Study of NOx Emissions of S.I. Engine Fueled with Different Kinds of Hydrocarbon Fuels and Hydrogen

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Abstract

Liquefied petroleum gas (LPG), Natural gas (NG) and hydrogen were used to operate spark ignition internal combustion engine Ricardo E6, to compare NOx emissions emitted from the engine, with that emitted from engine fueled with gasoline as a fuel.

The study was done when engine operated at HUCR for gasoline, compared with its operation at HUCR for each fuel. Compression ratio, equivalence ratio and spark timing were studied at constant speed 25rps.

The results appeared that NOx concentrations will be at maximum value in the lean side near the stoichiometric ratio, and reduced with moving away from this ratio for mixture at both sides, these concentrations were at its highest value when hydrogen used at CR=8:1, and got near to each other for the three hydrocarbon fuels used in the study, when the engine operated at HUCR for each fuel, but still hydrogen had maximum value, the main variable affect these concentrations was spark timing.

Keywords: liquefied petroleum gas, natural gas, hydrogen, compression ratio, Nox emissions, spark ignition engines.

1. Introduction

Thermal NOx formed by the stabilization of atmospheric nitrogen in oxidizing atmospheres at a high flame temperature exceeding 1573K or 1300 °C. Thermal NOx is generally produced during the combustion of both gases and fuel oils [1].

When the combustion is under fuel-lean conditions (with less air) and there is a rise in temperature, this will lead to an increase of NOx emissions due to increased oxygen radicals forming in the combustion process. However, when the combustion is under fuel-rich condition (with excess fuel) the oxidation reaction will involve the OH and H radicals [2].

High activation energies are required for the dissociation of oxygen molecules and the disengagement of the triple bond of nitrogen. This phenomenon causes the formation of thermal NOx to be largely dependent on the temperature, the degree of air to fuel mixing, the concentration of oxygen and nitrogen in the flame and duration of reaction occurred [3].

The environmental problems caused by NOx are now worldwide issues due to the seriousness of ozone reactivity and the amount of formation of smog. NOx combines with water vapor in clouds to produce acid rain which pollutes clean water sources and corrodes metals used in our daily life. Acid rain also harms the growth of organisms in the lake and disturbs the balance of the ecosystem both on land and at sea. Apart from that, acidified soil is the also the result of acid rain and it causes damage to the root system of trees, disabling the nutrient absorption process and disrupting the natural process of photosynthesis[4].

When NOx react chemically with other atmospheric gaseous compounds such as “Volatile organic compounds” (VOCs) under the sunlight, it will form smog. Smog is forefront to our environmental concerns as it reduces the visibility of surroundings and poses a health hazard to
humans which includes irritation of eyes, respiratory and cardiovascular problems such as asthma and headaches [5].

There are several factors which affect the formation of NOx in the engine and they are listed below:

The air-fuel ratio: plays a major role in determining the amount of emission of NOx as oxides of nitrogen are formed by the reaction of nitrogen in the fuel with oxygen in the combustion air. When the air to fuel ratio is greater than one which indicates that the combustion is in the lean condition, the fuel mixture has considerably less amount of fuel and excess amount of air. Engines designed for lean burning can achieve higher compression ratios and hence produce better performance. However, it will generate high amount of NOx due to the excess oxygen present in the air [6].

Combustion temperature: is also one of the primary factors that influence the formation of NOx. The formation of NOx is directly proportional to the peak combustion temperature, with higher temperatures producing higher NOx emissions from the exhaust [7].

The firing and quenching rates also influence the rate of NOx formation where a high firing rate is associated with the higher peak temperatures and thus increases the NOx emission. On the other hand, high rates of thermal quenching result in lower peak temperatures and contribute to the reduction of NOx emission [8].

Engine parameters such as load and speed of engine also influence the NOx emissions from the exhaust. When the engine is running under lean conditions, it emits less NOx. However, the nitric oxide (NO) emissions will consequently increase as the engine load increases. The effect of load becomes less significant when the engine is running close to stoichiometric air to fuel ratio. On the other hand, engine speed may increase or decrease the NO emissions as higher engine speed increases the burned gas mass fraction and thus offsets the peak temperature, depending on the exact engine conditions [9].

The term “Alternative Gaseous Fuels” relates to a wide range of fuels that are in the gaseous state at ambient conditions, whether when used on their own or as components of mixtures with other fuels. They have distinct superior merits to those of conventional liquid fuels in applications whether those for spark ignition or compression ignition engines. Additionally, most of these fuels can produce more favorable exhaust emission characteristics that can meet better the ever increasingly stringent emission regulations combined with enhanced power production efficiency and improved engine operational life [10].

The most common of the alternative fuels is natural gas that is usually made available after processing as “pipeline processed natural gas”. It is supplied for engine applications normally as compressed natural gas, (CNG), or occasionally in its cryogenic liquid form, (LNG). The composition of the gas in its natural untreated state varies widely depending on its source, treatment and local conditions. However, after it’s processing when destined for transport to its ultimate consumption points its composition becomes less widely variable and made up mostly of methane. Accordingly, much of the work and information available relating to natural gas as an engine fuel consider methane to be an adequate representation of the whole fuel [11].

Another common source of gaseous fuels involves the higher molecular weight components of natural gas in the form of Liquefied Petroleum Gases (LPG), which can be liquefied under pressure at ambient temperature. Usually, the main component of these fuel gases is n-propane. On this basis, often engine performance with pure or even commercial propane is considered to be represented adequately by engine operation with LPG gas mixtures [12].

Hydrogen as an engine fuel is well recognized to have unique and excellent combustion characteristics while producing effectively negligible exhaust emissions, except for NOx. Moreover, the addition of H2 to relatively slow burning fuels such as CH4 was shown to accelerate the flame propagation rates and extend the lean operational limits [13]. There is every indication that the use of hydrogen whether on its own or in combination with other fuels will be an attractive stage in the road towards achieving the “hydrogen economy”. This is perhaps despite the well recognized limitations associated with its engine application arising from the need to develop improved methods for its economic manufacture, ease of availability, storage and transport while ensuring the safety of its handling [14].

The aim of this work is studying the influence of some spark ignition engine parameters (like compression ratio, spark timing equivalence ratio) on resulted NOx emissions, when this engine was fueled with different gaseous fuels, and compare these emitted emissions with ones resulted from engine working with gasoline.
2. Experimental Technique

The investigation were carried out on single cylinder, 4-stroke spark ignition Ricardo E6 engine with variable compression ratio, spark timing and equivalence ratio, operated with gasoline, NG, LPG and hydrogen. Gasoline delivery system consists of the following parts, main fuel tank 6 liters capacity, supplementary fuel tank 1 liter capacity and gasoline carburetor. LPG delivery system consists of fuel tank (80 kg of LPG), fuel filter, solenoid valve, gaseous fuel flow rate measuring device (orifice plate), damping tank, gas carburetor. Hydrogen and NG supplying system was consist of gas cylinder, pressure regulator, chocked nozzles system as gas flow rate measuring device and as flame trap. Alcock air flow meter was used to measure air flow rate, speed was measured by tachometer. All the measuring devices were calibrated several times during the work.

The following instruments were used for the analysis of the emissions:

- A magnetic oxygen analyzer for \( \text{O}_2 \).
- A chemiluminescence analyzer for NO and \( \text{NO}_2 \).

The engine was operated with gasoline; NG, LPG and pure hydrogen. In practice, much of the gaseous fuels available are usually mixtures of various fuels and some diluents, constituents that can vary widely in nature and concentration, depending on the type of fuel and its origin. In this work the gasoline used was Iraqi Dora refinery production with octane No. 86, the LPG fuel produced from Al Taji Gas Company; consist of ethane 0.8%, 18.47% isobutane, 47.8% propane and 32.45% butane. NG used was produced from Iraqi Northern Gas Company; consist of 84.23% methane, 13.21% ethane, 2.15% propane, 0.15% isobutane, 0.17% n. butane and 0.03% pentane. Hydrogen produced from Al Mansur Company with 99.99% purity.

The very wide diversity in the composition of the gaseous fuels commonly available and their equally wide variety of their associated physical, chemical and combustion characteristics make the prediction and optimization of their combustion behavior in engines a more formidable task compared to conventional liquid fuels. Continued research is needed to provide more light on their suitability as engine fuels and understand better the roles of the many factors that control their behavior so as to achieve in practice the many potential superior benefits associated with their applications as engine fuels.

3. Discussion

3.1. Compression Ratio Effect

Fig. (1) shows the NOx resulted from gasoline engine for wide range of equivalence ratios and for several compression ratios, NOx increased in the lean side with the increase of CR, for equivalence ratio less than (\( \Theta = 0.9 \)), this was appeared by increased exhaust gas temperatures for these ratios, which increased from 525 to 585°C. These concentrations reduced in the rich side for equivalence ratios more than (\( \Theta = 1.1 \)), because of the increase in maximum cycle temperature with CR increased. For equivalence ratios (\( \Theta = 0.9-1.1 \)) where the engine produced the maximum brake power, NOx concentrations reduced with increased CR, because of interference of new parameter, It was the optimum spark ignition timing, with CR increased the mixture temperature increased inside combustion chamber, improving the burning and increasing the flame propagation velocity, causing the optimum spark timing to retard, to insure knock preventing. This operation reduces the NOx formation required time; this phenomenon will...
appear in Spark timing study clearly. NOx concentrations increased at CR=8.5:1 for these equivalence ratios range, because the CR effect prevailed OST effect and because of knock occurrence.

Fig. 2. Compression Ratio Effect on NOx Concentration for Wide Range of Equivalence Ratios, for LPG Fuel.

The same conditions appear in fig. (2) for LPG used as an engine fuel, with some extend in the lean equivalence ratios, making the CR effect obvious in this side for equivalence ratios less than $\phi=0.75$.

NG used as fuel in fig. (3), to show CR effect on NOx emitted by the engine, from the previous figures, the maximum value for NOx concentrations come within $\phi=0.95-0.98$ for NG, and for LPG between $\phi=0.92-0.95$, and for gasoline at $\phi=0.9 - 0.93$. The working at lean equivalence ratios less than $\phi=0.8$ gives accepted concentrations for USA and Europe emission limitations for 1996, with insured condition that burning failure will not happen.

Fig. 3. Compression Ratio Effect on NOx Concentration for Wide Range of Equivalence Ratios, for NG Fuel.

Fig. 4. Compression Ratio Effect on NOx Concentration for Wide Range of Equivalence Ratios, for Hydrogen Fuel.
Fig. 5. Comparison Between NOx Concentration for Wide Range of Equivalence Ratios for the Four Fuels Used in the Study at CR=8:1, Which is the HUCR for Gasoline.

Fig. 4 represents NOx emitted from the engine when fueled with hydrogen. Hydrogen engine gave high NOx concentrations for equivalence ratios between $\Theta=0.6-0.8$. In particular, hydrogen engine emitted high NOx concentrations compared with other fuels and this clear in fig. (5), which compares between the four used fuels at CR=8:1, LPG is the second higher NOx levels and gasoline the third one. Hydrogen has high flame propagation speed, this makes its burning very fast, causing high temperature and pressure inside the combustion chamber, with available formation time, and the required conditions for NOx formation were fulfilled. In the other hand, LPG has high heating value on mass basis, its flame speed a little more than gasoline, for these reasons it became the second. NG has a property of slow flame speed, and its heating value on mass basis is less than LPG and gasoline, for these reasons it became the last.

Fig. 6. Comparison Between NOx Concentrations for Wide Range of Equivalence Ratios for the Four Fuels Used in the Study When the Engine Worked at Each Fuel HUCR.

Fig. 7. Maximum NOx Concentrations Resulted with Compression Ratios Studied for Each Fuel.
Fig. (6) compares NOx concentrations emitted by the four fuels when each one of them fueled the engine at its HUCR. Hydrogen still precedes the others, especially in lean side, because of its high burning velocity. LPG still the second indicating its high heating value, and NG still the last demonstrating its low burning speed and low heating value on volume basis. The figure shows that NOx concentrations approached one another for the hydrocarbon fuels, when the engine worked at HUCR for each fuel, while hydrogen’s values moved away from them. This can be reached by referring to fig. (7), which represents the relation between CR and maximum NOx concentrations for all fuels used in this work.

3.2. Equivalence ratio effect

The figs. (1 to 6) show that NOx concentrations very low in extremely lean and in highly rich equivalence ratios, these concentrations increased highly in the lean side to reach its maximum value near the stoichiometric equivalence ratio from the lean side, after this value NOx concentrations reduced with mixture enrichment. In lean burn engines, increasing the air to fuel ratio decreases the NOx emissions. Extra air dilutes the combustion gases, thus lowering peak flame temperature and reducing thermal NOx formation. Oxygen availability and high burning temperature resulted from burning most of the fuel, also the time available for formation, all these conditions cause the NOx concentration to increase in the lean limit (Ø = 0.7-0.95).

NOx concentration reduced in the rich side with CR increased because of lack of oxygen needed for reactions, the high increase in burning temperatures, low NOx formation and dissociation equilibrium, all can be considered additional reasons of low NOx concentrations, where dissociation reactions freeze in the expansion stroke. Lowering the air-to-fuel ratio in rich burn engines limits oxygen availability in the cylinder, thus decreasing NOx emissions.

Hydrogen had extremely lean equivalence ratios less than Ø = 0.6, which gave very low NOx concentrations, these ratios can’t be reached by any other known fuel. Although hydrogen has low heating value on volume basis, resulted NOx in lean side higher than Ø = 0.65, was high compared with the other tested fuels, which had higher heating values than hydrogen, but hydrogen flame velocity proceeds flame velocities for other fuels in many steps (for hydrogen flame speed is between 2.65 – 3.4 m/s, for gasoline 0.34 m/s, for LPG 0.42 m/s and for NG 0.29 m/s), its burning and propagation increase combustion chamber pressure and temperature to very high levels, which can’t be reached by other fuels, and it will increase the NOx concentrations to these undesirable degrees. Hydrogen engine operation at equivalence ratios less than Ø = 0.6 emitted very low NOx concentrations, here the effect of little fuel quantity appeared, although of the high flame velocity. A fuel lean mixtures act as heat sinks lowers cylinder temperature and further reduces NOx formation.

3.3. Spark ignition effect

![Graph showing spark timing effect on NOx concentrations](image)

Fig.8. Studying Spark Timing Effect on NOx Concentrations for Specific Lean Equivalence Ratio, for Each Fuel Used in the Study, When the Engine Worked at Each Fuel HUCR.

Spark ignition effect on NOx concentrations for very lean equivalence ratios in exhaust gas was studied at HUCR and 1500 rpm engine speed, for four chosen lean equivalence ratios for each fuel, as fig. (8) represents, for gasoline Ø = 0.83 was chosen, Ø = 0.75 for LPG, Ø = 0.75 for NG and Ø = 0.7 for hydrogen. From the figure there was high reduction in NOx concentrations for all ratios, with retarding spark timing. NOx concentrations reduced about 42% when spark
timing was retarded 10°BTDC for gasoline fuel. For LPG the concentrations reduced 37% with retarding spark timing 10°BTDC from the optimum spark timing. For NG with the same condition NOx concentrations reduced 79%, for hydrogen reduced about 66% with spark timing retarded 10°BTDC.

The spark timing effect appeared clearly for equivalence ratios near stoichiometric (as fig. (9) shows), gasoline NOx concentrations reduced 42% when spark timing retarded 10°BTDC at equivalence ratio $\bar{\varnothing}=0.92$, for LPG, NOx concentrations reduced about 42% at $\bar{\varnothing}=0.95$ (near this ratio formed the maximum concentrations) for the same conditions, with NG as fuel, NOx concentrations reduced 70%, and for hydrogen the reduction was 50%.

The high reduction in NOx concentrations for NG due to its low burning velocity, which make spark timing effect on maximum temperature inside the combustion chamber obvious, the spark timing for NG always advanced compared with the other fuels.

Ignition or spark timing retard lowers NOx emissions by moving the ignition event to later in the power stroke. Because the combustion chamber volume is not at its minimum, the peak flame temperature will be reduced, thus reducing thermal NOx formation. Ignition timing retard is applicable to all engines. It is implemented in spark ignition engines by changing the timing of the spark.

Retarding spark timing effect on NOx concentration was very limited at rich equivalence ratios (as fig (10) shows), when spark timing retarded 10°BTDC gasoline NOx concentrations reduced only 12% at $\bar{\varnothing}=1.3$, at the same equivalence ratio but for LPG the concentrations reduced 15% when spark timing retarded 10°BTDC, when NG was used as a fuel at the same conditions, the NOx concentrations reduced 12.5%, but for hydrogen at $\bar{\varnothing}=1.3$ the spark timing became critical condition, where advancing or retarding the spark timing made abnormal combustion conditions, and caused engine failure, because of this there is no curve representing hydrogen behavior. The figures give emphasis that the spark timing effect is very limited at rich side because of oxygen lack.
4. Conclusions

1. NOx concentrations increased with CR increased at lean and rich sides. The maximum value for these concentrations reduced with CR increased.
2. NOx concentrations resulted from using hydrogen gave the maximum values compared with other fuels resulted concentrations, weather the engine run at HUCR for each fuel or at constant CR=8:1, because of its high burning velocity.
3. LPG fuel pass over gasoline and NG in emitted NOx, and win the second rank in higher NOx concentration.
4. Equivalence ratio can be used as restricting variable by operating engine with very lean mixtures.
5. Spark timing can be considered as the main factor in controlling NOx concentration resulted from the engine, when it works with one of the studied hydrocarbon fuels. Retarding the spark timing reduce NOx concentrations highly.
6. With hydrogen as engine fuel, changing spark timing from the optimum timing cause abnormal combustion, so the work will be limited with optimum timing, except for very lean equivalence ratios less than Ø =0.7, retarding spark timing appears its usual effect.

Nomenclature

LPG liquefied petroleum gas
NG natural gas
NOx nitrogen oxides
CR compression ratio
HUCR higher useful compression ratio
OST optimum spark timing
SIE spark ignition engine

5. References


دراسة ملوثات NOx لمحرك اشتعال بالشرارة يعمل بأنواع مختلفة من الوقود الهيدروكربوني والهيدروجين

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الخلاصة

استخدم الغاز النفطي المسال والغاز الطبيعي والهيدروجين لتشغيل محرك احتراف داخلي يعمل بالشارة نوع Ricardo E6 ومقدار ملوثات NOx والضغط ونسبة النفاخ الناتجة عند عمل المحرك بالغازولين.

تمت دراسة الملوثات الناتجة عند عمل المحرك بنسبة الانضغاط النافعة العليا للغازولين ونسبة اثناء بعضاً نسب الانضغاط النافعة العليا والوان ود. على حداد، ودرس تأثير نسبة الانضغاط والنسب النافعة وتوقيت الشرارة عند عمل المحرك بسرعة ثانية 1500 rpm.

أظهرت النتائج أن أعلى قيمة لملوثات NOx تكون دائماً في الجانب الضعيف، وقلل التراكيز بالإفراط عليه بالنسبة للنسبة تعابير الخيل، وأن هذه الملوثات تكون أعلى ما يمكن للغاز الهيدروجين عند نسبة انضغاط عالياً ونسبة نفاخ نافعة عالية على كل وك ود، ولكن نبقي الهيدروجين ذو أعلى قيمة لتركمير NOx، كما أن أكبر تأثير على هذه الملوثات كان توقيت الشرارة.