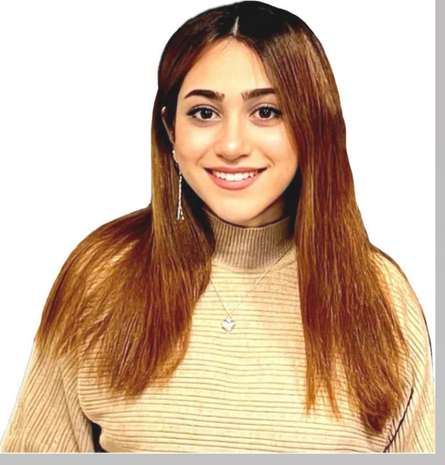

Thermodynamic Strategies for the Valorization of Steel Mill Gases: Pathways to Sustainable Methane Synthesis

Azita Etminan, Year 2 Ph.D.

Academic Supervisors: Professor Peter Holliman, Dr. Ian Mabbett

Industrial supervisor: Dr. Ciaran Martin, Tata Steel

Swansea University Prifysgol Abertawe | Steel and Metals Institute Sefydliad Dur a Metelau

Project Background

This research examines the transformation of CO and CO_2 from industrial gases (BFG, BOFG, COG) into valuable products, contributing to Carbon Capture and Utilization (CCU) efforts. Through carbon hydrogenation, it investigates producing methane, focusing on thermodynamic equilibrium analysis to optimize the process. The study employs the Gibbs free energy minimization method, highlighting the water gas shift reaction's role in converting CO to CO_2 and exploring dual hydrogenation processes for CO_2 methanation. It identifies optimal conditions for methane production and addresses the challenges, such as carbon formation, in applying CCU technologies.

Steelworks Gas composition

Table 1 shows dry composition of steel off-gas plant (ca. 6Mt/year). Direct carbon capture and utilization will use BFG, or BOFG COG as different feedstock alternatives to fossil fuel. The aim is to develop a novel processes which can reach high yields of valuable products to avoid CO_2 emissions whilst off-setting or exceeding production costs.

Table 1: Dry composition of steel off-gases.

%-vol	CO	CO_2	H_2	N_2	CH_4	O_2	CV (MJ/m^3)
BFG	22	23	5	50	-	-	4.2
COG	6	-	65	4	25	-	17
BOFG	75	19	-	5	-	1	9.5

Project goals

Process evaluation

- Thermodynamic feasibility investigation: Extracting thermodynamic data (Temp, Pressure, ΔG) for main and by-products reactions by HSC-Chemistry simulation.
- Parametric and lab aging studies: Flow rate, and feed gas composition for conceptual process optimization and process design

Catalyst material development, production, and testing

- • Manufacturing poison resistant and high activity catalysts for CCUS reactions.
- • Evaluating a highly efficient synthesis method for manufacturing at tonnage scale.
- • Laboratory apparatus set up.

Transformation of CO_2 into fuels

Fig .1 shows the Gibbs free energy versus temperature for different reactions towards CO &CO_2 utilization; syngas production, methanation, methanol synthesis and water gas shift reaction.

Fig. 1 shows how the Gibbs Free energy changes with temperature for different reactions.

Typically, a negative Gibbs free energy value suggests the spontaneous nature of a reaction. Accordingly, as depicted in Figure 1, the methanation of carbon dioxide is favored at temperatures less than or equal to 300 °C.

Moreover, considering the energy perspective, methane proves to be an excellent fuel, boasting a higher volumetric energy content than hydrogen, thus contributing to the reduction of greenhouse gas (GHG) emissions.

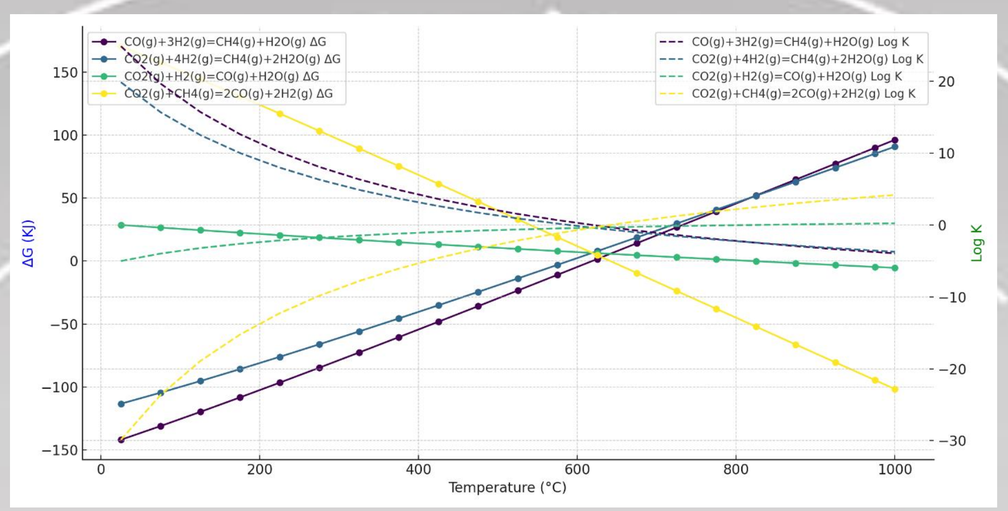

Fig .1: Reactions towards CO_2 utilization; ΔG VS Temperature- extracted by HSC-Chemistry.

CCUS reaction testing

All catalytic tests will carry out on a test rig set up at the Swansea University, SINTEC Lab (Fig. 2 below). The apparatus is designed
to work at temperatures up to 450 °C and pressures up to 10 bar. Two reactors will be set up to Take input gas feed and convert it into new products which will be analyzed by online GC.
Thermodynamic analyses of the WGS reaction and CO_2 hydrogenation are performed under diverse conditions, with an emphasis on using BFG, BOFG, and COG as inputs to meet the goals.

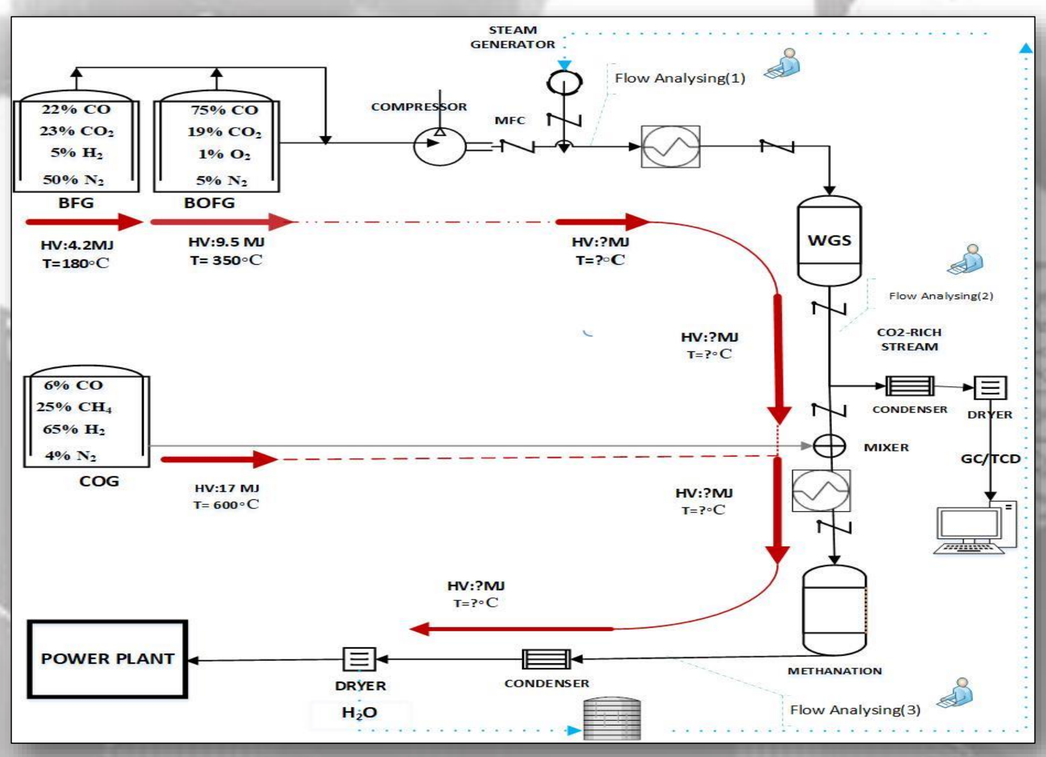

Fig .2: Possible reactor set up for CCUS testing.

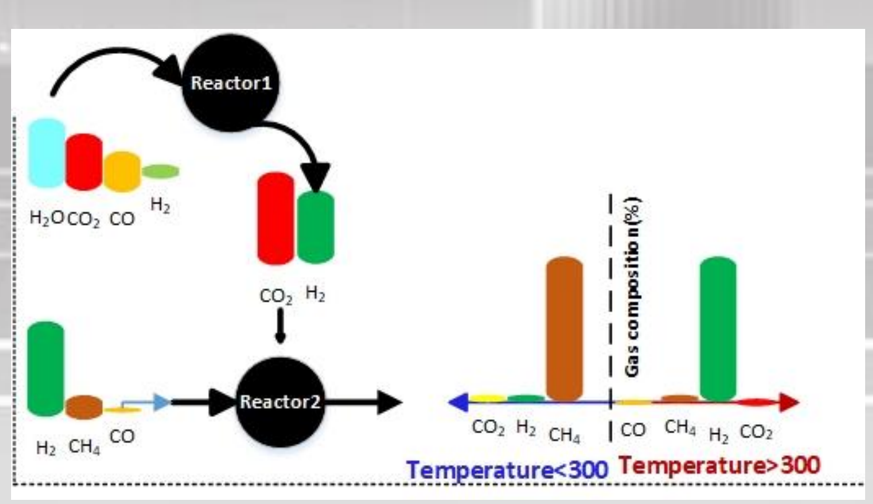

Fig .3: Possible products distribution for the simulated CCUS testing.

DATA Simulation by HSC-Chemistry

The HSC-Chemistry software serves as a robust simulation tool for predicting the input and output gas compositions of reactors in CCUS experiments. This involves leveraging the reaction equation and equilibrium composition features of HSC Chemistry for calculations. In this research, it was imperative to meticulously determine and outline the primary reactions expected to take place during the water-gas shift (WGS) and CO_2 hydrogenation processes. The analysis utilized the reaction equation and equilibrium composition functionalities within HSC Chemistry. The formula below is used to calculate the Gibbs free energy change ΔrGo (T) and the equilibrium constant Kp (T):

$$Kp = \exp\left(\frac{-\Delta rG(T)}{RT}\right)$$

$$\Delta rG°(T) = \Delta rH°(T) - T\Delta rS°(T)$$

$$\Delta rH°(T) = \Delta rHm(T) + \int_{298}^{T} \Delta rCp,m\,dT$$

$$\Delta rS°(T) = \Delta rSm(T) + \int_{298}^{T} \Delta rCp,m\,\frac{dT}{T}$$

- This research is exploring the spontaneous nature of reactions, as indicated by negative Gibbs free energy values. Specifically, the focus will be on conducting experiments to confirm that CO_2 methanation is most effective at temperatures of 300 °C or lower, as suggested by the simulation data. Additionally, parametric and lab aging studies, encompassing flow rate, feed/process gas composition, and heat balance, are explored for conceptual process optimization and design. This approach could be a game-changer in reducing industrial CO_2 emissions and advancing towards a more sustainable future.

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