

# Abstract

Carbon capture and sequestration (CCS), fuel switching (switching from coal to natural gas fired power) and renewables are some of the most promising means with which mankind can combat climate change.

Natural gas combined cycle (NGCC) power plants, which make use of both gas fired and steam cycle power generation are the most suitable and efficient fossil fuel power plants that can respond to renewable intermittence. Retrofitting the NGCC power plants with pre-combustion CSS allows the power plant to maintain its flexibility whilst capturing  $CO_2$  because pre-combustion capture occurs upstream; decoupled from the power cycle.

Power to gas (PtG) is a promising technology being developed to overcome renewable intermittence through electrical energy storage (EES). It involves feeding off peak renewable energy to a water electrolyser which splits water into  $H_2$  and  $O_2$  before using the  $H_2$  to valorise  $CO_2$  from an industrial emission source into renewable methane in a methanation unit. The methanation unit is composed of Sabatier reactors that need to have their temperature controlled through recycle of their product gasses. The electrolysis can either be conducted at high temperature using an equimolar feed in water and  $CO_2$  in what is known as high temperature co-electrolysis (HTCE) or it can be conducted at lower temperatures using only water as a feed in what is known as low temperature electrolysis (LTE). A major by-product from both processes is high temperature methanation heat from the Sabatier reactors.

This thesis presents studies on power to gas retrofitted to both LTE and HTCE electrolysers. The two processes were compared on: their ability to produce methane suitable for transportation in natural gas pipelines, their ability to produce renewable methane for onsite storage and their also compared on their energy and exergy efficiency's. The two setups were also retrofitted to a NGCC power plant which itself was retrofitted with a pre-combustion capture sorbent enhanced water gas shift carbon capture and sequestration upstream. No effort is made within the setup to make use of the available heat in the reforming section; with HRSG steam extraction supplying all the required steam for the reformer. This was done with the goal of determining the utility in retrofitting the high temperature methanation heat with the power plant steam cycle for waste heat recovery. The baseline and capture plant efficiencies were also determined and compared with what is stated in the literature.

A novel adaptation to an existing method for determining the physical exergy content of mass streams for flow sheet simulators was developed for ASPEN plus. The fundamental thermodynamic principles were first derived, before being interpreted according to the work of pioneers on the subject and then adapted for use in ASPEN plus. The adaptation involved developing a flow-sheet that could be used to acquire the important stream information from ASPEN plus which could then be used to conduct the calculations using excel or any other software of your choosing. A means of using the flowsheet to determine the thermal and pressure exergy components of the physical exergy of mass streams was also discussed.

Additionally, a novel means for the designing HRSG's for thermal power plants was developed that can be used with flowsheet simulators; a long-standing problem that has made research of power plant setups via simulation somewhat questionable until now. This technique was used to come up with a more accurate estimate for the efficiency penalty associated with pre-combustion carbon capture and sequestration on natural gas power plants. It was also used to determine the mechanical work that could be generated upon heat integration between the NGCC capture plant and the PtG retrofits. The technique developed could be implemented on a thermal power plant setup generating electricity from any hydrocarbon feed or waste heat stream with single or multi-pressure HRSG's. It will especially prove useful for fossil fuel power plants that utilise HRSG steam extraction to provide the necessary steam for their CCS retrofits as well as geothermal, and combined heat and power plants. It can also be used to determine the efficiency of nuclear power plants with greater accuracy through simulation.

The baseline NGCC power plant was simulated successfully and found to have a higher heating value [HHV] and lower heating value [LHV] efficiencies of 53.52% and 59.32% respectively which matched what is reported in the literature. Then the pre-combustion capture NGCC power plant was simulated and found to have lower than expected HHV and LHV efficiencies of 29.92% and 33.17% respectively. The LHV efficiency was 13.83% lower than what is reported in the literature of 47% and the HHV efficiency was 12.48% lower than what is reported in the literature of 42.4%. This disparity was attributed to the fact that a steam cycle flow-sheet for an NGCC pre-combustion capture power plant fitted with SEWGS is yet to be modelled in as much detail as it has in this thesis. This observation is backed by the exergy analysis (developed near the end of the study) conducted on the capture plant which found that the steam extracted for providing the necessary energy for the pre-combustion capture retrofit possess 35 MW of exergy. This amounts to 29.19% of the exergy available within the steam

that reports to the turbines which explains the larger than expected efficiency penalty. The accuracy with which the exergy analysis was able to account for the drop in power production proves that the method proposed for conducting exergy analysis for flow-sheet simulators works. There is much potential to improve the performance of the retrofitted plant, with the exergy analysis revealing that there is 42.29 MW in exergy within the mass stream reporting from the SEWGS flash unit within the pre-combustion capture retrofit. The pre-combustion capture retrofit contributes 13% to the irreversibility of the entire capture plant.

The molar composition of the product stream from the HTCE electrolyser is composed of: 38.8% carbon dioxide, 30.96% carbon monoxide and 30.24% hydrogen. This was attributed to the fact that only 48.3% of the water and  $CO_2$  fed was converted in the electrolyser, to produce  $H_2$ ,  $CO$  and  $O_2$  in an equimolar ratio according to the main reaction. When this product is used as feed to the methanation unit only one Sabatier reactor was needed to completely react all the hydrogen that was fed in. The final product failed to meet the specifications for pipeline transport with a methane composition of only 21% and a carbon dioxide composition of 76.53%. The Sabatier reactor reached a temperature of 313°C at the maximum Sabatier reactor recycle fraction of 0.9.

The composition of the product stream from the LTE electrolyser was composed entirely of hydrogen due to the fact that it had a conversion of 99.99% after being fed a stream composed of 100% water. Since the hydrogen stream reporting from the electrolyser is pure; all the carbon dioxide required for methanation was fed to first Sabatier reactor. To ensure that there was enough  $CO_2$  and  $CO$  to satisfy the reaction stoichiometry for complete reaction within the methanation unit; the flow of water to the electrolyser was adjusted so that the molar flow in hydrogen from the unit is 4 times the molar flow of  $CO_2$  added to three times the molar flow of  $CO$  coming from the capture plant. The molar composition of methane coming from the first Sabatier reactor was 70.87% and the temperature of the reactor was 436.16°C at the maximum recycle fraction of 0.9. The product from the second Sabatier reactor was able to reach a composition in methane adequate for pipeline transport of 95 mole% for a recycle fraction of 78% at a reactor temperature of 259°C.

A heat integration study determined that integrating the methanation heat in the HTCE PtG process with the HRSG in the pre-combustion capture NGCC power plant would reduce the LHV efficiency of the power plant by 48.85% to -15.68% whilst storing renewable energy. Another heat integration study determined that integrating the methanation heat in the LTE PtG

process with the HRSG in the pre-combustion capture NGCC power plant would improve the LHV efficiency of the power plant by 6.32% to 39.49% whilst storing renewable energy. The LTE NGCC pre-combustion capture setup was deemed an adequate renewable adaptation to the traditional NGCC peaker plant. HTCE was deemed unsuitable as source of waste heat.

A thermodynamic study determined that the efficiency of the HTCE electrolyser and the entire HTCE PtG processes were 31.49% and 42.21% with methane storage. The same study determined that the efficiency of the entire HTCE PtG processes will be 43.45% when the methane is prepared for pipeline transport instead. The exergy efficiency of the HTCE electrolyser and that of the entire HTCE PtG process were 87.07% and 84% respectively with methane storage. And the exergy efficiency of the entire HTCE PtG processes was 87% when the methane is prepared for pipeline transport. The electrolyser was found to contribute the most to the irreversibility within the retrofit (73%) and as a recommendation it is suggested that the temperature of the processes be lowered.

Another study determined that the efficiency of the LTE electrolyser and that of the entire LTE PtG processes were 83.52% and 55.95% respectively with methane storage. When methane is prepared for pipeline transport instead the efficiency of the entire processes was 56.79%. The exergy efficiency of the LTE electrolyser and that of the entire LTE PtG retrofit were found to be 83.23% and 83.71% respectively with methane storage. The exergy efficiency of the entire processes was found to be 84.30% when the methane was prepared for pipeline transport instead. The electrolyser was again found to contribute most to the irreversibility within the retrofit (91%) and as a recommendation it is suggested that the temperature of the process also be lowered.