ELECTRICALLY ASSISTED WATER SHIFT REACTION

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GlidArc-type plasma assisted water shift process of CO to H_2 can be performed at atmospheric pressure without any solid catalyst and at low (≤ 415°C) temperatures in a bench-scale 1.5 kW, 1.35 l reactor with 6 knife-shaped steel electrodes for the space velocity of the order of 1000 h^{-1}. Some 18 to 45 % of CO-to-H_2 shift rates are obtained for initial H_2O/CO = 0.93 to 2.7 mol/mol inputs.

1. Introduction

Methane reforming into hydrogen and carbon monoxide mixture (synthesis gas) is a very important way of natural gas transformation to more valuable products. When a catalytic steam reforming at 700-800°C under 15-40 bars is performed the following main process takes place :

$$CH_4 + H_2O = CO + 3\ H_2 \qquad (1)$$

giving a molar H_2/CO ratio in the synthesis gas close to 3. The reaction (1) may be more or less followed by so-called catalytic "water shift process" :

$$CO + H_2O = CO_2 + H_2. \qquad (2)$$

Reaction (2) is also industrially performed in separate reactors when rather hydrogen is sought as a main product. Use of catalysts in both processes is always linked to such difficulties like aging, poisoning or plugging due to impurities in natural gas, carbon deposit, etc.

In previous papers [1-4] we have already reported on electrically assisted CO_2 or steam reforming of methane to the synthesis gas which has been studied in our so-called Gliding Arc (GlidArc) reactor, a relatively cold, non-equilibrium and quite high-volume discharge working at atmospheric or higher pressures without any solid catalysts.

Interesting results have been obtained when an excess of steam is used in the methane reforming experiments where we obtain up to 66 vol. % of H_2, 13 % of CO, 7.3 % of CO_2 in products (at less than 1 % of C_2H_2 and non-transformed methane as balance). In all experiments the H_2/CO molar ratio ranges between 4.0 and 6.4 which is much higher as the theoretical ratio of 3 if only reaction (1) is considered. An excess of hydrogen (and a deficit of carbon monoxide at the same time). It is therefore interesting to check if really the side reaction (2) takes place in the GlidArc reactor, especially for higher steam/methane ratios in the entry gas mixture. In new trials the reactor has been therefore fed by a pure CO/steam mixture.

2. Experiment

Experimental set-up is presented on the Fig. 1 The GlidArc reactor consists of a cylindrical 1.35 l vessel made of stainless steel (80 mm dia.). Six knife-shaped steel electrodes are symmetrically put on the top of the vessel and around the gas-flow axis forming a large nozzle. The

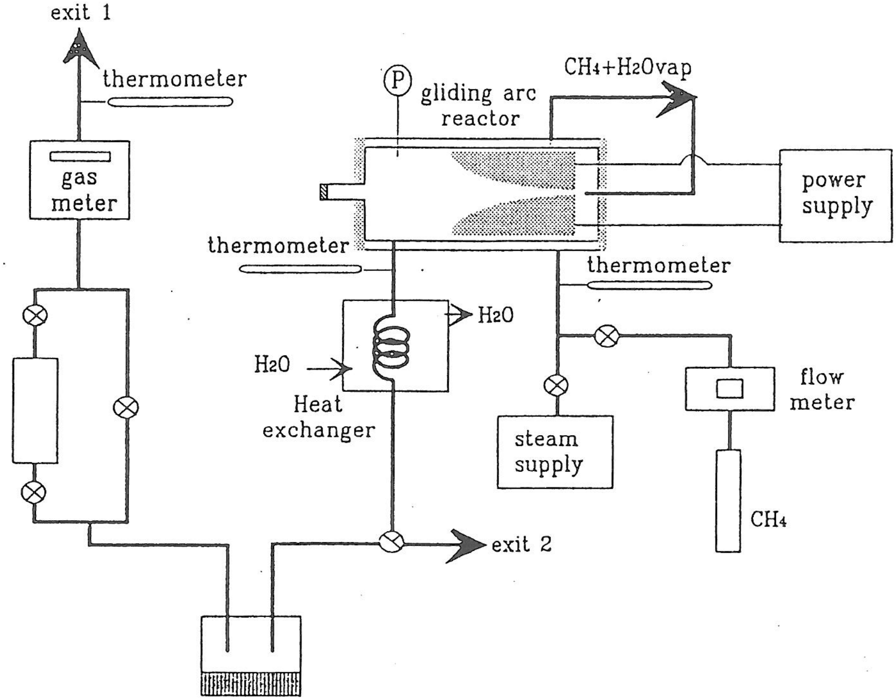

Fig. 1. Experimental set-up.

electrodes are supplied via a current-limited 10 kV transformers. Carbon monoxide and an excess of wet water vapor (at 105°C) are mixed together, slightly overheated in the vessel jacked and then injected between the reactor electrodes at atmospheric pressure. The mass input of CO is 4.8 to 14 g/min, the water mass flow and the electric power really dissipated in the reactor are almost constant around 8.5-9.6 g/min and 1.4-1.5 kW, respectively. The body of the reactor is slightly isolated thermally and the temperature of the exiting gas vary from 345 to 410°C.

The products are cooled to the room temperature in a water cooled heat exchanger, an excess of water is separated and then incondensable gas analyzed by gas chromatography (CH_4, CO_2, CO, H_2, C_2H_2 and C_2H_4 are considered).

3. Results

Some results of experiment are presented on Fig. 2. Up to 32 vol. % of hydrogen and almost equal amount of carbon dioxide (within a precision of our gas analysis) have been found in the gas product which means that the reaction (2) has indeed taken place at up to 45 % transformation rate of initial CO input.

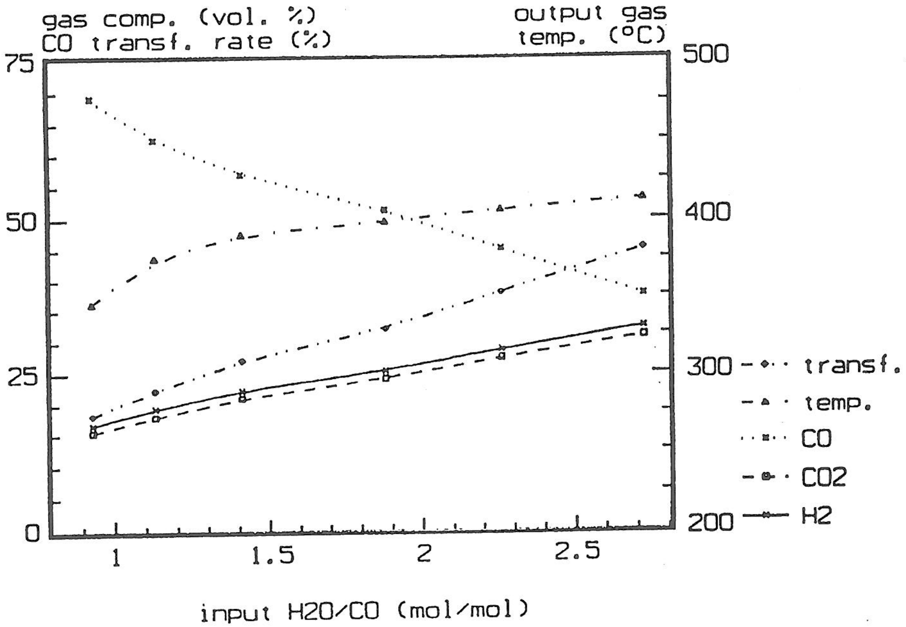

Fig. 2. Some results of the shift process performed in the laboratory scale GlidArc reactor at 1 atm.

Tab. 1 (where other data are the same as shown on the Fig. 2) presents the process energetics as a function of input H_2O/CO molar ratio. The SEI stands for the Specific Energy Input calculated from the total input molar flow of CO/H_2O mixture and dissipated power, and the SER means the Specific Energy Requirement to produce one mole of hydrogen.

Tab. 1. Energetics of the GlidArc plasma assisted shift process at a bench scale.

Run	1	2	3	4	5	6
Input H_2O/CO (mol/mol)	0.93	1.1	1.4	1.9	2.3	2.7
Dissipated power (kW)	1.4	1.4	1.4	1.4	1.5	1.5
SEI (kJ/mol $CO+H_2O$)	83	92	96	100	110	140
SER (kJ/mol H_2)	830	810	810	870	950	1100

4. Discussion

A comparison of our first feasibility study results to complete thermodynamic equilibrium calculations is based on a Limoges' computer program [5] for the same initial CO/H_2O mixtures heated for different temperatures. An example of such an equilibrium is given on Fig. 3 for the Run 3 conditions.

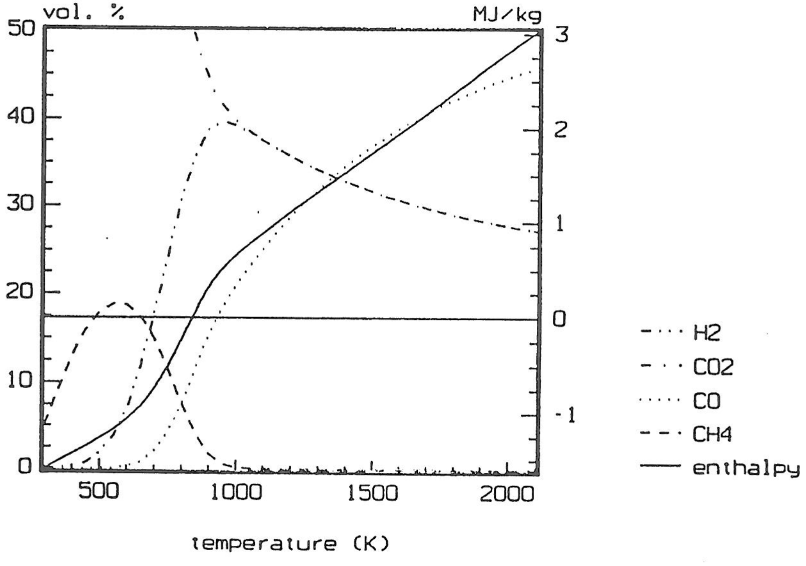

Fig. 3. Equilibrium concentrations and enthalpy of dry products of the shift reaction for an initial H_2O/CO = 1.41 mol/mol mixture (Run 3).

One sees that H_2 concentration in product reaches its maximum of 40 vol. % at 930 K but starting from 840 K the process becomes endothermal. At 930 K the theoretical energy cost of 1 mole of H_2 would be only 28 kJ. An optimal temperature for the process is comprised in a quite narrow range. Our H_2 concentration for the Run 3 is 22.2 % which corresponds to the equilibrium temperature of 735 K (when the output gas temperature was 663 K but our reactor is not an adiabatic one). Also, a contact time of the gas and plasma reactor was quite low (1.8 s) to let the gas to fully react. Similar data corresponding to all the runs are presented in Tab. 2.

Tab. 2. Comparison of experimental amounts of produced hydrogen to theoretical ones.

Run	1	2	3	4	5	6
$\left(\frac{H_2 \text{ produced (mol)}}{\text{initial CO (mol)}}\right)_{ex}$	0.195	0.240	0.285	0.336	0.396	0.471
equil. temp. (K)	750	750	735	725	725	725
reactor temp. (K)	618	648	663	671	678	685
contact time (s)	1.6	1.7	1.8	1.8	1.9	2.3
$\left(\frac{H_2 \text{ produced (mol)}}{\text{initial CO (mol)}}\right)_{th}$	0.544	0.608	0.675	0.758	0.805	0.845
equil. temp. (K)	960	940	930	910	890	880

5. Conclusions

Our first study on GlidArc-type plasma assisted water shift process clearly shows that the transformation of carbon monoxide to hydrogen is feasible at atmospheric pressure, without any solid catalyst and at quite low averaged temperatures in the reaction chamber.

6. References

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