# THERMAL OPTIMISATION OF A SORPTION ENHANCED REFORMING PLANT

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In this work, a simulation model of a $H_2$ production plant based on the sorption enhanced reforming process has been developed in order to carry out an exhaustive thermal analysis that will determine the best operating parameters of this process. These optimum issues imply not only maximising $H_2$ production but also reducing the external energy supply in the plant and therefore the energy penalty. The simulation model has been developed in Aspen Hysys and implies two interconnected fluidised bed reactors operating as reformer and regenerator.

The reformer has been simulated as an equilibrium reactor where the reforming and water gas shift reactions take place together with the carbonation reaction between the $CO_2$ produced from the CO conversion and the CaO coming from the regenerator. The $H_2$ produced from these reactions will be partially used by the catalyst contained in the solid stream coming from the calciner (NiO supported by $Al_2O_3$) to produce active catalyst. A visual basic code has been developed and integrated in the Aspen Hysys model in order to evaluate the equilibrium between the reactions explained above and the need for eliminating or introducing energy in this step. The operating conditions of the reformer have been maintained constant at 650ºC and atmospheric pressure, whereas three operating parameters will be modified to study its effect on the thermal analysis of the process: (1) steam-to-methane molar ratio in the gas stream fed into the reformer at 450ºC, (2) calcium-to-methane molar ratio between the solid and the gas stream entering the reformer; (3) mass of catalyst in the solid stream coming from the regenerator related to the mass of methane fed into the reformer.

There are two products from the reformer: the rich $H_2$ gas stream that will be purified and compressed up to a pressure value that would be dependant on its latest use, and the solid stream containing CaO without reacting, $CaCO_3$ and catalyst (Ni supported by $Al_2O_3$). To complete the loop, this solid stream is introduced in the calciner or regenerator in order to decompose the $CaCO_3$ previously formed. The calciner has been modelled as an adiabatic reactor where the energy needed for the calcination is supplied by additional methane burnt in oxy firing conditions. 900ºC and atmospheric pressure have been fixed as operating conditions in the calciner to assure that nearly complete calcination of this $CaCO_3$ is achieved and to avoid excessive degradation of the calcium based sorbent. The code developed for this reactor includes a semi-empirical calcination reaction model dependant on $CO_2$ concentration and temperature which has been fully characterised by multi-cycle TGA experiments. The fraction of $CaCO_3$ decomposed in the calciner will be determined by the solid residence time in the reactor and the additional fuel burnt with $O_2$. The presence of $CaCO_3$ in the product of the calciner will reduce the CaO available to react with $CO_2$ in the reformer and, as a result, the $H_2$ production in the

process would be affected. Due to the fact that methane is burnt with high purity $O_2$ in the calciner (95% $O_2$), part of the flue gas leaving the calciner at 900ºC has been cooled and recirculated again into the reactor to avoid high temperature flame inside the reactor. As a result of this heat exchange, it is possible to recover most of the energy introduced in the system and reduce therefore the energy penalty associated to the Ca-looping. Although it has not been considered that the capture capacity of the sorbent is reduced through the cycles, a minimum solid purge is made in the calciner (1% of the molar flow of methane in the reformer is purged as calcium in the calciner) and a fresh sorbent make-up flow is introduced in the system to maintain mass balances.

Once the simulation model was fully developed, it has been carried out a thermal analysis of the plant varying the three operating parameters mentioned above. In every simulated case, the following energy consumptions have been summarised:

(1) Evaporation and preheating of the steam fed into the reformer up to 150ºC before being mixed with the methane
(2) Preheating of the steam/methane mixture fed into the reformer up to 450ºC

Although steam evaporation represents more than a half of the energy requirements in the system, there are three main heat recovery stages in the process that exceed these consumptions and allow the design of a heat exchange network in each simulation case. These heat sources are:

(1) Energy recovered from the $H_2$ rich gas obtained in the reformer at 650ºC that is cooled down to 80ºC before entering into the condensation stage
(2) Energy recovered from the flue gas in the calciner that is cooled from 900ºC down to 230ºC before being split into the recycled flue gas in the calciner and the gas sent to the purification stage
(3) Energy recovered from the flue gas that has to be cooled down to 80ºC before being sent to the purification stage

The energy recovered in the flue gas recycled to the calciner is a high quality heat source because of its high temperature range and represents more than a half of the energy recovered in the system. Furthermore, it has been noticed that the sum of the energy consumptions in the system is lower than the energy recovered so a self-governed heat exchange network would be possible. To complete the thermal analysis the additional methane required in the calciner has to be included as well as the power requirements from the Air Separation Unit (ASU) that provides the $O_2$ stream fed into the calciner, the $CO_2$ purification and compression units ($CO_2$ CPU) and the $H_2$ compressor. The ASU, $CO_2$ CPU and $H_2$ compressor have not been simulated in the Aspen Hysys model and specific energy consumptions from literature have been considered. A thermal efficiency of the whole plant has been defined to determine the optimum operating parameters of model as well as to evaluate the penalty associated the energy sinks mentioned.