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STUDY THE TOXIC EFFECTS OF AROMATIC COMPOUNDS IN GASOLINE IN SAUDI ARABIA PETROL STATIONS

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ABSTRACT

Two gasoline samples of octane numbers 91 and 95 from Saudi Arabia petrol stations were studied statically and dynamically. This study was achieved at three different temperatures 20°C, 30°C and 50°C representing the change in temperatures of the different seasons of the year. Both the evaporated gases and liquid paraffinic including light aromatic hydrocarbons (BTEX) of gasoline samples inside the tank were subjected to analyze qualitatively and quantitatively via capillary gas chromatography. The stream composition of each gasoline sample was calculated by the combination of the liberated gases and the liquid gasoline fuel inside the car tank. The detailed hydrocarbon composition and the octane number of the studied gasoline samples were determined using detailed hydrocarbon analyzer. The idea of research is indicating the impact of light aromatic compounds in gasoline on the toxic effect of human and environment on the one hand, and on octane number of gasoline on the other hand. Although the value of octane number will be reduced but this will have a positive impact on the environment as a way to produce clean fuel.

Key words: Gasoline, Saudi Arabia petrol stations, Statically and dynamically, Light aromatic hydrocarbons, Capillary gas chromatography, Detailed hydrocarbon composition, Octane number.

INTRODUCTION

Gasoline is a mixture of over 200 petroleum-derived chemicals plus a few synthetic products that are added to improve fuel performance[1-4]. Gasolines come primarily from petroleum cuts with a range of boiling points from 38 to 150-205°C and a carbon number distribution of C_4-C_{12}[5,6]. The most important hazardous components of most gasoline fuels are benzene and many more compounds than just the better known BTEX alkyl benzenes

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(toluene, xylenes, and ethyl benzene). These aromatics are very harmful and carcinogenic compounds and their high volatility is the source of dangerous because it is easy to transmitted to humans by smell[7,8]. Workers at petrol station and factories that depend on gasoline exposed to the dangers of aromatic compounds liberated from gasoline fuel that have immediate and future effects of hand, these are articles have a direct relationship with octane number of gasoline fuel. The most common way people are exposed to benzene and other light aromatic hydrocarbons is when they fill their car with gasoline. Benzene evaporates quickly from contaminated water. Benzene vapors are present in exhaust from many industries and automobiles. People who live near highways or industries or petroleum station can be exposed to light aromatic hydrocarbons BTEX.

The abundance of aromatic compounds in air must be 0.2 ppm, and in water must be 0.1 ppb and if this proportion increased to 100 ppm the following things occur: (1) Shortness of breath and throat (2) headche, loss of balance (3) The effects on the liver and blood pressure (4) Irregular beat of the heart. The affects that occur after year:- (1) cancer which occurs after continuous exposure to benzene (2) effects on the nervous system and blood cells[9].

The impact of aromatic compounds on octane number to existence relationship between them[10-12]. It has been reduced aromatic compounds or separation part of the gasoline and reformat a small extent so do not affect the quality of fuel and efficiency of combustion within the engine and other words that it was abandoned for a fraction the value of the octane number, also, at the same time is a bad impact on the environment in terms of high pollutant by vehicle exhausts and petrol station. when the value of octane number will be reduced this will have a negative impact on the combustion of engine to a degree depend on the percentage of liberated light aromatics. In some times as away to reduce aromatic compounds are the product of gasoline with octane number unacceptable which can be way to produce clean fuel.

The capillary gas chromatography connected with flame ionization detector[13,14] plays an efficient analytical tool for complete analysis of gasoline fuel using selected ply siloxane capillary column[15].

The main goal of this work is the analysis of gasoline of 91 and 95-ON (octane number) statically and dynamically at three different temperatures 20^{o}C, 30^{o}C and 50^{o}C and study the impact of light aromatics on the human and on the octane number of engine motor.

EXPERIMENTAL

Sampling

For static studies, the volume 4 mL of each gasoline sample was selected for static studies at three different temperatures 20°C, 30°C and 50°C each temperature was kept at 30 min as constant time.

For dynamic studies (under shaking), the same volume of gasoline sample was taken and the shaking time is 30 min at each selected temperature.

Gas chromatography (GC)

The studied gasoline fuel samples of octane numbers 91 and 95 were subjected to gas chromatography. The instrument used was Clarus-500 gas chromatograph equipped with flame ionization detector (FID) and splitt-aplittless injector. Oven temperature was programmed from 100°C to 300°C at fixed rate of 3°C min^{-1}. HP-1 fused silica capillary column (30 m X 0.53 mm X 0.5 µm) was used for the analysis. Helium was used as carrier gas at flow rate 2 mL min^{-1}, the injector and detector temperatures are 300 and 325°C respectively.

Detailed hydrocarbon analyzer (DHA)

The studied gasoline samples were analyzed by the detailed hydrocarbon analyzer (DHA) of model Clarus-500 gas chromatograph. The instrument was equipped with a flame ionization detector, the system was provided with selective column and soft-ware for the DHA. The analyzer is a factory tested by Arnel (Job No 6477-AGC). The column used was tuned 100 m length and 0.25 mm internal diameter with a film thickness of 0.5 µm, the column was coated with polydimethyl siloxane as stationary phase. The analysis was done according to ASTM D-6730 standard method, the DHA data obtained was converted into PIONA results (i.e., paraffins, isoparaffins, olefins, naphthenes and aromatic percentages of each carbon number). The instrument settings were as follows: Carrier gas is helium at a flow rate of 1 mL min^{-1}. Oven Program (ramp 1): from 5°C (for 10 min) to 48°C (for 54 : 40 min) at a rate of 5°C min^{-1}. The initial temperature was maintained by CO_2 cryogenic system. Oven Program (ramp 2): from 48°C to 200°C (for 30:00 min) at a rate of 1.4°C min^{-1}. The values of octane numbers were calculated automatically from the detailed analysis of liquid gasoline fuels from DHA.

RESULTS AND DISCUSSION

Physical and chemical properties of gasoline

Information regarding the physical and chemical properties for the gasoline mixture is located in Table (1). In cases where data are not available for gasoline, ranges are given to indicate the different values for the individual components[16].

Table 1: Physical and chemical properties of gasoline[16]

Property	Information
Molecular weight	85 -100
Physical state	Liquid
Boiling point	Initially, 39°C after 10% distilled, 60°C after 50% distilled, 110°C after 90% distilled, 170°C final boiling point, 204°C
Density	0.7-0.8 g/cm
Color	Gasoline odor
Solubility in water at 20°C	Insoluble
Solubility in organic solvent	Absolute alcohol, ether, chloroform, benzene
Flash point	-46°C
Flammability limits	1.4-7.4%
Autoignition temperature	280-486°C
Explosive limits	1.3-6.0%

The capillary gas chromatographic analysis of the studied liquid gasoline fuels of octane numbers 91 and 95 were shown in Figs. 1 and 2. The chromatograms show the composition of gasoline mixture, normal paraffines, iso-paraffines and aromatics, the composition of gasoline contains hydrocarbons starting from ethane to pentadecane.

Summary reports of the studied gasoline samples of octane numbers (ON) 91 and 95 were achieved using the modern analytical GC technique named detailed hydrocarbon analyzer (DHA) and the results were given in Tables 2, 3. It has been found that the studied two gasoline samples of ON 91 and 95 contain aromatics 28.8 and 24.9 wt. %, respectively. The major amount of these aromatic are benzene and alkyl benzenes named BTEX (benzene, toluene, ethyl benzene and xylenes), and poly aromatics represents the minor amounts. The high volatility of the BTEX is the source of dangerous because it is easy to transmitted by smell to workers at petrol station and People who live near highways or petroleum station. These aromatics are very harmful and carcinogenic compounds.

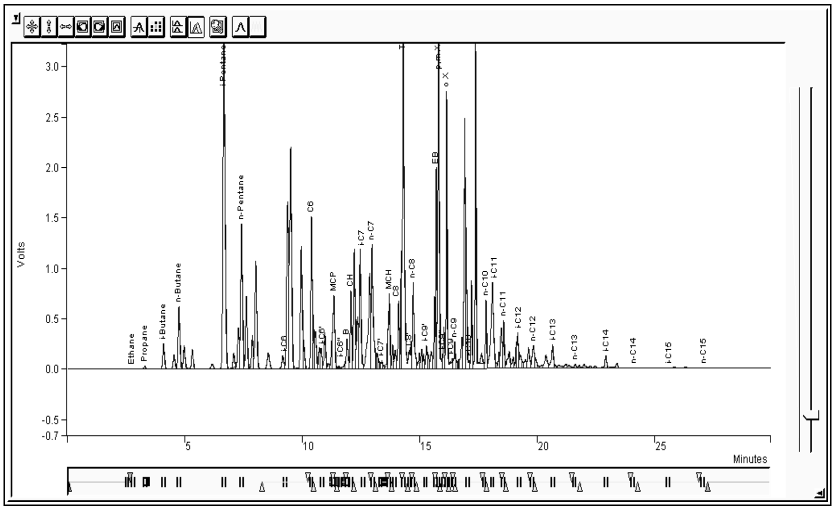

Fig. 1: Chromatogram of gasoline fuel of Octane Number 91

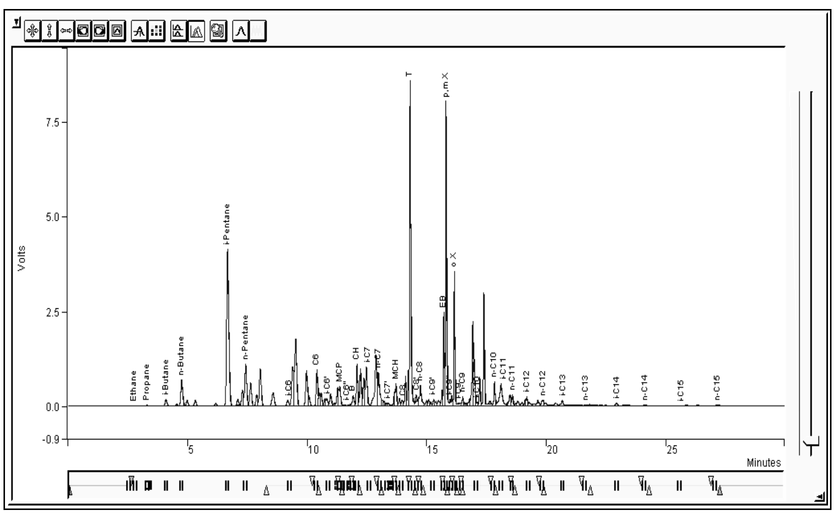

Fig. 2: Chromatogram of gasoline fuel of Octane Number 95

Gasoline is a volatile, flammable liquid obtained from distilling and refining petroleum, or crude oil, so, the compositions (paraffines, iso-paraffines and oliffines) of the studied gasoline samples are nearly the same, this was indicated from the total carbon and total hydrogen percentages given in Tables 2 and 3. The only differences in their compositions is the weight percentage of aromatics and the additive Tert Butyl Ether (TBE) to increase octane number.

Table 2: Summary report of gasoline sample of Octane No. 91

Group type	Total (Mass %)	Total (Vol. %)
Paraffins	10.544	11.766
I-paraffins	36.853	39.751
Olefins	13.911	14.919
Naphthenes	5.665	5.393
Aromatics	28.870	22.292
Total C14+:	0.000	0.000
Total unknowns	1.752	1.576
Grand total	100.000	100.000
methyl-t-butylether	4.405	4.303
Average molecular weight	87.571	
Relative density	0.679	
Vapor pressure (psi @ 100°F)	5.33	
Octane number (calculated)	90.44	
Percent carbon	86.045	
Percent hydrogen	13.156	
Bromine number	28.871	

Table 3: Summary Report of gasoline sample of Octane No. 95

Group type	Total (Mass %)	Total (Vol. %)
Paraffins	9.033	10.709
I-paraffins	37.500	40.701
Olefins	13.373	14.277
Naphthenes	10.427	9.662
Aromatics	24.961	20.753
Total C14+:	0.096	0.091
Total unknowns	2.269	2.155
Grand total	100.000	100.000
methyl-t-butylether	2.340	2.282
Average molecular weight	88.288	
Relative density	0.688	
Vapor pressure (psi @ 100°F)	5.74	
Octane number (calculated)	94.66	
Percent carbon	86.413	
Percent hydrogen	13.163	
Bromine number	27.221	

Statistical studies

GC studies of gas, liquid and stream composition of gasoline fuels 91 and 95 at 20^{o}C, 30^{o}C and 50^{o}C

Gas chromatographic analysis of gas and liquid in gasoline 91 and gasoline 95 statically at 20^{o}C, 30^{o}C and 50^{o}C was achieved and one example from them was given in Table 4. The composition of gas sample contains hydrocarbons starting from ethane to dodecane including light aromatics BETX, toluene followed by benzene represents the high value compared with other aromatics. Iso pentane and iso hexane represent the maximum mole percent in the liberated gas from gasoline inside tank, the rest of the percentage distributed on the other components. The composition of liquid sample in gasoline contains hydrocarbons starting from ethane to pentadecane including high percentage of light aromatics BETX. The weight percentages of the light aromatics BTEX are given in Tables 5 and 6. Toluene exhibits the highest percentage of aromatics than the other aromatics followed by xylenes. The stream composition was calculated by the combination of the all compositions of liberated gases and that in liquid gasoline inside the tank.

Table 4: Gas chromatographic analysis of a gas, liquid, and stream composition of gasoline sample (ON = 91) at 20°C

Components	Gas sample		Liquid sample		Stream composition	
	Mol. %	Wt. %	Mol. %	Wt. %	Mol. %	Wt. %
Ethane	0.033	0.014	0.011	0.003	0.011	0.004
Propane	1.054	0.638	0.027	0.012	0.039	0.018
i-Butane	5.782	4.609	0.429	0.261	0.491	0.299
Butene	1.311	1.009	0.149	0.088	0.163	0.096
n-Butane	15.659	12.481	1.972	1.200	2.130	1.300
i-pentane	43.086	42.631	14.321	10.814	14.653	11.096
pentene	0.886	0.852	1.587	1.165	1.579	1.162
n-Pentane	2.396	2.371	3.189	2.408	3.180	2.408
i-Hexanes	21.071	24.902	11.321	10.211	11.434	10.341
n-Hexane	1.615	1.909	2.457	2.216	2.448	2.214
Methyl cyclopentane	3.978	4.591	4.645	4.092	4.637	4.096
Benzene	0.606	0.649	2.040	1.668	2.023	1.659
Cyclohexane	0.405	0.467	2.087	1.839	2.068	1.827
Heptanes	0.893	1.228	8.072	8.466	7.989	8.402
Methyl cyclohexane	0.093	0.122	0.991	0.998	0.981	0.990

Cont…

Components	Gas sample		Liquid sample		Stream composition	
	Mol. %	**Wt. %**	**Mol. %**	**Wt. %**	**Mol. %**	**Wt. %**
Toluene	0.805	1.018	15.220	14.678	15.053	14.557
Octane	0.162	0.254	3.139	3.753	3.105	3.722
Ethyl-benzene	0.032	0.047	4.407	4.897	4.357	4.854
p, m-xylene	0.070	0.102	10.495	11.662	10.374	11.559
o-xylene	0.016	0.023	0.532	0.591	0.526	0.586
Nonanes	0.042	0.073	5.545	7.444	5.482	7.379
Decanes	0.004	0.007	4.531	6.748	4.479	6.689
Undecanes	0.001	0.003	2.075	3.395	2.051	3.365
Dodecanes	0.000	0.001	0.531	0.947	0.525	0.938
Tridecanes	0.000	0.000	0.173	0.335	0.171	0.332
Tetradecanes	0.000	0.000	0.046	0.095	0.045	0.094
Pentadecanes	0.000	0.000	0.006	0.014	0.006	0.014
Total	100.000	100.00	100.000	100.000	100.000	100.000
Mol. wt.	72.919		95.543		95.282	
Equ. liq. density	0.6364		0.7409		0.7398	
Total wt. of aromatic (BTEX)					1.765 mg	

The amounts of total light aromatics liberated from liquid gasoline fuels 91 inside care tank statically at 20^{o}C, 30^{o}C and 50^{o}C reaches 1.529%, 1.956% and 2.216%, respectively, and that of gasoline 95 are 0.822, 0.959 and 1.320, respectively. It is clear that the liberated light aromatics from liquid gasoline fuel inside car tank increase as a function of temperatures. These amounts have harmful effect on human health and environment and octane number, in addition the value of octane number was decreased followed by decreasing the efficiency of engine motor.

With respect to human health

The concentrations of total volatile aromatic compounds BETX liberated from liquid gasoline fuels 91 and 95 inside car tank are ranged from 0.822 to 2.216 %. These aromatics are very harmful and carcinogenic compounds and their high volatility is the source of dangerous because it is easy to transmitted to humans by smell. Workers at petrol station and people who live near highways or petroleum station can be exposed to these light aromatic hydrocarbons.

Occupational exposure limits (OEL) are set to protect workers from excessive exposure to toxic chemicals in the workplace[8]. An OEL defines the maximum average concentration of a chemical in the breathing zone acceptable for a normal 8-hour working day for 5 days a week. the OEL for benzene only has been ranging from 0.1 to 1 ppm in 2008[17]. Here we study the effect of all light aromatic hydrocarbons like benzene, toluene, ethyl benzene and xylenes (BTEX). So, the total concentration of BTEX has very harmful effect on workers at petrol station.

Table 5: GC of BETX (Wt. %) in gas, liquid and stream composition of gasoline sample (ON = 91) statically at 20°C, 30°C and 50°C

Temp.	Sample	B	T	E	X	Total BTEX	Octane No. before evaporation	Octane No. after evaporation
20°C	Gas	0.649	1.018	0.047	0.125	1.839	90.44	89.75
	Liquid	1.668	14.678	4.897	12.253	33.496		
	Stream composition	1.659	14.557	4.854	12.145	33.215		
30°C	Gas	0.753	1.055	0.040	0.108	1.956	90.44	89.67
	Liquid	2.108	13.776	3.650	15.417	34.951		
	Stream composition	2.081	13.515	3.576	15.103	34.275		
50°C	Gas	0.831	1.197	0.052	0.136	2.216	90.44	89.32
	Liquid	2.280	14.318	5.002	20.104	41.704		
	Stream composition	2.145	13.090	4.539	18.236	38.010		

Table 6: GC studies of gas, liquid, and stream composition of gasoline fuel 95 at 20°C, 30°C and 50°C

Temp.	Sample	B	T	E	X	Total BTEX	Octane No. before evaporation	Octane No. after evaporation
20°C	Gas	0.360	0.375	0.018	0.069	0.822	94.66	93.90
	Liquid	1.749	8.684	3.304	10.361	23.762		
	Stream composition	1.729	8.565	3.256	10.212	23.766		
30°C	Gas	0.416	0.444	0.022	0.077	0.959	94.66	93.82
	Liquid	2.072	11.230	3.317	17.100	33.719		
	Stream composition	2.016	10.869	3.206	16.530	32.621		
50°C	Gas	0.528	0.554	0.048	0.119	1.320	94.66	93.52
	Liquid	2.921	7.927	6.543	23.042	40.433		
	Stream composition	2.653	7.104	5.818	20.481	36.056		

With respect to octane number

The octane number of gasoline is one of the most important parameter determining the fuel quality. The octane number of a gasoline is a measure of its resistance to detonation[18,19]. The octane number of an engine is determined according to the engine design and compression ratio. The weather, driving conditions, and mechanical conditions of the engine are some examples that will be able to influence this requirement.

The percentage of the volatile aromatic compounds BETX is one of the main factors affecting the octane number value. So, the liberated aromatics from liquid gasoline fuel into the space above liquid inside car tank have pronounced effect on decreasing the octane number as given in Tables 5 and 6. This reflecting on decreasing the efficiency of combustion within the engine to the extent of liberated light aromatics from liquid gasoline fuel. The octane number decreases with increasing temperatures.

Dynamic Studies

GC studies of gas, liquid, and stream composition of gasoline fuels 91 and 95 dynamically at 20°C, 30°C and 50°C

Gas chromatographic analysis of BTEX in the gases liberated from liquid gasoline fuels of ON 91 and 95 inside care tank after shaking (dynamically) at 20°C, 30°C and 50°C were given in Tables 7 and 8. The composition of liberated gas sample contains the same hydrocarbons given above but with different percentages. Generally, the total light aromatic hydrocarbons in dynamic studies exhibit higher values than that in static studies, the percentages of BTEX increase as a function of shaking temperature.

Table 7: GC of BETX (Wt. %) in gas, liquid and stream composition of gasoline sample (ON = 91) dynamically at 20°C, 30°C and 50°C

Temp.	Sample	B	T	E	X	Total BTEX	Octane No. before evaporation	Octane No. after evaporation
20°C	Gas	0.696	1.041	0.037	0.110	1.884	90.44	89.63
	Liquid	1.789	12.290	2.583	8.682	25.344		
	Stream composition	1.762	12.007	2.519	8.465	24.753		
30°C	Gas	0.865	1.364	0.044	0.146	2.419	90.44	89.03
	Liquid	2.323	12.819	3.689	11.254	30.085		
	Stream composition	2.245	12.205	3.494	10.659	28.603		
50°C	Gas	1.011	2.279	0.065	0.183	3.538	90.44	88.45
	Liquid	2.244	7.693	6.944	16.516	33.397		
	Stream composition	2.075	6.953	6.004	14.284	29.316		

Table 8: GC of BETX (Wt. %) in gas, liquid and stream composition of gasoline sample (ON = 95) dynamically at 20°C, 30°C and 50°C

Temp.	Sample	B	T	E	X	Total BTEX	Octane No. before evaporation	Octane No. after evaporation
20°C	Gas	0.360	0.379	0.018	0.072	0.829	94.66	93.93
	Liquid	1.749	8.684	3.304	10.261	23.998		
	Stream composition	1.729	8.565	3.256	10.212	23.762		
30°C	Gas	0.416	0.444	0.022	0.077	0.959	94.66	93.82
	Liquid	2.072	11.230	3.317	17.100	33.719		
	Stream Composition	2.016	10.869	3.206	16.530	32.621		
50°C	Gas	0.528	0.554	0.048	0.119	1.249	94.66	93.67
	Liquid	2.921	7.927	6.543	23.042	40.433		
	Stream composition	2.653	7.104	5.818	20.481	36.056		

Toluene followed by benzene represents the high value compared with other light aromatics. Here toluene represents the highest percentage of aromatics followed by xylenes. The percentages of BTEX in the stream composition of gasoline samples 91 and 95 ranged from 23.762 to 36.056 %, these values are higher compared with that of static studies. So, these amounts have high bad effect on both human health and octane number.

The separated light aromatic compounds from liquid gasoline fuel in dynamic studies have bad effect on the workers at petrol station and people live near petrol station. Also, the separated aromatics in dynamic studies exhibit high effect on decreasing the value of octane number to an extent higher than in static studied as given in Tables 7 and 8. Also, the shaking temperature 50°C exhibits maximum separated BTEX percentages, therefore, harmful to the workers at petrol station and to the environment, and also, high decrease in octane number which accompanied with decrease the efficiency of combustion within the engine.

CONCLUSION

(i) The total liberated light aromatic hydrocarbons BTEX from gasoline fuel inside car tank in dynamic studies exhibit higher values than that in static studies may be due to the liberated gases increase with shaking. The percentages of BTEX increase as a function of shaking temperature. toluene followed by benzene represents the high value compared with other light aromatics.

(ii) The high volatility of the BTEX is the source of dangerous because it is easy to transmitted by smell to workers at petrol station and People who live near highways or petroleum station causing an immediate and future effects of hand and harmful to the environment. These liberated light aromatics from liquid gasoline fuel into the space above liquid fuel inside car tank produce a gasoline with octane number unacceptable which decrease the efficiency of combustion within the engine.

(iii) The liberating aromatic compounds in both static and dynamic studies exhibit higher values in summer than in winter due to the liberation of light aromatics increase as a function of temperatures. These accompanied with increasing the chance of suffering the workers at petrol station with harmful effect and decreasing the value of octane number.

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