

Kinetic Model of Steam Reforming for Heavy Tar Decomposition in Biomass Gasification

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Gasification technology as a feasible clean and efficient utilization technology has been developed to convert the low-grade energy resources like biomass into high value syngas. The generation of syngas is often accompanied by tar formation, which causes blockage in the downstream processing as tar condenses. The elimination of naphthalene and pyrene as heavy tar model compounds by steam reforming was studied by experiments in a horizontal tube reactor and simulation with CHEMKIN. A good agreement between the measured and calculated results of light gas products and soot was observed, and one can find that the reactivity of naphthalene is higher than that of pyrene in the presence of steam and most of carbon of both hydrocarbons convert into soot instead of light gaseous products. The reaction pathways of steam reforming were developed by sensitivity analysis and rate of production. Benzene and naphthalene, represented as precursor of light gas product, are dominated intermediate components of naphthalene and pyrene. The simplified reaction schemes including the reaction pathway as well as the associated kinetics were derived by CHEMKIN.

1. Introduction

To meet the rapidly growing demand of energy and deal with the consequent environmental issues, the gasification technology as a feasible clean combustion technology has been developed to convert biomass into high value syngas (Siwal et al., 2020). During gasification, many by-products are generated such as variable amounts of fly ash, volatile alkali metals and tar (Palma et al., 2013). In particular, tar formation often occurs in the syngas, causing blockage in the downstream processing as it condenses. It is desired to decompose the tar into gaseous products as much as possible during the gasification process.

Tar is a complex mixture of condensable hydrocarbons. According to its appearance, tars can be classified as the primary, secondary and tertiary ones. The primary tar mainly consists of oxygenated compounds and its formation takes place at a low temperature (673 - 873 K), like acetol and acetic acid (Fitzpatrick et al., 2009). The secondary tar containing phenolics and olefines, such as phenol, benzene and toluene, may be produced in a medium temperature range (873 - 1,073 K), while the tertiary tar comprising aromatic compounds is formed at high temperature range (1,073 - 1,273 K) (Ren et al., 2020). Heavy tars like large molecular PAHs are generally considered as the main tertiary tar (Apicella et al., 2017). Further effort is required to explore the decomposition of heavy tar.

Although many methods have been investigated to remove the tar from product gas (Ashok et al., 2020), steam reforming of tar seems to be the best way that can not only eliminate tar but also increase hydrogen yield. In case of steam reforming, the effects of operational conditions such as temperature, steam/carbon molar ratio and residence time on model compounds of the secondary such as benzene, toluene, naphthalene and phenol have been partly studied (Artetxe et al., 2017). However, the mechanisms and kinetics of their decomposition were often ignored. Very few data related to the kinetic parameters and reaction pathways were obtained. Given the complexity of reactions, the majority of the kinetic models obtained by experimental works were overall reaction, which were often determined by the overall weight loss of the tar or the light gaseous products such as CO, CH₄, and H₂. The work of Jess (1996) was one of the few that available presented an reaction scheme of

aromatic hydrocarbons (naphthalene, toluene and benzene) removal in the presence of steam and hydrogen was developed. In the scheme, naphthalene reforming was expressed as the light gaseous formation by cracking reactions and soot precursors formation by condensation reactions. The kinetic parameters of the formation of soot and cracking products have been calculated.

In this paper, naphthalene and pyrene, representing two-ring PAH and four-ring and above PAH, are used as model compounds of heavy tar in the steam reforming process. The comparison between the experimental results and the numerical predictions by CHEMKIN will be performed. Combined the results of experiments and simulations, a kinetic model including the reaction pathway as well as the associated kinetics is obtained for steam reforming of these model compounds.

2. Experimental approach

2.1 Experimental system

A schematic diagram of experiment system is shown in Figure 1. A horizontal corundum tube with inner diameter of 30 mm and length of 800 mm was placed inside an electric furnace heating by silicon molybdenum rods. The temperatures along the tube reactor were measured by a Pt-Rh thermocouple. The steam was vaporized in a steam generator and mixed with hydrocarbons (naphthalene, pyrene) evaporated by electric tracing band. Argon as a carrier gas flowed through the electric tracing band and pushed the mixture through the reaction zone with length of 300 mm when operation temperature reached the preset value. The mass flow rates of argon and steam were well controlled. The product gases were collected by gas storage bag after they passed through a condensing and drying tube. The gases were analyzed offline using gas chromatograph (GC). The soot was absorbed by quartz wool placed in the outlet of reactor and burned by oxygen in reaction zone. The content of soot was calculated by the combustion products analyzed by GC.

Reaction conditions of the experiments are listed in Table 1. Experiments were carried out at atmospheric pressure within a range of 1,273 - 1,673 K in reaction zone. Naphthalene as typical two ring polyaromatic hydrocarbons and pyrene as typical four ring polyaromatic hydrocarbons were used as model compound representing heavy tars.

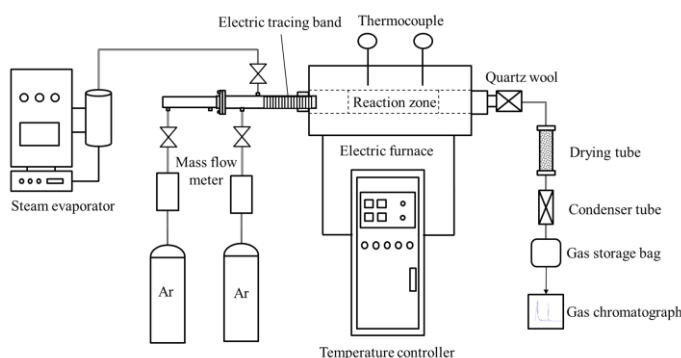


Figure 1: Experimental system of heavy tar steam reforming

Table 1: Reaction conditions of the experiments

Model compounds	Sample weight (mg)	Temperature (K)	Steam (vol%)	Residence time(s)
Naphthalene	10	1,273 - 1,673	30	2
Pyrene	10	1,373 - 1,673	30	2

2.2 Conversion

According to the previous work of Jess (1996), the reaction of aromatic hydrocarbons reforming can be summarized into two reaction pathways: (a) Cracking reactions of PAH leading to hydrocarbons with small carbon numbers; (b) Condensation reactions leading to soot precursors. The conversion of model compound j with carbon number $N_{C,j}$ cracking into light hydrocarbons (CO , CO_2 , CH_4) is defined as:

$$X_{c,j}(\%) = (n_{\text{CO},out} + n_{\text{CO}_2,out} + n_{\text{CH}_4,out}) / (n_{j,in} \cdot N_{C,j}) \times 100 \quad (1)$$

The yield of soot is calculated based on the amounts of CO and CO_2 when the collected sample is fully burnt. The conversion of model compound j forming soot precursors can be expressed as:

$$X_{s,j}(\%) = n_{soot,out} / (n_{j,in} \cdot N_{c,j}) \times 100 = (n_{CO,soot} + n_{CO_2,soot}) / (n_{j,in} \cdot N_{c,j}) \times 100 \quad (2)$$

The conversion of the model compound j can be calculated by:

$$X_j(\%) = X_{c,j} + X_{s,j} \quad (3)$$

3. Simulation calculation

Numerical simulation for heavy tar steam reforming was conducted using the Plug-flow Reactor module of CHEMKIN. A detailed chemical kinetic model for hydrocarbon combustion and polycyclic aromatic hydrocarbon developed by Richter and Howard (2002) was chosen. It was used to successfully predicted the thermal reactions of aromatic hydrocarbons from pyrolysis of solid fuels (Norinaga et al., 2011) and characteristics of partial oxidation of gas emitted from metallurgical coke ovens (Norinaga et al., 2010). The reaction conditions used in the simulation were consistent with the experimental conditions.

4. Results and discussion

4.1 Experiment and simulation analysis

Figure 2 shows the experimental conversion of PAHs, the cracking gas products and condensable deposited soot as a function of reference temperature T_R under the reaction conditions. It is found that polymerization and condensation lead to approximate 50 % carbons in PAH convert into soot precursors when temperature is up to 1673 K. Most of carbon of both of them convert into soot instead of light gaseous products. The main gaseous products were CO, CO₂ and CH₄. The content of soot was calculated by the amounts of combustion products (CO and CO₂) of the deposited soot precursors. With increasing temperature, the contents of soot, generated by naphthalene steam reforming, increases at first then decreases after 1,573 K. It is unraveled that the reaction of soot with steam at elevated temperature caused concentration of soot to decrease. The contents of soot of pyrene steam reforming rapidly increased in the temperature range from 1,373 K to 1,473 K, but only a slight increase was observed when temperature is up to 1,473 K. The possible reason is also the secondary cracking of soot with steam, while the reaction rate of soot formation is faster than decomposition rate of soot. Figure 2 also compares the conversion derived from the numerical simulation with those obtained by experiments in different temperature. Good agreements are found for both conversion of light gas products and soot. The overall conversion of pyrene is depended on the above two conversions, which is also predicted well.

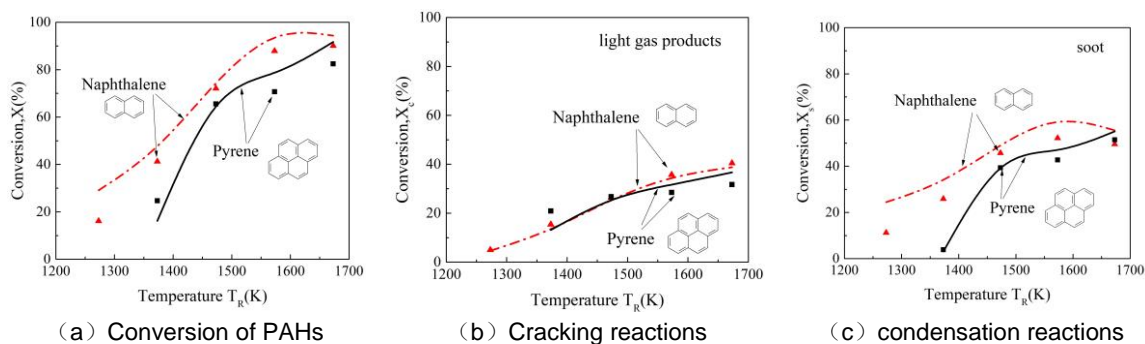


Figure 2: Conversion of naphthalene and pyrene at different temperatures (line-simulation, dot-experiment)

4.2 Reaction scheme

The steam reforming of heavy tar involves a set of complex reactions among PAH, product gases, steam, soot and intermediate products. However, no detailed kinetic modelling is available because of lack of information of intermediate products. In this section, the main reaction pathway for tar steam reforming was obtained by distributions of main components through CHEMKIN.

4.2.1 Naphthalene

Figure 3 gives the predicted distributions of main components in naphthalene steam reforming as a function of resident time (length of reactor) at 1,573 K. The reaction of aromatic hydrocarbons reforming are summarized into two reaction pathways. The first reaction pathway is the cracking reactions leading to hydrocarbons with

small carbon numbers, and the other one is condensation reactions accompanying with the growth of larger PAHs (soot precursors) (Figure 3b). As shown in Figures 3a and 3c, the consumption of naphthalene finishes in 0.5 s. Indene and benzene are two dominating intermediates of cleavage of naphthalene. Indene is a stable intermediate of naphthalene in gasification condition. The initial step of decomposition of naphthalene is naphthol formation by substitution reaction with steam. After that, naphthol is converted to indene through intermediate naphthoxy radical. Benzene as a key component of degradation of aromatic hydrocarbons is subsequently formed by deprivation carbons of indene. Consecutive reactions of benzene generate light gaseous products. The other direction of conversion of naphthalene is toward soot formation. In addition to the substitution reaction with OH radicals, the reaction of attack of H radicals that supplies naphthyl radical is also an important initial reaction for naphthalene steam reforming, leading to the formation of larger PAHs. The rate of naphthyl radical formation by attack of H radical proposed by Norinaga et al. (2011) is higher than that of naphthol formation by substitution reaction with OH radicals beyond 1,273 K. It means that more carbons in aromatic hydrocarbon are converted to soot than that in light gas products. This is strongly supported by the experimental results in Section 4.1. The concentrations of benzo[fluoranthene and coronene shown in Figure 3d are two largest ones among those of thirty-three PAHs, while their formation pathways are different. The combination of naphthalene with naphthyl radical results in the benzo[fluoranthene formation, whereby hydrogen is liberated. Coronene formation is based on the HACA (Hydrogen Abstraction and Acetylene Addition), which is a dominant pathway for the growth of PAHs up to the formation of soot. The mechanism of HACA means that one mole of hydrogen is removed while adding one mole of acetylene to form aromatic ring. The secondary cracking of soot precursors as PAHs with steam after 0.5 s is similar to process of naphthalene steam reforming. According to the experimental and stimulative results, a simplified reaction scheme for naphthalene steam reforming is developed, as shown in Figure 4. In the scheme, the detail of soot formation and decomposition is simplified, then indene and benzene are the dominated intermediates.

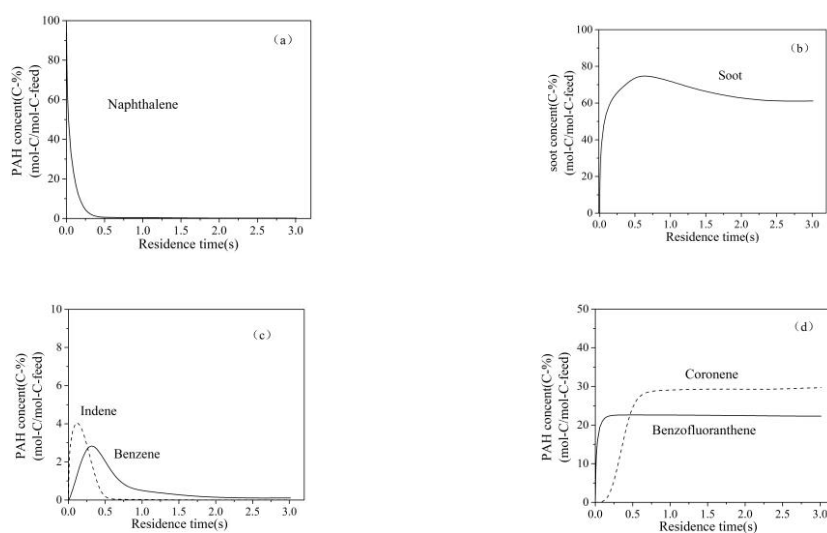


Figure 3: The concentration of main components in naphthalene steam reforming as a function of resident time (length of reactor) at 1573 K in numerical simulation

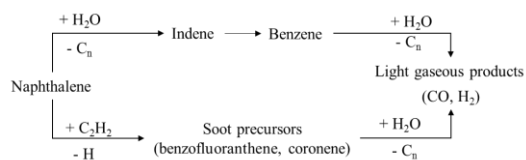


Figure 4: Simplified reaction paths for naphthalene steam reforming

4.2.2 Pyrene

Figure 5 gives the predicted distributions of main components in pyrene steam reforming as a function of resident time (length of reactor) at 1673 K. As shown in Figure 5a, there is still a small amount of residue at 2.0 s, which validates that the decomposition rate of pyrene is slower than that of naphthalene. Like decomposition

of naphthalene with steam, the steam reforming of pyrene is a complex process. The simulation results of important intermediates and soot are presented in Figure 5b and Figure 5d. Phenanthryl is a primary reaction product, resulting from the substitution reaction with OH radicals, whereby ethenone is liberated. Ethenone subsequently converts to CO and H₂. Phenanthryl can undergo hydrogenation reaction to phenanthrene, which is a stable intermediate in the first stage as shown in Figure 5c. Naphthalene is the second stage intermediate, formed by the reverse process of HACA reaction of phenanthryl, namely hydrogen addition and acetylene abstraction. The decomposition of naphthalene leads to light gaseous product, which is same with the explanation in Section 4.2.1. Likewise, the other direction of conversion of pyrene is toward soot formation. The presence of pyrenyl, resulting from the reaction of attack of H radicals, is assumed to be a precondition for soot formation. In case of pyrenyl, a reversible reaction occurs, namely formation of cyclopenta[cd]pyrene in the first 0.25 s and decomposition of that after as shown in Figure 5d. The reversible reaction slows down the reduction tendency of pyrene after 0.25 seconds. Similar to naphthalene, the main PAH of soot precursors in pyrene steam reforming is coronene based on results shown in Figure 5d. Naphthalene is the dominated intermediate and the detail of soot formation and decomposition is simplified. A simplified reaction scheme for pyrene steam reforming is shown in Figure 6.

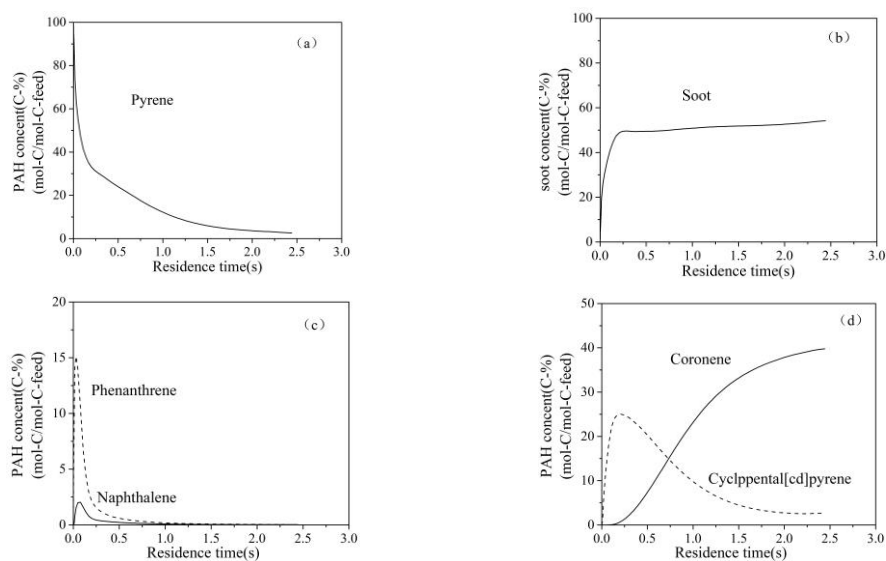


Figure 5: The concentration of main components in pyrene steam reforming as a function of resident time (length of reactor) at 1,673 K in numerical simulation

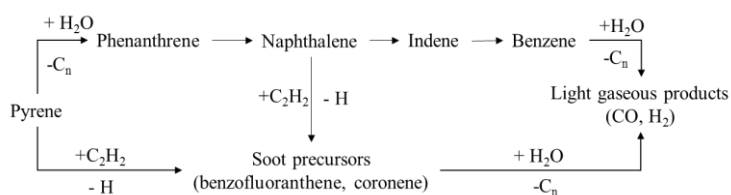


Figure 6: Simplified reaction paths for naphthalene steam reforming

4.3 Kinetic model

According to the simplified reaction scheme above, the primary and consecutive reactions have been given. However, due to lack of the concentration of intermediate products, it is hard to present the kinetic parameters of the primary reactions involving formation of the precursor of light gas product and soot in steam reforming. To obtain the complete the kinetic model of reaction scheme, the reaction rate of formation of precursor of light gas product r_c and the rate of soot formation r_s were determined from the simulations along length of tube (varied residence time) with varied reaction temperature. Benzene and naphthalene were represented as precursor of light gas product of naphthalene and pyrene. The kinetic parameters were calculated by the conversion rate of the primary products in different resident time and reaction temperature. The kinetic parameters of primary reactions of naphthalene and pyrene are summarized in Table 2. The reaction rates of consecutive reaction of decomposition of benzene, methane and soot are derived by the work of Jess (1996).

Table 2: Reaction conditions of the experiments

Reaction rate	Pre-exponential factor	Activation energy (kJ mol ⁻¹)
$r_{c,n} = dc_{C_6H_6}/d\tau _{C_{10}H_8 \rightarrow benzene}$	$2.72 \times 10^{13} m^{0.3} mol^{-0.1} s^{-1}$	360
$r_{s,n} = dc_{C_{soot}}/d\tau _{C_{10}H_8 \rightarrow soot}$	$2.66 \times 10^9 m^{0.9} mol^{-0.3} s^{-1}$	296
$r_{c,p} = dc_{C_{10}H_8}/d\tau _{C_{16}H_{10} \rightarrow naphthalene}$	$1.56 \times 10^8 m^{-0.3} mol^{0.1} s^{-1}$	250
$r_{s,p} = dc_{C_{soot}}/d\tau _{C_{16}H_{10} \rightarrow soot}$	$4.09 \times 10^{14} m^{-2.1} mol^{0.7} s^{-1}$	476

5. Conclusions

The steam reforming of naphthalene and pyrene in a horizontal tube reactor was carried out. The results showed that the reactivity of naphthalene is higher than that of pyrene in the steam reforming. Most of their carbon is converted into soot instead of light gaseous products. The numerical results predicted by CHEMKIN agree well with the experimental data under the given reaction conditions. The simplified reaction pathways of naphthalene and pyrene are developed by means of simulation. The reaction pathways of naphthalene and pyrene are similar. The substitution reaction with OH radicals is regarded as the first step of PAH steam reforming leading to precursor of light gas product, while the reaction of attack of H radicals that supplies the naphthyl or pyrenyl radical is a relatively important initial reaction for the formation of soot precursor. Benzene and naphthalene, represented as precursor of light gas product, are dominated intermediate components of naphthalene and pyrene. Consecutive reactions of these intermediates subsequently generate light gaseous products. Coronene is found to be the largest amount PAH among the thirty-three PAHs substitute of soot precursor. The simplified reaction schemes for naphthalene and pyrene steam reforming are developed and kinetic parameters of the primary reactions are derived.

Acknowledgements

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