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Evaluation for Leaded and Unleaded Gasoline as Hazardous Waste

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ABSTRA CT:

With the phase out of alkyl lead compounds as necessary additives for gasoline in order to raise its octane number, the alternative is to reformulate gasoline to have nearly same octane number but with other chemical structures . Such reformulated gasoline (RFG) is found to contain higher aromatics , benzene, isoparaffins, in comparison to leaded gasoline. Additionaly, this reformulated gasoline can also contain oxygenated additives. Accordingly, this paper is aiming at evaluation of emitted hazardous chemical compounds from car engines at fuel combustion.

Role of chemical structures for reformulated gasoline in emission of volatile organic compounds(VOC) and poisining materials are considered.

Key Words : *Alkyl Lead, Octane Number, Reformulated Gasoline, Oxygenated, Volatile Organic Compounds*

INTRODUCTION

Gasoline is a fuel for spark-ignited internal combustion engines. Generally, gasoline is contained hydrocarbons with widely different chemical structures and volatility. According to current trends in refiners there are different gasolines available in the markets and may have different performances and exhaust emission, which are affected by used engines .

In the worldwide refining industry, today, there are two important trends which are greatly affecting gasoline chemical and performance characteristics:

1. Refiners are working hard in order to convert every drop of crude oils, as received at the refiners, into valuable and usefuel products. Consequently, most refiners are now equipped with different conversion units, e.g. thermal cracking, catalytic cracking, hydrocracking, cocking, reforming, hydrofinishing, hydrotreating .... etc (1&2)[x] .
2. Refiners are pushing to increase quantities of unleaded gasolines on account of leaded gasolines. Environmental regulations in many countries are restricting the use of leaded gasolines.

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x Numbers in parentheses designated references at end of paper

Unleaded gasolines can be rich in some hydrocarbon components, basically aromatics and isoparaffins(3 & 4).

Factors affect gasoline composition and consequently its exhaust emission are the following ones (1-7) :

- Type of refined crude(s), e.g. paraffinic, asphaltenic, or mixed crudes.
- Applied refining and conversion technique(s)
- Ratio of different hydrocarbons in the gasoline blend, e.g. aromatics, naphthens, paraffins, olefins, diolefins, aromatic-olefins...etc.
- Presence of traces of non-hydrocarbon polar components in the gasoline blend, e.g. sulphur, nitrogen and oxygen compounds.

Most published works concerning gasoline compositions and their impact on exhaust emission are agreed on restricting gasoline compositions only on the following components and at such percentages (1-7):

- Paraffins, mainly branched chain alkylates, at percentage of 60-70% volume.
- Aromatics, mainly alkyl benzenes, at percentage of 25 - 40% volume. The Clean Air Act in USA restricts aromatics and benzene ($C_6 H_6$) in gasoline by only 25% and 1% volume respectively (6)
- Unsaturates and polar groups, can be variable, but in refiners equipped with hydrogenation treating units such components are usually not more than 5% volume (2&4).

The differences in exhaust emission due to variation in gasoline compositions, can be showed with the following features:

- Gasoline consumption rate
- Gasoline thermal and oxidative stability
- Emission gases, e.g. CO, NO_x, noncombustion hydrocarbons... etc.
- Emission of vo latile organic compounds (VOC)
- Startability problems , not only early in the morning but can also be all over the day
- Driveability problems

The aim of this paper is to compare leaded with unleaded gasoline concerning their hydrocarbon components and their tendency to form different exhaust emissions.

OCTANE NUMBER REQUIREMENTS AND UNLEADED GASOLINES

Octane number is a measure for gasoline knocking characteristic in spark-ignition engine. All types of new designed engines requested the increase in their compression ratios by the aim to improve their performance, power, speed, ..etc. It is a general role that the higher the engine comperession ratio, the higher the octane number requirement in gasoline.

Since 1921 tetraethyl lead (TEL) is incorporated in gasolines to increase their octane numbers. Due to the developments in engines TEL is increased in gasoluines from 0.1 ml/ liter in 1921 to reach about 0.6 ml/ liter in 1970. In some countries TEL percentage reached up to 0.9 ml/liter.

With the concern to reduce emission of pollutants from engine the Envirobmental Protection Agency (EPA) in USA issued many regulations and lows to reduce or restrict such emission.

Simultaneously a device is developed to reduce emission of carbon monoxide (CO), nitrogen oxides (NOx) and noncombustion hydrocarbons. This device is working on catalytic conversion for these pollutants, and accordingly it's commercial name is catalytic converter. Catalytic converter can achieve the following reduction:

- CO, to reduce by 96%.
- Non combustion hydrocarbons, to reduce by 96%.
- NOx, to reduce by 76%

In using of catalytic converters in med-seventies, leaded gasoline has resulted in catalytic poising under the effect of lead. Therefore, EPA in 1 st January 1978 took regulations to reduce TEL in gasolins, so lead can be lower than 0.2 ml/ liter and then to reduce to 0.1 ml/liter, in 1985, and to 0.05 ml/ liter in 1986, and finally to phase it out in 1988. USA is restricted for such reduction in TEL and then for phasing out. Japan also is producing all it's gasoline as unleaded.

To meet high octane number requirements in unleaded gasolines, it is essential to increase their content from aromatics and isoparaffins components.Additionaly, some oxygenated compounds (ethers, alcohols,...etc) can be added to get unleaded gasolines with high octane numbers.

REACTIVITY OF HYDROCARBON COMPONENTS ON HAZARDOUS EMISSION

Reactivity of gasoline components on hazardous emission can be ordered as shown in Figure 1.

Hazardous Emission

High Reactivity

- Diolefins
- Aromatic Olefins
- Olefins
- Aromatics
- Iso-Paraffins
- Naphathenes
- Paraffins

Low Reactivity

Fig1 : Reactivity of Gasoline Chemical Components on Deposits Formation

It is possible to explain such gradual decrease in reactivity of these components in hazardous emission according to the following:

- **Diolefins,** are considered as the highly reactive components. Presence of more than one double bond in the diolefins facilitate their reaction reactivity and can leed to formation of deposits and hazardous emission. Conjugated dienes are classified as very reactive components, e.g. 3 pentadiene [CH_2=C (CH_3) - CH = CH_2] and 1,3 butadiene (CH_2 = CH -CH= CH_2), especialy in presence of other olefins (4).

As a general trend in refiners, it is necessary to eliminate most unsaturates from gasoline compositions via hydrogenation processes. But such trend is not always possible to be implemented .

- **Aromatic-olefins and mono-olefins,** mono-olefins are coming in their reactivity after diolefins, but aromatic-olefins, due to their chemical configuration, are more reactive than simple olefins. All these olefins must be treated via hydrogenation in order to convert them to saturates.

By the aim of comparison, Table (1) includes percentages of olefins in both leaded and unleaded gasolines in some selected countries and regions . Accordingly, it is difficult to generalize the current trends in changing from leaded to unleaded gasolines, i.e. to increase or to reduce the contents of olefins in gasolines. It is quite clear that olefins contents are highly depending on the applied refining and treating units, e.g. distillation, reforming, isomerization, ...etc. Percentages of blended components in gasolines are also playing a major role. But in most countries, olefins content is carefully considered in order to inhibit their reactivity in hazardous emission.

- **Aromatics,** aromatic compounds in gasolines are presented in different percentages, mostly as alkyl benzenes. Table (2) shows the percentages of aromatics in both leaded and unleaded gasolines in some selected countries and regions. These figures show that most unleaded gasolines contain higher percentages of aromatics in order to achieve their high octane numbers requirements.

Combustion of aromatic compounds give exhaust emission full with volatile organic compounds (VOC), which are with carcinogenic effects. Such conclusion is pushing from the environmental point of view to reduce aromatics content in gasoline, especially aromatics with high boiling points. But low aromatics content requires the using of oxygenated additives in order to get gasolines with high octane numbers. USA restriction on aromatics content in gasolines by maximum of 25% volume is not yet achieved in most European Countries.

With regard to benzene (C_6 H_6) content in gasolines, also USA restriction of 1% volume benzene maximum is not yet applied in the European Countries. Table 3 includes benzene contents in both leaded and unleaded gasolines in some selected countries and regions.

- **Iso-paraffins,** Iso-paraffins can be with lower oxidation stability than n-paraffins according to their degree of branching . But generally, iso-paraffins are more stable than aromatics and olefins.The trend worldwide is to increase iso-paraffins contents in unleaded gasolines through reformate units.

- **Naphthens and paraffins,** are classified as the lowest reactive components in gasolines and can be accepted without restriction limits. These compounds have little impact on deposits formation and simultaneously their environmental problems are relatively limited. On other words, they are considered as environmentally friendly and acceptable components.

The polar groups (sulphur, nitrogen and oxygen compounds) are considered as highly reactive in deposits formation. The natural affinity of these compounds towards metals, (especialy hot metal surfaces) are catalysing the hazardous emission.

TRENDS TO REDUCE COMPONENTS WITH HAZARDOUS EMISSION

According to the previous reactivity classification of different hydrocarbon components in gasoline blends, the general trends in refiners, worldwide, are to work, as can as possible, to achieve the following:

- Increase total paraffins, mainly branched alkylates
- Enhance presence of isoparaffins
- Reduce aromatics
- Eliminate all polar groups
- Reduce unsaturates, as low as possible

In addition to these refiners trends, there is also worldwide acceptance for the following two concepts (1-7):

- Reducing unsaturates and polar components improve gasolines stability and reduce their tendency for hazardous emission.
- Reducing aromatic contents, especially high boiling point aromatics, can also give gasolines with lower tendency for hazardous emission.

Table 1 : Olefins Contents in Leaded and Unleaded Gasolines in Some Selected Countries and Regions (1994) (8).

Country	Leaded Gasolines % vol.	Unleaded Gasolines % vol.
France	1-26	1-24
Germany	2-12	3-10
UK	1-23	0-15
Italy	1-16	2-17
Egypt	0-2	0-3
Benelux (x)	4-14	1-16
Mid-Europe	1-17	1-11
Nordic Countries	0-12	1-14

(x) Benelux : Belgium, Netherland (Holland) and Luxembourg

Table 2 : Aromatics Contents in Leaded and Unleaded Gasolines in Some Selected Countries and Regions (1994)-(8)

Country	Leaded gasoline % Vol.	Unleaded gasoline % Vol.
France	22-46	31-54
Germany	31-47	84-51
UK	16-34	22-46
Italy	32-45	19-40
Egypt	10-49	46-56
Benelux (x)	24-43	31-50
Mid -Europe	32-45	30-48
Nordic Countries	34-49	25-40

(x) Benelux : Belgium, Netherland (Holland) and Luxembourg

GASOLINE ADDITIVES

Historically the development of fuels additives started in year 1921, as listed in Table 4. To achieve engine cleanliness, it is necessary to use detergent-dispersant additives. These additives are usually termed by the expression deposits control additives.

According to the US Interim requirements for deposit control additives, which is effective since 1 st January 1995, it is a must that (9):

- All gasolines must contain deposits control additives, at concentration equal to or more than the minimum recommended with the additives manufactures.
- To test fuels typical of in-use fuels, especially in deposits formation tendency.
- To caliberate all injectors at least quarterly.
- To document all gasoline transfers and status of additization.
- To maintain all documents for at least five years.
- To support minimum additive recommendation by testing via engine procedures.
- Potential fines are as high as 25 thousand US dollars per day for gasoline producers or blenders failing to add sufficient deposits control additives.

The most common types of detergent additives are: alkanol amines, amido amines. imidozalines, orthophosphates....etc. With regard to dispersent additives the well know types are: polyether amines, polybutene amines, polybutene succinimides, alkyl succinimides, hydroxyl polyamino carbomates, ...etc. The concept of using detergent-dispersant additives is that clean engine gives clean environment.

Table (3) : Benzene Contents in Leaded and Unleaded Gasolines in Some Selected Countries and Regions (1994)-(8)

Country	Leaded gasoline % Vol.	Unleaded gasoline % Vol.
France	0.3 - 4	0.2 - 4.3
Germany	0.5 - 4.3	0.7 - 4.6
UK	0.5 - 2.7	0.4 - 3.9
Italy	0.8 - 2.5	0.6 - 2.7
Egypt	1.5-3	1.5-4
Benelux (x).	0.6 - 4.7	0.8 - 2.8
Mid - Europe	1.5 - 4.2	0.6 - 4.2
Nordic Countries	0.4 - 4.3	0.9 - 3.5

(x) Benelux : Belgium, Netherland (Holland) and Luxembourg

Table (4) : Historical Development and Marketing of Gasoline Additives

Year	Additives
1923	Lead Antiknock
1926	Dyes
1928	Scavengers
1930	Antioxidants
1939	Metal Deactivators
1946	Corrosion Inhibirors
1950	Enticing
1953-1954	Detergents
1959	Manganese Antiknock
1965	Demulsifiers
1969	Tertiary Butyl Alcohol
1970	Detergents/Dispersants
1977	Ethanol
1979	Methyl Tertiary Butyl Ether
1980	Unleaded Deposits Control
1982	Flow Improvers

VOLATILE ORGANIC COMPOUNDS (VOC)

Definition of VOC is the following :

Organic copmound that contribute to ground level ozone formation. VOC include toxic comounds, oxygenated organic compounds and all volatile hydrocarbons, except ethane and methane.

VOC are classified as carcogenic and hazardous wastes, and must be reduced in engine exhaust emission, as much as possible.

Sources of emission for VOC are listed in Table (5). VOC chemical components are listed in Table (6). VOC increase with the increasing of reactive components, i.e. aromatics and benzene. Reducing of vapour pressure (i.e. decreasing percentage of volatile compounds) also leads to reduction in VOC.

Table 5: Sources of Emission for VOC

	%	
Exhaust Emission	37	
Evaporation	28 ↘	60
Running loss	32 ↗	
Refueling	3	
	100	

Table 6 : VOC Chemical Compostion

	WT.%
- Benzene (C_6H_6)	72.5
- Formaldehyde	11.4
- Acetaldhyde	8.1
- 1,3 Butadiene	5.1
- Polycyclic Organic Compounds	2.9
	100.0

CONCLUSIONS

This paper is discussing the reactivity of different hydrocarbon components, as existed in different gasolines, in hazardous emission . According to given data and results, it seems possible to conclude with the following:

- In spite that most refiners are expanding their production from unleaded gasolines, but still refiners are not capable to reduce content of reactive groups in composition of these gasolines towards hazardous emission.

- According to gained experience, addition of detergent dispersant additives is a must. Deposits formation in different engines parts can lead to many disadvantages and problems in engine operation, driveability, maintenance, and hazardous emission.

- The requirement of reduction in aromatics and unsaturates in unleaded gasolines, either to protect environment or reduce deposits must be balanced by oxygenated additives.

- Reduction of VOC must be carefully considered.

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