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An Experimental Study on the Influence of Ethanol and Automotive Gasoline Blends

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Abstract

The objective of this work is to investigate the production possibility of high octane environmental ethanol gasoline blends based on Euro specifications. The environmental gasoline is the key element to keep the environment safe and clean. Moreover, it reduces gas emissions after combustion of gasoline. One of the main methods to produce the environmental gasoline is blending gasoline with oxygenated compounds such as ethanol. Ethanol is chosen among other oxygenated compounds as it has a high influence on physico-chemical characteristics of gasoline rather than other oxygenated compounds. In addition, it has a high octane number as well as it is not polluting the environment and clean additive. In the experimental study, the choice of environmental gasolines are based on Euro-3 specifications for samples without ethanol blend and Euro-5 specifications for samples with ethanol blend; after upgrading. Various blend stocks have been prepared which have reformate, isomerate, full refinery naphtha (FRN), heavy straight run naphtha (HSRN), hydrocracked naphtha, heavy hydrocracked naphtha, coker naphtha and heavy coker naphtha. In this study, ASTM standard methods are performed for spark ignition fuels to characterize its physical and chemical properties. The results show that one has exhibited the optimum specifications of Euro-3 and thus its physico-chemical characteristics are 755.11 kg/m^3 of density, 55.88 of °API and 95 of RON, 88 of MON, 40% by volume of aromatic content and 0.66% by volume of benzene content. Moreover, ASTM distillation curve shows that the volume percentage at 150°C is 83. At the same time, the final boiling point (FBP) and recovery volume percent are 198°C and 96% respectively. While another sample has the poorest physical as well as chemical properties so that it is blended with ethanol to upgrade its characteristics. Therefore, the target is determining the optimum ethanol volume percent to be blended with poorest sample to yield the highest properties of gasoline. These blends are namely as E0, E5, E10, E15, E20. The results indicate that E5 is the optimum one for Euro-5 specifications after upgrading and thus its physico-chemical characteristics are 745.55 kg/m^3 of density, 58 of °API, 101 of RON, 98 of MON, 32.65% by volume of aromatic content and 0.47% by volume of benzene content. Moreover, ASTM distillation curve illustrates that the volume percentage at 150°C is 75. At the same time, the final boiling point (FBP) and recovery volume percent are 190°C and 97% respectively. In addition, its Reid vapor pressure equals 8.1 psi and the heat of combustion equals 35 MJ/L. In the final, Blending gasoline with ethanol is an essential issue concerning the production of environmental gasolines.

Keywords: Automotive; Gasoline; Fuel; Energy

Introduction

Nowadays the whole world has witnessed an industrial revolution in all fields, huge population growth and increase in energy consumption which have brought about an unsustainable situation. As a result, the pollution volume and impact have increased dramatically and thus reflect a bad impact on human's health. The increase in energy consumption has a direct influence to change in fuel prices in addition to a global environment as CO_2 and CO emissions increased significantly. The European Union stated that sector of transportation consumes about one third of total energy consumption [1].

This sector is mainly dependent on petroleum products (gasoline, diesel) as source of fuel. These fuels are considered a major contributor to greenhouse phenomena as they produce a high amount of greenhouse gases. Thus it becomes a necessity to find an alternative fuel instead of gasoline and diesel. This problematic situation is nearly the same in most developed and advance countries. That's why some countries have modified their fuel regulation in order to reduce CO_2 and CO emissions and keep environment clean as much as possible [2,3].

This fuel should be renewable and clean one to minimize greenhouse gases and produce an environmental fuel. Biofuels characterized by their production from renewable sources and considered as a clean fuel. It is biodegradable, and produces significantly less air pollution than fossil fuel. The fossil fuel exhaust is a potential carcinogen, since the use of bio-fuel has been found to reduce risks of cancer because it reduces the production of cancer-causing compounds, such as aromatics. Bio-fuel also produces less greenhouse gases such as CO_2. When either bio-fuel or petroleum is burned, the carbon content of the fuel returns to the atmosphere as CO_2. Plants grown to make ethanol for bio-fuel draw CO_2 out of the atmosphere for photosynthesis, causing a recycling process that result in less accumulation of CO_2 in the atmosphere. Thus, bio-fuel does not contribute to global warming in the same way that petroleum does [3-5].

In addition, Bio-fuel leads to produce exhaust NOx, hydrocarbons

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and smokes lower than a regular gasoline fuel. The gasoline fuel replacement is regulated by the amount of ethanol in the blend. Problems arise, however, due to the presence of water in the blend because commercially available ethanol is seldom found in an anhydrous state [6].

These biofuels can be used either as fuel or blending it with petroleum products. Using biofuels as an additive is much better as most of vehicles and other means of transportation are operated with petroleum products. The main standard fuel additives for gasoline are ethanol and ethyl tert-butyl ether (ETBE). The majority of advanced countries use both of them. Blending gasoline with ethanol has a great advantage as it decreases greenhouse gases significantly compared to pure gasoline and produces an environmental gasoline. Many studies have been done on ethanol gasoline blends to find the appropriate amount of ethanol. Various blending have been made to determine the optimum amount of ethanol that should be used [7-10]. A research study at Southern Illinois University has found that with bio-fuel blends engine power and specific fuel consumption slightly increase [11-14]. The aim of this study is to determine the optimum gasoline sample without any blending of oxygenated compounds based on Euro 3 specifications. Furthermore, the optimum sample is then blended with ethanol to find the optimum volume percent of ethanol based on Euro 5 specifications.

Methodology

The Experimental work is mainly a quantitative analysis to find out the optimum volume percent of ethanol added to gasoline to enhance its physical properties. This can fulfill by preparing various samples of gasoline with different volume percent from each cut (light naphtha, heavy naphtha, coker naphtha, reformate, isomerate and hydrocracker naphtha) and then applying experimental tests for the various gasoline samples (ASTM distillation, API, Reid vapor pressure, octane numbers, GC analysis). Furthermore, the optimum sample of gasoline based on Euro-3 specifications has been chosen as an environmental gasoline sample without any percentage of ethanol. Adding different volume percentages of ethanol to the gasoline sample No 5 to upgrade its physico-chemical characteristics have been achieved. Then experimental tests for the various gasoline-ethanol samples are applied (ASTM distillation, API, Reid vapor pressure, octane numbers, GC analysis). Moreover, the optimum oxygenated sample based on Euro-5 specifications has been chosen as an environmental gasoline sample with the optimum percentage of ethanol.

Experimental Work

This section is mainly showing a brief overview for the experimental work and procedures of each test conducted.

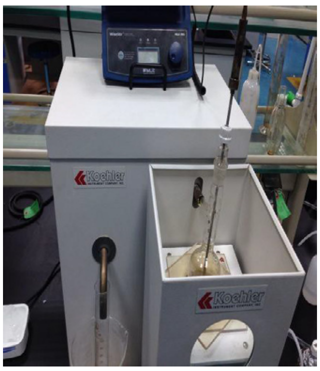

Figure 1: ASTM distillation apparatus.

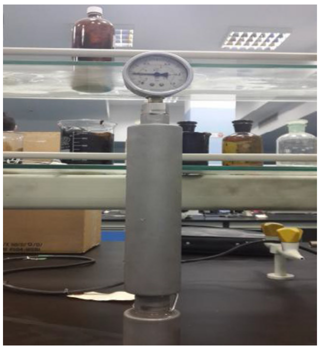

Figure 2: Reid vapor pressure apparatus.

Materials

This section is concerned with materials used in the experimental work. These materials are ethanol, isomerate, reformate, hydrocracker naphtha, heavy hydrocracker naphtha, coker naphtha, heavy coker naphtha, light straight run naphtha (LSRN), heavy straight run naphtha (HSRN), 50 ml volumetric flask and 50 ml Pycnometer.

ASTM distillation test

ASTM distillation is one of the main standard tests applied for crude oil and its products as shown in Figure 1 [16]. This test measures the temperature corresponding to volume percent evaporated from sample. The distillation of petroleum products is done in simple distillation equipment without fractionation column. The test is performed under atmospheric pressure for light products like gasoline, kerosene, diesel and heating oil. On the other hand for heavy cuts, reduced pressure is employed to decrease the boiling point of this cut. The results obtained from this test may be used to determine other physical properties like flash point.

Relative density or density

Specific gravity and API of crude oil and its products are considered two major properties which reflect the kind and price of products. As the API of the fraction is high, this indicates that the cut is light and contain valuable products so its price will be high and vice versa. The specific gravity is related with API by this relation:

$$\text{API} = \frac{141.5}{specific\ gravirty} - 131.5$$

Where specific gravity is defined as the density of the liquid cut over the density of water at specified temperature which is 60/60°F. As the specific gravity decreases, the value of the product increases as contents of light products increase [17].

Reid vapour pressure

Reid vapour pressure (RVP) of a cut or product is defined as the vapour pressure measured in a volume of air four time volume of liquid at 37.8°C which demonstrates in Figure 2 [18]. This property measures the vapour lock tendency occurring in a spark ignition engine operated with gasoline fuel in which excess vapours generated in line cause interruption in liquid fuel supplying to engine. Also it is important tool to estimate the hazard degree of fuel.

Heat of combustion using bomb calorimeter

Heat of combustion is one of the main characteristic that should be identified for hydrocarbons fuels. Combustion of fuels is either

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Figure 3: Oxygen bomb calorimeter.

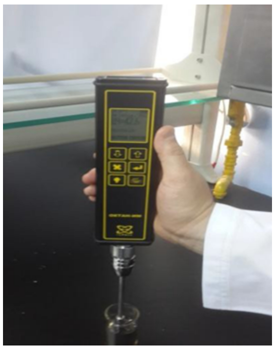

Figure 4: Octane-meter appartus.

Figure 5: Gas chromatography device.

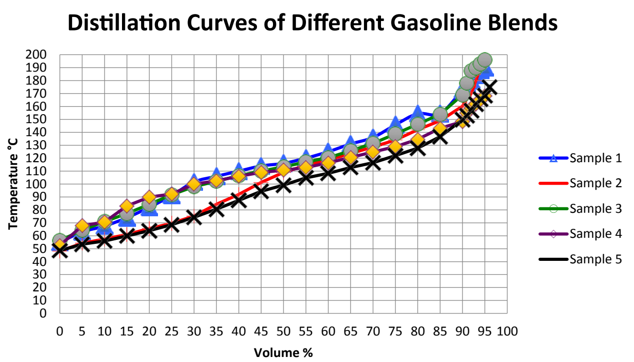

Figure 6: ASTM distillation for unleaded gasoline samples.

complete or incomplete combustion depending on the amount of oxygen. Always complete combustion is more desired than incomplete because it does not affect environment and cleaner than incomplete. Complete combustion of hydrocarbon fuels is an exothermic reaction and yields are carbon dioxide, water vapour and large amount of heat. The main aim of this test is to determine net heating value produced after combustion of fuel. A standard test is performed by ASTM using a bomb calorimeter to measure heat of combustion (Figure 3).

Octane numbers (RON and MON)

An octane number is considered one of the major properties in gasoline that must be determined accurately for motor fuels like gasoline [19,20]. This property has a great impact on motor performance and its life time so improving it is done continuously to keep it as high as possible. As the ability of motor or spark ignition engines increases to resist auto ignition the octane number of gasoline increases. The octane number of gasoline can be determined by measuring knocking value of this fuel and compared it to a mixture of iso octane (2, 2, 4, tri-methyl pentane) and normal heptane. The octane of pure n-heptane is assigned to be zero while octane of iso octane is assigned to be 100. For example a mixture of 80% iso octane and 20% n- heptane will have octane number 80. Hence if knocking value of gasoline fuel is corresponding to a mixture of 90% iso-octane and 10% n-heptane it means that gasoline fuel has octane number equal to 90. Octane number is classified into two types MON and RON. MON indicating the performance of engine at severe conditions and high speed may reach to 900 rpm (Figure 4). While RON is measuring performance of engine at smooth conditions and low speed may reach 600 rpm. AKI is the arithmetic average of RON and MON.

Detailed hydrocarbon analysis by gas chromatography (PIONA)

Detailed hydrocarbon test is one of the most main tests that should be performed for petroleum fractions. This test can be implemented on petroleum gases and naphtha cuts using a gas chromatography unit. This device consists of various units which are ordered in a certain sequence for the purpose of test. This test gives a detailed analysis for hydrocarbon family contents (paraffins, iso paraffins, olefins, naphthenes and aromatics) in petroleum fractions (Figure 5).

Results and Discussion

This section is mainly elaborating the results of experiments and giving an interpretation for what obtained in the experimental section.

ASTM distillation

According to Figure 6 which shows the volume % collected versus temperature, the following curves represent distillation curves for prepared gasoline samples as presented in Table 1. The distillation curves show the volume percent of volatile cuts with its corresponding temperatures. The curves represent mainly the initial, mid and final boiling points. The recovery of each sample reaches to 96% or 97% of total volume of samples and about 3% or 4% losses. The difference in distillation curves is due to the difference in each blend stock.

According to Figure 7, the following curves represent distillation curves for ethanol –gasoline blends as demonstrated in Table 2. The distillation curves show the volume percent evaporated with its corresponding temperature. The curves illustrate the initial, mid, and final boiling points. The recovery of each sample reaches to 96% or 97% of total volume of samples and about 3% or 4% loss. The difference in the behaviour of distillation curves is due to the volume percentages of ethanol.

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Density

The density values of unleaded gasoline samples are measured at 15.5°C. Table 3 shows density values of unleaded gasoline samples that presented in Table 1. Table 3 elaborates that the density of unleaded gasoline samples varies from (755 Kg/m^3 to 772.5 Kg/m^3). The density shows a variance as each sample differs from the other in the amount of blend-stocks used. As the lighter components increase in the sample, consequently its density decreases and vice versa. Sample 3 exhibits the optimum one according to Euro 3 specifications.

Blend-stocks, vol.%	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Reformate	52	60	51	51	36
Isomerate	12	9	8	8	17
FRN	17	10	13	-	17
HSRN	-	-	-	13	-
Hydrocracker naphtha	17	20	25	-	-
Heavy hydrocracker naphtha	-	-	-	25	25
Coker naphtha	2	1	3	-	5
Heavy coker naphtha	-	-	-	3	-

Table 1: Blend-stocks volume percent for unleaded gasoline samples.

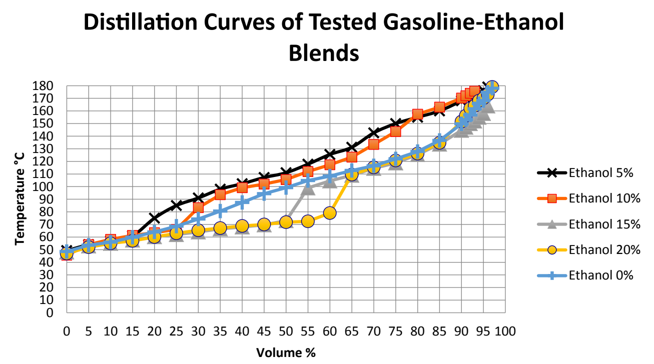

Figure 7: ASTM distillation of ethanol gasoline blends.

Blend-stocks, vol. %	E0	E5	E10	E15	E 20
FRN	17	16	15.5	14	14
Reformate	36	34	31.5	31	28
Isomerate	17	16	15.5	14	14
Hydrocracker naphtha	25	24	23	22	20
Coker naphtha	5	5	4.5	4	4
Ethanol	0	5	10	15	20

Table 2: Blend-stocks volume percent of ethanol gasoline samples.

Table 4 represents the results obtained for ethanol-gasoline blends (E0, E5, E10, E15 and E20). It appears from the results that density range from 739 Kg/m^3 to 754 Kg/m^3. The densities of E5 and E 10 are slightly smaller than the base gasoline sample by 0.66% and 1.4% respectively, while E15 and E 20 are slightly greater than base gasoline sample by 0.2% and 0.4% respectively. This indicates that as volumes of ethanol increase more than 10%, densities of samples increase and that does not sound good, while as volume percent of ethanol is 10 or less, the sample become lighter and that sounds good. So densities of E5 and E 10 are more desirable than E 15 and E 20. Eventually E5 will be the optimum blend based on Euro 5 specifications.

Reid vapour pressure

Reid vapour pressure is applied to all samples to obtain its Reid vapour pressure at 37.8°C. The experiment proves that E5 sample has a Reid vapour pressure equal 8.1 psi (Table 4). Euro standard for gasoline should be in the range from 8 to 9 psi. It is considered a physical property that should be taken into consideration especially in cold and hot countries. In cold countries RVP should have a high value to avoid operational problems in spark ignition engines. While as hot countries, RVP should be low to avoid excess vapours produced which may cause lock and interrupt liquid supply to engine.

Heat of combustion

According to Table 4, it means that everyone litre of sample E5 combusted gives calorific value equal to 35 MJ. This property is very essential to show that the thermal efficiency of the fuel is qualified or not. Also it is important for determining whether this fuel will be able to operate equipment, engine or not. Finally this test proves that sample E5 is qualified according to Euro 5 specifications.

Octane number (MON, RON)

Table 3 represents MON and RON for unleaded gasoline samples that are prepared according to proposed blend. The five samples show a high RON and MON except the sample 5. Sample 2 as well as sample 1 shows the highest octane number, but that does not mean sample

Test	Method	Unit	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Density @ 15.5°C	ASTM D1217-16	kg/m^3	768.1400	772.4280	755.1124 *(748-762) Euro-3*	769.1600	750.5480
RVP	ASTM D323-15a	Psi	7	7.5	8.4	7.2	8.6
RON	ASTM D2699-15a		95.6	98.2	95	90	88
MON	ASTM D2700-16		85.8	91.1	88	86	81.7
Aromatic	ASTM D6839-16	Vol. %	42.8420	46.6960	40 *(29-42) Euro-3*	40	32.6540
Paraffins	ASTM D6839-16	Vol. %	18.4680	16.3602	18.6639	18.6639	21.6228
Isoparaffins	ASTM D6839-16	Vol. %	25.2160	24.8070	26.3960	26.3960	27.8200
Naphthenes	ASTM D6839-16	Vol. %	11.8335	10.8500	12.9820	12.9820	15.1632
Olefins	ASTM D6839-16	Vol. %	1.6405	1.2868	1.9581	1.9581	2.7400
Benzene	ASTM D6839-16	Vol. %	0.68	0.78	0.66 *<1 Euro-3*	0.66	0.47
IBP	ASTM D86-04b	°C	55	48.1	56.3	52.4	48.5
T_{10}	ASTM D86-04b	°C	67.5	57.5	71	70.6	56
T_{50}	ASTM D86-04b	°C	116	109	113.3	110.7	99.2
FBP@ 96 Vol.%	ASTM D86-04b	°C	195	197	198 *(190-215) Euro-3*	170	174.8
Dist. @ 100 °C	ASTM D86-04b	Vol. %	30	45	34	30	50
Dist. @ 150 °C	ASTM D86-04b	Vol. %	75	85	83 *(81-87) Euro-3*	90	90

Table 3: Physico-chemical characteristics for unleaded gasoline samples.

Test	Method	Unit	E0	E5	E10	E15	E20
Density at 15.5°C	ASTM D1217-16	kg/m³	750.5480	745.5528 *(743-756) Euro-5*	739.3120	752.5500	754.1000
RVP	ASTM D323-15a	Psi	8.6	8.7 *(8.1-8.7) Euro-5*	8.8	7.9	7.4
RON	ASTM D2699-15a		88	101	106	103	97.6
MON	ASTM2700-16		81.7	98	105	102	89.5
Aromatic	ASTM D6839-16	Vol. %	32.6540	31.0910 *(29-35) Euro-5*	29.6855	28.1948	26.1013
Paraffins	ASTM D6839-16	Vol. %	21.6228	20.5910	19.6571	18.2024	18.0120
Isoparaffins	ASTM D6839-16	Vol. %	27.8200	26.4840	25.2909	24.0913	23.0232
Naphthenes	ASTM D6839-16	Vol. %	15.1632	14.4211	13.7847	13.1254	12.1240
Olefins	ASTM D6839-16	Vol. %	2.7400	2.5081	2.4909	2.0826	2.0121
Benzene	ASTM D6839-16	Vol. %	0.47	0.47 *<1 Euro-5*	0.46	0.46	0.45
IBP	ASTM D86-04b	°C	48.5	49.3	45.6	48.2	47
T_{10}	ASTM D86-04b	°C	56	57	58.2	55	55
T_{50}	ASTM D86-04b	°C	99.2	111	105.6	73	71.8
FBP@ 97 Vol.%	ASTM D86-04b	°C	178	190 *(190-210) Euro-5*	188	166	179
Dist. @ 100°C	ASTM D86-04b	Vol. %	50	38	40	55	64
Dist. @ 150°C	ASTM D86-04b	Vol. %	90	75	77.5	92.5	90
Heat of Combustion	ASTM D 4809-13	MJ/L	-	35	-	-	-

Table 4: Physico-chemical characteristics for ethanol gasoline blends.

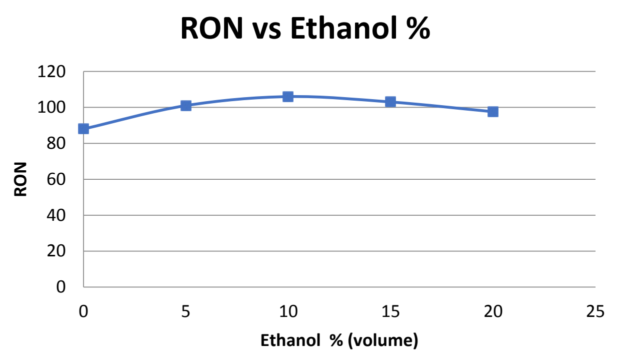

Figure 8: RON vs. Ethanol % by volume.

is matching Euro specifications. Further tests will determine the optimum sample.

According to Table 4, the following results show RON and MON of ethanol gasoline blend samples measured by octane-meter. RON of samples varies from 88 to 97.6 while MON varies from 81.75 to 105. The RON and MON shows a major variance in its value depending on volume % of ethanol added to the sample. RON and MON show an increase from the base gasoline for E5 and E10 while as it shows a decrease for E15 and E 20. The RON and MON for E5 and E10 are slightly higher than the base gasoline by 14%, 20.4%, 19.8%, and 28.4% respectively.

Figure 8 represents RON of ethanol gasoline samples with percentage of ethanol added. The curve indicates that RON is increasing until E 10 (a positive impact) and then RON begins to decrease. This proves that as the volume percent of ethanol exceed 10% by vol., RON begins to decrease. Therefore, there is no need to increase ethanol content above 10% as it has a negative impact on both RON and MON. Eventually, it has a main role in improving a spark ignition fuel if it is added within limited range.

Conclusions and Recommendations

This paper is discussing one of the main petroleum refinery issues which is the production of an environmental gasoline based on specifications of Euro-3 as well as Euro-5 using oxygenated compounds. The base gasolines in this work are mainly consists of various blend stocks produced by crude oil distillation, conversion process as well as upgrading processes. In more explanation, the Gasoline pool in this paper is mainly consists of straight run naphtha, isomerate, reformate, hydrocracker naphtha, coker naphtha, and ethanol. By comparing results of each sample, an optimum sample is chosen matching Euro-3 specifications. Also poorest sample in octane number is chosen to be blended with ethanol to enhance its physico-chemical characteristics. In addition, the choice of an optimum ethanol gasoline blend sample is based on Euro-5 specifications. Finally, it can be concluded the following points, by performing experimental results for both of base gasoline samples and ethanol gasoline blends:

a. The Production of environmental, clean and high octane number gasoline blends are the best solution for our environment.

b. The optimum unleaded gasoline sample matching Euro-3 specifications is the sample 3.

c. The optimum ethanol gasoline blend matching Euro-5 specifications is the sample E5.

d. Ethanol-gasoline-blends can be used as an alternative fuel for a variable speed spark-ignition up to 5 vol. % blends.

e. The high yield of gasoline production is based on different blend stocks not only straight run naphtha and reformate.

f. Using oxygenated compounds lead to reduce the aromatic content and consequently reduce carcinogenic compounds as well as improve octane numbers.

g. Maximizing the quality and quantity of an environmental gasoline according to standard European regulations (Euro-5).

h. An Environmental gasoline provides a great potential benefit to the refinery in view of minimizing operating costs, product quality improvement, safe and healthy living environment.

The following recommendations could be put for future work:

a. This research should be applied in the industry to prevent the hazards of air pollution.

b. The optimum composition of refinery gasoline blend should be applied for maximizing its quantity and quality with ethanol percentages.

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