Experimental and theoretical study of exhaust gas fuel reforming of Diesel fuel by a non-thermal arc discharge for syngas production

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Abstract: An experimental set-up has been developed to study two typical operating points of Diesel powered vehicle, corresponding to high load and low load points. A sensibility study over O/C ratio, injected electric current and mass flow rate have been carried out. The plasma reformer performances have been evaluated in terms of energy efficiency and conversion rate. At low engine load, an energy efficiency of 40% and a conversion rate of 95% have been reached which correspond to a syngas dry molar fraction of 25%. For the most favorable case, only 12 s are needed to regenerate the NOx trap catalyst. The 1D multistage kinetic model developed has shown good trend correlation with experimental results. It has been demonstrated that the oxygen from CO_2 and H_2O almost does not intervene in the exhaust gas Diesel fuel reforming. At the contrary, CO_2 and H_2O decrease temperatures, the kinetic reaction speed and the energy efficiency compared to PO_x reaction. To higher the temperature, more oxygen is needed but local combustion can happen and promote H_2O and CO_2 production.

Keywords: Plasma reformer, syngas, diesel fuel reforming, NO_x trap.

1. Introduction

In Europe, Euro stage VI regulation for Diesel engines will come into force in September 2014. This new regulation sets a 56 % reduction of NOx emissions compared to Euro stage V and forces car manufacturers to develop new efficient solutions. Three-Way Catalysts (TWC) used for gasoline engines after-treatment can efficiently decrease NOx emissions which operate under close to stoichiometric condition. However, TWC technologies become ineffective in Diesel engines since, in this case, exhaust gases have a high oxygen content.

For Diesel engines after-treatment, technologies based on NO_x trap catalysts are one of the technological solutions under development to meet the further emission regulations. The NO_x trap is based on a cyclic operating mode. In storage mode, the NO_x trap stores NO_x emitted from the engine on a catalyst material. Once full, the classical way to regenerate NO_x trap catalysts consists in operating the engine under rich combustion conditions for a short while in order to produce reducing species in the exhaust gas that will convert NO_x into N_2. This method is not totally satisfying since it suffers from a significant drawback known as oil dilution problem. To overcome oil dilution problem, it is possible to produce reducing species such as H_2 and CO by Diesel fuel reforming whose species will be used for NO_x trap regeneration. In this case, a part of the Diesel engine exhaust gas is by-passed to the reformer and is mixed with a small amount of Diesel fuel, which provides the necessary species to regenerate the NO_x trap catalyst. We present in this paper an alternative to catalytic reforming method consisting in using a non-thermal plasma torch. The plasma torches dedicated to reforming have been reviewed in [1]. Contrary to catalysts, plasma processes are non-sensitive to sulfur, light and compact device, and have short-transient time.

2. Experimental setup

The plasma reactor is composed of two consecutive zones: a plasma zone and a postdischarge zone. The plasma zone is the part where the arc plasma really takes place. The postdischarge zone is a passive zone, located downstream of the plasma zone where most of the reforming reactions ignited in the plasma zone continue to take place depending on their kinetic speed. The power supply is a resonant converter controlled in current [2]. The current can be precisely tuned in the range of 0.22-0.66 A. A high voltage is applied to the tip electrode (anode as we work in inverse polarity), and the cylinder electrode (cathode) is grounded. The cathode is a stainless steel cylinder with an 8 mm inner diameter and 75 mm long.

Both operating conditions studied are given in Tab. 1. They correspond to the exhaust gas composition of a diesel engine for two fuel/air equivalence ratios (Φ) of 0.66 (high load) and 0.32 (low load) for a Renault 2.0 L 16v dCi turbocharged engine.

Plasma reformer performances are analyzed in terms of energy efficiency and conversion rate. The energy efficiency is based on the LHV of syngas produced over the LHV of diesel fuel and plasma power. The conversion rate accounts for the fuel transformation and is an indicator of the mass balance on carbon atoms.

Table 1. *Operating conditions.*

Conditions	**1 High load**	**2 Low load**
Φ	0.66	0.32
O_2 ($\%_{mol}$)	6.8	13.9
N_2 ($\%_{mol}$)	75.8	77.4
CO_2 ($\%_{mol}$)	9.1	4.5
H_2O ($\%_{mol}$)	8.3	4.1

3. Results and Discussion

3.1. Influence of O/C ratio

In Fig. 1, for condition 2, the diesel fuel decomposition is higher than 80% for O/C greater than 1.3. The second operating condition (Φ = 0.32) reaches an energy efficiency of 40% against only 15% for the first one (Φ = 0.66). The strong difference in energy efficiencies is essentially due to the oxygen rate in the gas mixture, which is twice higher at low engine load, and CO_2 and H_2O, which are twice lower. In both cases, the temperature grows linearly with the O/C ratio. Oxygen has the role to bring energy to the system and allows reaching higher temperatures for low engine load.

In addition, at high load, an important part of calories are absorbed by CO_2 and H_2O present in high concentrations as in an EGR system. At low load, the higher the temperatures, the better the decomposition of diesel fuel, the faster the kinetic reactions, and, therefore, the better the energy efficiency.

The peak efficiencies are reached at an O/C greater than the PO_x stoichiometry reaction (respectively, for O/C equals 1.3 and 1.5 instead of O/C = 1). First, temperature is one of the most important parameters. As mentioned above, reforming reactions need a lot of energy to set quickly. More oxygen is needed to activate reforming reactions and thus a higher O/C ratio, but a part of this additional oxygen forms CO_2 (cf. Fig. 2). The nonhomogeneity of the plasma reformer can lead to a local combustion reaction that raises the temperature and leads to better performances, but higher CO_2 and H_2O production.

For each O/C ratio, Fig. 2 also shows that the plasma reformer promotes CO_2 production. The dry reforming reaction does not take place because a decrease of the CO_2 molar fraction compared to the initial composition is not observed. Concerning steam reforming, it maybe takes place when O/C is lower than 1. Indeed, the H_2 and CO molar fractions are quite high (4 and 8%, respectively) and the CO_2 fraction increases. For O/C lower than 1, the high excess of fuel induces a high production of CH_4 and a very low conversion rate, which can be associated with methanation. The CH_4 mole fraction must be decreased at maximum as it is a regulated pollutant. For O/C higher than 2, conditions are getting close to the combustion reaction and high temperature, and high CO_2 and low CH_4 production are observed. The H_2/C ratio of diesel fuel is equal to 0.92, and thus, generally more CO than H_2 is produced.

In condition 2 at O/C = 1.3, 15% and 8% dry molar fractions of CO and H_2, respectively, for a deposited power of 720 W have been reached. In these conditions, the dry molar fraction of CH_4 is only 1.6%.

The Euro V passenger car engines have to emit less than 180 mg/km of NO_x, and typically their real NO_x emission is close to 150 mg/km of NO_x. The Euro VI regulation imposes a NO_x emission lower than 80 mg/kg. Consequently, 70 mg/ kg of NO_x has to be treated by the NO_x trap. The homologation of European vehicles is based on NEDC (New European Driving Cycle), which is 11 km long. Assuming one regeneration during the cycle and that the NO_x emitted is essentially NO_2, the NO_x trap has to store 16.7×10^{-3} mol of NO_x. 5 mol of syngas are needed to reduce 1 mol of NO_x. Without scaling up the mass flow rate, in the second operating condition, 7×10^{-3} mol/s of syngas is produced and leads to a NO_x trap regeneration duration of 12 s, which is a very promising. On the contrary, the first condition leads to a NO_x trap regeneration duration of 45 s and is not competitive compared to catalytic processes.

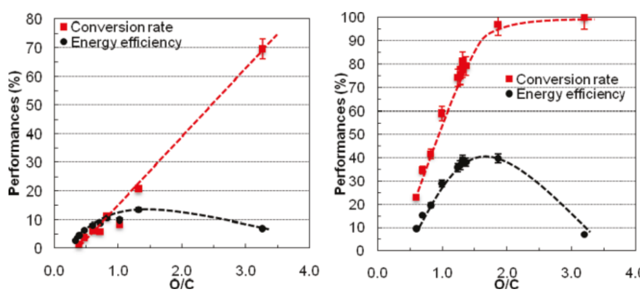

Figure 1. *Experimental performances as a function of O/C for both operating conditions (left, condition 1; right, condition 2).*

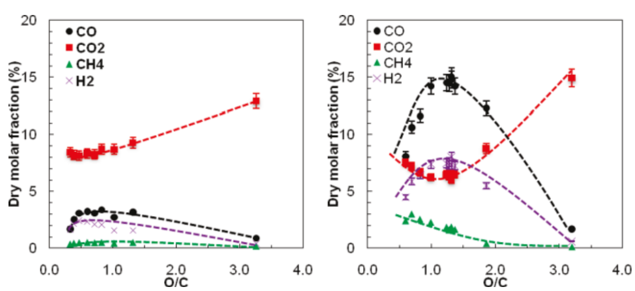

Figure 2. *Dry molar fraction as a function of O/C (left, condition 1; right, condition 2)*

3.2. Influence of the current

The monitoring of the input current directly affects the input power injected in the system. Fig. 3 shows the performances of the reformer as a function of input current. In the input current range [0.25-0.6 A], the deposited power varies quasi-linearly with the current as long as we stay in the glidarc zone. In NO_x trap regeneration conditions, the quasi-continuous regime, which gave the best results with ethanol, E85, and gasoline [3,4] cannot be reached anymore.

The performances at high load are quite low, and even a current of 0.6 A (P = 940 W) cannot reach an adequate temperature to quicken the PO_x reaction. At low load, the energy efficiency grows quasi-linearly with the input current and hence with the deposited power until 0.4 A. The energy efficiency and the conversion rate reached 31% and 58%, respectively, for I = 0.4 A and 35% and 60%, respectively, for I = 0.6 A while the deposited power rises from 730 to 1180 W.

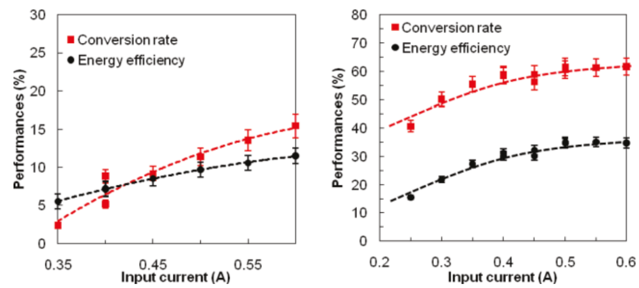

Figure 3. *Experimental performances as a function of input current (left, condition 1; right, condition 2).*

3.3. Influence of the exhaust gas flow rate

The influence of the exhaust gas mass flow rate has been studied in a range of 2.5-5% of the total exhaust gas mass flow rate. One can observe in Fig. 4 that the higher the exhaust gas flow rate, the lower the volume power injected and the lower the performances. The syngas molar flow rate is quasi-constant at 1.9×10^{-3} mol/s for the first engine condition. For the second condition, a better syngas molar flow rate is attained (4.8×10^{-3} mol/s) between 30×10^{-3} and 40×10^{-3} mol/s exhaust gas flow rate. This exhaust gas molar flow rate corresponds to a 3.5-4.5% range of total exhaust gas emitted by the engine.

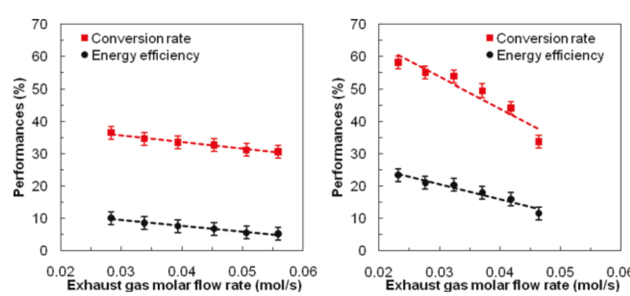

Figure 4. *Experimental performances as a function of exhaust gas flow rate(left, condition 1; right, condition 2).*

3.4. Comparison with a 1D multi-stage kinetic model

The 1D multistage model, presented in Fig. 5, has been detailed in [5]. This model is based on the following assumptions: (i) The medium is adiabatic. (ii) Only a fraction of reactants' inlet flow passes through the arc discharge. (iii) These two fractions, that is, cold and hot streams, respectively, are perfectly and instantaneously mixed at the reactor exit. The arc is modeled by a perfectly stirred reactor (PSR) where a homogeneous input power is applied. Finally, the postdischarge is modeled by means of plug flow reactor (PFR). The model uses the Chemkin II package [6]. The diesel fuel surrogate molecule used is *n*-heptane. The kinetic mechanism is composed of 160 species and 1540 reactions [7,8].

A shift in energy efficiency between experiments and the 1D model can be observed in Fig. 6. First, the energy efficiency discrepancy mainly comes from thermal losses. The model assumes the adiabaticity of the medium. Second, the perfect and instantaneous mix at the torch exit is far removed from the experimental torch exit, which is highly nonhomogeneous. Local nonhomogeneities could also appear in the reactor, leading to H_2O and CO_2 production instead of H_2 and CO. However, the model trends are similar to the experimental trends. For O/C higher than 1.5, the experiments and the 1D model are very close to thermodynamics results.

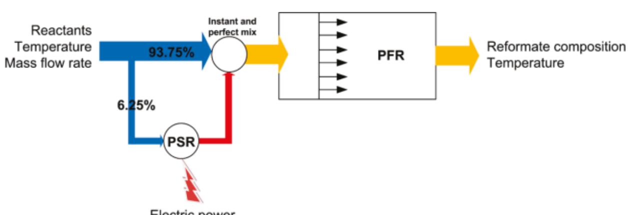

Figure 5. *Diagram of the 1D multistage kinetic model describing the low current plasma reformer.*

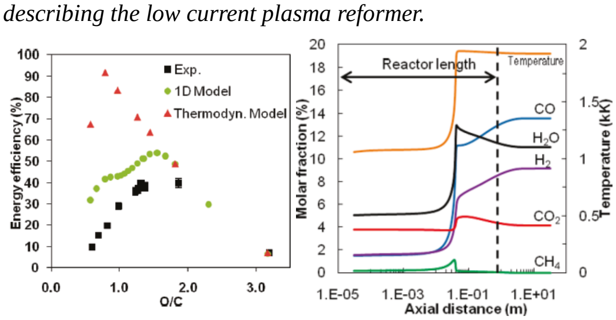

Figure 6. *Comparison between experimental data, 1D multistage model and thermodynamics for condition 2.*

4. Conclusions and Perspectives

An experimental set-up has been developed to study two typical operating points of Diesel powered vehicle, corresponding to high load and low load points. A sensibility study over O/C ratio, injected electric current and mass flow rate have been carried out. The plasma reformer performances have been evaluated in terms of energy efficiency and conversion rate. At low engine load, an energy efficiency of 40% and a conversion rate of 95% have been reached which correspond to a syngas dry molar fraction of 25%. The 1D multistage kinetic model developed has shown good trend correlation with experimental results.

It has been demonstrated that the oxygen from CO_2 and H_2O almost does not intervene in the exhaust gas Diesel fuel reforming. At the contrary, CO_2 and H_2O decrease temperatures, the kinetic reaction speed and the energy efficiency compared to PO_x reaction. To higher the temperature, more oxygen is needed but local combustion can happen and promote H_2O and CO_2 production.

For the most favorable case, only 12 s are needed to regenerate the NO_x trap catalyst. In the other case, a hybrid catalyst-plasma solution is envisaged.

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