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Pyrolysis behavior and kinetic study of phenol as tar model compound in micro fluidized bed reactor

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ABSTRACT

Thermal cracking characteristic of phenol as the model compound of biomass tar was investigated on a micro fluidized bed reactor. Pyrolysis kinetics for individual gaseous component, including hydrogen, methane, carbon monoxide and carbon dioxide were determined based on the iso-conversional and model-fitting approaches. Results indicated that carbon monoxide accounted for the biggest percentage of the total gas yield during pyrolysis of phenol. The evolution profiles of hydrogen energy and carbon monoxide were more affected by reaction temperature compared to methane and carbon dioxide. In the major conversion fraction from 20% to 80%, the apparent activation energies of methane (49.67 kJ/mol) and carbon dioxide (30.87 kJ/mol) were lower than that of hydrogen (145.2 kJ/mol) and carbon monoxide (53.35 kJ/mol). The most probable reaction mechanism for the formation of hydrogen and methane was three-dimension diffusion while chemical reaction and contracting sphere could describe the generation of carbon monoxide and carbon dioxide, respectively.

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Introduction

Gasification is generally viewed as one of the most promising options for converting biomass to gaseous biofuels. However, the generation of tar is a bottleneck problem during this thermo-chemical conversion process [1–3]. As a typical byproduct, tar will be condensed when the temperature is lower than its dew point, rendering the blockage of downstream equipments such as engines, filters and turbines [4], which will severely affect the stable operation of equipments

[5]. Besides, the generation of tar causes a partial loss of input energy [6,7]. Tar removal has been a key issue for utilizing biomass.

As one of the tar reduction methods, thermal cracking can convert tar into lighter gases with small molecules (e.g. hydrogen, methane and carbon monoxide) under high temperatures and certain residence time. This approach can reduce the content of tar without secondary pollution and waste of extra energy retained in the tar [8–10]. It is a potential method to improve the efficiency of thermo-chemical of

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biomass and get extensive studies. Additionally, with the presence of catalysts (e.g. acid catalysts, metal catalysts and activated carbon catalysts), the reaction temperature and residence time can be further decreased to reduce the energy consumption [11–13]. It should be noted that as high temperature is required to crack the tar, the concept of two-stage gasification facilities contributes to better results with respect to this issue. It usually separates the pyrolysis and gasification processes into two varied stages, and tar can be thermal decomposed into gases under higher temperatures by partial combustion of the volatiles between the two stages. This arrangement contributes to the production of gas products with a higher caloric value and lower tar content [14–16].

During this process, kinetic analysis is a promising way to elucidate the reaction mechanisms, which are usually investigated by thermogravimetric analysis (TGA) [17,18]. The thermogravimetric analyzer can monitor the evolution of sample mass in real time. However, the main disadvantage is that the sample needs to be feed into the reaction chamber at normal temperature and there is a small mass-lose before reaching the preset temperature. Besides, due to the limitation of structure and design principle, TGA could not be carried out under the condition of high gas velocity [19,20]. To address this deficiency brought by TGA, Institute of Process Engineering in Chinese Academy of Sciences, Shandong University and Shandong Baichuan Tongchuang Energy Company developed the micro fluidized bed reactor (MFBR). This instrument is mainly composed of a micro fluidized bed and a process mass spectrometer. It can send the samples into the reactor instantaneously when the temperature within the reactor is heated to the preset level. Therefore, the reaction time can be greatly shortened. The process mass spectrometer can analyze the relative concentration of gaseous products online. Then the kinetic parameters can be determined based on the evolution profiles of gaseous product under different temperatures. MFBR can minimize the inhibition of the diffusion and realize the isothermal reaction process in situ [21].

Tar is composed of numerous organic compounds with high boiling points. The main compositions of tar are polycyclic aromatic hydrocarbons (PAHs) in terms of phenol, toluene, benzene, naphthalene, anthracene and styrene [22–24]. Since the tar composition is extremely complex, most studies select one or two compounds of PAHs as the tar model compound, such as toluene [25,26], benzene [27,28] and naphthalene [29,30], but few studies are concerned with the compound of phenol, which is one of the major compositions of tar [31]. This work selected phenol as the tar model compound. The pyrolysis behavior of phenol was investigated in MFBR. Then the kinetic parameters as well as the most probable reaction mechanisms for the reaction processes were determined.

Methods

Experimental facility

Fig. 1 illustrates the schematic diagram of micro fluidized bed reactor system (MFBR). It is mainly composed of a sample

feeding system, a micro fluidized bed and a process mass spectrometer (Dycor ProLine, Ametek, USA). The feeding system is driven by an electromagnetic valve that can release about 10 ml gas per single pulse to send the sample into the reactor within 0.1 s. The pulsed gas originated from a compressed gas stream with the pressure of 0.2 MPa. The fluidized bed reactor is the key part of the MFBR, which is made of quartz and it is capable of bearing high temperatures around 1200 °C for a long time. The overall height and diameter of the fluidized bed reactor are 373 mm and 290 mm, respectively. The internal height and diameter of the reaction zone are 42 mm and 20 mm, respectively. The mass spectrometer can measure the relative content of gaseous products during the pyrolysis of tar online. The temperatures of the reactor and furnace, the pressures of the reactor as well as the actions of the sample feeding system are all controlled by the computer.

Experimental procedure

In this study, quartz sand was selected as the fluidization medium due to the poor catalytic influence on tar cracking. The particle sizes were ranged from 0.2 mm to 0.25 mm. At the beginning of each test, 3.0 g of quartz sand as the fluidizing medium was loaded into the fluidized bed reactor. 10 ± 0.1 mg phenol (Analytical pure, Tianjin Damao Chemical Reagent Factory, China) was placed at the sample-feeding system. After the system was sealed, the fluidizing gas, argon with 99.99% purity, was fed to the reactor to fluidize the quartz sand in the reactor. After several preliminary tests, the gas flow rate was kept at 500 ml/min to ensure all quartz sands were fully fluidized, providing an optimum reaction condition. Afterwards, the reactor was heated to the preset temperatures. Then the pulse valve of the sample-feeding system was switched on to inject the sample into the reaction zone in MFBR, which initiated the pyrolysis reactions. The evolution of produced gas was monitored online by a mass spectrometer. According to Fuentes-Cano et al. [29] and Jess [32], the thermal cracking of polycyclic aromatic hydrocarbons lead to hydrocarbons with smaller carbon numbers and the intermediates are formed only to a limited extent. Consequently, the light gases including hydrogen (H_2), methane (CH_4), carbon monoxide (CO) and carbon dioxide (CO_2) are investigated in the present study. The four gaseous products were all sampled in the entire reaction time to be analyzed via Micro-GC 3000 for quantifying the corresponding yield. The total gas yield was the sum of yields of the four gaseous products investigated in the present study.

According to Fagbemi et al. [33], the thermal cracking of tar is effective above 500 °C. Jess [32] concluded that the temperatures within 1200 °C were necessary for the thermal decomposition of aromatic hydrocarbons as tar model compounds. Dufour et al. [31] carried out a pyrolysis experiment of woody biomass in a quartz tubular reactor and investigated the evolution of aromatic tar composition as a function of reaction temperature. It was reported that with the temperature increasing from 700 °C to 1000 °C, the mole fraction of phenol in the total amount of quantified aromatic tar was gradually decreased from around 25% to 1%. Vivanpatarakij et al. [34] carried out a thermodynamic analysis of biomass gasification, and it was concluded that at a lower operating

Fig. 1 – Scheme for the micro fluidized bed reactor system.

temperature (973 K), phenol was the major tar component and at a higher temperature (1173 K), most phenol was thermal cracked into light gases. Therefore, the preset temperatures in the present study for thermal decomposition of phenol were selected between 750 °C and 950 °C with 50 °C intervals.

Kinetic methods

Activation energy is one of the most significant kinetic parameters evaluating the reactivity, which is usually calculated based on model-fitting method or model-free/iso-conversional method. The latter approach can determine the apparent activation energy without the assumption of reaction model, thus it can eliminate the inaccuracy of “kinetic compensation effect” [35] brought by the application of model-fitting method. Friedman-Reich-Levi method [36] is a typical iso-conversional method, which is used to determine the kinetic parameters in the present study. Since the pyrolysis of phenol in MFBR is a heterogeneous solid–state reaction, the global kinetics of the reaction can be described as [17,37]:

$$dx/dt = k(T) \times f(x) \quad (1)$$

where $k(T)$ is the rate constant of reaction, $f(x)$ is the differential reaction model, T is the reaction temperature, t is the reaction time, x is the conversion fraction of gas concentration. It was defined by the produced gas volume against the total gas volume at the end of the reaction [19], which can be calculated through:

$$x = \frac{\int_{t_0}^t V_i \times V dt}{\int_{t_0}^{t_e} V_i \times V dt} \times 100\% \quad (2)$$

where V_i is the volume rate of the gas product i , V is the volume rate of all gas products, t_0 is the start time of reaction, and t_e is the end time of reaction.

In Eq. (1), $k(T)$ is determined by Arrhenius equation:

$$k(T) = A \exp(-E_a/RT) \quad (3)$$

where E_a is the apparent activation energy, A is the pre-exponential factor, R is the universal gas constant.

Substituting of Eq. (3) into Eq. (1), then, taking the logarithm of both sides results in the expression for the Friedman-Reich-Levi method:

$$\ln(dx/dt) = -E_a/RT + \ln A + \ln f(x) \quad (4)$$

The points of $\ln(dx/dt)$ versus $1/T$ at different reaction temperatures can be fitted to a straight line, and the slope of the line corresponds to $-E_a/R$. Therefore, the apparent activation energy E_a can be finally deduced from the slope of the straight line.

The most probable reaction mechanism for pyrolysis of phenol in MFBR was evaluated based on the universal integral method [38,39], which is a typical model-fitting approach.

Eq. (1) can be further converted into Eq. (5) as:

$$dx/f(x) = k(T) \times dt \quad (5)$$

Taking the integration of the both sides of Eq. (5), and it can be further integrated into:

$$G(x) = \int_0^x \frac{dx}{f(x)} = k(T) \times t \quad (6)$$

where $G(x)$ is the integral reaction model. Based on Eq. (6), the points of $G(x)$ versus t at different reaction temperatures can be fitted to a straight line, and the slope of the line corresponds to $k(T)$.

Taking the logarithm of both sides of Eq. (3) can lead to the expression:

$$\ln k(T) = -E_a/RT + \ln A \quad (7)$$

Then based on Eq. (7), the plots between $\ln k(T)$ versus $1/T$ generate a straight line with the slope $-E_a/R$ to determine the

Table 1 – Product distribution for pyrolysis of phenol at different temperatures.

Temperature (°C)	750	800	850	900	950
Total gas yield (%)	65.27	68.78	73.22	79.16	83.21
H ₂ (%)	3.72	4.13	4.47	6.10	6.82
CH ₄ (%)	1.11	1.58	2.20	2.61	3.41
CO (%)	42.62	47.46	56.23	62.38	65.99
CO ₂ (%)	17.82	15.61	10.32	8.07	6.99

apparent activation energy once again. The most probable reaction model $G(x)$ can be determined based on the closeness of the value of apparent activation energies obtained from the universal integral method and Friedman-Reich-Levi approach.

Results and discussion

Product distribution

The yields of produced light gas at different reaction temperatures during pyrolysis of phenol in MFBR were shown in Table 1. It can be seen that CO was the major composition of pyrolysis gas mixture from phenol, which made up a large percentage of total gas yield. Horn et al. [40] carried out high-temperature shock-tube pyrolysis of phenol and CO was

observed to be the principal products, which is consistent with the present work. However, Jess [32] investigated the thermal degradation of aromatic hydrocarbons as tar model compounds, and it was reported that with increasing temperature, the organic cracking products from naphthalene were more converted to CO while CH₄ and C₂H₄ are the major cracking products from benzene. It suggests that the product distribution is also concerned with the chemical composition of the tar model compounds.

With increasing the reaction temperature, the total gas yield gradually increased from 65.27% at 750 °C to 83.22% at 950 °C. It suggests that the cracking reaction of tar model compound is favored at higher temperatures. However, the variations of gaseous products were not a monotonic trend. Specifically, the yield of H₂ increased gradually from 3.72% at 750 °C to 6.82% at 950 °C. This trend agrees well with the variation of H₂ yield during the pyrolysis of real biomass like straw [33] or model compound like toluene [11]. The yield of CH₄ and CO was also increased from 1.11% and 42.62% to 3.41% and 65.99%, respectively. A gradual decrease from 17.82% to 6.99% was observed for CO₂.

Pyrolysis behavior of phenol

Fig. 2 showed the effect of temperature on the relationship of the conversion fraction versus reaction time for different gaseous products (i.e. H₂, CH₄, CO and CO₂) during pyrolysis of

Fig. 2 – Evolution of conversion fractions versus reaction time at different temperatures for pyrolysis of phenol.

Table 2 – Apparent activation energies for individual gas during pyrolysis of phenol.

Gas	Conversion (wt.%)	R ²	SD	E _a (kJ/mol)	Gas	Conversion (wt.%)	R ²	SD	E _a (kJ/mol)
H ₂	20	0.924	0.043	15.29	CH ₄		0.905	0.042	20.83
	30	0.920	0.044	55.41			0.926	0.041	25.51
	40	0.982	0.021	117.5			0.943	0.036	29.69
	50	0.989	0.013	155.1			0.991	0.021	41.04
	60	0.991	0.011	211.1			0.983	0.019	65.82
	70	0.999	0.024	213.0			0.993	0.013	76.82
	80	0.934	0.022	249.1			0.986	0.027	87.95
	Average			145.2		Average			49.67
CO	20	0.947	0.042	1.578	CO ₂		0.988	0.003	0.077
	30	0.938	0.035	1.624			0.984	0.027	6.352
	40	0.993	0.039	18.03			0.993	0.048	11.66
	50	0.991	0.014	33.13			0.998	0.051	14.12
	60	0.993	0.027	55.78			0.983	0.018	21.48
	70	0.971	0.040	115.0			0.988	0.051	69.95
	80	0.949	0.039	148.4			0.994	0.044	92.44
	Average			53.35		Average			30.87

phenol in MFBR. The conversion fraction of 100% means the highest gas yield at the end of reaction. It can be seen that for all gas components, the conversion fractions increased rapidly within the first 10s, then tended to a slow growth. It is because that the model compound of phenol was sent into the reaction zone at the preset temperature rather than the ambient temperature. Thus a higher rate of heat and mass transfer could be fulfilled, enabling the fast decomposition of phenol into light gas, especially at the initial stage of reaction. It also indicates that the reaction in MFBR is mainly controlled by reaction kinetics rather than diffusion.

Reaction temperature is observed to be an influential factor affecting the evolution profiles of pyrolysis gas, especially for H₂ and CO. For the same gas component, the time spent on reaching the same level of conversion fraction was gradually shortened with increasing the reaction temperature from 750 °C to 950 °C. It can be also seen in Fig. 2 that during the pyrolysis of phenol, the releasing of gas components (CH₄ and

CO₂) was found to be faster than that of H₂ and CO due to the shorter reaction time. Therefore, a further kinetic analysis is necessary to elucidate this observation.

Kinetic analysis of pyrolysis of phenol

Table 2 illustrated the apparent activation energies (E_a) with fitting accuracy, including the square of correlation coefficient (R²) and standard deviation (SD) for different gas components during pyrolysis of phenol in MFBR. It can be seen in Table 2 that the apparent activation energies for all gas components increased gradually with the increased conversion fractions from 20% to 80%. It is consistent with the gas evolution profiles (Fig. 2) of pyrolysis of phenol in MFBR that the reaction rate at lower conversion fractions is faster than that of higher conversion fractions. The mean value of the apparent activation energies of CH₄ (49.67 kJ/mol) and CO₂ (30.87 kJ/mol) were lower than that of H₂ (145.2 kJ/mol) and CO (53.35 kJ/mol).

Table 3 – Typical reaction mechanisms for heterogeneous solid–state reaction.

Symbol	Reaction mechanism	f(x)	G(x)
G1	One-dimensional diffusion	1/2x	x ²
G2	Two-dimensional diffusion (Valensi)	$[-\ln(1-x)]^{-1}$	$x + (1-x)\ln(1-x)$
G3	Three-dimensional diffusion (Jander)	$1.5(1-x)^{2/3}[1-(1-x)^{1/3}]^{-1}$	$[1-(1-x)^{1/3}]^2$
G4	Three-dimensional diffusion (G-B)	$1.5[1-(1-x)^{1/3}]^{-1}$	$1-2x/3-(1-x)^{2/3}$
G5	Three-dimensional diffusion (A-J)	$1.5(1+x)^{2/3}[(1+x)^{1/3}-1]^{-1}$	$[(1+x)^{1/3}-1]^2$
G6	Nucleation and growth (n = 2/3)	$1.5(1-x) [-\ln(1-x)]^{1/3}$	$[-\ln(1-x)]^{2/3}$
G7	Nucleation and growth (n = 1/2)	$2(1-x) [-\ln(1-x)]^{1/2}$	$[-\ln(1-x)]^{1/2}$
G8	Nucleation and growth (n = 1/3)	$3(1-x) [-\ln(1-x)]^{2/3}$	$[-\ln(1-x)]^{1/3}$
G9	Nucleation and growth (n = 1/4)	$4(1-x) [-\ln(1-x)]^{1/3}$	$[-\ln(1-x)]^{1/4}$
G10	Autocatalytic reaction	x (1-x)	$\ln[x/(1-x)]$
G11	Mampel power law (n = 1/2)	$2x^{1/2}$	$x^{1/2}$
G12	Mampel power law (n = 1/3)	$3x^{2/3}$	$x^{1/3}$
G13	Mampel power law (n = 1/4)	$4x^{3/4}$	$x^{1/4}$
G14	Chemical reaction (n = 3)	(1-x) ³	$[(1-x)^{-2}-1]/2$
G15	Chemical reaction (n = 2)	(1-x) ²	(1-x) ⁻¹ -1
G16	Chemical reaction (n = 1)	1-x	-ln(1-x)
G17	Chemical reaction (n = 0)	1	x
G18	Contraction sphere	$3(1-x)^{2/3}$	$1-(1-x)^{1/3}$
G19	Contraction cylinder	$2(1-x)^{1/2}$	$1-(1-x)^{1/2}$

Note: A-J: Anti-Jander; G-B: Ginstling-Brounshtein.

Fig. 3 – Correlation of $G(x)$ versus t at different reaction temperatures for individual gas components.

A reaction with lower activation energy means less energy is required to break the chemical bonds between atoms and hence the reaction rate is faster, accompanied with a shorter residence time. Therefore, it accounts for the observation in Fig. 2 that the formation of gas components (CH_4 and CO_2) is easier than that of H_2 and CO during pyrolysis of phenol. Besides, the activation energies for individual gas components, 30.87–145.2 kJ/mol, are lower than, but within the range of activation energies for thermal decomposition of tar from real biomass [41,42] or tar model compounds [11,43] reported in the literature. In this study the activation energies of four gas components all varied greatly rather than remain stable at different conversion fractions. It suggests that the generation of different gaseous products during the pyrolysis of phenol may proceed with varied reaction mechanisms in the present study.

Table 3 illustrated the most common nineteen reaction models for heterogeneous solid–state reaction, which were applied in the present study [4,38,39]. Fig. 3 illustrated the correlation of $G(x)$ versus t at different reaction temperatures for individual gas components in MFBR. Based on the fitting accuracy, the four probable reaction models (Table 4) were selected first from the nineteen reaction models shown in Table 3. Afterwards, the most probable reaction model (Table 5) can be determined from the four probable models based on the closeness of the value of apparent activation energies obtained from the universal integral method and Friedman-Reich-Levi method. Table 5 verified the speculation that the

formation of individual gas components proceeded with different reaction mechanisms. Specifically, the mechanism of three-dimension diffusion could describe the evolution profiles of H_2 and CH_4 . Chemical reaction and contracting sphere are the most probable reaction mechanisms for CO and CO_2 , respectively. As pyrolysis proceeds with the conversion fractions increased correspondingly, the solid material will be decomposed from the superficial towards the center in various ways such as contracting sphere/cylinder, nucleation and growth. According to Font et al. [44], during this process, the complex physical and chemical interactions changed the composition of the reactant, and thus the active surface area of the reactant also changes due to the variations of solid depletion and pore structure. Additionally, the global reaction is the sum of various free radical reactions. The application of transition state theory [45,46] that can provide more basic information regarding the reaction rates of elementary chemical reactions, needing a further investigation.

Biomass tar is a complex mixture of organic compounds. According to the literature [4,47–51], the components of tar were divided into five classes based on the molecular weight of tar compounds: (1) GC-undetectable, (2) Heterocyclic aromatics (Pyridine, phenol, cresol, quinoline), (3) Aromatics (1 ring) (Xylene, styrene, toluene), (4) Light PAH compounds (2–3 ring) (Naphthalene, biphenyl, acenaphthylene, fluorenc, phenanthrene, anthracene), (5) Heavy PAH compounds (4–7 ring) (Fluoranthene, pyrene, chrysene, benzo[fluoranthene], benzo-pyrene, perylene). During the gasification process, the

Table 4 – Probable reaction models and kinetic parameters for individual gas during pyrolysis of phenol.

Gas	Temp	G(X)	G3	G7	G8	G10	Gas	Temp	G(X)	G4	G8	G15	G16
H ₂	750 °C	K(T)	0.006	0.039	0.021	0.047	CH ₄	750 °C	K(T)	0.010	0.077	3.525	0.647
		lnK(T)	−5.124	−3.248	−3.884	−3.053			lnK(t)	−4.624	−2.566	1.260	−0.436
		R ²	0.967	0.957	0.971	0.957			R ²	0.961	0.919	0.912	0.952
	800 °C	K(T)	0.008	0.049	0.026	0.061		800 °C	K(T)	0.009	0.066	2.630	0.521
		lnK(T)	−4.896	−3.013	−3.635	−2.790			lnK(t)	−4.764	−2.719	0.967	−0.651
		R ²	0.965	0.953	0.962	0.934			R ²	0.902	0.908	0.901	0.926
	850 °C	K(T)	0.005	0.035	0.017	0.040		850 °C	K(T)	0.005	0.039	1.944	0.357
		lnK(T)	−5.231	−3.357	−4.057	−3.233			lnK(t)	−5.327	−3.239	0.665	−1.031
		R ²	0.986	0.972	0.963	0.950			R ²	0.914	0.918	0.901	0.914
	900 °C	K(T)	0.005	0.033	0.016	0.037		900 °C	K(T)	0.005	0.038	1.814	0.341
		lnK(T)	−5.288	−3.410	−4.115	−3.289			lnK(t)	−5.362	−3.262	0.596	−1.078
		R ²	0.981	0.965	0.952	0.937			R ²	0.903	0.903	0.901	0.903
	950 °C	K(T)	0.009	0.063	0.030	0.071		950 °C	K(T)	0.003	0.029	1.954	0.320
		lnK(T)	−4.685	−2.768	−3.494	−2.645			lnK(t)	−5.726	−3.559	0.670	−1.138
		R ²	0.926	0.925	0.916	0.914			R ²	0.900	0.912	0.927	0.954
	E _a	kJ/mol	147.7	120.5	110.5	111.1		E _a	kJ/mol	47.08	36.78	55.12	21.53
CO	750 °C	G(X)	G3	G7	G15	G16	CO ₂	750 °C	G(X)	G3	G4	G7	G18
		K(T)	0.008	0.050	1.116	0.218			K(T)	0.023	0.012	0.150	0.028
		lnK(T)	−4.884	−2.996	0.109	−1.522			lnK(T)	−3.792	−4.397	−1.900	−3.574
	800 °C	R ²	0.969	0.965	0.918	0.931		800 °C	R ²	0.972	0.993	0.977	0.968
		K(T)	0.007	0.043	0.763	0.166			K(T)	0.036	0.017	0.246	0.039
		lnK(T)	−5.025	−3.149	−0.271	−1.797			lnK(T)	−3.313	−4.063	−1.402	−3.232
	850 °C	R ²	0.984	0.968	0.900	0.927		850 °C	R ²	0.998	0.995	0.992	0.992
		K(T)	0.005	0.034	0.710	0.144			K(T)	0.031	0.014	0.213	0.032
		lnK(T)	−5.265	−3.382	−0.343	−1.939			lnK(T)	−3.467	−4.261	−1.547	−3.433
	900 °C	R ²	0.979	0.965	0.900	0.905		900 °C	R ²	0.997	0.992	0.991	0.995
		K(T)	0.006	0.037	0.831	0.163			K(T)	0.033	0.015	0.228	0.035
		lnK(T)	−5.185	−3.295	−0.185	−1.814			lnK(T)	−3.409	−4.178	−1.479	−3.341
	950 °C	R ²	0.968	0.957	0.908	0.925		950 °C	R ²	0.995	0.990	0.998	0.996
		K(T)	0.006	0.040	1.071	0.195			K(T)	0.036	0.018	0.239	0.040
		lnK(T)	−5.124	−3.220	0.068	−1.637			lnK(T)	−3.792	−4.397	−1.900	−3.574
	E _a	kJ/mol	65.14	63.38	51.27	39.48		E _a	kJ/mol	27.67	26.34	34.51	31.63

Bold signifies the apparent activation energy determined by the universal integral method.

increased temperature promoted the thermal decomposition of tars of class 1 and class 2, while the concentration of class 3 and class 5 tars increased conversely. According to Sun et al. [52], part of heavy tar compounds was thermal degraded to light liquid compounds at the temperature of 500–600 °C. However, at higher temperatures (700–800 °C), the tar with heavy molecular weight was very resistant to cracking although the thermal cracking was the principal reaction of tar reduction. Since the tar compound of phenol investigated in the present study belongs to Class 2, the results obtained in the present study verified those conclusions above that with the increasing of temperature from 750 to 950 °C, the light tar of phenol was effectively cracked. Besides, it suggests that the approach of thermal cracking in a certain temperature is more

feasible for reduction of light tar instead of heavy tar, and the increased tar yield with increased temperature may originate from tar with heavy molecule weight during the gasification process. A detailed reaction kinetic study of different classes of tar components may help us get a more comprehensive knowledge of tar reduction during gasification process, which is recommended for future study.

Conclusions

The present study investigated the pyrolysis behavior of phenol as tar model compound in the micro fluidized bed reactor. Results indicated that the cracking reaction of phenol

Table 5 – Most probable reaction models and kinetics parameters for individual gas during pyrolysis of phenol.

Gas	E _a -FRL (kJ/mol)	E _a -UI (kJ/mol)	Reaction mechanism	G(X)
H ₂	145.2	147.7	G3	Three-dimensional diffusion (Jander)
CH ₄	49.67	47.08	G4	Three-dimensional diffusion (G-B)
CO	53.35	51.27	G16	Chemical reaction (n = 2)
CO ₂	30.87	31.63	G18	Contraction sphere

Note: FRL: Friedman-Reich-Levi method; UI: Universal Integral method.

was favored at higher temperatures, and reaction temperature was observed to be an influential factor affecting the evolution profiles of individual gaseous products, including hydrogen, methane, carbon monoxide and carbon dioxide. Pyrolysis kinetics were then carried out based on the iso-conversional and model-fitting approaches and the apparent activation energies for hydrogen, methane, carbon monoxide and carbon dioxide were 145.2 kJ/mol, 49.67 kJ/mol, 53.35 and 30.87 kJ/mol, respectively. The evolution of hydrogen and methane could be described by three-dimensional diffusion while chemical reaction and contracting sphere could account for the formation of carbon monoxide and carbon dioxide, respectively.

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Nomenclature

A	pre-exponential factor, s^{-1}
E	apparent activation energy, $kJ \cdot mol^{-1}$
f(x)	differential reaction model
G(x)	integral reaction model
k(T)	rate constant of reaction
R	universal gas constant, $8.3145 J \cdot mol^{-1} K^{-1}$
t	reaction time, s
t_0	start time of reaction, s
t_e	end time of reaction, s
T	reaction temperature, K
V_i	volume rate of the gas product i
V	volume rate of all gas products
x	conversion fraction of gas concentration, %

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