

Hydrogen Production from Biomass-Derived Syngas Using a Membrane Reactor Based Process

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ABSTRACT: Integrated gas combined (power generation) cycle (IGCC) power plants show promise for environmentally benign power generation. In these plants coal and/or biomass are first gasified into syngas, which is then processed in a water gas shift (WGS) reactor to further enhance its hydrogen content for power generation. However, impurities in the syngas, primarily H₂S, NH₃, various organic vapors, and tar-like species, are detrimental to catalyst life and must be removed before the gas enters the WGS reactor. This, then, means cooling the syngas for cleanup and then reheating it to the WGS reaction temperature. For use in various industrial applications, and potentially for CO₂ capture/sequestration, hydrogen purification is required. This, today, is accomplished by conventional absorption/adsorption processes, which results in significant process complexity and energy penalty for the overall plant. Ideally, one would like to establish a “one-box” process in which the syngas is fed directly into the WGS reactor, which then effectively converts the CO into hydrogen in the presence of all of the aforementioned impurities and delivers a contaminant-free hydrogen product. In this study, the development of such a process is described. It includes a catalytic membrane reactor (MR) making use of a hydrogen-selective, carbon molecular sieve membrane, and a sulfur-tolerant Co/Mo/Al₂O₃ catalyst. In this work, the membrane reactor’s behavior has been investigated for different experimental conditions and compared with the modeling results.

1. INTRODUCTION

Air pollution is today a serious problem throughout the world, with power-plant, factory, and vehicle emissions being major contributors. The use of hydrogen (H₂), as an alternative for fossil fuels, is broadly acknowledged as a potential means for reducing such pollution.¹ One of the benefits of adopting H₂ as an energy source, in addition to reducing CO₂ emissions, is that it can be produced from readily available and plentiful raw materials such as coal and renewable biomass; this then diminishes the need to use the world’s dwindling crude-oil resources. Coal is a key energy source for power generation in some of the largest world economies including the USA and China, where it is found as an abundant resource,² in addition to being a promising raw material to produce H₂. For that, coal must be first gasified with air or pure O₂ at high temperatures² to produce coal-gasifier off-gas (or syngas), containing as key species H₂, CO, CO₂, H₂O, CH₄, and other byproducts such as organic vapors, tars, H₂S, and NH₃, etc.,² the exact composition depending on the operating conditions, e.g., pressure, temperature, type of coal and oxidant used and their flow rates, and gasifier configuration, etc.²

To produce H₂ from syngas, it must be first cleaned of its contaminants that include, in addition to the compounds noted above, particulates such as coke, and inorganic matter known as ash² (for example, H₂S can be removed using solid sorbents,^{3–5} via catalytic conversion,⁶ or through solvent-based⁷ absorption). The cleaned syngas is then processed in a reactor to convert the CO, via its water gas shift (WGS) reaction with steam, into additional H₂ and CO₂ in order to produce pure H₂⁸ after the CO₂ is removed. When coal and/or biomass gasification and H₂ generation are combined with electricity production (e.g., via a

turbine or a fuel cell), the process is known as the integrated gas combined (power generation) cycle or IGCC.⁹ IGCC power plants are attracting interest today because they are well-suited for CO₂ capture for storage and sequestration (CCS).⁹

Biomass¹⁰ is another abundant raw material that also shows promise for H₂ production and for environmentally benign power generation via IGCC. The term encompasses a broad range of materials, including lignocellulosic products such as wood and wood waste, agricultural products and byproducts, food processing and municipal waste, and algae and various other aquatic plants, etc.¹¹ Moderately dried biomass can be used directly for electricity generation (e.g., via cofiring in coal power plants). Lignocellulosic materials can be used to produce liquid fuels (e.g., ethanol) via hydrolysis followed by fermentation of the resulting sugars.¹¹ A broader range of fuels can be produced via biomass pyrolysis,¹¹ though the process is still not commercial.

For environmentally benign power generation from biomass, IGCC offers the best option. As a renewable material, biomass offers during IGCC greater potential for CO₂ emissions reductions than coal. As in coal-based IGCC, biomass is first gasified to produce syngas containing similar main components as its coal-derived counterpart together with various impurities, including H₂S, NH₃, and high molecular weight (MW) compounds known as tars.^{12,13} For power generation, this syngas must be first cleaned of its contaminants and then be

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reacted in a WGS reactor to enrich its H_2 content. The WGS reaction is exothermic, its equilibrium conversion favored by low temperatures. Two reactors in series are typically used to overcome both equilibrium and kinetic limitations and to increase conversion.¹⁴ One, known as the high-temperature shift (HTS) reactor, operates at high temperatures using Fe/Cr-based catalysts, while the other, known as the low-temperature shift (LTS) reactor, operates at lower temperatures using a Cu/Zn-based catalyst.¹⁵ The WGS reactor product must be further processed in order to produce pure H_2 and a CO_2 stream ready for storage and sequestration. The whole process is complex and energy-intensive. In its place, our team has recently proposed instead a novel approach,¹⁶ termed the “one-box” process, that substitutes the conventional dual-bed WGS reactor process with a membrane reactor (MR). By using a hydrogen-selective carbon molecular sieve (CMS) membrane and a sulfided Co/Mo catalyst, which are both resistant to the syngas impurities, this process avoids the use of a separate syngas pretreatment as well as a H_2 purification step, thus simplifying design.

WGS membrane reactors (WGS-MR) are not new, however. Uemiya et al.¹⁷ were the first to study an atmospheric pressure Pd-membrane WGS-MR treating pure CO and using Ar as a sweep. At 400 °C (with a H_2O/CO ratio ~ 1) they achieved a maximum CO conversion of 96%. Since the WGS reaction requires high temperatures, most studies to date (with notable exceptions¹⁸) utilize high-temperature membranes including dense Pd,^{19–24} microporous silica,^{25–28} microporous zeolite,²⁹ and CMS membranes (CMSM).^{16,30–32} Pd or Pd-alloy WGS-MR have attracted most of the attention, starting with the early studies by Uemiya et al.¹⁷ Bi et al.²³ studied a MR operating at 375 °C and pressure of 1.2 bar with a simulated syngas feed (H_2 , 7%; CO , 25%; CO_2 , 15%; N_2 , 53%) and a N_2 sweep rate of 28.3 cm^3/min using a conventional Co/Cr catalyst and a porous glass supported Pd membrane. They obtained a maximum CO conversion of 98%. Augustine et al.³³ used a WGS-MR to treat a simulated syngas mixture (H_2 , 22.0%; H_2O , 45.4%; CO , 22.7%; CO_2 , 9.9%) with a dense Pd membrane supported on porous stainless steel (SS). They obtained a maximum CO conversion of 98% and H_2 recovery of 88% with a H_2O/CO ratio of 2.6 at the reactor temperature of 450 °C and a feed-side pressure of 14.4 bar for $GHSV = 2900 h^{-1}$ ($GHSV =$ gas hourly space velocity). Ma and co-workers³⁴ also studied the WGS reaction at temperatures in the range of 420–440 °C and pressures from 7 to 20 bar using a larger size composite Pd membrane, a simulated syngas (H_2 , 40%; CO , 42.2%; CO_2 17.8%), and H_2O/CO ratios ranging from 2.5 to 3.5. They obtained a maximum CO conversion of 98.1%, a H_2 recovery of 85.1% at 440 °C, and a $GHSV = 1130 h^{-1}$.

As the above studies indicate, and a recent concise review³⁵ also describes, Pd membranes, when used in WGS-MR, deliver high CO conversions and high-purity H_2 . Their main drawback for the WGS application, other than the limited availability of Pd which may ultimately, however, hinder their widespread use for this large-scale application, is that they are sensitive to syngas impurities, particularly H_2S which adversely affects them, even at single-digit parts per million levels. Exposure of Pd to H_2S was shown to reduce its permeability and to result in a surface scale of Pd sulfides³⁶ and pitting of the membrane surface.³⁷ Therefore, an exhaustive syngas cleanup step is necessary.^{38,39}

WGS-MRs using silica membranes have been studied as well and have also shown excellent performance.^{25–28} The drawback

with silica membranes for the WGS reaction is well-known, in that silica undergoes condensation in the presence of steam. Efforts to improve hydrothermal stability include membrane functionalization using surfactants to form a hydrophobic silica surface⁴⁰ and incorporation into the silica structure of various metals^{41,42} and carbon⁴³ during the preparation step; all of these efforts have, so far, found limited success, but silica membranes, on the other hand, show good potential for application to other reactions where steam is not required.^{44,45}

CMSM, as a result of challenges other types of membranes face with the WGS reaction, have attracted recent attention.^{16,30,31,39,46} They are made via the pyrolysis of polymeric precursors in various atmospheres, important conditions influencing their properties being as follows: (1) the type of precursor utilized,⁴⁷ (2) the pyrolysis conditions such as the atmosphere and heating protocols,⁴⁸ and (3) postpyrolysis modifications such as activation, oxidation, and stabilization.⁴⁹ Initial efforts by our group in using CMSM for the WGS reaction^{30,31} were important to prove that CMSM show good performance and stability in high-temperature steam. However, these early studies were performed with feeds not containing the impurities typically encountered in coal- and biomass-derived syngas. In our two most recent studies,^{16,46} CMSM were utilized to treat simulated coal-derived⁴⁶ and biomass-derived¹⁶ syngas containing realistic concentrations of H_2S and NH_3 . In these studies, sour-shift commercial catalysts^{50,51} were also used, and during the tests lasting more than a month, both membranes and catalysts exhibited good and stable performance in the temperature range of 250–350 °C (recently Dong and co-workers²⁹ used silylated zeolite membranes for the HTS reaction in the presence of H_2S ; though the reported steam stability of the silica surfaces contrasts prior studies by other groups, the results are nevertheless promising and will, hopefully, provide impetus for further development of these membranes).

In addition to H_2S and NH_3 , organic vapors and tars are also a concern for the WGS-MR processing biomass-derived syngas. Appropriate modifications in gasifier design and operating conditions along with using catalysts and additives, as well as novel technologies, such as supercritical water gasification,¹⁶ help minimize tar formation and also convert organic vapors into H_2 and CO via steam reforming. However, their presence in the syngas cannot be completely eliminated and must, therefore, be taken into account during the design of downstream systems for syngas cleanup and processing. High organic vapor concentrations were previously shown, for example, to be highly detrimental to polymeric membranes during the separation of syngas-relevant mixtures. For example, White et al.⁵² used polyimide membranes to separate a CO_2/CH_4 mixture saturated with toluene. The organic vapor reduced the selectivity by about 50%. Tanihara et al.⁵³ also reported similar selectivity losses ($\sim 85\%$) when separating an equimolar H_2/CH_4 mixture in the presence of toluene vapor.

Accumulation of the tars on the membrane surface and condensation of organic vapors within the membrane pore structure, thus blocking transport and leading to severe reductions in permeance, remained prior to our recent studies^{16,54} a key concern for the use of CMSM in biomass-derived syngas environments. An earlier study by Vu et al.⁵⁵ had hinted, however, that CMSM may be significantly more robust to the presence of organic vapors than their polymeric counterparts. They studied the influence of toluene (70 ppm) on the selectivity of a CMSM treating a (10% $CO_2/90\%$ CH_4)

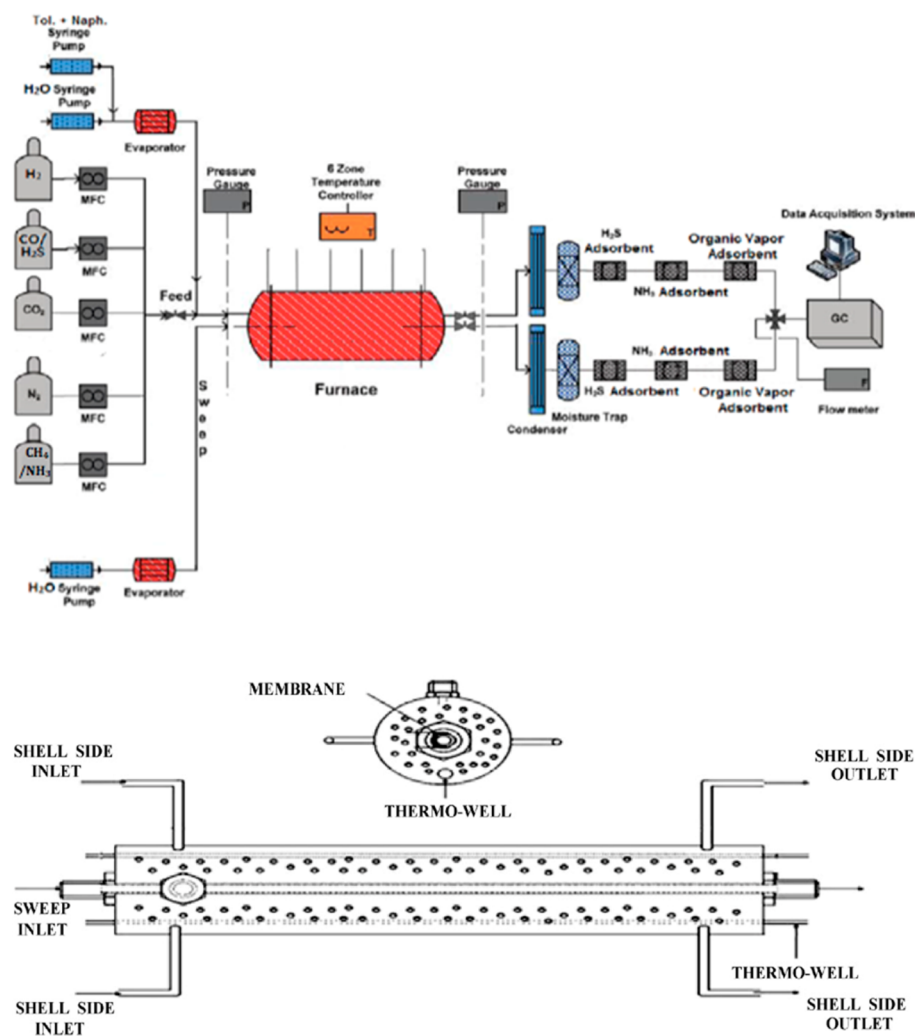


Figure 1. Experimental setup used in the membrane reactor experiments.

mixture at 3448 KPa and at 35 °C. In tests, lasting 60 h, the membrane showed stable performance, which Vu et al.⁵⁵ attributed to toluene's inability to enter the membrane nanopores.

During our laboratory-scale testing,¹⁶ the CMSM were exposed to simulated biomass-derived syngas containing realistic amounts of naphthalene, as a model tar, and toluene as a model organic vapor, these compounds selected based on prior literature work.⁵⁶ The membranes performed well¹⁶ with little impact on throughput/selectivity observed. However, operating temperature is key; stable performance is observed as long as the temperature stayed above 250 °C, with losses in performance observed for lower temperatures, becoming severe below 200 °C. These results were also validated in our field tests⁵⁴ with real coal-derived and/or biomass-derived syngas at the Department of Energy's (DOE's) National Carbon Capture Center (NCCC) facility with a pilot-scale CMSM module containing 86 membranes. Again, the membranes performed stably as long as the test temperature remained above 250 °C, with increasing losses in performance observed upon lowering the test temperatures.

The current plan by our team is to field-test the "one-box" process using the aforementioned 86-tube, pilot-scale module. Prior to, and in preparation for, such testing, however, our team recently completed a laboratory-scale investigation using a

single CMSM tube with properties similar to the membranes used to prepare the pilot-scale module. In these studies the membrane and catalyst were challenged with a simulated biomass-derived syngas that contained, in addition to H₂S and NH₃, realistic concentrations of a model organic vapor (toluene) and a model tar-like species (naphthalene). The results of these studies are detailed in this work and provide impetus and further motivation for undertaking the field-testing of the technology with real biomass-derived syngas on the way to eventual technology commercialization.

2. EXPERIMENTAL SYSTEM AND PROCEDURES

Figure 1 is a schematic of the MR experimental setup used to perform the WGS reaction experiments and the permeation tests reported here. For the experiments, the CMSM (25.4 cm long) is inserted in the middle of the tubular SS reactor and is sealed there with graphite o-rings and compression fittings. Commercial Süd-Chemie Co/Mo/Al₂O₃ C-25 WGS catalyst particles (~10 g) and inert quartz particles (~80 g) are crushed separately into smaller particles, their sizes sorted with mesh-screens in the range of 600–800 μm, and thoroughly mixed together and loaded in the annular volume between the membrane and the reactor housing; this is done in order to completely fill the reactor and be able to operate it under isothermal conditions. The experimental system consists of the

feed, reactor, and analysis sections. The feed section consists of gas cylinders, mass flow controllers (MFC), syringe pumps to deliver the water and the organic compounds (toluene and naphthalene), and the steam and organic vapor generating units. The reactor section includes the MR, a heating furnace, pressure gauges, two condensers and two moisture traps to remove the water and the organic vapors from the reject and permeate side streams, two traps to remove H₂S, two traps for removing NH₃, and another two traps to remove trace organic vapors from the same streams. The analysis section consists of an online gas chromatograph (GC) to analyze the concentration of the exit gas streams, two bubble flow meters (BFM) for measuring the total flow rates, and Draeger tubes for measuring the H₂S and NH₃ concentrations (via slip streams). For the liquid collected in the moisture trap, we measure the organic phase composition, after the water is removed, using a GC-MS instrument (Bruker GC450-MS300), making use of a 30 m DB-5 nonpolarized column. The analysis procedure starts at 50 °C, and the oven is kept at that temperature for 2 min. Then the oven temperature is increased to 250 °C, at 50 °C/min. After reaching 250 °C, the column was kept at that temperature for 4 min. The GC/MS was calibrated using toluene/naphthalene mixtures in methanol with a molar ratio from 1:1 to 16:1.

The reactor and a section of the feed and sweep lines (in order to preheat the feed and the sweep steams to the reactor temperature) are maintained at isothermal conditions in a six-zone furnace. The temperature in each zone is controlled via temperature controllers (TC) and thermocouples installed in six different locations in the bed. A sliding thermocouple is also used to monitor the temperature along the bed. MFC are used to control the flow rates of the feed and sweep streams. The pressure is controlled by adjusting the needle valves at the exit of the reactor and sweep sides. Pressure gauges are installed in the feed, reject, and permeate sides to monitor the pressure. Two syringe pumps, one for the feed and the other for the permeate side, are used to supply a controlled flow of water into the two steam-generating units. Another syringe pump and evaporator are combined to deliver the toluene and naphthalene vapors into the reaction system; the naphthalene is dissolved in the toluene at a predetermined concentration before being loaded into the syringe. These evaporator units are SS vessels packed with quartz beads in order to accelerate water/organic vapor evaporation and to dampen out fluctuations in their flow, if any. Heating tapes and TC are used to heat and control the temperature of the SS vessels. The steam generators along with the feed, sweep, permeate, and reject lines are insulated and "heat-traced" using heating tapes, their temperature also controlled with TC.

During the MR experiments, the gas streams exiting the reject and permeate sides flow through the condensers and then through the moisture traps to capture the water and the organic vapors, and through the adsorbent beds to remove H₂S and NH₃. The flow rates of the water-free and organics-free streams are then measured by BFM, and their composition is measured with an online GC. For the reactor experiments reported here, we use a simulated syngas with a composition (H₂/CO/CO₂/N₂/CH₄/NH₃/H₂S) = (0.67:1.00:1.00:2.67:0.2:0.00067:0.0006) typical of an air-blown biomass gasifier off-gas^{16,57} along with 0.8 vol % naphthalene and 6.4 vol % toluene added to the syngas feed, and a near stoichiometric H₂O/CO feed of 1.1. The same procedure is followed for the packed-bed reactor (PBR) experiments (to compare its performance with the MR)

and for measuring the catalytic reaction kinetics, the only difference being that the inlet and exit valves for the sweep gas are closed. The same system was also used for single-gas permeation studies to characterize the membrane properties. For such experiments, the sweep gas inlet is closed, gas flows into the feed side, and the permeate and reject stream flow rates are measured. For measuring the H₂O permeance, an Ar stream containing a predetermined concentration of water is fed into the system. The permeate stream then passes directly through an adsorbent bed where the water is captured. The amount of water that permeates is then calculated by measuring the weight of the adsorbent before and after water permeation.

Another key project goal was to further validate, by WGS-MR experiments, an isothermal MR model, previously developed and verified experimentally by our group for describing such reactors^{16,46} so that simulations can be performed to identify optimized reactor operating conditions (residence time, reactor pressure and temperature, and steam purge rate, etc.) for the various end-use applications. Further details about the model and key findings from its application can be found elsewhere.^{16,46}

3. RESULTS AND DISCUSSION

We previously tested the CMSM in the laboratory in the presence of toluene and naphthalene under nonreactive conditions¹⁶ as well as in the field where they were exposed to real coal-derived and/or biomass-derived syngas;⁵⁴ they were shown to perform well in both tests. The main goal in this study, therefore, was to test their ability to perform satisfactorily as well under reactive conditions in the presence of the aforementioned model impurities. Prior to the MR experiments, the membrane was characterized with single-gas permeation tests (our prior studies with CMSM indicate^{16,46} that mixed-gas permeances generally remain close to values measured with single-gas experiments, so no mixed-gas experiments were performed here). The permeances of various species, with respect to the inside membrane area (27.9 cm²), for the fresh membrane are shown in Table 1. Our experiments

Table 1. Single-Gas Permeation Data for the CMSM before and after the MR Experiments

gas	permeance (m ³ /(m ² ·hr·bar))	
	before	after
H ₂	2.21	2.04
CO	0.036	0.037
H ₂ O	not measured	0.73
CO ₂	0.073	0.079
CH ₄	0.007	0.007
N ₂	0.016	0.017

indicate that H₂S and NH₃ do not permeate through the membrane, and their permeance, therefore, was not included in Table 1 (In studies by our group in which the module and plumbing surfaces were specifically coated to avoid potential wall adsorption, the H₂S permeance was always found to lie between the permeances of N₂ and CH₄).

A key conclusion from our experiments, lasting for more than 8 weeks, is that the membrane exhibited robust behavior, with no notable changes observed over that period. Table 1, for example, shows the permeances of the various species measured via single-gas permeation tests (other than that for water, for which the permeance was measured as described above) after

all the reactor experiments were completed. The permeance of the less permeable species (CO, N₂, and CH₄) changed very little, and the permeance of H₂ decreased by ~7%, which is in line with our prior field-scale observations with these membranes.⁵⁴

Another goal of the study was to investigate the impact that the presence of an organic vapor and of a model tar-like species may have on catalyst performance. The reaction kinetics of this particular catalyst (Süd-Chemie Co/Mo/Al₂O₃ C-25 WGS catalyst) was extensively investigated previously by our group.^{16,46} Specifically, an empirical rate law, first proposed by Weller and co-workers^{58–61} and indicated below, was used to fit an extensive reactor data set that included studying syngas compositions corresponding to biomass and coal gasifiers, under a broad range of pressure, temperatures, and reactor residence times.

$$r_{\text{CO}} = A e^{-E/RT} P_{\text{CO}}^a P_{\text{H}_2\text{O}}^b P_{\text{CO}_2}^c P_{\text{H}_2}^d (1 - \beta) \quad (1)$$

$$\beta = \frac{1}{K_{\text{eq}}} \frac{(P_{\text{CO}_2} P_{\text{H}_2})}{(P_{\text{CO}} P_{\text{H}_2\text{O}})} \quad (2)$$

In the preceding expression r_{CO} is the reaction rate with respect to CO, T is the temperature. P_j is the partial pressure for component j , and K_{eq} is the overall reaction equilibrium constant. The values of the rate parameters (A , E , a , b , c , and d) have been reported elsewhere.^{16,46}

As reported in our previous papers,^{16,46} this empirical rate law performed well in fitting both our PBR and our MR data. However, the simulated syngas used in the present investigation contains a substantial amount of two model impurities (toluene and naphthalene), and their impact on the reaction kinetics of the catalyst was not known prior to this study (such impurities, for example, could have undergone catalytic cracking to produce coke that deactivates the catalyst or could have interfered, in some other way, with its WGS activity). For further investigation of this issue, additional reactor data were generated in this study and compared with the predictions of the empirical rate law (all of these experiments were carried out at 300 °C and a CO/H₂O = 1.1, which are the conditions utilized in the MR experiments reported here). The agreement between the data and the predictions from the empirical rate model are shown in Figure 2, which compares the experimentally measured conversions with the calculated conversions from the model. The experimental data agree well with the model indicating that under the conditions studied in this work the organic vapor and tar-like model impurities have no impact on catalytic activity. Furthermore, as noted previously, the catalyst activity remained stable, as manifested by the rate measurements spread throughout the 8 weeks of experiments (Figure 2). Since the empirical reaction rate model previously developed was shown to perform adequately, it was also utilized for all the reactor simulations reported in this paper, as discussed in the subsequent text.

One of the major potential advantages of the proposed one-box process is that it is a multifunctional system that combines the WGS reaction, the separation of the hydrogen product, and the removal of the various syngas impurities (H₂S, NH₃, organic vapors, and tars, etc.) into a single step. In particular, the ability of the CMSM to separate in situ the various syngas impurities offers great potential benefit in that it eliminates the need for using a warm-gas cleanup unit (WGCU) for removing these impurities from the syngas prior to its being processed in

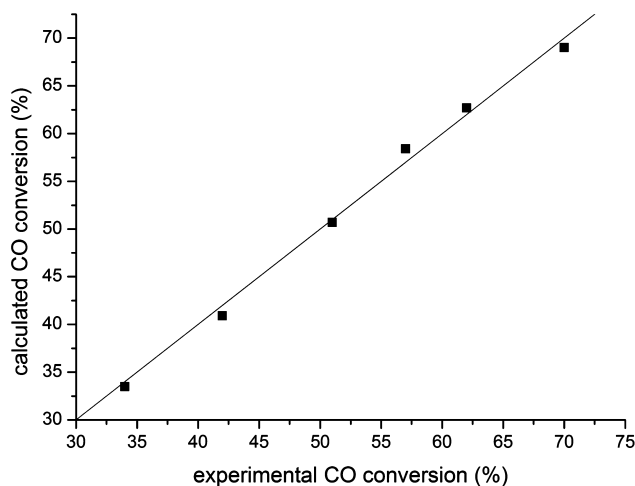


Figure 2. Experimental vs calculated CO conversions using the power-law rate expression^{16,46} under various packed-bed reactor experimental conditions (points, experiments; lines, simulations).

the WGS reactor. In our previous studies we reported on the ability of the CMSM to remove H₂S and NH₃.^{16,39,46,54} However, due to experimental limitations, we were not able to check their separation characteristics toward the organic vapors and the tar-like species. In this study, we have carried out a series of experiments in order to specifically check for the ability of such membranes to remove these types of impurities as well. Since these membranes are permeable to water (and also steam is used as the sweep gas) and toluene and naphthalene are somewhat soluble in water (see below), it is not straightforward to check the separation characteristics under reactive conditions. Instead, an experiment was carried out in which the CMS membrane was exposed to a flowing gas mixture of 6.4 vol % toluene in hydrogen at 300 °C and at 5 bar, and the gas phase exiting the permeate side (virtually pure hydrogen) was sampled via GC/MS for the presence of toluene. In these experiments we were unable to detect any toluene in the permeate stream (analytical instrument detection limit < 1 ppm). Thus, we conclude, based on these experiments, that toluene does not permeate through this tight-pore CMS membrane. Since naphthalene is a bigger molecule than toluene, hence one may also conclude (barring a set of unknown circumstances) that naphthalene (and the tar-like species in real syngas) will be unlikely to penetrate through the CMS membrane either.

In principle, through the use of condensers on the permeate side one could condense both water and the organic vapor and the tar-like species. However, no separate organic phase could ever be detected indicative that the CMSM does not allow such impurities to go through, and consistent with the toluene/hydrogen mixture permeation experiments described in preceding text. During the membrane reactor experiments, we collected the liquids from the condenser on the reject side and studied their volume and composition via GC-MS, as detailed in section 2. The key reason for doing that is so that we are able to investigate whether toluene and naphthalene react to a substantial extent in the WGS-MR and also whether they leak through to the permeate side during the process. These experiments, typically, involved carrying out the MR experiments for a certain period of time (while collecting all the condensable liquids produced) and then switching the feed flow into pure He gas, depressurizing the reactor, and under the

same temperature flushing the reactor system with He for an additional 8 h. Since the solution of naphthalene in toluene (a 1:8 molar ratio) has a lower density than water, the liquid phase collected consists of two phases, with the organic phase residing on the top. The organic phase is then carefully separated from the water phase and weighed. The total amount of organic phase collected corresponds to more than 95% of the amount of organic impurities (toluene + naphthalene) fed to the reactor during the period for which the liquid phase was collected and analyzed via GC-MS. The ratio of toluene/naphthalene in the organic phase collected from the reactor was 7.7:1. Given that toluene has a small but finite solubility in water (the toluene's solubility in water is 490 mg/L, and the naphthalene's solubility is 30 mg/L) and it is also volatile, it is not surprising that both the total amount of liquids but also the amount of toluene collected is somewhat smaller than the corresponding feed amounts (albeit less than 5%). Nevertheless, one can conclude from these results that neither one of these compounds gets substantially converted in the membrane reactor during the WGS reaction experiments, which is also in line with the experimental findings above that they do not impact the reaction kinetics, nor do they leak through the membrane to the permeate side; this is also a finding consistent with the permeation studies with the toluene in hydrogen mixtures noted previously.

Figure 3 shows the CO conversion as a function of $W_{\text{cat}}/F_{\text{CO}}$ (the weight of catalyst, which for these experiments is 10 g,

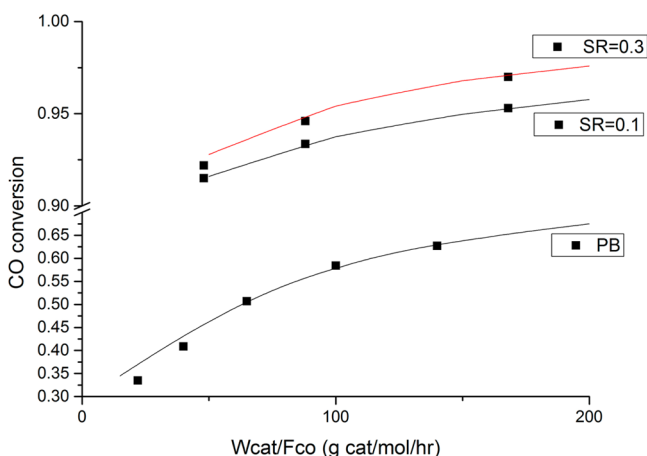


Figure 3. CO conversion under 3 bar of reactor pressure and at 300 °C for different sweep ratios (points, experiments; lines, simulations).

over the molar feed flow rate of CO) during the membrane reactor experiments for a feed pressure of 3 bar and two different sweep ratios (SR = 0.1 and 0.3). Shown in the same figure are the simulations based on the MR model using the independently measured reaction rate expression (eqs 1 and 2) and the membrane's permeances (the average values measured for the fresh membrane and the membrane after 8 weeks of experiments (see Table 1); for H_2S and NH_3 their permeances were set equal to zero). For comparison purposes, PBR experimental data and simulations are also shown in the same figure. A key observation from Figure 3 is that the model does an adequate job in describing both the MR as well as the packed-bed reactor experiments. The membrane reactor's conversion is higher than the packed-bed reactor's conversion, and both conversions increase with $W_{\text{cat}}/F_{\text{CO}}$ as expected. In

addition, increasing the sweep ratio also improves the reactor conversion.

Figure 4 shows the CO conversion as a function $W_{\text{cat}}/F_{\text{CO}}$ during the membrane reactor experiments for a different feed

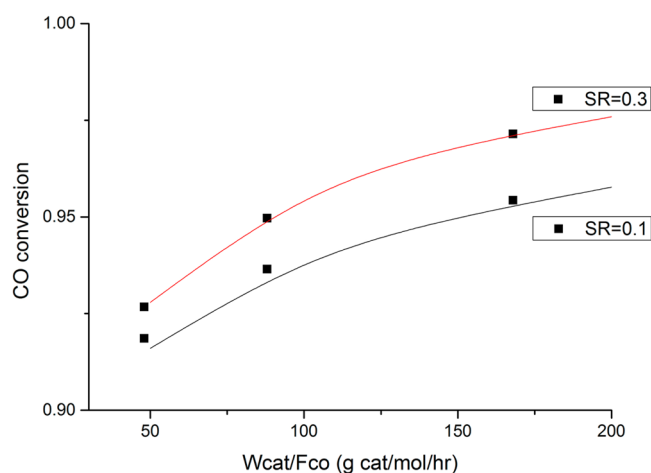


Figure 4. CO conversion under 5 bar of reactor pressure and at 300 °C for different sweep ratios (points, experiments; lines, simulations).

pressure of 5 bar and two different sweep ratios (SR = 0.1 and 0.3). Shown in the same figure, in addition, are the simulations based on the MR model. Once more, as Figure 4 indicates, the model does an adequate job in describing the MR. The membrane reactor's conversion again increases with $W_{\text{cat}}/F_{\text{CO}}$ and the sweep ratio. When comparing the results between Figures 3 and 4, it is clear that running the reactor at higher pressures benefits performance, an important result in terms of the eventual commercialization of the technology, since typical gasifiers are run at much higher pressures (20 bar and above). For further analysis and discussion about the effect of reactor pressure and the other operating conditions, please see refs 16 and 46.

Figure 5 shows the hydrogen recovery, defined as the fraction of total hydrogen that ends-up as part of the permeate stream,^{16,39} as a function of $W_{\text{cat}}/F_{\text{CO}}$ and the reactor pressure and sweep ratio. Shown on the same figure are also the recoveries calculated using the data-validated MR model. As

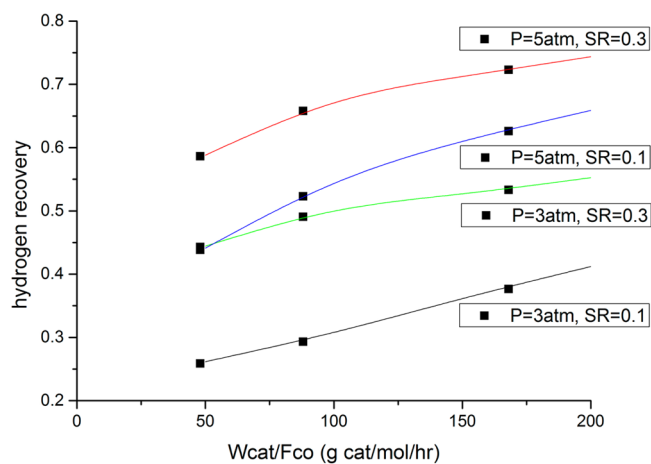


Figure 5. Hydrogen recovery under various experimental conditions (points, experiments; lines, simulations).

can be seen in Figure 5, the model does an adequate job, again, in describing the hydrogen recoveries for all conditions studied. As expected higher sweep ratios and reactor pressure increase H_2 recovery, and for a sweep ratio = 0.3 and a pressure of 5 bar, a H_2 recovery higher than 70% is achieved. The recoveries shown in Figure 5 are rather low due to limitations with the size of our laboratory system, which accommodates only one small-size CMS membrane—under optimized conditions (see discussion in the following text), recoveries in excess of 90% can be attained under realistic IGCC conditions.

Finally, Figure 6 shows the hydrogen purities (dry basis) in the permeate side as a function of W_{cat}/F_{CO} and the reactor

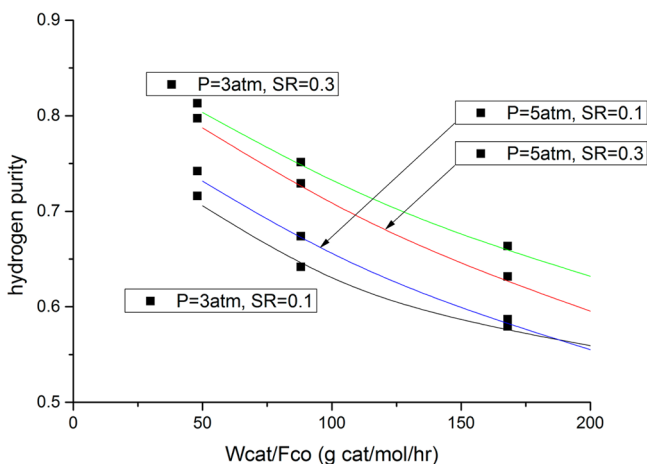


Figure 6. Permeate-side H_2 purity (dry basis) under various experimental conditions (points, experiments; lines, simulations).

pressure and sweep ratio. Shown on the same figure are also the hydrogen purities calculated using the data-validated MR model, which does a decent job in predicting the experimental values. As a result of the unoptimized laboratory-scale reactor operation, these purities are rather low—under optimized conditions,⁵⁴ purities in excess of 90% with a CO content of a few hundred parts per million can be attained under realistic IGCC conditions. The results in Figures 5 and 6 manifest the challenge one faces in optimizing such reactors, whereby conditions maximizing recovery may lead to diminished hydrogen purity. Thus, to optimize the reactor operating conditions, one needs a fine balance between W_{cat}/F_{CO} , the sweep ratio, and the reactor pressure in order to reach high CO conversion with acceptable hydrogen recovery and purity.

Since the model performs reasonably well in describing the experimental results, it can be used to further study the effect of various parameters on WGS-MR performance, in terms of reactor conversion, hydrogen recovery, and purity. The target here is to choose appropriate conditions which maximize both the CO conversion and H_2 recovery and minimize the CO content of the hydrogen product. Results of such process design and scale-up simulations have been presented elsewhere.^{16,39,46,54} For example, simulations, based upon membrane properties measured during field tests, demonstrate⁵⁴ that the one-box process, operating on a typical oxygen-blown gasifier off-gas, can deliver more than 90% hydrogen recovery at more than 90% purity (dry basis), and thus shows good promise for commercial application.

4. CONCLUSIONS

A novel MR system termed as the “one-box” process, in which syngas cleanup, hydrogen production via the WGS reaction, and product separation are combined in the same unit, was successfully utilized for producing hydrogen from a feed with a simulated biomass-derived syngas containing common impurities such as H_2S and NH_3 , a model organic vapor (toluene), and a model tar-like species (naphthalene). A single CMS membrane was used for the in situ hydrogen separation and syngas cleanup. The membrane was characterized in terms of its single-gas permeances, which were used for the model predictions. The CMS membrane stability was also investigated in the presence of these impurities, and the membrane proved to be stable under the experimental WGS reaction conditions.

The kinetics of the WGS reaction over a commercial Co/Mo/ Al_2O_3 sour-shift catalyst was also investigated in the presence of the organic vapor and of the model tar-like species as part of our study, and no impact of these impurities was observed. The performance of the MR (the one-box process) using such membranes and catalysts was investigated experimentally for a range of pressures and sweep ratios; the MR showed higher conversions compared with those of the traditional packed-bed reactor. Parallel modeling investigations indicated good agreement with the experimental data.

The proposed one-box process shows several advantages over the traditional packed-bed reactor system, including improvements in CO conversion and H_2 purity, while allowing one to perform the reaction in the presence of common impurities such as H_2S , NH_3 , organic vapor, and tar-like species, and being able to deliver a contaminant-free hydrogen product. Use of the process in hydrogen production from biomass-derived syngas should, therefore, result in considerable energy savings.

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Notes

The authors declare no competing financial interest.

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