

CHAPTER II

REVIEW OF LITERATURE

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1- Gasoline Basics :-

Gasoline is a complex mixture of hundreds of chemical compounds . It is primarily composed of hydrocarbons, which are molecules made up of different combinations of hydrogen and carbon . In simple terms, the internal combustion engine is a system of pistons and cylinders that transforms the chemical energy of gasoline into mechanical energy by oxidizing (combusting) hydrocarbons .The four-stroke internal combustion engine powers nearly all gasoline-fueled automobiles . Typically, a controlled mixture of atomized fuel and air is delivered to a cylinder; the mixture in the cylinder is compressed by a piston and then ignited by means of a spark plug. The resulting combustion drives the piston down, transmitting power to the crankshaft and thence to the wheels (Owen & Coley, 1995; Heywood, 1988) . This process results in exhaust gases, which include oxidizing carbon & hydrogen in the form of water and carbon dioxide (CO₂) as well as other combustion by-products, such as oxides of nitrogen (NO_x), carbon monoxide (CO), volatile organic compounds (VOC) and particulate matter (PM) .

Oxides of nitrogen (NO_x) are formed from the chemical reaction of ambient nitrogen and oxygen at the high temperatures present in the combustion chamber, while CO, VOC and PM are formed from unburned hydrocarbons resulting from incomplete combustion . Notably, VOC emissions result not only from the combustion of gasoline, but also from the evaporation of fuel in the gasoline tank, permeation through fuel lines and hoses and during refueling at the gasoline station . In automobiles, exhaust

PM is generally associated with older, poorly maintained cars, which consume lubricating oil, although VOC and NO_x contribute to secondary PM in the atmosphere . **(National Air Quality and Emission Trends Report, 1993; Paul Degobert, 1995)** .

Since the mandated de-leading of gasoline in the early 1970's, the regulation of motor fuels has been used in combination with vehicle emissions standards to reduce air pollutant emissions associated with motor vehicle use . In 1992, the federal government began to require that oxygen-containing chemical compounds (oxygenates) be added to some gasoline to reduce the CO emission that result from incomplete fuel combustion, particularly under cold weather conditions . The "oxyfuel" requirements apply to areas in violation of National Ambient Air Quality Standards (NAAQS) for CO and, as CO is a wintertime problem, require that gasoline sold in the wintertime contain 2.7 percent oxygen by weight **(Reyla, 1991; NESCAUM, 1998)** .

The reformulated gasoline RFG program was introduced as part of the Clean Air Act Amendments of 1990 for the primary purpose of reducing emissions of ozone precursors (mainly NO_x and VOCs) and toxic emissions from automobiles . The RFG contain 2 percent oxygen by weight . For a variety of reasons including cost, availability, ease of transport (especially in pipelines) and performance properties, MTBE has emerged as the primary oxygenate used in the most parts of the world to meet this requirement to date . To meet the 2 percent by weight requirement, MTBE is generally present in RFG at 11 percent by volume.

RFG must be formulated to meet a number of specifications (ASTM, D 4814-98 a) to ensure uniform fuel performance in a variety of vehicles and under widely different operating conditions . A particularly important parameter of gasoline performance is

octane . Higher octane gasoline is more resistant to knock . Knocking results in a loss of power and can lead to engine damage (**Owen & cole, 1995**) . Another important fuel parameter is volatility which is measured in units of pounds per square inch (psi) . Because highly volatile gasoline will evaporate more readily leading to excessive evaporative hydrocarbon (HC) emissions, both RFG and conventional gasoline are formulated to meet certain Reid Vapour Pressure (RVP) limits . If RVP is too low, vehicle start-up and running performance may be adversely affected, especially under cold-weather conditions. (**Downstream Alternatives, INC., 1996**) .

The formulation of gasoline to meet performance requirements and environmental standards is complex . Gasoline components have different octane and volatility characteristics; moreover, the properties of these constituents sometimes change in the presence of other fuel components . Similarly, some hydrocarbons are significantly more resistant to knock (i.e. higher in octane) than are others (**Stump et al, 1990; Furey, 1985**) . As it turns out, some amount of MTBE and/or ethanol would likely be used in gasoline even without an oxygenate mandate because both compounds function as octane-enhancer and blended into domestic gasoline as early as 1979 as substitute for lead .

The air quality goals of the reformulated gasoline program have been largely successful, providing an effective strategy for reducing pollutant emissions that continue to smog, CO, fine particulate matter, has, acid deposition and toxic air pollution (**NESCAUM, 1998**) . As a complement to vehicle emissions standards, the environmental regulation of fuels has played a critical role in advancing air quality objectives . Importantly, the benefits of cleaner fuels accrue immediately upon introduction of

the fuel . The benefits apply to all gasoline-powered engines, regardless of their age and design .

2- The Reformulated Gasoline :-

The primary purpose of the reformulated gasoline RFG program is to reduce motor vehicle emissions of ozone forming VOCs and NO_x during the summer months, as well as year-round emissions of certain toxic air pollutants . The RFG program was mandated to be implemented only in the nine cities in the U.S.A with the worst ozone air pollution problems . **(Los Angeles, San Diego, Chicago, Houston, Baltimor, Milwaukee, Philadelphia, Hartford, and New York city)** . In addition, may other areas with ozone levels exceeding the public health standards have requested to be included in the program on a voluntary basis . Essentially, the RFG is not a new gasoline but a new program . The main differences between RFG and conventional gasoline (CG), are in the levels of ingredients . Specifically, RFG's benzene and other aromatics levels are reduced . RVP is reduced in RFG only during the summer . The first phase, in effect from 1995 to 1999, and contain 2 wt.% oxygenate. The second phase of RFG program took effect on January 1, 2000 . In its phase II, RFG performance standards for VOC, which requires a reduction of no less than 25% from baseline emission **(California Environmental Protection Agency, 2000)** .

3- Gasoline and Driving Performance :-

Driveability is the term used to describe how an engine starts, warms up and runs. It is the assessment of a vehicle's response to the accelerator, relative to what the driver expects. Driveability problems include : hard starting, backfiring, rough idle, poor throttle response and stalling **(SAE, 1998; De Gobert, 1995; Heywood, 1988)** .

The key gasoline characteristic for good driveability is volatility. In cold weather, gasoline is blended to vapourise easily . This allows an engine to start quickly and run smoothly until it is warm . In warm weather, gasoline is blended to vapourise less easily to prevent vapour lock and minimize evaporation, which contributes to air pollution (**Hochhauser et al, 1993**) . It is important to note that there is no single best volatility for gasoline volatility must be adjusted for the altitude and seasonal temperature of the location where the gasoline will be used. Four properties are used to measure gasoline volatility : Vapour pressure, distillation profile, vapour-liquid ratio and driveability index . The fourth property is calculated from the distillation profile (**Doherty, 2001**).

Industry specifications developed by the American society for Testing and Materials (ASTM) define volatility classes in terms of vapour pressure and distillation temperature limits, and provide recommendations for selecting the appropriate volatility class for each area (ASTM-D 4814-98a) Reid vapour pressure (RVP) is the pressure measured in pounds per square inch (psi) using a specific instrument heated to 100°F (ASTM-D323) . A lower RVP indicates that the gasoline is less volatile. Typical gasoline vapour pressures range from 6 psi in the warmer summer months to 15 psi in the colder winter months .

Distillation temperature measurements involve heating a fuel and measuring the temperature at which a certain percentage of the sample evaporates . Engine performance has been correlated with an index using the temperatures for 10% (T10), 50% (T50) and 90% (T90) evaporation . To predict cold start and warm-up driveability, a driveability index (DI) equation has been developed using T in degrees Fahrenheit :

$$DI^{\circ}_F = 1.5 (T10) + 3.0 (T50) + (T90) \dots\dots\dots (1)$$

The DI varies with gasoline grade and season; the normal range is 850 to 1300 . Lower values of DI generally result in better cold-start and warm-up performance, but once good driveability is achieved, there is no benefit to further lowering the DI . The above equation was developed using data for conventional gasolines and has not been proven to be applicable to oxygenated gasolines (Hochhauser et al, 1995) . Excessively high T50 (low E100) can lead to poor starting and warm-up performance at moderate ambient temperatures.

The Co-ordinating Research council (CRC, U.S.) has continued to improve the DI equation (1) and to make it universally applicable (World Wide Fuel Charter, 2000) . CRC tested 29 test fuels: 9 all-hydrocarbon, 11 with 10 volume percent ethanol and 9 with 15 volume percent MTBE. Some important conclusions have been achieved from this CRC study that driveability problems increase for all fuel types as DI increases. An oxygen correction factor is required for higher driveability demerits for oxygenated gasoline as compared to all-hydrocarbon gasoline. Another Equation has been developed including the oxygen correction (World-Wide Fuel Charter, 2000).

$$DI^{\circ}_F = 1.5 (T10) + 3.0 (T50) + (T90) + (11 \times \text{wt\% Oxygen}) \dots(2)$$

In this equation temperatures are in degrees Celsius, and the following conversion formula is to be used (ASTM-D4814).

$$DI^{\circ}_C = (DI^{\circ}_F - 176) / 1.8 \dots\dots\dots(3)$$

At DI°_C levels higher than 550-570 driveability concerns increase dramatically . The oxygen correction factor, introduced in the above relation, to be applied for oxygenated gasolines which contain ether or alcohol oxygenates . Limited data on low and ultra low emission (LEV/ULEV) vehicles suggest that a similar oxygenate correction may be needed for ether-blended gasolines

(Pfalzgraf et al, 1996 & Otto et al, 1998) . The need for and the magnitude of correction will be determined as more data are needed (World-Wide Fuel Charter, 2000) .

The gasoline specification controls the volatility by setting limits for the vapour pressure, distillation profile and vapour-liquid ratio properties (ASTM-4814-98a) but does not include a DI requirement. Gasoline volatility not only affects a vehicle's driveability but also its hydrocarbon emissions-both evaporative and exhaust emissions (National Air Quality and Emission Trends Report, 1993; De Gobert, 1995) .

4- Gasoline and Antiknock Performance :-

Knock-free engine performance is as important as good driveability. Octane number is a measure of a gasoline's antiknock performance-its ability to resist knocking as it burns in the combustion chamber . There are two laboratory test methods to measure the octane number of a gasoline: the Research octane number (RON) and the Motor octane number (MON) . For a given gasoline, RON is always greater than MON . The difference between the two is called the sensitivity of the gasoline. There is a procedure to measure the antiknock performance of a gasoline in vehicles. The resulting value is called Road octane number (Rd ON) . Since vehicle testing is more involved than laboratory testing, there have been a number of attempts to predict Rd ON from RON and MON. The following relation has been developed (Chevron U.S.A. Inc. 2004; On Road Study, 1995) .

$$\text{Rd ON} = a (\text{RON}) + b (\text{MON}) + C$$

A good approximation for Rd ON sets $a = b = 0.5$ and $C = 0$, Yielding $(\text{RON} + \text{MON})/2$, commonly abbreviated $(R + M)/2$, which is called the Antiknock Index (AKI) . The performance of some vehicles correlates better with RON or MON alone than with the

combination of the two . Also, for a given vehicle, the correlation can vary with driving conditions. In general, the RON affects low to medium speed knock. The MON affects high speed knock. The RON of a gasoline is typically 8 to 10 number higher than the MON. For instance, an 87 octane gasoline typically has a MON of 82 and a RON of 92.

Most new cars are equipped with a device called a knock-sensor that detects knock and provides a signal to the electronic control module (ECM) . To eliminate the knock, the ECM retards the engine's timing, that is, it fires the spark plug later in the compression stroke. This reduces the peak cylinder pressure and, as a result, the tendency for autoignition . Loss of power due to the ECM's knock-elimination strategies can be prevented by using a gasoline with a higher AKI .

The octane number requirement (ONR) of an engine is defined as the octane number of the reference fuel that will give trace knock under the most severe speed and load conditions. Trace knock is the knock intensity that is just audible to the trained specialist .ONR usually is reported as on AKI value. Combustion chamber deposits increase ONR in two ways: increasing the combustion temperature and increasing the compression ratio **(Doherty, 2001; Chevron U.S.A. Inc. 2004)** .

Whether or not an engine knocks is dependent upon the octane quality of the fuel and ONR of the engine The ONR is affected by various engine design factors and in-use conditions **(Downstream Alternatives, Inc. 1996)**. Engines experience increased ONR when the ignition timing is advanced . The air/fuel ratio also affects ONR with maximum octane requirement occurring at an air/fuel ratio of about 14.7:1 . Enriching or enleaning from this ratio generally reduces octane requirement. Combustion temperature is also a factor, with higher combustion

temperatures increasing ONR . Additionally the exhaust gas recirculation rate can affect ONR . There are also atmospheric and climatic factors which influence ONR.

Since 1984, vehicles have been equipped with more sophisticated control systems, including sensors and engine management computers to measure and adjust for changes in air temperature and barometric pressure . These vehicles are designed to have the same AKI requirement at all elevations . Knock sensor systems are installed on many late-model engines . These systems, which temporarily retard spark timing to eliminate knocking, reduce power and acceleration . Using gasoline with an antiknock rating higher than that required to prevent knock or to prevent spark retardation by the knock sensor will not improve a vehicle's performance . Because different grades of gasoline have essentially the same heating value, they all provide the same power as long as their antiknock performance meets the engine's requirement .

Fuel economy is usually expressed as the number of miles traveled on one gallon of gasoline Relationship between fleet average fuel economy and heating value has been studied and the obtained results show that the average fuel economies are proportional to the heating values of the gasoline tested **(Hochhauser et al, 1993)** Conventional gasolines have always varied in heating value due to differences in formulations among batches and among refiners . Also, heating values varies by grade and by season . Gasolines which contain more aromatics have higher heating values . The heating value of winter gasoline is about 1.5% lower than summer gasoline because winter gasoline contains more volatile hydrocarbons **(California Air Resource Board, 1991)** .

Oxygenated gasolines have lower heating values than all-hydrocarbon gasolines because the heating values of the oxygenate components are lower than those of hydrocarbon they displace. The percent decrease in heating value is close to mass percent oxygen in the gasoline. For example, gasoline in carbon monoxide non-attainment areas must be oxygenated to a minimum of 2.7 mass% oxygen during four or five winter months. As a result, its heating value is about 2.7% lower than conventional gasoline (**Down stream Alternatives, Inc 1990; US-EPA, 1995; On-Road study, 1995**). Reformulated gasoline must be oxygenated year around to an average oxygen content of about 2.0 mass%. As a result, their heating values are about 2.0% lower than that of conventional gasoline. In addition, California phase 2 reformulated gasoline sets some limits on distillation temperatures and aromatics content, which have the secondary effect of lowering the density of the fuel. This reduces the heating value by about another 1%.

5- Environmentally Driven Changes in Gasoline :-

Over the past four decades, efforts to control the environmental impact of automobiles and the fuels that power them have proven increasingly complex. Many vehicle manufacturers have begun utilizing simple devices such as positive crankcase ventilation (PCV) valves, catalytic converters, exhaust gas recirculation (EGR) systems, evaporative emissions canisters, and an increasingly complex array of computer controls, modifications to air/fuel management systems, and various sensors (**Heywood, 1988; Pfalzgraf et al,1996; Otto et al, 1998; Hanel et al, 1996**). Vehicle manufacturers have also utilized engines with three or four valves per cylinder to improve fuel economy and reduce emissions (**National Air Quality, 1992**). Most of the vehicle emission reductions to date have been

achieved through vehicle Technology . However, attention has been increasingly directed to developing cleaner burning fuels . These efforts include removing or adding various components, reducing fuel volatility and will now include more complex compositional changes to gasoline .

Compositional change to gasoline is not a new concept . Over the years, gasoline composition has changed as a result of new refining technology, changes in crude oil feedstock, and variations in the demand for finished products. Recent changes, however have been driven by environmental considerations and this trend will continue . This will add to the difficulty of balancing environmental requirements with fuel performance standards .

The first environmentally driven change was the introduction of unleaded gasoline and the reduction in lead content of the leaded gasoline in the mid 1980's . In January 1, 1996 the addition of lead is no longer permitted . Next came the need to manufacture more unleaded gasoline and to phase out the use of lead . The refiners and petroleum industry responded to this need for the production of higher octane components through a variety of actions . These actions included the production of more reformat, FCC gasoline, alkylate, isomerate and also the addition of oxygenates (alcohols and ethers) to the gasoline . The need for oxygenates prompted some refiners to add units to make MTBE and other ethers . The refinery ether unit utilize isobutylene and isoamylenes, produced from refinery cat crackers, as a significant potential source for the production of these ethers (**Piel, 1989; Thomas, 1989, Piel and Thomas, 1990**) .

The use of more refining processes during the 1980s resulted in increased levels of aromatics, olefins/diolefins, and light components in gasoline. Aromatics include products such as benzene, a known cancer causing agent; toluene, a known toxin;

and xylenes which are the major contributors to smog formation . Olefins and diolefins present environmental concerns due to their contribution to smog formation, gum formation and deposits formation in the fuel injector and intake system. Light end components have a dramatic impact on fuel volatility which resulted in increased evaporative emissions . Evaporative emissions of hydrocarbons contribute to ground level ozone formation **(Colucci, 1989; Piel, 1989)**.

In January 1988, certain areas of Colorado become the first localities to mandate the use of oxygenated gasolines . By 1991, several other western cities had followed Colorado. The winter of 1992/1993 was the first year that the oxygenated gasoline programs were implemented on a nationwide basis . Oxygenated gasolines were extremely successful with impressive reductions in CO emissions **(Maples, 1993; EPA, 1993; EIA, 1998)** .

6- RFG Reduces Ground-Level Ozone :-

RFG program is one of the latest in a series of measures taken to provide cleaner burning automotive fuels and is first implemented in 1995 . RFG is often confused with oxygenated gasoline while both contain oxygenates, such as ethanol and MTBE, they are not exactly the same . Oxygenated Fuels are simply conventional gasolines with an oxygenate added . Oxygenated gasolines are sold during winter months to reduce CO emissions. Reformulated gasolines also contain oxygenates but under other compositional and property alterations to reduce ozone forming emissions . RFG is a year round program with slightly different versions of the fuel for summer and winter . All reformulated gasoline is oxygenated but not all oxygenated gasolines are RFG . It should also be noted that conventional

gasoline often contains 6-8 vol.% MTBE to boost octane (**Down Stream Alternatives, Inc., 1996**) .

In the presence of heat and sunlight, hydrocarbon emissions (both tailpipe and evaporative) react with NO_x to form ground level ozone . The requirements for reformulated gasoline are designed to reduce this reaction . A distinction should be made at this point with regard to reformulated gasoline as an ozone control strategy . Environmentally driven efforts are currently dealing with CFC (Chlorofluorocarbons) reclamation programs to reduce ozone depletion in the upper atmosphere, where it provides protection against harmful ultraviolet rays . However, at ground level, ozone is a respiratory irritant . It is particularly harmful to young children, the elderly, and those with respiratory conditions . Ozone is the principal ingredient in smog . Reformulated gasoline programs are directed toward reducing ground-level (lower atmosphere) ozone (**Lidderdale and Bohn, 2000; Lidderdale 1995; U.S.- EPA, 1998**) .

7- Oxygenates :-

RFG must contain an average of 2.0 weight percent oxygen (11.0 vol.% MTBE, 12.8 vol.% ETBE or TAME) . Oxygenated gasoline programs require winter grades to have an average of 2.7 weight percent oxygen (12.8 vol.% MTBE, 17.2 vol.% ETBE or TAME) . MTBE is manufactured by the chemical reaction of methanol and isobutylene. Similarly, ETBE is manufactured by the chemical reaction of ethanol and isobutylene . TAME is produced from the reaction of methanol and isoamylenes . These chemical reactions eliminate the unfavorable characteristics of methanol (**Piel, 1989; Thomas, 1989; Piel, 1990; Health Effect Institute, HEI, 2004**) .

As with the other oxygenates, the use of ethanol as a gasoline component will improve combustion and thereby reduce CO emissions . In U.S., ethanol has seen continued growth as a gasoline component since the late 1970s under the name gasohol **(Bykowski & Grabe, 1981, Furey, 1985; Yaccarino, 1989)** . Ethanol is approximately 35% oxygen so a 10 volume percent blend would contain approximately 3.5 weight percent oxygen . Blends exceeding 10 volume percent ethanol are not permitted by law, nor are they likely to occur, because ethanol costs much more than gasoline **(API, American Petroleum Inst., 2001)** . More recently, ethanol supporters have focused attention on ethanol's ability to replace MTBE . Other studies suggest that using ethanol can also slow global warming when compared with harmful gasoline component . **(Graham et al, 2000;EIA, 2001; EIA, 2002)**

Although the use of other oxygenates in gasoline is permitted, such use is not likely .The other alcohols and ethers permitted in gasoline are hampered by either high cost and/or unfavourable blending characteristics making their use in the near term very unlikely . While its is accepted that oxygenated fuels have the ability to improve octane quality, enhance combustion, and reduce exhaust emissions, refiners still harbour doubts regarding volatility, energy content (fuel economy), materials compatibility, and fuel system deposits. Extensive testing has been conducted in each of these areas and the effects of oxygenates are well studied .

8- Oxygen Content and Enleanment :-

Oxygenated fuels may contain up to approximately 2.7 weight% oxygen when blended with ether and 3.5 weight% oxygen when blended with ethanol . This level of oxygen further

enleans the fuel charge and the vehicles may display symptoms of enleanment (improper idle, engine dies) . This can usually be easily corrected by minor adjustments to enrich the air/fuel mixture **(Piel & Thomas, 1990; Piel, 1989)** .

Newer vehicles are equipped with onboard computer control systems . These systems include oxygen sensors, installed in the exhaust manifold, to determine the oxygen content of the exhaust gases . Vehicles equipped with onboard computers will compensate for the oxygen content of the fuel . The maximum level of oxygen permitted in gasoline through the sensor . He effects of fuel oxygen level on tailpipe emissions can be estimated from a number of emission test programs reported in the literature **(Piel, 1989)** . As expected, the oxygen in the fuel introduces an enleanment effect that significantl reduces CO and HC emissions Piel and Thomas (1990) have studied the effects of gasoline properties other than oxygen content in different reformulated blends . A conclusion has been reached that the properties associated with the alcohols are not as effective as ethers in reducing HC emissions .

9- Blending Refinery Streams :-

The final step in gasoline manufacture is blending the various streams into a finished product . Despite the diversity and ingenuity of the processes within a modern petroleum refinery, no single stream meets all the requirements of gasoline . It is not uncommon for the finished gasoline to be made up of five or six streams . Sometimes, to provide more flexibility, a stream is distilled into several fractions and each fraction is used as a separate blending component, for example fluid catalytic cracking (FCC) is distilled into FCC light and FCC heavy gasoline **(Chevron U.S.A. Inc., 2004)** .

Several factors make blending flexibility critical: The requirements of the gasoline specification (ASTM 4814) and the regulatory requirements are complex . Different marketing locations served by the refinery may have different performance and regulatory specifications . A blend must satisfy multiple internal inventory and economic requirements . Refiners use computerized blending programs to generate an optimized blend recipe . A computer program integrates all the performance, regulatory, economic and inventory requirements (**Hydrocarbon Processing, 1992**) .

10- MTBE Ground water Issue :-

A major issue regarding the use of MTBE concerns its detection at low levels in ground water in numerous locations . MTBE is very soluble and once released, it moves through soil and into water more rapidly, than other chemical compounds present in gasoline . Once in ground water, it is slow to biodegrade and is more persistent than other gasoline-related compounds . At greater depths, MTBE persists evaporation longer times (**Keller, Arther, 1998**) . The available data indicate that the primary source of MTBE in ground water has been oxy-fuel releases from leaking underground storage tank systems . Other significant source include leaking above ground storage tanks, fuel pipelines refueling and accidental spills .

In response to concerns about MTBE in domestic water wells in the United States, EPA formed a blue Ribbon Panel of experts from the health and scientific communities, the petroleum industry, water utilities and state and local governments . In addition to recommendation regarding the underground storage tank program and remediation programs, the panel recommended reducing the use of MTBE and Congressional action to remove the

2.0 wt.% oxygen requirement from the reformulated gasoline program (Doherty; 2001, **Blue Ribbon Panel on Oxygenates in gasoline's, 1999**) . The panel also recommended accelerated study of health effects and groundwater characteristics of compounds that may be used as replacements . some of these compounds include ETBE, MTBE, di-isopropyl ether (DIPE), ethanol, alkylate and aromatics (CEC, 1998; Hadder, 1999; Wang et al, 1999) .

Gasoline spilled and leaked into the environment is major source of water pollution . At elevated levels gasoline-MTBE blend can adversely affect the quality of drinking water, pose a threat to public health and threaten aquatic life . important report was prepared by Albine Environmental, Inc. and was extended for use by members of the California MTBE Research Partnership, the underground storage tanks (UST) management and operation practices . Over fifty suggestions for possible improvements and recommendations of UST experts were summarized from five documents which have been published by the State Water Resources Control Board (SWRCB, 1998, 1999) . Also, a survey of UST management and operation practice has been published by European Fuel Oxygenates Association (EFOA, 1999) .

11-Alternatives to MTBE :-

MTBE has been the leading ether-based oxygenate, other include ETBE . The primary alcohol oxygenates are ethanol and tert-butyl alcohol (TBA) . The extent to which any of these oxygenates might be used in place of MTBE would depend on availability, performance characteristics and cost relative to other alternatives . The long-term use of other ether-based oxygenates, such as ETBE and TAME for example, may be limited by the same water quality concerns that have prompted calls for a phase-

out of MTBE . As a class, ethers are soluble in water and resistant to biodegradation; consequently, ether contamination of soils and surface/ground water environments is difficult to remediate **(Interagency Assessment of Oxygenated Fuels, 1997)** . ETBE and TAME when leaked or spilled, are expected to behave much like MTBE . Among the alcohol alternatives, use of methanol is limited due to its toxicity . Furthermore, there is evidence that TBA may be carcinogenic .

More than any of the other oxygenate alternatives, ethanol widely considered to be the primary replacement option for MTBE. Moreover, ethanol is relatively low in toxicity compared to many other gasoline constituent, it biodegrades readily, and it does not present taste and odour issues when present at low concentrations in water **(NEIWPCC, 2001)** . However, like MTBE (Octane rating 110), ethanol (Octane rating 115-118) also function as an octane enhancer and can displace other, more toxic octane enhancers . Despite these similarities, replacing MTBE with ethanol will not be straight forward and is likely to result in other changes to the formulation of both RFG conventional gasoline . When MTBE is removed and ethanol is added to gasoline, the Reid Vapour pressure (RVP) increases and thus volatile organic compound (VOC) emissions increase . To counter the increase, the remaining base gasoline must be adjusted to a lower RVP. For the summer blends, the RVP of RFG must be reduced by 1.3 psi **(EIA, 2002)** . This is accomplished by removing the light materials which have high RVP **(EIA, 2001)** .

The refinery impacts of removing MBTE have been studied by Purvin & Gertz Inc. and Starto Inc. (alkylation process expert) studied the shift from MTBE to ethanol in two refineries . The results of this study have been reported elsewhere **(Graham et al, 2000)** . In summary, This study shows gasoline production losses

of 7-17 percent when MTBE is replaced with ethanol . Similar process has been done by the Energy Information Administration (EIA) . The main difference between these two process is that EIA used a higher percent of normal butane which has a very high RVP (EIA, 2002).

The EIA results found that the volume of total gasoline production from this refinery could easily restored to the MTBE volume levels with purchased alkylate was increased enough to match the prior MTBE-blended gasoline volumes and no emissions constrains occurred . The trouble some issue with the alkylate solution is whether adequate volumes of alkylate will be available for purchase from other U.S. refinery regions or internationally at a reasonable price during the startup of the MTBE bans .

The California Energy Commission (CEC), has developed California supply-demand balances and described some of their analyses in a presentation discussed how volume losses occur both due to less ethanol being used than MTBE and due to removal of pentanes to balance ethanol's high RVP during the low-RVP season (8 months per year in California) . The gap would need to be filled by importing alkylate (Gordon, 2001 b) . CEC also commissioned studies on monitoring refiner's plans and actions to eliminate MTBE and find additional supply (Anthony, 2002) .

Alkylate and iso-octane have frequently been discussed as attractive gasoline blend components to deal with supply issues if MTBE is eliminated . MTBE has an octane rating (R+M/2) of about 110, while alkylate is 92-94 and iso-octane is about 98 If MTBE is banned, the iso- butylene feed streams to refiner MTBE units will primarily be used to expand refinery alkylate production . The economics of conversion to iso-octane production makes this

less likely within refineries . Refiners could expand alkylate production using more C₃ or C₅ olefins not currently being alkylated, but most refiners do not see that occurring based on current alkylate economics (EIA, 2002) .

MTBE also is currently produced in large commercial plants outside of refineries . These commercial plants do not have a captive source of olefin feedstock's, and thus have a much different production cost structure . These plants could be converted to iso-octane or alkylate production (EIA, 2002) .

12- Substitution of Ethanol / for MTBE :-

The widespread substitution of ethanol for MTBE in reformulated and conventional gasoline blends has the potential to effect pollutant emissions from automobiles both directly and indirectly . These changes raise potential health concerns that must be considered in a comprehensive assessment of health impacts associated with the large-scale substitutions of MTBE by ethanol under the RFG program . This potential arises primarily from the generation of aldehydes as a by product of the oxidation of ethanol and also from ethanol's well- documented effects on fuel volatility (Marnett, 1998; Anderson et al, 1997; Tanner et al, 1998; Gaffney et al, 1997) .

Evidence on ambient air quality impacts from available monitoring studies is mixed. Studies performed in Denver Colorado (Anderson et al, 1997), Brazil (Gaffney et al, 1997) and New Mexico (Whitten, 1998) found that concentrations of formaldehyde and acetaldehyde during the winter of 1995/96, when nearly all gasoline was blended with ethanol, were not significantly different from those measured during the winter of 1988/89 when gasoline was blended with MTBE . Although these findings suffer from methodological shortcomings, Whitten found

evidence for increased acetaldehyde and peroxyacetyl nitrate (PAN) concentrations that may be attributed to ethanol use .

Gasoline-powered vehicle are an important source of reactive volatile organic compounds (VOC) and NO_x , which combine in the atmosphere in the presence of sunlight to form tropospheric (ground- level) ozone which is a powerful respiratory irritant . Emissions of NO_x and VOC from RFG would not be expected to change as a result of substituting ethanol for MTBE, since these emissions are limited by the performance requirements of the program . Moreover, according to the National Research Council (NRC), use of ethanol is also not expected to effect the overall reactivity, i.e., propensity to form ozone of specific VOCs emitted under different fuel scenarios (**National Research Council, 1999**) . The NRC did find that evaporative emissions from motor vehicles using ethanol-blended RFG could be significantly higher than for MTBE-blended RFG if RVP constrains were relaxed .

13-Health Hazards of Gasoline and Gasoline/MTBE BLENDS:-

MTBE has been used as an octane enhancer in the USA since 1979 at levels up to about 15% by volume without significant problems (**Arco, 1980; Kirwin and Galvin, 1983; EU, 1985**) . In 1992, due to the introduction of the 1990 clean Air Act amendments, the use of oxygenated fuels at higher levels was mandated in 37 specific areas of the USA (**US-EPA, 1991**) . During the winter of 1992 there were a number of complains from some of these areas that the use of gasoline/MTBE blends was associated with headaches, eye irritation, nausea, and dizziness . This was unexpected as previously there had been few complains, and there was little indication from studies in animals that MTBE

presented any unusual problems (Kuna, 1984; Scala, 1988; Von Burg, 1989; Ridlon, 1991; Sivak and Murphy, 1991) .

The toxicity of MTBE to animals has been extensively studied the acute toxicity in mammals is low by all routes tested (Sivak and Murphy, 1991) . MTBE is slightly irritating to the skin and eyes of rabbits and was negative in sensitization assays in guinea pigs (ARCO Chemical Company, 1980) . In a 90 day inhalation study, rats were exposed to MTBE vapours, there was no mortality nor any indications of significant toxicity at exposure levels up to 8000 ppm (Duffy, 1992; McKee & Molyneux, 1997) . In rabbits, no teratogenic or development toxicity was noted (Bevan, 1997) . The overwhelming evidence from mutagenicity studies indicates that MTBE does not affect genetic materials and is not considered to have mutagenic potential (McCoy and Johnson, 1995; Duffy, 1992).

14- Human Effects Related to Exposure to MTBE :-

There have been some worker complaints of odour, nausea, headache, and irritation of the eyes and respiratory tract . In general, these effects have been associated with exposures at levels greater than 100 ppm (Raabe, 1993a,b) . Also, a number of complaints were received during the winter of 1992-1993, a period of time during which the use of MTBE became widespread in the USA as a means of reducing carbon monoxide emissions . The complaints were concentrated in some commutes and were much less prevalent in others even when the gasoline contained similar levels of MTBE .

To address these complains, the EPA, API and several other organizations initiated a series of studies to more fully quantify MTBE exposures, and to try to relate these exposure levels to human effects. The data were discussed at a conference

(Raabe, 1993a) and the main findings were that: Exposures in non-occupational settings are much less than 1 ppm, although they could reach 10 ppm during refueling under unusual circumstances. Occupational exposures are usually less than 10 ppm, short-term, isolated exposures may reach 300 ppm . The epidemiological data do not generally support a causal relationship between subjective health effects and MTBE exposure . Controlled human exposures to MTBE at 1.4 and 1.7 ppm for 1 hour produced no clinically significant subjective or objective health effects .

A study in which volunteers was exposed to 18, 90 or 180 mg/m³ (equivalent to 5, 25 and 50 ppm) MTBE for 2 hours showed a dose unrelated increase in nasal peak expiratory flow . There were no signs of eye or mucous irritation in this study, nor were there any significant subjective effects (Johanson, 1995) . The study by Johanson et al. has been supported by other investigators, who exposed healthy male volunteers to 0, 25 and 75 ppm MTBE for one and three hours (Riihinaski et al, 1996) . It was concluded that mild symptoms, mainly a feeling of heaviness in the head and to a smaller extent slight mucous membrane irritation, was caused by exposure to MTBE at concentrations of 75 ppm for 3 hours .

15- Human Effects Associated with Exposure to Formulated Gasoline:-

Exposure to gasoline vapours at concentrations between 200 and 500 ppm can be irritating to the eyes at 500 ppm it can be irritating to the nose and throat and may produce symptoms of CNS . Depression, numbness and anaesthesia may occur following 15-60 minute exposures to 1000-5000 ppm vapour . Exposure to levels above 5000 ppm may result in loss of

consciousness, coma, and death . Epidemiological studies have revealed little evidence that exposure to gasoline is associated with significant adverse health risks except under condition of gasoline abuse (**McKee & Molyneux, 1997**) .

Two major European studies in Italy and Scandinavia have focused on MTBE exposures and levels in air in marketing . Personal exposures of shift duration for service station attendants ranged from 0.1 to 2.5 mg/m³, with averages in the range 0.4 to 0.7 mg/m³ (**Giacomello, 1996**) . Personal samples taken in four locations whilst customers were dispensing gasoline gave concentrations ranging from 0.2 to 245 mg/m³ with geometric means of 4.4 to 7.4 mg/m³ (**vainiotalo, 1996**) . These values relates to sample times of less than one minute .

Ambient levels of MTBE in air on service stations were also reported in these studies . (**Giacomello, 1996**) quoted average levels around pump units of 107 to 247 µg/m³ . (**Vainiotalo, 1996**) found levels that were higher by the pumps than at the service station perimeter, average levels being in the order of 200 to 1400 and 4 to 14 µg/m³ respectively . In these studies, average equals arithmetic mean . Data from north American studies by McCoy and Johnson for the API (1995), show that the average exposures in transport and distribution of gasoline, are consistent with the findings by McKee & Molyneux (1997) .

16- Some Health – related Questions :

Media reports, concerning the improvements in measured air quality, have not come without questions . In several cities, residents have complained of a variety of health effects from exposure to MTBE/gasoline exhaust . Headaches, dizziness, nausea, sore eyes, and respiratory irritation (**National Research Council, 1999, Keller, 1988**) . Addition studies have been

conducted by international health organizations, leading research universities and U.S. Environmental Protection Agency (EPA) . These studies confirm that MTBE reduces carbon monoxide, greenhouse gas emissions and smog forming compounds . **(Renewable Fuels Association, 1997; National Science and Technology Council, 1997; Keller, 1998) .**

The over whelming majority of scientific evaluations to date have not identified any health-related risks to humans from the intended use of MTBE in gasoline . Furthermore, MTBE does not accumulate in the body and it has not been shown to impair fertility, or damage a developing fetus or the genetic structure of cells . MTBE, like most chemicals, has the ability to cause some injury at extremely high dosages Extensive research indicates that the MTBE doses required to produce illness in laboratory animals are thousands of times greater than those to which humans could conceivably be exposed **(Health Issues, 2002) .**

For practical purposes, the interpretation of any health risks associated with the addition of MTBE to gasoline requires a comparison to the health risks associated with conventional gasoline . Some organizations include the U.S. Environmental Protection Agency (EPA), The American Petroleum Institute (API), and environmental groups such as the Natural Resources Defense Council (NRDC) and American lung Association (ALA), have all argued that current Knowledge suggests that MTBE is a less serious pollutant than the gasoline components it replaces **(McCarthy and Tiemann, 2001).**

According to these organization reports, the cancer risk from exposure to MTBE is substantially less than that for benzene, a minor constituent of gasoline that is classified as a known human carcinogen and more than 100 times less than that for 1, 3-

butadiene, a carcinogenic emission product of incomplete fuel combustion **(U.S. EPA, 1997)** .

Numerous governments and world-renowned independent health organizations have found no sufficiently compelling reason to classify MTBE as a possible cancer-causing agent for humans : The Department of Health & Human Services, National Toxicology Program voted in December 1998 not to list MTBE in its 9th report on carcinogens . The World Health Organization's International Agency for Research on Cancer determined in November 1998 that MTBE is not classified as a human carcinogen .The National Research Council in September 1998 concluded that exposure to MTBE could not cause kidney tumors for humans. California Science Advisory Board, determined in December 1998 that MTBE could not be considered carcinogenic or a developmental or reproductive toxicant . The European Union Risk Assessment on MTBE concluded in December 2000 that MTBE is not a human carcinogen . **(HOT TOPICS, 2002; Health Issues, 2002)** .

The Assumptions used by researchers from the University California (U.C.) in 1998 regarding the potential for widespread contamination of water supplies by MTBE are not supported by more recent data . The U.C. data was the basis for Governor Gray Davis' decision to ban the use of MTBE in 2003, due to concern about what had considered a threat to the environment . **(Governor Gray Davis, 1999)** . After four years of study by the European Union (EU) on assessing the potential risks of MTBE to both human health and to the environment, concluded that these is not a single peer-reviewed study that concludes that MTBE causes cancer in humans **(White and Knoll, 2002)** .