EMBEDDING SOLAR ENERGY IN ALUMINA USING STEAM REFORMING

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ABSTRACT

Solar energy is an abundant, yet dilute energy resource. In order to incorporate it into an industrial process such as the Bayer process it needs to be concentrated first and converted to a useable form. One such method is the use of solar thermal concentrator to focus the thermal energy to a single point, enabling high temperatures of up to 1000 °C to be achieved. In this form the solar energy can be used to drive endothermic chemical reactions resulting the thermal energy being converted to stored chemical energy. This solar fuel gas can be incorporated into the Bayer process wherever natural gas is currently combusted.

The fuel producing reaction is based on same chemical process used to produce more than 95% of the world's hydrogen and is therefore an extremely mature technology. Large commercial steam reformers produce more than 200,000 Nm^3/h of hydrogen in a single train. The reaction is widely practised commercially for the production of synthesis gases and H_2. It is highly endothermic and is generally conducted at temperatures in the range 800-950 °C and pressures in the range 0.5-3.3 MPa. Solar steam reforming is perhaps the most widely studied solar thermochemical option, with extensive on-sun experience by Australian and overseas investigators using a variety of reactor types with solar inputs ranging from 25–600 kWth.

This study examines the suitability of capturing solar energy through a solarised steam reforming processes and subsequently using the solar syngas products in place of other combustible gases for providing thermal energy to the Bayer process. Taking this approach allows a near seamless transition as the process remains virtually unchanged and provides a pathway to lower emission solar based energy sources.

The impact of the variability of the solar resource on the solar reforming process and flow-on impact to the Bayer process is presented and recommendations made to manage the variations. Further, specific parts of the Bayer process are identified that have shown compatibility with the new energy source.

1. INTRODUCTION

The worldwide average total energy consumption for the production of alumina is 11.2 GJ/t energy, with the production of steam for digestion, evaporation and pre-heating consuming 50% of this energy and combustion for calcination the remainder. In Australia, alumina production consumes 160 PJ of natural gas per year and is responsible for ~40% of Australia's CO_2 emissions from minerals processing.

An option for emissions reduction is the integration of solar energy, the most abundant renewable energy resource available on the earth, however its relative dilute energy density, which is less than 1000 w/m^2 and intermittency due to weather, day/night cycles and seasonal variations result in difficulties in integrating with traditional large scale mineral processing operations.

For electricity production, large scale solar energy systems in the hundreds of megawatts based on photovoltaic systems are now common place in suitable locations worldwide.

Even larger solar thermal systems are now coming online around the world, these systems are based on mirrors concentrating energy to a tower-based energy receiver where molten salt is heated to 590 °C and are capable of collecting gigawatts of thermal energy. The molten salt is stored in tanks until required before being used to generate steam for a typical Rankine based power cycle.

In order to successfully integrate solar energy into the Bayer process with minimal modification to the existing process, solar energy will need to be in a form similar to the

existing fuels source, typically natural gas. This paper presents one such process.

2. Solar Reforming as method capturing Solar Energy

This work focuses on the use of solar thermal systems to produce a solar enhanced syngas suitable for integration into existing alumina refineries with minimal modification. The process utilises the world's most common industrial process, steam reforming to chemically embed solar energy into the fuel gas.

2.1 Solar Thermal Systems

Solar thermal systems are divided into two distinct categories: linear focus and point focus. Both of these have been industrialised for the purposes of generating electricity using steam Rankine cycles.

Linear focus systems concentrate solar energy onto a long, linear receiver using either a parabolic trough or a linear Fresnel system. These systems can produce temperatures up to 500°C, and have a large industrial deployment of more than 3.5 GW for electricity generation, with more than 30 years of on-sun operating experience using the earliest systems.

Point focus systems concentrate solar energy onto to a single point using either a central tower or a dish. This enables much higher concentrations and temperatures to be achieved. Both towers and dishes track the sun in two dimensions, giving higher optical efficiencies than linear systems.

Figure 1. The Crescent Dunes CSP plant in the USA

Central tower systems focus the sun's thermal energy with thousands of tracking mirrors called heliostats. The heliostats focus concentrated sunlight on a receiver that sits on top of a tower positioned in the centre of the field. Central tower systems have been implemented at large sizes (up to 1.1 GWth) for utility-scale power generation seen in Figure 1, and are increasingly being adopted in the concentrating solar power (CSP) sector.

While tower-based systems typically operate with temperatures close to 600°C for electricity generation, they are capable of easily achieving temperatures up to 1000 °C and beyond and thus suitable for fuel processing.

2.2 Solar Chemistry processes

Industrial reforming of methane (CH_4) is used to produce more than 95% of the world's hydrogen and is therefore an extremely mature technology. The reaction is widely practised commercially for the production of synthesis gases and H_2. It is highly endothermic and is generally conducted at temperatures in the range 800-950°C and pressures in the range 0.5-3.3 MPa.

The primary reactions are the steam-methane reforming reaction and dry reforming reaction:

Steam reforming: $H_2O + CH_4 \rightarrow 3\ H_2 + 1\ CO$

CO_2 reforming (dry): $CO_2 + CH_4 \rightarrow 2\ H_2 + 2\ CO$

The use of solar thermal energy to provide the endothermic energy to drive the reactions has been studied by a number of researchers with great success (Agrafiotis et al., 2014) and is perhaps the most widely studied solar fuel process, with extensive on-sun experience by Australian and overseas investigators using a variety of reactor types with solar inputs ranging from 25–600 kWth.

The energy enhancement can be defined by comparing the energy content of the incoming natural gas against the energy content of the chemical products. CH_4 has a higher heating value (HHV) of 891 kJ/g-mol and a lower heating value (LHV) of 802 kJ/g-mol. The corresponding values for H2 are 286 kJ/g-mol (HHV) and 242 kJ/g-mol (LHV), and for CO is 283 kJ/g-mol. Overall, in ideal terms, the complete reforming of 1 g-mol of CH_4 by the steam reforming reaction generates 1 g-mol of CO and 3 g-mols of H_2. If this strongly endothermic process is driven using solar thermal energy, very significant embodiment of stored solar energy in the reaction products is attained with the product gas having a higher energy content of up to 28.4%, depending on the basis used and process conditions.

This enhanced fuel gas carries solar energy into any combustion process existing in the Bayer process, enabling a simple implementation of solar energy into the high temperature operations such as the caliciner.

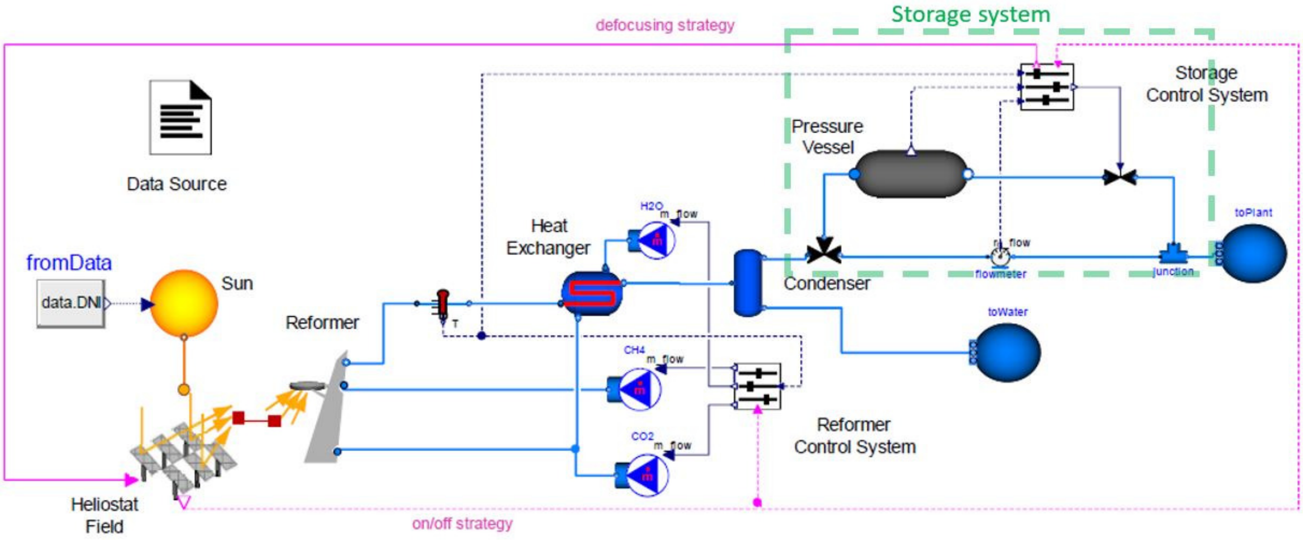

Figure 2: Modelica component diagram of the system model

2.3 Integration opportunities within the Bayer process

While the solar reforming of natural gas has been demonstrated as method of capturing solar energy in a fuel gas, the off-design performance of any solar energy system is obviously impacted by the prevailing weather and day/night operations. The obvious solution is to introduce a storage system where the enhanced fuel gas can be buffered for overnight operations however detailed analysis is required to ensure that any storage system is sufficient to service the needs of the calcination process.

Previously, coal gasification has been suggested as a method of replacing fuel gas with alternative energy sources. A gasifier is able to take a variety of solid fuels and covert them to syngas, a mix of predominately hydrogen, carbon monoxide and carbon dioxide. However, it has been identified that gas treatment is a critical step in this process as impurities present can impact on alumina quality. This previous work has concluded that clean syngas is a suitable fuel for the calcination and potentially may enhance the end alumina product.

The enhanced fuel gas produced by the solar reforming process will not have required clean up steps of a gasification process, but will be approximately similar composition, so may present similar alumina product quality improvements.

2.4 Dynamic Modelling of the solar thermal Steam Reforming process

To study the annual performance of a solar thermal steam reforming plant, it is necessary to understand how the variability of the solar resource affects the process. We developed a dynamic model for this purpose.

The model described in this section follows an object-oriented methodology based on equations and it was implemented in the Modelica language (Modelica Association, 2017). The main physical and chemical phenomena were identified and encapsulated into independent and reusable modules. These modules were interconnected graphically to build up the final system. This approach allows to study different plant configurations to improve the annual performance.

In this work, two different system models have been developed, one without storage and one with storage. Figure 2 depicts the final arrangement of both system models. These are composed by a data source, a sun, a reformer, a heat exchanger, a condenser, a control system, a temperature sensor, fluid sources and sinks. In addition, the storage system also includes a valve, a pressure vessel, a flowmeter, a pump and another control system.

A typical meteorological year data set in the TMY3-file format provides the input weather data necessary to run the system. This data is interpolated in the data source model. The sun model provides the Sun position and the direct normal irradiance to the heliostat field which calculates the total concentrated power into the reformer using a look-up table with the total optical efficiency of the field. This optical efficiency, which includes the cosine error, the reflectivity, the shading, the blocking, the attenuation and the spillage is provided by a third-party software (for example, SolarPILOT).

At the reformer, part of concentrated solar energy in transferred to the catalyzer and the gas which flows inside driving the methane reforming. Ideally, the flux distribution at the reformer is designed to provide a constant temperature in all the surface of the receiver. Under these conditions and taking into account that the incoming composition of the gas is automatically controlled to be constant, the reaction rates are only dependant by the temperature. To avoid the non-lineal system of equations of the equilibrium reaction, the reaction rates were tabulated per mole of methane and are calculated via spline interpolation as function of the temperature. This temperature is controlled by the reformer control system which manage the gas sources providing the suitable concentration and mass flow rate. Due to the high thermal inertia of the reformer, a pre-heat of the reformer is required before open the gas sources. This is done with the power coming from the heliostat field. When the reformer reaches the reference temperature (800 °C), the gas sources open and the mass flow rate of then are controlled by a proportional integer (PI) controller with reset. This PI controller hold the reformer temperature in the reference. The gas sources closes when the heliostat field is shut down.

To recover part of the heat of the reformer, a heat exchanger is placed at its exit. The steam used at the reforming is preheated in this device before it enters in the reformer with the outgoing reformer flow. Once the product gas leaves the heat exchanger, it flows to the condenser that after a fast condensation the water that was not consumed in the reforming reaction is removed form rest of the gases.

The product gas can be stored to be used with non-solar conditions as is shown in the Fig. 1b. A three-way valve placed at the exit of the condenser diverts part of the gas to the pressure vessel. In this storage device, the gas is compressed until a pressure limit (200 bar) and cooled up to the ambient temperature. The storage control system, allows to manage the discharge of the pressure vessel acting over a mass controlled valve. This system provide a constant a mass flow rate of product gas to the plant taking into account the amount of gas non diverted to the storage system and the pressure of the storage. When the pressure vessel reaches its maximum capacity, the defocussing of part of the heliostat field is required to guaranty the security of the plant. When the pressure at the vessel reaches its minimum value (the operating pressure of 8 bar), the discharge of gas stops.

The models of data source, Sun and heliostat field and pump are been re-used from the open source SolarTherm library (de la Calle et al., 2016) with some adaptations and extensions. This library provides suitable component models to perform annual simulations and the economic assessments of solar thermal plants. The heat exchanger model it is an adaption of the quasi steady-state model presented by Bonilla et al. (2017). Sources, boundaries, temperature sensor, flowmeter and junction are models available at the Modelica Standard Library (Modelica Association, 2017). The reformer, the condenser, the pressure vessel and the control systems were specifically developed for this work.

3. RESULTS AND DISCUSSION

3.1 Results from Dynamic Model

Dymola 2018 (Dassault Systemes, 2017) 2016) was the tool used for the Modelica implementations and simulations. The numerical solver used for the dynamic simulations has been DASSL (Petzold, 1983) whose absolute and relative tolerances were set to 10^{-4}. The simulation was performed using weather data from Learmonth, Western Australia, provided by EnergyPlus (NREL, 2018). The solar field plant was designed to provide 50 MW_{th} in nominal conditions. The plant is designed to have 8 bar of operating pressure and an inlet composition of 2.5 moles of H_2O per mol of CH_4.

Two different scenarios were tested with same plant features. At the first scenario, the alumina process requires 220 MW of high heating value (HHV) power. In this case, the solar reforming plant does not need storage, and model without storage was used. To guarantee the outlet power needed, a variable

amount of CH_4 was added at the output of the reforming plant.

Figure 3 shows the varying composition of the outlet power over the first three days of the year. The composition of the reformed gas is fixed because the control system allows to work in nominal conditions the most of the operating time. With these conditions, the molar fraction of the reformer outgoing gas is 0.027, 0.258, 0.055, 0.550 and 0.110 for the CH_4, H_2O, CO_2, H_2 and CO respectively. Therefore, the plant achieve an 87.1% of methane conversion in mass.

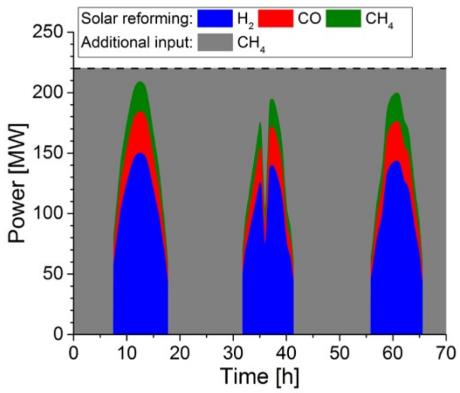

Figure 3. Composition of the outlet power in the first scenario.

Regarding the origin of the inlet power of the system, the main contribution is the CH_4 input as shown Figure .

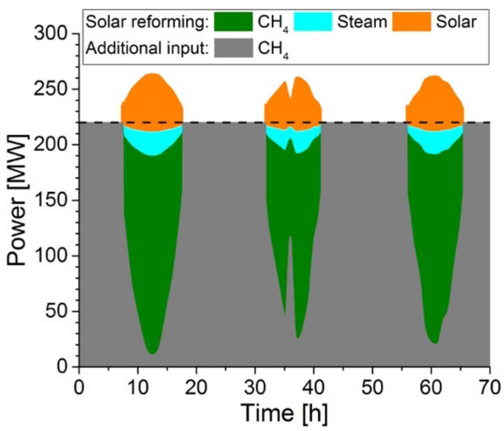

Figure 4. Composition of the inlet power in the first scenario.

The CH_4 contribution is divided in the one that goes to the reformer (green) and the additional CH_4 needed to meet with the power demand all the time. Additionally, the solar reforming process requires two more power inputs: one purely solar in the reformer (orange) and another to for boil the water used in the reforming (cyan). In this scenario, the CH_4 savings is around 3.7% in one year of operation.

At the second scenario, the alumina process requires a constant input of 90 MW. In this case the model with storage was used to guarantee the maximum solar energy income. In addition, a variable amount of CH_4 was added to meet the power demand.

Again, the simulations were performed over the first three days of the year. Figure 5 shows the varying composition of the outlet power where the 7 hour of storage has an important contribution. It is remarkable the lower contribution of additional CH_4 required in this scenario which is able to work without this support more than 12 hour per day in favourable solar conditions.

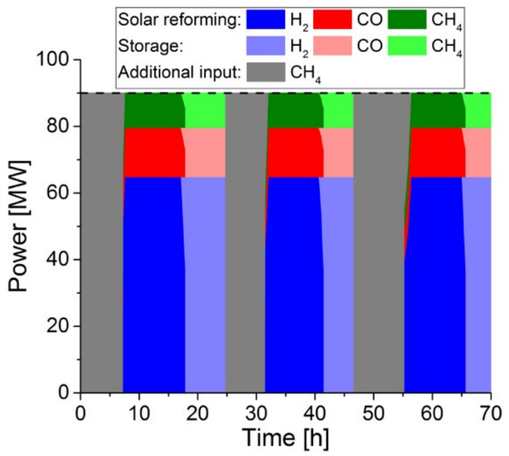

Figure 5. Composition of the outlet power in the second scenario.

Although the main contribution in the inlet power of the system is still the CH_4, this input is proportionally reduced with respect to the first scenario (Figure 6). The amount of solar and steam inputs are also reduced due to the partial defocussing of the heliostat field performed at the end of the first day. However, proportionally these contributions are higher than the first scenario. The compression power required to storage the gas is included although its contribution is lower in comparison with the rest inputs. This configuration allows to save around the 8.2% of the CH_4 consumption in one year of operation.

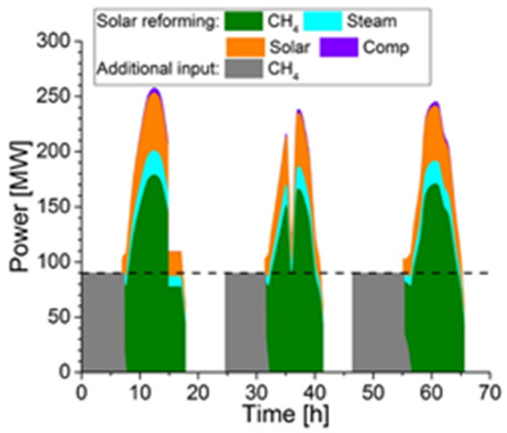

Figure 6. Composition of the inlet power in th second scenario.

3.2 Managing solar variations

The daily cycle of the sun results in variations in the thermal energy available to drive the solar reforming process, while the Bayer process is a 24/7 continuous process.

By oversizing the solar thermal system syngas production is above demand allowx`ing excess to be placed into storage enables a greater share of solar energy to be embedded into the calciner product.

Storage of gas is well established engineering process, with syngas storage first demonstrated for "town gas" in the 1800's, where a type of coal derided syngas was used in homes and industrial processes. This gas holder technology stored syngas at low pressures in large vessels sealed with water. While the technology is sound the mass of gas that can be stored is low due to the low storage pressure.

Most modern syngas storage is based on higher pressures systems, there are four types of systems that can be considered.

- Gasometer (low pressure)
- Above ground gas storage
- Pipeline storage
- Underground Caverns

The gasometer is essentially a modernised version of the original gas holder technology, Gasometers typically have a variable volume, through the use of a weighted movable cap, which provides gas output at a constant pressure. Gasometers operate at low pressure, with typical pressures in the range of 200-300mm water; maximum operating pressures are 1,000mm water. Typical volumes for large gasometers are about 50,000-70,000m^3, with approximately 60 m diameter structures; although the largest gasholder installed by one manufacturer was 340,000m^3. Gasometers have long operating lifetimes; the structure itself can operate for over 100 years, while the diaphragm that seals the gasometer has a lifetime of 200,000 strokes or approximately 10 years. A recent report from NREL suggest storage costs of \$340/m^3.

High pressure storage systems require the use of compressors, Syngas requires significantly higher compression energy than the equivalent natural gas storage due to the lower volumetric energy content in the syngas. Depending on the operating pressure, compression can introduce a significant energy cost onto the storage. Expansion turbines can be introduced to recover much of this energy at additional cost. High pressure systems are either traditional pressure vessel technology, or underground caverns. Pressure vessel technology is based on steel containment vessels and can be in the form of above ground storage vessels or pipeline-based storage. Above ground pressure vessels can range in capacity up to 14,000Nm^3 and cost from \$30-200 m^3. In areas with the solar plant is remote to the alumina process pipeline-based storage can be implemented. In pipeline-based storage the operating pressure of the pipeline is varied, in this case small increases in pressure can effectively store large amounts of gas at little additional cost.

Underground storage occurs in stable geological locations and is a common technique for storage of large quantities of gas. There are four underground formations in which gas can be stored under pressure: (a) depleted oil or gas field; (b) aquifers; (c) excavated rock caverns; and (d) salt caverns. Underground storage volumes in depleted oil and gas fields can be extremely large; volumes of gas stored exceed 10^9 m^3 and pressures can be up to 40 atm. Salt caverns, large underground voids that are formed by solution mining of salt as brine, tend to be smaller, typically around 10^6-10^7 m^3. Although smaller, salt caverns offer faster discharge rates and tend to be tighter than other underground formations, reducing leakage. The major issue with underground storage is the requirement for compatible sites with good solar resources. Costs of underground storage can be as low as \$10-20/Nm^3.

A newer concept for storage (Lavine et al., 2016) has been proposed which addresses the key issue of underground storage (compatible

geology with solar resource). In this concept, drilled shafts are lined with concrete and capped, enabling the advantages of an unground storage, without needing to locate large underground voids.

4. CONCLUSION

Solar thermal energy is an abundant resource that is now maturing to deliver gigawatts of energy in the power generation configuration. Capturing and integrating with an industrial process is challenging due to the inherent variability of the solar resource.

By adapting the existing solar thermal technology, high temperature endothermic reactions can be undertaken that absorb solar energy and effectively embed the energy within a fuel gas. In this case a steam reforming reaction is used to capture the energy.

The steam reforming reaction, a widely practiced industrial process produces a syngas with over 25% solar enhancement that can be utilised in the existing burner systems with the calciner and steam generators that form part of the Bayer process for alumina production. Solid fuel derived syngas via gasification has previously being examined as a fuel source with positive impacts on the alumina quality.

A model developed to illustrate some of the challenges that a variable energy resource such as solar introduce has shown that the while a direct solar to process connection achieves an annual carbon dioxide reduction of 3.7 %, introducing a syngas storage enables this to be reduction to be 8.7%. Further work optimising the storage and solar field size is expected to yield large reductions.

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