

Synthetic fuels production by graphite-assisted electrolysis

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Introduction

Hydrogen produced by water electrolysis is considered as the best energy carrier to adjust the balance between the generation of power source by renewable primary energy and energy demand for end-use. Further advantages are foreseen with the use of carbon-assisted electrolysis. This is due to the electrochemical participation of carbon in the reaction, the electrolysis process would potentially require about 1/3 the electrical energy with the balance of 2/3 coming from the chemical energy of carbon in comparison with conventional water electrolysis where all the energy input is electric [1, 2]. Carbon is oxidized to CO₂ on the anode and hydrogen is produced at the cathode. Generally, carbon sources for anodic reaction are graphite, activated carbon and coal. In this work, low temperature electrochemical gasification of graphite in alkaline and acid solutions was explored, taking into account experimental conditions where the faradaic overall current has a significant contribution from carbon oxidation reactions. Results indicate adequate molar gases fraction for the production of syngas and the production of small chain hydrocarbons, obtained at laboratory prototype level.

Experimental

Laboratory studies were conducted in an undivided planar cell with graphite electrodes with 25 cm² geometrical area. Cyclic voltammetry and polarization curves were instrumental to establish optimum operational conditions for adequate molar gases fraction for the production of syngas. Conditions were extrapolated to work with a 45W prototype using a 5 cell graphite stack with 150 cm² of total geometric anode area which was purpose-built and tested.

The prototype allows for electrolyte recirculation, temperature control up to 80 °C and pressure control up to 1bar. Facilities for gas conditioning before injection into the chromatograph were also incorporated. See figure 1. Gas production was implemented under intensiostatic control at 1-3 A. Gaseous product analysis was carried out using a gas chromatograph Micro GC 300 from Agilent.



Figure 1. Laboratory prototype used in this work, including the electrolyzer unit, with a stack of 5 cells, and facilities for temperature, pressure, solution recirculation and gas conditioning.

Results

Using the best conditions for testing obtained in the laboratory cell, regarding electrode spacing, alkali or acid concentration, potential for maximum gas production, testing in a 45 W implemented prototype was carried out (Figure 1).

The effect of temperature on the current density at constant potential was monitored and registered as an Arrhenius plot, which exhibited two regions. This suggests a change in mechanisms at around 50 °C. Activation energies of 13.8 and 8.5 kJmol⁻¹ were estimated. The same tendency was found when the concentration of CO was analyzed as a function of temperature.

For alkaline conditions and following gas chromatography results at 60°C, gas composition amounts to 64 % H₂, 3.8 % CO₂, 2.4 % CO e 13.2 % O₂, with a gas production rate of 6-8 Lh⁻¹ for a potential of 22.2 V and a current of 2 A.

Given the possibility of graphite corrosion acceleration when using acid solutions, the prototype was tested in 1 M sulphuric acid. Polarization curves show a large difference in activation and ohmic resistance regions compared to alkaline conditions. The potential required for the current density of interest was only 60 % of that required for alkaline electrolysis. This was confirmed when working with the prototype. Gas composition was also favorable since the concentration of oxygen decreases to 3 % associated to an increase in the CO₂ concentration to 17.6 %. CO concentration was recorded to be 1.8 % and H₂ 72 %. Results obtained also indicated the presence of short chain hydrocarbons in the gas mixture, such as CH₄, C₂H₆ and C₂H₄, even at temperatures of 50 °C. See figure 2.

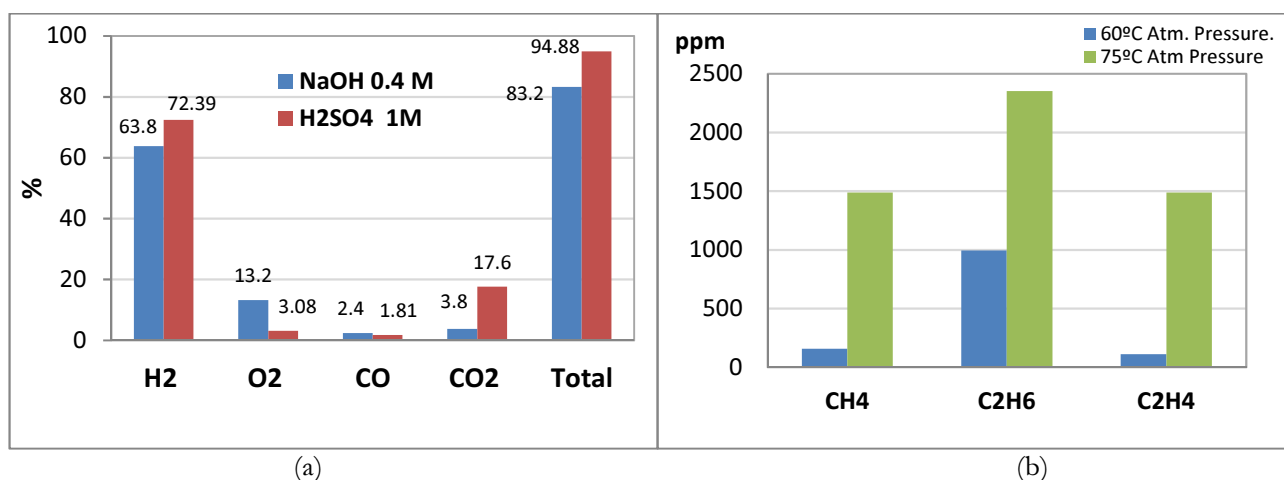


Figure 2. Main gas production (%) for alkaline and acid electrolysis at 60 °C and ambient pressure for graphite assisted electrolysis(a). Production of hydrocarbons (ppm) for acid electrolysis at 60 and 75 °C at atmospheric pressure.

Strategies for obtaining reduction in the overpotential and lower concentrations of oxygen in a less aggressive environment were sought. The effect of the presence of mediators such as iron salts will be discussed as well as the use of ionic liquid based electrolytes.

Final Remarks

Initial thorough laboratory study in a single cell reactor was carried out in order to establish optimum operational conditions for graphite assisted electrolysis yielding adequate molar gases fractions for the production of syngas, followed by implementation and testing of a 45 W prototype which uses a 5 cell stack with 150 cm² of total geometric anode area.

The electrochemical gasification of graphite in alkaline and acid solutions was explored, seeking the production of synthetic liquid fuels via syngas, in an electrolysis process characterized by the use of low temperatures and pressures.. Addition of mediators and the use of ionic liquids as electrolytes are explored. Results and the technological implications of the obtained advances are discussed.

Acknowledgements

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References

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