STUDY OF CO AND NOₓ EMISSIONS OF S.I.E FUELED WITH SUPPLEMENTED HYDROGEN TO GASOLINE

Miqdam T. Chaichan
Lecturer assistant, Mechanical Eng. Dep., University of Technology, Baghdad, Iraq

ABSTRACT
This paper includes study of CO and NOₓ emissions exhausted from single cylinder, 4-stroke S.I. engine, Ricardo E6, with variable compression ratio, spark timing and equivalence ratio, worked by supplementary hydrogen to gasoline.

The speed of 25 rps and higher useful compression ratio (HUCR) were chosen in studying the effect of wide range of equivalence ratios and spark timing on CO and NOₓ emissions submitted from engine.

The study showed that exhaust gas emissions depend mainly on equivalence ratio. The higher value of NOₓ concentrations was in lean side near the stoichiometric equivalence ratio, and reduced when getting far from this ratio.

CO concentrations were too small in the lean side, and the effect of equivalence ratio on it was too small in this side also, it increased in the rich side.

It was observed that retarding spark timing reduces the NOₓ concentrations by a large percentage; there was no effect of spark timing on CO concentrations.

The effect of speed on NOₓ concentrations was studied, and it was observed that these emissions became higher at medium speeds and reduced in higher and low speeds, CO concentrations increased with increasing speed also.

NOₓ concentrations increased with increasing hydrogen volumetric ratio in mixture while CO concentrations reduced by this increase.
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KEY WORDS
Hydrogen, gasoline, emission, nitric oxides, NOx, carbon monoxide, CO, compression ratio, equivalence ratio, spark timing, speed.

INTRODUCTION
Motor vehicle presently powered by conventional petroleum fuels consume about one-third of the world's oil consumption. The fast rates of depletion on the global oil supply system possess a threat to the transportation sector. Therefore, for the safe survival and growth of the existing vehicular network, substitutes to conventional petroleum fuels must be discovered (Akehurst, 2002).

Besides suffering from the problem of scanty global supply, the modern transportation system that is built on internal combustion engines also happens to be the major source of several health threatening pollutants. Therefore, an ideal long-term substitute to petroleum fuels should possess an infinite source potential and the least environmental pollution characteristics. Hydrogen fuel exactly caters to such need (Vianna, 2005).

A neat hydrogen – operated engine gives out water as main combustion product, it does not produce significant amount of CO, HCs, SOx, smoke, lead or other toxic metals, sulfuric acid deposition, ozone and other oxidants, benzene and other carcinogenic compounds, formaldehyde, CO2 and other greenhouse gases. In a well designed neat hydrogen fueled engine a very small portion of the lubricant cauting on the chamber walls is burnt thus producing negligible amount of hydrocarbon and carbon monoxide. However, in hydrogen- supplemented engines, some of these pollutions could be presents in proportions much smaller than that of the corresponding petroleum fueled engine (Das, 1990).

Oxide of nitrogen (NOx) happened to be the only major pollutant of concern, whether it is hydrogen specific or hydrogen supplemented engine (Shasby, 2004).

In addition to the above mentioned pollutant, a very small amount of hydrogen peroxide is also given out by a hydrogen engine under specific operation conditions (Das, 1991).

In this paper, however, we restricted to the effect of some major pollutants (CO and NOx), and the influence of some operational and designing parameters on them with respect to hydrogen supplemented engines.

The damaging effects of CO in preventing oxygen transport from the blood into the tissues are too well known to be further emphasized. Also, it has been found that CO also plays a critical role in increasing the concentration of several greenhouse gases and thus disturbs the climate effect (Vianna, 2005).

The present global level of CO is increasing and motor vehicles account for the major part of CO emissions in urban areas. It has been estimated that the level of CO in the lower atmosphere is increasing between 0.8 and 1.4% by year. CO and unburnt hydrocarbons (UBHC) will be intrinsically absent in a total hydrogen operated engine, however, they could be caused in hydrogen supplemented systems (Das, 1990).
(MacDonald, 1976) in his investigation studied the effect of CO emissions from hydrogen supplemented multi cylinder engine, it was observed that the CO level decreased within equivalence ratio of 0.55 and was increased with further leaning. This decrease in CO emission level was contrary to usual expectations. The possible explanation of such a trend, as given out by the investigator were that perhaps a hydrogen rich combustion seriously influenced "temperature and specific profile in the combustion chamber quench layer", thereby resulting in a change of the origin of CO. Additionally this situation could have "increased the hydroxyl radical concentration" which help in increase the rate of oxidation of CO to CO$_2$.

(Li Jing-ding and Lu Ying-qing, 1984) observed extremely low quantities of CO in the exhaust emitted out of their experimental engine set up, even though theoretically, no CO is supposed to be present, the CO emission level get decreased as the load is reduced in a practical operating engine system. It is a very difficult to get a perfect homogenous mixture.

This gives rise to some amount of CO. In addition, high temperature conditions and the dissociation effects of hydrogen in the engine cylinder result in resolving CO$_2$ to CO.

Recent research indicates that ozone (O$_3$) in the troposphere is the main gradients of smog. This gas is created in sunlight driven reactions involving nitrogen oxides (NOx). Controlling NOx is also essential to reduce the deposition of citric acid, which happen to be a principal component of acid rain (Das, 2005).

Mobile sources are responsible for the major contribution of NOx levels to the environment. Unfortunately, NOx happen to be the major pollutant of concern from hydrogen engines. Whether the engine is operating on a net hydrogen fuel or it happens to be a hydrogen-supplemented system, there is bound to be some level of NOx emissions (Murray, 1971).

The level of NOx emissions depend on combustion temperature, availability of oxygen, and time available for its kinetic process. It has been discovered that NOx level peak around stoichiometry due to higher combustion temperature and availability of sufficient oxygen. NOx emission is greatly influence by changes in equivalence ratio. It was also experimentally determined that spark timing which proved to be extremely important parameter for NOx production (Varde, 1984).

The compression ratio was observed to be influencing the level of NOx concentration. An increase in compression ratio results in higher level of NOx because of increase temperature conditions. This situation also leads to high flame speeds, which in consequence reduces the residence time. However, it was observed that between the two factors, such an increased temperature and decrease residence time, the effect of the former predominate thereby resulting in a high NOx level which higher compression ratio (Das, 1987).

The results reported by (Parks, 1976) on hydrogen enrichment observed that NOx reached a peek value at an equivalence ratio of around 0.8, as an overall effect of combustion temperature coupled with sufficient oxygen availability. As the mixture leaned beyond an equivalence ratio 0.8 and more oxygen became available, NOx still showed a decreasing trend because of lower combustion temperatures. It was thus observes, in general, leaner operation allowed by hydrogen addition to gasoline will reduce NOx emissions. However, the phenomenon of high flame temperature associated with hydrogen does influence its combustion temperature, which causes the increase of NOx emission at a given equivalence ratio.

A part from excessive spark advance (Murray, 1971), exhaust gas recirculation (Das, 1991), water injection (Das, 1987) and use of exhaust gas reduction catalysts (Das, 1990) have been successfully adopted for NOx control. Results of detailed study on the effects of diluents shows that both water injection and EGR are equally effective in reducing NOx levels (Das, 1990).

**EXPERIMENTAL TECHNIQUE**

The investigation were carried out on single cylinder ,4-stroke spark ignition Ricardo E6/US engine with variable compression ratio, spark timing and equivalence ratio , operated with
hydrogen enriched gasoline, hydrogen was supplied to air manifold by means of nozzles system and pressure regulator to achieve mixing rate.

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

- A non-dispersing infrared analyzer for CO.
- A magnetic oxygen analyzer for O₂.
- A chemiluminescence analyzer for NO and NO₂.

The engine was operated with pure gasoline, pure hydrogen and with hydrogen – gasoline mixtures, a wide range of equivalence ratio effect on emission concentrations at HUCR and 25 rps engine speed.

Engine performance studied to get HUCR for each fuel and for the mixtures, then start studying addition of hydrogen on volume basis where (hydrogen volume fraction, HVF= \( \frac{V_{H2}}{V_{H2}+V_{gasoline}} \)).

**DISCUSSION**

- **CR Effect**

  Engine was operated in different compression ratios starting from 6:1 to 9.0:1, with OST and 25 rps engine speed, for wide range of equivalence ratios, to study the effect of hydrogen supplementation for three volumetric fractions(HVF=0.3, 0.6, 0.9) to gasoline on NOx concentrations.

  The results shows constant effect, increasing hydrogen volumetric fraction increases NOx concentrations in lean side, and reduces in rich side, the maximum value of these concentrations increased. This is obvious in **fig. (1)**, which was chosen as a sample for this constant behavior, where 9:1 is HUCR for hydrogen – gasoline mixtures and HUCR for gasoline alone was 8:1.

  The increase of NOx concentrations in lean side because of three parameters: oxygen availability and high combustion speed because of hydrogen presence, and the high heating value of gasoline on volume basis. The decrease in NOx concentration in rich side because of oxygen lack, dissociation reactions with low reaction rate freeze, reaction time shortage, it also appear from the figure that mixture influenced in great manner with hydrogen supplementation.

  Compression ratio effect on mixture seems to be constant also, NOx concentrations increased in lean side and reduced in rich side with CR increase, because CR improvesCombustion operation and increase flame spreading velocity, and NOx concentration limited by two other parameters, which are oxygen availability and available reaction time.

  **Fig. (2)** shows the effect of changing CR from 6:1 to 9.0:1 on NOx concentration maximum value, for different hydrogen volumetric fractions in fuel, at OST and 25 rps engine speed.

  Increased HVF in fuel increases the maximum value of NOx concentration for HVF=90%, after that NOx reduces when engine operated with hydrogen fuel alone, this indicates the influence of high heating value of gasoline on volume basis.

  Increasing CR causes reduction in maximum value of NOx concentration, that is because of reduction in time available where OST retarded to get the best engine power and to avoid knock.

  Hydrogen was supplied in four volumetric fractions (HVF= 0.3, 0.6, 0.8, 0.9) to gasoline, and the study done for four different compression ratios (6, 7, 8, 9) to examine CO concentrations for wide range of equivalence ratios.

  The results conduct constant effect, hydrogen increase in mixture reduces CO concentration in exhaust gas, in rich side where CO concentrations are obvious, because of the reduction in carbon – to hydrogen atoms percentage in whole fuel.

  This is obvious in **figs (3 and 4)**, which was chosen as a sample for this constant behavior, where 8:1 is the HUCR for gasoline, and 9:1 is the HUCR for mixtures used in research.

  From the figures it is apparent that increasing CR increases CO concentrations in exhaust gas, because of reversed dissociation for CO₂ molecule to CO with increasing combustion temperature.
Equivalence Ratio Effect

Fig. (1) appears equivalence ratio effect on NOx concentrations, where NOx maximum value is at (Ø=0.96) with gasoline use, and with HVF increase in fuel it reaches (Ø=0.82) at HVF=0.9.

The fast reaction of hydrogen oxygen causes apparent lack of oxygen in combustion chamber, at the same time, this reaction gives very high temperature for equivalence ratios from Ø=0.8 to Ø=0.9. That is why the maximum NOx concentration is layed at values leaner than (Ø=0.96) when hydrogen added to gasoline.

Engine works at equivalence ratio leaner than Ø=0.7 gives very low NOx concentrations.

Figs. (3 and 4) conduct that CO concentration in exhaust gas are very low for equivalence ratios less than Ø=0.96, it reached approximatly zero at very lean equivalence ratios less than Ø=0.8, and it increased after this ratio; hydrogen addition reduces these concentrations as it been mentioned above.

Fig. (5) shows hydrogen addition effect on NOx concentrations, for specific chosen equivalence ratios when working with HUCR and 25 rps.

From the figure, increasing HVF increase NOx levels in lean side in large and obvious rate, this is appeared in equivalence ratios Ø=0.7 and Ø=0.8 curves, because of fulfillment of the following parameters: Oxygen availability, high combustion rate caused by hydrogen fast burning velocity and gasoline high heating value on volume basis, the later appeared to be the reason for NOx increase at Ø=0.8 more than that at Ø=0.7 although the two equivalence ratios are lean.

NOx levels decrease for equivalence ratios (Ø=1, 1.1, 1.3) although HVF increase, because of lack of oxygen needed for reactions and dissociation reactions increase.

- Speed effect

Figs. (6 to 8) show the effect of different speeds on NOx, for wide range of equivalence ratios, at different HVF's in fuel, at HUCR=9:1 and OST.

NOx concentrations were higher at medium speeds (25-30rps), and decrease at low speed (20 rps) and high speed (35 rps).

The maximum cycle temperature is low at low speeds, because of increased dilution and long combustion time, but in medium speeds NOx concentration increases, because of high cycle temperature, and in high speeds these concentrations go down because of shortage of time needed for oxygen and nitrogen reaction, also chemical dissociation increases because of high-rise in maximum cycle temperature.

Figs. (from 9 to 11) illustrate different speeds effect on CO levels for wide range of equivalence ratios and for different HVF's in fuel at HUCR and OST.

CO concentrations decrease with HVF increase in mixture, but with speed increase CO levels increase in exhaust gases, because of combustion temperature increase with speed increase, what increases in return dissociation reactions for CO₂ gas to CO, also, the short time required to oxide all CO gas to CO₂, lack of oxygen in combustion chamber in rich side.

- Spark timing effect

Spark timing give an advantage to gasoline – hydrogen mixtures, compared with hydrogen alone, when they are used in SIE. The engine operated with neat hydrogen as fuel need to change spark timing always to fit working equivalence ratio. Therefore, range of spark timing changing is very narrow and limited with existence of high-pressure rates before top dead centre, when timing is advanced away from its OST by few degrees and with hydrogen-air mixture pre-ignition when retarding the timing by few degrees. Pre-ignition do not happen to gasoline – hydrogen –air mixture, when retarding spark timing in any circumstances, but it happened only if high-pressure rates occur before top dead centre. In this case, a very high heat produced in combustion chamber causing hydrogen – gasoline mixture to burn before the spark plug ignited. Therefore, spark timing effect on NOx levels can be studied in hydrogen supplementation system, although it cannot be studied in neat hydrogen case.

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Fig. (12) shows the relation between NOx concentrations and spark timing degrees for three definite equivalence ratios (Ø=0.7, 0.8, 1.3) for mixture of air-gasoline and hydrogen, HVF=90%. This fraction was chosen because it gave the maximum NOx concentration at HUCR and 25 rps.

Retarding spark timing at equivalence ratio (Ø=0.7) by 15 degrees cause decrease in NOx concentration about 40%. At equivalence ratio Ø=0.8 where the maximum NOx levels laid near, retarding spark timing about 15 degrees cause degrease about 35%, but at Ø=1.3 NOx concentration reduced with same retarding degrees about 2.5%.

Retarding spark timing is a very important parameter for limiting and reduces NOx concentrations.

There was no effect of spark timing in CO concentrations.

CONCLUSIONS

- NOx concentrations increased with hydrogen supplementations to gasoline-air mixture at lean side for about 10 times, and decreased in rich side about 30%, the maximum value of this emission increased about 40% also.
- CO concentrations reduce with hydrogen supplementation to gasoline–air mixture in obvious manner at rich side at about 65%.
- NOx concentrations increase with CR increase in lean side and reduce in rich side. Also, the maximum concentrations reduce with hydrogen supplementation to gasoline-air mixture.
- CO concentrations in exhaust gas increase with CR increase.
- NOx concentration increase with speed increase from low (20 rps) to medium (25-30 rps) speeds, these concentrations decreases with speed increase from medium to high (35 rps) speed. In addition, CO concentration increases with speed increase.
- Retarding spark timing reduces NOx concentration in high percentage for lean equivalence ratio (about 40% at Ø=0.7), and for maximum values (35% at Ø=0.8). NOx concentrations reduce also in rich side for a little extent (about 2.5% at Ø=1.3).
- Spark timing do not affect CO concentrations.

REFERENCES


NOMENCLATURE
CO carbon monoxide
NOx Nitrogen oxides
Rps revolution per second
CR compression ratio
OST optimum spark timing
Ø equivalence ratio= (A/F)$_{stochiometric}/(A/F)_{actual}$

Fig. (1), the effect of hydrogen supplementation for three volumetric fractions to gasoline on NOx concentrations for wide range of equivalence ratios at HUCR and OST
**Fig. (2)**, the effect of changing CR from 6:1 to 9:0:1 on NOx concentration maximum value, for different hydrogen volumetric fractions in fuel, at OST and 25 rps engine speed

**Fig. (3)**, the effect of hydrogen supplementation for four volumetric fractions to gasoline on CO concentrations for wide range of equivalence ratios at CR=8:1, OST and 25 rps
Fig (4), the effect of hydrogen supplementation for three volumetric fractions to gasoline on CO concentrations for wide range of equivalence ratios at HUCR=9:1, OST and 25 rps.

Fig. (5), hydrogen addition effect on NOx concentrations, for specific chosen equivalence ratios when working with HUCR for each HVF and 25 rps.
**Fig (6)**, the effect of low speed (20 rps) on NOx concentrations, for wide range of equivalence ratios, at different HVF's in fuel, HUCR and OST.

**Fig. (7)**, the effect of medium speed (30 rps) on NOx concentrations, for wide range of equivalence ratios, at different HVF's in fuel, HUCR and OST.
Fig. (8), the effect of high speed (35 rps) on NOx concentrations, for wide range of equivalence ratios, at different HVF’s in fuel, HUCR and OST.

Fig. (9), the effect of low speed (20 rps) on CO concentrations, for wide range of equivalence ratios, at different HVF’s in fuel, HUCR and OST.

Fig. (10), the effect of medium speed (30 rps) on CO concentrations, for wide range of equivalence ratios, at different HVF’s in fuel, HUCR and OST.
Fig. (11), the effect of high speed (35 rps) on CO concentrations, for wide range of equivalence ratios, at different HVF's in fuel, HUCR and OST.

Fig. (12), the relation between NOx concentrations and spark timing degrees for three definite equivalence ratios (Ø=0.7, 0.8, 1.3) for mixture of air-gasoline and hydrogen, HVF=90%