

Estimation of chemical exergy of solid, liquid and gaseous fuels used in thermal power plants

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Received: 6 March 2013 / Accepted: 1 July 2013 / Published online: 27 July 2013
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Abstract This paper presents the methods for the calculation of chemical exergies of coal, heavy fuel oil and natural gas that are used as fuel in conventional thermal power plants. Calculations have shown that the chemical composition of the fuel greatly influences the value of its chemical exergy. In case of coal in which carbon and hydrogen are not combined together, an increase in both carbon and hydrogen contents increases its chemical exergy value. In case of heavy fuel oils, hydrogen–carbon ratio is the most influencing parameter in the chemical exergy value. An increase in hydrogen–carbon ratio in the fuel tends to increase its chemical exergy. In case of natural gases, a decrease in lighter hydrocarbon gas contents and an increase in heavier hydrocarbon gas contents tend to increase the chemical exergy value of the fuel. High moisture and/or ash contents also tend to lower the value of the chemical exergy.

Keywords Standard chemical exergy · Coal · Heavy fuel oil · Natural gas · Thermal power plant

List of symbols

Variables

G^0	Standard Gibbs function (kJ)
H^0	Standard enthalpy (kJ)
\bar{h}_d^0	Standard molar specific enthalpy of devaluation (kJ kmol ⁻¹)
m	Percent mass of a component
M	Molecular mass of a component
n	kmol of a component
(NCV) ⁰	Net calorific value of fuel (kJ kg ⁻¹)
P_0	Actual environmental pressure (Pa)
P_{00}	Partial pressure of a component in actual environment (Pa)
S^0	Standard entropy (kJ K ⁻¹)
T_0	Actual environmental temperature (K)
T_0	Standard temperature (K)

Greek letters

ψ_{Ch}^0	Standard specific chemical exergy (kJ kg ⁻¹)
φ	Ratio of standard specific chemical exergy to the net calorific value
Δ	Used for a change in any parameter

Subscripts

f	Fuel
p	Product
R	Reactant

Introduction

Energy is the major requirement of the people in a modern society. With industrial development, the energy consumption has been rising very rapidly and due to this, energy resources especially the fossil fuels are being

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consumed at a very high rate. This is also causing serious environmental problems due to pollution. In order that these resources may last longer and the pollution may be reduced, they should be used judiciously and efficiently. Optimum utilisation of energy resources thus becomes a compulsion for survival and to maintain the quality of life. This requires modifications and improvements in the existing power generation systems. Before any effort to modify a power generation system is undertaken, a thorough thermodynamic analysis of the system is necessary.

An analysis conducted on the energy flow can reveal the quantity and the location of energy loss. One can then take measures to avoid or reduce this energy loss. A traditional method of energy flow analysis is the energy balance calculation based on the first law of thermodynamics. This traditional method of analysis fails to consider changes in energy quality during a process which makes it unsatisfactory. It is now a well established fact that the thermodynamic analysis based on the second law of thermodynamics is quite useful in this regard. A thermodynamic function which Keenan [1] originally called availability was revived and a new name exergy was coined. Going by the history of exergy analysis [2], the developments in this direction began around the 1930s. Since then, a number of researchers have made contributions to the theory and practice of exergy analysis, e.g. [3–10]. Several papers have been published on exergy analysis of thermal systems such as steam power plants [11–13], gas-turbine cycles [14–16], Kalina cycle [17–20], absorption power/cooling combined cycles [21] and cogeneration [22].

As defined by Kotas [5], exergy of a steady stream of matter is equal to the maximum amount of work obtainable when the stream is brought from its initial state to the dead state by processes during which the stream may interact only with the environment. Exergy has two components—physical exergy and chemical exergy. Physical exergy is equal to the maximum amount of work obtainable when the stream of substance is brought from its initial state to the environmental state defined by p_0 and T_0 by physical processes involving only thermal interaction with the environment. Whereas, chemical exergy is equal to the maximum amount of work obtainable when the stream of substance under consideration is brought from the environmental state (p_0, T_0) to the dead state (p_{00}, T_0) by processes involving heat transfer and exchange of substances only with the environment. Alternatively, it can also be defined as the minimum amount of work necessary to synthesise and to deliver in the environmental state, the substance under consideration from the environmental substances by means of processes involving heat transfer and exchange of substances only with the environment.

Calculation of exergy values of a compound requires the reference exergies of the elements. Sussman [23], Kameyama et al. [24], Morris and Szargut [25], Szargut [26] and Rivero and Garfias [27] calculated the standard chemical exergy of some elements and compounds. Bilgen and Kaygusuz [28] explained the method for the calculation of the chemical exergies of coal-based fuels using the higher heating values.

The current study aims to provide comprehensive methodology for the estimation of chemical exergies of power plant fuels such as coal, heavy fuel oils and natural gas. Hopefully, this methodology and the calculated exergy data will be useful in the fossil fuel-fired power plants and coal mining industries and refineries.

Estimation of standard chemical exergy of coal

Ultimate analysis

Let the ultimate analysis of the coal be as follows:

Carbon, $m_{C,f}\%$; Hydrogen, $m_{H_2,f}\%$; Sulphur, $m_{S,f}\%$;
 Nitrogen, $m_{N_2,f}\%$; Oxygen, $m_{O_2,f}\%$; Moisture, $m_{H_2O,f}\%$
 and Ash, $m_{Ash,f}\%$

Molar composition per 100 kg of fuel

$$\text{Carbon (C)} \quad n_{C,f} = \frac{m_C}{M_C} \text{ kmol/100 kg of fuel} \quad (1)$$

$$\text{Hydrogen (H}_2\text{)} \quad n_{H_2,f} = \frac{m_{H_2}}{M_{H_2}} \text{ kmol/100 kg of fuel} \quad (2)$$

$$\text{Nitrogen (N}_2\text{)} \quad n_{N_2,f} = \frac{m_{N_2}}{M_{N_2}} \text{ kmol/100 kg of fuel} \quad (3)$$

$$\text{Sulphur (S)} \quad n_{S,f} = \frac{m_S}{M_S} \text{ kmol/100 kg of fuel} \quad (4)$$

$$\text{Oxygen (O}_2\text{)} \quad n_{O_2,f} = \frac{m_{O_2}}{M_{O_2}} \text{ kmol/100 kg of fuel} \quad (5)$$

$$\text{Water (H}_2\text{O)} \quad n_{H_2O,f} = \frac{m_{H_2O}}{M_{H_2O}} \text{ kmol/100 kg of fuel} \quad (6)$$

Composition of air

Air contains 21.0 % oxygen and 79 % nitrogen by volume. Therefore, for each kmol of oxygen $\frac{79}{21} = 3.7619$ kmol of nitrogen are involved.

Combustion equations for the combustible elements

$$n_{C,f}C + n_{C,f}O_2 \rightarrow n_{C,f}CO_2 \quad (7)$$

$$n_{H_2,f}H_2 + \frac{1}{2}n_{H_2,f}O_2 \rightarrow n_{H_2,f}H_2O \quad (8)$$

$$n_{S,f}S + n_{S,f}O_2 \rightarrow n_{S,f}SO_2 \quad (9)$$

Molar composition of the products for complete combustion of fuel

CO₂ $n_{CO_2,P}$ = CO₂ formed during the combustion of carbon
 = $n_{C,f}$ kmol/100 kg of fuel

H₂O $n_{H_2O,P}$ = H₂O formed during the combustion
 of hydrogen + H₂O present in the fuel
 = $(n_{H_2,f} + n_{H_2O,f})$ kmol/100 kg of fuel

SO₂ $n_{SO_2,P}$ = SO₂ formed during the combustion of sulphur
 = $n_{S,f}$ kmol/100 kg of fuel

N₂ N₂ does not take part in the combustion process

Therefore, N₂ in the products of combustion
 = N₂ present in the fuel + N₂ present in the
 air supplied

= N₂ present in the fuel + 3.7619 × O₂
 supplied by air

= N₂ present in the fuel + 3.7619

× (O₂ required for combustion
 – O₂ present in fuel)

$$n_{N_2,P} = n_{N_2,f} + 3.7619 \left(n_{C,f} + \frac{1}{2} n_{H_2,f} + n_{S,f} - n_{O_2,f} \right) \tag{10}$$

Net calorific value of fuel

The net calorific value of fuel is the lower heating value of the fuel which assumes the latent heat of vapourization of water in the reaction products is not recovered. It can be calculated by

$$\begin{aligned} (NCV)^0 &= -\text{Enthalpy of combustion} \\ &= - \left[\sum_P n_P \cdot \bar{h}_{d,P}^0 - \sum_R n_R \cdot \bar{h}_{d,R}^0 \right] \\ &= - \left[(n_{CO_2,P} \cdot \bar{h}_{d,CO_2}^0 + n_{H_2O,P} \cdot \bar{h}_{d,H_2O}^0 + n_{N_2,P} \cdot \bar{h}_{d,N_2}^0 \right. \\ &\quad \left. + n_{O_2,P} \cdot \bar{h}_{d,O_2}^0 + n_{SO_2,P} \cdot \bar{h}_{d,SO_2}^0) \right. \\ &\quad \left. - (n_{C,f} \cdot \bar{h}_{d,C}^0 + n_{H_2,f} \cdot \bar{h}_{d,H_2}^0 \right. \\ &\quad \left. + (n_{N_2,f} + n_{N_2,Air}) \cdot \bar{h}_{d,N_2}^0 + n_{S,f} \cdot \bar{h}_{d,S}^0 \right. \\ &\quad \left. + (n_{O_2,f} + n_{O_2,Air}) \cdot \bar{h}_{d,O_2}^0 + n_{H_2O,f} \cdot \bar{h}_{d,H_2O}^0) \right] \end{aligned} \tag{11}$$

Values of standard molar specific enthalpy of devaluation (\bar{h}_d^0) for various substances are given in Table 1. These values have been obtained from [5].

Table 1 Standard molar specific enthalpy of devaluation (\bar{h}_d^0) for various substances (source—Ref. [5])

Substance	State	$\bar{h}_d^0/\text{kJ kmol}^{-1}$
Argon (Ar)	Gas	0
Carbon (C)	Solid	393,780
Carbon dioxide (CO ₂)	Gas	0
Methane (CH ₄)	Gas	802,320
Ethane (C ₂ H ₆)	Gas	1,428,780
Propane (C ₃ H ₈)	Gas	2,045,380
Butane (C ₄ H ₁₀)	Gas	2,658,830
Hydrogen (H ₂)	Gas	242,000
Nitrogen (N ₂)	Gas	0
Oxygen (O ₂)	Gas	0
Sulphur (S)	Solid	724,580
Sulphur dioxide (SO ₂)	Gas	427,480
Water (H ₂ O)	Liquid	–44,030
Water (H ₂ O)	Gas	0

Chemical exergy of fuel

The ratio of standard specific chemical exergy to the net calorific value for solid fossil fuels without moisture content is given by [5]

$$\begin{aligned} \varphi_{dry} &= 1.0437 + 0.1882 \frac{m_{H_2,f}}{m_{C,f}} + 0.0610 \frac{m_{O_2,f}}{m_{C,f}} \\ &\quad + 0.0404 \frac{m_{N_2,f}}{m_{C,f}} \end{aligned} \tag{12}$$

For moist solid industrial fossil fuels containing sulphur, the standard chemical exergy is given by [5]

$$\psi_{Ch}^0 (\text{kJ kg}^{-1}) = \left[(NCV)^0 + 2442w \right] \varphi_{dry} + 9417 \cdot \left(\frac{m_{S,f}}{100} \right) \tag{13}$$

Estimation of standard chemical exergy of fuel oils

Ultimate analysis

Let the ultimate analysis of the fuel oil be as follows:

Carbon, $m_{C,f}\%$; Hydrogen, $m_{H_2,f}\%$; Sulphur, $m_{S,f}\%$;
 Nitrogen, $m_{N_2,f}\%$; Oxygen, $m_{O_2,f}\%$ and Ash, $m_{Ash,f}\%$

Molar composition per 100 kg of fuel, combustion equations for the combustible elements, molar composition of the products for complete combustion of fuel and net calorific value of fuel may be found using Eqs. (1) to (11) and the procedure given in Sect. 2 above.

Chemical exergy of fuel oil

The ratio of standard specific chemical exergy to the net calorific value for liquid fuels without moisture content is given by [5]

$$\varphi = 1.0401 + 0.1728 \frac{m_{H_2,f}}{m_{C,f}} + 0.0432 \frac{m_{O_2,f}}{m_{C,f}} + 0.2169 \frac{m_{S,f}}{m_{C,f}} \left(1 - 2.0628 \frac{m_{H_2,f}}{m_{C,f}} \right) \quad (14)$$

$$\text{Now, } \frac{\psi_{Ch,f}^0}{(\text{NCV})^0} = \varphi \quad (15)$$

$$\therefore \psi_{Ch,f}^0 = \varphi \cdot (\text{NCV})^0 \quad (16)$$

Estimation of standard chemical exergy of natural gas

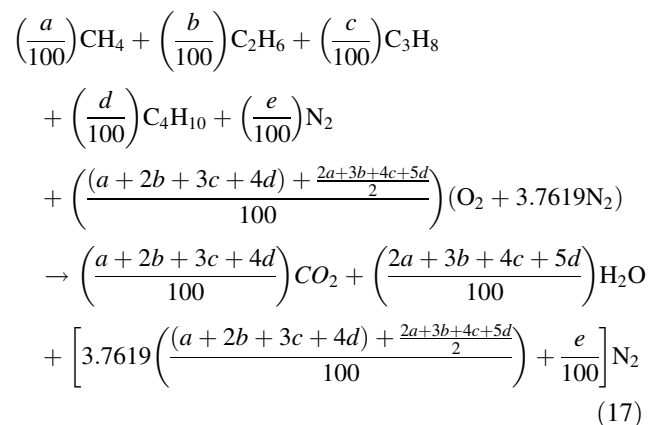
Volumetric analysis

Assuming the following volumetric analysis of the natural gas

$$\text{CH}_4 = a\%, \text{C}_2\text{H}_6 = b\%, \text{C}_3\text{H}_8 = c\%, \\ \text{C}_4\text{H}_{10} = d\% \text{ and } \text{N}_2 = e\%$$

Combustion equation for the fuel

The combustion equation for complete combustion of 1 kmol of natural gas of above composition can be written as



Standard molar specific chemical exergy of fuel

The general expression for standard molar specific chemical exergy of a gaseous fuel is

$$n_{\text{fuel}} \cdot \bar{\psi}_{Ch,\text{fuel}}^0 = -\Delta G^0 + \sum_{\text{P}} n_{\text{P}} \cdot \bar{\psi}_{Ch,\text{P}}^0 - \sum_{\text{R}} n_{\text{R}} \cdot \bar{\psi}_{Ch,\text{R}}^0, \quad (18)$$

where R stands for co-reactants and P stands for products.

$$\begin{aligned} \Delta G^0 &= \text{Change in Standard Gibbs function, kJ} \\ &= \Delta H^0 - T^0 \Delta S^0 \end{aligned} \quad (19)$$

$$\begin{aligned} &= \left(\sum_{\text{P}} n_{\text{P}} \cdot \bar{h}_{f,\text{P}}^0 - \sum_{\text{R}} n_{\text{R}} \cdot \bar{h}_{f,\text{R}}^0 \right) \\ &\quad - T^0 \left(\sum_{\text{P}} n_{\text{P}} \cdot \bar{s}_{\text{P}}^0 - \sum_{\text{R}} n_{\text{R}} \cdot \bar{s}_{\text{R}}^0 \right) \end{aligned} \quad (20)$$

The number of kmols of the components of the reactants and the products can be taken from the combustion Eq. (17) and used in the above equations. The values of the standard molar specific enthalpy of devaluation (\bar{h}_d^0) and the standard molar specific chemical exergy of the components of the reactants and the products can be taken from [5].

Results and discussion

The chemical exergy of some solid, liquid and gaseous fuels of standard composition can be obtained from the tables of standard chemical exergy. However, many such fuels have different composition and are multicomponent mixtures of very complicated compounds. Therefore, a proper methodology for the calculation of the exact chemical exergy of such fuels is to be followed.

In this study, some fossil fuels such as coal, heavy fuel oil and natural gas were considered for the calculation of chemical exergy. Tables 2, 3 and 4 show the ultimate analysis of the samples of some such fuels used in this study. Data of the standard enthalpy of devaluation, absolute entropy and the standard molar chemical exergy for various substances have been used in the calculations. These values have been taken from [5]. The calculated values of the standard chemical exergies of the considered fuels have also been presented in Tables 2, 3 and 4.

The results of the calculations indicate that the chemical composition of the fuel greatly influences the value of its

Table 2 Ultimate analysis of various samples of bituminous coal and calculated values of their chemical exergy

Coal sample	C/ %	H ₂ / %	O ₂ / %	N ₂ / %	S/ %	H ₂ O/ %	Ash/ %	$\psi_{Ch,f}^0/\text{kJ kg}^{-1}$
1	48.6	3.5	12	0.7	0.5	28.9	5.8	2.1699×10^4
2	61	4	3	2	1	4.5	24.5	2.6490×10^4
3	71.6	4.8	6.3	1.3	3.4	3.5	9.1	3.1715×10^4
4	73.4	5	6	1.5	3	3.5	7.6	3.2518×10^4
5	75	5.2	7	2	1	1	8.8	3.2982×10^4
6	78.2	5.5	10	1.5	0.6	1	3.2	3.4468×10^4

Table 3 Ultimate analysis of various samples of fuel oils, hydrogen–carbon ratio and calculated values of their chemical exergy

Oil sample	C/%	H ₂ /%	O ₂ /%	N ₂ /%	S/%	Ash/%	Hydrogen–carbon ratio	$\psi_{\text{Ch},f}^0/\text{kJ kg}^{-1}$
Crude oil	90	3.3	3	0.8	0.9	2	0.0367	3.5224×10^4
Heavy fuel oil 1	84	10	1.6	1.2	3.15	0.05	0.1190	4.2529×10^4
Heavy fuel oil 2	83.9	10.15	1.2	1.15	3.56	0.04	0.1210	4.2763×10^4
Heavy fuel oil 3	83.7	12.7	1.2	1.7	0.7	0	0.1517	4.5666×10^4
Heavy fuel oil 4	86.1	13.2	0	0	0.6	0.1	0.1588	4.6130×10^4

Table 4 Volumetric composition of various samples of natural gas and calculated values of their chemical exergy

Natural gas sample	CH ₄ /%	C ₂ H ₆ /%	C ₃ H ₈ /%	C ₄ H ₁₀ /%	N ₂ /%	$\bar{\psi}_{\text{Ch},f}^0/\text{kJ kmol}^{-1}$
1	93.9	3.6	1.2	1.3	0	9.0207×10^5
2	77.4	11.7	8.5	1.3	1.1	1.0436×10^6
3	67.4	16.8	15.8	0	0	1.1578×10^6
4	60.1	14.8	13.4	4.2	7.5	1.1331×10^6
5	54.3	16.3	16.2	7.4	5.8	1.2579×10^6

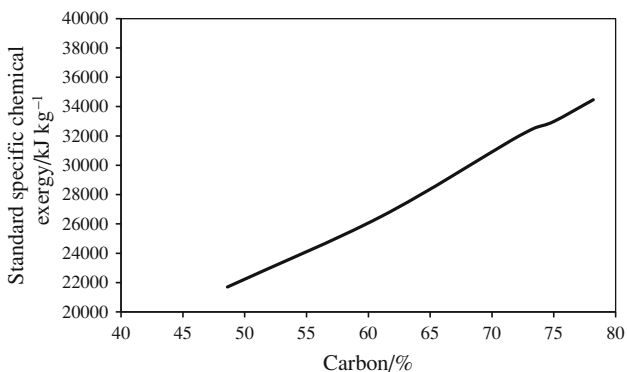


Fig. 1 Variation of standard specific chemical exergy of coal with its carbon content

chemical exergy. The exergy values are closely related to the carbon and hydrogen contents of these fuels. The variation of chemical exergy of coal with the variation in chemical composition has been presented in Table 2 and Figs. 1 and 2. Figure 1 shows the variation of chemical exergy with carbon content of coal while Fig. 2 shows the variation of chemical exergy with hydrogen content. It is clear from these results that in case of coal in which carbon and hydrogen are not combined together, an increase in both carbon and hydrogen contents increases its chemical exergy value. As indicated in Table 3, in case of heavy fuel oils, a decrease in carbon content and an increase in hydrogen content of the fuel increase its chemical exergy. This is because in fuel oils which are essentially hydrocarbons, hydrogen and carbon are combined together as a compound. So, in these fuels, hydrogen–carbon ratio is the

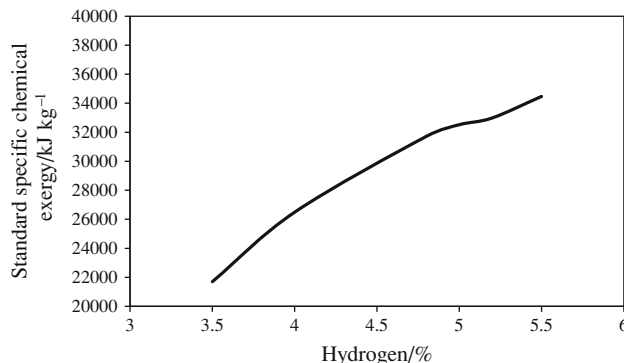


Fig. 2 Variation of standard specific chemical exergy of coal with its hydrogen content

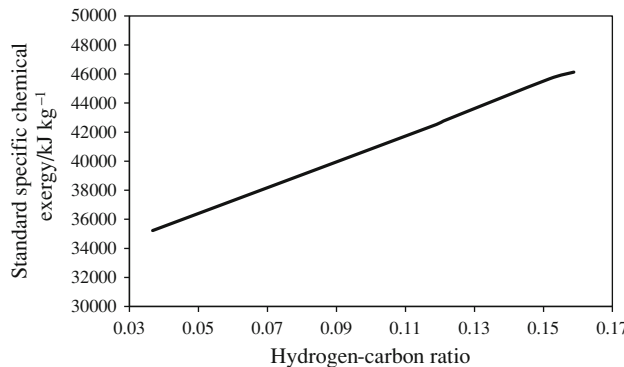


Fig. 3 Variation of standard specific chemical exergy of fuel oil with its hydrogen–carbon ratio

most influencing parameter in the chemical exergy. The variation of chemical exergy with hydrogen–carbon ratio is shown in Fig. 3. This variation is almost linear. It is clear that an increase in hydrogen–carbon ratio in the fuel increases its chemical exergy. As indicated in Table 4 that in case of natural gases which are essentially a mixture of hydrocarbon gases such as methane, ethane, propane and butane and incombustible gases such as nitrogen, a decrease in lighter hydrocarbon gas contents and an increase in heavier hydrocarbon gas contents tend to increase the chemical exergy value of the mixture. High moisture and/or ash contents also tend to lower the value of the chemical exergy.

Conclusions

Fossil energy resources are being consumed more and more owing to increasing energy demand of developed and developing countries. Therefore, wisely usage of resources and improving the efficiency of power generation systems is becoming a subject of increasing interest to all sectors of society in the industrialised nations. The designers and energy experts should consider the second law, or exergy in designing thermal systems. Exergy analysis enables one to evaluate quantitatively the causes of thermodynamic imperfections of thermal and chemical processes. Poor thermodynamic performance is the results of exergy losses in combustion and heat-transfer processes. In this paper, the methods for the calculation of chemical exergies of coal, heavy fuel oil and natural gas that are used as fuel in conventional thermal power plants have been presented. These methods and the calculated exergy values of the fuels considered will be useful to the analysts and researchers not only in conducting the second law analysis of the existing fossil fuel-fired power plants but also help in designing new energy-efficient plants. Use of fuels having high value of chemical exergy will improve the efficiency of these plants.

References

1. Keenan JH. Thermodynamics. New York: Wiley; 1940.
2. Rezac P, Metghalchi H. A brief note on the historical evolution and present state of exergy analysis. *Int J Exergy*. 2004;1:426–37.
3. Gaggioli RA, Petit PJ. Use the second law first. *Chemtech*. 1977;7:496–506.
4. Ahern JE. The exergy method of energy system analysis. New York: Wiley; 1980.
5. Kotas TJ. The exergy method of thermal plant analysis. London: Butterworths; 1985.
6. Szargut J, Morris DR, Steward FR. Exergy analysis of thermal, chemical, and metallurgical processes. New York: Hemisphere; 1988.
7. Moran MJ, Sciubba E. Exergy analysis: principles and practice. *ASME J Eng Gas Turbines Power*. 1994;116:285–90.
8. Moran MJ, Shapiro HN. Fundamentals of engineering thermodynamics. New York: Wiley; 2003.
9. Szargut J. Exergy method: technical and ecological applications. Southampton: WIT Press; 2005.
10. Dincer I, Rosen MA. Exergy: energy, environment and sustainable development. Oxford: Elsevier; 2007.
11. Dincer I, Al-Muslim H. Thermodynamic analysis of reheat cycle steam power plants. *Int J Energy Res*. 2001;25:727–39.
12. Aljundi IH. Energy and exergy analysis of a steam power plant in Jordan. *Appl Therm Eng*. 2009;29:324–8.
13. Singh OK, Kaushik SC. Variables influencing the exergy based performance of a steam power plant. *Int J Green Energy*. 2013; 10:257–84.
14. Badran O. Gas-turbine performance improvements. *Appl Energy*. 1999;64:263–73.
15. Khaliq A, Kaushik SC. Second-law based thermodynamic analysis of Brayton/Rankine combined power cycle with reheat. *Appl Energy*. 2004;78:179–97.
16. Tyagi SK, Chen J, Kaushik SC. Optimal criteria based on the ecological function of an irreversible intercooled regenerative modified Brayton cycle. *Int J Exergy*. 2005;2:90–107.
17. Kalina AI. Combined cycle system with novel bottoming cycle. *ASME J Eng Gas Turbines Power*. 1984;106:737–42.
18. El-Sayed YM, Tribus M. A theoretical comparison of the Rankine and Kalina cycles. *ASME Adv Energy Syst Div*. 1985; 1:97–102.
19. Kaushik SC, Singh OK. Evolution of Kalina cycle for efficient power generation: a review. *Int J Green Energy Environ*. 2011;1:30–46.
20. Singh OK, Kaushik SC. Energy and exergy analysis and optimization of Kalina cycle coupled with a coal fired steam power plant. *Appl Therm Eng*. 2013;51:787–800.
21. Zheng D, Chen B, Qi Y, Jin H. Thermodynamic analysis of a novel absorption power/cooling combined-cycle. *Appl Energy*. 2006;83:311–23.
22. Wang J, Dai Y, Gao L. Exergy analyses and parametric optimizations for different cogeneration power plants in cement industry. *Appl Energy*. 2009;86:941–8.
23. Sussman MV. Steady-flow availability and the standard chemical availability. *Energy*. 1980;5:793–802.
24. Kameyama H, Yoshida K, Yamauchi S, Fueki K. Evaluation of reference exergies for the elements. *Appl Energy*. 1980;11: 69–83.
25. Morris DR, Szargut J. Standard chemical exergy of some elements and compounds on the planet Earth. *Energy*. 1986;11(8): 733–55.
26. Szargut J. Chemical exergies of the elements. *Appl Energy*. 1989;32:269–86.
27. Rivero R, Garfias M. Standard chemical exergy of elements updated. *Energy*. 2006;31:3310–32.
28. 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.