Liquified Biomass Utilization in Water Co-electrolysis for Synthesis Gas Production

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Abstract— Developed within the scope of a collaborative R&DT project comprising the company GSYF, Lda, a 1 kW pilot unit aimed at recovery of previously liquefied biomass from lignocellulosic forest residues, later used as a carbon source in a co-electrolysis process, intended for the production of synthesis gas (H_2, CO, CO_2), also known as syngas. The syngas will be transformed into other value-added products, namely synthetic biofuels such as methane, methanol or biodiesel. This paper presents results on the research currently being carried out at ISEL with the objective of further advancing development on the pilot unit by the execution of optimization tests with and without addition of two different biomass types.

***Keywords*:** Syngas, Biomass, Water Electrolysis, Electrochemical process, Renewable energy, Biodiesel, methane production.

I. INTRODUCTION

Over the last decades the continuous increase in the world's energy needs resulted in growing consumption of non-renewable fuel sources (oil, natural gas, among others) and, consequently, greater environmental impacts. For this same reason, there is an increasing commitment to the development of alternative sustainable energy sources (biomass, solar and wind energy, among others). [1]

Currently, there is a significant push to create alternative fuels that are both innovative and cost-effective, with a specific focus on utilizing renewable sources. These aim to replace conventional oil-derived fuels in various applications, such as powering vehicles and generating electricity. [2]

Water electrolysis is an electrochemical process in which water (H_2O) is decomposed into hydrogen (H_2) and oxygen (O_2) gases by passing an electric current through it. Its primary application is the production of hydrogen, the lightest and most abundant chemical element in the Universe. Furthermore, hydrogen is an important compound for the modern industry due to its versatility and ability to be used as a clean-burning fuel. Its importance is expected to continue to grow in the coming years as the demand for clean energy sources increases. [3]

As part of Project "Clean Forest" and in cooperation with the company GSYF, Lda, this research aims to promote the development of a pilot (patented) system to produce syngas without separation of the generated gases. This novel process, intended as a positive contribution for reducing the dependence on fossil fuels, combines alkaline water electrolysis with the addition of a carbon source in the form of graphite composing the disks inside the stack and, also, added liquified biomass obtained from forest residues. [1]

Syngas has several potential uses for the modern industry, as it can be converted into other synthetic fuels, both gaseous like methane or liquid such as gasoline and diesel, through processes such as the Fischer-Tropsch or the methanol-to-gasoline conversion. It can also be used as a feedstock for the production of a wide range of chemicals, including methanol, ammonia, and acetic acid. In addition, syngas can be burned to generate electricity in gas turbines or internal combustion engines and substitute more expensive or scarce feedstocks in refinery processes, such as the hydrogen production taking place in petroleum refining. [4]

As displayed in Figure 1, the prototype unit consists of an electrolyte reservoir, a set of pressure and temperature sensors, a pump, a radiator with fan (in order to control the temperature of the process), a heating resistance, a moisture adsorption column and an electrolyzer consisting of a stack of 11 spaced graphite discs.
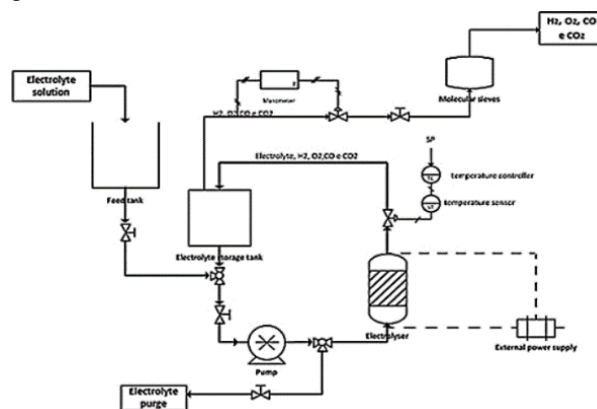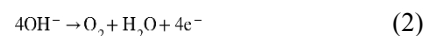

Fig. 1 Simplified flowsheet of the process [5]

The production of synthesis gas via electrochemical means is based on the following known reactions: [2]
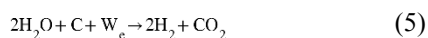
Cathode reactions:

$$2H_2O + 2e^- \rightarrow 2H_2 + 2OH^- \tag{1}$$

Anode reactions:

$$4OH^- \rightarrow O_2 + H_2O + 4e^- \tag{2}$$

$$2C + O_2 \rightarrow 2CO \tag{3}$$

$$2CO + O_2 \rightarrow 2CO_2 \tag{4}$$

Global reaction:

$$2H_2O + C + W_e \rightarrow 2H_2 + CO_2 \qquad (5)$$

Current experimental work focuses on carrying out optimization tests to determine the ideal conditions for the production of syngas to be used, in the future, as a feedstock for methane production. For this specific purpose, the syngas produced aims to have oxygen content as low as possible (to minimize the risk of catalyst deactivation during methanation) and a $CO_2:H_2$ ratio ideally close to the one associated with the conversion of CO_2 into methane (1:4).[2]

Two different biomass types were tested for two different concentrations (2.5 and 5 % (w/w)) in order to allow comparisons with each other and the respective performance with and without the use of any liquified biomass. In all tests the electrolyte used was a 1M solution of NaOH.

II. METHODOLOGY

The 1kW prototype plant has a stack with 12 cells (graphite bipolar electrodes), the distance between electrodes being 5 mm. The electrodes have a diameter of 117 mm (100 cm^2 area), and 5 mm thickness with 10 mm two holes to allow for circulation. The dimensions of each electrode can be found in Fig. 2.
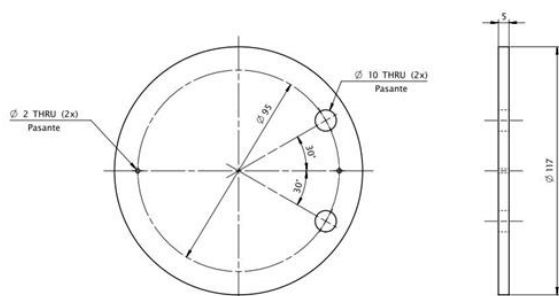

Fig. 2 Graphite disks dimensions/specifications

The electrolyte used is NaOH (1M). A pump is used to circulate the electrolyte from the reservoir to the stack. The electrolyte solution together with the produced gaseous phase leave the stack from the top and are guided through the tubes into the initial tank where the liquid phase is recirculated while the gaseous phase is separated and leaves the tank through a pressure valve. Since the produced gas phase leaving the tank still carries some steam, it needs to be passed through a cooling serpentine to condense the majority of the water that is then collected in the following drainable reservoir. The remaining gas exists from a second exit on the top of the reservoir and is passed through a cylindrical tank filled with molecular sieve (2.0-5.0 mm) to remove any remaining moisture. Following the removal of the majority his humidity, the gases enter a group of sensors to analyze and determine its pressure, temperature, remaining humidity as well as its composition. Control and adjustable operational parameters are: voltage/current, temperature and pressure, and the current of each.

With the goal of optimizing syngas production and its composition, three different groups of tests were executed, one without the addition of liquified biomass, one using a liquified sample of Acacia biomass and another using a sample of non-specified composition designated as Energreen. Each sample was diluted in the electrolyte solution at 2.5 and 5 % (W/W) and each one was tested within an interval of pressure (4 and 5 bar gauge) and temperature (100 and 110 ºC).

Each test was executed over a period of 3 hours with temperature, pressure, flow of gas produced, and current applied among other data, being monitored every of 15 minutes. To simplify the analysis and presentation the average of the 3 last measurements in stationary state was collected and presented as the shortened results for each test. Through these methods, it was possible to evaluate how the operational conditions affect the flow rate of gas produced and its composition (which constitute the most important set of results).

III. RESULTS

As a example, of the results obtained in each test, Fig.3 and Table I displays the variations in terms of compositions and the results collected throughout one of the tests respectively (in this case the one at 4 bar gauge at 100 ºC with 5% Acacia).
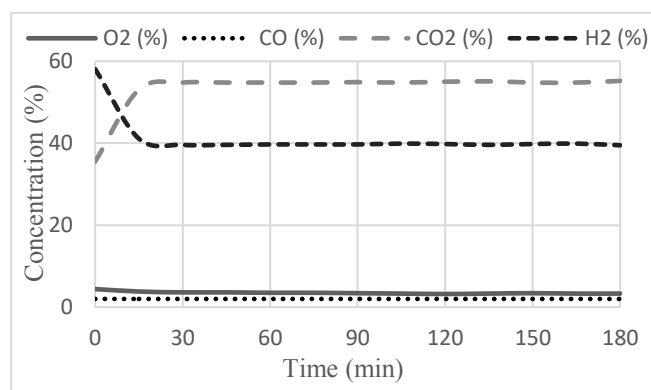

Fig. 3 Gas outlet composition over the duration of the test, 5% Acacia biomass, at 4 bar and 100 ºC

TABLE I
RESULTS COLLECTED, 5% ACACIA BIOMASS, AT 4 BAR AND 100 ºC;

Time (min)	T (°C)	P (bar)	V (V)	I (A)	O₂ (%)	CO (%)	CO₂ (%)	H₂ (%)	F (l/h)	W/f (Wh/L)
0	100.9	4.6	34.52	13.69	4.4	2.0	35.5	58.1	58.89	8.03
15	100.8	4.6	34.93	13.67	3.8	2.0	53.1	41.1	60.98	7.83
30	103.1	4.4	36.56	15.96	3.6	2.0	54.8	39.6	75.10	7.77
45	104.5	4.2	36.56	15.92	3.6	2.0	54.8	39.6	76.87	7.57
60	105.7	3.1	36.57	15.68	3.5	2.0	54.8	39.7	78.49	7.31
75	106.3	3.8	36.57	15.99	3.5	2.0	54.8	39.7	71.62	8.16
90	107.1	3.9	36.57	15.62	3.4	2.0	54.9	39.7	71.95	7.94
105	103.8	4.0	35.68	14.78	3.3	2.0	54.8	39.9	70.77	7.45
120	105.9	4.3	35.68	14.51	3.2	2.0	55.0	39.8	64.59	8.02
135	105.6	4.6	35.67	14.17	3.3	2.0	55.1	39.6	66.22	7.63
150	105.1	3.1	35.68	14.15	3.4	2.0	54.8	39.8	65.41	7.72
165	105.3	3.8	35.67	14.22	3.3	2.0	54.8	39.9	62.07	8.17
180	105.2	4.3	35.68	13.92	3.3	2.0	55.2	39.5	62.14	7.99

As way to resume the results of each individual test, Table II displays an average of the 3 last measurements in stationary state for each key parameter as well as a final $CO_2:H_2$ ratio to allow for a better comparison.

TABLE II
GLOBAL TESTS RESULTS

Carbon Source	Test Conditions	O_2 (%)	CO (%)	CO_2 (%)	H_2 (%)	F (l/h)	W/F (Wh/L)	$CO_2{:}H_2$ ratio
No biomass added	4 bar gauge; 100 ºC	4.1	1.8	25.4	68.7	46.84	10.58	1:2.71
	4 bar gauge; 110 ºC	3.5	1.8	26.2	68.5	44.95	11.39	1:2.61
	5 bar gauge; 100 ºC	8.8	2.1	29.6	59.5	57.19	8.62	1:2.01
	5 bar gauge; 110 ºC	6.7	2.1	31.8	59.4	61.79	7.92	1:1.87
2.5% Acacia biomass	4 bar gauges 100 ºC	3.9	2.0	34.5	59.6	67.53	7.05	1:1.72
	4 bar gauges 110ºC	2.1	2.0	42.6	53.3	62.92	6.71	1:1.25
	5 bar gauges 100 ºC	3.8	2.0	45.4	48.9	59.67	7.33	1:1.08
	5 bar gauges 110 ºC	3.4	2.0	53.4	41.1	62.64	7.17	1:0.77
5% Acacia biomass	4 bar gauges 100 ºC	3.3	2.0	54.9	39.7	63.21	7.96	1:0.72
	4 bar gauges 110 ºC	3.1	2.0	55.0	39.9	71.35	8.00	1:0.72
	5 bar gauges 100 ºC	4.0	2.0	53.8	40.1	63.91	8.85	1:0.75
	5 bar gauges 110 ºC	3.2	2.0	44.5	50.3	60.40	8.89	1:1.13
2.5% Energreen biomass	4 bar gauges 100 ºC	6.2	2.0	40.6	51.2	56.83	10.74	1:1.26
	4 bar gauges 110 ºC	3.2	2.0	46.0	48.7	65.88	6.25	1:1.06
	5 bar gauges 100 ºC	4.8	2.0	39.1	54.1	72.28	6.36	1:1.38
	5 bar gauges 110 ºC	3.0	2.0	46.7	48.3	63.32	6.72	1:1.03
5% Energreen biomass	4 bar gauges 100 ºC	4.1	2.0	40.6	53.3	67.68	7.34	1:1.31
	4 bar gauges 110 ºC	3.4	2.0	35.0	59.6	67.16	7.64	1:1.71
	5 bar gauges 100 ºC	4.2	2.0	36.5	57.4	62.35	8.33	1:1.57
	5 bar gauges 110 ºC	2.9	2.0	38.3	56.8	66.36	8.01	1:1.48

IV. CONCLUSION AND DISCUSSION OF RESULTS

By the analysis of the results, it can be concluded that, the additions of liquified biomass boosted CO_2 production leading to a significant increase in the its content within the gas outlet. As a consequence, it also lowered $CO_2{:}H_2$ ratio. Additionally, higher CO_2 production also requires more O_2 consumption, generating syngas with lower O_2 concentration.

Focusing on the production of syngas specifically for future use in methanation, the addiction of biomass, specifically Acacia shows favored results regarding the production of a syngas mixture while lowering its O_2 content. On the other hand, $CO_2{:}H_2$ ratios are farther from the ideal value when compared to the ideal 1:4, as expected. Although, this can be easily resolved either by a later addition of H_2 or alternatively by the partial removal of its CO_2 (with this still being an easier approach compared to removing the O_2).

Energreen, on the other hand, produced a more optimal CO_2/H_2 ratio (at the cost of lower O_2 consumption), and most importantly, has showed the best relation between energy consumed and gas production.

Regarding process condition, both biomasses showcased different behavior towards pressure, temperature, and its concentration. In the case of Acacia, the preferable conditions are 4 bar gauge at 110 ºC as these result in lower O_2 and energy consumption. Between the two tested concentrations, arguably the 2.5% mixture offered the best performance by having consistently the lowest energy expenditure while producing a more optimal $CO_2{:}H_2$ ratios.

In regards to Energreen, it is not as clear which of the two concentrations offers the best performance with 2.5% producing syngas at a lower energy cost and being close to 5% in terms of O_2 content but producing a less ideal $CO_2{:}H_2$ ratio. The same can be said for pressure and temperature. If the priority is the reduction of O_2 content, the observed ideal conditions were 5 bar gauge at 110 ºC. Although reducing energetic costs is deemed more important, than the best conditions were 4 bar gauge at 110 ºC.

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