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Kinetics study on biomass pyrolysis for fuel gas production*

CHEN Guan-yi(陈冠益)†1, FANG Meng-xiang(方梦祥)†2, ANDRIES, J.[1],
LUO Zhong-yang(骆仲泱)[2], SPLIETHOFF, H.[1], CEN Ke-fa(岑可法)[2]

(*[1] Section of Thermal Power Engineering, Department of Mechanical Engineering and Marine Technology, Delft University of Technology, the Netherlands*)
(*[2] Clean Energy and Environment Engineering Key Lab of MOE, Institute for Thermal Power Engineering, Zhejiang University, Hangzhou 310027, China*)

E-mail: †1 G.Chen@wbmt.tudelft.nl, †2 mxfang@cmee.zju.edu.cn

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Abstract: Kinetic knowledge is of great importance in achieving good control of the pyrolysis and gasification process and optimising system design. An overall kinetic pyrolysis scheme is therefore addressed here. The kinetic modelling incorporates the following basic steps: the degradation of the virgin biomass materials into primary products (tar, gas and semi-char), the decomposition of primary tar into secondary products and the continuous interaction between primary gas and char. The last step is disregarded completely by models in the literature. Analysis and comparison of predicted results from different kinetic schemes and experimental data on our fixed bed pyrolyser yielded very positive evidence to support our kinetic scheme.

Key words: Biomass, Pyrolysis, Kinetic study, Gas production
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INTRODUCTION

Since biomass is an abundant, inexpensive and renewable resource, its conversion to synthetic fuels and chemical products appears attractive. Among all kinds of biomass conversion routes, pyrolysis is being given increasing attention since the process is simple and may be optimised to produce different proportion of products for different end-users. In addition, pyrolysis is the first step of gasification. A good understanding of pyrolysis mechanism is therefore a basic prerequisite for controling the gasification process.

Biomass pyrolysis has been investigated extensively in the past decades and many kinetic models for biomass (mostly using wood) pyrolysis have been developed. High temperature pyrolysis of biomass for fuel gas production, however, is rarely reported in publications. Considering fuel gas has very flexible applications in gas turbine, gas engine, industrial furnace, and even fuel cell for the production of decentralised electricity for local consumers or as supplement for grid electricity, our focus is on biomass pyrolysis for fuel gas production.

There are three obstacles to direct application of the above-mentioned kinetic models into our case. First, every model has its specific experimental conditions, especially at low temperature and very low mass flow of volatiles; second, these models are based on very short residence time of the volatile phase in the reactor; third, biomass material itself is always case-dependent because of the complicated and varying composition. Therefore a characteristic kinetic model is necessary to be developed for our application.

The objective of the present work is to develop an innovative kinetic pyrolysis approach, i.e. overall kinetic pyrolysis (OKP) approach, based on fixed-bed pyrolysis of pine sawdust wastes at high temperature and long residence time of the volatile phase in the reactor for fuel gas production.

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LITERATURE REVIEW

Physically, bulk biomass pyrolysis can be viewed as a four-stage process, depending on the particle temperature, i.e. (a) below 100℃, no significant pyrolysis occurs; (b) 100 ℃ – 130 ℃, most moisture evaporates; (c) 130 ℃ – 450 ℃, primary pyrolysis occurs; (d) above 450 ℃, continuous devolatilization starts (Rav eendran *et al*., 1995; Chen, 1998). In fact this zonation scheme does not represent real pyrolysis behaviour which involves large scale overlapping of different stages. Furthermore, char-gasification reaction could occur following the fourth stage at temperature higher than 800℃.

Due to the above-mentioned complexity associated with the pyrolysis process and the varying composition of biomass materials, a large number of complex reactions are involved in the pyrolysis process and therefore it is impossible to obtain a widely accepted biomass pyrolysis model. For simplification, cellulose, a main composition of biomass, was first paid attention to by many researchers (Antal, 1995; Broido *et al*., 1975; Varhegyi *et al*., 1994; Zaror *et al*., 1988; Curtis *et al*., 1988). However, even very good cellulose pyrolysis models will still encounter serious difficulties when used directly for biomass pyrolysis. For this reason, different kinetic models for biomass pyrolysis were subsequently proposed. In general, biomass (and solid wastes) pyrolysis kinetic models (cellulose models included) can be divided into five categories:

(a) one-step, global model (Pyle *et al*., 1984; Samolado *et al*., 1991)

(b) one-step, multi-reaction model (Thurner *et al*., 1981; Koufopanos *et al*., 1989)

(c) two-step, semi-global model (Blasi, 1993; Font *et al*. 1990)

(d) chain growth model (Ahuja, 1996)

(e) multi-step, semi-global model (Leung, 1998)

The first category is a very simple correlation model and can be applied to predict well the weight-loss curve and therefore is welcomed by many researchers interested in the weight-change during biomass pyrolysis. The proportion of gas and tar yield is not given by this type of model. The second category can predict gas, tar and char yields, but not the decomposition of the primary products, and so, cannot be extended to systems different from the one which they were derived from. The suitable temperature for this type of model, for example, is limited to the range of 350 ℃ – 400 ℃ (Thurner *et al*., 1981). Compared with the first two categories, the third category is more suitable for kinetic description of biomass pyrolysis, since it includes the transformation of the primary degradation of the virgin materials and secondary decomposition of the primary products. This is the real case occurring in pyrolysis of biomass under temperature of higher than 500℃. Unfortunately this kind of model was set up on the basis of rapid quenching of the primary pyrolysis products and thus the interactions among primary products are neglected. The fourth category can satisfactorily give predicted results on the char yield of large particle biomass pyrolysis, but, for the case of small particles of feedstock, its precision is doubtful. Moreover, this model cannot predict tar or gas yield. The last category developed for scrap tire pyrolysis appears interesting, while only weight-loss rate can be predicted. In sum, all these models disregard the interactions such as char-gasification reaction among primary products. Char-gasification can be significant at high temperature, in particular for rice straw pyrolysis due to high alkaline and alkaline-earth metals originating in its composition. Alkaline metals always favour the char-gasification by the catalytic route below:

$$C + CO_2 \longrightarrow 2CO \qquad \text{(Reaction 1)}$$

$$C + H_2O \longrightarrow CO + H_2 \qquad \text{(Reaction 2)}$$

In addition, Klose and Wiest (1999) proposed a kinetic model, which included two-step reaction, but the second step involved two parallel decompositions of primary char and tar respectively.

KINETIC MODELLING

Kinetic characteristics of experimental conditions

In our experimental conditions characterized by high temperature and long residence time of volatiles in the reactor for fuel gas production (without inert carrier-gas), it was found that when a certain level of temperature was reached, sawdust particles always immediately released volatiles in gaseous phase which was always in the state of gas, and in the tar phase which could be condensed into the liquid phase. The tar phase started to decompose into gases at high temperature of 500 ℃ and above and even into carbon-containing deposition with the long residence time. The char-gasification was perceivably based on the comparison of measured char yield from two tests (one at very short residence time and the other for long residence time). Obviously those models mentioned above do not completely reflect the physical phenomena associated with the whole process of pyrolysis in our fixed bed reactor. Therefore the following steps have to be applied: Step 1, the degradation of the virgin biomass materials into primary products (tar, gas and semi-char); Step 2, the decomposition of the primary tar into secondary products (tar, char and gas); Step 3, the accompanying interaction (i.e. reaction 1 and 2) between primary gas and semi-char. Step 3 is normally very weak under experimental conditions applicable for previous models and thus usually ignored by previous researchers. However, at high temperature and long residence time, particularly with the help of the alkaline component inherent in biomass, this reaction could be very influential on the final product distribution and so cannot be neglected. The definition of tar, gas and char in the kinetic scheme is: for tar, only hydro-carbon compounds (C_3 + above), not including gaseous phase of steam; for gas, all gases (CO, CO_2, CH_4, H_2) which can't decompose under normal pyrolysis condition, and including gaseous phase of steam; for char, only solid residue, mostly of carbon. However for the experimental determination of the final pyrolysis product in the fixed bed, the H_2O is collected in liquid phase prior to the gas measurement and therefore only included in the tar yield. For the correspondence between the kinetic definition and experimental determination of pyrolysis products, the vapour is counted only in gaseous phase.

OKP model scheme

The basic principle of the OKP model proposed by us is shown in literature (Chen, 1998). The kinetic scheme incorporates three basic steps associated with our experimental conditions. Under our experimental conditions aimed at maximum production of medium calorific value gas, step 2 and step 3 exert significant influences on the final products formed, and thus attention is paid to them. Generally speaking, the OKP model describes in detail the significant secondary cracking of the primary pyrolysis product of tar and interaction between semi-char and gaseous phase which always exist irrespective of reaction temperature and residence time of the volatile phase. The adsorption, deposition, and char-gas reaction reported by Ahuja *et al*. (1996), cracking and repolymerization reactions revealed by Anthony and Howard (1976) are incorporated in this model.

Kinetic equations are described by the following ordinary differential equations.

$$\frac{dW_d}{dt} = -(k_1 W_d^{n1} + k_2 W_d^{n2} + k_3 W_d^{n3}) \qquad (1)$$

$$\frac{dC_1}{dt} = k_3 W_d^{n3} - k_4 C_1 \qquad (2)$$

$$\frac{dC_{21}}{dt} = \delta k_4 C_1 \qquad (3)$$

$$\frac{dC_{22}}{dt} = k_5 T_{a1} \qquad (4)$$

$$\frac{dG_{21}}{dt} = \delta k_4 G_1 \qquad (5)$$

$$\frac{dG_{22}}{dt} = k_6 T_{a1} \qquad (6)$$

$$\frac{dG_1}{dt} = k_2 W_d^{n2} - k_4 G_1 \qquad (7)$$

$$\frac{dT_{a1}}{dt} = k_1 W_d^{n1} - (k_5 + K_6 + k_7) T_{a1} \qquad (8)$$

$$\frac{dT_{a2}}{dt} = k_7 T_{a1} \qquad (9)$$

Where, W_d is degradable biomass weight, C_1 is primary char weight(kg), C_{21}, C_{22} are secondary char weight(kg), G_1 is primary gas weight (kg), G_{21}, G_{22} are secondary gas weight (kg), T_{a1} is primary tar weight (kg), T_{a2} is secondary tar weight (kg), δ is deposition coefficient representing the contacting situation of the surface C_1 and G_1; $k_j = A_j \exp(-E_j/RT)$; the initial conditions are: at time $t = 0$, $W_d = W_0$, $C_1 =$

$$C_{21} = C_{22} = G_{21} = G_{22} = T_{a1} = T_{a2} = 0$$

The residual weight at time t can be defined by:

$$M = W_b + C_1 + C_2 + C_{22} \qquad (10)$$

The final tar (T_a) yield and gas (G) yield can be derived from:

$$T_a = T_{a1} + T_{a2}$$
$$G = G_1 + G_{21} + G_{22}$$

The solution method

Under the isothermal condition (for our fixed bed, isothermal assumption is applicable), i.e. $T = T_0$, rate constant k_j ($k_1 - k_7$) defined by Arrhenius's law is a constant. The reaction order (n_1, n_2, n_3) is set to be 1.0, thus the set of ordinary differential equations together with the initial Eq. (10) can be solved by numerical methods (Chen, 1998).

The seven kinetic parameters plus a physical parameter are estimated by fitting Eqs. 1 – 9 to the weight-loss curve derived from an isothermal apparatus. The best fitting value is obtained by minimizing the sum of square function by means of a hybrid method combining features from the Newton-Raphson, steep-descent algorithm. It should be noted that the initial values of $k_1 - k_7$ are very crucial in order to achieve rapid convergence. The initial value of k_1, k_2, k_3 and k_5, k_6 can be derived from literature (Thurner and Mann, 1981; Blasi, 1993), however, it is impossible to evaluate the initial values of k_4, k_7 from previous publications. For simplification of calculation, k_7 is assumed to be the same value as that of k_6. Full details of obtaining the initial values of k_4 are shown in publication (Chen, 1998). Compared with the initial values of $k_1 - k_7$, the initial gas yield and tar yield appear more important as they both can influence the calculation process and also dominate the final pyrolysis product distribution. However, no reported experience with respect to them can be found in kinetic models available. Moreover, tar and gas yield cannot be easily obtained from the isothermal apparatus. In this work, the tar yield and gas yield were determined experimentally in our fixed-bed pyrolyser at temperature of 900℃. Obviously the experimental yield means the final yield, not instantaneous yield. However, during the iteration of numerical calculation the instantaneous yield of gas and tar is necessary, and therefore the assumption on this point is: instantaneous gas yield is proportional to the final gas yield by a magnitude of relative instantaneous carbon conversion rate ($\bar{X}_i$) which is a dimensionless ratio derived from the experimental data obtained in a laboratory-made isothermal apparatus and fixed bed pyrolyser together. The tar can be obtained by difference. The instantaneous carbon conversion rate is defined as:

$$X_i = \frac{W_0 - W_i}{W_0 - W_\infty}$$
$$\bar{X}_i = \frac{X_i}{X_\infty}$$

Here X_i is the instantaneous carbon conversion determined in the isothermal apparatus, X_∞ is the final carbon conversion obtained in the fixed bed pyrolyser.

EXPERIMENTAL SECTION

Isothermal experiments were carried out in an isothermal apparatus which was developed in our laboratory. In fact, it is an up-down furnace, with an instantaneous mass-change measurement. The main element of this device is a tubular ceramic reactor with 60 mm inner diameter and 500 mm in height. The tubular reactor is inserted vertically into an electrically heated tubular furnace. The sample material was placed in a stainless-steel mesh basket hung on a thermocouple which is connecting to the low part of the weight-loss analyzer. The weight-loss signal of the sample thus can be detected via the weight-loss analyzer at any time at a given operating temperature.

The fixed-bed reactor was made of stainless steel with inner diameter of 80 mm and horizontal height of 750 mm (Fig. 1). The reactor was divided into a pyrolysis zone at the bottom section and a tar-cracking zone at the upper section. In the pyrolysis zone, biomass particles were subjected to decomposition to form the primary products and were also subjected to reaction 1 and 2. In the cracking zone, only tar was decomposed there to form secondary products. The outlet of the pyrolysis reactor was connected to a condenser. The volatile phase flew into the condenser, then into a spherical dryer, and then into a water tank and a gas vent. The connecting tube before the condenser is always well-insulated to prevent tarry components from condensing.

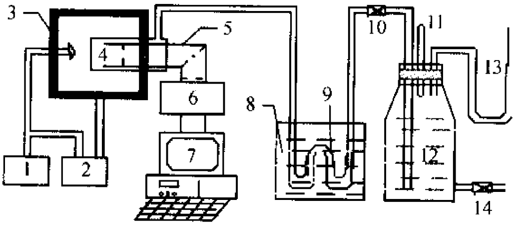

Fig.1 Fixed bed reactor

1. thermometer; 2. temperature controller; 3. electrical furnace; 4. pyrolysis reactor; 5. thermocouple; 6. Chessel recorder; 7. computer; 8. condenser; 9. U-tube; 10. regulator; 11. sample port; 12. gas tank; 13. U-tube; 14. regulator

The determination of hold time at a certain reaction condition is determined by ensuring that no further condensation occur in the cold traps. At the end of the experiment, the pyrolysis residue weighed to determine yields, and the gas yield is usually measured based on the variation of water tank volume and calibrated by the value from the volumetric flow-meter. The obvious features of our fix-bed reactor are: high operating temperature (800℃ – 950℃) and long residence time of volatiles (> 8s).

MODEL VALIDATION AND DISCUSSIONS

The possible variation in the ash content of various sample materials can lead to erroneous interpretation of the experimental data, so the biomass weight and residual weight reported in this paper were corrected as follows

M = Residual weight-Ash weight

W = Biomass weight-Ash weight

As mentioned above, kinetic data were obtained by fitting data with weight-loss from the isothermal apparatus based on the estimation of instantaneous gas and tar yields. The estimation of gas and tar yield involved in the kinetics of fixed bed reactor and of the isothermal apparatus, and therefore the kinetic data are expected to meet the operating conditions achieved in the isothermal apparatus where only weight-loss is concerned or in fixed bed where the gas yield and tar yield are of priority. The used biomass material was pine sawdust with the following approximate analysis data (wt. %): M, 12.27; A, 0.83; V, 70.55; FC, 16.35; with heating value of 18064 kJ/kg. The calculated kinetic parameters of pine sawdust calculated are shown in Table 1.

Table 1 Kinetic data calculated for pine sawdust pyrolysis at high temperature

Reaction	Frequency factor (A_j)	Apparent activation energy (E_j)	Deposition coefficient
k_1	110.7	5.95E+6	1.15
k_2	92.5	1.35E+5	
k_3	115.0	2.50E+6	
k_4	84.5	2.00E+5	
k_5	130.2	1.38E+5	
k_6	90.7	5.05E+6	
k_7	90.7	5.05E+6	

Fig. 2 shows the comparison of predicted weight-loss of sawdust particles against the results obtained experimentally in the isothermal apparatus at 900℃. It can be seen OKP model still can predict well the weight-change occurring in the isothermal apparatus although isothermal apparatus doesn't obviously involve in the secondary reaction and interactions of primary products. The good prediction is due to the fact that the solution of OKP model is still by fitting cal-

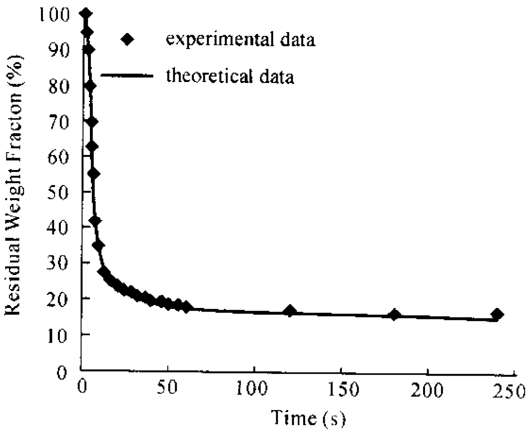

Fig. 2 Weight-loss predicted against experimental results in the isothermal apparatus for sawdust pyrolysis at 900℃

culated data with data from the isothermal apparatus.

The relationship between final gas yield and tar yield experimentally obtained in the fixed-bed pyrolyser at 900℃ and the theoretically calculated are shown in Table 2，showing good agreement of predicted results with experimental data. Based on the balance of total mass，the theoretically calculated char was somewhat lower than that experimentally obtained. The difference could be attributed to the overestimation of char-gasification reaction as low alkali content is associated with pine sawdust.

Table 2 Comparison of gas yield and tar yield for sawdust pyrolysis at 900℃

Item	Experimental Data（wt.%）	Theoretical Data（wt.%）
Gas yield	72.6	74.7
Tar yield	10.2	9.8

EVALUATION OF THE KINETIC MODELS

Most kinetic models that developed were based on different pyrolysis mechanisms，and found applicable to particular experimental conditions. There is no comprehensive evaluation on those kinetic models as there is no standard for such evaluation. A standard is proposed here based on the following items:

（a）A common total pyrolysis rate，$\bar{k}_p$，（$\mathrm{kg \cdot s^{-1}}$）is used，which is defined by the equation（11）. The value of $\bar{k}_p$ is determined by the kinetic representation of weight-time relationship，based on the range of temperature under isothermal conditions.

（b）$\bar{k}_p$ can be described as:

$$\int_{t_0}^{t_\infty} W'(t)\mathrm{d}t = -\bar{k}_p \Delta t_\infty \qquad (11)$$

and can be approximately expressed as:

$$\sum_{1}^{h} \frac{\Delta W_i}{\Delta t_i}\Delta t_i = -\bar{k}_e \Delta t_\infty \qquad (12)$$

Where ΔW_i = weight-loss during pyrolysis in a specific time zone $\Delta t_i(\bar{t}_{i-1}, \bar{t}_i)$; $\Delta t_\infty = t_\infty - t_0$，is the total pyrolysis time; $\bar{k}_e$ is defined by the equation（12）and its value is determined by the experimental data obtained in the isothermal conditions.

（c）Dimensionless pyrolysis rate $\bar{K}(=|\bar{k}_p - \bar{k}_e|/\bar{k}_e)$ is introduced.

The kinetic models can be evaluated by referring to $\bar{K}$ obtained above，which actually reprsents the deviation between data experimentally obtained in our fixed bed at high temperature of 900℃ and results theoretically predicted according to different kinetic schemes. Table 3 shows the comparison of different $\bar{K}$. As can be seen from this Table，OKP model minimizes the deviation. However other models，compared with OKP model，are simpler and lead to a simple computational process，and furthermore they appear very practical at low or middle heating rate（non-isothermal）of thermalgravimetric apparatus or of some tubular reactors for oil-like production，therefore they are still recommended for different specific cases.

Table 3 Calculated $\bar{K}$ values using different kinetic models for prediction of fixed-bed pyrolysis of pine sawdust

OKP model	Font *et al*.	Leung and Wang	Thurner and Mann	Ahuja *et al*.
<11%	<17%	<21%	<38%	<15%

CONCLUSIONS

The biomass pyrolysis kinetic model which incorporates the primary decomposition of the original biomass materials，the continuous decomposition of the primary products，and the interactions among the compositions of primary products has been developed here and is found to be accurate predicting the pyrolysis behaviour of pine sawdust in the fixed-bed reactor at high temperature. Compared with other kinetic models，OKP model predicts better for sawdust particles pyrolysis in the fixed bed at 900℃. The deviations between experimental and predicted pyrolysis rate are not so conspicuous for the applications of different models. However，it is believed that the deviation could be more serious when different kinetic models are used for the prediction of the gas yield from biomass pyrolysis in the fixed bed at high temperature.

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