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Analysis of reforming gas combustion in Internal Combustion Engine

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Abstract

The present paper deals with the study of the combustion of reforming gas in a small size Internal Combustion Engine. Therefore, mathematical models of both reforming process and internal combustion engine were implemented. In particular, steam reforming of glycerol to produce synthesis gas and spark ignition four strokes ICE were studied.

The reforming process mathematical model was verified using experimental data. Synthesis gas was used to feed the ICE with different syngas and engine configuration. On the basis of the comparison with the experimental results, it is possible to state that the mathematical model is validated.

Engine performance and pollutant emission evaluation was carried out using the integrated mathematical models with reference to the engine running on standard commercial fuel. The results highlight a reduction in engine performance and, at the same time a reduction of pollutant emissions in terms of CO and CO₂.

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Keywords: Glycerol steam reforming; ICE; H₂ production; syngas production; mathematical models;

1. Introduction

Biomass has recently received considerable attention as a potential substitute for fossil fuels in heat and power generation, as it allows for a reduction in environmental impact. In open literature it is possible to find several works on the innovative coupling between biomass gasification and fuel cells [1, 2, 3], whereas works on the coupling with

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traditional power generators, such as Internal Combustion Engines (ICE) and Gas Turbines (GT), are relatively scarce [4, 5]. The coupling of biomass conversion with more traditional power generators could be an easier way to gain, in the early stages, greater market-diffusion.

Moreover, a lot of researchers have been investigating new technologies to reduce fossil hydrocarbons use by increasing the production of fuels derived from vegetables biomasses. In this field, one of the most promising technology concerns the production of biodiesel from vegetable oils. This process is based on the transesterification of oils with a treatment that requires methanol, steam and electricity with some additional chemicals as sodium hydroxide, chlorum hydride, etc. Biodiesel is main product of this process and a mixture of glycerol and water (80/20, mass%) is generated as by-product. The amount of glycerol is a significant rate if compared to the biodiesel mass production. Biodiesel production has recorded an enormous growth in the last decade. The main drivers of this increase are the reducing dependence on imported oil and the reducing of greenhouse gas emission. Compared to diesel, the bio-fuel can be used in existing diesel engines without considerable modifications and it is compatible with existing fuel distribution infrastructure [6]. The European Union (EU) is world leader in production (67.9%) and consumption of biodiesel, followed by United States (17.8%) and Brazil [7]. The EU leadership is determined by the partial or total exemption of bio-fuels from taxes, which affect the price of traditional fuels [8].

On this scenario the present paper aims at studying the combustion of reforming gas in a small size ICE. Thus, mathematical models of glycerol steam reforming plant and ICE fed with obtained syngas were implemented and tested using experimental data.

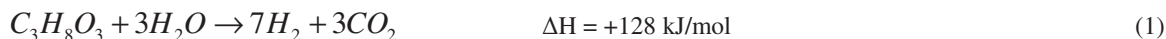
Nomenclature

\dot{m}	Boundary mass flux into volume
m	Mass of the volume
V	Volume
p	Pressure
ρ	Density
A	Flow area (cross-sectional)
A_s	Heat transfer surface area
e	Total internal energy (internal energy plus kinetic energy) per unit mass
H	Total enthalpy
h	Heat transfer coefficient
T_{fluid}	Fluid temperature
T_{wall}	Wall temperature
u	Velocity at the boundary
C_f	Skin friction coefficient
C_p	Pressure loss coefficient
D	Equivalent diameter
dx	Length of mass element in the flow direction (discretization length)
dp	Pressure differential acting across dx
S/C	Steam to carbon ratio ($\text{mol}_{\text{H}_2\text{O-in}}/\text{mol}_{\text{Carbon-in}}$)

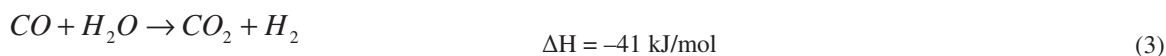
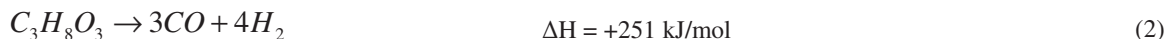
2. Hydrogen production by glycerol steam reforming

Biodiesel is becoming a promising fuel for diesel engines in wake of its renewable nature and environmental benefits. Different pathways can produce bio-diesel; however, glycerol (or glycerin) is a valuable by-product, which is formed during this process [9]. Glycerol has significant usage in pharmaceutical, cosmetic, soap and other industrial industries. However, with increased availability of glycerol, due to biodiesel production, the alternative utilization route needs to be explored otherwise this will lead to its disposal problem and may also affect the economics of biodiesel industry. For large scale production the best option would be to use the by-product as a fuel directly [9, 10]. Unlike methane [11], glycerol is a poor fuel, which does not burn in either petrol or diesel engines

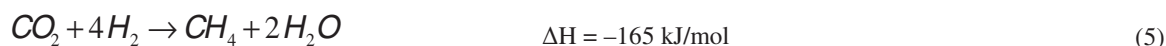
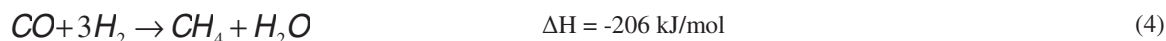
[12]. In the past, glycerol was blended with fuel oil and burnt as fuel. Practice that was abolished by European directive (waste incineration directive) because of pollution. Therefore, the alternative of use glycerol as a source of producing hydrogen could represent one promising way to use glycerol as energy fuel. In particular, syngas rich in hydrogen content can be produced from glycerol by steam reforming process that is the most common used method for producing hydrogen in the chemical industry. The overall steam reforming reaction apply to glycerol molecule ($C_3H_8O_3$), is represented as:



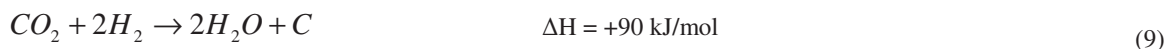
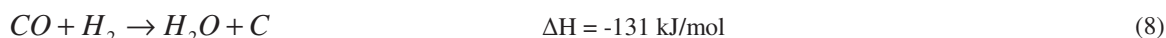
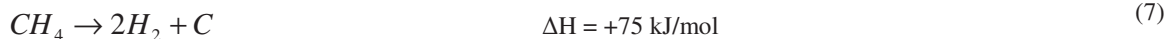
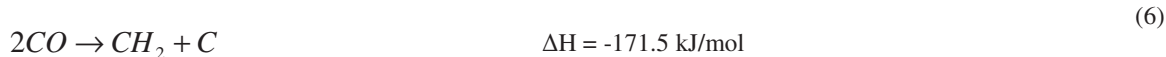
Thus, 7 mol H_2 /mol glycerol are produced as stoichiometric reaction. However, reaction in Eq. (1) may be viewed as the combination of the glycerol decomposition (cf. Eq. (2)) and water–gas-shift reaction (cf. Eq. (3)).



Eq. (1) is endothermic and results in an increase in the number of moles, therefore, high temperatures, low pressures, and high water/glycerol ratios in the feed favor H_2 production. The reverse reaction in Eq. (3), which leads to CO formation, is favored at high temperatures. The side reactions that lead to methane formation are represented as in Eq. (4) and Eq. (5) [13].



While CH_4 formation is favored at high pressures, its yield decreases as the temperature and water/glycerol ratio increase. Water reforms methane product into H_2 . The reverse reaction in Eq. (4), which denotes CH_4 steam reforming, is thermodynamically limited. Coke formation on the surface of the reforming catalyst is not uncommon. The reactions that may possibly lead to carbon formation are reported in equation from Eq. (6) to Eq. (9) [14].



Eq. (6) and Eq. (7) represent the decomposition of CO and CH_4 , whereas Eq. (8) and Eq. (9) denote the CO and CO_2 reactions with H_2 . Hydrogen production strongly depends on different operative conditions, such as water-to-glycerol feed molar ratio, temperature, and pressure. Therefore, the first step to understand the effect of the mentioned variables on hydrogen production and coke formation is a complete thermodynamic study of the glycerol-water system. In this way, studies carried out by authors led to demonstrate that the glycerol can be reformed to produce hydrogen rich gas mixture and then used for fuel cell application [2, 15]. Based on this preview activity, a more deep thermodynamic investigation on effect of the process variable on glycerol steam reforming process was dealt by Aspen Plus simulator process as following described.

2.1. Thermodynamic aspects

Aspen Plus simulator was used to carry out thermodynamic analysis of glycerol steam reformer process by means of a plant flowsheet divided in different parts. First part the inlet reactants (glycerol and water) are separately heated to reach the reaction temperature and further mixed and sent to the reforming reactor. This last one is composed by a

Gibbs reactor that calculates the equilibrium concentration of the reformed outlet stream. The last section represents a liquid separator necessary to separate the syngas from the liquid phase (mainly water with traces of organic by-products). This step is very important to feed correctly the internal combustion engine.

The equilibrium composition of the reformat gas obtained from the steam reforming system of glycerol was calculated using direct minimization of the Gibbs free energy. The primary components were $C_3H_8O_3$, H_2O , CO , CO_2 , H_2 , CH_4 , and C . The other intermediate compounds of the glycerol steam reforming, such as ethane, propane, methanol and ethanol, can be neglected. Over the temperature, pressure and S/C ratio range analyzed, the conversion of glycerol was always about 99.99%, thus it can be considered that the conversion was complete. As the reaction proceeds, the total Gibbs free energy decreases; the equilibrium condition is reached when the total Gibbs free energy (G_t) attains its minimum value. Therefore, the equilibrium composition can be determined by solving the minimization problem as follows:

$$\min_{n_i} (G^t)_{T,P} = \sum_{i=1}^C n_i \bar{G}_i = \sum_{i=1}^C n_i \left(G_i^0 + RT \ln \frac{\bar{f}_i}{f_i^0} \right) + n_s G_s \quad (10)$$

where G_i^0 is the Gibbs free energy of the species in standard conditions, C is the total number of components in the reaction system, n_i is the amount of each gaseous component, n_s is the number of carbon molecules involved in the carbon formation, and G_s is the Gibbs free energy of solid carbon. Based on the minimization problem of Gibbs free energy (as stated above) was solved to find the equilibrium composition of the reactive system. In particular, the reforming reactions modeled by Gibbs reactor and minimizing the free energy in order to calculate the syngas composition and the mole of carbon produced at a given conditions. The input data adopted for such calculations were: (i) pure glycerol; (ii) reagents inlet flow; (iii) reagents inlet temperature; (iv) reactor temperature; (v) reactor pressure equal to 1 bar. Fig. 1 shows the outlet dry syngas composition calculated by simulation of glycerol steam reforming process. As can be seen in Fig. 1, hydrogen production mainly increases with temperature in the range 623-923 K, successively it tends to decrease together with CO_2 , while the CO production sensitivity increases for all temperature range considered. Perhaps, this behavior can be explained by the reverse water gas shift reaction (Eq. 3). About methane conversion, it decreases when the temperature increase, this can be due to the methane steam reaction to produce carbon monoxide and hydrogen (reverse of Eq. 5). On the other hand, for all range of temperature slight differences was noted in terms of outlet stream distribution increasing the S/C ratio, even though the increase of hydrogen and carbon monoxide concentrations was evident. From the carbon formation point of view, Fig. 2 depicts the effects of the steam to carbon ratio (S/C) and the reformer temperature on carbon formation. It indicates the boundary of carbon formation for glycerol steam reforming, which is helpful to determine feasible conditions to avoid carbon formation. It is observed that carbon formation is thermodynamically inhibited at high temperatures for steam to carbon ratios higher than 2 mol/mol.

2.2. Experimental proof

In order to validate the thermodynamic model developed by Aspen Plus simulator, a series of glycerol steam reforming tests were carried out by CNR-ITAE micro-laboratory plant [15]. In particular, all catalytic experiments were performed in a temperature ranging from 823 to 1023 K, using a mixture of pure glycerol and water (steam to carbon ration (S/C) of 3 mol/mol) and a rhodium supported on alumina catalyst. The gas hourly space velocity ($GHSVC_3H_8O_3 = \text{catalyst bed volume}/\text{volume feed rate} = [m^3 m^{-3} h^{-1}]$) selected for the tests was of $5,000 h^{-1}$ in order to assure thermodynamic condition to catalytic performances. On line gas-chromatography analysis, both reagents and products, allowed to verify the carbon, hydrogen and oxygen balances. Thus, experimental data was compared in terms of syngas stream composition (on dry basis) to theoretical values estimated as above described (see Fig. 3).

Catalytic tests highlighted that the glycerol conversion to primary gaseous products (H_2 , CH_4 , CO and CO_2) increases with increasing of the operative temperature: 74% at 823K, about 87% at 923 K and finally 98.2% at 1023K. However, the conversion never reached 100%; this evidence can be attributed to the formation of other organic compounds such as acetone, acetaldehyde, ethanol, propanol, ethylene glycole, hydroxy-propane (detected into outlet liquid phase, not here reported).

Fig. 3 depicts hydrogen production clearly increased with the temperature, while the CH_4 presence drastically decreased from 4.8 mol% at 823 K to 0.18 mol% at 1023 K. On the other hand, CO_2 concentration was found to be

higher at 823 K (38.3 mol%), while CO production was found to be greater at 1023 K (about 18 mol%). This behavior it is due to steam reforming reaction, promoted by higher temperatures, that supports methane conversion to CO or CO₂ and H₂ in according to thermodynamic data [15, 16].

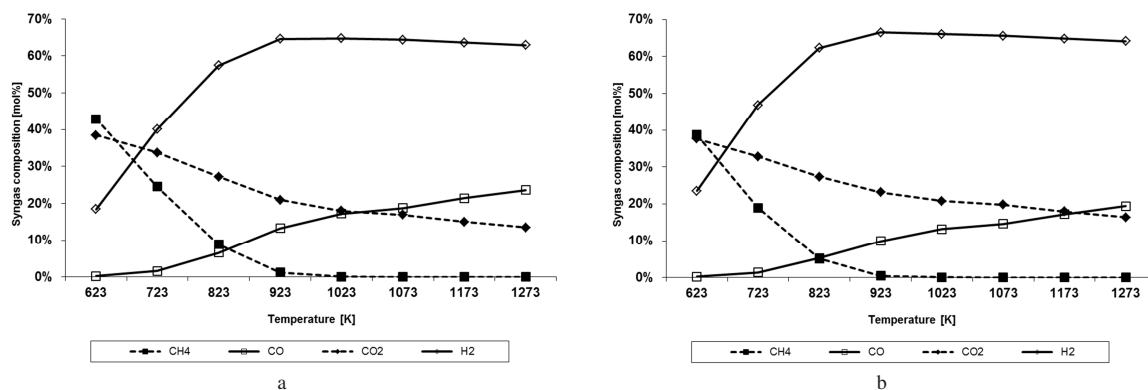


Fig. 1. Outlet gas compositions by glycerol steam reforming process as a function of reaction temperature, at equilibrium, calculated at: (a) S/C = 2 mol/mol; (b) S/C = 3 mol/mol.

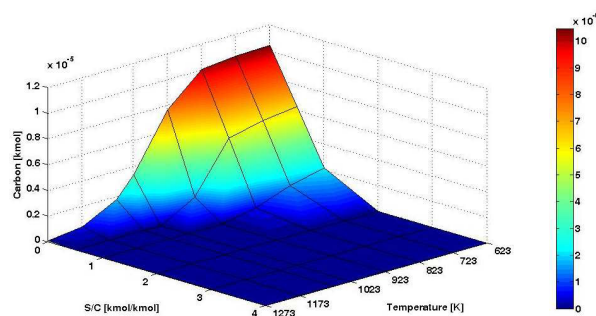


Fig. 2. Effect of S/C ratio and reaction temperature on theoretical carbon formation.

On the whole, experimental results seem to be in respect of reaction pathway proposed for other oxygenated molecule [14, 17], where the presence of the catalyst contributes with the temperature in the cleavage of C–C bonds. These last ones are accompanied by hydrogen evolution to form adsorbed carbon oxygenate on catalysts site, which further reacts with liquid water to release additional hydrogen and forms oxides of carbon. That suggests hydrogen production remains due to main reactions (water gas shift and methane reforming) and secondary reactions (dehydration, dehydrogenation) as appropriately considered in the thermodynamic calculations. Further, modest carbon deposition on used catalysts, from 1.4 mgCg⁻¹_{cat}×h at 873K to about 2.2 mgCg⁻¹_{cat}×h both to 923 K and 1023 K, were detected by CHNS elemental analysis after 15 hours of test. However, the coke formation rate was considered negligible referred to contact time of the flow gas-input (0.12 s) on catalytic bed load (0.02 g). On the basis of results above reported in terms of gaseous products composition, experimental data well fit with the thermodynamic analysis, especially at 923 K.

Therefore, by thermodynamic and experimental investigation it has been possible to reveal that optimal conditions for hydrogen production are: temperature of 923 K, pressure of 1 bar and water to glycerol molar ratio of 9:1. Under these conditions, methane production was very poor and coke formation was minimized, indeed catalytic information has shown stable activity.

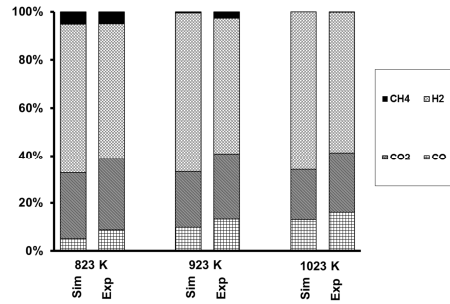


Fig. 3. Experimental and theoretical data comparison.

3. Engine mathematical model

One-dimensional approach [18, 19, 20] was used to create a small size engine mathematical simulation model. The engine model was built up as a four-cylinder inline spark ignition engine. The main geometrical characteristics of each cylinder are shown in Table 1.

Table 1. Main engine characteristics.

Description	Value
Bore	72 mm
Stroke	84 mm
Connecting Rod Length	129 mm
Compression Ratio	15
Engine Speed	3000 rpm

Concerning the flow model, it simultaneously solved the conservation of continuity, momentum and energy equations in one dimension. This means that all quantities determined are averages across the flow direction. The solutions were obtained using explicit time integration of Eq. 11, Eq. 12 and Eq. 13.

$$\frac{dm}{dt} = \sum_{\text{boundaries}} \dot{m} \quad (11)$$

$$\frac{d\dot{m}}{dt} = \frac{dpA + \sum_{\text{boundaries}}(\dot{m}u) - 4C_f \frac{\rho u |u| dx A}{2D} - C_p \left(\frac{1}{2} \rho u |u|\right) A}{dx} \quad (12)$$

$$\frac{d(me)}{dt} = -p \frac{dV}{dt} + \sum_{\text{boundaries}} (\dot{m}H) - hA_s(T_{\text{fluid}} - T_{\text{wall}}) \quad (13)$$

In order to study performance, combustion and emissions of an engine running on synthesis gas, a predictive combustion model (SI-turbulent flame) was used for the simulations [21]. A two-zone combustion model implemented within the GT-Power software [22] was used in the present work.

The combustion model takes into account the cylinder's geometry, spark-timing, air motion and fuel properties and provides detailed output of engine performance and emissions.

A direct optimization method [22] was used to determine optimal values of some engine parameters (Air-to-Fuel ratio, spark-timing and injection timing) suited to simulate the mathematical model running on synthesis gas.

The direct optimizer was built directly into the simulation solver; the solver used an algorithm to logically determine the input values for the next iteration based on feedback from results of prior iterations. The result of this optimization was a single set of parameter values that best met the optimization criteria. A discrete-grid algorithm method was chosen for searching optimum. This method reduced the search range into smaller ranges by $\frac{1}{2}$ until the optimum was found.

It was necessary to find new engine parameters different from those ones used for model running on gasoline, because of problems in combustion activation when running on synthesis gas. The misfiring is due to the very small low heating value of the syngas because of high content of non-combustible species into the fuel mixture. The optimization was performed using the maximum brake power as task value and the variation ranges of engine parameters shown in Table 2.

Table 2. Variation ranges of engine parameters and optimized values.

Description	Range	Optimized value
Air-to-Fuel Ratio	From 3 to 25	4
Spark-Timing [deg]	From -5 to -25	-11
Injection-Timing [deg]	From 380 to 420	405

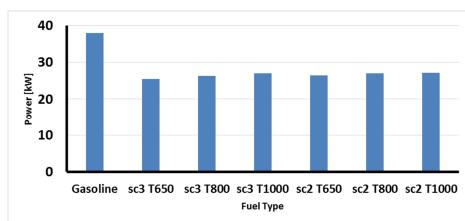
4. Results and discussion

Using the engine mathematical model several simulations were carried out to study the effects of syngas composition on engine performance, combustion and emissions. In particular, combustion in ICE running on different syngas type, as well as gasoline was studied. Fig. 4 shows performance (power, torque, efficiency and SFC) of the engine running on all analyzed syngas types. The nomenclature of each syngas composition is described by steam to carbon ratio (S/C) and temperature (T) values corresponding to syngas formation. In particular syngas compositions obtained with a S/C ratio of 2 and 3 at levels of temperature of 650, 800 and 1000 K were used for simulations. In the graphs reported in Fig. 4 performance of the engine running on gasoline are reported as reference.

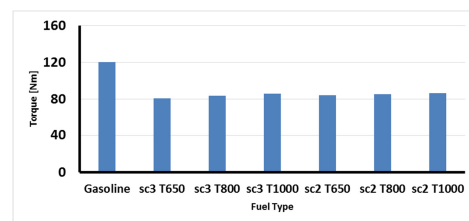
Observing the graphs in Fig. 4, running on syngas leads to a reduction of engine performance with respect to performance using gasoline. A reduction of about 30 % was registered.

Performance decrease is due to reduction of both in-cylinder pressure (see Fig. 5) and volumetric efficiency (Fig. 6). This behavior is evident using all studied fuel synthesis gases. In particular, a reduction of about 10% in pressure peak can be observed in Fig. 7, while in Fig. 6 a reduction more than 30 % in engine volumetric efficiency is evident. As it is possible to observe in the same figure the in-cylinder pressure peaks occur before in the combustion of syngas instead of gasoline. And this behavior is registered for all used syngas.

At the same time, a variation in in-cylinder temperatures was observed. In Fig. 8(a) in-cylinder temperature as function of crank angle is reported. Observing the graphs in Fig. 8(a) the syngas combustion produces lower in-cylinder temperature peaks (see also Fig. 8(b)), but higher in-cylinder mean temperatures as reported in Fig. 8(b). The increase in in-cylinder mean temperature is probably due to the increase in burn duration as it is possible to observe in Fig. 9. This behavior is evident for all studied syngas.



a



b

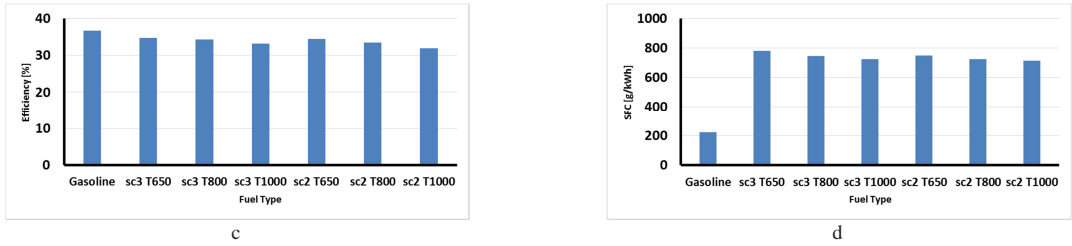


Fig. 4. Engine performance: (a) Power; (b) Torque; (c) Efficiency; (d) Specific Fuel Consumption.

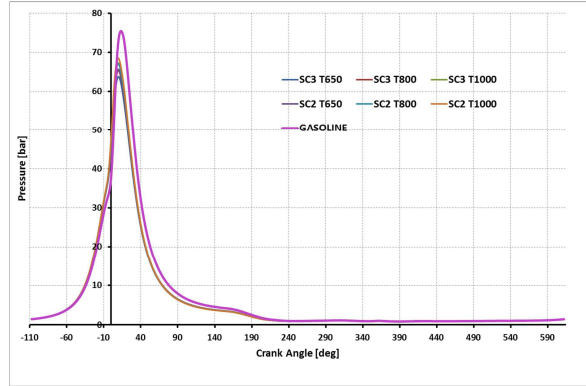


Fig. 5. In-cylinder pressure versus crank angle for different fuel types.

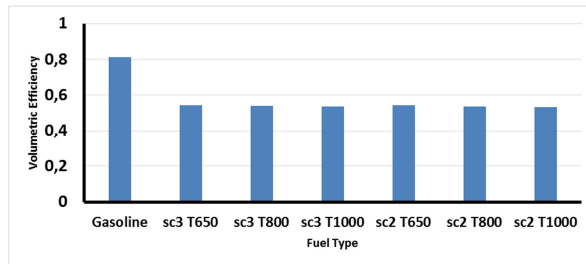


Fig. 6. Volumetric efficiency for different fuel types.

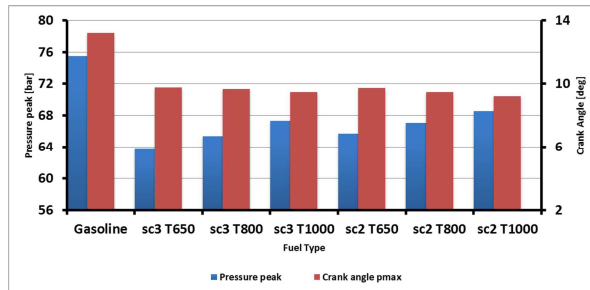


Fig. 7. In-cylinder pressure peaks, as well as crank angle they occur as function of fuel types.

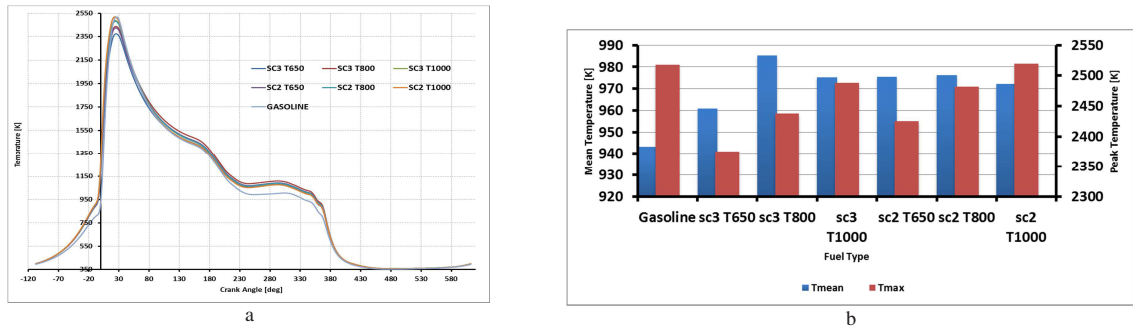


Fig. 8. (a) In-cylinder temperature versus crank angle; (b) In-cylinder peak and mean temperature.

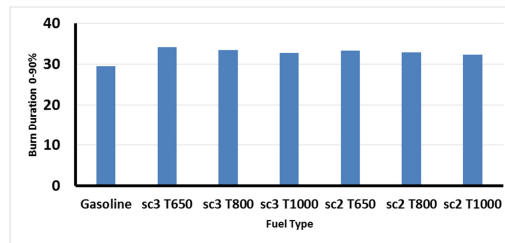


Fig. 9. Burn duration (0 – 90%) as function of fuel types.

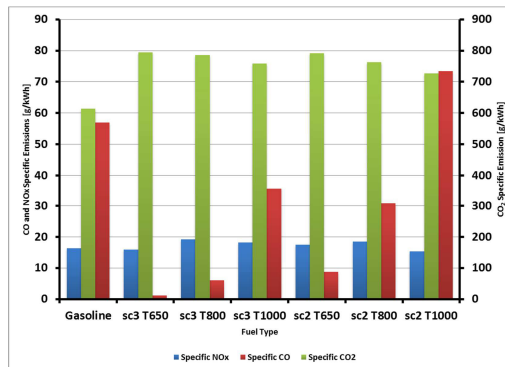


Fig.10. Specific emissions CO₂, CO and NO_x.

Concerning the pollutant emissions using synthesis gas, Fig. 10 shows CO₂, CO and NO_x specific emissions. As it is possible to see in the graphs reported in Fig. 10, using syngas as fuel produces an increase in specific CO₂ emissions. However, results analysis highlights that the increase in CO₂ emissions is related to the presence of CO₂ in the fuel mixture. Extrapolating the amount introduced with the syngas a reduction in specific CO₂ in the range from 30 % to 60 % is obtained. In any case, using glycerol from bio oil transformation process as feedstock of syngas production plant, a zero CO₂ emission by the global process is obtained. A reduction in CO emissions is registered as it is shown in Fig. 10. Increasing the reaction temperature in syngas production plant produce an increase in CO concentration in syngas. This is reflected in the engine specific CO emissions, as well. However, a strong reduction in CO emissions is observed for all used syngas in comparison with reference CO emissions (gasoline). Concerning NO_x emissions, Fig. 10 shows specific NO_x for different syngas type. As it is possible to observe in the figure specific NO_x emissions increase using syngas with respect to gasoline engine ones. This is due to the increase of in-cylinder mean temperature (see Fig. 8(b)). Observing the graph in the figure a slightly increase in engine specific NO_x emissions is registered for the two fuel mixture corresponding to a small increase in H₂ concentration (sc2T800 and sc3T800).

5. Conclusions

The process to get biodiesel from biological oils produces glycerol as byproduct. The latter can be processed using steam-reforming technique to generate synthesis gas. This syngas can be used to feed an ICE for electric energy generation and for mobility purposes. Thus, in this paper a mathematical model of the glycerol steam-reforming plant has been implemented and verified using experimental data. On the basis of the simulated and measured syngas compositions comparison, it is possible to state that the model is validated. Using the implemented model a parametric analysis as function of reaction temperature and S/C ratio was carried out. Obtained results highlighted that not all analyzed reaction temperature and S/C ratio combinations are suitable to run the plant and produce a useful syngas.

On the basis of the presented results, it can be seen that it is possible to feed a conventional spark ignition engine with synthesis gas from steam reforming of glycerol, accepting a reduction of engine performance. Moreover, using syngas to feed the engine leads to a reduction of pollutant emissions in terms of CO and CO₂. In conclusion, the goal of the present paper is the possibility to run a conventional spark ignition engine with low and inexpensive modifications using a syngas derived by a non-useful byproduct of biofuels production process.

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