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A Novel Approach to Enhance the Hydrogen Yield of Biomass Gasification Using CO$_2$ Sorbent

Hydrogen yield of conventional biomass gasification is limited by chemical equilibrium constraints. A novel technique that has the potential to enhance the hydrogen yield by integrating the gasification and absorption reactions has been suggested. The method involves gasification of biomass in presence of a CO$_2$ sorbent. Ethanol was used as the model biomass compound and CaO was the representative sorbent. Equilibrium modeling was used to determine the product gas composition and hydrogen yield. The analysis was done using ASPEN PLUS software (version 12.1) and the Gibbs energy minimization approach was followed. The effects of temperature, pressure, steam/ethanol ratio, and CaO/ethanol ratio on product yield were investigated. Three case studies were conducted to understand the effect of sorbent addition on the hydrogen yield. Thermodynamic studies showed that the use of sorbents has the potential to enhance the equilibrium hydrogen yield of conventional gasification by ~19% and reduce the equilibrium CO$_2$ content of product gas by 50.2%. It was also found that the thermodynamic efficiency of sorbent-enhanced gasification (72.1%) was higher than conventional gasification (62.9%). Sorbent-enhanced gasification is a promising technology with a potential to improve the yield and lower the cost of hydrogen production. [DOI: 10.1115/1.2747252]

Keywords: biomass, hydrogen, gasification, thermodynamics, sorbent

1 Introduction

In the next decade or two, hydrogen is expected to become a prominent energy carrier for stationary and mobile power generation applications [1,2]. The chemical energy stored in hydrogen can be converted to mechanical energy by combusting in an internal combustion (IC) engine or it can be directly converted into electricity by fuel cells without any carbon emissions and with minimal emission of other polluting gases. At present, the main process for hydrogen production is by catalytic steam reforming of methane [3]. Hydrogen produced from fossil fuel sources significantly contributes to the greenhouse gas emissions and environmental pollution. In order to have environment-friendly hydrogen, it must be produced from renewable resources. A number of different ways of producing renewable hydrogen are being investigated [4]. Of all the resources, biomass holds the greatest promise in the near future [4,5]. Thermochemical biomass gasification has been identified as a potential method for producing renewable hydrogen [6–8].

The authors carried out a basic thermodynamic analysis of biomass gasification in a previous study [9]. In that study, the favorable operating conditions for hydrogen production at thermodynamic equilibrium obtained by gasifying biomass were determined. The gasifier temperature, gasifier pressure, steam-to-biomass ratio (moles of steam per mole of biomass), and equivalence ratio (a measure of air supplied in biomass gasification) were varied over certain ranges and the product gas yield was found by the Gibbs energy minimization approach. It was concluded in the earlier study that steam biomass gasification produces a gas mixture rich in H$_2$, containing other gases such as CO, CO$_2$, CH$_4$, and small amounts of higher hydrocarbons. The high-

est hydrogen yield occurred at a gasification temperature of 1050 K. Lower temperature caused incomplete gasification thereby producing more hydrocarbons and less hydrogen. Higher temperature reduced the hydrogen yield due to reverse water gas shift reaction. Hence, the highest hydrogen yield has a temperature constraint. The optimum pressure was found to be atmospheric; higher pressures reduced the hydrogen yield while lower pressures did not offer any substantial increase in hydrogen. Hence, pressure too, imposes a constraint on the maximum hydrogen that can be produced from biomass. It was found that the steam-to-biomass ratio can be increased to give higher hydrogen yield, but this was at the cost of supplying extra steam. It was also observed that beyond a certain steam-to-biomass ratio, the hydrogen yield increased only marginally with most of the supplied steam going unreacted. Hence, in order to enhance the hydrogen yield of conventional biomass gasification, it was necessary to find new or improved techniques, which are simple, energy efficient, and inexpensive. The product gas coming out of the gasifier consists of gases other than hydrogen, such as CO, CO$_2$, and CH$_4$, and these need to be separated. Hence, the problem of gas separation also needs to be addressed.

In recent years, sorbents (such as calcium oxide) have been proposed to separate CO$_2$ and thereby increase the hydrogen yield of conventional steam methane reforming (SMR) and coal gasification processes. Hydrogen yield of more than 95% (dry molar basis) has been obtained experimentally in laboratory-scale steam methane reforming process [10]. Apart from high hydrogen yield, sorbent addition also offers other advantages, such as low reaction temperature, easy CO$_2$ separation, and a potential to lower the capital cost. In theory, the concept of using sorbents can be applied to any carbonaceous fuel, such as coal, heavy oils, biomass, or organic waste.

2 Sorbent-Enhanced Reforming

The concept of producing hydrogen by reforming hydrocarbons in the presence of a sorbent dates back to as early as 1868 [11]. In 1967, Curran et al. separated CO$_2$ at high temperature using cal-
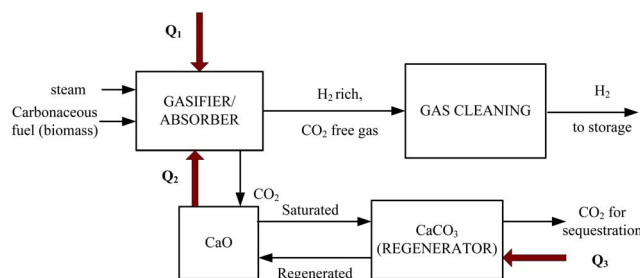
Fig. 1 Concept of sorbent-enhanced biomass gasification

cined dolomite [12]. More recently Balasubramanian et al. [10], Ortiz and Harrison [13] and Peng [14] have experimentally shown a novel method of improving hydrogen yield of conventional SMR and effectively separating CO_2. Lin et al. have proposed an innovative HyPr-RING (hydrogen production by reaction interaction novel gasification) technique that uses sorbents for producing hydrogen by gasification of coal [15–17]. The underlying concept of sorbent enhanced gasification is shown in Fig. 1. There are two main reactors in the process; first is the gasifier/absorber. Here, any carbonaceous fuel (in this case biomass) is supplied to the reactor to which steam is also being fed. The fuel reacts with steam to produce a gas mixture containing hydrogen, carbon monoxide, carbon dioxide, and some hydrocarbons (mainly methane). The carbon monoxide reacts with steam to produce additional hydrogen and CO_2 as per the water gas shift (WGS) reaction

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_R = -41.2 \text{ kJ/mol} \quad (1)$$

The calcium oxide sorbent, which is present in the gasifier, absorbs the carbon dioxide produced by the reforming reaction and gets converted to calcium carbonate as per the following reaction:

$$CaO + CO_2 \rightarrow CaCO_3 \quad \Delta H_R = -178.3 \text{ kJ/mol} \quad (2)$$

Heat released during the exothermic CO_2 absorption process is supplied to the endothermic steam gasification of biomass, thereby reducing the net external heat supplied to the gasifier. After some time, all the CaO gets converted to $CaCO_3$. The CaO is then regenerated by heating it in a regenerator (which is the other main reactor used in the process, refer to Fig. 2). The thermal energy for regeneration is supplied either by burning supplemental fuel or burning uncombusted char that remains in the calcium carbonate residue. The hydrogen produced may also have small amounts of impurities, such as carbon monoxide, methane, and tars. Hence, it is passed through a gas cleaning system (consisting of cyclones, filters, and possibly a hydrocarbon reforming catalyst bed) so as to obtain a clean gas that is rich in H_2. Through simultaneous gasification and CO_2 absorption, the equilibrium of the water gas shift reaction is shifted toward H_2. A typical woody
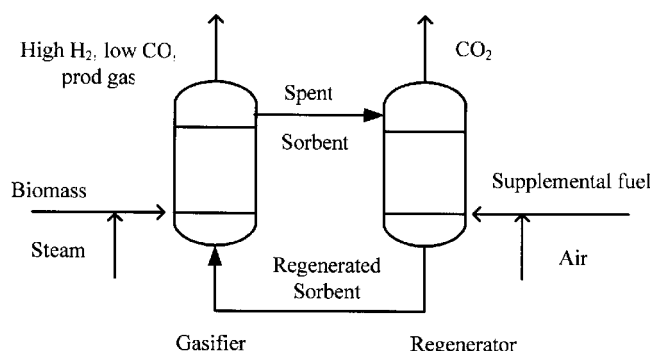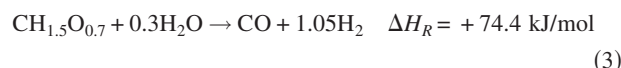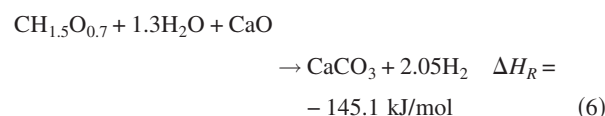

Fig. 2 Schematic of sorbent-enhanced gasification

biomass fuel can be represented as $CH_{1.5}O_{0.7}$ [6]. The reactions taking place in sorbent enhanced gasification for such a fuel can be written as follows:

$$CH_{1.5}O_{0.7} + 0.3H_2O \rightarrow CO + 1.05H_2 \quad \Delta H_R = +74.4 \text{ kJ/mol} \quad (3)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_R = -41.2 \text{ kJ/mol} \quad (4)$$

$$CaO + CO_2 \rightarrow CaCO_3 \quad \Delta H_R = -178.3 \text{ kJ/mol} \quad (5)$$

The overall reaction is given by Eq. (6), which represents the idealized sum reaction for sorbent enhanced gasification. Here, the formation of secondary products (methane, coke, and tar) is neglected. The regeneration of spent sorbent is given Eq. (7).

$$CH_{1.5}O_{0.7} + 1.3H_2O + CaO$$
$$\rightarrow CaCO_3 + 2.05H_2 \quad \Delta H_R = -145.1 \text{ kJ/mol} \quad (6)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H_R = +178.3 \text{ kJ/mol} \quad (7)$$

3 Simulation and Results

Sensitivity studies have been carried out in order to determine the effect of process variables on the equilibrium hydrogen yield. Ethanol was used as the model biomass compound and ASPEN PLUS software was used to model the process flow [18]. The motivation for using ethanol was based on the fact that the physical, thermodynamic, and transport properties for this biomass compound are well documented and are already built into ASPEN database. This makes it convenient to carry out the process simulations. The choice of ethanol as a model compound does not necessarily imply the biomass-ethanol-hydrogen route for producing hydrogen. Ethanol can be produced from renewable resources, such as corn, starch, sugarcane, cellulose, and waste materials from agro industry, using biological or other methods, and this is a subject matter of another study. A unique feature of using ethanol is that the biomass-ethanol-hydrogen systems are nearly CO_2 neutral. However, the availability of data and convenience of modeling a known process feed were the major factors behind choosing ethanol as the model biomass compound.

Broadly, three cases were analyzed as under:

- base case (no sorbent)
- reforming with sorbent in the reformer
- reforming with sorbent in the water gas shift (WGS) reactor

The process variables studied were temperature, pressure, steam/ethanol ratio, and CaO/ethanol ratio.

3.1 Case I: Ethanol Reforming (Base Case). The general reforming reaction between ethanol and steam can be written as

$$C_2H_5OH + H_2O \rightarrow Products \quad (8)$$

According to the thermodynamic considerations and experimental testing of ethanol steam reforming over Cu/Ni catalyst at temperatures above 600°C, the main products evolved are CH_4, H_2O, CO_2, CO, H_2, and solid carbon, C [19]. There are also trace amounts of ethylene and acetaldehyde. However, in the simulations, the concentration of products with two carbon atoms is found to be negligible compared to other products.

Referring to the simulation flow sheet in Fig. 3, ethanol and water are mixed (in MIXER) and heated (in HEATER) to a temperature of 700°C. The products are then sent to a Gibbs reactor (REFORMER), which is at the same temperature as HEATER and is maintained at atmospheric pressure. The reformation reaction yields a mixture of gases that flow into a cooling heat exchanger (COOLER), which is used to recover the waste heat from product
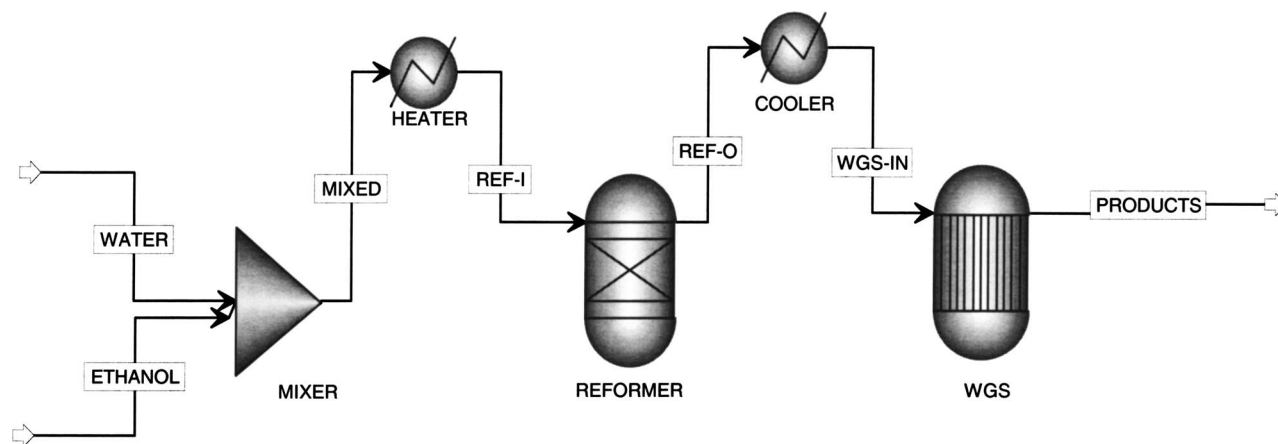
Fig. 3 Simulation flow sheet of conventional ethanol steam reforming (no sorbent) (case I)

gases. The gases then enter the second Gibbs reactor (WGS) in which water gas shift reaction takes place at 300°C to produce more hydrogen as per the following reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_R = -41.2 \text{ kJ/mol} \tag{9}$$

The results of the simulation are given in Table 1. All the gas yields for this case and the next two cases are given in kmols. The ethanol feed is kept fixed at 1 kmol. As shown in the results, the hydrogen yield by reforming is 4.69 kmol/kmol of ethanol feed. The hydrogen yield increases to 4.79 kmol/kmol of ethanol after the water gas shift reaction (WGS outlet). A sensitivity analysis was later carried out.

The steam-to-ethanol molar feed ratio was varied from 3 to 8, the temperature was varied from 500°C to 900°C, and the pressure was varied from 1 atm to 24 atm. The results of the sensitivity analysis are shown in Figs. 4–6. Figure 4 illustrates the effect of temperature on the product yield. The temperature has a significant effect on the equilibrium concentration of the products. As the reaction temperature increases, the hydrogen molar flow rate increases and reaches a maximum at 725°C. At the same temperature, methane yield reduces to a very small value. The increase of hydrogen yield is due to the reaction of ethanol with steam. As temperature increases the hydrocarbons (methane and higher) are reformed and converted to hydrogen. At still higher temperatures (more than 800°C), the water-gas shift reaction starts occurring in the reverse direction. This consumes the hydrogen and CO_2, and hence, the hydrogen yield starts reducing. Figure 5 shows the effect of varying reactor pressure on the product gas composition. It is seen that the steam reforming of ethanol is best done at atmospheric pressure. The effect of steam to ethanol molar ratio is

shown in Fig. 6 for a reforming temperature of 700°C. The addition of steam increases the hydrogen yield while reducing the methane and CO yields. Although high steam-to-ethanol ratio is favorable from hydrogen production point of view, it will be limited by the energy cost of the system.

3.2 Case II: Ethanol Reforming With Sorbent in Reforming Reactor. In this case, we analyze the addition of CaO to the steam ethanol reforming process. It is seen in Fig. 7, that CaO is an input to the REFORMER in addition to the ethanol and steam mixture. The following reaction takes place during the reforming process:

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s) \quad \Delta H_R = -178.3 \text{ kJ/mol} \tag{10}$$
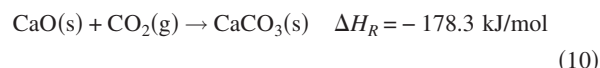
The separation of CO_2 from the gaseous phase will displace the equilibrium of the gas mixture to a higher hydrogen yield and a lower CO concentration. The products from the reformer are the same as case I, in addition CaO and $CaCO_3$ are present. The flow sheet of the simulation is shown in Fig. 7. The reformer products are sent to the separator (SEP) for separation of gases from solids. The gases, which include H_2, CO, CO_2, CH_4, and steam, are cooled to 300°C in the heat recovery exchanger (COOLER) and then enter the WGS reactor. The solids are sent to the regenerator (REGEN) in which $CaCO_3$ is thermally dissociated to CaO and CO_2 at 850°C. The results of the simulation in this case are shown in Table 2. The hydrogen yield in this case is higher than the base case. The total amount of hydrogen produced per kilomole of ethanol feed after the shift reactor is 5.7 kmols, which is almost 19% more than the no sorbent case (case I). The amount of

Table 1 Simulation results for case I

|	ETOH	WAT	MIX	REF-I	REF-O	WGS-IN	PROD
Temperature (°C)	25	25	25	700	700	300	300
Pressure (atm)	1	1	1	1	1	1	1
Vapor fraction (-)	0	0	0	1	1	1	1
Molar flow (kmol/h)	1	4	5	5	8.89	8.89	8.44
Mass flow (kg/h)	46.07	72.06	118.13	118.13	118.13	118.13	118.13
Enthalpy (kJ/h)	−292.6	−1129	−1421	−1045	−794.2	−920	−961
H_2 (kmol)					4.69	4.69	4.79
CO (kmol)					1.10	1.10	0.10
CO_2 (kmol)					0.84	0.84	1.53
Ethanol (kmol)	1		1	1	0.00	0.00	0.00
H_2O (kmol)		4	4	4	2.21	2.21	1.84
CH_4 (kmol)					0.05	0.05	0
C_2H_4 (kmol)					0	0	0.19
CH_3CHO (kmol)					0	0	0.00
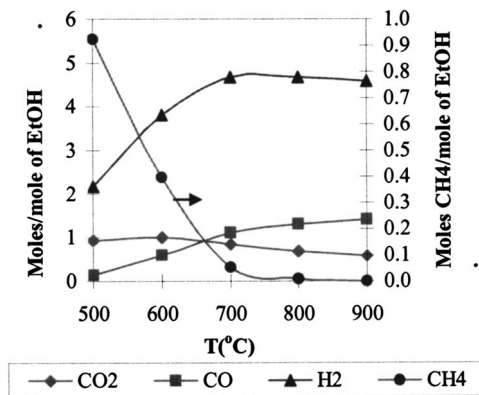
Fig. 4 Effect of reformer temperature on the product yield (steam/EtOH ratio=4, P=1 atm, no sorbent)

CO_2 in product gas is reduced from 1.53 kmol to 0.76 kmol due to the absorption by calcium oxide. A sensitivity analysis was later conducted. The temperature, pressure, and steam/ethanol ratio were varied over a wide range, and the product yield was determined as in case I.

The effect of temperature on the product yield is shown in Fig. 8. At temperatures lower than 750°C, the hydrogen production is greatly enhanced by the separation of CO_2; above this temperature the molar flows are similar to the previous case, meaning that the CO_2 separation reaction is no longer effective. Because of the exothermic nature of CO_2 separation reaction, it is favorable to operate at lower temperature. Hydrogen production is maximum at 650°C, which is approximately 100°C lower than the base case.

The effect of pressure on the product yield is shown in Fig. 9. Similar to the base case, operating the reactor at high pressure is not desirable due to the decrease in hydrogen yield. The steam/ethanol ratio is varied from 3 to 8. This ratio greatly enhances the steam reforming of ethanol in the presence of CaO. Figure 10 shows the results of varying this ratio at 700°C and atmospheric pressure.

The results are similar to the base case with higher amounts of hydrogen (~10%). Finally, the effect of varying the amount of sorbent on the product yield is shown in Fig. 11. The CaO/ethanol ratio of zero corresponds to the base case (no sorbent). As the amount of CaO is increased, it absorbs the carbon dioxide and is converted to $CaCO_3$. The carbon dioxide continues to be absorbed as it is produced until only a small amount (corresponding to equilibrium) remains. Beyond a certain CaO/ethanol ratio, the absorption is not effective. The amount of hydrogen produced increases up to the point where the CO_2 absorption is effective.
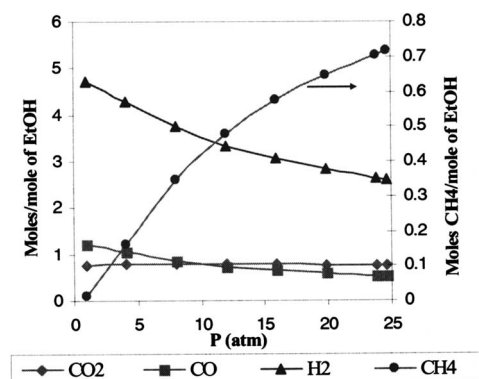
Beyond that point the increase in hydrogen yield is not significant.

Adding excess CaO is energy inefficient because it simply gets heated and cooled and does not help in CO_2 removal. Hence, it is essential to add only an optimum amount of CaO, as much as needed for removing all or most of the CO_2 from the product gas.

3.3 Case III—Ethanol Reforming With Sorbent in WGS Reactor. This is a variation of case II. Here the sorbent is placed in the WGS reactor, and hence, the water gas shift and CO_2 absorption reactions (both exothermic) take place in the same reactor (Fig. 12). The advantage of having CaO in the WGS reactor instead of REFORMER is that all the carbon oxides get absorbed, and therefore, we get pure hydrogen with only trace amounts of CO and CO_2 in the product gas. The gas may be used in a fuel cell or any other suitable application with minimal cleaning. Table 3 shows the simulation results for this case. It was observed from the results that the hydrogen yield for this case is much less than the hydrogen yield for case II (by almost 13%). It was also observed that the amount of heat energy to be supplied in this case is higher than the base case with only a marginal improvement (3.3%) in the hydrogen yield over the base case.

Although the WGS reactor rejects a large amount of heat, the temperature at which this heat is available is very low (300°C) and, thus, the quality of waste heat is poor. Hence, on the basis of no substantial increase in H_2 yield and much larger energy input than conventional gasification (heat is also supplied for regeneration of spent sorbent), this case was not analyzed further.

4 Energy Studies

An energy analysis was carried out to study the effect of sorbent addition on the hydrogen yield of cases I and II. In order to have a common base for comparison, the process conditions for both cases were kept the same and are given as follows:

Ethanol flow rate	1 kmol/h
Steam flow rate	4 kmol/h
Process pressure	1 atm
Reformer temperature	700°C
WGS reactor temperature	300°C
Regenerator temperature	850°C
CaO flow rate	3 kmol/h

A steam-to-ethanol molar ratio of four was chosen for the analysis. This is the stoichiometric amount of steam required per unit mole of ethanol feed. Higher steam-to-ethanol ratios will give higher hydrogen, but this will be at the cost of additional steam that needs to be supplied to the reformer. A lower steam-to-ethanol ratio would consume less energy, but at the same time, it produces less hydrogen. Hence, the stoichiometric amount was chosen for the analysis to get an idea of the efficiency of ethanol reforming for
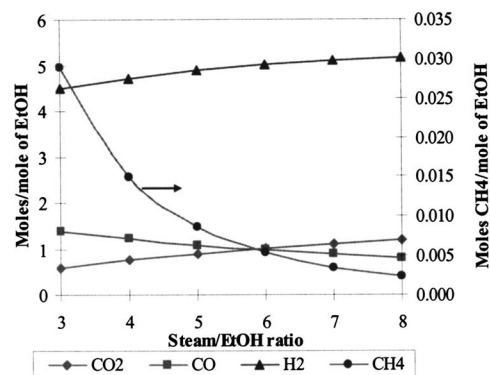

Fig. 5 Effect of reactor pressure on the product yield (steam/EtOH ratio=4, T=700°C, no sorbent)

Fig. 6 Effect of steam/EtOH ratio on product yield (T=700°C, P=1 atm, no sorbent)
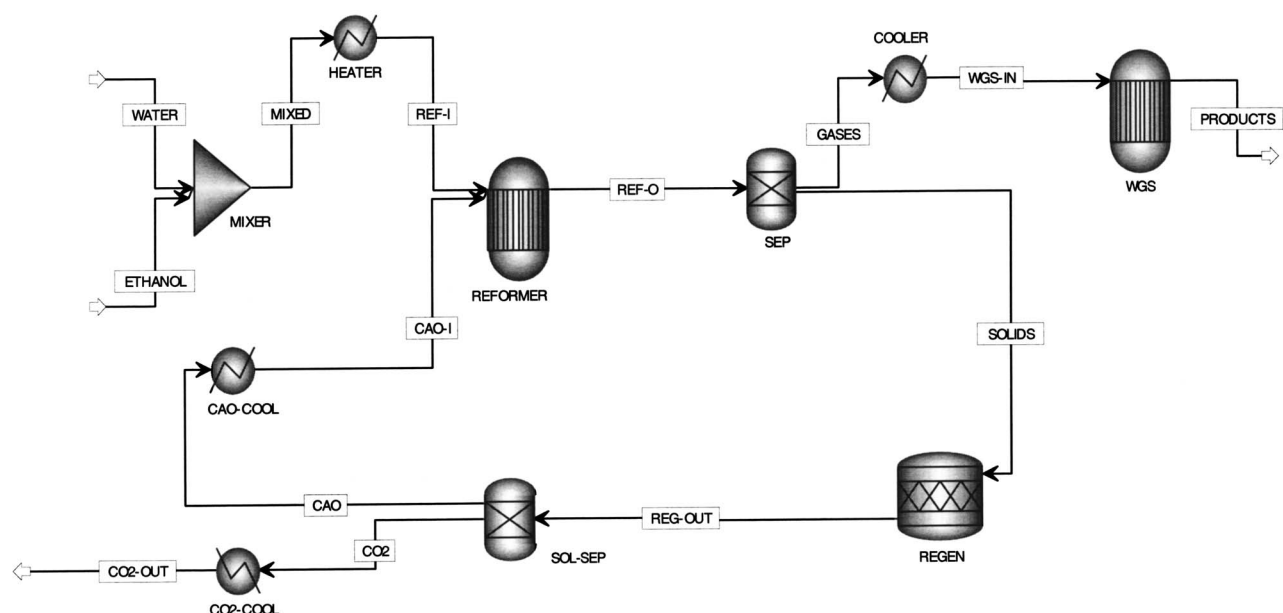
Fig. 7 Simulation flow sheet of ethanol steam reforming with CaO sorbent (sorbent placed in reformer) (case II)

hydrogen production for the two cases. The enthalpy of the various streams was calculated. The first law of thermodynamics was applied to all the reactors and heat exchangers, and the heat duty was then calculated. The product gas composition and the heat duties of the different reactors for the two cases are given in Table 4. The thermodynamic efficiency is then calculated as per the following definition:

$$\eta = \frac{\text{Energy Output}}{\text{Energy Supplied}} \quad (11)$$

$$\eta = \frac{\text{Lower Heating Value of Product gas}}{\text{LHV of biomass} + \text{External heat supplied}} \quad (12)$$

Here, the external heat supplied includes the following:

- heat input to the HEATER (used to produce steam-ethanol vapor mixture)
- heat input to the REFORMER
- heat input to the regenerator (REGEN) (applicable to sorbent case only)

The lower heating value of product gas is calculated as follows:

$$\text{LHV of gas} = n_{H_2} * \text{LHV}_{H_2} + n_{CO} * \text{LHV}_{CO} + n_{CH_4} * \text{LHV}_{CH_4} \quad (13)$$

Table 4 gives the product yield and heat duty of the different reactors. Table 5 gives the values of the input and output energies and the thermodynamic efficiency for the two cases. From Table 4, we observe that using sorbents increases the equilibrium H_2 yield of conventional gasification by about $\sim 19\%$ and reduces the equilibrium CO_2 content of product gas by 50.2%. It is also observed that the heat duty of the REFORMER is reduced by 42% as compared to conventional gasification.

5 Discussion of Results and Practical Considerations

The three case studies compared the effect of conventional ethanol reforming (case I) to sorbent-enhanced steam ethanol reforming when the sorbent was placed in the REFORMER (case II) and when it was placed in the WGS reactor (case III). The sensitivity studies showed that the hydrogen yield for case II is higher than case I for all temperatures in the range of $500-700\,^{\circ}$C. The CO_2 absorption reaction is exothermic, and if this reaction takes place in the reformer, it can supply heat in situ to the endothermic

Table 2 Simulation results for case II

	CAO-1	EtOH	GAS	MIX	PROD	REF-I	REF-O	SOL	WAT	WGS-I
Temperature (°C)	25	25	700	25	300	700	700	700	25	300
Pressure (atm)	1	1	1	1	1	1	1	1	1	1
Vapor fraction (-)	0	0	1	0	1	1	1	0	0	1
Mole flow (kmol/h)	3	1	7.83	5	7.80	5	10.83	3	4	7.83
Mass flow (kg/h)	168.2	46.1	69.9	118.1	69.9	118.1	286.4	216.5	72.1	69.9
Enthalpy (kJ/h)	−2006.4	−292.6	−418	−1421	−543	−1045	−2842	−2466	−1129	−502
H_2 (kmol)			5.28		5.70		5.28			5.28
CO (kmol)			0.58		0.09		0.58			0.58
CO_2 (kmol)			0.29		0.76		0.29			0.29
Ethanol (kmol)		1	0	1	0	1	0			0
H_2O (kmol)			1.65	4	1.19	4	1.65		4	1.65
CH_4 (kmol)			0.04		0.05		0.04			0.04
C_2H_4 (kmol)			0		0		0			0
CH_3CHO (kmol)			0		0		0			0
CaO (kmol)	3		0		0		1.90	1.90		0
$CaCO_3$ (kmol)			0		0		1.10	1.10		0
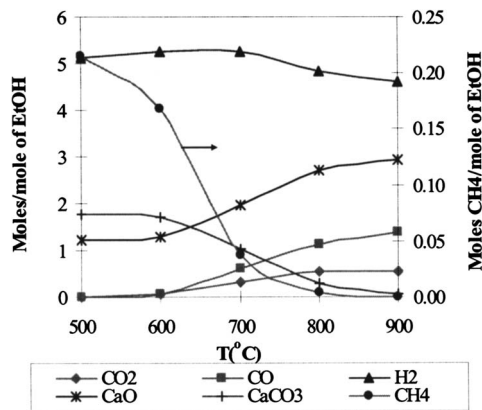
Fig. 8 Effect of reformer temperature on product yield (steam/EtOH=4, P=1 atm, CaO/EtOH=3)

Fig. 10 Effect of steam/EtOH ratio on the product yield (T =700°C, P=1 atm, CaO/EtOH=3)

ethanol reformation process. Hence, the net external heat required by the reformer is reduced. We saw in the energy and efficiency calculations that the reformer heat duty was reduced by 42% for case II as compared to case I. The reduced heat duty implies a compact reformer, and this would mean a reduction in the capital cost. If the exothermicity of the CO_2 absorption matches the endothermicity of ethanol reforming, the reformation step can become adiabatic. It was also observed in the sensitivity studies that the product gas has less CO and CO_2 in case II as compared to the conventional reforming of case I. If the sorbent can absorb all the CO (through water gas shift reaction) and CO_2, and reform the hydrocarbons in the product gas, many expensive downstream equipment, such as a WGS reactor and pressure swing adsorption unit, may not be needed (this is possible if all the CO first gets converted into CO_2 by the shift reaction, and later, all CO_2 is absorbed by the CaO sorbent). These would be replaced by a single reactor (regenerator) and less expensive gas cleaning equipment, such as cyclones, filters, and electrostatic precipitators for removing the residual impurities. Therefore, there is a potential to reduce the capital cost of hydrogen production by using sorbents. Hence, considering the improvement in hydrogen yield, in situ heat transfer in the reformer, and the possibility of reducing the capital costs, case II is better than case I.

In case III, the sorbent is placed in the WGS reactor, which is operated at 300°C. It is observed, in this case, that the product gas is rich in hydrogen without any CO or CO_2. This happens due to the sorbent, which is now placed in the WGS reactor, and it absorbs all the carbon oxides. In actual practice, however, it is ob-
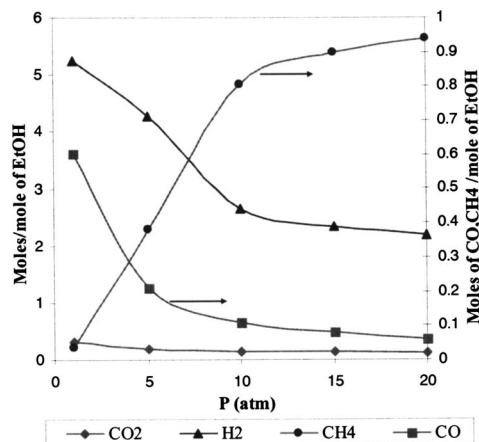
served that the kinetics of the CO_2 absorption reaction is very slow at temperatures below 500°C [20]. The kinetics of the reaction is most favorable in the temperature range 550–700°C. Although the case is theoretically attractive, from a practical standpoint there would be lot of carbon oxides in the product gas with either the same or marginal improvement in hydrogen yield as compared to case I. In case III, the heat released during the exothermic CO_2 absorption is available at a much lower temperature (300°C) than case II (700°C). This waste heat is of minimal utility as most other processes in the system operate at more than 300°C. Hence, based on the practical considerations and marginal improvement in hydrogen yield, case III was not considered for further study.

Sorbent enhanced biomass gasification has the potential to produce a hydrogen-rich gas stream that is depleted of carbon oxides. However, there are many concerns that need to be addressed for the process to have practical utility and one of them is the sulfur content in biomass feedstocks. Many biomass resources contain small amount of sulfur, which combines with oxygen to produce sulfur dioxide. The sulfur dioxide can further combine with calcium oxide to produce calcium sulfate as per the following reaction:

$$CaO + SO_2 + 0.5O_2 \rightarrow CaSO_4 \qquad (14)$$

Hence, in every cycle there will be loss of sorbent. This has to be compensated by make-up sorbent and separation of calcium sulfate from the residue. Tar formation during biomass gasification is another area of concern that needs to be addressed [7,21]. Tars are typically formed at low temperatures (below 400°C) and tend to settle on the catalyst bed typically during reactor startup.
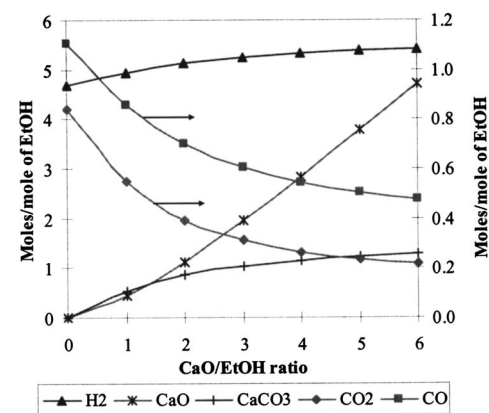

Fig. 9 Effect of pressure on product yield (steam/EtOH=4, T =700°C, CaO/EtOH=3)

Fig. 11 Effect of CaO/EtOH ratio on product yield (steam/EtOH ratio=4, T=700°C, P=1 atm)
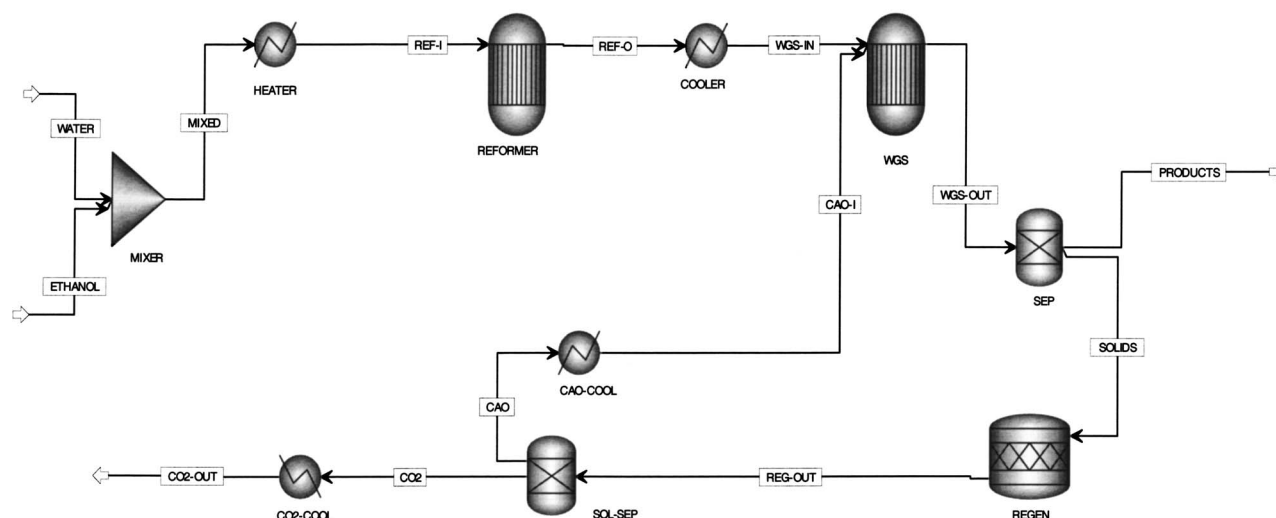
Fig. 12 Simulation of ethanol steam reforming including CaO sorbent (sorbent placed in WGS reactor) (case III)

There is also a possibility of tar deposition on the calcium oxide bed. In the past, some studies on the use of dolomites (calcium and magnesium salts) have shown that they have tar-reforming capability [22]. Calcium oxide is produced from dolomites by calcination followed by removal of magnesium compounds. It is expected that calcium oxide, like dolomites, also has some tar-reforming abilities. However, this needs to be ascertained by actual experimental studies.

In actual biomass gasification systems, the biomass would most likely be in solid fibrous form, such as wood pellets or peanut shells. This has to be mixed with the calcium oxide sorbent. The sorbent may be in the form pellets or in powder form. Powdered sorbent provides more surface area but is prone to attrition and carry over by flow of flue gases. Pelletized sorbent has the advantage of being less prone to carry over; however, it provides less surface area than powdered sorbents. The choice of the physical form of sorbent would also affect the product gas composition and the quantity of make-up sorbent that needs to be added for losses due to attrition and carry over.

The objective of the present work was to conduct a theoretical study on the use of sorbents for hydrogen production from biomass. However, as we have seen above, there are many practical considerations that must be addressed in order to make the sorbent enhanced biomass gasification process a mature technology that is commercially attractive.

6 Summary and Conclusions

Sorbent-enhanced gasification is a novel concept for producing a hydrogen-rich gas from carbonaceous fuels. It has already been demonstrated at the laboratory scale for producing hydrogen by steam methane reforming. In principle, the concept can be applied to any carbon-containing fuel including biomass. The potential advantages of SEG are as follows:

- higher hydrogen yield
- lower operating temperature as compared to conventional gasification
- reduced CO_2 in product gas
- less equipment needed and, thus, reduced capital costs (It is hypothesized that sorbent-enhanced gasification or reforming will require less equipment, due to combination of reactions, than conventional, and hence, there is a possibility of reducing the capital cost.)

Table 3 Simulation results of case III

	CAO-1	EtOH	MIX	PROD	REF-I	REF-O	SOL	WAT	WGS-I	WGS-O
Temperature (°C)	25	25	25.00	300	700	700	300	25	300	300
Pressure (atm)	1	1	1	1	1	1	1	1	1	1
Vapor fraction (-)	0	0	0	1	1	1	0	0	1	1
Mole flow (kmol/h)	3	1	5	6.74	5	8.89	3	4	8.89	6.74
Mass flow (kg/h)	168.2	46.1	118.1	41.7	118.1	118.1	244.7	72.1	118.1	41.7
Enthalpy (kJ/h)	−1881	−292.6	−1421	−251	−1045	−794	−2717	−1129	−920	−334
Mole flow (kmol/h)										
C_2H_4				0		0			0	0
H_2 (kmol)				4.95		4.68			4.68	4.95
CO (kmol)				0		1.10			1.10	0
CO_2 (kmol)				0		0.84			0.84	0
Ethanol (kmol)		1	1	0	1	0			0	0
H_2O (kmol)			4	1.52	4	2.21		4	2.21	1.52
CH_4 (kmol)				0.26		0.05			0.05	0.26
C_2H_4 (kmol)										
CH_3CHO (kmol)										
CaO (kmol)	3			0		0	1.26		0	0
$CaCO_3$ (kmol)				0		0	1.74		0	0

Table 4 Comparison of energy consumption in biomass gasification with and without sorbent

Output yield	Case I	Case II
	(kmol/kmol of ethanol)	
H_2	4.79	5.70
CO	0.1	0.09
CO_2	1.53	0.762
CH_4	0.00	0.05
H_2O	1.84	1.19
Heat Duty	(kW)	
HEATER	+108.6	+108.6
REFORMER	+65.9	+38
COOLER	−33.9	−27.9
WGS	−15.8	−6.7
REGEN	NA	+61.2
CO_2-COOL	NA	−12.4
CAO-COOL	NA	−34.9

Table 5 Thermodynamic efficiency and Heat input

	Case I	Case II
LHV of product gas (kJ/h)	1176.3×10^3	1435.9×10^3
LHV of biomass (kJ/h)	1242×10^3	1242×10^3
Total heat supplied (kJ/h)	628.1×10^3	748.2×10^3
Thermodynamic efficiency	62.9%	72.1%

This paper reports a theoretical study of hydrogen production by steam reforming of ethanol. It was observed that the hydrogen yield substantially improves if the reformation is carried out in presence of a sorbent. This happens due to the equilibrium shifting in favor of hydrogen. Based on the encouraging results obtained from theoretical studies, the authors are conducting an experimental investigation of the process. However, there are some important areas that need to be addressed, chief among them are the following:

- form of sorbent (powder or pellet) and how it is mixed with the biomass feedstock
- sorbent loss due to formation of calcium sulfate
- tar-reforming ability of calcium oxide sorbent
- energy consumed during regeneration
- kinetics of the CO_2 absorption and desorption processes

Acknowledgment

Nomenclature and Abbreviations

EtOH	=	ethanol/ethanol process stream in ASPEN flow sheet
GAS	=	"gases" stream in ASPEN flow sheet
LHV_x	=	lower heating value of species x (kJ/mol)
MIX	=	"mixed" stream in ASPEN flow sheet
P	=	pressure (atm)
T	=	temperature (K)
PROD	=	"product" stream in ASPEN flow sheet
PSA	=	pressure swing adsorption
SEG	=	sorbent-enhanced gasification
SMR	=	steam methane reforming
SOL	=	"solids" stream in ASPEN flow sheet
WAT	=	"water" stream in ASPEN flow sheet
WGS	=	water gas shift (-)
WGS-I	=	WGS reactor inlet stream in ASPEN flow sheet
WGS-O	=	WGS reactor outlet stream in ASPEN flow sheet
WGS	=	water gas shift (−)
n	=	number of moles (mol)

Greek

ΔH_R	=	heat of reaction (kJ/mol)
η	=	thermodynamic efficiency (%)

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