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Alcohols treatment using a Statarc reactor to produce syngas

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Abstract—This work is devoted to the plasma steam-reforming of various alcohols: methanol, ethanol and phenol. The plasma reactor is an elementary stationary discharge, which allows us to perform physical diagnostics and chemical analysis of the produced species. The arc is formed between two electrodes made of graphite. The liquid reactants (alcohol + water) are injected in the reactor and are vaporized directly in the upper electrode. Main studied parameters on the gas production are the inlet liquid flow rate, the alcohol mole fraction and the nature of the alcohol. Gas analyses are performed on the outlet gas and the dry gas obtained after a cold trap. From the chemical and the electrical diagnostics, the consumed power to produce 1 kg of H₂ is calculated. Main produced species in the dry gas are H₂, CO, CO₂, CH₄ and C₂ species are also detected depending on the inlet alcohol in the liquid mixture. To note the effects of the inlet composition of the liquid, we report also the dry gas composition as functions of inlet H/C and H/O ratios.

Keywords— Steam reforming, syngas, alcohol, biomass, non-thermal plasma

I. INTRODUCTION

A lot of studies show that hydrogen has a high potential as a fuel for electricity generation and transportation purposes. Overall, the catalytic reactors are used to produce H₂ from alcohol production. Some authors have also performed the possibility to use plasma reactor for hydrogen production from water and hydrocarbons, alcohol or biomass with high H₂ yields with limited costs [1-5]. This paper is devoted to a comparative study of syngas (H₂+CO) production from various alcohol (methanol vegetable or ethanol) H₂ yields and energetic cost in function of hydrogen sources are presented. The non thermal plasma used is a laboratory scale experimental device static discharge. Others products are obtained and analyzed: CO, CO₂, CH₄ and C₂ species.

II. EXPERIMENTAL SET-UP

The plasma reactor used in this work has been previously described [2,6,7]. The used discharge is called Non-Thermal Arc, NTA [8]. Discharge reactor includes a quartz tube (400 mm length; 30 mm inner diameter) containing two electrodes made of graphite. The conical extremities of the two electrodes are settled opposite each other and the electrode gap is 10 mm. The liquid mixture is injected through the upper electrode into the non-thermal plasma reactor (Fig. 1).

A syringe pump is used to adjust the flow rate from about 30 to 130 mL/h (at room temperature). The graphite electrodes are heated by the discharge and the liquid is entirely vaporized during its flow in the upper electrode. The moles of the reactants in the inlet liquid or in the inlet gas mixtures have the same values in the liquid phase and in the vapor phase, respectively. Three alcohols diluted in water have been studied in this paper: methanol, ethanol

and phenol. The mole fractions of alcohol have been varied in the inlet liquid mixtures from 0.09 to 0.55 and from 0.06 to 0.49 in methanol mixtures and ethanol mixtures, respectively. In the experiments from phenol, the inlet alcohol mole fractions remain low due to its low solubility in water.

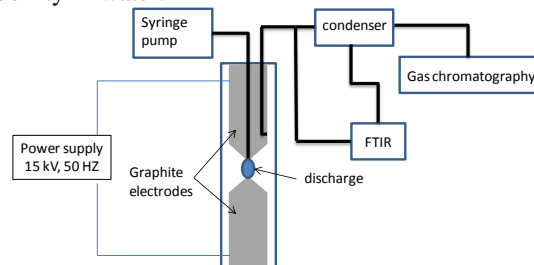


Fig. 1. Schematic reactor experimental.

The gas discharge is powered by a 50 Hz high-voltage transformer with leakage flux. AUPEM SEFLI high voltage transformer: primary 230 V, secondary 20 kV, I₂=155 mA). The current and voltage waveforms are measured and are recorded on a digital oscilloscope. From the current and voltage data, the power is calculated and the energy cost of production H₂ can be estimated. Typical plots of voltage and current as functions of the time are previously given [6,7]. At a maximum of current (about 230 mA), a quasi constant voltage is observed (900 V). Periodic high voltages peak are observed at the zero current transition of the alternating current.

At the outlet of the reactor, chemical analyses of the exhaust gas are performed. Total gas or dry gas (after condenser trap) is measured by using FTIR or GC. To quantify the concentrations of the species in the dry gas, the exhaust gas is injected into a cryogenic trap (-20°C) then in a gas phase chromatography analyzer (GC-Varian CP 3800). The obtained gas after the cold trap is called dry gas.

H₂, CO, CO₂, CH₄, C₂H₂, C₂H₄ and C₂H₆ are quantified. Infra-Red Transform Fourier (FTIR) analyses

are also done on the wet gas at the outlet of the reactor to measure non-consumed alcohol and water and to evaluate the concentrations of the produced species in the outlet wet gas

III. RESULTS

A. Gas analyses

First results are about the exhaust gases without condenser. Figure 2 displays FTIR spectrum obtained after a methanol-water treatment by NTA. Main detected species are CH_4 , CO , CO_2 , remaining CH_3OH and H_2O . For all alcohols studied, produced species are the same.

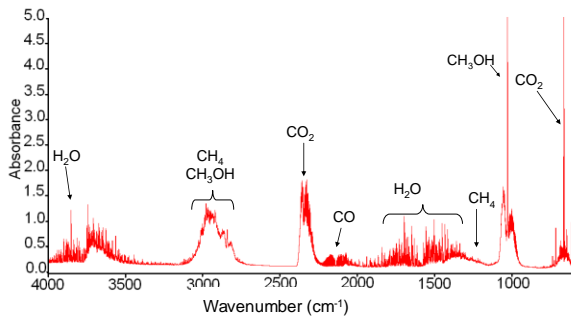


Figure 2: wet outlet gas IRTF spectrum. Inlet liquid: $\text{H}_2\text{O}+\text{CH}_3\text{OH}$, Flow rate: 75.3mL/h.

In figures 3 and 4, we report the exhaust gases composition as functions of the methanol or ethanol mole fractions in the injected mixture, respectively.

We can note that when the inlet alcohol mole fraction increases, high rises of H_2 and CO concentrations can be obtained, up to 45% and 20% in mol, respectively. In the same time, remaining alcohol concentration increases too.

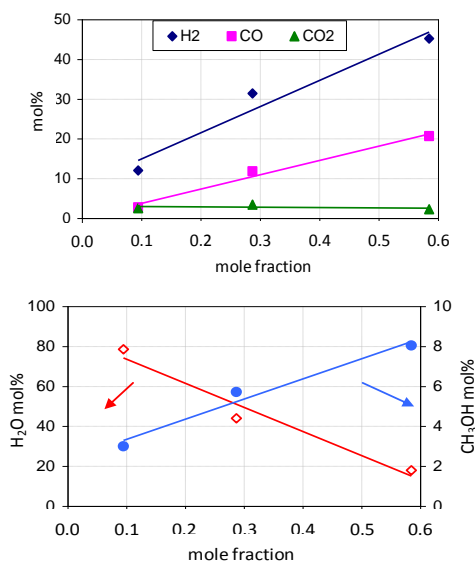


Fig. 3: Wet outlet gas composition in mol% as a function of the inlet methanol mole fraction. Inlet liquid flow rate=75.3 mL/h.

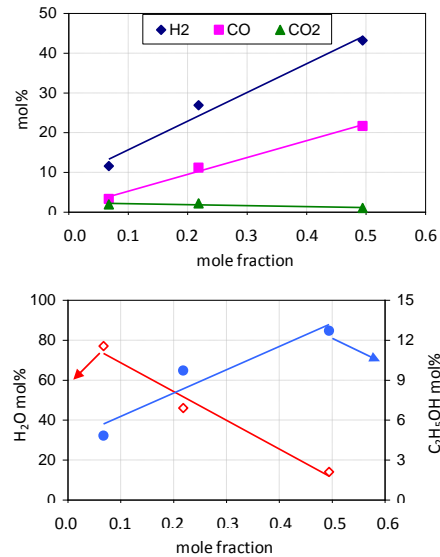


Fig. 4 : Wet outlet gas composition in mol% as a function of the inlet ethanol mole fraction. Inlet liquid flow rate=75.3 mL/h.

To increase the concentration of interesting species as H_2 or CO for fuel applications, it is possible to condense exhaust gas as described in figure 1. In our experiments, we can trap remaining water and alcohol. H_2 , CO and CO_2 concentrations are increased in the dry gas as displayed in figures 5 and 6. In these figures, the dry gases composition are reported as functions of the inlet liquid flow rate and various inlet alcohols mole fractions from methanol and ethanol treatments, respectively.

High concentrations of H_2 , CO and CO_2 are obtained. Concentrations of these species are about 60-66%, 14-24% and 7-16%, respectively and are functions of the flow rate and alcohol concentration in the inlet mixture. Variations of H_2 , CO and CO_2 mol% in the dry gas can be described as follow from both alcohols mixtures: a rise of the flow rate and X_{alcohol} leads to a decrease of produced H_2 and CO_2 . On the other hand, in the same time, overall CO increases.

When X_{alcohol} increases (up to 0.21 for methanol mixtures and 0.16 for ethanol mixtures), CO and CO_2 concentrations do not seem to be affected by a rise of the flow rate.

Minor species are also measured which are CH_4 and C_2 species. These species concentrations are not reported in this paper [7]. We have observed that C_2 species are more produced from ethanol mixtures but their concentration remain low ($<1.5\%$ in mol) and C_2H_4 and C_2H_2 maximum is observed for the highest flow rate and alcohol concentration. From methanol mixtures, concentrations of C_2 are lower than $4 \cdot 10^{-2}$ in mol%.

From these results we can observe that CO and CO_2 have opposite trends. Thus, constant $\text{CO}+\text{CO}_2$ sums, in mol%, are measured in dry gas when the flow rate varies for a given inlet X_{alcohol} . Values of $\text{CO}+\text{CO}_2$ sum are lightly lower from ethanol mixtures because more CH_4 and C_2 species are produced in the same time than from methanol steam-reforming.

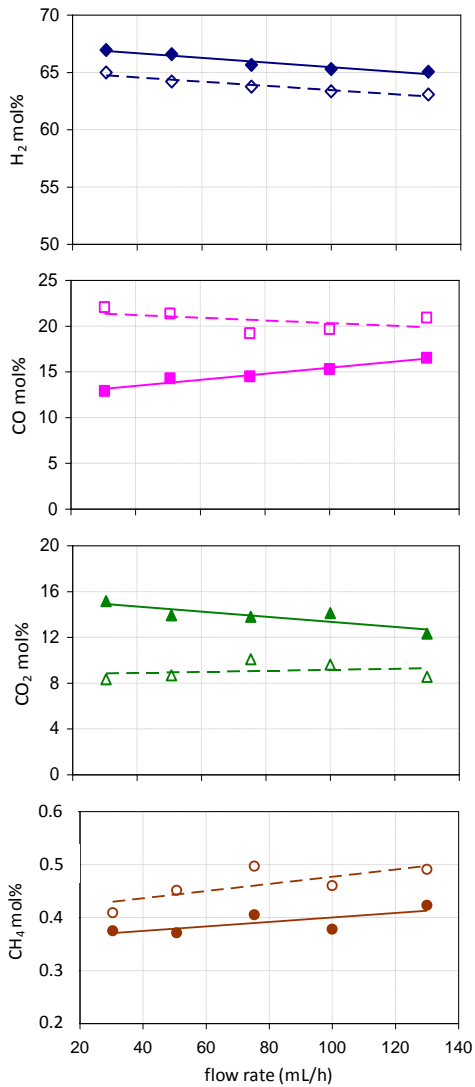


Fig. 5. H₂, CO, CO₂, CH₄ mol% of the dry gas vs. inlet liquid flow rate. Open symbols: X_{CH₃OH}=0.09; full symbols: X_{CH₃OH}=0.21.

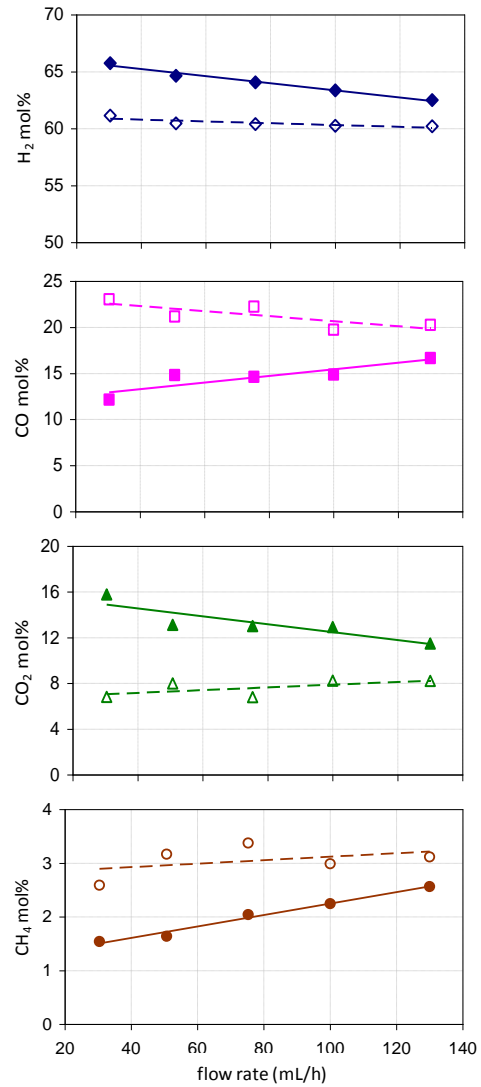


Fig. 6. H₂, CO, CO₂, CH₄ mol% of the dry gas vs. inlet liquid flow rate. Open symbols: X_{C₂H₅OH} = 0.09; full symbols: X_{C₂H₅OH} = 0.16.

To complete the experiments on alcohols treatments to produce syngas, the phenol steam-reforming reaction has been studied. In figure 7, the dry gas composition as a

function of the flow rate is presented figure 7. Due to its low solubility, the maximum studied X_{phenol} is 1.8.10⁻², corresponding to its higher solubility in water.

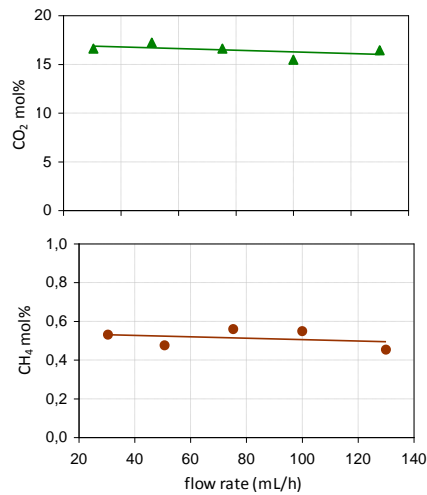
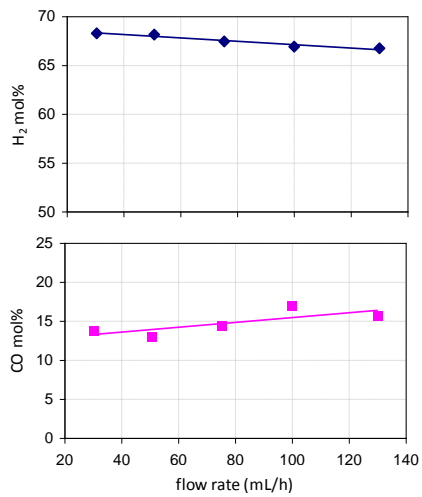


Fig. 7. H₂, CO, CO₂, CH₄ mol% of the dry gas vs. inlet liquid flow rate. Open symbols: X_{C₆H₅OH} = 0.018

In the phenol treatments, a rise of the total flow rate leads to slight variation of the exhaust dry gas composition: H_2 and CO_2 decrease and CO increases. Mol% values of H_2 , CO and CO_2 are about 66%, 14% and 16%, respectively. These values are in the same order of magnitude that the results obtained from methanol and ethanol experiments. In the wet exhaust gas, H_2O is the main outlet species due to the high dilution of phenol in the inlet water. Thus, % H_2 is close to 8 mol% in the wet gas.

B. H_2/CO ratio

H_2/CO ratio is taken into account to evaluate the efficiency of the syngas production. Next figures (fig 8) display H_2/CO ratios in various inlet parameters and alcohols nature. H_2/CO ratio highly depends on inlet parameters. From ethanol or methanol mixtures, similar trends are observed: For $X_{alcohol}=0.09$, a rise of the inlet flow rate leads to a decrease of H_2/CO ratio from about 5 to 4 when the flow rate increases from 25 to 130 mL/h. For higher $X_{alcohol}$, H_2/CO slightly increases up to about 3. For phenol-water treatments, the inlet alcohol concentration is low and obtained H_2/CO is between 5 and 4 depending on the flow rate.

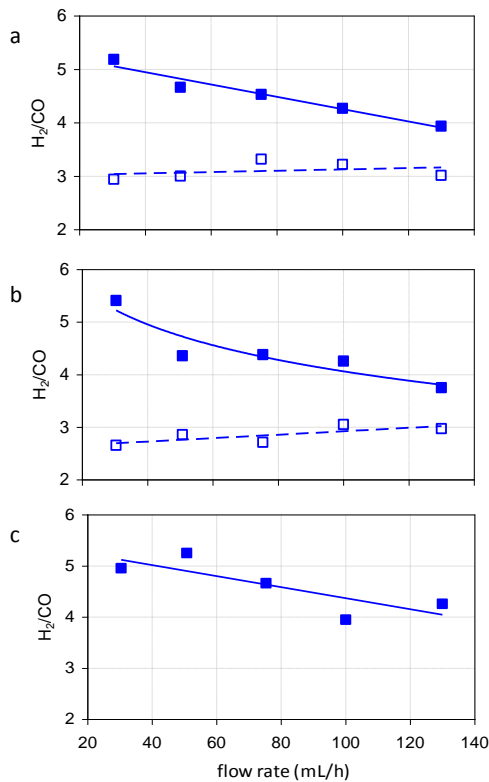


Fig. 8. H_2/CO ratios vs. flow rate. a) CH_3OH+H_2O ; b) $C_2H_5OH+H_2O$; Open symbols: $X_{alcohol}=0.09$; full symbols: $X_{alcohol}=0.16$ for ethanol and 0.21 for methanol. c) $C_6H_5OH+H_2$; $X_{alcohol}=0.018$.

We can observe that when $X_{alcohol}$ in the inlet mixture decrease, *i.e.* alcohol is more diluted, produced H_2 is kept at about same levels and CO is less produced. H_2 can be produced from alcohol and H_2O decomposition whereas CO is only produced from alcohol decomposition in the ethanol steam-reforming reaction:
 $C_2H_5OH + H_2O \rightarrow 2 CO + 4 H_2$

Moreover, when alcohol is more diluted in the inlet liquid mixture, the produced CO is more consumed by water in the water gas shift reaction to produce CO_2 :
 $CO + H_2O \rightarrow CO_2 + H_2$

C. Energy costs

From the outlet dry gas composition and the measured power, one can estimate the energy cost to produce 1kg H_2 in the dry gas. For this, it is necessary to know the flow rate of the produced dry gas. Figure 9 displays exhaust dry gas flow rate as a function of the alcohol mole fraction. For each alcohol, more $X_{alcohol}$ increases, in the inlet mixture, more the produced dry gas flow rate increases. This is due to that the exhaust gas is less condensate in the cold trap because less water is injected in the inlet mixture.

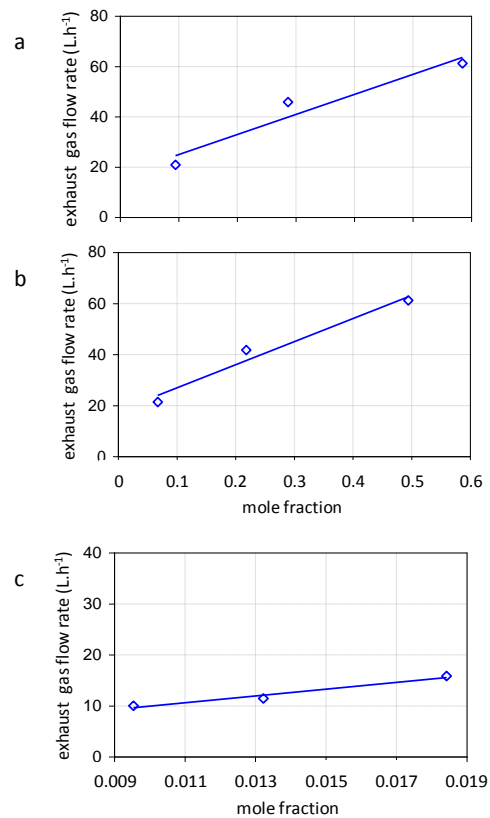


Fig. 9. Exhaust dry gas flow rate vs. alcohol mole fraction. a) CH_3OH+H_2O ; b) $C_2H_5OH+H_2O$; c) $C_6H_5OH+H_2$. Inlet flow rate=75.3 mL/h.

One can observe that for ethanol and methanol treatments, high dry gas flow rates can be obtained (from 20 to 60 $L.h^{-1}$) for the highest $X_{alcohol}$ in the inlet mixture. One other hand, from phenol mixtures, low dry gas flow rates are produced; this is explained because phenol is highly diluted in water in the inlet mixtures therefore almost the outlet gas is water vapor which is condensate in the cold trap.

From these experimental results, the energetic cost to produce one kg of H_2 , EC_{H_2} , can be calculated. EC_{H_2} evaluates the efficiency of the processes and is expressed as follow: $EC_{H_2} = Et / m_{H_2}$

where E_t is the electrical energy consumed per hour to produce a given mass of H_2 (m_{H_2}).

n dry exhaust gas, % H_2 has a constant level with the flow rate. When the flow rate increases with a same amount of H_2 in the gas, in % mol, implies a decrease of the energy cost to produce 1kg of H_2 , EC_{H_2} .

Figures 10 display EC_{H_2} . The energy cost is calculated for an inlet flow rate of 75.3 mL/h and as functions of $X_{alcohol}$. EC_{H_2} decreases when $X_{alcohol}$ increases; this is due to a produced gas where water vapor in mol% is weak.

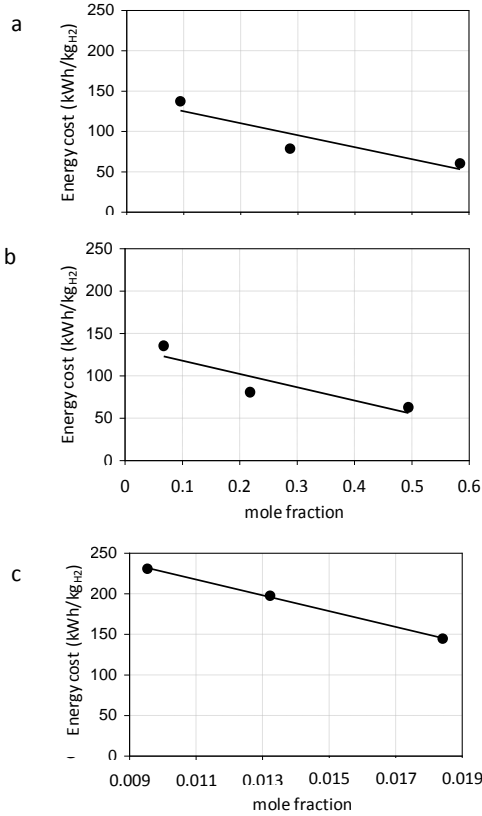


Fig. 10. Energy cost to produce 1kg of H_2 vs. alcohol mole fraction. a) CH_3OH+H_2O ; b) $C_2H_5OH+H_2O$; c) $C_6H_5OH+H_2O$. Inlet flow rate=75.3 mL/h.

One can observe that EC_{H_2} values are high in comparison to the electrolysis process (56 kWh/kg $_{H_2}$). Nevertheless, in electrolysis, only H_2 is produced whereas in our process, H_2 and CO are produced. These species can be used in turbine gas.

From our results, losses energy in our reactor have been estimated. To evaluate the losses, vaporization energy (to vaporize inlet liquid mixtures) and reaction energy are take into account. Energy losses, E_l , are calculated from the next expression:

$$E_l = E_t - E_r - E_{vap}$$

Where, E_t is the total energy injected in the plasma, calculated from injected power .

$$P = \frac{1}{T} \int_0^T u(t).i(t) dt$$

E_r is the steam-reforming reaction energy and E_{vap} is the consumed energy to vaporise the inlet liquid mixture.

In table 1, we present the various energy for ethanol steam reforming.

Table 1. Energies implied in the process.

X C_2H_5OH	Time (h)	E_t (Wh)	Evap (Wh)	E_r (Wh)	E_l (Wh)
0.07	0.012	1.77	0.94	0.121	0.709
0.22	0.006	1.01	0.48	0.115	0.415
0.49	0.004	0.76	0.32	0.112	0.328

One can observe that a rise of the inlet alcohol mole fraction leads a decrease of the energy losses, because E_t highly decrease in these mixtures. This decrease is due to a decrease of the conductance because less water vapor is in the plasma [7]. Same trends are observed for other alcohols treatments.

About half of the total energy injected in the reactor is lost. It is possible to reduce the energy costs by varynig of the inlet mixture. From these results, it will be interesting to optimize our statarc reactor which is not insulated. Thus, the efficiency of the process can be improved by decreasing of the losses energy.

D. Effects of the alcohols nature

From the experimental results presented in this paper, we can observe that the dry gas composition is about the same whatever the inlet alcohol mole fraction. It is interesting to study if the inlet atomic elementary composition plays a role. Thus, we studied the effects of the alcohols nature on dry gas composition by considering the inlet atomic composition of the mixtures.

We report, figures 11, H_2 , CO and CO_2 mol% as functions of the inlet H/C and H/O ratios. Ratios are calculated from the inlet mixtures composition by considering that all the injected liquid is vaporized through upper electrode. Thus, liquid moles and vapor moles of ethanol and water are the same. An increase of the inlet alcohol concentration leads to a decrease of H/C and a rise of H/O values.

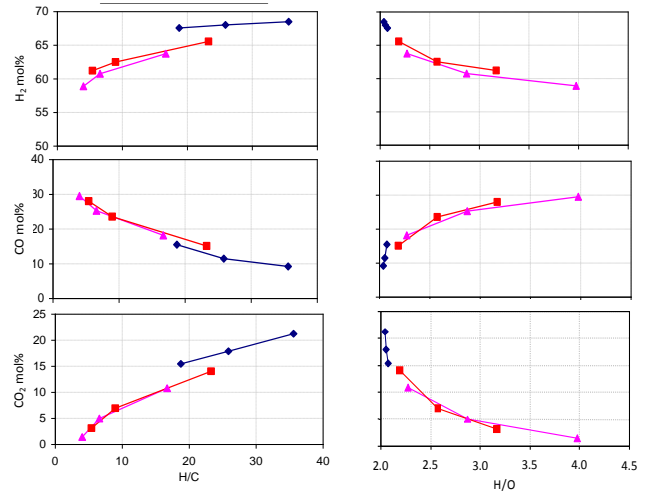
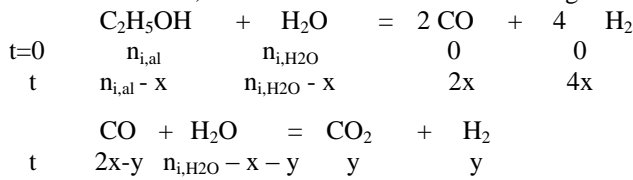


Fig. 11. H_2 , CO, CO_2 mol% vs. inlet H/C and H/O ratios. \blacktriangle methanol+ H_2O ; \blacksquare ethanol+ H_2O ; \blacklozenge phenol+ H_2O .

A rise of H/C and H/O have antagonists effects on produced species concentrations. H_2 and CO_2 concentrations increase when H/C increases or H/O

decreases. CO concentrations decrease for H/C increasing or H/O decreasing. A H₂+CO gas enrichment of the exhaust gas is promoted when the alcohol concentration decreases in the inlet mixture. Alcohol nature, at given H/C and H/O values, have not significant effects on the species concentrations.

In dry gas, the gas composition corresponds to only the produced species: CO, H₂ and CO₂. Remaining reactants, alcohol and water, are not take into account. Thus, if the conversion rates are not complete, we can only take into account the moles of the produced species in the dry phase gas. In first approximation we can estimate mol% of the produced species and main implied mechanisms by considering, only, the alcohol steam-reforming reaction and the water gas shift reaction. For example, for the ethanol treatment, the two reactions are the following:



y values are calculated from experimental %CO/%CO₂ ratio, R. R is linked, in the two reactions model to y; R=(2-y) / (y) in the ethanol treatment

Calculated H₂, CO and CO₂, in mol%, are not dependent on x values. Thus, in first approximation, x value in our calculations is equals to 1.

Moreover, y corresponds to the progress variable of the water gas shift reaction. A rise of y corresponds to a rise of the CO consumption produced from the alcohol steam-reforming reaction.

In the tables 2 and 3, we report for two inlet liquid flow rates, mol% of the produced species in the dry gas from the two previous reactions.

Table 2. y, mol% of H₂, CO and CO₂; X_{ethanol}=0.09

Inlet flow rate (mL/h)	y	H ₂ (mol%)	CO (mol%)	CO ₂ (mol%)
30	1.12	71.9	12.2	15.84
130	0.81	70.6	17.3	11.98

Table 3. y, mol% of H₂, CO and CO₂; X_{ethanol}=0.16.

Inlet flow rate (mL/h)	y	H ₂ (mol%)	CO (mol%)	CO ₂ (mol%)
30	0.45	69	23.9	7.1
130	0.57	69.6	21.6	8.7

The model gives us more produced H₂ than in experimental conditions. Overall, trends of the dry gas composition are well described by these two reactions.

From these data, we can observe that the water gas shift reaction depends on the inlet alcohol mole fraction, a rise of X_{ethanol} leads to a decrease of y, corresponding to a decrease of the water mole fraction in the inlet mixture. In these conditions, CO is more produced in comparison to CO₂. Progress variables of the water gas shift reaction highly depends on the inlet flow rate for the lowest X_{alcohol}. A rise of the flow rate implies a decrease of the residence time in the plasma then produced CO will be less consumed to lead to a CO₂ production.

In mixtures where alcohol is more diluted as phenol+water mixtures a similar model has been established. The results are given in table 4.

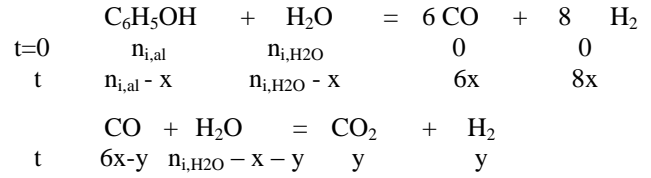


Table 4. y, mol% of H₂, CO and CO₂; X_{phenol}=0.018.

Inlet flow rate (mL/h)	y	H ₂ (mol%)	CO (mol%)	CO ₂ (mol%)
30	3.28	64.8	15.7	19
130	3.07	65.3	17.1	18

From the simplified model, calculated composition is close to experimental ones. As presented in tables 2 and 3, we can observe that for low X_{alcohol} in the inlet mixtures, the water gas shift reaction is promoted; from phenol mixtures, high y values are obtained.

III. CONCLUSION

Alcohol steam-reforming from a non-thermal arc is an interesting pathway to produce H₂ and syngas. The CO and CO₂ concentrations are in accordance with usual thermo-chemical techniques. The nature of the inlet reactants and its concentration are studied on produced species in dry and in wet exhaust gas. Energy cost to produce H₂ highly depends on alcohol concentration in the inlet mixture. The efficiency of the experimental reactor can be improved by the losses energy reduction. Nature of the inlet alcohol does not play a role on the mol% composition of the dry gas are presented and the effects of the inlet atomic composition. The experimental results can be modeled by two overall reactions: alcohol steam-reforming and water gas shift reaction. The progress variable of the water gas shift reaction is linked to the residence time and the inlet alcohol mole fraction. Nevertheless, the stationary non-thermal arc is particularly interesting for the direct treatment of hydrogenated liquids and hydrocarbons by plasma.

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