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Carbon dioxide reforming of methane with a free energy minimization approach

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Abstract−Carbon dioxide reforming of methane to syngas is one of the primary technologies of the new poly-generation energy system on the basis of gasification gas and coke oven gas. A free energy minimization is applied to study the influence of operating parameters (temperature, pressure and methane-to-carbon dioxide ratio) on methane conversion, products distribution, and energy coupling between methane oxidation and carbon dioxide reforming methane. The results show that the methane conversion increases with temperature and decreases with pressure. When the methane-to-carbon dioxide ratio increases, the methane conversion drops but the H_2/CO ratio increases. By the introduction of oxygen, an energy balance in the process of the carbon dioxide reforming methane and oxidation can be realized, and the CO/H_2 ratio can be adjusted as well without water-gas shift reaction for Fischer-Tropsch or methanol synthesis.

Key words: Coal Poly-generation, Carbon Dioxide Reforming of Methane, Free Energy Minimization, Thermodynamics Equilibrium

INTRODUCTION

Synthesis gas is a versatile feedstock for methanol, Fischer-Tropsch syntheses and dimethyl ether (DME) [1]. The traditional technology to produce synthetic-gas is steam reforming [2,3]. This process has dominated synthetic-gas production for many years. Although steam reforming is continuously enhanced by improving the catalysts, operation conditions and heat transfer to achieve better performance, an unavoidable drawback of this process is that the H_2/CO ratio of 3 : 1 obtained by steam reforming of methane is higher than that needed for Fischer-Tropsch or methanol synthesis [4].

The reforming reaction of methane with carbon dioxide to synthesis gas is a very attractive route for chemicals production. This is because an H_2/CO ratio of 1 : 1 is obtained from the reforming reaction. Considerable research efforts over the past few years have been directed towards the development of active and selective catalysts for the CO_2 reforming of CH_4 [5,6]. The other fact which cannot be ignored is that a mass of coke has been consumed in the world but abundant CH_4 in the coke oven gases has not been employed effectively, which contributes to the waste of resources. In addition, to meet the need of the Fischer-Tropsch or methanol synthesis, a water-gas shift reaction is necessary in the current poly-generation system on the individual basis of gas, which results in technological complexity and more emissions of CO_2.

Against this background the new poly-generation system on the basis of gasification gas and coke oven gas has been designed, as is shown in Fig. 1. In the new poly-generation, reforming of methane from coke oven gas is performed, with CO_2 from gasification gas (for example from spout-fluid bed coal gasifiers [7-9]). A decrease of two greenhouse gases and simultaneous production of a synthesis gas can be achieved. So it is of environmental and economic significance.

Numerous studies on the kinetics, catalysts activation and carbon deposition in the reforming process have largely been reported [10-12]. But studies on the reforming reactor system are scanty at best.

A free energy minimization approach is applied widely in the simulations of mass balance, energy balance and phase balance. Li et al. developed a non-stoichiometric equilibrium model based on free energy minimization to predict the performance of a circulating fluidized bed coal gasifier [13]. Zhang et al. studied the phase balance of Li/SF-6 gas-liquid fuel combustion on free energy minimization [14]. By means of the approach, Li et al. modeled and predicted the occurrence and migration mechanism of alkali metal during the coal-fired process [15].

In the present work, free energy minimization is applied to study the influence of operating parameters (temperature, pressure and methane-to -carbon dioxide ratio) on the methane conversion, products distribution, and energy coupling between methane oxidation and carbon dioxide reforming methane. The results will be regarded as the theory basis for designing the reforming reactor.

POLY-GENERATION ENERGY SYSTEM AND THE MODEL

1. Poly-generation Energy System on the Basis of Gasification Gas and Coke Oven Gas

A schematic diagram of the new poly-generation energy system on the basis of gasification gas and coke oven gas appears in Fig. 1. Coal may be classified into two types according to the components and characters of coal. One is gasification coal applied to produce gasification gas. The other is coke coal to produce coke oven gas. The mixture, which consists of gasification coal, steam, and O_2 from an air separator, is pressurized and heated to produce gasification gas with partial gasification. The pressure and temperature are adjusted to about 25 atm and 1,373 K, respectively. The species of gas-

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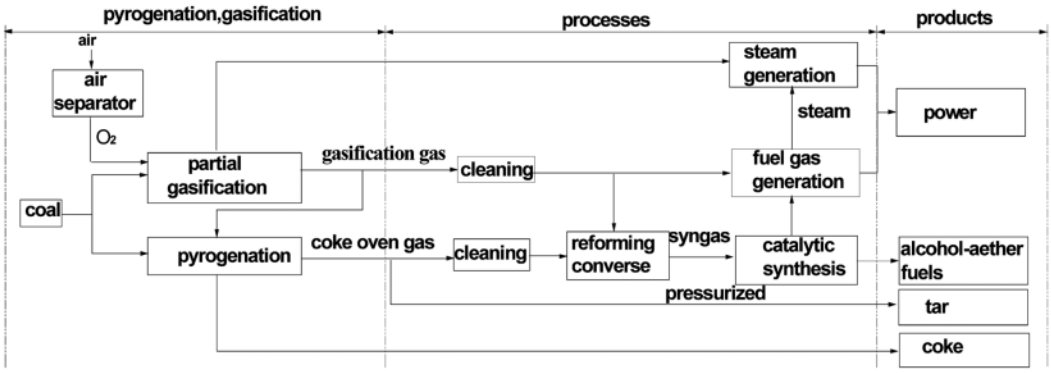

Fig. 1. A schematic diagram of the new poly-generation energy system.

ification gas involve mainly CO (35%), H_2 (40%) and CO_2 (20%). The heat needed for the gasification and heating is supplied by coal partial combustion. High pressure steam produced is used to generate electricity. After cleaning and desulfurization, the majority of the gasification gas enters a gas turbine to generate power, and the residual as the fuels of pyrogenation process and chemical synthesis feedstock. When heated by partial gasification gas combustion, coke coal is decomposed to produce coke, tar and coke oven gas. The primary species of coke oven gas involve CO (5-8%), H_2 (55-60%) and CH_4 (23-27%). Cleaning measures are taken to eliminate tar and sulfur of the coke oven gas. According to the proportion required, the pressurized coke oven gas (>25 atm) is mixed with gasification gas to enter a reforming reactor where carbon dioxide reforming of methane occurs. CO and H_2 from the reforming reactor are pressurized to meet the requirement of synthesizing alcohol fuels. The release gas enters the gas turbine to generate electricity.

2. The Model of Reforming Reaction

To simplify the problem, only 21 species are considered: C(g), CH, CH_2, CH_3, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, H, H_2, O, O_2, CO, CO_2, OH, H_2O, H_2O_2, HCO, HO_2, C(s). The species involve C, H and O. The gaseous species form a homogeneous phase, while C is considered to be single-specie phase. The free energy minimization of the reactor system is the criterion for judging the thermodynamic equilibrium of the reaction.

The RAND algorithm has been used because it can reduce the working matrix of the problem to (K+Π) by (K+Π), where K and Π represent the number of elements and phases, respectively. The mathematical aspects of this algorithm are well documented [16-18]. The algorithm allows the change in moles of a species in the m-th iteration to be expressed explicitly as

$$\delta n_i^{(m)} = n_i^{(m)}\left(\sum_{k=1}^{K} a_{ik}\psi_k + u_\alpha - \frac{\mu_i^{(m)}}{RT}\right) \quad \text{for multi-species phases;}$$

$$\delta n_i^{(m)} = u_\alpha n_i^{(m)} \quad \text{for single-species phases:}$$

$$(i=1, 2, \ldots, N;\ k=1, 2, \ldots, K;\ \alpha=1, 2, \ldots, \Pi) \tag{1}$$

N designates the total number of species; $n_i^{(m)}$ denotes the moles of species i in the m-th iteration; a_{ik} is the coefficient in the species-element matrix. ψ_k is a function related to the Lagrange multiplier; u_α is the phase split of δn_i, defined as

$$u_\alpha = \sum_{i=1}^{N} \delta n_{i\alpha}^{(m)} / n_i^{(m)} = \delta n_{t\alpha}^{(m)} / n_t^{(m)} \tag{2}$$

Where the subscript t means total; a refers to the phase to which a species belongs.

The set of simultaneous algebraic equations includes K linear equations regarding element abundance:

$$\sum_{k=1}^{K}\sum_{i=1}^{N} a_{ik} a_{ij} n_i^{(m)} \psi_k + \sum_{\alpha=1}^{\Pi} b_{j\alpha}^{(m)} u_\alpha = \sum_{i=1}^{N} a_{ij} n_k^{(m)} \frac{\mu_i^{(m)}}{RT} + b_k - b_k^{(m)} \quad (j=1, 2, \ldots, K) \tag{3}$$

The Π supplementary equations for different phases are:

$$\sum_{k=1}^{K} b_{k\alpha}^{(m)} \psi_k - n_{z\alpha} u_\alpha = \sum_{i=1}^{N} n_{i\alpha}^{(m)} \frac{\mu_{i\alpha}^{(m)}}{RT} \quad (\alpha=1, 2, \ldots, \Pi) \tag{4}$$

The initial element abundance vector b is calculated from the feedstock. The k-th element of the b-vector at the m-th iteration is

$$b_k^{(m)} = \sum_{i=1}^{N} a_{ik} n_i^{(m)} \tag{5}$$

Mass balance constraints are imposed at every iteration during solution of Eqs. (1)-(5). The difference $(b_k - b_k^{(m)})$ is added to the right-hand side of Eq. (3) to eliminate error accumulation during the iteration process [16].

The enthalpy balance of the process can be written as

$$\sum_{l}^{L} m_l \Delta H_{f,feed,298}^0 + \sum_{l}^{L} m_l H_{feed}(T_{feed,l}) = \sum_{i}^{N} n_i \Delta H_{f,prod,298}^0 + \sum_{i}^{N} n_i H_{prod}(T) + Q + \Delta H(T). \quad (l=1, 2, \ldots, L) \tag{6}$$

for any temperature T. The two terms on the left-hand side are the total heat of formation and the total enthalpy of all feed streams, respectively. The first two terms on the right-hand side represent the total heat of formation and total enthalpy of all product species, respectively. The heat removed by heat transfer surfaces is denoted as Q. The final term, ΔH(T), denotes the system net enthalpy accumulation as a function of temperature. The system is adiabatic if Q=0. If ΔH(T) is positive the system adjusts its equilibrium temperature to a higher level.

The chemical potential of species i is:

$$u_i = RT\left[\ln\left(\frac{\phi_i P}{P_0}\right) + \ln(X_i) + G_i^0(T, P_0)\right] \tag{7}$$

Gibbs free energy function G of the system is expressed as a linear combination of chemical potential of each component

$$G=\sum_{i=1}^{K} n_i u_i \tag{8}$$

The bounds on variables are:

$$0 \le n_i \le n_{iT} \tag{9}$$

Under given temperature and pressure, at equilibrium G should be global minimum with n_i satisfying elemental mass balance, enthalpy balance and non-negativity requirements.

The main reaction in the reforming process

$$CH_4+CO_2=2CO+2H_2 \qquad \Delta H=247.1\ \text{kJ/mol} \tag{10}$$

Possibly the secondary reactions [19,20]

$$CO+3H_2=CH_4+H_2O(g) \qquad \Delta H=-205\ \text{kJ/mol} \tag{11}$$

$$CO+3H_2O(g)=CO_2+H_2 \qquad \Delta H=-41.1\ \text{kJ/mol} \tag{12}$$

$$CH_4=C+2H_2 \qquad \Delta H=86.3\ \text{kJ/mol} \tag{13}$$

$$C+CO_2=2CO \qquad \Delta H=159.9\ \text{kJ/mol} \tag{14}$$

$$C+H_2O(g)=CO+H_2 \qquad \Delta H=118.7\ \text{kJ/mol} \tag{15}$$

$$C+2H_2O(g)=2H_2+CO_2 \qquad \Delta H=-89.8\ \text{kJ/mol} \tag{16}$$

$$C+O_2=CO_2 \qquad \Delta H=-123.1\ \text{kJ/mol} \tag{17}$$

$$H_2+0.5O_2=H_2O(g) \qquad \Delta H=-241.2\ \text{kJ/mol} \tag{18}$$

By the introduction of oxygen, firstly the oxidation reaction of CH_4 occurs. In the process of oxidation, the O_2 has been consumed completely. CO_2 and $H_2O(g)$ reforming of the residual CH_4 occur to produce H_2 and CO [21]. The oxidation reaction can be written as

$$CH_4+2O_2 \xrightarrow{\text{completely oxidated}} 2H_2O(g)+CO_2 \qquad \Delta H=-241.2\ \text{kJ/mol} \tag{19}$$

ΔH of Eqs. (10)-(19) denotes the heat of reactions by the net enthalpy accumulation at 1 atm pressure and 298 K. If ΔH is positive, it shows the reaction is endothermic; if negative, the reaction is exothermic.

RESULTS AND DISCUSSIONS

1. The Effect of the Reactor Operating Temperature

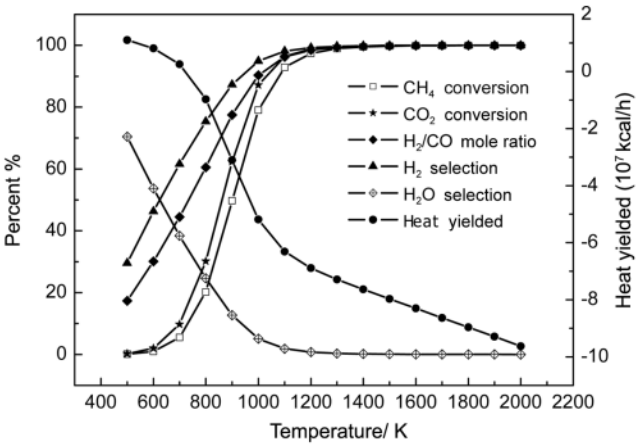

Fig. 2. Conversions etc. as a function of reaction temperature.

The temperature ranges from 500 to 2,000 K. The reactants, CH_4 and CO_2, are fed with 1000 kmol/h, respectively. The effect of operating temperature on the equilibrium state is shown in Fig. 2 for a gas pressure of 1 atm. Observed CO_2 conversions are consistently higher than CH_4 conversions. As the conversions of CH_4 and CO_2 increase with temperature, the ratio H_2/CO and H_2 selectivity rise as well. But steam selectivity decreases with temperature, where H_2 selectivity is defined as the ratio of H in H_2 to H in converted CH_4. Steam selectivity is defined as the ratio of H in steam to H in converted CH_4.

That may be the contributions of the CO_2 reforming reaction and the reverse water-gas shift reaction. Partial H_2 produced are consumed with the reverse reactions (12) and (16). So the ratio of H_2/CO is below 1 but it rises with temperature. With increasing temperature up to about 1,200 K, it is close to 1 and the conversions of reactants can be at most 100%. The heat needed for the system grows as the temperature increases.

Fig. 3 shows the effect of system temperature on the predicted amount of steam under the reaction conditions as Fig. 2. Below 900 K, the amount of steam strongly increases with temperature. However, it decreases for temperatures of 900 K and above.

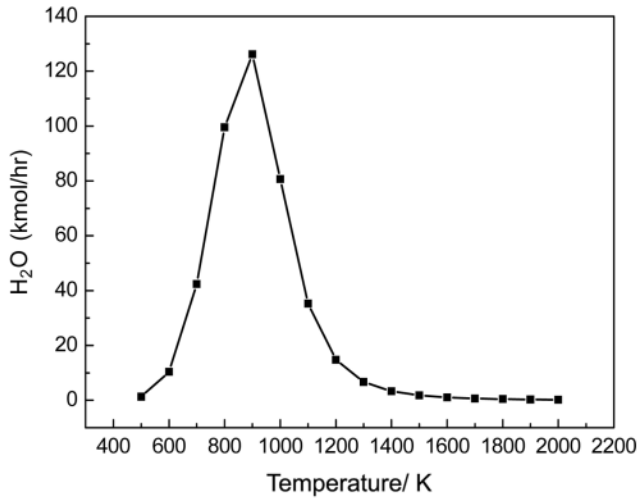

Fig. 3. Steam yielded as a function of reaction temperature.

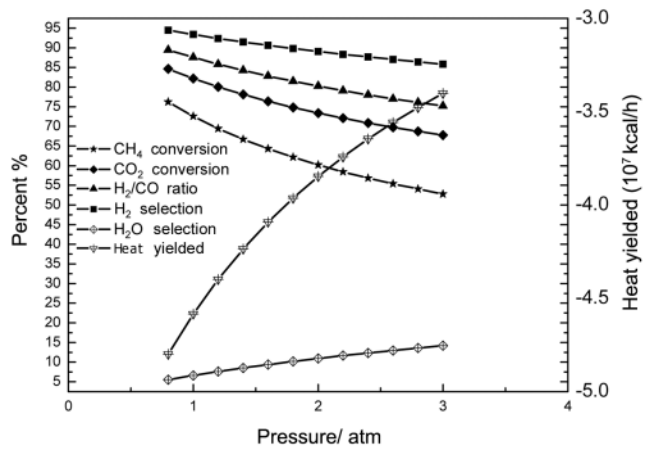

Fig. 4. Conversions etc. as a function of reaction pressure.

The carbon deposition occurs in the reforming process due mainly to methane and carbon dioxide decomposition. But it's little along as carbon elimination reactions (Eq. (14) etc.) occur.

2. The Effect of the Reactor Operating Pressure

Reactor pressure ranges from 0.8 to 3 atm. The reactants, CH_4 and CO_2, are fed with 1000 kmol/h, respectively. The effect of operating pressure on the equilibrium state is shown in Fig. 4 for temperature of 973 K. The reactant conversions, H_2/CO ratio and H_2 selectivity decrease with pressure. A decreasing in the heat needed was observed too. Whereas, the steam selectivity increases with pressure. At a gas pressure of 0.8 atm, about 75% of CH_4 is converted and the heat needed for the system is close to 4.8×10^7 kcal. When the pressure up to 3 atm, the heat needed is 3.5×10^7 kcal but the CH_4 conversion is only 52%. So a higher pressure is not suitable for CO_2 reforming reaction.

3. The Effect of the CH_4/CO_2 Ratio

The effect of the CH_4/CO_2 ratio on the system under conditions of 1 atmosphere pressure and 973 K of temperature is presented in Fig. 5. It shows that the CH_4 conversion and steam selectivity are decreased by the increasing CH_4/CO_2 ratio. On the other hand, the CO_2 conversion and H_2 selectivity are increased. At a CH_4/CO_2 ratio of 2 and above, there is little steam to be produced. The H_2/CO ratio was close to 1 gradually with the CH_4/CO_2 ratio.

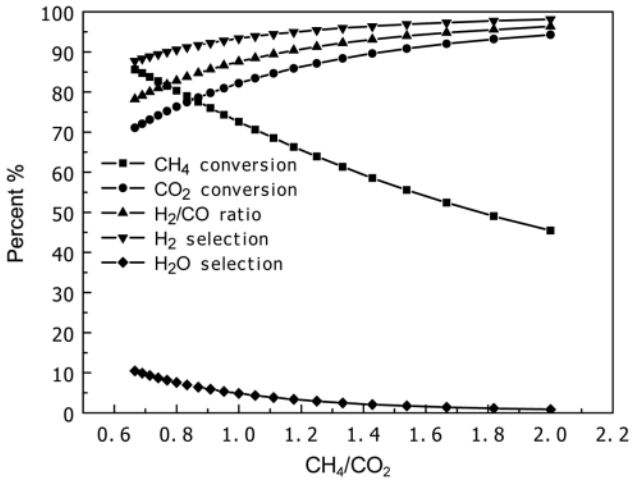

Fig. 5. Conversions etc. as a function of CH_4/CO_2 ratio.

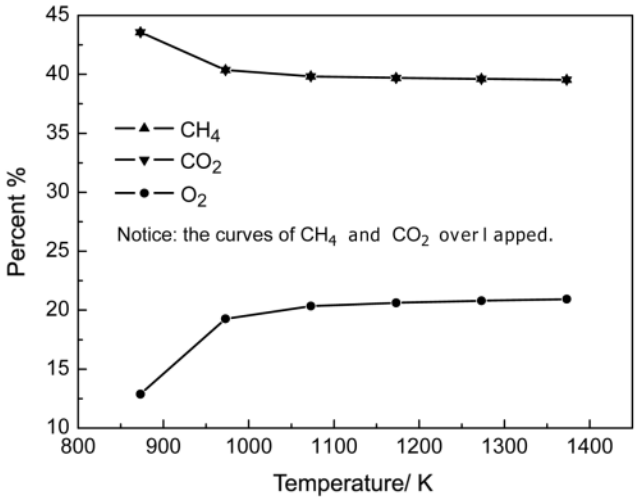

Fig. 6. Variation of feedstock gas composition with temperature.

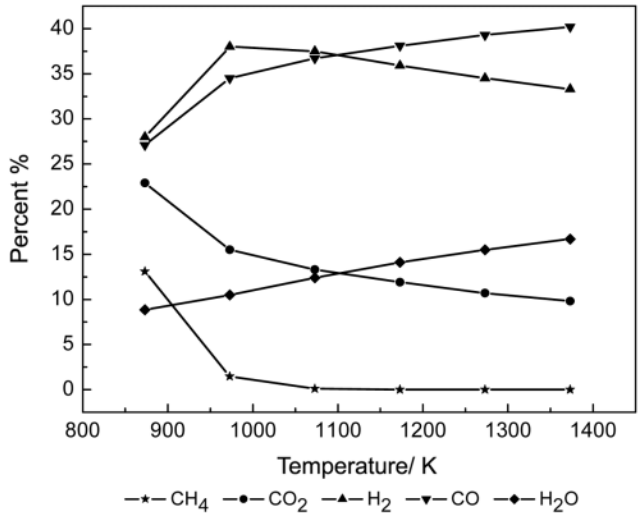

Fig. 7. Variation of equilibrium gas composition with temperature.

4. The Effect of O_2

By the introduction of oxygen, coupling between the carbon dioxide reforming of methane and methane oxidation was studied. It is assumed that the energy balance can be realized when the exothermic oxidation reaction is combined with the endothermic reforming process. Fig. 6 shows mole fractions of the feedstock for a gas pressure of 1 atm. The equilibrium composition is shown in Fig. 7. It appears from Fig. 6 that the fractions of CH_4 and CO_2 strongly decrease and O_2 increases with increasing temperature up to 970 K. At a temperature of about 970 K, the fraction of H_2 reaches its maximum in the equilibrium gas mixture. Above 970 K, the variation of feedstock gas composition with temperature becomes slight. Again, conversion of CH_4 is close to 100%, which is higher than CO_2, and the increment of O_2 is mainly to maintain the higher temperature in the reforming reactor. Below 1130 K, the amount of H_2 is higher than that of CO. The molar ratio of CO to H_2 can be adjusted well to meet the requirement of later chemical synthesis. The whole system may avoid the temperature rising rapidly compared with CH_4 partial oxidation to syngas [22].

Fig. 7 also shows that the fractions of H_2 and CO_2 decrease while CO and H_2O increase. This is attributed to the reverse reaction (11).

CONCLUSIONS

1. The effect of temperature and pressure on the reforming reaction is remarkable. The conversions of CH_4 and CO_2 increase with temperature but decrease with pressure. Reforming of methane can never be optimal based on thermodynamic equilibrium at higher pressure.

2. At about 900 K H_2O is close to its maximum value, which influences the H_2 selection. So the reaction temperature is not feasibly controlled at 900 K.

3. By the introduction of oxygen, an energy balance can be realized when the exothermic oxidation reaction is combined with the

endothermic reforming process, and the molar ratio of CO to H_2 can be adjusted as well to adapt chemical synthesis. Moreover, local temperature rising suddenly in methane partial oxidation reaction can be avoided.

4. Results will be the reference to design and optimize the reactors of methane reforming in the poly-generation energy system on the basis of gasification gas and coke oven gas.

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NOMENCLATURE

G_i^0 : standard-state Gibbs free energy of the i-th species [J/mol]
0 : initial
a_{ij} : coefficient in element species matrix representing species i containing element j
f : feed
H : enthalpy [KJ]
i : species index
j, k, l : component, element, feed stream indices
K : total number of elements considered
L : total number of feed streams considered
m : current number of iterations
m_l : mass of the l-th feed stream [kg]
N : total number of species considered
n : moles of a species [mol]
n_t : total moles in system [mol]
n_{za} : inert moles in phase a [mol]
P : pressure [N/m^2]
P_0 : standard-state pressure [N/m^2]
Q : heat transferred to environment per unit mass of fuel [kJ/kg]
R : ideal gas constant 8.314 [J/mol/K]
T : thermodynamic temperature [K]
u_α : phase split of differential change in total moles of the system
X_i : molar fraction of species i

Greek Letters

ΔH : change in system enthalpy [kJ/kg]
μ_i : chemical potential of species i [kJ/mol]
ψ_k : function related to Lagrange multiplier
ΔH_f^0 : heat of formation [kJ/mol]
ϕ_i : fugacity coefficient of species i
u_a : phase split of differential change in total moles of the system
α : a phase index
Π : total number of phases considered

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