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# Stoichiometric Approach to the Analysis of Coal Gasification Process

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## 1. Introduction

Coal is a solid fuel and less convenient for storage and transportation than petroleum and natural gas. In addition, it usually holds undesirable compounds containing S, N, and so on. Gasification converts coal into  $H_2$ , CO, and  $CH_4$  by the reaction with gasifying agents such as  $O_2$  and  $H_2O$ . There are three types of commercialized processes, 1) fixed bed gasifier: lump coal is gasified in a shaft reactor at  $900\sim 1000^\circ C$ , 2) fluidized bed gasifier: crashed coal is gasified in a fluidized reactor at around  $900^\circ C$ , and 3) entrained bed gasifier: pulverized coal is gasified by burner system at  $1350\sim 1600^\circ C$ . In order to improve the performance of  $500\sim 2000t/d$  plants, operating conditions should be appropriately determined and controlled based on the understanding of chemical reaction process that occurs in gasifier. It has been believed that coal supplied to gasifier is decomposed thermally to produce gases such as  $H_2$ , CO,  $CO_2$ ,  $H_2O$ , and  $CH_4$ , tar, and char. Tar and char react with  $O_2$  and  $H_2O$  supplied to form  $H_2$ , CO,  $CO_2$  and  $CH_4$ . However, it is quite difficult to understand gasification mechanism only based on the kinetics of above reactions.

An equilibrium constant has been often used to understand the composition of gasification products. It is, however, only available to the stable state, and therefore inapplicable to the analysis of transient composition of gases in operation, which is constantly fluctuating.

As mentioned above, the chemical process in a large scale gasifier cannot be perfectly explained by kinetics and equilibrium. Composition of gases produced by gasification is a very clear indicator of the chemical state in the gasifier. We propose a stoichiometric method to analyze the reaction process of coal gasification.

## 2. Derivation of chemical reaction formula

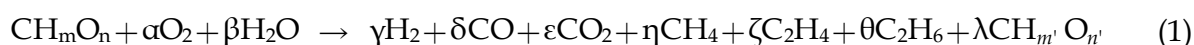
A gasification reaction is composed of various kinds of chemical processes such as pyrolysis of coal, decomposition of tar, oxidation of char, combustion of gas, shift reaction, and formation of various organic compounds. In order to elucidate the reaction process, the method to delve into the composition of gas for information on the reaction state in the reactor needs to be established. As has been mentioned, kinetic and equilibrium theories are not available for this purpose.

## 2.1 Molecular formula of coal

Coal scientists imagine a coal to be a complex of heterogeneous macromolecular compounds composed of aromatic rings, aliphatic chains, and various kinds of functional groups containing heteroatoms such as O, N, and S. One of the problems to express the reaction formula of gasification is how we express the molecular formula of coal. Even if a relatively accurate reaction formula could be obtained, it would not be available for investigation of practical analysis. Since the molecular structure of most of product is very simple, the chemical process may be discussed sufficiently based on the  $\text{CH}_m\text{O}_n$  regardless of the detailed structure of coal molecule.

## 2.2 Estimation of reaction formula

We express the gasification reaction by formula (1), where  $\text{CH}_m\text{O}_n$  and  $\text{CH}_{m'}\text{O}_{n'}$  are coal and tar respectively.



Equations concerning elemental balance for C, H and O for formula (1) are described as (2), (3) and (4) respectively.

$$1 = \delta + \varepsilon + \eta + 2\zeta + 2\theta + \lambda \quad (2)$$

$$m + 2\beta = 2\gamma + 4\eta + 4\zeta + 6\theta + m'\lambda \quad (3)$$

$$n + 2\alpha + \beta = \delta + 2\varepsilon + n'\lambda \quad (4)$$

Let the total moles of product gases in formula (1) be equal to  $\Sigma$ .

$$\Sigma = \gamma + \delta + \varepsilon + \eta + \zeta + \theta \quad (5)$$

When the concentrations of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$  (dry and  $\text{N}_2$  free) are represented by  $p$ ,  $q$ ,  $r$ ,  $s$ ,  $t$ , and  $u$  respectively, the mole number of each gases is described as follows.

$$\text{H}_2 \quad ; \quad \gamma = p \Sigma \quad (6)$$

$$\text{CO} \quad ; \quad \delta = q \Sigma \quad (7)$$

$$\text{CO}_2 \quad ; \quad \varepsilon = r \Sigma \quad (8)$$

$$\text{CH}_4 \quad ; \quad \eta = s \Sigma \quad (9)$$

$$\text{C}_2\text{H}_4 \quad ; \quad \zeta = t \Sigma \quad (10)$$

$$\text{C}_2\text{H}_6 \quad ; \quad \theta = u \Sigma \quad (11)$$

A sampling gas for analysis has usually been drawn out from the main stream of product gas, passed into cooler to remove condensable  $\text{H}_2\text{O}$  and tar, and then measured its volume by gas meter and analyzed its composition by various kinds of analyzer. Yield of tar has been evaluated as its moles per unit volume of gas produced. The molar yields of tar is presented by  $v$ ,  $\lambda$  in formula (1) is described as equation (12) that is written in the same form as that of equation (6) ~ (11).

$$\lambda = v \Sigma \quad (12)$$

Consequently, we obtain ten solutions,  $\alpha \sim \eta$  and  $\Sigma$ , mathematically because we could prepare eleven equations from (2) to (12).

Equation (2) is rewritten as (13) by employing (7) ~ (12).

$$1 = q \Sigma + r \Sigma + s \Sigma + 2t \Sigma + 2u \Sigma + v \Sigma \quad (13)$$

(13) is rearranged to equation (14).

$$\Sigma = \frac{1}{q + r + s + 2t + 2u + v} \quad (14)$$

Yields of gases and tar,  $\gamma \sim \lambda$  in (1) are expressed by equation (15) ~ (21).

$$\text{H}_2 \quad ; \quad \gamma = \frac{p}{q + r + s + 2t + 2u + v} \quad (15)$$

$$\text{CO} \quad ; \quad \delta = \frac{q}{q + r + s + 2t + 2u + v} \quad (16)$$

$$\text{CO}_2 \quad ; \quad \varepsilon = \frac{r}{q + r + s + 2t + 2u + v} \quad (17)$$

$$\text{CH}_4 \quad ; \quad \eta = \frac{s}{q + r + s + 2t + 2u + v} \quad (18)$$

$$\text{C}_2\text{H}_4 \quad ; \quad \zeta = \frac{t}{q + r + s + 2t + 2u + v} \quad (19)$$

$$\text{C}_2\text{H}_6 \quad ; \quad \theta = \frac{u}{q + r + s + 2t + 2u + v} \quad (20)$$

$$\text{Tar} \quad ; \quad \lambda = \frac{v}{q + r + s + 2t + 2u + v} \quad (21)$$

The expression for  $\beta$  in formula (1) is written from (3) as follows;

$$\beta = \gamma + 2\eta + 2\zeta + 3\theta + 0.5m'\lambda - 0.5m$$

When  $\gamma$ ,  $\eta$ ,  $\zeta$ ,  $\theta$ , and  $\lambda$  of above equation are substituted by the expression of (15), (18), (19), (20), and (21) respectively, equation (22) is obtained.

$$\text{H}_2\text{O} ; \beta = \frac{p + 2s + 2t + 3u + 0.5m'}{q + r + s + 2t + 2u + v} - 0.5m \quad (22)$$

Expression of  $\alpha$  is written by following equation from (4).

$$\alpha = \frac{\delta + 2\varepsilon + \beta + n'\lambda - n}{2}$$

When  $\delta$ ,  $\varepsilon$ ,  $\beta$ , and  $\lambda$  are substituted by (16), (17), (21), and (22) respectively, equation (23) is obtained.

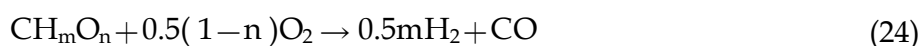
$$\alpha = \frac{(-p + q + 2r - 2s - 2t - 3u) - 0.5m'v + n'v}{2(q + r + s + 2t + 2u + v)} + 2.5m - 0.5n \quad (23)$$

### 3. Feature of this method

Since every equation used to evaluate  $\alpha \sim \lambda$  has been derived from (2), (3), and (4) without any arbitrary assumption and approximation, it may be applicable to any practical process. Since the left side of (1) is the reactant of gasification, and the right side is product, although (1) is written in the simplest form, it expresses exactly the material balance of gasification. Therefore, we can readily estimate the molar amounts of  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$  from  $\gamma$ ,  $\delta$ , and  $\eta$  to judge whether the molar ratio of  $\text{O}_2$  or  $\text{H}_2\text{O}$  to coal is appropriate or not from  $\alpha$  or  $\beta$ . In addition, each value of  $\alpha \sim \lambda$  is estimated simultaneously by arithmetic calculations using the values of concentration of each gas and H/C and O/C ratios of coal and tar. Formula (1) seems to be also obtained from the flow rates of coal, gasifying agents, and each gas produced. The carbon conversion for practical process has been usually found to be less than 100%, however, the accuracy of industrial instruments to control each flow rates of raw materials (coal,  $\text{O}_2$ , and  $\text{H}_2\text{O}$ ) or to measure that of products (gas, tar, drain, ash, and residual char) are insufficient to get a formula satisfying the law of conservation of mass.

### 4. Analysis of reaction formula obtained

We consider that a reference standard should be necessary to elucidate the reaction process concealed in formula (1). We tried to prepare the reaction formula expressed in mathematical form by a theoretical approach for this purpose. The quantitative details of formula (1) obtained from composition of gas becomes apparent by the comparison with a theoretical formula which is derived from (24) by mathematical means.



#### 4.1 Hypotheses for the chemical process

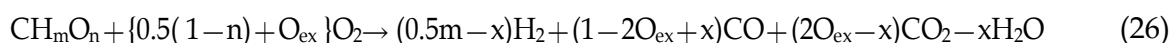
We assumed that the reaction process of gasification has been divided for convenience into two categories, namely partial oxidation and secondary reaction. Coal is converted into  $H_2$ ,  $CO$ ,  $CO_2$ , and  $H_2O$  by the reaction with  $O_2$  and  $H_2O$ . Most solid-gas reactions except for hydrogenation described later are classified in it. In secondary reaction step, the gas produced by partial oxidation changes its composition by shift reaction and formation of organic compounds. We transform standard reaction formula (24) mathematically according to both steps mentioned above and derived a formula having the same form of formula (1).

#### 4.2 Partial oxidation step

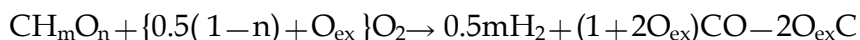
The amount of  $O_2$  in (24), i.e.  $0.5(1-n)$ , is regarded as a standard amount of  $O_2$  for gasification.  $\alpha$  in (1) is written as bellow.

$$\alpha = 0.5(1-n) + O_{ex} \quad (25)$$

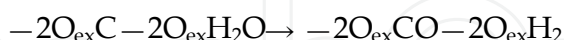
In the case of  $O_{ex} > 0$ , it can be assumed that coal is firstly gasified with  $0.5(1-n)O_2$  and converted into product gas, i.e.,  $0.5mH_2 + CO$ . Then  $2O_{ex}$  mole of the product gas is burned with  $O_{ex}$  mole of  $O_2$ ,  $2O_{ex}$  mole of  $H_2O$  and  $CO_2$  in total was generated. When moles of  $H_2$  burned is taken as variable  $x$ , that of  $CO$  is presented as  $(2O_{ex} - x)$  and reaction formula after partial oxidation step was written as follows;



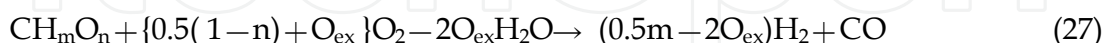
In the case of  $O_{ex} < 0$ , since  $\alpha$  is not enough to complete (24),  $-2O_{ex}$  of residual carbon is produced intermediately. The reaction is expressed by following formula.



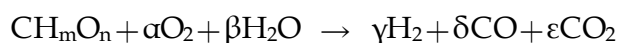
$-2O_{ex}C$  in above formula should be gasified with  $-2O_{ex}H_2O$  as follows;



The final formula after partial oxidation step is estimated as follows;



On the other hand, we can understand the partial oxidation step in further detail from a broader standpoint of view. Since it is stipulated that organic constituents are not produced in the partial oxidation, formula can be expressed as follows.



The elemental balance of this formula is given below.

$$1 = \delta + \varepsilon \quad (C)$$

$$m + 2\beta = 2\gamma \quad (\text{H})$$

$$n + 2\alpha + \beta = \delta + 2\varepsilon \quad (\text{O})$$

The calculation,  $2(\text{C}) + 0.5(\text{H}) - (\text{O})$  was performed.

$$\begin{array}{rcl}
 2(\text{C}) & : & 2 = 2\delta + 2\varepsilon \\
 0.5(\text{H}) & : & 0.5m + \beta = \gamma \\
 + ) & -(\text{O}) & : -n - 2\alpha - \beta = -\delta - 2\varepsilon \\
 \hline
 & & 2(1 + 0.25m - 0.5n) - 2\alpha = \delta + \gamma
 \end{array}$$

As theoretical moles of  $\text{O}_2$  for complete combustion of coal is defined by  $\mu$  ( $\mu = 1 + 0.25m - 0.5n$ ), the equation that shows the relationship between the sum of  $\text{H}_2$  and  $\text{CO}$  produced and amount of  $\text{O}_2$  reacted is obtained.

$$(\gamma + \delta) = 2\mu - 2\alpha$$

When the both side is divided with  $\mu$  and let  $\alpha/\mu$  be replaced by  $\chi$ , (28) is obtained.  $\chi$  is called oxygen ratio and generally used in the analysis of combustion.

$$(\gamma + \delta)/\mu = 2 - 2\chi \quad (28)$$

$(\text{O}) - (\text{C})$  is performed, equation (29) is obtained.

$$\begin{array}{rcl}
 (\text{O}) & : & n + 2\alpha + \beta = \delta + 2\varepsilon \\
 + ) & -(\text{C}) & : -1 = -\delta - \varepsilon \\
 \hline
 & & \varepsilon - \beta = 2\alpha - (1 - n)
 \end{array}$$

$$(\varepsilon - \beta)/\mu = 2\chi - (1 - n)/\mu \quad (29)$$

Since  $\beta$  is moles of  $\text{H}_2\text{O}$  decomposed,  $-\beta$  means that produced. Therefore,  $(\varepsilon - \beta)$  in equation (29) indicates the sum of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  produced in the case of  $\chi > 0.5(1 - n)/\mu$ .

In the case of  $\chi \leq 0.5(1 - n)/\mu$ , the following equation is valid where  $-\varepsilon$  means moles of  $\text{CO}_2$  decomposed.

$$(\beta - \varepsilon)/\mu = (1 - n)/\mu - 2\chi \quad (30)$$

The variations of  $(\gamma + \delta)/\mu$ ,  $(\varepsilon - \beta)/\mu$ , and  $(\beta - \varepsilon)/\mu$  are exhibited graphically against  $\chi$  in Fig. 1.

(28) is represented by black solid line with slope -2, (29) is done by red solid one with slope 2, and (30) is done by blue dotted lines with slope -2. Since  $\mu$  and  $\chi$  are the parameters that have been commonly used in the theoretical analysis of combustion, Fig. 1 allows us to investigate the partial oxidation step from the macroscopic point of view that covers not only gasification but also combustion. The partial oxidation step can be realized as general comprehension of oxidation process of coal based on Fig. 1.

Partial oxidation step can be further subdivided into various elemental reaction such as pyrolysis, combustion of C and H in coal, water-gas reaction, and Boudouard reaction. Taking all these into account, however, the reaction model may complicate analysis of gasification too much and may be far from practical application.

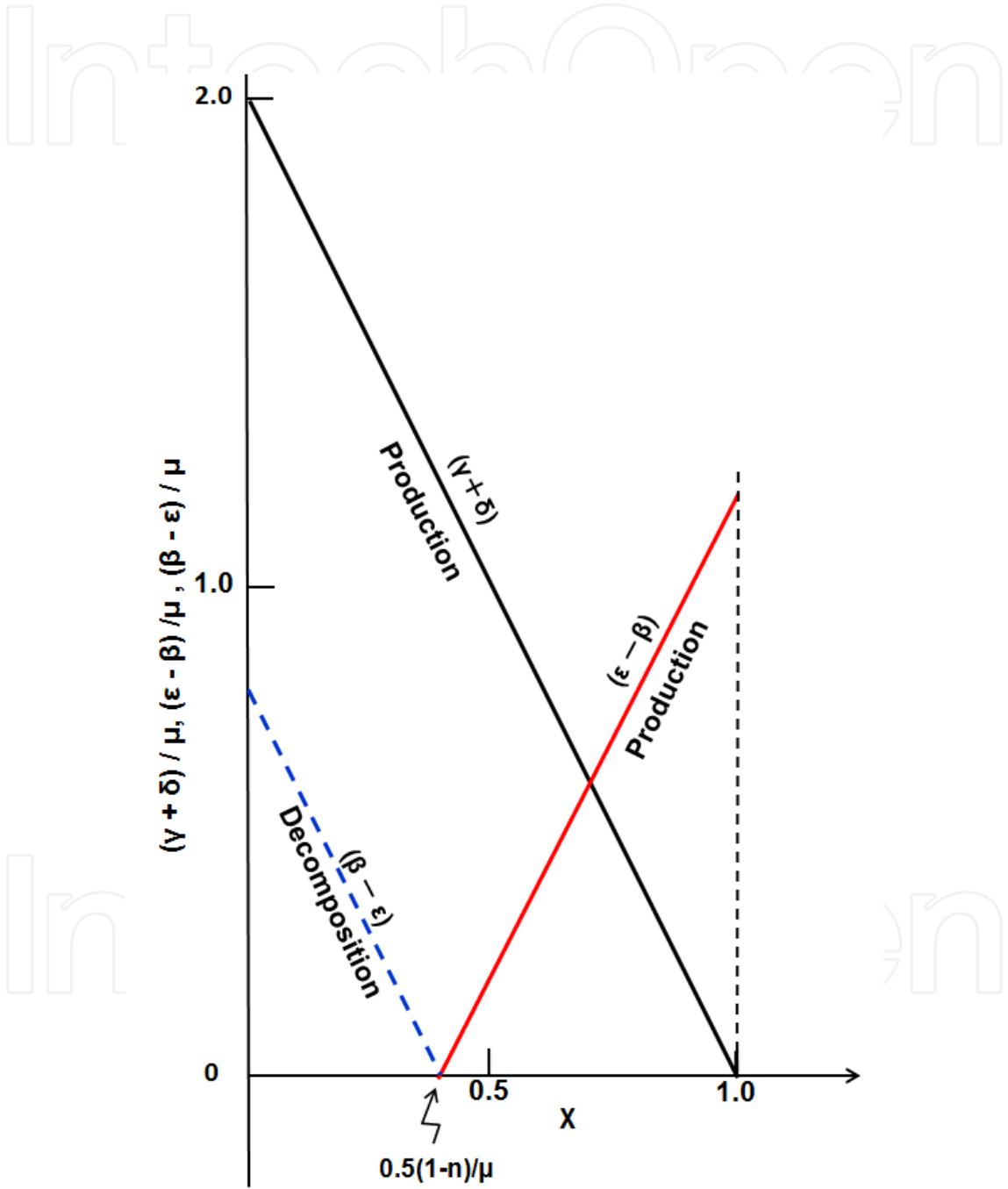
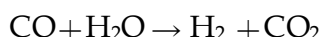


Fig. 1. Stoichiometry of partial oxidation step.

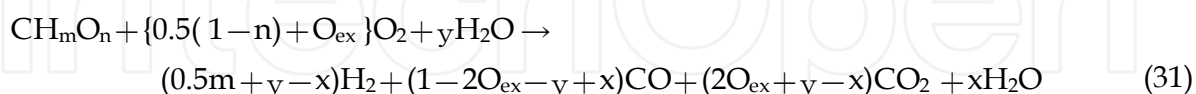


### 4.3 Shift reaction

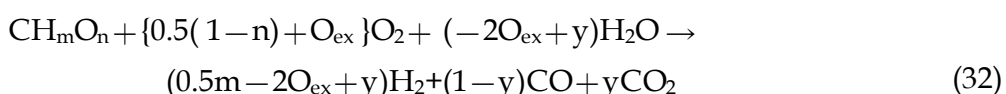
In the case of shift reaction, we can easily express the variation of yields of CO, H<sub>2</sub>O, H<sub>2</sub>, and CO<sub>2</sub> numerically based on its reaction formula.



In the case of  $O_{\text{ex}} > 0$ , let  $y$  be moles of CO caused shift reaction, formula (26) is modified as follows;



In the case of  $O_{\text{ex}} \leq 0$ , formula (28) is modified as follows;

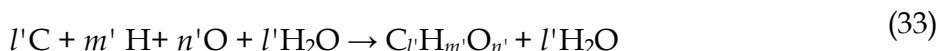


### 4.4 Formation of organic compounds

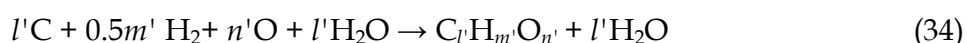
Organic constituent such as CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> are produced by the synthetic reaction as well as pyrolysis of coal and hydrogenation reaction. There is no question that the synthetic process is classified as secondary reaction step. However, the idea that pyrolysis and hydrogenation are also classified in the same step appears doubtful.

The formulae of pyrolysis, hydrogenation, and synthetic reaction are described as follows;

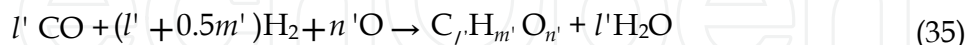
Pyrolysis:



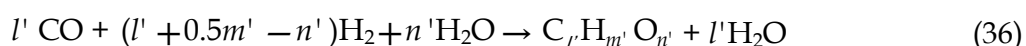
Hydrogenation reaction:



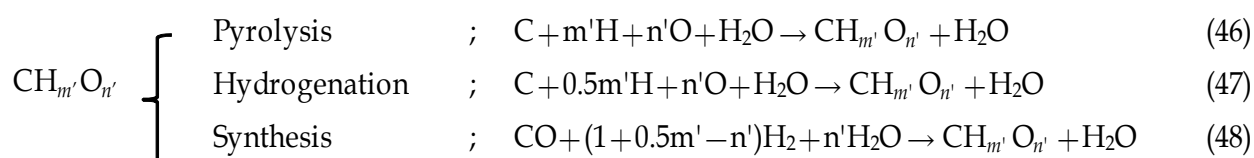
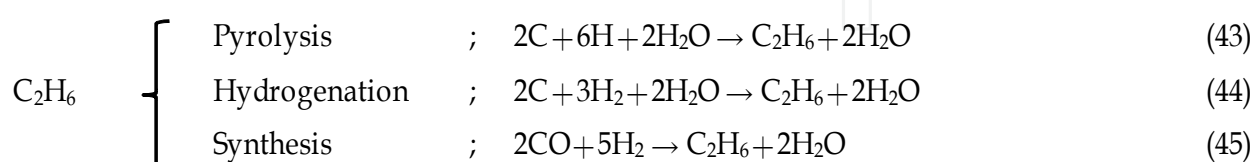
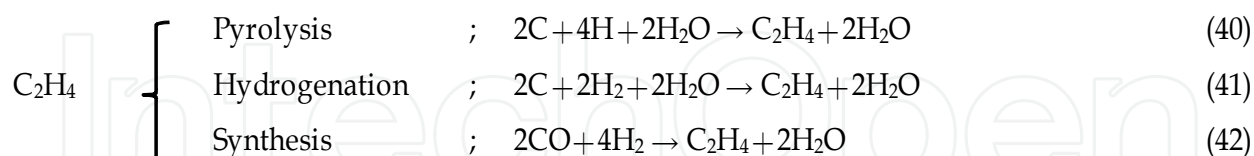
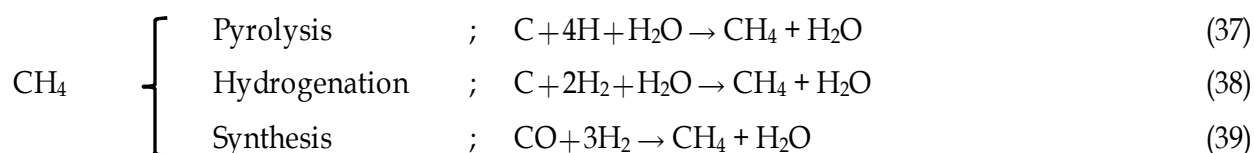
Synthetic reaction:



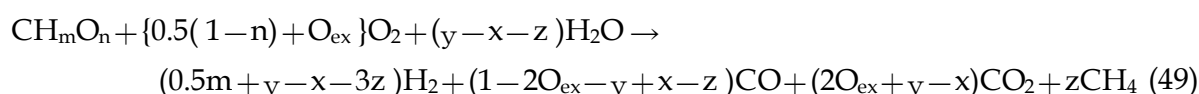
Where  $\text{C}_{l'}\text{H}_{m'}\text{O}_{n'}$  is organic compound and  $l'\text{H}_2\text{O}$  is moisture in an atmosphere. When  $m'\text{H}$  in the left side of (33) cause  $0.5m'\text{H}_2$ , it changes into (34). When water-gas reaction is occurred between  $l'\text{C}$  and  $l'\text{H}_2\text{O}$  in the left side of (34), it turns into formula (35). In other words, it means that the effect of the formation of organic compound on the yields of other inorganic components can be appreciated mathematically according to formula (35). Since O atom in the product gas is very reactive, however, it readily reacts with H<sub>2</sub>. Therefore, formula (35) is finally altered as follows;



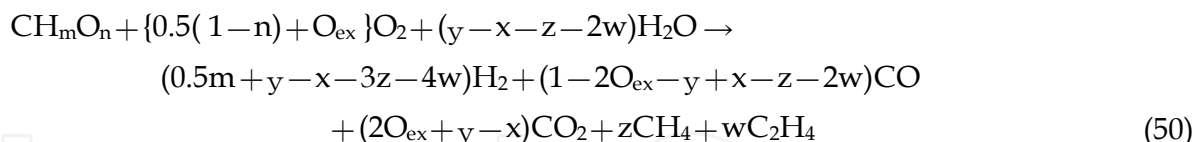
The difference in formation processes of organic compounds in (1) is shown as follows;



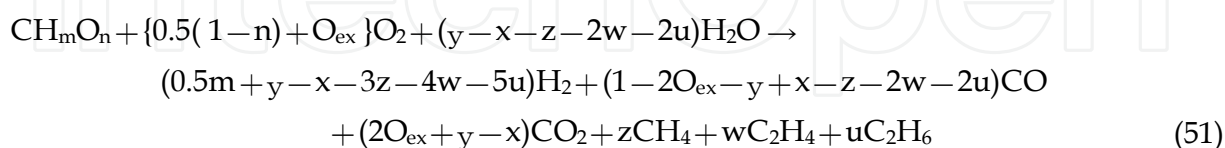
In the case of  $\text{O}_{\text{ex}} > 0$ , when  $z$  mole of  $\text{CH}_4$  is formed, formula (31) is modified.



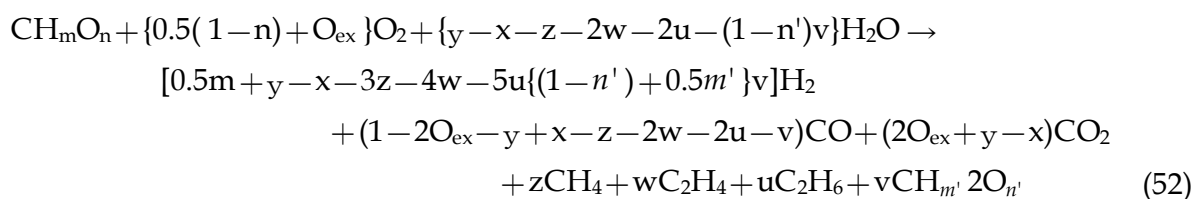
When  $w$  mole of  $\text{C}_2\text{H}_4$  is formed, (49) is transformed into (50) according to (42).



When  $u$  mole of  $\text{C}_2\text{H}_6$  is formed, (50) is modified to (51) according to (45).



When  $v$  mole of  $\text{CH}_{m'}\text{O}_{n'}$  is formed, (51) is transformed into (52) according to (48).



In the case of  $O_{ex} < 0$ , formula (32) is transformed step by step along the reaction formulae in which  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ , and  $CH_m'O_{n'}$  are synthesized.

$$CH_mO_n + \{0.5(1-n) + O_{ex}\}O_2 + (-2O_{ex} + y - z)H_2O \rightarrow$$
$$(0.5m - 2O_{ex} + y - 3z)H_2 + (1 - y - z)CO + yCO_2 + zCH_4 \tag{53}$$

When  $w$  mole of  $C_2H_4$  is formed according to formula (42), the formula is as follows.

$$CH_mO_n + \{0.5(1-n) + O_{ex}\}O_2 + (-2O_{ex} + y - z - 2w)H_2O \rightarrow$$
$$(0.5m - 2O_{ex} + y - 4w)H_2 + (1 - y - z - 2w)CO + yCO_2 + zCH_4 + wC_2H_4 \tag{54}$$

When  $u$  mole of  $C_2H_6$  is formed according to formula (45), the formula is as follows.

$$CH_mO_n + \{0.5(1-n) + O_{ex}\}O_2 + (-2O_{ex} + y - z - 2w - 2u)H_2O \rightarrow$$
$$(0.5m - 2O_{ex} + y - 4w - 5u)H_2 + (1 - y - z - 2w - 2u)CO$$
$$+ yCO_2 + zCH_4 + wC_2H_4 + uC_2H_6 \tag{55}$$

When  $v$  mole of  $CH_m'O_{n'}$  is formed according to formula (48), the formula is obtained as (41).

$$CH_mO_n + \{0.5(1-n) + O_{ex}\}O_2 + \{-2O_{ex} + y - z - 2w - 2u - (1-n')v\}H_2O \rightarrow$$
$$[0.5m - 2O_{ex} + y - 4w - 5u - \{(1-n') + 0.5m'\}v]H_2 + (1 - y - z - 2w - 2u - v)CO$$
$$+ yCO_2 + zCH_4 + wC_2H_4 + uC_2H_6 + vCH_m'O_{n'} \tag{56}$$

(52) and (56) show the stoichiometric structure of coal gasification. We can investigate the chemical process of gasification from a stoichiometric point of view that is different from conventional kinetic or chemical equilibrium viewpoint.

4.5 Evaluation of practical value of each variable

The numerical expression of each component is shown in Table 1.

(1)	(52) : $O_{ex} \geq 0$	(56) : $O_{ex} < 0$
$\alpha$	$0.5(1-n) + O_{ex}$	$0.5(1-n) + O_{ex}$
$\beta$	$y - x - z - 2w - 2u - (1-n')v$	$-2O_{ex} + y - z - 2w - 2u - (1-n')v$
$\gamma$	$0.5m + y - x - 3z - 4w - 5u - \{(1-n') + 0.5m'\}v$	$0.5m - 2O_{ex} + y - 4w - 5u - \{(1-n') + 0.5m'\}v$
$\delta$	$1 - 2O_{ex} - y + x - z - 2w - 2u - v$	$1 - y - z - 2w - 2u - v$
$\varepsilon$	$2O_{ex} + y - x$	$y$
$\eta$	$z$	$z$
$\zeta$	$w$	$w$
$\theta$	$u$	$u$
$\lambda$	$v$	$v$

Table 1. Comparison of each coefficient in (1) with (52) and (56)

The functions that express the inorganic components or  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\varepsilon$  differ appreciably with the sign of  $O_{ex}$ . In the case of  $O_{ex} > 0$ , the value of  $O_{ex}$  is calculated by equation (25) and that of

$z$ ,  $w$ ,  $u$ , and  $v$  are found to be equal to  $\eta$ ,  $\zeta$ ,  $\theta$ , and  $\lambda$  respectively. Following equation is obtained relating to the value of  $x$  and  $y$ .

$$\varepsilon = 2O_{\text{ex}} + y - x \quad (57)$$

Since the value of  $x$ , i.e. quantity of  $H_2$  burned with  $O_{\text{ex}}O_2$ , cannot be determined only from the results of ultimate analysis and gas analysis, we assume reasonable value of  $x$  based on the rate of combustion of  $H_2$  and  $CO$ . When gasifying temperature is too low to maintain the combustion rate of  $CO$ , only  $H_2$  seems to be virtually burned. In this case,  $x$  become  $2O_{\text{ex}}$  and equation (58) is valid.

$$x = 2O_{\text{ex}} \quad (58)$$

When (58) is substituted in (57), (59) is obtained.

$$y = \varepsilon \quad (59)$$

In usual gasification, the product gas in (24) is burned with  $O_{\text{ex}}O_2$  as it is,  $x$  is calculated by  $2O_{\text{ex}}\{0.5m/(1+0.5m)\}$  and equation (60) is obtained.

$$y = \varepsilon - 2O_{\text{ex}} + \{mO_{\text{ex}}/(1+0.5m)\} \quad (60)$$

In the case of  $O_{\text{ex}} < 0$ , we can find the relation,  $y = \varepsilon$ , from Table 1. Since the quantity of  $O_2$  is not enough to satisfy the standard reaction formula,  $CO_2$  cannot be produced by the combustion of  $CO$ .

The quantity of  $H_2$  or  $CO_2$  formed by shift reaction has never been evaluated. Our approach can account for the contribution of shift reaction to the composition of gas based on the rational assumption of the quantity of  $H_2$  burned.

## 5. Application to underground coal gasification

The principle of underground coal gasification (UCG) is shown schematically in Fig. 2.

UCG is a process that gasifies coal in seam with  $O_2$  or air injected through a borehole drilled from the surface. The gas produced is withdrawn to the surface through another borehole. In recent years, UCG technique is advanced drastically by application of horizontal digging technique developed in oil excavation, and several commercial processes have been scheduled.

It is difficult to insert various sensors to measure temperature, pressure, flow rate of gas from ground surface into reacting spots. Chemical phenomenon occurred in UCG has not been well understood compared with surface gasification processes because of the lack of information described above. Therefore, the reaction formula, heat of gasification, and adiabatic temperature of UCG should be helpful to understand the reaction process. We applied our method to the data of gas composition and ultimate analysis of coal obtained by UCG tests carried out at five China mines, and investigated the feature of each chemical processes.

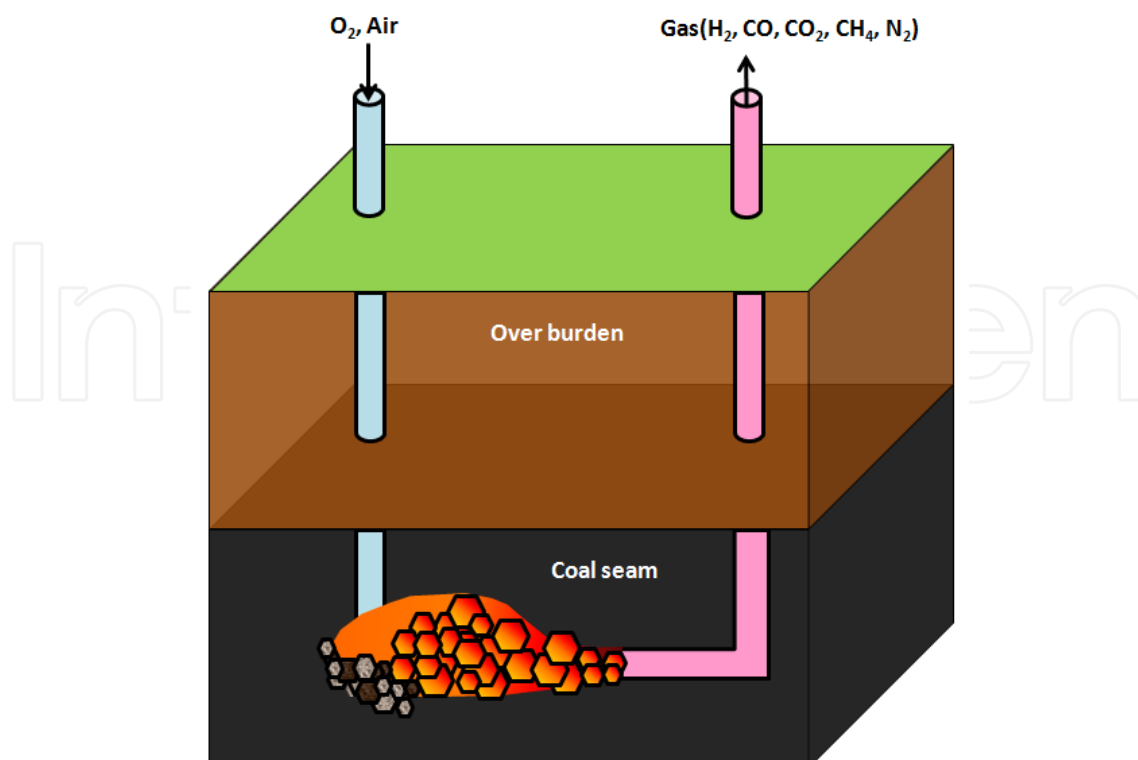


Fig. 2. The scheme of UCG

### 5.1 Reaction formula and heat of reaction

Composition of gas in the data reported by China University of Mining and Technology consists of  $H_2$ ,  $CO$ ,  $CO_2$ ,  $CH_4$ , and  $N_2$ , and none of the other hydrocarbons nor tar were measured.



The value of  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\varepsilon$ , and  $\eta$  in (1') is estimated by equation (23), (22), (15), (16), (17), and (18) respectively.

Heat of reaction of gasification,  $h_r$  (kcal/mol-coal) is calculated by (61).

$$h_r = \gamma h_{H_2} + \delta h_{CO} + \eta h_{CH_4} - h_{Coal} \quad (61)$$

Here,  $h_{Coal}$ ,  $h_{H_2}$ ,  $h_{CO}$ , and  $h_{CH_4}$  are molar combustion heats (kcal/mol) of coal,  $H_2$ ,  $CO$ , and  $CH_4$  respectively. The values of  $h_{H_2}$ ,  $h_{CO}$ , and  $h_{CH_4}$  are -68.32, -67.64, and -212.80 kcal/mol respectively.

### 5.2 Estimation of adiabatic temperature

In the case of UCG, it is presumed that  $h_r$  generated is partly transferred to the wall made of coal or char. As the heat conducted to the wall is utilized in water gas reaction, pyrolysis, drying, and preheating of coal effectively. Consequently, the reactor of UCG can be thought as adiabatic one, and most of  $h_r$  turns to the sensible heat of gas in the reactor.

Gas in the reactor consists of the products presented in right side of formula (1'), N<sub>2</sub>, and H<sub>2</sub>O. The total moles of product gas, i.e. Σ in (1'), is expressed by  $\Sigma = 1/(q + r + s)$  as shown in equation (13), the yield of N<sub>2</sub> per 1 mol of coal gasified is defined by ζ.

$$\zeta = \frac{(\text{Concentration of N}_2)}{(q + r + s)}$$

The amount of residual H<sub>2</sub>O remained in the reactor is expressed by θ. In the case of UCG, it is difficult to estimate θ precisely based on the result of gas analysis. We estimate θ based on the equilibrium relationship of shift reaction.

$$K = \frac{[H_2][CO_2]}{[CO][H_2O]}$$

The relationship between equilibrium constant of shift reaction and temperature is shown in Table 2.

T(°C)	K	T(°C)	K	T(°C)	K
350	2.075×10 <sup>1</sup>	700	1.549×10 <sup>0</sup>	1050	5.162×10 <sup>-1</sup>
400	1.177×10 <sup>1</sup>	750	1.257×10 <sup>0</sup>	1100	4.647×10 <sup>-1</sup>
450	7.319×10 <sup>0</sup>	800	1.042×10 <sup>0</sup>	1150	4.222×10 <sup>-1</sup>
500	4.887×10 <sup>0</sup>	850	8.801×10 <sup>-1</sup>	1200	3.870×10 <sup>-1</sup>
550	3.453×10 <sup>0</sup>	900	7.553×10 <sup>-1</sup>	1250	3.576×10 <sup>-1</sup>
600	2.553×10 <sup>0</sup>	950	6.574×10 <sup>-1</sup>	1300	3.329×10 <sup>-1</sup>
650	1.959×10 <sup>0</sup>	1000	5.793×10 <sup>-1</sup>		

Table 2. Equilibrium constant of shift reaction

Heat of product gas, Q<sub>sh</sub> is calculated by the integration of thermal capacity of each component gas, which is given by following eq., Cp = a+bT+cT<sup>2</sup>+dT<sup>3</sup> (kcal/kg-mol-deg), from 298K to gasification temperature T. The values of a ~ d of each gas are shown in Table 3.

Gas	a	b×10 <sup>2</sup>	c×10 <sup>5</sup>	d×10 <sup>9</sup>
H <sub>2</sub>	6.952	-0.04576	0.09563	-0.2079
CO	6.726	0.04001	0.1283	-0.5307
CO <sub>2</sub>	5.316	1.4285	-0.8362	1.784
CH <sub>4</sub>	4.75	1.2	0.303	-2.630
C <sub>2</sub> H <sub>4</sub>	0.944	3.735	-1.993	4.22
C <sub>2</sub> H <sub>6</sub>	1.648	4.124	-1.530	1.74
N <sub>2</sub>	6.903	-0.03753	0.193	-0.6861
H <sub>2</sub> O	7.7	0.04594	0.2521	-0.8387

Table 3. The values of a ~ d to estimated Cp of gas

Taking account of residual water equilibrated with [H<sub>2</sub>], [CO], and [CO<sub>2</sub>], adiabatic gasification temperature or T<sub>ad</sub> that satisfies Q<sub>sh</sub> = h<sub>r</sub> was estimated by the rule of trial and error.

5.3 Analysis of chemical process

We estimated reaction formula of gasification, heat of reaction, and gasification temperature of UCG carried out at Fuxin mine, Xinghe mine, Liuzhuang mine, Ezhuang mine, and Xiyang mine in China. The results of ultimate analysis and molecular formulae estimated for five coals were shown in Table 4 with their heating values.

Coal mine CH <sub>m</sub> O <sub>n</sub>	Ultimate analysis (%-daf)					Molecular formula CH <sub>m</sub> O <sub>n</sub>	Heating Value (MJ/mol)
	C	H	O	N	S		
Fuxin coal	79.7	5.35	12.91	1.36	0.68	CH <sub>0.806</sub> O <sub>0.121</sub>	0.486
Xinghe coal	81.67	5.57	9.08	1.39	1.7	CH <sub>0.818</sub> O <sub>0.083</sub>	0.532
Liuzhuang coal	82.66	5.63	8.85	1.47	1.09	CH <sub>0.817</sub> O <sub>0.080</sub>	0.493
Ezhuang coal	82.87	5.68	9.22	1.4	0.83	CH <sub>0.822</sub> O <sub>0.083</sub>	0.498
Xiyang coal	92.34	3.22	2.48	1.17	0.79	CH <sub>0.418</sub> O <sub>0.020</sub>	0.512

Table 4. Ultimate analysis, molecular formula and heating values of coals

As an example of analysis of chemical process of UCG, results for Ezhuang mine are summarized below. The daily variation of the concentration of each gas components is shown in Fig. 3.

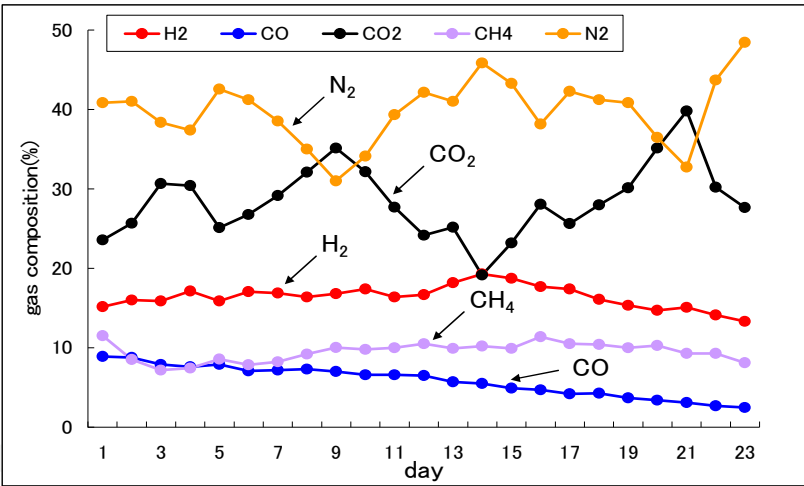


Fig. 3. The daily variation of the concentration of each gas

The change in the each coefficient of reaction formula (1') with elapse of time was shown in Fig. 4. Value of  $\alpha$  may be applicable to estimate the amount of coal gasified. Therefore, total volume of the cave formed in coal seam can be estimated by the integrated value of  $\alpha$ .

Value of  $\beta$  is important information to understand the reaction mechanism quantitatively.

The linear relationship was found in the plots of the values of other coefficients against  $\alpha$  as shown in Fig. 5 and 6.

Figs. 5 and 6 show that yields of combustible gas such as H<sub>2</sub>, CO, and CH<sub>4</sub> decreased in proportion to increase of oxygen reacted. The quantity of H<sub>2</sub>O reacted decreased with  $\alpha$  in the same way. On the other hand, the yield of CO<sub>2</sub> increased with  $\alpha$ . It was thus proved that

$\alpha$  was responsible for the formation of every component gas in the case of UCG carried out in Ezhuang mine.

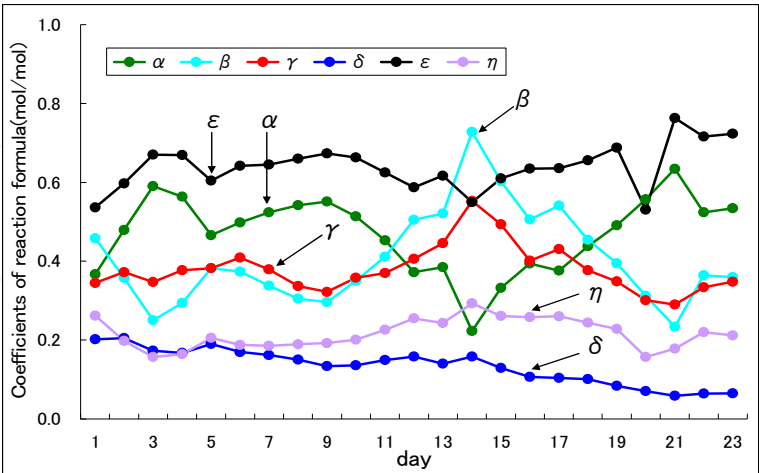


Fig. 4. Change in the coefficients with the elapse of time

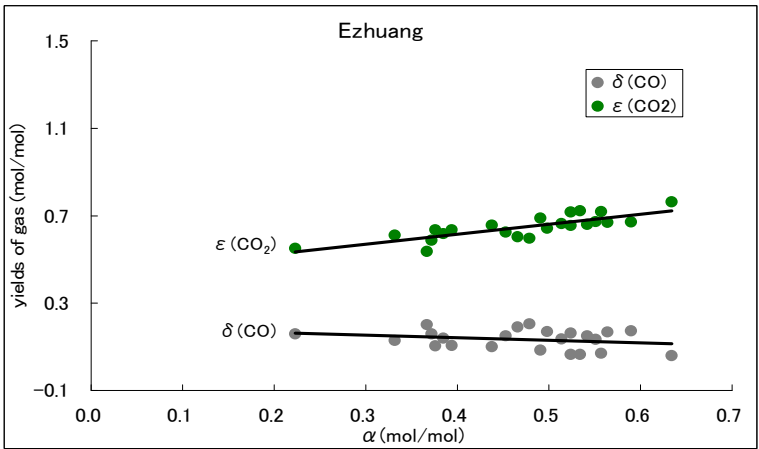


Fig. 5. Relationship between  $\alpha$  and other coefficient

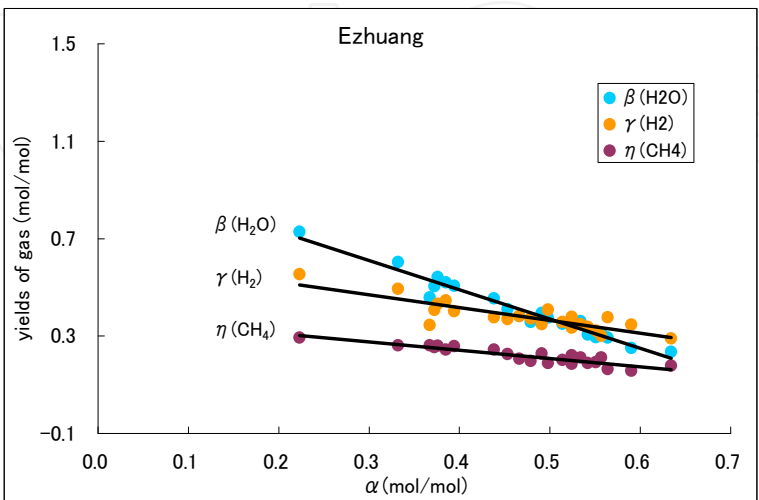


Fig. 6. Relationship between  $\alpha$  and other coefficient



The change in  $h_r$  and  $T_{ad}$  with elapse of time was shown in Fig. 7.

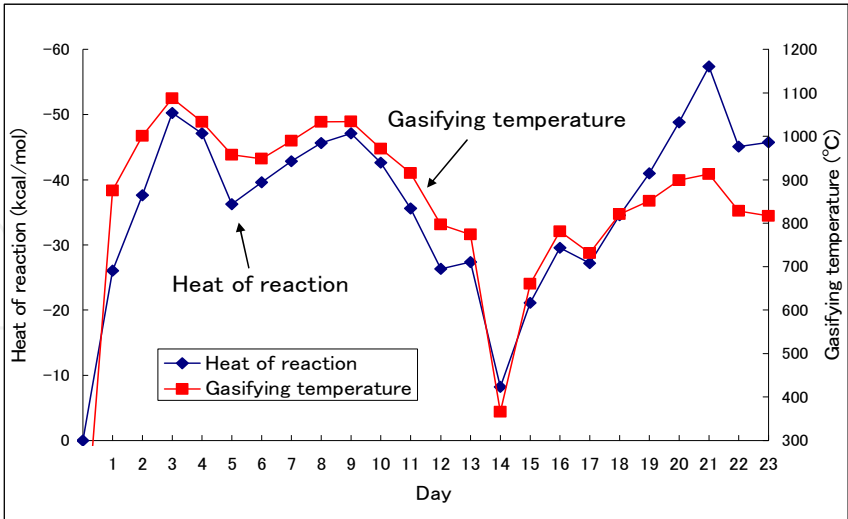


Fig. 7. Change in  $h_r$  and  $T_{ad}$  with elapse of time

Fig. 8 indicates the plot of  $h_r$  vs.  $\alpha$ , and  $T_{ad}$  vs.  $\alpha$ . A plot of  $h_r$  vs.  $\alpha$  gave a straight line, but that of  $T_{ad}$  vs.  $\alpha$  was widely scattered. The distribution of plots may be attributed to the uncertainty in the estimation of residual  $H_2O$  in product gas, which was calculated from equilibrium of shift reaction. It is presumed that the gas composition in UCG reactor has not been attained to chemical equilibrium. The approach to improve the reliability of estimation for  $T_{ad}$  without depending upon the equilibrium theory has not been reported. Our attempt might be the first to predict the temperature of UCG reactor.

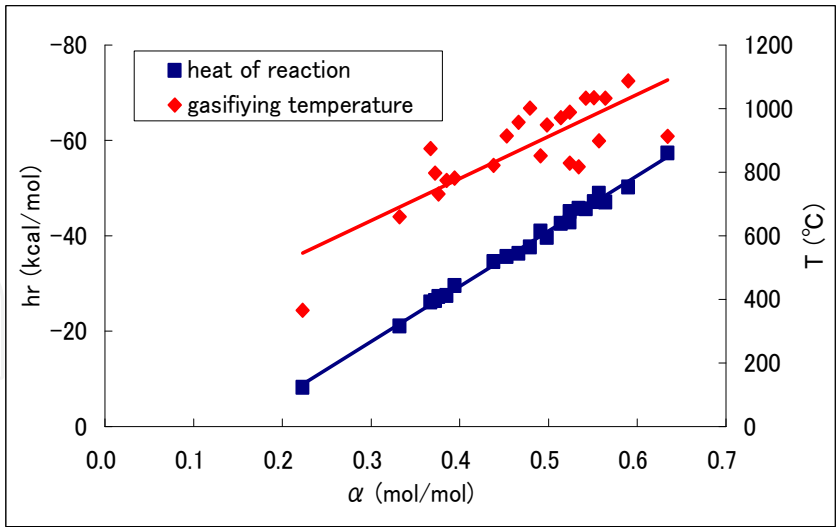


Fig. 8. indicates the plots of  $h_r$  vs.  $\alpha$ , and  $T_{ad}$  vs.  $\alpha$ .

5.4 Comparison of reaction process in five coal mines

We compared the result of analysis of the data of UCG carried out at five coal mines. Average compositions of gases produced by UCG processes are listed in Table 5.

Coal mine	Average compositions of gases (%)					
	O <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>
Fuxin	0.71	8.28	16.5	7.01	5.18	57.68
Xinghe	-	21.72	8.82	13.59	2.64	53.36
Liuzhuang	1.49	14.77	13.98	10.73	3.69	55.31
Ezhuang	0	16.42	5.83	28.47	9.48	39.8
Xiyang	0.2	9.3	9.2	9.2	7.2	64.7

Table 5. Average compositions of gases produced by UCG

The mean value of each coefficient of reaction formula of UCG is shown in Table 6.

The average coefficients of reaction formula and indicators of gasification (mol/mol)								
Coal mine	$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$	$\eta$	O <sub>ex</sub>	y
Fuxin	0.347	0.247	0.287	0.573	0.245	0.182	-0.093	0.244
Xinghe	0.333	0.688	0.882	0.348	0.545	0.108	-0.126	0.520
Liuzhuang	0.376	0.399	0.537	0.499	0.365	0.135	-0.084	0.319
Ezhuang	0.477	0.397	0.375	0.133	0.650	0.217	0.019	0.583
Xiyang	0.171	0.717	0.363	0.359	0.359	0.281	-0.319	0.354

Table 6. The average coefficients of reaction formula of gasification

The result of analysis of the data obtained by fixed bed gasifier which is a conventional surface process is summarized in Table 7 as a reference.

The average coefficients of reaction formula and indicators of gasification(mol/mol)								
Prosess	$\alpha$	$\beta$	$\gamma$	$\delta$	$\epsilon$	$\eta$	O <sub>ex</sub>	y
Wilputte	0.337	0.316	0.515	0.705	0.183	0.112	-0.122	0.183
Riley-Morgan	0.428	0.370	0.517	0.707	0.284	0.009	-0.048	0.284
Riley-Morgan	0.407	0.256	0.560	0.658	0.279	0.062	-0.020	0.279
Riley-Morgan	0.433	0.215	0.503	0.723	0.224	0.053	-0.022	0.224
Lurgi	0.331	0.224	0.623	0.466	0.396	0.136	0.018	0.018

(Chemistry of Coal Utilization, Elliott.M.A.Editor, p1615)

Table 7. The coefficients of reaction formula of surface fixed bed gasification

Value of each coefficient in Table 7 distributed in narrower range compared with Table 6. Comparing to the fixed bed process, the value of  $\alpha$  of four mines except for Xiyang were around the same as well as those of fixed bed. The relatively small  $\alpha$  of Xiyang may be due to its different chemical composition and heating value as shown in Table 4.

The partial oxidation process is considered to be practically governed by the value of O<sub>ex</sub>. On the other hand, the secondary reaction proceeded more actively compared to surface fixed bed gasification.

The change in  $h_r$  with elapse of time for five mines is shown in Fig. 9.

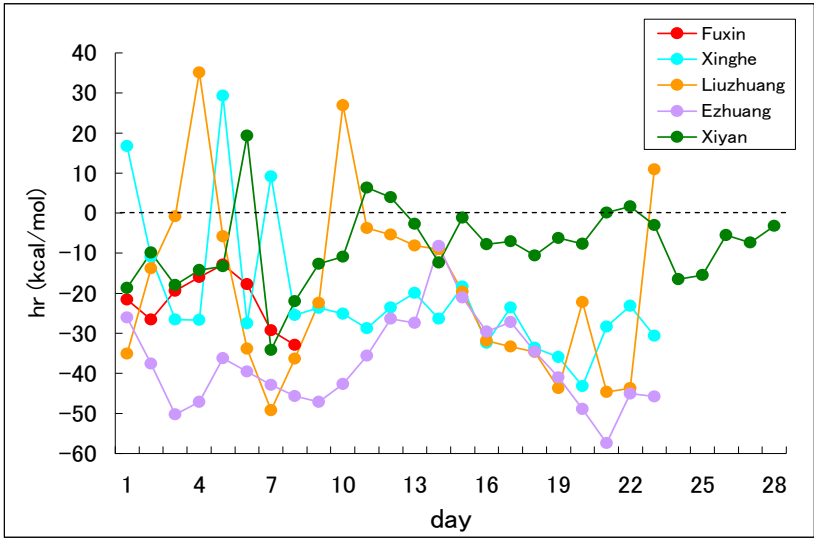


Fig. 9. The change in  $h_r$  with elapse of time

Although the rate of air supply is nevertheless kept constant during every tests,  $h_r$  repeated increase and decrease. It occasionally rose into positive value indicating that the endothermic reaction process proceeded.

The relationship between  $h_r$  and  $\alpha$  is shown in Fig. 10. As plots in the region of  $h_r > 0$  stays the same straight line characteristic for each coal mine, it is indicated that  $h_r > 0$  has not accidentally obtained. Positive value of  $h_r$  is assumed to be attributed to excessive water gas reaction promoted by the heat accumulated at the wall of gasifier. The periodic fluctuation of  $h_r$  may indicate an essential feature of actual UCG reactions.

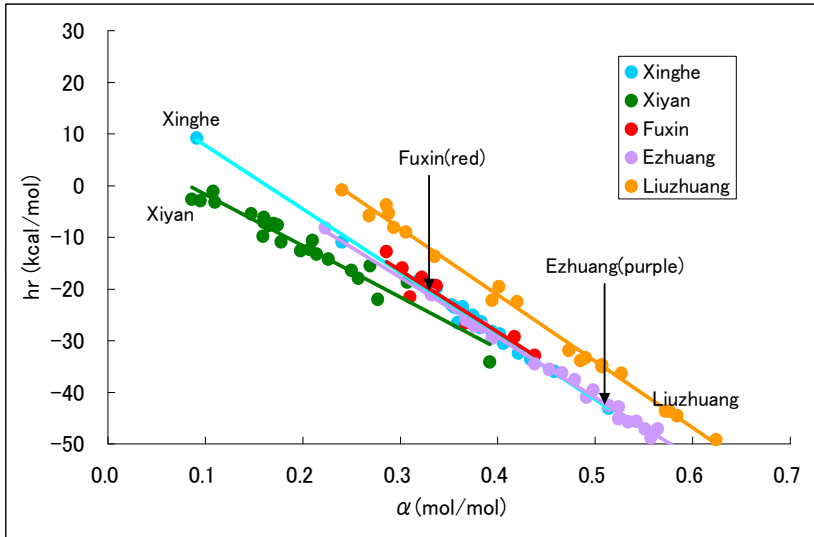


Fig. 10. Relationship between  $\alpha$  and  $h_r$

Relationship between  $\alpha$  and  $\beta$  was shown in Fig. 11.

The plot of  $\alpha$  vs.  $\beta$  gave a straight line in all coal mines.  $O_{ex}$  in UCG is almost zero or negative as shown in Table 9. In the case of  $O_{ex} < 0$ ,  $-2O_{ex}H_2O$  was consumed in water gas

reaction to compensate the lack of  $O_2$ . Therefore, the amount of water reacted basically increased in proportion to the reduction of oxygen reacted. Besides, it is considered that progress of shift reaction and formation of  $CH_4$  influenced on the slope of each straight line.

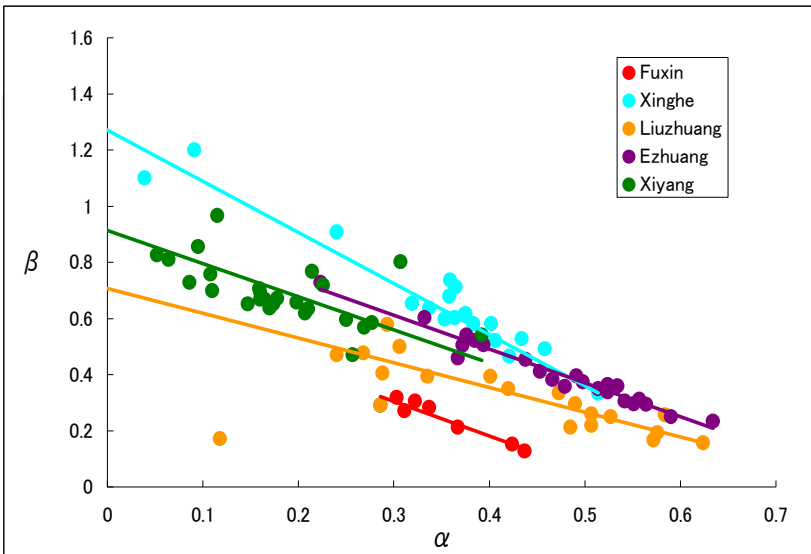


Fig. 11. Relationship between  $\alpha$  and  $\beta$

Plot of  $y$  vs.  $\alpha$  for each mine is shown in Fig. 12.

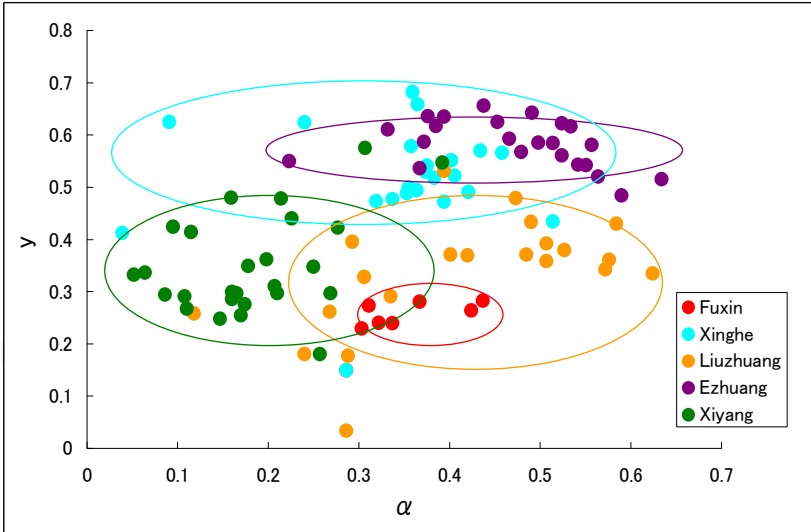


Fig. 12. Relationship between  $\alpha$  and  $y$

Since the plots scattered in the range indicated by ellipse and the linearity was hardly found, it is considered that shift reaction was not affected by partial oxidation.

The plot of  $\eta$  vs.  $\alpha$  is shown in Fig. 13.

A relatively linear relationship is found to exist between  $\eta$  and  $\alpha$  showing decrease in  $\eta$  along with increase in  $\alpha$ . This is presumably a result of thermal effect on the stability of  $CH_4$

determined by the chemical equilibrium. Average  $\eta$  of Xiyang mine is found to be 0.281mol/mol, which is much larger than results of other mines as shown in Table 6. As carbon content of Xiyang coal is 92.34%, it should be classified as anthracite. It is generally accepted that most of H atoms in molecular structure of anthracite are combined with C atoms directly at the rim of aromatic rings, and very limited numbers of methyl group or hydrocarbon chains exist. This means that  $\text{CH}_4$  is produced by hydrogenation or synthesis reaction between  $\text{H}_2$  and  $\text{CO}$ , not by pyrolysis. It is well known that hydrogenation occurs only with high pressure  $\text{H}_2$ . Therefore, it is considered that  $\text{CH}_4$  is mainly produced by synthetic route in the case of this coal.

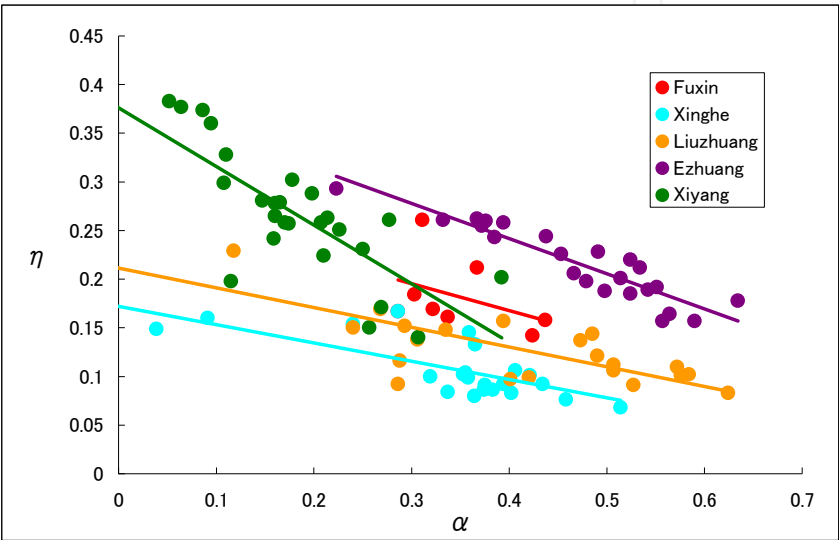


Fig. 13. Relationship between  $\alpha$  and  $\eta$

Plots of  $\gamma$ ,  $\delta$ , and  $\varepsilon$  vs.  $\alpha$  are shown in Figs. 14, 15, and 16.

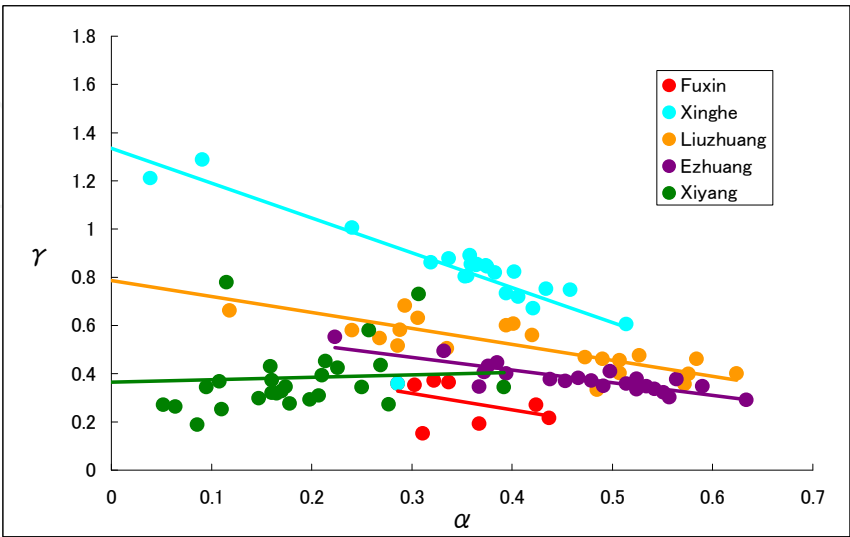


Fig. 14. Relationship between  $\alpha$  and  $\gamma$

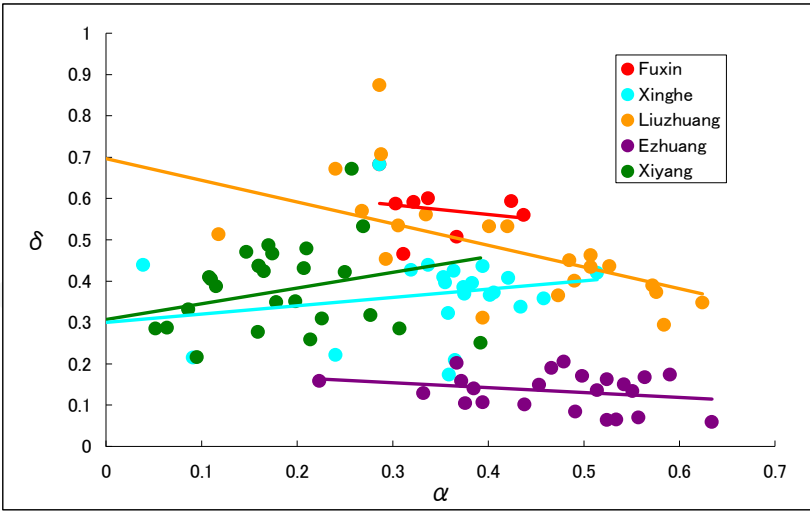


Fig. 15. Relationship between  $\alpha$  and  $\delta$

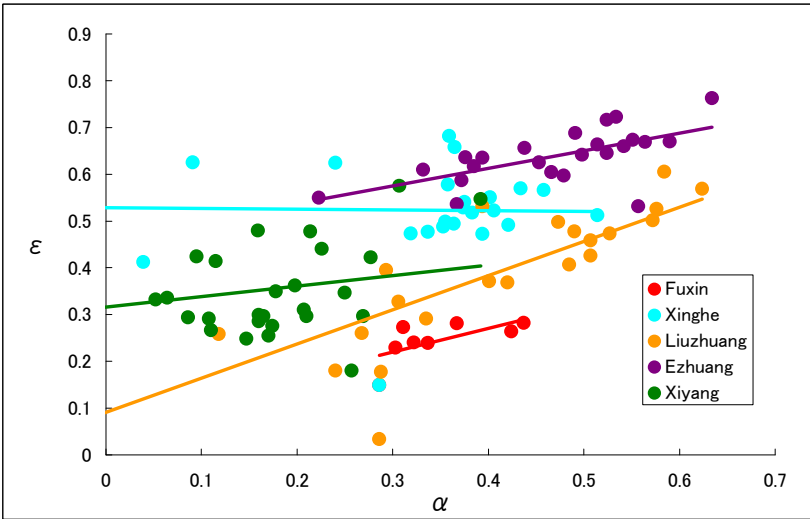


Fig. 16. Relationship between  $\alpha$  and  $\epsilon$

Amounts of  $H_2$  and  $CO$  have been used as indicator to estimate chemical process of surface gasification. For example, the yields of  $H_2$  and  $CO$  are expected to increase with decrease in the amount of  $O_2$  reacted. Such tendency, however, was not found in the plots of  $\gamma$  vs.  $\alpha$  and  $\delta$  vs.  $\alpha$  presumably due to the appreciable progress of secondary reaction. In the case of UCG, we need to evaluate the amounts of  $H_2$ ,  $CO$ , and  $CO_2$  after estimation of the effect of secondary reaction.

6. Conclusion

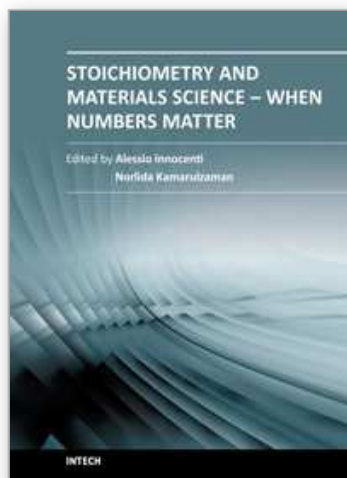
It is generally accepted that gasification consists of more than five chemical processes such as pyrolysis, partial oxidation of char, further decomposition of tar, secondary reactions, and combustion of char or gas. It is obviously difficult to simulate actual coal gasification precisely by applying reliable scientific analysis of fundamental experiment. Since coal gasification is a very complicated both from experimental and theoretical points of view, its chemical process cannot be completely understood merely by the accumulation of kinetic data.

Our method described here may be the first one that can scientifically elucidate reaction process based on the stoichiometry using gas composition obtained at a practical gasification plant. Since this method is constructed based on stoichiometry of the reaction formula without any arbitrary assumption and approximation, it is applicable to any gasification process regardless of the type of gasifier or a rank of coal used. The feature of this study is to elucidate gasification mathematically based on material balance of coal gasification reactions which was traditionally used to calculate carbon conversion and cold gas efficiency. The mathematical reaction formula derived in this study offered a novel point of view to estimate practical reactions that occur in a gasifier more precisely and it should help to attain optimum operation condition in practical gasification plant.

As a good example of the application of our method, results of the analysis of UCG is introduced. Actual operation data of UCG carried out at five mines in China was investigated by our method. We have consequently succeeded to obtain the reaction formula of gasification, progress of shift reaction, reaction heat of gasification, and adiabatic gasification temperature. These results allow us to understand the partial oxidation step and secondary reaction step of UCG.

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## **Stoichiometry and Materials Science - When Numbers Matter**

Edited by Dr. Alessio Innocenti

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The aim of this book is to provide an overview on the importance of stoichiometry in the materials science field. It presents a collection of selected research articles and reviews providing up-to-date information related to stoichiometry at various levels. Being materials science an interdisciplinary area, the book has been divided in multiple sections, each for a specific field of applications. The first two sections introduce the role of stoichiometry in nanotechnology and defect chemistry, providing examples of state-of-the-art technologies. Section three and four are focused on intermetallic compounds and metal oxides. Section five describes the importance of stoichiometry in electrochemical applications. In section six new strategies for solid phase synthesis are reported, while a cross sectional approach to the influence of stoichiometry in energy production is the topic of the last section. Though specifically addressed to readers with a background in physical science, I believe this book will be of interest to researchers working in materials science, engineering and technology.

### **How to reference**

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