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Multi-Scale Modeling and Simulation of Intensified Reactive-Separation Processes for Hydrogen Production and CO2 Capture via the Water-Gas Shift Reaction (WGSR)

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Publication Date
2018

Peer reviewed|Thesis/dissertation
Multi-Scale Modeling and Simulation
of Intensified Reactive-Separation Processes
for Hydrogen Production and CO₂ Capture
via the Water-Gas Shift Reaction (WGSR)

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Chemical Engineering

by

Secgin Karagoz

2018
ABSTRACT OF THE DISSERTATION

Multi-Scale Modeling and Simulation of Intensified Reactive-Separation Processes for Hydrogen Production and CO₂ Capture via the Water-Gas Shift Reaction (WGSR)

by

Secgin Karagoz

Doctor of Philosophy in Chemical Engineering

University of California, Los Angeles, 2018

Professor Vasilios Manousiouthakis, Chair

As a result of fossil fuels-based energy production, reducing atmospheric carbon dioxide emissions has become an urgent issue. Especially, carbon capture and storage (CCS) technology, being one of the leading processes to reduce total carbon emissions, has become increasingly important. Hydrogen is an important energy carrier, and hydrogen-based technologies have increased in importance recently due to the worldwide focus on green processes.

The Integrated Gasification Combined Cycle (IGCC) is a promising technology supplying clean energy at affordable prices. The IGCC process is currently being coupled with CCS technologies. However, using CCS technologies in power generation processes is a great challenge, necessitating the intensification of the coupled IGCC-CCS process. Process intensification (PI), leads to substantially smaller, cleaner, and more energy efficient processes,
and is a prominent topic, receiving significant attention in recent years. As part of intensifying a process, integration of multiple operations (e.g., reaction and separation) in a single unit is often carried out, to improve the existing process efficiency, and to reduce energy consumption, and unwanted output/by-product generation.

The objective of this work is to demonstrate the process intensification potential of a technology, containing one or more water gas shift (WGS) reactor components seamlessly integrated with other plant components. We investigate the applicability of various (alternative to the conventional process) novel and efficient reactor configurations that include self-standing adsorptive reactor (AR)/membrane reactor (MR), and the combination of a MR-LTSR-AR-adsorptive separator (AS)-membrane separation (MS) units (herein after referred to as the LTSR-MS/LTSR-AS/AS-LTSR-AS/MR-AS/AS-MR-AS/MR-AR systems). The proposed WGS reactor technologies have the potential to generate highly efficient and ultra-compact processes, by producing H₂ for use in IGCC with simultaneous CO₂ capture.

Innovative designs of the proposed processes are determined based on the comprehensive modeling and design of the selected IGCC plant’s section. Comprehensive, multi-scale, multi-phase, computational fluid dynamics (CFD) models are developed for reaction/separation processes. Developed models quantify the many complex physicochemical phenomena occurring within the process, thus providing the basis to better understand, and intensify the overall system. Model predictions are generated for a broad range of operating conditions and design parameters, thus enabling a comparative performance assessment of the proposed process versus a conventional process for the proposed IGCC application.
The dissertation of Secgin Karagoz is approved.

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2018
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ACKNOWLEDGEMENTS

All the praises belong to GOD, blessing me with the ability to pursue my graduate studies, seek knowledge and having patience.

I would like to express my gratitude to my advisor, Professor Vasilios I. Manousiouthakis, and Professor Theo T Tsotsis. I would also like to thank Professor Dante Simonetti, and Professor Philippe Sautet and Professor Ertugrul Taciroglu for serving on my doctoral committee.

I would like to thank my colleagues, including Flavio Da Cruz, Masih Jorat, Nicholas Margull, Jack Lowd, and Chuanjun Jiao.

I would like to thank my parents Zeynep and Mehmet Karagoz, and my sibling Sezgin Karagoz for their encouragement of me throughout my Ph.D.

Financial support through DOE grant DE-FE0026423 “A High Efficiency Ultra-Compact Process for Pre-Combustion CO₂ Capture” is gratefully acknowledged. Financial support from The Republic of Turkey Federal Agency for Support and Evaluation of Graduate Education within the Ministry of Education of Turkey is also gratefully acknowledged.


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• Elcicek H., Akdogan E., Karagoz S. The Use of Artificial Neural Network for Prediction

• Ashkan Garshasbi, Huanhao Chena, Mingyuan Caoa, Seçgin Karagöz, Richard J. Ciora,
  Jr.,Paul Kt Liuc, Vasilios I. Manousiouthakis, Theodore T. Tsotsis. Membrane-based
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• Seçgin Karagöz, Flavio Eduardo da Cruz, Theodore T. Tsotsis, Vasilios I.
  Manousiouthakis. Multi-Scale Membrane Reactor (MR) Modeling and Simulation for the
  Water Gas Shift Reaction. Chemical Engineering & Processing: Process Intensification
  (2018).

• Seçgin Karagöz, Theodore T. Tsotsis, Vasilios I. Manousiouthakis. Energy
  intensification of H₂ generation and CO₂ capture/utilization by a novel adsorptive reactor

Chapter 1. Introduction

Fossil fuels (coal, petroleum, and natural gas) are the major sources (over 60% in 2016) for energy production in the United States [1]. About 6,870 million metric tons (MMT) of greenhouse gas are emitted into the atmosphere each year because of the fossil fuels based energy production actions, over 80% of which is in the form of CO$_2$ [2]. As a result of this process, the world is facing the serious environmental problems, and, thus, reducing the carbon emissions has become a urgent issue. Especially, carbon capture and storage (CCS) technology, being one of the leading processes to reduce total carbon emissions, has become increasingly important. CCS involves capturing CO$_2$ emitted from the burning of fossil fuels, safely transporting it and storing it underground.

Hydrogen is an important energy carrier for both mobile and stationary power generation applications and has numerous other industrial uses[3-4]. Hydrogen-based technologies have increased in importance recently due to the worldwide focus on green processes. Hydrogen has the potential to become the leading energy carrier [5-6], especially due to its fuel cell technology applications [7], which are increasingly gaining global attention [8] as promising mobile transportation alternatives. Hydrogen can be produced from both renewable and non-renewable energy sources [9], such as solar energy, liquid hydrocarbons, coal, biomass, and natural gas, with the latter being the most commonly used resource for hydrogen production [8-9]. Production cost is likely to be a key factor that determines the widespread use of hydrogen in the future, with significant reduction in production cost being beneficial to the further development and growth of the hydrogen economy [2, 9-10].

Integrated Gasification Combined Cycle (IGCC) is a promising technology in a manner of supplying clean energy at affordable prices. The IGCC process is currently being coupled with
carbon capture technologies [11-12]. However, using of CO₂ capture/sequestration technologies in power generation processes is a great challenge [13-14]. According to the U.S. National Energy Technology Laboratory (NETL), the efficiency of an IGCC power plant with CO₂ capture decreases approximately 15-20% compared to an IGCC power plant without CO₂ capture [17]. The conventional IGCC process with carbon capture (see Figure 1) generates electricity from a solid or liquid fuel, by (1) converting the fuel into syngas (a mixture rich in CO, CO₂, H₂, H₂O, CH₄) at high pressures, (2) cleaning up the produced syngas from problematic impurities (e.g., COS, H₂S, HCl, Hg, etc.), (3) converting the remaining CO into CO₂ by utilizing a sequence of reactors where the Water Gas Shift Reaction (WGSR) takes place, (4) separating the resulting H₂ and CO₂ mixture, (5) generating electricity in a combined-cycle power block consisting of a gas turbine and a steam turbine, (6) and drying and compressing the CO₂ for sequestration purposes.

Figure 1. Simplified block flow diagram of a conventional IGCC power-plant with CO₂ capture.

The heterogeneously-catalyzed WGSR is an industrially important commercial chemical process [15-16]. The WGSR has been historically well-studied and finds today a broad range of industrial applications [5-16]. It is one of the most crucial steps in hydrogen production processes, enabling further hydrogen enrichment and carbon monoxide (CO) conversion both in power generation and in petrochemical plants [5, 15, 17]. The WGSR has also gained renewed attention recently, in both industrial and academic sectors, due to its potential use as a main route
for hydrogen production, in environmentally-friendly, integrated gas combined cycle (IGCC) coal power plants [18-19]. There has been, therefore, a recent significant increase in hydrogen production and purification related WGSR studies, aiming to improve existing technologies, and to potentially develop new processes that can reduce production costs.

The WGSR, Eq.(1), is exothermic, reversible, and equilibrium-limited in nature.

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \left( \Delta H_{298K}^0 = -41.1 \text{ kJ/mol} \right) \]  

Its operating temperature is the result of a compromise between the high CO equilibrium conversions attainable at low temperatures, and the high CO reaction rates attainable at high temperatures. Its operating pressure is the result of a compromise between the high compression costs, and the high CO reaction rates attainable at higher pressures, as the equilibrium conversion is pressure-independent given that there is no change of moles accompanying the reaction.

The WGSR is, typically, carried out in the presence of low-temperature heterogeneous catalysts (known as low-temperature shift catalysts or LTS, operating in the range of 200-300 °C), or high-temperature shift catalysts (HTS, operating in the range of 300-450 °C). Commercial LTS catalysts typically contain Cu, Zn, Cr, Al and Co-Mo oxides, while HTS catalysts typically contain Fe, Cr oxides [20-21]. To overcome both kinetic and equilibrium limitations, the WGSR is typically carried out in a sequence of two reactors, one operating at high temperatures (HTSR) and the other at low temperatures (LTSR), with inter-stage cooling, [22-24]. For pure hydrogen production, the process requires a downstream separation step to remove the by-product CO\(_2\) and any unreacted CO. Thus, the overall reaction/separation WGSR process is well-suited for application of novel intensification concepts, integrating reaction and separation into a single unit. Such process intensification has the potential to improve efficiency.
and economics, through decreased operating temperatures, higher CO conversion levels, and reduced capital costs associated with lower catalyst use and lower downstream separation loads.

Process intensification (PI) is a prominent topic, receiving significant attention recently. Stankiewicz and Moulijn [26] define PI as “Any chemical engineering development that leads to a substantially smaller, cleaner, and more energy efficient technology.” According to Stankiewicz and Moulijn [26], process intensifying equipment and process intensifying methods are two main areas of PI. As part of the intensification procedure, integration of multiple operations (e.g., reaction and separation) in a single unit is a robust tool to improve the existing process’ efficiency, reduce energy consumption, and unwanted outputs/by-products. Such intensification has the potential to enhance process efficiency/economics by offering drastic process technologies improvements, regarding a variety of metrics [10, 24-25].

PI encompasses several techniques (adsorption, absorption, and membranes) to accomplish such intensification [26-29]. Especially, adsorptive reactor (AR) and membrane reactor (MR) receive considerable attention to removal, and recovery of the produced gases from fuel gas. The reaction products (e.g., H₂, CO₂) is selectively removed by the adsorbent and membrane, so the equilibrium is shifted to the product side, enabling higher conversions and the produced gas capture processes to be combined in one single step. Operating at lower reaction temperatures, reducing material costs, increasing operation safety, eliminating the need for excess steam in the reaction, minimizing the need for downstream purification and reducing the amount of catalyst for the desired conversion level are the other remarkable features of these technologies [1, 5, 7, 9]. However, the MR-or-AR-based technologies separates only one of the reaction’s products (e.g., H₂ or CO₂). On the other hand, the integrated separation of the
reaction’s products creates a synergy, significantly increases the process efficiency such as higher reaction rates, yields and selectivity [1, 5].

The objective of this work is to demonstrate the process intensification potential of a technology, contains one or more water gas shift (WGS) reactor components seamlessly integrated with other plant components. The concept of process intensification potential can be attained by any conceivable design employing the same technology. We investigate the applicability of various (alternative to the conventional high temperature shift reactor-HTSR+ low temperature shift reactor-LTSR) novel and efficient reactor configurations that include self-standing adsorptive reactor (AR)/membrane reactor (MR), and the combination of a MR-LTSR-AR-adsorptive separator (AS)-membrane separation (MS) units (herein after referred to as the LTSR-MS/LTSR-AS/AS-LTSR-AS/MR-AS/AS-MR-AS/MR-AR systems). As demonstrated in Figure 2, the sequential design allows these units to be connected through variety of configurations. The syngas produced through gasification of coal is directed to these units and the outlet of units can be mixed to deliver cleared syngas with certain specifications for energy generation. The final cleaned syngas stream produced by the treatment skid will go through a heat and power generation unit consisting of hydrogen turbines, producing energy to match the target levels defined by the performance attributes. The proposed WGS reactor technologies have potential to generate a highly efficient and ultra-compact processes by producing H₂ for use in IGCC with simultaneous CO₂ capture.
Figure 2. Simplified proposed block flow diagram of an IGCC power-plant with CO₂ capture.

Innovative design of the proposed processes is determined based on the comprehensive modeling and design of the selected IGCC plant’s section. Comprehensive, multi-scale, multiphase, computational fluid dynamics (CFD) models are developed for general, reaction/separation, steady-state/cyclic processes, a process intensification mainstay. Developed models quantify the many complex physicochemical phenomena occurring within the process, and thus providing the basis to better understand, and intensify the overall system. Model predictions are generated for a broad range of operating conditions (e.g., reactor temperature, inlet gas composition, feed pressure, and inlet gas flow rate) and design parameters (e.g., weight of catalyst, weight of adsorbent, gas permeance, and membrane area), thus enabling a comparative performance assessment of the proposed process versus a conventional process for the proposed IGCC application.

2.1. Introduction

A conventional Integrated Gasification Combined Cycle (IGCC) power generation plants convert coal into syngas (containing CO/H$_2$/CO$_2$ with small amounts of CH$_4$ and impurities) via a high-pressure gasifier in the presence of steam and oxygen. In industry, water gas shift reactors consist of two different temperature stages, the high-temperature shift reactor (HTSR) and the low-temperature shift reactor (LTSR) with a cooling process between them is a recommended for the operation of hydrogen generation. The process gas stream passes from the reformer system through the adiabatic two-stage water gas shift reactors’ system, such as Figure 3. The high-temperature water gas shift reactor (HTSR) is carried out between the ranges of 300 °C – 450 °C. On the other hand, the low-temperature water gas shift reactor (LTSR) is performed between the ranges of 200 °C – 300 °C. In the HTSR, a fast CO consumption is favored and then, the gas stream passes through an inter-stage cooling system. LTSR stage follows the cooling system, where is favored the approach to equilibrium conversions. This system (HTSR + Cooling +LTSR) enables to reach higher CO conversions and desired level of hydrogen production. Thus, most of the CO is consumed in the HTSR, and rest of the CO content is converted LTSR. Subsequently, the CO$_2$ is removed from the stream usually through an absorber with amine-based solvents prior to undergoing compression for future transport and sequestration. The resultant stream is hydrogen rich and mixed with nitrogen diluent before entering an F-class gas-turbine to produce power. In the United States, the current efforts demonstrate that coal-based power production in IGCC will continue in the foreseeable future, and while current technology has significantly reduced SO$_2$, NO$_x$, and p.m. emissions, CO$_2$
emissions continue to be a problem. For this reason, a significant efforts in both academia and industry are shown on CCS technology as the primary process for the reduction of domestic and global CO$_2$ emission from coal power plants. However, the current CCS systems require additional energy compared to projects without CCS. According to the U.S. National Energy Technology Laboratory (NETL), the efficiency of an IGCC power plant with CO$_2$ capture decreases approximately 15-20% compared to an IGCC power plant without CO$_2$ capture [15]. Thus, further improvement and development are required for CCS technology to achieve acceptable market levels. For this reason, the novel hybrid alternative processes are proposed in this work as a more efficient and realizable alternative to standard pre-combustion CCS technology.

**Figure 3. A Conventional Process, HTSR+LTSR.**

The main focus, in this work, is investigation of the applicability of various (alternative to the conventional high temperature shift reactor-HTSR+ low temperature shift reactor-LTSR) novel and efficient reactor configurations that include self-standing adsorptive reactor (AR)/membrane reactor (MR), and the combination of a MR-LTSR-AR-adsorptive separator (AS)-membrane separation (MS) units (herein after referred to as the LTSR-MS/LTSR-AS/AS-LTSR-AS/MR-AS/AS-MR-AS/MR-AR systems). The sequential design allows these units to be connected through variety of configurations. In the following sections of this chapter, innovative design aspects of the variety of configurations, as alternative proposed processes, will be analysed and discussed. Having flexible, multi-component syngas clean-up and multi-product production systems, minimizing the greenhouse gas (CHG) capture and disposal costs associated
with current IGCC plants via the adoption of the innovative unitary/modular WGS reactive-separations technology, minimizing capital and operating costs, maximizing the profitability of IGCC power plant by increasing their power generation capacity are the possible outcomes of the novel designs. Our philosophy in modularization for coal-based power generation is to adopt unit operations which (i) are uniquely suitable for modularization, e.g., the aforementioned membrane- and adsorption-based reactors and separators, because of insignificant scale-down penalty, (ii) offer process intensification features, e.g., by combining WGS and gas separation into one unit of WGS/MR, to compensate for the potential penalty as a result of modularization, and (iii) constitute a self-contained unit, so mass production can be achieved to reduce the capital cost.

Multi-scale model and simulation based detailed investigation, and the obtained key results of the proposed processes will be represented in the later chapters. The models (PBR, MR, MS, AR, AS, etc.) to be employed (and potentially further augmented) in this work are based on long-standing, well established scientific/engineering principles, such as total mass, component mass, momentum, and energy conservation. The expressions quantifying various terms in the equations (Dusty Gas Model and Maxwell-Stefan Model for diffusion, Ergun for momentum losses, etc.), are also well established, and result in the models having a small number of adjustable parameters, thus extending their range and applicability. In addition, the WGS MR and AR models have been experimentally validated as part of a current DOE project of the proposing team. The efforts will include the identification and potential development of comprehensive mathematical models for each component of the proposed energy system, which will be integrated into a novel IGCC plant for the purposes of reducing CHG emissions, and cost.
2.2. WGSR Intensification through the reactive-or-separation of hydrogen

LT-MRs (depicted in Figure 4) in series and multistage reactors (HTSR/MS/LTSR/MS) in series, as shown in Figure 5, are potential alternatives to conventional hydrogen production system. Integrating reaction and separation during WGSR process is well-suited for application of novel intensification concepts. Such process intensification has the potential to improve efficiency and economics, through decreased operating temperatures, higher CO conversion levels, and reduced capital costs associated with lower catalyst use and lower downstream separation loads. In this work, LTMRs in series and multistage reactor’s systems are proposed as alternatives to the conventional process under the section of WGSR Intensification through the reactive-or-separation of hydrogen.

![Proposed Alternative Process 1](image1.png)

**Figure 4. An Alternative Process 1, HTSR+MS+LTSR+MS in series.**

![Proposed Alternative Process 2](image2.png)

**Figure 5. An Alternative Process 2, LT-MR+LT-MR in series.**

The conventional approach, PBRs incorporate interstage coolers, is not ideal, and MR technology offers an improved approach which is the “controlled delivery” feature offered by a membrane. With this feature, the process able to deliver water/stream to internal locations where water is needed as a coolant and/or as a reactant, while the excess steam can be released through permeation. As a result, the reactor can be kept in an optimal temperature range while
maximizing CO conversion and H₂ recovery. Moreover, steam released to the permeate side with H₂ can be reused as a diluent in the turbine. Membrane-based power generation can improve the net power generation efficiency with carbon capture and reduce capital cost over conventional IGCC process (i.e., IGCC with dual-stage Selexol). For the MR and MS units/modules, selection of the membrane with optimal permeance and selectivity at the anticipated operating temperature and pressure, identifying the optimal membrane size (e.g., number of tubes, size, diameter), configuration (e.g., dead-end vs. open-end, membrane spacing, etc.), and mode of operation (co-current vs. countercurrent, sweep or no sweep, adiabatic vs. non-adiabatic, with or without interstage cooling), selecting the optimal operating conditions (e.g., pressure, temperature, space time, etc.) are major design aspects, effect whole plant efficiency.

2.3. WGSR Intensification through the reactive-or-separation of carbon dioxide

The WGSR and CO₂ adsorption are carried out simultaneously in an AR, since it is packed with both catalyst and adsorbent pellets. The adsorbent selectively removes CO₂ continuously from the bulk gas phase, shifting forward the WGSR equilibrium towards more product formation. The AR holds the promise of intensifying IGCC plants (depicted in Figure 6) by combining multiple units into one. At the same time, the AR requires dynamic operation, since the adsorbent’s capacity is not limitless, and adsorbent regeneration is required. Thus, in this work two times are defined in regard to the AR’s reaction/adsorption operation: (1) the minimum time of operation, which is defined as the time that CO₂ is first detected at the reactor exit, and (2) the maximum time of operation, which is the time for which the corresponding time-averaged mass flowrate of carbon exiting the AR during the entire reaction/adsorption phase up to that point reaches maximum 10% (a common carbon capture goal for IGCC plants) of the constant mass flowrate of carbon entering the AR during the same period. In our proposed AR
system (depicted in Figure 7), we have minimum two ARs operating simultaneously; this is due to the cyclical nature of the AR operation, which consists of a reaction/adsorption phase and a desorption phase. At any given time, one of the reactors is fed with syngas, which undergoes the WGSR and CO₂ adsorption, and generates a carbon-depleted gas consisting of water and hydrogen, while the other reactor is fed with steam, which induces CO₂ desorption from the CO₂-rich adsorbent pellets, and generates a stream consisting of CO₂ and H₂O. This operation mode is referred to as one step, and in the subsequent step the reactor roles are reversed. Figure 7 depicts one such step of the two AR system operation, whereby the white-colored valves are open, and the black-colored valves are closed, while in the next step the status of these valves is reversed. The duration of each step of the AR operation can then be quantified in terms of the aforementioned operating times.

Figure 6. An Alternative Process 3, ARs in parallel.

Figure 7. Detailed Representation of the Proposed ARs in parallel.
In this work, LTSR/AS sequence in a modular form (Figure 8) is considered as an alternative process 4 compared to based-case process of LTSR+HTSR sequence process. In the proposed process 4, each module is consisted of LTSR followed by minimum two AS, operate simultaneously due to the cyclical nature of an adsorptive reactor’s operation. During process, reaction takes place in LTSR while separation is carried out in AS (selective to CO$_2$), and this is repeated along each module. A LTSR is packed with low temperature shift catalyst while an AS is packed with Hydrotalcite adsorbent. A possible advantage of this process over the AR-based processes is utilizing all available catalyst in LTSR since the half of the catalyst in AR process is not used because of desorption step, so this alternative process may ensure opportunity to intensify process by saving catalyst.

**Figure 8. An Alternative Process 4, Modular LTSR+AS in series.**

Modifying the alternative process 4 by installing AS in front of modular process gives rise to another alternative process (AS/LTSR/AS sequence) in a modular form (Figure 9). This alternative modular form creates possibility having more efficient process over the alternative process 4 such as saving more catalyst.
For the AR/AS unit/modules, the adsorbent with the maximum working capacity under the select operating conditions, identifying the optimal mode of operation (PSA vs. TSA vs. combined TSA/TSA, adiabatic vs. non-adiabatic, etc.), optimal operating conditions (temperature, pressure, maximum and minimum operating times) and optimal catalyst/adsorbent weights are major design aspects, determines the overall plant efficiency.

2. 4. WGSR Intensification through the reactive-or-separation of hydrogen and carbon dioxide

Such a hybrid system combining MR and an AR in tandem (a MR followed by a AR combination) [31] is the most likely ones to meet that success criterion of the avoiding the need to use a 2-stage Selexol process. A key advantage of our proposed system integrated in IGCC plant (Figure 10) is that it provides a high-pressure CO$_2$ stream ready for sequestration.

In the proposed process (MR+AR), reaction and separation are carried out in MR (selective to H$_2$) and AR (selective to CO$_2$) simultaneously. An AR is packed with catalyst and adsorbent pellets while a MR is usually composed by a metal pipe, one or more membrane tubes assembled, and the reaction zone, catalyst pellets are packed, is localized between the metal pipe internal wall and the membrane external surface. During the process, reaction’s products (e.g. H$_2$, CO$_2$) continuously removed from the bulk gas phase by shifting the chemical equilibrium to more product formation. The use of MR/AR that demonstrates on improvement upon IGCC process by combining multiple existing units into a single step. The proposed process (depicted

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**Figure 9. An Alternative Process 5, Modular AS+LTSR+AS in series.**
in Figure 11), leads a significant reduction on the electricity production cost compared the baseline capture approaches. Again, for this design, two operating times are defined in regard to the AR’s reaction/adsorption operation: (1) the minimum time of operation, which is defined as the time that CO$_2$ is first detected at the reactor exit, and (2) the maximum time of operation, which is the time for which the corresponding time-averaged mass flowrate of carbon exiting the AR during the entire reaction/adsorption phase up to that point reaches 10% (a common carbon capture goal for IGCC plants) of the constant mass flowrate of carbon entering the AR during the same period. Basically, defining the minimum and maximum operating times creates the AR operating flexibility of sifting between 100-90 % CO$_2$ capture.

In our proposed system (depicted in Figure 11), we have one MR followed by two AR, operate simultaneously due to the cyclical nature of an adsorptive reactor’s operation. Indeed, the AR’s operation consists of a reaction/adsorption phase and a desorption phase. Thus, continuous operation necessitates the use of at least two reactors. In step one, the syngas gas is fed into the first MR, and H$_2$ is separated. In step two, the MR exit gas mixture is fed into the AR, and CO$_2$ is adsorbed. While this is occurring, the other adsorptive reactor is flushed with steam and desorption takes place producing a stream consisting of CO$_2$ and H$_2$O. The resulting products of the system are a carbon-depleted syngas consisting of water and hydrogen from the first reactor, and a mixture of water and carbon dioxide from the second reactor. Step 3 is identical to step 2 except that the reactor tubes’ functions are now reversed; the tube where reaction/adsorption took place in step 2 will now undergo desorption, while the tube where desorption took place in step 2 will now undergo reaction/adsorption. In the step 3, the white (open) valves are switched to black valves (closed), and black valves are switch to the whites.
An important advantage of the proposed process is its reduced energy consumption, compared to the conventional process that utilizes a Dual-stage Selexol unit to separate the carbon dioxide from the syngas exiting the WGSR. Indeed, the conventional process generates a pure CO\textsubscript{2} stream at approximately 1 bar, which must then be compressed to approximately 150 bar [32] for sequestration/utilization purposes. This compression step consumes a significant portion of the power produced by the power plant. In contrast, the AR operates at much higher pressures (>20 bar), which are close to the power plant’s gasifier’s operating pressures, and naturally delivers the pure CO\textsubscript{2} stream at these higher pressures, thus attaining significant energy savings. During the desorption step, the obtained CO\textsubscript{2}/H\textsubscript{2}O gas mixture (at the exit of the reactor) is separated at the same pressure as the reactor exit, and the separated high-pressure H\textsubscript{2}O is recycled in the desorption step, without the need for repeated compression.

Figure 10. An Alternative Process 6, LT-MR+AR in series.

Figure 11. A Detailed Representation of the proposed MR/AR Sequence Process.
A configuration of LT-MR/AS sequence in a modular form (depicted in Figure 12) is a promising technology, as a seventh alternative process. In this process design (MR+AS), reaction/separation is performed in MR (selective to H₂), and separation is carried out in AS (selective to CO₂). During the process, reaction’s products (e.g. H₂) continuously removed from the bulk gas phase by shifting the chemical equilibrium to more product formation. The use of MR/AS has potential to intensify process by saving a significant amount of catalyst. Compared to AR and LT-MR/AR sequence process, the major advantage of this design is that all available amount of the catalyst can be used in MR since half of the catalyst does not process in AR system due to desorption step. Thus, this design increases the possibility to intensify process by reducing reactor volume, packed with catalyst.

**Figure 12. An Alternative Process 7, Modular LT-MR+AS in series.**

As a final option, by adding extra AS module in front of LT-MR/AS module, another alternative process is obtained (depicted in Figure 13) as AS/LT-MR/AS configuration.

**Figure 13. An Alternative Process 8, Modular AS+LT-MR+AS in series.**
2.5. Economic and environmental impact of the proposed processes

The proposed project develops and applies novel process intensification approaches (modeling, design, preliminary optimization of reaction separation processes) to IGCC WGSR’s section in order to develop a novel, modular technology, aiming to convert coal into economical and environmentally friendly being energy. Through the use of novel designs, the work aims to not only reduce cost of power generation, but to also have a greater reduction in CO\textsubscript{2}. A key success metric for optimal design is to avoid the need to use a 2-stage Selexol process. The proposed process, provides an advantage of being flexible, producing higher purity gases (>95%), capturing CO\textsubscript{2} (>90%), and reaching higher conversions (>95%).

An important advantage of the proposed CO\textsubscript{2} based separation process is its reduced energy consumption, compared to the conventional process that utilizes a Dual-stage Selexol unit to separate the carbon dioxide from the syngas exiting the WGSR. Indeed, the conventional process generates a pure CO\textsubscript{2} stream at approximately 1 bar, which must then be compressed to approximately 150 bar [32] for sequestration/utilization purposes. This compression step consumes a significant portion of the power produced by the power plant. In contrast, the AR operates at much higher pressures (>20 bar), which are close to the power plant gasifier’s operating pressure, and naturally delivers a pure CO\textsubscript{2} stream at these higher pressures, attaining significant energy savings.

During the AR/AS desorption step, the obtained CO\textsubscript{2}/H\textsubscript{2}O gas mixture (at the exit of the reactor) is separated at the same pressure as the reactor exit, and the separated high-pressure H\textsubscript{2}O is recycled in the desorption step, without the need for repeated compression. Indeed, CO\textsubscript{2} compression is a significant contributor to the energetic cost of carbon capture systems. The cumulative efficiency of the compressor train is highly dependent on the variables of individual
compressor efficiency, pressure ratio and inlet temperature/pressure. In this work, a four-compressor sequence with four coolers (Figure 14) is considered, and CO$_2$ is considered a constant compressibility factor gas, for which the minimum total annualized cost of a series of adiabatic compressors and coolers is known, [33].

![Figure 14. The configuration of a four section CO$_2$ compression system.](image)

The comparative compressor sequence power requirement for the IGCC process employing either a conventional WGSR system or the proposed AR/AS is shown in Figure 15. The traditional to AR/AS compressor power requirement is equal to one for atmospheric AR/AS operation and can exhibit as much as 73% reduction for an AR/AS exit pressure of 40 bar.

![Figure 15. Compressor power requirement vs. AR exit pressure (taken as the initial compressor pressure)](image)
Integration of the proposed AR/AS system within the IGCC attains a more efficient CCS than those currently proposed, that can nevertheless deliver carbon capture as high as 100 \%, thus reducing the environmental impact of coal power plants.

The other key advantages of the proposed technology include lower operating temperatures, lower steam requirements, reduced catalyst cost, and a high-purity product stream. The AR/MR systems operate at lower reaction temperatures since low-temperature WGS catalyst is used in process (no need for high temperature operation and catalyst anymore), so this reduces material costs and increases operation safety. Compared to conventional process, the AR/MR operation reduces required catalyst amount. The AR/MR operation reduces the need for excess steam in the reaction. To attain a minimum 95 \% CO conversion, our simulation proposes that the conventional process requires high H\textsubscript{2}O/CO ratios (around 5) as HTSR feed (at 593 K). In this work, the study of various H\textsubscript{2}O/CO ratios suggests the use of H\textsubscript{2}O/CO ratios greater than 1.5 is enough to reach more than 95\% conversions for AR process (at 523 K). The proposed process reduces the need for downstream CO\textsubscript{2} separation and enables production of high purity H\textsubscript{2} and CO\textsubscript{2} (greater than 95 \%). The above establish clearly that the proposed process is superior, from an economic, environmental and power generation perspective, to currently proposed CCS technologies for IGCC plants.

3.1. Introduction

The study of multiphase transport/reaction phenomena is, of course, of interest to a wide range of separation and reactor applications [33–36] involving simultaneous heat, momentum, and multi-component mass transport [37–39]. The most marked characteristic of such multiphase systems is their nonlinear nature, which requires the quantification of a set of multiple, coupled nonlinear differential equations for the problem solution, a task that entails a complex set of technical challenges [37]. For reactors, accounting for all such phenomena dictates the use of the so-called heterogeneous models [40–42] rather than the simplified pseudo-homogeneous models [34]. The most crucial advantage of using such models in the modeling of reactors and separators, is their ability to solve transport equations separately for each phase (bulk reactor phase, catalysts, adsorbents, membranes), explicitly accounting for gradients inside of each phase and between phases, and thus providing satisfactory results in the context of one-dimensional simulation (axial) even though the reactor/separator has typically a higher spatial dimensionality [43].

A key component of such an effort is the development of an effective model that will allow for the design of such reactors based on the scale-up of laboratory systems. Several modeling studies of the WGSR-MR [44–60] and WGSR-AR [61–68] have been previously published in literature. However, all these models do not explicitly account for the reaction/transport within the catalyst/adsorbent pellets themselves and, instead, consider a constant catalyst pellet effectiveness factor along the reactor’s length. This may be an adequate assumption for lab-scale AR/MR, that utilize powdered catalysts to eliminate internal transport
limitations, but it is unlikely to be valid for commercial reactors which must employ larger size pellets to avoid large pressure drops, particularly under the high-pressure conditions of the IGCC application. For such reactors, one expects the effectiveness factor to vary substantially along the length of the reactor. Moreover, thermal effects are typically neglected and isothermal operation is assumed, which is again consistent with the conditions prevailing (or approached) for most of the lab-scale studies. However, isothermal operation is unlikely for commercial-scale systems. In fact, due to the high exothermicity of the WGSR, heat management is a key design consideration and constraint for both traditional packed-bed reactors as well as MR, particularly for the high-pressure IGCC conditions of interest in this study. The goal of this work, therefore, is the development of a multi-scale MR model, that overcomes these technical literature limitations, by capturing in detail the species/energy transport phenomena within the porous catalyst/adsorbent pellets, themselves, and their dependence on the pellet’s location along the reactors’ length, as well as the species/energy transport phenomena in the reactor’s bulk phase. Throughout this work, the local and the axially-averaged effectiveness factors, for both the catalyst and adsorbent pellets, are calculated through multiple operating cycles and for various pellet sizes.

3. 2. Multiscale Mathematical Model Approach

A membrane reactor is typically composed of the reactor module (made usually out of stainless steel), containing in its interior one (for typical lab-scale systems) or multiple (for pilot-scale or field-scale units) membrane tubes commonly assembled inside the module in a concentric fashion. The reaction zone, i.e., the region where catalyst pellets are packed, is localized in between the MR module internal wall and the membranes’ external surface. For the WGSR-MR under study here, H₂ transports from the reaction zone through the selective CMS membrane towards the membrane permeation zone, thus shifting the chemical equilibrium and
resulting into more CO\textsubscript{2} and H\textsubscript{2} being formed. In the permeation zone, the hydrogen is carried away by a sweep gas (steam, in our studies) flowing either co-currently or counter-currently to the reacting mixture. A schematic of such a MR is shown in Figure 16.

![Schematic of Membrane Reactor](image)

*Figure 16. 1-D Representation of control volumes in a Membrane Reactor.*

From a physical standpoint, the MR in Figure 16 can be described as a multi-scale, multiphase system that encompasses different process functions in various regions of the device. Here, the reaction zone in the MR is modeled at two different scales: the so-called microscale, which considers pellet-scale features, including average pore size, reaction rates, pellet material properties, and pellet shape; and the macroscale, which considers reactor scale features including membrane module dimensions, membrane tube characteristics, and catalyst packing void fraction. The permeation zone is modeled at the macroscale level only, as in the MR configuration studied here it contains no catalyst and/or adsorbent pellets.

In the model, these MR regions are modeled as individual domains, so that one can properly assess the contribution of each of their parameters to the overall system. Regardless of the length scale, phase, or region of the system, conservation laws must hold. Thus, in the derivation of the MR model equations, the Reynolds Transport Theorem (RTT) is applied separately to each of the MR domains: the pellet domain, the reactor domain, and the permeation
zone domain. Pellet and reactor domains are part of the reaction zone, describing its microscale and macroscale behavior, respectively. The permeation zone is a macroscale domain featuring counter-current or co-current removal of the hydrogen.

The AR system (depicted in Figure 17) is modeled at two different scales: the pellet scale, which considers all catalyst/adsorbent pellet features, including average pore size, reaction/adsorption kinetic rates, pellet material properties, and pellet shape; and the reactor scale, which considers such features, as reactor dimensions, catalyst/adsorbent packing void fraction, and others. In addition, the AR is considered to comprise of three domains: the catalyst pellet domain, adsorbent pellet domain, and the reactor domain (bulk gas phase).

![Figure 17. 1-D Representation of control volumes in a Membrane Reactor.](image)

The resulting steady-state/time-dependent equations are implemented in the COMSOL software package and solved simultaneously in all aforementioned domains along the length of the AR and MR, using the finite element method (FEM). A schematic representation of the model information flow for MR and AR is presented in Figure 18 and 19. The adsorbent and/or catalyst pellet domains are distributed along the reactor axis, contributing source terms to the reactor domain equations, while receiving information regarding the reactor gas conditions prevalent at the pellet boundary. Indeed, solution of the differential equations describing the
system behavior in the pellet interior requires information from the pellet boundary. On the other hand, solution of the differential equations describing the system behavior in the reactor interior requires source term information related to the pellet boundary. Information regarding gas pressure, temperature, velocity, and species’ concentrations in the reactor domain, is provided to the catalyst and adsorbent pellet domains, and temperature and species flux information in the catalyst and adsorbent pellet domains is provided to the reactor domain. The solution of the overall differential equation system is carried out in a simultaneous matter. At the end of this process, temperature, pressure, and species profiles are known at each axial location within the reactor domain, and at each pellet domain radial, reactor domain axial local pair.

\[ \text{Figure. 18. Multiscale Modeling Approach in MR.} \]
The CFD model employs a uniform (fine) mesh in the reactor domain, and a non-uniform mesh with 8000-unit cells (shown in Figure 20) in the catalyst and adsorbent pellet domains. For the radial direction of both catalyst and adsorbent pellet, we use a predefined distribution with element ratio, it provides much smaller unit cells through the surface of the pellets. Halving of the mesh size did not yield any noticeable changes in the obtained results.
In order to gauge the impact of the underlying transport and reaction (catalyst pellet) and sorption (adsorbent pellet) processes, instantaneous effectiveness factors are calculated. They are defined as ratios of the real uptake rate (due to combined transport and reaction or adsorption) of a given species by the catalyst/adsorbent pellet over the same uptake rate in the absence of transport limitations, i.e., when the gas phase concentration within the particle is the same with that prevailing at the pellet’s external surface.

3.3. Pellet-Scale Modeling (Catalyst/Adsorbent/Quartz Pellets)

This section covers the derivation of Reynold’s Transport Theorem (RTT) based pellet scale model equations. The differentiation among the various MR and AR domains are practiced by assigning the following designation: \( c \)-catalyst pellet, \( a \)-adsorbent pellet, \( q \)-quartz pellet (inert quartz particles are used to dilute the catalyst phase to be able to attain isothermal conditions in MR), \( r \)-reactor domain, and \( per \)-permeation domain. Table 1 contains the definition of the various geometric parameters: They include the volumetric fraction which is defined as the differential volume occupied by phase \( \gamma \) within domain \( \alpha \) divided by the respective differential volume of domain \( \alpha \). Similarly, one can use the same approach to define the area fraction, as the ratio of the differential area occupied by phase \( \gamma \) within domain \( \alpha \) to the differential area of the respective domain \( \alpha \). The area to volume factor is defined as the differential contact area between two phases within the same domain, e.g., \( \gamma_1^a \) and \( \gamma_2^a \), divided by the respective differential volume of phase \( \alpha \).
Then, the total mass conservation equations for catalyst domain-phase pairs in MR/AR systems and adsorbent domain-phase pairs in the AR system are shown in equations (5) through (8) below:

**Catalyst-Fluid:**

\[
\frac{\partial}{\partial t} \left( \sum_{i=1}^{N_{f,i}} \rho_{f,i}^\gamma \right) + \nabla \cdot \left( \sum_{i=1}^{N_{f,i}} \rho_{f,i}^\gamma \dot{\nu}_{f,i}^\gamma \right) = 0 \quad ; \quad i = 1, \nu
\]  

**Catalyst-Solid:**

\[
0 = \frac{\partial \rho_i^\gamma}{\partial t}
\]  

**Adsorbent-Fluid:**

\[
-M_i \frac{\partial \rho_{f,i}^\gamma}{\partial t} = \rho_{f,i}^\gamma \dot{w}_{f,i}^\gamma + \nabla \cdot \left( \rho_{f,i}^\gamma \dot{v}_{f,i}^\gamma \right) \quad ; \quad i = 1, \nu
\]  

**Adsorbent-Solid:**

\[
M_i \frac{\partial \rho_{f,i}^\gamma}{\partial t} = \rho_{f,i}^\gamma \dot{w}_{f,i}^\gamma + \nabla \cdot \left( \rho_{f,i}^\gamma \dot{v}_{f,i}^\gamma \right) \quad ; \quad i = 1, \nu
\]  

The species mass conservation equations for catalyst domain-phase pairs in MR/AR systems and adsorbent domain-phase pairs in the AR system are shown in equations (9) through (12) below:

**Catalyst-Fluid:**

\[
M_i \frac{\partial \rho_{f,i}^\gamma}{\partial t} = \dot{e}_{f,i}^\gamma \left( \rho_{f,i}^\gamma \dot{v}_{f,i}^\gamma \rho_i^\gamma \right) + \nabla \cdot \left( \dot{e}_{f,i}^\gamma \nabla \left( N_{f,i}^\gamma \right) \right) \quad ; \quad i = 1, \nu
\]  

**Catalyst-Solid:**

\[
0 = \frac{\partial \rho_{j,i}^\gamma}{\partial t} \quad ; \quad i = 1, \nu
\]  

**Adsorbent-Fluid:**

\[
-M_i \frac{\partial \rho_{f,i}^\gamma}{\partial t} = \dot{e}_{f,i}^\gamma \left( \rho_{f,i}^\gamma \dot{w}_{f,i}^\gamma \rho_i^\gamma \right) + \nabla \cdot \left( \dot{e}_{f,i}^\gamma N_{f,i}^\gamma \rho_i^\gamma \right) \quad ; \quad i = 1, \nu
\]  

**Adsorbent-Solid:**

\[
M_i \frac{\partial \rho_{f,i}^\gamma}{\partial t} = \dot{e}_{f,i}^\gamma \left( \rho_{f,i}^\gamma \rho_i^\gamma \right) \quad ; \quad i = 1, \nu
\]
**Dusty Gas Model (DGM):**

Quantification of the combined diffusion-convection mass flux \( N_{f,j}^{a} \) of species \( i \) within the pellet domain is carried out using the Dusty Gas Model (DGM). In general, the most industrial multiphase reactors run under the reactions condition involving more than two species. Thus, advanced multicomponent flux models are required to model species diffusion such as the Dusty Gas Model to reach the level of accurate modeling of the transport mechanisms and reaction kinetics [42]. The Dusty Gas Model takes into account the three species’ transport mechanisms; continuum (or regular) derived using the Maxwell-Stefan equations, viscous diffusion (or convection), Knudsen diffusion. Continuum diffusion is the movement of species due to concentration gradients, viscous diffusion is the movement of species due to pressure gradients, and Knudsen diffusion is the movement of species due to concentration gradients in the presence of small pore walls. Thermal diffusion is not considered in this work [69-70]. The resulting DGM constitutive equations, relating the combined (convective and diffusive) molar fluxes in systems with walls, with the underlying species’ concentration gradients, are:

\[
- \frac{1}{N_i} \sum_{j=1}^{N} \left( \frac{c_{f,j}^{a}}{D_{f,j}^{a}} N_{f,j}^{a} - \frac{c_{f,j}^{a}}{D_{f,j}^{a}} N_{f,j}^{a} \right) \frac{N_{f,j}^{a} c_{f,j}^{a}}{D_{f,j}^{a}} = \nabla c_{f,j}^{a} + \sum_{j=1}^{N} \left( 1 + \frac{P_{j}^{a}}{D_{f,j}^{a} \mu_{j}^{a}} \right) \nabla P_{j}^{a} \quad ; \quad i = 1, N_s
\]

The combined molar fluxes \( \vec{N}_i \; i = 1, N_s \), combined mass fluxes \( \vec{J}_i \; i = 1, N_s \), and velocities \( \vec{v}_i \; i = 1, N_s \) for the \( i \)th species, are defined as \( \vec{N}_i = c_i \vec{v}_i \; i = 1, N_s \), \( \vec{J}_i = M_i c_i \vec{v}_i \; i = 1, N_s \). By defining the gas mixture’s molar average velocity \( \bar{v} = \sum_{i=1}^{N_s} \frac{c_i}{\sum_{j=1}^{N} c_j} \bar{v}_i \) and average mass velocity \( \bar{u} = \sum_{i=1}^{N_s} \frac{M_i c_i}{\sum_{j=1}^{N} M_j c_j} \bar{v}_i \), one can decompose the combined molar (mass) fluxes into convective \( c_i \vec{v} \; i = 1, N_s \) (\( M_i c_i \bar{u} \; i = 1, N_s \)) and diffusive \( n_i = c_i (\vec{v}_i - \vec{v}) \; i = 1, N_s \) (\( \vec{J}_i = M_i c_i (\vec{v}_i - \bar{u}) \; i = 1, N_s \)) components, as follows:
\[
\begin{align*}
\bar{n}_i &= c_i (\bar{v}_i - \bar{v}) = \bar{N}_i - c_i \bar{v} = \bar{N}_i - c_i \sum_{j=1}^{N} c_j \bar{v}_j, \quad i = 1, N, \\
\bar{j}_i &= M_i c_i (\bar{v}_i - \bar{u}) = \bar{J}_i - M_i c_i \bar{u} = \bar{n}_i - M_i c_i \sum_{j=1}^{N} M_j c_j \bar{v}_j, \quad i = 1, N
\end{align*}
\]

(14)  
(15)

The DGM can be written in matrix equation form for the \( N_s \) species as following:

\[
\begin{array}{c}
\begin{bmatrix}
\bar{n}_1 \\
\bar{n}_2 \\
\vdots \\
\bar{n}_{Ns}
\end{bmatrix}
= \\

\begin{bmatrix}
\sum_{j=1}^{Ns} D_{ij}^{c} + 1 \\
\sum_{j=1}^{Ns} D_{ij}^{c} \\
\vdots \\
\sum_{j=1}^{Ns} D_{ij}^{c}
\end{bmatrix}
\begin{bmatrix}
\bar{c}_1 \\
\bar{c}_2 \\
\vdots \\
\bar{c}_{Ns}
\end{bmatrix}
= \\

\bar{N}
\end{array}
\]

Then a DGM effective diffusivity matrix can be defined as \( D^{DGM} \) and give rise to the equation

\[
\bar{N} = -D^{DGM} \cdot \bar{\nabla}X
\]

\[
(16)
\]

**Maxwell-Stefan Model (MSM) and Wilke Model (WM):**

Alternative to DGM, diffusive fluxes are also calculated by using the Maxwell-Stefan Model and Wilke Model in pellet domains. The impact of various diffusion models (Maxwell-Stefan, Wilke, Dusty Gas) on the predictions of a multi-scale reactor/separator mathematical
model is discussed in Chapter 4. The Maxwell-Stefan equation can be given in the following form:

\[
\vec{v}_i = \sum_{j=1}^{N_i} \frac{x_i x_j}{D_{ij}} \left( \frac{1}{\rho_j} \frac{\vec{J}_j}{\rho_i} - \frac{1}{\rho_j} \frac{\vec{J}_j}{\rho_j} \right) + (w_i - x_i) \left( \nabla \frac{P}{P} \right) + \sum_{j=1}^{N_i} \frac{x_i x_j}{\rho_j D_{ij}} \left( \frac{D_j^p}{w_j} - \frac{D_j^p}{w_i} \right) \left( \nabla \frac{T}{T} \right)
\] (17)

The Wilke Model can be given in the following form:

\[
\vec{J}_i = -D_m^a \nabla \rho_i \alpha, \quad \text{where } D_m^a = \frac{1-w_i^c}{M \sum_{j=1}^{N_i} D_{ij}^a}
\] (18)

The species \( i \) volumetric generation rate in the pellet-fluid subsystem is quantified by the underlying reaction, and adsorption rates. Eq. (19) reflects the relation between the volumetric and the specific generation rates for the pellet domains.

\[
R_{f,i}^a = \varepsilon_{f,v}^a \rho_i^a \mathcal{R}_{f,i}^a
\] (19)

For the energy equation development in the pellets’ domain presented here, the solid phase is considered stagnant, and the potential and kinetic energies, the work done by the fluid onto the solid, and the energetic effect of interphase viscous friction are all considered negligible. Also, radiation-based energy transport is not considered to be essential for this application. Fourier’s law is used to account for heat conduction, and the reacting mixture’s enthalpy is calculated using an ideal gas mixture assumption.

\[
\begin{align*}
\text{Pellet-Fluid: } & \begin{cases}
-q_i^p \varepsilon_{f,A}^p \lambda_{f,A}^p \nabla T_f^p \\
- \sum_{i=1}^{n} \varepsilon_{f,A}^p C_{f,i} \left( \frac{1}{M_i} \nabla \frac{T_f^p}{T_f^p} \right) \\
- \sum_{i=1}^{n} h^p R_{f,i}^p + \sum_{j=1}^{N_i} \frac{\varepsilon_{f,v}^p C_{f,i}^p}{\varepsilon_{f,v}^p \rho_i^p} \nabla T_f^p
\end{cases} \\
= & \begin{cases}
\sum_{i=1}^{n} \varepsilon_{f,v}^p \rho_i^p \left( \varepsilon_{f,v}^p C_{f,i}^p \right) \frac{\partial T_f^p}{\partial t} \\
+ \sum_{i=1}^{n} \varepsilon_{f,v}^p \rho_i^p \left( \varepsilon_{f,v}^p C_{f,i}^p \right) \left( \nabla \frac{T_f^p}{T_f^p} \right)
\end{cases}
\end{align*}
\] (20)
**Pellet-Solid:**

\[ q_{f\rightarrow s}^p + \nabla \cdot \left[ \epsilon_{f,A}^p \lambda_f^p \nabla T_f^p \right] = \epsilon_{f,V}^p \rho_f^p C_V^p \frac{\partial T_f^p}{\partial t} \]  

(21)

The proximity of the solid and fluid phases in the pellets domains induce a high heat transfer coefficient between the two phases, which in turn leads to a common temperature \( T^\alpha \) for the pellet’s solid-fluid composite system. The resulting composite energy equation is given by Eq.(22).

\[
\begin{align*}
\nabla \cdot \left[ \sum_{\gamma \in \{s,f\}} \left( \lambda^\alpha \nabla T^\alpha \right) \right] - \sum_{\gamma \in \{s,f\}} \nabla \cdot \left( \epsilon_{\gamma,V}^\alpha \rho_{\gamma}^\alpha C_V^\alpha \right) n_{\gamma,j}^\alpha \cdot \nabla T^\alpha
\end{align*}
\]

\[
\begin{align*}
&= \left[ \epsilon_{\gamma,V}^\alpha \rho_{\gamma}^\alpha C_V^\alpha + \sum_{i=1}^{n_{\gamma}} \frac{1}{M_i} \epsilon_{\gamma,V}^\alpha \rho_{\gamma_i}^\alpha C_i^\alpha \right] \frac{\partial T^\alpha}{\partial t}
\end{align*}
\]

(22)

The momentum conservation equation for each domain-phase pair as a function of the mass average velocity \( \bar{v}_\gamma^\alpha \) of phase \( \gamma \) within the domain \( \alpha \) is shown in Eq.(23) to (24).

**Pellet-Fluid:**

\[
\overline{S_f^\gamma} = \frac{1}{S_f^\gamma} \left[ \frac{\partial}{\partial t} \left( \epsilon_{f,V}^\gamma \sum_{i=1}^{n_{\gamma}} w_{f,i}^\gamma \rho_{f,i}^\gamma \bar{v}_{f,i}^\gamma \right) + \nabla \cdot \left( \epsilon_{f,V}^\gamma \sum_{i=1}^{n_{\gamma}} \sum_{j=1}^{n_{f,j}} \rho_{f,i}^\gamma \bar{v}_{f,i,j}^\gamma \right) \right] \quad \text{for } i = 1,\nu
\]

(23)

**Pellet-Solid:**

\[
\overline{S_s^\gamma} = 0 \quad \text{for } i = 1,\nu
\]

(24)

In this study, we consider steady-state (MR)/dynamic (AR) reactive transport in the pellet domains, a spherical pellet, homogeneous porous structure along the pellet, a mean pore diameter, a constant reaction kinetics and reaction orders over the entire range of conditions simulated, and no side reaction occurs. For the pellet-fluid subsystem, a source term for the momentum balance is obtained by adding the DGM for all species.

For the pellet domains, the simplified molar-based equations are shown in Tables 2 and 3, together with the set of initial and boundary conditions which are presented in Tables 4 and 5.
Table 2. Molar-based catalyst pellet-scale model equations- MR (Steady-State).

Constitutive laws

Continuity equation:

\[ \sum_{i=1}^{2} R_{f,j}^e r^2 = \frac{d}{dr} \left( c_{f,j}^e r^2 v_{f,j}^e \right) \]  
(25)

Component mass conservation:

\[ R_{f,j}^e r^2 = \frac{d}{dr} \left[ c_{f,j}^e r^2 \left( x_{f,j}^e c_{f}^e v_{f,j}^e + J_{f,j} \right) \right] \]  
(26)

Diffusion model (DGM):

\[ -\frac{1}{\sum_{j=1}^{2} c_{f,j}^p D_{q}^{\phi}} \sum_{j=1}^{2} \left( \frac{c_{f,j}^p D_{q}^{\phi}}{D_{q}^{\phi}} J_{f,j} - \frac{c_{f,j}^p D_{q}^{\phi}}{D_{q}^{\phi}} J_{f,j}^{p} \right) - \frac{J_{f,j}^{p}}{D_{k}^{\phi}} = \frac{d}{dr} c_{f,j}^p - \frac{d}{dr} c_{f,j}^{p,\text{sat}} + \frac{c_{f,j}^p}{\sum_{j=1}^{2} c_{f,j}^{p,RT}} \left( 1 + \frac{p_{c}^p}{D_{k}^{\phi} \mu_{f,j}^p} \right) \frac{d}{dr} p_{c}^p \]  
(27)

Energy conservation:

\[ \left( \sum_{i=1}^{2} \varepsilon_{f,i}^e X_{f,i}^e C_{f,j}^e \right) v_{f,j}^e \frac{dT^{e}}{dr} + \sum_{i=1}^{2} \varepsilon_{f,i}^e X_{f,i}^e \rho_{i}^{e} R_{f,j}^{e} = \frac{d}{dr} \left( \varepsilon_{f,j}^e \frac{dT^{e}}{dr} \right) - \sum_{i=1}^{2} \varepsilon_{f,i}^e \left( \frac{1}{M_{i}} C_{f,i}^{e} \right) \frac{d}{dr} T^{e} \]  
(28)

Table 3. Molar-based adsorbent pellet-scale model equations- AR (Dynamic).

Constitutive laws

Continuity equation:

\[ -\sum_{i=1}^{2} R_{f,j}^a = \frac{d}{dt} \left( \varepsilon_{f,j}^a r^2 \sum_{i=1}^{2} \varepsilon_{f,j}^a \right) + \frac{d}{dr} \left( \varepsilon_{f,j}^a r^2 \varepsilon_{f,j}^a v_{f,j}^a \right) \]  
(29)

Component mass conservation:

\[ -R_{f,j}^a = \frac{d}{dt} \left( \varepsilon_{f,j}^a r^2 c_{f,j}^a \right) + \frac{d}{dr} \left[ \varepsilon_{f,j}^a r^2 \left( x_{f,j}^a c_{f}^a v_{f,j}^a + J_{f,j}^{a} \right) \right] \]  
(30)

Diffusion model (DGM):

\[ -\frac{1}{\sum_{j=1}^{2} c_{f,j}^p D_{q}^{\phi}} \sum_{j=1}^{2} \left( \frac{c_{f,j}^p D_{q}^{\phi}}{D_{q}^{\phi}} J_{f,j} - \frac{c_{f,j}^p D_{q}^{\phi}}{D_{q}^{\phi}} J_{f,j}^{p} \right) - \frac{J_{f,j}^{p}}{D_{k}^{\phi}} = \frac{d}{dr} c_{f,j}^p - \frac{d}{dr} c_{f,j}^{p,\text{sat}} + \frac{c_{f,j}^p}{\sum_{j=1}^{2} c_{f,j}^{p,RT}} \left( 1 + \frac{p_{c}^p}{D_{k}^{\phi} \mu_{f,j}^p} \right) \frac{d}{dr} p_{c}^p \]  
(31)

Energy conservation:
For the energy equation development in the inert quartz pellet, the solid phase is considered stagnant, and the potential and kinetic energies, the work done by the fluid onto the solid, and the energetic effect of interphase viscous friction are all considered negligible. The resulting composite energy equation is given by Eq. (35).

\[ 0 = \nabla \cdot \left[ \left( \rho_s^a \right) \nabla T^a \right] \quad (35) \]

The set of initial and boundary conditions for the solution of the quartz pellet scale model equations is presented in Table 1.
Table 5. Boundary conditions for inert pellet-scale model equations.

<table>
<thead>
<tr>
<th>Boundary conditions:</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_r = -λ^r \nabla T^r = 0 ) for ( r = 0 )</td>
</tr>
<tr>
<td>(-h^r (T^r - T^s) = Q^s ) for ( r = r^s )</td>
</tr>
</tbody>
</table>

\[ (36) \]

3.4. Reactor-Scale (Bulk Gas) Modeling

3.4.1 Membrane Reactor (MR)

3.4.1.1 Reaction Zone

In MR-reaction zone, quartz is considered a rigid solid body with constant mass for lab-scale reactor simulations. Assuming no structural changes during reaction inside of the pellet, stagnant solid phase, no phase changing in the reaction mixture, the total mass conservation equation for reaction zone in the MR system is shown in Eq. (37) to (38).

Reactor-Fluid:

\[ \sum_{i=1}^r S^r_{f-per,i} = \frac{\partial}{\partial t} \left( \epsilon_{f,y}^r \rho_f^r \right) + \nabla \cdot \left( \epsilon_{f,A}^r \rho_f^r v_f^r \right) \]  
\[ (37) \]

Reactor-Solid:

\[ 0 = \frac{\partial}{\partial t} \left( \epsilon_{i,s}^r \rho_i^r \right) \]  
\[ (38) \]

The species mass conservation equation for reaction zone obtained from the RTT are shown in Eq. (39) to (40).

Reactor-Fluid:

\[ \overline{S}^r_{f-per,i} + M_i R_{f,i} = \frac{\partial}{\partial t} \left( \epsilon_{f,y}^r w_f^r \rho_f^r \right) + \nabla \cdot \left( \epsilon_{f,A}^r \left( w_f^r \rho_f^r v_f^r + n_f^r \right) \right) \]  
\[ ; \ i = 1, ν \]  
\[ (39) \]

Reactor-Solid:

\[ 0 = \frac{\partial}{\partial t} \left( \epsilon_{i-s}^r \rho_i^r \right) \]  
\[ ; \ i = 1, ν \]  
\[ (40) \]

The source term \( \overline{S}^r_{f-per,i} \) represents the species mass lost in reaction zone through permeation zone at the control surface \( CS^per \) of the permeation domain.

\[ \overline{S}^r_{f-per,i} = \begin{cases} J_{f,i}^{per} & \text{if } 1D \\ 0 & \text{if } 2D \text{ or } 3D \end{cases} \]  
\[ (41) \]
The solution-diffusion model is used to describe the permeation through membrane. In this model, permeation is proportional to the difference between the species’ partial pressure at the tube and shell sides, gas boundary layer resistance near the membrane surface is neglected, and infinitely selective membrane is assumed. The integration of Henry’s law (solubility) and Fick’s law (diffusion) results in Eq.(42) for the flux of the permeating species [71].

\[
\overline{J}_j^{\text{per}} = \frac{D \cdot S \cdot \Delta p_j}{\delta} = \frac{P_e \cdot \Delta p_j}{\delta}
\]  

(42)

In Eq.(42), \(D\) is the diffusion coefficient of the species on the membrane side, \(S\) is the gas solubility, \(\Delta p_j\) is the difference between the jth species partial pressure at tube and shell side, \(\delta\) is the membrane thickness, and \(P_e\) is the so-called permeability coefficient.

The species flux through membrane can be represented by using the Sieverts’ Law [4]:

\[
\overline{J}_j^{\text{per}} = \frac{P}{\delta} \left[ \left( p_{j,t}^{\text{top}} \right)^n - \left( p_{j,s}^{\text{top}} \right)^n \right] \in CS^{\text{per}}
\]  

(43)

The Arrhenius Law expresses the relation between the permeability and the temperature;

\[
P_e = P_e^0 \exp \left( -\frac{E_p}{R \cdot T} \right)
\]  

(44)

According to the the Sieverts’ Law and the Arrhenius Law, the flux increases by decreasing the membrane thickness and increasing the temperature. Many studies have verified the applicability of the Sieverts' law to CMS membranes.

The momentum conservation equation for each domain-phase pair as a function of the mass average velocity \(\overline{v}_j^\gamma\) of phase \(\gamma\) within the domain \(\alpha\) is shown in Eq.(45) to (46).

**Reactor-Fluid:**

\[
\overline{S}_j^\gamma = \frac{\partial}{\partial t} \left( \epsilon_{j,\gamma}^\alpha \rho_j^\gamma \overline{v}_j^\gamma \right) + \nabla \cdot \left( \epsilon_{j,\gamma}^\alpha \rho_j^\gamma \overline{v}_j^\gamma \overline{v}_j^\gamma \right)
\]  

(45)

**Reactor-Solid:**

\[
\overline{S}_j^\gamma = 0
\]  

(46)
The source term $S^\alpha_f$ typically consists of Reynold stresses, body forces, momentum exchange, mass exchange, equilibrium and non-equilibrium pressure, and average stresses.

For the energy equation development in all MR domains presented, solid phase is considered stagnant, and the potential and kinetic energies, the work done by the fluid onto the solid, and the effect of interphase viscous friction are all considered negligible. Also, radiation-based energy transport is not considered to be essential for this application. Fourier’s law is used to account for heat conduction, and the reacting mixture’s enthalpy is calculated using an ideal gas mixture assumption. Then, the energy equations for each domain-phase pair in the system are presented in Eq.(47) to (48).

$$\begin{align*}
\text{Reactor-Fluid:} & \quad -q'_{f\to r} - q'_{f\to per-f} + \nabla \cdot \left( e'_{f,A} \lambda_f \nabla T_f \right) \\
& \quad - \sum_{i=1}^n \left[ e'_{f,A} \left( \frac{1}{M_i} C'_{p,i} \right) \eta_{f,A} \cdot \nabla T_f \right] \\
& \quad - \sum_{i=1}^n \left[ \rho_f \left( \frac{1}{M_i} \right) \tilde{v}_{f,A} \cdot \nabla \left( e'_{f,A} \eta_{f,A} \right) \right]
\end{align*}$$

$$\begin{align*}
& = \left\{ e'_{f,A} \rho_f \left( \sum_{i=1}^n \frac{e'_{f,A}}{C'_{p,i}} C_{p,i} \right) \frac{\partial T_f}{\partial t} \right. \\
& \quad \left. + e'_{f,A} \rho_f \left( \sum_{i=1}^n \frac{\eta_{f,A}}{C'_{p,i}} C_{p,i} \right) \tilde{v}_{f,A} \cdot \nabla T_f \right\} \\
& \quad \left( 47 \right)
\end{align*}$$

$$\begin{align*}
\text{Permeation-Fluid:} & \quad q'_{r\to per-f} + \nabla \cdot \left( \lambda_f \nabla T_{f,per} \right) \\
& \quad = \left\{ \rho_f \left( \sum_{i=1}^n \frac{\eta_{f,per}}{C'_{p,per}} C_{p,per} \right) \frac{\partial T_{f,per}}{\partial t} \right. \\
& \quad \left. + \rho_f \left( \sum_{i=1}^n \frac{\eta_{f,per}}{C'_{p,per}} C_{p,per} \right) \tilde{v}_{f,per} \cdot \nabla T_{f,per} \right\} \\
& \quad \left( 48 \right)
\end{align*}$$

In this work, the heat exchanged among the fluid, solid phases in reaction zone and permeation zone, $q'_{f\to r}$, is composed of six terms: the enthalpy carried by the species’ mass flux between the reactor and the pellet domains at the control surface $CS^r$ of the pellet domain, Eq.(50); the enthalpy carried by the species’ mass flux between the reactor and the permeation domains at the control surface $CS^{per}$ of the permeation domain, Eq.(51); the convective heat flux exchanged between the fluid in the reactor and the pellet solid phase at the control surface $CS^r$ of the pellet domain, Eq.(52); the convective heat flux exchanged between the fluid in the reactor and the
quartz solid phase at the control surface $CS^s$ of the quartz domain, Eq.(53); a source term $q'_f$ that accounts for any external heat flux crossing the considered reactor control surface $CS^r$, Eq.(54); and a source term $q'_i$ that accounts for any internal heat flux crossing the considered permeation control surface $CS^{per}$, Eq.(55).

$$q'_{f \rightarrow s} = q'_{me} + q'_{nper} + q'_f + q'_q + q'_i$$  \hspace{1cm} (49)$$

$$q'_{nper} = e'_{s \rightarrow V} \left( \frac{A'}{e'_{r, V}} \right) \sum_{i=1}^{r} \left( \frac{1}{M_i} \tilde{h}'_{i, A} \tilde{e}'_{i, A, N_i} \right) \in CS^s$$  \hspace{1cm} (50)$$

$$q'_{nper} = \left( \frac{A^{per}}{V^r} \right) \sum_{i=1}^{r} \left[ \frac{1}{M_i} (N_i^{per} \tilde{h}'_{i, A} - \tilde{h}'_{i, A}) \right] \in CS^{per}$$  \hspace{1cm} (51)$$

$$q'_i = e'_{s \rightarrow V} \left( \frac{A'}{e'_{r, V}} \right) \left[ \tilde{e}'_{s, A} h'^{s} \left( T'_f - T^s \right) \right] \in CS^s$$  \hspace{1cm} (52)$$

$$q'_q = e'_{q \rightarrow V} \left( \frac{A'}{e'_{r, V}} \right) \left[ \tilde{e}'_{s, A} h'^{q} \left( T'_f - T^s \right) \right] \in CS^s$$  \hspace{1cm} (53)$$

$$q'_e = \left\{ \begin{array}{ll} \frac{4}{d^q} U^{p} (T'_f - T^p) \text{ if } 1D \\ 0 \text{ if } 2D \text{ or } 3D \end{array} \right\} \in CS^r$$  \hspace{1cm} (54)$$

$$q'_i = \left\{ \begin{array}{ll} \frac{A^{per} U^{per}}{V^r} (T'_f - T^{per}) \text{ if } 1D \\ 0 \text{ if } 2D \text{ or } 3D \end{array} \right\} \in CS^{per}$$  \hspace{1cm} (55)$$

In the application of the adiabatic case on the MR, we consider globally adiabatic reactor (with respect to the environment, no external coolant or heater or $q'_e = 0$). However, we utilize the Eq.(54) to express the heat flux between reaction zone and environment for the non-adiabatic reactor case.

The reactor configuration is given by a one-dimensional tubular reactor with no axial dispersion, thus radial concentration and temperature gradients are neglected. Gradients
explicitly inside of each phase and between phases are satisfied on one-dimensional reactor simulation (axial), even though the system has a higher dimensionality [43].

The cross-sectional average momentum equation can be written as [34], [72]:

\[
\frac{\partial}{\partial t} \left( \epsilon_{f,v} \rho_f \bar{v}_f \right) + \nabla \cdot \left( \rho_f \bar{v}_f \bar{v}_f \right) = \left\{ -\epsilon_{f,v} \nabla p_f + \epsilon_{f,v} \rho_f \bar{g} + \nabla \cdot \bar{v}_f \left( \mu_f' \left( \nabla \bar{v}_f + (\nabla \bar{v}_f)^T \right) \right) + \epsilon_{f,v} \left( K_D \bar{v}_f + K_v \bar{v}_f^2 \right) \right\}
\]

(56)

The process is steady-state and the gravity term is neglected in horizontal tube. The bed friction in porous reactor plays the main role in pressure drop of the bed. Also, the gas phase velocity is normally not very large [34], [72]. Because of these factors the momentum equation can be reduced to the following form:

\[
\nabla p_f = -K_D \bar{v}_f - K_v \bar{v}_f^2 = \nabla p_f = -150 \frac{(1 - \epsilon_{f,v})}{\epsilon_{f,v}} \frac{(1 - \epsilon_{f,v})}{\epsilon_{f,v}} \frac{(1 - \epsilon_{f,v})}{\epsilon_{f,v}} \frac{(1 - \epsilon_{f,v})}{\epsilon_{f,v}} \frac{(1 - \epsilon_{f,v})}{\epsilon_{f,v}} \frac{(1 - \epsilon_{f,v})}{\epsilon_{f,v}} \rho_f \bar{v}_f \bar{v}_f
\]

(57)

where \( K_D \) and \( K_v \) are constants for the viscous and kinetic pressure drop [34].

For the reactor domain (reaction zone), the molar-based conservation equations are presented in Table 6, coupled with the set of boundary conditions which presented in Table 7.

Table 6. Molar-based reactor-scale model equations.

<table>
<thead>
<tr>
<th>Bulk-gas constitutive laws</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Continuity equation:</strong></td>
</tr>
<tr>
<td>[ \epsilon_{i,v} \frac{A_i}{V_i} \sum_{i=1}^N \left( \epsilon_{f,v} f_{f,i} \right)^{\epsilon_{i,v}} - N_T \frac{A_{per}}{V_i} \sum_{i=1}^N \left( J_{per}^{f,i} \right)^{\epsilon_{i,v}} = \frac{d}{dz} \left( \epsilon_{f,v} \epsilon_{i,v} \bar{v}_f \bar{v}_f \right) ]</td>
</tr>
</tbody>
</table>

(58)

| **Component mass conservation:** |
| \[ \epsilon_{i,v} \frac{A_i}{V_i} \left( \epsilon_{f,v} f_{f,i} \right)^{\epsilon_{i,v}} - N_T \frac{A_{per}}{V_i} \left( J_{per}^{f,i} \right)^{\epsilon_{i,v}} = \frac{d}{dz} \left( \epsilon_{f,v} \epsilon_{i,v} \bar{v}_f \bar{v}_f \right) + \frac{d}{dz} \left( \epsilon_{f,v} \epsilon_{i,v} \bar{v}_f \bar{v}_f \right) \] |

(59)

| **Diffusion model (Stefan-Maxwell):** |
\[ \sum_{j=1}^{m} \left[ \frac{x_{f,j}'}{D_{q}} + \frac{1}{\rho_{f,j}} \left( \frac{1}{\rho_{f,j}} - \frac{1}{\rho_{f,j}'} \right) \right] = \frac{d}{dz} x_{f,j}' + \left( \frac{x_{f,j}' - w_{f,j}}{p_{f}'} \right) \frac{d}{dz} p_{f}' + \sum_{j=1}^{m} \left[ \frac{x_{f,j}'}{\rho_{f,j}' D_{q}} \left( \frac{\bar{D}_{f}'}{w_{f,j}' - w_{f,j}} \right) \right] \frac{1}{T_{f}'} \frac{d}{dz} T_{f}' \]  

\textbf{Momentum conservation:} 
\[ \frac{d p_{f}'}{dz} = -150 \frac{\mu_{f}'}{(e_{f,Y})} \frac{(1-e_{f,Y})^{2}}{d_{p}^{2}} - 1.75 \frac{(1-e_{f,Y})}{(e_{f,Y})} \rho_{f}' v_{f}' v_{f}' \]  

\textbf{Energy conservation:} 
\[ \begin{bmatrix} -e_{e,v} \left( \frac{A'}{e_{f,v}} V ' \right) \left[ e_{e,www}^{v} \left( T_{f}' - T' \right) \right] \\ -e_{e,v} \left( \frac{A'}{e_{f,r} V '} \right) \left[ e_{e,www}^{v} \left( T_{f}' - T' \right) \right] \\ -e_{e,v} \left( \frac{A'}{e_{f,v} V '} \right) \left( \sum_{j=1}^{m} \frac{1}{M_{j}} \left( \tilde{R}_{f,j}' - \tilde{R}_{f,j}'^{R} \right) \right) \\ - \left( \frac{A_{p}'}{V '} \right) \sum_{j=1}^{m} \left( J_{f,j}' \left( \tilde{R}_{f,j}' - \tilde{R}_{f,j}' \right) \right) \end{bmatrix} = \begin{bmatrix} \left( \sum_{j=1}^{m} e_{f,j} C_{p,j} \right) \left( v_{f}' \frac{dT_{f}'}{dz} \right) \\ \left( \frac{\lambda_{f}'}{V '} \right) \left( T_{f}' - T_{f}^{R} \right) + \delta \left( \frac{4}{d_{f}^{2}} \right) U \left( T_{f}' - T^{B} \right) \end{bmatrix} \]  

\( \delta = \begin{cases} 1 & \text{if Wall - isothermal} \\ 0 & \text{if Adiabatic} \end{cases} \)  

<table>
<thead>
<tr>
<th>Boundary Conditions:</th>
</tr>
</thead>
</table>
| \( \bar{V}_{f}' = \bar{V}_{f}' \) | \( \bar{V} T_{f}' = 0 \) 
| \( p_{f}' = \bar{P}_{f}' \) | \( \bar{V} p_{f}' = 0 \) for \( z = 0, J_{f}' = 0 \) for \( z = L \)  
| \( x_{f,j}' = x_{f,j}' \) | \( \bar{V} x_{f,j}' = 0 \)  
| \( T_{f}' = T_{f}' \) |  

Table 7. Boundary conditions for reactor-scale model equations.  

\section{3. 4. 1. 2. Permeation Zone} 

Following the same strategy as previous sections, the total mass conservation equation for permeation zone in the MR system is shown in Eq. (64).  

\textbf{Permeation-Fluid:} 
\[ - \sum_{j=1}^{m} S_{f,j}' = \frac{\partial}{\partial t} \left( \rho_{f}' \bar{v} \right) + \bar{V} \cdot \left( \rho_{f}' \bar{v} \bar{v} \right) \]  

40
The species mass conservation equation for permeation domain obtained from the RTT are shown in Eq. (65).

\[ \frac{\partial}{\partial t} (\rho_{j}^{\text{per}} v_{f,j}^{\text{per}}) + \nabla \cdot \left( \rho_{j}^{\text{per}} v_{f,j}^{\text{per}} v_{f,j}^{\text{per}} \right) ; \quad i = 1, \nu \]  

(65)

The momentum conservation equation for permeation zone as a function of the mass average velocity \( \overline{v_{\gamma}} \) of phase \( \gamma \) within the domain \( \alpha \) is shown in Eq. (66).

\[ \overline{S}_{f,j \rightarrow \text{per} - f}^{\text{per}} = \frac{\partial}{\partial t} \left( \rho_{j}^{\text{per}} \overline{v_{f,j}^{\text{per}}} \right) + \nabla \cdot \left( \rho_{j}^{\text{per}} \overline{v_{f,j}^{\text{per}} v_{f,j}^{\text{per}}} \right) \]  

(66)

The source term \( \overline{S}_{f,j}^{\text{per}} \) in Eq. typically consists of Reynold stresses, body forces, momentum exchange, mass exchange, equilibration and non-equilibrium pressure, and average stresses.

Then, the energy equation for permeation zone is presented in Eq. (67).

\[ q_{f,j \rightarrow \text{per} - f}^{\prime} + \nabla \cdot \left( \lambda_{f}^{\text{per}} \overline{\nabla T_{f}^{\text{per}}} \right) = \left\{ \rho_{f}^{\text{per}} \left( \sum_{i=1}^{\nu} c_{f,i}^{\text{per}} c_{V,i}^{\text{per}} \right) \frac{\partial T_{f}^{\text{per}}}{\partial t} - \frac{\partial p_{f}^{\text{per}}}{\partial t} \right\} + \rho_{f}^{\text{per}} \left( \sum_{i=1}^{\nu} c_{f,i}^{\text{per}} c_{P,i}^{\text{per}} \right) \overline{v_{f,j}^{\text{per}}} \cdot \overline{\nabla T_{f}^{\text{per}}} \right\} \]  

(67)

For the permeation zone domain, conservation equations are presented in Table 8, while their boundary conditions are presented in Table 9.

*Table 8. Molar based permeation zone model equations.*

<table>
<thead>
<tr>
<th>Bulk Gas Constitutive laws</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Continuity Equation:</strong></td>
</tr>
<tr>
<td>[ N_{T} \frac{A_{f}^{\text{per}}} {V} \sum_{i=1}^{\nu} \left[ J_{f,i}^{\text{per}} \right] \frac{d}{dz} \left( \chi_{f,i}^{\text{per}} c_{f}^{\text{per}} v_{f,i}^{\text{per}} \right) ]</td>
</tr>
<tr>
<td>[ (68) ]</td>
</tr>
<tr>
<td><strong>Component mass conservation:</strong></td>
</tr>
<tr>
<td>[ N_{T} \frac{A_{f}^{\text{per}}} {V} \left</td>
</tr>
<tr>
<td>[ (69) ]</td>
</tr>
<tr>
<td><strong>Momentum conservation:</strong></td>
</tr>
</tbody>
</table>
\[
\frac{d}{dz} \left( \rho_f^{\text{per}} v_f^{\text{per}} \right) = - \frac{d p_f^{\text{per}}}{dz} + \mu_f^{\text{per}} \frac{d^2 v_f^{\text{per}}}{dz^2}
\]

(70)

**Energy conservation:**

\[
\begin{aligned}
\frac{d}{dz} \left( \frac{\rho_f^{\text{per}}}{V_f^{\text{per}}} \frac{d T_f^{\text{per}}}{dz} \right) + \frac{A_f^{\text{per}} U_f^{\text{per}}}{V_f^{\text{per}}} (T_f' - T_f^{\text{per}}) + \\
\left( \frac{A_f^{\text{per}}}{V_f^{\text{per}}} \sum_{i=1}^{r_f} \left( J_f^{\text{per}} \left( h_f^{\text{ad},i} - h_f^{\text{per},i} \right) \right) \right)^{\text{per}} = \sum_{i=1}^{r_f} x_f^{\text{per},i} C_f^{\text{per},i} \left( \frac{d T_f^{\text{per}}}{dz} \right)
\end{aligned}
\]

(71)

**Table 9. Boundary conditions for permeation zone model equations.**

**Boundary conditions:**

\[
\begin{align*}
v_f^{\text{per}} &= \left( v_f^{\text{per}} \right)_m \\
p_f^{\text{per}} &= \left( p_f^{\text{per}} \right)_m \\
x_f^{\text{per}} &= \left( x_f^{\text{per}} \right)_m \\
T_f^{\text{per}} &= \left( T_f^{\text{per}} \right)_m
\end{align*}
\]

(72)

3.4.2 Membrane Separation

Taking away the reactivity of the membrane reactor creates another system, called membrane separation (MS). All the relations (derived in the previous sections) is valid for MS without having reactive feature of the equations.

3.4.3 Adsorptive Reactor (AR)

Similar to the MR model development, the total mass conservation equation for the reactor domain-phase pair is shown below in Eq. (73) to (74), where in equation 74 \( \varepsilon_s^{e} \) represents the solid phase fraction inside the reactor, as opposed to \( \varepsilon_s^{c} \) in equation 8 which represents the solid phase fraction inside a single adsorbent pellet.

**Reactor-Fluid:**

\[
- \sum_{i=1}^{r_f} S_f^{\text{ad},i} = \frac{\partial}{\partial t} \left( \varepsilon_f^{c} \rho_f^{c} \right) + \nabla \cdot \left( \varepsilon_f^{c} \rho_f^{c} v_f^{c} \right)
\]

(73)

**Reactor-Solid:**

\[
\sum_{i=1}^{r_f} S_f^{\text{ad},i} = \frac{\partial}{\partial t} \left( \varepsilon_s^{c} \rho_s^{c} \right)
\]

(74)
The species mass conservation equation for the reactor domain-phase pair is shown in Eq. (75) to (76).

**Reactor-Fluid**:

\[
\overrightarrow{S}_{fad,i}^{r} = \overrightarrow{M}_{i}^{r} + \frac{\partial}{\partial t}\left( \overrightarrow{e}_{i}^{r,v} \overrightarrow{w}_{f,i}^{r} \rho_{i}^{r} \right) + \nabla \left[ \overrightarrow{e}_{i}^{r,v} \left( \overrightarrow{w}_{f,i}^{r} \rho_{i}^{r} \overrightarrow{v}_{f}^{r} + \overrightarrow{n}_{f,i}^{r} \right) \right], i = 1, \nu
\]  

(75)

where, in this work, the gradient terms are one-dimensional, and the term \(\overrightarrow{n}_{f,i}^{r} = -\overrightarrow{e}_{i}^{r,v} D_{z} \nabla w_{f,i}^{r}\) accounts for axial dispersion.

**Reactor-Solid**:

\[
\overrightarrow{S}_{fad,i}^{s} = \frac{\partial}{\partial t}\left( \overrightarrow{e}_{i}^{s,v} \overrightarrow{w}_{s,i}^{s} \rho_{i}^{s} \right) \quad i = 1, \nu
\]  

(76)

The source term \(\overrightarrow{S}_{fad,i}^{r}\) represents the species mass lost from the bulk gas phase through adsorption. The species \(i\) volumetric generation rate in the reactor-fluid subsystem is quantified by Eq. (77) and (78), which enforces its equality to the product of a surface to volume adjustment ratio times the overall \(i\)th species combined diffusion-convection mass flux, at the control surface \(CS^{\alpha}\) of the pellet domain.

\[
R'_{f,i}^{r} = \overrightarrow{e}_{i}^{r,v} \frac{A'^{r}}{\overrightarrow{e}_{i}^{r,v} V^{r}} \left[ \left( \overrightarrow{e}_{f,A}^{r} N_{i}^{r} \right)^{CS^{r}} \right]
\]  

(77)

\[
-S'_{fad,i}^{r} = \overrightarrow{e}_{i}^{r,v} \frac{A'^{r}}{\overrightarrow{e}_{i}^{r,v} V^{r}} \left[ \left( \overrightarrow{e}_{f,A}^{r} N_{i}^{r} \right)^{CS^{r}} \right]
\]  

(78)

The momentum conservation equation for the reactor domain-phase pair as a function of the mass average velocity \(\overrightarrow{v}_{f}^{r}\) of phase \(\gamma\) within the domain \(\alpha\) is shown in Eq. (79) to (80).

**Reactor-Fluid**:

\[
\overrightarrow{S}_{f}^{t} = \frac{\partial}{\partial t}\left( \overrightarrow{e}_{i}^{r,v} \rho_{i}^{r} \overrightarrow{v}_{f}^{r} \right) + \nabla \left[ \overrightarrow{e}_{i}^{r,v} \left( \rho_{i}^{r} \overrightarrow{v}_{f}^{r} \overrightarrow{v}_{f}^{r} \right) \right]
\]  

(79)

**Reactor-Solid**:

\[
\overrightarrow{S}_{f}^{t} = \frac{\partial}{\partial t}\left( \overrightarrow{e}_{i}^{s,v} \rho_{i}^{s} \overrightarrow{v}_{f}^{s} \right) + \nabla \left[ \overrightarrow{e}_{i}^{s,v} \left( \rho_{i}^{s} \overrightarrow{v}_{f}^{s} \overrightarrow{v}_{f}^{s} \right) \right]
\]  

(80)

The cross-sectional average momentum equation can be written as:

\[
\frac{\partial}{\partial t}\left( \overrightarrow{e}_{i}^{r,v} \rho_{i}^{r} \overrightarrow{v}_{f}^{r} \right) + \nabla \left[ \overrightarrow{e}_{i}^{r,v} \rho_{i}^{r} \overrightarrow{v}_{f}^{r} \overrightarrow{v}_{f}^{r} \right] + \left[ -\overrightarrow{e}_{i}^{r,v} \nabla \rho_{i}^{r} + \overrightarrow{e}_{i}^{r,v} \rho_{i}^{r} \overrightarrow{g} + \overrightarrow{e}_{i}^{r,v} \left( \overrightarrow{k}_{D} \overrightarrow{v}_{f} + \frac{\mu_{i}^{r} \left( \nabla \overrightarrow{v}_{f}^{r} + \left( \nabla \overrightarrow{v}_{f}^{r} \right)^{T} \right)}{2} \right) \right] + \overrightarrow{e}_{i}^{r,v} \left( \overrightarrow{k}_{s} \overrightarrow{v}_{f}^{s} + \frac{\mu_{i}^{s} \left( \nabla \overrightarrow{v}_{f}^{s} + \left( \nabla \overrightarrow{v}_{f}^{s} \right)^{T} \right)}{2} \right)
\]  

(81)
The process is steady-state and the gravity term is neglected in horizontal tube. The bed friction in porous reactor plays the main role in pressure drop of the bed. Also, the gas phase velocity is normally not very large. Because of these factors the momentum equation can be reduced to the following form;

\[
\vec{V} \rho_f \vec{V}_f = -K_D \vec{V}_f - K_v \vec{V}_f^2 - \vec{V} p_f = -150 \frac{(1 - e_{f,y}^r)^2}{(e_{f,y}^r)^3 d_p^2} - \mu_f 1.75 \frac{(1 - e_{f,y}^r)}{(e_{f,y}^r)^3 d_p} \rho_f \vec{V}_f \vec{V}_f
\]  

(82)

where \( K_D \) and \( K_v \) are constants for the viscous and kinetic pressure drop.

For the reactor domain’s fluid phase, the RTT derived energy balance is shown in Eq. (83).

\[
\begin{align*}
\begin{cases}
q_{f,\rightarrow s} + \vec{V} (e_{f,A}^r \vec{V} T_f^r) \\
- \sum_{i=1}^{n} \left[ \frac{1}{M_i} \tilde{C}_{p,i} (e_{f,A}^r n_{f,i}) \right] \\
- \sum_{i=1}^{n} \left[ \frac{1}{M_i} \tilde{h}_{f,i} \vec{V} (e_{f,A}^r n_{f,i}) \right]
\end{cases}
&= \begin{cases}
\varepsilon_{f,y}^r \left( \sum_{i=1}^{n} \frac{1}{M_i} \rho_f^r C_{v,i}^r \right) \frac{\partial T_f^r}{\partial t} \\
- \frac{\partial}{\partial t} (e_{f,y}^r p_f^r) \\
+ \varepsilon_{f,A}^r \left( \sum_{i=1}^{n} \frac{1}{M_i} \rho_f^r C_{p,i}^r \right) \vec{V}_f \vec{V} T_f^r
\end{cases}
\end{align*}
\]

(83)

In this work, the energy exchanged between the fluid, and solid phases is composed of five “heat” terms, Eq. (84): the enthalpy carried by the species’ mass flux between the reactor and the catalyst-pellet domains, Eq. (85); the convective heat flux exchanged between the fluid in the reactor and the catalyst-pellet solid phase, Eq.(86); the enthalpy carried by the species’ mass flux between the reactor and the adsorbent-pellet domains, Eq. (87); the convective heat flux exchanged between the fluid in the reactor and the adsorbent-pellet solid phase, Eq.(88); a source term \( q_{f,\rightarrow s} \) that accounts for any external heat flux crossing the considered reactor control surface \( CS^r \) for one dimensional models, Eq. (89);

\[
q_{f,\rightarrow s} = q_{f,\rightarrow s,1} + q_{f,\rightarrow s,2} + q_{f,\rightarrow s,3} + q_{f,\rightarrow s,4} + q_{f,\rightarrow s,5}
\]  

(84)

\[
q_{f,\rightarrow s,1} = \sum_{i=1}^{n} \left[ \frac{A^c}{\varepsilon_{f,y}^r V^r} \left( \frac{1}{M_i} \tilde{h}_{f,i} e_{f,A}^r N_i^r \right) \right]_{CS^r}
\]  

(85)
\[ q'_{c,2} = \varepsilon'_{c,2,Y} \left( \frac{A'}{\varepsilon'_{c,Y} V^c} \right) \left[ \varepsilon'_{r,A} h^r \left( T'_f - T'' \right) \right]^{CSr} \]  
\[ (86) \]

\[ q'_{c,1} = \varepsilon'_{c,1,Y} \left( \frac{A^r}{\varepsilon'_{c,Y} V^r} \right) \sum_{j=1}^{v} \left[ \frac{1}{M'_j} \bar{h}'_{j,A} \varepsilon'_{j,A} N'_i^{CSr} \right] \]  
\[ \left[ 1 \right] \]  
\[ (87) \]

\[ q'_{a,2} = \varepsilon'_{a,2,Y} \left( \frac{A^a}{\varepsilon'_{a,Y} V^a} \right) \left[ \varepsilon'_{a,A} h^a \left( T'_f - T'' \right) \right]^{CSr} \]  
\[ (88) \]

\[ q'_{a} = \begin{cases} \frac{A'U'}{V^r} \left( T'_f - T'' \right) & \text{if 1D} \\ 0 & \text{if 2D or 3D} \end{cases} \]  
\[ (89) \]

For the reactor domain, the molar-based conservation equations are presented in Table 10, coupled with the set of boundary conditions which presented in Table 11.

**Table 10. Molar-based AR-scale model equations.**

<table>
<thead>
<tr>
<th>Bulk Gas Constitutive laws</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Continuity Equation:</strong></td>
</tr>
<tr>
<td>Reactor-Fluid:</td>
</tr>
</tbody>
</table>
| \[ \sum_{i=1}^{v} \varepsilon'_{i,Y} A_i^r \left[ \left( \varepsilon'_{r,A} N'_i^{CSr} \right) \right]\] + \[ \sum_{i=1}^{v} \varepsilon'_{i,Y} A_i^a \left[ \left( \varepsilon'_{a,A} N'_i^{CSa} \right) \right]\] = \[ \frac{d}{dt} \left( \varepsilon'_{r,A} c'_r \right) + \frac{d}{dz} \left( \varepsilon'_{r,A} c'_r v'_r \right) \]  
\[ (90) \]  

| Component mass conservation: |
| Reactor-Fluid: |
| \[ \left[ \varepsilon'_{a,Y} A_i^a \right] \left[ \left( \varepsilon'_{a,A} N'_i^{CSa} \right) \right] \] + \[ \varepsilon'_{a,Y} A_i^a \left[ \left( \varepsilon'_{a,A} N'_i^{CSa} \right) \right] \] = \[ \frac{d}{dt} \left( \varepsilon'_{a,Y} x'_r, c'_r \right) + \frac{d}{dz} \left[ \varepsilon'_{a,Y} \left( x'_r, c'_r v'_r + n'_r, A \right) \right] \]  
\[ (91) \]  

| Momentum conservation: |
| \[ \frac{dP'_f}{dz} = -150 \mu'_f \left( 1 - \varepsilon'_{f,Y} \right)^2 \left( 1 - \varepsilon'_{f,Y} \right) -1.75 \left( 1 - \varepsilon'_{f,Y} \right) - \rho'_f v'_f v'_f \]  
\[ (92) \]  

| Energy conservation: |
Table 11. Initial and boundary conditions for reactor-scale model equations.

**Initial Conditions:**

\[
\begin{align*}
    w_{f,i}^* &= (w_{f,i}^*)_w \\
    w_{f,n,0}^* &= w_{f,N,0}^* = 0.5, \\
    T_{f}^* &= (T_{f}^*)_w, \\
    p_{f}^* &= (p_{f}^*)_w \\
\end{align*}
\]

for \( t = 0, \ \forall z \) (94)

**Boundary Conditions:**

\[
\begin{align*}
    \bar{v}_{f}^* &= (\bar{v}_{f}^*)_in \\
    p_{f}^* &= (p_{f}^*)_in \\
    -\varepsilon_{f,v} D_n \bar{w}_{f,i}^* &= - \left( (w_{f,i}^*)_in - w_{f,i}^* \right) \\
    -\lambda^* \bar{v}_{f}^* &= -\varepsilon_{f,k} \bar{p}_{f}^* \left( \sum_{i} c_{f,i} C_{f,i} \right) \left( \bar{v}_{f}^* \right)_in \left( T_{f}^* - T_{f}^* \right) \\
\end{align*}
\]

\[\bar{v}_{f}^* = 0, \ \bar{p}_{f}^* = 0 \] for \( z = 0, \ \bar{v}_{f}^* = 0 \) for \( z = L \) (95)

3.4.4. Adsorptive Separation

Taking away the reactivity of the adsorptive reactor creates adsorptive separation (AS) system. All the relations (related the AR) is valid for AS without having reactive feature of the equations.
3.5. General Equations

At moderate pressures, the regular diffusion, effective diffusion coefficients \(D_{ij}^{\text{eff}}\) \(i=1,N;\ j=1,N; j \neq i\) employed in the above equations, are estimated using the binary regular diffusion coefficients predicted by Chapman-Enskog theory [73-74], combined with a correction factor accounting for the length and tortuosity of the diffusion path. The equations to estimate the binary diffusion coefficient for polar and non-polar gas mixtures are based on Poling, Praunitz and O’Connell’s [75]. For ideal gas mixtures, Stefan-Maxwell diffusivities and the binary diffusivities are almost identical [34]. The employed equations are shown in Table 12 and 13:

**Table 12. Binary diffusion coefficient estimation.**

<table>
<thead>
<tr>
<th>Binary mixture of non-polar gases (i) and (j) [75]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Binary diffusion coefficient:</strong> (D_{ij} = \left( \frac{0.00266}{p \sigma_i^2 \sigma_j^2} \right) \sqrt{\frac{T_i}{M_{ij}}} )</td>
</tr>
<tr>
<td><strong>Effective Binary diffusion coefficient:</strong> (D_{ij}^{\text{eff}} = \left( \frac{\epsilon_{ij}}{\epsilon} \right) D_{ij} )</td>
</tr>
<tr>
<td><strong>Reduced molecular mass:</strong> (M_{ij} = 2 \left[ \frac{1}{M_i} + \frac{1}{M_j} \right]^{-1} )</td>
</tr>
<tr>
<td><strong>Lennard-Jones dimension:</strong> (\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} )</td>
</tr>
<tr>
<td><strong>Collision integral:</strong> (\Omega_{ij} = \left{ \begin{array}{l} \frac{1.06036}{(T_i^<em>)^{0.1561}} + \frac{0.193}{\exp\left(0.47635T_i^</em>\right)} \ + \frac{1.03587}{\exp\left(1.52996T_i^<em>\right)} + \frac{1.76474}{\exp\left(3.89411T_i^</em>\right)} \end{array} \right} )</td>
</tr>
<tr>
<td><strong>Reduced temperature:</strong> (T_i^* = \frac{k_i T}{\hat{\epsilon}_{ij}} )</td>
</tr>
<tr>
<td><strong>Lennard-Jones energy:</strong> (\hat{\epsilon}_{ij} = \left( \hat{\epsilon}_i \hat{\epsilon}_j \right)^{1/2} )</td>
</tr>
</tbody>
</table>
Table 13. Binary diffusion coefficient estimation.

<table>
<thead>
<tr>
<th>Binary mixture of polar gases $i$ and $j$ [75]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Binary diffusion coefficient:</strong> $D_{ij}^{\text{polar}} = \frac{0.00266}{p(\sigma_{ij}^{\text{polar}})^2 \Omega_{ij}^{\text{D,polar}} \sqrt{T^3}}$</td>
</tr>
<tr>
<td><strong>Effective Binary diffusion coefficient:</strong> $D_{ij}^{\text{eff}} = \left( \frac{\rho_i}{\tau} \right) D_{ij}$</td>
</tr>
<tr>
<td><strong>Lennard-Jones dimension:</strong> $\sigma_{ij}^{\text{polar}} = \left( \sigma_{ij}^{\text{polar}} \sigma_{ij}^{\text{polar}} \right)^{1/2}$</td>
</tr>
<tr>
<td>$\sigma_k^{\text{polar}} = \left( \frac{1.585V_k^b}{1+1.3(\delta_k^{\text{polar}})^2} \right)^{1/3}$ ; $k = i, j$</td>
</tr>
<tr>
<td><strong>Collision integral:</strong> $\Omega_{ij}^{\text{polar}} = \Omega_{ij}^{\text{D}} + \frac{0.19(\delta_{ij}^<em>)^2}{T_{ij}^</em>}$</td>
</tr>
<tr>
<td><strong>Stockmayer potential:</strong> $\delta_{ij}^* = \left( \delta_{ij}^{\text{polar}} \delta_{ij}^{\text{polar}} \right)^{1/2}$</td>
</tr>
<tr>
<td>$\delta_k^{\text{polar}} = \frac{1.94 \times 10^3 (\tilde{\mu}_k)^2}{V_k^b T_k^b}$ ; $k = i, j$</td>
</tr>
<tr>
<td><strong>Reduced temperature:</strong> $T_{ij}^* = \frac{k_B T}{E_{ij}^{\text{polar}}}$</td>
</tr>
<tr>
<td><strong>Lennard-Jones energy:</strong> $\tilde{\varepsilon}<em>{ij}^{\text{polar}} = \left( \frac{\tilde{\varepsilon}</em>{ij}^{\text{polar}}}{\tilde{\varepsilon}<em>{ij}^{\text{polar}}} \frac{\tilde{\varepsilon}</em>{ij}^{\text{polar}}}{\tilde{\varepsilon}_{ij}^{\text{polar}}} \right)^{1/2}$</td>
</tr>
<tr>
<td>$\frac{\tilde{\varepsilon}_k^{\text{polar}}}{k_B} = 1.18 \left[ 1 + 1.3(\delta_k^{\text{polar}})^2 \right] T_k^b$ ; $k = i, j$</td>
</tr>
</tbody>
</table>

In the equations presented in Tables 12 and 13, pressure has units of the bar, temperatures are in K, and the resulting binary diffusivities have units of cm2/s.

The constitutive laws and other model equations can be found in Table 14 and 15.
Table 14. General model equations.

Partial pressure of species $i$:  
\[ p_i^p = c_i^p \hat{R}T \]  
(113)

Dalton’s law:  
\[ p^p = \sum_{i=1}^{u} p_i^p \]  
(114)

Total molar concentration:  
\[ c_f^\alpha = \sum_{i=1}^{u} c_{f,i}^\alpha \]  
(115)

Total mass concentration:  
\[ \rho_f^\alpha = \sum_{i=1}^{u} \rho_{f,i}^\alpha \]  
(116)

Molar fraction of species $i$:  
\[ x_{f,i}^\alpha = \frac{c_{f,i}^\alpha}{c_f^\alpha} \]  
(117)

Mass fraction of species $i$:  
\[ w_{f,i}^\alpha = \frac{\rho_{f,i}^\alpha}{\rho_f^\alpha} = \frac{x_{f,i}^\alpha M_i}{M_n} \]  
(118)

Combined mass flux of species $i$:  
\[ \overline{N}_{f,i}^\alpha = \overline{n}_{f,i}^\alpha + \rho_{f,i}^\alpha \overline{v}_f^\alpha \]  
(119)

Combined molar flux of species $i$:  
\[ \overline{J}_{f,i}^p = \overline{j}_{f,i}^p + \rho_{f,i}^p \overline{v}_f^p \]  
(120)

Effective binary diffusion coefficient:  
\[ D_{ij}^{\text{eff}} = e_{f,A}^\alpha D_{ij} \]  
(121)

Knudsen diffusion coefficient$^8,34$:  
\[ D_{jk} = e_{f,A}^p \left( \frac{2 d_{\text{pore}}^p}{3} \right) \sqrt{\frac{\hat{R}T}{2\pi M_i}} \]  
(122)

Knudsen diffusion coefficient$^{28}$:  
\[ B_0 = e_{f,A}^p \left[ \left( \frac{d_{\text{pore}}^p}{32} \right) \right] \]  
(123)

Tortuosity:  
\[ \tau = \frac{e_{f,X}^p}{e_{f,A}^p} \]  
(124)
Volumetric fraction (two-phase system):
\[ \varepsilon_{f,V} + \varepsilon_{p-s,V} + \varepsilon_{q-s,V} = 1 \] (125)

Surface fraction (two-phase system):
\[ \varepsilon_{f,V} + \varepsilon_{c-s,V} + \varepsilon_{q-s,V} = 1 \] (126)

The interphase heat-transfer and mass transfer coefficients are calculated using the correlations [43]:
\[ Nu = 2 + 1.1Pr^{1/3}Re^{0.6} \] (127)
\[ Sh = 2 + 1.1Sc^{1/3}Re^{0.6} \] (128)

Table 15. General model equations-2.

Dimensionless Groups:
\[ Nu = \frac{\frac{hd}{\lambda_f}}{\lambda_f}, \quad Re = \frac{\frac{\nu_f}{\rho_f}d_f}{\mu_f}, \quad Pr = \frac{C_{p,f}\mu_f}{\lambda_f} \] (129)

The viscosity of Gas Mixture:
\[ \mu_f = \sum_{i=1}^{r} x_{f,i} \mu_{f,i}^0(T), \quad \phi_{ij} = \frac{\left[1 + \left(\frac{\mu_{f,i}^0(T)}{\mu_{f,j}^0(T)}\right)^{1/2} \left(M_i/M_j\right)^{1/4}\right]^2}{8\left(1 + \left(M_i/M_j\right)^{1/2}\right)^{1/2}} \] [76] (130)

Thermal Conductivity:
\[ \lambda_f^p = \varepsilon_{f,V}^p \lambda_f^p + \varepsilon_{f,s}^p \lambda_f^p \] (131)
\[ \lambda_f^c = \lambda_f + \varepsilon_{f,V}^c \lambda_{f,eff}, \quad \lambda_c = \varepsilon_{p-s}^c \lambda_{p-s} + \varepsilon_{c-s}^c \lambda_{c-s} \] (132)

Thermal Conductivity of Pure Gases:
\[ \lambda_{f,i}^c = A_i + B_i T + C_i T^2 + D_i T^3 \] [77] (133)

Thermal Conductivity of Gas Mixture:
\[ \lambda_f^c = \sum_{i=1}^{r} x_{f,i} \lambda_{f,i}^c(T), \quad \phi_{ij} = \frac{\left[1 + \left(\frac{\mu_{f,i}^0(T)}{\mu_{f,j}^0(T)}\right)^{1/2} \left(M_i/M_j\right)^{1/4}\right]^2}{8\left(1 + \left(M_i/M_j\right)^{1/2}\right)^{1/2}} \] [76] (134)

The effective axial conductivity:
\[
\frac{\lambda_{f,\text{eff}}}{\lambda_f} = \frac{\lambda_0}{\lambda_f} + 0.75(Pr)(Re), \quad \frac{\lambda_0}{\lambda_f} = \epsilon_{f,V} + \frac{1 - \epsilon_{f,V}}{0.139 \epsilon_{f,V} - 0.0339 + \frac{2}{3} \left( \frac{\lambda_f}{\lambda_f} \right)} \tag{43}
\]

Specific Heat Capacity of Pure Gases:

\[
C^a_{p,j} = a_{0,j} + a_{1,j} t + a_{2,j} t^2 + a_{3,j} t^3 + a_{4,j} t^4, \quad t = \left( \frac{T}{1000} \right) \tag{78}
\]

Specific Heat Capacity of Gas Mixture:

\[
C^a_{p,f} = \sum_{i=1}^{1} \chi_{f,i}^a M_i C^a_{p,i} \tag{76}
\]

Standard Enthalpy of Gases:

\[
\tilde{h}_{f,i}^a = \tilde{\Phi}_{i}^a + a_{0,i} t + a_{1,i} \frac{t^2}{2} + a_{2,i} \frac{t^3}{3} + a_{3,i} \frac{t^4}{4} - \frac{a_{4,i}}{4} \quad t = \left( \frac{T}{1000} \right) \tag{78}
\]

### Table 16. Properties dependence.

<table>
<thead>
<tr>
<th>Property description</th>
<th>Dependence in the simulation</th>
<th>Pellet</th>
<th>Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid phase viscosity</td>
<td>( \mu_f^a = \mu_f^a \left( T^p, { c_i^p } \right) )</td>
<td>( \mu_f^a = \mu_f^{p'} \left( T', { c_i^{p'} } \right) )</td>
<td></td>
</tr>
<tr>
<td>Fluid phase conductivity</td>
<td>( \lambda_f^a = \lambda_f^a \left( T^p \right) )</td>
<td>( \lambda_f^a = \lambda_f^{p'} \left( T', p', { c_i^{p'} } \right) )</td>
<td></td>
</tr>
<tr>
<td>Binary diffusion coefficients</td>
<td>( D_0^p = D_0^p \left( T^p, p^p \right) )</td>
<td>( D_0^p = D_0^{p'} \left( T', p' \right) )</td>
<td></td>
</tr>
<tr>
<td>Knudsen diffusivities</td>
<td>( D_{\text{K}} = D_{\text{K}} \left( T^p \right) )</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Species ( i ) heat capacity</td>
<td>( C^a_{p,i} = C^a_{p,i} \left( T^p \right) )</td>
<td>( C^a_{p,i} = C^a_{p,i} \left( T^p \right) )</td>
<td></td>
</tr>
<tr>
<td>Species ( i ) molar enthalpy</td>
<td>( \tilde{h}<em>{f,i}^a = \tilde{h}</em>{f,i}^a \left( T^p \right) )</td>
<td>( \tilde{h}<em>{f,i}^a = \tilde{h}</em>{f,i}^{p'} \left( T' \right) )</td>
<td></td>
</tr>
</tbody>
</table>

### 3.6. Catalyst/Adsorbent Effectiveness Factor Definitions and Quantification

In this study we calculate, through the employed multiscale model temporal effectiveness factors both for the catalyst as well as the adsorbent pellet. The temporal effectiveness factor for the \( i \)th species is defined by Eq. (139), the superscript \( \zeta \) refers either catalyst or adsorbent pellet.
\[ \eta^c_i = \frac{\left( \sum_{j \in S} e_j^c N_j^c \right) \cdot \overline{\mu} dA'}{\sum_{i \in CV} M_i e_i^c \rho_{i,a} \bar{R}_i^c dV} \]

Similarly, the length-averaged effectiveness factor is given by Eq. (140):

\[ \eta^{\text{ave}}_i(z) = \frac{\int_0^z \left( \frac{A_i^c e_i^c}{V e_i^c} \right) \left( \sum_{j \in S} e_j^c N_j^c \right) \cdot \overline{\mu} dA'\right) (z) dz}{\int_0^z \left( \frac{A_i^c e_i^c}{V e_i^c} \right) \left( \sum_{i \in CV} M_i e_i^c \rho_{i,a} \bar{R}_i^c \right) (z) dz} \]

This allows one to quantify the impact of the various transport and sorption/reaction processes, and also enables the assessment of behavioral and quantitative changes during the transition from lab-scale to industrial-scale pellet sizes. The catalyst or adsorbent effectiveness factor for species i is defined as the ratio of that species’ mass flow rate entering the pellet’s surface, over the calculated mass generation/consumption rate for the same species in the absence of transport limitations at the prevailing conditions at the pellet’s surface. For the catalyst pellet, the effectiveness factors of all species are equal, since there is only one reaction (WGSR) taking place in the pellet with equal stoichiometric coefficients for all species. For the adsorbent pellet, there is only effectiveness factor for CO₂ as it is the only adsorbed species. The dynamic nature of the AR process suggests that the net species mass flow at the pellet’s surface accommodates not only the reaction occurring in the catalyst pellet (or the adsorption occurring in the adsorbent pellet), but also helps meet the same species’ accumulation needs within the pellet’s pores. This suggests that early in the AR’s operation, when the accumulation needs are the largest, the values of the temporal effectiveness factor may be greater than one.
Chapter 4. Intensification of Steady-State Processes for WGSR based Hydrogen Production via Multi-scale Modeling and Simulation

4.1. Introduction

In the flow of this chapter, the rigorous Dusty Gas, the rigorous Maxwell–Stefan and Wilke models are used to describe diffusion fluxes in the reactor and the pellet scales. In most of the studies in the literature, it is recognized that the simplification on the application of the Dusty Gas Model (DGM), and assumptions of uniform temperature and pressure gradients throughout the spherical pellet. However, we have calculated the temperature and the pressure gradients along the spherical pellet to validate the assumptions above, and the Dusty Gas Model is rigorously applied in the pellet model equations solution. Then, numerical studies is applied on the WGSR’s systems for the production of hydrogen. The multi-scale model results give a practical insight into the WGSRs systems from the viewpoint of industrial operation for hydrogen generation and provides a detailed numerical insight into the transport phenomena with multiscale studies in porous media (pellet and reactor scales) on each system. For the concept of micro design, the effect of some design parameters (mean pore diameter, volumetric porosity, tortuosity factor etc.) and various species’ flux models (Maxwell-Stefan model, dusty gas model and Wilke model) on process performance is studied. Especially, variation on the catalysts’ effectiveness factors (high temperature shift/low temperature shift catalysts) are demonstrated along the reactor length for the various aforomentioned design parameters and flux models.

In the second section, the multi-scale model is used in simulating the MR’s effectiveness in transforming coal-derived syngas into a H₂-rich stream and a CO₂-rich stream, thus intensifying the WGSR. Model predictions are generated for a broad range of operating conditions (e.g., reactor temperature, inlet gas composition, feed pressure, and inlet gas flow
rate) and design parameters (e.g., weight of catalyst, gas permeance, and membrane area), thus enabling a comparative performance assessment of the MR versus a conventional PBR for the proposed IGCC application.

In the third section of this chapter, macro process design and intensification studies are carried out on various hydrogen production processes. The applicability of various (alternative to the conventional high temperature shift reactor-HTSR/low temperature shift reactor-LTSR in series) novel and efficient reactor configurations that include the combination of the steady-state MR-HTSR-LTSR-MS systems (herein after referred to as the (proposed HTSR/MS/LTSR/MS and LTMRs) systems) are investigated.

4.2. Conventional Hydrogen Production via High-temperature and Low-temperature Water-Gas Shift Reactors’ system

In industry, water gas shift reactors consist of two different temperature stages, the high-temperature shift reactor (HTSR) and the low-temperature shift reactor (LTSR) with a cooling process between them is a recommended for the operation of hydrogen generation. The high-temperature water gas shift reactor (HTSR) is carried out between the ranges of 300 °C – 450 °C. On the other hand, the low-temperature water gas shift reactor (LTSR) is performed between the ranges of 200 °C – 300 °C. Depending on the reaction temperature, specific catalysts are used for each reactor types. Typically, Cu–ZnO–Al2O3 based catalysts and Fe3O4 –Cr2O3–CuO based catalysts are used for LTSR and HTSR in industry, respectively. In the HTSR, a fast CO consumption is favored and then, the gas stream passes through an inter-stage cooling system. LTSR stage follows the cooling system, where is favored the approach to equilibrium conversions. This system (HTSR + Cooling +LTSR) enables to reach higher CO conversions and
desired level of hydrogen production. Thus, most of the CO is consumed in the HTSR, and rest of the CO content is converted LTSR.

The kinetics of the WGS reaction has gained growing interest in recently. There are various studies in the literature reported different rate expressions and mechanisms of the WGSR (Langmuir-Hinshelwood, Redox and empirical – Power-law). When we consider all these, empirical-power-law rate expression is preferred by most of the researchers [24], [79]. While a commercial Co-Mo/Al₂O₃ is selected catalyst type for LTSR, commercial Fe₂O₃-Cr₂O₃ catalyst is used for HTSR in this study. The parameters of the empirical model are obtained based on the experimental results, and the reaction rate can be described by Arrhenius Law to ensure a prediction the rate of reaction computationally. Table 17 represents empirical power-law rate expression with Arrhenius Law, and reaction and equilibrium equations.

\[ r_j = k_0 \exp \left( -\frac{E_a}{RT} \right) \frac{P_{CO}^{m} P_{H_2O}^{n} P_{CO_2}^{q} P_{H_2}^{q}}{1 - \frac{P_{CO} \cdot P_{H_2}}{K_{eq} \cdot P_{CO_2} \cdot P_{H_2O}}} \] (141)

\[ r_j = k_0 \exp \left( -\frac{E_a}{RT} \right) c_{CO}^{m} c_{H_2O}^{n} c_{CO_2}^{q} c_{H_2}^{q} \left( 1 - \frac{1}{K_{eq}} \cdot \frac{c_{CO} \cdot c_{H_2}}{c_{CO_2} \cdot c_{H_2O}} \right) \] (142)

\[ K_{eq} = \exp \left( \frac{4577.8}{T} - 4.33 \right) \] (143)

All reported simulations were carried out with a syngas composition of \((H_2/CO/H_2O/CO_2/CH_4/H_2S) = (2.7637/1.00/a/2.1528/0.8/0.05)\), where \(1 < a < 5\), which is a typical composition of a coal/oxygen-blown gasifier off-gas. We applied the aforementioned empirical power law rate expressions for the WGSR in the packed-bed reactor simulations using a commercial Co/Mo/Al₂O₃ and Fe₂O₃-Cr₂O₃ catalysts’ physical properties and characteristics.
Table 18 and 19 shows the parameters used in the solution of the catalyst pellet and reactor scales’ model equations. Thermal conductivity of the spherical pellet and the gas mixture, specific heat capacity of the gas mixture and standard enthalpies of the gases varies with temperature.

### Table 18. Parameters Used in Simulation (LTSR).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of catalyst</td>
<td>592.68</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>Pellet void fraction</td>
<td>0.2-0.7</td>
<td>-</td>
</tr>
<tr>
<td>Pellet radius</td>
<td>0.004</td>
<td>m</td>
</tr>
<tr>
<td>Surface area of catalyst</td>
<td>160-220*10$^3$</td>
<td>m$^2$/g</td>
</tr>
<tr>
<td>Pore volume of catalyst</td>
<td>0.55-0.65*10$^{-6}$</td>
<td>m$^3$/g</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>1.4285-5</td>
<td>-</td>
</tr>
<tr>
<td>Mean pore diameter</td>
<td>6.3*10$^{-7}$-10$^{-9}$</td>
<td>m</td>
</tr>
<tr>
<td>Inlet pressure</td>
<td>10-30</td>
<td>bar</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>493-573</td>
<td>K</td>
</tr>
<tr>
<td>Reactor length</td>
<td>7</td>
<td>m</td>
</tr>
<tr>
<td>Chemical model parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$l$</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>$m$</td>
<td>0.29</td>
<td>-</td>
</tr>
<tr>
<td>$n$</td>
<td>-0.07</td>
<td>-</td>
</tr>
<tr>
<td>$q$</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>$k_0$</td>
<td>6.3</td>
<td>mol/atm$^{l+m+n+q}$h/g</td>
</tr>
<tr>
<td>$E_a$</td>
<td>5.9</td>
<td>kcal/mol</td>
</tr>
</tbody>
</table>

### Table 19. Parameters Used in Simulation (HTSR).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of catalyst</td>
<td>1008</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>Pellet void fraction</td>
<td>0.2-0.7</td>
<td>-</td>
</tr>
<tr>
<td>Pellet radius</td>
<td>0.004</td>
<td>m</td>
</tr>
<tr>
<td>Surface area of catalyst</td>
<td>61*10$^3$</td>
<td>m$^2$/g</td>
</tr>
<tr>
<td>Pore volume of catalyst</td>
<td>0.35*10$^{-6}$</td>
<td>m$^3$/g</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>1.4285-5</td>
<td>-</td>
</tr>
<tr>
<td>Mean pore diameter</td>
<td>6.3*10$^{-7}$-10$^{-9}$</td>
<td>m</td>
</tr>
<tr>
<td>Inlet pressure</td>
<td>10-40</td>
<td>bar</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>573-673</td>
<td>K</td>
</tr>
<tr>
<td>Reactor length</td>
<td>7</td>
<td>m</td>
</tr>
<tr>
<td>Chemical model parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$l$</td>
<td>0.74</td>
<td>-</td>
</tr>
<tr>
<td>$m$</td>
<td>0.47</td>
<td>-</td>
</tr>
</tbody>
</table>
The local influence of three design parameters (volumetric porosity, tortuosity, and mean pore diameter) of the catalytic pellet were investigated in definition of the molecular fluxes by the rigorous Maxwell-Stefan model (MSM) and dusty gas model (DGM), and the simpler Wilke model. Given the complexity of a real porous structure, which contains networks of pores with very different diameters and layouts, those parameters are usually average values from experimental data such as the media’s pore size distribution. The effect of the design parameters on reaction rate can be seen in Figures 21-24 for high temperature shift catalyst and low temperature shift catalyst. As expected, the reaction rate is proportional to mean pore diameter and pellet’s volumetric porosity increase for both high temperature and low temperature catalysts. The local influence of the design parameters on the low temperature catalyst is more apparent compared to high temperature catalyst. The effective Knudsen and bulk diffusivities decrease by increase of tortuosity factor and dropping of pellet void fraction. DGM-based simulations include both the effect of Knudsen and bulk diffusivities, and this influence can clearly be seen in Figures 21-22. The effective Knudsen diffusion in DGM is proportional to the pore size and independent of process pressure. Thus, it is expected to obtain influence on DGM-based simulation results by varying pore diameter. This influence is shown in Figures 23-24 since the overall process results changes by varying the mean pore diameter. On the other hand, the effective bulk diffusivities are independent of pore size and inversely propositional to pressure, so both MSM and WM don’t include Knudsen diffusion. Therefore, the simulation results shouldn’t have affected by varying pore size in MSM and WM-based simulations, and

<table>
<thead>
<tr>
<th>n</th>
<th>-0.18</th>
<th>-</th>
</tr>
</thead>
<tbody>
<tr>
<td>q</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>k₀</td>
<td>2623.4 (m²/mol)⁻¹.s⁻¹</td>
<td></td>
</tr>
<tr>
<td>Eₐ</td>
<td>80 kJ/mol</td>
<td></td>
</tr>
</tbody>
</table>
Figure 23-24 represent this concept for both flux models. The prediction of the MSM and WM are very close each other. However, there are significant deviations between the DGM and MSM-WM couple (Figures 21-22). As a result, it is possible to propose that the process is influenced by Knudsen diffusion, and the DGM model is therefore preferable to the SMS and WM for both HT and LT catalysts’ modeling.

**Figure 21. Reaction rate along the pellet radius for various design parameters and flux models.**

HTS-catalyst mean pore diameter: 12.6 nm.

**Figure 22. Reaction rate along the pellet radius for various design parameters and flux models.**

LTS-catalyst mean pore diameter: 12.6 nm.
Figure 23. Figure 4: Reaction rate along the pellet radius for various design parameters and flux models. HTS-catalyst, void fraction=0.35, tortuosity factor=2.857.

Figure 24. Reaction rate along the pellet radius for various design parameters and flux models. LTS-catalyst, void fraction=0.35, tortuosity factor=2.857.

Figure 25. H₂ mole fraction along the reactor length (Left) and pellet radius (Right) for various reactor positions (mean pore diameter: 12.6 nm, void fraction: 0.35).
The influence of different molecular flux models on H\(_2\) mole fraction along the reactor length and pellet radius for both HTSR and LTSR is depicted in Figure 25 and 26. The H\(_2\) profiles through the reactor length and pellet radius is overestimated by WM compared to the DGM and MSM. Then, it is reasonable to reach conclusion the weakness of the WM compared to two rigorous flux models. According the overall reactor results, it seems Knudsen diffusion is more dominant in HT catalyst compared to LT catalyst. Figure 27 shows the mass and mole averaged velocities for the mole based dusty gas model of HT and LT catalysts. In the physical sense, the mass averaged velocity in the mole-based model should be zero across the pellet
surface, so the results in Figure 27 meets this expectation. Based on the averaged mass and molar velocities, it is easy to say that the diffusion fluxes clearly dominate over the convective fluxes. As a result, assumption of the neglecting the convective flux terms in the model’s equations of the pellet is a quite reasonable. In the WGSR, one mole CO and H₂O react to produce one mole CO₂ and H₂. Thus, the sum of the total fluxes must be equal zero through the pellet radius, so Figure 27 again demonstrates this expectation.

**Figure 28. Effectiveness factor axial profiles for various design parameters, VF: void fraction and MPD: mean pore diameter. (HTSR-Up and LTSR-Down)**

Unlike most WGSR literature studies, which assume constant catalyst pellet effectiveness factors, this work employs the DGM to quantify the effectiveness factor for pellets situated along the HTSR and LTSR reactor axes. Given the WGSR stoichiometry, all species’ effectiveness factors are equal. Figure 28 demonstrates that, as expected, at any fixed axial HTS/LTS reactor
location, the effectiveness factor decreases as the pellet void fraction reduces. Figure 28, also, demonstrates that for adiabatic operation the effectiveness factor decreases along both the HTSR and LTSR lengths since the reacting mixture’s temperature increases along the length of both the PBRs, thus accelerating the intrinsic kinetics of the WGSR more than the diffusivities of all species, which in turn increases the effectiveness factor’s denominator more than its numerator. On the other hand, mean pore diameter doesn’t have significant effect on effectiveness factor for both HTSR and LTSR.

In the rest of the simulations, rigorous DGM is used as molecular flux model in pellet scale while MSM is applied in reactor scale. The integrated gasification combined cycle (IGCC) generates electricity from a solid or liquid fuel. IGCC power plants have similar technology as modern gas fired power plants. IGCC power plants are widely considered being a promising and clean power generation technology. Initial step in IGCC is converting the fuel to syngas which is a mixture of hydrogen and carbon monoxide. Hydrogen production from syngas can be enhanced by the exothermic shift reaction. In the conventional method, WGS catalysts operated sequentially in two stages at two different temperature levels in the presence of \( \text{H}_2\text{S} \) followed by separation of the \( \text{CO}_2 \) from the hydrogen. As final stage, electricity is generated in a combined cycle power block consisting of a gas turbine process and a steam turbine process which includes a heat recovery steam generator. The CO conversion evaluation along the combined reactor’s length for the combined HTSR and LTSR system can be seen in Figure 29 for various operating conditions. The CO conversion is reached the level of 95% if the reaction temperature of the HTSR is kept at 593 K and \( \text{H}_2\text{O}/\text{CO} \) ratio of 5, and LTSR temperature is 493 K. The aforementioned operating conditions and 95% conversion is defined as base case scenario for the
HTSR/LTSR system. Operating both HTSR and LTSR at higher pressure and H$_2$O/CO ratios promote to reach complete or higher-level conversions.

The resulting HTSR’s exit for the cases (1), (2), (3) and (4) is fed into the LTSR for each set of simulation conditions 493 K, 523 K and 573 K.

Figure 30 shows the temperature profiles’ evaluations along the combined reactor’s length for the combined HTSR and LTSR system. In our multi-scale model, we calculated the temperature profiles of catalyst-pellet and bulk gas phase in the PBR. Minimum and maximum temperature differences, between the bulk gas phase and catalyst pellet, along the reactor length for the adiabatic reactor simulations can be expressed as 2-0.02 K (WM), 1.55-0.035 K (MSM), 1.2-0.05 K (DGM) for HTSR, and 2.8-0.3 K (WM), 2.7-0.25 K (MSM), 2.1-0.5 K (DGM) for LTSR.
Various local design parameters and species’ flux models (Maxwell-Stefan, Wilke, Dusty Gas) are applied on multi-scale reactive-separator mathematical models to predict the performance of steady-state hydrogen production systems. The following results are obtained along the simulations: (1) for various design parameters (mean pore diameter, volumetric porosity, and tortuosity factor), the prediction of the MSM and WM are very close each other in both HT and LT catalysts. However, the significant deviation is observed in transition from MSM-WM to DGM. These results suggest that Knudsen diffusion has significant impact on pellet-scale performance, and it is recommended to use DGM for pellet scale simulations under the selected parameters, (2) a small but significant differences is obtained in the mole fraction profiles of hydrogen along the reactor axis for various flux model application. WM overestimates H$_2$ mole fraction compared to the DGM (average excess estimations are 2.78 % for LTSR and 2.6 % for HTSR) and MSM (average excess estimations are 1.31 % for LTSR and 1.1 % for HTSR). The simulated results expose the limitations and weakness of the WM compared to two rigorous flux models. (3) Various design parameters have significant impact on the effectiveness factor calculations, and calculated effectiveness factor profiles varies axially.
4.3. Multi-Scale Membrane Reactor (MR) Simulation for the Water Gas Shift Reaction

One promising way to accomplish the process intensification for the WGSR is through the use of membranes in multifunctional reactors, known as membrane reactors (MR), for simultaneous production, separation, and purification of hydrogen from syngas mixtures [25], [80-81]. In such reactors, a H₂-selective membrane is used to enhance the WGSR rate, and to potentially overcome thermodynamic equilibrium conversion limitations by selectively removing hydrogen from the reaction mixture. The use of MR technology for WGSR, potentially, offers unique advantages that include the production of high-purity hydrogen, lower operating temperatures and steam requirements, reduced catalyst costs, increased operation safety, and no need for a further downstream hydrogen purification step [82-84].

Inorganic hydrogen-selective membranes are typically utilized in catalytic MR, because they are capable of functioning at the high temperatures and pressures such reactors operate under. They include both dense (Pd and Pd-alloy) and microporous (silica, zeolite, and carbon molecular sieve) membranes [4], [9]. Pd and Pd-alloy membranes have been studied extensively [6], [25] in MR applications involving H₂ production. Their high selectivity towards hydrogen (infinite, theoretically) results in high CO conversions and high hydrogen purity when they are used in WGSR-MR. Pd membranes are, however, sensitive to impurities (e.g., H₂S) found in the syngas from coal gasification involved in the IGCC technology, which is the subject of the present investigation. Our focus here is on carbon molecular sieve (CMS) membranes, which have attracted attention, in the past, for gas separation applications, and have also found recent use by our team and others in MR for the WGSR, where they have proven stable in the presence
of high-temperature and high-pressure steam and other impurities (e.g., H₂S, NH₃, organic vapors, tars, etc.), and have been shown to deliver high-purity hydrogen [85].

We utilized a commercial Co-Mo/Al₂O₃ shift catalyst that has been shown to exhibit high activity and stability for the low-temperature shift process. The catalyst kinetics were investigated, and a global rate expression was developed, which is shown in Table 20.

**Table 20. Model rate Equations.**

<table>
<thead>
<tr>
<th>Reaction Rate:</th>
<th>[ r_j = k_w \left( \frac{p_{CO} \cdot p_{H₂ₕ}}{p_{H₂}} \cdot \frac{p_{CO₂}}{K_{eq}} \right) ]</th>
<th>(144)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ K_{eq} = \exp \left( \frac{4577.8}{T} - 4.33 \right) ]</td>
<td>(145)</td>
<td></td>
</tr>
</tbody>
</table>

Model simulations were carried out under conditions similar to those employed during the lab-scale MR investigation [28]. Specifically, we studied as a feed a syngas with composition (H₂/CO/CO₂/CH₄) = (2.76/1.00/2.15/0.84), which is typical of coal/oxygen-blown gasifier off-gas and H₂O/CO feed ratios in the range of 1 - 2.50. We investigated feed temperatures in the range of (493.15 - 573.15 K) and feed pressures of (10-25 bar). Table 21 summarizes the parameter values, used in the model’s solution. The key objective of the present paper is to extend the application of the model to larger catalyst particle sizes, ranging in diameter from 0.06 cm - 0.6 cm, to investigate whether there are intraparticle concentration and temperature gradients that one needs to be concerned about. These larger size particles are likely to be utilized in the field-testing of pilot-scale units, and, of course, eventually in commercial systems.

We investigate two different cases here: A case (termed wall-isothermal), in which we assume that the reactor is immersed in an oven whose temperature (equal to the reactor wall temperature as well) is maintained constant, and a second case in which the reactor is operated under adiabatic conditions. For the first case, which is typical of the operation of lab-scale reactors, in
the present simulations (but also in practice) the feed temperature is always set equal to the furnace temperature. Operation under adiabatic conditions, due to its simplicity, is likely to be the preferred mode of operation during pilot-scale and commercial operation.

Table 21. Parameter Values Used in Simulation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of catalyst [28]</td>
<td>592.68 kg/m³</td>
<td></td>
</tr>
<tr>
<td>Pellet void fraction [28]</td>
<td>0.35561</td>
<td>-</td>
</tr>
<tr>
<td>Pellet radius</td>
<td>0.0003-0.005 m</td>
<td></td>
</tr>
<tr>
<td>Surface area of catalyst [28]</td>
<td>160-220*10⁵ m²/g</td>
<td></td>
</tr>
<tr>
<td>Pore volume of catalyst [28]</td>
<td>0.55-0.65*10⁻⁶ m³/g</td>
<td></td>
</tr>
<tr>
<td>Tortuosity</td>
<td>2.8121</td>
<td>-</td>
</tr>
<tr>
<td>Mean pore diameter [28]</td>
<td>6.3*10⁻⁹ m</td>
<td></td>
</tr>
<tr>
<td>Inlet pressure</td>
<td>1-2.5 MPa</td>
<td></td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>493-573 K</td>
<td></td>
</tr>
<tr>
<td>Reactor/membrane diameter ratio</td>
<td>5.579</td>
<td>-</td>
</tr>
<tr>
<td>Number of membranes</td>
<td>1-4</td>
<td></td>
</tr>
<tr>
<td>Reactor length</td>
<td>0.254 m</td>
<td></td>
</tr>
<tr>
<td>Reactor void fraction</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>Overall heat transfer coefficient (U''')</td>
<td>227 W/m²·K</td>
<td></td>
</tr>
<tr>
<td>Heat transfer coefficient (U''')</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Chemical Kinetic rate parameters k_w</td>
<td>1.66*10⁻⁶ mol/(g·s·atm)</td>
<td></td>
</tr>
<tr>
<td>Gas Permeance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>1</td>
<td>m³/m²·hr·bar</td>
</tr>
<tr>
<td>CO</td>
<td>0.0125 m³/m²·hr·bar</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.025 m³/m²·hr·bar</td>
<td></td>
</tr>
<tr>
<td>CH₄</td>
<td>0.00806 m³/m²·hr·bar</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>0.333</td>
<td>m³/m²·hr·bar</td>
</tr>
</tbody>
</table>
4.3.1. Effectiveness factor phenomena

Figure 31. Effectiveness factor axial profiles for various pellet sizes. MR results (Top), PBR Results (Bottom). Wcat/FCO: 70 (g*h/mol) and Wquartz/Wcat: 7. For the MR we use no sweep, and the permeate-side pressure is 1 bar.

Figure 31 plots the effectiveness factor (defined in the conventional way as the ratio of the real reaction rate in a catalyst particle divided by the hypothetical rate that would result if conditions inside the particle were the same as those prevailing at the particle’s surface) for both the MR (top) and the PBR (bottom) along the reactor axis. Figure 31 demonstrates that, as expected, at any fixed axial PBR and MR location, the effectiveness factor decreases as the pellet diameter increases. Figure 31 shows that for the adiabatic operation the effectiveness factor decreases along the length for both the MR and the PBR. The same is true for the wall-
isothermal MR for which the effectiveness factor also decreases along the reactor’s length. For the wall-isothermal PBR, however, the effectiveness factor increases along the reactor’s length. A possible explanation for the behavior observed during adiabatic operation is that the reacting mixture’s temperature increases along the length of both the PBR (see Figure 35) and the MR (see Figure 38), thus accelerating the intrinsic kinetic rates (see Figure 39) of the WGSR more than the diffusivities and the transport rates of all species increase due to these temperature increases, thus resulting in stronger diffusional limitations as one moves down the length of the reactor. On the other hand, in the wall-isothermal operation, the reacting mixture’s temperature barely increases along the length of both the PBR and the MR. Thus, in the PBR, the WGSR reaction rate (see Figure 39) slows down more due to reactant depletion than the species diffusion rate does, resulting in an axially increasing effectiveness factor. On the other hand, in the MR the WGSR reaction rate (see Figure 39) does not slow down as significantly, due to hydrogen depletion from the reaction zone, while the diffusion rate does, again mostly due to hydrogen depletion, thus resulting in an axially decreasing effectiveness factor. Figure 31 also illustrates that the effectiveness factors are lower in the MR than in the PBR and also decrease significantly (by over 20%) in the axial direction for both adiabatic and wall-isothermal operation, thus placing in question the commonly employed constant effectiveness factor assumption.
4. 3. 2. Species’ concentration/temperature profiles, and reaction rate in PBR/MR (pellet and reactor scales)

Figure 32. Axial molar flow rates (wall-isothermal PBR-Left) and pellet species concentration radial profiles at various PBR locations (Right). $W_{\text{cat}}/F_{\text{CO}}: 70$ (g*h/mol) and $W_{\text{quartz}}/W_{\text{cat}}: 7$.

Figure 33. Axial molar flow rates (adiabatic PBR-Left) and pellet species concentration radial profiles at various PBR locations (Right). $W_{\text{cat}}/F_{\text{CO}}: 70$ (g*h/mol) and $W_{\text{quartz}}/W_{\text{cat}}: 7$.

Figures 32 and 33 show the PBR axial species molar flow rates (Left) and the local-pellet radial species concentrations at three different locations in the reactor (Right), for the wall-isothermal and adiabatic cases, respectively. The relatively flat radial species concentration profiles, and the fact that they do not vary by much along the PBR’s length, are consistent with the values of the PBR effectiveness factor (0.9) for the 0.4 cm diameter pellets (see Figure 32).
Figure 34 (left) shows the catalyst-pellet’s surface and bulk gas phase temperature axial profiles along the adiabatic PBR’s length (for these simulations the thermal conductivity is set equal to 1 W/(m*K)). Due to the exothermicity of the WGSR, the temperature of the gas rises by ~35 K from the entrance to the exit of the reactor. The average difference between the catalyst-pellet and gas phase temperatures along the length of the PBR is ~1.1 K, pointing out that the impact of external heat transfer limitations is rather small. Figure 34 (right) shows the catalyst-pellet temperature radial profiles at several axial PBR locations. The temperature gradients are again rather small, with the maximum temperature difference between the pellet’s center and surface occurring always at the PBR inlet and varying from 0.032 K to 2.05 K, as the solid thermal conductivity ranges from 10 W/(m*K) to 0.1 W/(m*K). This range is wide enough to encompass any catalyst solid conductivity values within the considered temperature range, given that the catalyst’s chemical composition is CoO: 3-4 wt%, MoO₃: 13-15 wt% and Al₂O₃: 80-85 wt%, the thermal conductivity of Al₂O₃ (with MgO additive) varies between 6 W/(m*K) to 10 W/(m*K) as the temperature varies between 700 K to 500 K, respectively, [86], and the ratios of MgO/CoO and Co/Mo conductivities are approximately 2.5, [87], and 0.9, [78], respectively.
Figure 35. Axial molar flow rates (isothermal MR Reject Left-up and permeate Left-down) and pellet species concentration radial profiles at various MR locations (Right). No-sweep, permeate side pressure: 1 bar, $W_{\text{cat}}/F_{\text{CO}}$: 70 (g*h/mol) and $W_{\text{quartz}}/W_{\text{cat}}$: 7.
Figures 35 and 36 show the MR axial species molar flow rates in the reaction zone (Left-up), and permeation zone (Left-down) and the local-pellet radial species concentrations (Right), for the wall-isothermal and adiabatic cases, respectively. As expected, in contrast to the PBR cases (Figures 32 and 33) where the concentration of H\(_2\) rises along the length of the reactor, in the MR reject side the H\(_2\) concentration decreases right from the inlet of the reactor with a corresponding increase in concentration in the MR permeate side. The radial species concentration profiles (on the right) become progressively steeper, axially, along the MR’s length, which is consistent with the lower values of the MR effectiveness factor one also observes along the length of the reactor (0.9 at the MR inlet to 0.48-0.57 at MR outlet, see Figure 31) for the 0.4 cm diameter pellets. For the adiabatic MR case the radial concentration profiles are a bit steeper than those for the wall-isothermal case, which is consistent again with the smaller effectiveness factors observed.
Figure 37. Adiabatic MR axial temperature profiles (Left) and pellet radial temperature profiles for various MR locations and solid thermal conductivities (Right). No-sweep, permeate side pressure: 1 bar, $W_{\text{cat}}/F_{\text{CO}}$: 70 (g*h/mol) and $W_{\text{quartz}}/W_{\text{cat}}$: 7.

Figure 37 (left) illustrates the axial catalyst-pellet and gas phase temperature profiles in the reaction zone (the MR reject side), and the axial gas phase temperature profile in the permeation zone for the adiabatic MR, and for a catalyst thermal conductivity value of $W=1$ W/(m*K). There are differences between the catalyst-pellet and gas phase temperatures in the MR reject side (maximum difference ~6 K), as well as between the gas phase temperatures in the reject and the permeate sides (maximum difference ~12 K). Figure 37 (right) also shows the difference between the catalyst pellet temperature at any given radial location and that of its surface, for several axial MR locations, and catalyst thermal conductivity values. The maximum temperature difference, between the pellet’s center and surface, occurs always at the MR inlet and varies from 0.075 K to 6.1 K, as catalyst thermal conductivity decreases from 10 W/(m*K) to 0.1 W/(m*K).
Figure 38 illustrates the intrinsic WGSR kinetic rates along the length of the MR and PBR reactors. In the first half of these reactors, the MR rates are significantly higher than the PBR rates, since the permeation of hydrogen in the MR reduces the rate of the WGSR’s reverse CO forming reaction. Further, the reaction rates in the adiabatic reactors are higher than in the isothermal ones, due to the increased temperatures observed in the adiabatic reactors. In the second half of the reactors these trends are reversed, since the higher rates observed in the first half of the reactors have led to reactant depletion in the second half.
4.3.3. Sweep effect on MR performance

Figure 39. Conversion (Left) and gas-phase axial temperature profiles (Right) for the PBR (wall-isothermal and adiabatic) and MR (wall-isothermal and adiabatic), the latter reactor employing various sweep ratios as indicated on the Figures. Permeate-side pressure: 1 bar, inlet permeation zone temperature: 553 K, $W_{\text{cat}}/F_{\text{CO}}$: 70 (g*h/mol) and $W_{\text{quartz}}/W_{\text{cat}}$: 7.

Figure 39 illustrates the effect on MR performance of employing steam as a sweep stream on the reactor’s permeate side. For the conditions in Figure 40 ($W_{\text{cat}}/F_{\text{CO}}$ =70) when employing a MR without any sweep instead of a PBR operating under the same conditions, leads to approximately 98% and 112% increase in the conversion (over the PBR case) at the exit of the reactor for the adiabatic and isothermal cases, respectively. Using steam as a sweep agent further improves conversion, as can be seen from Figure 39 (left) for both the wall-isothermal and adiabatic MR cases, as is to be expected, since the use of low-pressure (and relatively inexpensive) steam as a sweep improves the H$_2$ transport rate across the membrane but also reduces the loss of high-pressure (expensive) steam from the reaction zone to the permeation zone. As can be seen in Figure 39 (Right), another positive effect of sweeping is the cooling effect provided to the reactor, as the steam in this case acts as a cooling medium. The downstream H$_2$/H$_2$O separation can be readily carried out, using cooling/flashing/heating operations, thus suggesting sweeping as a promising process operation alternative.
4.3.4. $W_{cat}/F_{CO}$ inlet ratio effect on MR performance

Next, the effect of the $W_{cat}/F_{CO}$ ratio on MR conversion and temperature (Figure 40), and on an MR over PBR performance improvement metric (Figure 41), is discussed. In the underlying simulations, $W_{cat}/F_{CO}$ is varied by keeping the amount of catalyst $W_{cat}$ constant, while varying the inlet molar flow rate $F_{CO}$. As shown in Figure 40, both the PBR and MR conversions are monotonically increasing functions of the $W_{cat}/F_{CO}$ ratio, for both the wall isothermal, and adiabatic cases. As $W_{cat}/F_{CO}$ increases from 70 to 130, conversion increases from approximately 25 % to 35% (28 % to 40 %) for the wall-isothermal (adiabatic) PBR, and from approximately 52 % to 75 % (55 % to 77%) for the wall-isothermal (adiabatic) MR. Figure 40 also illustrates that as the $W_{cat}/F_{CO}$ ratio increases from 70 to 130, the adiabatic PBR outlet temperature increases from 590K to 602K, while the adiabatic MR outlet temperature remains within a range of 607 K to 611 K.
Figure 41. MR intensification metric for various $\text{W}_{\text{cat}}/F_{\text{CO}}$ ratios. Permeate side pressure: 1 bar, and $\text{W}_{\text{quartz}}/\text{W}_{\text{cat}}$: 7.

To better understand the relative effect of the $\text{W}_{\text{cat}}/F_{\text{CO}}$ ratio on MR conversion versus PBR conversion, an MR over PBR intensification metric is introduced, defined as a percentage increase in conversion, i.e. as the ratio of the difference of MR conversion from PBR conversion over PBR conversion, and denoted as $(X_{\text{MR}}-X_{\text{PBR}})/X_{\text{PBR}}$. As shown in Figure 42, the functional dependence of $(X_{\text{MR}}-X_{\text{PBR}})/X_{\text{PBR}}$ on $\text{W}_{\text{cat}}/F_{\text{CO}}$ can be divided into three regions. In the first region ($40 \leq \text{W}_{\text{cat}}/F_{\text{CO}} \leq 60$), an intensification metric of about 1.17 is obtained, but the PBR ($\leq 25\%$) and MR ($\leq 48\%$) conversions are relatively low. In the third region ($180 \leq \text{W}_{\text{cat}}/F_{\text{CO}} \leq 200$) hydrogen production rates are low, but again an intensification metric of about 1.17 can be obtained that is higher than performance improvement limiting values of 0.91 for the adiabatic MR and 0.65 for the wall-isothermal MR, which are obtainable for $\text{W}_{\text{cat}}/F_{\text{CO}}$ ratios above 800. Finally, in the second region ($60 < \text{W}_{\text{cat}}/F_{\text{CO}} < 140$), the MR intensification metric is minimum around a $\text{W}_{\text{cat}}/F_{\text{CO}}$ value of about 105 for both wall-isothermal and adiabatic cases, albeit the value of this minimum is high (about 1.1 for the wall isothermal case, and 0.91 for the adiabatic
case), and is accompanied by reasonable values for both conversions and hydrogen production rates.

4. 3. 5. Inlet temperature effect on MR performance

Figure 42 illustrates the effect of varying the temperature at the reactor inlet on the conversion, and temperature profiles for both PBR and MR, demonstrating that higher temperatures yield higher conversions, for the same $W_{\text{cat}}/F_{\text{CO}}$ ratios. This is explained by the increased temperatures throughout the reactor, see Figure 42 (left), which in turn lead to a reaction rate acceleration. In particular, increasing the reactor inlet temperature from 523 K to 553 K (523 K to 573 K) improves conversion by around 6% (12%) for both the wall-isothermal (~6%) and adiabatic MR (12%). One concern here is for the temperatures not to exceed the safe operating temperature for the WGS sour-shift catalyst, which is reported by the manufacturer to be ~613 K.
4.3.6. Permeation and retentate zone inlet pressure effect on MR performance

Figure 43. Conversions (Left) and gas-phase axial temperature profiles (Right) for various permeation zone pressures. Inlet permeate side temperature: 553 K, $W_{cat}/F_{CO}: 70 \text{ (g*h/mol)}$ and $W_{quartz}/W_{cat}: 7$.

Figure 43 illustrates the effect on MR performance of varying the permeate side pressure, while keeping the sweep ratio, and all other conditions constant. Increasing the permeate-side pressure reduces CO conversion, as it decreases the hydrogen permeation rate through the membrane. Correspondingly the reactor temperatures decrease as well. One advantage, of course, of running the MR with a higher permeate side pressure is to avoid a compression step downstream needed in the use of the $H_2$ product for power generation (e.g., in hydrogen turbines).

Figure 44. Conversions (Left) and gas-phase axial temperature profiles (Right) for various retentate side pressures. Inlet permeate side temperature: 553 K, $W_{cat}/F_{CO}: 70 \text{ (g*h/mol)}$ and $W_{quartz}/W_{cat}: 7$.
Figure 44 shows the effect on MR performance of varying the retentate side pressure, while keeping the all other conditions constant. Decreasing the retentate-side pressure reduces CO conversion and the hydrogen permeation rate through the membrane. Correspondingly the reactor temperatures decrease from 25 bar to 20 bar, but the exit reactor temperatures at 20 and 15 bar are obtained almost same.

4.3.7. **Sweep stream inlet temperature effect on MR performance**

![Figure 45. Conversions (Left) and gas-phase axial temperature profiles (Right) for various sweep stream inlet temperatures. Permeate-side pressure: 1 bar, \( W_{\text{cat}}/F_{\text{CO}} \): 70 (g\(^{\circ}\)h/mol) and \( W_{\text{quartz}} / W_{\text{cat}} \): 7.](image)

As mentioned earlier, sweeping with steam not only reduces hydrogen partial pressure in the permeation zone (and thus increases its transport rate), but also has the added benefit of acting as a coolant to remove the exothermic heat of the reaction. Figure 45 shows the effect of varying the sweep stream temperature while keeping all other conditions the same. Surprisingly, varying the inlet temperature of the sweep from 553 K to 453 K leaves the reactor conversion virtually unaffected but lowers the reaction zone temperature by \(~10\) °C.

Multi-scale modeling and simulations are carried out for a high-pressure membrane reactor employing carbon molecular sieve membranes and used for hydrogen production via the water gas shift reaction. The influence of several operating conditions and design parameters on reactor performance is quantified. Rigorous evaluation of the catalyst effectiveness factors in the
PBR and MR environments, demonstrates that they are not constant but vary significantly along the reactors’ length and that catalyst pellets of the same diameter exhibit different effectiveness factors. Numerical simulations employing catalyst solid thermal conductivity values in the range one would expect for common WGSR catalysts (published values for such properties are presently sorely lacking, however), indicate that values in the lower part of range lead to non-negligible temperature gradients within the catalytic pellet, but nevertheless these gradients have no major impact on the calculated catalyst effectiveness factors. On the other hand, sweep gas pressure/temperature and membrane area have a significant impact on the MR’s behavior. Both adiabatic and wall-isothermal reactor simulations were performed to investigate the comparative performances of the various MRs. In general, the adiabatic MR gives higher conversion values as compared to the wall-isothermal MR for the same operating conditions due to the temperature dependent acceleration of the reaction rate, along the reactor length.

4. **HTSR/LTSR sequence versus proposed HTSR/MS/LTSR/MS sequence and proposed LTMRs in series**

In the last part of this section, the study focuses on the comparison of various hydrogen production processes (baseline, proposed process 1 and proposed process 2), for process design and intensification purposes. Process intensification (PI) encompasses any chemical engineering development offering drastic process technologies improvements, in regard to a variety of metrics. Such intensification has the potential to improve process efficiency and economics. As part of the intensification procedure, integration of multiple operations (e.g., reaction and separation) is used as a robust tool to improve the existing process’ efficiency, reduce energy consumption, and unwanted outputs/by-products. In this study, we chose process reactive
volume reduction (process catalyst amount reduction) and H\textsubscript{2} production rate increment as process intensification metrics and a comparison criterion among three aforementioned systems.

A number of simulations are carried-out of the integrated HTSR-LTSR system, and the resulting HTSR’s exit is fed into the LTSR for each set of simulation. This design is used as the baseline to which our proposed MR/MS-based plants will be compared. The performance summary (CO conversion evaluation along the combined HTSR/LTSR reactor’s length) of the baseline design can be seen in Figure 29 for various operating conditions. The obtained simulation results suggest (consistent with industry) that CO conversion reaches 95%, if the HTSR’s inlet conditions are kept at 593 K (adiabatic process)-H\textsubscript{2}O/CO ratio of 5, and the LTSR’s inlet temperature at 493 K (adiabatic process). Thus, the total CO conversion of 95 % is chosen as key design criteria for a comparative study between the baseline and alternative processes.

In the first alternative process (multistage system), the membrane separation (MS) used as an intermediate tool to separate H\textsubscript{2} from HTSR exit stream and then, the stream is sent through LTSR. The intermediate membrane separation creates a synergy that significantly increases overall process efficiency and results in higher conversion. Membrane area have a significant impact on the MS/MR’s performance, and it is also a key design parameter to define the capital cost of MS/MR. To illustrate this impact, we performed the simulations for various intermediate MS separation factors such as 60%, 75% and 90% (separation of H\textsubscript{2}, produced in HTSR). We applied the same procedure for LTMRs (performed 60%, 75% and 90% separation of H\textsubscript{2}, produced in the first LTMR). On the other hand, we reached the process performance of having >90% H\textsubscript{2} separation in total for the all cases. Figure 46 represents CO conversion along the HTSR-MS-LTSR system. As can be seen in Figure 46 (Right), intermediate MS increases the
total conversion performance of the process approximately 9% (60% H₂ separation), 12% (75% H₂ separation) and 17% (90% H₂ separation). Moreover, multistage system enables to reach 95% CO conversion criteria for the operating conditions of HTSR’s H₂O/CO ratios of 3 and 4. However, the ratio of 5 must be utilized for the conventional system to reach same amount of total CO conversion.

*Figure 46. Multistage (HTSR/MS/ LTSR/MS) system’s conversion evaluation along the combined reactor’s length*. 

*The resulting HTSR’s exit for the cases (1), (2) and (3) is fed into the LTSR for each set of simulation conditions of 0%, 60%, 75%, and 90% H₂ (produced in the HTSR and separated in the intermediate MS) separation.*
<table>
<thead>
<tr>
<th>Process Conditions</th>
<th>Process Outcomes</th>
<th>Intensification Metrics</th>
</tr>
</thead>
</table>
| **Conventional Process (Baseline)** | 1- HTSR-adiabatic (593 K, 40 bar and H₂O/CO=5)  
2- Cooling to 493 K  
3- LTSR-adiabatic (493 K, 30 bar) | 95% Conversion  
(baseline-used catalyst amount and produced H₂ rate are calculated) | Catalyst Amount Metric=1 (baseline)  
H₂ Production Rate Metric=1 (baseline) |
| **Proposed Process 1 (HTSR/MS/LTSR/MS)** | 1- HTSR-adiabatic (593 K, 40 bar)  
2- Membrane separation of 60%, 75% and 90%-H₂ (obtained at the exit HTSR)  
3- Cooling to 493 K  
4- LTSR-adiabatic (493 K, 30 bar)  
5- Membrane separation of H₂ to reach total >90% separation | 95% Conversion  
>90% H₂ Separation  
(1- Fix H₂ production rate as baseline and calculate the reduction in the amount of catalyst 2- Fix the amount of catalyst as baseline and calculate the increase in H₂ production rate) | Catalyst Amount Metric=0.89 (60% H₂ separation), 0.8 (75% H₂ separation) and 0.68 (90% H₂ separation)  
H₂ Production Rate Metric=1.15 (60% H₂ separation), 1.45 (75% H₂ separation) and 1.7 (90% H₂ separation) |
| **Proposed Process 2 (LTMR/LTMR)** | 1- LTMR-adiabatic (523 K, 40 bar) and separation of 60%, 75% and 90%-H₂  
2- Cooling to 523 K  
3- LTMR-adiabatic (523 K) and separation of H₂ to reach total >90% separation | 95% Conversion  
>90% H₂ Separation  
(1- Fix H₂ production rate as baseline and calculate the reduction in the amount of catalyst 2- Fix the amount of catalyst as baseline and calculate the increase in H₂ production rate) | Catalyst Amount Metric=0.61 (60% H₂ separation), 0.56 (75% H₂ separation) and 0.45 (90% H₂ separation)  
H₂ Production Rate Metric=1.22 (60% H₂ separation), 1.55 (75% H₂ separation) and 1.9 (90% H₂ separation) |

*Figure 47. The summary of process conditions, process outcomes and intensification metrics.*

The summary of process conditions, process outcomes and intensification metrics for conventional process, alternative process 1 and alternative process 2 is depicted in Figure 47. For design aspects, a membrane reactor consists of a pressure vessel that houses several membrane bundles, each bundle consisting of multiple CMS membrane tubes. These bundles typically consist of CMS membrane tubes, whose dimensions are an inner and outer diameter of 3.5mm and 5.7mm respectively, and a length of 1m (Figure 48). A membrane reactor (MR) consists of 1400 bundles in parallel (1 m of each) and 9800 bundles in total (7 m reactor—Figure 13). 60%, 75% and 90% H₂ (produced in the first LTSR) separations are achieved by varying the number of tubes in the first LTMR and then, reject’s side gas mixture is fed through the second LTMR. Again, above 90% H₂ separation performance is achieved in the third alternative process.
Figure 48. A schematic of the configuration for the sequence of MRs.

Same syngas composition as conventional process is used as the feed to the MR. In the simulations, the membrane permeances (m³/m².h.bar) were taken to be: H₂=1; CO=0.0125; CO₂=0.025; CH₄=0.00806, H₂O=0.333, which are typical of values we measure with high-quality CMS membranes prepared by our industrial collaborators in this project (Media and Process Technology, Inc.). In MS simulations, we used same membrane characteristics and removed reaction zone (catalyst) effect from system.

Process catalyst reduction trend among the hydrogen production systems is depicted in Figure 49 for various intermediate H₂ separation levels of 60%, 75% and 90%. H₂ production rate are kept constant to obtain results in Figure 49 for all three systems. Approximately 11% (conventional→ proposed 1)/18% (conventional→ proposed 2), 20% (conventional→ proposed 1)/25% (conventional→ proposed 2) and 32% (conventional→ proposed 1)/40% (conventional→ proposed 2) of reactive volume reduction is obtained for the H₂ separation levels of 60%, 75% and 90%, respectively. Similarly, approximately 11% (conventional→ proposed 1)/39% (conventional→ proposed 2), 20% (conventional→ proposed 1)/44%
(conventional→ proposed 2) and 32% (conventional→ proposed 1)/55% (conventional→ proposed 2) of catalyst amount reduction is obtained for the H₂ separation levels of 60%, 75% and 90%, respectively.

![Bar charts showing catalyst amount reduction for various H₂ separation factors.](image)

**Figure 49.** Process catalyst amount reduction for various H₂ separation factors.
Figure 50. Process H$_2$ production rate increment for various H$_2$ separation factors.

H$_2$ production rate increase (for constant amount of catalyst) in the hydrogen production systems is shown in Figure 50 for various H$_2$ separation levels of 60%, 75% and 90%. Transition from conventional process to proposed 1 and proposed 2 increases the H$_2$ production rate significantly. The values of 15% - 22% (60% separation), 45% - 55% (75% separation) and 70% - 90% (90% separation) are obtained for different systems.

Process intensification-aimed comparative study is performed for various hydrogen production processes. The multi-scale simulation results show that the both proposed alternative processes 1 and 2 are superior then the conventional process, and promising substitutes.

5.1. Introduction

In this chapter, the main goal is to carry out multiscale modeling and simulation studies for both the adsorption and desorption steps of an AR carrying out the WGSR. This multiscale model enables the quantification of catalyst and adsorbent effectiveness factors within the reactor environment, obviating the commonly employed assumption that these factors are constant. Simulations of the AR’s alternating adsorption-reaction/desorption operation, using the proposed model, illustrate rapid convergence to a long-term periodic solution. The obtained simulation results quantify the influence of key operating conditions and design parameters (e.g., reactor temperature/pressure, \( \frac{W_{\text{cat}}}{F_{\text{CO}}} \), \( \frac{W_{\text{ad}}}{F_{\text{CO}}} \), \( \frac{F_{\text{H2O}}}{F_{\text{CO}}} \) ratios and pellet size) on the AR’s behavior. They also demonstrate, for pellet diameters used at the industrial scale, significant temporal and axial variation of the catalyst/adsorbent pellet effectiveness factors. Finally, the energetic intensification benefits of the proposed AR process over conventional WGSR packed-bed reactors are quantified. The feasibility of the sorption-enhanced WGSR reactor is established, as well as the energetic benefits resulting from lower CO\(_2\) compression needs resulting from the elimination of the need of a separate CO\(_2\) removal step.

5.2. Results and Discussion

In our simulations, we utilized a commercial Co-Mo/Al\(_2\)O\(_3\) shift catalyst features that has been shown to exhibit high activity and stability for the low-temperature shift process. The catalyst kinetics were investigated, and the global rate expression developed in [28] is employed as shown in equations (146), (147). In the spirit of [88], the intrinsic adsorption reaction rate of the adsorbent employed in the AR is considered to depend linearly on the difference between the
adsorbed CO\textsubscript{2} concentration and its equilibrium value. The employed adsorption rate expressions are shown in equations (148), (149). The relevant WGSR and adsorption rate parameters are shown in Table 22.

Table 22. Chemical model equations.

\begin{align*}
\text{Reaction Rate:} & \quad r_j = k_a \left( \frac{p_{CO} \cdot p_{H_2O}}{p_{H_2}} - \frac{p_{CO}}{K_{eq}} \right) \quad (146) \\
K_{eq} &= \exp \left( \frac{4577.8}{T_f^\circ} - 4.33 \right) \quad (147) \\
\text{Adsorption Rate:} & \quad \overline{R}_{f,a} = k_w (q_{eq} - q_i) \quad (148) \\
\text{Langmuir Adsorption Isotherm:} & \quad q_{eq} = \frac{m_b p_i}{1 + b p_i} \quad (149)
\end{align*}

We carried out the simulations using an inlet feed composition of (H\textsubscript{2}/CO/H\textsubscript{2}O/CO\textsubscript{2}/N\textsubscript{2}/CH\textsubscript{4}) = (0.51/1.00/a/0.36/2.28/0.1), which corresponds to a coal-derived syngas (from an air-blown gasifier) intermixed with steam, at a (H\textsubscript{2}O/CO) ratio equal to a, where 1.1 < a < 3. To initiate the AR simulation, we consider that the AR is first pressurized to operating pressure by an equimolar steam/inert gas (N\textsubscript{2}) mixture and heated to the desired temperature with the aid of this gas mixture. Once the reactor and pellet domain interiors reach the equimolar H\textsubscript{2}O/N\textsubscript{2} mixture composition, then the reactor feed is switched to the specified syngas composition, and time is considered to be t=0.

The following parameter ranges are considered: Wall-isothermal temperature (inlet temperatures: 523-573 K); pressure (5-25 bar); W\textsubscript{cat}/F\textsubscript{CO} value of 17-245 (where W\textsubscript{cat} is the weight of catalyst and F\textsubscript{CO} is the inlet flow rate of CO); W\textsubscript{ad}/F\textsubscript{CO} value of 98-1,470 (where W\textsubscript{ad} is the weight of adsorbent); W\textsubscript{ad}/W\textsubscript{cat} value of 1-10. Table 4 shows the parameter values used in the solution of model equations. The values reported in Table 23 correspond to a commercial Co-
Mo/Al₂O₃ shift catalyst and a hydrotalcite adsorbent, where rate constant is from [28] and the adsorption parameters were fitted based on experimental data [89].

Table 23. Parameter Values Used in Simulation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of catalyst</td>
<td>592.68</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Density of adsorbent</td>
<td>1.780</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Catalyst pellet void fraction</td>
<td>0.35561</td>
<td>-</td>
</tr>
<tr>
<td>Adsorbent pellet void fraction</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>Catalyst/adsorbent pellets radius</td>
<td>0.00035-0.005</td>
<td>m</td>
</tr>
<tr>
<td>Surface area of pellets</td>
<td>160-220*10⁵</td>
<td>m²/g</td>
</tr>
<tr>
<td>Pore volume of pellets</td>
<td>0.55-0.65*10⁻⁶</td>
<td>m³/g</td>
</tr>
<tr>
<td>Mean pore diameter of catalyst</td>
<td>6.3*10⁻⁹</td>
<td>m</td>
</tr>
<tr>
<td>Mean pore diameter of adsorbent</td>
<td>6.3*10⁻⁷</td>
<td>m</td>
</tr>
<tr>
<td>Reactor diameter</td>
<td>0.03175</td>
<td>m</td>
</tr>
<tr>
<td>Reactor length</td>
<td>0.1397</td>
<td>m</td>
</tr>
<tr>
<td>Heat transfer coefficient (U₉₅₀)</td>
<td>227</td>
<td>W/m²·K</td>
</tr>
<tr>
<td>Chemical Kinetic rate parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k_w</td>
<td>1.683*10⁻⁶</td>
<td>mol/(g·s·bar)</td>
</tr>
<tr>
<td></td>
<td>1.722*10⁻⁵</td>
<td></td>
</tr>
<tr>
<td>kₐ</td>
<td>0.0058</td>
<td>1/s</td>
</tr>
<tr>
<td>mₐCO₂</td>
<td>2.9526</td>
<td>kg/mol</td>
</tr>
<tr>
<td>bₐCO₂</td>
<td>3.96</td>
<td>1/bar</td>
</tr>
</tbody>
</table>

5. 2. 1. Effectiveness factor phenomena in catalyst and adsorbent pellets

Figure 51 (top) illustrates the local temporal catalyst effectiveness factor profiles in the AR (for two different pellet sizes), while Figure 49 (bottom) shows the axially-averaged effectiveness factor profiles. Both the local and the axially-averaged effectiveness factors decrease appreciably as the pellet size increases, as expected. Note also that the effectiveness factors increase with time as one transitions from the AR mode into the PBR mode of operation as adsorbent saturation is reached.
Figure 51. Catalyst pellet instantaneous-local effectiveness factor (Top) and catalyst pellet axially-averaged effectiveness factor (Bottom) vs. time for various pellet sizes. (523 K, 25 bar and \( \frac{W_{\text{cat}}}{F_{\text{CO}}} = 88 \) g*h/mol).

Figure 52 (top) illustrates the local temporal adsorbent pellet effectiveness factor profiles in the AR (for two different pellet sizes), while Figure 52 (bottom) shows the axially-averaged effectiveness factor profiles. For times up to around 2,000 sec, the adsorbent axially-averaged effectiveness factor decreases with increasing adsorbent pellet size. After 2,000 sec, the effectiveness factors for the various pellet sizes become equal and approximately zero, indicating that the adsorbent pellets are nearing their full capacity. Changing adsorbent pellet size from-lab scale to industrial-scale leads to average effectiveness factor declines of approximately 30%. Fig. 8 (top) shows the local effectiveness factor behavior of the adsorbent pellet along the AR length at various operating times. At small operating times, and in the first 30% of the reactor’s length, an effectiveness factor above 3 and 1.5 for pellet sizes 0.035 and 0.5 cm, is observed, indicating that a significant part of the incoming flux into the adsorbent pellet is for accumulation purposes,
i.e., for filling the pore space with gas. The effectiveness factor values trend downwards at larger operating times, as the adsorbent pellets in the AR begin to saturate with adsorbed CO$_2$. The effectiveness factor values are also small at longer reactor lengths, even at small operating times, as CO$_2$ is scarce at these lengths and times, due to its adsorption at the earlier part of the AR.

The AR operation is cyclical in nature. Figure 51 shows the adsorbent pellet’s axially-averaged effectiveness factor profiles for four consecutive operating cycles. As it can be seen in this Figure, the adsorbent pellet’s effectiveness factor profile reaches its long-term behavior within about four cycles.

**Figure 51.** Adsorbent pellet’s axially-averaged effectiveness factor profiles for four consecutive operating cycles. (523 K, 25 bar and $W_{cat}/F_{CO}=88$ g*$h$/mol).

**Figure 52.** Adsorbent pellet instantaneous-local effectiveness factor (Top) and adsorbent pellet axially-averaged effectiveness factor (Bottom) vs time for various pellet sizes. (523 K, 25 bar and $W_{cat}/F_{CO}=88$ g*$h$/mol).
5.2.2. Species’ profiles through the radius of the catalyst and adsorbent pellets

Figure 52 shows the CO\textsubscript{2} radial molar profiles in the adsorbent pellet at three different axial locations in the AR bed. Figure 53 shows the radial molar profiles of the various species including CO\textsubscript{2} in the catalyst-pellet at the same exact locations. In the initial times of the adsorption/reaction cycle, there are sharp concentration gradients within the adsorbent pellets, which become flat at later times in the cycle when the adsorbent saturates and the CO\textsubscript{2} adsorption rate approaches zero. Our simulations confirm that for the experimental conditions investigated and the catalyst and adsorbent materials the total pressure and temperature gradients prevailing across the pellets are quite small.

For example, the simulations for lab-scale to industrial scale pellet sizes (particle diameter 0.07-1 cm) yield that the pressure variation between the pellet’s surface and center is in the range of 9.5×10\textsuperscript{-5} bar → 55.3×10\textsuperscript{-3} bar, depending on reactor operating conditions and location within the reactor. Similarly, the temperature variation between the pellet’s surface and center is found to be in the range of 0.1K → 0.59 K.
5.2.3. Temperature profiles along the reactor length

The temperature profiles of the catalyst-pellet, adsorbent-pellet, and bulk gas phase in the AR are shown in Figure 54. The minimum and maximum temperature differences along the reactor length for various operating times are found to be 0.1 K - 2.35 K between the bulk gas phase and the catalyst pellet, and 0.01-0.3 K between the bulk gas phase and the adsorbent pellet.
The biggest temperature differences between the bulk gas phase and the catalyst pellet, and the bulk gas phase and the adsorbent pellet, are observed near the reactor inlet.

![Temperature Profiles](image)

*Figure 56. AR time-averaged temperature axial profiles.*

The temperature differences among the catalyst-pellet, adsorbent-pellet, and bulk gas phase along the reactor length for various pellet diameters are shown in Figure 55. Increasing the pellet diameter causes higher temperature differences between the catalyst/adsorbent pellet and the bulk gas, but these differences are reduced along the reactor length.

![Temperature Profiles](image)

*Figure 57. AR average temperature axial profiles for various pellet sizes. (W_{cat}/F_{CO}=88 g*h/mol).*

Increment of the pellet size increases the heat transfer limitations among the domains and reduces the heat transfer coefficient between the pellets and bulk gas phases. It was found that the calculated minimum and maximum heat transfer coefficients between the pellets and bulk gas phase are 200-278, 107-144, 56-71 and 32-38 W/m²*K for the particles 0.7, 2, 6 and 10 mm.
5.2.4. Parametric studies in AR

Figure 58. AR exit CO₂ mole fraction and CO conversion vs operating time for various operating temperatures. (W_cat/F_CO=88 g*h/mol)

Figure 56 (left) shows the CO₂ exit concentration as a function of operating time for three different feed temperatures, while Figure 56 (right) shows the corresponding reactor conversion profiles.

Figure 59. AR exit CO₂ mole fraction and CO conversion vs operating time for various operating pressures. (W_cat/F_CO=88 g*h/mol)

The effect of the presence of the adsorbent is clear from these Figures, with the AR showing close to 100% conversion while the adsorbent is still fresh and effectively removes the CO₂ produced by the WGSR shifting the reaction equilibrium towards the product side. Eventually, the adsorbent gets completely saturated and the AR ends operating as a PBR. From Figure 56 it can be concluded that the selected operating temperatures (523 K-573 K) do not have a significant effect on AR performance. Figure 57 (left) shows the CO₂ exit concentration as a function of operating time for three different reactor pressures, while Figure 57 (right) shows the
corresponding reactor conversion profiles. As the operating pressure increases from 15 bar to 40 bar, 95 % CO conversion can still be attained, although the minimum and maximum operating times decrease significantly, since the number of CO\(_2\) moles entering the reactor increases as the pressure increases and the inlet volumetric flow rate is kept constant. The AR exit CO\(_2\) mole fraction and CO conversion versus operating time for various F\(_{CO}\) are shown in Figure 58 (while W\(_{cat}\) and W\(_{ad}\) are kept constant, inlet velocity is changed). The molar flow rate is a key operational parameter in the AR process.

![Figure 60. AR exit CO\(_2\) mole fraction and CO conversion vs operating time for various W\(_{cat}\)/F\(_{co}\) and W\(_{ad}\)/F\(_{co}\) ratios.](image)

Reducing the inlet syngas velocity results in an increase in H\(_2\) purity, CO conversion, and the minimum/maximum AR operational times. Starting from the value of 44 W\(_{cat}/F_{CO}\) (W\(_{ad}/F_{CO}=264\)), the minimum CO conversion of 95% is obtained approximately at 1,450 sec, which is considered long enough for practical AR operation. Minimum and maximum operating times at 400 sec and 1,500 sec for the same W\(_{cat}/F_{CO}\) value, are obtained, so the value of 44 W\(_{cat}/F_{CO}\) can be considered as a practical operating condition for a WGSR AR. Increasing the value of W\(_{cat}/F_{CO}\) from 44 to 132 yields minimum and maximum operating times of 700 sec and 2,100 sec.

The AR exit CO\(_2\) mole fraction and CO conversion versus operating time for various H\(_2\)O/CO ratios are shown in Figure 59. CO conversion, CO\(_2\) breakthrough time and high purity
H₂ production are favored by higher H₂O/CO ratios. As Figure 59 shows, increasing the H₂O/CO ratios from 1.1 to 3 improves CO conversion with the AR mode of operation lasting for significantly longer times. The study of various H₂O/CO ratios suggests the use of H₂O/CO ratios greater than 1.5 for the attainment of CO conversion levels greater than 95%. The AR exit CO₂ mole fraction and CO conversion versus operating time for various W₀/W₁ ratios are shown in Figure 60 (in the simulations, the catalyst amount is kept constant, while the adsorbent amount is varied).

![Graphs showing CO₂ mole fraction and CO conversion vs operating time for various H₂O/CO ratios.](image)

**Figure 61. AR exit CO₂ mole fraction and CO conversion vs operating time for various H₂O/CO ratios.**

(W₀/F₀ = 88 g/h/mol)

The adsorbent/catalyst ratio has a significant effect on CO conversion and H₂ product purity. Indeed, as the adsorbent/catalyst ratio increases, higher H₂ purity and higher operational time before breakthrough are obtained. CO conversions greater than 95% are attainable for W₀/W₁ ratios larger than 1. The AR exit CO₂ mole fraction and CO conversion versus operating time for
various pellet diameters are shown in Figure 61. The pellet size is also a crucial factor for AR performance, since both the reaction and the adsorption rates can be limited by intraparticle transport for larger size pellets. As shown in Figure 61, the simulations for pellet diameters of 0.7, 2, 6 and 10 mm, suggest that a relatively small effect of varying pellet diameter on CO$_2$ breakthrough time, and a much more pronounced effect on CO conversion. In addition, it is found that the AR outlet CO$_2$ mole fraction time profiles become steeper at breakthrough times, for smaller pellet diameters, due to lower mass transfer limitations within the pellet.

![Figure 63. AR exit CO$_2$ mole fraction and CO conversion vs operating time for various pellet diameters.](image)

(W$_{cat}$/F$_{CO}$=88 g*h/mol)

In Figure 62, the [0, 1] and [1, 2] x-axis intervals illustrate AR CO$_2$ loading axial profiles during the adsorption/desorption parts of the AR’s 1st operating cycle for the switch times (400s and 1500 s). Correspondingly, [2, 3] and [3, 4] represent the 2nd cycle; [4, 5] and [5, 6] the 3rd cycle; [6, 7] and [7, 8] the 4th cycle and [8, 9] and [9, 10] the 5th cycle. In this case, the minimum and maximum operating times observed as 400 sec and 1,500 sec. Figure 62 shows that AR reactor operates at steady-state conditions through the fourth cycle for the operating times 400 sec and 1,500 sec. In other words, the amount of adsorbed CO$_2$ for each adsorption/desorption cycle approaching the constant value through the fourth cycle. Therefore, these results create the possibility of operating AR cyclically for any reasonable selected operating times.
Figure 64. AR CO$_2$ loading axial profiles for 2 switch times and 5 operating cycles.

5.3. Conclusions

A multiscale model of an AR has been developed and simulated, to demonstrate its energetic and other intensification characteristics, as applied to the transformation of coal gasifier syngas into hydrogen/carbon-dioxide rich mixtures, using the WGSR. The presented dynamic model considers reaction and transport phenomena in the catalyst/adsorbent pellet, and reactor domains, and demonstrates significant variation of catalyst and adsorbent effectiveness factors along the AR’s length for industrially-sized pellets. The obtained simulations also enable quantification of the energetic intensification benefits of the proposed AR system over conventional WGSR packed bed reactors. The influence of several operating conditions and design parameters on reactor performance is quantified. $W_{\text{cat}}/F_{\text{CO}} - W_{\text{ad}}/F_{\text{CO}}$, $H_2O/CO$, $W_{\text{ad}}/W_{\text{cat}}$
ratios and pressure have a significant impact on the AR’s behavior and reaching operational goals. The adsorption/desorption cyclic studies demonstrate that the process reaches the steady-state operating conditions through the certain number of cycles for any reasonable selected operating times.
Chapter 6. A Novel Membrane Reactor (MR)/Adsorptive Reactor (AR) Process

6.1. Introduction

The objective of this chapter is the modeling and simulation of a novel process, consisting of a membrane reactor (MR)/adsorptive reactor (AR) sequence that intensifies equilibrium limited reactions and associated separation processes. We aim to demonstrate the feasibility of the proposed overall process via process intensification with the MR and/or AR units, so as to eliminate the need for use of complex and costly unit operations, e.g., two-stage Selexol. In the direction of the mentioned target, we develop and apply design, modeling and preliminary optimization of each individual units and overall process. Firstly, comprehensive, multi-scale, multiphase, computational fluid dynamics (CFD) models are developed quantifying the many complex physicochemical phenomena occurring in each units, and thus providing the basis to better understand, and intensify the overall reaction/separation, steady-state/cyclic processes. Secondly, we carry out simulations in order to study the influence of the individual units’ operating and design parameters. For the MR component, we investigate the effect of the temperature, pressure, W_cat/F_CO ratio, inlet H2O/CO molar ratio, sweep case, permeate side pressure, sweep ratio, and the H2O/H2 separation factor (SF) on MR’s performance. For the AR module, we investigate the impact of operating and design conditions (W_cat/F_CO ratio, inlet H2O/CO molar ratio, etc.). Then, the individual modular components and overall system are analyzed to carry out preliminary optimization, such optimization entails characterizing the acceptable ranges (defining the minimums and maximums) in terms of the operating and design parameters to meet the selected success criteria for the process.
6. 2. Case Study

As demonstrated in Figure 63, we investigate the applicability of a novel and efficient reactor configuration, the sequence of low temperature membrane reactor (LT-MR)/ adsorptive reactor (AR). The syngas produced through gasification of coal is directed to these units and the outlet of units can be mixed to deliver cleared syngas with certain specifications for energy generation. The final cleaned syngas stream produced by the treatment skid will go through a heat and power generation unit consisting of hydrogen turbines, producing energy to match the target levels defined by the performance attributes. The proposed process has potential to generate a highly efficient and ultra-compact processes by producing H₂ for use in IGCC with simultaneous CO₂ capture.

6. 2. 1. Membrane Reactor Studies

A simulated coal-derived syngas with composition (H₂:CO:CO₂:N₂:CH₄:H₂S:H₂O = 0.51:1.00:0.36:2.28:0.1:0.0031:1.1) was fed to the retentate side of the MR. The W_cat/F_CO_0 values in the MR were varied within a range of 20-95 g-cat*h/mol-CO, by changing the MR inlet flowrate, while the MR was considered to operate at a temperature of 250 ºC and a pressure of 25 bar. In the simulations, membrane permeances, in m³/m².h.bar, were: H₂=1; CO=0.0027; CO₂=0.0018; CH₄=0.0027, H₂O=0.333.
6. 2. 1. 1. Species molar flow rates and mole fractions in MR

![Graph](image)

**Figure 66. MR molar flow rates vs W_cat/F_CO_0. Sweep ratio: 0.1, permeate pressure: 4 bar.**

Figures 64-65 illustrate the MR outlet molar flow rates and species mole fractions as a function of W_cat/F_CO_0, for both reaction and permeation zones. The total inlet and outlet molar flow rates are also shown in Figure 64, for simulation consistency verification purposes.

![Graph](image)

**Figure 67. MR outlet species mole fractions vs W_cat/F_CO_0. Sweep ratio: 0.1, permeate pressure: 4 bar.**
6. 2. 1. 2. CO conversion, H$_2$ recovery, H$_2$O/CO outlet molar ratio and CO$_2$ lost in MR

Repeated simulations of the presented multiscale model were carried out, for various values of the sweep ratio and permeate side pressure, to quantify these parameters’ effect on MR performance, and thus identify appealing operating conditions and process designs that meet such operating constraints as CO$_2$ lost <10 % and outlet H$_2$O/CO ratio >1.1.

Figures 66-69 (sweep ratio variation) and 70-73 (permeate side pressure variation) illustrate MR outlet CO conversion, H$_2$O/CO outlet molar ratio, H$_2$ recovery and CO$_2$ lost in the MR, as a function of $W_{\text{cat}}/F_{\text{CO}_0}$.

As shown in Figures 66 and 68, CO conversion and H$_2$ recovery are increasing functions of $W_{\text{cat}}/F_{\text{CO}_0}$ for fixed steam sweep ratio, and also increasing functions of steam sweep ratio for fixed $W_{\text{cat}}/F_{\text{CO}_0}$. Indeed, Figures 66 and 68 illustrate that CO conversion (H$_2$ recovery) increases from 38.5 % (67 %), at 30 $W_{\text{cat}}/F_{\text{CO}_0}$ and no sweep ratio, to 85 % (95 %), at 95 $W_{\text{cat}}/F_{\text{CO}_0}$ and 0.3 sweep ratio. Conversion and H$_2$ recovery increase with increasing steam sweep ratios, since steam sweeping lowers permeate H$_2$ partial pressure enhancing H$_2$ transport across the membrane, and reduces the loss of high-pressure steam (a reactant) from the reaction zone to the permeation zone. This effect is ever more dominant for higher $W_{\text{cat}}/F_{\text{CO}_0}$ values.

As mentioned earlier, a goal for the proposed MR-AR process is to capture at least 90% of the carbon in its feed. Thus, a maximum 10 % CO$_2$ loss is allowed through the MR’s membrane. Figure 8 demonstrates that the max CO$_2$ loss through the MR membrane is 1.9 %, due to the low CO$_2$ permeability through the membrane. Thus this goal of the MR-AR process can readily be met.
Figure 67 illustrates that the MR outlet H\textsubscript{2}O/CO molar ratio is an increasing function of the steam sweep ratio for fixed W\textsubscript{cat}/F\textsubscript{CO\_0}, but a convex function of W\textsubscript{cat}/F\textsubscript{CO\_0} for fixed steam sweep ratio, with the minimum occurring around 50 W\textsubscript{cat}/F\textsubscript{CO\_0}, and being in the order of 0.07 for no sweep and 0.15 for 0.3 sweep ratio, while the maximum is about 0.5 and occurs at low (about 25) W\textsubscript{cat}/F\textsubscript{CO\_0}. These are all unacceptably low H\textsubscript{2}O/CO molar ratios, since in the proposed MR-AR process, the MR’s outlet serves as the AR’s inlet, and a value of 1.1 is considered to be the minimum allowable H\textsubscript{2}O/CO molar ratio of MR’s exit for an acceptable catalyst activity in the AR. These low H\textsubscript{2}O/CO molar ratios at the MR exit are attributable to the low steam permeate pressure of 1 bar, which leads to H\textsubscript{2}O transport from the reactive zone to the permeate zone. Increasing the permeate side pressure is thus a possible solution to this problem of low H\textsubscript{2}O/CO molar ratios at the MR outlet. In the next section, the effect of increasing permeate side pressure on exit H\textsubscript{2}O/CO molar ratios is discussed.

*Figure 68. CO conversion vs. W\textsubscript{cat}/F\textsubscript{CO\_0}. *

*Figure 69. Exit H\textsubscript{2}O/CO ratio vs. W\textsubscript{cat}/F\textsubscript{CO\_0}. *
6.2.1.3. Permeate side pressure effect on CO conversion, H₂ recovery, H₂O/CO outlet molar ratio and CO₂ lost in MR

Figures 70 and 72 illustrate that at 0.1 steam sweep ratio, CO conversion (H₂ recovery) is an increasing (increasing) function of W_cat/F_CO_0 for fixed permeate-side pressure, and an increasing (decreasing) function of permeate-side pressure, for fixed W_cat/F_CO_0. Indeed, Figure 70 illustrates that CO conversion increases from about 40 %, at 20 W_cat/F_CO_0, to 77 % (84 %), at 95 W_cat/F_CO_0 and 1 bar (5 bar) permeate-side pressure. Figure 72 on the other hand, shows that H₂ recovery increases from about 45 % (70 %) at 20 W_cat/F_CO_0 and 5 bar (1 bar) permeate-side pressure, to 60 % (93 %), at 95 W_cat/F_CO_0 and 5 bar (1 bar) permeate-side pressure.

As Figure 73 demonstrates, the max CO₂ loss through the MR membrane is again 1.9 %, thus ensuring that the MR-AR process goal of maximum 10 % CO₂ loss in the MR continues to be satisfied at high permeate side pressures.

*Permeate inlet temperature:453 K, permeate side pressure:1 bar.
Figure 71 illustrates that the MR outlet H₂O/CO molar ratio is an increasing function of the permeate side pressure for fixed W_cat/F_CO_0, but a convex function of W_cat/F_CO_0 for fixed permeate side pressures, with the minimum occurring around 50 (25) W_cat/F_CO_0, and being about 0.15 (1.2) for 1bar (5 bar) permeate side pressure, while at 95 W_cat/F_CO_0 the MR outlet H₂O/CO molar ratio is 0.2 (2.45) for 1bar (5 bar) permeate side pressure.

Based on the above simulation results, an appealing permeate-side pressure of 4 bar is identified, for which H₂ recovery only decreases by at most 25 %, CO conversion increases by at least 7 %, CO₂ loss decreases by about 18 %, and H₂O/CO molar ratios increase by a factor of 2 to 9 times, easily becoming larger than 1.1, as permeate side pressure increases from 1 bar to 4 bars.
* Permeate inlet temperature: 453 K, permeate side pressure: 1 bar, sweep ratio: 0.1.

6. 2. 1. 4. Temperature profiles in MR

* Permeate inlet temperature: 453 K, permeate side pressure: 1 bar, sweep ratio: 0.1.

Figure 74 illustrates that the MR axial temperature profiles for the retentate and permeate gas phases, and for the catalyst-pellet domain, are all increasing functions of \( \text{W}_{\text{cat}}/\text{F}_{\text{CO}_0} \). Figure 74 also illustrates that the difference between the retentate gas phase and the permeate gas
phase (catalyst-pellet domain) temperatures is +11 K (-8 K) for 20 $W_{\text{cat}}/F_{\text{CO}}$, and +0.5 K (-0.5 K) for 100 $W_{\text{cat}}/F_{\text{CO}}$.

6.2.2. Connecting MR with AR

Having identified above that an MR featuring a sweep ratio of 0.1 and permeate side pressure of 4 bar has appealing characteristics, a set of AR simulations was carried out for an AR fed by the retentate stream of an MR with 0.1 sweep ratio, 4 bar permeate side pressure, and a range of MR $W_{\text{cat}}/F_{\text{CO}}$ values. For each considered AR feed, a number of AR simulations are carried out for a range of AR $W_{\text{cat}}/F_{\text{CO}}$ values (50-200 g-cat*h/mol-CO), a range of AR $W_{\text{ad}}/W_{\text{cat}}$ values (4-10), and operating conditions of 250 °C, and 25 bars.

6.2.2.1. MR- $W_{\text{cat}}/F_{\text{CO}}$ and AR- $W_{\text{cat}}/F_{\text{CO}}$ effect on minimum/maximum AR operating times and corresponding average total conversions

The cyclical nature of an AR’s operation, suggests that the time for which the AR operates in reaction/adsorption mode is of great significance for AR process economics, flexibility and safety. It is therefore important to know the AR’s minimum and maximum operating times. Figure 75 illustrates that the minimum and maximum AR operating times are increasing functions of AR $W_{\text{cat}}/F_{\text{CO}}$, for various AR inlets, each of which is obtained for a different MR $W_{\text{cat}}/F_{\text{CO}}$ ratio. The minimum (maximum) time increases from about 200 s (300 s) for 80 MR $W_{\text{cat}}/F_{\text{CO}}$ and 50 AR $W_{\text{cat}}/F_{\text{CO}}$ ratio, to about 1500 s (2000 s) for 20 MR $W_{\text{cat}}/F_{\text{CO}}$ and 200 AR $W_{\text{cat}}/F_{\text{CO}}$ ratio. Figure 75 also illustrates that the minimum and maximum AR operating times are decreasing functions of MR $W_{\text{cat}}/F_{\text{CO}}$, for a fixed AR $W_{\text{cat}}/F_{\text{CO}}$ ratio. Indeed, as MR-$W_{\text{cat}}/F_{\text{CO}}$ increases, CO conversion at the MR exit increases, resulting in a higher CO$_2$ AR inlet flowrate, which then requires lower AR-$W_{\text{cat}}/F_{\text{CO}}$, and thus lower minimum and maximum AR operating times.
The minimum time of operation, defined as the time that CO$_2$ is first detected at the AR exit.

The maximum time of operation, defined as the time for which the time-averaged mass flowrate of carbon exiting the AR during the entire reaction/adsorption phase (including the carbon lost through the membrane) reaches 10%.

Figure 76 illustrates that the total (both MR and AR) time-averaged CO conversions, over both the minimum and maximum AR operating times, are increasing functions of AR W$_{cat}$/F$_{CO}$, for various AR inlets, each of which is obtained for a different MR W$_{cat}$/F$_{CO}$ ratio. As mentioned earlier, one of the most important success criteria for the proposed process is obtaining at least 95% total CO conversion through the combined MR/AR
system. However, as can be seen in Figure 76, the total min-95% CO conversion is not acquired for all cases and AR-W_cat/F_CO_0 values. The total conversion decreases, while the value of MR-W_cat/F_CO_0 decreases. The CO conversion averaged over the minimum (maximum) operating times shown in Figure 76- Left (Figure 15-Right), values of 75, 110, 200 (100, 190, >200) AR-W_cat/F_CO_0 are needed to attain 95 % total conversion for MR-W_cat/F_CO_0 values of 80,60,50, respectively. These results suggest that 95 % conversion can be attained either running MR at higher MR-W_cat/F_CO_0 values (around 70-80) and mid-range values of AR-W_cat/F_CO_0 (around 90-100) or running MR at mid-range MR-W_cat/F_CO_0 values (around 50-60) and higher values of AR-W_cat/F_CO_0 (above 200). Increasing the inlet H2O/CO molar ratio would be another alternative to achieve higher total conversions. Starting the MR at higher inlet H2O/CO molar ratios may have the following effects: (1) increasing MR conversion for lower MR-W_cat/F_CO_0 values, (2) decreasing permeate side pressure (increasing H2 recovery and CO2 lost through membrane), (3) having higher MR outlet H2O/CO values yields higher average toAR CO conversions, (4) increasing excess use of steam and decreasing production rate.
6.2.2. Wad/Wcat effect on minimum/maximum AR operating times and corresponding average total conversions

![Graphs showing AR CO2 breakthrough time and AR maximum operation time vs AR-W_cat/F_CO_0 values for various Wad/Wcat values. MR W_cat/F_CO_0=60.]

**Figure 79.** AR CO2 breakthrough time (Left) and AR maximum operation time (Right) vs AR-W_cat/F_CO_0 values for various Wad/Wcat values. MR W_cat/F_CO_0=60.

![Graphs showing exit-average total (MR+AR) CO conversion vs AR-W_cat/F_CO_0 values for various Wad/Wcat values. MR W_cat/F_CO_0=60.]

**Figure 80.** Exit-average total (MR+AR) CO conversion vs AR-W_cat/F_CO_0 values for various Wad/Wcat values. MR W_cat/F_CO_0=60.

The effect of Wad/Wcat on the AR’s minimum and maximum operating times and average total conversions is shown in Figures 77-78. As expected, CO2 breakthrough time and max operating times are favored by higher Wad/Wcat ratios. Increasing the Wad/Wcat ratios from 4 to 10 increases the CO2 breakthrough time from 500 sec to 2500 sec and the maximum
operating time from 700 sec to 2800 sec. All these results suggest that the MR-AR system easily meets the >95% H₂, CO₂ purity, >90% CO₂ capture, and >95% CO conversions criteria, demanded for IGCC power plants.

In this chapter, a comprehensive, multi-scale, computational fluid dynamics (CFD) based model for the novel membrane reactor-adsorptive reactor process is developed, and simulated. Repeated model simulations are carried out, to study the influence of the individual units’ operating and design parameters and to characterize acceptable ranges for these parameters, so as to meet predefined process performance specifications. These detailed simulation results suggest that the novel MR-AR process sequence readily fulfills carbon capture system (CCS) targets on CO conversion, H₂ purity, and CO₂ capture, and therefore represents a promising pre-combustion capture alternative for IGCC power plants.
Chapter 7. High efficiency unitary-modular process intensification

7.1. Introduction

The objective of this work is the multi-scale model simulation based design of alternative modular and intensified technologies for power plants containing one or more water gas shift reaction (WGSR) components. We investigate the applicability of different novel and efficient reactor configurations that include self-standing adsorptive reactors (ARs in parallel- base case), and combinations of low temperature membrane reactor (LTMR)- low temperature shift reactor (LTSR)- adsorptive reactor (AR)- adsorptive separator (AS) units (herein after referred to as the LTSR-AS, AS-LTSR-AS, LTMR-AS, AS-LTMR-AS, LTMR-AR unitary-modular systems). Comprehensive, multi-scale, multi-phase, computational fluid dynamics (CFD) models are employed to capture the behavior of these general, reaction/separation, steady-state/dynamic processes. Two intensification metrics are used for a comparative evaluation of alternative designs, and the most promising designs are identified.

In this study, we employ two intensification metrics, IM1 and IM2, as comparison criteria among alternative systems. IM1 is the ratio of the total mass of catalyst that needs to be purchased for process operations to be initiated in the considered design, over the corresponding catalyst quantity in the baseline design. These masses are capital cost surrogates related to catalyst purchases, and thus IM1 is a capital cost related intensification metric. IM2 is the ratio of the total mass of catalyst that is in a reactive environment at any given time in the considered design, over the corresponding catalyst quantity in the baseline design. Catalysts have a finite lifetime, T, after which they are no longer functional. Relevant quantities often used in relation to a catalyst’s lifetime are the Turnover Number, TON, defined as moles of reactant transformed into product by one mole of catalyst active sites before catalyst becomes deactivated, and the
Turnover Frequency, TOF, defined as moles of reactant transformed into product by one mole of catalyst active sites per unit time. These quantities satisfy the relation TON=TOF*T. Defining as \( N_M \) the moles of catalyst active sites over the mass of the catalyst, then suggests that the moles of reactant transformed into product by an M amount of catalyst over a period of time T, after which the catalyst becomes inactivated, is \( \text{TOF} \times T \times N_M \times M \). Thus the mass of catalyst that is in a reactive environment at any given time in a considered design, is a surrogate for the design’s operating cost related to the catalyst’s replacement. Therefore, IM2 is an operating cost related intensification metric. IM1 and IM2 are therefore both equal to 1 for the baseline design, which consists of two AR’s operating in parallel, with one AR being in reaction mode, while the other AR is in regeneration mode. An alternative process is considered to be superior to the baseline design, if both its metrics are less than 1. Similarly, an alternative process is superior to another alternative process, if both its metrics are lower than the corresponding metrics of the other process. It may also be the case that a process is superior to another process in regard to one metric but inferior in regard to another metric.

7.2. Results and Discussion

7.2.1. AR Process

We carried out the simulations using an inlet feed composition of \((\text{H}_2/\text{CO}/\text{H}_2\text{O}/\text{CO}_2/\text{CH}_4) = (2.76/1.00/3/2.15/0.84)\), which corresponds to a coal-derived syngas (from an air-blown gasifier) intermixed with steam.
Figure 81. AR exit CO$_2$ mole fraction (Left) and CO conversion (Right) vs operating time. (W$_{cat}$/F$_{CO}$=140 g*h/mol, Wall-isothermal).

From Figure 81 (Left), the AR operation time, defined as the time that CO$_2$ is first detected at the reactor exit, is shown to be around 35 min. The average CO conversion in the AR (Figure 81-Right) is 98.33%, and it is evident from this level of conversion that the presence of the adsorbent significantly augments AR performance by shifting the reaction equilibrium towards the product side. Eventually, the adsorbent becomes completely saturated and the AR ceases operating as a PBR. For the remainder of this chapter, the aforementioned AR performance criteria (35 min operating time and 98.33% CO conversion) is used as a based-case scenario. The obtained intensification metrics for the baseline are both (IM1 and IM2) 1.

Figure 82. AR CO$_2$ loading for switch time 35 min and 5 operating cycles.

Figure 82 illustrates the captured CO$_2$ in the AR for adsorption and desorption steps for various operating cycles. For each cycle, a subtraction of the remaining CO$_2$ during the
desorption step from the captured \( \text{CO}_2 \) during the adoption step in the AR gives the net adsorbed \( \text{CO}_2 \) for each cycle. Figure 82 shows that the AR reactor operates at steady-state conditions by the fourth cycle. In other words, the amount of adsorbed \( \text{CO}_2 \) for each adsorption/desorption cycle approaches the constant value during the fourth cycle. Therefore, these results confirm the possibility of operating the AR cyclically for any reasonable operating time.

7.2.2. AR Process Low Temperature Shift Reactor (LTSR)/Adsorptive Separation (AS) Sequence in a Modular Form

In this study, we consider an LTSR/AS sequence in a modular form (Figure 83) as an alternative process (modular process 1) to the baseline AR process. In our proposed process 1, each module consists of an LTSR followed by two AS units, operating simultaneously due to the cyclical nature of an AS unit’s operation. During operation, the reaction takes place in the LTSR while the separation is carried out in the AS unit (selective to \( \text{CO}_2 \)). These steps are repeated within each module. A LTSR is packed with low temperature shift catalyst while an AS unit is packed with Hydrotalcite adsorbent. The operating conditions (Feed composition, inlet pressure/temperature, etc.) considered for the LTSR/AS sequence are identical to the AR process. A potential advantage of this process, over the latter, is the utilization of all available catalyst in the LTSR. Since half of the catalyst in the AR process remains unused during the desorption step, this alternative sequence leads to increased intensification of the process through reduction of the total catalyst amount.
Figure 83. An alternative modular process I.

![Diagram of LTSR and AS processes](image)

**Figure 84.** LTSR conversion (Left-Adiabatic) and AR exit CO\(_2\) mole fraction (Right-wall isothermal) for single module process. (\(W_{\text{cat}}/F_{\text{CO}}=140 \text{ g}\cdot\text{h/mol}\)).

Figure 84 illustrates the CO conversion (Left) in the LTSR and CO\(_2\) exit mole fraction in the AS unit for a single module. Like the AR process, the operating time of the AS unit is about 35 min. Even though all the available catalyst (same amount of catalyst used in AR process) is utilized, 76.7% conversion is achieved in the LTSR for a single module. Based on these results, it is obvious that a single module LTSR/AS process is inferior to the AR process.
The effect of increasing the number of modules is substantial (Figure 85), with the LTSR showing around 97.16% conversion (26.67% increase in conversion for same amount of catalyst) in the 6th module. Indeed, the increasing number of modules provides higher conversions but 95.43% of the 26.67% conversion improvement is observed at the transition from one module to two modules. Figure 85 suggests that utilizing a minimum of two modules in the process is enough to achieve a desirable/significant increase in conversion. However, an obtained conversion of 97.16%, with six modules, is still less than the AR process conversion of 98.33%

For the LTSR/ AS sequence in a modular form, while the IM1 is 1, the IM2 is 2.

**Figure 85. LTSR conversion vs number of modules in process.**

**Figure 86. Effectiveness factor axial profile in LTSR.**

Figure 86 illustrates the effectiveness factor (the ratio of the real reaction rate in a catalyst particle divided by the hypothetical rate that would result if conditions inside the particle were
the same as those prevailing at the particle’s surface) for the LTSR along the reactor axis. Figure 86 indicates that for the adiabatic reactor condition the effectiveness factor decreases along the length (0.9→0.775). A possible explanation for the behavior observed during adiabatic operation is that the reacting mixture’s temperature increases along the length, thus accelerating the intrinsic kinetics of the WGSR more than the diffusivities and the transport rates of all species, thus resulting in stronger diffusional limitations as one moves down the length of the reactor.

Process Conditions:
LT-MR (523 K, 25 bar)
Cooling to 523 K
AS-Adsorption (523 K, 25 bar)
AS-Desorption (723 K, 25 bar)

Process Outcomes:
97.16% Conversion
35 min of operating time
Separation CO2 at 25 bar
66.6% Compressor Power Reduction

Comparison Metric:
IM1=1
IM2=2

7.2.3. Adsorptive Separation (AS)/Low Temperature Shift Reactor (LTSR)/Adsorptive Separation (AS) Sequence in Modular Form:

AS/LTSR/AS sequence in a modular form is considered as second alternative process. Starting from the second module (depicted in Figure 87), the process has the same configuration as LTSR/AS sequence, but the first module is only composed of minimum two AS units, operates simultaneously.

Figure 87. An alternative modular process 2.
Figure 88 indicates the effect of the number of modules on the performance of alternative process 2. Modification (adding an AS unit in front of the first LTSR) of the alternative process 1 improves the single LTSR conversion from 76.7% to 92% (19.95% enhancement). Also, a conversion enhancement of 97.16% →98.682% is obtained through the 6-modular LTSR sequence. The alternative process 2 achieves the same conversion as the AR process when a minimum of 7 modules are employed. When the average AR process conversion of 98.33% (base case) is attained, the alternative process 2 saves around 6-7% of catalyst (Fig. 12-Right) with a configuration of 7-10 modules. The IM1 and IM2 are 0.93 and 1.86 for AS/LTSR/AS sequence in a modular form.

7.2.4. Low Temperature Membrane Reactor (LT-MR)/Adsorptive Separation (AS) Sequence in Modular Form

A configuration of LT-MR/AS sequence in a modular form (depicted in Figure 90) is a promising technology, as a third alternative to AR process. In this process (MR+AS), reaction/separation is performed in MR (selective to H₂), and separation is carried out in AS.
(selective to CO₂). During the process, reaction’s products (e.g. H₂) continuously removed from the bulk gas phase by shifting the chemical equilibrium to more product formation. The use of MR/AS has potential to intensify process by saving a significant amount of catalyst. Compared to AR process, the major advantage of this design is that all available amount of the catalyst can be used in MR since half of the catalyst does not process in AR system due to desorption step. Thus, this design increases the possibility to intensify process by reducing reactor volume, packed with catalyst.

For design aspects, a membrane reactor consists of a pressure vessel that houses several membrane bundles, each bundle consisting of multiple CMS membrane tubes. These bundles typically consist of CMS membrane tubes, whose dimensions are an inner and outer diameter of 3.5mm and 5.7 mm respectively, and a length of 1m (Figure 89). A membrane reactor (MR) consists of 1400 bundles in parallel (1 m of each) and 9800 bundles in total (7 m reactor-Figure 13). 60%, 75% and 90% H₂ (produced in the first LTSR) separations are achieved by varying the number of tubes in the first LTMR and then, reject’s side gas mixture is fed through the second LTMR. Again, above 90% H₂ separation performance is achieved in the third alternative process.
Figure 89. A schematic of the configuration for the sequence of MRs and 1-D Representation of control volumes in a Membrane Reactor.

Same syngas composition as conventional process is used as the feed to the MR. In the simulations, the membrane permeances (m³/m².h.bar) were taken to be: H₂=1; CO=0.0125; CO₂=0.025; CH₄=0.00806, H₂O=0.333, which are typical of values we measure with high-quality CMS membranes prepared by our industrial collaborators in this project (Media and Process Technology, Inc.). The detail about the derivation of the MR model equations and simulation results can be found in the previous publication of our group (see [17]). In MS simulations, we used same membrane characteristics and removed reaction zone (catalyst) effect from system.

Figure 90. An alternative modular process 3.
The CO conversion (Left) in the LT-MR and CO₂ exit mole fraction (Right) of the AS unit for a single module is shown in Figure 91. Throughout this chapter, we keep the operating time around 35 min as the same amount of adsorbent is used for all simulations. Although all the available catalyst (same amount of catalyst used in AR process) is utilized, a single LT-MR achieves maximum 97.8% conversion (less than AR conversion of 98.33%). However, when we increase the module number to 2, almost full conversion (99.7%) is achieved by the proposed process 3. Besides H₂, other species such as CO, CO₂, H₂O and CH₄ can also pass through the permeate side, so up to 1% of CO is lost during the membrane separation process. Thus, we must consider the real MR conversion to be 98.7%. In conclusion, these results suggest that minimum two modular configuration must be employed to reach the desired improvement for the process. A decisive design aspect of the alternative process 3 is a conversion limit for the first LT-MR in module 1. Decreasing the conversion in first LT-MR (designing the MR to deliver a specified conversion) from 80% to 5% results in a reduction of the required amount catalyst by more than 6% (see Figure 92).
Figure 92. Catalyst Reduction vs first LT-MR conversion.

Figure 93. Effectiveness factor axial profile in LT-MR.

Figure 93 shows the changes of the effectiveness factor in the MR along its length. Also, it decreases significantly in the axial direction, thus raising significant doubts over the commonly employed constant effectiveness factor assumption. The obtained IM1 and IM2 are 0.3066 and 0.6212 for LT-MR/AS sequence in a modular form.

**Process Conditions:**
- LT-MR (523 K, 25 bar)
- Cooling to 523 K
- AS-Adsorption (523 K, 25 bar)
- AS-Desorption (723 K, 25 bar)

**Process Outcomes:**
- 98.7% Conversion
- 35 min of operating time
- Separation CO2 at 25 bar
- 66.6% Compressor Power Reduction

**Comparison Metric:**
- IM1 = 0.3066
- IM2 = 0.6212
7. 2. 5. Adsorptive Separation (AS)/Low Temperature Membrane Reactor (LT-MR)/Adsorptive Separation (AS) Sequence in Modular Form

As another option to LT-MR/AS sequence in a modular form, we add extra AS module in front of LT-MR/AS module (depicted in Figure 94) to observe the effect on the process performance. Indeed, AS places a significant synergy on the process performance, so AS/LT-MR/AS configuration accomplishes 99.8% conversion (Figure 95), and 72% catalyst reduction in a single LT-MR unit. The real MR conversion is around 99% after a subtraction of the lost CO through the membrane. These results give the IM1 and IM2 as 0.28 and 0.5656. In conclusion, these results suggest that two modular configurations is sufficient to reach desired improvement for the process.

*Figure 94. An alternative modular process 4.*
7.2.6. Low Temperature Membrane Reactor (LT-MR)/Adsorptive Reactor (AR) in Sequence

We consider LT-MR/AR in sequence (Figure 96) as a final alternative process. The process reduces 52% of catalyst and attains 99.1% conversion. LT-MR/AS sequence is the most efficient process by having IM2 of 0.486. However, the configuration of LT-MR/AR achieves IM1 of 0.48 (less than the configurations of LT-MR/AS and AS/LT-MR/AS) because of the unused amount of catalyst.

Figure 95. LTMR conversion for single AS/LT-MR/AS module.
Figure 96. LT-MR conversion (Left-Adiabatic) for single LT-MR.

7.3. Conclusions

In this study, a process intensification-aimed comparative study is performed for a variety of WGSR technologies. The obtained multi-scale simulation results can be summarized as follows:

1- Based on the intensification metric of IM1, AS/LT-MR/AS, LT-MR/AS and LT-MR/AR are the most promising substitute processes compared to the baseline ARs. The IM1 based comparison results in the following order: AS/LT-MR/AS (IM1=0.28, 99% conversion- 2 modules)> LT-MR/AS (IM1=0.3066, 98.7% conversion- 2 modules)> LT-MR/AR (IM1=0.48, 99.1% conversion- 1 module)> AS/LTSR/AS (IM1=0.93, 98.68% conversion- 10 modules)> **ARs (IM1=1, 98.63% conversion)** >LT SR/AS (IM1=1, 97.16% conversion).

2- The IM2 based comparative study delivers LT-MR/AR as the most efficient configuration by IM2 of 0.486. The IM2 based comparison results in the following order:
LT-MR/AR (IM2=0.486, 99.1% conversion - 1 module) > AS/LT-MR/AS (IM2=0.5656, 99% conversion - 2 modules) > LT-MR/AS (IM2=0.6212, 98.7% conversion - 2 modules) > ARs (IM2=1, 98.63% conversion) > AS/LTSR/AS (IM2=1.86, 98.68% conversion - 10 modules) > LTSR/AS (IM2=2, 97.16% conversion).
Chapter 8. A Hybrid Adsorptive-Membrane Reactor (HAMR) for Intensification of the Water-Gas Shift (WGS) Reaction Process

8.1. Introduction

The Hybrid Adsorptive-Membrane Reactor (HAMR) is a dynamically operated process, which consists of a metal tube containing one or more tubular membranes. In this chapter, a mathematical model of HAMR is developed and simulated. The aim of this effort is to intensify the water gas shift (WGS) reaction process for hydrogen production. Indeed, the coupling of reaction and separation in the HAMR process can substantially improve reactant conversion, product selectivity, and can even yield near pure products. In addition, for reversible reactions such as the WGS, the HAMR process can be designed so as to deliver reactant conversions that exceed even equilibrium conversions attainable in conventional reactors. The proposed HAMR model equations are developed in the dimensionless form, and the effect of the key dimensionless group is studied on the HAMR performance. To this end, the performance of the traditional packed bed reactor (PBR), membrane reactor (MR) and adsorptive reactor (AR) is compared to the HAMR.

8.2. HAMR System

8.2.1. Design of the HAMR

A HAMR is composed of the reaction-adsorption and permeation zones. In addition, the reaction-adsorption zone, localized in between internal wall of the HAMR module and the membrane tubes’ external surfaces, is comprised of three domains: the catalyst-pellet, adsorbent-pellet, and bulk gas phase domains. Each HAMR module (depicted in Figure 97) consists of multiple CMS membrane tubes (85 tubes), whose dimensions are an inner and outer diameter of 3.5mm and 5.7mm respectively, and a length of 1m. A parallel and series combination of these
HAMR modules results an industrial scale HAMR unit. A typical industrial-scale HAMR unit may include approximately 1000 HAMR module in total. In HAMR, simultaneous reaction-separation process take place. During the process, the reaction products are continuously removed from the bulk gas phase (membrane tube is selective to H\(_2\) and adsorbent is selective to CO\(_2\)). In the permeation zone, the hydrogen is carried away by a sweep gas (steam, in this study) flowing either co-currently or counter-currently to the reacting mixture.

\[
\begin{align*}
\text{Catalyst Pellet} & \quad \text{Adsorbent Pellet} \\
\text{Sweep: H}_2\text{O} & \quad \text{Sweep: H}_2 \\
\text{Reactant: CH}_4, \text{H}_2, \text{CO, CO}_2, \text{H}_2\text{O, H}_2\text{S} & \quad \text{Products: CH}_4, \text{H}_2, \text{CO, CO}_2, \text{H}_2\text{O, H}_2\text{S} \\
\end{align*}
\]

\[\text{Reaction Zone} \quad \text{Permeation Zone} \]

**Figure 97. 1-D Representation of control volumes in a HAMR module.**

8.2.2. Integration of the HAMR System in Power Generation Process

A conventional Integrated Gasification Combined Cycle (IGCC) power generation plants convert coal into syngas (containing CO/H\(_2\)/CO\(_2\) with small amounts of CH\(_4\) and impurities) via a high-pressure gasifier in the presence of steam and oxygen. The process gas stream passes from the reformer system through the adiabatic two-stage water gas shift reactors’ system. In industry, water gas shift reactors consist of two different temperature stages, the high-temperature shift reactor (HTSR) and the low-temperature shift reactor (LTSR) with a cooling process between them is a recommended for the operation of hydrogen generation. This system (HTSR + Cooling +LTSR) enables to reach higher CO conversions and desired level of hydrogen production. Thus, most of the CO is consumed in the HTSR, and rest of the CO
Subsequently, the CO$_2$ is removed from the stream usually through an absorber with amine-based solvents prior to undergoing compression for future transport and sequestration. The resultant stream is hydrogen rich and mixed with nitrogen diluent before entering an F-class gas-turbine to produce power. In the United States, the current efforts demonstrate that coal-based power production in IGCC will continue in the foreseeable future, and while current technology has significantly reduced SO$_2$, NO$_x$, and p.m. emissions, CO$_2$ emissions continue to be a problem. For this reason, a significant efforts in both academia and industry are shown on CCS technology as the primary process for the reduction of domestic and global CO$_2$ emission from coal power plants. However, the current CCS systems require additional energy compared to projects without CCS. According to the U.S. National Energy Technology Laboratory (NETL), the efficiency of an IGCC power plant with CO$_2$ capture decreases approximately 15-20% compared to an IGCC power plant without CO$_2$ capture. Thus, further improvement and development are required for CCS technology to achieve acceptable market levels. For this reason, the novel hybrid alternative process (HAMR) is proposed in this work as a more efficient and realizable alternative to standard pre-combustion CCS technology. As demonstrated in Figure 98, we study in this paper the applicability to the IGCC process of a novel and efficient HAMR process. In the process scheme in Figure 98, the syngas produced through gasification of coal is directed into the HAMR system that produces a hydrogen-rich stream for power generation and a pure, high-pressure CO$_2$ stream ready for sequestration. The hydrogen-rich stream produced by the HAMR skid goes through a heat and power generation unit consisting of hydrogen turbines, producing energy to match the target levels defined by the performance attributes. Thus, the proposed process has the potential to become a highly efficient and ultra-compact process that produces H$_2$ for use in IGCC with simultaneous CO$_2$ capture.
WGSR has also gained renewed interest recently, in both the industrial and academic sectors, due to its potential use as a main route for hydrogen production in environmentally-friendly IGCC coal power-plants, as noted above. There has been, therefore, a recent significant increase in WGSR-related studies, aiming to improve existing technologies and to potentially develop new processes that can reduce production costs.

The WGSR and CO$_2$/H$_2$ separation are carried out simultaneously in a HAMR. Therefore, the HAMR holds the promise of intensifying IGCC plants by combining multiple units into one. Due to dynamic operation feature, HAMR can be utilized in the flexible operating times (between the minimum and maximum operating times). While the minimum time of operation is defined as the time that CO$_2$ is first detected at the reactor exit, the maximum time of operation can be defined as the time for which the corresponding time-averaged mass flowrate of carbon exiting the HAMR during the entire reaction/adsorption phase up to that point reaches 5% (a common carbon capture goal for IGCC plants) of the constant mass flowrate of carbon entering the AR during the same period. In our proposed HAMR system (depicted in Figure 98), we have two HAMRs operating simultaneously; this is due to the cyclical nature of the AR operation, which consists of a reaction/adsorption phase and a desorption phase. At any given time, one of the reactors is fed with syngas, which undergoes the WGSR and CO$_2$ adsorption, and generates a carbon-depleted gas consisting of water and hydrogen, while the other reactor is...
fed with steam, which induces CO₂ desorption from the CO₂-rich adsorbent pellets, and generates a stream consisting of CO₂ and H₂O. This operation mode is referred to as one step, and in the subsequent step the reactor roles are reversed.

Having flexible, multi-component syngas clean-up and multi-product production system, minimizing the greenhouse gas (CHG) capture and disposal costs associated with current IGCC plants via the adoption of the reactive-separations technology, minimizing capital and operating costs, maximizing the profitability of IGCC power plant by increasing their power generation capacity are the possible outcomes of the HAMR system. The conventional process generates a pure CO₂ stream at approximately 1 bar, which must then be compressed to approximately 150 bar for sequestration/utilization purposes. This compression step consumes a significant portion of the power produced by the power plant. In contrast, the HAMR operates at much higher pressures (>20 bar), which are close to the power plant gasifier’s operating pressure, and naturally delivers a pure CO₂ stream at these higher pressures, attaining significant energy savings.

During the HAMR desorption step, the obtained CO₂/H₂O gas mixture (at the exit of the reactor) is separated at the same pressure as the reactor exit, and the separated high-pressure H₂O is recycled in the desorption step, without the need for repeated compression. Indeed, CO₂ compression is a significant contributor to the energetic cost of carbon capture systems. Integration of the proposed HAMR system within the IGCC attains a more efficient CCS than those currently proposed, that can nevertheless deliver carbon capture as high as 100 %, thus reducing the environmental impact of coal power plants.

There are several other key advantages of the proposed technology with favorable economic impact. They include lower operating temperatures, lower steam requirements,
reduced catalyst use, and high-purity product streams. The AR system operates at lower reaction temperatures, since only low-temperature WGS catalyst is used in the process, as there is no need for high temperature operation and catalyst anymore, thus reducing material costs and increasing process safety. Compared to the conventional process, the AR process reduces catalyst and steam use, since it can attain conversions that exceed even equilibrium conversions attainable in traditional HTSR+LTSR sequences. Further, the proposed HAMR process reduces the need for downstream CO₂ separation and enables production of H₂ and CO₂ with high purity greater than 95%.

8. 2. 3. Multi-scale Modeling of the HAMR

From a physical standpoint, the HAMR is a multi-scale, multiphase system that encompasses different process functions in various regions of the device. The reaction zone in the HAMR is modeled at two different scales: the so-called microscale, which considers catalyst/adsorbent pellet-scale features, including average pore size, reaction/adsorption rates, material properties, and shape; and the macroscale, which considers reactor scale features including membrane module dimensions, membrane tube characteristics, and catalyst/adsorbent packing void fraction. The permeation zone is modeled at the macroscale level only, as in the HAMR configuration studied here it contains no catalyst and/or adsorbent pellets.

In the multi-scale approach, HAMR is modeled as individual domains and sub-domains, so that one can properly assess the contribution of each of their parameters to the overall system. While catalyst pellet, adsorbent pellet, bulk gas phase in reaction zone and bulk gas phase in permeation zone are considered individual domains, solid and fluid phases in catalyst/adsorbent pellet are counted as sub-domains. The Reynolds Transport Theorem (RTT) is applied separately to each of these domains and sub-domains to obtain conservation equations. The resulting time-
dependent equations are implemented in the COMSOL software package and solved simultaneously in all three aforementioned domains along the length of the HAMR, using the finite element method (FEM).

The catalyst and adsorbent pellet domains are distributed along the reactor axis, contributing source terms to the reactor domain equations, while receiving information regarding the reactor gas conditions prevalent at the pellet boundary. Indeed, solution of the differential equations describing the system behavior in the pellet interior requires information from the pellet boundary. On the other hand, solution of the differential equations describing the system behavior in the reactor interior requires source term information related to the pellet boundary. Information regarding gas pressure, temperature, velocity, and species’ concentrations in the reactor domain, is provided to the catalyst and adsorbent pellet domains, and temperature and species flux information in the catalyst and adsorbent pellet domains is provided to the reactor domain. The solution of the overall differential equation system is carried out in a simultaneous matter. At the end of this process, temperature, pressure, and species profiles are known at each axial location within the reactor domain, and at each pellet domain radial, reactor domain axial local pair.

In order to gauge the impact of the underlying transport and reaction (catalyst pellet) and sorption (adsorbent pellet) processes, instantaneous effectiveness factors are calculated. They are defined as ratios of the real uptake rate (due to combined transport and reaction or adsorption) of a given species by the catalyst/adsorbent pellet over the same uptake rate in the absence of transport limitations, i.e., when the gas phase concentration within the particle is the same with that prevailing at the pellet’s external surface.
8. 3. Dimensionless Mathematical Formulation

In the derivation of the model’s equations, the Reynolds Transport Theorem is applied separately to each of the domains. Geometrical parameters of volumetric porosity \((\varepsilon_v = \text{volume of voids/total volume})\), area porosity \((\varepsilon_a = \text{area of voids/total area})\) and area-to-volume factor \((\varepsilon_t = \text{area of porous wall/total volume})\) are used in the derivation of these model’s equations.

To facilitate spatial integration in the development of a general mathematical model, a differential volume occupied by each phase is correlated with a differential volume of the respective system. For the catalyst pellet, this relation defines what is known as volumetric porosity, while the volumetric void fraction is used for this relationship in the reactor. Similarly, for the surface integration in a multiphase system, one can use the same approach to define a correlation between the differential area occupied by each phase and the respective system’s differential area, determining the area porosity and area void fraction, for the pellet and the reactor systems respectively. The catalyst pellet, adsorbent pellet, reactor domain and permeation domain are identified by the superscripts \(c\), \(a\), \(r\) and \(per\). The catalyst-adsorbent pellets and reactor domains composed by solid or fluid phases, identified by the subscripts \(f\), and \(s\) respectively. The symbols \(\gamma\) and \(\alpha\) will represent phases and domains, respectively.

8. 3. 1. Dimensionless Variables

First, dimensionless variables are defined. The model will be presented in terms of these dimensionless variables.

\[
R_i^\alpha = \frac{R_i^c}{R_i^a}, \quad c_i^\alpha = \frac{c_i^c}{c_i^a}, \quad \bar{v}^\alpha = \frac{v^c}{v^a}, \quad \bar{r}^\alpha = \frac{r^c}{r^a}, \quad \bar{N}_i^\alpha = \frac{N_i^c}{N_i^a}, \quad \bar{c}^\alpha = \frac{c^c}{c^a}, \quad \bar{T}^\alpha = \frac{T^c}{T^a}, \quad \bar{P}^\alpha = \frac{P^c}{P^a},
\]

\[
\bar{x}^\alpha = \frac{x^c}{x^a}, \quad \bar{p}^\alpha = \frac{p^c}{p^a}, \quad \bar{c}_p^\alpha = \frac{c_{p,i}^c}{c_{p,i}^a}, \quad \bar{v}^\alpha = \frac{v^c}{v^a}, \quad \bar{a}^\alpha = \frac{a^c}{a^a}, \quad \Delta \bar{H}^\alpha = \frac{\Delta H^c}{\Delta H^a}, \quad \bar{c}_i^\alpha = \frac{c_i^c}{c_i^a}, \quad \bar{T}^\alpha = \frac{T^c}{T^a}, \quad \bar{j}_{\text{per}}^\alpha = \frac{j_{\text{per},c}}{j_{\text{per},a}}.
\]
\[ \bar{T}_{\text{per}} = \frac{J_{i\text{per}}}{J_{i}}, \quad \bar{V} = \frac{V_{i}}{V_{j}}, \quad \bar{n}_{i} = \frac{n_{i}^{l}}{n_{j}^{l}}, \quad \bar{z} = \frac{z}{z_{j}}, \quad \bar{P} = \frac{P_{i}}{P_{j}}, \quad \bar{h}_{i}^{l} = \frac{h_{i}^{l}}{h_{j}^{l}}, \quad \bar{T}_{\text{per}} = \frac{T_{i\text{per}}}{T_{j}}, \quad \bar{x} = T_{i\text{per}} = \frac{T_{j}}{T_{\text{per}}}, \quad \bar{\lambda} = \frac{\lambda_{i}}{\lambda_{j}}. \]

8. 3. 2. Molar based catalyst/adsorbent pellet-scale model equations

The final component mass, energy and momentum conservation equations of the catalyst and adsorbent pellets can be expressed as following;

8. 3. 2. 1. Component mass conservation

**Adsorbent Pellet Fluid:**

\[ -R_{f,i}^{a} = \frac{\partial}{\partial t} \left( e_{f,V,i}^{a} c_{i}^{a} \right) + \nabla \cdot \left( e_{f,A,i}^{a} N_{i}^{a} \right) \Rightarrow \]

\[ \frac{\bar{R}_{i}^{a}}{e_{f,A,i}^{a} N_{i}^{a}_{i}} \bar{R}_{i}^{a} = \frac{e_{f,V,i}^{a} \bar{v}_{i}^{a}}{e_{f,A,i}^{a} N_{i}^{a}_{i}} \bar{c}_{i}^{a} + \frac{1}{\bar{r}^{2}} \frac{\partial \left( \bar{r}^{2} N_{i}^{a} \right)}{\partial \bar{r}} \Leftrightarrow D_{i}^{a} \bar{R}_{i}^{a} = \frac{\partial \bar{c}_{i}^{a}}{\partial \bar{t}} + \frac{1}{\bar{r}_{i} \bar{r}^{2}} \frac{\partial \left( \bar{r}^{2} N_{i}^{a} \right)}{\partial \bar{r}}; \quad i = \text{CO}_{2} \quad (150) \]

**Catalyst Pellet Fluid:**

\[ -R_{f,i}^{c} = \frac{\partial}{\partial t} \left( e_{f,V,i}^{c} c_{i}^{c} \right) + \nabla \cdot \left( e_{f,A,i}^{c} N_{i}^{c} \right) \Rightarrow \]

\[ \frac{\bar{R}_{i}^{c}}{e_{f,A,i}^{c} N_{i}^{c}_{i}} \bar{R}_{i}^{c} = \frac{e_{f,V,i}^{c} \bar{v}_{i}^{c}}{e_{f,A,i}^{c} N_{i}^{c}_{i}} \bar{c}_{i}^{c} + \frac{1}{\bar{r}^{2}} \frac{\partial \left( \bar{r}^{2} N_{i}^{c} \right)}{\partial \bar{r}} \Leftrightarrow D_{i}^{c} \bar{R}_{i}^{c} = \frac{\partial \bar{c}_{i}^{c}}{\partial \bar{t}} + \frac{1}{\bar{r}_{i} \bar{r}^{2}} \frac{\partial \left( \bar{r}^{2} N_{i}^{c} \right)}{\partial \bar{r}}; \quad i = 1, N_{s} \quad (151) \]

8. 3. 2. 2. Energy conservation

**Adsorbent Pellet Fluid:**

\[ \left\{ \nabla \cdot \left[ \lambda^{a} \bar{\nabla} T^{a} \right] + (-\Delta H_{\alpha}^{a} \cdot R_{\alpha}^{a}) \right\} = \left\{ e_{f,V,i}^{a} \rho_{s} C_{V,s}^{a} + \sum_{i=1}^{N_{s}} e_{f,V,i}^{a} C_{P,s}^{a} \frac{\partial T^{a}}{\partial \bar{t}} \right\} \Rightarrow \]

\[ + \left[ \sum_{i=1}^{N_{s}} e_{f,V,i}^{a} C_{P,s}^{a} \bar{v}_{i}^{a} \right] \bar{\nabla} T^{a} \]
\[
\begin{align*}
&\left\{ \frac{\bar{\lambda}^a}{\dot{\varepsilon} C_i C_r} \frac{\partial}{\partial \bar{T}^a} \left[ (\bar{\lambda}^a) \frac{\partial \bar{T}^a}{\partial \bar{T}} \right] + \frac{(\Delta \bar{H}^a \bar{R}^a)}{\dot{\varepsilon} C_i C_r} \frac{\partial \bar{T}^a}{\partial \bar{T}} \right\} = \left\{ \frac{\varepsilon^a}{\dot{\varepsilon} C_i C_r} \frac{\partial \bar{T}^a}{\partial \bar{T}} \right\} + \frac{\partial \bar{T}^a}{\partial \bar{T}} \right) \\
&\Rightarrow \frac{1}{\pi \bar{P}^a} \cdot \frac{\partial}{\partial \bar{T}} \left[ (\bar{\lambda}^a) \frac{\partial \bar{T}^a}{\partial \bar{T}} \right] + \pi \bar{P}^a \cdot (\Delta \bar{H}^a \bar{R}^a) = \frac{\partial \bar{T}^a}{\partial \bar{T}} + \frac{1}{\pi \bar{P}^a} \cdot \frac{\partial \bar{T}^a}{\partial \bar{T}}, \quad \text{rx = Adsorption} 
\end{align*}
\]

Catalyst Pellet Fluid:

\[
\begin{align*}
&\left\{ \bar{\nabla} \cdot \left[ (\bar{\lambda}^c) \bar{\nabla} \bar{T}^c \right] + \frac{(\Delta \bar{H}^c \bar{R}^c)}{\dot{\varepsilon} C_i C_r} \frac{\partial \bar{T}^c}{\partial \bar{T}} \right\} = \left\{ \frac{\varepsilon^c}{\dot{\varepsilon} C_i C_r} \frac{\partial \bar{T}^c}{\partial \bar{T}} \right\} + \left[ \sum_{i=1}^{\nu} \frac{\varepsilon^i C_i C_r}{\dot{\varepsilon} C_i C_r} \bar{P}^i \bar{T}^i \right] \cdot \bar{\nabla} \bar{T}^c \\
&\Rightarrow \frac{1}{\pi \bar{P}^c} \cdot \frac{\partial}{\partial \bar{T}} \left[ (\bar{\lambda}^c) \frac{\partial \bar{T}^c}{\partial \bar{T}} \right] + \pi \bar{P}^c \cdot (\Delta \bar{H}^c \bar{R}^c) = \frac{\partial \bar{T}^c}{\partial \bar{T}} + \frac{1}{\pi \bar{P}^c} \cdot \frac{\partial \bar{T}^c}{\partial \bar{T}}, \quad \text{rx = WGSR} 
\end{align*}
\]

The initial and boundary conditions for the solution of conservation equations is represented as following;

\[
\begin{align*}
\begin{cases}
c_i^a = \left( c_i^a \right)_{in} & \bar{c}_i^a = 1 \\
T^a = T_r^a = T_{in} & \bar{T}^a = \bar{T}_r^a = 1 \\
P^a = \left( P^a \right)_{in} & \bar{P}^a = 1 \\
Q_r = -\bar{\lambda}^a \bar{\nabla} \bar{T}^a = 0 & \text{for } \bar{T} = 0, \forall r \\
\bar{\nabla} \bar{P}^a = 0 & \text{for } \bar{T} = 0, \forall r
\end{cases}
\end{align*}
\]
Boundary Conditions:

\[
\begin{align*}
N_i^a &= 0 \\
\bar{Q}_r &= -\lambda^a \bar{V} T^a = 0 \quad \text{for } r = 0 & \Rightarrow & \quad N_i^a &= 0 \\
\bar{V} P^a &= 0 \\
\frac{\partial P^a}{\partial r} &= 0
\end{align*}
\]

\[
\frac{k_m}{Sh^a} \left( \bar{c}_i^r - \bar{c}_i^a \right) = \bar{N}_i^a
\]

\[
\frac{h^a r^2}{\lambda^a} \left( \bar{T} - \bar{T}_i^a \right) = -\frac{\partial \bar{T}^a}{\partial r} + \left( \sum_{j=1}^{n} \bar{C}_j^a \bar{v}_j^a \bar{r}^a \right) \frac{\lambda^a}{Pe^a}
\]

\[
Sh^a \cdot \left( \bar{c}_i^r - \bar{c}_i^a \right) = \bar{N}_i^a
\]

\[
Nu^a \cdot \left( \bar{T} - \bar{T}_i^a \right) = -\frac{\partial \bar{T}^a}{\partial r} + Pe^a \cdot \bar{T}^a \quad \text{for } \bar{r} = 1
\]

\[
\bar{P}^a = \bar{P}_r
\]

8.3.3. Molar based reactor-scale model equations

The final component mass, energy and momentum conservation equations of the reactor domain can be expressed as following;

8.3.3.1. Component mass conservation

Reactor-Fluid:
\[
\begin{align*}
- N_T \frac{A_{\text{per}}}{V_f} \left[ \mathcal{J}_{f,i} \right] + \epsilon_{a-s,V} \frac{A^a}{\epsilon_{a-V}^a} \left[ \left( \mathcal{E}^a_{f,A} \mathcal{N}^a_{e-i} \right)^{CS^a} \right] = \frac{\partial}{\partial t} \left( \epsilon_{f,i} \mathcal{E}^i_{f,i} \right) + \nabla \cdot \left[ \epsilon_{f,A} \left( \mathcal{E}^i_{f,i} \mathcal{N}^i_{f,i} \right) \right] \Rightarrow \\
\end{align*}
\]

Momentum conservation:

\[
\bar{v} P' = -150 \frac{\mu_f^i \left(1 - \epsilon_{f,i}^e \right)^2 \mathcal{V}_f^i}{\left( \epsilon_{f,i}^e \right)^3 d_p^2} - 1.75 \frac{\left(1 - \epsilon_{f,i}^e \right) \rho_f^i \mathcal{V}_f^i}{\left( \epsilon_{f,i}^e \right)^3 d_p} \Rightarrow \\
\frac{d \bar{P}^i}{d \bar{z}} = -150 \frac{\mu_f^i \left(1 - \epsilon_{f,i}^e \right)^2 \mathcal{V}_f^i}{\left( \epsilon_{f,i}^e \right)^3 d_p^2 \bar{P}^i} - 1.75 \frac{\left(1 - \epsilon_{f,i}^e \right) \mu_f^e \mathcal{V}_f^i}{\left( \epsilon_{f,i}^e \right)^3 d_p \bar{P}^i} \frac{\mu_f^i}{\bar{R}} \Rightarrow \frac{d \bar{P}^i}{d \bar{z}} = -\pi_s - \pi_g \cdot R_c \quad (158)
\]

8.3.3.2. Energy conservation

Reactor-Fluid:
\[
\begin{align*}
\left(-\varepsilon''_{a,NY} \left( \frac{A'}{\varepsilon_{a,NY} V'} \right) \left[ \varepsilon'_{a,N} A' \left( T''_i - T'' \right) \right] \right) & + \left(-\varepsilon''_{u,NY} \left( \frac{A'}{\varepsilon_{u,NY} V'} \right) \left[ \varepsilon'_{u,N} A' \left( T''_i - T'' \right) \right] \right) \\
\left(-\varepsilon''_{a,NY} \left( \frac{A'}{\varepsilon_{a,NY} V'} \right) \left[ \sum_{j=1}^N \frac{1}{M_j} \tilde{j}'_f, \varepsilon'_{a,N} \tilde{j}'_f, \tilde{J}'_f \right] \right) & + \left(-\varepsilon''_{u,NY} \left( \frac{A'}{\varepsilon_{u,NY} V'} \right) \left[ \sum_{j=1}^N \frac{1}{M_j} \tilde{j}'_f, \varepsilon'_{u,N} \tilde{j}'_f, \tilde{J}'_f \right] \right) \\
\left(-\varepsilon''_{a,NY} \left( \frac{1}{M_f} C_{P,j} \right) \tilde{n}'_f, V'{\nabla}T_f \right) & - \left( \frac{A}{V'} \right) \sum_{j=1}^N \left( \tilde{j}'_f, \varepsilon'_{a,N} \tilde{j}'_f, \tilde{J}'_f \right) \\
\end{align*}
\]

\[
\begin{align*}
\left(\frac{\partial}{\partial t} \left( \frac{\varepsilon'_{f,NY} \varepsilon'_{f,N} V'}{\tilde{A}'_f \tilde{A}'_f} \right) - \frac{\partial}{\partial t} \right) & = \left(\frac{\varepsilon'_{f,NY} \varepsilon'_{f,N} V'}{\tilde{A}'_f \tilde{A}'_f} \right) \\
\left(\frac{\partial}{\partial t} \left( \frac{\varepsilon'_{f,NY} \varepsilon'_{f,N} V'}{\tilde{A}'_f \tilde{A}'_f} \right) - \frac{\partial}{\partial t} \right) & = \left(\frac{\varepsilon'_{f,NY} \varepsilon'_{f,N} V'}{\tilde{A}'_f \tilde{A}'_f} \right) \\
\left(\frac{\partial}{\partial t} \left( \frac{\varepsilon'_{f,NY} \varepsilon'_{f,N} V'}{\tilde{A}'_f \tilde{A}'_f} \right) - \frac{\partial}{\partial t} \right) & = \left(\frac{\varepsilon'_{f,NY} \varepsilon'_{f,N} V'}{\tilde{A}'_f \tilde{A}'_f} \right) \\
\left(\frac{\partial}{\partial t} \left( \frac{\varepsilon'_{f,NY} \varepsilon'_{f,N} V'}{\tilde{A}'_f \tilde{A}'_f} \right) - \frac{\partial}{\partial t} \right) & = \left(\frac{\varepsilon'_{f,NY} \varepsilon'_{f,N} V'}{\tilde{A}'_f \tilde{A}'_f} \right) \\
\end{align*}
\]

\[\left(\frac{\partial}{\partial t} \left( \frac{\varepsilon'_{f,NY} \varepsilon'_{f,N} V'}{\tilde{A}'_f \tilde{A}'_f} \right) - \frac{\partial}{\partial t} \right) = \left(\frac{\varepsilon'_{f,NY} \varepsilon'_{f,N} V'}{\tilde{A}'_f \tilde{A}'_f} \right) \]
The initial and boundary conditions for the solution of conservation equations is represented as following:

**Initial Conditions:**

\[
\begin{align*}
\bar{c}_i' &= \left(\bar{c}_i'\right)_{in} \\
\bar{T}' &= \left(\bar{T}'\right)_{in} \quad \text{for } t = 0, \forall z \\
\bar{P}' &= \left(\bar{P}'\right)_{in} \\
\bar{v}' &= \left(\bar{v}'\right)_{in} \\
\bar{P}' &= \left(\bar{P}'\right)_{in}
\end{align*}
\]

**Boundary Conditions:**

\[
\begin{align*}
-\epsilon_{i,v} D_z \bar{v}c_i' &= \left(\bar{v}'\right)_{in} \cdot \left(\left(\bar{c}_i'\right)_{in} - c_i'\right) \\
\bar{v}' &= 1 \\
\bar{P}' &= 1 \\
\bar{v}T' &= -\kappa T' = -\epsilon_{i,A} \left(\sum_{j=1}^{n_i'} c_{i,j} C_{p,j} \left(\bar{v}'\right)_{in} \cdot \left(\bar{T}'\right)_{in} - T'\right) \\
\frac{d\bar{T}'}{dz} &= \left(1 - \bar{T}'\right) \\
\frac{d\bar{P}'}{dz} &= \left(1 - \bar{P}'\right)
\end{align*}
\]

Initial and boundary conditions for reactor-scale model equations

The initial and boundary conditions for the solution of conservation equations is represented as following:

**Initial Conditions:**

\[
\begin{align*}
\bar{c}_i' &= \left(\bar{c}_i'\right)_{in} \\
\bar{T}' &= \left(\bar{T}'\right)_{in} \quad \text{for } t = 0, \forall z \\
\bar{P}' &= \left(\bar{P}'\right)_{in} \quad \text{for } \bar{T} = 1, \forall \bar{z}
\end{align*}
\]

**Boundary Conditions:**

\[
\begin{align*}
\bar{v}' &= \left(\bar{v}'\right)_{in} \\
\bar{P}' &= \left(\bar{P}'\right)_{in} \quad \text{for } \bar{v} = 1 \\
\bar{T}' &= -\kappa T' = -\epsilon_{i,A} \left(\sum_{j=1}^{n_i'} c_{i,j} C_{p,j} \left(\bar{v}'\right)_{in} \cdot \left(\bar{T}'\right)_{in} - T'\right) \\
\frac{d\bar{T}'}{dz} &= \left(1 - \bar{T}'\right) \\
\frac{d\bar{P}'}{dz} &= \left(1 - \bar{P}'\right)
\end{align*}
\]
8. 3. 4. Molar based permeation zone model equations

The final component mass, energy and momentum conservation equations of the reactor domain can be expressed as following:

8. 3. 4. 1. Component mass conservation

\[ N_T \frac{A_v^T}{V_T} \sum_{i=1}^{v} \left[ J_{f,i} \right]^e z \frac{\partial}{\partial t} \left( \varepsilon_{f,i} V_i c_i^{per} \right) + \nabla \cdot \left( c_i^{per} \nabla V_i v^{per} \right) \Rightarrow \]

\[ N_T \frac{A_v^T}{C_i^{per} V_T} \sum_{i=1}^{v} \left[ J_{f,i} \right]^e z \frac{\partial}{\partial t} \left( \varepsilon_{f,i} V_i c_i^{per} \right) \frac{\gamma_i^{per}}{V_i^{per}} + \frac{d}{dz} \left( \overline{c_i^{per}} \nabla V_i \right) \Rightarrow \]

\[ \frac{D_{a,i}^{per}}{\pi_{21}} J_{f,i} \nabla \left( \overline{c_i^{per}} \nabla V_i \right) = \frac{\partial \overline{c_i^{per}}}{\partial t} + \frac{1}{\pi_{21}} \frac{d}{dz} \left( \overline{c_i^{per}} \nabla V_i \right) \]

8. 3. 4. 2. Momentum conservation

\[ \nabla \cdot \left( \rho_f^{per} \nabla V_f^{per} V_f^{per} \right) = -\nabla P^{per} + \mu_f^{per} \nabla^2 V_f^{per} \Rightarrow \]

\[ \frac{\pi_{21}}{\mu_f^{per}} \frac{d}{dz} \left( \overline{P_f^{per}} \nabla V_f^{per} V_f^{per} \right) = -\frac{\pi_{21}}{\mu_f^{per}} \frac{d}{dz} \overline{P_f^{per}} + \frac{d^2 V_f^{per}}{dz^2} \]

\[ R_e^{per} \frac{d}{dz} \left( \overline{P_f^{per}} \nabla V_f^{per} V_f^{per} \right) = -\pi_{22} \frac{d}{dz} \overline{P_f^{per}} + \frac{d^2 V_f^{per}}{dz^2} \]

8. 3. 4. 3. Energy conservation

\[ \nabla \left( \frac{A_v^T}{V_T} \overline{T_f^{per}} \right) + \frac{A_v^T}{V_T} \left( T_f^{per} - T_f^{per} \right) \frac{\partial}{\partial t} \left( \sum_{i=1}^{v} \frac{c_i^{per} C_{V,i}}{V_i^{per}} \right) \frac{\partial T_f^{per}}{\partial t} - \frac{\partial P_f^{per}}{\partial t} + \]

\[ \left( \frac{A_v^T}{V_T} \sum_{i=1}^{v} \left( J_{f,i} \left( h_i^{per} - h_i^{per} \right) \right) \right) \frac{\partial V_f^{per}}{\partial t} \left( \overline{T_f^{per}} \right) \Rightarrow \]
Initial and boundary conditions for permeation zone model equations

The initial and boundary conditions for the solution of conservation equations is represented as following:

**Initial Conditions:**

\[
\begin{align*}
\bar{c}_i' &= 1 \\
\bar{T}' &= 1 \quad \text{for } \bar{t} = 0, \ \forall \bar{z} \\
\bar{P}' &= 1
\end{align*}
\]

**Boundary Conditions:**

\[
\begin{align*}
\bar{v}_f' &= 1 \\
\bar{P}_p' &= 1 \quad \text{for } \bar{z} = 0, \ \frac{d\bar{T}_p}{d\bar{z}} = 0 \\
\bar{c}_i' &= 1 \\
\bar{T}_p' &= 1
\end{align*}
\]

\[
\begin{align*}
\bar{P}_p' &= 1 \quad \text{for } \bar{z} = \bar{z}'
\end{align*}
\]

8.4. Results and Discussions

A coal-derived syngas with composition \((\text{H}_2:\text{CO}:\text{CO}_2:\text{N}_2:\text{CH}_4:\text{H}_2\text{S}:\text{H}_2\text{O} = 0.51:1.00:0.36:2.28:0.1:0.0031:1.5)\) is used as the feed to the HAMR. The HAMR was
considered to operate at a temperature of 250 °C (simulations are carried out under adiabatic case) and a pressure of 25 bar. In the simulations, the membrane permeances (m³/m².h.bar) were taken to be: H₂=1; CO=0.0027; CO₂=0.0018; CH₄=0.0027, H₂O=0.333, which are typical of values we measure with high-quality CMS membranes. The values reported in Table 4 correspond to a commercial Co-Mo/Al₂O₃ shift catalyst and a hydrotalcite adsorbent.

### Table 24. Parameter Values Used in Simulation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of catalyst</td>
<td>592.68</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Density of adsorbent</td>
<td>1.780</td>
<td>kg/m³</td>
</tr>
<tr>
<td>Catalyst pellet void fraction</td>
<td>0.35561</td>
<td></td>
</tr>
<tr>
<td>Adsorbent pellet void fraction</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Catalyst/adsorbent pellets radius</td>
<td>0.00035-0.005</td>
<td>m</td>
</tr>
<tr>
<td>Surface area of pellets</td>
<td>160-220*10⁶</td>
<td>m²/g</td>
</tr>
<tr>
<td>Pore volume of pellets</td>
<td>0.55-0.65*10⁻⁶</td>
<td>m³/g</td>
</tr>
<tr>
<td>Mean pore diameter of catalyst</td>
<td>6.3*10⁻⁹</td>
<td>m</td>
</tr>
<tr>
<td>Mean pore diameter of adsorbent</td>
<td>6.3*10⁻⁷</td>
<td>m</td>
</tr>
<tr>
<td>Reactor diameter</td>
<td>0.03175</td>
<td>m</td>
</tr>
<tr>
<td>Reactor length</td>
<td>0.1397</td>
<td>m</td>
</tr>
<tr>
<td>Heat transfer coefficient ( Uₚₑᵣ )</td>
<td>227</td>
<td>W/m²·K</td>
</tr>
<tr>
<td>Chemical Kinetic rate parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>kₖₜ</td>
<td>1.683*10⁻⁶,</td>
<td>mol/(g·s·bar)</td>
</tr>
<tr>
<td>kₙₜ</td>
<td>1.722*10⁻⁵ [28]</td>
<td></td>
</tr>
<tr>
<td>mₖₐ</td>
<td>0.0058 [27]</td>
<td>1/s</td>
</tr>
<tr>
<td>mₖₐ</td>
<td>2.9526 [27]</td>
<td>kg/mol</td>
</tr>
<tr>
<td>bₖₐ</td>
<td>3.96 [27]</td>
<td>1/bar</td>
</tr>
</tbody>
</table>
8. 4. 1. Species mole fractions, and comparison among the HAMR, AR (Adsorptive Reactor), MR (Membrane Reactor) and PBR (Packed Bed Reactor)

8. 4. 2. CO conversion, H₂ recovery, and CO₂ lost in HAMR

Averaged 93.66% CO conversion (depicted in Figure 100-left) and steady-state conversion of 89% (represents also MR) is attained in HAMR along the 4000 sec. On the other hand, averaged 69% CO conversion (depicted in Figure 100-left) and steady-state conversion of 66% (represents also PBR) is obtained in AR along the 4000 sec. These results demonstrate that HAMR has significant advantage over AR, MR and PBR under the same conditions.

Figure 100 (right) illustrate the H₂ recovery (which is defined here as the molar flow rate of H₂ exiting the MR permeate side divided by the total molar flow rate of H₂ exiting the MR), and total CO₂ lost (ending-up) in the MR permeate side. As shown in Figure 100, approximately 95 % of H₂ recovery is obtained in HAMR by the effect of membrane separation. However,
approximately 15% of the CO\textsubscript{2} is lost through the membrane after reaching full capacity of the adsorbent.

*Figure 100. CO conversion, H\textsubscript{2} recovery, and CO\textsubscript{2} lost. Sweep ratio: 0.1, permeate pressure: 1 bar.*

**The effect of $D'_{a,i}$ on CO conversion, H\textsubscript{2} recovery, and CO\textsubscript{2} lost in HAMR**

The effect of the $D'_{a,i}$ on HAMR performance is shown in Figure 101. Decreasing the value of $D'_{a,i}$ from the base-case to 0.5*base-case reduces the conversion approximately 25%. Moreover, decreasing the value of $D'_{a,i}$ from the base-case to 0.5*base-case reduces the H\textsubscript{2} recovery approximately 15%, and the CO\textsubscript{2} lost through membrane approximately 45%.

*Figure 101. The effect of $D'_{a,i}$ CO conversion, H\textsubscript{2} recovery, and CO\textsubscript{2} lost in HAMR. Sweep ratio: 0.1, permeate pressure: 1 bar.*
The effect of $D'_{a,2}$ CO conversion, $H_2$ recovery, and $CO_2$ lost in HAMR

The effect of the $D'_{a,2}$ on HAMR performance is shown in Figure 102. Increasing the value of $D'_{a,2}$ from the 0.5*base-case to 2*base-case increases the conversion approximately 23%. Increasing the value of $D'_{a,2}$ from the 0.5*base-case to 2*base-case doesn’t have significant effect on $H_2$ recovery. However, it decreases the CO2 lost around 100%.

Figure 102. The effect of $D'_{a,2}$ CO conversion, $H_2$ recovery, and CO2 lost in HAMR. Sweep ratio: 0.1, permeate pressure: 1 bar.

The effect of $D'_{a,3}$ CO conversion, $H_2$ recovery, and $CO_2$ lost in HAMR

The effect of the $D'_{a,3}$ on HAMR performance is depicted in Figure 103. $D'_{a,3}$ doesn’t have significant effect on HAMR performance.
Figure 103. The effect of $D_{a.3}$, CO conversion, H2 recovery, and CO2 lost in HAMR. Sweep ratio: 0.1, permeate pressure: 1 bar.

The effect of $P_e$ CO conversion, H2 recovery, and CO2 lost in HAMR

The effect of the $P_e$ on HAMR performance is depicted in Figure 104. Increasing the value of $P_e$ from the 0.67*base-case to 1.33*base-case drops the conversion approximately 25%. Increasing the value of $P_e$ from the 0.5*base-case to 2*base-case doesn’t have significant effect on CO2 lost. However, it decreases the H2 recovery around 8%.

Figure 104. The effect of $P_e$ CO conversion, H2 recovery, and CO2 lost in HAMR. Sweep ratio: 0.1, permeate pressure: 1 bar.
Nomenclature

English Symbols

\( \Lambda^p (m^2 \text{ of domain } p) \) Area of the control surface of domain \( p \)

\( \Lambda'^p (m^2) \) Cross section area of the tubular reactor

\( B_{\alpha} (m^2) \) Viscous flow parameter of domain \( p \)

\( c_{\gamma,i}^\alpha \left( \frac{\text{mol of species } i \text{ in phase } \gamma \text{ within domain } \alpha}{m^3 \text{ of phase } \gamma \text{ within domain } \alpha} \right) \) Species’ \( i \) molar density of phase \( \gamma \) within domain \( \alpha \)

\( c_{\gamma}^\alpha \left( \frac{\text{mol of phase } \gamma \text{ within domain } \alpha}{m^3 \text{ of phase } \gamma \text{ within domain } \alpha} \right) \) Total molar density of phase \( \gamma \) within domain \( \alpha \)

\( C_{p,i}^\alpha \left( \frac{J \text{ of species } i \text{ in phase } \gamma \text{ within domain } \alpha}{(mol \cdot K) \text{ of the } i^{th} \text{ component of phase } \gamma \text{ within domain } \alpha} \right) \) Species’ \( i \) molar specific heat at constant pressure of phase \( f \) within domain \( \alpha \)

\( C_{V,i}^\alpha \left( \frac{J \text{ phase } s \text{ within domain } \alpha}{(mol \cdot K) \text{ of phase } s \text{ within domain } \alpha} \right) \) Species’ \( i \) molar specific heat at constant volume of phase \( s \) within domain \( \alpha \)

\( CS^\alpha (m^2 \text{ of domain } \alpha) \) Control surface of domain \( \alpha \)

\( CV^\alpha (m^3 \text{ of domain } \alpha) \) Control volume of domain \( \alpha \)

\( D_{\gamma ij}^\alpha \left( m^2 \text{ of phase } f \text{ within domain } \alpha \right) \) Species’ \( i \) and \( j \) binary diffusion coefficient of phase \( \gamma \) within domain \( \alpha \)

\( D_{\gamma ij}^{\alpha p} \left( m^2 \text{ of domain } p \right) \) Species’ \( i \) and \( j \) effective binary diffusion coefficient in domain \( p \)

\( D_{k,i}^{\alpha} \left( \text{total } m^3 \text{ of domain } p \right) \) Species’ \( i \) Knudsen diffusion coefficient in domain \( p \)

\( D_{i r}^f \left( m^2 \text{ of phase } f \text{ within domain } r \right) \) Species’ \( i \) thermal diffusion coefficient of phase \( f \) within domain \( r \)

\( d^p (m) \) Diameter of the catalytic pellet

\( d_{\text{mean}}^p (m) \) Mean pore diameter in domain \( p \)

\( d^r (m) \) Diameter of the tubular reactor

\( F_{\text{CO}} (mol/h) \) Inlet CO molar flow rate

\( h^\alpha \left( \frac{J \text{ from phase } f \text{ within domain } \alpha}{(m^2 \cdot K) \text{ of phase } s \text{ within domain } \alpha \cdot s} \right) \) Interfacial heat transfer coefficient between phase \( f \) within domain \( \alpha \) and phase \( s \) within domain \( \alpha \)

\( H_{\gamma}^\alpha \left( \frac{J \text{ of phase } \gamma \text{ within domain } \alpha}{kg \text{ of phase } \gamma \text{ within domain } \alpha} \right) \) Mass specific enthalpy of phase \( \gamma \) within domain \( \alpha \)
\[ \tilde{H}^i_{\alpha} \left( \frac{J \text{ of species } i \text{ in phase } f}{\text{mol of species } i \text{ in phase } f} \right) \]  
Species' \( i \) standard molar enthalpy of formation

\[ \tilde{h}^i_{\gamma,\alpha} \left( \frac{J \text{ of phase } \gamma \text{ within domain } \alpha}{\text{mol of phase } \gamma \text{ within domain } \alpha} \right) \]  
Species' \( i \) molar enthalpy of phase \( \gamma \) within domain \( \alpha \)

\[ \lambda_{\gamma}^i \left( \frac{J \text{ of phase } \gamma \text{ within domain } \alpha}{(m \cdot K) \text{ of phase } \gamma \text{ within domain } \alpha} \right) \]  
Thermal conductivity of phase \( \gamma \) within domain \( \alpha \)

\[ \bar{\tilde{j}}^i_{\gamma,\alpha} \left( \frac{\text{kg of species } i \text{ in phase } \gamma \text{ within domain } \alpha}{(m^2 \text{ of phase } \gamma \text{ within domain } \alpha) \cdot s} \right) \]  
\( i \)th species diffusion molar flux in phase \( \gamma \) within domain \( \alpha \)

\[ \bar{\tilde{j}}^i_{\gamma,\alpha} \left( \frac{\text{kg of species } i \text{ in phase } \gamma \text{ within domain } \alpha}{(m^2 \text{ of phase } \gamma \text{ within domain } \alpha) \cdot s} \right) \]  
\( i \)th species combined diffusion-convection molar flux in phase \( \gamma \) within domain \( \alpha \)

\[ k_w \text{ (m/s)} \]  
Mass transfer coefficient

\[ L \text{ (m)} \]  
Length of the tubular reactor

\[ M_i \text{ (kg of } i/\text{mol of } i) \]  
\( i \)th species molar mass

\[ \# \text{ (dimensionless)} \]  
Unit vector direction of the differential area \( dA \) of the \( CS \).

\[ \bar{\tilde{n}}^i_{\gamma,\alpha} \left( \frac{\text{kg of species } i \text{ in phase } \gamma \text{ within domain } \alpha}{(m^2 \text{ of phase } \gamma \text{ within domain } \alpha) \cdot s} \right) \]  
\( i \)th species diffusion mass flux in phase \( \gamma \) within domain \( \alpha \)

\[ \bar{\tilde{N}}^i_{\gamma,\alpha} \left( \frac{\text{kg of species } i \text{ in phase } \gamma \text{ within domain } \alpha}{(m^2 \text{ of phase } \gamma \text{ within domain } \alpha) \cdot s} \right) \]  
\( i \)th species combined diffusion-convection mass flux in phase \( \gamma \) within domain \( \alpha \)

\[ p_{\gamma}^i \left( \frac{J \text{ of phase } f \text{ within domain } \alpha}{m^2 \text{ of phase } f \text{ within domain } \alpha} \right) \]  
Pressure of phase \( \gamma \) within domain \( \alpha \)

\[ Q_{\gamma}^i \left( \frac{J \text{ of phase } \gamma \text{ within domain } \alpha}{(m^2 \text{ of phase } \gamma \text{ within domain } \alpha) \cdot s} \right) \]  
Heat flux into phase \( \gamma \) within domain \( \alpha \)

\[ q_{f \rightarrow s}^i \left( \frac{J \text{ from phase } f \text{ to } s \text{ within domain } \alpha}{(m^2 \text{ of domain } \alpha) \cdot s} \right) \]  
Heat transferred from phase \( f \) to \( s \) within domain \( \alpha \)

\[ q_{f \rightarrow p}^i \left( \frac{J \text{ from phase } f \text{ to } p \text{ within domain } \alpha}{(m^2 \text{ of domain } \alpha) \cdot s} \right) \]  
Heat transferred from phase \( f \) to \( p \) within domain \( \alpha \)

\[ q_r^i \left( \frac{J \text{ from domain } r \text{ to domain } p}{(m^2 \text{ of domain } r) \cdot s} \right) \]  
Heat transferred from domain \( r \) to domain \( p \) due to convection.

\[ q_q^i \left( \frac{J \text{ from domain } r \text{ to domain } q}{(m^2 \text{ of domain } r) \cdot s} \right) \]  
Heat transferred from domain \( r \) to domain \( q \) due to convection.
Heat transferred from the exterior to domain \( r \).

Heat transferred from the interior to domain \( per \).

Heat transferred from domain \( r \) to domain \( p \) due to mass flux

Heat transferred from domain \( r \) to domain \( per \) due to mass flux

\( R^\alpha \left( \frac{\text{mols of species } i \text{ in phase } \gamma \text{ within domain } \alpha}{(\text{m}^3 \text{ of domain } \alpha) \cdot \text{s}} \right) \) \( i \)th species volumetric generation rate in phase \( \gamma \) within domain \( \alpha \)

\( \bar{R}^\alpha_{f,\gamma} \left( \frac{\text{mols of species } i \text{ in phase } f \text{ within domain } p}{(\text{kg of phase } s \text{ within domain } p) \cdot \text{s}} \right) \) \( i \)th species phase \( s \) specific generation rate in phase \( f \) within domain \( p \)

\( \bar{R}(J/\text{mol.K}) \) Universal gas constant

\( r(m \text{ of domain } p) \) spatial variable of domain \( p \)

\( r^\varphi (m) \) Radius of the pellet

\( S^\alpha_{\gamma} \left( \frac{\text{kg of phase } \gamma \text{ within domain } \alpha}{(\text{m}^2 \text{ of domain } \alpha) \cdot \text{s}^2} \right) \) Momentum source term of phase \( \gamma \) within domain \( \alpha \)

\( S^\alpha_{\gamma \rightarrow \gamma'} \left( \frac{\text{J of phase } \gamma \text{ to } \gamma' \text{ within domain } \alpha}{(\text{m}^2 \text{ of domain } \alpha) \cdot \text{s}^2} \right) \) Interphase energy transfer source term in domain \( \alpha \)

\( S^\alpha_{\gamma \rightarrow \gamma, \varphi} \left( \frac{\text{kg of phase } f \text{ within domain } \alpha}{(\text{m}^2 \text{ of domain } \alpha) \cdot \text{s}^2} \right) \) Interphase mass transfer source term in domain \( \alpha \)

\( T^\alpha_{\gamma}(K) \) Temperature of phase \( \gamma \) within domain \( \alpha \)

\( T^\alpha(K) \) Temperature of the composite phase in domain \( \alpha \)

\( T^\varphi(K) \) Temperature of the furnace

\( \overrightarrow{T^\alpha_{\gamma}} \left( \frac{\text{kg of phase } \gamma \text{ within domain } \alpha}{(\text{m}^2 \text{ of phase } \gamma \text{ within domain } \alpha) \cdot \text{s}^2} \right) \) Viscous momentum flux tensor of phase \( \gamma \) within domain \( \alpha \)

\( U^\varphi \left( \frac{\text{J transferred from domain } r \text{ to furnace}}{(\text{m}^2 \cdot K \text{ of interphase contact}) \cdot \text{s}} \right) \) Global heat transfer coefficient between the furnace and domain \( r \)
\[ U_{\text{per}} \left( \frac{J \text{ transferred from domain } r \text{ to domain } \text{per}}{\left( \text{m}^2 \cdot \text{K} \right) \text{ of interphase contact}} \cdot \text{s} \right) \] 
Heat transfer coefficient between the domain per and domain \( r \)

\[ V^p \left( \text{m}^3 \text{ of domain } p \right) \] 
Total volume of domain \( p \)

\[ \overline{v}_\gamma^\alpha \left( \text{m/s} \right) \] 
Mass average velocity of the phase \( \gamma \) within domain \( \alpha \)

\[ v_{\gamma,i}^\alpha \left( \text{m/s} \right) \] 
\( i \)th species velocity in phase \( \gamma \) within domain \( \alpha \)

\[ w_{\gamma,i}^\alpha \left( \frac{\text{kg of species } i \text{ in phase } \gamma \text{ within domain } \alpha}{\text{kg of phase } \gamma \text{ within domain } \alpha} \right) \] 
\( i \)th species mass fraction in phase \( \gamma \) within domain \( \alpha \)

\[ W_{\text{cat}} \left( \text{g} \right) \] 
Amount of catalyst

\[ W_{\text{quartz}} \left( \text{g} \right) \] 
Amount of quartz

\[ x_{\gamma,i}^\alpha \left( \frac{\text{mol of species } i \text{ in phase } \gamma \text{ within domain } \alpha}{\text{mol of phase } \gamma \text{ within domain } \alpha} \right) \] 
\( i \)th species molar fraction in phase \( \gamma \) within domain \( \alpha \)

Greek symbols:

\[ \varepsilon_{\gamma}^\alpha \left( \frac{\text{m}^3 \text{ of phase } \gamma \text{ within domain } \alpha}{\text{total m}^3 \text{ of domain } \alpha} \right) \] 
Volumetric fraction of phase \( \gamma \) within domain \( \alpha \)

\[ \varepsilon_{\gamma, \alpha}^\alpha \left( \frac{\text{m}^2 \text{ of phase } \gamma \text{ within domain } \alpha}{\text{total m}^2 \text{ of domain } \alpha} \right) \] 
Surface fraction of phase \( \gamma \) within domain \( \alpha \)

\[ \rho_{\gamma}^\alpha \left( \frac{\text{kg of phase } \gamma \text{ within domain } \alpha}{\text{m}^3 \text{ of domain } \alpha} \right) \] 
Mass density of phase \( \gamma \) within domain \( \alpha \)

\[ \rho_{\gamma,i}^\alpha \left( \frac{\text{kg of species } i \text{ in phase } \gamma \text{ within domain } \alpha}{\text{m}^3 \text{ of domain } \alpha} \right) \] 
\( i \)th species mass concentration in phase \( \gamma \) within domain \( \alpha \)

\[ \tau \left( \frac{\text{m of diffusion pathlength in phase } f \text{ within domain } \alpha}{\text{m of CV length in domain } \alpha} \right) \] 
Tortuosity of phase \( f \) within domain \( \alpha \)

\[ \mu_\gamma^\alpha \left( \frac{\text{kg of species } i \text{ in phase } \gamma \text{ within domain } \alpha}{\text{m of phase } \gamma \text{ within domain } \alpha} \cdot \text{s} \right) \] 
Viscosity of phase \( f \) within domain \( \alpha \)

\[ \nu \left( \text{dimensionless} \right) \] 
Total number of species in the phase-domain

\[ \Phi_{\gamma}^\alpha \left( \frac{\text{J of phase } \gamma \text{ within domain } \alpha}{\text{kg of phase } \gamma \text{ within domain } \alpha} \right) \] 
Mass specific potential energy of phase \( \gamma \) within domain \( \alpha \)

\[ \lambda^\alpha \left( \text{J within domain } \alpha / \text{m}^2 \cdot \text{K} \cdot \text{s} \right) \] 
Conductivity within domain \( \alpha \)
Bibliography


