

# A unified correlation for estimating specific chemical exergy of solid and liquid fuels

Guohui Song, Jun Xiao, Hao Zhao, Laihong Shen\*

Key Laboratory of Energy Thermo-conversion and its Process Monitoring and Control of Ministry of Education, School of Energy & Environment, Southeast University, Nanjing 210096, Jiangsu Province, PR China

## ARTICLE INFO

### Article history:

Received 23 September 2011

Received in revised form

5 February 2012

Accepted 9 February 2012

Available online 10 March 2012

### Keywords:

Chemical exergy

Standard entropy

Solid and liquid fuels

Organic matter

Inorganic matter

Ash

## ABSTRACT

This paper presents a unified simple correlation for estimating specific chemical exergy of solid and liquid fuels on dry basis. The specific chemical exergy of a dry fuel was split into two contributions: chemical of exergies of organic matter and inorganic matter, respectively. To estimate chemical exergy of organic matter, a correlation for estimating standard entropy of organic matter of solid and liquid fuels was derived using 162 data points. A system of linear equations for estimating the numbers of moles of selected inorganic compounds from ash analysis data was established for estimating chemical exergy of inorganic matter. Statistical comparison shows that both chemical exergies of inorganic matter and ash can be properly neglected compared with the specific chemical exergy of dry solid and liquid fuels. The validation shows that the unified correlation is reliable and accurate. The method and results presented in this paper can be adopted to develop correlations for estimating specific chemical exergy of solid and liquid fuels based on various reference environmental models.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

Specific chemical exergy is an important fuel property in exergy analysis and performance optimization of energy conversion systems. Generally, chemical exergy of gaseous fuels can be calculated straightly by the basic method [1], of which main species can be determined experimentally. However, it is nearly impossible to calculate specific chemical exergy of carbon-based solid and liquid fuels using the basic approach, because carbon-based fuels often contain a wide variety of species with complex bond interactions and unknown thermodynamic properties [2]. To estimate specific chemical exergy of fuels, a few correlations have been proposed, which can be divided into two categories:

### 1.1. Correlations between chemical exergy and calorific value

Rant [3] proposed a constant ratio of chemical exergy to calorific value for solid and (separately) liquid fuels. However, the calculation for different organic substances showed the ratio depends

significantly on the chemical composition [4]. Szargut and Styrylska [4] corrected Rant's correlations by taking the chemical composition of fuels into account using statistical method. And a few correlations between the ratio of specific chemical exergy to lower heating value and the chemical composition of fuels were proposed, including one correlation for gaseous fuels, four correlations for liquid fuels or compounds, five correlations for solid fuels or compounds, respectively. Although Szargut and Styrylska's correlations have been commonly used for evaluation of chemical exergy of fuels in previous works [5–8], there are some drawbacks. Firstly, the correlations do not involve the effect of nitrogen on liquid fuels and sulfur on solid fuels, respectively, because of the lack of relevant thermodynamic data. Secondly, the states of some organic compounds had been mistaken in Szargut's source data [1] according to the new edition of handbook of organic chemistry [9], e.g., 1,2,4,5-Tetramethylbenzene, Pentamethylbenzene, 1,1-Diphenylethane, Diphenyl ether, which are in liquid state at reference state, had been processed as solids; gaseous *n*-Octadecane had been processed as solid; and Tridecane, Tetradecane, Pentadecane, Hexadecane, Methylcyclopentane, Propylcyclohexane, Butylcyclohexane and Propylbenzene, which are in gas state at reference state, had been processed as liquids. Finally, the correlations are limited to Szargut's reference environmental (R.E.) model theoretically.

\* Corresponding author. Tel.: +86 25 83795598; fax: +86 25 83793452.  
E-mail address: [lhshen@seu.edu.cn](mailto:lhshen@seu.edu.cn) (L. Shen).

## 1.2. Semi-empirical correlations derived from Gibbs free energy relations

Using Gibbs free energy relations, empirical data, and assuming the entropy of a fuel is equivalent to the sum of the entropies of the constituent elements, Shieh and Fan [10] presented a simple correlation for estimating the specific chemical exergy of structurally complicated materials. However, the estimation of standard entropy of the materials in Shieh and Fan's method did not perform entirely correctly [11]. However, Stepanov [11] recommended the method for practical use. Stepanov [11] and Bilgen [12] corrected the correlation for coal or coal liquids by introducing Ikumi et al. [13] and Eisermann et al.'s [14] correlations for estimating standard entropy of coal or coal liquids, respectively. However, the correlations are tedious to use and limited in scope of application, which were derived from standard entropies of relevant organic molecules of coals or coal liquids. The semi-empirical correlation based on Gibbs free energy relations can be modified to any R.E. model and has a more simple form compared with that of Szargut and Styrylska's correlations. Song et al. [15] proposed a simple correlation for estimating standard entropy of organic matter in biomass, and then corrected Shieh and Fan's method for biomass. And the results indicate that this method has a high accuracy for biomass validated by Szargut and Styrylska's correlations. Unfortunately, its applicability is theoretically limited to biomass.

Additionally, little attention has been paid to chemical exergy of inorganic matters in fuels [3,10–12]. The chemical exergy of ash, which could be usually neglected, has been treated approximately as that of inorganic matter [1]. However, ash is the inorganic residue that results from the complete combustion (or oxidation) of fuels, and the thermodynamic properties of inorganic matter and ash are not equal though the weights are similar. Song et al. [15] has evaluated the influence of inorganic matters on chemical exergy of biomass based on a simple assumption on the original state of inorganic matter-forming elements, i.e. Si, Al, Fe and Ti were assumed to present as oxides while Ca, K, P, Mg, S and Na as elements. However, the chemical composition of minerals in coal or biomass is actually much complex. The simple assumption on the original state of inorganic matter-forming elements by Song et al. could not describe the nature of the inorganic matter in coal or biomass well. The chemical exergy of inorganic matter still needs more sufficient studies.

To the authors' knowledge, standard chemical exergy of water has been reported in all R.E. models, only estimation of specific chemical exergy of solid and liquid fuels on dry basis (db) needs to be investigated. The objective of the present work is to develop a practical correlation for estimating specific chemical exergy of various solid and liquid fuels (db) with sufficient consideration on inorganic matter.

## 2. Derivation of the method

The derivation associated with inorganic matter, to some extent, was not performed perfectly in Shieh and Fan' work [10]. A clear derivation is presented in this study. Dry fuels can be regarded for many purposes as consisting of two classes of materials: (a) mainly a range of organic constituents, broadly referred to as 'organic matter'; (b) and a range of minerals and other inorganic constituents, broadly referred to as 'inorganic matter'. By ignoring the effect of mixing, specific chemical exergy of a fuel (db)  $ce_{db}$  is calculated as follows:

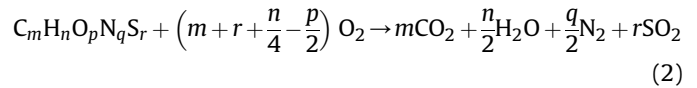
$$ce_{db} = CE_{OM} + CE_{IM} \quad (1)$$

where  $CE_{OM}$  and  $CE_{IM}$  are chemical exergies of organic matter and inorganic matter of a fuel (db), respectively.

The organic matter-forming elements in fuels are mainly C, H, O, N and S, which can be measured by ultimate analysis. And the inorganic matter-forming elements in fuels are commonly Al, Ca, Fe, K, Mg, Na, P, S, Si and Ti, of which the oxides can be identified by high-temperature ash (HTA) analysis [16–18]. Other elements in fuels (e.g. Cl, Mn) were ignored in this study for their relatively very low concentrations or difficulties in measuring.

### 2.1. Chemical exergy of organic matter

Through a complete combustion at the reference state, the organic matter ( $C_mH_nO_pN_qS_r$ ) in 1 kg of a fuel (db) reacts with oxygen to produce carbon dioxide, water, nitrogen and sulfur dioxide; that is,



where the subscripts  $m$ ,  $n$ ,  $p$ ,  $q$  and  $r$  mean numbers of atoms of elements C, H, O, N and S in the organic matter, respectively, i.e.:

$$m = \frac{10C}{12.011} (\text{mol}) \quad (3)$$

$$n = \frac{10H}{1.008} (\text{mol}) \quad (4)$$

$$p = \frac{10O}{15.999} (\text{mol}) \quad (5)$$

$$q = \frac{10N}{14.007} (\text{mol}) \quad (6)$$

$$r = \frac{10S}{32.066} (\text{mol}) \quad (7)$$

where C, H, O, N and S represent carbon, hydrogen, oxygen, nitrogen and sulphur contents of the fuel, respectively, in wt% (db).

Then chemical exergy of organic matter can be expressed as follows [1,10]:

$$CE_{OM} = m\epsilon_{CO_2} + \frac{n}{2}\epsilon_{H_2O} + \frac{q}{2}\epsilon_{N_2} + r\epsilon_{SO_2} - \left(m + r + \frac{n}{4} - \frac{p}{2}\right)\epsilon_{O_2} - \Delta C_r^0 \left(\text{kJ} \cdot \text{kg}^{-1}\right) \quad (8)$$

where  $\epsilon_{CO_2}$ ,  $\epsilon_{H_2O}$ ,  $\epsilon_{N_2}$ ,  $\epsilon_{SO_2}$  and  $\epsilon_{O_2}$  are standard chemical exergies of carbon dioxide, liquid water, nitrogen, sulfur dioxide and oxygen, respectively, in  $\text{kJ mol}^{-1}$  (Table 1).  $\Delta C_r^0$  represents the change in the Gibbs free energy from the combustion process at the reference state:

$$\Delta C_r^0 = \Delta H_r^0 - T_0 \Delta S_r^0 \quad (9)$$

where  $\Delta H_r^0$  refers to the heat of reaction of the combustion process, for the above reaction, which is equal to the negative of higher heating value [10], i.e.:

$$\Delta H_r^0 = -HHV \quad (10)$$

$\Delta S_r^0$  represents the change in the standard entropy and can be calculated by entropy equation of the combustion process, i.e.:

$$\Delta S_r^0 = m \cdot s_{CO_2}^0 + \frac{n}{2} s_{H_2O}^0 + \frac{q}{2} s_{N_2}^0 + r \cdot s_{SO_2}^0 - \left(m + r + \frac{n}{4} - \frac{p}{2}\right) s_{O_2}^0 - S_{OM}^0 \left(\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}\right) \quad (11)$$

**Table 1**  
Standard chemical exergy and standard entropy of the products of organic matter.

Substance	$\epsilon/\text{kJ mol}^{-1}$	$s^0/\text{kJ mol}^{-1} \text{K}^{-1}$
CO <sub>2</sub>	19.87	0.214
H <sub>2</sub> O <sub>l</sub>	0.95	0.070
O <sub>2</sub>	3.97	0.205
N <sub>2</sub>	0.72	0.192
SO <sub>2</sub>	310.93	0.248

l: liquid phase.

where  $s_{\text{CO}_2}^0$ ,  $s_{\text{H}_2\text{O}}^0$ ,  $s_{\text{N}_2}^0$ ,  $s_{\text{SO}_2}^0$  and  $s_{\text{O}_2}^0$  are standard entropies of carbon dioxide, water, nitrogen, sulfur dioxide and oxygen at reference state, respectively, in  $\text{kJ mol}^{-1} \text{K}^{-1}$  (Table 1).  $S_{\text{OM}}^0$  represents standard entropy of organic matter, in  $\text{kJ K}^{-1} \text{kg}^{-1}$  dry fuel. It should be noted that the standard pressure for entropy is 0.1 MPa in thermo chemistry [19], which is different from the reference pressure of Szargut's R.E. model (1 atm). However, the difference between specific entropies of gaseous substances at 0.1 MPa and 1 atm is  $0.109 \times 10^{-3} \text{kJ mol}^{-1} \text{K}^{-1}$  [19], which is negligibly small compared with the values of standard entropies listed in Table 1. Similarly, the influence of pressure difference on standard Gibbs free energy of formation can also be ignored properly. In this study, the data at 0.1 MPa were employed directly.

By substituting the Eqs. (9), (10) and (11) into (8), the chemical exergy of organic matter can be expressed as follows:

$$\begin{aligned}
 CE_{\text{OM}} = m & \left[ (\epsilon_{\text{CO}_2} + T_0 s_{\text{CO}_2}^0) - (\epsilon_{\text{O}_2} + T_0 s_{\text{O}_2}^0) \right] \\
 & + \frac{n}{2} \left[ (\epsilon_{\text{H}_2\text{O}} + T_0 s_{\text{H}_2\text{O}}^0) - \frac{1}{2} (\epsilon_{\text{O}_2} + T_0 s_{\text{O}_2}^0) \right] \\
 & + \frac{p}{2} (\epsilon_{\text{O}_2} + T_0 s_{\text{O}_2}^0) + \frac{q}{2} (\epsilon_{\text{N}_2} + T_0 s_{\text{N}_2}^0) \\
 & + r \left[ (\epsilon_{\text{SO}_2} + T_0 s_{\text{SO}_2}^0) - (\epsilon_{\text{O}_2} + T_0 s_{\text{O}_2}^0) \right] \\
 & + \text{HHV} - T_0 S_{\text{OM}}^0 \left( \text{kJ} \cdot \text{kg}^{-1} \right)
 \end{aligned} \quad (12)$$

Considering the negligible contribution of ash content to HHV, Channiwala and Parikh' correlation for estimating HHV of solid, liquid and gaseous fuels (db) was applied in this study [20], i.e.:

$$\begin{aligned}
 \text{HHV} = & 0.3491C + 1.1783H + 0.1005S - 0.1034O \\
 & - 0.0151N - 0.0211A \left( \text{MJ} \cdot \text{kg}^{-1} \right)
 \end{aligned} \quad (13)$$

$0\% \leq C \leq 92.25\%$ ,  $0.43\% \leq H \leq 25.15\%$ ,  $0.00\% \leq O \leq 50.00\%$ ,  $0.00\% \leq N \leq 5.60\%$ ,  $0.00\% \leq S \leq 94.08\%$ ,  $0.00\% \leq A \leq 71.4\%$ ,  $4.745 \text{ MJ kg}^{-1} \leq \text{HHV} \leq 55.345 \text{ MJ kg}^{-1}$ , where C, H, O, N, S and A represent carbon, hydrogen, oxygen, nitrogen, sulphur and ash contents of a fuel, respectively, in wt% (db).

Ikumi et al. [13] and Eisermann et al. [14] have proposed correlations for estimating standard entropy of coal or coal liquids, respectively. However, the correlations are tedious to use and limited in scope of application. Battley et al. [21,22] have measured the standard entropy of lyophilized cells of *Saccharomyces cerevisiae* at 298.15 K and then correlated the standard entropy of dried biomass (in  $\text{J C mol}^{-1} \text{K}^{-1}$ ) with the atomic entropies of the atoms comprising the biomass. It is also tedious to employ the formula in the present work. Though Song et al. [15] proposed a simple correlation for estimating standard entropy of biomass on dry ash-free basis, its applicability is limited to biomass theoretically. Thus, new correlations for estimating  $S_{\text{OM}}$  is essential for derivation of correlations for estimating  $CE_{\text{OM}}$  based on the thermodynamic framework of Gibbs free energy relations.

## 2.2. Chemical exergy of inorganic matter

Inorganic matter of coal, biomass and petroleum, etc, contains a range of minerals and other inorganic constituents. Chemical composition of high-temperature ash can be regarded as that of inorganic matter of fuels produced from coal, biomass or crude oil. In principle, specific chemical exergy of inorganic matter or ash is calculated as follows, respectively [1]:

$$ce_{\text{mixture}} = \sum x_i \epsilon_i + RT_0 \sum (x_i \ln x_i) \left( \text{kJ} \cdot \text{mol}^{-1} \right) \quad (14)$$

where  $x_i$  and  $\epsilon_i$  represent the mole fraction and standard chemical exergy of the species  $i$  in inorganic matter or ash, respectively.  $R$  is the universal gas constant,  $0.0083145 \text{ kJ mol}^{-1} \text{K}^{-1}$ .

The standard chemical exergy of a compound ( $\epsilon_{\text{compound}}$ ) is calculated as follows [1]:

$$\epsilon_{\text{compound}} = \Delta G_f^0 + \sum n e_j \epsilon_j \left( \text{kJ} \cdot \text{mol}^{-1} \right) \quad (15)$$

where  $\Delta G_f^0$  is the standard Gibbs free energy of formation of the compound,  $n e_j$  is the numbers of atom of the constitute element  $j$ ,  $\epsilon_j$  represents the standard chemical exergy of the constitute element  $j$ , in  $\text{kJ mol}^{-1}$ .

Huggins [23] and Ward [24] have summarized the principal minerals found in coal and low temperature ash (LTA), respectively. Suárez-García et al. [25] and Werkelin et al. [26] have investigated the inorganic matter in vegetable and woody biomass, respectively. However, there is still scarce quantitative report on chemical composition of inorganic matter in coal, biomass or other fuels. Thus, estimating chemical exergy of inorganic matter still needs a sufficient study.

## 3. Correlations for estimating standard entropy and chemical exergy of organic matter

### 3.1. Standard entropy of organic matter

Standard entropy of organic matter has been estimated from that of the structural, biologically important or relevant organic molecules in previous works [13–15]. And the same method was applied in this study. A large range of organic molecules relevant to coal, biomass, petroleum, shale oil, gasoline, diesel, coal and biomass tar, synthetic liquid fuels made from coal for biomass, etc, were collected from the published literature [1,13,14,21,22,27–29]. Then the molecules with available standard entropies were selected as source data samples. Finally, there are 99 and 63 data points were collected for solid and liquid organic molecules, respectively, as tabulated in Tables 2 and 3.

Although there are many mathematical models for regression [20], a correlation in the form of a first order polynomial, which is similar to that of Eq. (13), is the most apt. Due to the mathematical characteristic, the correlation can be used for estimating not only the specific standard entropy of organic molecules, but also standard entropy of organic matter in solid or liquid fuels by substituting the ultimate analysis (db). Thus, correlations in the form of a first order polynomial were derived statistically based on the standard entropies of organic molecules collected in this study. Three statistical parameters were employed as evaluating parameters, which are defined as follows:

$$\text{Average bias error (ABE)} = \frac{1}{n} \sum_{i=1}^n \frac{v_E - v_R}{v_R} \times 100\% \quad (16)$$

**Table 2**  
Standard entropy of organic molecules relevant to solid fuels at 298.15 K.

Name	Formula	$s^0/\text{kJ K}^{-1} \text{kg}^{-1}$
Urea	CH <sub>4</sub> ON <sub>2</sub>	1.742
Oxalic acid	C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	1.334
Dicyanodiamide	C <sub>2</sub> H <sub>4</sub> N <sub>4</sub>	1.538
Glycine	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> N	1.379
Melamine	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub>	1.182
L-Lactic acid	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	1.579
D-Lactic acid	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	1.593
L-Alanine	C <sub>3</sub> H <sub>7</sub> O <sub>2</sub> N	1.450
L-Serine	C <sub>3</sub> H <sub>7</sub> O <sub>3</sub> N	1.419
Alloxan	C <sub>4</sub> H <sub>2</sub> O <sub>4</sub> N <sub>2</sub>	1.313
Maleic acid	C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>	1.373
Fumaric acid	C <sub>4</sub> H <sub>4</sub> O <sub>4</sub>	1.431
Allantoin	C <sub>4</sub> H <sub>6</sub> O <sub>3</sub> N <sub>4</sub>	1.233
Succinic acid	C <sub>4</sub> H <sub>6</sub> O <sub>4</sub>	1.488
Creatinine	C <sub>4</sub> H <sub>7</sub> ON <sub>3</sub>	1.483
Aspartic acid	C <sub>4</sub> H <sub>7</sub> O <sub>4</sub> N	1.278
Glycylglycine	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub> N <sub>2</sub>	1.438
L-Asparagine	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub> N <sub>2</sub>	1.321
Creatine	C <sub>4</sub> H <sub>9</sub> O <sub>2</sub> N <sub>3</sub>	1.445
Hypoxanthine	C <sub>5</sub> H <sub>4</sub> ON <sub>4</sub>	1.070
Xanthine	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub> N <sub>4</sub>	1.059
Adenine	C <sub>5</sub> H <sub>5</sub> N <sub>5</sub>	1.118
Guanine	C <sub>5</sub> H <sub>5</sub> ON <sub>5</sub>	1.060
Uric acid	C <sub>5</sub> H <sub>5</sub> O <sub>3</sub> N <sub>4</sub>	1.024
L-Proline	C <sub>5</sub> H <sub>9</sub> O <sub>2</sub> N	1.425
L-Glutamic acid	C <sub>5</sub> H <sub>9</sub> O <sub>4</sub> N	1.279
DL-Alanyl glycine	C <sub>5</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub>	1.460
L-Glutamine	C <sub>5</sub> H <sub>10</sub> O <sub>3</sub> N <sub>2</sub>	1.335
L-Valine	C <sub>5</sub> H <sub>11</sub> O <sub>2</sub> N	1.527
Methionine	C <sub>5</sub> H <sub>11</sub> O <sub>2</sub> NS	1.551
1,2-Dinitrobenzene	C <sub>6</sub> H <sub>4</sub> O <sub>4</sub> N <sub>2</sub>	1.287
1,3-Dinitrobenzene	C <sub>6</sub> H <sub>4</sub> O <sub>4</sub> N <sub>2</sub>	1.314
Phenol	C <sub>6</sub> H <sub>6</sub> O	1.530
Hydroquinone	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1.273
Catechol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1.364
Resorcinol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1.341
Pyrocatechol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	1.270
L-Cystine	C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	1.347
α-D-Glucose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	1.177
α-D-Galactose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	1.140
L-Sorbose	C <sub>6</sub> H <sub>12</sub> O <sub>6</sub>	1.226
L-Leucine	C <sub>6</sub> H <sub>13</sub> O <sub>2</sub> N	1.586
L-Isoleucine	C <sub>6</sub> H <sub>13</sub> O <sub>2</sub> N	1.586
2-Nitrobenzoic acid	C <sub>7</sub> H <sub>5</sub> O <sub>4</sub> N	1.247
3-Nitrobenzoic acid	C <sub>7</sub> H <sub>5</sub> O <sub>4</sub> N	1.227
4-Nitrobenzoic acid	C <sub>7</sub> H <sub>5</sub> O <sub>4</sub> N	1.257
Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	1.372
o-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	1.290
m-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	1.281
p-Hydroxybenzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	1.272
Phthalic acid anhydride	C <sub>8</sub> H <sub>4</sub> O <sub>3</sub>	1.188
o-Phthalic acid	C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>	1.252
Hippuric acid	C <sub>9</sub> H <sub>9</sub> NO <sub>3</sub>	1.336
Phenylalanine	C <sub>9</sub> H <sub>11</sub> O <sub>2</sub> N	1.300
L-Phenylalanine	C <sub>9</sub> H <sub>11</sub> O <sub>2</sub> N	1.293
L-Tyrosine	C <sub>9</sub> H <sub>11</sub> O <sub>3</sub> N	1.181
Naphthalene	C <sub>10</sub> H <sub>8</sub>	1.302
Durene	C <sub>10</sub> H <sub>14</sub>	1.840
2-Methylnaphthalene	C <sub>11</sub> H <sub>10</sub>	1.547
L-Tryptophan	C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	1.229
Hippurylglycine	C <sub>11</sub> H <sub>12</sub> N <sub>2</sub> O <sub>4</sub>	1.330
Pentamethylbenzene	C <sub>11</sub> H <sub>16</sub>	1.870
Biphenyl	C <sub>12</sub> H <sub>10</sub>	1.335
Diphenyl	C <sub>12</sub> H <sub>10</sub>	1.340
Diphenylether	C <sub>12</sub> H <sub>10</sub> O	1.375
Diphenylamine	C <sub>12</sub> H <sub>11</sub> N	1.666
Hexamethylbenzene	C <sub>12</sub> H <sub>18</sub>	1.848
Sucrose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	1.052
β-Lactose	C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	1.128
Benzophenone	C <sub>13</sub> H <sub>10</sub> O	1.346
Diphenylcarbinol	C <sub>13</sub> H <sub>12</sub> O	1.330
Anthracene	C <sub>14</sub> H <sub>10</sub>	1.164
Phenanthrene	C <sub>14</sub> H <sub>10</sub>	1.188
1,2-Diphenylethene	C <sub>14</sub> H <sub>12</sub>	1.390

**Table 2 (continued)**

Name	Formula	$s^0/\text{kJ K}^{-1} \text{kg}^{-1}$
Stilbene	C <sub>14</sub> H <sub>12</sub>	1.393
Dibenzyl	C <sub>14</sub> H <sub>14</sub>	1.478
Pyrene	C <sub>16</sub> H <sub>10</sub>	1.112
Fluoranthene	C <sub>16</sub> H <sub>10</sub>	1.140
1,4-Diphenyl-2-butene-1,4-dione	C <sub>16</sub> H <sub>12</sub> O <sub>2</sub>	1.351
1,4-Diphenyl-1,4-butanedione	C <sub>16</sub> H <sub>14</sub> O <sub>2</sub>	1.363
Hexadecanoic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	1.764
1-Hexadecanol	C <sub>16</sub> H <sub>34</sub> O	1.864
Triphenylene	C <sub>18</sub> H <sub>12</sub>	1.116
2,3-Benzanthracene	C <sub>18</sub> H <sub>12</sub>	0.943
Naphthacene	C <sub>18</sub> H <sub>12</sub>	1.120
Triphenylamine	C <sub>18</sub> H <sub>15</sub> N	1.240
Triphenylmethane	C <sub>19</sub> H <sub>16</sub>	1.277
Triphenylmethanol	C <sub>19</sub> H <sub>16</sub> O	1.265
Perylene	C <sub>20</sub> H <sub>12</sub>	1.050
Triphenylethylene	C <sub>20</sub> H <sub>16</sub>	1.310
Coronene	C <sub>24</sub> H <sub>12</sub>	0.940
1,3,5-Triphenylbenzene	C <sub>24</sub> H <sub>18</sub>	1.200
Tetracosane	C <sub>24</sub> H <sub>50</sub>	1.920
Tetraphenylmethane	C <sub>25</sub> H <sub>20</sub>	1.160
Pentacosane	C <sub>25</sub> H <sub>52</sub>	1.900
Dotriacontane	C <sub>32</sub> H <sub>66</sub>	1.888
Tritriacontane	C <sub>33</sub> H <sub>68</sub>	1.888
Anhydrous bovine zinc insulin	C <sub>508</sub> H <sub>752</sub> O <sub>150</sub> N <sub>130</sub> S <sub>12</sub>	1.315
Anhydrous bovine chymotrypsinogen A	C <sub>1077</sub> H <sub>1736</sub> O <sub>343</sub> N <sub>304</sub> S <sub>12</sub>	1.350

$$\text{Average absolute error (AAE)} = \frac{1}{n} \sum_{i=1}^n \left| \frac{v_E - v_R}{v_R} \right| \times 100\% \quad (17)$$

$$\text{Coefficient of determination } (R^2) = 1 - \frac{\sum_{i=1}^n (v_E - v_R)^2}{\sum_{i=1}^n (v_R - \bar{v}_R)^2} \quad (18)$$

where  $v_E$  and  $v_R$  denote estimated and reference values, respectively. AAE indicates the average error of a correlation, and a lower AAE value means a smaller error of the correlation. ABE indicates the average bias error of the correlation, and a positive ABE value implies an overall overestimation while a negative one means an overall underestimation. The smaller the absolute value of the ABE is, the smaller the bias of the correlation.  $R^2$  indicates the level of explained variability in the model. It is commonly used as a guideline to measure the accuracy of the model. The higher  $R^2$  is, the better the fitting is.

Three correlations for estimating standard entropy of organic matter in solid and/or liquid fuels were derived and expressed as follows:

for solid organic matters:

$$s_{OM,S}^0 = 0.0086c + 0.0780h + 0.0106o + 0.0103n + 0.0118s \left( \text{kJ} \cdot \text{K}^{-1} \cdot \text{kg}^{-1} \right) \quad (19)$$

$$20.00\% \leq c \leq 95.97\%, 1.42\% \leq h \leq 14.88\%, 0.00\% \leq o \leq 71.08\%, 0.00\% \leq n \leq 66.63\%, 0.00\% \leq s \leq 26.69\%.$$

for liquid organic matters:

$$s_{OM,L}^0 = 0.0068c + 0.1567h + 0.0268o + 0.0551n + 0.0329s \left( \text{kJ} \cdot \text{K}^{-1} \cdot \text{kg}^{-1} \right) \quad (20)$$

$$26.10\% \leq c \leq 93.46\%, 4.38\% \leq h \leq 16.38\%, 0.00\% \leq o \leq 69.52\%, 0.00\% \leq n \leq 34.12\%, 0.00\% \leq s \leq 51.61\%.$$

for solid and liquid organic matters:

$$s_{OM,SL}^0 = 0.0038c + 0.1659h + 0.0109o + 0.0045n + 0.0316s \left( \text{kJ} \cdot \text{K}^{-1} \cdot \text{kg}^{-1} \right) \quad (21)$$

**Table 3**  
Standard entropy of organic molecules relevant to liquid fuels at 298.15 K.

Name	Formula	$s^0/\text{kJ K}^{-1} \text{kg}^{-1}$
Formic acid	CH <sub>2</sub> O <sub>2</sub>	2.802
Methanol	CH <sub>4</sub> O	3.971
Methyl alcohol	CH <sub>4</sub> O	4.026
Acetonitrile	C <sub>2</sub> H <sub>3</sub> N	3.645
Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	2.664
Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	2.662
Ethanthiol	C <sub>2</sub> H <sub>6</sub> S	4.765
Dimethyl sulfide	C <sub>2</sub> H <sub>6</sub> S	3.170
Ethanol	C <sub>2</sub> H <sub>6</sub> O	3.496
Ethylene glycol	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	2.690
Acetone	C <sub>3</sub> H <sub>6</sub> O	3.451
n-Propionic acid	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	2.592
Thiophene	C <sub>4</sub> H <sub>4</sub> S	2.153
2-Butanone	C <sub>4</sub> H <sub>8</sub> O	3.312
Ethyl acetate	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	2.944
Butyric acid	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	2.569
Butyl mercaptan	C <sub>4</sub> H <sub>10</sub> S	3.060
Diethyl sulfide	C <sub>4</sub> H <sub>10</sub> S	2.983
2-Methylthiophene	C <sub>5</sub> H <sub>6</sub> S	2.226
3-Methylthiophene	C <sub>5</sub> H <sub>6</sub> S	2.224
Furfuryl alcohol	C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>	2.196
Cyclopentanol	C <sub>5</sub> H <sub>10</sub> O	2.390
Pentanoic acid	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	2.544
Benzene	C <sub>6</sub> H <sub>6</sub>	2.218
Benzenethiol	C <sub>6</sub> H <sub>6</sub> S	2.022
Phenol	C <sub>6</sub> H <sub>6</sub> O	1.626
Aniline	C <sub>6</sub> H <sub>7</sub> N	2.054
Cyclohexene	C <sub>6</sub> H <sub>10</sub>	2.632
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	2.428
Cyclohexanol	C <sub>6</sub> H <sub>12</sub> O	1.993
n-Hexane	C <sub>6</sub> H <sub>14</sub>	3.435
Toluene	C <sub>7</sub> H <sub>8</sub>	2.398
Benzyl alcohol	C <sub>7</sub> H <sub>8</sub> O	2.004
Cyclohexane, methyl-	C <sub>7</sub> H <sub>14</sub>	2.525
n-Heptane	C <sub>7</sub> H <sub>16</sub>	3.254
Styrene	C <sub>8</sub> H <sub>8</sub>	2.281
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	2.404
o-Xylene	C <sub>8</sub> H <sub>10</sub>	2.322
m-Xylene	C <sub>8</sub> H <sub>10</sub>	2.375
p-Xylene	C <sub>8</sub> H <sub>10</sub>	2.330
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	2.404
Ethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	2.503
n-Octane	C <sub>8</sub> H <sub>18</sub>	3.132
Indene	C <sub>9</sub> H <sub>8</sub>	1.844
1,2,3-Trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	2.311
1,2,4-Trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	2.365
1,3,5-Trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	2.276
Propylbenzene	C <sub>9</sub> H <sub>12</sub>	2.330
n-Nonane	C <sub>9</sub> H <sub>20</sub>	3.069
1,2,4,5-Tetramethylbenzene	C <sub>10</sub> H <sub>14</sub>	2.165
Prehnitene	C <sub>10</sub> H <sub>14</sub>	2.205
p-Cymene	C <sub>10</sub> H <sub>14</sub>	2.056
Pentamethylbenzene	C <sub>11</sub> H <sub>16</sub>	2.183
n-Decane	C <sub>10</sub> H <sub>22</sub>	2.991
1-Methylnaphthalene	C <sub>11</sub> H <sub>10</sub>	1.792
Pentamethylbenzene	C <sub>11</sub> H <sub>16</sub>	2.157
n-Undecane	C <sub>11</sub> H <sub>24</sub>	2.931
Biphenyl	C <sub>12</sub> H <sub>10</sub>	1.622
Diphenyl ether	C <sub>12</sub> H <sub>10</sub> O	1.711
n-Dodecane	C <sub>12</sub> H <sub>26</sub>	2.880
Diphenylmethane	C <sub>13</sub> H <sub>12</sub>	1.423
1,1-Diphenylethane	C <sub>14</sub> H <sub>14</sub>	1.863
Cetyl alcohol	C <sub>16</sub> H <sub>34</sub> O	2.502

correlations only for solid or liquid organic molecules are more accurate than the unified correlation Eq. (21). However, the statistical parameters of Eq. (21) indicate that the correlation may also be acceptable. The three correlations will be further compared later.

### 3.2. Chemical exergy of organic matter

By substituting Eqs. (19)–(21) with chemical composition data on dry basis into the Eq. (12), respectively, the practical correlations for estimating  $CE_{OM}$  ( $\text{kJ kg}^{-1}$ ) can be obtained as follows:

for solid fuels:

$$CE_{OM,S} = 362.008C + 1101.841H - 86.218O + 2.418N + 196.701S - 21.1A \quad (22)$$

for liquid fuels:

$$CE_{OM,L} = 362.545C + 1078.376H - 91.048O - 10.940N + 190.410S - 21.1A \quad (23)$$

for solid and liquid fuels:

$$CE_{OM,SL} = 363.439C + 1075.633H - 86.308O + 4.147N + 190.798S - 21.1A \quad (24)$$

The three correlations were applied to estimate chemical exergy of organic matter in solid and liquid fuels. Data of chemical composition of solid fuels were collected from Refs. [17,18], containing 37 and 86 data points for various coal and biomass, respectively (see [Supplementary information S.1](#)). There are few extended overviews on data of proximate and ultimate analyses of various liquid fuel, only minimum and maximum values of contents of C, H, O, N, S and A for petroleum, shale oil, oil from tar sands, crude benzol, synthetic liquid fuels made from coal or biomass, etc have been summarized [27,28]. In this study, 100 sets of data of ultimate analysis plus ash content for various liquid fuels (db) were generated randomly with constraint of the scope of the chemical composition summarized in Refs. [27,28] (see [Supplementary information S.2](#)). Although the data are not actual information of chemical composition of liquid fuels, it can be used for comparison of Eq. (22) or (23) with Eq. (24) as the same source data were employed.

Eq. (22) through (24) are restricted to the content ranges of the elements C, H, O, N and S for Eq. (19) through (21), respectively. For organic matter in a fuel, c, h, o, n and s in Eq. (19) through (21) can be represented by the ultimate analysis data on dry ash-free basis of the fuel. Then the ultimate analysis data (daf) for the solid and liquid fuels were firstly converted from that on dry basis (S.1 and S.2), a following comparison indicates that in respect of content ranges of the basic elements, Eq. (19) through (21) can completely satisfy the estimation of standard entropy of organic matter in the fuels presented in S.1 and S.2.

Fig. 1(a) presents the comparison between chemical exergy of organic matter in solid fuels estimated by Eqs. (22) and (24) (i.e.,  $CE_{OM,S}$  and  $CE_{OM,SL}$ ), respectively. The error band of  $\pm 0.8\%$  is shown on the figure to indicate the error limits, and the ABE and AAE are  $-0.336\%$  and  $0.338\%$ , respectively. Similarly, Fig. 1(b) shows the comparison between chemical exergy of organic matter in liquid fuels estimated by Eqs. (23) and (24) (i.e.,  $CE_{OM,L}$  and  $CE_{OM,SL}$ ), respectively, and the error band, ABE and AAE are  $\pm 0.32\%$ ,  $0.214\%$  and  $0.214\%$ , respectively. Together, the comparisons indicate chemical exergies of organic matter estimated by Eq. (22) or (23) are very similar to that by Eq. (24). Although Eq. (24) slightly underestimates chemical exergy of organic matter for solid fuels, and overestimates for liquid fuels, respectively, it can be employed

$20.00\% \leq c \leq 95.97\%$ ,  $1.42\% \leq h \leq 16.38\%$ ,  $0.00\% \leq o \leq 71.08\%$ ,  $0.00\% \leq n \leq 66.63\%$ ,  $0.00\% \leq s \leq 51.61\%$ , where c, h, o, n and s represent contents of elements C, H, O, N and S in organic molecules, respectively, in wt%.

ABEs of Eqs. (19)–(21) are 0.757, 1.386 and 4.500, respectively; AAEs are 7.935, 10.063 and 17.338, respectively; and  $R^2$  are 0.6385, 0.7192 and 0.6116, respectively. The results show that the



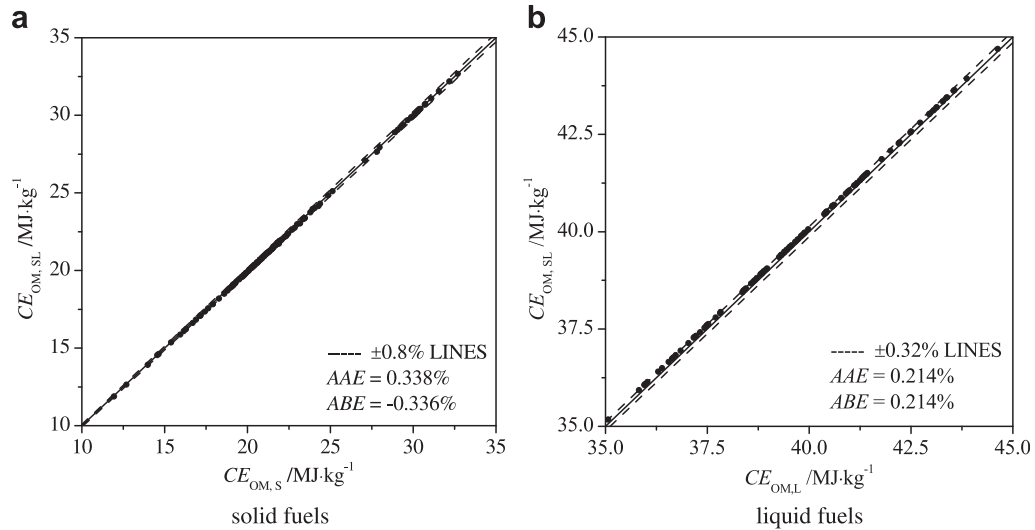


Fig. 1. Comparison of chemical exergy of organic matter in (a) solid and (b) liquid fuels estimated by correlations  $CE_{OM,S}$  and  $CE_{OM,L}$  with that by  $CE_{OM,SL}$ , respectively.

for estimating chemical exergy of organic matter for both solid and liquid fuels.

#### 4. Estimation of chemical exergies of inorganic matter

The principal minerals found in coal and LTA have been summarized by Huggins [23] and Ward [24]. In this study, 49 varieties of inorganic compounds were selected for inorganic matter in coal (Table 4). The actual inorganic matter in biomass could be divided into detrital (terrigenous) and authigenic genetic classes. The chemical composition of detrital inorganic matter was approximated by that in soil [30]; the chemical composition of authigenic genetic inorganic matter including ions has been studied by Suárez-García et al. [25] and Werkelin et al. [26] 36 varieties of inorganic substance, including some ions, were selected as constituents for inorganic matter in biomass (Table 5). Data pertaining to standard Gibbs free energy of formation were mainly collected from Refs. [31–34]. Other compounds were estimated by Chermak and Rimstidt's method for silicate minerals or the ideal mixing model [34]. Standard chemical exergies of  $Al^{3+}$ ,  $Ca^{2+}$ ,  $Fe^{3+}$ ,  $K^+$ ,  $Mg^{2+}$ , and  $Na^+$  were approximately substituted by that of the corresponding element. This may slightly overestimate chemical exergy of inorganic matter in biomass. The standard chemical exergy of  $MgP_2O_7$  was approximately estimated based on exergy equation of reaction using data of  $\Delta G_f^0$  of  $P_2O_4^{2-}$ , and  $\Delta G_f^0$  of  $MgP_2O_7^{2-}$  and  $MgP_2O_7$  reported by Goldberg and Tewari [35]. Standard chemical exergies of various inorganic compounds founded in coal or biomass were calculated by Eq. (15) as listed in Tables 4 and 5, respectively. Standard chemical exergies of the oxides in HTA were listed in Table 6.

There is rare quantitative report on chemical composition of inorganic matter in coal, biomass, or other fuels. And the contents of the inorganic compounds may differ largely from one variety to another variety of fuels. It is impossible to directly estimate chemical exergy of inorganic matter by Eq. (14). In recent years, Vassilev et al. [16–18] have presented some systematic and extended overviews on high-temperature ash composition of varieties of coal and biomass. We have noted that by taking the numbers of atoms of the ten elements in an individual compound as a coefficient, where the coefficient of an element can be regarded as zero if a compound does not contain the element; and taking the numbers of moles of elements Al, Ca, Fe, K, Mg, Na, P, S,

Si and Ti per kg of ash as constant terms (see Supplementary information S.3), a system of linear equations can be established to express the numbers of moles of the inorganic compounds. For inorganic matter of coal, the system of linear equations consists of 10 equations in 49 variables. For inorganic matter of biomass, the system of linear equations consists of 10 equations in 36 variables. The systems could be conveniently written in matrix form as follows:

$$\begin{bmatrix} a_{1,1} & a_{2,2} & a_{1,3} & \dots & a_{1,n} \\ a_{2,1} & a_{2,2} & a_{1,3} & \dots & a_{2,n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ a_{m,1} & a_{m,2} & a_{m,3} & \dots & a_{m,n} \end{bmatrix} \times \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{bmatrix} = \begin{bmatrix} b_1 \\ b_2 \\ \vdots \\ b_m \end{bmatrix} \quad (25)$$

where  $a_{ij}$  represents the number of atoms of element  $i$  in an inorganic compound  $j$ .  $b_1 \sim b_m$  refers to the numbers of moles of elements Al, Ca, Fe, K, Mg, Na, P, S, Si and Ti per kg of ash, respectively.  $x_1 \sim x_n$  refers to the numbers of moles of the inorganic substances, respectively.  $m = 10$ , and  $n = 49$  or 36 for coal or biomass, respectively. The constraint of the systems is that all  $x_j$  is nonnegative number. The other elements presented in selected inorganic compounds, e.g. C, H and O, were not considered as constraint conditions.

The systems have infinite solutions, which can be regarded as possible chemical compositions of inorganic matter of coal or biomass. Computer algorithms have been developed based on MATLAB to solve the system of linear equations, which employed the rand function provided by MATLAB [36] and the substitution method. 100 sets of solutions for an individual ash sample were obtained. Then chemical exergy of inorganic matter corresponding to 1 kg of ash was calculated with the solutions and the average value was used in this study. Then specific chemical exergy of a fuel (db)  $ce_{db}$  can be calculated by Eqs.(1) and (24).

The proportions of chemical exergies of inorganic matter ( $CE_{IM}$ ) and ash ( $CE_{Ash}$ ) to specific chemical exergy ( $ce_{db}$ ) were evaluated by the following two parameters  $r_{Ash}$  and  $r_{IM}$ :

$$r_{Ash} = \frac{CE_{Ash}}{ce_{db}} \times 100\% \quad (26)$$

$$r_{IM} = \frac{CE_{IM}}{ce_{db}} \times 100\% \quad (27)$$

**Table 4**

Standard Gibbs energy of formation and standard chemical exergy of principal minerals found in coal and LTA.

Name	Formula	$\Delta G_f^\circ/\text{kJ mol}^{-1}$	$\epsilon/\text{kJ mol}^{-1}$
Pyrope	$\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	-5934.5	120.57
Almandine	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	-4942.0	355.93
Chlorite <sup>a</sup>	$\text{Fe}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$	-6350.9	657.31
Clinoptilolite-K <sup>a</sup>	$(\text{NaK})_6(\text{SiAl})_{36}\text{O}_{72} \cdot 20\text{H}_2\text{O}$	-28332.9	908.44
Clinoptilolite-Na <sup>a</sup>	$\text{K}_{0.99}\text{Na}_{2.86}\text{Al}_5\text{Si}_{22.09}\text{O}_{53.56} \cdot 15.43\text{H}_2\text{O}$	-27233.2	689.63
Jarosite	$\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	-3318.7	129.19
Natrojarosite <sup>a</sup>	$\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$	-3159.3	258.67
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	-3797.5	-18.41
Ankerite <sup>a</sup>	$\text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2$	-966.9	52.69
Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	-6337.1	48.08
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	-4007.9	28.40
Heulandite <sup>a</sup>	$\text{CaAl}_2\text{Si}_7\text{O}_{18} \cdot 6\text{H}_2\text{O}$	-9603.7	151.51
Crandallite <sup>a</sup>	$\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$	-5509.3	170.31
Calcite	$\text{CaCO}_3$	-1128.5	19.12
Aragonite	$\text{CaCO}_3$	-1127.4	20.22
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	-2161.3	31.91
Anhydrite	$\text{CaSO}_4$	-1321.8	24.61
Bassanite	$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	-1436.1	29.34
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-1797.0	25.59
Pyrrhotite	$\text{Fe}_{0.875}\text{S}$	-98.9	838.02
Pyrite	$\text{FeS}_2$	-160.1	1430.99
Marcasite	$\text{FeS}_2$	-158.4	1432.69
Goethite	$\text{FeO}(\text{OH})$	-491.8	7.22
Coquimbite <sup>a</sup>	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$	-4397.0	344.80
Hematite	$\text{Fe}_2\text{O}_3$	-744.4	15.55
Magnetite	$\text{Fe}_3\text{O}_4$	-1012.7	126.23
Siderite	$\text{FeCO}_3$	-682.8	110.41
Wuestite	$\text{FeO}$	-251.4	127.58
Rozenite <sup>a</sup>	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$	-1773.5	170.90
Szomolnokite <sup>a</sup>	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$	-1062.0	168.06
Ilmenite	$\text{FeTiO}_3$	-1155.5	134.11
Illite <sup>a</sup>	$\text{K}_{1.5}\text{Al}_4(\text{Si}_{6.5}\text{Al}_{1.5})\text{O}_{20}(\text{OH})_4$	-10623.6	345.11
Muscovite	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	-5603.6	-43.49
Sanidine	$\text{KAlSi}_3\text{O}_8$	-3745.8	-10.53
Spinel	$\text{MgAl}_2\text{O}_4$	-2176.6	41.51
Magnesioferrite	$\text{MgFe}_2\text{O}_4$	-1329.6	61.71
Periclase	$\text{MgO}$	-569.3	62.06
Hexahydrate	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	-2631.2	41.68
Smectite <sup>a</sup>	$\text{Na}_{0.33}(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$	-6022.8	72.04
Montmorillonite <sup>v</sup>	$\text{Na}_{0.7}\text{Mg}_{0.7}\text{Al}_{1.3}\text{Si}_8\text{O}_{20}(\text{OH})_2$	-9697.5	146.43
Glauberite <sup>a</sup>	$\text{Na}_2\text{Ca}(\text{SO}_4)_2$	-2595.0	39.87
Thenardite	$\text{Na}_2\text{SO}_4$	-1269.8	18.63
Dawsonite	$\text{NaAlCO}_3(\text{OH})_2$	-1786.0	-2.60
Analcime	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	-3090.0	-4.67
Albite	$\text{NaAlSi}_3\text{O}_8$	-3711.6	-6.28
Quartz	$\text{SiO}_2$	-856.3	1.78
Anatase	$\text{TiO}_2$	-883.2	27.43
Rutile	$\text{TiO}_2$	-888.8	21.83
Boehmite	$\text{AlO}(\text{OH})$	-918.4	-5.98

<sup>a</sup>  $\Delta G_f^\circ$  is estimated by Chermak and Rimstidt' method for silicate minerals or the ideal mixing model summarized in ref [34].

The results were presented graphically at Fig. 2(a) and (b) for coal and biomass, respectively. For coal (Fig. 2(a)),  $CE_{IM}$  is normally less than  $CE_{Ash}$ , and  $r_{Ash}$  and  $r_{IM}$  are within 3.2% and 2.3%, respectively, and have mean values of 0.4% and 0.2%, respectively. For biomass (Fig. 2(b)),  $CE_{IM}$  is normally greater than  $CE_{Ash}$ ,  $r_{Ash}$  and  $r_{IM}$  are within 5.7% and 8.5%, respectively, and have mean values of 0.6% and 0.8%, respectively. The results indicate that for practical use both the chemical exergies of ash and inorganic matter of coal and biomass can be ignored. For both coal and biomass,  $r_{Ash}$  and  $r_{IM}$  normally increase with the increase of  $A$  (Fig. 2). It seems that  $r_{Ash}$  and  $r_{IM}$  may be too large to neglect beyond the maximum value of  $A$  (about 50 wt.%) in this study. However, Fig. 2 also clearly shows that the differences between  $r_{Ash}$  and  $r_{IM}$  are even smaller. This observation indicates that the change in chemical exergy of inorganic matter

**Table 5**

Standard Gibbs energy of formation and standard chemical exergy of principal inorganic substances found in woody and vegetable biomass.

Name	Formula	$\Delta G_f^\circ/\text{kJ mol}^{-1}$	$\epsilon/\text{kJ mol}^{-1}$
Aluminium ion <sup>b</sup>	$\text{Al}^{3+}$		790.39
Corundum	$\text{Al}_2\text{O}_3$	-1582.3	4.45
Gibbsite	$\text{Al}(\text{OH})_3$	-1154.9	-4.39
Boehmite	$\text{AlO}(\text{OH})$	-918.4	-5.98
Diaspore	$\text{AlO}(\text{OH})$	-922.7	-10.28
Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	-3797.5	-18.41
Calcium ion <sup>b</sup>	$\text{Ca}^{2+}$		731.40
Calcite	$\text{CaCO}_3$	-1128.5	19.12
Whewellite <sup>a</sup>	$\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	-1754.4	281.59
Dolomite	$\text{CaMg}(\text{CO}_3)_2$	-2161.3	31.91
	$\text{CaMg}_3(\text{SO}_4)_4$ <sup>a</sup>	-4769.6	309.95
Apatite	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	-6337.1	48.08
Anhydrite	$\text{CaSO}_4$	-1321.8	24.61
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-1797.0	25.59
Ferric iron <sup>b</sup>	$\text{Fe}^{3+}$		376.99
Hematite	$\text{Fe}_2\text{O}_3$	-744.4	15.55
Goethite	$\text{FeO}(\text{OH})$	-491.8	7.22
Pyrite	$\text{FeS}_2$	-160.1	1430.99
Potassium ion <sup>b</sup>	$\text{K}^+$		366.66
Muscovite	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	-5603.6	-43.49
	$\text{KCaPO}_4$ <sup>a</sup>	-1706.6	260.87
Fairchildite <sup>a</sup>	$\text{K}_2\text{Ca}(\text{CO}_3)_2$	-2196.5	100.70
Sylvite	$\text{KCl}$	-408.8	81.94
Monopotassium phosphate	$\text{KH}_2\text{PO}_4$	-1415.7	56.42
Dipotassium phosphate	$\text{K}_2\text{HPO}_4$	-1636.5	84.20
	$\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ <sup>a</sup>	-3694.7	223.01
Arcanite	$\text{K}_2\text{SO}_4$	-1437.7	-89.37
Magnesium ion <sup>b</sup>	$\text{Mg}^{2+}$		629.37
Nequeohite	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	-1723.8	36.06
	$\text{Mg}_2\text{P}_2\text{O}_7$ <sup>c</sup>		1012.23
Sodium ion <sup>b</sup>	$\text{Na}^+$		336.71
Natrofairchildite <sup>a</sup>	$\text{Na}_2\text{Ca}(\text{CO}_3)_2$	-2179.9	57.31
Halite	$\text{NaCl}$	-384.0	76.72
Quartz	$\text{SiO}_2$	-856.3	1.78
Anatase	$\text{TiO}_2$	-883.2	27.43
Rutile	$\text{TiO}_2$	-888.8	21.83

<sup>a</sup>  $\Delta G_f^\circ$  is estimated by Chermak and Rimstidt' method for silicate minerals or the ideal mixing model summarized in ref [34].

<sup>b</sup> Standard chemical exergy of the ion is approximately substituted by that of the element.

<sup>c</sup> Standard chemical exergy was approximately estimated by exergy equation of reaction using  $\Delta G_f^\circ$  of  $\text{P}_2\text{O}_7^{4-}$  and  $\Delta G_f^\circ$  of  $\text{MgP}_2\text{O}_7^-$  and  $\text{MgP}_2\text{O}_7$  reported by Ref [35].

from the combustion process is quite small compared with the specific chemical exergy of the fuel. It confirms that chemical exergies of ash and inorganic matter can be neglected properly for coal and biomass. Additionally, the average ratio of  $CE_{IM}$  to  $CE_{Ash}$  is about 0.54 or 1.40 for coal or biomass, respectively. This quantitative relationship between inorganic matter and ash has potential applications in exergetic life cycle or exergoenvironmental analyses.

The chemical composition of the inorganic matter of coal can be approximately used as that of liquid fossil fuels, e.g. crude oil. The high-temperature ash can be regarded as the inorganic matter of the liquid fuels produced from coal or biomass. And considering

**Table 6**

Standard Gibbs energy of formation and standard chemical exergy of the oxides in HTA.

Substance	$\Delta G_f^\circ/\text{kJ mol}^{-1}$	$\epsilon/\text{kJ mol}^{-1}$
$\text{SiO}_2$	-856.444	1.64
$\text{CaO}$	-603.509	129.88
$\text{K}_2\text{O}$	-322.766	412.54
$\text{P}_2\text{O}_5$	-1355.675	377.12
$\text{Al}_2\text{O}_3$	-1582.271	4.48
$\text{MgO}$	-568.943	62.42
$\text{Fe}_2\text{O}_3$	-742.294	17.66
$\text{SO}_3$	-371.017	242.00
$\text{Na}_2\text{O}$	-379.090	296.32
$\text{TiO}_2$	-889.406	21.22

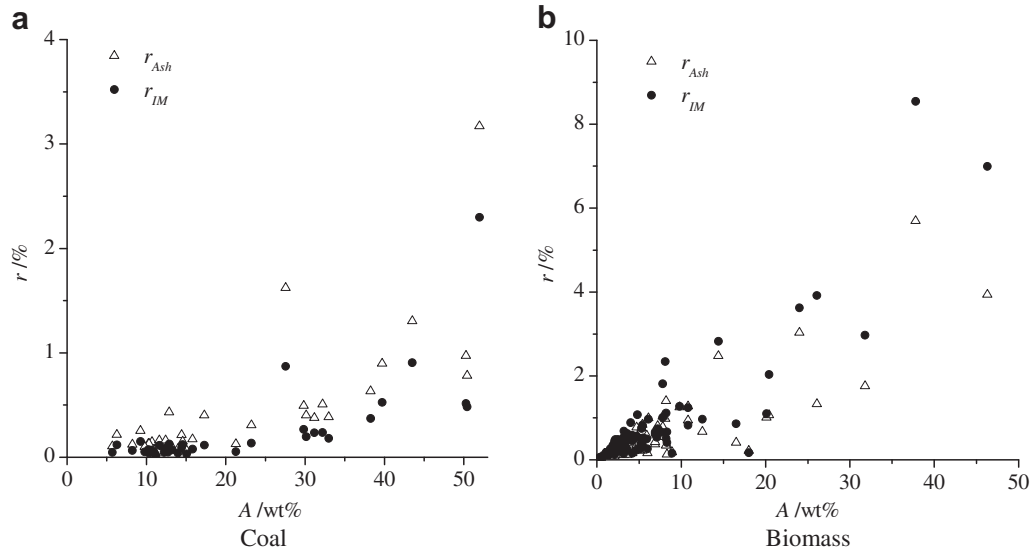


Fig. 2. Proportions of chemical exergy of ash and inorganic matter to  $ce_{db}$  of (a) coal and (b) biomass, respectively.

liquid fuels commonly have much smaller ash content, it may be concluded that chemical exergies of ash and inorganic matter for both various solid and liquid fuels could be ignored properly. Furthermore, the other properties of inorganic matter could also be estimated by this mathematical method.

**5. Unified correlation for estimating specific chemical exergy of solid and liquid fuels**

By ignoring chemical exergy of inorganic matter, specific chemical exergy of a solid or liquid fuel (db) is the chemical exergy of the organic matter of the fuel. Then a unified correlation for estimating specific chemical exergy of solid and liquid fuels (db) is as follows:

$$ce_{db} = 363.439C + 1075.633H - 86.308O + 4.147N + 190.798S - 21.1A \text{ (kJ}\cdot\text{kg}^{-1}) \quad (28)$$

where C, H, O, N, S and A represent carbon, hydrogen, oxygen, nitrogen, sulphur and ash contents of a fuel, respectively, in wt% (db). According to our source data, Eq. (28) is applicable to various coal, biomass, petroleum, shale oil, oil from tar sands, crude benzol, synthetic liquid fuels made from coal or biomass, i.e.,  $27.33\% \leq C \leq 89.10\%$ ,  $2.46\% \leq H \leq 14.00\%$ ,  $1.10\% \leq O \leq 46.92\%$ ,  $0.00\% \leq N \leq 9.27\%$ ,  $0.01\% \leq S \leq 5.54\%$ ,  $0.00\% \leq A \leq 51.96\%$ .

Theoretically, the correlation is simultaneously restricted by the content ranges of the correlations for estimating HHV, i.e. Eq. (13) and standard entropy of organic matter, i.e., Eq. (21), respectively. In the case of solid or liquid fuels with contents exceeding the ranges based on the source data in this study, the application of Eq. (28) should be judged by the content ranges for both Eqs. (13) and (21).

Szargut and Styrylska’s correlations [4] have been commonly used for evaluating chemical exergy of technical fuels. The validation of the present correlation Eq. (24) in this study was carried out by comparison of the values of  $ce_{db}$  over 223 data points estimated by Szargut and Styrylska’s method and the proposed correlation,

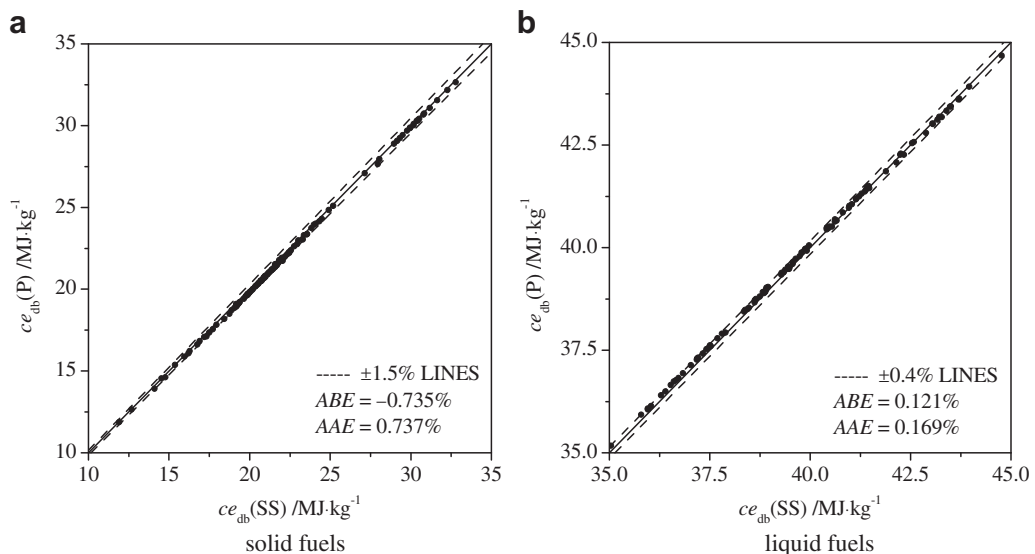


Fig. 3. Comparison between  $ce_{db}$  of (a) solid and (b) liquid fuels estimated by the proposed correlation (P) and Szargut and Styrylska’s method (SS), respectively.



respectively. The results were presented graphically at Fig. 3(a) and (b) for solid and liquid fuel (db), respectively.

Fig. 3(a) presents the comparison for solid fuels. The error band of  $\pm 1.5\%$  is shown on the figure to indicate the error limits, and the ABE and AAE are  $-0.735\%$  and  $0.737\%$ , respectively. Similarly, Fig. 3(b) shows that the error band, ABE and AAE for liquid fuels are  $\pm 0.4\%$ ,  $0.121\%$  and  $0.169\%$ , respectively. The results indicate the proposed correlation with simple form is accurate and reliable.

The present correlation for estimating specific chemical exergy of solid and liquid fuels mainly suffers from the limitations of the unified correlation for estimating HHV. For solid and liquid fuels, the predictions of HHV correlation does not hold good for (i) the fuels with chemical contents beyond the specified ranges of C, H, O, N, S and Ash; (ii) combustible material likes certain category of leather, plastic, rubber and minerals where oxygen penetration for combustion of C, H and S is difficult either due to very strong C-H bond or due to very high ash content [20]. However, these limitations can be corrected by substituting more accurate correlations or data of HHV into Eq. (12) for a special variety of fuel.

The proportions of  $CE_{Ash}$  and  $CE_{IM}$  to  $ce_{db}$  have been checked based on Kameyama et al., van Gool, Zheng et al., Rivero and Garfias, and Bilgen's R.E. models, respectively [37–41] and the same conclusions have been observed. Thus, the chemical exergy of inorganic matter and ash can be ignored based on the mentioned R.E. models [37–41]. In principle, the previous correlations are limited to their R.E. models or the specified fuels [3,4,10–12,15]. However, with the mentioned conclusion on inorganic matter, the present method can be easily modified for all solid and liquid fuels based on any R.E. models above by substituting the data of standard chemical exergies of carbon dioxide, liquid water, nitrogen, sulfur dioxide and oxygen based on the R.E. model.

## 6. Conclusions

A unified correlation for estimating specific chemical exergy of solid and liquid fuels (db) was proposed on Szargut's R.E. model, which is based on the exergy and entropy equations of reaction, Gibbs free energy relations, a modified estimation of standard entropy of organic matter of solid and liquid fuels and a mathematical model for estimating chemical composition of inorganic matter from HTA analysis data. The following conclusions were obtained from the present work:

- (1) Three correlations in the form of a first order polynomial for estimating the standard entropy of organic matter in solid and/or liquid fuels were derived statistically from the standard entropies of organic molecules relevant to solid and liquid fuels.
- (2) A mathematical model for estimating the numbers of moles of inorganic compounds from HTA analysis data was established. Statistical results show that: (a) chemical exergies of ash and inorganic matter are very negligibly small compared with specific chemical exergy of coal or biomass (db), averagely; (b) difference between chemical exergies of ash and corresponding inorganic matter is even smaller. Both chemical exergies of ash and inorganic matter can be neglected properly for various solid and liquid fuels, which are at least applicable to Szargut, Kameyama et al., van Gool, Zheng et al, Rivero and Garfias, and Bilgen's R.E. models.
- (3) Specific chemical exergy of a solid or liquid fuel (db) is approximately equal to chemic exergy of the organic matter of the fuel. A unified correlation for estimating specific chemical exergy of solid and liquid fuels (db) on Szargut's R.E. model was proposed, i.e.:  $ce_{db}(\text{kJ kg}^{-1}) = 363.439C + 1075.633H - 86.308O + 4.147N + 190.798S - 21.1A$ . It has a simple form and thus is convenient to use. The validation indicates that the proposed correlation is accurate and reliable.

- (4) The method and results on standard entropy of organic matter and chemical exergy of inorganic matter can be adopted for various R.E. models, and then the unified correlation for estimating specific chemical exergy of solid and liquid fuels based on that R.E. model can be easily modified.

## Acknowledgment

This work was supported by the Special Fund for Major State Basic Research Projects of China (2010CB732206). The authors would like to thank Miss Lijuan Zheng, Pennsylvania State University, and Mr. Zhuangzhi Wu, Central South University, for their help on documents collection, Mr. Deshan Liang, Beijing University of Science and Technology, for his help on acceleration of the algorithm for solving the uncertain linear systems.

## Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.energy.2012.02.016.

## Nomenclature

AAE	average absolute error
ABE	average bias error
CE	chemical exergy, $\text{kJ kg}^{-1}$
ce	specific chemical exergy, $\text{kJ mol}^{-1}$ or $\text{kJ kg}^{-1}$
db	dry basis
G	Gibbs free energy, $\text{kJ mol}^{-1}$ or $\text{kJ kg}^{-1}$
H	enthalpy, $\text{kJ kg}^{-1}$
HHV	higher heating value
HTA	high-temperature ash analysis
LTA	low-temperature ash analysis
ne	amount of atoms of an element
p	pressure, kPa
R	gas constant, $0.0083145 \text{ kJ mol}^{-1} \text{ K}^{-1}$
$R^2$	coefficient of determination
r	percent, %
S	entropy, $\text{J mol}^{-1} \text{ K}^{-1}$ or $\text{kJ kg}^{-1} \text{ K}^{-1}$
s	specific entropy, $\text{J mol}^{-1} \text{ K}^{-1}$ or $\text{kJ kg}^{-1} \text{ K}^{-1}$
T	temperature, K
x	mole fraction
v	value of a parameter

## Greek symbols

$\Delta$	change
$\epsilon$	standard chemical exergy

## Superscript

o	standard state in thermo chemistry
---	------------------------------------

## Subscripts

0	reference state
E	estimated value
f	formation
i	species i
IM	inorganic matter
L	liquid fuels
OM	organic matter
R	reference value
r	reaction
S	solid fuels
SL	solid and liquid fuels

## References

- [1] Szargut J, Morris DR, Steward FR. Exergy analysis of thermal, chemical, and metallurgical processes. New York: Hemisphere Publishing Corporation; 1988.
- [2] Hermann WA. Quantifying global exergy resources. Energy 2006;31:1685–702.
- [3] Rant Z. Towards the estimation of specific exergy of fuels (in German). Allg Wärmetech 1961;10:172–6.
- [4] Szargut J, Styrylska T. Approximate evaluation of the exergy of fuels (in German). BWK 1964;16:589–96.
- [5] Feng W, van der Kooij HJ, de Swaan Arons J. Biomass conversions in subcritical and supercritical water driving force, phase equilibria, and thermodynamic analysis. Chem Eng Process 2004;43:1459–67.
- [6] Panopoulos KD, Fryda L, Karl J, Poulou S, Kakaras E. High temperature solid oxide fuel cell integrated with novel allothermal biomass gasification Part II: exergy analysis. J Power Sources 2006;159:586–94.
- [7] Prins MJ, Ptasinski KJ, Janssen FJJG. From coal to biomass gasification: comparison of thermodynamic efficiency. Energy 2007;32:1248–59.
- [8] Karamarkovic R, Karamarkovic V. Energy and exergy analysis of biomass gasification at different temperatures. Energy 2010;35:537–49.
- [9] Gokel GW. Dean's handbook of organic chemistry. 2nd ed. New York: McGraw-Hill; 2004.
- [10] Shieh JH, Fan LT. Estimation of energy (enthalpy) and exergy (availability) contents in structurally complicated materials. Energy Source Part A 1982;6:1–46.
- [11] Stepanov VS. Chemical energy and exergy of fuels. Energy 1995;20:235–42.
- [12] Bilgen S, Kaygusuz K. The calculation of the chemical exergies of coal-based fuels by using the higher heating values. Appl Energy 2008;85:776–85.
- [13] Ikumi S, Luo CD, Wen CY. A method of estimating entropies of coals and coal liquids. Can J Chem Eng 1982;60(4):551–5.
- [14] Eisermann W, Johnson P, Conger WL. Estimating thermodynamic properties of coal, char, tar and ash. Fuel Process Technol 1980;3(1):39–53.
- [15] Song G, Shen L, Xiao J. Estimating specific chemical exergy of biomass from basic analysis data. Ind Eng Chem Res 2011;50:9758–66.
- [16] Vassilev SV, Vassileva CG. A new approach for the classification of coal fly ashes based on their origin, composition, properties, and behaviour. Fuel 2007;86:1490–512.
- [17] Vassilev SV, Vassileva CG. A new approach for the combined chemical and mineral classification of the inorganic matter in coal. 1. Chemical and mineral classification systems. Fuel 2009;88:235–45.
- [18] Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the chemical composition of biomass. Fuel 2010;89:913–33.
- [19] Chase MW. NIST-JANAF thermochemical tables. 4th ed. Washington DC and Woodbury NY: American Chemical Society; 1998.
- [20] Channiwala SA, Parikh PP. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 2002;81(8):1051–63.
- [21] Battley EH, Putnam RL, Boerio-Goates J. Heat capacity measurements from 10 to 300 K and derived thermodynamic functions of lyophilized cells of *Saccharomyces cerevisiae* including the absolute entropy and the entropy of formation at 298.15 K. Thermochim Acta 1997;298:37–46.
- [22] Battley EH. An empirical method for estimating the entropy of formation the absolute entropy of dried microbial biomass for use in studies on the thermodynamics of microbial growth. Thermochim Acta 1999;326:7–15.
- [23] Huggins FE. Overview of analytical methods for inorganic constituents in coal. Int J Coal Geol 2002;50:169–214.
- [24] Ward CR. Analysis and significance of mineral matter in coal seams. Int J Coal Geol 2002;50:135–68.
- [25] Suárez-García F, Martínez-Alonso A, Fernández Llorente M, Tascón JMD. Inorganic matter characterization in vegetable biomass feedstocks. Fuel 2002;81(9):1161–9.
- [26] Werkelin J, Skrifvars BJ, Zevenhoven M, Holmbom B, Hupa M. Chemical forms of ash-forming elements in woody biomass fuels. Fuel 2010;89:481–93.
- [27] Harker JH, Backhurst JR. Fuel and energy. New York: Academic Press; 1981.
- [28] Sarkar S. Fuels and combustion. 3rd ed. Boca Raton: CRC Press; 2009.
- [29] Milne TA, Evans RJ, Abatzoglou N. Biomass gasifier "tars": their nature, formation, and conversion. NREL/TP-570-25357; 1998.
- [30] Bolt GH, Bruggenwert MGM. Soil chemistry. Amsterdam: Elsevier Scientific Publishing Co; 1978.
- [31] Robie RA, Hemingway BS. Thermodynamic properties of minerals and related substances at 298.15 K and 1 bar (105 pascals) pressure and at higher temperatures. Washington DC: U.S. Geological Survey; 1979.
- [32] Lin C. Manual for thermodynamic properties of minerals and related substances. Beijing: Scientific Press; 1985.
- [33] Barin I. Thermochemical data of pure substances. 3rd ed. New York: VCH; 1995.
- [34] Valero A, Valero A, Vieillard P. The thermodynamic properties of the upper continental crust: exergy, Gibbs free energy and enthalpy. Energy; 2011. doi:10.1016/j.energy.2011.06.012.
- [35] Goldberga RN, Tewari YB. Thermochemistry of the biochemical reaction: {pyrophosphate(aq) + H<sub>2</sub>O(l) = 2 phosphate(aq)}. J Chem Thermodyn 2002;34:821–39.
- [36] Deng W. Info instruction manual for MATLAB. 2nd ed. Beijing: Posts & Telecom Press; 2010.
- [37] Kameyama H, Yoshida K, Yamauchi S, Fueki K. Evaluation of reference exergy for the elements. Appl Energy 1982;11:69–83.
- [38] van Gool W. Thermodynamics of chemical references for exergy analysis. Energy Convers Manage 1998;39(16–18):1719–28.
- [39] Zheng D, Wu X, Song Z, Chen M, Yu Y, Ren X, et al. Technical guides for exergy analysis in energy system (in Chinese). Chinese industrial standard GB/T 14909-2005; 2005.
- [40] Rivero R, Garfias M. Standard chemical exergy of elements updated. Energy 2006;31:3310–26.
- [41] Bilgen S. Calculation and interpretation of the standard chemical exergies of elements using the chemical reference species. Acta Phys Chim Sin 2009;25(8):1645–9.