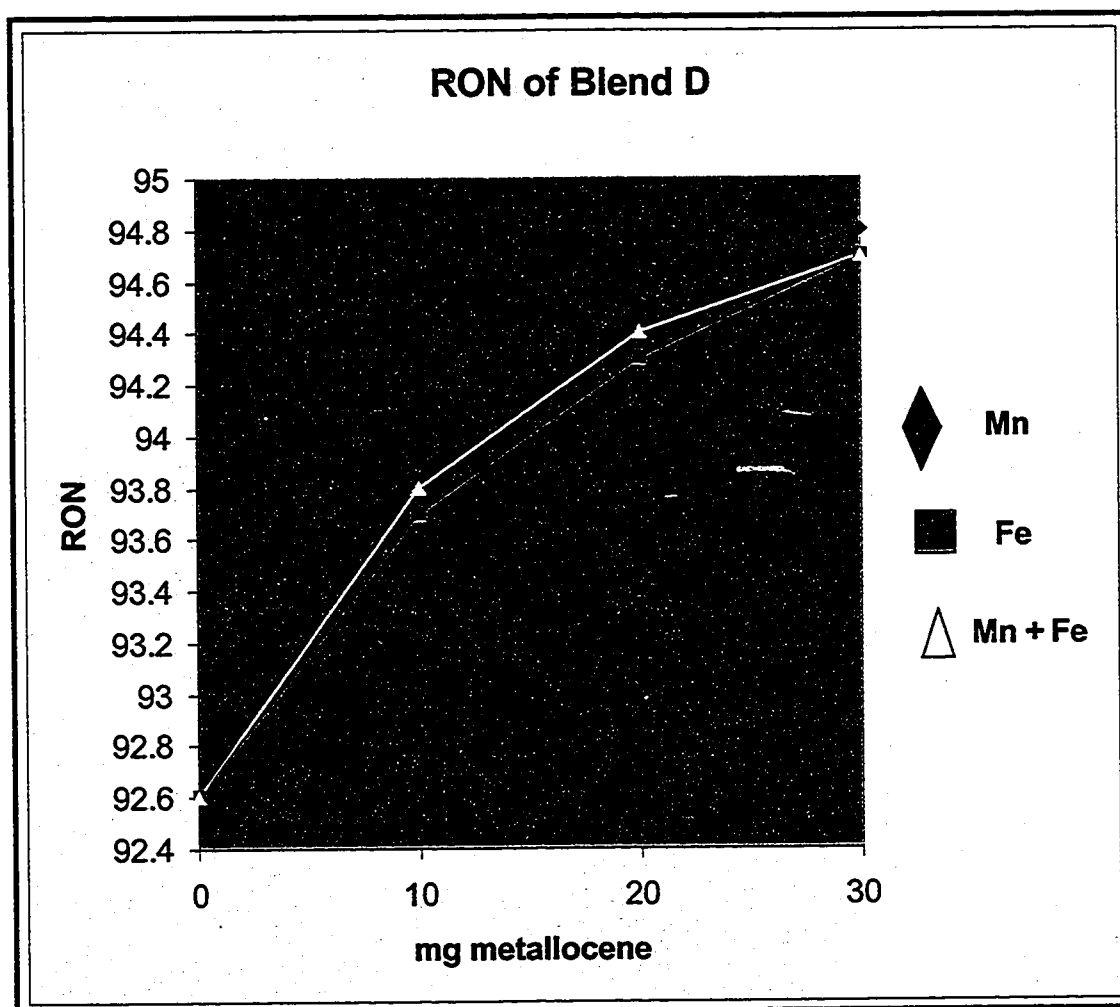
CHAPTER 8

ECONOMICAL EVALUATION

TSD[Technology Service Department] performed an economic evaluation of MMT using the collected laboratory testing of MMT octane responses and the Linear Program [LP]. The results of the LP revealed that a net savings of $39.7 MM per year [includes cost of MMT] could be achieved by blending a combination of MMT and MTBE into the gasoline pool versus utilizing MTBE as the sole octane enhancer additive. The cost of the MMT will be approximately $20 MM per year. By using a combination of MMT and MTBE, the purchase of MTBE could be reduced from 14,000 BPD to 7,000 BPD.

FPD [Facility Planning Department] recently completed an economic evaluation of MMT and concluded that a combination of MMT and MTBE would result in a net savings of $20 MM per year. This cost savings is considered conservative as the octane response was based upon a very conservation increase of 1.7 RON for a MMT addition rate of 18 mg Mn/liter. Once again the FPD economic evaluation even though it is conservative reveals significant potential savings by utilizing a combination of MMT and MTBE within the gasoline pool rather than using MTBE as the only octane enhancer additive. OSPAS completed an economic evaluation of DCI versus MMT, and found comparable results for both additives, assuming equivalent pricing.

CHAPTER 9

ENVIRONMENTAL ASPECTS

DCI is a flammable solid, while MMT has a flash point of 96 °C. DCI is non-toxic, which makes it very attractive when compared to MMT TEL, or IPC. DCI is much less toxic than MMT, which is considered toxic from ingestion, inhalation, and dermal contact. EPD [Environmental Protection Department] reviewed various environmental studies associated with the use of MMT. Upon completion of their review, EPD concurred with utilizing MMT as an octane enhancer provided a limit of 18 mg/l of metallic manganese is established. As with majority of fuel additives, much discussion has taken place over the years regarding the effect of MMT on the environment. In June 1995, the well-respected firm Research Triangle Institute [North Carolina] performed a fifteen-month extensive study on the environmental impact that MMT has on a large North American city [Toronto]. The reason Toronto was chosen is due to the prevalent use of MMT in its automobiles, its large population, and the large range of traffic conditions. The conclusions from this extensive study are as follows:

- Personal exposure levels to manganese [from all sources] in Toronto are well below the US EPA's and Health Canada's most stringent health guidelines.

- Manganese level in the environment due to the use of MMT does not appear to be a measurable source of manganese personal exposures in Toronto.

- The results of the RTI study agrees with the findings of prior studies performed by Health Canada which concluded "airborne manganese resulting from the combustion of MMT in gasoline powered vehicles is not entering the Canadian environment in quantities or under conditions that may constitute a health risk".

CHAPTER 10

CONCLUSION & RECOMMENDATIONS

Economic evaluations performed by TSSD, OSPAS, and FPD have shown significant savings in using a combination of DCI, MMT and MTBE versus using MTBE as the sole gasoline additive. The additive is a proven octane enhancer and has been successful used in western countries for over twenty years. Environmental agencies and fuel specialists have found no adverse effects in utilizing MMT and as a result the additive is permitted for use within the gasoline pool of North America, South Africa, Russia, China and some European countries. The manganese content within the gasoline pool will be less than twenty times the existing lead levels allowed with TEL. MMT is considerable less hazardous than TEL and the quantity required to increase the octane pool is significantly less than the current lead specifications.

Ferrocene (DCI) is already approved for use in Europe, Australia, Germany, and the Philippines, and has a long history of use. At levels up to 30 mg/liter, has no adverse effect on engine performance, catalytic converters, or the environment. Ferrocene (DCI) is considered to have no significant human health effects either in pure form of from its combustion products.

We recommended that DCI and MMT be permitted as gasoline additives to enhance the octane of the gasoline pool within Saudi Arabia. The decision to choose DCI or MMT, or a combination of the two, should be based on purchase price and economics, as well as toxicological considerations, since their engine performance data indicates that they are equivalent.

APPENDIX I.

THESIS RESEARCH PROPOSAL

Study of Octane Enhancers For Unleaded Gasoline: Tetraethyl Lead, Methyl-Cyclopentadienyl Manganese Tricarbonyl, Dicyclopentadienyl Iron, and Iron Pentacarbonyl

MS THESIS RESEARCH PROPOSAL

By
Farhan Al-Shahrani
ID # 941429

DEPARTMENT OF CHEMISTRY
COLLEGE OF SCIENCE

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
DHAHRAN, SAUDI ARABIA

May, 2001

Study Octane Enhancers For Unleaded Gasoline: Tetra-Ethyl Lead, Methyl Cyclopentadienyl Manganese Tricarbonyl, Dicyclopentadienyl Iron, and Iron Pentacarbonyl.

Introduction:

This is a proposal to study the efficacy, synergism, advantages, economics, environmental, and mechanical impact of metallane combustion and octane improvers in combination with oxygenates on Saudi Arabian fuels. Various fuel streams to be studied include reformate, light straight run naphtha, butanes, pentanes, hydrocracker naphtha, FCC Gasoline, and Natural Gasoline. These additives include Tetra-Ethyl Lead [TEL] {1}, Methyl-Cyclopentadienyl Manganese Tricarbonyl [MMT] {2}, Dicyclopentadienyl Iron [DCI] {3}, and Iron pentacarbonyl [IPC] {4}. The effect of these additives along with MTBE on gasoline octane number and its different specifications will be the main objective of this study.

Literature Review:

Spark knock, so called because it is influenced by the timing of the spark, is one f the most important forms of abnormal combustion; it determines, to some extent, the efficiency that can be achieved in an engine. The higher the compression ratio, the better the thermal efficiency, but the grater the tendency for spark knock to occur and so the higher the fuel octane quality that is required. By retarding the ignition timing, the tendency for knock will decrease [and vice versa], but going beyond a certain limit can adversely affect power output. This response to ignition timing distinguishes it form other forms of abnormal combustion such as preignition or run-on.

Even vehicles operating on a fuel for which they have been designed will sometimes knock, and this may be due to a number of factors such as excessive deposit formation in the combustion chamber, over advancement of the ignition timing,

particularly severe driving conditions, or a combination of several factors during manufacture in which the production tolerances all conspire to increase octane requirement. Of course, it can also be dure to the fuel being of a poorer quality than specified.

Nowadays, it is usual to define octane quality using at least two octane parameters and sometimes three. These are: Research Octane Number [RON], motor Octane Number [MON], and a number concerned with the distribution of Research Octane quality through the boiling range of gasoline. Gasoline is specified by Antiknock Index which is the average of the RON an MON of the fuel, i.e.:

Antiknock index = ½ [RON+MON]

Most Gasoline have higher RON than MON, and the difference between these two ratings is called the "sensitivity". Octane number refers to the ability of a gasoline fuel to resist the tendency to pre-ignite. In gasoline engines, air and fuel are compressed in a piston chamber. Because of the compression the mixture becomes very hot. At the right time, the spark from the spark plug will ignite the air/fuel mixture and this will provide power to the engine. If the fuel has a low octane number the heat generated by compressing the mixture can cause the mixture to ignite before it is supposed to. This is called 'knocking' and it is not good for the engine. The tendency of a fuel to knock is a function of the chemistry of the fuel. Aromatics have high octane numbers, normal paraffins have low octane numbers. [1-5] Engine knock is caused by a premature second ignition in an Internal Combustion [IC] engine, which occurs at a location away for the initial ignition. The theory, mechanism and phenomenon of knock in spark ignition internal combustion engines have been the subject of intense investigations. [1-5] The

knock properties of many different hydrocarbon fuel components, as well as amine, oxygen, phosphorus, and other hetroatom organic derivatives have been studied and reported in a variety of private and public investigations. [6-10] The search for metallane and metallocene replacements for lead antiknocks has been extensively studied by different fuel research centers. [11-14]
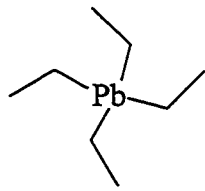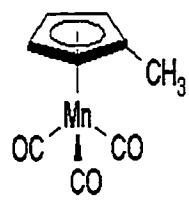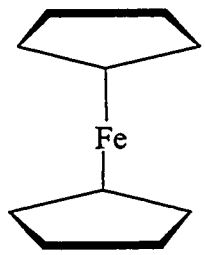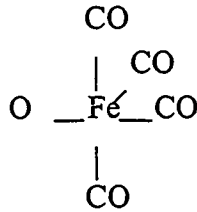
While considering the use of fuel additives, the investigators have to be aware of the impact of the fuel on engine and exhaust performance, wear, deposits, and emissions. [48-50] In addition, the fuel researcher must consider the improvement of octane with additives such as oxygenates or metallanes as compared with other strategies such as refining and blending, and these approaches must be considered. [51-58] Many studied were carried out in different aspects of metallane and metallocene compounds in order to enhance their usage as an anti-knock additives in gasoline and to increase the octane value. These studied covered metallane and metallocene reactions, mechanisms, synthesis, stability, and properties. [28-41]

Lead alkyls are still the most important antiknock additives, even though they are being phased out in many countries for environmental reasons. They usually represent the most economical way to achieve required octane levels. With unleaded gasoline the required octane levels are generally obtained by more severe refining but this reduce noxious emission from exhaust gases is well documented and, because lead poisons the catalysts used to achieve this and is itself toxic, it is both inevitable and desirable that lead compounds in gasoline should be phase out. Nevertheless, they are still used in many countries because the use of lead alkyls reduced gasoline manufacturing costs and crude usage. They function, as do all organometallic antiknocks, by decomposing at the

appropriate temperature in the combustion cycle to form a cloud of catalytically active metal-oxide particles. These particles interrupt the chain branching reactions which lead to the rapid combustion known as knock. [44]

Although over the years there have been many investigations into possible organometallic antiknock compounds to replace lead alkyls, the nearest to a successful alternative that has been found is MMT. This compound is more effective than lead on a metal concentration basis. It can only be used at relatively low concentrations [below about 0.0165 g Mn/L] because of problems with fuel instability, deposit build-up in engines, lack of response at higher concentrations and its adverse effect on hydrocarbon emissions from catalyst-controlled cars. [42-44]

Some other effective alternative metallic antiknocks in addition to lead and MMT contains iron and were used in U.S and Europe during 1930s. They are in a form of either Iron Pentacarbonyl [IPC] or Ferrocene [Dicyclopentadienyl iron] [DCI]. At low concentration, they both showed a reasonable increase in RON. [44-47] Although other metals have been shown to have antiknock effectiveness, they have generally failed for a number of reasons including combustion chamber and spark plug deposits, toxicity, wear, and cost-effectiveness. The following proposed compounds of metallane and metallocenes will be under this study.

(structure)	(structure)	(structure)	(structure)
TEL	**MMT**	**DCP**	**IPC**
(1)	**(2)**	**(3)**	**(4)**

Instrumentation:

Research Octane Number [RON] Engine:

RON is determined in a single cylinder variable compression ratio engine that operates at 600 rpm with a 125 °C inlet air temperature at standard barometric pressure. Spark advance is fixed at 13 degrees BTDC. In a real world engine, RON is necessary to satisfy part throttle knock problems. A good quality racing gasoline has a RON in the range of 110 to 115. The difference in the spread of RON is not very important to racing engines. The test and hardware were originally developed in 1931. The hardware was revised in 1946 with procedural changes made until the late 1960's.

Motor Octane Number [MON]:

MON is determined in a single cylinder engine similar to the RON engine with a few changes that make operating conditions more severe and therefore the octane numbers are lower. The MON engine runs at 900 rpm with a 300 °C mixture temperature. Spark advance varies with compression ratio. In a real world engine, MON is necessary to satisfy octane demands at wide-open throttle. This is a very important number for

racing engines since they spend a high percentage of their lives under high speed and high load conditions. Racing engines cannot afford to be short on octane quality, since detonation or preignition will quickly reduce a racing engine to junk.

The motor octane appetite of an engine with 13:1 compression ratio and a four inch bore varies with operating conditions but is normally around 101. Good quality racing Gasoline have MON in the range of 100 to 115. If your engine requires a 101 MON, it is of no value to use a gasoline that has a 115 MON. To cover yourself for extreme conditions, it is wise to have an octane cushion but there is no advantage to using a very high-octane quality product if you do not need it. The MON test was originally developed in 1932. Major hardware changes were made in 1948 with procedural changes made until the late 1960's.

Present State of the Problem:

With the elimination of lead from the gasoline pool worldwide, refiners now rely on oxygenates like Methyl Tertiary Butyl Ether [MTBE] , Ethyl Tertiary Butyl Ether [ETBE], Tetra Amyl Methyl Ether [TAME], Di Iso Propyl Ether [DIPE], Di Methyl Ether [DME], and Methanol, to increase octane of the reformate, naphtha, and FCC gasoline blends, to achieve acceptable octane levels. New metallane additives are now being introduced, such as Iron Penta Carbonyl [IPC] , Di Cyclo Pentadienyl Iron [DCI], and Methylcyclopentadienyl Manganese Tricarbonyl [MMT], which will be blended with Tertiary Ethyl Lead [TEL] , oxygenates, and hydrocarbons. Carriers, antioxidants, detergents, dyes, and deposit control additives are also present in gasoline. Gasoline in Saudi Arabia is exposed top long periods of storage at elevated temperatures, and interactions among additives are likely to occur, causing gum formation, peroxides,

sludge, and octane loss. The effect of different additves on the gasloine specification is important to overcome any fouling in gasoline as a clean and safe fuel.

Objectives:

The objective of this study is to develop data and record observations of the efficacy, synergism, advantages, economics, environmental, and mechanical impact of metallane combustion and octane improvers in combination with oxygenates like MTBE on Saudi Arabian fuels. Various fuel streams to be studied include reformate, light straight run naphtha, butanes, pentanes, hydrocracker naphtha, FCC Gasoline, Pyrolysis Gasoline, and Natural Gasoline. These additives include Tetra-Ethyl Lead [TEL] (1), Methyl-Cyclopentadienyl Manganese Tricarbonyl [MMT] (2), Dicyclopentadienyl Iron [DCI] (3), and Iron pentacarbonyl [IPC] (4). The affect of different additives and oxygenates on different gasoline specifications will be included to ensure the production of clean and efficient gasoline.

Proposed Procedures:

The proposed four metallane compounds are octane improvers currently commercially available from Alcor Chemie Vertriebs Associated Octel, Novaktan, and Ethyl Corp., and under study by R&DC/Saudi Aramco. Ethanol and MTBE are available from SABIC. Fuel components are available from Ras Tanura, Jeddah, Yanbu, Riyahd, and Rabigh Refienries.

Most of investigations will be performed at the Lab R&D Center using equipment from the Crude Evaluation Unit and the Advanced Instruments Unit. Some support will be sought from Refining, Domestic Marketing Tech Service, Process Engineering, and Environmental Engineering. Consultants [unpaid] from Octel, Novaktan, Ethyl, UOP,

Fina, Star Enterprise, and Atlantic Richfield will be utilized in this study. Octane Measurements will be performed at the Ras Tanura Refinery Engine Laboratory using their CRC Waukasha Research Octane Engine and the rest of preparation and measurements will be performed in the Lab R&D Center/ Saudi Aramco.

The scope of this study include the following:

- o Identify and assemble candidate additives and fuel components. Candidate additives will include lead, iron, and manganese and possibly other new candidates.

Fuel Components will include butanes, pentanes, hydrocracker naphtha, straight run naphtha, reformate, and FCC, and natural gasoline. Oxygenates include MTBE and Ethanol

- o Determine metal level of additives. Measure physical properties of fuel, along with octane and composition.

- o Prepare fuel blends that contrast and compare effects of additives, oxygenates, sensitivities, synergisms, and interactions.

- o Study the effect of different additives and oxygentates in different concentrations on the gasoline specificaions.

APPENDIX II

DATA SHEETS FOR METALLANES

TETRAETHYL LEAD				
Synonyms				
Lead tetraethyl TEL Tetraethyl plumbane				
Formula	$Pb[C_2H_5]_4$			
Formula mass	323.45			
Physical properties.				
Melting pt. [°C]	-136.8		Solubility in water	0.02 mg/100ml
Boiling pt. [°C]	200 [decomposes]		Flash point [°C]	77
Specific gravity	1.7		Autoignition temp. [°C]	110
V.P. [mm Hg]	0.15		Upper explosive limit [%]	
Vapor density	8.6		Lower explosive limit [%]	1.8
Registry numbers.				
CAS	78-00-2		NFPA rating [0-4]	
EINECS	201-075-4		Health	3
RTECS	TP4550000		Flammability	2
RCRA	P110		Reactivity	3
UN	1649			
UN Guide	131		Exposure limits	
UN Hazard Class	6.1		OSHA PEL: TWA 0.075 mg/m³ skin NIOSH REL: TWA 0.075 mg/m³ skin NIOSH IDLH: 40 mg/m³ [as Pb]	
Description.				
Colorless liquid or dyed red, orange or blue with a slight musty odor.				
Hazards.				
The vapor is heavier than air. Decomposes on heating above 110 C and under influence of light producing toxic fumes: carbon monoxide, lead. Reacts violently with strong oxidizers, acids, halogens, oils and fats causing fire and explosion hazard. Attacks rubber and some plastics and coatings.				

METHYLCYCLOPENTADIENYL MANGANESE TRICARBONYL

Synonyms				
MMT				
Tricarbonyl[methylcyclopentadienyl]manganese				

Formula	$C_9H_7MnO_3$			
Formula mass	218.1			

Physical properties.				
Melting pt. [°C]	2.2		Solubility in water	Insoluble
Boiling pt. [°C]	231.7		Flash point [°C]	110
Specific gravity	1.39		Autoignition temp. [°C]	
V.P. [mm Hg]	7		Upper explosive limit [%]	
Vapor density			Lower explosive limit [%]	

Registry numbers.				
CAS	12108-13-3		NFPA rating [0-4]	
EINECS	235-166-5		Health	
RTECS	OP1450000		Flammability	
RCRA			Reactivity	
UN	2810			
UN Guide	153		Exposure limits	
UN Hazard Class	6.1		TLV [as Mn]: ppm; 0.2 mg/m³ [skin] [ACGIH 1994-1995]. OSHA PEL: C 5 mg/m³ NIOSH REL: TWA 0.2 mg/m³ skin	

Description.
Yellow to dark-orange liquid with a faint, pleasant odor.

Hazards.
On combustion, forms toxic or irritating fumes including manganese oxides and carbon monoxide. Decomposes under influence of light. Class IIIB Combustible Liquid.

DICYCLOPENTADIENYL IRON

Synonyms				
Ferrocene bis[Cyclopentadienyl]iron Iron dicyclopentadienyl				

Formula	$[C_5H_5]_2Fe$			
Formula mass	186.03			

Physical properties.				
Melting pt. [°C]	173		Solubility in water	Insoluble
Boiling pt. [°C]	249		Flash point [°C]	
Specific gravity			Autoignition temp. [°C]	
V.P. [mm Hg]			Upper explosive limit [%]	
Vapor density			Lower explosive limit [%]	

Registry numbers.				
CAS	102-54-5		NFPA rating [0-4]	
EINECS	203-039-3		Health	
RTECS	LK0700000		Flammability	
RCRA			Reactivity	
UN				
UN Guide			Exposure limits	
UN Hazard Class			NIOSH REL: TWA 10 mg/m^3 [total] TWA 5 mg/m^3 [resp] OSHA PEL: TWA 15 mg/m^3 [total] TWA 5 mg/m^3 [resp]	

Description. Orange, crystalline solid with a camphor-like odor.

Hazards. Ammonium perchlorate, tetranitromethane, mercury[II] nitrate. Combustible Solid.

IRON PENTACARBONYL			
Synonyms Iron carbonyl Pentacarbonyliron			
Iron carbonyl Pentacarbonyliron			
Formula	Fe[CO]$_5$		
Formula mass	195.9		
Physical properties.			
Melting pt. [°C]	-20	Solubility in water	Insoluble
Boiling pt. [°C]	103	Flash point [°C]	-15
Specific gravity	1.49	Autoignition temp. [°C]	
V.P. [mm Hg]	40	Upper explosive limit [%]	12.5
Vapor density	6.8	Lower explosive limit [%]	3.7
Registry numbers.			
CAS	13463-40-6	NFPA rating [0-4]	
EINECS	236-670-8	Health	2
RTECS	NO4900000	Flammability	3
RCRA		Reactivity	1
UN	1994		
UN Guide	131	Exposure limits	
UN Hazard Class	6.1	TLV [as Fe]: 0.1 ppm; 0.23 mg/m^3 [STEL : 0.2 ppm; 0.45 mg/m^3] [ACGIH 1994]. NIOSH REL: TWA 0.1 ppm [0.23 mg/m^3] ST 0.2 ppm [0.45 mg/m^3]	
Description. Colorless to yellow to dark-red, oily liquid.			
Hazards.			
The vapor is more dense than air. It may travel along the ground and be ignited at a distant location. May explode on heating. The substance may spontaneously ignite on contact with air. Decomposes on heating, on burning or under influence of light producing toxic gases including iron oxides and carbon monoxide. The substance is a strong reducing agent and reacts violently with oxidizers. Class IB Flammable Liquid. marine pollutant.			

REFERENCES

1. Gary, James H., and Handwerk, Glen E., Petroleum Refining: Technology and Economics, Second Edition, Marcel Dekker, New York, 1984.8.

2. Martinie, Gary D., Al-Khawajah, Anwar A., Dutta, Tamal K., Al-Solemi Bandar, ARI 670-03/96, Evaluation of UOP R-72/56 Staged Reformer Catalyst for Jeddah Refinery, February 20, 1997.

3. Phillips 66 Reference Data for Hydrocarbons and Petro-Sulfur Compounds, Phillips Petroleum Company, Bullitin No. 521, Bartellsville, OK, 1962.

4. Livingston, H. K., Knock Resistance of Pure Hydrocarbons in Correlations with Chemical Structure, Ind. & Eng. Chemnistry, 43 [12], 2834-2840.

5. Hunt, John M., Petroleum Geochemistry and Geology, pp 48-52, W. H. Freeman and Company, San Francisco, 1979.

6. Knocking Characteristics of Pure Hydrocarbons, American Petroleum Institute Project 45, ASTM Special Technical Publication 225, Philadelphia, 1955.

7. Owen, Keith, and Coley, Trevor, Automotive Fuels Reference Book Second Edition, pp 99-160, Society of Automotive Engineers, Warrendale, Pennsylvania, 1995.

8. Downs, D., and Walsh, A. D., Knock in Internal Combustion Engines, Nature, Vol. 163, p 370, 1949.

9. Downs, D., and Pigneguy, J. H., an Experimental Investigation into Pre-Ignition in the Spark Ignition Engine, Proceedings of the Institution of Automotive Engineers, London, June 21, 1950.

10. Downs, D., Griffiths, S. T., and Wheeler, R. W., Pre-Flame Reactions in the Spark Ignition Engine, Journal of The Institute of Petroleum, January, 1963.

11. Downs, D., Walsh, A. D., and Wheeler, R. W., A Study of the Reactions that Lead to Knock in the Spark Ignition Engine, Philosophical Transactions of the

Royal Society, Series A. Mathematical and Physical Sciences, No. 870, Vol. 243, pp.463-524, July 19, 1951.

12.   Walsh, A. D., Knock in Spark Ignition Engines in Low Temperature Oxidations, pp 285-327, NATO, Ed. W. Jost, Gordon and Breach, London,

13.   Unzelman, G. H., Forster, E. J., Burns, A. M., Are There Substitutes for Lead Antiknocks? American Petroleum Institute 36th Midyear meeting, San Francisco, May 14, 1971.

14.   Lease, C. A., Octane Value of Oxygenates, Arco Petroleum Products Company, Harvey Technical; Center, October 18, 1979.

15.   Supply and Cost of Alternatives to MTBE in Gasoline, Publication No. P300-98-013, California Energy Commission Staff Report, October, 1998

16.   Marker, T. L., Keesom, W. H., Schmidt, R., Davis, S., and Marinangeli, R., Low Cost Diisopropyl Ether Production, Conference on Clean Air Act and Reformulated Gasoline, Washington, October 9-11, 1994.

17.   Hinkamp, J.B. Study Rates Alcohols as Octane Blending Agents. Sept. 12, 1983. Oil and Gas Journal, pp. 170-178.

18.   Mackinven, R., A Search for an Ashless Replacement for Lead in Gasoline, Thornton Research Centre, Shell International Petroleum Company, Ltd., Jahrestagung, DGMK, Germany, October, 1974.

19.   Hartley, Frank R., and Patai, Saul, the Chemistry of the Metal Carbon Bond, Vol. 1, Wiley, New York, 1982.

20.   Kitman, Jamie Lincoln, the Secret History of Lead, The Nation, March 30, 2000.

21.   Kotz, John C., Editor, Transition Metal Organometallic Compounds, Plenum Press, New York, 1986.

22.   Lyne, P. D., Mingos, D. P., Zeigler, T., Molecular Orbital Analysis of the Intermediates and Products generated by the Photooxidation of Iron Pentacarbonyl, Inorganic Chemistry, 1993, 32 pp 4783-4789.

23. Cotton, F. A., and Wilkenson, Geoffery, Inorganic Chemistry, Fifth Edition, McMillin, New York, 1990.

24. Vlasov, P. A., Zaslonko, I. S., and Karasevich, V. N., and Yu, K., Iron Cluster Thermal Decomposition and Ionization, Smirnov Semenov Institute of Chemical Physics Russian Acadamy of Sciences, 177977 Moscow, Kosygin Street 4. Russia.

25. Mulqueen, Simon, The Impact of Emission System Durability of Plutocen G Treated Gasoline, Associated Octel, Feb. 2000, Bletchly, UK.

26. Laveskog, Anders, Emission Test of Gasoline Containing Ferrocene, AB Svensk Bilprovning, Motortestcenter, May 1993, Haninge, Sweden.

27. Peters, Lutz, Investigation of Otto EngineExhausts Resulting from the Combustion of Fuel with Added Ferrocene, Franhofer Instute, July 1996, Hanover, Germany.

28. Czerwinski, J., Mosimann, T., and Matter, U., Tests of fine Particle Emissions from Cars with SI Engines with Increased Additive Concentrations, College of Engineering, Bern Acadamy, Dec. 1998, Bern, Switzerland.

29. Czerwinski, J., Napoli, S., Mosimann, T., and Matter, U., Studies of the Fine Particulate Emissions from Cars with Petrol Engines using the Additive Plutocen, Eidg. Technische Hochschule Zurich, Jan. 2000, Zurich, Switzerland.

30. Russell, Trevor, Requirements for New Gasoline Additives, Presentation to Saudi Aramco, Sept. 15, 2000, Al-Khobbar, Saudi Arabia.

31. U.S. Environmental Protection Agency. 1985. Decision not to regulate manganese under the Clean Air Act. Federal Register 50, 32627.

32. Zayed, J. et al. 1993. Occupational and environmental exposure of garage workers and taxi drivers to airborne manganese arising from the use of MMT. Am. Ind. Hyg. Assoc. 55: 53-58.

33. Anderson, G.E., A.S. Rosenbaum and L.A. Gardner. 1991. Modeling of Manganese Exposure in Mobile Populations. Systems Applications International, San Rafael, CA.

34. Brault, N., S. Loranger, F. Courchesne, G. Kenndy and J. Zayed. 1994. Bioaccumulation of manganese in plants: influence of MMT as gasoline additive. Sci. Total Environ. 153: 77-84.

35. Benson, J.D., et. al. 1979. Results of Coordinating Research Council MMT Field Test Program. SAE Paper 790706.

36. Faggan, J.E., J.D. Bailie, E.A. Desmond and D.L. Lenane. 1975. An Evaluation Of Manganese As An Antiknock In Unleaded Gasoline. SAE Paper 750025.

37. Hollrah, D.P. and A.M. Burnes. MMT Increases Octane While Reducing Emissions. March 11, 1991. Oil and Gas Journal, pp. 86-91.

38. Hollrah, D.P. and A.M. Burns, 1990. Gasoline Blending in the '90's: Problems and Options. NPRA Paper FL-90-114.

39. Sabotka & Company, Inc. 1990. Analysis of the effects on the refining industry of allowing HiTEC 3000 as an additive in gasoline.

40. Turner, Mason & Company. 1989. Reduced refinery emissions and costs vis HiTEC 3000 in unleaded gasoline. Appendix 6 of May 9, 1990 Ethyl submission in support of waiver application to the U.S. EPA.

41. Turner, Mason & Company. 1991. Study of effects of HiTEC 3000 use on refinery operations. Appendix 14 of the November 26, 1991 Ethyl submission in support of waiver application to the U.S. EPA.

42. Aradi, A.A., J.W. Roos, B.F. Fort, Jr., E.E. Lee and R.I. Davidson. 1994. The Physical And Chemical Effect Of Manganese Oxides On Automobile Catalytic Converters. SAE Paper 940747.

43. Benson, Jack D., and Steinbrink, Ranier, Gasoline Quality Required for Future Low Emission Vehicles, Fifth Int. Symmposium on Performance Evaluation of Automotive Fuels and Lubricants, Goteborg, Sweden, May 13-16, 1997.

44. Benson, Jack D., Spark Plug Validation Tests with MMT, General Moters R&D Dept. Publication, Warren, Michigan, Jan. 27, 1997.

45. Yolanda, Robert, Ethyl MMT Test Programs, Presentation to Saudi Aramco, July

12, 2000, Dhahran, Saudi Arabia.

46. Hollorah, Donald, MMT Overview, Presentation to Saudi Aramco, July 12, 2000, Dhahran, Saudi Arabia.

47. Vandendome, Patrick, Combustion of MMT, Presentation to Saudi Aramco, July 12, 2000, Dhahran, Saudi Arabia.

48. Pellizzari, R. E., et al, Executive Summary, Manganese Exposure Study [Toronto], Research Triangle Institute, June 30, 1998, Research Triangle Park, NC.

49. Wood, Grace, and Egyed, Marika, Risk Assesment for the Combustion Products of MMT in Gasoline, Environmental Health Directorate, Health Canada, Dec. 6, 1994.

50. Abbott, P.J. 1987. Methylcyclopentadienyl Manganese Tricarbonyl [MMT] in Petrol: the Toxicological Issues. The Science of the Total Environment 67: 247-255.

51. Ulrich, C.E., W. Rinehart and M. Brandt. 1979. Evaluation of the chronic inhalation toxicity of a manganese oxide aerosol III - pulmonary function, electromyograms, limb tremor and tissue manganese data. Am. Ind. Hyg. Assoc. J. 40: 349-353.

52. ATSDR [Agency for Toxic Substances and Disease Registry]. 1992. Toxicological Profile for Manganese and Compounds. TP-91/19.

53. Toxicological Profile for Manganese. U.S. Department of Health and Human Services September 1997.

54. Nielsen, F.H. Ultra Trace Minerals. Modern Nutrition in Health and Disease 8th Ed., 1994;275-277.

55. Rodier, J. Manganese poisoning in Moroccan miners. British Journal of Industrial Medicine 1955;12:21-35.

56. Mena, I., Marin, O., Fuenzalida, S., Cotzias, G.C. Chronic manganese poisoning. Neurology 1967;17:128.

57. Mena, I., Court, S., Fuenzalida, S., Papavasiliou, P.S., Cotzias, G.C. Modification of chronic manganese poisoning: Treatment with L-Dopa or 5-OH tryptophan. New England Journal of Medicine 1970;11:405.

58. Roels, H., Lauwerys, R., Buchet, J.P., Genet, P., Sarhan, M.J., Hanotiau, I., deFays, M., Bernard, A., Stanesou, D. Epidemiological survey among workers exposed to manganese: Effects on lung, central nervous system and some biological indices. American Journal of Industrial Medicine 1987;11:307-327.

59. Menkes, D.B., Fawcet, J.P. Too easily lead? Health effects of gasoline additives. Environmental Health Perspectives 1997;105[3]:270-3.

60. Davis, J.M. Methylcyclopentadienyl manganese tricarbonyl: Health risk uncertainties and research directions. Environmental Health Perspectives 1998;106[51]:191-201.

61. Zheng, Wei; Ren, Sean; Graziano, J.H. Manganese inhibits mitochondrial aconitase: a mechanism of manganese neurotoxicity. Brain Research 1998;799:334-352.

62. Gavin, Claire E.; Gunter, Karlene K.; Gunter, Thomas E. Mn2+ sequestration by mitochondria and inhibition of oxidative phosphorylation. Toxicology and Applied Pharmacology 1992;115:1-5.

63. Galvani, Pietro; Fumagalli, Pietro; Santagostino, Angela. Vulnerability of mitochondrial complex I in PC12 cells exposed to manganese. European Journal of Pharmacology 1995;293:377-383.

64. Martinie, Gary D. and Al-Ghamdi, Mohammed, Evaluation Of Tetraethyl Lead Octane Blending Component And Impurities By [207]Pb Nuclear Magnetic Resonance, Saudi Aramco Technical Exchange meeting, March, 1997, Dhahran, KSA.

65. Axenrod, T., and Webb, G. A., Nuclear Magnetic Resonance of Nuclei Other than Protons, Wiley, New York, 1974, Chapter 23.

66. Granger, Pierre, Brevard, Christian, Devaul, Marguerite, Fast Direct Measurements of $^1J_{PbPb}$ and its Variation with Substitution at the Lead Atom, Journal of Magnetic Resonance, 76, 232-240 [1988].

67. Granger, Pierre, and Harris, Robin K., <u>Multinuclear Magnetic Resonance in Liquids and Solids-Chemical Applications</u>, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1990.

68. Hays, G. R., Gilles, D. G., Blaauw, L. P., and Clague, A. D. H., <u>Field Dependent Relaxation in ^{207}Pb NMR, Journal of Magnetic Resonance</u>, 45, 102-107 [1981].

69. Pregosin, P. S., <u>Transition Metal Nuclear Magnetic Resonance</u>, Elsevier Publishing Co., Amsterdam, 1991.

70. Gordon, Arnold J., and Ford, Richard A., <u>the Chemists Companion</u>, Wiley Interscience, New York, 1972.

71. Harris, Robin. K., and Mann, B. E., <u>NMR and the Periodic Table</u>, Academic Press, New York, 1981.

72. Harris, R.K. in <u>Encyclopaedia of Nuclear Magnetic Resonance</u>, D.M. Granty and R.K. Harris, [eds.], vol. 5, John Wiley & Sons, Chichester, UK, 1996.

73. Maciel, Gary, <u>Nuclear Magnetic Resonance of Metals</u>,

74. Crompton, T. R., <u>Gas Chromatography of Organometallic Compounds</u>, Plenum Press, New York, 1982.

75. Martinie, G. D., and Skahan, D.J., <u>Measurement of MTBE quality by Gas Chromatography</u>, ARCO Chemical Company, Research and Development Report, Dept. of Analytical Chemistry, First Quarter, 1986.

76. Martinie, G. D., and Washall, T. A., <u>Effect of T-Butyl Hydroperoxide and Di-Allyl Peroxide Impurities in MTBE on Gasoline Octane</u>, ARCO Chemical Company, Research and Development Report, Dept. of Analytical Chemistry, Third Quarter, 1988.

VITA

Farhan Mohammad Al-Shahrani attained B.A. degree in Industrial Chemistry from King Fahd University of Petroleum and Minerals in 1998. His experience includes five years with Saudi Arabian Oil Company (Saudi Aramco); as a Lab Scientist at the Research and Development Canter in Dhahran, the Kingdom of Saudi Arabia. He worked in the Crude and Product Evaluation Unit, Chromatography Unit and lately assigned to be a member of the Fuel Team in the Technology & Research Division. He served as a chairman of the exhibition committee of the 5th International Chemistry in Industry Conference and Exhibition held in the Kingdom of Bahrain from Oct. 14 to 16, 2002. He is currently an active member of the American Chemical Society (ACS) as well as a member of the Board of Directors for the local Saudi Chapter of ACS.