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To cite this version:
Khadija Arabi, Olivier Aubry, Ahmed Khacef, Jean Marie Cormier. Alcohols treatment using a Statarc reactor to produce syngas. International Symposium on Non-Thermal/Thermal Plasma Pollution Control Technology & Sustainable Energy, ISNTPT-8, Jun 2012, Camaret sur mer, France. pp., 2012. <hal-00823057>

HAL Id: hal-00823057
https://hal.archives-ouvertes.fr/hal-00823057
Submitted on 16 May 2013

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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 liquid inlet 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.

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 peaks 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 C6H6 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 CH₄, CO, CO₂, remaining CH₃OH and H₂O. For all alcohols studied, produced species are the same.

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 H₂ and CO concentrations can be obtained, up to 45% and 20% in mol, respectively. In the same time, remaining alcohol concentration increases too.

To increase the concentration of interesting species as H₂ 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. H₂, CO and CO₂ 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 H₂, CO and CO₂ 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 H₂, CO and CO₂ 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 H₂ and CO₂. 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 CO₂ concentrations do not seem to be affected by a rise of the flow rate.

Minor species are also measured which are CH₄ and C₂ species. These species concentrations are not reported in this paper [7]. We have observed that C₂ species are more produced from ethanol mixtures but their concentration remain low (<1.5% in mol) and C₅H₁₀ and C₆H₁₂ maximum is observed for the highest flow rate and alcohol concentration. From methanol mixtures, concentrations of C₂ are lower than 4.10⁻² in mol%.

From these results we can observe that CO and CO₂ have opposite trends. Thus, constant CO+CO₂ sums, in mol%, are measured in dry gas when the flow rate varies for a given inlet X_alcohol. Values of CO+CO₂ sum are lightly lower from ethanol mixtures because more CH₄ and C₂ species are produced in the same time than from methanol steam-reforming.
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. Due to its low solubility, the maximum studied X_{phenol} is $1.8 \times 10^{-2}$, corresponding to its higher solubility in water.

Fig. 5. H₂, CO, CO₂, CH₄ mol% of the dry gas vs. inlet liquid flow rate. Open symbols: $X_{phenol}=0.09$; full symbols: $X_{phenol}=0.12$.

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

Fig. 7. H₂, CO, CO₂, CH₄ mol% of the dry gas vs. inlet liquid flow rate. Open symbols: $X_{phenol} = 0.018$. 
In the phenol treatments, a rise of the total flow rate leads to slight variation of the exhaust dry gas composition: H₂ and CO₂ decrease and CO increases. Mol% values of H₂, CO and CO₂ 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, H₂O is the main outlet species due to the high dilution of phenol in the inlet water. Thus, %H₂ is close to 8 mol% in the wet gas.

B. H₂/CO ratio

H₂/CO ratio is taking into account to evaluate the efficiency of the syngas production. Next figures (fig 8) display H₂/CO ratios in various inlet parameters and alcohols nature. H₂/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 H₂/CO ratio from about 5 to 4 when the flow rate increases from 25 to 130 mL/h. For higher X_alcohol, H₂/CO slightly increases up to about 3. For phenol-water treatments, the alcohol concentration is low and obtained H₂/CO is between 5 and 4 depending on the flow rate.

![Fig. 8. H₂/CO ratios vs. flow rate. a) CH₃OH+H₂O; b) C₂H₅OH+H₂O; c) C₆H₅OH+H₂; X_alcohol=0.09 for ethanol and 0.21 for methanol. c) C₆H₅OH+H₂; X_alcohol=0.018.](image)

We can observe that when X_alcohol in the inlet mixture decrease, i.e. alcohol is more diluted, produced H₂ is kept at about same levels and CO is less produced. H₂ can be produced from alcohol and H₂O decomposition whereas CO is only produced from alcohol decomposition in the ethanol steam-reforming reaction: 

\[ C₂H₅OH + H₂O \rightarrow 2 \text{CO} + 4 \text{H}_2 \]

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 CO₂:

\[ CO + H₂O \rightarrow CO₂ + H₂ \]

C. Energy costs

From the outlet dry gas composition and the measured power, one can estimate the energy cost to produce 1kg H₂ 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) CH₃OH+H₂O; b) C₂H₅OH+H₂O; c) C₆H₅OH+H₂; Inlet flow rate=75.3 mL/h.](image)

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 H₂, EC_H₂, can be calculated. EC_H₂ evaluates the efficiency of the processes and is expressed as follow: 

\[ EC_{H₂} = \frac{E_t}{m_{H₂}} \]
where $E_t$ is the electrical energy consumed per hour to produce a given mass of H$_2$ ($m_{H2}$).

In 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$_{H2}$.

Figures 10 display EC$_{H2}$. The energy cost is calculated for an inlet flow rate of 75.3 mL/h and as functions of $X_{alcohol}$. EC$_{H2}$ decreases when $X_{alcohol}$ increases; this is due to a produced gas where water vapor in mol% is weak.

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 varying the inlet mixture. From these results, it will be interesting to optimize our statoric 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.

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

<table>
<thead>
<tr>
<th>$X_{C2H5OH}$</th>
<th>Time (h)</th>
<th>$E_t$ (Wh)</th>
<th>Evap (Wh)</th>
<th>Er (Wh)</th>
<th>$E_v$ (Wh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.07</td>
<td>0.012</td>
<td>1.77</td>
<td>0.94</td>
<td>0.121</td>
<td>0.709</td>
</tr>
<tr>
<td>0.22</td>
<td>0.006</td>
<td>1.01</td>
<td>0.48</td>
<td>0.115</td>
<td>0.415</td>
</tr>
<tr>
<td>0.49</td>
<td>0.004</td>
<td>0.76</td>
<td>0.32</td>
<td>0.112</td>
<td>0.328</td>
</tr>
</tbody>
</table>

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.

Fig. 10. Energy cost to produce 1kg of H$_2$ vs. alcohol mole fraction.

- a) $C2H5OH+H2O$; b) $C2H5OH+H2$; c) $CH4OH+H2$.

Inlet flow rate=75.3 mL/h.

Fig. 11. H$_2$, CO, CO$_2$ mol% vs. inlet H/C and H/O ratios.

- $\triangle$ methanol+$H2$; $\bullet$ ethanol+$H2$; $\odot$ phenol+$H2$.
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:

\[ \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} = 2 \text{CO} + 4 \text{H}_2 \]

Table 2 gives y, mol% of H₂, CO and CO₂ in the dry gas from the two previous reactions.

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

<table>
<thead>
<tr>
<th>Inlet flow rate (mL/h)</th>
<th>y</th>
<th>H₂ (mol%)</th>
<th>CO (mol%)</th>
<th>CO₂ (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1.12</td>
<td>71.9</td>
<td>12.2</td>
<td>15.84</td>
</tr>
<tr>
<td>130</td>
<td>0.81</td>
<td>70.6</td>
<td>17.3</td>
<td>11.98</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Inlet flow rate (mL/h)</th>
<th>y</th>
<th>H₂ (mol%)</th>
<th>CO (mol%)</th>
<th>CO₂ (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.45</td>
<td>69</td>
<td>23.9</td>
<td>7.1</td>
</tr>
<tr>
<td>130</td>
<td>0.57</td>
<td>69.6</td>
<td>21.6</td>
<td>8.7</td>
</tr>
</tbody>
</table>

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 depend on the inlet flow rate for the lowest X_{ethanol}. 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.

\[ \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} = 6 \text{CO} + 8 \text{H}_2 \]

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

<table>
<thead>
<tr>
<th>Inlet flow rate (mL/h)</th>
<th>y</th>
<th>H₂ (mol%)</th>
<th>CO (mol%)</th>
<th>CO₂ (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3.28</td>
<td>64.8</td>
<td>15.7</td>
<td>19</td>
</tr>
<tr>
<td>130</td>
<td>3.07</td>
<td>65.3</td>
<td>17.1</td>
<td>18</td>
</tr>
</tbody>
</table>

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_{ethanol} 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.

REFERENCES