

## NUMERICAL STUDY OF THE PERFORMANCES OF A NATURAL GAS SI ENGINE WITH EXHAUST GAS-STEAM FUEL REFORMER

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### Abstract

*A steady, equilibrium mathematical model of the system: natural gas engine and steam-exhaust gas reformer is developed and programmed in Matlab. The modelled process of the reforming is carried out on the nickel/aluminium catalyst Ni/MgAl<sub>2</sub>O<sub>4</sub>. Natural gas, exhaust gas from the engine and steam consist substrates in this process. The main products of the reforming are hydrogen and carbon monoxide. Hydrogen is a very promising fuel for internal combustion engines. Thanks to its high flame speed and low flammability limit, the addition of hydrogen to the conventional fuel results in a considerable reduction of NO<sub>x</sub> production. The model is used to investigate the influence of temperature and proportions between reagents on the process. The analysed parameters are: the pressure generated in the engine working in the hybrid, NO<sub>x</sub> production by the engine, reforming products by reformer co-operating with engine.*

### 1. Introduction

Nowadays, European legislation on internal combustion engines emissions is more and more rigorous. Natural gas being a clean burning and plentiful resource is, in many ways, a good alternative fuel to perform these current and future requirements [1]. This fuel gives lower emissions of carbon monoxide and unburned hydrocarbons. The problem is that natural gas - fuelled engines can produce undesirably high NO<sub>x</sub> emission. Of course, one can argue, that in simple terms NO<sub>x</sub> is a by-products of a good and efficient combustion. The rate of NO<sub>x</sub> formation depends exponentially on temperature and is a function of oxygen availability [1].

The process being the subject of this article is an exhaust gas – steam reforming of natural gas. It is a technique where hydrocarbon fuels is decomposed mostly into hydrogen, carbon dioxide, carbon monoxide in reaction with water and exhaust gas from the engine over a solid phase catalyst. The reformed fuel reach in hydrogen, carbon monoxide and inert gases, let to reduce a combustion temperature and gives, thanks to presence of hydrogen, a higher flame speed and low flammability limit of the fuel. These two advantages are not negligible taking in consideration that reformed fuel contains a bigger quantity of inert gases, so is more difficult to burn. The addition of hydrogen allowed a significant extension in the lean operating limit of the engine, compared with operation on conventional fuel alone [1].

The concept explored in this study involves the use of reformed fuel (mix of natural gas and reformed gas) to reduce NO<sub>x</sub> emissions. Effects of use of such fuel on the engine work have been analysed. A computer program on Matlab platform was developed for the computational analysis of the behaviour of the hybrid: engine – exhaust gas-steam reformer.

### 2. Fuel exhaust gas steam reforming

The conception of the process is as follow (see Figure 1).

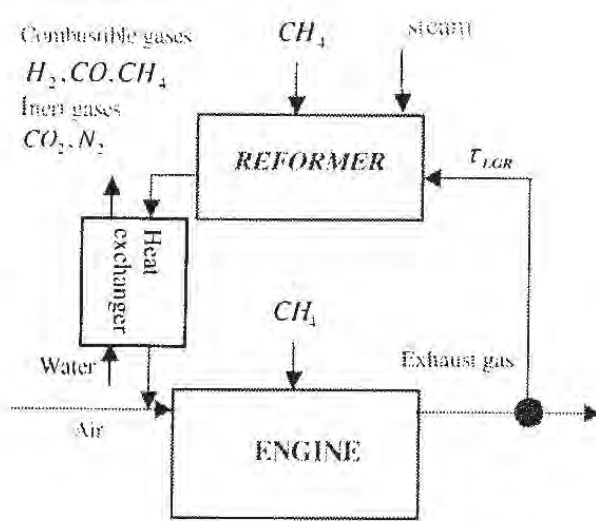


Fig. 1. Engine – reformer system

- Reforming of the natural gas composed mostly from  $CH_4$  is executed on the nickel/aluminium catalyst  $Ni/MgAl_2O_4$ .
- The catalytic reformer unit does a steam reforming of  $CH_4$  using exhaust gas from the engine and steam from an external source.
- The quantity of steam taken to the reforming in the model is 5% (apart from the chapter 4.1 where it varies between 2 and 8 %) of the total amount of the fuel consumed by the engine. In this case, if the volume of the fuel tank is 50 litres, the volume of a tank of water would be 2,5 l. It can be located in a place accessible to the user of the vehicle to enable him a systematic refilling of water.
- Exhaust gas produced by the engine is in a small percentage  $\tau_{EGR}$  (tested in this study within the range from 2% to 8% of a global quantity of the produced exhaust gas) input to the reformer.
- The quantity of natural gas reformed in the reformer is equal to less than 5% (tested 1% and 5%) of the natural gas burned in the engine.
- The best range of temperatures for this process lies between 800 and 1200 K. These temperatures are impossible to obtain from exhaust gas because their temperature is nearly constant and lies between 350 and 410 C. Even if the temperature of exhaust gas can attain the temperature of 600 C, after leaving the exhaust port, the temperature of the exhaust gas falls quickly. Taking in consideration the above, the reformer should be heated artificially. There are three possible methods of heating the reactor: either by an electrical heater or by a furnace burning a reformed fuel or natural gas or by the reaction of partial oxidation inside reformer achieved by adding air or  $O_2$  to the substrates stream [3].
- The produced reformed gas is composed mostly from  $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$  and  $H_2O$ .

## 2. 1. ZINOX - SI engine model

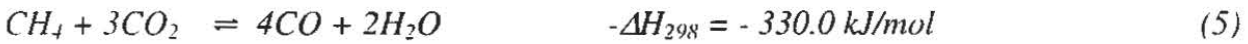
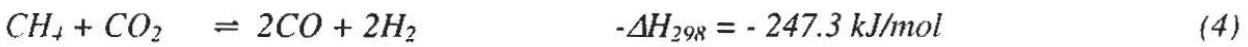
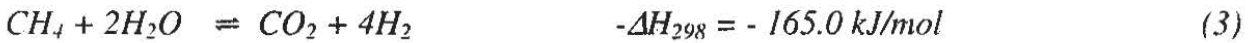
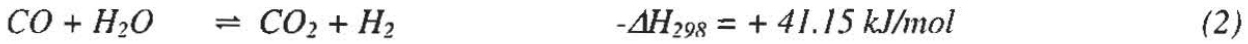
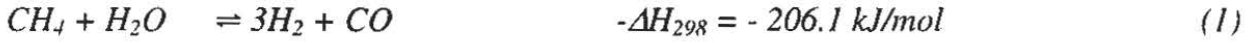
In order to model the SI engine cycle, the thermodynamic zero-dimensional, two zones model was developed. Such a model belongs to the second generation of the engine models and was fully developed by Heywood (1986), Ferguson (1988) and others researchers [6]. This model was extended with the  $NO_x$  production Zeldovich model [4]. A program called ZINOX was developed by Teodorczyk (1998 & 2000).

The input data to the ZINOX engine model are given below:

COMPRESSION RATIO, R	9.00	BURNING ANGLE, THETAB (deg)	60.00
BORE, B (cm)	8.00	START OF IGNITION, THETAS (deg)	-12.00
STROKE, S (cm)	7.00	MEAN EQUIVALENCE RATIO, PHI	1.00
HALF STROKE TO BORE RATIO, EPS	27	RESIDUAL MASS FRACTION, F	.05
ENGINE SPEED, RPM (rev/min)	1500	INITIAL PRESSURE, P1 (bar)	1.00
HEAT TRANSFER COEFFICIENT, H (J/m**2/K)	600	INITIAL TEMPERATURE, T1 (K)	350.00
BLOWBY COEFFICIENT, C (1/S)	.80	WALL TEMPERATURE, TW (K)	400.00

## 2. 2. Reformer Model – Chemical equilibrium

A simplified theoretical, chemical, thermodynamic model of the reformer has been built on the assumption that all reactions reach equilibrium and that the process is steady (the warm up and the starting up of the reactor was not taking into consideration). The possible reactions occurring among  $CH_4$ ,  $CO_2$ ,  $CO$ ,  $H_2$ ,  $H_2O$  are mentioned in the article of Xu and Froment [7]. In this model, five reactions were considered:



One should take into consideration in order to decide which reactions should be put in the model is whether this reaction is independent or not.

One of the major parameter characterising chemical environments is the number of independent reactions [4]. An independent chemical reaction has a stoichiometric equation which is not a linear combination of other stoichiometric equations of reactions taking place in the given chemical environment. We can conclude that reaction (3) is a linear combination of reactions (1) and (2). Addition of these two equations by sides gives reaction (3). In similar way, the reaction (4) is a linear combination of reactions (1) and (2). Also reaction (5) is the linear combination of the reactions (1) and (2). Taking in consideration the above, five original equations (1-5) are reduced to just two independent reactions (1) and (2). Even if other reactions take place, considering only independent reactions, one can obtain the same results (the same products) like considering all reactions.

Since only two of the three reactions are linearly independent, we can describe this problem with two conversion variables (6 and 7) which can be defined as:

$$x_{CH_4} = \frac{F_{CH_4,0} - F_{CH_4}}{F_{CH_4,0}} \quad x_{CO_2} = \frac{F_{CO_2} - F_{CO_2,0}}{F_{CH_4,0}} \quad (6 - 7)$$

Where the  $F$  indicates molar flow rate. In terms of these two conversion variables, the molar flow rates are defined. Molar flow rates and partial pressures of the species are given in [2]. Substituting these partial pressures into the rate equations would give us the reaction rates in terms of two conversion variables. Reaction kinetics on the surface could be represented by two reactions with Langmuir-Hinshelwood style rate expressions [7]:

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO \quad r_1 = \frac{\frac{k_1}{p_{H_2}^{2.5}} (p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_1})}{(DEN)^2} \quad (8)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad r_2 = \frac{\frac{k_2}{p_{H_2}} (p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_2})}{(DEN)^2} \quad (9)$$

$$DEN = 1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + \frac{K_{H_2O}P_{H_2O}}{P_{H_2}} \quad (10)$$

The 16 parameters (8 pre-exponential factors, 2 activation energies, 2 heat of reaction and 4 heats of adsorption) determined by Xu and Froment [7] are given in Table 1. In order to calculate the equilibrium composition, one should assume that the reactions' velocities (8) and (9) are equal to 0:  $r_1 = r_2 = 0$ . It results from the fact that the equilibrium is a stable chemical state. In equilibrium, the effects of the reactions proceeding in opposite directions should balance reciprocally.

Table 1

	A(k <sub>1</sub> )	A(k <sub>2</sub> )	A(K <sub>1</sub> )	A(K <sub>2</sub> )	A(K <sub>CO</sub> )	A(K <sub>H<sub>2</sub></sub> )	A(K <sub>CH<sub>4</sub></sub> )	A(K <sub>H<sub>2</sub>O</sub> )
Value	4.225·E <sup>15</sup>	1.955·E <sup>6</sup>	4.707 E12	1.142 E-2	8.23·E-5	6.12·E-9	6,64·E-4	1,77·E5
Unit	Kmol·bar <sup>1/2</sup> / (Kg catalyst · h)	Kgmol / Bar·kg catalyst·h)	Bar <sup>2</sup>		Bar <sup>-1</sup>	Bar <sup>-1</sup>	Bar <sup>-1</sup>	
	E <sub>a</sub> (k <sub>1</sub> )	E <sub>a</sub> (k <sub>2</sub> )	ΔH(K <sub>1</sub> )	ΔH(K <sub>2</sub> )	ΔH(K <sub>CO</sub> )	ΔH(K <sub>H<sub>2</sub></sub> )	ΔH(K <sub>CH<sub>4</sub></sub> )	ΔH(K <sub>H<sub>2</sub>O</sub> )
kJ/mole	240.1	67.13	224.0	-37.3	-70.65	-82.90	-38.28	88,68

### 3. Results for reformer

Simulations were done for the proportion between reagents as  $\frac{F_{H_2O}}{F_{CH_4}} = 3.5$   $\frac{F_{H_2O}}{F_{Exhaust\ gas}} = 10$ .

Exhaust gas steam fuel reforming simulations were done for a range of temperatures from 300 K to 1500 K. The goal of this simulation was to characterise the sensibility of the process to the temperature. As one can easily see on Fig. 2, the minimal temperature in which the effects of this process are visible is about 720 K (in fact the reforming starts in the temperature 552 K, but the transformation in temperatures below 720 K is very weak).

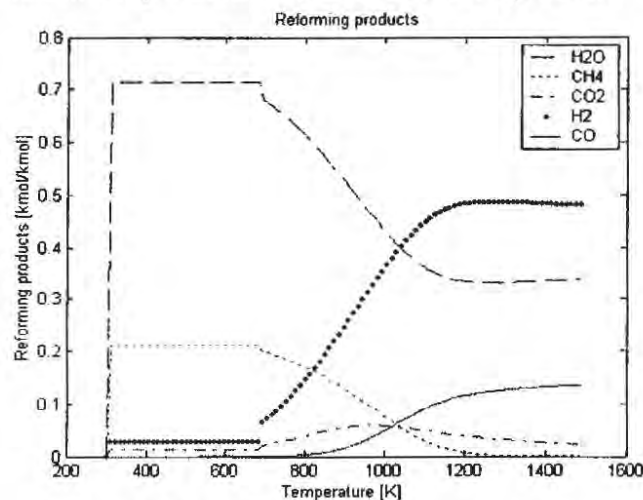


Fig. 2. Reforming products versus temperature

The maximal transformation is obtain for the temperature 1450 K Maximal production of  $H_2$  take place in the temperature of 1350 K. Figure 2 shows that the amount of  $H_2$  at the temperature 1300 K does not exceed 0.5 of the molar fraction. However in this temperature

there is a significant synthesis of  $NO_x$ . For this reason the realistic operational temperature will be close to 1000 K. At this temperature the production of  $H_2$  is about 0.28 of the molar fraction. The synthesis of the  $CO$  is about 0.03 kmol/kmol. A very weak production of  $CO$  can be caused by the fact that in the studied model  $CO$  is synthesised in the reaction no 1 and is one of the substrates in the reaction no 2. So, there is a production and a conversion of  $CO$  at the same time. Another obvious tendency on the figure 2 is that the proportion of the  $CO_2$  decreases with temperature when  $CO$  increases. This is due to the reaction no 1, which occurs in high temperature 1000 K and to the reaction no 2 which is more likely to happen in the temperature 750 K.

#### 4. Numerical Results for Engine – Reformer Model

In order to initiate calculations by the code consisting of two blocks, ZINOX4 – engine simulator and Equilibrium – reformer simulator one assumes that in the first iteration, the cylinder of the engine is fulfilled with 0,105 moles of  $CH_4$ . This is the quantity of fuel needed to burn 1 mole of air.

The plot shown on Fig. 3 was obtained by changing the stream of the exhaust gas put into the reformer. The exhaust stream varied from 2% to 8% of global quantity of exhaust gas produced by the engine (calculations were performed for 2%, 4%, 6% and 8%). The computer code executes 3 iterations for every EGR percentage, so the 12 lines are drafted in the plot. However, only 9 lines are visible. The reason for this is that for each EGR percentage, the code starts with fulfilling the cylinder by  $CH_4$  and air only. For the same conditions of engine work, the lines for these loupes superpose. The supply with only  $CH_4$  and air is represented by the line situated on a top of the chart. It is easy to state that the pressure, and in consequence, the work produced by the engine diminish for the application of reforming process. Higher the EGR percentage, smaller the pressure generated by the engine, the lost for 2% of EGR consists about 15% of the total pressure generated by the engine. For 8% of EGR it is 19%. As we can see on the Fig. 4, higher is the EGR stream put into the reformer, lower is the pressure in the cylinder. This phenomenon is connected to the fact that higher EGR to the reformer causes lower combustion temperature. The temperatures of the combustion are lower of about 160 – 200 K (it depends, of course, on EGR percentage). It results from the fact that the exhaust gas contains a big quantity of inert gases such as  $N_2$  and  $CO_2$  which do not take part in combustion and at the same time consist a considerable mass of gas mix put to the engine.

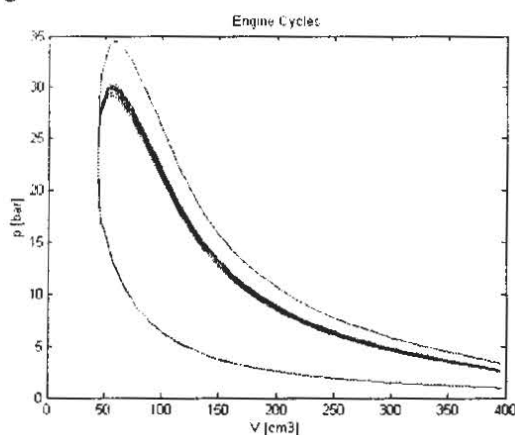


Fig. 3. Engines cycles for different values of the exhaust gas recirculation to the reformer

The comparison between direct exhaust gas recirculation to the engine and application of the exhaust gas- steam

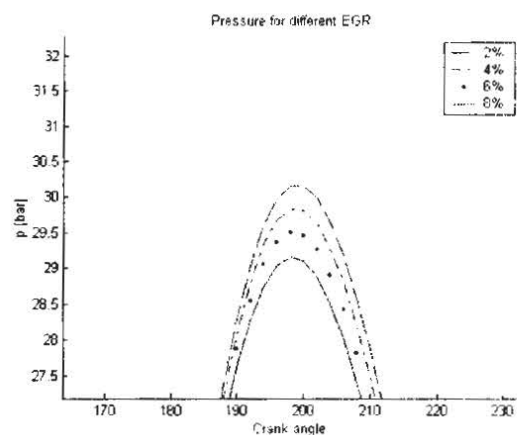


Fig. 4. In-cylinder Peak Pressure versus Crank Angle

reforming was done (Fig. 5). As one can easily notice on the Fig. 5, the production of  $NO_x$  in the case of the reforming process

application is much smaller than for the process of the EGR to the engine. For the taken engine set, the  $NO_x$  production (engine without reforming and without direct EGR to the reforming) generated by Zinox is 2192 ppm. Comparing it with the  $NO_x$  production obtained for engine with exhaust gas recirculation (dashed line on the fig. 6), one can see that this process gives for EGR 2%, the  $NO_x$  production lower of about 30%. For 4% EGR, it is 60%. For the system engine - reformer, for 2% of EGR, the  $NO_x$  production is of 82% lower. So the studied process gives more than 50% of improvement in comparison to the EGR recirculation to the engine. Of course, this is accompanied by the fall of the in-cylinder pressure, so the fall of the produced work. For the reforming process with the 2% EGR, the fall of the pressure is of about 10%.

In Fig.6, representing composition of the reformed fuel,  $CH_4$  is the sum of the  $CH_4$  from the reformer and the  $CH_4$  added to the engine. One can see that the quantity of the  $N_2$  in reforming products rises, higher is the EGR. It is understandable when we take in consideration that the exhaust gas contains a big quantity of  $N_2$  from the air. The molar fraction of  $H_2$  decreases, higher is EGR to the reformer. One could explain it by the fast increase of the molar flow of  $N_2$ . Another reason for this

#### 4. 1. Changing steam stream

Figures 7 and 8 show the molar composition of the reformed gas at the exit of the reformer for varied steam stream. For 1% of  $CH_4$  put to the reformer, there is a visible tendency that the  $H_2$  concentration almost does not rise, bigger is the stream of the steam (Fig. 7). This is not the case for 5% of  $CH_4$  put to the reformer:  $H_2$  production rises, bigger is the quantity of steam. (Fig.8). The conclusion is that the quantity of steam and the quantity of the  $CH_4$  put to the reformer should be pretty much the same. As far as the pressure generated in the cylinder is concerned, the fall of the pressure seems to be smaller for this proportion of reagents.

tendency is that  $H_2$  is generated in reactions of  $CH_4$  with  $H_2O$ , so the augmentation of the exhaust gas stream does not have a strong influence on the  $H_2$  production, even if the exhaust gas contains a certain quantity of  $H_2O$ .

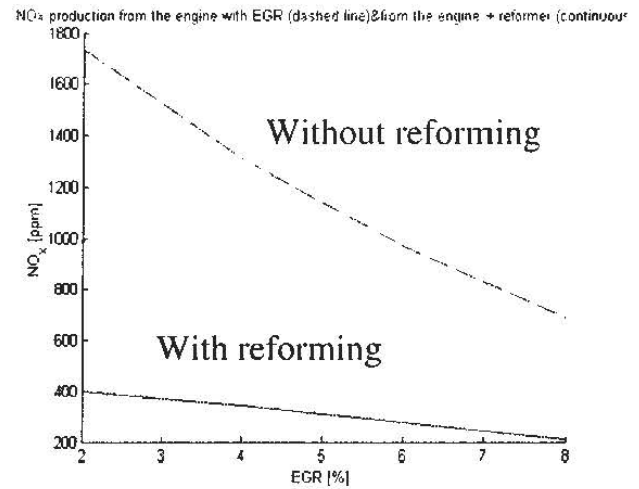


Fig. 5.  $NO_x$  versus EGR

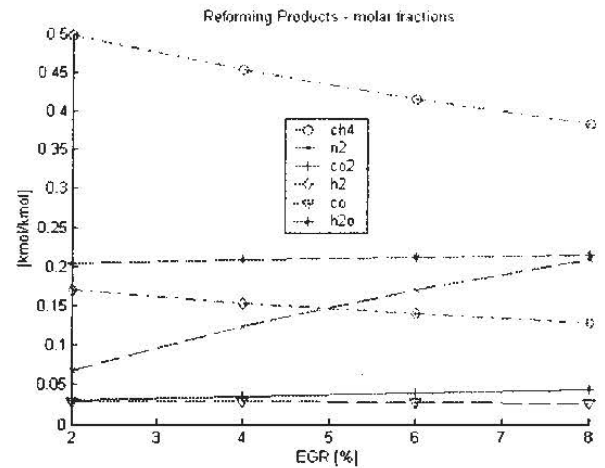


Fig. 6. Reforming products in molar fraction for different exhaust gas recirculation to the reformer.

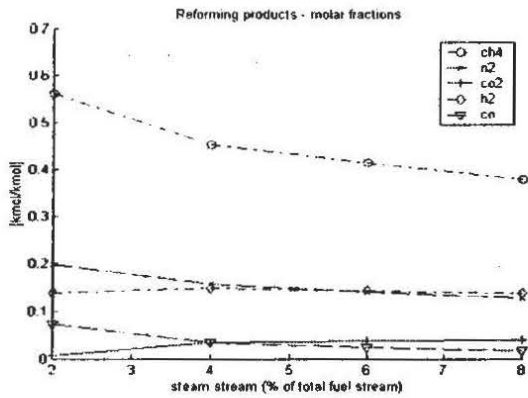


Fig. 7. Reforming products for different values of steam stream put to the reformer. The quantity of the CH<sub>4</sub> put to the reformer is equal to 1% of the quantity of CH<sub>4</sub> put to the engine.

#### 4. 2. Exhaust gas reforming (no steam)

The case of the reforming without steam was studied. Fig. 9 shows that the loss of the pressure in the case of the reforming without steam is smaller than for the reforming with steam. For 2% EGR for the reforming using steam, the loss is 4,2 bars, for the reforming without steam 2 bars. The Fig. 10 represents the products of the reforming process for different values of the EGR. The maximal production of hydrogen is smaller that for exhaust-gas-steam reforming. The maximal one is obtained for 4% of the EGR. The reduction of the emission is 52% for 8% of EGR. NO<sub>x</sub> reduction is smaller than this obtained for exhaust-gas steam reforming (Fig. 11).

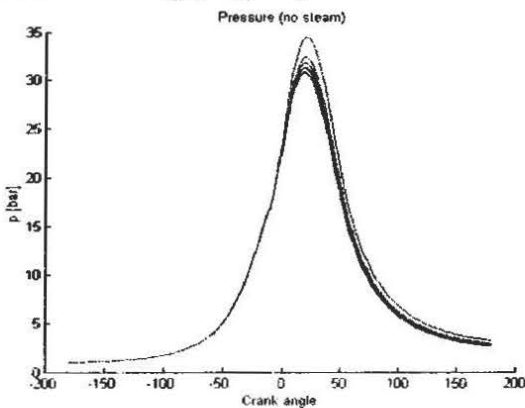


Fig. 9. In-cylinder pressure for different values of the exhaust gas recirculations to the reformer

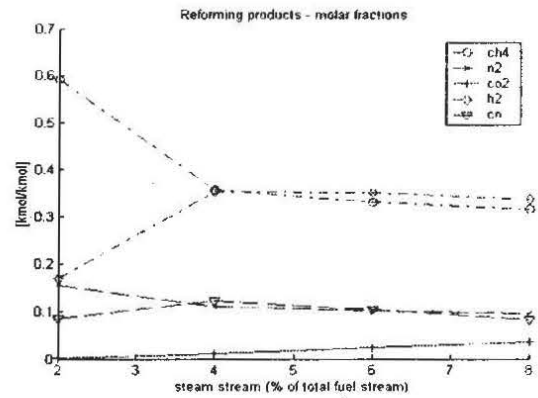


Fig. 8. Reforming products versus steam stream. The quantity of the CH<sub>4</sub> put to the reformer is equal to 5% of the quantity of CH<sub>4</sub> put to the engine.

varing from 2% to 8%. No steam added to the reformer.

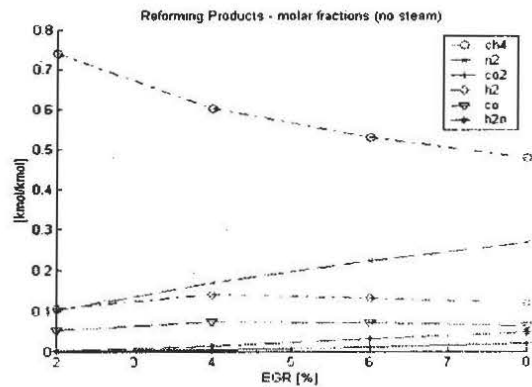


Fig. 10. Reforming products for different values of EGR to the reformer. No steam added

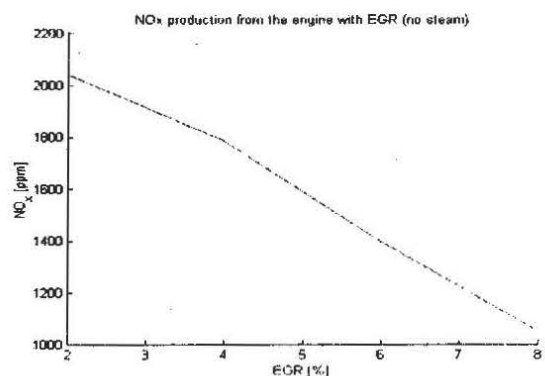


Fig. 11. NO<sub>x</sub> production for different values of EGR to the reformer. No steam added.

## 5. Conclusions

The interest to do on-board reforming seems to be the diminishing of the  $NO_x$  emission. This aim is achieved but at the sacrifice of the engine work.

The production of  $H_2$  depends strongly on temperature. The maximum tested temperature is 1000 K. Achievement of this temperature requires an additional heating of the reformer. It can be done by combustion of the fuel or by the reaction of partial oxidation inside reformer achieved by adding air or  $O_2$  to the substrates stream. The calculations of heating power were performed. The calculated heating power to rise the temperature of exhaust gases of 400 K (from 600 K to 1000 K) is 37 W by one cylinder. Taking in consideration that the power of the engine, for 8% of the exhaust gas used to the reforming process, is 3.24 kW, the needed power consists only about 1% of the produced power.

The performed tests show that the quantity of exhaust gas does not have a strong effect on the quantity of produced hydrogen.

A different steam quantity to the reformer was tested. The production of the hydrogen rises quickly for higher steam quantity until the point at which the ratio between them is 1:1. This is the most recommended relation between components.

The reforming without additional steam was also tested. Results show that the production of hydrogen, as well as, the reduction of  $NO_x$  in this process is smaller than in the case of the steam-exhaust gas reforming.

The exhaust gas-steam reforming seems to be more effective as far as  $NO_x$  reduction is concerned then direct EGR to the engine.

Taking into considerations that the reformer model is an equilibrium model, so the ideal one, the results obtained are maximal.

Future research should concentrate on the elaboration of a more sophisticated unsteady, three-dimensional model of the hybrid engine-reformer taking into consideration the warm-up phase and starting-up of the reformer.

### Notation:

$A(k_i)$	– preexponential factor of rate coefficient, $k_i$	
$A(K_i)$	– preexponential factor of adsorption constant, $K_i$	
$E_1, E_2$	– activation energy of reaction I and II kJ/mol	
$F_{CH_4}, F_{CO_2}$	– molar feed rate of $CH_4$ and $CO_2$	kmol/h
$K_1, K_2$	– equilibrium constant of reaction I and II	
$K_{CO}, K_{H_2}, K_{CH_4}$	– adsorption constants for $CH_4$ , $CO$ and $H_2$ , $bar^{-1}$	
$K_{H_2O}$	– dissociative adsorption of $H_2O$	
$k_1, k_2$	– rate coefficient of reaction I and II	$kmol \cdot bar^{1/2} / (kg\_cat \cdot h)$ $kmol / (kg\_cat \cdot h \cdot bar)$
$p_j$	– partial pressure of component j	bar
$R$	– gas constant	kJ/kmol
$r_1, r_2$	– rates of reactions I and II	kmol/kg_cat*h
$T$	– temperature	K
$x_{CH_4}$	– conversion of $CH_4$	kmol $CH_4$ / kmol $CO_2$ fed
$x_{CO_2}$	– conversion of $CO_2$	kmol $CH_4$ / kmol $CO_2$ fed



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