Thermodynamic Approaches for Achieving Net Zero in Steel Mill Emissions: Methane Production via Sustainable Processes

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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.

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.

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.

BFG	COG	BOFG
22% CO	6% CO	75% CO
23% CO_2	65% H_2	19% H_2
5% H_2	25% CH_4	5% N_2
50% N_2	4% N_2	

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.

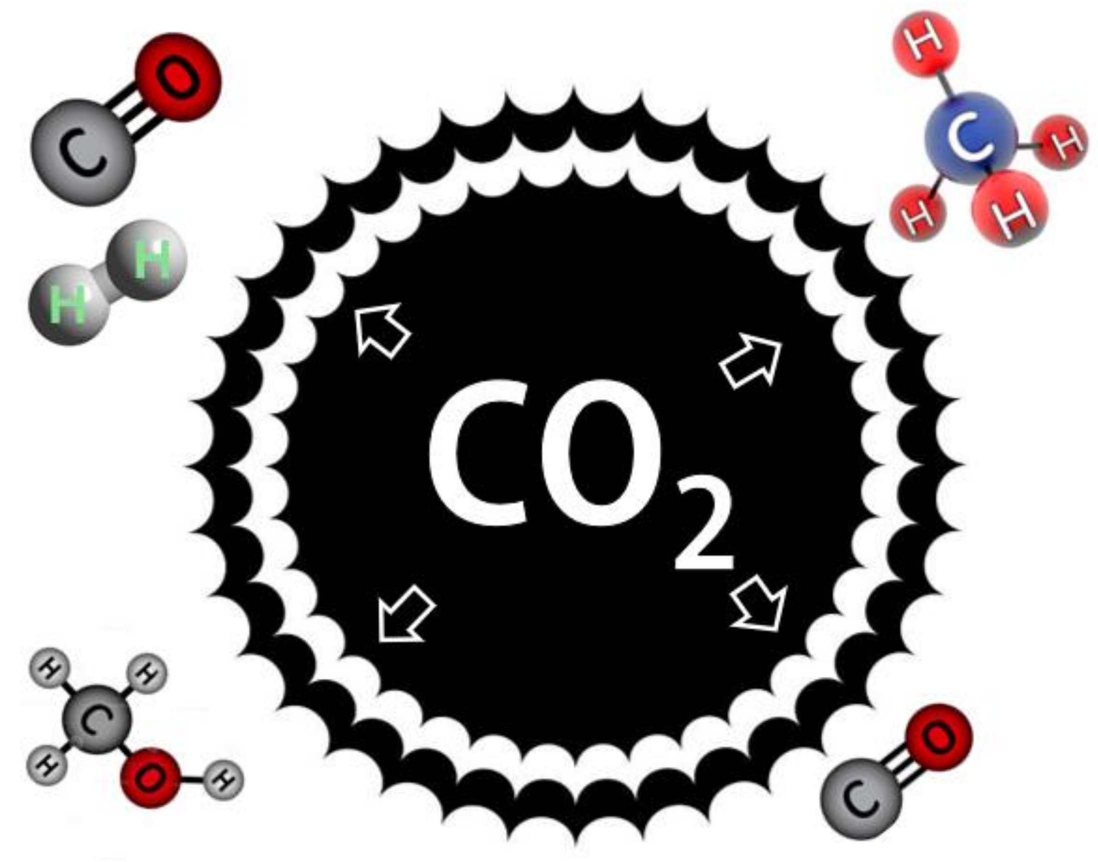

Fig .1: Reactions towards CO_2 utilization.

Fig .1 shows the different reactions towards CO &CO_2 utilization; syngas production, methanation, methanol synthesis and water gas shift reaction. Typically, a negative Gibbs free energy value suggests the spontaneous nature of a reaction which the methanation of carbon dioxide has the lowest ΔG and is favored at temperatures less than or equal to 300 °C. 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 $\Delta_r G^o$ (T) and the equilibrium constant Kp (T):

$$Kp = exp(\frac{-\Delta_r G(T)}{RT})$$

$$\Delta_r G^o(\boldsymbol{T}) = \boldsymbol{\Delta r H^\circ(T) - T\Delta_r S^\circ(T)}$$

$$\Delta_r H^\circ(T) = \Delta_r Hm(T) + \int_{298}^{T} \Delta_r Cp,mdT$$

$$\Delta_r S^\circ(T) = \Delta_r Sm(T) + \int_{298}^{T} \Delta_r Cp,m\frac{dT}{T}$$

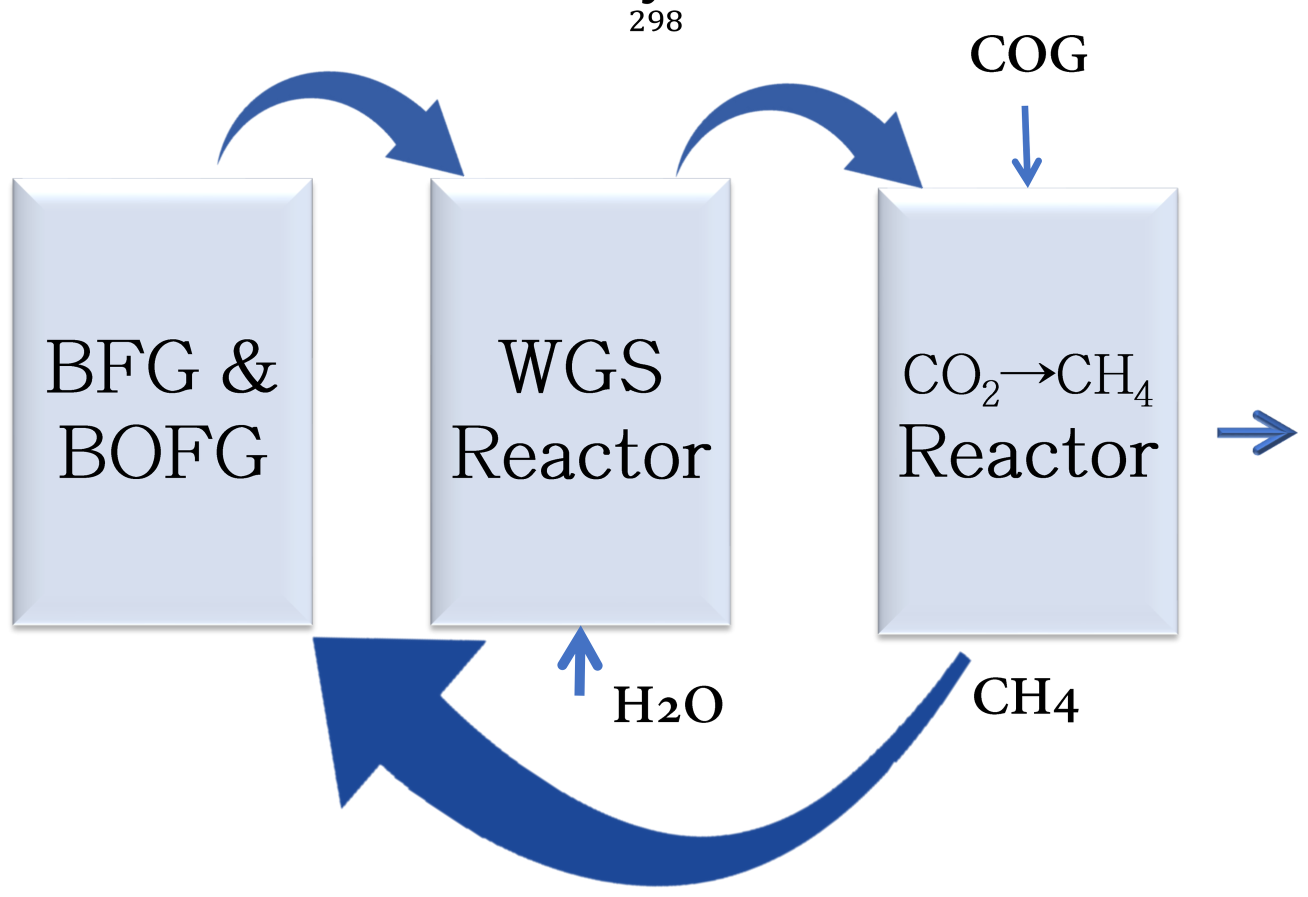

Fig .2: Possible reactor set up for CCUS testing.

CCUS reaction testing

All catalytic tests will carry out on a test rig set up at the Swansea University, SINTEC Lab (Fig. 2). 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.

Conclusion

Our simulation data indicates complete CO_2 conversion and high CH_4 yield(Figure 3) in optimized thermodynamic conditions. 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. This approach could be a game-changer in reducing industrial CO_2 emissions and advancing towards a more sustainable future.

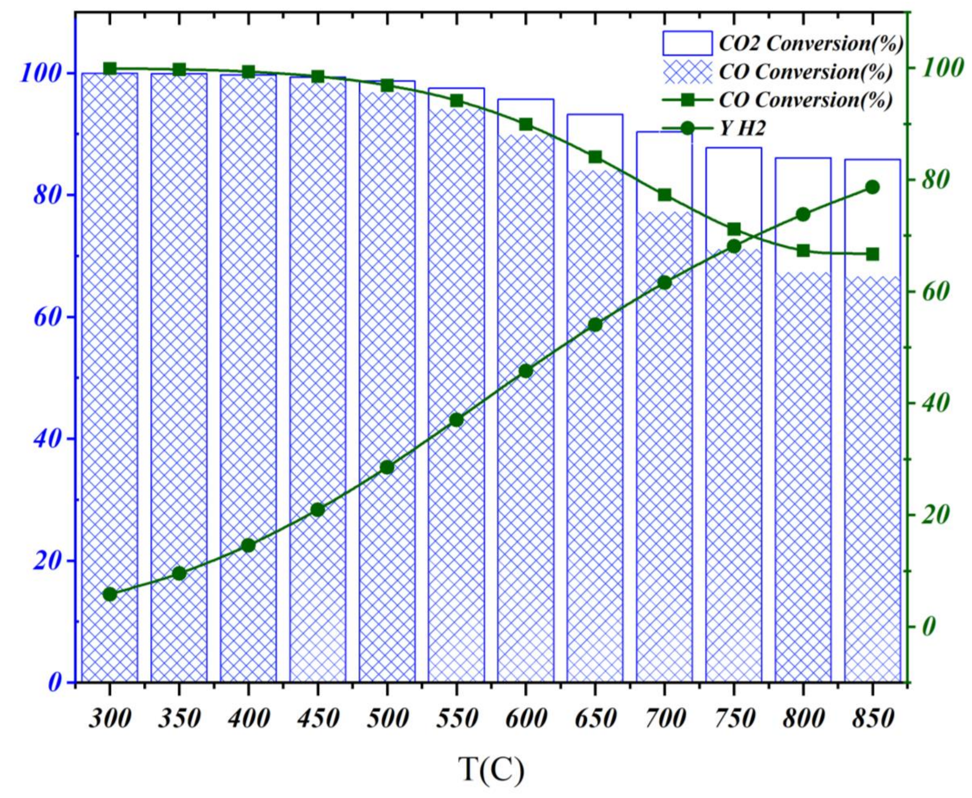

Fig .3: CO_2 & CO conversion and CH_4 yield vs Temperature.

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