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THERMODYNAMIC ANALYSIS OF BIOGAS FIRED CHEMICAL LOOPING COMBUSTION WITH SUPERCRITICAL CO_2 CYCLE FOR POWER GENERATION WITH CO_2 CAPTURE.

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Abstract: *According to the Intergovernmental Panel on Climate Change (IPCC), electric-power generation continues to represent the largest source of CO_2 emissions, and among the available options for reducing net CO_2 emissions to the atmosphere carbon capture and storage (CCS) technologies would play a major role mitigating the global warming problem. Currently, the most promising options for capturing CO_2 efficiently for power plants are pre-combustion capture, post-combustion capture and oxy-fuel combustion. Nevertheless, this technologies present both technical and financial drawbacks that limit its commercial implementation on a large scale, such as the large amount of energy required for CO_2 capture, or the energy penalty associated with the air separation unit (ASU). Chemical looping combustion (CLC) is an emerging technology with inherent CO_2 separation that is not affected by these energy penalties and achieve CO_2 capture rates above 90%, with potential to reach so-called negative CO_2 emissions when biomass is used as fuel. On the other hand, CO_2 exhibits attractive properties such as high density, low viscosity, low toxicity, and flammability index, making it an interesting working fluid option for power generation cycles. The integration of a supercritical CO_2 Brayton cycle in a CLC process is characterized by its simplicity, economic advantages, compact size, and high efficiency compared to conventional power cycles, so it has great potential for commercialization. This work evaluates the thermodynamic performance of a proposed power plant through simulation using Aspen Plus. The net efficiency of the power plant cycle is expected to be around 50% and a total efficiency around 80% with more than 95% carbon capture.*

Keywords: *Chemical Looping Combustion, Supercritical CO_2 Brayton cycle, Biogas, Power generation, CCS.*

1. INTRODUCTION

Nowadays it has become required to implement measures against the continuous high greenhouse gas emissions, in order to reduce the climate change trend. Amongst the principal species composing these gases, carbon dioxide (CO_2) is said to be found in high concentrations, being emitted from the burning of fuel to provide electricity. According to the Intergovernmental Panel on Climate Change (IPCC), (2005); combined the manufacturing industries and energy production sectors are responsible for approximately 60 % of the greenhouse gas emissions, therefore carbon capture & storage (CCS) technologies could perform an important role to reduce the emission of such species.

According to the IPCC,(2005) CCS technologies combined with the application of biomass as energy source fuels in powerplants could possess the likelihood to achieve, to what is known as “negative carbon emissions”, reducing considerably carbon dioxides gas concentrations, due to the capability of biomass to capture carbon dioxide during its growth.

Amongst the most advanced CCs technologies; Pre-combustion Capture, Post-combustion capture and oxy-fuel combustion capture are some that were developed and are still available as of today.

The pre-combustion capture, consist primarily of a fuel pre-treatment; being coal gasification or the reformation of a natural gas by means of oxygen, in order to obtain a synthesis gas mostly composed of carbon monoxide (CO), CO_2, and hydrogen gas (H_2). Afterwards it is combined with steam, for the de CO undergoes conversion and carbon dioxide is obtained. This generates a stream consisting of CO_2 and H_2, where an absorbent is employed to physically remove the carbon dioxide and hydrogen is consumed for energy production (Kanniche et al., 2010).

The post-combustion capture removes the carbon dioxide composed inside the gases generated post-combustion, at the outlet, engaging either a Pulverized Coal (PC) cycle or Natural Gas Combine Cycle (NGCC). According to Kanniche

et al., (2010), CO_2 extraction is performed by a range of methods such as; adsorption, membrane separation, cryogenic separation and chemical absorption; being the most developed to date.

Oxy-combustion capture performs the combustion, by burning fuel inside atmospheres with high O_2 presence, generating gases mainly composed of CO_2 and water vapor H_2O. Given the high temperatures during this stage, this promotes; a meaning amount of the combustion gases to be redirected into the combustion chamber, encouraging to employ unreacted O_2, reducing the concentration of residual O_2 in the flue gas (Markewitz et al. 2012). As for the unutilized remaining flow, it is processed to perform the CO_2 removal, which is subsequentially stored, from the water and non-condensable gases.

Several challenges must be surmounted to apply these mechanisms at an industrial scale, particularly due to the high energy penalty associated with the CCS processes described, as per Chao et al. (2021).

The pre-combustion capture technology is highly developed at an industrial scale. However, its integration into the IGCC system has presented ongoing availability issues (Kanniche et al., 2010). According to Kheirinik et al., (2021), the investment for a pre-combustion power plant costs 1.6 times more than a powerplant incorporating an oxy-fuel combustion system, given that it is a very tough process requiring sophisticated operation units, therefore its construction and operation becomes expensive.

Merkel TC, et al., (20019) highlited the high energy penalty associated to post-combustion capture using amine solvent absorption, consuming around 30% of the power generated with respect to a 90% carbon capture from the flue gas. Furthermore, Merkel et al., (2010), denoted a consumption approximately 16% for the same percentage with respect to carbon capture, for the preliminary results of the system suggested.

The oxy-fuel combustion appears to be an adequate method for energy purposes at powerplants, however it requires large volumes of high purity O_2, which implicates the use of a complex and intensive; with respect to use of energy, separation process. According to Chorowski & Gizicki, (2015) even with cryogenic systems, which offers high efficiencies for gas separation, the air separation unit (ASU) presents a reduction in net thermal efficiency, being at least 7%, due to energy consumption mainly associated to the operation of air compressors.

Chemical Looping Combustion (CLC) process is an energy conversion technique, which can be operated employing different types and states of fuel, whether it presents itself solid, liquid or as a gas, achieving reduced CO_2 emissions, given that it fulfils carbon capture up to 90% in efficiency with no energy penalties (Czakiert et al., 2022). This process is conducted inside two inter-connected reactors, being the air reactor or oxidation reactor, where the atmospheric air oxidizes the oxygen carrier (OC) as soon they come into contact, and the combustion reactor, which reduces the OC as the fuel reacts with the oxygen, provided by the oxygen carrier itself. As in the oxy-combustion, the fuel burning in O2 rich atmosphere, generates combustion gases mainly constituting of CO_2 and H_2O, which can be separated by means of condensation.

Biogas is considered as a renewable energy source, mainly produced from organic matter found in agricultural waste, sewage sludge and food scraps. According to Zanette, (2009), biogas is mainly constituted of methane (CH_4) and CO_2, also containing small concentration of other species such as; sulfuric acid and ammonia. It is produced mainly by anaerobic digestion, where organic matter undergoes decomposition promoted by the microorganisms that break it down at different stages, where CH_4 is considered as a by-product. As well as providing clean energy, it portrays great availability as a fuel inside the region, as Freddo et al., (2022) denotes, Brazil has demonstrated great potential for biogas production, operating more than 750 plants and 44 in the implementation during 2021. Based on such data, studies such as (Milkiewicz, 2021), indicated a growth of 20% compared to the 2020 data with respect to the number of operational plants around the country.

CO_2 is a known compound given its non-flammability and thermal stability. In its supercritical state, the CO_2 suffers an increase in its density, requiring small amount of work for its compression, therefore, according to Marchionni et al., (2017), this allows a reduction with respect to the dimensions for the machinery required, while achieving high cycle efficiencies.

Supercritical CO_2 (sCO_2) Brayton cycles portrays an efficient power generation compactly; according to the simulation of (Khallaghi et al., 2019) developed in Aspen Plus this technique linked with the CLC is able to achieve a net efficiency of 51.4%, higher than the 48.7& obtain from the Staged Oxy-fuel Natural Gas Combined Cycle (SOF-NGCC) plant, he employed as reference.

The current work evaluates a Brayton cycle configuration using sCO_2 through Aspen Plus simulations. The objective is to determine the most efficient configuration for power generation using a biogas-fired CLC-sCO_2 process.

2. PROCESS DESCRIPTION AND SIMULATION

The analysis for this work was done performing process simulations in Aspen Plus V11 ® software, designating the Peng Robinson equation of state as the thermodynamic model with the Boston Mathias modification. The fuel supply designated was biogas, adopting a composition of 60% CH_4 and 40% CO_2; disregarding the small concentration of ammonia (NH_3) and hydrogen sulfide (H_2S) to null their effects in the reactor equilibrium. iron(III) oxide (Fe_2O_3) was appointed as the oxygen carrier, oxidizing inside the fuel reactor (FR) as it comes into contact with the fuel, subsequentially being reduced into iron(II) oxide/iron(II,III) oxide form (FeO/Fe_3O_4), producing a gas flow named GAS

1 (H_2, CO, H_2O, CO_2, CH_4). A cyclone is modeled with the SSplit block to assuming a total separation of the gas flow from the solid flow. Inside the Air Reactor (AR) the species FeO/Fe_3O_4 reacts with the air as the oxygen carrier suffers oxidation returning into Fe_2O_3, which releases a gas stream named GAS2 (N, O_2 in low concentrations, meaning depleted air). The products obtained inside the AR are separated as it was done in the FR; employing a cyclone. The temperature of the gaseous streams produced GAS1 and GAS2 are used to supply energy the sCO_2 power cycles.

The feed flows corresponding to the air and biogas streams are set to 25°C and atmospheric pressure, at the start of the process, afterward two block compressors (COM1 and COM2) pressurize the respective streams to 1.2 bar; an isobaric process is considered, in order to neglect pressure, drop effects inside the equipment. The RGibbs model was set to simulate the combustion and air reactor, following the equilibrium reactor method minimizing the Gibbs energy, assuming adiabatic processes. Figure 1 shows the block diagram simulated in the Aspen Plus software, as explained in this section.

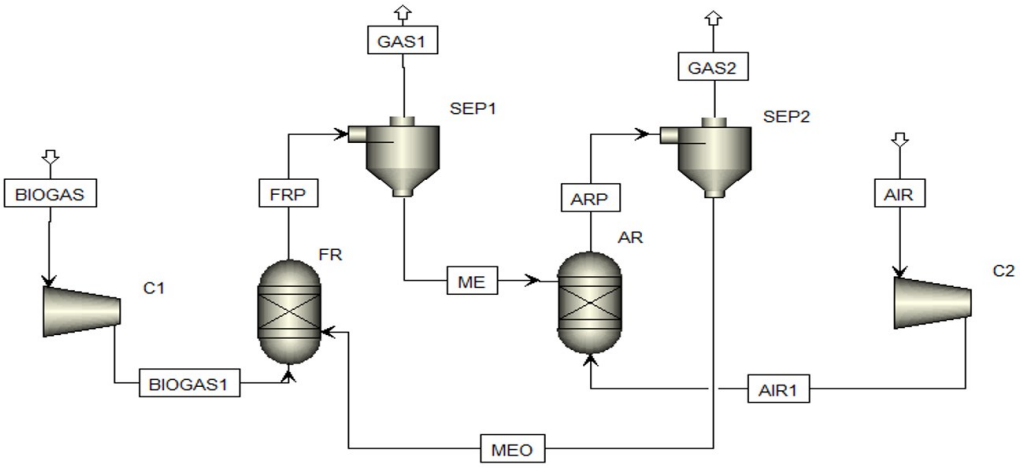

Figure 1. Simulation portrayal of the CLC-sCO2 process fed with biogas in the Aspen Plus software.

Table 1 exhibits each of the components and characteristics of the feed flows of the reactors respectively during the process. The block representing the oxygen carrier and outlet flows produced at the reactor are illustrated in Table 2, such provide the composition of each respectively.

Flow name	Composition (mole fraction)	Pressure (bar)	Temperature (°C)	Flow (kmol/h)
BIOGAS	0.6 CH_4; 0.4 CO_2	1	25	1
BIOGAS1	0.6 CH4; 0.4 CO_2	1.2	25	1
AIR	0.21 O_2; 0.79 N_2	1	25	13-18
AIR1	0.21 O_2; 0.79 N_2	1.2	25	13-18

Table 1: Composition and component of the respective system feed flows

Flow name	Composition
FRP	Feo/Fe_3O_4 + Flue gases
ARP	Fe_2O_3 + Depleted air
ME	Feo/Fe_3O_4
MEO	Fe_2O_3

Table 2: Composition corresponding each reactor outlet flow

Inside the air reactor (AR) the oxygen carrier oxidizes when it comes in contact with the atmospheric air, therefore an exothermic reaction takes place, afterwards it is separated from the depleted air GAS1 in a cyclone entering the fuel reactor, this time coming in contact with the fuel causing its combustion. Such cycle is repeated as the reduced oxygen

carrier exits the fuel reactor, being separated from the product gases GAS2 and recycled to the air reactor, meaning the oxygen carrier is subject to an ongoing oxidation and reduction process.

To perform the simulation both reactors were modeled as adiabatic equilibrium reactors, using the RGibbs blocks, for the compressors; their modelling was made using the Comp block, while the separators were done employing SSplit blocks.

Power generation was provided by means of two supercritical CO_2 Brayton cycles (sCO_2-1 y SCO_2-2), in which the heat transfer is supplied from the hot gas flows (GAS1 and GAS2) from the reactors. In Figure 2 is shown a flowsheet in the Aspen simulator of the sCO_2 cycles studied for the proposed work. The CO_2 stream that eventually enters the turbine (TUR) is heated by the hot gas (HOTGAS), coming from the reactors which then enters the heat exchanger (HEATER). As the flow 9 exits the turbine it goes through two heat exchangers and splits into flow 4 and flow 12, in order to promote efficiency in the compression process the flow 4 is compressed in COM2, while the flow 12 undergoes a decrease in its temperature before entering compressor COM1; which afterwards passes through the LHR heat exchanger for temperature recovery and then mixes with flow 5; entering the HTR heat exchanger before finally going into the HEATER and repeating the cycle..

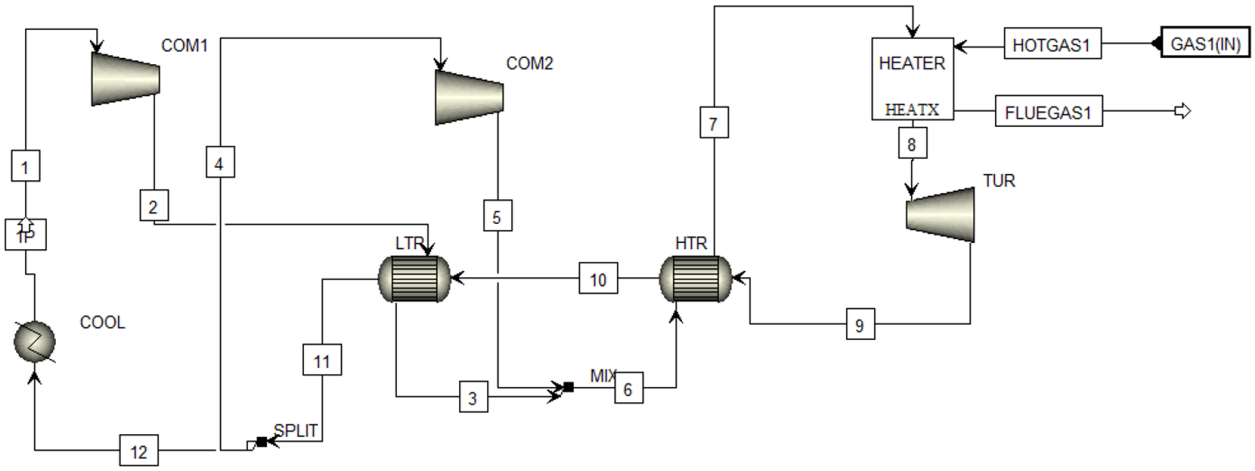

Figure 2: sCO_2 cycle with recompression flowsheet simulation in Aspen Plus.

3. RESULTS AND DISCUSSION

The first parametric analysis was performed varying the air inlet flow rate, while the fuel and oxygen carrier flow rates were set constant. For the total flow rates of BIOGAS and MEO values of 1kmoh/h and 8kmol/h were set respectively. As shown in Figure 3, the presence of FeO increased considerably, with respect to the parameters settings presented, corresponding to values lower than 8 kmol/h in the air inlet to the AR, therefore the oxygen inside the fuel reactor is not sufficient for the biogas combustion to occur completely to obtain high concentration of CH_4, H_2 and CO in the flue gas, such can be observed in Figure 4. Alternatively, as the air reactor flow rate is equal or higher than 8 kmol/h, complete oxidation of the oxygen carrier takes place and the MEO flow is primarily composed of Fe_2O_3 and the oxygen supply inside the fuel reactor is sufficient for the fuel to undergo complete combustion.

For the second parametric analysis the oxygen carrier flow was studied to evaluate the process, the fuel flow rate was set constant at a value of 1 kmol/h, while the MEO flow fluctuated along with the AIR flow where the ratio (air flow)/(OC flow) >1 was maintained. It is observed that the oxygen supply for the fuel reactor is insufficient for the fuel to reach fuel combustion and GAS2 temperature does not exceed 600 °C, when the MeO flow presents values lower than 4 kmol/h. For such reaction to occur, the MEO flow rate value must be equal or greater than 4 kmol/h along with the AIR flow rate being greater than 7 kmol/h, nevertheless such ratios result in temperatures above the iron oxide melting point in both fuel and air reactors, such phenomena can be countered increasing the AIR flow.

As it is possible to operate with a MEO flow rate higher than 8 kmol/h, there are some limitations to such conditions; mainly being that it leans to unreacted Fe_2O_3 being present inside the ME flow leaving the fuel reactor, foretelling that there is an excessive OC flow for the amount of fuel used. Figure 5, shows the presence of FeO in the ME flow.

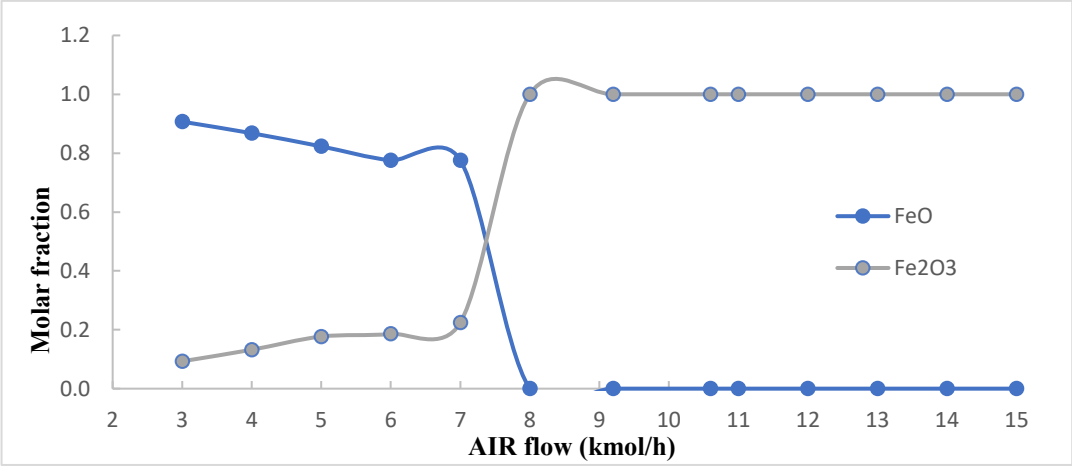

Figure 3. MeO flow composition for different AIR flow rates.

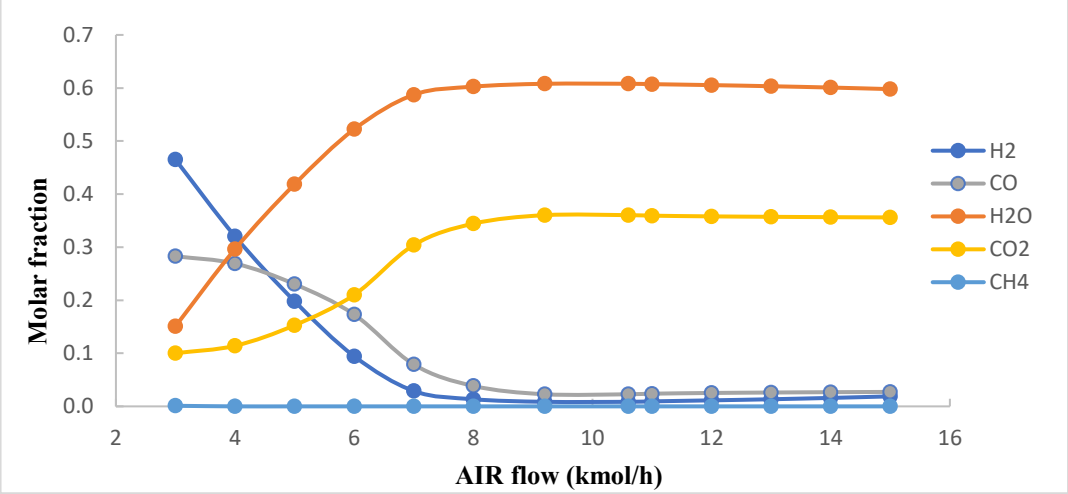

Figure 4: GAS1 flow composition for different AIR flow rates.

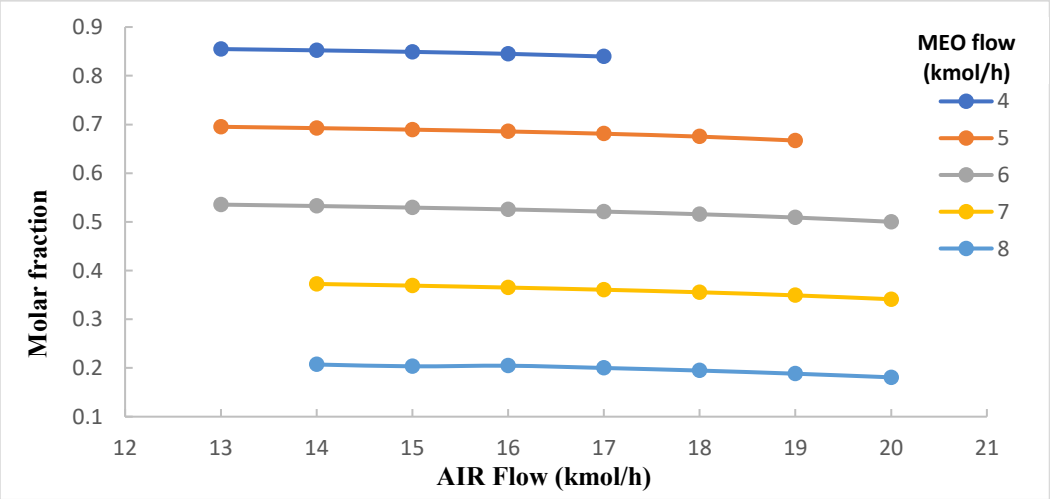

Figure 5: FeO presence at the ME flow rates.

Bases on the results, it was determined that an input of 1 kmol of BIOGAS, a MEO flow rate between 4 and 8 kmol/h along what AIR flow rate between 14 and 18 kmol/h are adequate in order to accomplish a complete fuel combustion, while conserving both reactor at temperatures below the melting points of iron oxides, as in Figure 6 and 7.

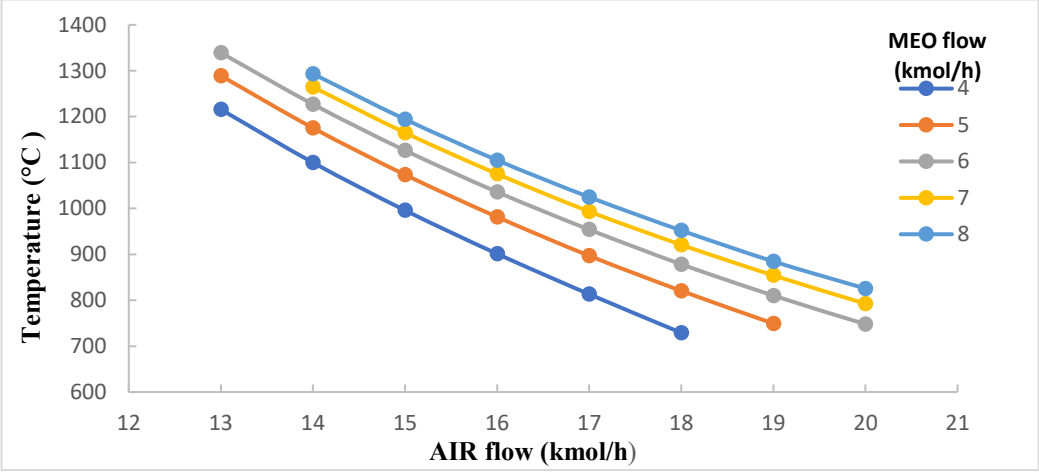

Figure 6: Fuel Reactor temperature corresponding to different MEO flow rates.

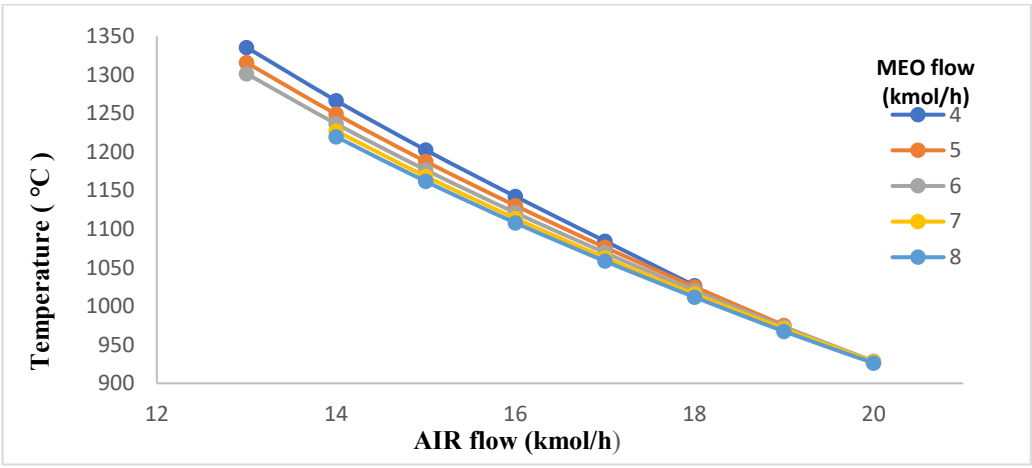

Figure 7: Air Reactor temperature for the different MEO flows rates.

To evaluate the impact of these parameters on the total net power output of the sCO_2 cycles, a combinatorial analysis was conducted using the collected results. Table 3 summarizes information on the parameters analyzed.

Cycle	Variable	Unit	Value
CLC	AIR flow	kmol/h	14-18
	MEO flow	kmol/h	4-8
	BIOGAS flow	kmol/h	1
sCO_2 - 1	Flow 8 temperature	°C	500-650
	Flow 8 pressure	bar	74-120
	Flow 9 pressure	bar	180-250
	CO_2 mass flow	kg/h	310-410
sCO_2 - 2	Flow 8 temperature	°C	500-650
	Flow 8 pressure	bar	500-650
	Flow 8 pressure	bar	74-120
	CO_2 mass flow	kg/h	1300-1800

Table 3: Variables considered in the combinatorial analysis.

As in previous analyses, the fuel flow rate of BIOGAS will remain constant at 1 kmol/h.

The temperature of Stream 8 indicates the temperature of the CO_2 in its supercritical state upon exiting the heat exchanger HEATER and prior to entering the turbine TUR.

The pressures from streams 8 and 9 correspond to the inlet and outlet turbine pressures for both supercritical CO_2 cycles.

The variation in CO_2 mass flow rates in the power cycles results from the difference in GAS1 and GAS2 flows from the FR and AR reactors, correspondingly.

The highest net power values for power cycle 2 (sCO_2-2) align with AIR flow rate values around 14.5 kmol/h, illustrated in Figure 8. The pattern proposes that higher net power values can be obtained from lower AIR flow rates, but this implies the presence of temperatures above 1200 °C in the AR. On the other hand, alterations of the FE2O3 molar flow of the CLC cycle, do not seem to have a significant impact on the net power obtained for the power cycles studied.

The power output of the sCO_2-1 and sCO_2-2 power cycles is depicted in Figures 8 and 9, demonstrating a direct correlation with turbine inlet temperature. The maximum output power is consistently achieved at temperatures between 550 and 575 °C. This applies to both cycles, with the power of the sCO_2-1 cycle surpassing that of sCO_2-2.

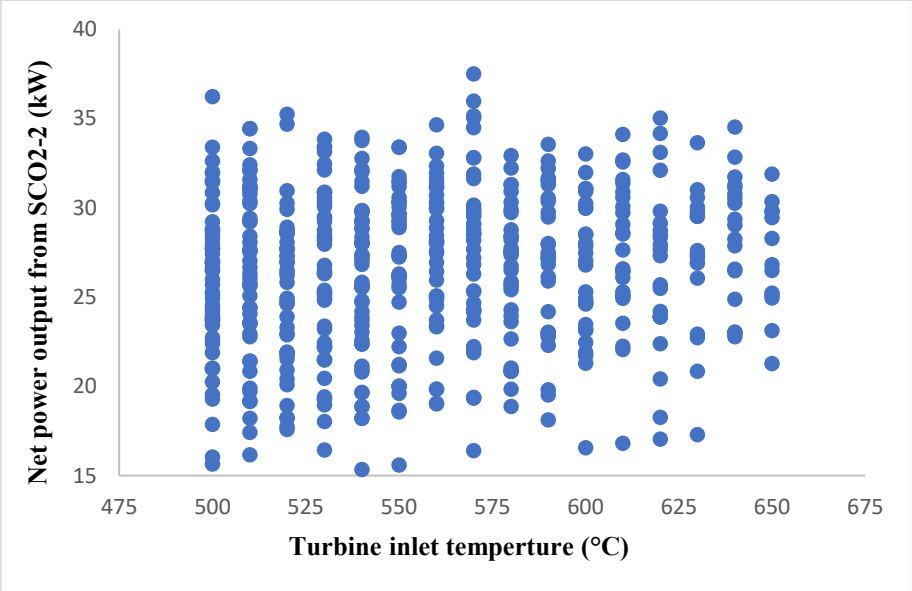

Figure 8: Net power output from sCO_2- cycle 1, for different AIR flow values

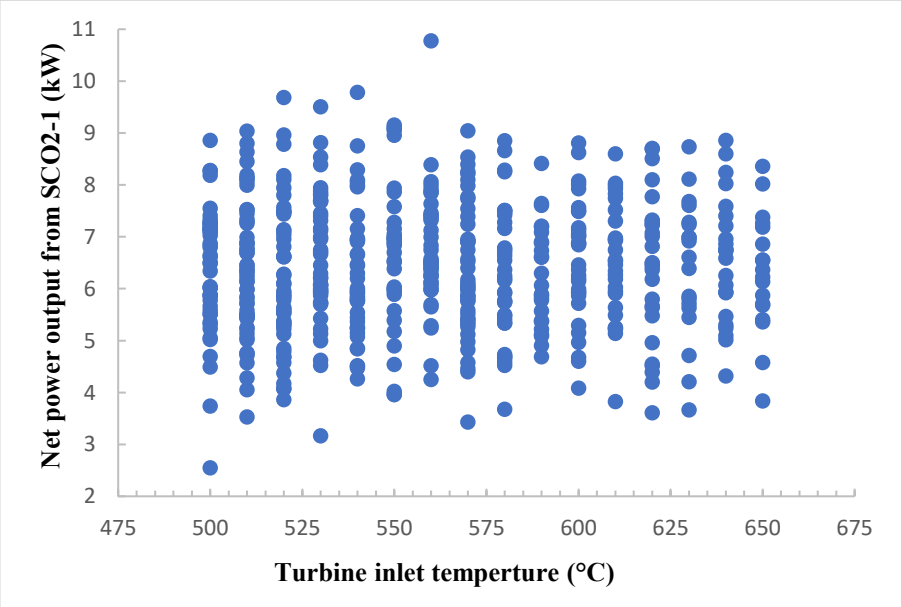

Figure 9: Net power output from sCO_2- cycle 2, for different AIR flow values.

Figure 10 presents the correlation between the useful power extracted from the sCO_2-2 cycle and the input AIR flow rate in the CLC cycle. The maximum useful power output is achieved at an AIR flow rate of 14.5 kmol/h. For the conditions examined in this study, attempting to maximize the useful power output of the sCO_2-2 cycle when operating with AIR flow rates lower than 14 kmol/h results in temperatures exceeding 1200 °C in the AR. While for airflows greater than 16.5 kmol/h, the net power of the cycle tends to decrease due to the temperature reduction experienced by GAS2 coming out of the AR.

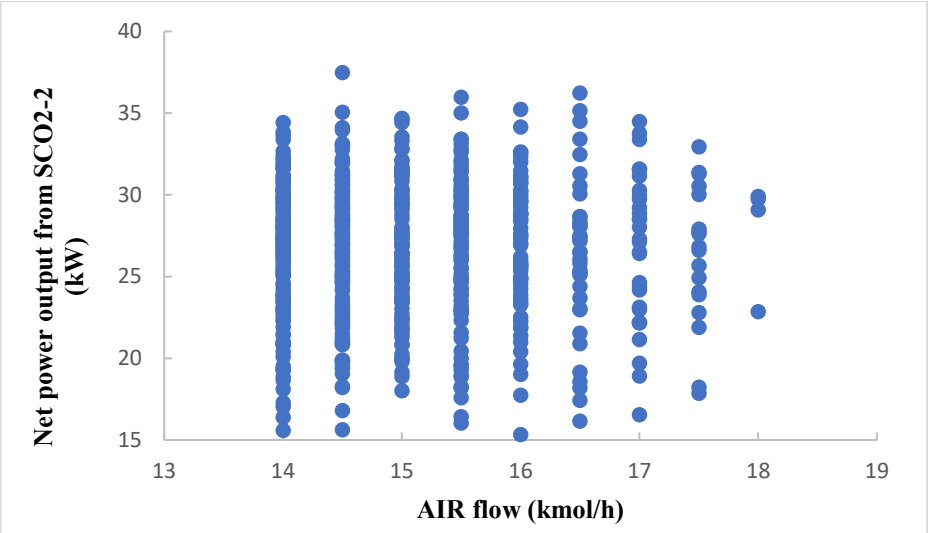

Figure 10 - Net power output from sCO_2-2 cycle for different inlet air flows to the AR.

As seen in Figures 11 and 12, both graphs depict a seemingly increasing trend in both the maximum and minimum values of the extracted liquid power per cycle as the inlet pressure of supercritical CO_2 in the turbine increases. Both the maximum and minimum values demonstrate this trend. Maximum levels of power were achieved at pressures of 230 and 240 bars.

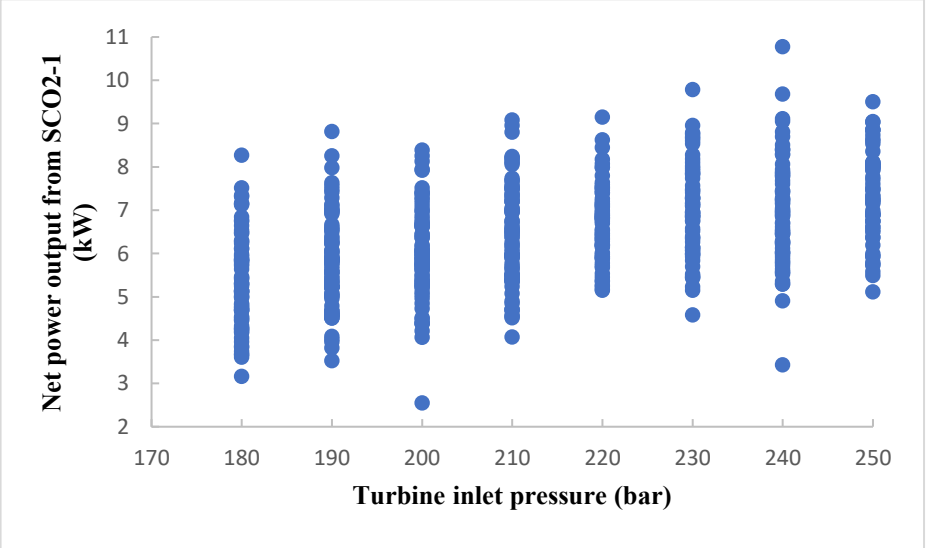

Figure 11 - Net power output from sCO_2-1 cycle for different turbine inlet pressure.

As for the CO_2 stream regarding cycle 1, Figure 13 exposes the increase in net power output as the CO_2 molar flow increases. While the results gathered from the $sCO_2 - 2$ indicate that the maximum useful power point is achieved for a CO_2 flow rate of 36.36 kmol/h, as shown in Figure 14 below.

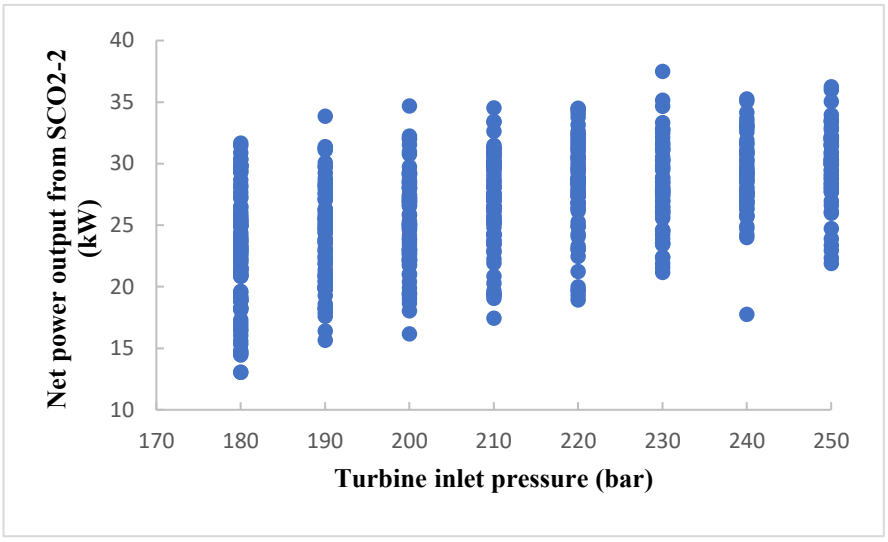

Figure 12 - Net power output from sCO_2-2 cycle for different turbine inlet pressure.

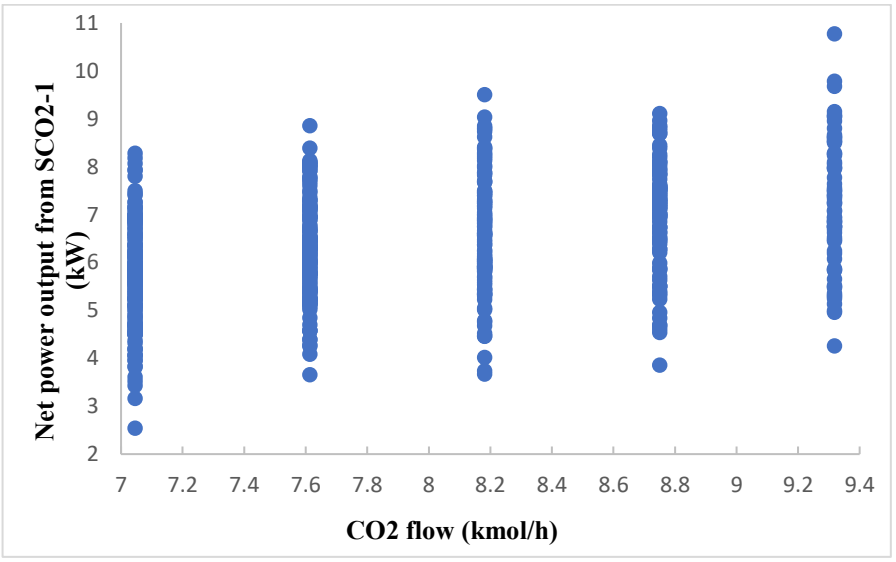

Figure 13 - Net power output from sCO_2-1 cycle as function of CO_2 flow rate.

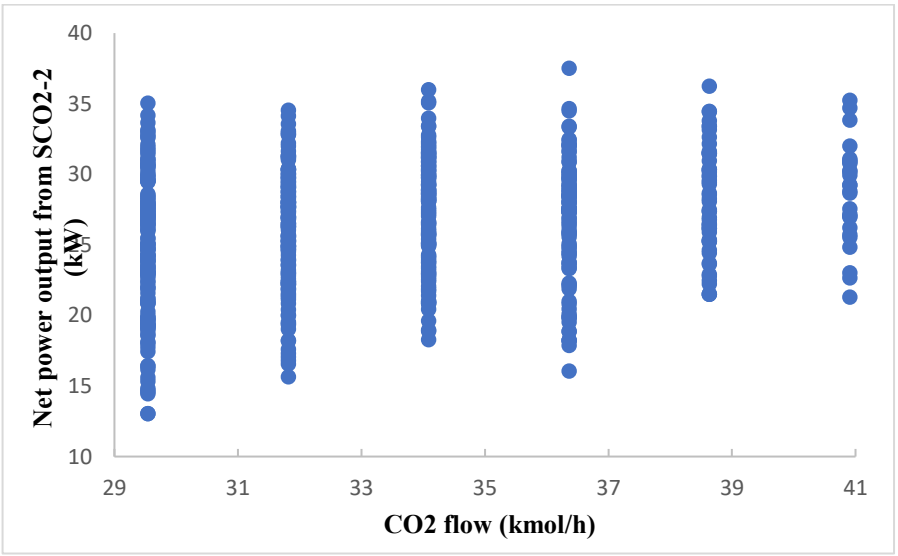

Figure 14 - Net power output from sCO_2-2 cycle as function of CO_2 flow rate.

4. CONCLUSIONS

The proposed CLC process, fed with biogas at a flow rate of 1 kmol/h required a minimum OC flow rate of 3 kmol/h for complete combustion to occur, however, this provokes the complete reduction of the whole Fe_2O_3 stream, therefore a minimum flow of 4 kmol/h is advised.

In the other hand, operating with OC flow rates higher than 8 kmol/h only result in significant Fe_2O_3 presence in the ME flow, between the air and combustion reactor, meaning it has no significant effect in the useful power obtained.

The AIR flow rate must be at least 14 kmol/h, so the reactors' temperatures manage to be below the iron oxides' melting point. Higher flow rates reduce the AR temperature as function of the OC molar flow.

The maximum liquid power gathered from the sCO_2-1 was 10.77 kW, in regard to an air input rate of 14.5 kmol/h in the oxidation reactor, with a CO_2 molar flow rate of 9.3 kmol/h entering the turbine at 560°C at a 240-bar pressure. The results indicate that, for these same conditions, higher CO_2 flow rates can result in increases in liquid power for this cycle. As for the sCO_2-2 cycle, temperatures of 570 *C and 230 bar pressure, with CO_2 flow rate of 36.36 kmol/h end up in a useful power of 37.5 kW.

5. ACKNOWLEDGEMENTS

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