A Multi-Objective Optimization Approach to Polygeneration Energy Systems Design

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Polygeneration, typically involving co-production of methanol and electricity, is a promising energy conversion technology which provides opportunities for high energy utilization efficiency and low/zero emissions. The optimal design of such a complex, large-scale and highly nonlinear process system poses significant challenges. In this article, we present a multiobjective optimization model for the optimal design of a methanol/electricity polygeneration plant. Economic and environmental criteria are simultaneously optimized over a superstructure capturing a number of possible combinations of technologies and types of equipment. Aggregated models are considered, including a detailed methanol synthesis step with chemical kinetics and phase equilibrium considerations. The resulting model is formulated as a non-convex mixed-integer nonlinear programming problem. Global optimization and parallel computation techniques are employed to generate an optimal Pareto frontier. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 1218–1234, 2010
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Introduction

The current global environment of ever-increasing oil depletion and green-house gas (GHG) emissions makes it urgent to seek technologies which can reliably reduce the pressure on oil based liquid fuels and carbon dioxide emissions.[1] Polygeneration,[2] a multiple-input, multiple-output energy system that produces electricity and chemicals, is one such potential energy conversion technology, which is both cost-effective and environmental friendly, hence providing an alternative towards meeting increasing energy demands and environmental constraints simultaneously. A schematic flowsheet of a typical polygeneration plant[3] is shown in Figure 1. It involves gasification of coal, biomass, petroleum coke, or other feedstocks that can be gasified, using high pressure oxygen produced in an air separation unit (ASU). Gasification products mainly comprise synthesis gas, or syngas, slug, and ash. Syngas contains hydrogen, carbon monoxide, carbon dioxide, steam, and other components in trace. Mineral materials in feedstocks are converted to slug, a by-product which can be sold to the market as building material. Ash mixed with crude syngas is separated in a particulate removal unit, usually a gas scrubber. Sulphur compounds and other components which are harmful to downstream reactors and catalysts are removed thereafter. Removed sulphur compounds could be converted to elemental sulphur and sold as another by-product. Then the clean syngas is split into two streams. One stream undergoes a chemical synthesis process to produce liquid fuels, which

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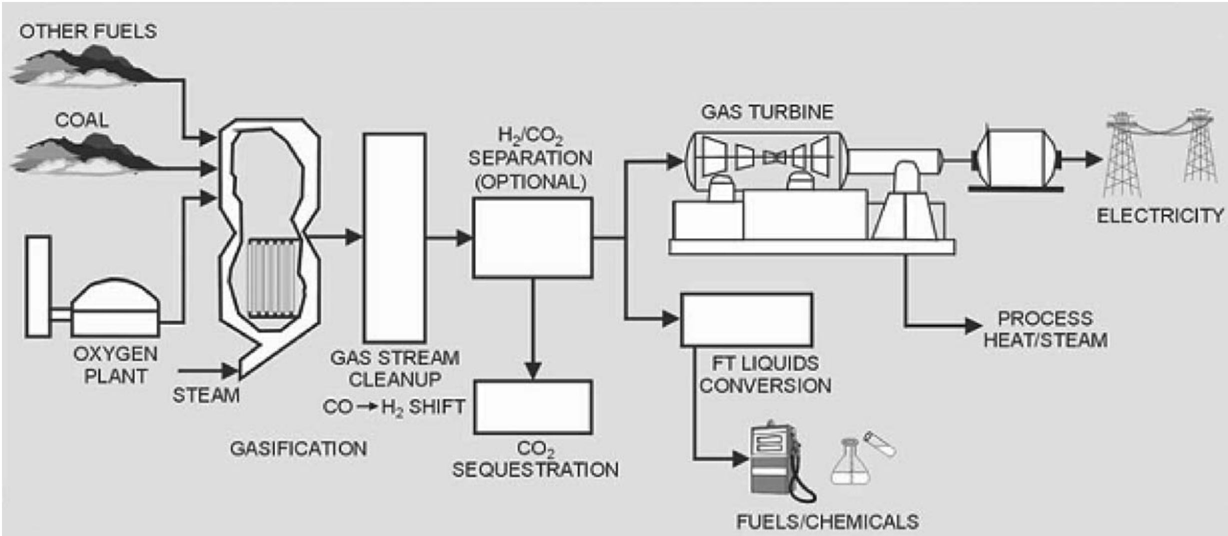

Figure 1. A schematic flowsheet of a polygeneration plant.[3]

could be Fischer-Tropsch (FT) oil, methanol, dimethyl ether (DME), and hydrogen. The other stream of syngas, joined by unconverted syngas from the chemical synthesis part, is fed into the combustion chamber of a gas turbine. There it combusts with high pressure air from an air compressor to produce high temperature and high pressure gas, which then expands in the turbine and drive a generator connected with the gas turbine to produce electricity. Thermal energy in the flue gas from the gas turbine is further exploited through a heat recovery steam generator (HRSG) and steam turbines.

The energy conversion efficiency of a polygeneration plant is typically higher than that of conventional stand-alone plants which produce the same products, as a result of more efficient energy utilization (according to energy quality) and higher degree of process integration. For instance, the production costs of methanol in a methanol/electricity polygeneration plant could be 40% lower than that in a stand-alone methanol plant because of increased overall energy conversion efficiency.[4]

Polygeneration also provides opportunities to realize a low/(almost) zero emissions system by placing a precombustion carbon dioxide capture and sequestration (CCS) unit between the gasification unit and chemical synthesis unit. The CCS unit could be combined with the water-gas shift reactor of the chemical synthesis unit, see in Figure 1. Conventionally, the function of the water gas shift reactor is to adjust the mole composition of the syngas and make it favourable to downstream chemical synthesis, via the following water gas shift reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \text{(r1)}$$

Alternatively, CCS device could be added to the process after the shift reactor to capture and sequestrate carbon dioxide in syngas. Because of the high concentration of carbon dioxide in the syngas produced by a gasifier, this option is less energy-intensive and more cost-effective than capturing and sequestrating carbon dioxide in a conventional pulverized coal power plant, in which only post-combustion is possible and carbon dioxide is extremely diluted by large amount of nitrogen, making it much more difficult to separate. Although CCS adds extra costs to the entire process, this could be partially compensated due to the increase in efficiency.

Designing such a complex polygeneration process clearly constitutes a formidable task, especially considering the following issues:

- Alternative types of technologies and equipment for each functional part of a polygeneration process—here a challenge is on how to represent and determine an optimal combination of technologies, their compatibility, and the like.
- High degree of mass and energy coupling and integration—in the gasification, chemical synthesis, and power generation parts of the process. Issues here include the accurate calculation of thermodynamic properties, such as enthalpy and entropy, and the highly nonlinear mathematical formulations that such calculations typically result in.
- The chemical synthesis unit poses particular challenge—the unit deals with syngas of different mole compositions produced from various types of gasifiers and feedstocks. A mechanistic model here will be most helpful to appropriately represent chemical kinetics and phase equilibrium within the synthesis reaction.
- Economic and environmental criteria—here, a multi-objective optimization framework is clearly needed if convincing quantitative arguments have to be established for the economic and environmental behaviours of a complex polygeneration process. Such an optimization setting should also consider the presence of nonconvexity in the nonlinear parts of the model, which will require the use of appropriate global optimization methods and tools.

Some of these issues have been partly addressed in our previous works. At the strategic level Lin et al.[5] proposed optimal planning strategies for a polygeneration complex over a long-term horizon time—a superstructure which captures potential technologies along with a suitable mixed-

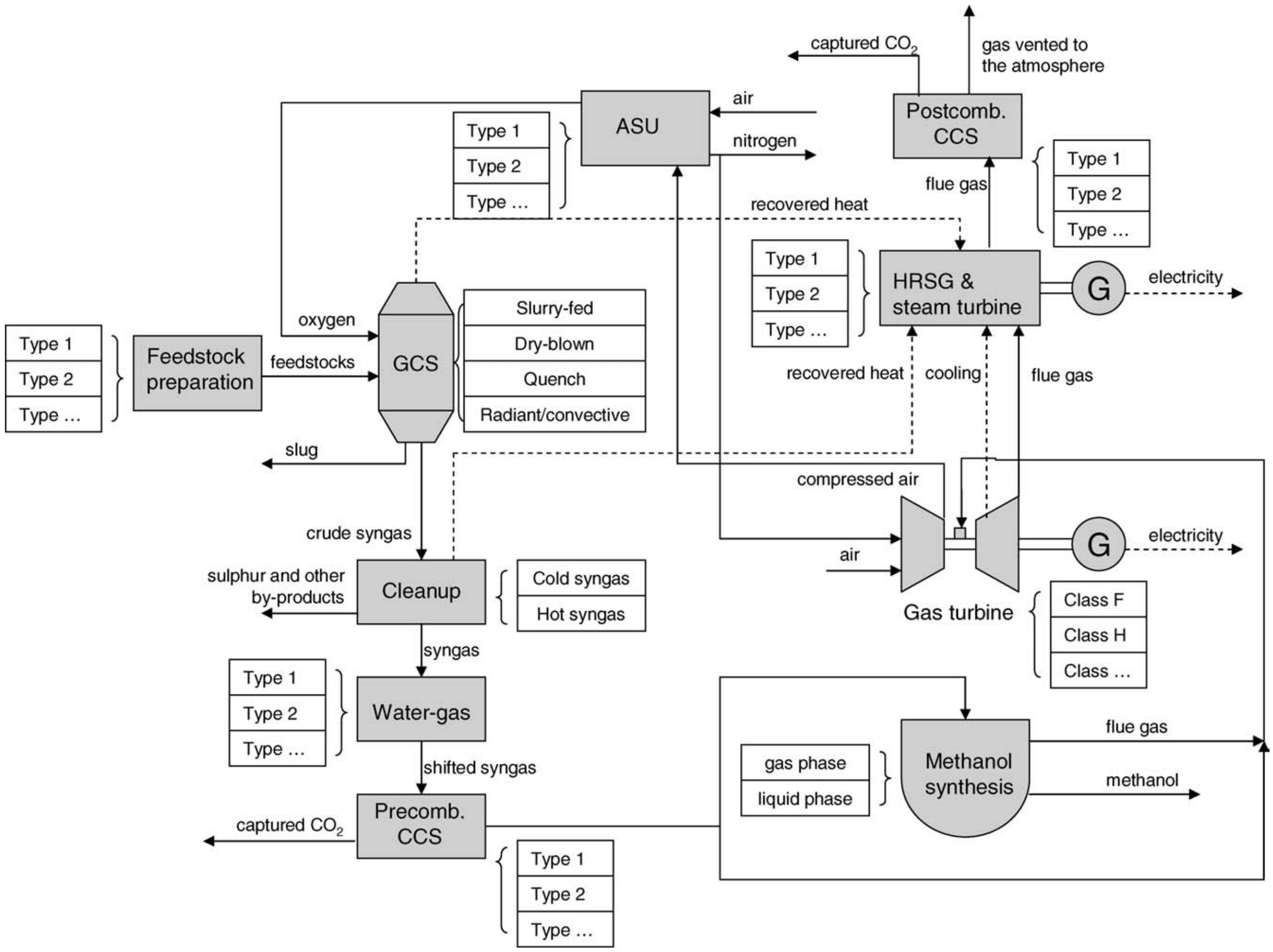

Figure 2. A superstructure representation of a polygeneration process.

integer optimization solution strategy. At the design level, Liu et al.[6] considered a polygeneration process comprising different interconnected functional units within corresponding mass and energy balance. Despite these achievements, however, a comprehensive holistic approach for the optimal design of polygeneration processes is still lacking. This is the main objective of this work.

In particular, we propose a multiobjective mixed-integer nonlinear programming (MINLP) formulation of a typical polygeneration process operating over a (long-term) horizon time. A typical polygeneration complex for the combined production of methanol and electricity has been selected to illustrate the methodology. Net present value (NPV) of the plant over its overall operating horizon is selected as the economic objective function, while a cradle-to-gate life cycle assessment based GHG emission indicator is considered as the environmental objective function. The polygeneration process is presented as a network of several interconnected functional blocks. Each block involves alternative technologies or types of equipment as candidates, the resulting superstructure captures all possible technical combinations (within the postulated set). For all blocks except the methanol synthesis one, mass and energy balances are established for all input and output streams. For the methanol synthesis block, the model involves chemical kinetics and phase equilibrium relationships to handle the different mole compositions of inlet syngas resulted from different technologies implemented in upstream blocks. The entire operating horizon time is discretized into a number of discrete time intervals, where all time-variant parameters are considered as piecewise constant functions (over these time intervals).

Table 1. Design and Operational Variables

Design Variables	
y	Selection of Technologies or Types of Equipment
cap	Capacity of a functional block
Operational Variables	
$ma_{b\text{-}cp,drc,i}(t)$	Mass flowrate of coal as feedstock over each time interval
$m_{b\text{-}c1}(t)$	Flowrate of sequestrated carbon dioxide in pre-combustion CCS over each time interval
$m_{b\text{-}c2}(t)$	Flowrate of sequestrated carbon dioxide in post-combustion CCS over each time interval
$r_{cp}(t)$	Split ratio of syngas between chemical and power generation blocks over each time interval
$r_{ws}(t)$	Ratio of shifted syngas over each time interval

This article is organized as follows. First, the superstructure representation of the polygeneration process is illustrated, followed by the detailed mathematical formulation for each functional block, together with the analytical expressions determining the economic and environmental objective functions. A case study is then presented in detail, which outlines the solution procedure involving a global optimization search and parallel computational studies to accelerate the solution time.

Process Superstructure Representation

A generic polygeneration process is divided into several functional blocks, where each block could involve several technology options. This forms a superstructure of the polygeneration process, as shown in Figure 2, featuring the following blocks:

- Air separation unit. This block prepares oxygen for an oxygen-blown gasifier. Part of the nitrogen produced could be fed to the gas turbine block to mitigate NO*x* formation.
- Feedstock preparation block. This block prepares slurry for a slurry-fed gasifier or pulverized feedstock for a dry-blown gasifier.
- Gasification chamber and syngas scrubber (GCS). Raw feedstocks are gasified in this block to produce crude syngas. Mineral components in the feedstocks are converted to slug and ash and removed from the crude syngas. Some of the sensible heat of the crude syngas could be recovered, depending on the selection of equipment, for instance, through a radiant/convective syngas cooler.
- Syngas cleanup unit. Sulphur compounds, chloride compounds, fine particles, and other hazardous components in crude syngas are removed in this block.
- Water gas shift block. In this block, mole composition of the syngas is adjusted via the water-gas shift reaction shown in (r1) to meet the requirement of downstream chemical synthesis.
- Precombustion CO_2 capture and sequestration. Concentrated carbon dioxide in syngas after the water-gas shift reaction can be separated out and sequestrated.
- Methanol synthesis. A split or the whole stream of the syngas goes through this block for methanol synthesis. The synthesis reaction is catalyzed. Depending on the phase of inert medium, it could be either gas phase synthesis or liquid phase synthesis.
- Gas turbine block. Unconverted syngas from the methanol synthesis block, together with any bypassed fresh syngas, combusts in this block, producing high-pressure high-temperature gas to drive a turbine to produce power. Depending on the temperature and pressure at the inlet of the turbine, there could be several alternative classes of gas turbines, for instance F class, H class, and so on.[7]
- HRSG and steam turbine block. A HRSG recovers heat from flue gas coming out of the gas turbine block, producing steam which drives a set of steam turbines to produce more power.
- Postcombustion CO_2 capture and sequestration. Carbon dioxide in the flue gas can be separated and captured in this block.

Based on this process superstructure representation, a detailed mathematical model is developed in the purpose of selecting the most optimal design and operational variables. These variables represent the degree of freedom of the model, as summarized in Table 1.

Mathematical Model

First, the operating horizon is discretized into n_t time intervals, denoted as

$$t = \{t_1, t_2, \dots t_{n_t}\}$$

In each time interval, mass and energy balances are established for all functional blocks. Aggregated models are considered to establish input–output relationships based on a reference variable, for each functional block. A more detailed mechanistic model is considered for the methanol synthesis block to appropriately capture the chemical kinetics and phase equilibrium relationships.

Mass flowrate of each stream is denoted by a variable with four subscripts, referring respectively to the block it relates to, the technology adopted by the block, components comprising the stream, and its position in the block (inlet or outlet). A subscript is null if the term it refers to does not exist. Subscripts are given as a part of the name of a variable, whilst sets in a parenthesis that follows denote the space where the variable is defined upon. Nomenclature for all variables, parameters and subscripts are listed in Notation.

Functional blocks

Air Separation Unit. The ASU block has two input streams, namely atmospheric air and compressed air extracted from the gas turbine block, and three output streams, namely oxygen stream flowing to the gasifier block, nitrogen stream fed back to the gas turbine block, and vented nitrogen. The following mass balances are considered.

The total inlet air stream is selected as a reference variable for the ASU block:

$$m_{\mathrm{b\_as,air,i}}(t) = m_{\mathrm{b\_as,aia,i}}(t) + m_{\mathrm{b\_as,aic,i}}(t) \tag{1}$$

$$m_{\mathrm{b\_as,air,i}}(t) = m_{\mathrm{b\_as,oxy,o}}(t) + m_{\mathrm{b\_as,nit,o}}(t) \tag{2}$$

The amount of inlet air provided by the gas turbine compressor is represented by an integration rate β_{ir}:

$$m_{\mathrm{b\_as,aic,i}}(t) = m_{\mathrm{b\_as,air,i}}(t) \cdot \beta_{\mathrm{ir}} \tag{3}$$

Mass balance for oxygen:

$$m_{\mathrm{b\_as,air,i}}(t) \cdot X_{\mathrm{air}}(j) = m_{\mathrm{b\_as,oxy,o}}(t) \cdot X_{\mathrm{aox}}(j) + m_{\mathrm{b\_as,nit,o}}(t) X_{\mathrm{ani}}(j), \; j = \mathrm{O_2} \tag{4}$$

Mole and mass flowrates of oxygen and nitrogen components in the outlet oxygen stream are listed below.

$$m_{\mathrm{b\_as,o\vec{x}y,o}}(j,t) = m_{\mathrm{b\_as,oxy,o}}(t) \cdot X_{\mathrm{aox}}(j), \quad j = \mathrm{O_2, N_2} \tag{5}$$

$$\mathrm{ma}_{\mathrm{b\_as,o\vec{x}y,o}}(j,t) = \mathrm{ma}_{\mathrm{b\_as,o\vec{x}y,o}}(j,t) \cdot MW(j), \quad j = \mathrm{O_2, N_2} \tag{6}$$

$$ma_{b\_as,oxy,o}(t) = \sum_{j=O_2,N_2} ma_{b\_as,o\vec{x}y,o}(j,t) \quad (7)$$

Coal Preparation. The coal preparation block preprocesses coal for the downstream gasifier block. Depending on the gasification technology, either coal slurry or oxygen-blown pulverized coal is prepared. The inputs comprise coal, oxygen, and water. The output is either coal slurry or oxygen-blown pulverized coal. The mass flowrate of the dry coal component at the inlet is selected as the reference variable. Mass balances between all inlet and outlet streams are as follows:

$$ma_{b\_cp,t\_gs,csl,o}(ag,t) = \alpha_{csl/drc}(ag) \cdot ma_{b\_cp,t\_gs,drc,i}(ag,t) \quad (8)$$

$$ma_{b\_cp,t\_gs,oxy,o}(ag,t) = \alpha_{oxb/drc}(ag) \cdot ma_{b\_cp,t\_gs,drc,i}(ag,t) \quad (9)$$

Gasifier Chamber and Syngas Scrubber. The gasifier and scrubber block includes several technical options. The selection (or not) of each technology is represented by a binary variable y_{ag}, while the additional logical constraint

$$\sum_{ag} y_{b\_gs}(ag) \leq 1 \quad (10)$$

enforces that only one technology can be selected (at most).

Mass balance constraints on the total flowrate of coal are given by

$$ma_{b\_cp,drc,i}(t) = \sum_{ag} ma_{b\_cp,t\_gs,drc,i}(ag,t) \quad (11)$$

With upper bound/lower bound constraints as follows

$$0 \leq ma_{b\_cp,t\_gs,drc,i}(ag,t) \leq y_{b\_gs}(ag) \cdot UB \quad (12)$$

And total flowrate of coal to all types of gasifiers (although only one could be selected) is given by:

Inputs to this block comprise coal slurry or oxygen-blown pulverized coal, oxygen from the ASU block, steam or water injection from the steam turbine to the gasification chamber, and making-up water to the syngas scrubber. Outputs are crude syngas, slag slurry, and blown-down water. Each gasifier requires a specific amount of oxygen to gasify the inlet coal, using the flowrate of inlet coal as the reference variable:

$$ma_{b\_gs,t\_gs,oxy,i}(ag,t) = \alpha_{oxy/drc}(ag) \cdot ma_{b\_cp,t\_gs,drc,i}(ag,t) \quad (13)$$

Oxygen streams split to all gasifiers come from the ASU block:

$$\sum_{ag} ma_{b\_gs,t\_gs,oxy,i}(ag,t) = ma_{b\_as,oxy,o}(t) \quad (14)$$

Flowrates of steam/water injection, making-up water, slag slurry, and blown-down water are proportional to the reference variable, given by:

$$ma_{b\_gs,t\_gs,swi,i}(ag,t) = \alpha_{swi/drc}(ag) \cdot ma_{b\_cp,t\_gs,drc,i}(ag,t) \quad (15)$$

$$ma_{b\_gs,t\_gs,mkw,i}(ag,t) = \alpha_{mkw/drc}(ag) \cdot ma_{b\_cp,t\_gs,drc,i}(ag,t) \quad (16)$$

$$ma_{b\_gs,t\_gs,bld,i}(ag,t) = \alpha_{bld/drc}(ag) \cdot ma_{b\_cp,t\_gs,drc,i}(ag,t) \quad (17)$$

$$ma_{b\_gs,t\_gs,ssl,o}(ag,t) = \alpha_{ssl/drc}(ag) \cdot ma_{b\_cp,t\_gs,drc,i}(ag,t) \quad (18)$$

Mass balance between the crude syngas and all other streams is established as follows:

$$\begin{aligned} ma_{b\_gs,t\_gs,csg,o}(ag,t) + ma_{b\_gs,t\_gs,ssl,o}(ag,t) &= ma_{b\_cp,t\_gs,drc,i}(ag,t) + ma_{b\_cp,t\_gs,csl,o}(ag,t) \\ &+ ma_{b\_cp,t\_gs,oxy,o}(ag,t) + ma_{b\_gs,t\_gs,oxy,i}(ag,t) \\ &+ ma_{b\_gs,t\_gs,mkw,i}(ag,t) + ma_{b\_gs,t\_gs,bld,i}(ag,t) \quad (19) \end{aligned}$$

Primary components in the crude syngas are H_2, CO, CO_2, H_2O, N_2, and H_2S, involving five elements: C, H, O, N, S. From mass balances for all the five elements, together with a mass relationship between H_2 and CO in the crude syngas, mole flowrates of each component in the crude syngas are determined through Eq. (20–26):

$$\frac{ma_{b\_cp,t\_gs,drc,i}(ag,t) \cdot UA(C)}{MW(C)} = m_{b\_gs,t\_gs,c\vec{s}g,o}(ag,CO,t) + m_{b\_gs,t\_gs,c\vec{s}g,o}(ag,CO_2,t) \quad (20)$$

$$\begin{aligned} &\frac{ma_{b\_cp,t\_gs,drc,i}(ag,t) \cdot UA(H)}{MW(H)} + 2 \cdot \frac{ma_{b\_cp,t\_gs,csl,o}(ag,t) + ma_{b\_gs,t\_gs,mkw,i}(ag,t) + ma_{b\_gs,t\_gs,bld,i}(ag,t)}{MW(H_2O)} \\ &= 2 \cdot m_{b\_gs,t\_gs,c\vec{s}g,o}(ag,H_2,t) + 2 \cdot m_{b\_gs,t\_gs,c\vec{s}g,o}(ag,H_2O,t) + 2 \cdot m_{b\_gs,t\_gs,c\vec{s}g,o}(ag,H_2S,t) \\ &+ 2 \cdot \frac{ma_{b\_gs,t\_gs,ssl,o}(ag,t) - ma_{b\_cp,t\_gs,drc,i}(ag,t) \cdot UA(ash)}{MW(H_2O)} \quad (21) \end{aligned}$$

$$\begin{aligned} &\frac{ma_{b\_cp,t\_gs,drc,i}(ag,t) \cdot UA(O)}{MW(O)} + 2 \cdot (m_{b\_gs,t\_gs,oxy,i}(ag,t) + m_{b\_cp,t\_gs,oxy,o}(ag,t)) \cdot X_{aox}(O_2) + \frac{ma_{b\_gs,t\_gs,bld,i}(ag,t)}{MW(H_2O)} \\ &= m_{b\_gs,t\_gs,c\vec{s}g,o}(ag,H_2O,t) + m_{b\_gs,t\_gs,c\vec{s}g,o}(ag,CO,t) + 2 \cdot m_{b\_gs,t\_gs,c\vec{s}g,o}(ag,CO_2,t) + \\ &\frac{ma_{b\_gs,t\_gs,ssl,o}(ag,t) - ma_{b\_cp,t\_gs,drc,i}(ag,t) \cdot UA(ash)}{MW(H_2O)} \quad (22) \end{aligned}$$

$$\frac{\mathrm{ma}_{\mathrm{b\_cp,t\_gs,drc,i}}(\mathrm{ag},t)\cdot \mathrm{UA}(N)}{\mathrm{MW}(N)} + 2\cdot (m_{\mathrm{b\_gs,t\_gs,oxy,i}}(\mathrm{ag},t) + m_{\mathrm{b\_cp,t\_gs,oxy,o}}(\mathrm{ag},t))\cdot X_{\mathrm{aox}}(\mathrm{N_2}) = 2\cdot m_{\mathrm{b\_gs,t\_gs,c\vec{s}g,o}}(\mathrm{ag},\mathrm{N_2},t) \quad (23)$$

$$\frac{\mathrm{ma}_{\mathrm{b\_cp,t\_gs,drc,i}}(\mathrm{ag},t)\cdot \mathrm{UA}(S)}{\mathrm{MW}(S)} = m_{\mathrm{b\_gs,t\_gs,c\vec{s}g,o}}(\mathrm{ag},\mathrm{H_2S},t) \quad (24)$$

$$m_{\mathrm{b\_gs,t\_gs,c\vec{s}g,o}}(\mathrm{ag},\mathrm{H_2},t) = \alpha_{\mathrm{hyd/cm}}\cdot m_{\mathrm{b\_gs,t\_gs,c\vec{s}g,o}}(\mathrm{ag},\mathrm{CO},t) \quad (25)$$

Finally, crude syngas exiting all gasifiers is mixed up for further cleaning in downstream cleanup units.

$$m_{\mathrm{b\_gs,c\vec{s}g,o}}(\mathrm{is},t) = \sum_{\mathrm{ag}} m_{\mathrm{b\_gs,t\_gs,c\vec{s}g,is}}(\mathrm{ag},\mathrm{is},t) \quad (26)$$

Syngas Cleanup Unit. The input to this block is crude syngas, and its output comprises sweet syngas and element sulphur. The crude syngas is split into all available alternative syngas cleanup units:

$$m_{\mathrm{b\_gs,c\vec{s}g,o}}(\mathrm{is},t) = \sum_{\mathrm{ac}} m_{\mathrm{b\_cu,t\_cu,c\vec{s}g,i}}(\mathrm{ac},\mathrm{is},t) \quad (27)$$

Again, only one syngas cleanup unit should be selected at most. Appropriate logical constraints are considered:

$$\sum_{\mathrm{ac}} y_{\mathrm{b\_cu}}(\mathrm{ac}) \le 1 \quad (28)$$

$$0 \le m_{\mathrm{b\_cu,t\_cu,c\vec{s}g,i}}(\mathrm{ac},\mathrm{is},t) \le y_{\mathrm{b\_cu}}(\mathrm{ac})\cdot \mathrm{UB} \quad (29)$$

Efficiency of removing each component from the crude syngas is denoted as β_{cu}, and the flowrate of each component in the outlet sweet syngas is given by

$$m_{\mathrm{b\_cu,t\_cu,s\vec{s}g,o}}(\mathrm{ac},\mathrm{is},t) = (1-\beta_{\mathrm{cu}}(\mathrm{ac},\mathrm{is}))\cdot m_{\mathrm{b\_cu,t\_cu,c\vec{s}g,i}}(\mathrm{ac},\mathrm{is},t) \quad (31)$$

After cleanup, sweet syngas from all units goes to a mixer:

$$m_{\mathrm{b\_cu,s\vec{s}g,o}}(\mathrm{is},t) = \sum_{\mathrm{ac}} m_{\mathrm{b\_cu,t\_cu,s\vec{s}g,o}}(\mathrm{ac},\mathrm{is},t) \quad (31)$$

The mixed sweet syngas is then split into two streams, one flowing to the downstream methanol synthesis block and the other entering the gas turbine block. The split ratio, namely the chemical-power ratio r_{cp}, basically determines the production rates of methanol and electricity and it is a significant variable for operating and controlling the entire process. Here, for mathematical reasons (to avoid numerical difficulties such as division by zero), we introduce an equivalent variable, r_{cm}, representing the ratio between the chemical stream and the main stream before split, as follows:

$$r_{\mathrm{cm}}(t) = \frac{r_{\mathrm{cp}}(t)}{r_{\mathrm{cp}}(t)+1} \quad (32)$$

Flowrates of the chemical stream and the power stream are given by

$$m_{\mathrm{b\_cu,s\vec{s}c,o}}(\mathrm{is},t) = r_{\mathrm{cm}}(t)\cdot m_{\mathrm{b\_cu,s\vec{s}g,o}}(\mathrm{is},t) \quad (33)$$

$$m_{\mathrm{b\_cu,s\vec{s}p,o}}(\mathrm{is},t) = (1-r_{\mathrm{cm}}(t))\cdot m_{\mathrm{b\_cu,s\vec{s}g,o}}(\mathrm{is},t) \quad (34)$$

Water–Gas Shift Reactor. Input to this block is a split of the chemical stream of sweet syngas, and its output is a stream of shifted syngas. First, the chemical stream of sweet syngas is further split into two steams, one going through the water-gas shift reactor and the other bypassing it.

$$m_{\mathrm{b\_ws,s\vec{s}s,i}}(\mathrm{is},t) = r_{\mathrm{ws}}(t)\cdot m_{\mathrm{b\_cu,s\vec{s}c,o}}(\mathrm{is},t) \quad (35)$$

$$m_{\mathrm{b\_ws,s\vec{s}n,o}}(\mathrm{is},t) = (1-r_{\mathrm{ws}}(t))\cdot m_{\mathrm{b\_cu,s\vec{s}c,o}}(\mathrm{is},t) \quad (36)$$

The conversion rate of carbon monoxide, denoted as β_{CO}, is constrained by chemical equilibrium. Its maximum value is set to be 90% throughout this model.[8]

$$\Delta m_{\mathrm{CO}}(t) = m_{\mathrm{b\_ws,s\vec{s}s,i}}(\mathrm{is},t) - m_{\mathrm{b\_ws,s\vec{s}s,o}}(\mathrm{is},t),\ \mathrm{is}=\mathrm{CO} \quad (37)$$

$$\Delta m_{\mathrm{CO}}(t) \le \beta_{\mathrm{CO}}\cdot m_{\mathrm{b\_ws,s\vec{s}s,i}}(\mathrm{is},t),\ \mathrm{is}=\mathrm{CO} \quad (38)$$

$$m_{\mathrm{b\_ws,s\vec{s}s,o}}(\mathrm{is},t) = m_{\mathrm{b\_ws,s\vec{s}s,i}}(\mathrm{is},t) + \Delta m_{\mathrm{CO}}(t),\ \mathrm{is}=\mathrm{H_2},\mathrm{CO_2} \quad (39)$$

$$m_{\mathrm{b\_ws,s\vec{s}s,o}}(\mathrm{is},t) = m_{\mathrm{b\_ws,s\vec{s}s,i}}(\mathrm{is},t),\ \mathrm{is}=\mathrm{N_2},\mathrm{H_2O},\mathrm{H_2S} \quad (40)$$

Steam required by the water gas shift reaction is extracted from the steam turbine, and its amount is equal to Δm_{CO}. This will lead to a decrease of the work generated by the steam turbine. Temperature and pressure of the extracted steam would match those of the water gas shift reaction, denoted as T^{wg} and P^{wg}. Its enthalpy is a function of its temperature, whilst its dependence on pressure is negligible, denoted as $h^{T^{\mathrm{wg}}}$. This stream of extracted steam would have generated Δh^{wg} work if it had not been used for water gas shift reaction, given by

$$\Delta h^{\mathrm{wg}} = h^{T^{\mathrm{wg}}} - h^{P^*,x^*} \quad (41)$$

where P^* and x^* are pressure and steam quality at the exit of the steam turbine.

Taking the standard conditions for water gas shift reactions and steam turbines, i.e., T^{wg} being set to 473 K, P^* 0.049 bar, and x^* 0.9, the unit work loss Δh^{wg} is 9144 kJ/kmol. The whole work loss due to the steam extract is then given by:

$$\Delta w^{\mathrm{wg}}(t) = \Delta m_{\mathrm{CO}}(t)\cdot \Delta h^{\mathrm{wg}} \quad (42)$$

After the water-gas shift reaction, the shifted and bypassed syngas mix up again, with this stream being the inlet gas for the downstream carbon dioxide capture block.

$$m_{\mathrm{b\_c1,s\vec{s}g,i}}(\mathrm{is},t) = m_{\mathrm{b\_ws,s\vec{s}s,o}}(\mathrm{is},t) + m_{\mathrm{b\_ws,s\vec{s}n,o}}(\mathrm{is},t) \tag{43}$$

Precombustion Carbon Dioxide Capture. Input to this block is sweet syngas, and its outputs are syngas and captured carbon dioxide. The amount of captured carbon dioxide, $m_{\mathrm{b\_c1}}(t)$, is a process-wide variable to be selected. The upper limit of CO_2 recovery rate, denoted as $\beta^{\mathrm{pre}}_{CO_2}$, determines the maximum amount of carbon dioxide that can be separated, given by:

$$m_{\mathrm{b\_c1}}(t) \le \beta^{\mathrm{pre}}_{CO_2} \cdot m_{\mathrm{b\_c1,s\vec{s}g,i}}(\mathrm{is},t),\ \mathrm{is} = CO_2 \tag{44}$$

Considering the fact that the CO_2 recovery rate is between 95% and 100% for most precombustion CCS technologies,[9,10] $\beta^{\mathrm{post}}_{CO_2}$ is set to 100% for simplicity. The flowrate of the outlet steam of this block is given by

$$m_{\mathrm{b\_c1,s\vec{s}g,o}}(\mathrm{is},t) = m_{\mathrm{b\_c1,s\vec{s}g,i}}(\mathrm{is},t) - m_{\mathrm{b\_c1}}(t),\ \mathrm{is} = CO_2 \tag{45}$$

$$m_{\mathrm{b\_c1,s\vec{s}g,o}}(\mathrm{is},t) = m_{\mathrm{b\_c1,s\vec{s}g,i}}(\mathrm{is},t),\ \mathrm{is} = H_2, CO, H_2O, N_2, H_2S \tag{46}$$

The energy penalty caused by the carbon dioxide separation step is accounted for in the electricity generation section.

Methanol Synthesis. Two mechanistic models are considered for the gas phase and liquid phase methanol synthesis based on chemical kinetics and phase equilibrium proposed by Lee,[11] to handle different mole compositions of the inlet sweet syngas resulted from different gasification technologies used upstream.

First, the sweet syngas is split between gas and liquid phase methanol synthesis. Only one technology can be selected.

$$m_{\mathrm{b\_c1,s\vec{s}g,o}}(\mathrm{is},t) = \sum_{\mathrm{am}} m_{\mathrm{b\_ms,t\_ms,s\vec{s}g,i}}(\mathrm{am},\mathrm{is},t) \tag{47}$$

$$0 \le m_{\mathrm{b\_ms,t\_ms,s\vec{s}g,i}}(\mathrm{am},\mathrm{is},t) \le y_{\mathrm{b\_ms}}(\mathrm{am}) \cdot \mathrm{UB} \tag{48}$$

$$\sum_{\mathrm{am}} y_{\mathrm{b\_ms}}(\mathrm{am}) \le 1 \tag{49}$$

- Gas phase methanol synthesis:

With the inherent difficulty of removing reaction heat, a strict constraint is imposed on the mole composition of inlet syngas to control the amount of reaction heat released for the gas phase methanol synthesis via setting an upper limit to the carbon to hydrogen ratio, as follows:

$$\begin{aligned} &m_{\mathrm{b\_ms,t\_ms,s\vec{s}g,i}}(\mathrm{GP},H_2,t) - 2 \cdot m_{\mathrm{b\_ms,t\_ms,s\vec{s}g,i}}(\mathrm{GP},CO,t) \\ &\quad \cdot m_{\mathrm{b\_ms,t\_ms,s\vec{s}g,i}}(\mathrm{GP},CO_2,t) \ge (y_{\mathrm{b\_ms}}(\mathrm{GP}) - 1) \cdot \mathrm{UB} \end{aligned} \tag{50}$$

Only two reactions are independent from the three reactions taking place in a methanol synthesis reactor (r2 to r4 shown below). Here, we select (r2) and (r3) as the two independent ones.

$$CO + 2H_2 \longrightarrow CH_3OH \tag{r2}$$

$$CO_2 + H_2 \longrightarrow CO + H_2O \tag{r3}$$

$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O \tag{r4}$$

Mole flowrates of all components in the product gas and their mole compositions are expressed in terms of production rates of CH_3OH and H_2O, denoted as Δm_{meh} and Δm_{wat}, and stoichiometric coefficients of reaction (r2) and (r3), as follows

$$\begin{aligned} m_{\mathrm{b\_ms,t\_ms,p\vec{g}m,o}}(\mathrm{am},j,t) &= m_{\mathrm{b\_ms,t\_ms,s\vec{s}g,i}}(\mathrm{am},j,t) \\ &\quad + \upsilon_1(j)\Delta m_{\mathrm{meh}} + \upsilon_2(j)\Delta m_{\mathrm{wat}},\ j = \mathrm{is} \cap \mathrm{im} \end{aligned} \tag{51}$$

Mole fractions of all components in the product gas are given by

$$ym_{\mathrm{p\vec{g}m}}(\mathrm{am},\mathrm{im},t) = \frac{m_{\mathrm{b\_ms,t\_ms,p\vec{g}m,o}}(\mathrm{am},\mathrm{im},t)}{\sum_{\mathrm{im}} m_{\mathrm{b\_ms,t\_ms,p\vec{g}m,o}}(\mathrm{am},\mathrm{im},t)} \tag{52}$$

Fugacity coefficients of each component in the gaseous mixture are expressed in terms of mole fraction, critical temperature and pressure, and reaction temperature and pressure, as follows

$$\ln\phi(\mathrm{am},\mathrm{im},t) = \frac{9T_c(\mathrm{im})P}{128P_c(\mathrm{im})T}\left(1 - \left(\frac{T_c(\mathrm{im})}{T}\right)^2\right) ym_{\mathrm{p\vec{g}m}}(\mathrm{am},\mathrm{im},t) \tag{53}$$

The chemical equilibrium constants of reactions (r2) and (r3) are given below, in terms of mole fractions and fugacity coefficients of reactants.

$$K_1 = \frac{\mathrm{ym}_{\mathrm{p\vec{g}m}}(\mathrm{GP},CH_3OH,t)\phi(\mathrm{GP},CH_3OH,t)}{P^2\mathrm{ym}_{\mathrm{p\vec{g}m}}(\mathrm{GP},CO,t)\mathrm{ym}^2_{\mathrm{p\vec{g}m}}(\mathrm{GP},H_2,t)\phi(\mathrm{GP},CO,t)\phi^2(\mathrm{GP},H_2,t)} \tag{54}$$

$$K_2 = \frac{\mathrm{ym}_{\mathrm{p\vec{g}m}}(\mathrm{GP},CO,t)\mathrm{ym}_{\mathrm{p\vec{g}m}}(\mathrm{GP},H_2O,t)\phi(\mathrm{GP},CO,t)\phi(\mathrm{GP},H_2O,t)}{\mathrm{ym}_{\mathrm{p\vec{g}m}}(\mathrm{GP},CO_2,t)\mathrm{ym}_{\mathrm{p\vec{g}m}}(\mathrm{GP},H_2,t)\phi(\mathrm{GP},CO_2,t)\phi(\mathrm{GP},H_2,t)} \tag{55}$$

On the other hand, empirical equations of equilibrium constants K_1 and K_2 are given by the following expressions:

$$\log_{10}K_1 = \frac{3921}{T} - 7.971\log_{10}T + 2.499\times10^{-3}T - 2.953\times10^{-7}T^2 + 10.2 \tag{56}$$

$$\ln K_2 = 4.33 - \frac{8240}{T+460} \tag{57}$$

Thus relationships between component properties and reactor properties can be established through Eqs. 54–57.

- Liquid phase methanol synthesis:

For liquid phase methanol synthesis, equations of chemical equilibrium are set up for the liquid phase where catalytic reactions take place.

Table 2. Property Coefficients

Coefficient	Value	Coefficient	Value	Coefficient	Value
$T_c(H_2)$	33.2 K	$T_c(CO)$	134.5 K	$T_c(CO_2)$	304.2 K
$T_c(N_2)$	126.2 K	$T_c(CH_3OH)$	513 K	$T_c(H_2O)$	647 K
$P_c(H_2)$	13.0 bar	$P_c(CO)$	35.0 bar	$P_c(CO_2)$	73.8 bar
$P_c(N_2)$	34.0 bar	$P_c(CH_3OH)$	81.0 bar	$P_c(H_2O)$	220.6 bar
$a(H_2)$	−11.12	$b(H_2)$	1438.02	$c(H_2)$	1.90
$a(CO)$	88.99	$b(CO)$	−6417.13	$c(CO)$	−11.63
$a(CO_2)$	4.24	$b(CO_2)$	−629.76	$c(CO_2)$	0
$a(N_2)$	3.53	$b(N_2)$	−105.82	$c(N_2)$	0
$a'(CH_3OH)$	5.16	$b'(CH_3OH)$	1569.61	$c'(CH_3OH)$	−34.85
$a'(H_2O)$	3.56	$b'(H_2O)$	643.75	$c'(H_2O)$	−198.04
a_{oil,H_2}	−0.451	$a_{\mathrm{oil,CO}}$	12.7	a_{oil,CO_2}	−13.3
a_{oil,N_2}	0	a_{oil,CH_3OH}	37.3	a_{oil,H_2O}	0
b_{oil,H_2}	0.00567	$b_{\mathrm{oil,CO}}$	−0.107	b_{oil,CO_2}	0.117
b_{oil,N_2}	0	b_{oil,CH_3OH}	−0.335	b_{oil,H_2O}	0
c_{oil,H_2}	0	$c_{\mathrm{oil,CO}}$	0.000201	c_{oil,CO_2}	−0.000258
c_{oil,N_2}	0	c_{oil,CH_3OH}	0.00076	c_{oil,H_2O}	0
$a_{H_2,\mathrm{oil}}$	0.0476	$a_{\mathrm{CO,oil}}$	0.0903	$a_{CO_2,\mathrm{oil}}$	0.321
$a_{N_2,\mathrm{oil}}$	0	$a_{CH_3OH,\mathrm{oil}}$	−1.011	$a_{H_2O,\mathrm{oil}}$	0
$b_{H_2,\mathrm{oil}}$	−0.000732	$b_{\mathrm{CO,oil}}$	−0.000330	$b_{CO_2,\mathrm{oil}}$	−0.00298
$b_{N_2,\mathrm{oil}}$	0	$b_{CH_3OH,\mathrm{oil}}$	0.0183	$b_{H_2O,\mathrm{oil}}$	0
$c_{H_2,\mathrm{oil}}$	0	$c_{\mathrm{CO,oil}}$	-4.58×10^{-6}	$c_{CO_2,\mathrm{oil}}$	6.60×10^{-6}
$c_{N_2,\mathrm{oil}}$	0	$c_{CH_3OH,\mathrm{oil}}$	-5.40×10^{-5}	$c_{H_2O,\mathrm{oil}}$	0

$$K_1 = \frac{x_{\mathrm{p\vec{g}m}}(\mathrm{CH_3OH},t)k_{\mathrm{H}}(\mathrm{CH_3OH})\gamma(\mathrm{CH_3OH})}{x_{\mathrm{p\vec{g}m}}(\mathrm{CO},t)x^2_{\mathrm{p\vec{g}m}}(\mathrm{H_2},t)k_{\mathrm{H}}(\mathrm{CO})k^2_{\mathrm{H}}(\mathrm{H_2})\gamma(\mathrm{CO})\gamma^2(\mathrm{H_2})} \tag{58}$$

Henry's law constant k_{H} is given as follows.

$$k_{\mathrm{H}}(\mathrm{im}) = 10e^{a(\mathrm{im})+\frac{b(\mathrm{im})}{T}+c(\mathrm{im})\ln(T)},\ \ \mathrm{im} = \mathrm{H_2, CO, CO_2, N_2} \tag{59}$$

$$k_{\mathrm{H}}(\mathrm{im}) = 10^{\frac{a'-b'}{T+c'}} \cdot \phi(\mathrm{im}),\ \ \mathrm{im} = \mathrm{CH_3OH, H_2O} \tag{60}$$

Activity coefficient γ for each reactant in the liquid phase, a solution comprising all reactants and inert oil, is obtained using the following expression.

$$\begin{aligned}\ln\gamma(\mathrm{im},t) =\ & 2A_{\mathrm{oil,im}}x_{\mathrm{p\vec{g}m}}(\mathrm{im},t)x_{\mathrm{oil}}(\mathrm{oil},t) + A_{\mathrm{im,oil}}x^2_{\mathrm{oil}}(\mathrm{oil},t) \\ & - 2\sum_{\mathrm{im}}(A_{\mathrm{oil,im}}x^2_{\mathrm{p\vec{g}m}}(\mathrm{im},t)x_{\mathrm{oil}}(\mathrm{oil},t) \\ & + A_{\mathrm{im,oil}}x_{\mathrm{p\vec{g}m}}(\mathrm{im},t)x^2_{\mathrm{oil}}(\mathrm{oil},t))\end{aligned} \tag{61}$$

$$\sum_{\mathrm{im}} x_{\mathrm{p\vec{g}m}}(\mathrm{im},t) + x_{\mathrm{oil}}(\mathrm{oil},t) = 1 \tag{62}$$

where

$$A_{\mathrm{oil,im}} = a_{\mathrm{oil,im}} + b_{\mathrm{oil,im}}(T-273.15) + c_{\mathrm{oil,im}}(T-273.15)^2 \tag{63}$$

$$A_{\mathrm{im,oil}} = a_{\mathrm{im,oil}} + b_{\mathrm{im,oil}}(T-273.15) + c_{\mathrm{im,oil}}(T-273.15)^2 \tag{64}$$

With activity coefficients and fugacity coefficients available, phase equilibrium relationships between gaseous and liquid phases are established as

$$x_{\mathrm{p\vec{g}m}}(\mathrm{im},t)\gamma(\mathrm{im},t)k_{\mathrm{H}}(\mathrm{im}) = \mathrm{ym}_{\mathrm{p\vec{g}m}}(\mathrm{LP},\mathrm{im},t)\phi(\mathrm{LP},\mathrm{im},t)P \tag{65}$$

The production rate of methanol is given by

$$m_{\mathrm{b\_ms,mep,o}}(t) = \sum_{\mathrm{am}} m_{\mathrm{b\_ms,t\_ms,p\vec{g}m,o}}(\mathrm{am},\mathrm{im},t),\ \ \mathrm{im} = \mathrm{CH_3OH} \tag{66}$$

Property coefficients used in this block are listed in Table 2.

Gas Turbine. Inputs to the gas turbine block include fuel gas, atmosphere air to the air compressor, nitrogen recycled from the ASU block, and steam injection from the steam turbine. Its outputs are flue gas leaving the turbine, compressed air to the ASU block, and mechanical work generated by the turbine.

The fuel gas input comprises two parts: flue gas from the methanol synthesis block and the power stream of the fresh sweet syngas after the cleanup unit, as follows

$$m_{\mathrm{b\_gt,f\vec{u}g,i}}(j,t) = \sum_{\mathrm{am}} m_{\mathrm{b\_ms,t\_ms,p\vec{g}m,o}}(\mathrm{am},j,t) + m_{\mathrm{b\_cu,s\vec{s}p,o}}(j,t),\quad j = \mathrm{is} \cap \mathrm{im} \cap \mathrm{ig} \tag{67}$$

Then it is split into all available alternative gas turbines. Again only one of them should be selected.

$$m_{\mathrm{b\_gt,f\vec{u}g,i}}(\mathrm{ig},t) = \sum_{\mathrm{agt}} m_{\mathrm{b\_gt,t\_gt,f\vec{u}g,i}}(\mathrm{agt},\mathrm{ig},t) \tag{68}$$

$$0 \le m_{\mathrm{b\_gt,t\_gt,f\vec{u}g,i}}(\mathrm{agt},\mathrm{ig},t) \le y_{\mathrm{b\_gt}}(\mathrm{agt}) \cdot \mathrm{UB} \tag{69}$$

$$\sum_{\mathrm{agt}} y_{\mathrm{b\_gt}}(\mathrm{agt}) \le 1 \tag{70}$$

The lower heating value (LHV) of the fuel is used as the reference variable, given by

$$lhv_{\mathrm{b\_gt,t\_gt,fug,i}}(\mathrm{agt},t)=\sum_{\mathrm{ig}}\mathrm{LHV}(\mathrm{fug})\cdot m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{fug}},\mathrm{i}}(\mathrm{agt},\mathrm{ig},t) \tag{71}$$

The LHV of H_2 and CO are 122.68 and 10.11 MJ/kg, respectively, and the LHV of all other components in the fuel gas are zero.

Flowrates of inlet air, nitrogen and steam injection are calculated from the lower heating value:

$$m_{\mathrm{b\_gt,t\_gt,air,i}}(\mathrm{agt},t)=\alpha_{\mathrm{air/lhv}}(\mathrm{agt})\cdot lhv_{\mathrm{b\_gt,t\_gt,fug,i}}(\mathrm{agt},t) \tag{72}$$

$$m_{\mathrm{b\_gt,t\_gt,nit,i}}(\mathrm{agt},t)=\alpha_{\mathrm{nit/lhv}}(\mathrm{agt})\cdot lhv_{\mathrm{b\_gt,t\_gt,fug,i}}(\mathrm{agt},t) \tag{73}$$

$$m_{\mathrm{b\_gt,t\_gt,stm,i}}(\mathrm{agt},t)=\alpha_{\mathrm{stm/lhv}}(\mathrm{agt})\cdot lhv_{\mathrm{b\_gt,t\_gt,stm},i}(\mathrm{agt},t) \tag{74}$$

Total flowrates of each component in all inlet streams are given by

$$\begin{aligned}m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{ig},t)&=m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{fug}},\mathrm{i}}(\mathrm{agt},\mathrm{ig},t)\\&+(m_{\mathrm{b\_gt,t\_gt,air,i}}(\mathrm{agt},t)-m_{\mathrm{b\_as,aic,i}}(t))\cdot X_{\mathrm{air}}(\mathrm{O_2}),\ \ \mathrm{ig}=\mathrm{O_2}\end{aligned} \tag{75}$$

$$\begin{aligned}m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{ig},t)&=m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{fug}},\mathrm{i}}(\mathrm{agt},\mathrm{ig},t)\\&+(m_{\mathrm{b\_gt,t\_gt,air,i}}(\mathrm{agt},t)-m_{\mathrm{b\_as,aic,i}}(t))\cdot X_{\mathrm{air}}(\mathrm{N_2})\\&+m_{\mathrm{b\_gt,t\_gt,N_2},i}(\mathrm{agt},t),\ \ \mathrm{ig}=\mathrm{N_2}\end{aligned} \tag{76}$$

$$\begin{aligned}m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{ig},t)&=m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{fug}},\mathrm{i}}(\mathrm{agt},\mathrm{ig},t)\\&+m_{\mathrm{b\_gt,t\_gt,stm,i}}(\mathrm{agt},t),\ \ i=\mathrm{H_2O}\end{aligned} \tag{77}$$

$$\begin{aligned}m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{ig},t)&=m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{fug}},\mathrm{i}}(\mathrm{agt},\mathrm{ig},t),\\&\quad i=\mathrm{H_2,CO,CO_2}\end{aligned} \tag{78}$$

Assuming that complete combustion takes place in the combustion chamber of a gas turbine, the flowrates of components in the flue gas are given by mass balances over all elements, as follows:

$$\begin{aligned}m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{H_2},t)&+m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{H_2O},t)\\&=m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{o}}(\mathrm{agt},\mathrm{H_2O},t)\end{aligned} \tag{79}$$

$$\begin{aligned}2m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{O_2},t)&+m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{H_2O},t)\\&+m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{CO},t)+2m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{CO_2},t)\\&=2m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{o}}(\mathrm{agt},\mathrm{O_2},t)+m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{o}}(\mathrm{agt},\mathrm{H_2O},t)\\&+m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{o}}(\mathrm{agt},\mathrm{CO_2},t)\end{aligned} \tag{80}$$

$$\begin{aligned}m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{CO},t)&+m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{CO_2},t)\\&=m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{o}}(\mathrm{agt},\mathrm{CO_2},t)\end{aligned} \tag{81}$$

$$m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{agt},\mathrm{ig},t)=m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{o}}(\mathrm{agt},\mathrm{ig},t),\ \ \mathrm{ig}=\mathrm{N_2} \tag{82}$$

$$m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{o}}(\mathrm{agt},\mathrm{ig},t)=0,\ \ \mathrm{ig}=\mathrm{H_2,CO} \tag{83}$$

$$m_{\mathrm{b\_gt,}\vec{\mathrm{gas}},\mathrm{o}}(\mathrm{ig},t)=\sum_{\mathrm{agt}}m_{\mathrm{b\_gt,t\_gt,}\vec{\mathrm{gas}},\mathrm{o}}(\mathrm{agt},\mathrm{ig},t) \tag{84}$$

The mechanical work generated by a gas turbine is obtained from the turbine's internal efficiency as follows

$$w_{\mathrm{b\_gt}}(\mathrm{agt},t)=\eta_{i,\mathrm{b\_gt}}(\mathrm{agt})\cdot lhv_{\mathrm{b\_gt,t\_gt,fug,i}}(\mathrm{agt},t) \tag{85}$$

HRSG and Steam Turbine. Streams carrying enthalpy into the HRSG and steam turbine block include the flue gas leaving the gas turbine block, the heat recovered in the gasifier chamber and scrubber block, the heat recovered in the syngas cleanup unit, and all miscellaneous heat recovered elsewhere in the process. The enthalpy in these streams is given as follows

$$h_{\mathrm{b\_gt,t\_gt,gas,o}}(\mathrm{agt},t)=lhv_{\mathrm{b\_gt,t\_gt,fug,i}}(\mathrm{agt},t)-w_{\mathrm{b\_gt}}(\mathrm{agt},t) \tag{86}$$

$$h_{\mathrm{b\_st,gas,i}}(t)=\sum_{\mathrm{agt}}h_{\mathrm{b\_gt,t\_gt,gas,o}}(\mathrm{agt},t) \tag{87}$$

$$h_{\mathrm{b\_gs,t\_gs,rch,o}}(\mathrm{ag},t)=\alpha_{\mathrm{rch/b\_gs}}(\mathrm{ag})\cdot \mathrm{ma}_{\mathrm{b\_gs,t\_gs,csg,o}}(\mathrm{ag},t) \tag{88}$$

$$h_{\mathrm{b\_cu,t\_cu,rch,o}}(\mathrm{ac},t)=\alpha_{\mathrm{rch/b\_cu}}(\mathrm{ac})\cdot \mathrm{ma}_{\mathrm{b\_cu,t\_cu,csg,i}}(\mathrm{ac},t) \tag{89}$$

$$h_{\mathrm{b\_st,rch,i}}(t)=\sum_{\mathrm{ag}}h_{\mathrm{b\_gs,t\_gs,rch,o}}(\mathrm{ag},t)+\sum_{\mathrm{ac}}h_{\mathrm{b\_cu,t\_cu,rch,o}}(\mathrm{ac},t) \tag{90}$$

$$h_{\mathrm{b\_st,rcm,i}}(t)=\alpha_{\mathrm{rcm/gas}}\cdot \mathrm{ma}_{\mathrm{b\_gt,gas,o}}(t) \tag{91}$$

The mechanical work generated in this block is given by:

$$w_{\mathrm{b\_st}}(t)=\eta_{\mathrm{i,b\_st}}\cdot(h_{\mathrm{b\_st,gas,i}}(t)+h_{\mathrm{b\_st,rch,i}}(t)+h_{\mathrm{st,rcm,i}}(t)) \tag{92}$$

Postcombustion Carbon Dioxide Capture. Input to this block is flue gas coming out of the HRSG, and its outputs are captured carbon dioxide and the remaining part of the flue gas. The amount of captured carbon dioxide, $m_{\mathrm{b\_c2}}(t)$, is a process-wide variable to be selected. The upper limit of CO_2 recovery rate, denoted as $\beta^{\mathrm{post}}_{\mathrm{CO_2}}$, determines the maximum amount of carbon dioxide that can be separated, given by:

$$m_{\mathrm{b\_c2,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{ig},t)=m_{\mathrm{b\_gt,}\vec{\mathrm{gas}},\mathrm{o}}(\mathrm{ig},t) \tag{93}$$

$$m_{\mathrm{b\_c2}}(t)\le\beta^{\mathrm{post}}_{\mathrm{CO_2}}\cdot m_{\mathrm{b\_c2,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{ig},t),\ \ \mathrm{ig}=\mathrm{CO_2} \tag{94}$$

Considering the fact that the CO_2 recovery rate is below 90% for most postcombustion CCS technologies,[9,10] $\beta^{\mathrm{post}}_{\mathrm{CO_2}}$ is set to 90%. The flowrate of the outlet steam is given by

$$m_{\mathrm{b\_c2,}\vec{\mathrm{gas}},\mathrm{o}}(\mathrm{ig},t)=m_{\mathrm{b\_c2,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{ig},t)-m_{\mathrm{b\_c2}}(t),\ \ \mathrm{ig}=\mathrm{CO_2} \tag{95}$$

$$m_{\mathrm{b\_c2,}\vec{\mathrm{gas}},\mathrm{o}}(\mathrm{ig},t)=m_{\mathrm{b\_c2,}\vec{\mathrm{gas}},\mathrm{i}}(\mathrm{ig},t),\ \ \mathrm{ig}=\mathrm{O_2,N_2,H_2O} \tag{96}$$

Energy penalty caused by the carbon dioxide separation step is accounted in the electricity generation section.

Production rates

Production rates of primary products, i.e., methanol and electricity, and by-products are calculated in this section.

Production of Methanol. The production rate of methanol is obtained from the methanol synthesis block, as follows

$$\mathrm{ma}_{\mathrm{meh}}(t) = \mathrm{MW}(\mathrm{CH_3OH}) \cdot m_{\mathrm{b\_ms,meh,o}}(t) \tag{97}$$

Methanol should meet its market demand in each period, given by

$$\mathrm{ma}_{\mathrm{meh}}(t) \geq \Phi_{\mathrm{meh}}(t) \tag{98}$$

Electricity Generation. Gross mechanical work is generated in the process from the gas and steam turbines. After deduction of the compression work consumed in the ASU, in the CO_2 capture block, and other auxiliary equipment, net mechanical work is obtained.

The gross mechanical work is given as follows

$$w_{\mathrm{grp}}(t) = \sum_{\mathrm{agt}} w_{\mathrm{b\_gt}}(\mathrm{agt}, t) + w_{\mathrm{b\_st}}(t) \tag{99}$$

The compression work consumed in the ASU comprises three parts, namely compression work for the inlet air, the oxygen product and nitrogen, given as follows

$$w_{\mathrm{aia}}(t) = \alpha_{\mathrm{w/aia}} \cdot \mathrm{ma}_{\mathrm{b\_as,aia,i}}(t) \tag{100}$$

$$w_{\mathrm{aio}}(t) = \alpha_{\mathrm{w/aio}} \cdot \mathrm{ma}_{\mathrm{b\_as,aio,o}}(t) \tag{101}$$

$$w_{\mathrm{ain}}(t) = \alpha_{\mathrm{w/ain}} \cdot \mathrm{ma}_{\mathrm{b\_as,ain,o}}(t) \tag{102}$$

The work consumption in precombustion and postcombustion CO_2 capture blocks are given by

$$w_{\mathrm{b\_c1}}(t) = \alpha_{\mathrm{w/c1}} \cdot \mathrm{ma}_{\mathrm{b\_c1}}(t) \tag{103}$$

$$w_{\mathrm{b\_c2}}(t) = \alpha_{\mathrm{w/c2}} \cdot \mathrm{ma}_{\mathrm{b\_c2}}(t) \tag{104}$$

The work consumed by other auxiliary equipment is given as a fraction of gross mechanical work generation, as follows

$$w_{\mathrm{aux}}(t) = \alpha_{\mathrm{w/aux}} \cdot w_{\mathrm{grp}}(t) \tag{105}$$

The net mechanical work production is obtained as a summation of all the mechanical work, together with the work loss resulted by steam extraction for the water gas shift reaction, as follows

$$\begin{aligned} w_{\mathrm{net}}(t) = w_{\mathrm{grp}}(t) - w_{\mathrm{aia}}(t) - w_{\mathrm{aio}} - w_{\mathrm{ain}} - w_{\mathrm{b\_c1}}(t) \\ - w_{\mathrm{b\_c2}} - w_{\mathrm{aux}}(t) - \Delta w^{\mathrm{wg}}(t) \end{aligned} \tag{106}$$

Using the mechanical efficiency of the generator, the net electricity production rate is given by

$$\mathrm{elc}(t) = \eta_{\mathrm{m}} \cdot w_{\mathrm{net}}(t) \tag{107}$$

Again, the electricity production rate should meet its market demand in each period, as follows

$$\mathrm{elc}(t) \geq \Phi_{\mathrm{elc}}(t) \tag{108}$$

Production of Sulphur as a By-Product. Production rate of sulphur is given as a product of sulphur removal rate and its content in the inlet coal, as follows

$$\mathrm{ma}_{\mathrm{sul}}(t) = \alpha_{\mathrm{sul/drc}} * (\mathrm{ma}_{\mathrm{b\_cp,drc,i}}(t) * \mathrm{UA}(S)) \tag{109}$$

Objective Functions. An economic objective, NPV, is calculated from initial capital costs of the process and its profit over the operating horizon. Initial capital costs comprise the purchase of primary equipment, auxiliary equipment, civil/structure/architectural costs, engineering fees and contigency, interest occured during construction period, and starting-up costs. Profit over the operating horizon is calculated by discounting the net profit in each time interval to the starting point of the operating horizon and summing them up.

The purpose of the environmental objective is to provide an objective measurement of the environmental behaviour of a polygeneration plant over its life time, comprising all primary types of emissions produced from both plant operation and all previous stages. Based on this, all sorts of damage assessments can be conducted according to specific interest and purposed, for instance, impacts on climate change, ecotoxicity effects, and depletion of natural resources. A cradle-to-gate GHG emissions indicator is established over the operating horizon, on a CO_2-equivalent basis. It comprises three parts:

- GHG emissions produced within the process during operation
- GHG emissions produced throughout mining, extraction, and other preprocessing phases of feedstocks
- GHG emissions produced during equipment production and plant construction

Net Present Value. The NPV of the process is obtained by subtracting the total capital requirement up to the starting point of process operation from the summation of net profit in each period discounted to the same time point.

The calculation of the total capital requirement results from the investment cost calculations of primary equipment in all functional blocks. For each block, there is a reference capacity and investment cost. Size effects are considered by a size factor. The capacity of each block is expressed in terms of a primary stream, as follows

- ASU—oxygen production rate
- coal preparation—coal flowrate
- gasifier and scrubber—coal flowrate
- syngas cleanup unit—clean syngas production rate
- water-gas shift reactor—flowrate of inlet syngas
- precombustion CO_2 capture—flowrate of captured CO_2
- methanol synthesis—methanol production rate

- gas turbine—mechanical work generation
- HRSG and steam turbine—mechanical work generation
- postcombustion CO_2 capture—flowrate of captured CO_2

The investment cost of each block is given by

$$\mathrm{inv}(p,q)=\delta\mathrm{inv}(p,q)\left(\frac{\mathrm{cap}(p,q)}{\delta\mathrm{cap}(p,q)}\right)^{n},\quad p=\mathrm{block},q=\mathrm{technology}$$

In all operating periods, the capacity of each block should be greater than the operating flowrate of the corresponding stream, denoted by z, upon which the capacity is defined, as follows

$$\mathrm{cap}(p,q)\geq z(p,q,t),\ \ p=\mathrm{block},q=\mathrm{technology},t=\mathrm{period} \tag{111}$$

The investment cost for all primary equipment is then expressed as the summation over all functional blocks using all technologies, as follows

$$\mathrm{inv}_{\mathrm{eqp}}=\sum_{p,q}\mathrm{inv}(p,q),\ \ p=\mathrm{block},q=\mathrm{technology} \tag{112}$$

Investment costs for bulk plant items, including water system, civil, structure, architecture, piping, control and instrumentation, and electrical systems, are given by

$$\mathrm{inv}_{\mathrm{bk}}=\alpha_{\mathrm{bk/equ}}\cdot\mathrm{inv}_{\mathrm{equ}} \tag{113}$$

Process plant cost is obtained from costs of equipment and bulk plants items, as follows

$$\mathrm{inv}_{\mathrm{ppc}}=\mathrm{inv}_{\mathrm{eqp}}+\mathrm{inv}_{\mathrm{bk}} \tag{114}$$

Engineering fees and project contingency are given by

$$\mathrm{inv}_{\mathrm{efc}}=\alpha_{\mathrm{efc/ppc}}\cdot\mathrm{inv}_{\mathrm{ppc}} \tag{115}$$

Total plant cost is then given by their summation, as follows

$$\mathrm{inv}_{\mathrm{tpc}}=\mathrm{inv}_{\mathrm{ppc}}+\mathrm{inv}_{\mathrm{efc}} \tag{116}$$

Interest occurred during the construction period is obtained as

$$\mathrm{inv}_{\mathrm{ist}}=\alpha_{\mathrm{ist/tpc}}\cdot\mathrm{inv}_{\mathrm{tpc}} \tag{117}$$

Finally, the total plant investment is

$$\mathrm{inv}_{\mathrm{tpi}}=\mathrm{inv}_{\mathrm{tpc}}+\mathrm{inv}_{\mathrm{ist}} \tag{118}$$

Miscellaneous investment costs, including prepaid royalties, initial catalyst and chemical inventory, startup costs, spare parts, working capital, and land use, is given by

$$\mathrm{inv}_{\mathrm{mis}}=\alpha_{\mathrm{mis/tpi}}\cdot\mathrm{inv}_{\mathrm{tpi}} \tag{119}$$

The total capital requirement of a plant is given by

$$\mathrm{inv}_{\mathrm{tcr}}=\mathrm{inv}_{\mathrm{tpi}}+\mathrm{inv}_{\mathrm{mis}} \tag{120}$$

In each period, O and M costs includes purchase of feedstocks, sequestration of CO_2, and other fixed cost. Purchase of feedstocks is obtained as the product of capacity factor (availability), operating time within the period, price of feedstocks, and consumption rate, as follows

$$\mathrm{omc}_{\mathrm{drc}}(t)=\lambda(t)\cdot\tau(t)\cdot\zeta_{\mathrm{drc}}(t)\cdot\mathrm{ma}_{\mathrm{b\_cp,drc,i}}(t) \tag{121}$$

The cost of CO_2 sequestration is given as the product of capacity factor, unit cost of sequestration, and rate of sequestration, as follows

$$\mathrm{omc}_{\mathrm{seq}}(t)=\lambda(t)\cdot\tau(t)\cdot\zeta_{\mathrm{seq}}(t)\cdot\mathrm{ma}_{\mathrm{b\_c1,s\vec{s}g,o}}(\mathrm{is},t),\ \ \mathrm{is}=\mathrm{CO_2} \tag{122}$$

Fixed O and M costs are obtained as a fraction of the total capital requirement, given by

$$\mathrm{omc}_{\mathrm{fix}}(t)=\lambda(t)\cdot\alpha_{\mathrm{fix/tcr}}\cdot\mathrm{inv}_{\mathrm{tcr}} \tag{123}$$

Income in each period comes from the sales of electricity and methanol (and sulphur as a by-product), given by

$$\mathrm{inc}_{\mathrm{elc}}(t)=\lambda(t)\cdot\tau(t)\cdot\zeta_{\mathrm{elc}}(t)\cdot\Phi_{\mathrm{elc}} \tag{124}$$

$$\mathrm{inc}_{\mathrm{mep}}(t)=\lambda(t)\cdot\tau(t)\cdot\zeta_{\mathrm{mep}}(t)\cdot\Phi_{\mathrm{mep}} \tag{125}$$

$$\mathrm{inc}_{\mathrm{sul}}(t)=\lambda(t)\cdot\tau(t)\cdot\zeta_{\mathrm{sul}}(t)\cdot\mathrm{ma}_{\mathrm{sul}}(t) \tag{126}$$

The net income in each period is thus obtained as follows

$$\mathrm{inc}_{\mathrm{net}}(t)=(\mathrm{inc}_{\mathrm{elc}}(t)+\mathrm{inc}_{\mathrm{mep}}(t)+\mathrm{inc}_{\mathrm{sul}}(t))-(\mathrm{omc}_{\mathrm{drc}}(t)+\mathrm{omc}_{\mathrm{seq}}(t)+\mathrm{omc}_{\mathrm{fix}}(t)) \tag{127}$$

After discounting the net income in all periods to the starting point of project, the net present value is obtained as follows

$$\mathrm{npv}=\sum_{t}\frac{\mathrm{inc}_{\mathrm{net}}}{(1+r)^{\tau(t)}}-\mathrm{inv}_{\mathrm{tcr}} \tag{128}$$

Equation 128 is used as the economic objective function to be maximized.

Coefficients used in the calculation of the economic objective function are listed in Table 3.

GHG Emissions. Emissions of three GHG gases, denoted as e, namely CO_2, CH_4, and NO_x, are calculated from the following three stages:

- cradle-to-gate emissions during feedstock production, including extraction and transportation to site

Table 3. Coefficients for Calculation of the Economic Objective Function

Coefficient	Value
n	0.7
$\alpha_{bk/equ}$	0.34
$\alpha_{efc/ppc}$	0.25
$\alpha_{ist/tpc}$	0.112
$\alpha_{mic/tpi}$	0.053
r	0.1

- emissions produced during equipment production, installation and plant construction
- emissions produced throughout the plant operating period

Cradle-to-gate emissions during feedstock production and precessing procedure are obtained from corresponding emission inventory and consumption rate of feedstocks. Inventories of all the three emissions during coal production and precessing, denoted as γ_{fds}, are taken from European Reference Life Cycle Data System (ELCD),[12] which are obtained from official statistical data of EU-25 countries. Inventories for CO_2, CH_4, and NO_x are 0.0154, 0, 3.85×10^{-5} kilogramme per kilogramme of coal produced, respectively. Emissions from this category are calculated as:

$$\mathrm{ghg}_{\mathrm{fds}}(e) = \sum_t \lambda(t) \cdot \tau(t) \cdot \gamma_{\mathrm{fds}}(e) \cdot \mathrm{ma}_{\mathrm{b\_cp,drc,i}}(t) \qquad (129)$$

Emissions produced during the equipment production, installation and plant construction are obtained as the product of the investment cost of the equipment or the construction procedure and a corresponding emission inventory, which is calculated using the Economic Input-Output Life Cycle Assessment (EIO-LCA) method. The EIO-LCA method estimates the materials and energy resources required for, and the environmental emissions resulting from, activities in an economy, and it provides emission inventories on an economic basis, i.e., the amount emissions produced by investing a unit amount on a certain type of equipment or constructing a certain type of plant. Values of these EIO-LCA emission inventories are obtained from Ref. 13, denoted as γ_{eqp} and γ_{con}, respectively. Emissions from this category are calculated as:

$$\mathrm{ghg}_{\mathrm{eqc}}(e) = \sum_{p,q} \gamma_{\mathrm{eqp}}(p,q,e) \cdot \mathrm{inv}(p,q) + \gamma_{\mathrm{con}}(e) \cdot \mathrm{inv}_{\mathrm{bk}},$$
$$p = \text{block}, q = \text{technology} \qquad (130)$$

Emissions produced throughout the plant operating period can be calculated either directly or via corresponding reference variables. Carbon dioxide emissions of this category are given by:

Table 4. Ultimate Analysis of Illinois #6 Coal, wt %, Dry Basis

C	H	N	S	O	Ash
71.7	5.1	1.4	2.8	7.8	11.2

Table 5. Prices of Feedstocks and Products

		Price
Feedstocks	Coal	65 \$/tonne
Products	Methanol	343 \$/tonne
	Electricity	0.06 \$/kWh
	Sulphur	82.7 \$/tonne

$$\mathrm{ghg}_{\mathrm{opt}}(CO_2) = \sum_t \lambda(t) \cdot \tau(t) \cdot \mathrm{ma}_{\mathrm{b\_c2,g\vec{a}s,o}}(CO_2, t) \qquad (131)$$

Emissions of SO_2 are obtained from the sulphur removal rate, as follows:

$$\mathrm{ghg}_{\mathrm{opt}}(SO_2) = 2\sum_t \lambda(t) \cdot \tau(t) \cdot (1 - \alpha_{\mathrm{sul/drc}})$$
$$* \, \mathrm{ma}_{\mathrm{b\_cp,drc,i}}(t) * \mathrm{UA}(S) \qquad (132)$$

Emissions of NO_x are calculated using the mechanical work generated by the gas turbine as the reference variable, as follows:

$$\mathrm{ghg}_{\mathrm{opt}}(NO_x) = \sum_{\mathrm{agt},t} \lambda(t) \cdot \tau(t) \cdot \alpha_{\mathrm{NO_x/wgt}} \cdot w_{\mathrm{b\_gt}}(\mathrm{agt}, t) \qquad (133)$$

Overall emissions of each kind are the summation of those produced during each phase discussed earlier, as follows:

$$\mathrm{ghg}(e) = \mathrm{ghg}_{\mathrm{fds}}(e) + \mathrm{ghg}_{\mathrm{eqc}}(e) + \mathrm{ghg}_{\mathrm{opt}}(e) \qquad (134)$$

Emissions of CO_2, SO_2, and NO_x have different impacts on the green house gas effect. According to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC), their impact factors are 1, 0, and 310 respectively, on a hundred year time scale.[14] Denoting the

Table 6. Technology Alternatives Considered for Functional Blocks

Block	Symbol of Technical Alternative	Definition
Gasification chamber and sysgas scrubber	Q	Oxygen-blown, coal slurry fed, quench for crude syngas cooling
	RC	Oxygen-blown, coal slurry fed, radiative and convective heat exchanger for crude syngas cooling
	H	Oxygen-blown, coal slurry fed, radiative and convective heat exchanger for crude syngas cooling, compatible with hot syngas cleanup
Syngas cleanup unit	CQ	Cold syngas cleanup, compatible with quench gasifier
	CRC	Cold syngas cleanup, compatible with radiative and convective gasifier
	CH	Hot syngas cleanup
Methanol synthesis	G	Gas phase methanol synthesis
	L	Liquid phase methanol
turbine	GTH	H-class gas turbine

Table 7. Values of Key Parameters for Each Functional Block

Block	Parameter	Value
ASU	β_{ir}	50%
	$X_{aox}(O_2)$	0.95
	$X_{aox}(N_2)$	0.05
	$X_{ani}(O_2)$	0.011
	$X_{ani}(N_2)$	0.989
	δ_{cap}	29.3 kg/s oxygen
	δ_{inv}	53.6×10^6 \$
	$\gamma_{eqp}(CO_2)$	16.8 tonne/10^6 \$
Coal preparation	$\alpha_{csl/drc}$	0.5
	$\alpha_{oxb/drc}$	0
	δcap(G–Q)	31.6 kg/s coal
	δcap(G–RC)	31.1 kg/s coal
	δcap(G–H)	28.8 kg/s coal
	δinv(G–Q)	27.7×10^6 \$
	δinv(G–RC)	27.3×10^6 \$
	δinv(G–H)	25.9×10^6 \$
	$\gamma_{eqp}(CO_2)$	16.8 tonne/10^6 \$
Gasifier chamber and syngas scrubber	$\alpha_{oxy/drc}$	0.923
	$\alpha_{swi/drc}$	0
	$\alpha_{mkw/drc}$(G–Q)	0.54
	$\alpha_{mkw/drc}$(G–RC)	0.124
	$\alpha_{mkw/drc}$(G–H)	0.103
	$\alpha_{bld/drc}$(G–Q)	2.098
	$\alpha_{bld/drc}$(G–RC)	0.45
	$\alpha_{bld/drc}$(G–H)	0
	$\alpha_{ssl/drc}$(G–Q)	0.59
	$\alpha_{ssl/drc}$(G–RC)	0.536
	$\alpha_{ssl/drc}$(G–H)	0.156
	δcap(G–Q)	31.6 kg/s coal
	δcap(G–RC)	31.1 kg/s coal
	δcap(G–H)	28.8 kg/s coal
	δinv(G–Q)	32.9×10^6 \$
	δinv(G–RC)	79×10^6 \$
	δinv(G–H)	63.6×10^6 \$
	$\gamma_{eqp}(CO_2)$	16.8 tonne/10^6 \$
Syngas cleanup	$\beta_{cu}(ac,H_2O)$	1
	$\beta_{cu}(ac,CO_2)$	0.27
	$\beta_{cu}(ac,H_2S)$	1
	δcap(CGCU–Q)	58.1 kg/s syngas
	δcap(CGCU–RC)	62.8 kg/s syngas
	δcap(HGCU)	72.9 kg/s syngas
	δinv(CGCU–Q)	37.3×10^6 \$
	δinv(CGCU–RC)	30.6×10^6 \$
	δinv(HGCU)	65.0×10^6 \$
	$\gamma_{eqp}(CO_2)$	16.8 tonne/10^6 \$
Precombustion CCS	$\alpha_{w/c1}$	0.173 kWh/kg CO_2
	δcap	17.5 kg/s
	δinv	26.5×10^6 \$
	$\gamma_{eqp}(CO_2)$	16.8 tonne/10^6 \$
Methanol synthesis	T(GP)	523 K
	T(LP)	523 K
	P(GP)	70 bar
	P(LP)	50 bar
	δcap(GP)	12.4 kg/s methanol
	δcap(LP)	12.4 kg/s methanol
	δinv(GP)	15.6×10^6 \$
	δinv(LP)	30.0×10^6 \$
	$\gamma_{eqp}(GP,CO_2)$	16.8 tonne/10^6 \$
	$\gamma_{eqp}(LP,CO_2)$	16.8 tonne/10^6 \$
Gas turbine	$\alpha_{air/lhv}$(GT–H)	0.782 kg/MJ
	$\alpha_{nit/lhv}$(GT–H)	0.0473 kg/MJ
	$\alpha_{stm/lhv}$(GT–H)	0.0147 kg/MJ
	η_{i,b_gt}(GT–H)	0.405
	δcap(GT–H)	282.2 MW
	δinv(GT–H)	54×10^6 \$
	$\gamma_{eqp}(GT–H,CO_2)$	39.5 tonne/10^6 \$
	$\gamma_{eqp}(GT–H,SO_2)$	2.49 tonne/10^6 \$
	$\gamma_{eqp}(GT–H,NO_x)$	0.649 tonne/10^6 \$
HRSG and steam turbine	α_{rch/b_gs}(G–Q)	0 MW/(kg/s)
	α_{rch/b_gs}(G–RC)	0.819 MW/(kg/s)
	α_{rch/b_gs}(G–H)	0.728 MW/(kg/s)
	$\alpha_{rch/b–cu}$(CGCU–Q)	0.182 MW/(kg/s)
	$\alpha_{rch/b–cu}$(CGCU–RC)	0 MW/(kg/s)
	$\alpha_{rch/b–cu}$(HGCU)	0 MW/(kg/s)
	$\alpha_{rcm/gas}$	0.399 MW/(kg/s)
	$\eta_{i,b–st}$	0.306
	δcap	154.6 MW
	δinv	45.5×10^6 \$
	$\gamma_{eqp}(CO_2)$	39.5 tonne/10^6 \$
	$\gamma_{eqp}(SO_2)$	2.49 tonne/10^6 \$
	$\gamma_{eqp}(NO_x)$	0.649 tonne/10^6 \$
Postcombustion CCS	$\alpha_{w/c2}$	0.288 kWh/kg CO_2
	δcap	17.5 kg/s
	δinv	26.5×10^6 \$
	$\gamma_{eqp}(CO_2)$	16.8 tonne/10^6 \$
Electricity generation	$\alpha_{w/aia}$	0.399 MW/(kg/s)
	$\alpha_{w/aio}$	0.229 MW/(kg/s)
	$\alpha_{w/ain}$	0.134 MW/(kg/s)
	$\alpha_{w/ccd}$	1.482 MW/(kg/s)
	$\alpha_{w/aux}$	0.023
	η_m	0.985
Sulphur recovery	$\alpha_{sul/drc}$	0.99
Plant construction	$\gamma_{eqp}(CO_2)$	209 tonne/10^6 \$
	$\gamma_{eqp}(NO_x)$	0.626 tonne/10^6 \$

impact factors by σ, the overall green house gas effect of all emissions are given on a CO_2 equivalent basis, as follows:

$$\text{ghg}_{CO_2\text{eqv}} = \sum_e \sigma(e) \cdot \text{ghg}(e) \tag{135}$$

Equation 135 is used as the environmental objective function to be minimized.

Model Summary and Its Solution as a Multi-Objective Optimization Problem. The model is formulated as

$$\begin{aligned} \min \quad & U \begin{cases} f_1 = -\text{npv} \\ f_2 = \text{ghg}_{CO_2\text{eqv}} \end{cases} \\ \text{s.t.} \quad & \text{Eq. 1–135} \end{aligned} \tag{p}$$

This is a multiobjective optimization (MOO) problem for decision making. The goal is to obtain U, the decision maker's utility function, which comprises the two objective functions to be minimized simultaneously. Its optimal solutions satisfy the condition that any further decrease of one objective function will always cause increase of the other objective function, the so called Pareto optimality.

This MOO problem is converted into a set of conventional single objective optimization problems using the ϵ-Constraint method.[15] Firstly, problem (p) is solved with only objective function one, f_1, as follows:

$$\begin{aligned} \min \quad & f_1 = -\text{npv} \\ \text{s.t.} \quad & \text{Eq. 1–135} \end{aligned} \tag{p1}$$

By solving problem (p1), an optimal solution can be obtained, denoted as $\vec{x}_1^*$. The maximum of objective function

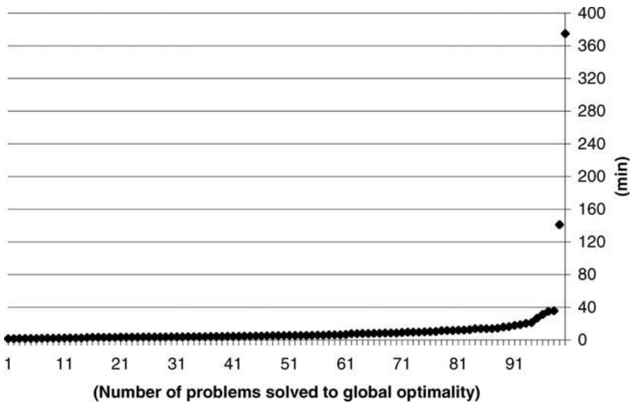

Figure 3. Computation solution times to global optimality.

two, f_2, is obtained at this optimal point $\vec{x}_1^*$, as any value higher than this for f_2 will not decrease the value of f_1. This maximum of f_2 is denoted as follows:

$$\theta^{\mathrm{U}} = f_2(\vec{x}_1) \tag{136}$$

After this, another optimization problem is established with f_2 only, as follows:

$$\begin{aligned} \min \quad & f_2 = \mathrm{ghg}_{\mathrm{CO_2eqv}} \\ \text{s.t.} \quad & \text{Eq. 1–135} \end{aligned} \tag{p2}$$

By solving problem (p2), another optimal solution is obtained, denoted as $\vec{x}_2^*$. At this point, f_2 reaches its minimum, denoted as:

$$\theta^{\mathrm{L}} = f_2(\vec{x}_2^*) \tag{137}$$

The (feasible) bounds of f_2 are then defined by θ^{L} and θ^{U}, as $[\theta^{\mathrm{L}}, \theta^{\mathrm{U}}]$. Then this region is divided equally into N intervals by a set of points, denoted as:

$$\{\theta^{\mathrm{L}}, \theta^1, \theta^2, \ldots, \theta^q, \ldots, \theta^{N-1}, \theta^{\mathrm{U}}\} \tag{138}$$

where

$$\theta^q = \theta^{\mathrm{L}} + \frac{\theta^{\mathrm{U}} - \theta^{\mathrm{L}}}{N}, \; q = 1, 2, \ldots, N-1 \tag{139}$$

Then, problem (p) can be converted into the following set of single objective optimization problems:

$$\begin{aligned} \min \quad & f_1 = -\mathrm{npv} \\ \text{s.t.} \quad & f_2 \le \theta \\ & \text{Eq. } 1 - 135 \\ & \theta \in \{\theta^{\mathrm{L}}, \theta^1, \theta^2, \ldots, \theta^q, \ldots, \theta^{N-1}, \theta^{\mathrm{U}}\} \end{aligned} \tag{p3}$$

Case Study

A case study has been conducted using the proposed approach for a coal-based polygeneration plant that produces methanol and electricity.

Illinois #6 coal is used as the main fuel feedstock, and its ultimate analysis is shown in Table 4. Market demand for electricity is 400 MW, and market demand for methanol is considered 500 tonne per day. Element sulphur is sold to the market as a by-product. Prices of feedstocks and products in the first time interval are listed in Table 5. Prices in the following time intervals are adjusted according to inflation rate, given by Eq. 140, where r_{inf} is the annual inflation rate, 3% in this case study. An operating horizon of 10 years is assumed, and it is divided into three time intervals of equivalent length. Plant availability is set to be 0.85. Technology alternatives of four primary functional blocks are considered. Symbols representing these technical alternatives and their definitions are listed in Table 6. Values of key parameters for each functional block are listed in Table 7. These data are obtained from Refs. 11, 16.

$$\zeta(t) = (1 + r_{\mathrm{inf}})^{\tau(t-1)} \cdot \zeta(t-1) \tag{140}$$

The overall mathematical model corresponds to a nonconvex MINLP model involving 9 binary variables, 1252 continuous variables, 1162 equality constraints, and 194 inequality constraints. The optimization is performed in GAMS[17] using BARON[18] as the MINLP solver. The model involves nonconvex bilinear, trilinear, and fractional terms (also with exponential terms). Before solving the problem, the variables and constraints are properly scaled so that values of all variables and coefficients fall in the range of −100 to 100. Priorities are assigned to binary variables and some key continuous variables with great impact on the computational performance in conducting the Branch-and-Reducing algorithm within BARON. These continuous variables include coal flowrate, split ratio of syngas between chemical and power generation parts, ratio of shifted syngas, and flowrates of carbon dioxide separation in both CCS blocks.

The computational results indicate that it takes 201 and 519 s, respectively, on a 3.31 GHz CPU to solve the two

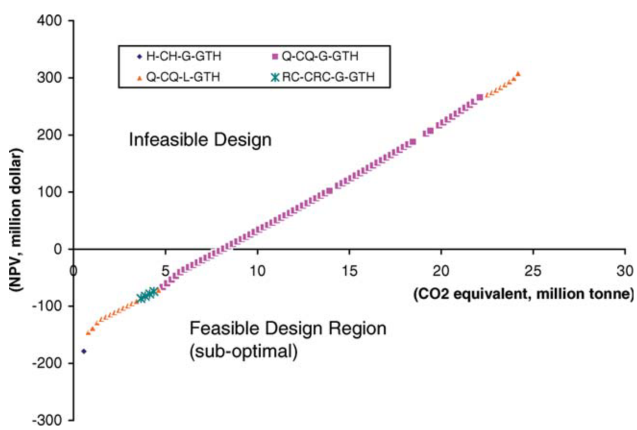

Figure 4. Pareto curve for polygeneration energy systems design.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

single-objective optimization problems shown in (p1) and (p2). After obtaining these two bounds, the whole interval in divided into 100 sub-intervals, as shown in Eq. 138. These problems are solved in parallel on a 274-CPU cluster with an average CPU speed of 2.03 GHz and total memory of 329.6 GB. The computation times for solving each one of the 100 problems to global optimality is shown in Figure 3. As can be seen, 98 problems are solved to global optimality within 40 min.

The optimal results obtained are used to generate the optimal Pareto curve, the frontier that separates the feasible and infeasible design space, shown in Figure 4. As can be seen, out of the 18 possible combinations of technologies listed in Table 6, only four appear in the Pareto curve. The different types of equipment and technologies that are needed to meet specific design targets are listed below:

- Hot gas cleanup technology should only be used when the emission constraint is extremely strict.
- A combination of quench gasification, cold gas cleanup, and liquid phase methanol synthesis technologies is suitable for conditions where the environmental constraints are either significantly loose or very tight. With a relaxed environmental constraint, this technological combination is chosen due to low requirements on initial capital investment. With a tight environmental constraint, however, it becomes again preferable due to its corresponding minimum requirements on the composition of inlet syngas entering the methanol synthesis reactor.
- Gas phase methanol synthesis, with either a radiative and convective gasifier or a quench gasifier, appears to be the most viable design. It is superior to other types of designs in most circumstances where the emission constraint is neither too strict nor too loose.

Conclusions

A superstructure based multiobjective mixed-integer optimization methodology is proposed for the design of polygeneration energy systems where both profitability and environmental impacts are taken into account, based on which Pareto trade-off curves can be obtained to guide the design process. Trade-offs between the economic and environmental objectives show that certain technological combinations are superior to others under circumstances where specific constraints are considered important. To enhance the accuracy of the model, all key parameters used in this modeling and optimization framework are collected from industrial demonstration plants. Optimization under uncertainty is another option if further improvements on the accuracy of optimization results are required. On the computation side, the study shows that reasonable computation times can be achieved for the solution of such large-scale multiobjective nonconvex MINLP problems, with the appropriate utilization of advanced global optimization tools, preprocessing, and parallel computation techniques.

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Notation

Binary variables

y = selection of equipment using a technology, 1 for selection, 0 otherwise

Continuous variables

Δm_{CO} = converted carbon monoxide in water gas shift reaction
Δm_{meh} = production rate of methanol in methanol synthesis block
Δm_{wat} = production rate of water in methanol synthesis block
Δw^{wg} = total work loss resulted by steam extraction for water gas shift reaction
ϕ = fugacity coefficient
cap = capacity of a functional block
elc = electricity generation, MW
ghg_{CO_2eqv} = green house gas emissions on a CO_2 equivalent basis, tonne
ghg_{eqc} = emissions from equipment production and plant construction, tonne
ghg_{fds} = emissions from feedstock production, tonne
ghg_{opt} = emissions during plant operation, tonne
h = enthalpy flowrate, MJ/s (MW)
inc = income
inv = investment cost for equipment
lhv = flowrate of lower heating value, MJ/s (MW)
m = mole flowrate, kmol/s
ma = mass flowrate, kg/s
npv = net present value
omc = O & M cost
r_{cm} = ratio between chemical stream and main stream of sweet syngas
r_{cp} = chemical-power ratio
r_{ws} = fraction of chemical stream of sweet syngas that undergoes water-gas shift reaction
w = mechanical work
x = mole fraction for liquid phase
ym = mole fraction for gaseous phase
z = streams upon which capacity of a block is defined

Parameters

Δh^{wg} = unit work loss resulted by steam extraction for water gas shift reaction
Φ = market demand for each primary product
$\alpha_{air/lhv}$ = ratio between mass flowrate of inlet air and the LHV of inlet fuel
$\alpha_{bld/drc}$ = mass ratio between blown down water and inlet coal for a gasifier
$\alpha_{bk/eqp}$ = ratio between investment costs for bulk items and equipment
$\alpha_{csl/drc}$ = mass ratio between water and coal in coal slurry
$\alpha_{efc/ppc}$ = ratio between engineering fees & project contingency and process plant cost
$\alpha_{fix/tcr}$ = ratio between fixed O & M cost and total capital requirement
$\alpha_{hyd/cm}$ = mass ratio between H_2 and CO in crude syngas
$\alpha_{ist/tpc}$ = ratio between interest and total plant cost
$\alpha_{mkw/drc}$ = mass ratio between making-up water and inlet coal for a gasifier
$\alpha_{nit/lhv}$ = ratio between mass flowrate of inlet nitrogen and the LHV of inlet fuel
$\alpha_{NO_x/wgt}$ = ratio between NO_x emissions and mechanical work generated by the gas turbine
$\alpha_{oxb/drc}$ = mass ratio between oxygen and coal in oxygen-blown pulverized coal feed
$\alpha_{oxy/drc}$ = mass ratio between inlet oxygen and coal steams to a gasifier
α_{rch/b_cu} = heat recovery rate in the syngas cleanup unit block
α_{rch/b_gs} = heat recovery rate in the gasifier chamber & scrubber block
$\alpha_{rcm/gas}$ = ratio between miscellaneous recovered heat and flowrate of gas turbine flue gas
$\alpha_{ssl/drc}$ = mass ratio between slag slurry from the syngas scrubber and inlet coal to a gasifier

$\alpha_{stm/lhv}$ = ratio between mass flowrate of steam injection and the LHV of inlet fuel
$\alpha_{sul/drc}$ = recovery rate of sulphur
$\alpha_{swi/drc}$ = mass ratio between steam/water injection and inlet coal for a gasifier
$\alpha_{w/aia}$ = ratio between compression work and mass flowrate of atmosphere air for ASU
$\alpha_{w/ain}$ = ratio between compression work and mass flowrate of nitrogen for ASU
$\alpha_{w/aio}$ = ratio between compression work and mass flowrate of oxygen for ASU
$\alpha_{w/aux}$ = ratio between work consumed by auxiliary equipment and gross mechanical work generation
$\alpha_{w/c1}$ = ratio between work consumption and captured carbon dioxide for precombustion CCS
$\alpha_{w/c2}$ = ratio between work consumption and captured carbon dioxide for postcombustion CCS
β_{CO} = conversion rate of carbon monoxide in water gas shift reaction
$\beta_{CO_2}^{pre}$ = recovery rate of carbon dioxide in precombustion CCS
$\beta_{CO_2}^{post}$ = recovery rate of carbon dioxide in postcombustion CCS
β_{cu} = fraction of removal for a component in the crude syngas through a syngas cleanup unit
β_{ir} = integration rate between the ASU block and the gas turbine block
γ_{con} = emission inventory for plant construction
γ_{eqp} = emission inventory for equipment production
γ_{fds} = cradle-to-gate emission inventory for feedstock production
η_i = internal efficiency
η_m = mechanical efficiency
λ = capacity factor (availability)
θ = interval point for an objective function in ϵ-Constraint method
θ^L = lower bound of an objective function in ϵ-Constraint method
θ^U = upper bound of an objective function in ϵ-Constraint method
σ = impact factors of a greenhouse gas on a CO_2 equivalent basis
τ = operating time
υ = stoichiometric coefficient
ζ = price
A = coefficient for calculation of activity coefficient of a component solved in inert oil
K = equilibrium constant
LHV = lower heating value
MW = molecular weight
P = pressure
P^* = pressure at the exit of a steam turbine
P^{wg} = pressure of water gas shift reaction
P_c = critical pressure
T = temperature
T^{wg} = temperature of water gas shift reaction
T_c = critical temperature
UA = ultimate analysis of coal, comprising C, H, O, N, S, ash, w.t.%
UB = upper bound
X_{air} = mole composition of atmosphere
X_{ani} = mole composition of nitrogen stream produced in ASU
X_{aox} = mole composition of oxygen stream produced in ASU
a = coefficient for calculation of Henry's law constant
a' = coefficient for calculation of Henry's law constant
$a_{im,oil}$ = coefficient for calculation of activity coefficient
$a_{oil,im}$ = coefficient for calculation of activity coefficient
b = coefficient for calculation of Henry's law constant
b' = coefficient for calculation of Henry's law constant
$b_{im,oil}$ = coefficient for calculation of activity coefficient
$b_{oil,im}$ = coefficient for calculation of activity coefficient
c = coefficient for calculation of Henry's law constant
c' = coefficient for calculation of Henry's law constant
$c_{im,oil}$ = coefficient for calculation of activity coefficient
$c_{oil,im}$ = coefficient for calculation of activity coefficient
h = enthalpy
k_H = Henry's law constant
n = size factor
r = discount rate
r_{inf} = inflation rate
x^* = steam quality

Sets

ac = syngas cleanup technologies
ag = gasification technologies
agt = gas turbine technologies
am = methanol synthesis technologies, GP for gas phase, LP for liquid phase
e = green house gas emissions: CO_2, CH_4, and NO_x
ia = components in the air: O_2, N_2
ig = components in fuel and flue gas of a gas turbine: O_2, N_2, H_2O, H_2, CO, CO_2
im = components in product gas of methanol synthesis: N_2, H_2O, H_2, CO, CO_2, CH_3OH
is = components in syngas: H_2, CO, CO_2, H_2O, N_2, H_2S
t = time interval

Subscripts

Functional Blocks

b_as = air separation unit
b_c1 = precombustion CO_2 capture
b_c2 = postcombustion CO_2 capture
b_cp = coal preparation
b_cu = syngas cleanup unit
b_ms = methanol synthesis
b_gs = gasifier chamber and scrubber
b_gt = gas turbine
b_st = steam turbine
b_ws = water gas shift reactor

Technologies

t_cu = syngas cleanup technologies
t_gs = gasification technologies
t_gt = gas turbine technologies
t_ms = methanol synthesis technologies, GP for gas phase, LP for liquid phase

Components

air = overall air flow
aia = atmosphere air
aic = compressed air
bld = blown down water
csg = crude syngas
csl = coal slurry
drc = dry coal
elc = electricity
fug = fuel gas
gas = gas
mep = methanol product
mis = miscellaneous heat recovered
mkw = making up water
nit = nitrogen
oil = inert oil in liquid phase methanol synthesis
oxy = oxygen
pgm = product gas from methanol synthesis block
rch = recovered heat
rcm = miscellaneous recovered heat
seq = CO_2 sequestration
ssc = sweet syngas for chemical synthesis
ssl = slag slurry
ssn = non-shifted sweet syngas
ssp = sweet syngas for power generation
ssg = sweet syngas
sss = shifted sweet syngas
stm = steam
sul = element sulphur
swi = steam/water injection

Positions

i = inlet
o = Outlet

Miscellaneous

aux = auxiliary equipment
efc = engineering fees and project contingency
eqp = equipment
fix = fixed O & M cost
grp = gross production
ist = interest
net = net production rate/income
ppc = process plant cost
tpc = total plant cost
tpi = total plant investment

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