

Novel process design and techno-economic simulation of methanol synthesis from blast furnace gas in an integrated steelworks CCUS system

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ABSTRACT

A novel process design and techno-economic performance assessment for methanol synthesis from Blast Furnace Gas (BFG) is presented. Methanol synthesis using BFG as a feedstock, based on direct CO₂ hydrogenation at commercial scale was simulated using Aspen Plus software to evaluate its technical performance and economic viability. The applied process steps involve first conditioning BFG using adsorption based desulfurisation, water-gas shift, dehydration, then separation of components into N₂, CO₂ and H₂ rich streams using pressure swing adsorption. The H₂ stream and a fraction of the CO₂ stream are fed to a methanol synthesis system, while the remaining CO₂ may be considered for geological storage in a Carbon Capture, Utilization and Storage (CCUS) case, or not in a Carbon Capture Utilization (CCU) case. Techno-economic analysis confirms methanol production from BFG is economically attractive under certain conditions, with Levelized Cost of Methanol production (LCOMeOH) calculated to be 344.61 £/tonne-methanol, and costs of CO₂ avoided of – 20.08 £/tonne-CO₂ for the CCU process and 9.01 £/tonne-CO₂ for the CCUS process when using a set of baseline engineering assumptions. Sensitivity analysis of the process simulation explores opportunities for optimising the methanol synthesis system in terms of the impact of reactor size and/or recycle ratio on LCOMeOH. Economic viability of the CCU(S) processes is also found to be highly dependent on the cost of the feedstock BFG. Future cost savings as compared to business-as-usual steel production by 2030 in consideration of expected increases in the carbon price are estimated to be 10.59 £/tonne-steel for CCU and 24.61 £/tonne-steel for CCUS.

1. Introduction

The iron and steel industry represents the largest energy consuming manufacturing sector in the world, with average specific emissions being 1.83 tonnes of CO₂ per tonne of steel and global crude steel production reaching 1.8 Gt for the year 2018, up by 4.6 % compared to 2017 [1]. The enormous CO₂ footprint of steel production, which accounts for between 7 % and 9 % of anthropogenic CO₂ emissions [2] must be substantially reduced. Around 70 % of the steel produced nowadays is obtained via the combined Blast Furnace - Basic Oxygen Furnace (BF-BOF) route, with more than 90 % of the CO₂ emissions coming from three by-product gases; i.e., BFG, Coke Oven Gas (COG) and Basic Oxygen Furnace Gas (BOFG) and sinter production [3]. Although steel-making energy intensity has been reducing through energy efficiency, process optimization and fuel substitution measures, such innovations can only lead to a reduction of around 15 % in CO₂ emissions. Other alternative processes, such as Direct Reduced Iron (DRI) using natural

gas or electric arc furnaces are only applicable for certain types of steel and can only reduce emissions by 25 %. The hydrogen based DRI approach can only achieve efficient emissions reduction when large amounts of renewable electricity are made available to the steel industry [4].

Carbon Capture, Utilization and Storage (CCUS) has the potential to achieve a more drastic and feasible reduction of CO₂ emissions from the iron & steel industry needed to achieve net-zero emissions targets. A broad range of CCUS technologies have been proposed to target gas streams in the iron and steel industries [5–8] which are currently under development at different Technology Readiness Levels (TRLs). Emerging CO₂ capture technologies for iron and steel application are based on post-combustion, pre-combustion or top gas recycle concepts, encompassing advanced solvents [9–11], membranes [12], new solid sorbents for Pressure Swing Adsorption (PSA)/Vacuum Pressure Swing Adsorption (VPSA) [13] and calcium looping [14]. Issues regarding stability of functional materials (under real industrial conditions), the role and fate

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of impurities, environmental impacts (e.g. fugitive emissions other than the CO₂), retrofitability of existing steel mill plants, energy consumption (and nature of such energy; i.e. electricity vs thermal) need rigorous quantitative estimation.

Given that BFG represents the greatest volumetric flow on a steelworks, it is hence a particular focus of attention for CCUS applications. BFG has low calorific value ($\sim 3.5 \text{ MJ/m}^3$) consisting mainly of $\sim 55 \text{ vol} \% \text{ N}_2$, $\sim 21 \text{ vol} \% \text{ CO}_2$, $\sim 21 \text{ vol} \% \text{ CO}$ and $\sim 3 \text{ vol} \% \text{ H}_2$. Along with the other off-gases, BFG is currently used as a fuel gas on a typical steelworks for reheating purposes and in combined heat and power plants; otherwise, it is flared after gas cleaning. The combustion of low calorific value BFG for generating heat and power is known to be highly inefficient with carbon intensities being 6 times higher than the European average [4]. In addition to applying conversion and capture processes to separate CO₂ for permanent geological storage to reduce steel's CO₂ intensity, there is currently great interest in using by-product steel gases to produce high value commodity chemicals instead of power and heat [6]. Steel industry operators view such Carbon Capture and Utilization (CCU) applications as commercially attractive because they could provide additional revenue streams that may lower the overall costs of CO₂ mitigation.

Methanol is a particularly attractive candidate for steel off-gas valorisation given its suitability as a transition fuel, with 31 % of the 98 Mt of current global demand being used in fuel applications. 65 % of methanol produced today is however used as a precursor for the production of other chemicals such as formaldehyde and acetic acid or more recently in the MTO process to produce olefins such as ethylene and propylene. Such secondary chemicals are then used to produce a vast range of plastics, resins, along with construction and other materials for everyday use [15]. Some material applications of methanol may represent a pathway for long term sequestration of CO₂ in consideration of the natural degradation half-lives for some plastics which range from centuries (e.g. ~ 250 years for land buried HDPE bottles) to millennia (e.g. ~ 5000 years for HDPE land buried pipes) [16]. Recently, a framework for assessing the compatibility of CO₂ utilization products was proposed by de Kleijne et al. [17] based on the CO₂ source (i.e. fossil, atmospheric or biogenic), TRL and 'CCU lifetime'. Despite the mitigation potential of long lived CO₂ sink materials, their environmental proliferation and potential for circularity must be seriously taken into consideration. In 2005, the Nobel Prize laureate, George Olah, proposed a future methanol economy as an alternative to the hydrogen economy [18]. Proponents of a methanol economy point to the cheapness of production, fuel safety due to low volatility, low toxicity and rapid biodegradation if spilled in the environment, ease and economy of storage compared to compressed hydrogen and the ability to quickly integrate use and distribution with existing infrastructure. Methanol production therefore presents one of the few opportunities for utilization of CO₂ and industrial off-gases where there is sufficient market demand given the diverse range of its applications.

Conventional methanol production is based on generating industrial syngas, comprising varying amounts of H₂, CO and CO₂, obtained via coal gasification and/or natural gas reforming. The CO and CO₂ components undergo hydrogenation reactions to produce methanol typically over CuO/ZnO/Al₂O₃ commercial catalysts [19]. Some of the earliest commercial methanol production processes from the 1920s to 1940s were based on direct catalytic hydrogenation using CO₂ obtained as a by-product of fermentation [20] and other processes [21]. In recent years, there has been an increasing interest in methanol production from steel off-gases [22–28] and other forms of CO₂ utilization based methanol production such as power-to-X [29–33]. These studies in the main consider enrichment of (blended) steelworks off-gases with hydrogen or biomass derived syngas in order to enable methanol synthesis. Indeed, methanol production from steelworks off-gases has been considered since the early 80s [34]. Commercial technology to produce methanol from COG already exists and has progressed particularly in China. In 2019, COG accounted for 17 % of feedstock for Chinese methanol

production [35]. Given the composition of BFG and the stoichiometry of methanol synthesis, adding H₂ from a suitable source [27] or separating some CO/CO₂ are necessary steps for achieving a viable process route, while some designs consider removal of N₂ as an inert impurity in high concentration for improving the process. Recent research in the FResMe project [36], demonstrated a whole process that enables CCUS in the steel industry involving improved methanol production for use as a marine fuel, by integrating the Sorption Enhanced Water Gas Shift (SEWGS) CO₂ capture technology.

Given that many future routes to alternative methanol production will be based on the direct CO₂ hydrogenation route, Lurgi have recently developed suitable high activity catalysts for this process [37]. The Icelandic company Carbon Recycling International produces methanol with Lurgi processes, using CO₂ extracted and purified from the flue gases of a nearby geothermal power plant and hydrogen obtained by alkaline water electrolysis using renewable electricity. This industrial scale plant has been operating since 2012 and has a capacity of 4000 tonnes methanol/yr [38]. This process exhibits a number of advantages over the conventional syngas route. Synthesis reaction impurities (typically higher alcohols, esters, ethers and ketones) are limited to water and dissolved CO₂ in crude methanol, which then allows for use of a single methanol distillation unit. A less intense exotherm is experienced in the reactor unit compared to the syngas reaction; which allows the use of a tube cooled reactor with lower cost, higher efficiency and relative simplicity of operation, while avoiding the use of multiple reactors in series, which may be required with adiabatic or cold-shot reactors to achieve suitable conversions. An improved heat distribution within the methanol reactor also helps to prevent catalyst sintering. The process based on direct CO₂ hydrogenation also has some disadvantages as compared to the conventional process which include larger reactor sizes due to CO₂-syngas being less reactive than CO-syngas and greater by-product water production due to the reaction stoichiometry.

This paper presents the development of the preliminary design and process simulation of a BFG-to-methanol process based on direct CO₂ hydrogenation with or without additional compression, transport and storage of excess CO₂. The process route considered in the present work is based on the application of CCUS to BFG alone (i.e., pre-conditioning steps integrated with CO₂ capture and storage are applied to achieve the stoichiometric ratio of H₂/CO_x necessary for methanol synthesis). Technology with TRL high enough to be feasibly deployed by the early 2030s is selected. The study also aims to achieve a high overall carbon mitigation rate from the targeted BFG through methanol synthesis, CO₂ storage and process integration based on stream recycling while applying insights gleaned from operational experience in BFG conditioning and separation, and methanol synthesis and purification when using CO₂ as a feedstock. The study also holds relevance to hydrogen production from BFG. The process has been developed using Aspen Plus V10 process simulation software for calculation of the mass and energy balances required to assess the technical viability. Integrating the mass and energy balances with engineering cost models allowed for the further assessment of the process's techno-economic viability in light of process capital costs, the operating costs, including feedstock costs, and the current market selling price of methanol. Sensitivity analysis is applied around the methanol synthesis system in terms of reactor size and recycle ratio in order to determine most cost-effective system parameters through assessment of the LCOMeOH and CO₂ Avoidance Cost (CAC). The advantages of implementing such a process in view of future carbon pricing is also assessed by comparing CCU and CCUS options to the business-as-usual case and assessing the impact on the cost of steel production.

2. Methodology

This investigation entails a modelling study needed to understand the fundamentals of the BFG-to-methanol process and to investigate the overall process economics. The utilised techniques and assumptions are

described in the following sections.

2.1. Basis of calculation and system boundaries

In the present work, a gas conditioning system and methanol production plant were considered based on 265 kN m³/h of BFG, equivalent to 340 tonne/h, being available for CCU(S). This is premised on diversion of the BFG ordinarily destined for the power plant in a typically sized BF-BOF integrated steelworks [39]. How the energy that would have been generated using this amount of BFG as a fuel source is replaced will have implications for the system environmental and techno-economic metrics, where options include the use of renewables (e.g. wind or solar) and potential energy generation efficiency improvements. The technical and economic performance of the BFG-to-methanol process is assessed as represented in Fig. 1. The process modelling focusses on a gas conditioning and separation system along with a methanol synthesis and distillation system. In the economic analysis, the cost of BFG and value of product methanol along with possible costs of CO₂ disposal through compression, transport and geological storage are assumed. Steam which is consumed by the process is considered to be raised from waste heat in the core iron and steel-making industrial processes and is part of the economic assessment but not directly simulated. Electricity consumed by process operations is assumed to come from an external source with appropriate costs attributed.

2.2. BFG-to-methanol process design and simulation

In this work, a BFG-to-methanol plant was simulated using Aspen Plus V10 based on the process flow diagram presented in Fig. 2. The process route was selected based on recommendations available in the literature about various aspects of conditioning BFG and methanol synthesis using either industrial syngas or CO₂ + H₂. Unit operations were selected with high enough TRL to be deployable at scale prior to 2030.

BFG exiting the primary and secondary gas cleaning systems typically present on a steelworks, contains 5–15 ppm_v of sulfur species, comprising a mixture of H₂S and COS. The sulfur content of BFG needs to be minimised to protect downstream catalysts for chemical processing applications. For fuel production or chemical production using syngas, the downstream synthesis catalyst sulfur tolerance dictates the required level of sulfur removal. For certain applications such as Fischer-Tropsch

(FT) synthesis using Co or Fe based catalysts, Tijmensen et al. [40] report H₂S + COS tolerance of below 0.01 ppm, while Boerrigter and Uil [41] report a total sulfur tolerance of below 1 ppm. Cu based catalysts for methanol synthesis generally have slightly higher tolerance to sulfur poisoning compared to those used for FT [42]. A range of technologies exist for desulfurisation of industrial gases, which include wet scrubbing or dry adsorption. Examples of wet scrubbing based on physical absorption are the Rectisol process, which uses refrigerated methanol as a solvent, and the Selexol process using a solvent comprising a mixture of dimethyl ethers of polyethylene glycol. These processes are complex, characterised by high costs and therefore mainly used at large-scale for streams with high H₂S concentrations [43]. Typical examples for dry processes are the adsorption of H₂S on ZnO or removal of impurities by activated carbon. Dry processes are used presently for low inlet concentrations (normally < 50 ppm) and can be commonly found in industry, e.g. refineries, as guard beds. In particular, ZnO is a widely used adsorbent for H₂S removal from gas streams such as natural gas or syngas at mid to high temperatures (200–450 °C) [44]. Current research investigates regeneration of ZnO sorbents by flushing with air or dilute O₂ but a characteristic of dry adsorption processes is that the used adsorbent is spent after use and has to be disposed of or requires reprocessing for recycling. ZnO adsorption is selected as the desulfurisation technique in the present flowsheet (Fig. 2).

In the present process, BFG is compressed up to 6 bar and sulfur compounds are removed by adsorption using ZnO. The BFG is pre-heated and steam is added before it undergoes the Water Gas Shift (WGS) in a conventional two-stage process consisting of a high-temperature shift (operating at 300–436 °C, 6 bar) and a low-temperature shift (200 °C, 6 bar), in both of which, the following WGS reaction takes place:



The first step is catalysed by an iron oxide/chromium catalyst whereas in the second stage it is promoted by using a catalyst based on Cu/ZnO (Al₂O₃). A major limitation of Fe-based HTS catalysts is their low volumetric activity. As such, the CO conversion generally does not reach equilibrium under HTS conditions. This therefore requires that the HTS catalyst be operated in the kinetic rather than equilibrium regime in order to avoid excessive catalyst bed volume [45]. However, the WGS is slightly exothermic and, as such, the equilibrium conversion increases with decreasing temperature, where complete CO conversion is possible at lower temperatures of around 200 °C [46]. Thus, the thermodynamic

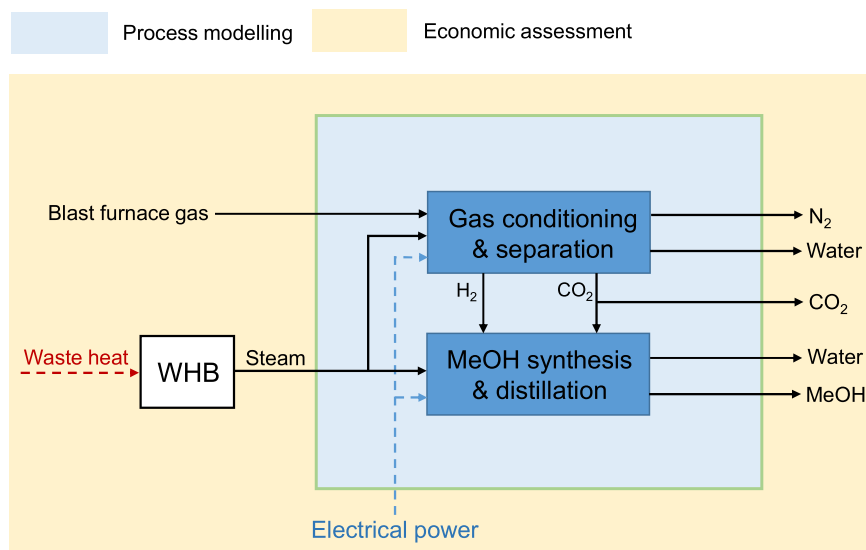


Fig. 1. System boundary of the BFG-to-methanol CCU(S) plant (green line). Blue section represents the part considered for process modelling; yellow part represents the part considered for economic assessment; WHB: Waste Heat Boiler.

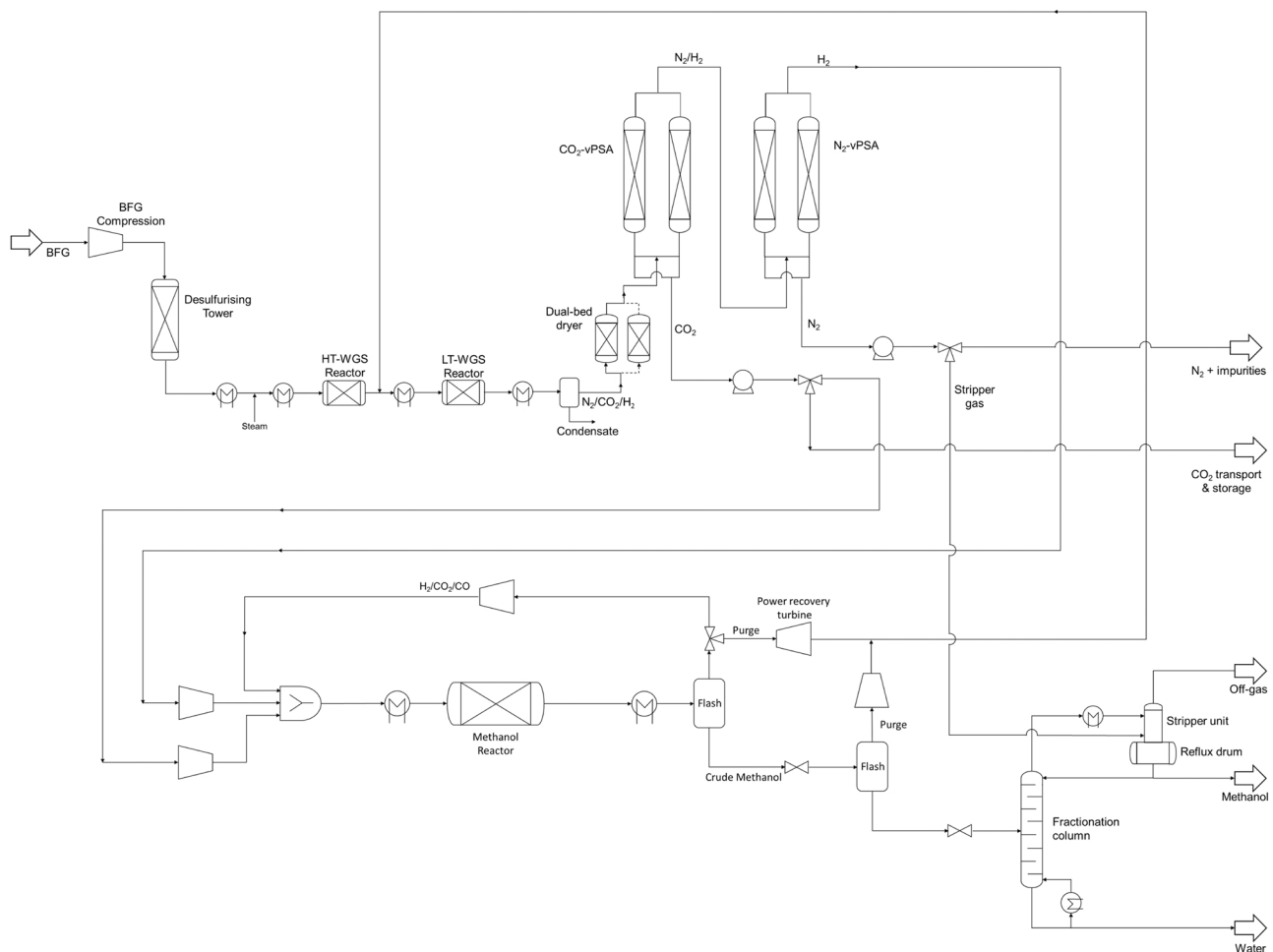


Fig. 2. Process flow diagram for the BFG-to-methanol process by direct CO₂ hydrogenation.

equilibrium limitation can be overcome by using the second step WGS at low temperatures (LT-WGS). For these reasons, a Plug Flow Reactor (PFR) module considering reaction kinetics is selected to model the HT-WGS while the LT-WGS maybe more simply approximated using an equilibrium reactor model. The H₂O: CO ratio at the HT-WGS inlet is 2.3, which is high enough to suppress methanation reactions [47]. The HT-WGS reactor was simulated using the kinetic model derived by Hla et al. [48], represented by Eqs. (2)–(3):

$$\log_{10}K = -2.1498 + 0.0003855T + \frac{2180.6}{T} \quad (4)$$

Eqs. (2)–(4) were implemented in Aspen Plus, by using the recast parameters provided by Patra et al. [50] that are accepted by the formalism in the software's framework.

Due to the presence of steam in the second WGS reactor effluent, an aqueous phase (condensate) condenses out of the cooled shift converted

$$r = 10^{0.659 \pm 0.0125} \exp\left(\frac{-88 \pm 2.18}{RT}\right) P_{CO}^{0.9 \pm 0.041} P_{H_2O}^{0.31 \pm 0.056} P_{CO_2}^{-0.156 \pm 0.078} P_{H_2}^{-0.005 \pm 0.006} (1 - \beta) \quad (2)$$

where r is the rate of the WGS reaction ($\text{mol g}_{\text{cat}}^{-1} \text{s}^{-1}$), P_{CO} , P_{H_2O} , P_{CO_2} and P_{H_2} are the respective partial pressures of CO, H₂O, CO₂ and H₂ (kPa), R is the Universal Gas Constant ($\text{kJ mol}^{-1} \text{s}^{-1}$), T is temperature (K), and β is the approach to equilibrium as defined by:

$$\beta = \frac{P_{CO_2} P_{H_2}}{K P_{CO} P_{H_2O}} \quad (3)$$

where K is the equilibrium constant and can be calculated using the following correlation given by Callaghan [49]:

BFG stream. The condensate is separated from the cooled shift converted BFG stream in a condensate drum. After removal of condensate, the shift converted BFG stream is passed to a drying system for dehumidification by contact with silica-alumina gel. WGS of BFG is advantageous in the context of downstream separation because the elimination of CO from gas mixture removes the need for the difficult CO/N₂ separation which is a well-known bottleneck in gas processing; however, a disadvantage is that some energy will be lost in the WGS process. The shift converted and dried BFG stream containing mostly N₂, CO₂ and H₂ is next separated mainly into separate components to a certain degree of purity, but each still containing some impurities, using a two-stage VPSA system. In the first stage separation, CO₂ is mainly adsorbed onto a sorbent at

pressure while the remaining $N_2 + H_2$ mixture passes through the system. Once the sorbent has reached capacity for adsorbed CO_2 , feed to the system ceases and the CO_2 is desorbed under reduced pressure. The second stage system similarly separates H_2 and N_2 by adsorption/desorption of N_2 . The CO_2 stream leaving the PSA system is divided into two streams. The larger CO_2 stream (approximately 75 %) is compressed and transported to geological storage via pipeline (note that the CO_2 compression and storage system is considered beyond the battery limit in the present study). The smaller CO_2 stream is used as a feedstock to the methanol synthesis area of the plant along with the H_2 stream leaving the second PSA stage. The N_2 stream exiting the VPSA system is considered for further use as a sparging gas in the methanol purification section and potentially for other uses in the steelworks. The PSA system was modelled using the simple SEP Aspen Plus unit and based on the performance data for BFG separation available from the Course50 project [13] and that of water gas shifted biomass derived syngas [51]. The CO_2 PSA system was based on the use of the sorbent Zeolum F-9H, achieving a desorbed CO_2 purity of 96 vol% and CO_2 recovery of 80 %. The N_2/H_2 PSA towers are similarly sized, with a 4 unit system and use CaX sorbent with an assumed H_2 purity of 99.99 vol% and H_2 recovery of 85 %.

In the methanol synthesis section of the plant, the feed gases are compressed up to the reactor feed pressure using several compression stages with intercooling. The pressurised feed is then heated and fed to the reactor where methanol is synthesised over a commercial Cu/ZnO/ Al_2O_3 catalyst. The CO_2 hydrogenation reaction (5) and the Reverse Water Gas Shift (RWGS) reaction (6) are considered to occur in the methanol synthesis reactor:



The methanol synthesis reactor is modelled as a PFR using the Langmuir-Hinshelwood-Hougen-Watson (LHHW) expression to calculate the reaction rate constants r_{MeOH} and r_{RWGS} ($kmol\ kg_{cat}^{-1}\ s^{-1}$) for the CO_2 hydrogenation reaction (6) and the RWGS reaction (7), respectively:

$$r_{MeOH} = k_{MeOH} \frac{(p_{CO_2} p_{H_2}) - (1/K_{pMeOH})(p_{CH_3OH}/p_{H_2})}{\left(1 + K_a(p_{H_2O}/p_{H_2}) + K_b\sqrt{p_{H_2}} + K_c p_{H_2O}\right)^3} \quad (7)$$

$$r_{RWGS} = k_{RWGS} \frac{p_{CO_2} - (1/K_{pRWGS})(p_{CO} p_{H_2O}/p_{H_2})}{\left(1 + K_a(p_{H_2O}/p_{H_2}) + K_b\sqrt{p_{H_2}} + K_c p_{H_2O}\right)} \quad (8)$$

where k_i are the kinetic factors ($kmol\ kg_{cat}^{-1}\ s^{-1}\ Pa^{-1}$) or ($kmol\ kg_{cat}^{-1}\ s^{-1}\ Pa^{-1}$), K_{pi} are the equilibrium constants (dimensionless or Pa^{-2}) calculated using expressions provided by Graaf et al. [52], and $K_{a/b/c}$ are the adsorption constants (Pa^b). Additionally, the kinetic pre-factor needs to be presented in the form of Eq. (9) and the other terms need to be adapted into the form of Eq. (10).

$$k_i = k_{i,0} \exp\left(-\frac{E_i}{RT}\right) \quad (9)$$

$$\ln K_i = A_i + \frac{B_i}{T} \quad (10)$$

The reaction rate parameters provided by Vanden Bussche and Froment [53] with the unit conversions provided by Lücking for these and the equilibrium constant expressions [54] are implemented in the Aspen Plus model.

The effluent from the reactor section undergoes phase separation where the reaction products are condensed using a cooler and settled in a flash vessel while the unreacted gases are recycled, pressurised and mixed with the reactor feed. Part of the unreacted gas stream is purged

in order to prevent the accumulation of impurities in the system. Methanol is separated from water in a distillation column. The H_2O-CH_3OH distillation column in the Aspen Model flowsheet is modelled using the Winn-Underwood-Gilliland method based DSTWU module and the design parameters suggested by Pérez-Fortes et al. [32] as a first attempt with the addition of an N_2 sparging vessel to assist in the removal of excess CO_2 in solution from the methanol product. More rigorous calculations can be performed using the RadFrac module for carrying out equilibrium-stage and hydraulics modeling. Other operations in the Aspen Plus flowsheet, such as compressors, heat-exchangers and flash vessels were modelled using the standard available modules. The SRK property model is the recommended model for this system [55] because methanol production takes place above 10 bar pressure. The free water method STEAMNBS was also selected.

The overall energy efficiency of the process was calculated as defined in Eq. (11):

$$\eta = \frac{\dot{m}_{CH_3OH} LHV_{CH_3OH} + Q_{>200^\circ C} + E_{TUR}}{\dot{m}_{BFG} LHV_{BFG} + \dot{m}_{STEAM-WGS} C_{ps} + Q_{HEAT} + E_{COMP} + E_{VAC}} \% \quad (11)$$

where \dot{m}_{CH_3OH} , \dot{m}_{BFG} and $\dot{m}_{STEAM-WGS}$ are the flowrates of methanol, BFG and steam supplied to the WGS reactor, respectively, while $Q_{>200^\circ C}$ and Q_{HEAT} are the recoverable heat and heat supplied to heaters in the process (including the reboiler), respectively, E_{TUR} is the electricity generated by the turbine, and E_{COMP} and E_{VAC} are the electricity consumed by the compressors and vacuum pumps, respectively.

2.3. Techno-economic evaluation

2.3.1. Process plant capital cost estimates

Feasibility estimates of process plant capital costs typically obtain accuracy in the range of $\pm 30\%$ [56]. Purchased and installed equipment costs were obtained using a combination of estimation methods available in the literature and using the Aspen Process Economic Analyzer. The currency presented is 2019 GBP. Capital costs generated using the Aspen Process Economic Analyzer were based on 2019 USD; a conversion factor of 0.78 was applied to convert from 2019 USD into 2019 GBP. The sizing and equipment and installed costs of the following unit operations were obtained using the Aspen Process Economic Analyzer: compressors, turbine, heaters, coolers/condensers, flash vessels and distillation columns.

The desulfurization column was sized assuming it to have a service life of 6 months, after which the sorbent is replaced and disposed of, with assumed adsorption capacity of 39 kg of sulfur per 100 kg of zinc oxide before it reaches its saturation limit [57]. The HT-WGS and methanol synthesis reactors were sized according to Gas Hourly Space Velocity (GHSV) within range advised in literature with reactor conversion calculated using the kinetic methods described in Section 2.2. Industrially relevant GHSV in the LT-WGS of $2000\ h^{-1}$ is used for sizing in the present work. The dehydration unit was sized by comparison to natural gas processing and is based on a 3 tower system (2 towers on adsorption, 1 on regeneration) containing type 4A 4×8 mesh beads with lifetime of 3 years [58]. The PSA units were scaled according to some recommendations made in the COURSE50 project [13].

The vessel costs of ZnO desulfurization beds, WGS reactors, dehydration and PSA units, in addition to the capital costs of vacuum pumps were determined according to the methodologies given by Loh et al. [59] and using a module factor of 2.3 for converting vessel costs to installed costs. The capital cost of the methanol synthesis reactor was obtained using the relation provided by Luyben [60] with a module factor of 3.75. Initial sorbent and catalyst charge costs are included in capital costs while replacements are considered in Operations and Maintenance (O&M) costs. Values for sorbent and catalyst costs for ZnO desulfurization beds [61], WGS [62] and methanol synthesis reactors [32], dehydration and PSA units [63] were taken from a variety of sources and are listed in the Table 1.

Table 1

Costs and values of streams, materials and utilities used for the techno-economic analysis.

Element	Cost/value	Source
Process streams		
Blast Furnace Gas	3.48 £/tonne	[67]
Methanol (gate price)	383.1 £/tonne	[32]
CO ₂	− 17.5 £/tonne	[69]
Utilities		
Electricity	66.55 £/MW h	[70]
Natural gas	16.57 £/MW h	[70]
MP and superheated steam	5.94 £/MW h	[68]
LP steam	4.3 £/tonne	[68]
Heat credit	4.46 £/MW h	*
Cooling water	0.9857 £/MW h	[71]
Catalysts and Sorbents		
ZnO guard bed	10,675 £/m ³	[61]
HT-WGS	£6899.79 £/m ³	[62]
LT-WGS	£6899.79 £/m ³	[62]
Molecular sieve	622.02 £/m ³	[63]
CO ₂ -PSA	828 £/t	[63]
N ₂ -PSA	828 £/t	[63]
Methanol synthesis	88.25 £/kg	[32]

* Heat credit is attributed to cooling operations above 200 °C from the steam price × 0.75.

The Process Facilities Capital (PFC) was obtained by summing the installed equipment costs in each of the listed plant areas. The Total Plant Cost (TPC) was obtained by adding indirect costs of engineering and home office fee (10 % of PFC), general facilities fee (15 % of PFC), project contingency (20 % of PFC) and process contingency (5 % of PFC) to the PFC. The Total Capital Requirement (TCR) includes the total plant cost, prepaid royalties (0.5 % of PFC), allowance for funds during construction (4.5 % of the TPC), preproduction fees (1 month of O&M costs) and inventory capital (0.5 % of the TPC).

2.3.2. Process plant operations and maintenance cost estimates

The O&M costs include the variable and fixed operating costs. Variable O&M (VOM) costs cover material, by-products and waste streams sale or disposal, consumables (i.e. catalysts and sorbents) and utilities. The cost of BFG is subject to some uncertainty because of the inefficiency of power generation when used as a fuel. Sub-critical power plants which are typically present on an integrated steelworks fire BFG in combination with other off-gases, COG and BOFG, and natural gas, with reported net electrical efficiencies of 32 % [64]. This contrasts with much higher electrical efficiencies of Combined Cycle Gas Turbines (CCGTs) firing natural gas of 52–63 % [65]. However, replacing conventional steelworks power plants with a CCGT to be run on the same fuel mix would raise net electrical efficiency by 8–10 points to about 40–45 % [66]. Although detailed modelling of the power plant is beyond the scope of the present work, significant efficiency improvements in the steelworks power plant are assumed to result through diverting BFG for methanol synthesis, fuel switching in the steelworks power plant to a mix which is mainly composed of CH₄/H₂ and the replacement of a subcritical unit with a CCGT. This efficiency saving is reflected in the boundary price of BFG which takes a literature value of 3.48 £/tonne (converted from RMB) [67] that is significantly lower than the equivalent reference thermal value of natural gas by a factor 3–4. For the purposes of calculating overall steelworks environmental metrics, power plant efficiency improvements for CCU(S) cases are assumed to lead to a 68 MW saving of natural gas consumption in that section of the plant. Low Pressure (LP), Medium Pressure (MP) and superheated steam that feed different parts of the process are assumed to be risen from waste heat available from the steelworks core industrial processes using a cost value recommended by Roussanaly et al. (5.94 £/MW h) [68] while a credit for process heat recovery at 0.75 times the steam price was also assumed. A gate price for methanol (383.1 £/tonne) [32], adjusted for currency and inflationary measures, was adopted in the present work to

determine the profitability of the process as compared to the LCOMeOH. In the CCUS case, a CO₂ disposal cost encompassing CO₂ compression, transport and geological storage was assigned a median value recommended by ZEP (17.5 £/tonne) [69]. The electricity price is taken from the first quarter of 2020 (66.55 £/MW h) [70] with assumed zero CO₂ emissions contribution. Utility consumption rates were calculated using the extracted unit duties from the Aspen Plus flowsheet. N₂ has numerous uses on a steel plant, e.g. as an inert purging gas; however, no value has been assigned to the N₂ stream produced in the present process because it is of low purity (containing 74.3 vol% N₂) and significant amounts of CO₂ and H₂. The large volume flow of the N₂ rich stream may also be prohibitive to its total utilisation. Any value or cost of disposal of the other streams emanating from the BFG-to-methanol process have been considered negligible. The prices of catalysts and sorbents were assumed from a variety of sources as listed in Table 1. The values in Table 1 were adjusted from sources for year and currency as appropriate.

The Fixed O&M (FOM) costs, associated with operating labour, holidays, shift allowance and national insurance, maintenance costs (including maintenance labour), and also general administration and support costs associated with laboratory charges, distribution and marketing, and R&D. The annualised capital costs were calculated on the basis of a 30 year project lifetime.

LCOMeOH was calculated according to the following formula:

$$\text{LCOMeOH} = \frac{\text{TAC}}{\dot{m}_{\text{MeOH}} \times 8322} \quad (12)$$

where \dot{m}_{MeOH} is the mass flowrate of methanol out of the process (tonne/h) and TAC refers to the Total Annualised Capital given by:

$$\text{TAC} = \text{TCR} \times \text{ACCR} + \text{VOM} + \text{FOM} \quad (13)$$

The Annualised Capital Charge Ratio (ACCR) is given by:

$$\text{ACCR} = \frac{r(1+r)^n}{(1+r)^n - 1} \quad (14)$$

where r is the project interest rate (0.05 [72]) and n is the plant lifetime. CAC was calculated through consideration of the impact of implementing CCU(S) cases on the CO₂ intensity of steel (tonne CO₂/tonne steel) and Cost of Steel Production (CoSP) (£/tonne steel) as compared to a set of baseline assumptions for a reference business-as-usual steelworks using the following formula:

$$\text{CAC} = \frac{(\text{CoSP})_{\text{CCU(S)}} - (\text{CoSP})_{\text{ref}}}{(\text{tonne CO}_2/\text{tonne steel})_{\text{ref}} - (\text{tonne CO}_2/\text{tonne steel})_{\text{CCU(S)}}} \quad (15)$$

3. Results of the process simulation and techno-economic analysis

In this section, the results of the process simulation, technical performance and techno-economic feasibility are presented. In addition, sensitivity analysis of the methanol synthesis reactor system and cost parameters is used to identify optimal process parameterisation and understand the process economics.

3.1. BFG-to-methanol process simulation

An illustration of the flowsheet developed in Aspen Plus for the BFG-to-methanol process is available in the supplementary electronic information along with the full stream table generated by the program. BFG, compressed to 6 bar, first enters the ZnO adsorbent desulfurization tower with the requirement to reduce the ~ 10 ppm_v contaminant to < 1 ppm_v, leading to a H₂S removal rate of 3.72 kg/h. In the case of BFG desulfurization, the amount of ZnO adsorbent needed per hour is 9.54 kg, and for a service lifetime of 6 months, 41,785.2 kg of ZnO is estimated. For a bulk density of ZnO of 1.35 g/cm³ [57], a bed volume of 30.95 m³ is determined with dimensions of 2.52 m diameter and 6.21 m

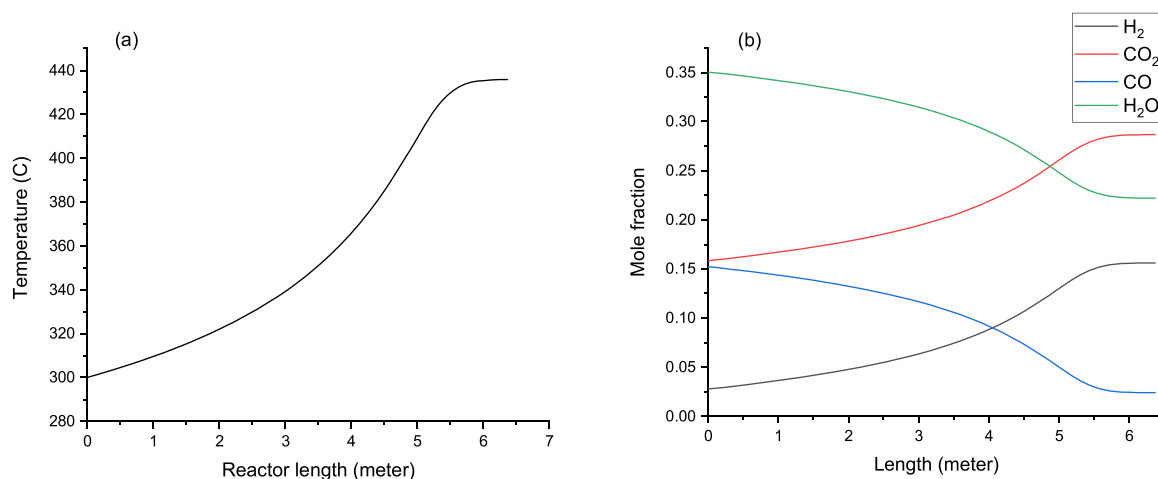


Fig. 3. Temperature profile (a) and chemical species profiles (b) along the length of the HT-WGS reactor.

height. 2 vessels are deployed with one in adsorption mode and the other on standby at any given time. Following desulfurization, heating and mixing with steam, the simulated flowrate of BFG + steam into the HT-WGS reactor is 381,278 N m³/h. A reactor with a bed diameter of 2 m and length of 6.37 m results in a volume of 20 m³ and corresponds to a GHSV of 38,079 h⁻¹. These design parameters are sufficient to reach equilibrium following Hla et al. kinetics [48] under the conditions in the adiabatic reactor as illustrated in Fig. 3. Temperature rises in the adiabatic reactor from 300 to 436 °C and the exit concentration of CO is 2.4 mol%. The calculated volumetric flowrate into the LT-WGS reactor is 403,299 N m³/h. These values result in a reactor volume of 336 m³, 5.1 m diameter and length 16.45 m.

After cooling and removing condensate from the shifted BFG, it flows to a dehydration unit for further water removal. In cases of PSA for CO₂ and N₂ separation, feed is assumed to enter the units at 2 bar pressure, while desorption occurs at 0.1 bar via the use of vacuum pumps. The recovered H₂ and around 25 % of the recovered CO₂ is next sent to the methanol synthesis loop. Since H₂ and CO₂ are withdrawn from the PSA systems at different pressures of 0.1 bar and 2 bar respectively, both streams are separately pressurised to 4 bar before being mixed in the 3:1 stoichiometric proportions and pressurised further by multistage compression with interstage cooling until 76 bar. Prior to being fed into the methanol synthesis reactor, the feed stream is mixed with the unused reactant recycle stream and heated to 210 °C. Methanol synthesis is simulated in a tube-cooled reactor under isothermal conditions and

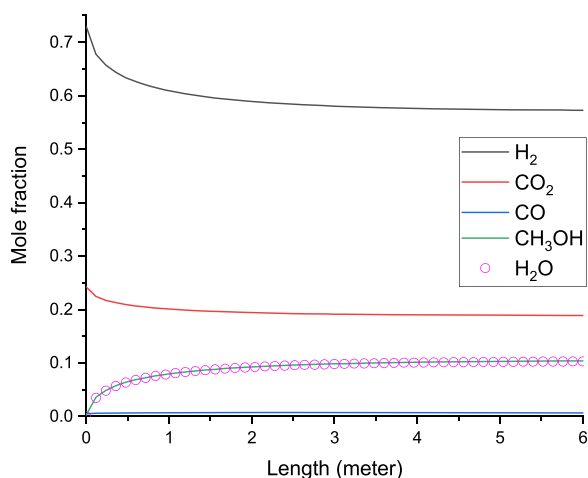


Fig. 4. Chemical species profiles along the length of the methanol synthesis reactor.

cooled using process water. The amount of catalyst utilised is 20,865 kg of Cu/ZnO/Al₂O₃. The obtained total fixed bed volume is 16.05 m³, which corresponds to a GHSV of 23,028 h⁻¹. As can be seen in Fig. 4, most of the conversion occurs in the first half of the reactor. Therefore, a reduction in the catalyst bed volume may be considered.

The gas phase effluent leaves the methanol synthesis reactor at 210 °C, with a CH₃OH content of 10.3 vol%. The conversion of CO₂ into methanol is 35.1 %. 2.4 % of the incoming CO₂ is converted to CO due to the RWGS reaction (6). The methanol synthesis reactor effluent is next cooled down to 35 °C in a heat exchanger, allowing for the condensation of the majority of CH₃OH and water so that gas and liquid phases can be separated in a flash vessel. The gas stream arising from the flash vessel, which is composed mainly of H₂ and CO₂, is compressed and recycled back to the reactor. 15 % of this recycle stream is purged to avoid the accumulation of inert gases in the methanol synthesis loop. The condensed methanol and water is reduced to 1.2 bar pressure. The released gas is separated in another flash vessel and purged. The two purged streams are collected where power is recovered from the high pressure stream in a turbine when the pressure is reduced to 6 bar and while the low pressure stream is compressed to the same pressure. The two streams are combined and returned to the feed of the LT-WGS reactor since they contain small quantities of CO. The condensate mixture of CH₃OH and water with a CH₃OH concentration of 49.3 wt%. The liquid stream is then fed to the methanol distillation column.

The methanol distillation unit is modelled with 52 equilibrium stages, with the feed introduced at stage 43 (counted from top). A reflux ratio of 0.35 and a reboiler duty of 12.82 MW, are required to reach the design specifications of CH₃OH purity (H₂O; top < 100 ppm) and CH₃OH recovery (CH₃OH; top 99.99 mol%). The calculated height is 31.7 m. The top methanol product stream is sparged with a portion of the N₂ rich stream emanating from N₂ PSA system in order to remove residual dissolved CO₂ and meet the product purity of 99.9 mol%. The spent sparge gases are purged. Finally, the liquid CH₃OH product stream leaves the process.

Table 2 shows the BFG-to-methanol process mass balance in terms of the inputs and outputs to the overall system. Around ~ 340 tonnes/h of BFG results in 22.7 tonnes/h of methanol being produced with purity of 99.9 mol%. The production rate of methanol is equivalent to typical commercial scale of 190 ktonnes/year. Around 0.09 tonnes/day of sulfur needs to be removed from the system, while 75 % of the CO₂ is diverted to compression, transport and geological storage in the CCUS case or mixed with stack gases and emitted to atmosphere in the CCU case.

Table 3 shows the overall energy balance of the BFG-to-methanol process. The largest sources of electricity consumption at 77.9 MW are the compressors with the PSA vacuum pumps contributing ~ 46 % to

Table 2
Stream mass balance based on inputs and outputs to the CCUS system.

Component	BFG-in	Steam-in	Sulfur-out			Condens.-out	Dryer-out
			(tonne/h)				
CO ₂	118	–	–	–	6.61 × 10 ⁻³	–	
CO	72.4	–	–	–	–	–	
N ₂	145	–	–	–	4.10 × 10 ⁻⁶	–	
H ₂	0.947	–	–	–	–	–	
H ₂ O	–	107	–	–	57.7	3.19	
CH ₃ OH	–	–	–	–	3.52 × 10 ⁻²	–	
H ₂ S	3.72 × 10 ⁻³	–	–	3.72 × 10 ⁻³	–	–	
CH ₄	4.21 × 10 ⁻³	–	–	–	–	–	
O ₂	0.629	–	–	–	–	–	
HE	4.37 × 10 ⁻⁴	–	–	–	–	–	
AR	2.71	–	–	–	1.79 × 10 ⁻⁶	–	

Component	N ₂ -out	CO ₂ T&S-out	Offgas-out			Bottoms-out	Methanol-out
			(tonne/h)				
CO ₂	48	146	0.972	–	–	2.51 × 10 ⁻²	
CO	0.7	1.14 × 10 ⁻²	1.03 × 10 ⁻²	–	–	7.39 × 10 ⁻⁶	
N ₂	141	2.30	2.07	–	–	1.36 × 10 ⁻³	
H ₂	1.09	0.118	1.60 × 10 ⁻²	–	–	5.71 × 10 ⁻⁶	
H ₂ O	–	–	–	–	14.6	1.32 × 10 ⁻³	
CH ₃ OH	–	0.118	2.79	–	2.55 × 10 ⁻³	22.7	
H ₂ S	–	–	–	–	–	–	
CH ₄	4.08 × 10 ⁻²	6.66 × 10 ⁻⁴	5.99 × 10 ⁻⁴	–	–	1.75 × 10 ⁻⁶	
O ₂	0.61	9.96 × 10 ⁻³	8.96 × 10 ⁻³	–	–	1.82 × 10 ⁻⁵	
HE	4.24 × 10 ⁻⁴	6.92 × 10 ⁻⁶	6.24 × 10 ⁻⁶	–	–	–	
AR	2.62	4.28 × 10 ⁻²	3.85 × 10 ⁻²	–	–	7.67 × 10 ⁻⁵	

Table 3
Overall energy balance of the CCUS system.

Process units/streams	Energy flux (MW)
Compressors/vacuum pumps	77.9
Energy recovery turbine	– 0.89
Heaters	23.8
Coolers	– 188.0
Methanol reactor	– 13.6
Distillation column:	
Condenser	– 12.0
Reboiler	12.8
BFG-in	235.1
WGS reactor steam-in	82.0
N ₂ -out	38.7
CO ₂ -T&S-out	6.2
Off-gas-out	16.9
CH ₃ OH-out	145

this, followed by the first BFG compression stage contributing ~ 30 % and the remaining 24 % made up by the methanol synthesis loop compression stages. Some power (0.89 MW) can be recovered in from the purge stream energy recovery turbine. The contribution to energy consumption through heating throughout the system is lower than compression, with 12.8 MW consumed by the distillation column reboiler and 23.8 MW consumed by the other heaters distributed throughout the plant. A total of 213.6 MW of heat must be removed from

Table 4
BFG-to-methanol major unit vessel and catalyst capital costs.

Reactor	Type	Volume (m ³)	Vessel cost (£k)	Initial catalyst cost (£k)	No of vessels	Installed cost	Ref.
ZnO Bed	Vertical	30.95	£36.7k	£660.8 k	2	£1490.4k	[59]
HT-WGS	Adiabatic	20	£42.9k	£138.0 k	1	£236.7k	[59]
LT-WGS	Adiabatic	336	£123.1k	£2318.3 k	1	£2601.4k	[59]
Molecular Sieve	Vertical	24	£30.8k	£14.9 k	3	£257.4k	[59]
CO ₂ -PSA	Horizontal	213.63	£86.3k	£54.4 k	12	£3033.6k	[13,59]
N ₂ -PSA	Horizontal	213.63	£86.3k	£54.4 k	12	£3033.6k	[13,59]
CH ₃ OH	Tube-cooled	16	£1724.6k	£1841.3 k	1	£8308.7k	[60]

the process by cooling in heat exchangers, the methanol reactor and the distillation column condenser, indicating the possibility for heat integration within the methanol synthesis plant or energy export to the steel plant or other surrounding heat sinks. The energy flows of energy containing streams, calculated on a lower heating value basis or specific enthalpy of steam (160 °C and 6 bar) in the case of steam fed to the water gas shift reactor are also presented in Table 3. The feed streams of BFG and steam account for 235.1 and 82 MW of energy added to the process. The most significant energy flow out of the process is unsurprisingly the methanol product accounting for 145 MW of energy removed. Smaller amounts of energy are lost through the nitrogen rich stream (38.7 MW), the CO₂ stream sent for transport and storage (6.2 MW) and the off-gas stream from the methanol purification section 16.9 (MW) due to their residual H₂ and CO contents.

Calculation of the overall process energy efficiency yielded a value of 76.4 %. The efficiency is the same in the CCU and CCUS cases due to the CO₂ compression system being beyond the system boundary; however, in actuality energy requirements for compression in the CCUS case will be highly significant.

3.2. Techno-economic evaluation

The spreadsheet used to perform the techno-economic evaluation of the BFG-to-methanol process is available in the supplementary electronic information. Table 4 shows the capital costs in terms of the vessel costs (calculated with respect to vessel volumes), initial catalyst and

Table 5

BFG-to-methanol process equipment capital costs as calculated by Aspen Plus V10.

Item	No of items	Total equipment purchase cost (£k)	Total Installed costs (£k)
Compressors	8	£44,304.1 k	£46,575.3 k
Turbine	1	£305.7 k	£414.5 k
Heaters	3	£696.5 k	£1275.3 k
Coolers/condensers	8	£2023.5 k	£3848.2 k
Flash vessel	3	£231.1 k	£580.1 k

sorbent charge and the total final installed costs. Of these vessels, the most expensive unit is the methanol synthesis reactor, at an installed cost of £8.3m followed by the PSA system at ~ £6m the LT-WGS reactor at £2.6m. The capital cost of the 52 stage distillation column was calculated by the Aspen Plus Economic Analyzer, resulting in a purchase cost of £372.7k and an installed cost £600.9k.

Table 5 gives the equipment costs of the compressors, turbine, heaters, coolers, condensers and flash vessels. Of these items, the most costly category of equipment are compressors with installed costs totalling ~ £46.6m; of these, by far the most expensive item is the BFG compressor with installed cost at £28.9m. Centrifugal vacuum pumps were costed according to the method given by Loh [59], resulting in installed costs ~ £2.0m and ~ £5.2m for the CO₂ and N₂ systems, respectively (4 pumps are needed for each system). The summary of the process capital costs is given in Table 6 with a TCR of £127.4m.

Table 7 shows the VOM costs for the BFG-to-methanol process. Significant costs are incurred from the use of electricity for compressors and vacuum pumps throughout the process with total cost equalling 43.1 m £/yr. Another major operating cost listed in Table 7 relates to the use of LP steam as feed to the HT-WGS reactor, which is equivalent to 3.8 m £/yr, while the use of superheated steam to heat the BFG prior to being fed to the WGS system incurs 637 k£/yr. The total heating cost through the use of steam, including for the distillation column reboiler, amount to 1.8 m£/yr. In the current analysis, a significant amount of medium grade heat (> 200 °C) equivalent to ~ 175 MW is assumed to be usefully recoverable or able to be integrated in the process, leading to a total heat credit of - 6.5 m£/yr. The need to remove 13.18 MW of lower grade heat (< 200 °C) from the process using cooling water costs 206.5 k£/yr. The need to replace the ZnO bed every 6 months, the HT-WGS catalyst every 2.5 years, the LT-WGS every 6 years, the molecular sieve sorbent every 3 years, the PSA sorbents every 5 years and the methanol synthesis catalyst every 4 years incurs another VOM cost of 1.84 m£/yr. The total VOM costs are 43.95 m£/yr.

The FOM costs are shown in Table 8. The total operating labour cost was calculated on the basis of 5 process operators on a salary of 40 k£/yr with a 50 % addition for holiday, shift allowance, national insurance, pension and other overheads. The maintenance cost was calculated as

Table 6

BFG-to-methanol process capital cost summary.

Plant area	Process facilities capital	Total plant cost	Total capital requirement
ZnO bed	£1.49m	£2.24m	£2.35m
WGS	£2.84m	£4.26m	£4.48m
PSA + vacuum pumps	£13.48m	£20.22m	£21.30m
Methanol system*	£26.61m	£39.92m	£42.05m
BFG Compression	£29.28m	£43.93m	£46.27m
Heat exchangers	£3.85m	£5.77m	£6.08m
Flash vessels	£0.58m	£0.87m	£0.92m
Total	£78.13m	£117.2m	£127.4m[†]

* Methanol system comprises synthesis reactor, distillation and compressor units.

[†] Includes preproduction fees equal to 1 month of VOM + FOM.

Table 7

BFG-to-methanol Variable Operations & Maintenance (VOM) costs.

Process items	Cost element	Variable O&M cost
<i>BFG Compressor</i>		
	Electricity	13.1 m£/yr
<i>Turbine</i>		
	Electricity	- 493.1 k£/yr
<i>ZnO bed</i>		
	Replacement sorbent	660.8 k£/yr
<i>WGS section</i>		
	HTS catalyst replacement	55.2 k£/yr
	LTS catalyst replacement	386.4 k£/yr
	LP steam feed	3.83 m£/yr
	Heaters superheated steam	637.3 k£/yr
	Coolers heat credit	- 4.11 m£/yr
<i>PSA section</i>		
	Molecular sieve sorbent	14.9 k£/yr
	CO ₂ sorbent	130.5 k£/yr
	N ₂ sorbent	130.5 k£/yr
	Vacuum pumps electricity	19.7 m£/yr
	Coolers heat credit	- 1.20 m£/yr
<i>Methanol synthesis section</i>		
	Compression electricity	10.39 m£/yr
	Cooling water for coolers	108.1 k£/yr
	Feed heater steam	540.8 k£/yr
	Reactor cooling water	111.6 k£/yr
	CH ₃ OH catalyst replacement	460.3 k£/yr
	Cooler heat credit	- 1.2 m£/yr
	Distillation cooling water	98.4 k£/yr
	Distillation steam	633.8 k£/yr
	Total variable O&M cost	43.95 m£/yr

Table 8

BFG-to-methanol Fixed Operations & Maintenance (FOM) costs.

Cost element	Fixed O&M cost
Total operating labour cost	300 k£/yr
Maintenance cost	2.34 m£/yr
Maintenance labour	937.62 k£/yr
Admin & support labour	371.3 k£/yr
Total Fixed O&M cost	3.02 m£/yr

2 % of the total plant cost, while maintenance labour comprises 40 % of the maintenance cost. Admin & support labour is calculated as 40 % of the maintenance and operating labour. The total FOM costs equate to 3.02 m£/yr.

Table 9 shows the Key Performance Indicators (KPIs) for the performance of the BFG-to-methanol CCU(S) processes in the context of their impacts on the overall integrated steelworks performance. The application of the CCU process alone would result in a modest reduction of overall steelworks emissions of 9.3 % with a corresponding steel CO₂ intensity of 1.66 tonne CO₂/tonne steel while deeper reductions of 42 % are achievable when the remaining separated CO₂ is sent to geological storage in the CCUS case with an overall avoidance of 1.5 Mtonne CO₂/yr. The equivalent CO₂ captured from the targeted BFG is 13.4 % and 76.4 % for the CCU and CCUS cases, respectively, with the remaining carbon mainly in the form of CO₂ predominantly leaving the process with the N₂ rich stream. With the current set of assumptions adopted, the CCU process is found to be profitable to a degree, leading to a lower LCOMeOH than the methanol gate selling price and total sales revenue generated of 72.4 M£/yr and resulting in a small decrease in the steel production cost. Where the equivalent CO₂ contained in methanol is considered avoided, a negative value of CAC is reported - 20.08 £/tonne CO₂ for the CCU case. However, the added penalty costs of CO₂ compression, transport and storage in the CCUS case leads to an overall increase in steel production of 6.67 £/tonne steel and CAC of 9.01 £/tonne CO₂ using the nominal set of assumptions. The increased production costs in the CCUS case may be offset, however, when one considers the potential future carbon taxation price as will be discussed in

Table 9

Key performance indicators for the BFG-to-methanol CCU and CCUS cases.

Metric	Business-as-usual	CCU case	CCUS case
Steel CO ₂ intensity (tonne CO ₂ /tonne steel)	1.83	1.66	1.07
Steelworks emission reduction potential (%)	–	9.3	42
£ Steel production cost (£/tonne steel)	383.33	379.86	390
Steel production rate (Mtonne steel/yr)	2.1	2.1	2.1
Annual steel production cost (M£/yr)	803.4	796.1	817.9
Steelworks CO ₂ emissions (Mtonne CO ₂ /yr)	3.84	3.47	2.23
Methanol production rate (ktonne/yr)	–	188.9	188.9
CO ₂ equivalent in methanol (ktonne/yr)	–	259.9	259.9
Methanol sales revenue (M£/yr)	–	72.4	72.4
CO ₂ to geological storage (Mtonne/yr)	–	–	1.24
BFG carbon capture rate (%)	–	13.4	76.4
Annual CO ₂ T&S fee (M£/yr)	–	–	21.7
LCO _{MeOH} (£/tonne)	–	344.61	459.54
CAC* (£/tonne)	–	– 20.08	9.01

* Includes a CO₂ saving of 102.2 ktonne/yr achieved through sub-critical unit to CCGT power plant switching conversion related efficiency improvements

the following section.

3.3. Sensitivity analysis

In this section, the sensitivity of a set of process and cost parameters on the technical and economic performance is described and analysed. In a first analysis (SA-1), reactor volume was decreased from its nominal value of 16.05 m³ incrementally down to 1.85 m³ with GHSV then ranging 23,000–300,000 h⁻¹; simultaneously, the CO₂ split fraction (i.e. the fraction of captured CO₂ diverted to methanol production) was incrementally increased from its nominal value of 0.25–0.277 in order to maintain the reactor feed CO₂: H₂ ratio in 1: 3 proportions. In a second analysis (SA-2), the reactor volume was adjusted in the same range as the first analysis but resulted in a higher maximum GHSV of 330,000 h⁻¹ due to differences in flowrate; the recycle split fraction (i.e. the fraction of separated unreacted reactor effluent gas that is recycled and mixed with the reactor feed) was simultaneously adjusted from its

nominal value of 0.85 up to 0.929 for maintaining the same reactor feed component ratio. In a third analysis (SA-3), the recycle split fraction was incrementally increased from 0.85 up to 0.984 while adjusting the CO₂ split fraction from 0.25 to 0.2193 to maintain the reactor feed component ratio. In a fourth analysis (SA-4), the BFG price was adjusted in the range – 1.25 to 11.75£/tonne, where the upper limit represents the thermal equivalent natural gas price taken from the first quarter of 2020 [70]. In a final analysis (SA-5), the impact of a predicted future carbon price [73] on the KPIs was assessed.

The results of the first 4 sensitivity analysis cases (SA-1–SA-4) are shown in Figs. 5–7, while future predicted GB carbon price and the impact of these prices on cost of steel production for business-as-usual, CCU and CCUS scenarios (SA-5) are shown in Fig. 8.

As shown in Fig. 5a, as the reactor volume decreases and GHSV therefore increases, the reactor conversion per pass decreases from ~ 35 % at ~ 23,000 GHSV h⁻¹ to < 22.5 % at GHSV > 300,000 h⁻¹ with similar results for SA-1 and SA-2, albeit with the results extended to

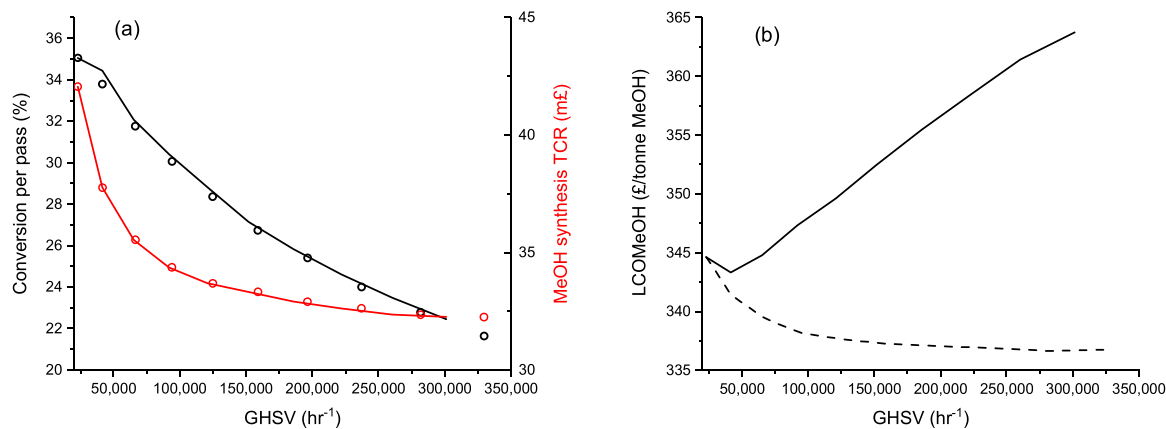


Fig. 5. Comparison of the impacts of the sensitivity of methanol synthesis reactor GHSV while maintaining feed component ratio for SA-1 and SA-2. Graph (a) – methanol synthesis reactor conversion per pass (black line – SA-1; black open circles – SA-2); methanol synthesis system TCR (red line – SA-1; red open circles – SA-2). Graph (b) – CCU case LCO_{MeOH} for SA-1 (solid line) and SA-2 (dashed line).

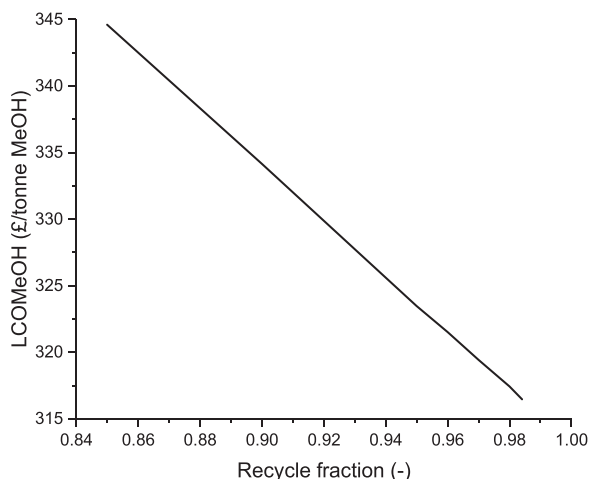


Fig. 6. Sensitivity of methanol synthesis loop recycle fraction on LCOMeOH.

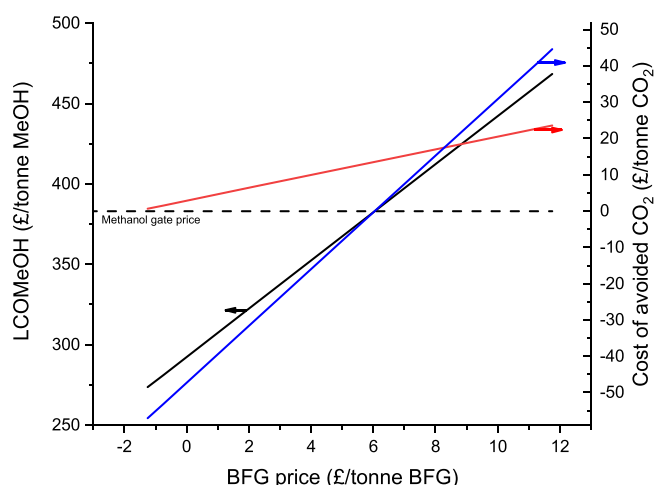


Fig. 7. Sensitivity of BFG price on LCOMeOH (black line) and CAC for the CCU case (blue line) and CCUS case (red line). The dashed line represents the methanol gate selling price.

slightly higher values of GHSV in SA-2 due to differences in flowrate. Fig. 5a also shows that the TCR of the methanol synthesis system decreases initially steeply as GHSV increases from the nominal cost of

~ 42 m£ and then levels off at lower costs of ~ 32 m£ with only minor differences between SA-1 and SA-2 analyses. Fig. 5b shows the comparison of the impact of reactor volume size variation on the CCU case LCOMeOH for SA-1 and SA-2. In SA-1, the LCOMeOH decreases from 344.61 to 343.33 £/tonne as methanol reactor GHSV is increased from ~ 24,000 to ~ 40,000 h⁻¹ due to the substantial cost savings in the methanol unit; however, the overall trend in this analysis is for increasing LCOMeOH as GHSV increases due to lowering production rate caused by loss of material through purge. In SA-2, increasing the GHSV resulted in decreasing LCOMeOH due to lowering methanol unit costs and marginally increasing production rate connected to an increased rate of recycle in the methanol synthesis loop without loss of material through purge. The LCOMeOH keeps decreasing down to 336.64 £/tonne as GHSV is increased to ~ 260,000 h⁻¹ and then increases thereafter.

Fig. 6 shows the effect of increasing methanol synthesis loop recycle fraction while decreasing the CO₂ split fraction for the purposes of maintaining the component feed ratio. The benefit of increasing the recycle split fraction is clear with LCOMeOH decreasing significantly to 316.47 £/tonne at the maximum recycle fraction of 0.984, while adopting this value leads to the best process performance observed over the range of parameters studied. This trend is caused by an increase in production rate over this range despite the corresponding reactor inlet N₂ concentration increase from 2 % to 13 %. This means that dilution effects of N₂, as predicted by the applied kinetic model, are outweighed by the increase in overall conversion rate effect that the increased recycle rate has over the range investigated.

Fig. 7 shows the effect of BFG price variation on LCOMeOH and CAC for the CCU(S) cases (SA-4). Under the present set of assumptions, methanol synthesis at a steelworks presents a cost effective solution for CO₂ mitigation when the BFG price is below 6.10 £/tonne since the LCOMeOH is below the methanol gate price at these conditions. This value of the BFG price coincides with the transition of CAC from negative to positive values in the CCU case, ranging from - 57.06 to 44.57 £/tonne of CO₂ over the range of values considered. In the CCUS case, CAC remains positive over the range considered reaching a maximum of 23.62 £/tonne. The minimum value of CAC in the CCUS case of 0.65 £/tonne occurs with a negative BFG price of ~ 1.25 £/tonne. Such a case could only be considered plausible when diverting BFG for methanol synthesis would lead to such drastic increases in efficiency of the power generation section of the steelworks that it would result in a net decrease in steelworks energy imports where the related cost savings would also pay for any corresponding power plant upgrades. At BFG prices above 8.29 £/tonne, CCUS is the most cost effective method of CO₂ mitigation but it should be borne in mind that this approach is the most ambitious

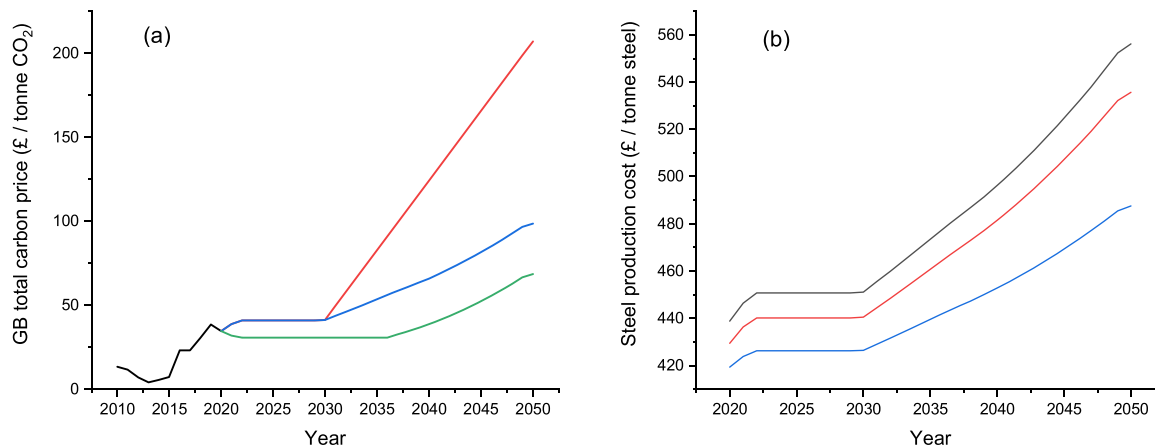


Fig. 8. Impact of future GB carbon price on steel production cost under business-as-usual, CCU and CCUS cases. Graph (a) – National Grid Future Energy Scenarios projected GB total carbon price [73] (black line – history; red line – high case; blue line – base case; green line – low case. Graph (b) – steel production cost under base case carbon pricing (black line – business-as-usual case; red line – CCU case; blue line CCUS case).

for emissions reduction at all conditions.

Fig. 8 shows the impact of the projected GB carbon price on the cost of steel production (SA-5). The projected GB carbon pricing (Fig. 8a) is taken from National Grid Future Energy Scenarios [73] and presents high, low and base cases, where in the present work, the latter is adopted for elucidating the impact on the steel production costs for the steelworks CCU(S) scenarios as compared to a business-as-usual scenario. The 2022 GB carbon price of 41 £/tonne CO₂ is higher than the nominal CAC for both CCU and CCUS cases. This means application of CCU(S) is already favourable under current market conditions when carbon pricing is considered with CCU and CCUS achieving steel production prices of 440.13 and 426.23 £/tonne-steel, respectively, as compared to the business-as-usual price of 450.69 £/tonne-steel. As shown in Fig. 8b, the CCUS case is the most economically favourable at all projected times due to the greater amount of CO₂ avoided with the cost saving compared to business-as-usual becoming more marked as time progresses, estimated at 2030 to be 10.59 £/tonne-steel for CCU and 24.61 £/tonne-steel for CCUS and then reaching 68.53 £/tonne-steel for CCUS by 2050

4. Summary and conclusions

CCUS processes will play an important part in global warming mitigation by capturing CO₂ and then storing it in geological formations and/or using it to make products that otherwise would be manufactured from fossil fuels. Amongst a number of chemical compounds that can be synthesised from CO₂ and H₂, methanol is an attractive option due to its ease of storage and its diverse range of applications, including fuel and base chemical for follow-on chemical processes.

In this study, a BFG-to-methanol plant based on direct CO₂ hydrogenation, comparable in production rate to average sized conventional methanol production facilities was developed with the aid of Aspen Plus V10 in order to obtain the mass and energy balances needed to evaluate its technical performance and economic viability. The plant produces from a BFG stream present on a steelworks, industrial-grade CH₃OH at a production rate of ~ 190,000 tonnes/yr. The BFG-to-methanol process is technically feasible and can operate using available technology and equipment that currently exists on other chemical process facilities. The applied process steps involve desulfurisation of BFG followed by 2-stage WGS, dehydration, then separation into N₂, CO₂ and H₂ rich streams. 25 % of the separated CO₂ stream is used for utilisation with all of the H₂ at stoichiometric 1:3 feedstock proportions in a methanol synthesis system. The developed industrial-scale BFG-to-methanol process consumes 340 tonnes/h of BFG. The conversion per pass of CO₂ in the catalytic reactor is ~ 35 %, while the total amount of CO₂ converted in the methanol synthesis section is 61 %.

A detailed cost analysis of the process was also undertaken in this study. The most expensive unit in the BFG-to-methanol process is the compression system, with the initial BFG compressor alone having an installed cost at £28.9 m. The total equipment installed cost is £78.1 m while the TCR is £127.4 m. VOM costs are dominated by the use of electricity for compressors and steam used for the WGS process. The cost of the BFG feedstock is also significant at 9.85 m£/yr when using the price adopted in the current analysis of 3.48 £/tonne.

For the calculation of KPIs, CCU and CCUS cases were considered which were identical in all except for the addition of a disposal cost for excess CO₂ in the CCUS case, comprising compression, transport and geological storage costs. The BFG-to-methanol process route appears to be an economically attractive means of CO₂ abatement under current market conditions when using the assumptions adopted in the present study. In the presented nominal scenario, the LCOMeOH in the CCU case is calculated to be 344.61 £/tonne which is lower than the assumed selling price at 383.1 £/tonne, meaning this variant of the process could generate revenue. Due to this, the calculated CAC costs are extremely low for the CCUS case at 9.01 £/tonne and even negative in the CCU case at - 20.08 £/tonne CO₂. When using a set of baseline assumptions for a business-as-usual case, the CO₂ abatement potential of CCU is modest,

however, only reducing CO₂ emissions in a steelworks by 9.3 %. The CCUS process is able to achieve a more substantial CO₂ emissions reduction at 41 %.

Sensitivity analysis has shown that options to improve the process performance as compared to nominal design include reducing the reactor size and increasing the methanol synthesis loop recycle ratio. The economic viability of the BFG-to-methanol is highly dependent on the cost of the feedstock BFG with break-even at 6.10 £/tonne in the CCU case. The degree to which heat produced by the process can be usefully integrated is also a practical concern for economic viability. Considering the co-selling possibility of the produced N₂ rich by-product stream could increase the final profitability of the overall process. The cost of electricity will also play an important role due to the energy intensive nature of the BFG and CO₂-syngas compression steps. Given the current and a future base-case carbon pricing in the United Kingdom, the proposed process routes are preferable to business-as-usual with the CCUS route offering the greater cost savings which reach 68.53 £/tonne of steel by 2050.

A recommendation for future work is to investigate ways to reduce the energy consumption or reduce energy costs of the process (e.g. through heat integration). Other areas for future investigation include the consequences of diversion of low energy content BFG stream away from combined heat and power production where options for higher efficiency electricity production from other off-gases and natural gas in an integrated in a steel plant may be possible. Policy options for promoting methanol production away from heavily fossil fuel dependent routes should also be investigated.

CRedit authorship contribution statement

Richard Porter: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Writing – original draft. **Paul D. Cobden:** Conceptualization, Investigation, Supervision, Writing – review & editing. **Haroun Mahgerefteh:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jcou.2022.102278](https://doi.org/10.1016/j.jcou.2022.102278).

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