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An Integrated System of Gasoline Reformer and Three Way Converter for On-board hydrogen Production

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ملخص: تمت دراسة إعادة تشكيل (تحسين) البنزين باستخدام غازات العادم لإنتاج الهيدروجين على متن السيارة باستخدام نظام مدمج يتكون من محسن للوقود يستخدم مادة مساعدة على التفاعل مدمج مع المحول الثلاثي لغازات العادم (TWC) مركب على محرك ذي ست أسطوانات (V6) يعمل على نظام اشعال الشحنة المتجانسة بالكبس (HCCI). يتم ادخال الغاز الناتج من المحسن إلى المحرك كوقود مكمل لتحسين أداء المحرك و تقليل أكاسيد النيتروجين في العادم. ولتحديد الظروف المثالية للمحرك و المحسن الملحق به بحيث ينتج أكبر قدر من الهيدروجين أخذين في الاعتبار الكفاءة الحرارية. تم اختبار تأثير نسبة الأكسجين إلى الكربون في الخليط الداخل للمحسن و كذلك ظروف تشغيل المحرك المختلفة ، و قد اتضح أن درجة حرارة نواتج التفاعل عند مخرج المحسن مرتبطة بإنتاج الهيدروجين حيث تم الحصول على تراكيز تصل إلى 12.8 % من الهيدروجين في نواتج المحسن و ذلك باستخدام البنزين التجاري الخالي من الرصاص. كما وجد بعض الهيدروكربونات في نواتج المحسن ، مما يدل على عدم حدوث تحسين كامل للبنزين . أجريت التحاليل باستخدام جهاز (NDIR) . هذا التصميم المدمج الجديد للمحسن و المحول الثلاثي لغازات العادم يمكن إدخاله ضمن دائرة إعادة إدخال غازات العادم (EGR) وذلك لتوسيع الحدود الدنيا لنافذة التشغيل لنظام إشعال الشحنة المتجانسة بالكبس .

Abstract**:** On-board exhaust gas assisted gasoline reforming has been investigated using a compact prototype system consisting of a fuel reformer integrated with a three way catalytic converter (TWC) connected to a V6 engine running at homogeneous charge compression ignition (HCCI) mode, the integrated fuel reformer and TWC were designed and constructed to supply reformed exhaust gas recirculation (REGR) stream to the gasoline-fuelled HCCI V6 engine as supplement fuel to improve engine performance and reduce NO_x emissions.

To find the optimum operating conditions of the engine-reformer system (in terms of hydrogen production and thermal efficiency), the effect of oxygen to carbon ratio (O_2/C) in the reactor input mixture, and the different engine operating conditions were investigated. The reactor outlet temperature appears to be strongly correlated to the production of hydrogen. Concentrations up to 12.8 % of hydrogen in the reformer products were achieved from commercial unleaded gasoline. Uncompleted reforming of gasoline was assumed from significant quantities of hydrocarbons in the product measured by Non-Dispersive Infrared (NDIR). This novel design of an integrated fuel reformer and three-way catalytic converter

(TWC) that can be fitted in the EGR loop was applied to extend the lower boundary of the (HCCI) operating window.

Keywords: Hydrogen, Exhaust gas reforming, Gasoline reforming.

1. INTRODUCTION

Hydrogen is foreseen by some as an important environmentally friendly energy carrier. However, this cannot be always the case until all the technical problems associated with producing and handling hydrogen are solved and the infrastructure requirements are established. Hydrogen use in internal combustion (IC) engines in small quantities as an addition to main fuel can improve combustion and engine performance. Small quantities of hydrogen can be produced on-board by fuel reforming (i.e. gasoline) in contact with engine exhaust gas (source of heat and reactants e.g. O_2, H_2O, CO_2) over a Johnson Matthey proprietary Rh based reforming catalyst coated onto a metallic monolith substrate solid catalyst.

Gasoline has evolved through the last few decades in order to improve combustion efficiency and engine emissions, but some gasoline components which are essential to improve the octane number (such as aromatics) are still unfavourable to reforming processes and after treatment systems performance. On-board production of small amounts of hydrogen to be used for internal combustion (IC) engines in order to improve its combustion or after-treatment units is an achievable solution [1,2]. Numerous partial oxidation auto-thermal reforming studies have been carried out to determine the ease of converting these fuels into syngas. O'Connor et al. [3] studied the partial oxidation of cyclohexane, n-hexane, 75 mol% i-octane: 25 mol% toluene mixture, pure i-octane and commercial gasoline using a Rhodium based catalyst. High yield of synthesis gas was successfully produced. Production of syngas decreased with toluene additions and production of methane and propylene was noticed. Kopasz et al. [4] carried out an experimental study on auto-thermal reforming of gasoline and some individual components of gasoline using a micro reactor system. The results revealed that aromatic components require higher temperature (800^{o}C) and longer contact time compared to paraffinic components, while naphthenic components can be reformed at shorter contact time but higher temperatures are required compared to paraffinic components. They also reported that for n-octane, increasing the temperature from 700-800 ^{o}C leads to a decrease in the hydrogen yield, while hydrocarbons of C1-C_3 were noticed in the reformer products. Kopasz et al. [5] investigated the effect of fuel composition on reforming behaviour using blends of paraffins, naphthenic and aromatic hydrocarbons. The results indicated that fuel blends with high aromatic content and high naphthenic content were more difficult to reform and the aromatics and naphthenes were also found to have an impact on the kinetics of paraffins reforming in the blend. Both the naphthenic and aromatic fuels were more sensitive to temperature than the paraffinic fuel. Cracknell et al. [6] studied the reforming of a number of pure components species that are typically present in gasoline. The reforming experimental results revealed that toluene and cyclohexane require the highest temperatures and the olefin species require the lowest temperatures for the maximum yield of hydrogen. The results also indicated that higher molecular weight olefins are more difficult to reform than other components. These findings supported the idea of producing a gasoline which is easy to reform and suitable for spark ignition engines.

Fuel reforming on-board using real commercial gasoline and exhaust gas from a HCCI engine running on gasoline is a great challenge to achieve but offers significant potential advantages when a fuel reformer is placed in the exhaust gas recirculation (EGR) loop and the reformate is used as reformed EGR (REGR). Despite of the relatively low hydrogen concentration in the gas product of the reactor due to high dilution of nitrogen inherent in the exhaust gas, hydrogen concentration of 10-20% is high enough for REGR [7, 8].

A study of fuel reforming, using exhaust gas from a HCCI engine fuelled with commercial grade unleaded gasoline was carried out to optimize the operating parameters of the integrated fuel reformer and TWC in terms of hydrogen yield and thermal efficiency.

The task is to produce hydrogen that is to be used as a component of the re-circulated exhaust gas fed into the intake manifold of of a gasoline fuelled HCCI engine

2. EXPERIMENTAL SETUP

2.1 Test engine

The multi cylinder engine used for this research is the Jaguar AJV6 direct injection 3 litre swept volume research engine having 11.3 geometric compression ratios. Throughout this research natural aspiration was implemented. The engine is equipped with cam profile switching mechanism to switch between SI (high lift, long duration) and HCCI (low lift, short duration) modes. The variable cam timing systems give the possibility of changing the cam timing of the intake and exhaust cams within a range of 60 crank angle degrees. Negative valve overlap was used to increase the amount of retained exhaust gas in the cylinder to achieve HCCI combustion. The engine is connected to an EC38 eddy current dynamometer and a DSPACE-based system coupled to a computer using MATLAB/SIMULINK software is used to control the engine parameters during operation and to record engine data. The on-board fuel reformer integrated with the TWC is connected to the engine as shown in Figures

1a,1b and gasoline fuel evaporator is shown in Figure 1c.

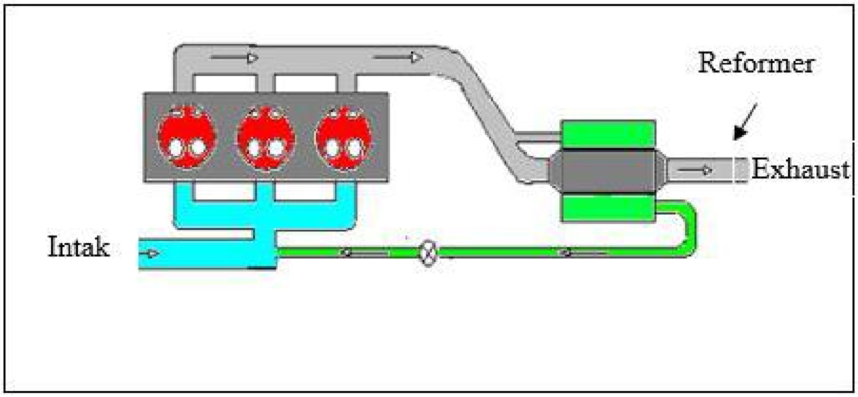

Figure (1a). Schematic of on line reformer

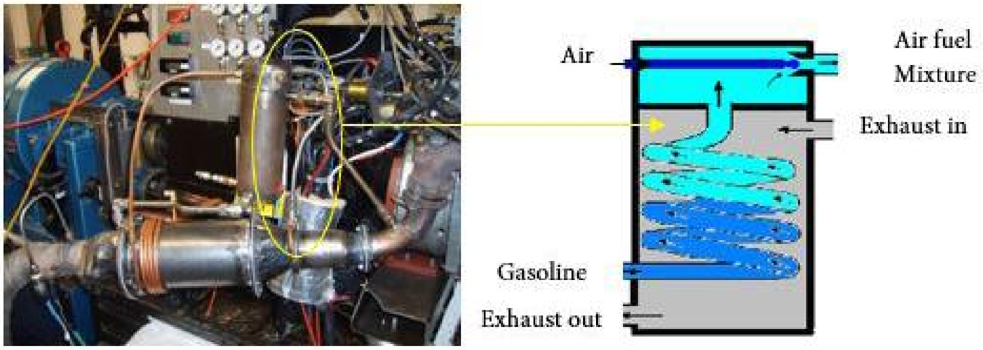

Figure (1b). The integrated reformer connected to V6 engine

Figure (1c). Gasoline evaporator schematic

2.2 Fuel used

The fuel used was commercial unleaded gasoline having RON 95. Saturated hydrocarbons contribute to 43.82% of total fuel composition. Out of these the largest fraction was iso-paraffins (36.07 % of total fuel) and iso-octane was the most abundant of the iso-paraffins. The second largest component was the aromatics contributing in total 32.29% of the fuel composition. Toluene and trimethyl-benzene were the most abundant aromatic components. Olefins contribute only 11.53% and naphthenes contribute the lowest share of 3.66% of the total fuel composition.

2.3 Combined fuel reformer-TWC system

On-board fuel reformer integrated with the TWC as shown in Figure 2 was used. A Johnson Matthey proprietary Rh based reforming catalyst was uniformly coated onto a metallic monolith substrate. The combined reformer has been designed and built in a concentric shape with the three-way catalytic converter (TWC) as a core and the reformer in annular shape outside the TWC. Such design requires very little extra space beyond the baseline catalytic converter, while under stoichiometric engine operating conditions the reformer can utilise the heat generated in the TWC to further improve the reforming process efficiency and hydrogen production. Fuel evaporator was connected to the reformer as described in earlier publication [9] which also gives more detail on the design.

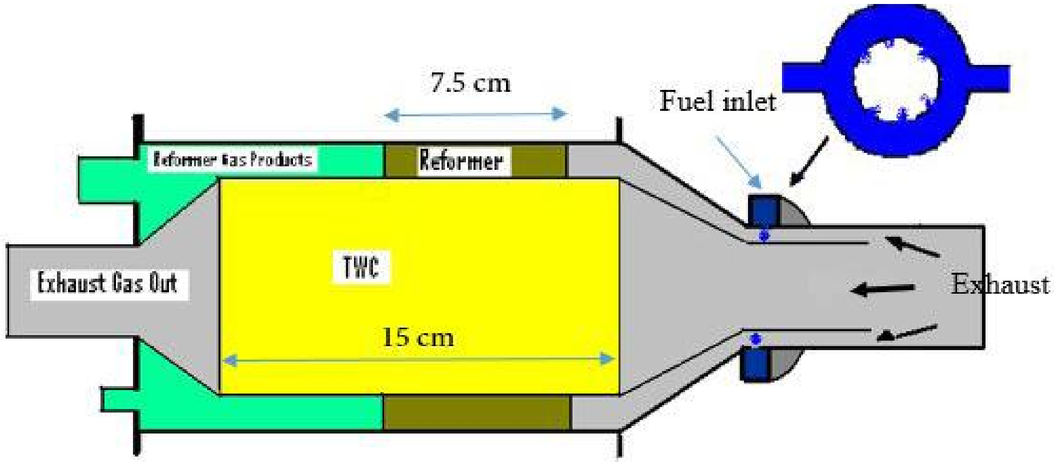

Figure (2). Schematic of the integrated fuel reformer and TWC

2.4 Emissions and reformate analysis

The Gases were analysed by Non-Dispersive Infrared (NDIR) to measure carbon monoxide, carbon dioxide, nitric oxides and hydrocarbons and oxygen (electrochemical method). Hydrogen was measured using a HP 5890 series gas chromatograph equipped with a thermal conductivity detector was connected on line. The apparatus was calibrated using certified gases (10% H_2 in N_2 and 30% H_2 in N_2).

2.5 Experimental procedure

Gasoline was added to the reformer using a micro gear pump with a built-in flow meter. Air was added at the outlet of the fuel vaporizer to ensure adequate mixing with the fuel vapour. Temperatures were measured along the reactor using K-type thermocouples. The integrated fuel reformer and TWC were designed and constructed to supply reformed exhaust gas recirculation (REGR) stream to the gasoline-fuelled HCCI V6 engine in order to extend the bottom range of HCCI operation window. The integrated reactor was tested at different engine conditions as given in Table 1. The analysis of the exhaust gas leaving the engine at each condition is given in Table 2. Table 3 shows a comparison between the gas mixture composition at the fuel reformer inlet and the gas products composition at the reformer outlet for the five tested engine conditions on dry bases.

Table (1). Engine operating conditions

	Cond.1	Cond.2	Cond.3	Cond.4	Cond.5
Engine speed (rpm)	1500	1500	1500	2000	2500
Engine load IMEP (bar)	4.0	3.2	4.0	3.7	3.6
Excess air ratio (λ)	1.2	1.2	1.0	1.2	1.2
Exhaust temp.(°C)	395	370	420	390	405

Table (2). Exhaust gas composition (before adding air and fuel) for different engine operating conditions, dry base

	Cond.1	Cond.2	Cond.3	Cond.4	Cond.5
CO vol %	0.07	0.07	0.5	0.06	0.06
CO_2 vol %	12.1	10.7	14.2	12.0	12.1
O_2 vol %	4.0	5.8	0.8	4.2	3.9
NO_x ppm	168	18	201	35	85
HC* ppm	255	253	208	145	141

*Hydrocarbons are hexane equivalent as measured by NDIR

Table (3). The reactor inlet and outlet gas composition % for the tested engine conditions at fuel flow rate 35ml/min to the reactor

Engine condition	Gas mixture composition % at the reactor inlet (dry bases)				Product gas mixture composition % at the reactor outlet (dry bases)			
	O_2	CO	CO_2	H_2	O_2	CO	CO_2	H_2
1	9.66	0.05	8.06	0.0	0.4	9.3	10.0	10.8
2	10.86	0.05	7.17	0.0	1.0	8.0	9.9	12.8
3	7.50	0.33	9.47	0.0	0.5	3.5	12.9	5.8
4	9.80	0.04	8.00	0.0	0.2	7.3	10.9	9.0
5	9.60	0.04	8.10	0.0	0.3	7.1	11.2	9.3

3. RESULTS AND DISCUSSION

3.1 Effect of engine conditions on reformer products

Gasoline was fed to the reactor in gaseous phase after being mixed with the added air. Fixed flow rate of 40 l/min of air was added to the exhaust gas entering the reformer for all engine conditions to promote partial oxidation to supply the required enthalpy for steam reforming. Constant exhaust gas flow rate of 80 l/min was applied for all tested engine conditions, the reactor pressure and the gas hourly space velocity (GHSV) were 1.0 bar and 25000 hr-1 respectively. The amount of fuel fed to the reformer was increased gradually from 10-35 ml/min to identify the optimum fuel flow rate at which maximum hydrogen production was achieved.

Figures 3 and 4 show a comparison between the reformer product compositions when using exhaust gas from the five tested engine conditions. The reformate composition at 35 ml/min flow rate of gasoline into the reactor is shown in Table

3 for the tested five engine conditions. The highest hydrogen concentration was 12.8% when using exhaust gas from engine condition “2” and the lowest concentration was 5.8% when using exhaust gas from engine condition “3”. This is attributed to oxygen content which will enhance partial oxidation and consequently increase the reactor temperature. Figure 4 shows the same products for the five engine conditions at fuel flow rate to the reactor 20 ml/min. The hydrogen concentration in the reformate was lower for all engine test conditions with maximum concentration of 9.3% achieved by using exhaust gas from engine condition “1” while the lowest concentration of 5.7% was achieved when using exhaust gas from engine condition “3”. From these results; it is clear that O_2/C ratio has strong effect on hydrogen production.

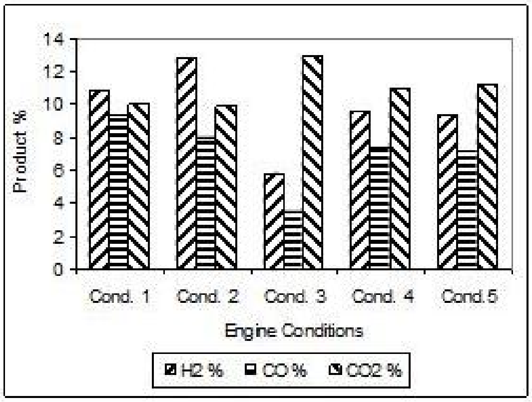

Figure (3). Reactor product gas composition at different engine conditions, for fuel flow rate of 35 ml/min (liquid)

3.2 Temperature profiles

The reactor temperature has to be brought to a maximum value by partial oxidation to provide the reservoir of enthalpy required by the endothermic steam reforming reaction. Following that maximum, the temperature will drop gradually to the equilibrium temperature of the reactor by feeding enthalpy into the steam reforming reaction which is the most important for hydrogen production. Figures 5 and 6 show the maximum temperature as a function of fuel input flow rate and the axial distribution of temperature in the reformer respectively.

The reactor outlet temperature is the most difficult parameter to control due to its dependence on engine conditions, O_2/C, H_2O/C ratios and GHSV as it is shown in Figures 7 and 8. It can be seen clearly from Figure 6 that engine condition affects the reactor equilibrium temperature. At low O_2/C ratio at the reactor inlet a difference of about 40 °C in the outlet temperature was observed between engine conditions “3” and “4”, while at higher O_2/C ratio the corresponding temperature difference

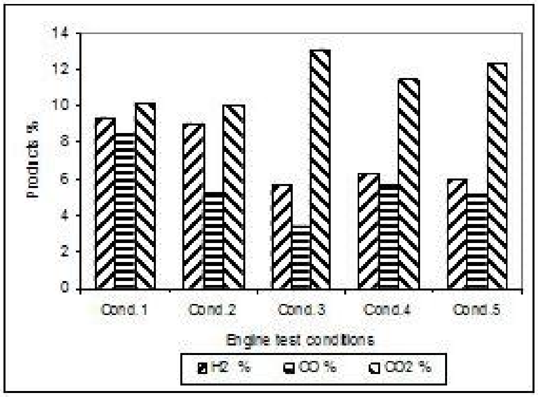

Figure (4). Reactor product gas composition at different engine conditions, for fuel flow rate of 20 ml/min (liquid)

approaches 80°C. The temperature differences are much larger than the differences in the incoming engine exhaust temperatures and it seems that the pattern does not follow the inlet temperature pattern. Figure 8 indicates clearly that at lower O_2/C ratios at the reactor inlet, resulting in lower reactor equilibrium temperatures, higher proportion of hydrogen is produced. At the equilibrium temperature of 638°C, corresponding to O_2/C ratio of 0.27, the maximum hydrogen content of 10.8% was achieved.

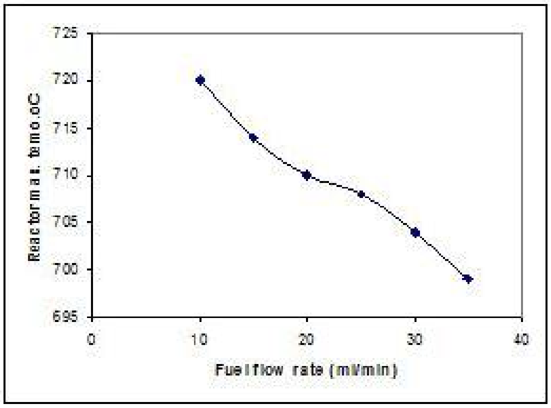

Figure (5). Maximum temperature at the reactor inlet as a function of fuel input flow rate.

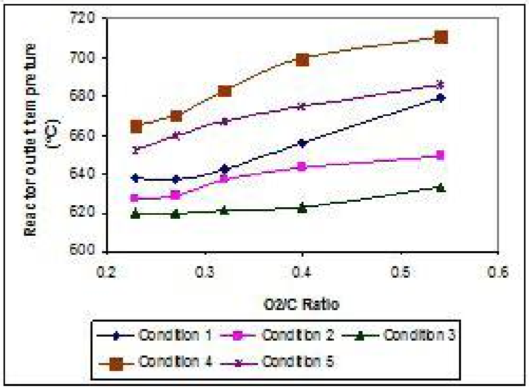

Figure (7). Reactor outlet temperature vs. O_2/C ratio for different engine conditions.

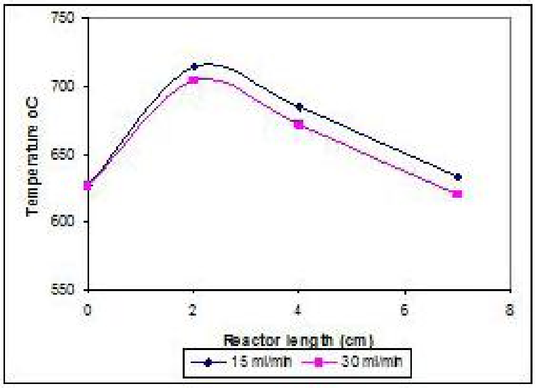

Figure (6). Temperature distribution along the length of the reformer at different fuel flow rates while using exhaust gas from engine condition "3".

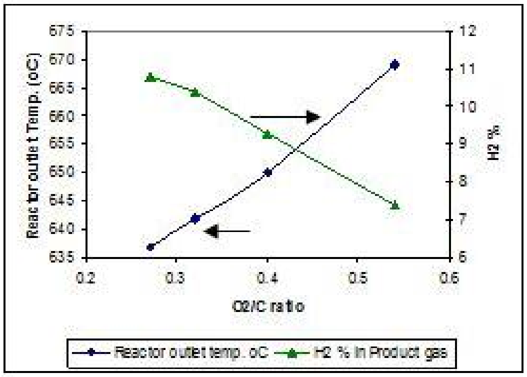

Figure (8). Hydrogen production and reactor outlet temperature vs. O_2/C ratio, exhaust from an engine operated under condition "1"

3.3 Process efficiency

The thermal efficiency of reforming is a ratio of the calorific value of the product that can be used divided by the calorific value of the fuel introduced to the reformer. The fuel reformer was made to convert a hydrocarbon fuel to hydrogen and other products. The enthalpy content of the exhaust gas can be excluded from the accounting because it is a waste.

Because the reformer products will be introduced to the ICE as REGR, other combustible products in addition to hydrogen such as carbon monoxide and hydrocarbons can release more energy in the engine and thus these contribute to the reforming process efficiency, thus the efficiency can be calculated from the following equation.

$$\eta(\%) = \frac{LHV_{H_2} \times \dot{m}_{H_2} + LHV_{co} \times \dot{m}_{co} + LHV_{Hydrocarbon} \times \dot{m}_{Hydrocarbon}}{LHV_{fuel} \times \dot{m}_{fuel}} \times 100$$

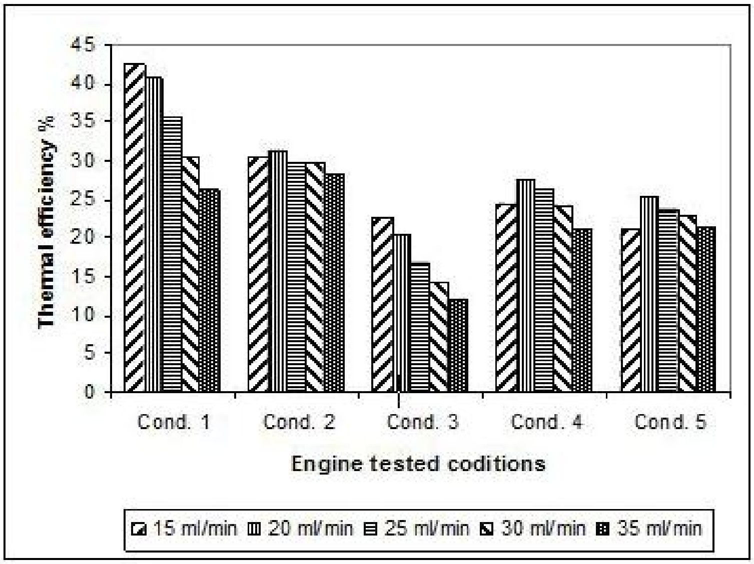

Figure (9). Reformer thermal efficiency for different engine test conditions and different fuel flow rates to the reformer

Due to difficulty in quantifying the mass of hydrocarbons existing in the reformer products the efficiency presented here was calculated taking into account only hydrogen and carbon monoxide. Figure 9 shows the thermal efficiency of the integrated reformer at different engine test conditions for the different fuel flow rates supplied to the reformer at each test condition. It is clear that the thermal efficiency is very low and that increasing the fuel flow rate to the reformer does not increase the thermal efficiency even though the concentration of hydrogen produced is increased.

4-CONCLUSION

Experimental results have revealed that on board exhaust gas assisted gasoline reforming at typical operating conditions of an HCCI engine can be achieved at reactor maximum temperatures below 750 °C and O_2/C ratio in the range of 0.3-0.4 using exhaust gas from a gasoline-fuelled HCCI engine.

The O_2/C ratio at the reactor inlet is one of the important parameters that influence hydrogen production. Varying the O_2/C ratio in the range of 0.2-0.5, by adjusting the fresh air and fuel flow rates at the reactor inlet, changes hydrogen production significantly with a peak value of about 12.8% achieved at O_2/C ratio of approximately 0.29.

The low value of steam to carbon ratio limits the steam reforming process and thus the potential for hydrogen production.

Different engine operating conditions affect the exhaust gas composition at the reformer inlet and consequently the reactor product composition is affected.

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