



Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Article

Targeting efficient biomass gasification

Saneliswa Magagula^{1,2}, Jiangze Han^{3,4}, Xinying Liu^{1,4}, Baraka C. Sempuga^{1,4,*}¹ Institute for the Development of Energy for African Sustainability (IDEAS), University of South Africa, Science Campus, Florida, Johannesburg 1710, South Africa² Department of Chemistry, University of Puerto Rico, Rio Piedras Campus, San Juan, PR 00931, USA³ College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang 050018, China⁴ International Joint Laboratory of New Energy, Hebei University of Science and Technology, Shijiazhuang 050018, China

ARTICLE INFO

Article history:

Received 31 May 2020

Received in revised form 11 November 2020

Accepted 13 November 2020

Available online 1 January 2021

Keywords:

Biomass

Gasification

Gasification thermodynamics

Biomass conversion efficiency

Process targeting

ABSTRACT

The sustainability of biomass use as a primary energy source depends on the efficiency of its conversion processes. The key contributing factors are well understood, owing to extensive experimental and theoretical modeling efforts in literature. In this manuscript, we present a systematic study of the thermochemical conversion route that allows us to target desirable outcomes when converting biomass to other fuels and products. Using process synthesis techniques that include material, energy and work balances, we identify the best targets to consider for highly efficient processes given specific constraints. Our analysis shows that by supplying the right amount of oxygen, a 100% carbon conversion efficiency can be achieved for certain applications that require gas as product. If the objective is to obtain a cleaner fuel from biomass, converting it to char is most efficient in terms of carbon and energy conversion. According to our analysis, an energy neutral biomass gasification process is theoretically possible over a wide range of H₂ and CO production rates. We demonstrate its feasibility by simulating the process on Aspen Plus[®]. The simulation reveals that with heat integration, we can achieve the energy neutral target at a hydrogen production rate of 0.9 mol/mol biomass. We further show that even at zero energy requirement, biomass gasification processes can have excess chemical potential, which can be recovered as useful work or conserved by producing more H₂. Adding low temperature heat in the form of steam at 102 °C gives an 8% gain in chemical potential conservation and increases the hydrogen production rate by 60%. The insights revealed in this work allow for better decision making in early stages of process design, and consequently, more efficient biomass gasification processes.

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1. Introduction

Biomass can be converted to other forms of energy through thermochemical and biological methods. The thermochemical route includes pyrolysis, gasification, and hydrothermal liquefaction [1–3]. This route offers a variety of gaseous and liquid products that can be used as fuels or as feedstock for other processes [4,5]. According to the International Energy Agency, bioenergy accounts for 30% of the growth in renewables consumption for the period 2018–2023 and will remain the primary source of renewable energy in 2023 [6]. European countries have shown a strong move towards the use of biomass in the mix of renewables as a primary source of energy [7]. However, the sustainability of biomass supply and the efficiency in biomass use remain significant

challenges [8]. As biomass consumption increases across the globe, its efficient use will become more critical for it to be a sustainable primary energy resource.

Thermochemical biomass conversion is inherently inefficient- it consumes energy that is often supplied by burning part of the feed material, producing CO₂ at the expense of the desired products such as CO and H₂. Numerous research publications have explored ways to address this with reactor design, experimental investigations, as well as developing thermodynamic and kinetic models [9–13]. These studies have led to an appreciable understanding of the factors that influence biomass conversion reactions and their associated energies. Although some crucial aspects such as tar reduction, carbon conversion, hydrogen yield, gas quality, energy efficiency, and catalysis have received much attention [9–11,14], there is still a need for a more systematic approach to study and develop biomass conversion technologies. With a more insightful understanding of the processes, we can identify opportunities to improve their efficiency.

* Corresponding author at: Institute for the Development of Energy for African Sustainability (IDEAS), University of South Africa, Science Campus, Florida, Johannesburg 1710, South Africa.

E-mail address: sempubc@unisa.ac.za (B.C. Sempuga).

A systems approach can potentially give the most effective assessment of different biomass processes. Goffe *et al.* [15] have recently shown this by highlighting various publications where authors reported significantly different indices while studying similar processes. They attributed this to a limitation in the way that performance indicators are defined, for instance, not stipulating whether the evaluation considered integration or addition of matter. In this regard, Goffe *et al.* suggested a method for determining upper-performance limits based on stoichiometry and the energy balance of a biomass conversion system. The method uses what is termed an objective approach, which allows identifying the most appropriate processes and products for a specific biomass type (defined by the ratio of carbon and hydrogen content). The method provides a holistic analysis where one can assess the process and reveal opportunities for improvement.

In this work, we apply a similar approach, looking at processes from a systems point of view in order to explore possible performance targets worth considering during the design process. Targets here represent limits of performance for a given process, which can be set in terms of either material balance or energy and work potential requirements. In particular, we use process synthesis targeting techniques, which include potential work analysis (availability) as both a performance indicator and a target in addition to the material and energy balances employed by Goffe *et al.*

The targeting techniques in this work have been used extensively to analyze processes by determining feasible regions in terms of material, heat, and work balances [16–21]. In this manuscript, we demonstrate that this approach provides insight into biomass gasification/pyrolysis and makes it possible to identify the best targets to consider during the early stage of design, and that can result in highly efficient processes. Typically, the optimization of biomass gasification occurs after the designer has decided on the structure and critical parameters of the process. The design process often precludes a critical understanding of the interactions between the parameters and how they affect process performance in terms of production, energy, and work (exergy or availability) efficiency. Our analysis seeks to determine the best possible outcome for a biomass gasification process given specific constraints at the conceptual stage of design, maximizing opportunities for innovation. Using targeting techniques, we demonstrate that theoretically, an energy-neutral biomass gasification process is possible. We also show that biomass has enough chemical potential to produce more desired products beyond the limits set by energy constraints. We further attempt to achieve the targets by developing and simulating a flowsheet in Aspen Plus®.

2. Method

We use three fundamental tools, namely: material, energy, and work (availability or exergy) balance, to set up specific targets for the gasification process. The common practice is using these tools to analyze existing processes and to assess their performance; however, the approach in this work is to use them as synthesis tools in identifying and setting up possible performance targets during the early stage of process design.

2.1. The attainable region for biomass gasification

We begin by determining the attainable region: the material balance region that sets the limit of all possible outcomes from a given feed. The next step is to identify the optimum process within the attainable region and its associated energy and work requirements. Fig. 1 represents the general overall material balance of a woody biomass gasification process. The carbon, hydrogen, and oxygen ratio in biomass was averaged from several different types

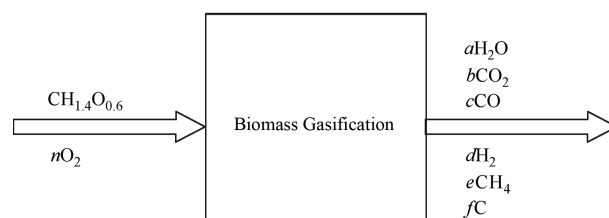
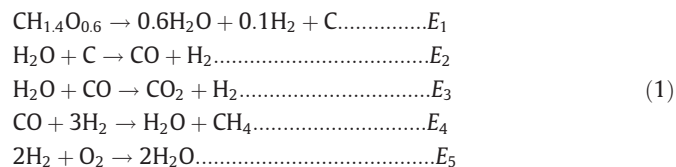


Fig. 1. Overall material balance for biomass gasification.

of woody biomass [22] to obtain a representative chemical formula. The formula excludes nitrogen and sulfur impurities as their quantities are so small that they will not affect the results of the high-level mass, energy, and work analysis of the process. We derive the enthalpy and the Gibbs energy of formation for biomass from the heating value and entropy correlations given by Song *et al.* (2011) [23,24]. The Supplementary Material document contains details on deriving the molecular formula and estimating the thermodynamic properties of biomass.

Oxygen is considered as a possible feed material to supply energy to the process by either burning some of the feed biomass or undesired by-products. At this stage, the possible product components include H_2O , CO_2 , CO , H_2 , CH_4 , and C . Typically, gasification processes also produce significantly small amounts of other components such as C_2H_4 , C_2H_6 , nitrogen, sulfur compounds, tars, and ash. The analysis in this work does not consider these components since they will not have a significant influence on the overall mass, energy, and work balance of the process. However, tars, although in small quantities, can cause significant operational problems and can prevent the adoption of biomass gasification in applications requiring ultra-clean gas. The current work does not intend to solve the tar production problem in biomass gasification. It instead seeks to gain insight into the process and improve its efficiency in the production of the desired products. Considering these impurities at this stage will make the analysis unnecessarily complicated without a significant influence on the material, energy, and work requirement, as well as the structure of the process. Research and technologies for removing sulfur and tars from gasification processes exist [25–29], which propose relatively simple methods that can be implemented during the detailed design phase without significant changes in the process structure.

Obtaining the attainable region requires deriving a set of independent material balances (IMB), which represent all possible outcomes from a biomass gasification process. Eq. (1) represents one of the possible sets of IMB.



E_j represents the extent of material balance j . Note; although the material balances are in the form of reactions, they may not necessarily be the reactions occurring during biomass gasification. They are simply a set of material balances representing all possible outcomes from the system. From the set in Eq. (1) we can express the molar amount of each component in the product stream of the gasification process as follows:

$$n_i = n_i^0 + \sum_{ij} \nu_{ij} E_j \tag{2}$$

n_i = moles of component i in the product from the gasification process

n_i^0 = moles of component i in the feed stream to the gasification process

v_{ij} = stoichiometric coefficient of component i in the material balance equation j in Eq. (2)

E_j = the extent to which the material balance j proceeds (similar to the extent of reaction) in Eq. (2).

We define $N_i = n_i - n_i^0$ to be the net moles of component i , leaving or entering the gasification process. Thus, Eq. (2) can be written as follows:

$$N_i = \sum_{ij} v_{ij} E_j \quad (3)$$

Eq. (3) yields eight independent material balance equations (one for each component) and 13 variables, which include eight components and five extents. Therefore, the system has five degrees of freedom, which presents an opportunity to set up five targets simultaneously within the material balance feasible region.

With so many degrees of freedom, the challenge is to identify optimal targets within a multidimensional system. One way of overcoming this problem is to systematically narrow down the search for optimal targets to specific sub-regions of interest; for example, by simultaneously fixing the production rate of H_2 , CO_2 , and C per mole of biomass fed. In this way, we can narrow down the system to a two-dimensional sub-region with one degree of freedom where one can determine an optimal target. The disadvantage of this method is that one is not able to show all the possibilities and thus can easily miss better targets and solutions. Alternatively, we can formulate an optimization problem and use linear programming to find a solution within specific sub-regions determined by setting specific constraints on the system. This method reduces the need to fix the variables and thus increases the possibility of finding a better solution. In this work, we have adopted the latter method to explore several targets of interest in biomass conversion.

2.2. Linear programming for targeting: material balances

To reformulate the material balance system into an optimization problem, we set a basis for the system—per mole of biomass consumed (mol BM), and we assume that the conversion of biomass to other products is complete. Therefore,

$$n_{CH_{1.4}O_{0.6}}^0 = E_1 = 1$$

We also set the production rate of H_2 per mole of biomass consumed (mol/mol BM) as the independent variable. Setting the basis of calculations and choosing an independent variable reduces the dimension of the system to 3 degrees of freedom, which we now use to formulate the linear programming problem.

The material balance equation in matrix form becomes:

$$\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & -1 & -2 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & -1 & 1 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & -1 & -1 & 2 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & -1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} N_{H_2O} \\ N_{CO_2} \\ N_{CO} \\ N_{CH_4} \\ N_C \\ N_{O_2} \\ E_2 \\ E_3 \\ E_4 \\ E_5 \end{bmatrix} = \begin{bmatrix} 0.6 \\ 0 \\ 0 \\ 0 \\ 0.1 - N_{H_2} \\ 0 \\ 1 \\ 0 \end{bmatrix}$$

In setting up the targets, we consider two cases (constituting two material balance sub-regions) for the biomass conversion process:

– **Minimizing the production rate of C at selected fixed production rates of H_2 subject to material balance constraints.** Minimizing carbon production is significant because, in general, biomass carbon conversion to gaseous products is considered one

of the essential performance indicators. Thus, we can look at targets that minimize the production rate of C (Char), which would represent the process with high carbon conversion.

$$\text{for } N_{H_2} = [0 \ 1]; \min N_C \text{ subject to } \begin{cases} \mathbf{A}N_d^T \leq 0 \\ \mathbf{A}_{eq}N^T = \mathbf{b}_{eq} \end{cases}$$

– **Minimizing the production rate of CO_2 at selected production rates of H_2 subject to material balance constraints.** In general, minimizing CO_2 production is desirable not only to reduce the carbon emission footprint of the process but also to improve the calorific value of the product gas.

$$\text{for } N_{H_2} = [0 \ 1]; \min N_{CO_2} \text{ subject to } \begin{cases} \mathbf{A}N_d^T \leq 0 \\ \mathbf{A}_{eq}N^T = \mathbf{b}_{eq} \end{cases}$$

$\mathbf{A}N_d^T \leq 0$ is the inequality constraint matrix, which imposes individual components to either be in the product or feed stream only, or both if not constrained. For example, we impose the O_2 to be a feed only by limiting N_{O_2} to the negative region. No constraint is placed on the water as it can be used as both feed and product. However, the rest of the components are constrained to be products only. Thus, $\mathbf{A}N_d^T \leq 0$ is expressed as follows:

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} N_{H_2O} \\ N_{CO_2} \\ N_{CO} \\ N_{CH_4} \\ N_C \\ N_{O_2} \end{bmatrix} \leq \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

The equation, $\mathbf{A}_{eq}N^T = \mathbf{b}_{eq}$ is the equality constraint and is set to represent the material balance constraints given above.

One could also look at the cases where CO_2 and CH_4 are available as feedstock to the gasification process by relaxing their constraints. However, this is beyond the scope of this work.

2.3. Linear programming solution for targeting: energy and work balances

In general, gasification processes consume energy. They, therefore, require feeding O_2 to burn part of the feed material and produce the energy in the form of heat (Q) as needed to drive endothermic reactions. The minimum amount of energy required is equivalent to the change in enthalpy across the process (ΔH).

$$\Delta H_P = \sum_i n_i \hat{H}_i - \sum_i n_i^0 \hat{H}_i \quad (4)$$

\hat{H}_i is the molar enthalpy of component i .

Eq. (4) can be expressed in terms of net-amount of components in and out of the gasifier as follows:

$$\Delta H_P = \sum_i N_i \hat{H}_i \quad (5)$$

For a fully energy integrated process, which has no energy losses to the environment and requires only the minimum energy input, we can assume that the feed and the product streams are at ambient (or reference) temperature T_0 . This assumption is valid if we further assume that the feed and product streams have the same heat capacity, such that they can exchange heat to cool down the product stream to ambient temperature and heat the feed stream to the reactor temperature without the need for additional heat transfer from outside the process. In reality, the feed and product streams have different compositions and, consequently, have different heat capacities. However, since the sensible heat needed to either cool or heat the stream to the required temperature is often small compared to the heat of reaction, it will not have a significant influence on the analysis at this point. We will only

consider it in the simulation. Furthermore, in real processes, there are always energy losses due to limitations in equipment design. Since these losses are variable, depending on the level of design flaws, we do not consider them at this point where we seek to determine the best targets for the process. However, we can consider them as deviations from the target at a later stage of design, which is beyond the scope of this work. Under these assumptions, we can calculate the energy requirement as the change of the enthalpies of formation across the process:

$$\Delta H_p = \sum_i N_i \Delta \hat{H}_{fi}(T_0) \quad (6)$$

$\Delta \hat{H}_{fi}(T_0)$ is the molar enthalpy of formation of component i at the reference temperature T_0 . It follows from Eq. (6) that when $\Delta H_p > 0$, energy must be supplied to the process and when $\Delta H_p < 0$, energy must be removed from the process.

The quality of energy required by a process is as crucial as its amount. We express the *quality* of energy as the amount of energy available that is equivalent to mechanical work (w_s), which we will refer to as shaft work. Thus, we define the work requirement of a process (w_p) as the amount of energy equivalent to mechanical work, needed by the process. Several authors [19,30–33] have shown that this energy is determined by the change in Gibbs free energy across the process (ΔG_p).

Similar to the enthalpy and under the same assumptions, we can show that:

$$w_p = \Delta G_p = \sum_i N_i \Delta \hat{G}_{fi}(T_0) \quad (7)$$

$\Delta \hat{G}_{fi}(T_0)$ is the molar Gibbs free energy of formation of component i at the reference temperature T_0 . It also follows from Eq. (7) that when $\Delta G_p > 0$, work (w_p) must be supplied to the process and when $\Delta G_p < 0$, work must be removed, meaning the process has the potential to produce mechanical work.

Ideally, one should target negative values for ΔH_p and ΔG_p since positive values mean that energy and work (w_p) must be supplied to the process from an external source. Unless renewable sources of energy are available, the process may require using a portion of the feed material as fuel to meet its energy and work requirements, by feeding more oxygen to produce more unwanted products (CO_2 , H_2O).

The energy requirement analysis of biomass conversion is often used to assess the performance of existing processes. The method in this paper uses not only the energy requirement but also the work requirement (which takes into account the quality of the energy) along with the material balance to identify and set targets for biomass conversion. Energy considerations do not provide extra degrees of freedom, but rather help in narrowing the system further to sub-regions of more considerable significance. Therefore, we can reformulate the optimization problem to include energy and work balances. We look at the cases where we constrain the system for zero energy or work requirement by setting $\Delta H_p = 0$ kJ or $\Delta G_p = 0$ kJ as an additional constraint to the system while minimizing the production rate of CO_2 or C as previously discussed.

The significance of the $\Delta H_p = 0$ kJ target for biomass conversion is that material balances with zero energy requirements are identified, and become targets for the process design. Although a zero energy requirement process might be challenging to achieve in real processes, the resulting material balance will set the basis and targets for the process design, resulting in a fundamentally efficient process. The remaining task would be to optimize the equipment designs, the energy, and mass integration to minimize deviations from the target.

On the other hand, the significance of $\Delta G_p = 0$ kJ is of great importance, although often overlooked. It relates to the conservation of the chemical potential of the feed materials during their

conversion into products. The chemical potential is an indication of the quality of energy that a chemical substance carries (or chemical availability). Thus, there is an opportunity to produce useful work when the chemical potential of the product is less than that of the feed ($\Delta G_p < 0$ kJ). The difference represents the maximum work available. Not recovering the work potential will make the process irreversible; as a consequence, the process will have a more significant adverse impact on the environment.

Recovering the work potential as useful work will induce additional capital and operating cost, but could be beneficial from the environmental and economic perspective if the cost to benefit ratio is favorable. However, avoiding a decrease in work potential between the feed and product materials in the first place, could lead to the best economic and environmental outcome. No real system will be able to achieve $\Delta G_p = 0$ kJ. However, knowing the target material balance for $\Delta G_p = 0$ kJ will direct design decisions and optimization objectives to a more efficient process.

To account for energy and work balances, we reformulate the optimization problem as follows:

$$\text{for } N_{\text{H}_2} = [0 \ 1]; \min N_{\text{C}}(\text{or } N_{\text{CO}_2}) \text{ subject to } \begin{cases} \mathbf{A}\mathbf{N}^T \leq 0 \\ \mathbf{A}_{\text{eq}}\mathbf{N}^T = \mathbf{b}_{\text{eq}} \\ \Delta H_p = 0 \\ \text{or} \\ \Delta G_p = 0 \end{cases}$$

Note that $\Delta H_p = 0$ kJ and $\Delta G_p = 0$ kJ targets cannot be set simultaneously since these two are linearly dependent through the material balance.

2.4. Process simulation

Using Aspen Plus®, we develop and simulate a process based on the results obtained in and Figs. 4 and 5. The simulation flowsheet is developed to either reach a specific material balance target or an energy target which can cover a range material balances. The integration of the chosen target into the simulation starts by first fixing the basis of material balance calculations, in this case 1 mole of biomass in the feed. Then, an attempt is made to achieve the material and energy target by adjusting the amount of feed components, by adjusting the reaction operating temperature within the allowable range set by the reaction model used, by optimizing the energy integration, and by using separation and recycles where necessary.

In this work we target first an energy-neutral process and zero char production. In the second case, we attempt to push H_2 production beyond the limit set by the energy-neutral process by supplying low-temperature energy. In this way, we convert the excess chemical potential of the energy-neutral process to hydrogen to improve the overall efficiency. For both cases, the structure of the flowsheet is the same (Fig. 2), but the differences are in the material flowrates, energy flows, and temperatures.

We use a combination of empirical and equilibrium models to simulate the gasification process in Aspen plus®. According to a recent review by Safarian *et al.* [34] 66% of authors have used equilibrium models for gasification. When they combined mathematical modeling with process simulation, they yielded a reasonably accurate representation of the gasification process that gives a high degree of insight and accurate economic analysis. The structure of the model we have used in this work (Fig. 2) is similar to the models in the review by Safarian *et al.* It consists of three main parts, each using a different model appropriate for the specific stage of gasification. The pyrolysis section predicts the yield of volatile matter (VM), tars, and char. The char then undergoes complete combustion to produce heat and flue gas containing CO_2 and H_2O . The flue gas is either sent out as a by-product or sent for gasification as VM and tars mixture where it reacts and reaches chem-

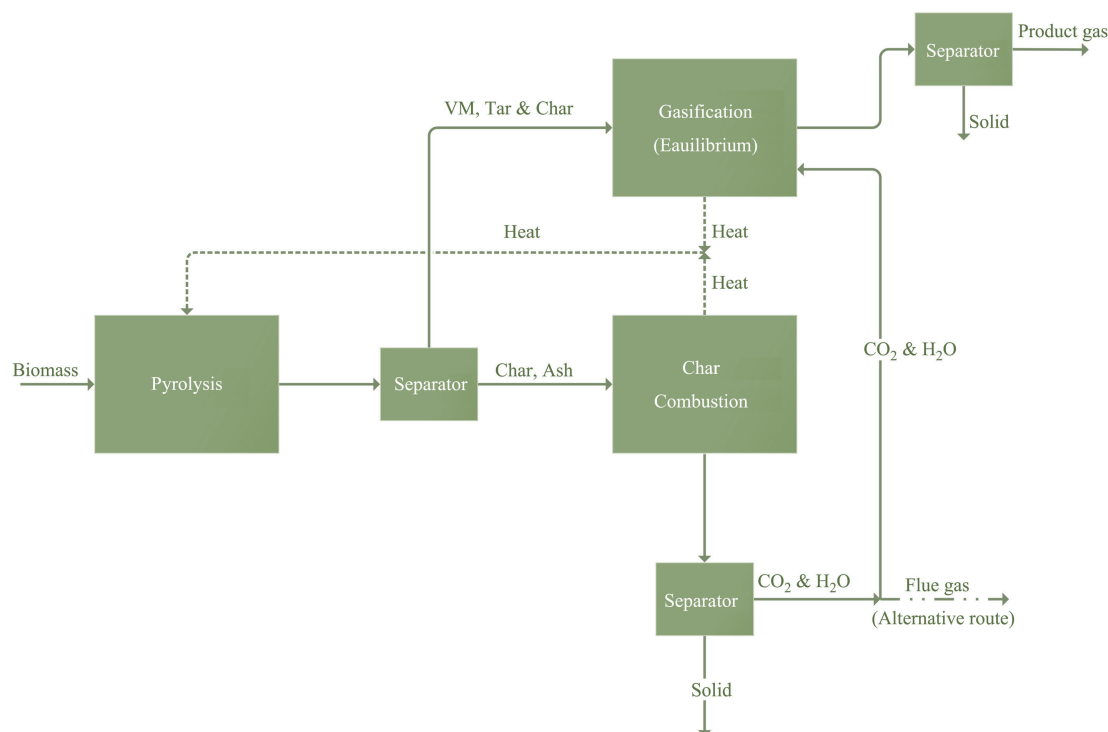


Fig. 2. Aspen simulation model.

ical equilibrium to yield the product gas. The char combustion section produces the heat required to drive reactions in the pyrolysis and gasification sections.

In the Aspen simulation, biomass is modeled using ultimate and proximate analyses on a dry and ash-free basis, averaged from several biomass compositions data given in Qian *et al.* [22]. The simulation flowsheets consist of three main sections, which are assumed to operate at 0.1 MPa:

- **The pyrolysis section** uses an RYield reactor to simulate the conversion of feed biomass to gas, tar, and char. A Fortran calculator determines the values of the input variables for the RYield reactor to predict the yield and composition of the product gas, tar, and char. In the Fortran calculator, we use an empirical model that Neves *et al.* developed using experimental data from different kinds of biomass pyrolysis processes at temperatures ranging from 200 °C to 1000 °C [35]. The model predicts the yield of char and gas as well as the gas composition and tar content for a given ultimate and proximate analysis of biomass, and pyrolysis temperature. We simulate the pyrolysis as an adiabatic process (zero heat load) by fixing the reactor temperature and adjusting the temperature of the feed stream. The hot gas stream from the combustion and equilibrium reactors provides the necessary heat for the pyrolysis feed stream to reach the required temperature.
- **The combustion section** uses an RStoich reactor to model the complete or partial combustion of the char produced in the pyrolysis section depending on the amount of oxygen fed to the process. We also model the RStoich reactor as an adiabatic process and send the hot flue gas and the unreacted carbon to the equilibrium reactor.
- **The gasification section** uses an RGibbs reactor to model the equilibrium composition from the reaction of the pyrolysis gas, tar, and the combustion flue gases. We also simulate the RGibbs reactor as an adiabatic process, and thus the equilibrium temperature is variable and depends on the temperature of the feed streams.

The heat recovery section uses a series of heat exchangers to cool the product stream down to a temperature as close to ambient as possible by exchanging energy with the feed streams of biomass, water, and oxygen. A minimum temperature approach of 5 °C is maintained to avoid any temperature crossing within the heat exchanger.

3. Results and Discussion

3.1. Biomass gasification targeting minimum char and CO₂ production

Significant differences are apparent in biomass gasification when targeting minimum char and minimum CO₂ production [Fig. 3 (a) and (b), respectively]. If the aim is to minimize the production of char, then it is possible to eliminate both char and CO₂ products [Fig. 3 (a)] to achieve 100% carbon conversion to CO. However, the process will require a significant amount of oxygen feed and will produce a large amount of water. The need for oxygen decreases with increasing H₂ production rate, as does the water production. On the other hand, if the aim is to minimize CO₂ [Fig. 3 (b)], then the production of char is considerably high at low H₂ production rates, and carbon conversion to CO is significantly low. The need for oxygen is minimal at the lower end of the H₂ production rate. Both cases produce water at the same rate and require water supply when H₂ production exceeds 0.7 mol/mol BM.

The energy implications of these targets are also significant, as shown by their respective ΔH and ΔG plots. For example, in Fig. 3 (a), the maximum H₂ production rate without any energy required ($\Delta H = 0$ kJ) is 0.6 mol/mol BM, while in (b), this value is lower at 0.18 mol/mol BM; because of the low carbon conversion to gases in (b). Consequently, (b) has a high char production rate while (a) has no char production. Moreover, the high carbon conversion in (a) results in more substantial amounts of energy release compared to (b), as evidenced by the higher values of ΔH and ΔG . Thus, the targets in (a) will be less energy efficient unless the process is

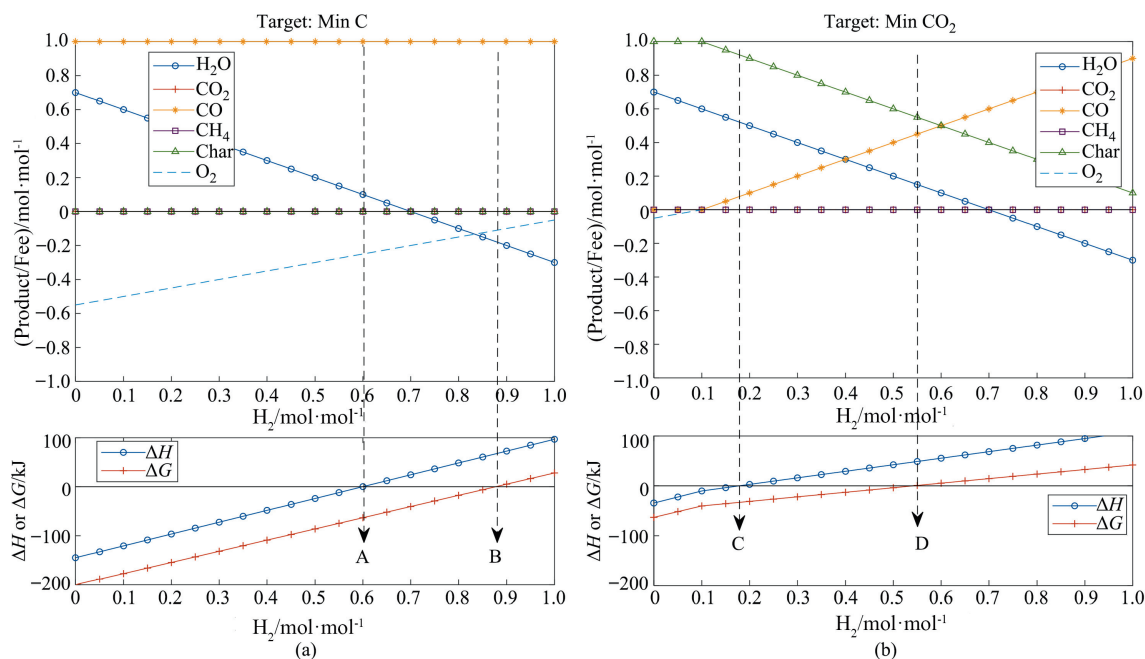


Fig. 3. Solutions for biomass gasification targeting (a) minimum C (Char) and (b) minimum CO₂ production rate as a function of H₂ production rate per mole of biomass, with their respective ΔH and ΔG.

optimized to recover as much useful work as possible or change the material balance to the optimum point, which in this case is at A—the point of zero energy release. All the targets to the left of A will release energy and are potentially inefficient since the recovery of useful energy (work) is not guaranteed if the temperature gradients within the process are not favorable. A better alternative is to avoid producing excess energy by targeting higher H₂ production rates. On the other hand, the targets in (b) would be suitable for char production applications; the potential for energy conservation is high but with low H₂ and CO production rates. Here, most of the energy is stored as chemical energy in char.

Another significant result in both (a) and (b) is that the ΔG line crosses zero (points B and D respectively) at a higher H₂ production rate than the ΔH line (points A and C). Therefore, the targets in both (a) and (b) are ΔH limited (or energy limited). Consequently, energy supply from an external source is necessary to increase the H₂ production rate past their limit at points A and C.

As previously discussed, the chemical potential of a process is conserved at ΔG = 0 kJ. Negative ΔG values, between points A-B in (a), and between C-D in (b), mean that there is chemical potential available to either recover as useful work or conserve as chemical potential stored in the product materials. The latter option could be more efficient than the former from the energy and material conservation perspective. It could also be more cost-effective than the alternative, which requires a work recovery system. If the chemical potential is not recovered or conserved, it will be lost by making the process more irreversible with much adverse environmental impact. The positive ΔH values, between points A-B in (a), and between C-D in (b), mean energy input is necessary in order to recover or conserve the available chemical potential. If a low-quality energy source is available, such as heat at low temperature, then in the case of (a), the maximum production rate of H₂ can increase from 0.6 to approximately 0.88 mol/mol MB (47% increase). Moreover, in the case of (b), the maximum production rate of H₂ can increase from 0.18 to about 0.54 mol/mol MB (200% increase). The production rate of CO in (b) can increase from about 0.08 to about 0.44 mol/mol MB.

The choice of a target depends on the application and objectives that one would want to achieve. In general, high efficiencies in

both material and energy is desirable in terms of capital and operating costs as well as environmental impacts. If one is looking at syngas production for applications that require gas, then Fig. 3 (a) shows that high carbon conversion efficiencies (100%) are possible with just the correct amount of oxygen supply. The hydrogen conversion, as well as the energy efficiencies, will be high at a high H₂ production rate, with 100% hydrogen conversion efficiency corresponding to the 0.7 mol/mol BM mark for the H₂ production rate.

On the other hand, if the aim is to convert biomass into a cleaner fuel, then Fig. 3 (b) suggests that converting it to char could be a better option in terms of carbon conversion and energy conversion efficiencies. In this case, hydrogen efficiency is less critical since the aim is not to produce hydrogen. However, there is an opportunity to co-produce char and H₂, which could be a better option as one can convert low quality energy into chemical energy. The latter is possible, for example, by feeding low-temperature steam, if available, into the process to increase the production rate of H₂.

We have seen that the material balance sub-regions in Fig. 3 are ΔH limited. This fact sets a limit on the maximum H₂, CO, and char production. These limits are not necessarily the same in other sub-regions. To explore this, we add a constraint to the linear programming problem by setting ΔH = 0 kJ, while minimizing the production of char or that of CO₂. We then visualize the results in Fig. 4.

3.2. Targeting minimum char and CO₂ production with no energy consumption

The material balance targets in Fig. 4 are all energy neutral. The results in Fig. 4 (a) show that complete carbon conversion to gas is possible at no energy penalty over a wide range of H₂ and CO production rates. Carbon efficiency (defined as the ratio of carbon in the desired product over the total carbon in BM) is highest below the H₂ production rate of 0.6 mol/mol BM, where the complete conversion of carbon to CO and CH₄ is possible. Maximum CO production occurs at an H₂ production rate of 0.6 mol/mol BM, with a 100% carbon conversion to CO (point E). Higher H₂ production rates up to 1.75 mol/mol BM (point F) are possible but come with a proportional CO₂ production at the expense of CO. For all these targets,

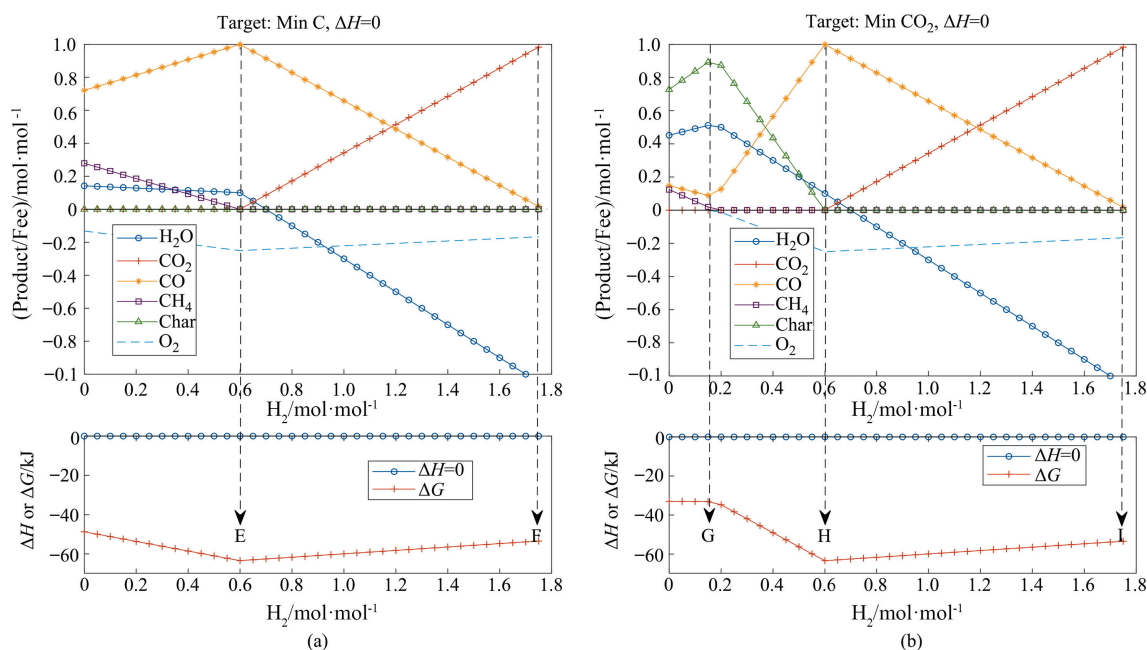


Fig. 4. Material and energy balance targets for biomass conversion that minimizes the production of char (a) and CO_2 (b) with no energy consumption ($\Delta H = 0 \text{ kJ}$).

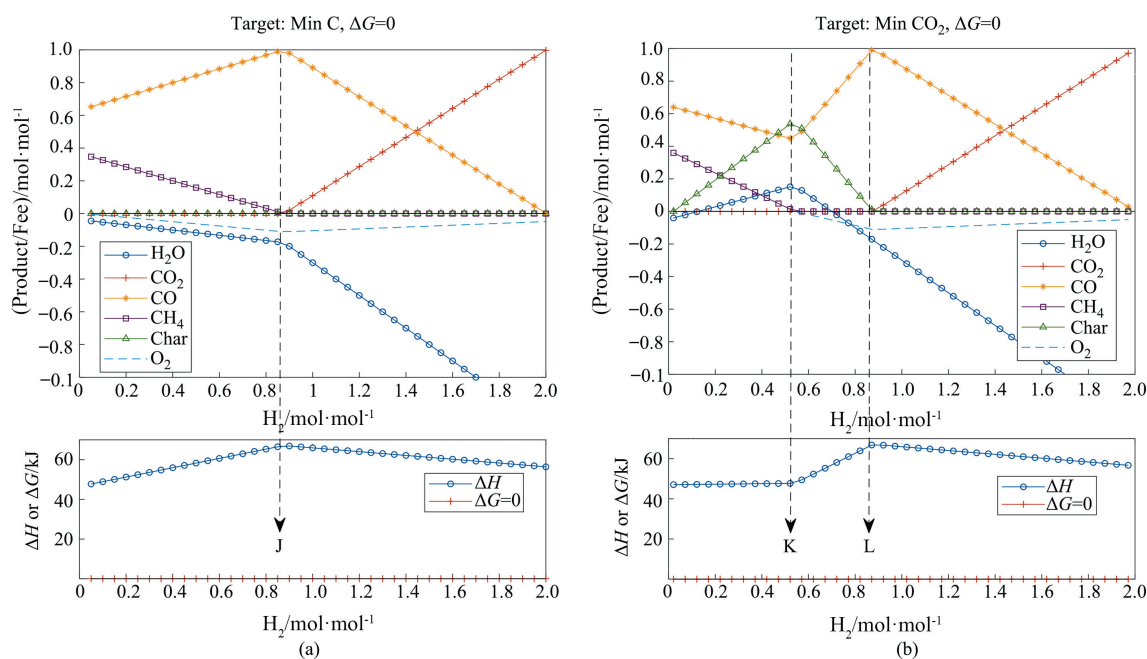


Fig. 5. Material and energy balance targets for biomass conversion that minimizes the production of char (a) and CO_2 (b) with no work potential input ($\Delta G = 0 \text{ kJ}$).

O_2 feed is necessary, but H_2O feed is only necessary at higher H_2 production rates.

The results in Fig. 4(b) show that char can also be produced from biomass at no energy cost up to a maximum of 0.89 mol/mol BM (point G). At this point, the H_2 and CO production rates are lower, and no O_2 feed is required. Increasing the H_2 production rate will lead to the same results as those obtained in Fig. 4(a). For example, CO_2 production is also inevitable above the H_2 production rate of 0.6 mol/mol BM . The maximum H_2 production rate is also at 1.75 mol/mol BM (point I), corresponding to zero CO production.

A crucial result in Fig. 4 is that ΔG is negative across the two material balance sub-regions, implying that these sub-regions are energy limited and not work (or chemical potential) limited. Therefore, as was discussed previously, there is an opportunity to either recover the work potential as useful energy or store it as chemical potential by increasing the production rate of the desired products (H_2 , CO , or char).

Recovering the chemical potential as useful work is possibly less efficient and quite difficult. It could require a heat engine configuration where at one point in the process, heat from an external

source enters at low temperature. At another point, the same amount of heat leaves the process at a higher temperature than the temperature of the entry point. The net effect is that no additional energy is added to the process while recovering the available chemical potential in the form of heat at a high temperature. Splitting the process into two steps is necessary for the heat engine configuration to be possible; an endothermic step that accepts heat at a low temperature, and an exothermic step that rejects heat at a high temperature. Matching the energies and temperature between these two steps may prove to be complicated— an inevitable source of inefficiency.

3.3. Targeting minimum char and CO₂ production with no work requirement

An alternative way to recover the available chemical potential is to store it in the product components (H₂, CO, and char) of the process. Setting the target to $\Delta G = 0$ kJ instead of $\Delta H = 0$ kJ in the linear programming formulation will yield material balances for complete chemical potential conservation, as shown in Fig. 3. These targets clearly require energy input since, as was shown previously, the biomass conversion process is energy limited. However, they do not require any work input because ΔG is zero. In other words, the process does not require high-quality energy, and therefore, a source of low-temperature heat is sufficient for any of the targets in Fig. 5. In principle, the temperature of the heat can be as low as 25 °C. However, because of practical limitations, the minimum temperature of the heat might need to be higher than 100 °C, which is by any industrial standard low-quality heat.

Fig. 5 shows that, if low quality heat is available, the production rate of H₂ at the maximum CO production rate (point J) can increase up to 0.85 mol/mol BM—a 42% rise compared to point E in Fig. 4 (a). Moreover, the maximum H₂ production rate increases by 14% from 1.75 [point F, Fig. 4 (a)] to 2 mol/mol BM with the same CO₂ production rate. Fig. 5 (b) shows similar results at maximum CO and H₂ production rates, as in Fig. 5 (a). However, the

maximum char production rate decreases by 40% from 0.89, at point G in Fig. 4 (b), to 0.54 mol/mol BM at point K in Fig. 5 (b).

It is clear that there are great opportunities to improve biomass conversion efficiency for applications such as syngas, hydrogen, and char production. More importantly, the conversion can happen at zero energy cost. If a source of low-quality energy is available such as concentrated solar energy (CSP) or waste heat from other processes, the production limits can be pushed even further by using the excess chemical potential resulting from the energy-neutral process.

3.4. Simulation results

Fig. 6 shows the Aspen Plus flowsheet simulation results of an energy-neutral biomass gasification process (Process 1). The objective was to achieve one of the targets in Fig. 4. The simulation results show that an energy-neutral process is feasible with heat integration between the feed and the product streams. The resulting material balance does not match any of the targets in Fig. 4, possibly because the temperature of the product stream in the simulation is 62 °C. In comparison, the temperature basis in Fig. 4 is 25 °C. Therefore, the simulation is slightly exothermic with respect to the basis of calculations. The average temperatures in the pyrolysis and gasification are 645 °C and 635 °C, respectively, at an oxygen feed rate of about 0.19 kmol/kmol BM and water feed rate of 0.35 kmol/kmol BM. The net availability (AV), calculated as the difference between the AV flow of the product stream and the sum of the AV flows of the feed streams, represents the lost work (or chemical potential) associated with the current material balance. It is equivalent to ΔG across the process.

As previously discussed, the main objective of the work-neutral target ($\Delta G = 0$ kJ) is to recover the excess chemical potential associated with the energy-neutral case where $\Delta G < 0$ kJ and $\Delta H = 0$ kJ. Since the biomass gasification process is energy limited, an attempt to recover or conserve the chemical potential will require the process to accept energy in the form of heat. The second simulation case (Process 2) in Fig. 7, is an attempt to conserve a por-

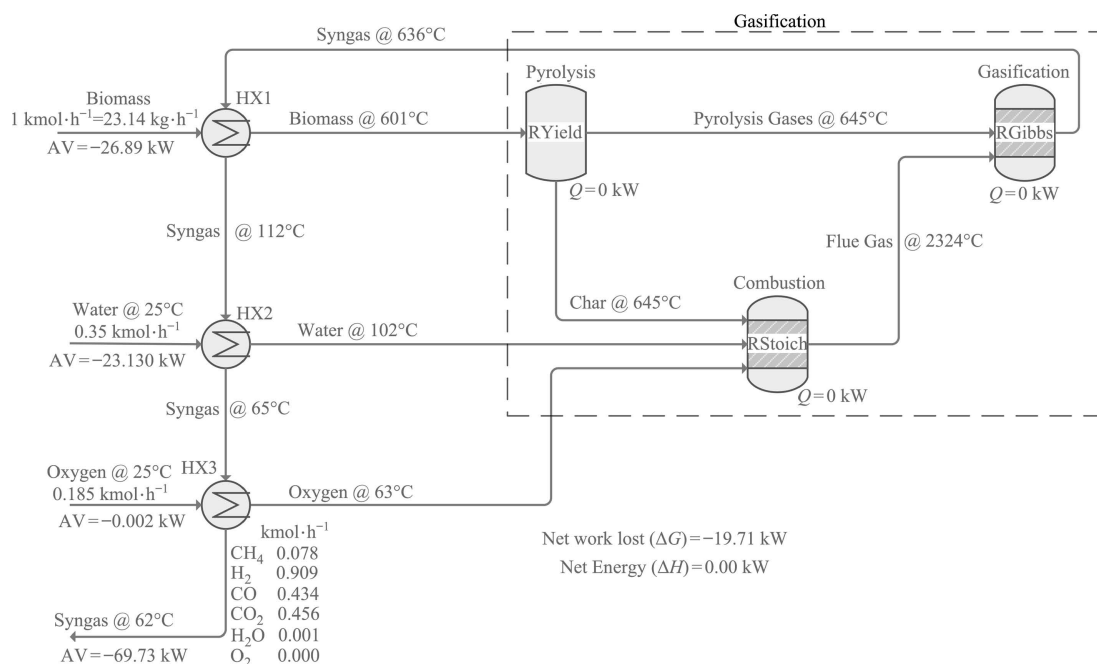


Fig. 6. Process 1: Aspen Plus simulation flowsheet and results for an energy-neutral biomass gasification process, depicting the temperature and the availability (AV) of the inlet and outlet streams to the process.

tion of the excess chemical potential by increasing the production rate of H_2 .

One way of supplying energy is by using the feed material to carry the energy with it into the process. However, the amount of energy carried in this way is limited by the material heat capacity and feed rate. The latter is fixed by the overall material balance. Endothermic reactions would be the best way of supplying energy to the process using less material. However, endothermic reactions often require heat to be supplied at high temperatures. In this work, we use the latent heat of the feed water to supply low-temperature heat (102°C) to the process. An external source of heat (Q_{external}) supplies the energy required to vaporize liquid feed water at 102°C and 100 kPa. Heat recovered by cooling the hot product stream is used to pre-heat the feed water to its boiling point of 102°C .

The simulation results in Fig. 7 (Process 2) show a limit of $0.74 \text{ kmol} \cdot (\text{kmol BM})^{-1}$ for the feed water. The amount of energy required to evaporate this water is about 6.2 kW of heat supplied at 102°C through HX4. The targets in Fig. 5 show that the required energy input to conserve the chemical potential entirely is in the range $45\text{--}70 \text{ kJ} \cdot \text{mol}^{-1}$, equivalent to a range of $12.5\text{--}19.44 \text{ kW}$ per $1 \text{ kmol} \cdot \text{h}^{-1}$ of biomass in the simulation in Fig. 7. Thus, the energy supplied via the water evaporator (HX4) is approximately 32%–48% of the energy needed to recover the chemical potential of the process entirely.

The results of process 2 show that supplying 6.2 kW of heat by evaporating the feed water at 102°C increases the hydrogen production rate to about 1.45 mol/mol BM , equivalent to about 60% rise from 0.90 mol/mol BM , the hydrogen production rate of Process 1 in Fig. 6. The average temperatures in the pyrolysis and gasification are now 700°C and 660°C , respectively, at an oxygen feed rate of about 0.18 mol/mol BM . The net lost work potential (or chemical potential) calculated as the difference of the AV flows between the feed and product stream is now -16.71 kW , equivalent to about 15% reduction compared to the work potential lost in Process 1 at -19.07 kW . However, the net gain in chemical potential conservation is about 1.67 kW , taking into account the

availability carried into the process by supplying heat at 102°C , implying that an 8% gain in chemical potential conservation yields a 60% increase in H_2 production rate.

Zhang *et al.* [36] have reviewed several processes of biomass steam gasification to produce hydrogen and have looked at their performance in terms of hydrogen production per kg of biomass as well as in terms of the exergy efficiency calculated based on hydrogen production rate. Zhang *et al.* reported a hydrogen production rate ranging from 6.56 to $32.94 \text{ mol} \cdot \text{kg}^{-1}$ of biomass for different biomasses with wood residue at $27.86 \text{ mol} \cdot \text{kg}^{-1}$. If we compare this value with the simulation results for Process 1 (Fig. 6), we can see a production rate of $39.28 \text{ mol} \cdot \text{kg}^{-1}$ representing nearly 40% increase in hydrogen yield. This significant improvement is attributable to energy neutral material balance target and the heat integration effort to achieve it.

If we now consider the simulation results of Process 2 (Fig. 7) we can see a hydrogen production rate of $62.71 \text{ mol} \cdot \text{kg}^{-1}$, representing a 125% improvement compared to value of $27.86 \text{ mol} \cdot \text{kg}^{-1}$ for wood residue reported by Zhang *et al.* This large improvement is attributable to the additional low quality energy that is supplied to the process, which, by using the available chemical potential in the biomass, allows feeding a higher water to biomass ratio (0.58) to produce more hydrogen compared to the processes reported in Zhang *et al.* that have a water to biomass ratio of 0.2.

If we further compare the exergy efficiencies using the same method of calculations as in Zhang *et al.* We can show that the exergy efficiency of Process 1 is 50.13% and that of that of Process 2 is 78.95%, representing significant improvement compared to 32.92% exergy efficiency for wood residue reported in Zhang *et al.*

These results show that there are significant opportunities for improving biomass gasification. The targeting tools presented in this work provide insight and better understanding of biomass conversion processes, thereby incentivizing further research and development in process flowsheet and equipment design to achieve higher efficiencies that would lead to better conservation of biomass resources.

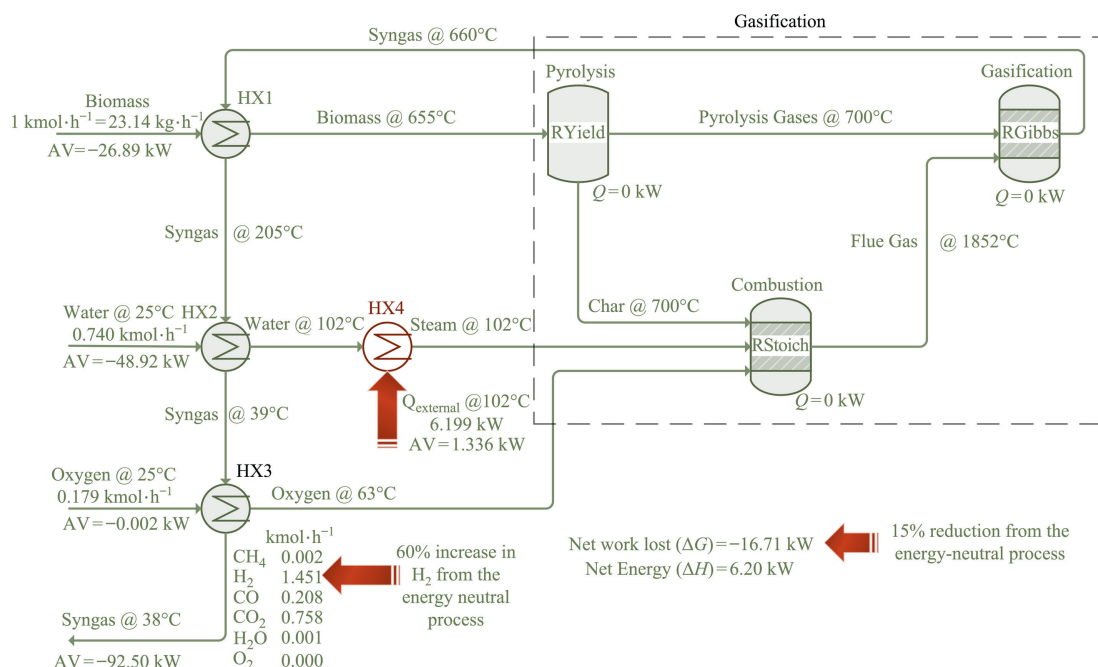


Fig. 7. Process 2: Aspen Plus flowsheet and simulation results of a biomass gasification process that conserves part of the available chemical potential by taking in low-quality heat to increase the production of hydrogen.

4. Conclusions

Material, heat, and work (or exergy) balances have been used to set up targets towards efficient biomass gasification. By reducing the multidimensionality of the system to simpler optimization problems, linear programming tools allowed us to explore these targets of interest, such as minimizing C and CO₂ production. Consequently, we demonstrated significant potential to improve biomass gasification for various applications. For instance, by supplying the right amount of oxygen, a 100% carbon conversion efficiency can be achieved at no energy cost over a wide range of H₂ and CO production rates. If a cleaner fuel from the biomass is desired, converting it to char is most efficient in terms of carbon and energy conversion. Up to 0.89 mol/mol BM of char can be produced in an energy-neutral process. Co-producing char and H₂ is also shown to be possible and attractive in terms of converting low-quality energy into chemical energy.

Using an Aspen Plus® simulation, we have demonstrated that an energy-neutral biomass gasification process is feasible with heat integration, and can be achieved at a hydrogen production rate of 0.9 mol/mol BM. More importantly, we have shown that even at zero energy requirement, biomass gasification processes can possess excess chemical potential, which can be recovered as useful work or even better conserved by producing more desired products such as H₂. According to our simulation, an 8% gain in chemical potential conservation yields a hydrogen production rate of 1.45 mol/mol BM, 60% higher than the energy neutral target. More process design techniques must be explored to attain higher chemical potential conservation and get closer to the target than what is achieved in the Aspen simulation. These results pave a way towards achieving significant improvement in biomass gasification efficiency.

The targeting method we have used in this work has some limitations in that, it assumes complete energy integration within the process and does not account for the separation energy for processes that requires separation. Consequently, it does not guarantee that an identified target is feasible when the underlying assumptions are lifted. These limitations emanate largely from the lack of better technology in equipment designs and in catalysis. Thus, the targets that cannot be achieved at this point, can alternatively be used to guide research and technology development towards more efficient processes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to acknowledge the financial support from University of South Africa, Hebei University of Science and Technology and South Africa National Research Foundation (113648).

Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cjche.2020.11.027>.

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