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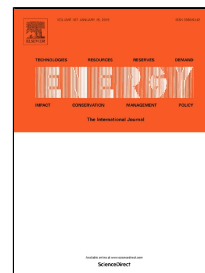
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Simulation and evaluation of utilization pathways of biomasses based on thermodynamic data prediction

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Abstract

It is important to evaluate the utilization pathways of biomasses as there are different multiple choices for various types of biomasses. A method using the functional exergy efficiency as a unified protocol is proposed to evaluate the effectiveness of energy utilization in three utilization pathways of biomasses: pyrolysis, oxygen gasification and anaerobic digestion. The results show that straws are more suitable than manures used in the pyrolysis process. Functional exergy efficiencies of the oxygen gasification process of six biomasses are all higher than those of the pyrolysis process. The functional exergy efficiencies of the manures have increased, becoming close to those of straws. For the anaerobic digestion process, the functional exergy efficiencies of straws are generally lower than that of manures. Manures with low lignin content (chicken manure in this study) are more suitable as the feedstock of anaerobic digestion process. The functional exergy efficiencies of anaerobic digestion are lower than those of the pyrolysis and gasification processes while the temperature exceeds 850 °C.

Keywords: Biomass utilization, Gibbs energy minimization, PBMP model, Process evaluation, Functional exergy efficiency

1. Introduction

Alterations to the climate due to temperature rise caused by the greenhouse effect pose a risk to humanity, and other species. Greenhouse gas emissions from anthropogenic activities such as the

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burning of fossil fuels for power generation are major contributors to the climate change. This necessitates a switch from conventional to renewable power sources, e.g. solar photovoltaic, wind, biomass and hydroelectric generation [1], among which biomass is one of the most important energy sources in near future [2]. Biomass energy is a CO₂-zero energy that does not interfere with the global carbon itself [3]. If the biomass is not used effectively, however, it will cause serious environmental pollution [4]. Therefore, the utilization of biomass has triple advantage of energy conservation, emission reduction and resource utilization.

Biomass resources include wood and wood wastes, agricultural crops and their waste byproducts, municipal solid waste, animal wastes, waste from food processing and aquatic plants and algae [5]. From the proximate analysis or ultimate analysis of biomass, the composition of biomasses varies depending on the types of biomasses considered and even for the same types of biomasses they may vary at different regions and seasons. The chemical conversion technologies for utilizing biomass can be divided into three basic categories: direct combustion processes, thermochemical processes (pyrolysis process, gasification process and direct liquefaction), biochemical processes (anaerobic digestion and alcoholic fermentation). Different utilization pathways and various types of biomasses lead to issues such as the lack of unified protocol to evaluate the biomass utilization. For example, is one type of corn stovers suitable for pyrolysis utilization, or gasification utilization, or anaerobic digestion utilization? In this study, we focus on how to evaluate the utilization pathways of biomasses with respect to energy utilization. The method is, thus, to simulate different utilization pathways and then to evaluate the effective utilization of energy based on the simulation results.

The thermochemical conversion process can be simulated by kinetic mathematical models [6], artificial neural networks models [7], and equilibrium models [8]. The Gibbs energy minimization method is one of the equilibrium models, and it does not involve specific chemical reaction equations and has a high degree of thermodynamic consistency [9]. High accuracy of thermodynamic data is a prerequisite of process simulation results obtained from the Gibbs energy minimization method. The biochemical conversion processes are simulated by rate-limitation step models [10], anaerobic digestion No.1 [11], artificial neural networks models [12], and practical biochemical methane potential (PBMP) model [13] in the literature. In this study, the PBMP model is selected for the process of methane production evaluation to assess the performance of an anaerobic digester.

In the field of power plants, exergy efficiency is used to evaluate the effective utilization of energy and can be divided into two different approaches (a brute-force or functional exergy efficiency). A brute-force exergy efficiency for any system is defined as the ratio of the sum of all output exergy terms to the sum of all input exergy terms. Compared with the brute-force exergy efficiency, a functional exergy efficiency for any system is defined as the ratio of the exergy associated with the desired energy output to the exergy associated with the energy expended to achieve the desired output [14]. For thermochemical processes, the main criteria of the effective utilization of energy are the loss of exergy (Ex_{loss}) and brute-force exergy efficiency [15, 16]. However, for the biochemical utilization of biomasses in order to obtain biogas, any exergy analysis is basically not considered because of the difficulty to determine the exergy of fermentation broth, biogas slurry and biogas residue. Therefore, output to input ratio of energy efficiency is selected as an effective indicator of energy utilization [17]. Since the energy efficiency is based on the first law of thermodynamics, so it cannot truly reflect the utilization of energy. As we all know, the main tasks of thermochemical conversion and anaerobic digestion of biomass are to produce syngas and biogas, respectively. Therefore, the functional exergy efficiency (desired outputs are syngas and biogas, respectively) instead of the brute-force exergy efficiency is extended to evaluate the utilization pathways of biomasses in this study.

The main objective of this study is to compare different utilization pathways of various biomasses. It is necessary to predict thermodynamic data of biomasses as their types and compositions vary. Based on thermodynamic data prediction, the pyrolysis and oxygen gasification processes of biomasses are simulated by the Gibbs energy minimization method. Biogas data of anaerobic digestion process are obtained through the PBMP model. The functional exergy efficiencies of utilization pathways of biomasses are evaluated based on the process simulation results. The innovative aspects of this study are related to the following two points: (1) The functional exergy efficiency concept was extended to evaluate utilization pathways of biomasses; (2) Process simulation and energy evaluation are based on the thermodynamic data predicted by the high accurate models of higher heat value (*HHV*) [18] and chemical exergy [19] of dry biomass. In summary, only with the help of the composition of biomasses, utilization pathways of biomasses can be simulated and evaluated based on thermodynamic data prediction.

2. Material and methods

2.1. System boundary and definition of the functional exergy efficiency

It is necessary to define the system boundary before evaluating the energy performance. When the system boundary is defined, the exergy or energy balance equation can be formulated. There are several different system boundaries that may be used in estimating the energy performance of a biogas plant [17]. In this study, system boundaries of pyrolysis, oxygen gasification and anaerobic digestion processes of biomasses are shown in Figs. 1-3, respectively, and then their functional exergy efficiencies were defined accordingly.

2.1.1. Pyrolysis process

The pyrolysis process of biomass is shown in Fig. 1 and the dashed box is the system boundary (System I). The exergy input of the system is the exergy of biomass $Ex_{wb,total}$, the exergy input of drying process ($Ex_{heat1,total}$) and pyrolysis reactor ($Ex_{heat2,total}$), and the exergy output of the system is exergy of the syngas ($Ex_{syngas,total}$). Based on the system boundary, the functional exergy efficiency of pyrolysis process is defined as follows:

$$\eta_l = \frac{Ex_{syngas,total}}{Ex_{wb,total} + Ex_{heat1,total} + Ex_{heat2,total}} \quad (1)$$

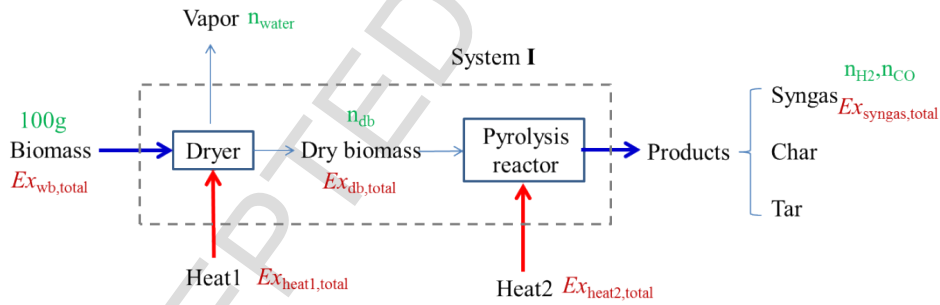


Fig. 1. Schematic diagram of the pyrolysis process of biomass

2.1.2. Oxygen gasification process

The oxygen gasification process of biomass is shown in Fig. 2 and the dashed box is the system boundary (System II). The slight different between pyrolysis and oxygen gasification is oxygen added into gasification reactor. The exergy input of the system is the exergy of biomass $Ex_{wb,total}$, the exergy of oxygen ($Ex_{O_2,total}$), the exergy input of drying process ($Ex_{heat3,total}$) and gasification reactor

($Ex_{heat4,total}$), and the exergy output of the system is the exergy of the syngas ($Ex_{syngas,total}$). Based on the system boundary, the functional exergy efficiency of oxygen gasification process is defined as follows:

$$\eta_{II} = \frac{Ex_{syngas,total}}{Ex_{wb,total} + Ex_{O_2,total} + Ex_{heat3,total} + Ex_{heat4,total}} \quad (2)$$

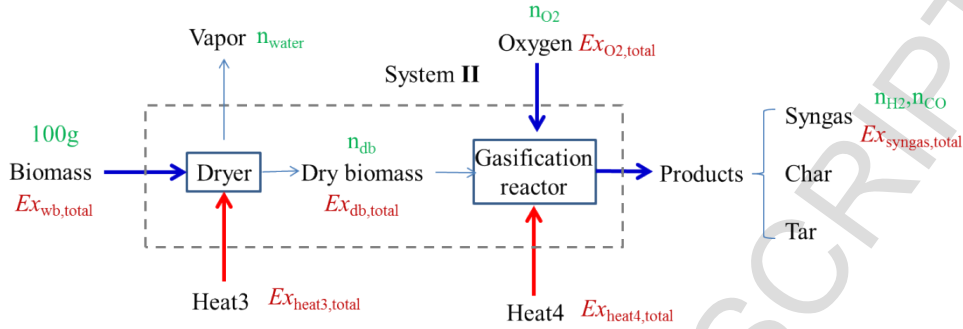


Fig. 2. Schematic diagram of the oxygen gasification process of biomass

2.1.3. Anaerobic digestion process

The anaerobic digestion process of biomass is shown in Fig. 3 and the dashed box is the system boundary (System III). The exergy input of the system is the exergy of biomass $Ex_{wb,total}$, the exergy input of anaerobic digestion reactor ($Ex_{heat5,total}$), and the exergy output of the system is the exergy of the biogas ($Ex_{biogas,total}$). Based on the system boundary, the functional exergy efficiency of anaerobic digestion process is defined as follows:

$$\eta_{III} = \frac{Ex_{biogas,total}}{Ex_{wb,total} + Ex_{heat5,total}} \quad (3)$$

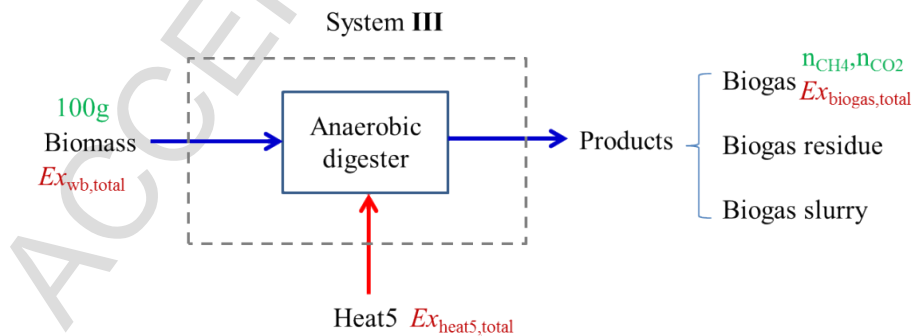


Fig. 3. Schematic diagram of the anaerobic digestion process of biomass

2.2. Assumptions in process simulation and evaluation

The following assumptions have been made for facilitating the process simulation and evaluation

calculations:

- (1) The mass of biomass is taken as 100 g in all utilization pathways of biomasses.
- (2) Simulation results of thermochemical and biochemical processes are given based on 100 g dry biomasses to eliminate the effect of moisture.
- (3) For the simulation of thermochemical conversion processes with the Gibbs energy minimization method, char is represented by carbon and ash.
- (4) Biogas is assumed to the mixture of CH₄ and CO₂ as other gases such as H₂S are very little, usually less than 1%.
- (5) The energy consumptions of the processes such as drying are all expressed as exergy by converting energy into exergy via Carnot efficiency.
- (6) The temperature for drying process in thermochemical conversion processes is assumed as 100 °C.
- (7) Specific heat capacity of fermentation broth in anaerobic process is assumed to that of water for the total solid of fermentation broth is 5%.
- (8) All gaseous components are ideal gas.

2.3. Process simulation

2.3.1. Simulation of thermochemical conversion processes

The thermochemical conversion processes are simulated by the Gibbs energy minimization method [20, 21] as follows:

$$\Delta_f H_{m,i}^o + \int_{298.15}^T c_{p,i} dT + T \left(S_{m,i}^o + \int_{298.15}^T \frac{c_{p,i}}{T} dT \right) + RT \ln \left(\frac{n_i}{n_{total}} \right) + \sum_k \lambda_k a_{ik} = 0 \quad (i=1,2,3,\dots,w) \quad (4)$$

where $\Delta_f H_{m,i}^o$, $S_{m,i}^o$, $c_{p,i}$, and R are the standard molar enthalpy of formation, the standard molar entropy, heat capacity, and the universal gas constant, respectively. n_{total} is the total number of moles of all species i . w represents the equilibrium equation refers to each species. As a result of the calculation from Eq. (4), the equilibrium composition n_{H_2} and n_{CO} produced from the pyrolysis and oxygen gasification processes are obtained at the given temperature.

According to Eq. (4), the values of standard molar enthalpy of formation ($\Delta_f H_m^o$), standard molar entropy (S_m^o) and heat capacity (c_p) are necessary for the calculation of the Gibbs energy minimization method. The following equations are used for dry biomass:

$$\Delta_f H_{m, CxHyOzNzSb}^{\circ} = -32.762C - 141.781H - 9.258S + 87.4\left(\frac{1}{3}C + H\right) \text{ kJ} \cdot \text{mol}^{-1} \quad (5)$$

$$\begin{aligned} S_m^{\circ} &= M \times (0.0055C + 0.0954H + 0.0096O + 0.0098N + 0.0138S) \\ &= 0.1 \times (0.0055C + 0.0954H + 0.0096O + 0.0098N + 0.0138S) \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned} \quad (6)$$

$$\begin{aligned} C_p &= 0.001M c_p = 0.1(-212.928 + 4.8567T) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ &= 10^{-4}(-212.928 + 4.8567T) \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned} \quad (7)$$

The simulation of the thermochemical conversion processes is described in detail in section 1.1 in the Appendix.

2.3.2 Simulation of anaerobic digestion process

In this study, the PBMP model is used to simulate the anaerobic digestion process, using the following equation:

$$\begin{aligned} \text{PBMP} \left(\frac{\text{mL CH}_4}{\text{g biomass}} \right) &= (80.4 - 2.70\text{Lignin})\% \times \frac{22400 \times TS\% \left(\frac{C}{24} + \frac{H}{8} - \frac{O}{64} - \frac{3N}{112} \right)}{100} \\ &= (80.4 - 2.70\text{Lignin})\% \times 224TS\% \times \left(\frac{C}{24} + \frac{H}{8} - \frac{O}{64} - \frac{3N}{112} \right) \text{ mL} \cdot \text{g}^{-1} \end{aligned} \quad (8)$$

where Lignin means the lignin content of biomass, *TS* means the total solid of biomass. With the help of Eq.(8), the volume and amount of CH₄ can be calculated by Eqs.(9) and (10).

$$\begin{aligned} V_{\text{CH}_4} &= 100 \times \text{PBMP} \left(\frac{\text{mL CH}_4}{\text{g wb}} \right) \\ &= (80.4 - 2.70\text{Lignin})\% \times 22400TS\% \times \left(\frac{C}{24} + \frac{H}{8} - \frac{O}{64} - \frac{3N}{112} \right) \text{ mL} \end{aligned} \quad (9)$$

$$\begin{aligned} n_{\text{CH}_4} &= V_{\text{CH}_4} / 22.4 \times 10^3 \\ &= (80.4 - 2.70\text{Lignin})\% \times TS\% \times \left(\frac{C}{24} + \frac{H}{8} - \frac{O}{64} - \frac{3N}{112} \right) \text{ mol} \end{aligned} \quad (10)$$

The simulation of the anaerobic digestion process is described in detail in section 1.2 in the Appendix.

2.4. Process evaluation

In this study, the process evaluation of three utilization pathways of biomasses is performed with the use of the functional exergy efficiency. Therefore, it is necessary to calculate the exergy of related substances and processes, and the corresponding equations are provided in Table 1. The derivation of these equations and further details are provided in section 2 of the Appendix.

Table 1 Exergy calculated in the utilization pathways of biomasses – the important equations.

	Pyrolysis	Oxygen gasification	Anaerobic digestion	
Biomass (wb)	$Ex_{wb} = 92.072 \left(\frac{1}{3}C + H \right) \text{ kJ} \cdot \text{mol}^{-1} [19]$ $Ex_{wb, \text{total}} = n_{db} Ex_{db} + n_{\text{water}} Ex_{\text{H}_2\text{O}} = (TS/100) Ex_{db} + ((100-TS)/18) Ex_{\text{H}_2\text{O}}$ $= 92.072 \left(\frac{1}{3}C + H \right) \times TS\% + 5.278 \times (1-TS\%)$			
Dryer	$Ex_{\text{heat1, total}} = n_{\text{water}} Ex_{\text{heat1}}$ $= 5.556(1-TS\%) \left(1 - \frac{T_0}{T_{\text{Dry}}} \right) \times$ $\left(\int_{T_0}^{373.15} 0.001 C_{p, \text{H}_2\text{O}} dT + 40.668 \right)$ $Ex_{\text{heat3, total}} = Ex_{\text{heat1, total}}$			
Reactor	$Ex_{\text{heat2, total}}$ $= TS\% \times \left(1 - \frac{T_0}{T_I} \right) \times$ $\int_{T_0}^{T_I} 0.001 C_{p, \text{db}} dT$	$Ex_{\text{heat4, total}} = Ex_{\text{heat4, O}_2, \text{ total}} + Ex_{\text{heat4, db, total}}$ $= TS\% \times \left(1 - \frac{T_0}{T_{II}} \right) \int_{T_0}^{T_{II}} 0.001 C_{p, \text{db}} dT$ $+ TS\% \times \left(1 - \frac{T_0}{T_{II}} \right) \int_{T_0}^{T_{II}} 0.001 C_{p, \text{db}} dT$	$Ex_{\text{heat5, total}} = m_{\text{broth}} e_{\text{heat5}}$ $= 0.02TS \times \left(1 - \frac{T_0}{T_{III}} \right) \times 4.2 \times (T_{III} - T_0)$	
Gas product	$Ex_{\text{syngas, total}} = Ex_{\text{total}}^{ph} + Ex_{\text{total}}^{ch} = \left(n_{\text{H}_2} Ex_{\text{H}_2}^{ph} + n_{\text{CO}} Ex_{\text{CO}}^{ph} \right)$ $+ \left(n_{\text{H}_2} \left(e_{\text{H}_2}^{ch} + RT_0 \ln x_{\text{H}_2} \right) + n_{\text{CO}} \left(e_{\text{CO}}^{ch} + RT_0 \ln x_{\text{CO}} \right) \right)$			$Ex_{\text{biogas, total}} = n_{\text{total}} Ex^{ch} = n_{\text{CH}_4} e_{\text{CH}_4}^{ch}$

where n_{db} and Ex_{db} represent number of moles and exergy of dry biomass, respectively. m_{broth} is the mass of fermentation broth in the anaerobic digestion process of biomass.

2.5. Biomass scenarios

Low-valued biomass such as straws and manures are very rich worldwide. If these biomasses are not handled properly, they will cause serious environmental pollution problems [4]. Therefore, we selected three kinds of common straws and three kinds of manures [22] in this study to compare different utilization processes of biomass. The physical and ultimate analysis of biomasses is listed in Table 2. It can be seen that the values of TS% of manures are lower than that of straws, which means that the moisture content of manures is greater than that of straws. It also should be mentioned that the lignin content of dairy manure is the highest.

Table 2 Physical and ultimate analysis of biomasses

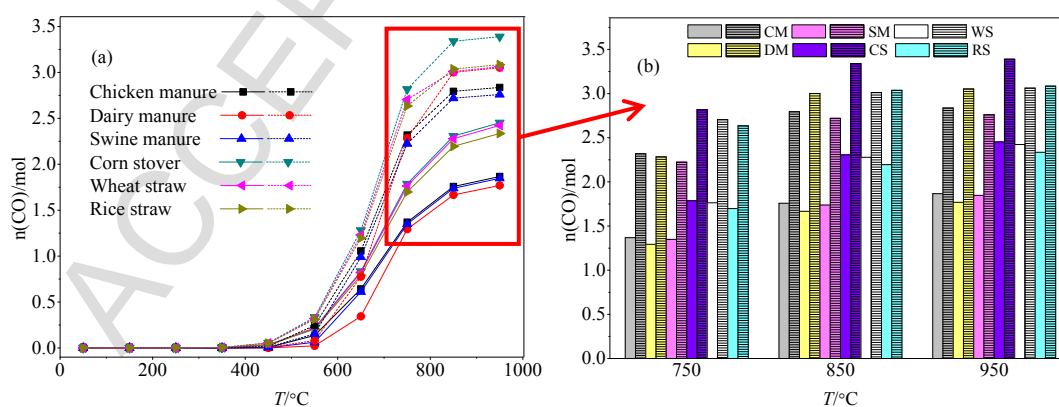
Biomass	Abbreviation	TS%	VS%	VS/TS%	Lignin	Ash	C	H	O	N
Chicken manure	CM	25.9	19.5	75.3	1.6	24.7	35.9	5.1	30.5	3.4
Dairy manure	DM	38.5	28.8	74.8	17.4	25.2	37.6	5.1	28.9	2.8
Swine manure	SM	30.4	22.0	72.4	4.3	27.6	34.8	4.7	30.3	2.2
Corn stover	CS	84.9	76.9	90.6	10.3	9.4	43.2	5.9	40.2	0.8
Wheat straw	WS	90.5	77.9	86.1	7.6	13.9	39.9	5.7	39.6	0.4
Rice straw	RS	92.9	81.6	84.6	10.8	15.4	39.7	5.4	38.2	0.9

3. Results and Discussion

3.1. Process simulation results

3.1.1. Simulation results of thermochemical conversion processes

Although the moisture contents of six biomasses are different, the biomasses were dried before pyrolysis or oxygen gasification reactor. Therefore, the pyrolysis and oxygen gasification processes of same amount (100 g in this study) of six dry biomasses were calculated via the Gibbs energy minimization method to compare the simulation results, as shown in Fig. 4. The simulation results of pyrolysis and oxygen gasification processes (equivalence ratio (ER) is set as 0.2 in this study, as defined in Eq. (A12) in the Appendix) are respectively represented by the solid line and dash one in Fig. 4 (a) and Fig. 4 (c). The amount of CO produced from the pyrolysis (without grid) and oxygen gasification (with grid) processes at 750, 850 and 950 °C in Fig. 4(a) is shown in detail in Fig. 4(b).



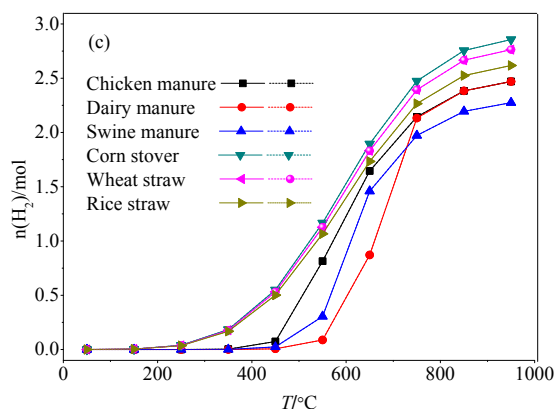


Fig. 4. Simulation results of the pyrolysis (solid line) and oxygen gasification processes (dash line) of six dry biomasses

It can be seen that the amounts of CO and H₂ increase with the temperature increasing in both pyrolysis and oxygen gasification processes in Fig. 4(a) and 4(c). As shown in Fig.4 (a), for the pyrolysis process, the amounts of CO produced from straws are higher than those from manures. For the same types of biomasses, the amounts of CO are almost same. As shown in Fig.4 (a) and Fig.4 (b), for the oxygen gasification process, the amounts of CO produced from six dry biomasses increase dramatically, especially corn stover, which means that the addition of oxygen agent has a significant effect on the amounts of CO in the products. The amount of CO of corn stover is the highest in the oxygen gasification process due to its highest carbon content in all biomasses. As shown in Fig.4 (c), for the pyrolysis process, the amounts of H₂ produced from straws are higher than those from manures, which is same to the trend of the amounts of CO. Compared with the pyrolysis process, the amounts of H₂ obtained from the oxygen gasification process are not changed, which is different to the trend of the amounts of CO. All above simulation results reveal that the high carbon element content of biomass is a necessary condition for its oxygen gasification.

As shown in Fig. 4(c), it should be noted that the amount of H₂ produced from both pyrolysis and oxygen gasification processes of dairy manure increases dramatically in the range of 650 to 850 °C, which leads to the reversion between the amount of H₂ produced from dairy manure and that from swine manure while the temperature exceeds 750 °C. The phenomenon might be caused by that the lignin content of dairy manure is higher than that of swine manure. This is in accordance with the conclusion that compared with cellulose and hemicellulose, the cracking and deformation of lignin released out much more H₂ at a higher temperature [23].

To study the effect of carbon content in biomass on the amount of syngas, the simulation results of the amounts of syngas produced by pyrolysis process of six dry biomasses at the temperature of 850 °C and their carbon contents are drawn in Fig. 5. It can be seen that the carbon content has a nearly positive effect on the amount of syngas, which means the high carbon content of biomass is also beneficial to its pyrolysis process.

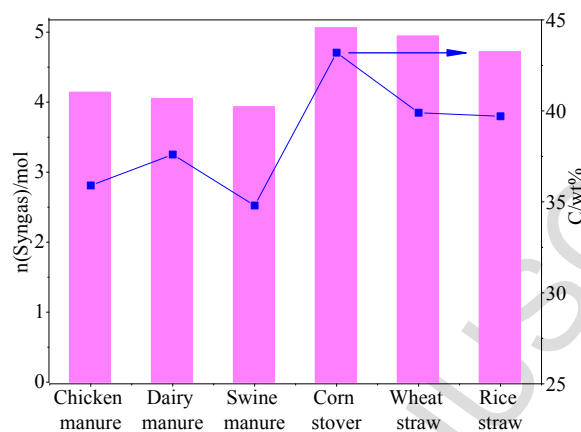


Fig. 5. Relationship between the carbon content in six dry biomasses and the amount of syngas produced by the pyrolysis process at 850 °C

3.1.2. Simulation results of biochemical conversion process

Although the moisture content and TS of six biomasses are different, TS of all biomasses in Table 2 is higher than that of fermentation broth (level of 5% TS is selected in this study), which means that the TS% of six biomasses in fermentation broth is same. Therefore, the simulation results of anaerobic digestion process of 100 g six dry biomasses are set and shown in Fig. 6.

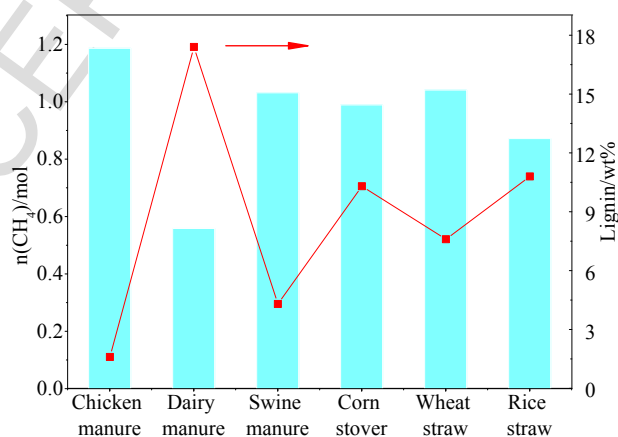


Fig. 6. Simulation results of the anaerobic digestion process of six dry biomasses

The amounts of CH₄ produced from anaerobic digestion of 100 g straws change little while those from manures vary significantly instead. The amounts of CH₄ obtained from chicken manure and dairy manure are the highest and lowest, respectively. The amount of CH₄ produced from anaerobic digestion of 100 g swine manure is similar to that from three straws. According to Eq. (10), the amount of CH₄ is related to the lignin and element content. In order to study the effect of lignin content on the amount of CH₄, the lignin contents (wt%) of biomasses are also shown by points connected by a line in Fig. 6. Although the lignin content of swine manure is lower than that of wheat straw, the amount of CH₄ obtained from swine manure is also lower. It can be seen that there is a nearly negative relationship between the amounts of CH₄ and their lignin contents. All above indicates that the lignin content is the main factor that affects the amounts of CH₄ produced compared with element contents.

3.2. Process evaluation result

3.2.1. Pyrolysis process

According to the relevant calculation formulas of exergy in the section 2.4, the values of exergy of biomass $Ex_{wb,total}$, the exergy input in the drying process $Ex_{heat1,total}$, the exergy input in the pyrolysis reactor $Ex_{heat2,total}$ and the exergy of syngas product $Ex_{syngas,total}$ in pyrolysis process of six biomasses (100 g) are shown in Fig. 7 (a).

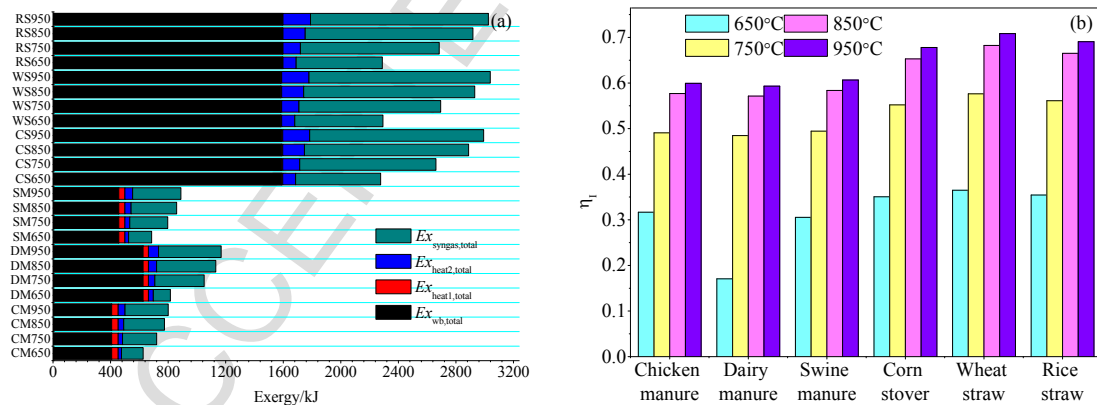


Fig. 7. Exergy (a) in and functional exergy efficiencies (b) of the pyrolysis process of six biomasses at different temperatures

In Fig. 7(a), the numbers following the abbreviated letters indicate the pyrolysis temperature. For example, CM650 means that the pyrolysis process of chicken manure is at 650 °C. As can be seen from Fig. 7(a), for the exergy of biomass $Ex_{wb,total}$ (black bar), the exergies of straws are nearly same, this is

mainly due to their moisture contents are close to each other. In contrast, the exergies of manures are different, in which the exergy of dairy manure is the largest for its lowest moisture content (highest total solid) in manures. The exergies required for manures are larger than those for straws in the drying process ($Ex_{\text{heat1,total}}$, red bar) due to their moisture contents. The values of the exergies of drying process of straws can be negligible due to their low moisture contents, therefore they (red bar) cannot be found in Fig.7(a). For the same types of biomasses, although the higher the pyrolysis temperature, the more exergy the gas products ($Ex_{\text{syngas,total}}$, dark cyan bar) will be due to the increase of the amount of syngas, the exergy input in the pyrolysis reactor ($Ex_{\text{heat2,total}}$, blue bar) also increases as the pyrolysis temperature increases.

The functional exergy efficiencies of pyrolysis process of six biomasses at different temperatures are shown in Fig. 7(b). For the same types of biomasses, the functional exergy efficiencies increase as the pyrolysis temperature increases. Compared with chicken manure and swine manure, the functional exergy efficiency of dairy manure is the lowest at 650 °C and becomes nearly the same to that of chicken manure and swine manure at 750, 850 and 950 °C. This is due to the high lignin content of dairy manure. The cracking and deformation of lignin releases out much more H₂ at a higher temperature [23], which leads to higher exergy of syngas produced. It should be mentioned that from 650 to 950 °C of pyrolysis temperature, the functional exergy efficiencies increase slower and slower. In general, the functional exergy efficiencies of straws are higher than those of manures at different pyrolysis temperatures. At 950 °C, the functional exergy efficiencies of manures and straws can reach about 0.6 and 0.7, respectively.

The relationship between the functional exergy efficiencies of pyrolysis process of six biomasses at different temperatures and their amounts of syngas produced is shown in Fig. 8. It can be seen that their trends are different. The largest value of functional exergy efficiencies belongs to wheat straw, while the largest amount of syngas is produced by corn stover instead. The functional exergy efficiency of dairy manure is the lowest and the amount of syngas produced by swine manure is the lowest instead. The different trends between functional exergy efficiencies and their amounts of syngas produced are due to both pyrolysis reaction and the drying process. The latter is very important as different exergies are caused by the varied moisture contents of manures and straws. Moreover, for the same amounts of biomasses, the largest amount of syngas produced does not mean the optimum process for the input of

energy and the type of biomasses is different. Therefore, a wrong result will appear if the amount of syngas produced is set as the unified protocol.

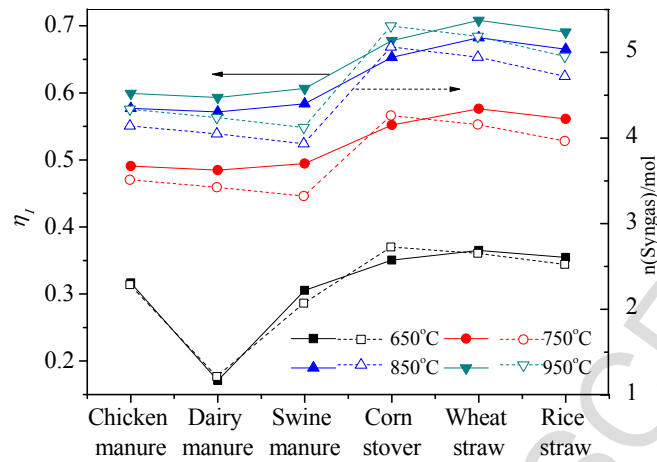


Fig. 8. Relationship between the functional exergy efficiencies (solid line) of pyrolysis process of six biomasses at different temperatures and their amounts of syngas produced (dash line)

3.2.2. Oxygen gasification process

According to the relevant calculation formulas of exergy in the section 2.4, the values of exergy of biomass $Ex_{wb,total}$, the exergy input in the drying process $Ex_{heat3,total}$, the exergy input in the gasification reactor $Ex_{heat4,total}$ and the exergy of syngas product $Ex_{syngas,total}$ in oxygen gasification process of six biomasses (100 g) are shown in Fig. 9.

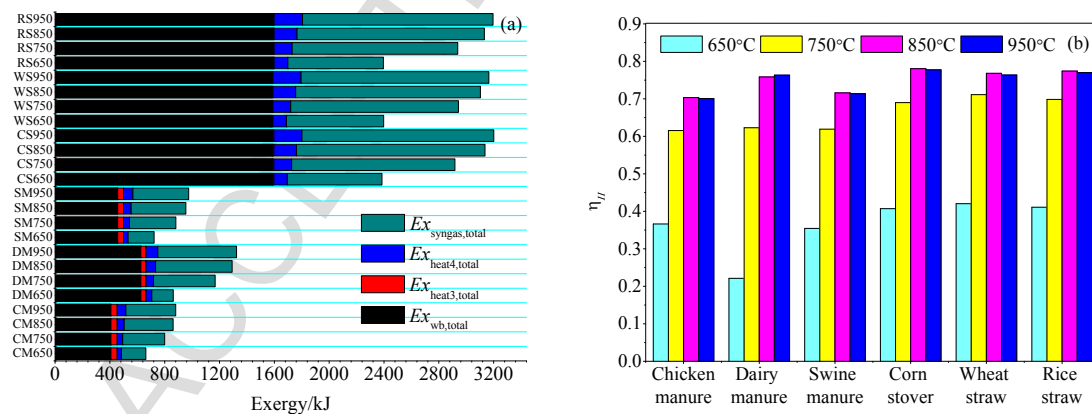


Fig. 9. Exergy (a) in and functional exergy efficiencies (b) of the oxygen gasification process of six biomasses at different temperatures

The numbers following the abbreviated letters indicate the oxygen gasification temperature. Same to

the pyrolysis process, due to the different moisture contents, the exergies required for manures are larger than those for straws in the drying process ($Ex_{\text{heat3,total}}$, red bar). The values of the exergies of drying process of straws can be negligible due to their low moisture contents. Therefore, they (red bar) cannot be found in Fig. 9(a). Similar to the pyrolysis process, for the same types of biomasses, the higher the gasification temperature, the more exergy the gas product ($Ex_{\text{syngas,total}}$, dark cyan bar) and the exergy input in the gasification reactor ($Ex_{\text{heat4,total}}$, blue bar) will be. The difference is that the exergy of the syngas produced from pyrolysis process is more than that from oxygen gasification process. This is mainly due to the increase of the amount of CO in syngas caused by oxygen agent addition.

The functional exergy efficiencies of oxygen gasification of the six biomasses at different temperatures are shown in Fig. 9(b). Similar to the pyrolysis process, the higher the gasification temperature, the larger the functional exergy efficiencies for the oxygen gasification process of the same types of biomasses. However, the picture changes little after 850 °C, and the functional exergy efficiencies slightly decrease at 950 °C, which is different to the pyrolysis process. This is mainly due to the increase of the exergy required for heating the oxygen added. This illustrates that 850 °C is suitable temperature for the oxygen gasification process of six biomasses. Above 850 °C, compared with the pyrolysis process, the functional exergy efficiencies of the manures have increased, becoming close to those of straws. In the high temperature region (>850 °C), the functional exergy efficiencies of six biomasses are all more than 0.7 and the maximum values is 0.77 (corn stover).

Unlike what was the case with the pyrolysis process, for manures, the functional exergy efficiencies of dairy manure at 850 and 950 °C are the lowest in the pyrolysis process but the highest in the oxygen gasification process, as shown in Fig. 9(b) and 10. This is due to the relative high carbon content in dairy manure, which leads to the increase of CO generated. Compared with the pyrolysis process, the functional exergy efficiencies of the oxygen gasification process are much greater at each temperature, as shown in Fig. 10. This is due to the addition of oxygen at an ER of 0.2 in the oxygen gasification process, so that the amount of CO in the syngas continues to increase.

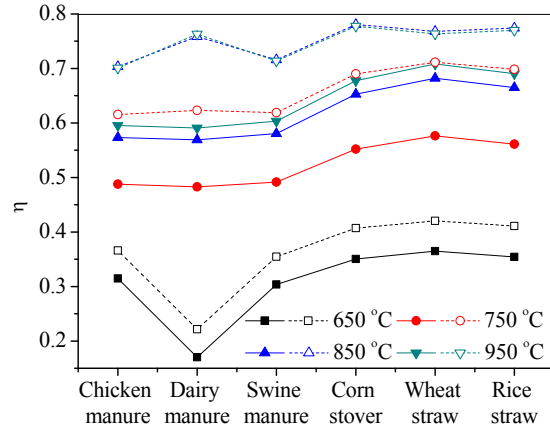


Fig. 10. Comparison of functional exergy efficiencies of pyrolysis process (solid line) and that of the oxygen gasification process (dash line) of six biomasses at different temperatures

3.2.3. Anaerobic digestion process

According to the relevant calculation formulas of exergy in the section 2.4, the values of exergy of biomass $Ex_{wb,total}$, the exergy input in the anaerobic digestion reactor $Ex_{heat5,total}$ and the exergy of biogas product $Ex_{biogas,total}$ in anaerobic digestion process of six biomasses (100 g) are shown in Fig. 11

(a). The exergy input to the anaerobic digestion reactor ($Ex_{heat5,total}$, red bar) is almost negligible due to the temperature difference of 12 °C between anaerobic digestion temperature and ambient one. Although the exergy of chicken manure and swine manure are less than dairy manure, more biogas is generated than dairy manure. This phenomenon is mainly due to the high lignin content in dairy manure, resulting in a decrease in the degradation rate of dairy manure and hence the exergy of gas product is low. The exergy of the biogas of anaerobic digestion of wheat straw is more than that of corn stover and rice straw is also due to its low lignin content.

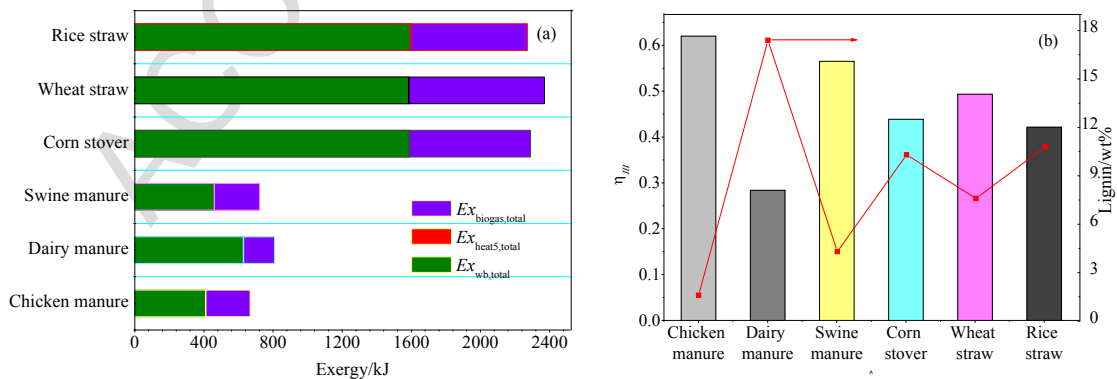


Fig. 11. Exergy (a) in and functional exergy efficiencies (b) of the anaerobic digestion process of six

biomasses

The low exergy for biogas obtained from dairy manure can also be seen from the comparison of the functional exergy efficiencies of anaerobic digestion process of six biomasses shown in Fig. 11(b). The functional exergy efficiencies of the anaerobic digestion process of manures except dairy manure are higher than those of straws. The highest and lowest functional exergy efficiency is the anaerobic digestion process of chicken manure (0.6) and dairy manure (0.29). Among the three straws, the functional exergy efficiencies of anaerobic digestion process of rice straw and corn stover is close to each other, the functional exergy efficiency of wheat straw shows the higher value. Therefore, the chicken manure is more suitable to be used as the feedstock of anaerobic digestion due to the highest functional exergy efficiency. Manures except dairy manure are better than straws while used as feedstock of anaerobic digestion. The relationship between lignin content and functional exergy efficiency is also studied and shown in Fig. 11(b). It can be seen that there are also a nearly negative relationship between the values of functional exergy efficiencies and their lignin contents. The reason is that the exergy input of anaerobic digestion reactor is the only one needed and the value can be neglected. Therefore, the trend of functional exergy efficiencies is same to that of the amount of biogas produced by different biomasses.

Compared with the pyrolysis and oxygen gasification processes, the functional exergy efficiencies of anaerobic digestion are lower than those of the pyrolysis and gasification processes at the temperature above 850 °C for the organic matter entering the biogas residue, which is mainly due to the lignin content in biomass cannot be degradable in anaerobic digestion process but can be converted in thermochemical conversion processes at high temperatures. Therefore, an important route of improving the biogas production of the anaerobic digestion process is to reduce the lignin content such as via pretreatment of biomass [24].

4. Conclusions

With the help of the composition of biomasses, utilization pathways of biomasses are simulated and evaluated successfully based on predicted thermodynamic data. The conclusions are listed as follows:

(1) For the pyrolysis and oxygen gasification processes, the trend of the amount of syngas produced is different to the functional exergy efficiency, while the trend of the amount of biogas produced and

the functional exergy efficiency is the same for anaerobic digestion process.

(2) According to the functional exergy efficiencies, straws are more suitable than manures used in the pyrolysis process for their lower moisture content. The higher the temperature ($<950\text{ }^{\circ}\text{C}$), the greater the functional exergy efficiencies are.

(3) Functional exergy efficiencies of the oxygen gasification process of six biomasses are all higher than those of the pyrolysis process. A suitable temperature for the oxygen gasification process of six biomasses is $850\text{ }^{\circ}\text{C}$. The functional exergy efficiencies of dairy manure at 850 and $950\text{ }^{\circ}\text{C}$ show the lowest value in the pyrolysis process but the highest value in the oxygen gasification process. In the high temperature region ($>850\text{ }^{\circ}\text{C}$), compared with the pyrolysis process, the functional exergy efficiencies of the manures have increased, becoming close to those of straws. The functional exergy efficiencies of six biomasses are all more than 0.7 and the maximum values is 0.77 (corn stover).

(4) For the anaerobic digestion process, the functional exergy efficiencies of straws are generally lower than that of manures. Manures with low lignin content (chicken manure in this study) are more suitable as the feedstock of anaerobic digestion process. The functional exergy efficiencies of anaerobic digestion are lower than those of the pyrolysis and gasification processes at temperature above $850\text{ }^{\circ}\text{C}$.

The significant of this study is to propose a method to compare different utilization pathways of various biomasses based on the composition of biomasses directly.

Acknowledgements

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Appendix

1. Process simulation

1.1. Simulation of thermochemical conversion

1.1.1. Input of drying process

Based on the assumption that the mass of biomass was taken as 100 g in all utilization pathways of biomasses, the mass of dry biomass (db) and water were calculated by Eqs. (A.1) and (A.2), respectively.

$$m_{db} = m_{wb} \times TS\% = TS \text{ g} \quad (\text{A.1})$$

$$m_{water} = m_{wb} \times (1 - TS\%) = 100 - TS \text{ g} \quad (\text{A.2})$$

where m_{db} , m_{wb} and m_{water} are the mass of dry biomass, biomass and water, respectively. TS represents total solid in biomass.

Due to the fact that the calculation of heat capacity, standard molar enthalpy of formation and so on is based on mole, the mass of dry biomass and water was transferred to mole basis. It should be noted that the molecular weight of dry biomass was taken as $100 \text{ g} \cdot \text{mol}^{-1}$ and their chemical formula were determined accordingly in this study.

$$n_{db} = m_{db} / 100 = TS / 100 = TS\% \text{ mol} \quad (\text{A.3})$$

$$n_{water} = m_{water} / 18 = (100 - TS) / 18 = 5.556(1 - TS\%) \text{ mol} \quad (\text{A.4})$$

where n_{db} and n_{water} are the moles of dry biomass and water, respectively.

1.1.2 Gibbs energy minimization

The total Gibbs energy of the system is written as follows [20, 21]:

$$G_{T,p}^t = g(n_1, n_2, n_3, \dots, n_i, \dots, n_w) \quad (i=1,2,3,\dots,w) \quad (\text{A.5})$$

where $G_{T,p}^t$ is the total Gibbs energy of the system and n_i is referred to each species (mol). The problem is to find the set of n_i for which the total Gibbs energy of system is minimized. The material balance for each elements present in the system is given by

$$\sum_i n_i a_{ik} = A_k \quad (\text{A.6})$$

where a_{ik} is the number of atoms of the k th element present in each molecule of the chemical species i , A_k is the total number of atomic masses of the k th element in the system.

The Gibbs energy of the system is minimized with the Lagrange method by using the elemental mass balances as subsidiary constraints. Therefore, a new function is derived by adding Eqs. (A.5) and (A.6),

$$F = G_{T,p}^t + \sum_k \lambda_k \left(\sum_i n_i a_{ik} - A_k \right) \quad (\text{A.7})$$

where λ_k are the Lagrange multipliers. The minimum value of F is occurred when the partial derivative with respect to each species approaches to zero at specified temperature and pressure,

$$\frac{\partial F}{\partial n_i} = \frac{\partial G_{T,p}^t}{\partial n_i} + \sum_k \lambda_k a_{ik} = 0 \quad (\text{A.8})$$

where $\frac{\partial G_{T,p}^t}{\partial n_i}$ is known as chemical potential (μ_i), therefore, the following equation can be obtained.

$$\mu_i + \sum_k \lambda_k a_{ik} = 0 \quad (\text{A.9})$$

The chemical potential is defined as [20, 21],

$$\begin{aligned} \mu_i &= \Delta_f G_{m,i} + RT \ln \left(\frac{n_i}{n_{total}} \right) = \Delta_f H_{m,i} + TS_{m,i} + RT \ln \left(\frac{n_i}{n_{total}} \right) \\ &= \Delta_f H_{m,i}^o + \int_{298.15}^T c_{p,i} dT + T \left(S_{m,i}^o + \int_{298.15}^T \frac{c_{p,i}}{T} dT \right) + RT \ln \left(\frac{n_i}{n_{total}} \right) \end{aligned}$$

(A.10)

where $\Delta_f H_{m,i}^o$, $S_{m,i}^o$, $c_{p,i}$, R are the standard molar enthalpy of formation, the standard molar entropy, heat capacity, and the universal gas constant respectively. n_{total} means the total mole of all species i .

Putting Eq. (A.10) in Eq. (A.9) gives,

$$\Delta_f H_{m,i}^o + \int_{298.15}^T c_{p,i} dT + T \left(S_{m,i}^o + \int_{298.15}^T \frac{c_{p,i}}{T} dT \right) + RT \ln \left(\frac{n_i}{n_{total}} \right) + \sum_k \lambda_k a_{ik} = 0 \quad (i=1,2,3,\dots,w) \quad (4)$$

The above equation represents w equilibrium equations referring to each species present in the system. As a result of the calculation by Eq. (4), the equilibrium composition n_i (such as n_{H_2} and n_{CO} obtained from pyrolysis and oxygen gasification in this study) of the multi-phase system at given temperature is obtained.

The thermodynamic equilibrium of coal gasification was analyzed via the Gibbs energy minimization method and the detailed calculation steps were shown [21]. The Equilibrium amount of products of pyrolysis and oxygen gasification calculated by the Gibbs energy minimization method was

rewritten for biomass as follows:

The calculation is structured using the species in the product mixture taken from literature [25] and they are presented in Table A.1.

Table A.1 List of species considered in the calculation

Species										
C(g)	CH	CH ₂	CH ₃	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	H	H ₂
O	O ₂	CO	CO ₂	OH	H ₂ O	H ₂ O ₂	HCO	HO ₂	N	N ₂
NCO	NH	NH ₂	NH ₃	N ₂ O	NO	NO ₂	CN	HCN	HCNO	S(g)
S ₂ (g)	SO	SO ₂	SO ₃	COS	CS	CS ₂	HS	H ₂ S	C(s)	S(s)

Therefore the global reaction for both pyrolysis and oxygen gasification of dry biomasses (represented by $C_xH_yO_zN_aS_b$) can be written as,



where x, y, z, a, b are respectively the moles of carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulfur (S) in 100 g of dry biomass. $x=C/12, y=H, z=O/16, a=N/14$, and $b=S/32$ for unit conversion. C, H, N, S are determined by ultimate analysis (wt%, db), and the O content usually serves as an indicator to differentiate the sum of the percentages of C, H, N, S and that of the ash ($O = 100 - C - H - N - S - \text{Ash}$).

ER means equivalence ratio and is defined as follows.

$$ER = \frac{\text{Moles of actual oxygen assumption}}{\text{Stoichiometric ratio}} \quad (\text{A.12})$$

where the stoichiometric ratio is defined as the moles of oxygen needed to combust 1 mole of biomass, $x + \frac{y}{4} - \frac{z}{2} + b$ mol in this study. The values of ER for pyrolysis process and oxygen gasification process are 0 and 0~1, respectively.

All the species are combination of five basic elements i.e. carbon, hydrogen, oxygen, nitrogen and sulfur. Therefore, initially five constrain mass balances are written that represent each element conservation in the system, as given by Eq. (A.6).

Carbon balance:

$$n_C + n_{CH} + n_{CH_2} + n_{CH_3} + n_{CH_4} + 2n_{C_2H_2} + \dots + n_{CS_2} + n_{CS} = x \quad (\text{A.13})$$

Hydrogen balance:

$$n_{CH} + 2n_{CH_2} + 3n_{CH_3} + 4n_{CH_4} + 2n_{C_2H_2} + \dots + n_{HS} + 2n_{H_2S} = y \quad (\text{A.14})$$

Oxygen balance:

$$n_{\text{O}} + 2n_{\text{O}_2} + n_{\text{CO}} + 2n_{\text{CO}_2} + n_{\text{OH}} + \dots + 3n_{\text{SO}_3} + n_{\text{COS}} = z + 2ER\left(x + \frac{y}{4} - \frac{z}{2} + b\right) \quad (\text{A.15})$$

Nitrogen balance:

$$n_{\text{N}} + 2n_{\text{N}_2} + n_{\text{NCO}} + n_{\text{NH}} + n_{\text{NH}_2} + \dots + n_{\text{HCN}} + n_{\text{HCNO}} = a \quad (\text{A.16})$$

Sulfur balance:

$$n_{\text{S}} + 2n_{\text{S}_2} + n_{\text{SO}} + n_{\text{SO}_2} + n_{\text{SO}_3} + \dots + n_{\text{H}_2\text{S}} + n_{\text{S(s)}} = b \quad (\text{A.17})$$

Now using Eq. (4) a set of equations are written for each species present in the products. A formulation for few species are shown below,

For methane:

$$\Delta_{\text{f}}H_{\text{m,CH}_4}^{\circ} + \int_{298.15}^T c_{p,\text{CH}_4} dT + T \left(S_{\text{m,CH}_4}^{\circ} + \int_{298.15}^T \frac{c_{p,\text{CH}_4}}{T} dT \right) + RT \ln \left(\frac{n_{\text{CH}_4}}{n_{\text{total}}} \right) + (\lambda_1 + 4\lambda_2) = 0 \quad (\text{A.18})$$

For hydrogen:

$$\Delta_{\text{f}}H_{\text{m,H}_2}^{\circ} + \int_{298.15}^T c_{p,\text{H}_2} dT + T \left(S_{\text{m,H}_2}^{\circ} + \int_{298.15}^T \frac{c_{p,\text{H}_2}}{T} dT \right) + RT \ln \left(\frac{n_{\text{H}_2}}{n_{\text{total}}} \right) + (2\lambda_2) = 0 \quad (\text{A.19})$$

For carbon monoxide:

$$\Delta_{\text{f}}H_{\text{m,CO}}^{\circ} + \int_{298.15}^T c_{p,\text{CO}} dT + T \left(S_{\text{m,CO}}^{\circ} + \int_{298.15}^T \frac{c_{p,\text{CO}}}{T} dT \right) + RT \ln \left(\frac{n_{\text{CO}}}{n_{\text{total}}} \right) + (\lambda_1 + \lambda_3) = 0 \quad (\text{A.20})$$

For solid C:

$$\Delta_{\text{f}}H_{\text{m,C}}^{\circ} + \int_{298.15}^T c_{p,\text{C}} dT + T \left(S_{\text{m,C}}^{\circ} + \int_{298.15}^T \frac{c_{p,\text{C}}}{T} dT \right) + RT \ln \left(\frac{n_{\text{C}}}{n_{\text{total}}} \right) + \lambda_1 = 0 \quad (\text{A.21})$$

n_{total} in Eqs. (A.18)-(A.21) means the total mole of all species and can be calculated by,

$$n_{\text{total}} = n_{\text{C}} + n_{\text{CH}} + n_{\text{CH}_2} + n_{\text{CH}_3} + n_{\text{CH}_4} + n_{\text{C}_2\text{H}_2} + \dots + n_{\text{S(s)}} + n_{\text{C(s)}} \quad (\text{A.22})$$

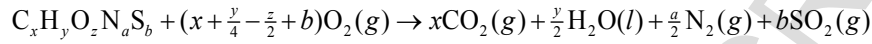
The model is comprised of 49 unknown that include 44 product species moles, 5 Lagrange multipliers (λ_1 , λ_2 , λ_3 , λ_4 and λ_5). Therefore, in order to calculate the unknowns, 49 equations are required. 5 equations come from the mass balance of elements from Eqs. (A.13)-(A.17), 44 equations are included using Eq. (4) and demonstration of these equations are presented in Eqs. (A.18)-(A.21).

1.1.3 Estimating thermodynamic data of dry biomass

According to Eq. (4), the values of standard molar enthalpy of formation ($\Delta_f H_m^o$), standard molar entropy (S_m^o) and heat capacity (c_p) of dry biomass are necessary to the calculation by the Gibbs energy minimization method.

① Estimating standard molar enthalpy of formation ($\Delta_f H_m^o$)

The combustion reaction between dry biomass and oxygen in oxygen bomb calorimeter is described by:



The value of energy change of combustion reaction in oxygen bomb calorimeter is higher heat value (HHV , $\text{kJ} \cdot \text{kg}^{-1}$, based on dry biomass), then,

$$\begin{aligned} -0.001M \times HHV = & x\Delta_f H_{m,CO_2}^o + \frac{y}{2}\Delta_f H_{m,H_2O(l)}^o + \frac{a}{2}\Delta_f H_{m,N_2}^o + b\Delta_f H_{m,SO_2}^o \\ & - \Delta_f H_{m,C_xH_yO_zN_aS_b}^o - (x + \frac{y}{4} - \frac{z}{2} + b)\Delta_f H_{m,O_2}^o \end{aligned} \quad (A.23)$$

where M is molecular weight of dry biomass, $100\text{g} \cdot \text{mol}^{-1}$. $\Delta_f H_{m,C_xH_yO_zN_aS_b}^o$, $\Delta_f H_{m,CO_2}^o$, $\Delta_f H_{m,H_2O(l)}^o$, $\Delta_f H_{m,N_2}^o$, $\Delta_f H_{m,SO_2}^o$ and $\Delta_f H_{m,O_2}^o$ are standard molar enthalpy of formation of dry biomass, carbon dioxide, liquid water, nitrogen, sulfur dioxide and oxygen, then,

$$\begin{aligned} \Delta_f H_{m,C_xH_yO_zN_aS_b}^o = & x\Delta_f H_{m,CO_2}^o + \frac{y}{2}\Delta_f H_{m,H_2O(l)}^o + \frac{a}{2}\Delta_f H_{m,N_2}^o + b\Delta_f H_{m,SO_2}^o \\ & - (x + \frac{y}{4} - \frac{z}{2} + b)\Delta_f H_{m,O_2}^o + 0.001M \times HHV \end{aligned} \quad (A.24)$$

Where $\Delta_f H_{m,CO_2}^o$, $\Delta_f H_{m,H_2O(l)}^o$, $\Delta_f H_{m,N_2}^o$, $\Delta_f H_{m,SO_2}^o$ and $\Delta_f H_{m,O_2}^o$ can be looked up from data handbook [26], and their values were listed in Table A.2. HHV can be given by experimental data or prediction model. For the types and composition of biomasses varied, HHV was estimated by the high accurate model proposed in our previous study [18] and the equation was listed as follows.

$$HHV = 874.08 \left(\frac{1}{3} C + H \right) \text{ kJ} \cdot \text{kg}^{-1} \quad (A.25)$$

Table A.2 Thermodynamic data of substances involved in the calculation of biomass's enthalpy

Substance	CO ₂	H ₂ O	N ₂	SO ₂	O ₂
$\Delta_f H_{m,i} / \text{kJ} \cdot \text{mol}^{-1}$	-393.505	-285.830	0	-296.813	0

$$\begin{aligned} \Delta_f H_{m,C_xH_yO_zN_aS_b}^o = & -393.505x - 142.915y - 296.813b + M \times 0.001 \times 874.08 \left(\frac{1}{3} C + H \right) \\ = & -393.505x - 142.915y - 296.813b + 0.874M \times \left(\frac{1}{3} C + H \right) \end{aligned} \quad (A.26)$$

According to the definition of x , y and b , the final calculation equation of standard molar enthalpy of formation of dry biomass was obtained.

$$\Delta_f H_{m,CxHyOzNsSb}^{\circ} = -32.762C - 141.781H - 9.258S + 87.4\left(\frac{1}{3}C + H\right) \text{ kJ} \cdot \text{mol}^{-1} \quad (5)$$

It has been verified that HHV can be predicted by Eq. (A.25) with the element contents in dry biomass in our previous study [18], so it is reasonable and accurate that the standard molar enthalpy of formation of dry biomass is calculated by Eq. (5) with element contents.

② Estimating standard molar entropy S_m°

Song et al. [27] developed a relationship between standard entropy and composition of 27 types of solid biomolecules and proposed the specific entropy of dry biomass as follows.

$$s^{\circ} = 0.0055C + 0.0954H + 0.0096O + 0.0098N + 0.0138S \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} \quad (A.27)$$

In this study, the calculation is based on mole, then Eq. (A.27) was expressed as:

$$\begin{aligned} S_m^{\circ} &= M \times (0.0055C + 0.0954H + 0.0096O + 0.0098N + 0.0138S) \\ &= 100 \times (0.0055C + 0.0954H + 0.0096O + 0.0098N + 0.0138S) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ &= 0.1 \times (0.0055C + 0.0954H + 0.0096O + 0.0098N + 0.0138S) \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned} \quad (6)$$

③ Estimating heat capacity C_p

Heat capacity of dry biomass and temperature showed a good linear relationship [28] and the proposed specific heat capacity of dry biomass as follows.

$$c_p = 1113.68 + 4.8567(T - 273.15) = -212.928 + 4.8567T \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1} \quad (A.28)$$

Then, Eq. (A.28) after unit conversion is written as.

$$\begin{aligned} C_p &= 0.001M c_p = 0.1(-212.928 + 4.8567T) \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ &= 10^{-4}(-212.928 + 4.8567T) \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned} \quad (7)$$

1.2. Simulation of anaerobic digestion

In order to simulate the anaerobic digestion of biomass, first of all, the mass of input fermentation broth needs to be given. Hassan et al. [29] proposed a level of 5% solids (TS%) at mid-temperature anaerobic digestion when co-fermented with chicken manure and wheat straw. According to mass balance,

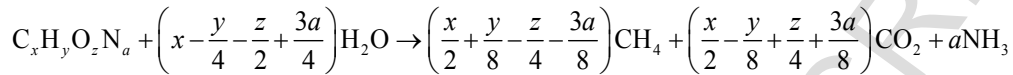
$$5\% \times m_{\text{broth}} = 100 \times TS\% \quad (A.29)$$

where m_{broth} represents mass of fermentation broth, g. 100 in the right of Eq.(A.29) means the mass of biomass.

Therefore, the mass of fermentation broth is as follows.

$$m_{\text{broth}} = 20TS \quad \text{g} \quad (\text{A.30})$$

In this study, the PBMP model was used to simulate the anaerobic digestion process. The theoretical biochemical methane potential (TBMP) represented the maximum biomethane yield per volatile solid (VS). To get the TBMP, the organic carbon in biomass was assumed to be transferred into CH_4 and CO_2 (two main composition of biogas) completely during the anaerobic digestion process. Therefore, the reaction in the anaerobic digestion of biomass was written as follows [13]:



According to the definition of the TBMP, we can obtain the following equation,

$$\text{TBMP} \left(\frac{\text{mL CH}_4}{\text{g VS}} \right) = \frac{22.4 \times 1000 \times \left(\frac{x}{2} + \frac{y}{8} - \frac{z}{4} - \frac{3a}{8} \right)}{12x + y + 16z + 14a} \quad \text{mL} \cdot \text{g}^{-1} \quad (\text{A.31})$$

When considering the actual digestion conditions, biomass can't be degraded completely by microorganisms during the digestion process, so in order to get the PBMP, an important factor needs to be taken into account, namely the biodegradability (BD) [13]. In this study, a linear correlation (Eq. (A.32)) [22] was used to estimate the BD of biomass.

$$\text{BD} = (80.4 - 2.70\text{Lignin})\% \quad (\text{A.32})$$

Then the PBMP can be calculated from the TBMP and BD by Eq. (A.33):

$$\begin{aligned} \text{PBMP} \left(\frac{\text{mL CH}_4}{\text{g VS}} \right) &= \text{BD} \times \text{TBMP} \\ &= (80.4 - 2.70\text{Lignin})\% \times \frac{22.4 \times 1000 \times \left(\frac{x}{2} + \frac{y}{8} - \frac{z}{4} - \frac{3a}{8} \right)}{12x + y + 16z + 14a} \\ &= (80.4 - 2.70\text{Lignin})\% \times \frac{22.4 \times 1000 \times \left(\frac{\text{C}}{24} + \frac{\text{H}}{8} - \frac{\text{O}}{64} - \frac{3\text{N}}{112} \right)}{\text{C} + \text{H} + \text{O} + \text{N}} \quad \text{mL} \cdot \text{g}^{-1} \end{aligned} \quad (\text{A.33})$$

Actually, comparing to the PBMP per VS, we are more concerned with the PBMP per biomass. According to the definition of VS and TS, Eq.(A.34) can be obtained.

$$\text{C} + \text{H} + \text{O} + \text{N} = \frac{\text{VS}}{\text{TS}} \times 100 \quad (\text{A.34})$$

Therefore,

$$\begin{aligned} \text{PBMP} \left(\frac{\text{mL CH}_4}{\text{g VS}} \right) &= (80.4 - 2.70 \text{Lignin}) \% \times \frac{22400 \times \left(\frac{\text{C}}{24} + \frac{\text{H}}{8} - \frac{\text{O}}{64} - \frac{3\text{N}}{112} \right)}{\frac{\text{VS}}{\text{TS}} \times 100} \\ &= (80.4 - 2.70 \text{Lignin}) \% \times \frac{22400 \times \text{TS} \% \left(\frac{\text{C}}{24} + \frac{\text{H}}{8} - \frac{\text{O}}{64} - \frac{3\text{N}}{112} \right)}{\text{VS}} \text{mL} \cdot \text{g}^{-1} \end{aligned} \quad (\text{A.35})$$

Then, PBMP per biomass can be calculated by Eq. (8):

$$\begin{aligned} \text{PBMP} \left(\frac{\text{mL CH}_4}{\text{g wb}} \right) &= (80.4 - 2.70 \text{Lignin}) \% \times \frac{22400 \times \text{TS} \% \left(\frac{\text{C}}{24} + \frac{\text{H}}{8} - \frac{\text{O}}{64} - \frac{3\text{N}}{112} \right)}{100} \\ &= (80.4 - 2.70 \text{Lignin}) \% \times 224 \text{TS} \% \times \left(\frac{\text{C}}{24} + \frac{\text{H}}{8} - \frac{\text{O}}{64} - \frac{3\text{N}}{112} \right) \text{mL} \cdot \text{g}^{-1} \end{aligned}$$

(8)

The volume and mole of biogas can be obtained by Eq.(9) and Eq.(10) respectively for the mass of biomass is 100g.

$$\begin{aligned} V_{\text{CH}_4} &= 100 \times \text{PBMP} \left(\frac{\text{mL CH}_4}{\text{g wb}} \right) \\ &= (80.4 - 2.70 \text{Lignin}) \% \times 22400 \text{TS} \% \times \left(\frac{\text{C}}{24} + \frac{\text{H}}{8} - \frac{\text{O}}{64} - \frac{3\text{N}}{112} \right) \text{mL} \end{aligned} \quad (9)$$

$$\begin{aligned} n_{\text{CH}_4} &= V_{\text{CH}_4} / 22.4 \times 10^3 \\ &= (80.4 - 2.70 \text{Lignin}) \% \times \text{TS} \% \times \left(\frac{\text{C}}{24} + \frac{\text{H}}{8} - \frac{\text{O}}{64} - \frac{3\text{N}}{112} \right) \text{mol} \end{aligned} \quad (10)$$

2. Calculating exergy for process evaluation

The total exergy value of substance equals to the sum of all kinds of exergy values [30],

$$Ex = Ex^{ki} + Ex^{po} + Ex^{ph} + Ex^{ch} \quad (\text{A.36})$$

where Ex^{ki} , Ex^{po} , Ex^{ph} and Ex^{ch} denote the exergy flow rate of kinetic energy, potential energy, physical energy and chemical energy, respectively. Neglecting the kinetic exergy ($mV^2/2$) and potential exergy (mgZ), the exergy flow rate of gas can be simplified as,

$$Ex = Ex^{ph} + Ex^{ch} \quad (\text{A.37})$$

Exergy of heat input is calculated by Eq. (A.38):

$$Ex_{\text{heat}} = \left(1 - \frac{T_0}{T} \right) Q \quad \text{kJ} \quad (\text{A.38})$$

where $\left(1 - \frac{T_0}{T} \right)$ means the Carnot efficiency, Q is the energy of heat input, kJ.

2.1. Exergy of biomass $Ex_{\text{wb,total}}$

The exergy of biomass is equal to chemical exergy for its physical exergy is 0 [31]. The exergy of

biomass is composed of the exergy of dry biomass and that of liquid water. In this study, the specific chemical exergy of dry biomass was calculated by Eq. (A.39) proposed by our previous study [19].

$$e_{db} = 920.72\left(\frac{1}{3}C + H\right) \text{ kJ}\cdot\text{kg}^{-1} \quad (\text{A.39})$$

Eq. (A.40) can be obtained via unit conversion for the molecular weight of dry biomass (taken as $100 \text{ g}\cdot\text{mol}^{-1}$):

$$\begin{aligned} Ex_{db} &= 0.1e_{db} \\ &= 0.1 \times 920.72\left(\frac{1}{3}C + H\right) \\ &= 92.072\left(\frac{1}{3}C + H\right) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned} \quad (\text{A.40})$$

The molar exergy of liquid water is $0.95 \text{ kJ}\cdot\text{mol}^{-1}$, then, the total exergy of 100 g biomass was obtained.

$$\begin{aligned} Ex_{wb,\text{total}} &= n_{db} Ex_{db} + n_{\text{water}} Ex_{\text{H}_2\text{O}} \\ &= (TS/100) Ex_{db} + ((100 - TS)/18) Ex_{\text{H}_2\text{O}} \\ &= 92.072\left(\frac{1}{3}C + H\right) \times TS\% + 0.95 \times 5.556(1 - TS\%) \\ &= 92.072\left(\frac{1}{3}C + H\right) \times TS\% + 5.278 \times (1 - TS\%) \text{ kJ} \end{aligned} \quad (\text{A.41})$$

It has been verified that exergy can be predicted by Eq. (A.39) with the element contents in dry biomass in our previous study [19], so it is also reasonable and accurate that the exergy of biomass is calculated by Eq. (A.41) with element contents.

2.2. Exergy input of drying process

Drying process of biomass can be divided into two stages, heating biomass to $100 \text{ }^\circ\text{C}$ and $100 \text{ }^\circ\text{C}$ water to vapor, their energy is $\int_{T_0}^{373.15} C_{p,\text{H}_2\text{O}} dT$ and $\Delta_{\text{vap}} H_m$ ($40.668 \text{ kJ}\cdot\text{mol}^{-1}$), respectively.

$$Ex_{\text{heat1}} = \left(1 - \frac{T_0}{T_{\text{Dry}}}\right) \left(\int_{T_0}^{373.15} C_{p,\text{H}_2\text{O}} dT + \Delta_{\text{vap}} H_m\right) \text{ kJ}\cdot\text{mol}^{-1} \quad (\text{A.42})$$

where T_{Dry} is drying temperature ($100 \text{ }^\circ\text{C}$ in this study), T_0 is ambient temperature ($25 \text{ }^\circ\text{C}$ in this study), $\left(1 - \frac{T_0}{T_{\text{Dry}}}\right)$ means Carnot efficiency, $C_{p,\text{H}_2\text{O}}$ represents the molar heat capacity of liquid water, $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

The exergy used to dry 100 g biomass in pyrolysis process is as follows:

$$\begin{aligned} Ex_{\text{heat1},\text{total}} &= n_{\text{water}} Ex_{\text{heat1}} \\ &= n_{\text{water}} \left(1 - \frac{T_0}{T_{\text{Dry}}}\right) \left(\int_{T_0}^{373.15} C_{p,\text{H}_2\text{O}} dT + 40.668\right) \\ &= 5.556(1 - TS\%) \left(1 - \frac{T_0}{T_{\text{Dry}}}\right) \left(\int_{T_0}^{373.15} C_{p,\text{H}_2\text{O}} dT + 40.668\right) \text{ kJ} \end{aligned} \quad (\text{A.43})$$

Exergy input of drying process of gasification process $Ex_{\text{heat3,total}}$ is equal to that of pyrolysis process $Ex_{\text{heat1,total}}$.

2.3. Exergy input of reactor

2.3.1. Exergy input of pyrolysis reactor $Ex_{\text{heat2,total}}$

Input exergy to heat and maintain biomass in pyrolysis reactor was calculated by Eq. (A.44):

$$Ex_{\text{heat2}} = \left(1 - \frac{T_0}{T_I}\right) \int_{T_0}^{T_I} C_{p,\text{db}} dT \quad \text{kJ} \cdot \text{mol}^{-1} \quad (\text{A.44})$$

where $C_{p,\text{db}}$ is molar heat capacity of dry biomass (calculated by Eq.(7)), $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. T_I represents the pyrolysis temperature in the reactor.

Then, the total input exergy of pyrolysis reactor can be calculated,

$$\begin{aligned} Ex_{\text{heat2,total}} &= n_{\text{db}} Ex_{\text{heat2}} \\ &= TS\% \times \left(1 - \frac{T_0}{T_I}\right) \int_{T_0}^{T_I} C_{p,\text{db}} dT \quad \text{kJ} \end{aligned} \quad (\text{A.45})$$

2.3.2. Exergy input of gasification reactor $Ex_{\text{heat4,total}}$

The heat input to the gasification process primarily brings biomass and oxygen to the gasification temperature T_{II} . Calculation formula of input exergy of gasification process for heating biomass is same to that of pyrolysis process except the heat temperature.

$$Ex_{\text{heat4, db, total}} = TS\% \times \left(1 - \frac{T_0}{T_{II}}\right) \int_{T_0}^{T_{II}} C_{p,\text{db}} dT \quad \text{kJ} \quad (\text{A.46})$$

Calculation formula of input exergy for heating oxygen is as follows: (the amount of oxygen added is determined by equivalence ratio (ER))

$$Ex_{\text{heat4, O}_2} = \left(1 - \frac{T_0}{T_{II}}\right) \int_{T_0}^{T_{II}} C_{p,\text{O}_2} dT \quad \text{kJ} \cdot \text{mol}^{-1} \quad (\text{A.47})$$

The amount of oxygen added to 100 g of biomass gasification is set to n_{O_2} , then the total exergy input required was calculated by Eq. (A.48):

$$Ex_{\text{heat4, O}_2, \text{total}} = n_{\text{O}_2} \left(1 - \frac{T_0}{T_{II}}\right) \int_{T_0}^{T_{II}} C_{p,\text{O}_2} dT \quad \text{kJ} \quad (\text{A.48})$$

Therefore, the calculation formula of the total of exergy input is as follows:

$$Ex_{\text{heat4,total}} = Ex_{\text{heat4, O}_2, \text{total}} + Ex_{\text{heat4, db, total}} \quad \text{kJ} \quad (\text{A.49})$$

2.3.3. Exergy input of anaerobic digestion $Ex_{\text{heat5,total}}$

The specific exergy required for heating the anaerobic digestion process is,

$$e_{\text{heat5}} = \left(1 - \frac{T_0}{T_{III}}\right) \int_{T_0}^{T_{III}} c_{p,\text{broth}} dT \quad \text{kJ} \cdot \text{kg}^{-1} \quad (\text{A.50})$$

where T_{III} is the temperature of anaerobic digestion, °C. $c_{p,\text{broth}}$ is the specific heat capacity of fermentation broth (not the biomass), $\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$. In this study, the specific heat capacity of the fermentation broth is assumed to be equal to that of water for the amount of water is dominant in the fermentation broth ($TS=5\%$).

Then, the calculation formula of the total exergy is as follows:

$$\begin{aligned} Ex_{\text{heat5},\text{total}} &= m_{\text{broth}} e_{\text{heat5}} \\ &= 20TS \times \left(1 - \frac{T_0}{T_{III}}\right) \int_{T_0}^{T_{III}} 4.2 dT \quad \text{J} \\ &= 0.02TS \times \left(1 - \frac{T_0}{T_{III}}\right) \times 4.2 \times (T_{III} - T_0) \quad \text{kJ} \end{aligned} \quad (\text{A.51})$$

2.4. Exergy of gas [32]

The molar physical exergy of gas is calculated by Eq. (A.52):

$$Ex^{ph} = (H - H_0) - T(S - S_0) \quad (\text{A.52})$$

where H and S are the molar enthalpy and entropy of gas under working condition, H_0 and S_0 are the molar enthalpy and entropy of gas at the standard reference state.

Difference of molar enthalpy ($H-H_0$) and difference of molar entropy ($S-S_0$) are denoted as:

$$H - H_0 = \int_{T_0}^T C_p dT \quad \text{kJ} \cdot \text{mol}^{-1} \quad (\text{A.53})$$

$$S - S_0 = \int_{T_0}^T \frac{C_p}{T} dT - R \ln \frac{p}{p_0} \quad \text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \quad (\text{A.54})$$

where, R is the general gas constant, $8.314 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. C_p is the molar heat capacity at constant pressure, $\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. p is the pressure under working condition, $p_0=0.1 \text{ MPa}$ is the pressure at the standard reference state.

Finally, the calculation formula of molar physical exergy of gas for omitting the effect of pressure is as follows:

$$Ex^{ph} = \int_{T_0}^T C_p dT - T_0 \int_{T_0}^T \frac{C_p}{T} dT \quad \text{kJ} \cdot \text{mol}^{-1} \quad (\text{A.55})$$

The molar chemical exergy of gas is calculated by Eq.(A.56):

$$Ex^{ch} = \sum x_i (e_i^{ch} + RT_0 \ln x_i) \quad \text{kJ} \cdot \text{mol}^{-1} \quad (\text{A.56})$$

where x_i is the mole fraction of the i -th component in the gas. e_i^{ch} is the molar chemical exergy of i -th component, $\text{kJ} \cdot \text{mol}^{-1}$.

2.4.1. Exergy of syngas $Ex_{\text{syngas,total}}$

Syngas is composed of H_2 and CO , therefore, the physical exergy of syngas can be calculated.

$$Ex_{\text{total}}^{ph} = n_{H_2} Ex_{H_2}^{ph} + n_{CO} Ex_{CO}^{ph} \text{ kJ} \quad (\text{A.57})$$

where $Ex_{H_2}^{ph}$ and Ex_{CO}^{ph} are the molar physical exergy of CO and H_2 , their values are calculated by Eq.(A.55).

According to Eq. (A.56), the calculation formula of molar chemical exergy of syngas is,

$$Ex^{ch} = x_{H_2} (e_{H_2}^{ch} + RT_0 \ln x_{H_2}) + x_{CO} (e_{CO}^{ch} + RT_0 \ln x_{CO}) \text{ kJ} \cdot \text{mol}^{-1} \quad (\text{A.58})$$

where

$$x_{H_2} = \frac{n_{H_2}}{n_{\text{total}}} = \frac{n_{H_2}}{n_{H_2} + n_{CO}} \quad (\text{A.59})$$

$$x_{CO} = \frac{n_{CO}}{n_{\text{total}}} = \frac{n_{CO}}{n_{H_2} + n_{CO}} \quad (\text{A.60})$$

Then the chemical exergy of syngas is calculated by Eq. (A.61).

$$\begin{aligned} Ex_{\text{total}}^{ch} &= n_{\text{total}} Ex^{ch} \\ &= n_{H_2} (e_{H_2}^{ch} + RT_0 \ln x_{H_2}) + n_{CO} (e_{CO}^{ch} + RT_0 \ln x_{CO}) \text{ kJ} \end{aligned} \quad (\text{A.61})$$

Finally, according to Eq. (A.37), the total exergy of syngas is calculated by Eq. (A.62).

$$Ex_{\text{syngas,total}} = Ex_{\text{total}}^{ph} + Ex_{\text{total}}^{ch} \text{ kJ} \quad (\text{A.62})$$

2.4.2. Exergy of biogas $Ex_{\text{biogas,total}}$

The temperature of mesophilic anaerobic digestion is 37°C , which is very close to the environment (25°C , 1atm). Therefore, the physical exergy of biogas is negligible in this study. For biogas product of anaerobic digestion of biomass, only CH_4 is the target product, then the specific exergy of biogas can be calculated as follows:

$$Ex^{ch} = x_{CH_4} e_{CH_4}^{ch} \text{ kJ} \cdot \text{mol}^{-1} \quad (\text{A.63})$$

$$x_{CH_4} = \frac{n_{CH_4}}{n_{\text{total}}} = \frac{n_{CH_4}}{n_{CH_4} + n_{CO_2}} \quad (\text{A.64})$$

According to Eq. (A.37), the total exergy of biogas can be calculated.

$$Ex_{\text{biogas,total}} = n_{\text{total}} Ex^{ch} = n_{CH_4} e_{CH_4}^{ch} \text{ kJ} \quad (\text{A.65})$$

Nomenclature

BD biodegradability of biomass

C_{p,H_2O} molar heat capacity of liquid water, $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

$C_{p,db}$ molar heat capacity of dry biomass, $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

C_{p,O_2} molar heat capacity of oxygen, $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$

$c_{p,broth}$ specific heat capacity of fermentation broth, $\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$

Ex_{heat1} molar exergy input of drying process, $\text{kJ}\cdot\text{mol}^{-1}$

$Ex_{heat1,total}$ exergy input of drying process of 100g biomass in pyrolysis process, kJ

Ex_{heat2} molar exergy input of pyrolysis reactor, $\text{kJ}\cdot\text{mol}^{-1}$

$Ex_{heat2,total}$ exergy input of pyrolysis reactor for 100g biomass, kJ

$Ex_{heat3,total}$ exergy input of drying process of 100g biomass in gasification process, kJ

$Ex_{heat4, db, total}$ exergy input for heating dry biomass in gasification reactor for 100g biomass, kJ

Ex_{heat4, O_2} molar exergy input for heating oxygen, $\text{kJ}\cdot\text{mol}^{-1}$

$Ex_{heat4, O_2, total}$ exergy input for heating oxygen in gasification reactor for 100g biomass, kJ

$Ex_{heat4, total}$ exergy input of gasification reactor for 100g biomass, kJ

$Ex_{heat5, total}$ exergy input of anaerobic digestion for 100g biomass, kJ

$Ex_{biogas, total}$ total exergy of biogas, kJ

$Ex_{syngas, total}$ total exergy of syngas, kJ

$Ex_{wb, total}$ total exergy of 100 g biomass, kJ

Ex_{db}	molar chemical exergy of dry biomass, $\text{kJ}\cdot\text{mol}^{-1}$
e_{db}	specific chemical exergy of dry biomass, $\text{kJ}\cdot\text{kg}^{-1}$
$e_{\text{heat}5}$	specific chemical exergy required for heating the anaerobic digestion of biomass, $\text{kJ}\cdot\text{kg}^{-1}$
$G_{T,p}^t$	total Gibbs energy of the system, $\text{kJ}\cdot\text{mol}^{-1}$
HHV	higher heat value, $\text{kJ}\cdot\text{kg}^{-1}$
M	molecular weight of dry biomass, $\text{g}\cdot\text{mol}^{-1}$
m_{db}	mass of dry biomass, g
m_{wb}	mass of biomass, g
m_{water}	mass of water, g
m_{broth}	mass of fermentation broth, g
n_{db}	mole of dry biomass, g
n_i	equilibrium composition is referred to each species, mol
n_{water}	mole of water, mol
n_{CH_4}	mole of biogas, mol
PBMP	practical biochemical methane potential
Q	energy of heat input, kJ
S_m^o	standard molar entropy, $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
R	universal gas constant, $8.314 \times 10^{-3} \text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
TS	total solid
T_{Dry}	drying temperature, $^{\circ}\text{C}$
T_0	ambient temperature, $^{\circ}\text{C}$
T_I	pyrolysis temperature in the reactor, $^{\circ}\text{C}$
T_{II}	gasification temperature in the reactor, $^{\circ}\text{C}$
T_{III}	temperature of anaerobic digestion reactor, $^{\circ}\text{C}$
VS	volatile solid
V_{CH_4}	volume of biogas, mL
$\Delta_f H_m^o$	standard molar enthalpy of formation, $\text{kJ}\cdot\text{mol}^{-1}$
$\Delta_{\text{vap}} H_m$	molar enthalpy of vaporization, $\text{kJ}\cdot\text{mol}^{-1}$

Greek symbols

- η_I functional exergy efficiency of pyrolysis process
- η_{II} functional exergy efficiency of oxygen gasification process
- η_{III} functional exergy efficiency of anaerobic digestion process

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- ▶ Functional exergy efficiency is extended as unified protocol in biomass utilization
- ▶ Thermodynamic data of biomasses are predicted by high accurate models
- ▶ Thermochemical and biochemical conversion are simulated via different methods
- ▶ Utilization pathways of biomasses are compared based on functional exergy efficiency

ACCEPTED MANUSCRIPT