

Integrated Process Configuration for High-Temperature Sulfur Mitigation during Biomass Conversion via Indirect Gasification

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ABSTRACT: Sulfur present in biomass often causes catalyst deactivation during downstream operations after gasification. Early removal of sulfur from the syngas stream post-gasification is possible via process rearrangements and can be beneficial for maintaining a low-sulfur environment for all downstream operations. High-temperature sulfur sorbents have superior performance and capacity under drier syngas conditions. The reconfigured process discussed in this paper is comprised of indirect biomass gasification using dry recycled gas from downstream operations, which produces a drier syngas stream and, consequently, more-efficient sulfur removal at high temperatures using regenerable sorbents. A combination of experimental results from NREL's fluidizable Ni-based reforming catalyst, fluidizable Mn-based sulfur sorbent, and process modeling information show that using a coupled process of dry gasification with high-temperature sulfur removal can improve the performance of Ni-based reforming catalysts significantly.

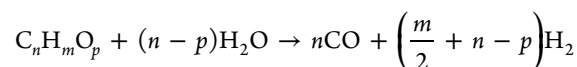
INTRODUCTION

Syngas is used industrially to produce various useful chemicals and fuels.¹ In addition to the desired constituents (CO and H₂), syngas produced via gasification of biomass contains hydrocarbons, tars, and contaminants such as sulfur.² Sulfur content in biomass-derived syngas can be in the 20–600 ppmv range³ and early removal after gasification can be beneficial. Sulfur and other contaminants can deactivate catalysts used in downstream syngas cleanup via reforming.⁴ Catalysts used in subsequent steps of the process, such as those for synthesis, also have stringent requirements on allowable contaminant levels (ppb to low ppm levels).^{1,5} Efficient and cost-competitive ways to remove these contaminants and produce clean syngas are key requirements for the commercial utilization of biomass-derived syngas for fuels and chemicals production.

Figure 1 shows a generalized process flow diagram of a biorefinery with adaptations for indirect gasification. *This process flow will vary depending on the specific products and technologies used.* An air separation unit for oxygen supply is not necessary in an indirect gasification system, which is the biggest difference between this system and gasifiers using direct heat transfer via partial oxidation;⁶ consequently, a steam reformer is used instead of an autothermal reformer to avoid any oxygen supply requirements. Note that because oxygen addition is not required, and heat transfer occurs indirectly in the gasifier, this configuration allows for the use of different gas compositions for biomass fluidization, including dry gases, as proposed in this paper. Figure 1 depicts a dual-bed circulating indirect gasification system⁷ with a gasifier and a combustor. In the dual-bed system, biomass is fed to the gasifier and hot olivine (or another solid heat-transfer material) from the combustor is used as the source of gasifier heat. Other methods of indirect heat transfer are also possible.⁸ The syngas from the gasifier is separated from the solids using cyclones and sent to the steam reformer for conversion of tars and hydrocarbons.⁹ The reformer serves the dual purpose of removing undesirable condensable tars¹⁰ to avoid fouling downstream equipment and

producing additional CO and H₂ from the tars and hydrocarbons that exit the gasifier. The solids separated in the gasifier cyclones, which include olivine and unconverted carbon in the form of char, are sent to the combustor of the dual-bed system. The char is combusted to heat the olivine. The hot olivine is separated from the ash produced during char combustion and then sent back to the gasifier. The combustor is fluidized using air, and the gasifier is commonly fluidized using steam.⁷

Steam reforming is an endothermic operation used for the conversion of tars and hydrocarbons to CO and H₂ in the presence of suitable catalysts.¹¹ A generalized reforming reaction is shown here:



Note that the reformer is depicted as a generic block in Figure 1. In practice, it will be necessary to ensure proper particulates removal, which may include filtration to sustain desired flow characteristics and performance in a fixed-bed reactor. The other alternative is to use a fluidized-bed reactor to alleviate the problem of particulates plugging the reactor. NREL has developed and demonstrated an attrition-resistant reforming catalyst in a fluidized bed at a pilot scale; the reformer follows two cyclones for the removal of particulates from syngas exiting the gasifier.⁴

In the process shown in Figure 1, heat is recovered from syngas exiting the reformer. The syngas is then scrubbed and compressed before it is sent for acid gas removal, where CO₂ is removed to make the syngas composition suitable for the synthesis reactor. Some H₂S is also removed with the CO₂ in the acid gas removal process. The syngas may then be polished using a ZnO bed to adjust H₂S levels for the synthesis reactor.

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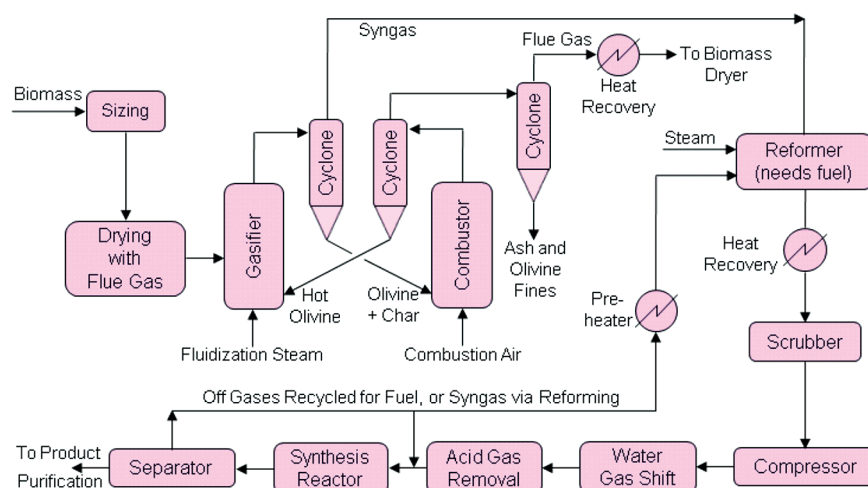
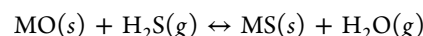


Figure 1. Generalized process flow diagram of a biorefinery with syngas from indirect gasification used to synthesize products. The order of some of the unit operations may be different and some steps may be added or eliminated, based on the specific product from a process.

The clean syngas is sent to the synthesis reactor, after further compression if necessary. The design may also include a water gas shift (WGS) reactor to achieve the desired H_2 :CO ratio for the synthesis reaction. After synthesis, the unconverted off gases are recovered and split between two or more streams, with some of the off-gases being directly recycled to the synthesis reactor after recompression and the remainder being sent back to the reformer to produce CO and H_2 or to be used as fuel to support the endothermic reforming reactions. Sending a portion of the off-gas stream to the reformer or elsewhere in the process to change its chemical composition before recycle, or purging after combustion, is usually necessary to prevent the buildup of byproducts formed in the synthesis reactor.

The aim of the reformer is to convert most of the tars and other hydrocarbon species, including methane produced in the gasifier, into CO and H_2 . The reforming catalyst typically consists of transition metals such as Ni or precious metals such as Pt or Rh¹² as the active catalyst. The Ni-based catalysts are more susceptible to deactivation by sulfur than the noble metal catalysts are. It has been shown that the adsorption of hydrogen sulfide on metal leads to the blocking of catalytically active sites.⁵ It is generally well-known that sulfur is a catalyst poison. However, because of the many other contaminants in biomass-derived syngas, it is not definitive that tackling the sulfur alone in biomass-derived syngas will sustain catalyst performance. Nonetheless, as discussed in a previous publication⁴ and also shown in this research, lowering the sulfur content in biomass-derived syngas does improve reforming performance of the catalyst. Thus, the removal of sulfur from the syngas produced in the gasifier before sending it to the reformer can be beneficial if done in a cost-effective manner. Sulfur removal processes that occur at high temperatures (700–900 °C), close to the gasification and reforming temperatures, can be located between the gasifier and reformer to avoid a thermal cycle and additional high-temperature heat-transfer equipment.

High-temperature sorbents can be used to remove H_2S .³ H_2S is the primary sulfur species in syngas,² because of the reducing environment during gasification, and removal of H_2S can help protect and improve the performance of downstream catalysts. The key reaction between H_2S and metal oxide sorbents is the following:¹³



The thermodynamic equilibrium toward H_2S removal is usually favored at lower temperatures and lower moisture contents.^{14,15} If moisture can be minimized, then the H_2S removal capacity of the sorbent can be significantly enhanced, even at high temperatures.

Significant research has been conducted on developing high-temperature sulfur sorbents for coal syngas cleanup,^{3,16} and prior work has informed our choices of sorbents. It was found that some sorbents (e.g., zinc oxide,¹⁷ iron and copper-based materials¹⁸) tend to face the problem of vaporization or reduction to metallic form at high temperatures, rendering them less effective. Extensive research for coal desulfurization was conducted with the aim of developing materials that are stable and retain good sulfur reactivity at high temperatures and in highly reducing environments. To that end, zinc titanate, which is a zinc-based material that does not volatilize easily up to temperatures of 700–800 °C,^{19,20} and copper chromite, which is a material that has the lowest reducibility of all the copper-oxide based materials,^{21,22} were developed. Other materials that also show great promise at high temperatures are based on manganese^{15,23–30} and rare-earth elements.^{21,31–36} The manganese-based material is of particular interest to us, because even though it does show some initial deactivation, it was one of the few sorbents that have been tested for hundreds of sulfidation–regeneration cycles.^{28,30}

■ EXPERIMENTAL SECTION

Sulfur Sorbent and Reforming Catalyst. A Mn-based sorbent was used for sulfur removal. The sorbent was prepared by incipient impregnation by the addition of manganese acetate solution on a fluidizable attrition-resistant alumina support supplied by CoorsTek (Golden, CO).³⁷ The support contains >90% alumina, 5.2% SiO_2 , and 2.5% MgO. Further details of the preparation have been discussed by Cheah et al.²⁹ The manganese content on the sorbent was 8.3% (by weight).

The reforming catalyst used for the tests has the same alumina support as that for the sulfur sorbent. Its composition is 5.6% Ni, 3.6% Mg, and 0.4% K (by weight), with the balance being the support material. Further details of the catalyst are provided by Yung et al.⁴

Sorbent and Reforming Catalyst Tests. A Micro-Activity Test System (MATS), shown in Figure 2, was used to gather experimental data for the Mn-based sulfur sorbent and Ni-based reforming catalyst.

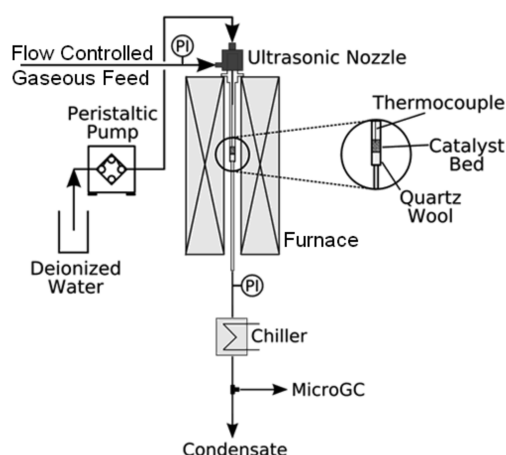


Figure 2. Schematic of the Micro-Activity Test System (MATS) arrangement.

The sorbent or catalyst was supported on ~ 0.2 g of quartz wool inside a 9.6-mm-inner-diameter (9.6-mm-ID) quartz tube, and test gases and water were fed in a down-flow configuration. Typically, 0.5 g of sorbent was used with dry gases and 5 g of sorbent was used for gases with steam. The experiments were run for 1–12 h to determine steady-state sulfur retention capacity. Approximately 1 g of reforming catalyst and a steam-to-carbon ratio of 4 were used for the reforming tests with ethylene and H_2S . The targeted gas composition and gas hourly space velocity (GHSV) were maintained using mass-flow controllers in the flow paths from the gas sources. The desired temperature was maintained by the surrounding furnace via a feedback control loop. Further details of the MATS system are available in the literature.²⁹

The simulated syngas composition used for the tests is shown in Table 1. This composition was used for tests with the sorbent and also for tests where the sorbent was upstream of the reforming catalyst.

Table 1. Simulated Syngas Composition

gas	composition (mole basis)
H_2S	394 ± 3 ppmv
CO	$10.5\% \pm 0.5\%$
H_2	$10.5\% \pm 0.5\%$
CH_4	$6.3\% \pm 0.3\%$
CO_2	$8.3\% \pm 0.3\%$
C_2H_4	$1.7\% \pm 0.1\%$
C_6H_6	370 ± 16 ppmv
H_2O	varied
inert	balance

Determination of Sulfur Retention in Sorbents. The S/Mn molar ratio in the sorbent after it was sulfided for 12 h in dry syngas was determined using two methods. The first method used direct elemental measurement of both Mn and S in the sorbent. Mn content in the sorbent was determined using inductively coupled plasma–optical emission spectrometry (ICP-OES). Sulfur content in the post-reaction sample was

analyzed with a LECO TruSpec Sulfur Add-On Module, where the sulfur in the sample was completely converted to SO_2 and the concentration of SO_2 measured. In the second method, the amount of sulfur removed from the syngas was determined by numerical integration of the amount of sulfur removed from the syngas stream over time (that is, by integrating the sulfur breakthrough curves). The S/Mn molar ratio for the dry syngas experiments determined using the numerical integration method was $\sim 9\%$ higher than that obtained from direct elemental sulfur measurements. The standard deviation for direct elemental measurement of sulfur in the dry syngas, done in triplicate, was $\sim 3\%$. The experimental direct elemental measurement method for sulfur measurement did not work well with the low-sulfur-content sorbents obtained from the experiments with moist syngas, because the measurement uncertainty was high when the sulfur content was low. The results from the numerical integration method, which were shown to be within 10% of the results from the elemental analysis method with dry syngas, were deemed more reliable for determination of sulfur retention with moist syngas.

RESULTS AND DISCUSSION

Sulfur Sorbent Performance. The reduction in sulfur retention capacity of the Mn-based sorbent with increasing moisture was experimentally quantified (Table 2) for three moisture contents, using the gas composition shown in Table 1.

Table 2. Sulfur Retention Capacity of Mn-Based Sorbent at Various Moisture Contents at 700 °C

moisture (mole basis)	S/Mn molar ratio
dry	0.95 (0.87 ^a)
8%	>0.07
45%	0.004

^aValue using direct elemental S measurement.

The significant reduction in the sorbent's capacity for H_2S removal with increased moisture shows that the Mn-based sorbent is more effective at lower moisture contents. Thus, dry conditions can facilitate increases in removal efficiency and reduce equipment sizes and required sorbent inventory.

Another experiment measured H_2S breakthrough at different moisture contents using the Mn sorbent. Results of that test (Figure 3) quantify the extended time without H_2S break-

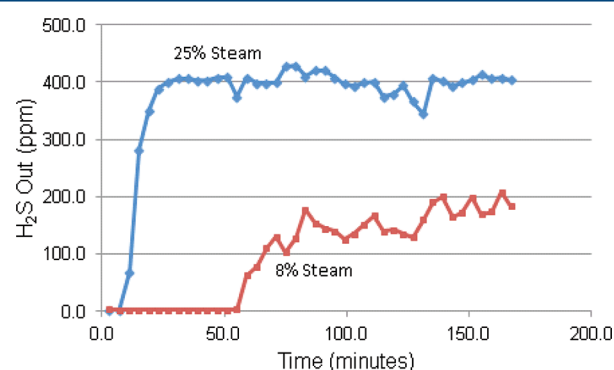


Figure 3. Exit H_2S concentration after simulated syngas at two steam contents (8 and 25 vol %) was sent through a Mn-based sorbent bed in the MATS setup. Key test conditions: temperature = 700 °C, GHSV = $15\,000\text{ h}^{-1}$, inlet $\text{H}_2\text{S} \approx 394$ ppmv.

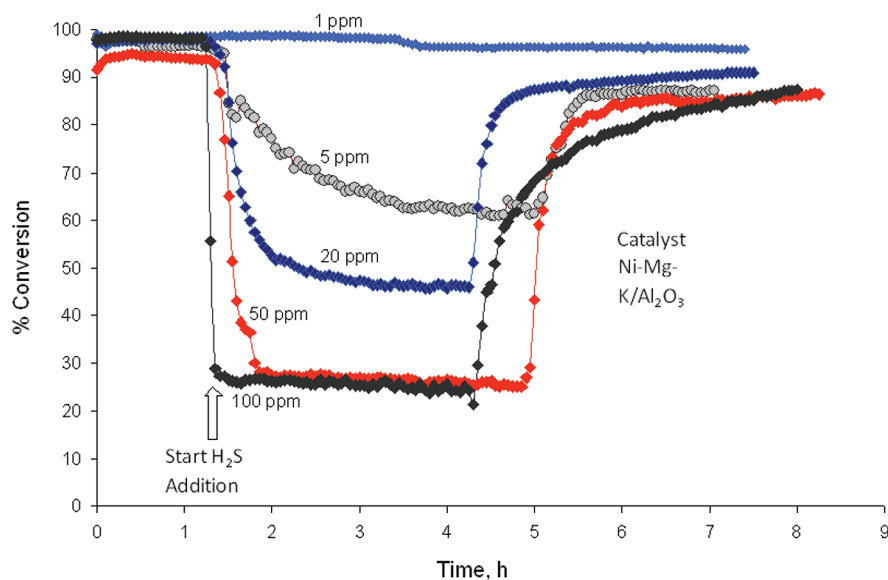


Figure 4. Ethylene conversion using a Ni-based reforming catalyst⁴ in the presence of various levels (ppmv) of H₂S. The drop in activities after 1 h corresponds to the introduction of H₂S. The revival of activities between 4 h and 5 h corresponds to the removal of H₂S from the inlet stream. Experiments were conducted on the MATS system at GHSV = 90 000 h⁻¹, steam to carbon ratio = 4, and temperature range = 820–850 °C.

through when using drier gases. For the 8 vol % steam case, the average H₂S in the cleaned syngas during the first 55 min, before there was significant H₂S breakthrough, was 2.4 ppmv, with a standard deviation of 0.2. The sulfur loading at the point of sulfur breakthrough beyond the 2–3 ppmv range was 0.14 g S/100 g sorbent.³⁸ The tests were conducted with ~394 ppmv of H₂S (Table 1). Syngas from woody feedstocks typically contains <100 ppmv of H₂S²; therefore, significant sulfur breakthrough should take longer with woody feedstocks.

Although the sulfur loading of 0.14 g S/100 g sorbent is small, the sorbent requirement should be evaluated in the context of biomass-derived syngas, the sulfur content of which is much lower than that of syngas from coal. As mentioned previously, sulfur in biomass-derived syngas is in the 20–600 ppmv range. This range is 50 times lower than sulfur (H₂S) in syngas from coal, which has a range of ~0.1–3 vol % (see Table 1 in the work of Ben-Slimane et al.¹⁵). Detailed studies of equilibrium sulfur retention in Mn material containing ~40 wt % Mn using simulated coal-derived syngas showed ~10 wt % sulfur retention (10 g S/100 g sorbent) under high-temperature conditions. Based on the sulfur concentration in coal-derived syngas, which is 50 times higher, compared to that in biomass-derived syngas, the sorbent loading requirement by weight per molar flow of syngas for the coal experiments¹⁵ is in the same order of magnitude as the biomass-derived syngas desulfurization results using the NREL sorbent. Note that with the simulated biomass-derived syngas (8% moisture), the outlet H₂S concentration in the cleaned syngas is much lower (2–3 ppmv) than with the simulated coal-derived syngas.¹⁵ This lower concentration is necessary for the downstream applications of the biomass-derived syngas proposed in this paper.

Effect of Sulfur on Ni-based Steam Reforming Catalysts. The effect of contaminants in biomass-derived syngas on the reforming performance of the Ni-based catalyst mentioned above is discussed in detail by Yung et al.⁴ The effect of H₂S on ethylene reforming using the same catalyst is shown in Figure 4, while subsequent (Figure 5) discussions focus on methane, which is the most difficult component to

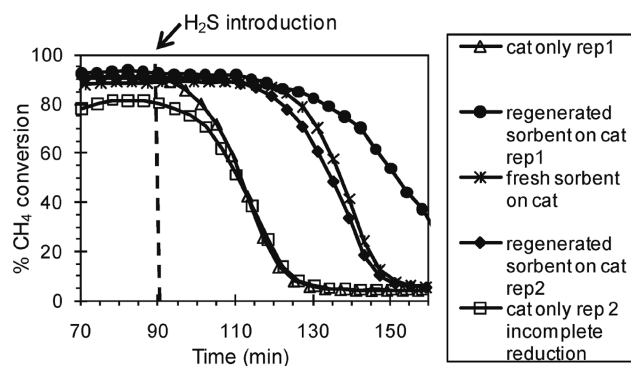


Figure 5. Methane conversion during three sets of experiments for steam reforming of simulated syngas with 59.4% steam: (1) catalyst unprotected by sorbent, (2) catalyst protected by upstream fresh sorbent, and (3) catalyst protected by upstream regenerated sorbent. Reaction conditions: temperature 750 °C, GHSV with respect to the sorbent 6600 h⁻¹. The improvement of reforming performance (methane conversion) when using an upstream sulfur sorbent compared to the “cat(alyst) only” tests shows the potential benefit of using an effective sulfur sorbent upstream of the reformer. (Reprinted with permission from ref 29. Copyright American Chemical Society, 2011.)

reform in syngas. After methane, ethylene is usually the second-most predominant component from indirect biomass gasification that must be reformed.^{2,7,39} Pure ethylene spiked with H₂S is also capable of simulating the sulfur-induced deactivation during reforming of benzene and higher-molecular-weight tar species; it has been postulated that the reforming mechanism of higher-molecular-weight aromatics proceeds via initial cracking to C₁ and C₂ molecules.⁴⁰ In addition, ethylene was much easier to introduce in the MATS system than the higher-molecular-weight species were. Note that the molar proportions of benzene and higher-molecular-weight compounds and tars are significantly lower than methane and ethylene in biomass-derived syngas.³⁹ Recent measurements of benzene and tars using a molecular beam mass spectrometer (MBMS) at NREL’s pilot plant, before and

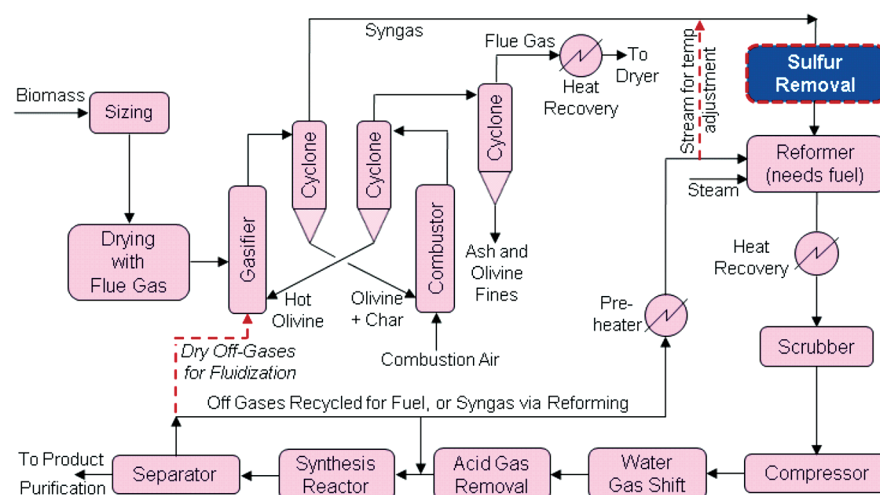


Figure 6. Modified version of process flow diagram shown in Figure 1. Modifications (shown by dashed lines) include the use of dry off gases from the synthesis reactor for biomass fluidization in the gasifier and sulfur removal from the syngas exiting the gasifier.

after fluidized steam reforming of biomass-derived syngas, have shown that all of these higher-molecular-weight species² are completely converted in the presence of NREL's reforming catalyst within detection limits (5–35 mg/Nm³, varying with the tar species) of the MBMS, even in the presence of sulfur in biomass-derived syngas.

Cheah et al.²⁹ demonstrated further evidence of the beneficial effects on the Ni-based reforming catalyst upon upstream removal of H₂S from simulated syngas. The experiments were conducted by placing the sulfur sorbent upstream of the reforming catalyst in the MATS system, and the results indicated that the reforming catalyst was able to maintain high levels of methane conversion for much longer periods with an upstream sulfur sorbent. The abundance of methane in syngas from an indirect biomass gasifier,² and its stable molecular structure, makes methane conversion a key indicator of good overall reforming performance. Low methane conversion in the reformer has a negative economic impact on the overall conversion process,³⁹ unless methane is a desired product, such as for biopower.

The longer period of better reforming performance (Figure 5) in the cases with an upstream sulfur sorbent corresponds to the time necessary for H₂S breakthrough through the sorbent. Details demonstrating that the sorbent does not have any reforming activity are in Cheah et al.²⁹ Cheah et al.²⁹ also showed that the sulfur sorbent could be effectively regenerated using combinations of steam and air and thus has potential for application in a continuous circulating system with regeneration. Longer term tests, including regeneration, will be conducted in the future with this sorbent. Mn-based sorbents have been shown to be robust and maintain performance through multiple cycles during tests with simulated coal-derived syngas.^{24,30}

Process Modifications. Because fluidization steam and moisture present in the biomass feed are the main contributors to the moisture in syngas from indirect gasification, the moisture content can be controlled by changing the fluidization medium and drying the biomass. Biomass drying can be energy- and capital-intensive, and economic tradeoffs must be considered to determine the optimal moisture content. Recent studies at the Idaho National Laboratory suggest that 10%

moisture in woody biomass may be a preferred moisture level after feedstock processing⁴¹ (see Table B-4 in ref 41).

Dry process gases can be used instead of steam⁴² for biomass fluidization in order to limit the moisture introduced into the gasifier (see Figure 6). Tests have shown that the steam added for fluidization does not have any significant impact on carbon conversion;⁷ the primary impact of the steam is on the syngas composition, because of the water-gas shift (WGS) and, to a lesser extent, from additional reforming reactions. Recycled off-gas compositions from simulated Fischer–Tropsch^{43,44} and mixed-alcohol⁴⁵ processes show that they are dry and can be used in the process schematic shown in Figure 6. This concept relies on the availability of clean, dry off-gases from the downstream synthesis reactor. However, such gases may not be available in sufficient quantities from all synthesis processes to meet the requirements for biomass fluidization in the indirect gasifier. For example, in a methanol production process, there is high overall conversion of syngas within the synthesis reactor loop, and therefore a lower quantity of gases is available for recycle.^{46,47} In such cases, recycling part of the cleaned syngas stream from the scrubber (see Figure 6 for location) to the gasifier, after water knockout, instead of sending the full stream to the synthesis reactor, will result in increases in production costs, primarily because of the increase in equipment sizes and heat recovery. A cost-benefit analysis will be necessary to justify the use of this proposed process reconfiguration. The availability of dry process gases will be specific to the process design; for example, a fixed-bed Fischer–Tropsch process will have sufficient off-gases, because of low conversion, whereas a slurry-reactor Fischer–Tropsch process will have higher conversions and smaller amounts of off-gases to recycle.⁴⁸ With a slurry reactor, a combination of reactor off-gases and fuel gases recovered during product separation, along with some supplementary syngas after the scrubber, will be sufficient to meet the biomass gasifier fluidization requirements (based on estimates from the process shown in Bibber et al.⁴⁴).

In cases where dry process gases are available for recycle to the gasifier (e.g., a mixed-alcohol process⁴⁵), the equipment size impact of this proposed process modification is expected to be negligible. In any case, the unreacted gas stream will likely need to be sent to the reformer to modify its composition. The overall volume of process streams will not change if these

unreacted dry gases replace the fluidizing steam in the gasifier, and the entire process steam requirement is introduced directly in the reformer (Figure 6), instead of the steam being distributed between the gasifier and reformer (Figure 1).

Predictions of syngas moisture content using correlations⁴⁵ (see Appendix G of ref 45) developed from indirect gasification test data⁷ show that the moisture contents in syngas produced by dry gasification of 5 and 10 wt % moisture feed are ~4.6 and 9.5 vol %, respectively. As expected, the predicted moisture content is higher with steam fluidization; for a steam-to-bone dry biomass ratio of 0.4 w/w and a feedstock moisture content of 5 wt %, the predicted moisture in the syngas is 40 vol %.³⁹ As shown in Figure 3, relatively efficient removal of sulfur at high temperatures is possible with drier syngas. The reformer will require additional steam to compensate for the amount not added to the gasifier; the main criteria dictating the amount of steam added to the process is the desired H₂:CO ratio in the synthesis reactor.¹ The final syngas composition after the reformer will remain almost unchanged by this process reconfiguration.

It is desirable to have synergy between the operating temperatures of the gasifier and the reformer, to avoid expensive heat-transfer equipment and the associated thermal loss. The typical operating range of the indirect biomass gasifier depicted in Figure 1 is 700–850 °C.⁷ Catalytic steam reforming of biomass-derived syngas has been conducted at temperatures of 550–900 °C.¹¹ Thus, it is desirable to operate a sulfur sorbent system in the 700–900 °C range, because this unit will be placed between the gasifier and reformer. Also, cooling the gasifier outlet (Figure 1) to temperature ranges of 400–750 °F (~205–400 °C), which is typical of conventional zinc-oxide sorbent processes,¹³ will risk equipment fouling due to tar condensation. Steam reforming reactions are thermodynamically favored at higher temperatures, with the detrimental effects of H₂S on reforming catalysts also being shown to decrease at higher reforming temperatures,¹¹ so it is prudent to utilize the heat from the gasifier products during reforming. As shown in Figure 6, the conditions in the sorbent unit can be adjusted for optimal performance by upstream mixing of a slip stream of the dry recycled gases, which can help lower the temperature and also further reduce the overall moisture content of the feed. In any case, heat input will be necessary during reforming to maintain high temperatures and compensate for the endothermic reactions. The data shown for 8% steam in Figure 3 and Table 2 are in the range of relevance for such a process configuration. Also, as mentioned in the Introduction, in the context of reforming, very efficient particulate removal beyond the gasifier cyclones will be necessary for fixed-bed sorbent systems, whereas fluidized-bed systems will be more tolerant to the presence of particulates. NREL's attrition-resistant fluidizable sorbent that has been described above is still in the early stages of testing and can potentially alleviate extreme particulate removal requirements.

CONCLUSION

High-temperature sulfur removal is possible in an integrated biomass conversion process with dry gases used for fluidization during indirect gasification. There are significant energy benefits¹³ of using such a regenerative sulfur sorbent process over conventional liquid scrubbing processes where the syngas must be cooled before sulfur removal. Early sulfur removal after the gasifier can also benefit processes that use Ni-based steam reforming catalysts after the gasifier; potential benefits include

higher conversion of hydrocarbons, increased catalyst longevity due to less sulfur poisoning, and reduced reformer operating temperatures.

This process reconfiguration can be applied to any integrated biomass conversion process where a suitable dry gas stream is available for gasifier fluidization, for example, the production of hydrogen from biomass⁴⁹ where the dry off gases from pressure swing adsorption can be used for biomass fluidization in the gasifier.

The demonstrated use of the relatively inexpensive fluidizable and regenerable Mn-based sorbent on attrition-resistant alumina support for high-temperature sulfur removal makes this a good candidate for bulk industrial use. Further experiments will be necessary to determine and improve long-term performance of the sorbent. Also other materials, with and without Mn, for high-temperature biomass-derived syngas desulfurization are being studied to improve the sorbent's capabilities.

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Notes

The authors declare no competing financial interest.

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