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Kinetic Study on Steam Gasification of Thai-Lignite Using a Drop Tube/Fixed Bed Reactor (DT/FBR)

K. Sangtong-Ngam[*], M.H. Narasingha[+1]

Abstract – *Coal gasification has been considered worldwide as a promising process for energy production. However, there are a few works on the Thai-lignite gasification, especially on direct gasification. To increase a better understanding for a design and practical gasification process of Thai lignite, the kinetics study using a drop tube/fixed bed reactor (DT/FBR) is therefore of interest. The results from the study show that, for the isothermal pyrolysis of Thai lignite at temperature of 750, 800, and 850 ºC, the pyrolysis reaction completed over the range of reaction times from 5 s to 30 s, and the char yields decreased when increasing the reaction temperature. In case of steam-*N_2 *mixing gasification, the char yields were found to continuously decrease with increasing in the reaction time. This is because of the progress of gasification reaction. The char yields were also found to decrease with an increase in reaction temperature due to the fact that the gasification process is an endothermic reaction. By observation, the reactivity of steam-*N_2 *gasification of Thai lignite consisted of two periods. The early period was strongly affected by the mineral matter, which could be attributed to the zero order reaction as shown in term of rate constant at reaction time = 0 and overall rate constant for the loss of active catalytic species, whereas the latter period was noticed to be well described by the random pore model, which is a function of the conversion and the growing of pore surface areas. In addition, the steam gasification rates obtained from experiments were found to be corresponding to the total gasification rate obtained by calculations.*

Keywords – Direct steam gasification, drop tube/fixed reactor, kinetics, Thai lignite.

1. INTRODUCTION

Energy problem is one of the most important problems for Thailand in this decade. This is because the conventional-fuel demand has already reached its critical situation. Coal gasification has been considered worldwide as a promising process for energy production. Such process can also be considered for Thailand since there are still quite a number of coal reserves in Thailand, especially lignite in approximately 870.05 million tons from various coal mines such as Mae Moh, Krabi, Saba Yoi, and Sin Pun [1], [2]. Moreover, this process allows a mitigation of greenhouse effects when concerning on environmental aspect. Recently, coal gasification has been attracting more attentions as part of an integrated gasification-combined cycle (IGCC) technology that gives efficiency for an electrical production about 45% with the potential of 60% in the near future [3], [4].

The coal gasification is a process of converting carbon and volatile matter in coal into a fuel gas, in which consists of "syngas" (hydrogen and carbon monoxide) and methane, by using gasifying agents and controlling conditions of both temperature and pressure (at a given sufficient time). It can be divided into two important steps: i) initial rapid pyrolysis of coal (devolatilization) to produce char, tar and gases, and ii) subsequent gasification of the char generated [5]–[9]. In fact, the char gasification step is a controlling step of overall conversion process as it has much slower reaction rate when compared with the rapid pyrolysis step. The char gasification undergone by conditions that are different from the pyrolysis conditions is called ex-situ char gasification [5], [7], [10], [11]. The ex-situ char gasification is normally operated by running gasification of char samples that have already been cooled down to ambient temperature. The major drawback of this process is that the char samples need to be re-heated up again for the gasification after having been cooled down and this therefore can lower the gasification reactivity. In an attempt to avoid such problem, a direct gasification of untreated coal (in-situ char gasification) has gained much attention because the kinetics and behaviors of the direct gasification are nearly conditions of a practical reactor. The direct coal gasification processes are typically conducted at severe conditions such as high temperature and high heating rate and the coal particles in a practical gasifier undergo pyrolysis and gasification continuously at the same conditions.

In order to have an efficient coal-gasification process, a better understanding in kinetics and behaviors of the coal gasification is in much of need. The kinetics and behaviors of coal gasification can be investigated by several methods, such as a thermogravimetric analysis, a drop tube furnace and a drop tube/fixed bed reactor. The thermogravimetric analyzer (TGA) is generally used to investigate the gasification reactivity at low temperature and low heating rate, whereas the drop tube furnace (DTF) is ordinarily used to investigate at high temperature and high heating rate. However, the DTF has its difficulty to measure the retention time and particle temperature of

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char particles when they are dropped to char collector. But this problem can be solved with the drop tube/fixed bed reactor (DT/FBR, a fixed bed equipped with a drop tube reactor), which has recently been developed to study the gasification. As the retention time and particle temperature of reaction can be well measured by the DT/FBR, the high heating rate up to 10^3-10^5 °C s^{-1} [9], [12] and high temperature can also be provided as well as the practical reactor.

In this paper, since there are only a few works on the direct Thai-lignite gasification, the kinetics and behaviors of Thai-lignite gasification using a drop tube/fixed bed reactor (DT/FBR) is therefore of interest and studied. With the similar operating conditions to the practical reactor and the other advantages of the DT/FBR, the kinetic investigations obtained from this study can be employed for a scale-up design of the process in order to acquire the practical gasification process or plant for Thai lignite with an optimum use in a near future.

2. METHODOLOGY

Sample preparation

Thai lignite from Mae Moh Mine (Lampang province, north of Thailand) was used for this research work. Raw lignite samples were ground and sieved to 75 microns and then dried in a vacuum oven at 70 °C for 24 hours as a preparation step. The proximate analysis of samples is illustrated in Table 1. To obtain demineralized-lignite samples, the raw lignite samples were treated by chemical extraction with HCl and HF, respectively, at 60 °C and 3 hours for each chemical.

Experimental Set-up of a Drop Tube/Fixed Bed Reactor (DT/FBR)

A schematic diagram of the DT/FBR is shown in Figure 1. The reactor consists of three main parts; i) an outer quartz tube with 16 mm I.D., ii) an inner quartz tube with 10 mm I.D., and iii) an injector (sample holder) with 4 mm I.D. Quartz wool was placed in the inner quartz tube at the lower end. The injector was connected at the top end of the inner quartz tube, in which the end of the injector was directly passed through the inner quartz tube to a reaction zone.

Thai-lignite samples were isothermally gasified with the steam-N_2 mixture in the DT/FBR at three different temperatures; 750, 800, and 850 °C, and high heating rate. For each run, approximately 50 mg of lignite sample would be placed into the sample holder together with pressurized carrier gas, N_2, at 5 bars. A pure N_2 gas (at atmospheric pressure) was then continuously fed into the inner quartz tube at a flow rate of 300 ml/min during the heating of reactor to a desired temperature. At the desired temperature, the steam-N_2 mixture would be continuously supplied into the inner quartz tube for 20 minutes at a flow rate ratio of 300:300 ml/min between steam and N_2. When a steady condition of the reactor has been reached, a lower valve of the sample holder would instantaneously open and the lignite particles would be injected after that into the reaction zone and fixed on the quartz wool by natural expansion of the pressurized carrier gas. Subsequently, the nascent char would be formed by rapid pyrolysis and then continuously gasified with steam at a range of reaction time 5-6000 seconds for each temperature. This reaction can be terminated by immediately changing the steam-N_2 mixture to the cooled N_2 at flow rate of approximately 800-1000 ml/min, while the reactor has to be immediately cooled by a heating rate range at 100–150 °C/min. In this study, only pure N_2 gas was used as gasifying agent at a flow rate of 300 ml/min for pyrolysis of Thai lignite. After the temperature of reactor has reached the room temperature at approximately 25 °C, all char particles would be removed from the inner quartz tube and the mass of the particles would be measured. The experimental data in each condition have been repeated at least twice before illustration.

Morphological Analysis

The crystalline properties of the samples were analyzed by Powder X-ray Diffraction Method (XRD) with a Diffractometer (Bruker AXS Model D8 Discover). The X-ray patterns were recorded by using Cu Kα radiation. The power supply was maintained at 40 kV and 40 mA. Peaks were obtained by step at 2θ, scan speed at 0.3 second/step and increment at 0.025 degree. Peaks of crystal structures were indicated by comparison with data of reference materials in library of the machine. The porous char particles were observed by a Scanning Electron Microscope (SEM; JEOL, JSM-5800LV).

Table 1. Proximate analysis of Thai lignite from Mae Moh Mine

	Proximate analysis [% dry basis]		
	Volatile maters	Fixed carbon	Ash
Thai-lignite (TLN)	38.0	22.2	39.8
Demineralized Thai-lignite (DTLN)	47.2	50.3	2.47
Morwell*	51.5	46.6	1.9

* Obtained from the work of Hashimoto *et al*. 1986.

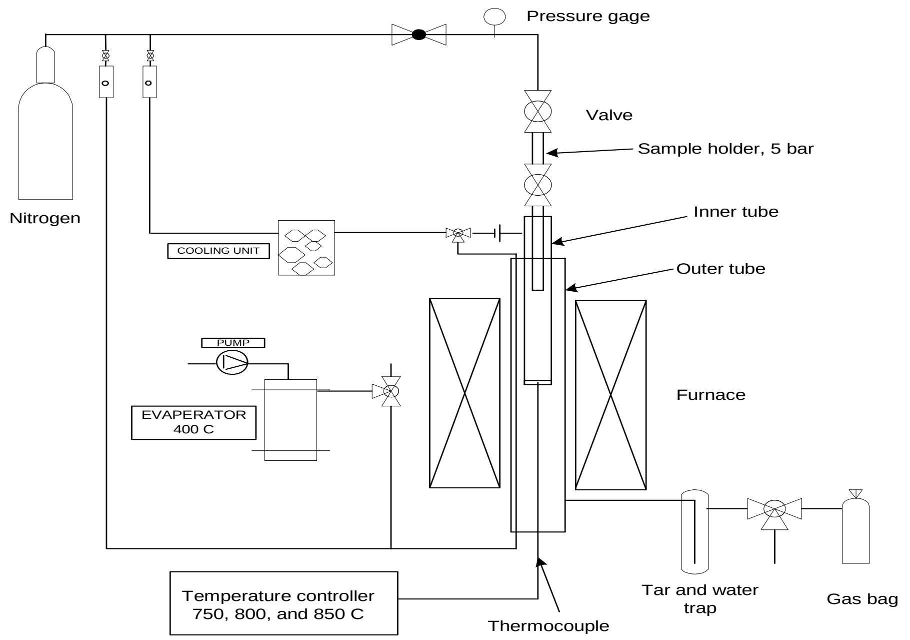

Fig. 1. A schematic diagram of a Drop Tube/Fixed Bed Reactor (DT/FBR) for steam-N_2 mixing gasification of Thai-lignite

3. RESULTS AND DISCUSSION

Characteristics of Pyrolysis and Steam Gasification of Thai lignite (TLN) and Demineralized Thai lignite (DTLN)

Thai-lignite samples (TLN) were isothermally conducted for pyrolysis and steam-N_2 mixing gasification by the DT/FBR at three different temperatures. Figures 2A–2C show the results on the char yields and the remaining solid from process as a function of reaction time at various temperatures. It is found that char yields from the pyrolysis process at various reaction temperatures rapidly decreased over a range of reaction time at 0-30 s. After that, over the range of reaction time at 30-6,000 s, the char yields were nearly constant at 59%, 57.5%, and 56% for temperatures at 750, 800, and 850 °C, respectively. As seen in Figure 2C, char yields from the steam-N_2 mixing gasification gradually decreased over the range of reaction time at 0-100 s, and then changes to decrease slightly after the reaction time was arrived at 100 s until completed reaction at 6,000 s.

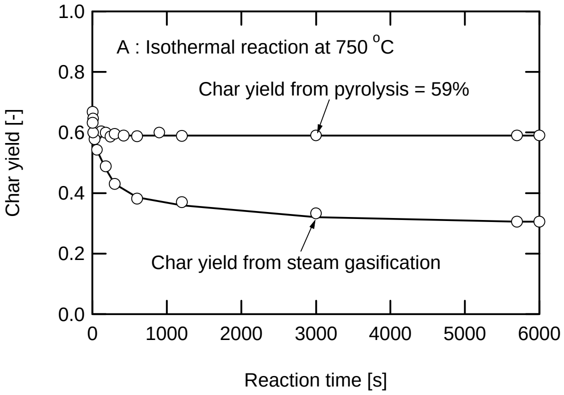

Fig. 2A. The relationship between char yields and reaction time at atmospheric pressure using the drop tube/fixed bed reactor, temperature =750 °C

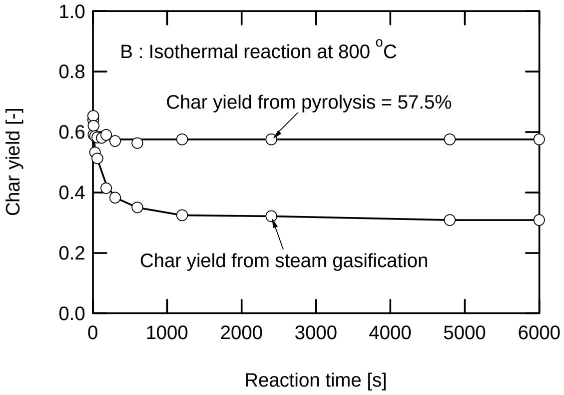

Fig. 2B. The relationship between char yields and reaction time at atmospheric pressure using the drop tube/fixed bed reactor, temperature = 800 °C

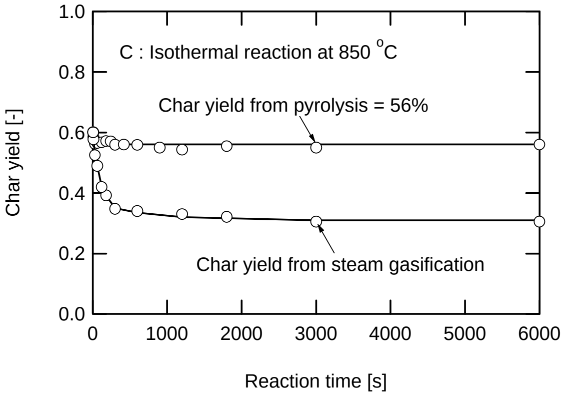

Fig. 2C. The relationship between char yields and reaction time at atmospheric pressure using the drop tube/fixed bed reactor, temperature = 850 °C

From the above findings, it can be suggested that the pyrolysis process can complete within 30 s. In case of steam-N_2 mixing gasification, it can be noticed that the char yields decrease when increasing the reaction time due to the progress of char gasification reaction. These results are found to be corresponding to the work of Bayarsaikhan *et al.* [9], in which a Victoria brown coal (Lay Yong, from the Lartrobe Valley in Victoria, Australia) was investigated by a drop tube/fixed bed reactor. It is reported that, at pyrolysis temperature of 900 ºC, the yield of the Victoria brown coal char was nearly constant over the range of pyrolysis time at 5-10,800 s, and the yield decreased when increasing the heating rate and/or decreasing the total system pressure. By looking at the effect of temperature on char yields, as shown in Figures 2A-2C, it is found that the char yields slightly decrease with increasing in the pyrolysis temperature. This is due to the fact that pyrolysis is a thermal cracking process; therefore, structure of material is more broken with an increasing in the reaction temperature. The solid yield will then be decreased when increasing the temperature. For the steam-N_2 mixing gasification, char yields at reaction time 50 minutes is found to be 33%, 32% and 30% [dry basis] for the reaction temperature at 750, 800, and 850 ºC, respectively. It is observed that the char yields decrease with increasing in reaction temperature due to the fact that the reactants have more energy for converting to products as the reaction of gasification is an endothermic reaction.

The values of char yields at various temperatures as illustrated in the Figures 2A-2C were used to calculate the conversion, *X* (dry-ash free basis), by the Equation 1:

$$X = 1 - \left[\frac{W_{char} - W_{moisture} - W_{ash}}{W_{raw} - W_{moisture} - W_{ash}} \right] \qquad (1)$$

Actually, the conversion from coal gasification process (X_{sg}) is the summation between the pyrolysis step (X_p) and char gasification step (X_{nchar}); therefore, conversion of nascent char from the char gasification step can be defined as Equation 2:

$$X_{sg} = X_p + (1 - X_p) X_{nchar} \qquad (2)$$

The conversion of nascent char during the gasification step, X_{nchar}, was used for kinetic analysis in this investigation. The relationship between loss of nascent char conversion, $1\text{-}X_{nchar}$, and the progress of reaction time at three different temperatures (750, 800, and 850 ºC) is illustrated in Figure 3.

It is found that the $1\text{-}X_{nchar}$ shows a rapidly decrease when increasing the reaction time from 5 s up to a range of reaction time at 60-100 s. After that, it turns to a slightly decreased until the completion of reaction at the reaction time nearly 6,000 s for all employed conditions. The steam-N_2 mixing gasification of demineralized Thai-lignite, DTLN, was also conducted to investigate the effect of mineral matter on the kinetics of steam-N_2 gasification. The relationship between the $1\text{-}X_{nchar}$ of DTLN and progress of reaction time at reaction temperatures 850 ºC is illustrated in Figure 4. As seen in Figure 4, the $1\text{-}X_{nchar}$ shows a slightly decreased fashion over the range of reaction time from 0 to 30 s, and turns then to decrease rapidly over the range of reaction time from 30 s up to 200 s. Finally, the $1\text{-}X_{nchar}$ slightly decreases again and maintain nearly at $1\text{-}X_{nchar} = 0$ when the reaction completes.

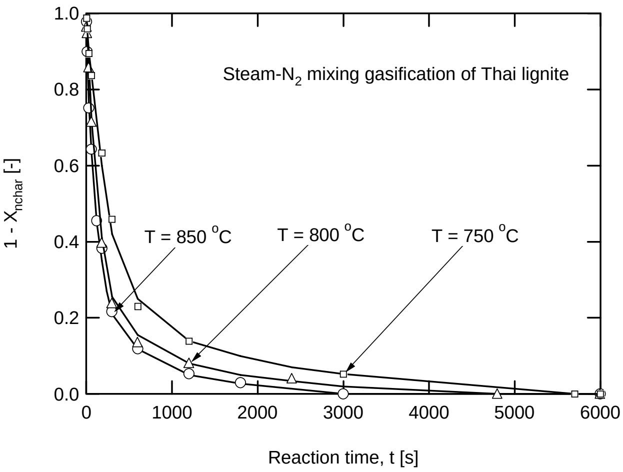

Fig. 3. The relationship between the $1\text{-}X_{nchar}$ and the reaction time of Thai-lignite (TLN) at three different temperatures 750, 800, and 850 ºC.

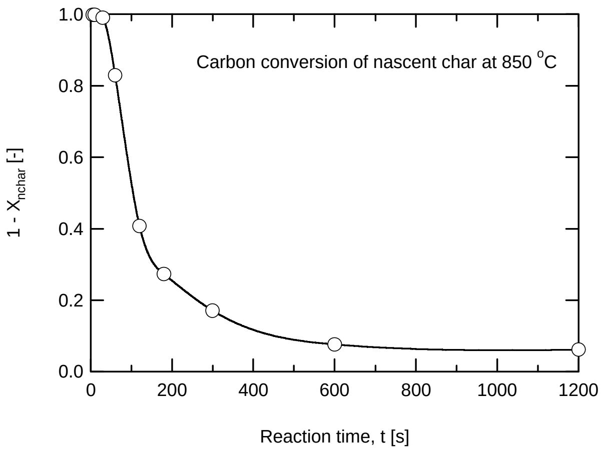

Fig. 4. The relationship between the loss of nascent char conversion, $1\text{-}X_{nchar}$, and the reaction time of demineralized Thai-lignite (DTLN) at reaction temperatures 850 ºC

From the above results, it can be proposed that the reactivities of steam-N_2 mixing gasification are affected by mineral matters as presented in form of ash. These behaviors are found to be corresponding to the behaviors of char gasification, as presented in previous researches [9], [14]–[16]. It, therefore, can be presumed that the reactivity of steam-N_2 mixing gasification for TLN also consists of two steps; i) over the range of the X_{nchar} at 0-0.2, and ii) at 0.2-1. However, effects of mineral matters on the reactivity of steam gasification for TLN will be discussed in next section.

Effects of Mineral Matters on Reactivity of Thai-lignite Steam-N_2 Mixing Gasification

In order to clarify the effects of mineral matters on reactivity of steam-N_2 mixing gasification for TLN, specific gasification rate (r_{sg}) is obtained by Equation 3.

$$r_{sg} = \frac{dX_{nchar} / dt}{(1 - X_{nchar})} \qquad (3)$$

Figure 5 shows the specific gasification rates of TLN ($r_{sg,\ TLN}$) and DTLN ($r_{sg,\ DTLN}$). It is found that the $r_{sg,\ TLN}$ continuously decreases with increasing in the X_{nchar}. The $r_{sg,\ TLN}$ reaches the highest at 0.025 s^{-1} when $X_{nchar} = 0$, and then gradually decreases over the range of the X_{nchar} from 0 up to 0.2. For X_{nchar} at 0.2-1, the $r_{sg,\ TLN}$ changes again to decrease slightly until the completion of reaction. In contrast, the values of $r_{sg,\ DTLN}$ at various conversions are found to continuously increase with progress of X_{nchar} from 0 to 0.4. Subsequently, it tends to decrease over the range of X_{nchar} from 0.4 to the completion of reaction at 1. It can be seen that the highest specific reaction rate of DTLN is reached at 0.013 s^{-1} when $X_{nchar} = 0.4$.

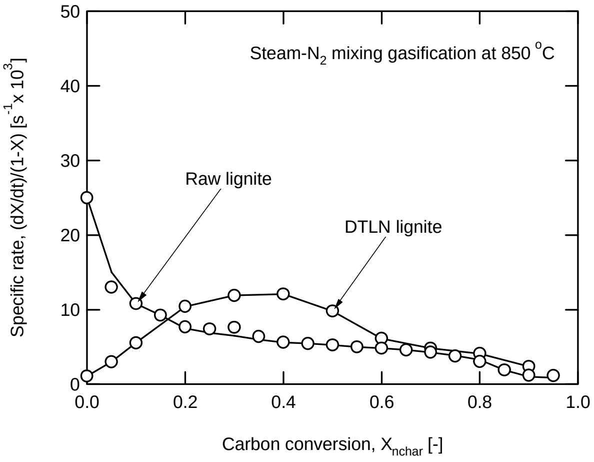

Fig. 5. The specific gasification rate of the steam-N_2 mixing gasification for Thai-lignite, $r_{sg,\ TLN}$, and demineralized Thai-lignite, $r_{sg,\ DTLN}$, at the reaction temperature 850 ºC and atmospheric pressure

In addition, the behavior of specific gasification rate of TLN is found to be similar to that of DTLN at the latter period over a range of X_{nchar} from 0.6 to 1. However, the behaviors of both samples are quite different at the early period of reaction as the specific gasification rate of TLN is much higher than the specific gasification rate of DTLN. These results are found to be well corresponding to those of many researchers [9], [14]–[16]. They reported that the gasification rate consists of a catalytic gasification and a non-catalytic gasification, and also suggested that the loss of catalytic activity was caused by volatilization and/or deactivation of inherent mineral matters.

As the result of all previously mentioned, it can be summarized that the reactivity of steam-N_2 mixing gasification of TLN is affected by the mineral matters which can act as catalysts in early period of reaction. In order to clarify the deactivation of mineral matters that act as catalysts, the X-ray diffraction (XRD) patterns of solid residuals from pyrolysis and steam-N_2 mixing gasification, also called char product, were conducted by utilizing X-Ray diffractometer (Bruker AXS Model D8 Discover). The XRD patterns of char products from pyrolysis and direct gasification at temperature 850 ºC are shown in Figure 6. It can be observed that the peaks of crystal structures of char product from direct gasification are more detected than those of char product from pyrolysis, especially on peaks of $MgFe_2O_4$, Fe_2O_3 and CaS. From this finding, it can be suggested that some kinds of the inherent mineral matters, such as magnesium, iron, and calcium, lost their activities by the formation of crystal structures.

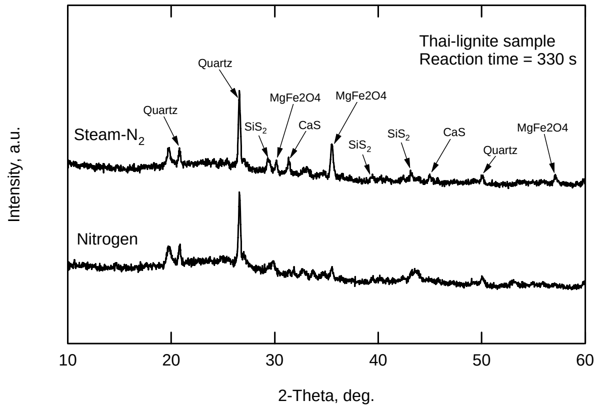

Fig. 6. X-ray diffraction (XRD) patterns of char product from pyrolysis and steam-N_2 gasification, conducted by the DT/FBR

For this study, volatilizations of inherent mineral matters as represented in formation of ash were also investigated by calculation of relative ash following the simple equation show in Equation 4.

$$Relative\ ash\ [\%] = [Ash_{solid}\ x\ Solid\ yield]/100 \qquad (4)$$

It is accounted that the relative ashes of raw Thai-lignite, pyrolysis solid of Thai lignite, and steam-N_2 gasification solid of Thai lignite are 37%, 31%, and 27%, respectively. Also the losses of mineral matters of TLN are found to be devolatiled by 6% and 10% during pyrolysis and gasification process, respectively.

In summary, it can be proposed that the mineral matters of TLN act as catalyst at the early period of the reaction and deactivate with the progress of reaction. The deactivation of catalytic gasification can be caused by devolatization and deactivation during gasification process. This summary is in broad agreement with the result from [9].

Kinetic Model of the Steam Gasification Process

From the results in the previous section, it can be indicated that the reactivity of steam-N_2 gasification of TLN at 850 ºC generally consists of two periods or reactions; i) at a range of conversion from 0–0.2, and ii) at a range of conversion from 0.2 to 1. The first period of reaction is affected by the mineral matters in raw Thai-lignite, which act as catalysts for the steam gasification. The second period of reaction is regarded as the non-catalytic gasification. The combination of these two periods of reaction presents the total gasification rate. A zero order reaction has been proposed for kinetic study of the catalytic gasification. The rate of catalytic gasification is considered to be a function of the amount of the active mineral species, but independent from the amount of the conversion. The catalytic gasification rate can be expressed by the following equations:

$$\frac{dX_{nchar}}{dt} = k_{cat} \qquad (5)$$

$$k_{cat} = k_{cat,0} \exp(-k_{deact} t) \qquad (6)$$

k_{cat} is the rate constant of the catalytic gasification reaction

$k_{cat,\,0}$ is the rate constant at $t = 0$, k_{deact} is the overall rate constant for the loss of active catalytic species.

$$\ln\left(\frac{dX_{nchar}}{dt}\right) = \ln k_{cat,0} - k_{deact}t \qquad (7)$$

The $k_{cat,\,0}$ and k_{deact} can be calculated by method of linearization. Equation 7 is the linearized equation from Equation 6, in which the $k_{cat,\,0} = 0.02$ s^{-1} and $k_{deact} = 0.085$ s^{-1} are obtained from intersection and slope of the strength line, respectively. Table 2 shows the kinetic parameters of this system at three different temperatures (750, 800, and 850 ºC).

Table 2. The kinetic parameters of the steam-N$_2$ gasification of Thai lignite at three different temperatures

Temperature (ºC)	$K_{cat,\,0}$ (s^{-1})	K_{deact} (s^{-1})	$k_{ncat,\,0}$ (s^{-1})	Ψ (-)
850	0.0200	0.085	0.0017	10
800	0.0074	0.022	0.0015	6
750	0.0030	0.012	0.0009	3

When looking at non-catalytic gasification, the rate is, in contrary, a function of the conversion. Many models have been used to describe the behavior of the reaction in this period [9], [10], [17]. But the random pore model has been applied in this study for the investigation in the non-catalytic gasification of TLN (in-situ gasification) due to the better results than those obtained by the other models. The random pore model does consider physical structural changes during the progress of gasification reaction. The random overlapping of pores' surfaces does the reaction on the areas available for reaction. The equations of this model [11], [18] are as follows:

$$\frac{dX_{nchar}}{dt} = k_{ncat,0}(1 - X_{nchar})[1 - \psi\ln(1 - X_{nchar})]^{1/2} \qquad (8)$$

where $k_{ncat,\,0}$ is a rate constant at $t = 0$ and Ψ is a parameter related to the pore structure of the unreacted sample ($X = 0$).

Equation 8 is then linearized, as illustrated in Equation 9, to get the kinetic parameters of the random pore model ($k_{ncat,\,0}$ and Ψ).

$$\left[\frac{dX_{nchar}/dt}{1 - X_{nchar}}\right]^2 = k_{ncat,0}^{\ 2} - k_{ncat,0}^{\ 2}\psi\ln(1 - X_{nchar}) \qquad (9)$$

The slope of straight line and its intercept point can be used to calculate $k_{ncat,\,0}$ and Ψ, respectively. It is found that the $k_{ncat,\,0}$ and Ψ for TLN steam-N$_2$ mixing gasification at 850 ºC are 0.0017 s^{-1} and 10, respectively, which also shown in Table 2.

The combination of Equations 6 and 8 can provide the total gasification rate of reaction which consists of the catalytic gasification and the non-catalytic gasification as following:

$$\frac{dX_{nchar}}{dt} = k_{cat,0}\exp(-k_{deact}t) + k_{ncat,0}(1 - X_{nchar})[1 - \psi\ln(1 - X_{nchar})]^{1/2} \qquad (10)$$

Figure 7 shows the comparison between the calculated data (based on equation 10) and the experimental data at reaction temperature of 850 ºC.

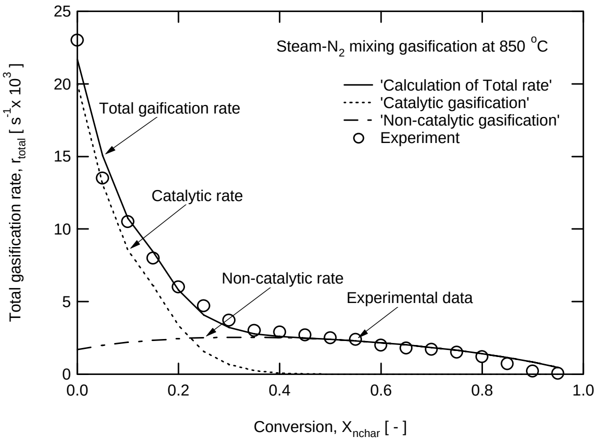

Fig. 7. Comparison between the calculated data and the experimental data of steam-N$_2$ mixing gasification of Thai lignite at reaction temperature 850 ºC

As seen in the figure, the calculated data are well corresponding to the experimental data. Equation 11 then represents the curve of the calculated data presented in Figure 7.

$$\frac{dX_{nchar}}{dt} = 0.02\exp(-0.085\,t) + 0.0017\,(1 - X_{nchar})[1 - 10\,\ln(1 - X_{nchar})]^{1/2} \qquad (11)$$

It can be concluded that the kinetics of steam-N$_2$ gasification at 850 ºC for TLN at the early period of reaction is strongly affected by mineral matters, which can be attributed by the zero-order reaction shown in the terms of $k_{cat,\,0}$ and k_{deact}, whereas the kinetics at the latter period of reaction can be well described by the random pore model which is a function of the conversion and the growing of pore surface area. Moreover, the reactivity of each period can separately occur as two parallel reactions that can be presented by different kinetic constants.

Morphological Analysis for Steam-N$_2$ Gasification of Thai-lignite

In order to gain a better understanding in kinetics of Thai-lignite gasification, especially on non-catalytic gasification, it is important to also have a clear view of morphological changes during the gasification process. The information obtained from [19] indicated that parent coal properties were still significant in determining the final char morphology and its kinetics. Therefore, Scanning Electron Microscopy (SEM) was selected in this study to acquire pictures of char particles coming from different conditions in order to clarify the kinetics of steam-N$_2$ mixing gasification for Thai lignite.

SEM photographs of raw Thai-lignite are shown in Figures 8A and 8B. As seen in Figure 8A, it can be confirmed that all studied particle sizes were less than 75 microns, which can reduce effects of heat and mass transfer during reaction progress. Unfortunately, pore structure can not be clearly observed on the surface area of particles as illustrated in Figure 8B.

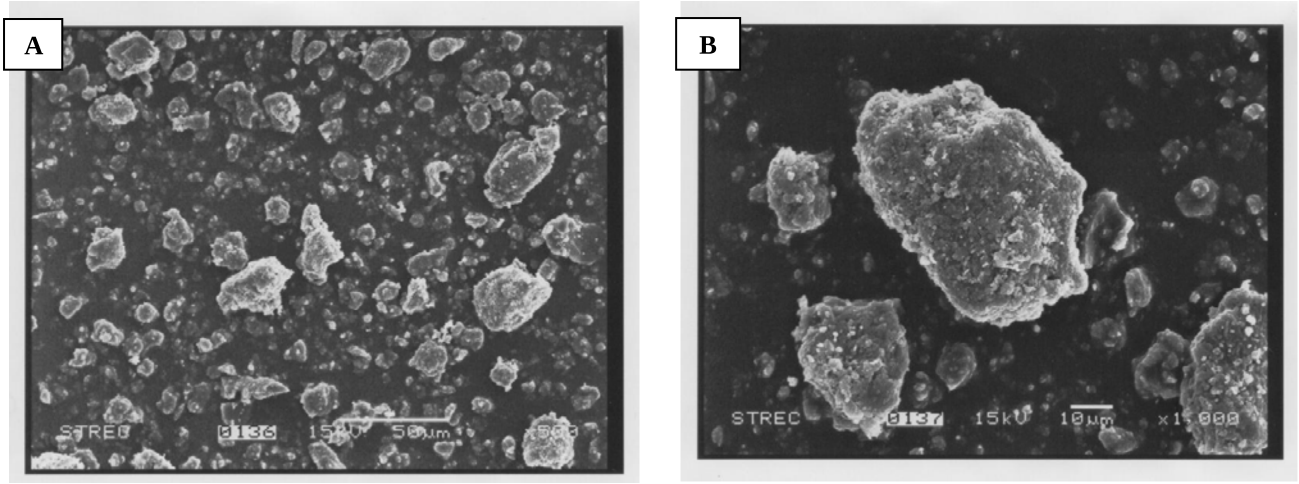

Fig. 8A and 8B. SEM photographs of raw Thai-lignite

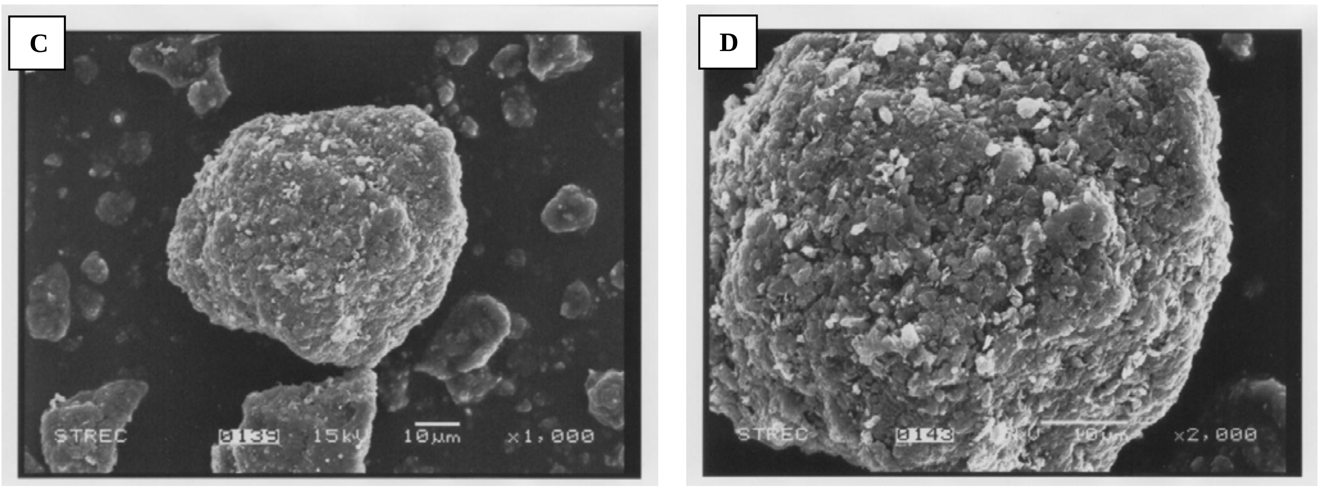

Fig. 8C and 8D. SEM photographs of char sample from pyrolysis at 850 ºC

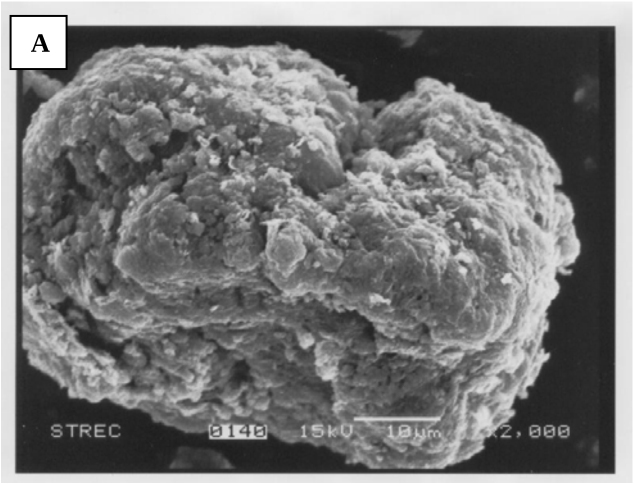

Fig. 9A. SEM photograph of char sample from steam-N_2 gasification at 850 ºC and 30 s

Figures 8C and 8D show SEM photographs of char particles from pyrolysis at 850 ºC, as they represent the raw-char materials for subsequent gasification step. It is found that char particles seem to be swelling or more porous. This is due to the fact that the volatile matters are immediately released from inside particles during pyrolysis step. The SEM photograph of char particles from steam-N_2 gasification at 850 ºC and 30 s is illustrated in Figure 9A, showing that the char particles at 30 s became rough/sponge particles, and more porous surfaces can be observed on the particle surface area. This can be suggested that the reactive gas (steam) diffuse into surface area and inside of pore structures.

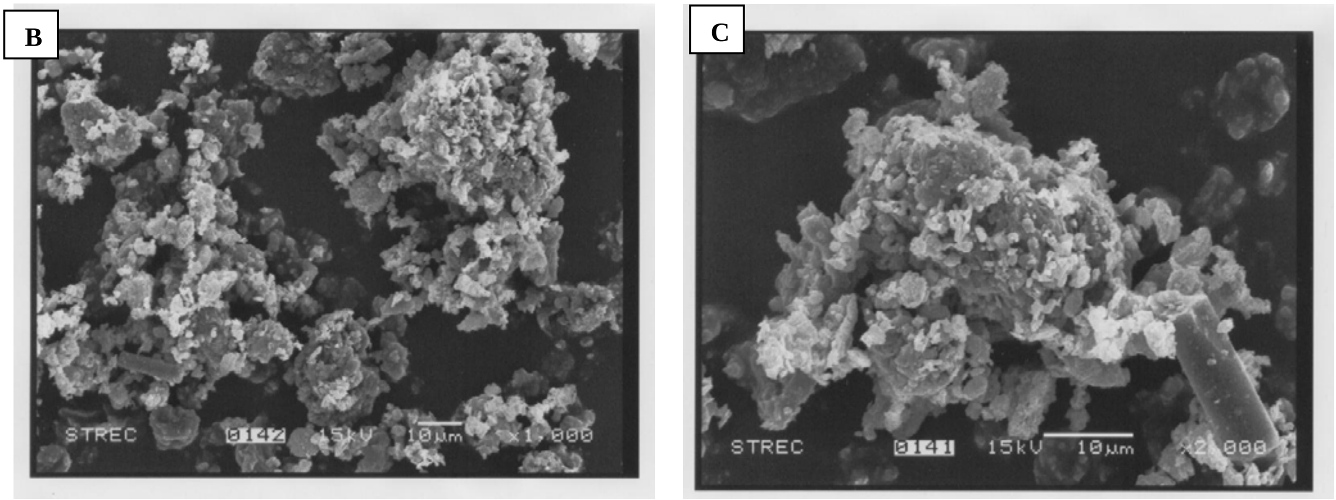

Fig. 9B and 9C. SEM photographs of char sample from steam-N_2 gasification at 850 °C and 330 s

From the results that were observed through all SEM photographs, the morphological changes of char particles during steam gasification in this study can be noticed as the following:

1) The swelling/porous particles were formed by the release of volatile matters from inside particle during pyrolysis step.
2) Steam would then diffuse into the surface and the inside of pore structure to react with the active sites at the edges of carbon crystallites, resulting in formation of spongy structures as represented by pictures of char from gasification at 30 s. It is presumed that the reaction rate of non-catalytic gasification increases in the early period of reaction due to the growing of pore structures that can lead to an increase in the reactive surface area.
3) The reaction would be decreased, after it rose to the highest, by the overlapping of pore's structures with the progress of gasification reaction. This can be supported by the decay in structures as presented in SEM photographs of char from gasification at 330 s.

According to the statements above, it can be therefore confirmed that the random pore model is a better model for the investigation on the gasification rate, especially on the non-catalytic gasification, which can be proved by those SEM photographs.

4. CONCLUSION

To increase a better understanding for a design and practical gasification process of Thai lignite, the kinetics study using a drop tube/fixed bed reactor (DT/FBR) is therefore of interest and studied. The results from the study show that, for the isothermal pyrolysis of Thai lignite at temperature of 750, 800, and 850 ºC, the pyrolysis reaction completed over the range of reaction times from 5 s to 30 s, and the char yields decreased when increasing the reaction temperature. In case of steam-N_2 mixing gasification, the char yields were found to continuously decrease with increasing in the reaction time. This is because of the progress of gasification reaction. The char yields were also found to decrease with an increase in reaction temperature due to the fact that the gasification process is an endothermic reaction. By observation, the reactivity of steam-N_2 gasification of Thai lignite consisted of two periods. The early period was strongly affected by the mineral matter, which could be attributed to the zero order reaction as shown in term of rate constant at $t = 0$ and overall rate constant for the loss of active catalytic species, whereas the latter period was noticed to be well described by the random pore model, which is a function of the conversion and the growing of pore surface areas. In this study, the steam gasification rates obtained from experiments were found to be corresponding to the total gasification rate obtained by calculations. The gasification rate of steam-N_2 mixing gasification which is the combination between the catalytic gasification and non-catalytic gasification can be expressed as follows:

$$\frac{dX_{nchar}}{dt} = 0.02\exp(-0.085\,t) + 0.0017\,(1 - X_{nchar})\left[1 - 10\ln(1 - X_{nchar})\right]^{1/2}$$

In addition, SEM photographs of char particles were also conducted to clarify behaviors of steam-N_2 mixing gasification for Thai lignite. From the results, it can be confirmed that the random pore model can be used for the study of Thai-lignite gasification rate, especially on the non-catalytic gasification.

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NOMENCLATURE

k_{cat}	Rate constant of catalytic gasification reaction, s^{-1}
$k_{cat,\,0}$	Rate constant of catalytic gasification reaction at $t = 0$, s^{-1}
k_{deact}	Overall rate constant for the loss of active catalytic species, s^{-1}

$k_{ncat,\,0}$	Rate constant of non-catalytic gasification reaction at $t = 0$, s^{-1}
r_{sg}	Specific rate of gasification, s^{-1}
t	Time, s
T	Temperature, ºC
W_{ash}	Weight of remaining ash, mg.
W_{char}	Weight of remaining char at t, mg
$W_{moisture}$	Weight of moisture in sample , mg.
W_{raw}	Weight of sample at $t=0$, mg.
X	Char conversion, dry-ash free basis
X_{nchar}	Conversion of nascent char from char gasification step
X_p	Conversion of coal in the N_2 flow (pyrolysis)
X_{sg}	Conversion from steam-N_2 gasification process
Ψ	Parameter related to the pore structure of the unreacted sample
DTLN	Demineralized Thai-lignite
DTF	Drop Tube Furnace
DT/FBR	Drop Tube/Fixed Bed Reactor
I.D.	Inner diameter
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analyzer
TLN	Thai-lignite
XRD	X-ray diffraction

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