Production of synthesis gas obtained via alkaline water electrolysis and added biomass

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Abstract

This paper presents the results of the research currently being carried out at ISEL with the objective of developing new electrochemistry-based processes to obtain renewable synthetic fuels from alkaline water electrolysis using a carbon source. In the developed process, the gas mixture obtained from alkaline water electrolysis and a carbon source is not separated into their components but rather is introduced into a catalyzed reactor, in order to achieve conversion to synthetic 2nd generation biofuels, such as biomethane, biomethanol, bio-dimethyl ether, etc. Tests have been previously executed in a pilot electrolyzer and reactor of 1 kW, and are now being scaled up to a pilot electrolyzer and reactor of 5 kW, producing 250 l/h CH_4, as an intermediate step to a pilot of 100 kW.

Keywords: Water electrolysis; synthesis gas; biofuels

I. INTRODUCTION

It is well known that electricity cannot be stored in large quantities as such, but an alternative way of energy storage can be to convert electricity, particularly the one generated from renewable sources, like wind or solar, into chemical compounds. This procedure is a good solution to the currently existing problems of excess electricity in the grid. This paper describes a further new approach to new technology, previously reported by the authors [1] capable of producing syngas in a single step, without separation of the elementary gases, produced during the water alkaline electrolysis. It is called co-electrolysis of water, under the alkaline process, using a carbon source to directly produce the syngas mixture, at low temperatures and pressures, thus requiring significative fewer amounts of energy inputs [2-3]. This previous approach, uses graphite electrodes, as a source of carbon, that is further oxidized, during the electrolysis process, to carbon monoxide and carbon dioxide which are present in the generated gas mixture (syngas), and, efficiently converts electricity from renewable sources (mainly wind or solar, or when this electricity is in excess in the electrical grid, or in off-peak hours). Thus, this new technology is able to convert electricity into syngas, which is an intermediate for the generation of synthetic 2nd G biofuels, which was already demonstrated [4]. The main drawback is the (small) consumption of the graphite electrodes and its relatively high cost, which could be avoided if steel electrodes are used together with an additional carbon source, such as liquefied biomass, to be added to the electrolyzer. Concerning the use of liquefied biomass, some results from preliminary trials have been recently published elsewhere [5] and point out that, the process needs enhancement, such as the use of solid catalysts. In this new process, the gas obtained from electrolysis is not separated into its components and, it's introduced into a reactor together with a specific content of a previous mixture of cork/eucalyptus splinter liquefied biomass, at normal pressure and different temperatures. The gas is released upon contact with the biomass, thus resulting in a syngas, which is a mixture consisting essentially of carbon monoxide, hydrogen, carbon dioxide, and some remains of unreacted oxygen. In this work, the behavior of operational parameters such as biomass content, temperature, and the use of different amounts of acidified zeolite HY catalyst was investigated. In the performed tests, it was found that, in addition to the syngas, methane was also produced, with significant content.

The purpose of using samples of different kinds of liquified biomass of cork and/or eucalyptus bark, with and without the correspondent sugars solubilized in an aqueous solvent, was to investigate if, there was a significant influence on the output syngas/methane produced, at the methanation reactor, as well, the influence of temperature and catalyst content in this process. The temperature range chosen for this study must be significantly lower than the typical temperatures used in the gasification process (700–800 °C). The advantage of this technology is located, precisely, in the utilization of lower/medium temperatures, when compared with the

IEECP'22, July 21-22, 2022, Oxford, United Kingdom

coal/biomass gasification and steam reforming processes, which produces, also, syngas. The utilization of lower temperatures will lead to significant input energy savings to the process and, as consequence, lower operating costs. On the other hand, the influence of using lower catalyst contents in the methanation process in this study is to see if the methane concentration will increase in these temperatures, with and without catalyst [6].

II. MAIN RESULTS

Regarding the production of syngas, Table 1 shows the results obtained with complementary experiences in the methane glass reactor, where this gaseous mixture is produced, with the methane generation, through the reaction between the electrolysis gas and, the liquified biomass. The results achieved and calculated were: the volumetric yields production of solid, liquid, and gas phases, respectively, the remaining biomass collected in the reactor (Yield$_{(liq.biom.)}$) after the elapsed time of 60 minutes, at different temperatures, the condensate (Yield$_{(cond.)}$) and, also, the gas mixture produced (Yield$_{(gas)}$).

Table 1. Experimental results obtained with complementary experiences in the syngas/methane reactor.

(ºC)	Vf$_{(liq.biom.)}$ (mL)	Yield$_{(liq.biom.)}$ (%)	Yield$_{(cond.)}$ (%)	Yield$_{(gas)}$ (%) $^{(*)}$
100	98	98.0	-	2.0
150	96	97.0	-	3.0
200	72	74.0	23.5	2.5

(*) – estimated considering the initial volume of 100 mL of liquified biomass minus the volumes of final liquified biomass and condensate produced.

Table 2 shows, at the end of 4 hours of experience, the correspondent final output values of the gas volumetric flow, as well, as the oxygen and methane volumetric contents in the produced gas mixture, for different reaction temperatures and different weight content (z. HY catalyst). To compare with another Y zeolite already prepared, ultra-stabilized with nickel (z. USY), it was also performed, two more experiments with this catalyst, which was supplied from another Portuguese university. The results achieved with USY zeolite do not show any significant improvement, mainly in the %CH$_4$ content, when compared with the acidified HY zeolite catalyst.

III. CONCLUSIONS

From this research work, it can be concluded that it is possible to produce syngas and methane, using this electrolysis system (Electrofuel), together with a fixed bed catalytic reactor to produce methanation (Sabatier process), with significantly fewer energy inputs when compared with the conventional thermochemical processes of syngas/methane production, like pyrolysis and gasification. Comparing the combined electrochemical/Sabatier process (10.38 kJ·mol^{-1}) with the pyrolysis one (14.29 kJ·mol^{-1}) and considering the same syngas/methane flow and the same gas composition, an increase of 38% in the input energy was observed. By another hand, in the comparison between the same combined process (10.38 kJ·mol^{-1}) with the gasification one (27.21 kJ·mol^{-1}), an increase of 162% in the input energy was observed, both values applied for each mole of syngas/methane mixture.

With the utilization of these combined electrochemical/Sabatier reactors, it's possible to reduce input energy to the system and, as consequence, reduce energetic (operating) costs.

Table 2. Experimental results in the methanation reactor, for different reaction temperatures and different weight content catalyst.

% (W$_{cat.}$/W$_{liq.biom.}$)	T (°C)	F (mL·min^{-1})	%O$_2$	%CH$_4$
A2, no catalyst	150	142.9	33.5	0.19
	200	150.0	32.0	0.45
	250	138.5	33.3	0.45
	300	138.5	32.0	2.08
A2, z. HY, 2%	150	145.2	33.8	0.25
	200	134.2	32.5	1.84
	250	145.2	32.2	4.16
	300	157.9	30.2	12.8
A2, z. HY, 4%	150	145.2	33.9	0.28
	200	145.2	32.5	3.98
	250	134.2	30.0	5.02
	300	138.5	22.2	33.9
A2, z. USY, 1%	200	125.0	33.1	0.17
A2, z. USY, 2%	200	132.4	33.1	0.26
A3, no catalyst	200	145.2	32.3	0.16
A4, z. HY, 4%	200	133.6	32.2	3.81

Regarding the methane production in this reactor, the operating conditions obtained so far, which enhanced and maximized its production was, a temperature of 300 °C and a weight heterogeneous catalyst content of 4% of zeolite HY. However, it should be noticed that there are compounds, in the produced gas, that were measurable by the portable sensors. It was possible to conclude also, that, z. HY catalyst was progressively deactivated, through the visualization of carbon particles deposition on the surface catalyst. Nevertheless, the catalyst can be reactivated, by calcination, to be used again in the Sabatier reaction, so it's possible to conclude that, the use of z. HY catalyst was clearly suitable in the Sabatier reaction (methanation process), at normal pressure and temperatures between 200–300 °C.

Besides, the use of acidified zeolite HY catalyst and higher temperatures increases methane production, which points out for further research steps comprising the increase of catalyst mass, and, to study the increase of pressure and temperature in a new laboratory prototype. It will also be of interest to investigate the use of other heterogeneous catalysts which may be more active such as other zeolites, acid clays, or bimetallic catalysts, as well, as study the production of other biofuels, like biomethanol, bio-DME, etc., regarding this electrolytic system.

IV. ACKNOWLEDGMENTS

This work was partially funded by FCT - Fundação para a Ciência e Tecnologia, Portugal, through project reference PCIF/GVB/0167/2018.

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