Optimising Methanol Production from Steel Manufacture Off-gases

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Introduction

The iron and steel industry represents the largest energy consuming manufacturing sector in the world with average emissions 1.83 tonnes of CO_2 per tonne of steel. The enormous CO_2 footprint of steel mills, which accounts for 8 % of anthropogenic CO_2 emission, must be substantially reduced.

A unique feature of the current steel making processes is the presence of energy containing residual gases; Coke Oven Gas (COG), Blast Furnace Gas (BFG) and Basic Oxygen Furnace Gas (BOFG) (figure 1 and table 1). In modern efficient plants, these gases are often used as a fuel within the plant to produce power or combined heat and power. Otherwise, CO is converted to CO_2 by combustion at the mouth of the furnaces, and through flaring after gas cleaning in furnaces.

There is great interest in utilising by-product steel gases to produce high value chemicals such as methanol, instead of heat and power (figure 2). Minimising the cost and improving the performance of the methanol synthesis process integrated with a steel plant is key to establishing its viability.

This poster presents an overview of the new project for optimising methanol production from steel manufacture off-gas and through experimental analysis of catalytic reaction and the use of process simulation.

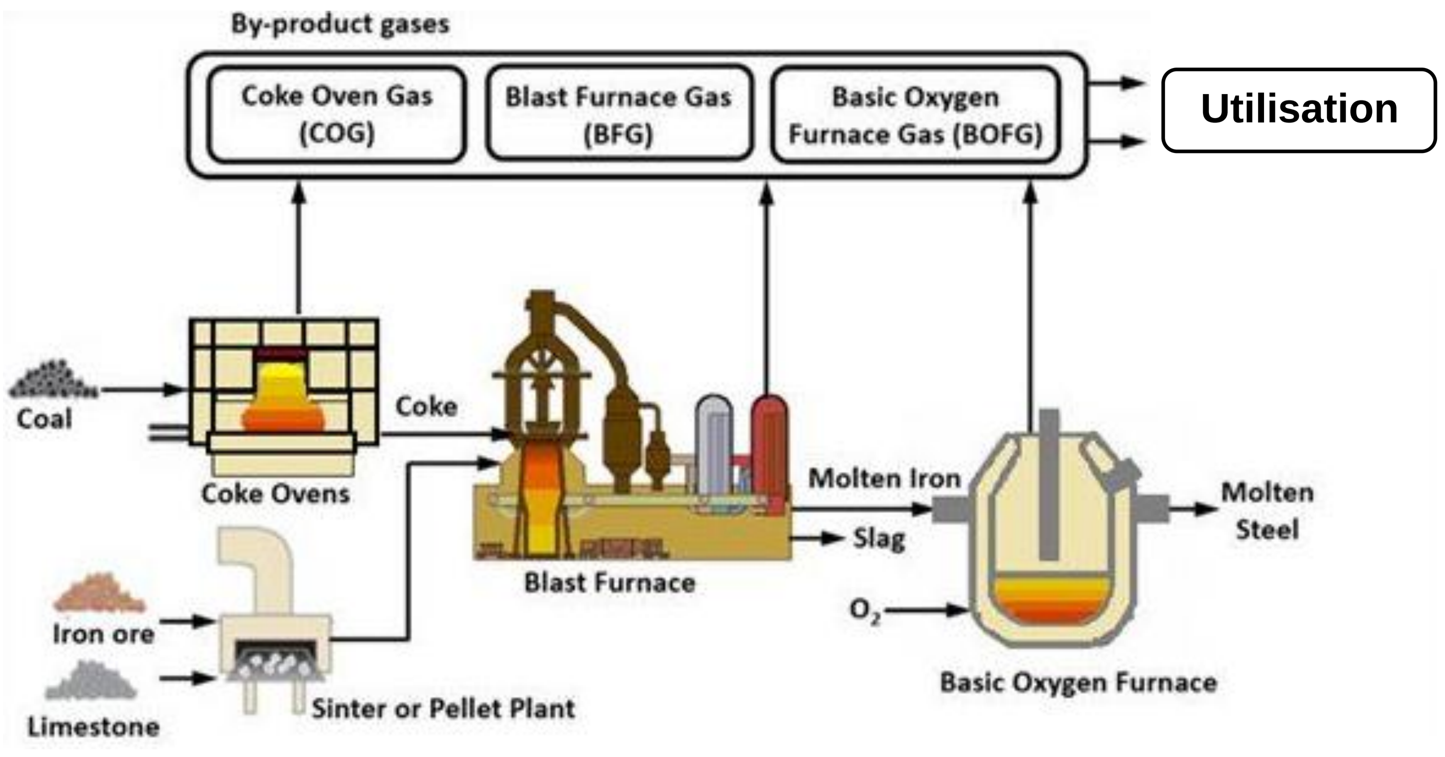


Figure 1. Schematic of steel making process and off-gas production [3].

Table 1. Steelworks off-gases properties.

	mol%		
Component	COG	BFG	BOFG
CO	6	20	58
CO_2	2	24	20
H_2	63	3	4
N_2	4	53	18
C_2H_6	3	0	0
CH_4	22	0	0
LHV (MJ/Nm^3)	17.5	2.85	7.6
Representative flowrate (kNm^3/hr)	40	366	28

Figure 3. The first Chinese COG-to-methanol plant Qujing City, Yunnan Province, 80 kt/a pure methanol, commissioned in 2006.

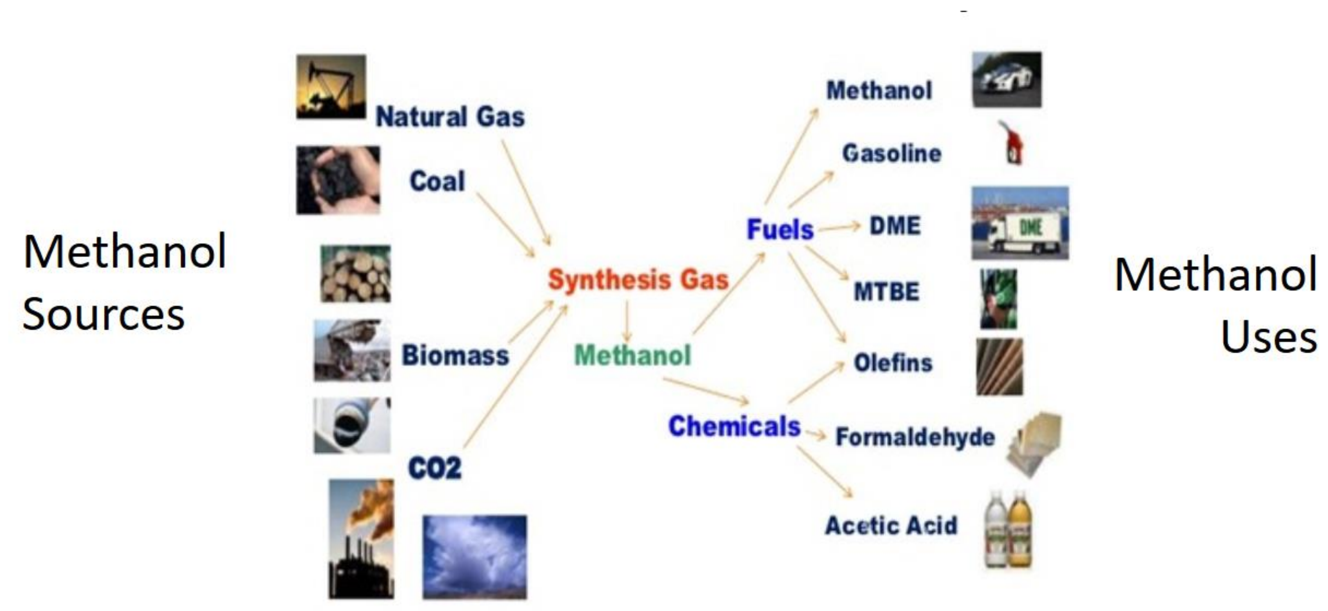


Figure 2. Sources and uses of methanol.

Figure 4. Methanol filling station, Aalborg, Denmark, opened in 2015.

Scientific and policy context

This project addresses the Priority Research Direction U1 “Valorizing CO_2 by Breakthrough Catalytic Transformations into Fuels and Chemicals” a key recommendation of the Mission Innovation - Carbon Capture Innovation Challenge through the substantial reduction of the cost of CO_2 utilisation [1].

The proposal is also aligned with the development of an anchor CCUS project, i.e. linking Tata Steel’s Port Talbot works with other South Wales industrial emitters, as outlined in the Carbon Capture Utilisation Cost Challenge Taskforce [2].

While carbon capture and utilisation (CCU) options may present a more modest contribution to achieving global CO_2 emission mitigation targets compared to permanent geological storage, there may be reasonable prospects in areas without readily available access to CO_2 storage sites

Project objectives

1. To investigate the effect of feed gas $CO/CO_2/H_2$ ratio and stream impurities relevant to residual steel gases including N_2, Ar, CH_4 NH_3 & H_2O on the methanol production process using selected catalysts
2. To study catalyst degradation, including morphology and composition following exposure to the BFG reaction environment using a range of analytical techniques
3. To construct and validate a catalytic reaction mechanism describing methanol synthesis from BFG
4. To assess the impact of catalyst and chemical reactor selection on methanol synthesis from BFG
5. To perform techno-economic simulations for assessing the cost of methanol production from BFG

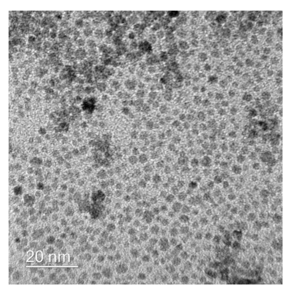
Experimental work

- Current work at UCL investigates methanol synthesis using novel Cu/CeO_2 and Cu/SiO_2 catalysts, as well as conventional $Cu/ZnO/Al_2O3$
- Novel catalysts can offer improved conversion and selectivity at higher CO_2 concentration
- **Fabrication method:** CeO_2 suspended in liquid and $Cu(NO_3)_2$ added, $NaNO_3$ added to cause precipitation and Cu^{2+} bonding to CeO_2 substrate.
- A range of analytical techniques can be applied to catalysts before and after reaction exposure: TEM, XPD, XPS, XAS, EPR

CeO_2 Nano-Spheres

1. (2g sodium acetate +2ml acetic acid) dissolve in 10ml water
2. 5ml $(NH_4)_2Ce(NO_3)_6$ dissolved in 1
3. Stirred for 10 min.

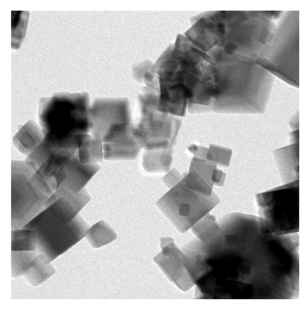
30min Air 0 bar



CeO_2 Cubes

1. 3ml of 0.2mol/L $Ce(NO_3)_3$+12ml of 9mol/L NaOH

24h Air 0 bar



50 – 100 nm

Experimental set-up

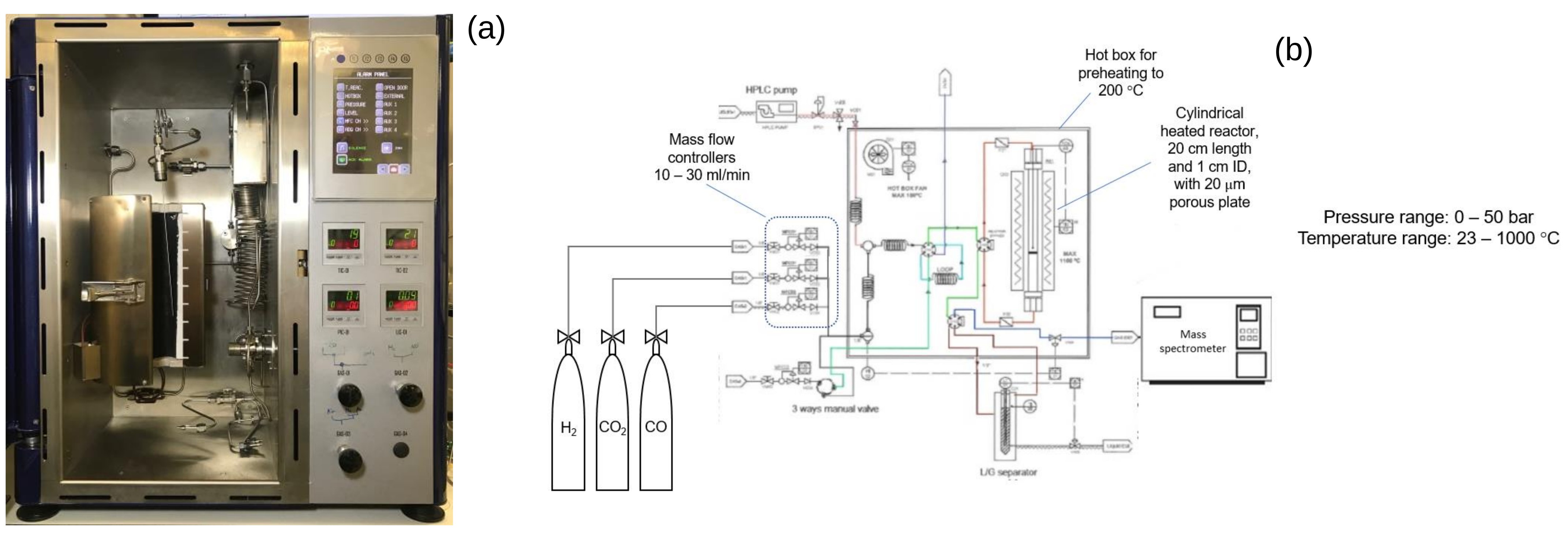


Figure 5. Microactivity reactor for real-time, in process activity and selectivity measurements of catalysts for methanol production; (a) photograph and (b) schematic diagram.

Methanol synthesis

Main catalytic reactions

Hydrogenation of carbon monoxide

1. $CO + 2H_2 \rightleftharpoons CH_3OH$ $\quad \Delta H_R$ = -90.55 kJ/mol

Hydrogenation of carbon dioxide

2. $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$ $\quad \Delta H_R$ = -49.43 kJ/mol

Reverse water-gas shift

3. $CO_2 + H_2 \rightleftharpoons CO + H_2O$ $\quad \Delta H_R$ = +41.12 kJ/mol

Favourable feed gas composition using conventional catalyst $Cu/ZnO/Al_2O_3$

4. $\dfrac{H_2 - CO_2}{CO + CO_2} \approx 2.1$

5. $\dfrac{H_2}{CO} = 2.4 - 2.5$

6. $\dfrac{CO_2}{CO} = 0.13 - 0.14$

Process modelling

Work-plan

- Development of process flowsheets involving conversion of BFG to methanol
- Calculation of process economics.
- Sensitivity analysis and optimisation.
- Testing of current reaction kinetics models and their extension to other catalysts.
- Detailed reactor modelling studies

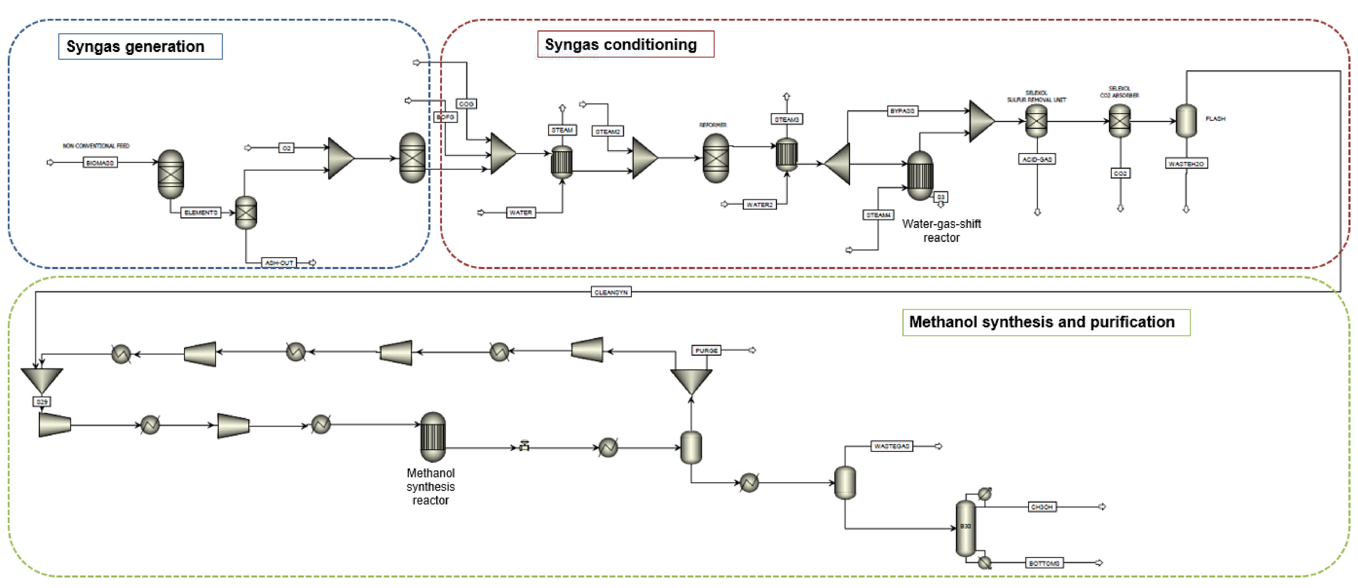


Figure 6. Example Aspen flowsheet for methanol production from COG, BOFG and Biomass.

Acknowledgements

This work is supported by the UK CCS Research Centre through the 2018 Flexible Funding Call. In-kind contributions from Tata Steel UK, Swerim AB and Johnson Matthey are gratefully acknowledged.

References

[1] Accelerating Breakthrough Innovation in CarbonCapture, Utilization, and Storage. Report of the Mission Innovation CarbonCapture, Utilization, and Storage Experts’ Workshop. Available online at: https://www.energy.gov/fe/downloads/accelerating-breakthrough-innovation-carbon-capture-utilization-and-storage

[2] https://www.gov.uk/government/groups/ccus-cost-challenge-taskforce

[3] W. Uribe-Soto, J.F. Portha, J.M. Commenge, L. Falk. A review of thermochemical processes and technologies to use steelworks off-gases. Renewable and Sustainable Energy Reviews 74 (2017) 809–823