



Full Length Article

Multiparameter-based product, energy and exergy optimizations for biomass gasification

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ARTICLE INFO

Keywords:

Biomass gasification
Gibbs free energy minimization
CO₂ conversion
Exergy Efficiency
Optimization

ABSTRACT

The thermodynamic modelling of biomass gasification was studied by using Gibbs free energy minimization approach. Different from the studies using the same approach, the simultaneous presence of all gasifying agents (air, H₂O and CO₂) was considered and a multiparameter optimization was applied to determine the synergetic effect of gasifying agents for hydrogen, syngas with a specific H₂/CO ratio and methane production. The performance of gasification was assessed by using technical and environmental performance indicators such as product yields, cold gas efficiency, exergy efficiency, CO₂ emission and the heat requirement of the gasifier. The results show that the simultaneous presence of gasifying agents does not create considerable changes in syngas yield, H₂ yield, methane yield, CGE and exergy efficiency while it allows to tune the H₂/CO ratio and the heat requirement of the gasifier. The highest syngas yield is observed at T > 1100 K and 1 bar and when SBR > 0.5 and/or CBR > 0.8 with the absence of air, at which CGE changes between 114% and 122% while exergy efficiency is between 77% and 86%. The results prove that CO₂ offers several advantages as a gasifying agent and suggests that CO₂ recycling from gasifier outlet is a useful option for the biomass gasification.

1. Introduction

Gasification is one of the techniques used to convert biomass-derived feedstock into valuable products that can be further processed for fuel and chemical production. It is important to know the relation between gasifier output and fuel and process conditions for maximizing the benefit from outputs. Thermodynamic models enable us to learn more about this relation with a reasonable error in a fast way. Thermodynamic models provide to calculate the maximum achievable yield of a desired product assuming that the residence time is high enough to reach equilibrium [1]. In fact, while it is practically not possible to achieve thermodynamic equilibrium except for high temperatures (>1500 K), the model still provides a reasonable prediction on product composition, especially for downdraft gasifier, which operates close to equilibrium conditions [1–4]. The thermodynamic equilibrium model can be mainly classified in two groups: (i) Stoichiometric method. (ii) Non-stoichiometric method. The stoichiometric method considers equilibrium constants of selected reactions and mass balances whereas non-stoichiometric method works based on Gibbs free energy minimization. Since all reactions occurring in the gasifier cannot be considered in the former, the latter is more preferable to minimize errors in the

prediction [3]. Gibbs free energy minimization also allows us to determine nitrogen- and sulfur-related pollutants (e.g. NH₃, H₂S) that are present at minor quantities in the gasifier outlet gas [5].

Gibbs free energy minimization (GEM) approach has been applied many times in the literature to determine outlet gas compositions of gasifiers for different fuel composition and operation conditions. Literatures on the thermodynamic modelling of biomass gasification based on GEM can be summarized as follows. Chaiwatanodom et al. [6] have studied the potential of CO₂ recycling for improving gasification performance at different temperature, pressure and oxygen to biomass ratio. Authors have used gasification efficiency factor (i.e. energy efficiency including energy required for CO₂ absorption from gasifier outlet) and CO₂ emission per syngas production (mol CO₂ /mol CO + H₂) as performance indicators. They found that the addition of CO₂ improves both gasification efficiency factor and CO₂ emission per syngas production at low temperature and high pressure. The highest performance was obtained when the CO₂/C ratio is between 0.1 and 0.2 at 800 °C.

Das et al. [7] have simulated co-gasification process with different coal to biomass ratio (CB) and investigated the effect of equivalence ratio (ER), the gasification temperature and CB on gas compositions. The study showed that the increase in the amount of coal of the feed results

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<https://doi.org/10.1016/j.fuel.2021.121208>

Received 10 December 2020; Received in revised form 30 May 2021; Accepted 3 June 2021

Available online 18 June 2021

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Nomenclature	
AFR	Air to fuel ratio
C	Mass fraction of carbon
C_p	Constant pressure specific heat capacity (kJ/kmol.K)
CBR	Carbon dioxide to biomass ratio
CC	Carbon conversion (%)
CGE	Cold gas efficiency (%)
ex	Molar specific exergy (kJ/kmol)
ex_{ch}	Molar chemical exergy (kJ/kmol)
ex_{ke}	Molar kinetic exergy (kJ/kmol)
ex_{pe}	Molar potential exergy (kJ/kmol)
ex_{ph}	Molar physical exergy (kJ/kmol)
ER	Equivalence ratio
ESY	Effective syngas yield (m ³ /kg biomass)
Ex_D	Exergy destruction (kJ)
Ex_Q	Exergy of heat (kJ)
f	Mole number of CO ₂ per kmol of biomass (kmol/kmol biomass)
G	Gibbs free energy (kJ)
g	Molar Gibbs free energy (kJ/kmol)
H	Mass fraction of hydrogen
h	Molar Enthalpy (kJ/kmol)
h^0	Molar enthalpy at standard conditions (kJ/kmol)
HHV	Higher heating value (MJ/kg)
k	Mole number of air per kmol of biomass (kmol/kmol biomass)
LHV	Lower heating value (MJ/kg)
m	Mass (kg)
M	Molar mass (kg/kmol)
N	Mass fraction of nitrogen
n	Mole number (kmol)
O	Mass fraction of oxygen
P	Pressure (bar)
Q	Heat supplied to the gasifier (kJ)
q	Heat supplied to the gasifier per kg of biomass (kJ/kg)
r	Mole number of H ₂ O per kmol of biomass (kmol/kmol biomass)
R	Gas constant (J/mol.K)
s	Molar Entropy (kJ/kmol.K)
s^0	Molar Entropy at standard conditions (kJ/kmol.K)
S	Mass fraction of Sulfur
SBR	Steam to biomass ratio
SY	Syngas yield (m ³ /kg biomass)
T	Temperature (K)
T^0	Standard temperature (298 K)
UFB	Utilization factor of biomass burned (%)
w	Mass fraction of moisture
x	Mole number of product
y	Mole fraction
Δh_f^0	Standard enthalpy of formation (kJ/kmol)
η_{ex}	Exergy efficiency
μ	Chemical potential (kJ/kmol)
<i>Subscripts – Superscripts</i>	
0	Standard state
air	Air
b	Biomass
ch	Chemical
daf	Dry and ash free
db	Dry basis
gas	Gas
i	Component
in	Inlet stream
ke	Kinetic energy
out	Outlet stream
pe	Potential energy
ph	Physical energy
stoich	stoichiometric
<i>Abbreviations</i>	
CSR	Carbon steam reforming
GEM	Gibbs free energy minimization
MDR	Methane dry reforming
MSR	Methane steam reforming
MSW	Municipal solid waste
SSR	Steam supply ratio
WGS	Water-Gas shift

in an increase in CO concentration, whereas a decrease in H₂ concentration. In addition, CO and H₂ concentrations increase with temperature and decrease with ER. Similar changes in CO and H₂ yields upon temperature and ER change was also observed in the study of Mozafari et al [8] and Ramzan et al. [9]. Mozafari et al [8] investigated the effect of pressure, temperature and air to fuel ratio (AFR) on the air gasification of waste tire. Authors have determined the optimum conditions for waste tire gasification as 0.1 bar, 1640 K and AFR of 0.46. Ramzan et al. [9] evaluated the gasification of different biomass waste (e.g. food waste, municipal solid waste (MSW) and poultry waste) in terms CGE and they found that the gasification of food waste has the highest CGE (71%) followed by municipal solid waste and poultry waste with CGE of 53 and 45% at optimum conditions, respectively.

Oliveira et al. [10] developed a model for gasification of MSW to evaluate the effect of air, biomass moisture, temperature and pressure on gas compositions and low heating value (LHV) of the outlet gas mixture under adiabatic and isothermal supercritical conditions. Model results indicated that the LHV of the gas mixture along with H₂ and CO concentrations increase with pressure in adiabatic condition while it increases with temperature in isothermal condition.

Doherty et al. [11] used ASPEN Plus with the restricted equilibrium model to determine the effect of ER, temperature, air preheating, biomass moisture and steam injection on gas composition and cold gas

efficiency (CGE) of the wood pellet gasifier. Their study showed that without air preheating, maximum CGE (i.e. 66.1%) is obtained at ER of 0.34–0.35 and at temperatures of 837–874 °C. Air preheating improves CO and H₂ production, thereby increasing CGE at low ER (<0.35). Steam injection was found to be effective for H₂-rich syngas production. The positive effect of steam addition on H₂ production was also observed in other studies in literature [12].

Mehrpooya et al. [13] also used a thermodynamic model in ASPEN Plus based on the restricted equilibrium model. Authors analyzed syngas yield, energy and exergy efficiencies of biomass gasification process consisting of several separate units such as preheating, drying, pyrolysis, char gasification and char oxidation. They found that biomass moisture is the parameter which has the highest impact on syngas yield and the highest exergy destruction belongs to drying stage. Authors also evaluated several biomass feedstocks in terms of exergy efficiency and showed that rice husk has the highest exergy destruction rate.

Dong et al. [14] investigated the influence of elemental composition of biomass, pressure, temperature and ER on gas composition, LHV value of gas outlet and exergy efficiency for straw gasification. They found that the exergy efficiency of the gasifier increases with temperature and the H/C ratio of biomass while it decreases with pressure and the O/C ratio of biomass. The gasifier pressure has a positive effect on LHV of gas and the pressure effect is more pronounced at high

temperatures. Similar effect was also observed in the study of Haryanto et al. [12], in which H₂ concentration increases with the pressure between 1 and 3 atm and above 1000 K.

Freitas et al. [15] tested the performance of algal biomass gasifier at supercritical conditions (240–300 bar, 700–1100 K) and they investigated the effect of co-reactant feeding (e.g. CO₂ and CH₄) along with temperature and pressure on the outlet gas composition. The results showed that the increase in temperature strongly improves H₂ production while the pressure has no significant effect on it. The addition of CH₄ and CO₂ as co-reactant results in a decrease in H₂/CO ratio.

Hemmati et al. [16] studied the thermodynamic analysis of supercritical gasification at 250–350 bar and 750–1100 K. They used glucose as a model compound for biomass and investigated the effects of temperature, pressure, and feedstock concentration on H₂ production. The study showed that H₂ production increases with temperature while it decreases with feedstock concentration and the effect of pressure is negligible. The enhanced H₂ yield at high temperatures was also observed in the study of Lu et al [17].

Gambarotte et al. [5] studied the effect of AFR and temperature on gas composition and LHV by considering that different nitrogen and sulfur containing compounds (e.g. NO, NO₂, NH₃, HCN, H₂S, SO₂, SO₃) form due to gasification along with typical gasification products (CO, H₂, CH₄, CO₂, H₂O). In the model developed by authors, the gasifier temperature is calculated based on AFR, assuming that there is no heat addition to the gasifier. The model results indicated that the gasifier temperature increases with AFR. The temperature increase gives rise to higher CO and N₂ concentrations whereas it reduces CO₂, CH₄ and H₂ concentrations. NH₃ and H₂S are the main nitrogen and sulfur containing pollutants in the gasifier outlet and their concentrations decrease by temperature.

Kuo et al. [18] have studied the comparison of gasification performances of raw bamboo and torrefied bamboo at 250 °C (TB250) and 300 °C (TB300) by using thermodynamic analysis. Authors analyzed the effect of ER and steam supply ratio (SSR) on CGE and carbon conversion (CC) of biomass feedstock treated differently. They found that torrefaction enhances syngas yield, which increases with the torrefaction temperature. The highest syngas yield is obtained when ER is between 0.2 and 0.3 and SSR is 0.9 for all biomass feedstock considered. TB250 was found to be the best when CC, CGE and syngas yield are considered simultaneously.

Madadian et al. [19] have investigated the effect of temperature, biomass moisture content and ER on CGE and high heating value (HHV) for the gasification of wood pellet with air. Their study showed that the optimum ER value is 0.31 for maximum CGE and HHV and at optimum ER HHV values are 3.8 and 8.7 MJ/m³ for the biomass moisture content of 35 and 5%, respectively.

Rodriguez-Alejandro et al. [20] have performed a parametric study by using a modified equilibrium model and non-equilibrium factors for biomass gasification of wood chips, dairy manure and sorghum. They studied the effect of temperature and ER on gas composition and LHV of gas. In their model tar formation was included as well. The results indicated that tar concentration decreases with temperature and ER.

Sreejith et al. [21] have studied the thermodynamic analysis of steam gasification with apricot stones used as biomass feedstock. Authors tried to determine optimum temperature and pressure for maximizing H₂ yield, LHV of the outlet gas and energy efficiency. They determined that the gasifier pressure does not have a significant impact on the H₂ yield while the increase in temperature causes a noticeable increase in H₂ concentration. The highest H₂ yield (63.5%) is obtained at 870 K and 1 bar. The highest LHV (15.5 MJ/m³) is obtained when the temperature and pressure are 1000 K and 4 bar. Energy efficiency shows a slight increase with the temperature and the highest efficiency (65.7%) is observed at 973 K. In another study by the same authors [22], optimal steam to biomass ratio (SBR) was investigated to get the highest H₂ yield, LHV and energy efficiency. They found that H₂ yield increase with SBR continuously in the range of SBR (0–2.5) considered. The maximum

H₂ concentration was found to be 71% at SBR of 2. Authors also noted that if three performance measures (i.e. H₂ yield, LHV, energy efficiency) are considered simultaneously, the optimal SBR is 0.8 and the corresponding energy efficiency is 56.5%.

Literature studies indicate that gasification models mainly use air and water (or steam) as oxidants and take biomass type, temperature, pressure, ER (or AFR) and SBR (SSR) as important gasifier parameters. Most of them evaluate gasifier performance based on CGE, HHV (or LHV) and carbon conversion values. Only a few model studies consider CO₂ as a co-reactant and exergy efficiency as a performance indicator [4,6,13,14] and investigate the effect of process parameters on pollutant concentrations [5]. None of these studies include a simultaneous consideration of multiple process parameters for the optimization of process conditions and explore the synergetic (or non-synergetic) effect of parameters on product yields, energy and exergy efficiencies. Therefore, multi-parameter-based optimization is needed for more complete assessment of gasification performance.

In the present work, we have studied the biomass gasification of sunflower pellet in the presence of air, H₂O, and CO₂ as oxidants via a mathematical model developed in MATLAB (version 2017b). We have investigated the simultaneous effect of process parameters such as temperature, pressure, equivalence ratio (ER), steam to biomass ratio (SBR), carbon dioxide to biomass ratio (CBR) on gas composition, gas yield (m³/kg biomass), cold gas efficiency (CGE), carbon conversion, pollutant concentrations and exergy efficiency of biomass gasification process by using Gibbs free energy minimization approach. We have also determined the optimum conditions to maximize specific products used in downstream processes, such as Fisher-Tropsch process for synthetic fuel synthesis, a boiler for heat generation, gas turbines and fuel cells for electricity generation. The main contribution of the study is to develop a new modelling approach which enables us to make an application-based optimization of several parameters simultaneously and to include carbon dioxide as an oxidant and exergy efficiency as a performance indicator.

2. Modeling approach

The biomass gasification model was developed by using Gibbs free energy minimization method. Biomass feedstock was first chosen. Then the overall gasification reaction and possible gasification products were specified. After setting atomic balances for carbon, oxygen, hydrogen, nitrogen and sulfur, Gibbs free energies of each compound at gasification temperature were formulated. Mole numbers of each compound were found at the minimum total Gibbs free energy value. When mole numbers of gasification products were fixed, performance indicators of the gasification (e.g. CGE, energy efficiency, exergy efficiency, carbon conversion) were defined. Assumptions and details of modelling steps are explained in the following sections.

2.1. Assumptions

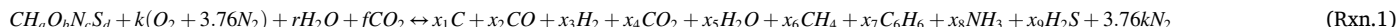
The following assumptions were used in the biomass gasification model:

- Gasification occurs in isothermal and steady-state conditions.
- The biomass feedstock is ash and moisture free.
- The biomass feedstock and oxidants (e.g. air, H₂O, CO₂) are fed to the gasifier at 25 °C and 1 atm.
- All product gases are assumed to show ideal gas behavior since the pressure of the gasifier is <10 bar.
- All nitrogen and sulfur content of biomass is converted to NH₃ and H₂S after gasification, respectively [11].
- The gasifier is perfectly isolated, i.e. there is no heat loss during gasification.
- Char only contains carbon. Ash is excluded in the model.

2.2. Biomass composition and gasification reactions

Sunflower pellet was chosen as a biomass feedstock. The ultimate (i.e. elemental) and proximate analysis results of sunflower pellet are taken from [23] and are shown in Table 1. Dry and ash free form of biomass was taken for the study and the biomass gasification analysis was performed per kmol of biomass. Based on proximate analysis the molecular formula of the biomass was determined by normalizing to 1 kmol of carbon atom. Nitrogen and sulfur contents of the biomass were included in the model.

The overall chemical reaction of the gasification is described as follows:



where a, b, c and d are the mole numbers of hydrogen, oxygen, nitrogen and sulfur per mole of carbon in biomass, respectively, while x_i represents the mole number of the products.

Biomass reacts with oxidants (e.g. air, water, carbon dioxide) to form char and a gas mixture containing producer gas (CO, H₂, CO₂, N₂), water (H₂O), methane (CH₄) and pollutants such as tar, ammonia (NH₃) and hydrogen sulfur (H₂S). Char is assumed to be 100% carbon. Benzene (C₆H₆) was used as a model molecule for tar compounds. All nitrogen and sulfur contents of the biomass were assumed to be converted into NH₃ and H₂S [11].

The chemistry of biomass gasification is quite complex, i.e., numerous chemical reactions occur during gasification. Important gasification reactions are listed in Table 2. These reactions mainly dictate the final gas composition depending on temperature, biomass/oxidant ratio, residence time and biomass composition. We used these reactions to understand our model results obtained in different conditions.

2.3. Gasification model

The gasification model was developed by using series of equations related to mass balance, Gibbs free energies of gaseous products and Lagrange multipliers based on the overall gasification reaction. Five mass balances were used in the model for each atom (C, H, O, N, S) included in the biomass formula as shown below:

$$\text{Carbon: } 1 + f = x_1 + x_2 + x_4 + x_6 + 6x_7 \quad (1)$$

$$\text{Hydrogen: } a + 2r = 2x_3 + 2x_5 + 4x_6 + 6x_7 + 3x_8 + 2x_9 \quad (2)$$

$$\text{Oxygen: } b + 2k + r + 2g = x_2 + 2x_4 + x_5 \quad (3)$$

$$\text{Nitrogen: } c + 7.52k = x_8 + 7.52k \quad (4)$$

$$\text{Sulfur: } d = x_9 \quad (5)$$

The non-stoichiometric method used in this study based on the minimization of total Gibbs free energy. The total Gibbs free energy is the sum of Gibbs free energy of 9 gaseous products indicated in reaction

Table 1
Ultimate (daf basis) and proximate analysis of sunflower pellets [23]

Ultimate analysis		Proximate analysis	
Character	Value (%)	Character	Value (%)
Carbon	52.1	Volatile Matter	65.2
Hydrogen	6.1	Fixed Carbon	19.5
Oxygen	41.0	Ash	4.1
Nitrogen	0.6	Moisture	11.2
Sulfur	0.1		

(1).

$$G = \sum_{i=1}^n \mu_i n_i \quad (6)$$

In equation (6), μ_i is the chemical potential of compound i and n_i is the corresponding mole number. The chemical potential of each compound is found by the following equation, under the assumption that each gaseous compound in the gas mixture behaves as an ideal gas.

$$\mu_i = g_i + RT \ln(P_i/P^0) \quad (7)$$

where g_i is the molar Gibbs free energy of compound i at a specific temperature and 1 atm pressure, P_i is the partial pressure of compound i

and P^0 is the standard pressure (i.e. 1 atm). Since we assumed that we have an ideal gas mixture, Dalton's law of partial pressure is applied:

$$\mu_i = g_i + RT \ln(y_i P/P^0) \quad (8)$$

where y_i is the mole fraction of gas i in the total gaseous product. The solid carbon was not included in this calculation. The molar Gibbs free energy of gases were calculated by using their molar enthalpy and molar entropy values at the specified temperature as follows:

$$g_i = h_i - Ts_i \quad (9)$$

$$h_i = \Delta h_f^0 + \int_{T^0}^T C_{p,i}(T) dT \quad (10)$$

$$s_i = s^0 + \int_{T^0}^T C_{p,i}(T) dT/T \quad (11)$$

where h_i and s_i are molar enthalpy and entropy of gas i , Δh_f^0 and s^0 are the standard molar enthalpy of formation and entropy for gas i at 298 K and 1 atm, respectively. $C_{p,i}$ is the constant pressure specific heat of gas i and T^0 is the standard temperature (298 K). The specific heats of gases were found by:

$$C_p = a + bT + cT^2 + dT^3 \quad (12)$$

where a, b, c and d are coefficients that vary depending on the compound. The values of these coefficients are taken from the literature

Table 2
Gasification reactions and their enthalpies at standard conditions (T = 298 K, P = 1 atm).

#	Reaction Type	Chemical Equation	Δh_{rxn}^0 (kJ/mol)
1	Boudouard	$C + CO_2 \leftrightarrow 2CO$	172
2	Carbon Steam Reforming (CSR)	$C + H_2O(g) \leftrightarrow CO + H_2$	131
3	Methanation	$C + 2H_2 \leftrightarrow CH_4$	-74.8
4	Partial Oxidation	$C + 1/2O_2 \leftrightarrow CO$	-111
5	Oxidation	$C + O_2 \leftrightarrow CO_2$	-394
6	Oxidation	$CO + 1/2O_2 \leftrightarrow CO_2$	-284
7	Oxidation	$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O(g)$	-803
8	Oxidation	$H_2 + 1/2O_2 \leftrightarrow H_2O(g)$	-242
9	Water-Gas Shift (WGS)	$CO + H_2O(g) \leftrightarrow CO_2 + H_2$	-41
10	Methane Dry Reforming (MDR)	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$	247
11	Methane Steam Reforming (MSR)	$CH_4 + H_2O(g) \leftrightarrow CO + 3H_2$	206

[24,25] for each gas compound (see Suppl. Info).

In addition to specific heats of gaseous compounds, the specific heat of carbon was also calculated to use in energy balance. Different from gaseous compounds, the specific heat of carbon was found by using the following equation [26]:

$$C_{p,C} = \left(4.03 + 1.14 \times 10^{-3} T - \frac{2.04 \times 10^5}{T^2} \right) \times 4.18 \quad (13)$$

2.4. Gasification parameters

The varying parameters in this study are temperature, pressure, equivalence ratio (ER), steam to biomass ratio (SBR) and carbon dioxide to biomass ratio (CBR). The latter three were defined as:

$$ER = \frac{m_{air}}{m_{air,stoich}} \quad (14)$$

$$SBR = \frac{m_w}{m_{b,daf}} \quad (15)$$

$$CBR = \frac{m_{CO_2}}{m_{b,daf}} \quad (16)$$

where m_{air} is the mass of air required for gasification, $m_{air,stoich}$ is the mass of air required for the stoichiometric combustion of biomass, $m_{b,daf}$ is the mass of dry and ash free biomass, m_w and m_{CO_2} are the mass of water and carbon dioxide, respectively. In order to determine the amount of stoichiometric air for the complete combustion, we assumed that in the stoichiometric combustion, the biomass is converted into CO_2 , H_2O , NO , N_2 and SO_2 [27]. The mole fraction of NO in all nitrogen-containing gas mixture ($NO + N_2$) is determined based on the ratio between the coefficient of nitrogen (1.51 MJ/kg) in the correlation used to calculate HHV value of the biomass (Eqn. (20)) and the heating value of NO (6.45 MJ/kg). The fraction of NO in the nitrogen containing gas mixture is found to be 0.234.

2.5. Solution approach

The equilibrium molar concentrations of the products ($x_i, i = 1, 2, \dots, 9$) are found by solving the following Gibbs free energy minimization problem, formulated as:

$$\min_x G \text{ in Eq (6)}$$

subject to constraints Eq (1)–(5)

The decision variable vector x is comprised of the molar concentrations of the products as described in Section 2.1. Given a set of operating conditions for temperature, pressure, ER, SBR and CBR, the nonlinear optimization problem above is solved by MATLAB constrained nonlinear optimization routine *fmincon*. The default *interior-point algorithm* is used in the *fmincon* routine, where the mass balance equalities are handled by the method of Lagrange multipliers. On an Intel Core i7 notebook PC with 8 GB RAM, a single optimization problem can be solved, on average, in 5 s. It was concluded that the optimization formulation and solution method presented above is sufficiently accurate and fast enough to find equilibrium concentrations.

2.6. Performance indicators

The gasification performance was evaluated by using several indicators such as carbon conversion, gas yield, cold gas efficiency (CGE), energy and exergy efficiencies. The carbon conversion efficiency presents the amount of carbon in the biomass material which converted into gases. Carbon conversion (CC) is calculated from:

$$CC(\%) = \left(1 - \frac{m_{C,residue}}{m_{C,b}} \right) \times 100 \quad (17)$$

Gas yield is another important parameter, which shows how much

gas is produced per kg of biomass and found by:

$$GasYield = \frac{n_{gas,total} \times R \times T_0}{P \times m_b} \quad (18)$$

The cold gas efficiency (CGE) shows the heat potential of the gas relative to biomass heat potential. CGE is calculated from:

$$CGE(\%) = \left(\frac{\sum m_{gas,i} \times LHV_{gas,i}}{m_b \times LHV_b} \right) \times 100 \quad (19)$$

where LHV_b and LHV_{gas} are low heating value of biomass and gaseous compound, respectively. Lower heating value of biomass in MJ/kg was calculated from higher heating value, which was found by using the following correlation:

$$LHV_b^{db} = HHV_b - 2.4 \times 8.9H \quad (20)$$

where 2.4 MJ/kg is the latent heat of vaporization of water and 8.9 kg/kg is the stoichiometric ratio of water to hydrogen [28]. The higher heating value of biomass was determined by:

$$HHV_b = 34.91C + 117.83H + 10.05S - 1.51N - 10.34O \quad (21)$$

where C, H, S, N and O are the mass fractions of carbon, hydrogen, oxygen and sulphur, respectively, as determined by ultimate analysis on a dry and ash free (daf) and numbers are in MJ/kg [28].

The CO_2 emission per the produced syngas ($CO + H_2$) after the gasification was evaluated to determine CO_2 production potential for the processes using CO_2 as a feedstock including the gasification itself via recycling and/or to gain insight about the relative effect of the process on greenhouse gas emission. The CO_2 emission of the gasification is described as follows:

$$CO_2Emission = \frac{n_{CO_2}}{n_{CO} + n_{H_2}} \quad (22)$$

Exergy efficiency is one of the important performance indicators in this study. It represents how much work potential is lost during gasification. The exergy efficiency of the gasification is found by using the following equation:

$$\eta_{ex} = \frac{\sum n_{out} ex_{out}}{Ex_Q + \sum n_{in} ex_{in}} \quad (23)$$

where the flow exergy of each component on an unit molar basis can be calculated from:

$$ex = ex_{ph} + ex_{ch} + ex_{ke} + ex_{pe} \quad (24)$$

where, ex_{ph} , ex_{ch} , ex_{ke} and ex_{pe} are the unit molar basis physical exergy, chemical exergy, exergies of kinetic and potential energies, respectively. While the exergies of kinetic and potential energies are neglected, the physical and chemical exergies can be found by:

$$ex_{ph} = (h - h_0) - T_0(s - s_0) \quad (25)$$

$$ex_{ch} = \sum y_i ex_{0,i} + RT_0 \sum y_i \ln \gamma_i \quad (26)$$

where $ex_{0,i}$, y_i and γ_i are the standard molar chemical exergy, molar fraction, and activity coefficient of substances, respectively. The standard chemical exergies of pure substances were taken from the literature [29–31] (see Suppl. Info). The activity coefficients were taken as 1, assuming that we have an ideal gas mixture.

The chemical exergy of biomass can be calculated by using following equation [30,31]

$$ex_b^{ch} = (M_b((LHV_b \times 1000 + 2442w)\rho + 9417S) \quad (27)$$

where LHV_b is the low heating value of biomass, w is the mass fraction of moisture, 2442 kJ/kg is the latent heat of vaporization of water, S is mass fraction of sulfur in biomass (as received basis), 9417 kJ/kg is the difference between the standard chemical exergy and the low heating value of rhombic sulfur, 1000 kJ/MJ is the unit conversion

factor, M_b is molar mass of biomass in kg/kmol and φ is defined for O/C < 2 as [32,33]:

$$\varphi = \frac{1.044 + 0.016H/C - 0.3493O/C(1 + 0.0531H/C) + 0.0493N/C}{1 - 0.4124O/C} \quad (28)$$

where H, C, O and N are mass fractions of hydrogen, carbon, oxygen and nitrogen in biomass. The exergy of heat in (Ex_Q) is found as follows:

$$Ex_Q = Q_{in} \left(1 - \frac{T_0}{T}\right) \quad (29)$$

where T_0 environment temperature (25 °C), T is the gasification temperature and Q_{in} is the heat supplied to the gasifier, which can be found by energy balance equation:

$$Q_{in} + \sum n_{in} h_{in} = \sum n_{out} h_{out} \quad (30)$$

In the energy balance equation, the enthalpy of biomass is calculated by:

$$h_b = h_{CO_2} + \frac{a}{2} h_{H_2O} + 0.234c \times h_{NO} + dh_{SO_2} + (LHV_b \times 1000 \times M_b) \quad (31)$$

where a, c and d are mass balances of biomass formula (Eqn. (2)–(5)), 0.234 is the mass fraction of NO in the nitrogen containing gas mixture (see section 2.4) and 1000 kJ/MJ is the unit conversion factor.

The exergy destruction, Ex_D , is found by as follows:

$$Ex_Q + \sum n_{in} ex_{in} = \sum n_{out} ex_{out} + Ex_D \quad (32)$$

In both energy and exergy balance equations, water is taken in the liquid state for cases including steam as the gasifying agent to include energy and exergy required to vaporize water in the calculations.

3. Results and discussion

The model presented in Section 2 is first validated by comparing its results with the related literature. Afterwards, the operating space of the gasification reaction is explored to get an insight for the performance indicators defined in Section 2.6 for air, steam and CO₂ gasification and for the gasification in the simultaneous presence of air, steam and CO₂. This is achieved by running the Gibbs free energy minimization problem on a 5-dimensional grid constructed by sampling temperature from 500 to 1500 K at 50 K increments (total of 21 test points), pressure from 1 bar to 10 bar at 1 bar increments (10 test points), ER from 0 to 0.5 at 0.1 increments (6 test points), SBR from 0 to 2.4 at 0.3 increments (9 test points), and finally CBR from 0 to 2.4 at 0.3 increments (9 test points). In total, $21 \times 10 \times 6 \times 9 \times 9 = 102.060$ test conditions are run. The findings from these tests are reported in the subsequent sections. At the end of this section, the synergetic effect of gasifying agents and the potential of CO₂ as a gasifying agent are discussed. For all conditions considered in this study, the tar concentration was found to be negligibly small (10^{-3} - 10^{-6} g/m³ gas). Therefore, the effect of process conditions on the tar concentration was not discussed in this study.

Table 3

The comparison of our model results with experimental and other model results reported in the literature for the air gasification of wood with a moisture content of 20% in dry basis at 1073 K. The numbers represent the mole fraction of gas in dry basis.

Gas	Present Work	Experiment [34]	Stoichiometric Model [35]	Non-stoichiometric Model [5]
H ₂	25.35	15.23	21.06	25.00
CO	23.73	23.04	19.61	21.57
CO ₂	10.54	16.42	12.01	11.73
CH ₄	0.02	1.58	0.64	0.04
N ₂	40.36	42.31	46.68	41.66

3.1. Model validation

The validation of the model was done by comparing our results with the experimental results published in the literature [34] for the air gasification of wood with a moisture content of 20% in dry basis at 1073 K and the results of stoichiometric and non-stoichiometric models obtained for the same conditions [5,35]. The comparison of the results is shown in Table 3. As seen from the Table, the CO concentrations in our model and the experiment are very similar while the model overestimates hydrogen production and underestimates methane production. This is typical behavior of equilibrium models, which was already explained in the literature [5,36]. This behavior is also clearly seen in other models indicated in Table 3, which show good agreement with our model.

The model was also compared with other literature studies to validate the model for steam gasification. We have chosen two model studies for the comparison [21,22,37]. The comparison of these models with experimental studies were already made and the typical weaknesses of the equilibrium model (e.g. overestimation of H₂ concentration and underestimation of CH₄ concentrations) were already discussed in the related publications. We compared our results with the related model results obtained at 1 bar with the SBR of 1 for 3 different temperatures. In order to make the comparison consistent, the same types of biomass feedstocks considered in the model studies were used. The comparison of the results is shown in Table 4. As seen from the Table, there is a good fit between our results and the results obtained in the study of Mahishi and Goswami [37] while the difference is more apparent between our results and the results obtained in the study of Sreejith et al. [21,22]. This difference can be explained by the reason that char was not considered as a gasifier product in the study of Sreejith et al. [21,22].

3.2. The effect of process parameters on the performances of air, steam and CO₂ gasification

The effect of temperature, pressure, ER, SBR and CBR on gas composition, pollutant concentrations and our performance indicators were investigated for air, steam and CO₂ gasification separately and optimum conditions were determined for each of them. The interested reader is referred to see Supplementary Information. The results show that air gasification gives the best performance at temperatures of 1000 ± 50 K when ER is 0.2 ± 0.02 considering technical and environmental performances of the system. At these conditions, syngas yield, CGE,

Table 4

The comparison of our model results and results reported in the literature for the steam gasification of different feedstocks at the same conditions (1 bar, SBR = 1).

Temperature (K)	BiomassType	Literature	Equilibrium Mole Number/ Mole Biomass			
			H ₂	CO ₂	CO	CH ₄
900	Wood	Mahishi and Goswami [37]	1.08	0.48	0.48	0.13
		Present Work	1.03	0.41	0.44	0.15
		Sreejith et al. [21,22]	0.98	0.35	0.59	0.1
1000	Wood	Present Work	1.06	0.44	0.43	0.13
		Mahishi and Goswami	1.3	0.31	0.68	0.04
		Present Work	1.3	0.3	0.68	0.02
1100	Wood	Sreejith et al.	0.8	0.13	0.78	0.08
		Present Work	1.29	0.34	0.65	0.015
		Mahishi and Goswami	1.27	0.26	0.75	0.08
1100	Wood	Present Work	1.29	0.25	0.75	0.001
		Sreejith et al.	0.74	0	0.97	0.07
		Present Work	1.28	0.28	0.72	0.001

exergy efficiency and CO₂ emissions are 1.73 m³/kg biomass, 90.8%, 79.4% and 0.035, respectively. Optimum steam gasification occurs when the temperature and SBR are 1100 ± 100 K and 0.5 ± 0.1. At these conditions, syngas yield, CGE, exergy efficiency and CO₂ emissions are 2.27 m³/kg biomass, 111%, 84% and 0.018, respectively. The best performance for CO₂ gasification is obtained when T and CBR are 1000 ± 100 K and 1 ± 0.1. At these conditions, syngas yield, CGE, exergy efficiency and CO₂ emissions are 2.27 m³/kg biomass, 117%, 84.7% and 0.114, respectively. The results indicate that CGE values exceeds 100% for steam and CO₂ gasification at the related conditions. This is expected since the CGE calculation only measures the heating value of gaseous products per the heating value of the fuel. It does not consider the energies of oxidant feed and the heat required for the process as energy inputs. In this respect, steam and CO₂ gasification at some SBR and CBR ratios gives a relatively higher H₂ and CO formation, thereby a higher cumulative heating value of the gas mixture than that of fuel (i.e. CGE values above 100%), as seen in the literature [6,18]. The results also show that gasifier pressure does not create a considerable effect on gas and pollutant concentrations relative to other parameters discussed except for methane concentrations, which will be discussed in Section 3.4.4.

3.3. Comparison of syngas yield for air, steam and CO₂ gasification

The analyses regarding air, steam and CO₂ gasification indicate that at high temperature (T > 1000 K), the syngas yield increases with SBR and CBR continuously while there is an optimum ER value suggesting that the syngas yield can be increased as much as possible with SBR and CBR. Since the syngas yield is directly proportional to CGE, the higher SBR and/or CBR gives higher syngas yield and CGE. However, this analysis disregards the amount of heat required for the process. Even if the high SBR and CBR values promote CO and H₂ producing reactions to occur, since these reactions are endothermic, they increase the amount of heat required for the process. This affects energy balance of the gasifier. In order to make a reasonable comparison of syngas yield produced at different SBR, CBR and ER, a new term, the effective syngas yield (ESY), is introduced in this part considering that the amount of heat required is met by burning a portion of biomass and the remaining biomass is used to produce syngas. ESY is defined as follows:

$$ESY = \left(1 - \frac{UFB}{100}\right) * SY \quad (33)$$

where UFB is the utilization factor of biomass burned and can be found by the following equation:

$$UFB = \frac{Q_m}{LHV_{biomass} \times m_{biomass}} \times 100 \quad (34)$$

The change of effective syngas yield as a function of ER, SBR, CBR and temperature are shown in Fig. 1. As seen from the figure, the highest effective syngas yield (1.4–1.6 m³/kg biomass) obtained in air, steam and CO₂ gasification are very close to each other. The highest yield is obtained in air gasification, which is followed by CO₂ and steam gasification in order. To get the highest effective syngas yield, air gasifier should operate at ER of 0.18–0.36 and between 1000 and 1400 K. Steam gasification gives the highest syngas yield at SBR of 0.2–0.8 and 1000–1400 K whereas the highest syngas yield in CO₂ gasification is obtained at CBR of 0.7–2 and at 1000–1300 K. Results suggest that even if the syngas yield increases with H₂O and CO₂ in steam and CO₂ gasification as opposed to air gasification, when the heat requirement of the gasifier is also taken into account, all gasification processes have optimum operation conditions to get the highest syngas yield.

3.4. Simultaneous optimization of process parameters

In this section, we consider all process parameters simultaneously for the optimization of process conditions and explore the synergetic (or non-synergetic) effect of parameters on several gasification outputs used in different downstream applications and energy and exergy efficiencies of the process. The optimization of process parameters was done for obtaining the highest syngas yield, hydrogen yield, methane yield, hydrogen and methane concentrations. The top 50 data converged after the optimizations and the related process parameters giving these maximum values were evaluated to gain insight about the dependency of maximum values on process parameters. Technical (e.g. CGE and exergy efficiency) and environmental (CO₂ emission per syngas produced) performance indicators and the heat requirement of the gasifier were also determined for each condition and included for the evaluation of the system performance. The range of desired outputs, process parameters and performance indicators obtained after each optimization are summarized in Table 5 and their corresponding discussion is

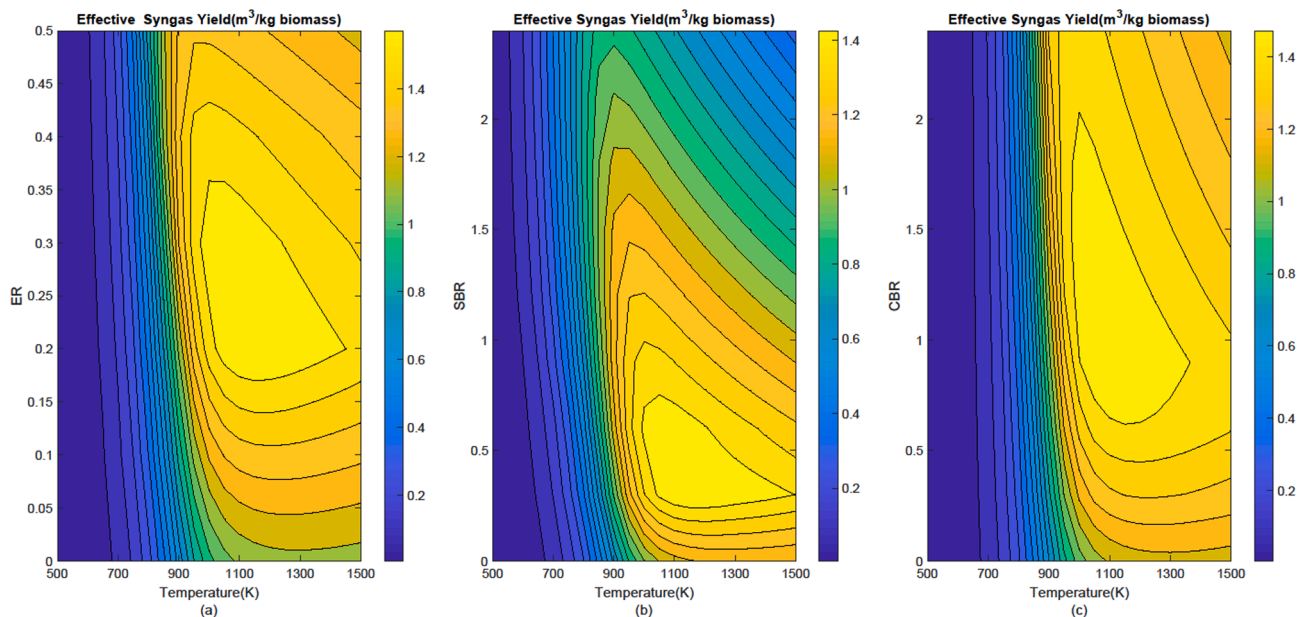


Fig. 1. The effect of ER, SBR and CBR on effective syngas yield.

Table 5

The range of process parameters, performance indicators for obtaining top 50 desired output in optimization.

Desired Output	T (K)	P (bar)	ER	SBR	CBR	Yield (m ³ /kg)*	H ₂ or CH ₄ Conc. (%)**	H ₂ /CO ratio	CGE (%)	η _{ex} (%)	CO ₂ e	q _{in} (kJ/kg)
Max Syngas Yield	1400–1500	1	0	0–2.4	0–0.6	2.27	0.43–1.4	0.2–1.7	114–122	77–86	0.20–0.57	9744–21690
Max Syngas Yield in near autothermal mode***	1000–1350	1–5	0.1–0.3	0–0.3	0–0.9	1.60–1.65	0.6–0.95	0.48–1.11	82–107	77–85	0–0.22	–960.8–4277
H ₂ /CO ratio = 2, max syngas yield	950–1500	1–10	0–0.1	1.2–2.1	0–2.1	2.05–2.27	1.37–1.52	2	102–113	75–82	0.14–0.7	9996–14980
H ₂ /CO ratio = 0.5, max syngas	1050–1500	1–10	0	0.3–0.9	1.5–2.4	2.25–2.27	0.75–0.77	0.5	119	82–86	0.18–0.41	8643–14400
Max H ₂ yield	900–1150	1–8	0	1.8–2.4	0–0.9	1.75–1.89	0.31–0.41	3.37–6.34	108–111	77–80	0.25–0.53	10450–14550
Max H ₂ concentration	1050–1500	1–10	0	0–0.6	0	0.68–1.34	0.50–0.53	1.05–1.5	71–114	59–86	0–0.1	2672–7460
Max CH ₄ yield	500	4–10	0	0.9–2.1	0–2.4	0.57	0.13–0.29	124–451.3	89	81–83	67–287	543–3491
Max CH ₄ concentration	600–800	2–10	0	0–0.6	0	0.25–0.55	0.35–0.37	2.62–33.11	40–90	40–84	2.3–23	–1991–382

*Yield represents syngas yield (m³ CO + H₂ / kg daf biomass) or H₂ or CH₄ yield (m³ / kg daf biomass) depending on the desired output.

**It represents the mole fraction of H₂ in the outlet gas mixture excluding N₂ sourced from the inlet air. For conditions giving max CH₄ yield and concentration (two rows at bottommost) it represents the mole fraction of CH₄.

*** Except for this case, all optimization were performed for the gasifier working in allothermal mode.

presented in the following subsections.

3.4.1. Process parameters optimization for the highest syngas yield

Syngas (CO and H₂) production is the main motivation of gasification processes. It is one of the key intermediates for the chemical industry since it can be converted to synthetic hydrocarbon fuels and chemicals via Fischer-Tropsch synthesis (FTS). Syngas is also important for heat and electricity generation via boiler, gas turbine and solid oxide fuel cell due to its high heating value. Due to the importance of syngas for the chemical and energy industry, one of the objectives of the optimization study is to determine conditions maximizing the syngas yield of biomass gasification. The top 50 syngas yields obtained from the optimization along with the related process parameters giving these yields are shown in Fig. 2. The figure shows that the maximum syngas yield is 2.27 m³/kg biomass and the syngas yield does not vary much with the change in process parameters in the first 50 data. All syngas yields are obtained at high temperature (1400–1500 K), low pressure (1–2 bar) and in the absence of air (ER = 0). Different from temperature, pressure and ER, the dependency of the syngas yield on SBR and CBR values are weak, i.e.

there is a little change in the syngas yield even if the variation in SBR and CBR values are high. This is expected since when the temperature is above 1100 K, SBR > 0.5 and/or CBR > 0.8, the syngas yield does not change with SBR and CBR values. The results suggest that in order to obtain a high syngas yield biomass gasifier should be operated at a high temperature (above 1100 K) and a low pressure and when SBR > 0.5 and/or CBR > 0.8 with the absence of air.

The change of the H₂/CO ratio and other performance indicators such as CGE, exergy efficiency CO₂ emission, the heat requirement of gasifier (q_{in}) and the percentage of biomass sacrificed to meet the heat requirement (UFB) obtained at the conditions giving maximum syngas yield were also evaluated and shown in Fig. 2. As seen from the figure, at the related conditions H₂/CO ratio changes between 0.2 and 1.7, and it strongly depends on SBR and CBR values. It increases with SBR values and decreases with CBR values. This means that H₂/CO ratio can be tuned by changing SBR and CBR values without a significant change in syngas yield at the conditions specified above. The other performance indicator that is strongly affected by SBR and CBR is CO₂ emission per syngas produced. CO₂ emissions varies between 0.2 and 0.57. The

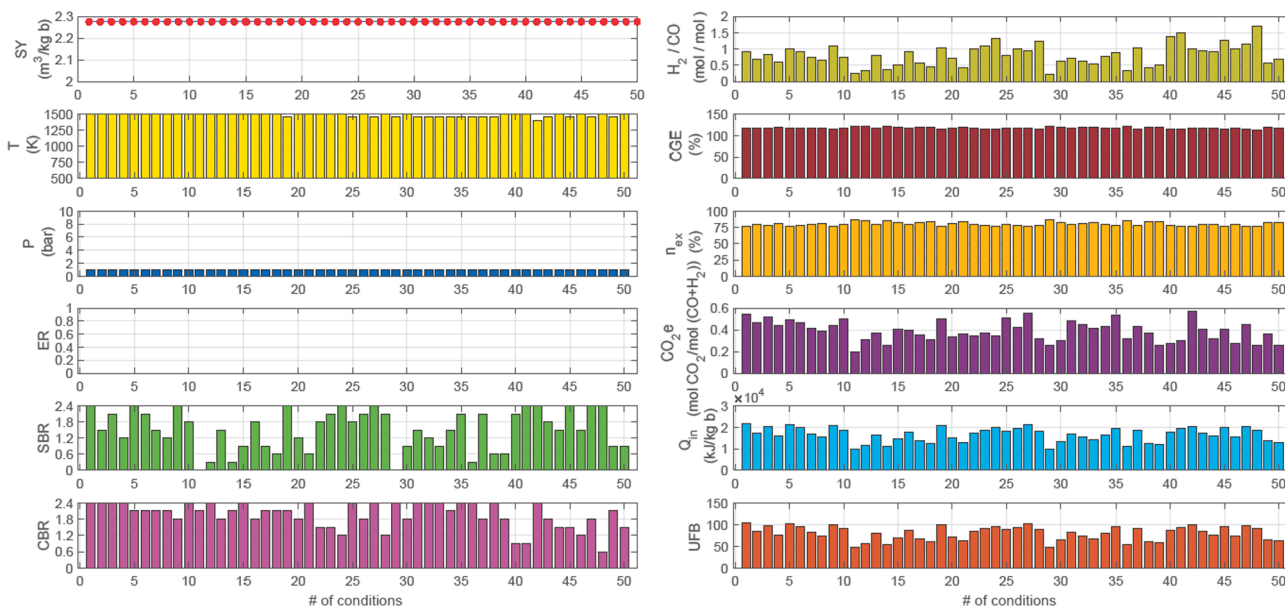


Fig. 2. The top 50 syngas yield at different T, ER, SBR, CBR and P along with performance indicators obtained at the related conditions.

highest CO₂ emission is observed when SBR and CBR are at the highest value due to the combined effect of Boudouard, carbon steam reforming and water–gas shift reactions (see Table 2). Different from the H₂/CO ratio and CO₂ emission, the change of CGE and exergy efficiency at different operation conditions are relatively small. CGE changes between 114 and 122% while exergy efficiencies are between 77 and 86%. The results demonstrate that at maximum syngas conditions energy and exergy efficiencies remain almost constant while the H₂/CO ratio and CO₂ emission per syngas produced changes dramatically depending on the change in SBR and CBR values. Since H₂O and CO₂ mainly promote endothermic reactions (Boudouard, RWGS, MSR and CSR in Table 2), the increases in SBR and CBR values result in an increase in the external heat requirement of the gasifier. The effect of SBR and CBR on the total heat requirement of the gasifier is almost the same if we exclude the vaporization heat of water. The heat requirement of the gasifier is 17000 kJ/kg biomass at maximum SBR (SBR = 2.4) in the absence of CO₂ (Figure S6) including the vaporization heat of water (5425 kJ/kg biomass) while it is 10000 kJ/kg biomass at maximum CBR (CBR = 2.4) in the absence of H₂O (Fig. 2, condition (29)). If one wants to burn a part of biomass feedstock to meet this heat requirement, 90% and 50% of biomass are burned for maximum SBR and CBR conditions, respectively. This indicates that obtaining a high syngas yield and any adjustment of H₂/CO ratio at max syngas conditions result in an extensive heat requirement.

The importance of heat requirement of the gasifier for obtaining a high syngas yield was already evaluated in the previous analysis. It is also interesting to know how the syngas yield and our performance indicator change when the gasifier is operated in the near autothermal mode, i.e., the biomass feedstock sacrificed for heat generation were not considered and the remaining biomass was evaluated for the calculation of syngas yield as we discussed in Section 3.3. We applied the same optimization and found out process conditions giving the top 50 syngas yield for the near autothermal gasification. Fig. 3 shows the top 50 effective syngas yield in the near autothermal mode, process parameters and performances indicators obtained at these conditions. The syngas yield in near autothermal mode changes between 1.60 and 1.65 m³/kg biomass, which is approximately 30% lower than that obtained from the gasifier operated in allothermal mode (the previous case). The operating conditions change as well in this mode. The top 50 syngas yield in near autothermal mode are obtained at moderate temperature (1000–1300 K) and when ER is around 0.2. The operating temperature can be

lowered in this range without a significant loss in syngas yield with increasing CBR values till to 0.9. The reason for that is related to the promotion effect of CO₂. Since CO₂ promotes CO-producing reactions such as methane dry reforming (MDR) and Boudouard reactions, it enables to obtain the same amount of syngas at lower temperatures.

At the maximum syngas conditions in near autothermal mode CGE values (82–107%) are 20% less than that obtained in allothermal mode due to lower syngas yield obtained. However, exergy efficiency obtained in near autothermal mode (77–85%) is almost the same with the one obtained in allothermal mode. Since the amount of decrease in syngas yield is balanced against the amount of decrease in the heat requirement, the exergy efficiency remains nearly unchanged. Similarly, the change in the H₂/CO ratio (0.47–1.15) and CO₂ emission (0–0.26) obtained for the near autothermal mode are relatively small compared to that obtained for the allothermal mode. This is related to the small variation in SBR and CBR values for this data set. One should note that the CO₂ emission sourced from the combustion of biomass sacrificed for meeting the heat requirement is not included in the CO₂ emission evaluated here.

3.4.2. Process parameters optimization for the highest syngas yield with the H₂/CO ratio of 2.0 or 0.5

The ratio of H₂/CO in syngas at the gasifier outlet is very important for hydrocarbon fuel production via FTS since it directly affects the process conditions and catalyst selection. The syngas with the H₂/CO ratio of 2.0 is preferred for FTS with cobalt catalyst due to its low WGS activity while FTS operation in the presence of iron catalyst requires the syngas with the H₂/CO ratio of 0.5 [38]. Therefore, the H₂/CO ratio were also considered in the optimization and process conditions of the biomass gasifier giving the highest syngas yield with H₂/CO ratio of 2.0 and 0.5 were determined. Fig. 4 indicates that the top syngas yields (2.05–2.27 m³/kg biomass) with the H₂/CO ratio of 2.0 (within ± 2% margin) are mainly obtained at high temperatures (1250–1500 K) and when SBR is on average 1.8. This is expected since the higher SBR promotes H₂ formation via endothermic carbon steam reforming reaction. Fig. 4 also shows that the operation temperature of the gasifier can be lowered till 950 K with the addition of CO₂, which promotes methane dry reforming and Boudouard reactions to happen. The operating conditions giving the top syngas yields with the H₂/CO ratio of 0.5 are different than those obtained for the H₂/CO ratio of 2.0. As seen from Fig. 5, the top syngas yields with the H₂/CO ratio of 0.5 are obtained at

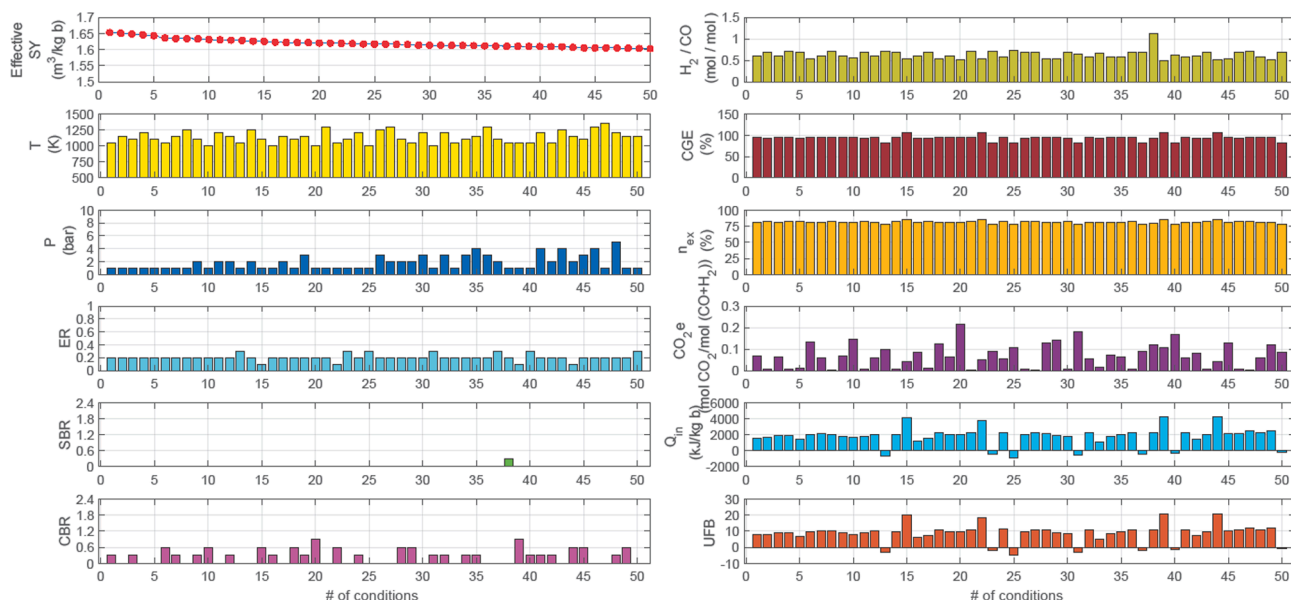


Fig. 3. The top 50 effective syngas yields at different T, ER, SBR, CBR and P along with performance indicators obtained at the related conditions.

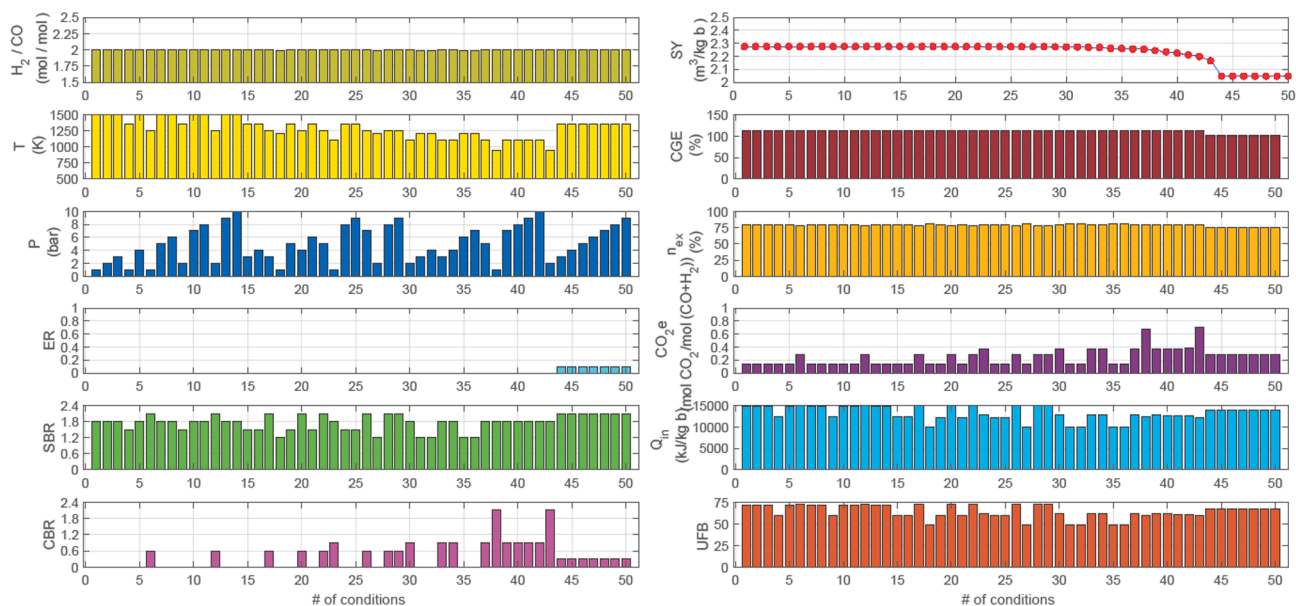


Fig. 4. The top 50 syngas yields with the H_2/CO ratio of 2.0 at different T, ER, SBR, CBR and P along with performance indicators obtained at the related conditions.

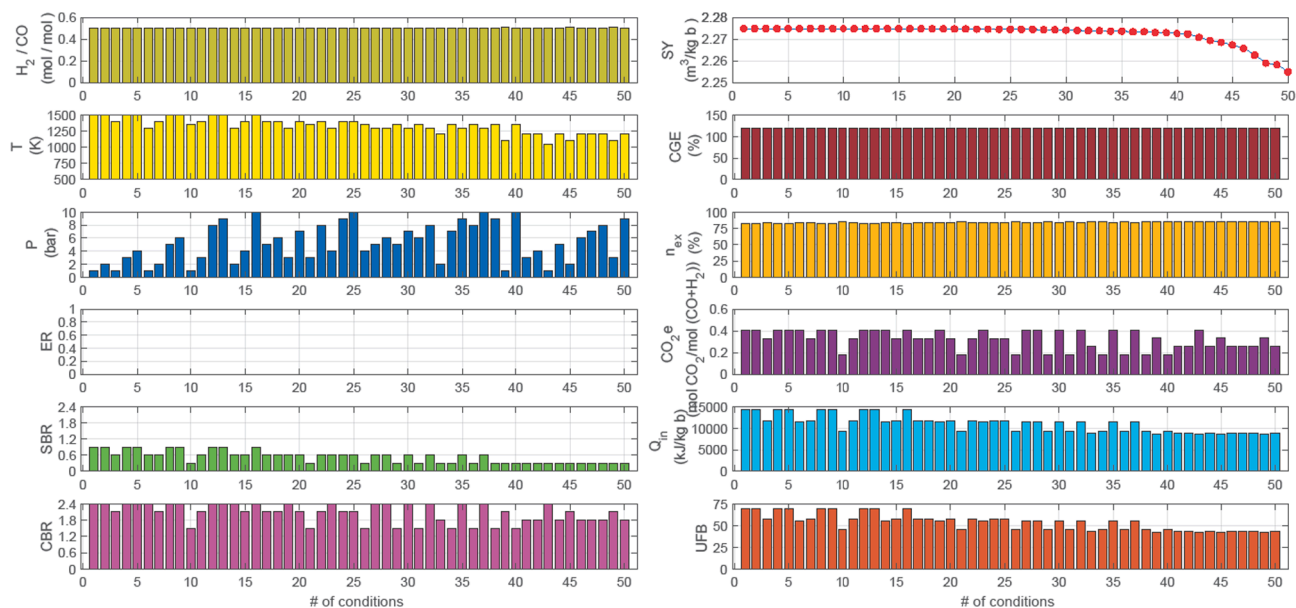


Fig. 5. The top 50 syngas yields with the H_2/CO ratio of 0.5 at different T, ER, SBR, CBR and P along with performance indicators obtained at the related conditions.

high CBR (>1.5), low SBR (<0.9) and relatively higher temperatures on average (1050–1500 K). Since CBR increases CO yield via Boudouard and reverse water–gas shift reactions, the H_2/CO ratio remain at around 0.5 at high CBR values. The results suggest that in order to obtain a high syngas yield with the H_2/CO ratio of 2.0, the biomass gasifier should operate at a high SBR (>1.2) and low CBR (<0.5) while for obtaining a high syngas yield with the H_2/CO ratio of 0.5 the gasification should occur at high CBR (>1.5) and low SBR (<0.9). For both conditions, syngas yields are around the same. CGE, exergy efficiency and CO_2 emission obtained at conditions giving high syngas yield with the H_2/CO ratio of 0.5 are a little bit higher than those obtained at conditions giving the high syngas yield with the H_2/CO ratio of 2.0 while a lower heat requirement is observed for the former. For both conditions, the pressure dependency of biomass gasification in terms of product yield is very weak, i.e., a large change in pressure (from 1 bar to 10 bar) does not create any significant effect on the H_2/CO ratio, suggesting that there is

no need to pressurize the gasifier for H_2/CO adjustment.

3.4.3. Process parameters optimization for the highest H_2 yield and concentration

Hydrogen is one of the most important products of biomass gasification, since it is used as a reactant in fuel cells for electricity generation with high efficiencies and transportation, in fertilizer production and in refineries for cracking of heavy hydrocarbon fragments. Its purity is also an important concern since some downstream applications require high hydrogen purity such as proton exchange membrane (PEM) fuel cells. We have determined top 50 process conditions to obtain high hydrogen yields and high hydrogen concentrations for the related downstream applications. Fig. 6 shows that the top H_2 yields vary between 1.75–1.89 m^3/kg biomass and they are observed at high SBR (>1.8), low CBR (<0.9) and between 900 and 1150 K in the absence of air. At these conditions, CGE and exergy efficiencies are 108–111% and 77–80%,

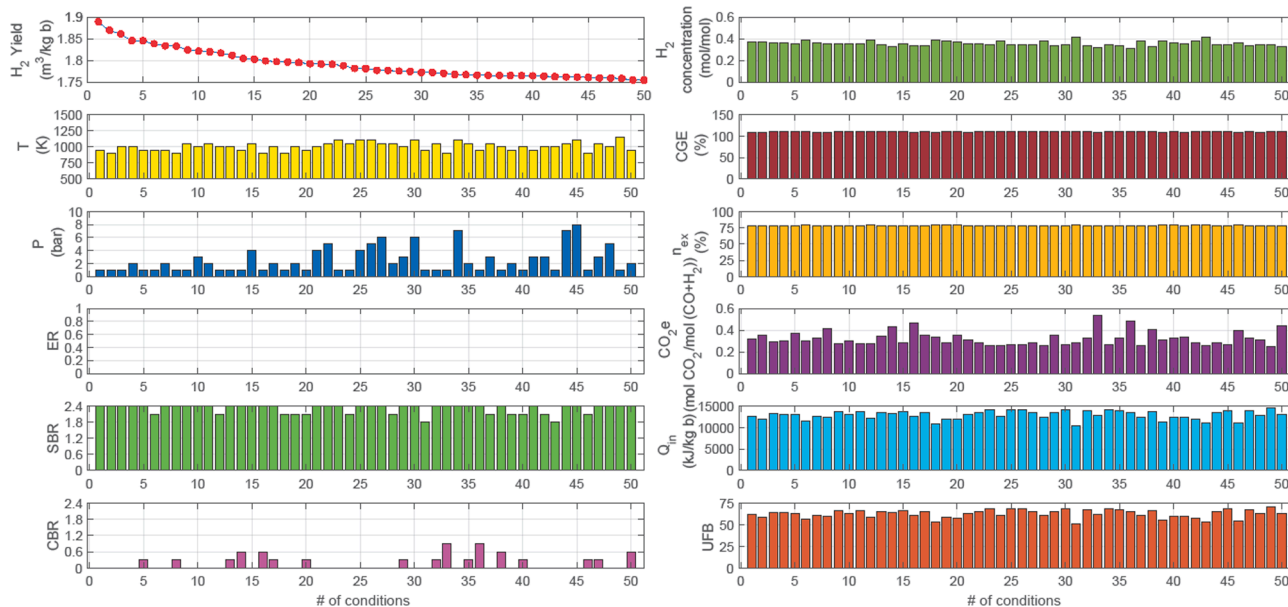


Fig. 6. The top 50 H_2 yields at different T, ER, SBR, CBR and P along with performance indicators obtained at the related conditions.

respectively. These numbers are very close to the ones obtained at maximum syngas yield conditions indicating that at both conditions similar CGE and exergy efficiencies are obtained. The similarity between two conditions is also valid for CO_2 emission. CO_2 emission at maximum H_2 yield conditions are between 0.25 and 0.53 which are close to the range observed for the CO_2 emission at the maximum syngas yield condition.

At the condition giving the top H_2 yields, H_2 concentration is between 0.31 and 0.41 suggesting that an extensive purification is required before the resulting mixture is used for fuel cell applications. H_2 can be obtained with a higher purification by simply changing operating conditions as seen from Fig. 7. The higher H_2 concentration (0.50–0.53) can be obtained at higher temperature (1050–1500 K) and lower SBR (0–0.6) in the absence of air and CO_2 . However, this results in a significant decrease in H_2 yield (0.68–1.34 m^3/kg biomass). Similarly, a lower CO_2 emission is observed at the conditions giving max H_2 concentration. The maximum CO_2 emission (0.1) is around fivefold less than

the one obtained at the conditions giving the maximum H_2 yield. At maximum H_2 concentration conditions, CGE and exergy efficiencies vary in a broader range depending on SBR value. When SBR is 0.6, both CGE and exergy efficiency are almost the same as the ones obtained at conditions giving the maximum H_2 yield. However, in the absence of steam, CGE and exergy efficiencies drop >30 and 20%, respectively. Since both maximum H_2 yield and maximum H_2 concentration are obtained in the presence of H_2O and CO_2 and in the absence of air, at the related conditions the gasifier requires an external heat source. The heat requirement for conditions giving the maximum H_2 yield is between 10,450 and 14450 kJ/kg biomass, i.e., approximately 50 and 70% of biomass feedstock should be burned to meet this heat requirement. The lower limit can be achieved either by decreasing the SBR or CBR value. The former is more effective in terms of heat reduction. The heat requirement for conditions giving the maximum H_2 concentration is less than that for conditions giving the maximum H_2 yield. It varies between 2672 and 7460 kJ/kg, which corresponds to 15% and 35% of biomass

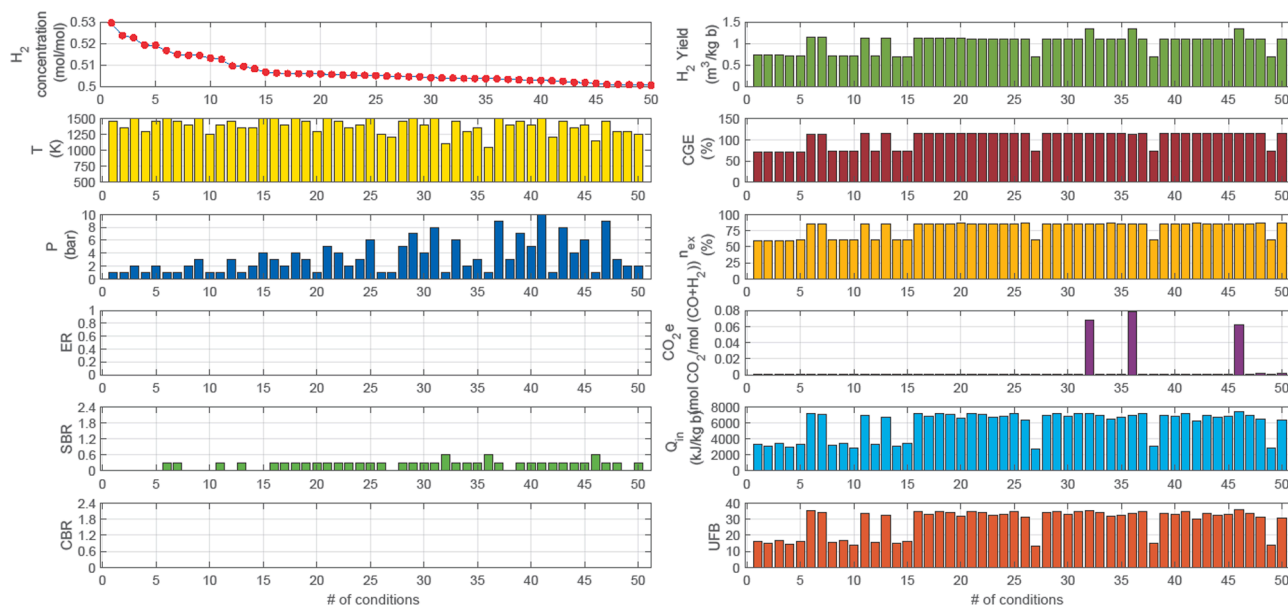


Fig. 7. The top 50 H_2 concentrations at different T, ER, SBR, CBR and P along with performance indicators obtained at the related conditions.

sacrificed to burn. The lower limit can be achieved in the absence of steam. As SBR increases, the heat requirement increases as well. However, one should consider that a higher SBR results in improvements in CGE and exergy efficiencies up to 40% and 30%, respectively, due to the increase in H₂ yield. As seen for conditions giving the highest syngas, the dependency of H₂ yield and concentration on pressure is so small that this effect can be neglected.

3.4.4. Process parameters optimization for the highest CH₄ yield and concentration

Methane is also one of the important gas products, which is used extensively in the current energy infrastructure for residential and industrial heating, electricity generation and transportation. Even if the main motivation of biomass gasification is to produce syngas or producer gas, it is important to know the methane production potential of the gasifier and optimum operation conditions giving the highest methane yield and concentration. Figs. 8 and 9 show process conditions giving the top 50 CH₄ yields and concentrations along with performance indicators obtained at these conditions. As seen in Fig. 8, the highest methane yield is around 0.57 m³/kg biomass and it is observed at low temperature (500 K) and high pressure (>4 bar) when SBR is on average 1.2. Since at low temperature both reverse methane steam and dry reforming reactions favor the reactant side due to the exothermicity of reactions, a higher methane yield is obtained at lower temperatures. Different from the previous analyses, the effect of pressure on the methane yield and concentration is pronounced. The methane yield increases with the pressure since for both reverse methane dry and steam reforming reactions the differences in mole numbers of products and reactants are significantly positive (Le Chatelier's principle). Therefore, low temperatures and high pressures are preferred to obtain high methane yield. At these conditions, the maximum methane concentration that can be attained is 29%. This number can be increased to 37% by increasing the temperature up to 800 K and decreasing SBR value below 0.6 (Fig. 9). However, this leads to a twofold decrease in methane yield thereby resulting in more than twofold decrease in CGE and exergy efficiencies. The heat duty of the gasifier also changes dramatically when operation conditions are switched to conditions giving the high CH₄ concentrations. At the maximum CH₄ yield conditions, the gasifier requires an external heat source (up to 3491 kJ/kg biomass) while at the maximum CH₄ concentration conditions the gasifier mostly produces heat (1991 kJ/kg biomass). Since the former

proceeds in the presence of water and water mainly promotes endothermic reactions (carbon and methane steam reforming), the gasifier operates in endothermic mode while the reverse happens for the latter.

3.4.5. Process parameters optimization for the highest CGE and exergy efficiencies

Cold gas efficiency indicates how much energy is transferred from the solid feedstock to gaseous products during gasification. It is important to know conditions giving the highest CGE for downstream applications such as boiler and gas turbine since higher CGE means higher energy available for heat and electricity generation. CGE provides a quantitative assessment on the energy transfer during biomass gasification, but the transfer of the quality of energy (or ability to get useful work) is also an important metric for all processes, which is evaluated by exergy efficiency. Therefore, exergy efficiency was also included in the optimization and process conditions giving the top CGE and exergy efficiencies were evaluated. Optimization results show that process parameters giving the top CGE and exergy efficiencies are similar with those giving the top syngas yield. Since CGE and exergy efficiencies are mainly affected by H₂ and CO yield due to their relatively high heating values (LHV_{H2} = 120 MJ/kg, LHV_{CO} = 10.1 MJ/kg) and chemical exergies (see Table 4), the maximum CGE (122%) and exergy (86%) efficiencies are obtained at conditions where the syngas yield is maximized. Therefore, we refer to Section 3.4.1 for discussions on conditions giving the top CGE and exergy efficiencies.

3.5. The synergetic effect of gasifying agents

One of the objectives of this study is to determine the synergetic effect of air, steam and CO₂ as gasifying agents on product yields, energy and exergy efficiencies and to make the value of CO₂ more apparent as a gasifying agent. The individual evaluation of each gasifying agent with respect to temperature (Suppl. Info) and simultaneous consideration of all of them (Section 3.4) indicate that there is no significant synergetic effect of gasifying agents for product yields and energy and exergy efficiencies. The highest syngas yield (2.27 m³/kg biomass) is obtained in the absence of air when SBR and CBR are maximum (Fig. 2), but the same value can be also obtained when one of them is absent and the other one is at maximum (Figure S6 and S9). Similar behaviors are observed for H₂ and CH₄ yields and concentrations. The maximum H₂ and CH₄ yields and concentrations are observed in the absence of air and

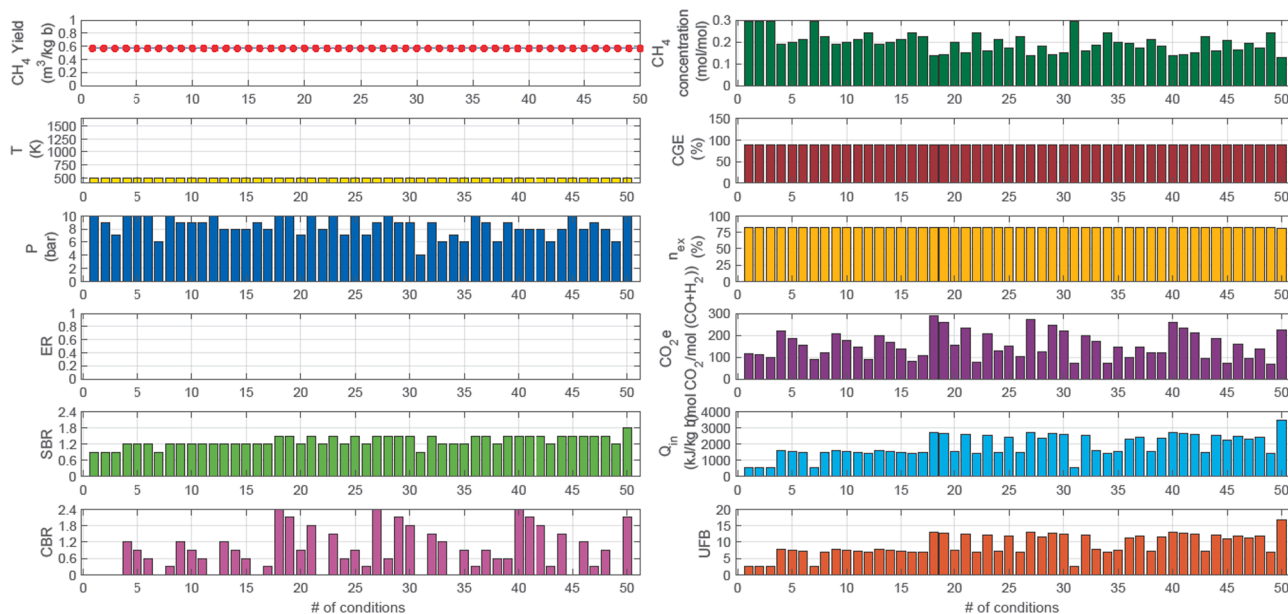


Fig. 8. The top 50 CH₄ yields at different T, ER, SBR, CBR and P along with performance indicators obtained at the related conditions.

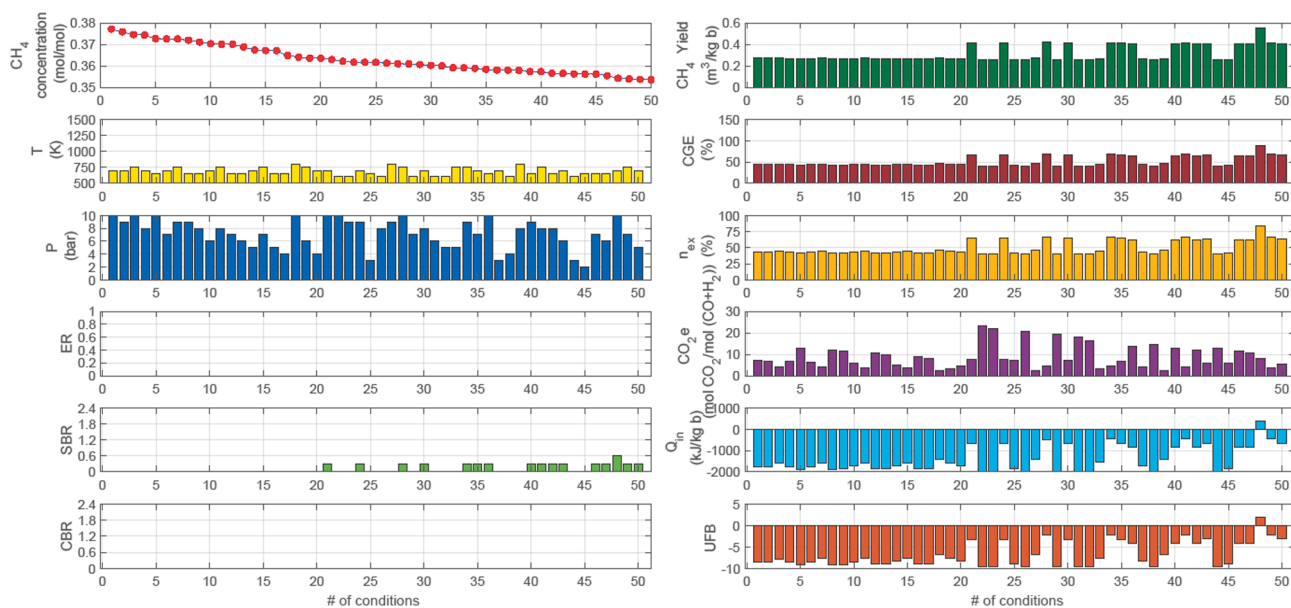


Fig. 9. The top 50 CH_4 concentrations at different T, ER, SBR, CBR and P along with performance indicators obtained at the related conditions.

CO_2 suggesting that there is no synergetic effect between air, CO_2 and H_2O for product yields. The synergetic effect is also absent for CGE and exergy efficiency since these values can be maximized in the absence of air and H_2O (Fig. 2, condition (11) and (29)).

3.6. The importance of CO_2 as a gasifying agent

Gasification processes mainly use air, oxygen, steam or the mixture of them as gasifying agents, but CO_2 has also a potential for the gasifying agent. It is produced in the gasification, and recycling CO_2 to the gasifier inlet can lower CO_2 emission, thereby minimizing the environmental impact of the gasification process. In this study, the effect of CO_2 as a gasifying agent along with air and steam on product yields, energy and exergy efficiencies was evaluated and the advantages of CO_2 utilization in the gasification were determined. The results show that CO_2 gasification shows a better performance than steam gasification in terms of the energy requirement of the process. In other words, less heat supply is required for CO_2 gasification than steam gasification for the same syngas yield even if the heat of vaporization is excluded when H_2O is introduced in the liquid state. CO_2 is also important for H_2/CO adjustment. The top syngas yield with the H_2/CO ratio of 0.5 can only be obtained in the presence of CO_2 , which is important for FTS operation working in the presence of iron catalyst. Another advantage of CO_2 utilization is to decrease the gasification temperature in the near autothermal mode. The gasifier temperature can be lowered in the presence of CO_2 without a significant loss in syngas yield and a significant change in the heat requirement. This can be important for durability of the reactor since high temperature exposure for long time can damage the reactor and decrease the useful life-time.

4. Conclusions

We have studied thermodynamic modelling of the biomass gasification in the presence of different gasifying agents such as air, steam and CO_2 by using Gibbs free energy minimization approach via MATLAB. We have investigated the synergetic effect of gasifying agents for syngas, H_2 and CH_4 production and we have evaluated the technical and environmental performances of the gasification by using product yields, cold gas efficiency, exergy efficiency and CO_2 emission. Optimum process conditions were first determined for air, steam and CO_2 gasification separately and then the multiparameter optimizations were carried out for

the gasification in the simultaneous presence of all gasifying agents to maximize syngas yield, H_2 yield, CH_4 yield and energy and exergy efficiencies. Main conclusions derived from the study are summarized below:

- The optimization gives the highest syngas yield ($2.27 \text{ m}^3/\text{kg}$ biomass) at $T > 1100 \text{ K}$ and low pressure (1 bar) and when $\text{SBR} > 0.5$ and/or $\text{CBR} > 0.8$ with the absence of air. At the related conditions, CGE changes between 114 and 122% while exergy efficiencies are between 77 and 86%. CO_2 emissions varies between 0.2 and 0.57.
- The optimization study made for the gasifier operating in near autothermal mode shows that the syngas yield changes between 1.60 and $1.65 \text{ m}^3/\text{kg}$ biomass and is obtained at moderate temperature (1000–1300 K) and when ER is around 0.2. This yield is approximately 30% lower than that obtained from the gasifier operated in allothermal mode.
- The top H_2 yield varies between $1.75\text{--}1.89 \text{ m}^3/\text{kg}$ biomass with H_2 concentration of 0.3–0.4 and they are observed at high SBR (>1.8), low CBR (<0.9) and between 900 and 1150 K in the absence of air. At these conditions, CGE, exergy efficiency and CO_2 emission are 108–111%, 77–80% and 0.25–0.53, respectively.
- The top H_2 concentration (0.50–0.53) can be obtained at temperatures of 1050–1500 K and low SBR (0–0.6) in the absence of air and CO_2 . However, H_2 yield decreases significantly ($0.68\text{--}1.34 \text{ m}^3/\text{kg}$ biomass) compared to that obtained at max H_2 yield conditions.
- The highest methane ($0.57 \text{ m}^3/\text{kg}$ biomass) is observed at low temperature (500 K) and high pressure (>4 bar) when SBR is on average 1.2. At these conditions, CGE, exergy efficiency and CO_2 emission are 89%, 81–83%, 67–287, respectively. At these conditions, the maximum methane concentration that can be attained is 29%. This number can be increased to 37% by increasing the temperature till to 800 K and decreasing SBR value below 0.6.
- The maximum CGE (122%) and exergy (86%) efficiencies are obtained at conditions where the syngas yield is maximized.
- There is no significant synergetic effect between the gasifying agents (e.g. air, steam and CO_2) for product yields, energy and exergy efficiencies.
- CO_2 offers several advantages as a gasifying agent: (i) CO_2 gasification requires less external heat compared to H_2O gasification even if the vaporization heat of water is excluded. (ii) CO_2 can be used to tune H_2/CO ratio towards lower ratios without sacrificing syngas

yield. (iii) The gasifier temperature can be lowered in the presence of CO₂ without having a significant lose in yield and increase in heat requirements.

CRedit authorship contribution statement

Basar Caglar: Conceptualization, Methodology, Writing - original draft, Supervision. **Duygu Tavsanci:** Software, Formal analysis, Visualization. **Emrah Biyik:** Methodology, Software, Validation, Writing - review & editing.

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

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors. We would like to sincerely thank the reviewers and editor for their valuable and constructive comments, which helped us in improving the quality of the paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2021.121208>.

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