The application of a genetic algorithm to estimate kinetic parameters for biomass pyrolysis from thermogravemetric data

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Abstract:
A kinetic study of the pyrolysis process of rice straw was investigated using a thermogravimetric analysis, TGA and the weight loss was measure in nitrogen atmosphere. The samples were heated over a range of temperature from 298 K to 973 K with three different heating rates of 5, 10 and 15 K min^{-1}. The kinetic triplet parameters such as activation energy E, pre-exponential A and reaction model f(α) were obtain by model fitting method which are exercised till date for evaluating the optimum overall kinetics parameters usually applied traditional gradient base optimization techniques but associated with major drawback of attaining global optimum due to uncertainties in selection of initial guess. To overcome such uncertainties and drawbacks, we have, applied the modern evolutionary optimization method (Genetic Algorithms, GA technique) for 14 models to attain the globally optimum kinetic parameters using the experimental TGA data and we did compare the experimental and simulated data to expect the possible mechanism to occur during pyrolysis. As rice straw case studies, the suitability of the models is also tested using the AIC score. 3D diffusion model is the best suited one and it also predicted the experimental TGA data successfully. The Avarami-Erofe'ev nucleation models also show good AIC score and well predicted the experimental TGA data.

Keywords: *Kinetic triplet parameters; Thermogravimetric analysis; Rice straw; Genetic Algorithm*

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1. Introduction

An understanding of biomass pyrolysis can give rise to a development of biomass conversion process. Since pyrolysis is the first step of biomass conversion such as gasification, liquefaction, carbonization and combustion, its sound understanding is significant for the effective use of biomass. For engineering applications, knowledge of the pyrolysis kinetics is essential for predicting the pyrolysis behavior of biomass material as well as designing the suitable reactor design and operating condition which the correctness of the kinetic expression heavily depends upon reliable evaluation of kinetic parameters from the decomposition behavior under different conditions of temperature and/or environment.

The model-fitting methods that are exercised till date for evaluating the optimum overall kinetics parameters usually applied traditional gradient base optimization techniques but associated with major drawback of attaining global optimum due to uncertainties in selection of initial guess. And to overcome such uncertainties and drawbacks, we have, applied the modern evolutionary optimization method (genetic algorithms, GA technique) for 14 reaction model, can be chosen to fit experimental. It is possible that the obtained kinetics parameters describes the rate-limiting step of the decomposition process and recommended that this approach is acceptable for engineering applications.

Therefore, in the present work, we have reported pyrolysis kinetics of rice straw for different heating rates employing the GA techniques to get the globally optimum overall kinetics triplet parameters (activation energy, *E*; pre-exponential factor, *A* and reaction model, *f(α)*) using direct integration technique of temperature integral. All 14 different physic-chemical models available are used coupled with GA to find out the best one that predicts the experimental data well. In addition to that, Akaike Information Criteria (AIC) is also applied to choose the most appropriate reaction model. Thus, applying GA in the present work, we tried to establish the reaction mechanism involved during pyrolysis of rice straw sample mentioned above and correspondingly reported the globally optimized kinetic parameters.

2 Experimental and methodology

2.1 Experimental

Thermogravimetric analysis, TGA was performed using Perkin Elmer, Pyris1 analyzer. To maintain pyrolysis conditions, high purity nitrogen was used as the carrier gas with 50 ml min^{-1} of volume flow rate. TGA for drying step had a heating rate of 10 K min^{-1} for all analysis, while pyrolysis step were performed at three different heating rates: 5, 10 and 15 K min^{-1}. The composition based on proximate and ultimate analyses are shown in Table 1. During the heating, the mass of the rice straw and furnace temperature were dynamic record.

Table 1 Characteristic of rice straw

Proximate analysis (wt %)				Ultimate analysis (wt %)			
Moisture	Volatile	Fix carbon	Ash	C	H	N	O
9.79	65.78	13.97	10.46	45.56	7.00	0.77	46.67

2.2 Kinetic analysis

The kinetic analysis of biomass pyrolysis under non-isothermal, usually based on Eq. (1).

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (1)$$

where *A* is the pre-exponential factor, *E* is the activation energy are the Arrhenius parameters. *R* is the gas constant, β is the heating rate. The Arrhenius parameters, together with $f(\alpha)$ the reaction model, are called the kinetic triplet. A typical plot (α, T) co-ordinates of the sets of experimental data. Two straight lines $T = T_m$ and $T = T_n$, drawn on the plots from Fig. 1, will determine on each curve, a pair of values of α, i.e. (α_{m1}, α_{n1}),…, (α_{m5}, α_{n5}). With the help of these pairs and using various conversion functions, such given in Table 3, the values of F_{mn1}, F_{mn2},…,F_{mn5} can be computed according to Eq. (2), and for each conversion function, $f(\alpha)$, several values are obtained.

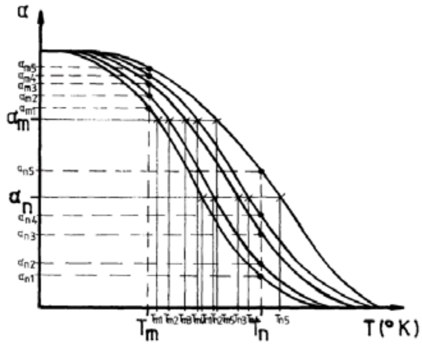

Fig. 1 TG curves corresponding to a reaction using different heating rates (Popescu, 1996).

The integral form of Eq. (1) is, then

$$\int_{\alpha_m}^{\alpha_n} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta}\int_{T_m}^{T_n} \exp(-E/RT)dT \quad (2)$$

where α_m, α_n are the two different degrees of conversion and T_m, T_n are their corresponding temperatures. By using the notations

$$F(\alpha)_{mn} = \int_{\alpha_m}^{\alpha_n} \frac{d\alpha}{f(\alpha)} \quad \text{and} \quad I(T)_{mn} = \frac{A}{\beta}\int_{T_m}^{T_n} \exp(-E/RT)\,dT \quad (3)$$

2.3 Kinetic parameters optimization

The objective function used in case of multiple heating rates of TGA curves to calculate optimum values of kinetic parameters for total J data points and total L heating rates by minimization of square of deviation between experimental mass $\lfloor M_{Exp}(T) \rfloor$ and calculated mass $[M_{Cal}(T)]$ is given by Eq. (4).

$$(A, E) = \sum_{l=1}^{L} \left[\sum_{j=1}^{J} \left[M_{\exp,l,j} - M_{cal,l,j} \right] \right]^2 \tag{4}$$

where j and l denote the data point and heating rate, respectively. The values of $M_{cal}(T)$ calculated for each single value of $\alpha_{l,j}$ are as follows:

$$M_{cal,l,j} = M_{\exp,l,0} - \alpha_{l,j} \left(M_{\exp,l,0} - M_{\exp,l,\infty} \right) \tag{5}$$

where $M_{\exp,l,0}$ is the initial point and $M_{\exp,l,\infty}$ is the final point of lth heating rate. All 14 models involved two parameters optimization since in those models A and E values are optimized by employ a conversion parameter that active over at the same temperatures on curves recorded for a reaction carried out at various heating rates. This allows separate Arrhenius Eq. to be summed together as show in Eq. (6).

$$\frac{dm}{dt} = \sum_{i=1}^{k} \left(\frac{A}{\beta} \exp\left(-E/RT_\alpha\right) \cdot f(\alpha) \right) \quad \text{and} \quad \alpha_{l,j}(T_\alpha) = \frac{m_{i,0} - y_i(T_\alpha)}{m_{i,0} - m_{i,f}} \tag{6}$$

Where k is number of reactions, and for each conversion i: A is the pre-exponential factor, E is the activation energy, $y_i(T_\alpha)$ is the mass fraction remaining at temperature T_α and $\alpha_{l,j}(T_\alpha)$ is the conversion at temperature T_α. Note that the conversion has a value of 0 before the reaction begins and continuously increases until the reaction is complete, at which point the value is 1. Typically, conversion parameters are manually identified by visual analysis of TGA mass loss rate, while the pre-exponential factor, A and the activation energy, E are solved using GA (Holland, 1975) in MATLAB 7.6.0(R2009a). Akaike's Information Criteria (Saha et al., 2008) is also applied to choose the appropriate reaction model.

$$\text{AIC} = N \ln\left(\frac{SS}{N}\right) + 2K \tag{7}$$

Where N is number of data points, K the number of parameters plus one and SS is sum of square of the difference between the calculated mass and experimental mass.

3. Results and discussion

3.1 Thermogravimetric analysis

Pyrolysis of the rice straw samples was carried out at 5, 10 and 15 K min^{-1}. The temperature at which $\alpha = 0$ (T_{w0}), the temperature at which decomposition starts and $\alpha \approx 0.1$ (T_d), the temperature at which the maximum weight loss rate occurs (T_m) and the temperature at the end of the pyrolysis step ($T_{w\infty}$) are reported in Table 2 for each case of experiments.

Table 2 Experimental condition for rice straw TGA study

Rice straw (mg)	Heating rate (K min^{-1})	Temperature Range (K)	Residue (%)	T_{w0} / T_d / T_m / $T_{w\infty}$
5.475	5	370 - 900	28.205	393.128 / 496.951 / 564.909 / 873.556
9.558	10	370 - 900	27.255	379.310 / 502.912 / 574.297 / 873.117
6.995	15	370 - 900	28.477	397.077 / 507.808 / 581.473 / 873.185

Fig. 2 represent α versus T curves for pyrolysis of rice straw at several heating rates. It is observed from the Fig.s that the curves show constant pattern behavior at different heating rates. A quick thermal decomposition is observed in the range of T_d to T_{w0} and the highest decomposition rate is observed at ~ T_m, as reported in Table 2. After this quick increase, the solid continues to decompose smoothly and slowly until the end of the experiment. Higher heating rate finishes the decomposition faster. The thermal decomposition behavior is almost similar except for a difference in T_m, is attributed to the fact of similar reaction mechanism, which is the basis of multi-heating rate approach for kinetics analysis.

The *dα/dT* versus *T* curves. Heating rate affects DTG curve positions, maximum decomposition rate and location of maximum T_m peaks. When heating rate increases, starting and final temperature of pyrolysis region also increase. Maximum point of TG and DTG curves are shifted towards higher temperature. This can be explained on the basis of heat transfer limitation. During the analysis, at low heating rate, a larger instantaneous thermal energy is provided to the system and longer time may be required for the purge gas to reach equilibrium with the temperature of the sample. While at the same time and in the same temperature region a higher heating rate has a short reaction time and therefore the temperature needed for the sample to decompose is also higher. This causes the maximum rare curve to shift to the right (Slopiecka et al., 2012).

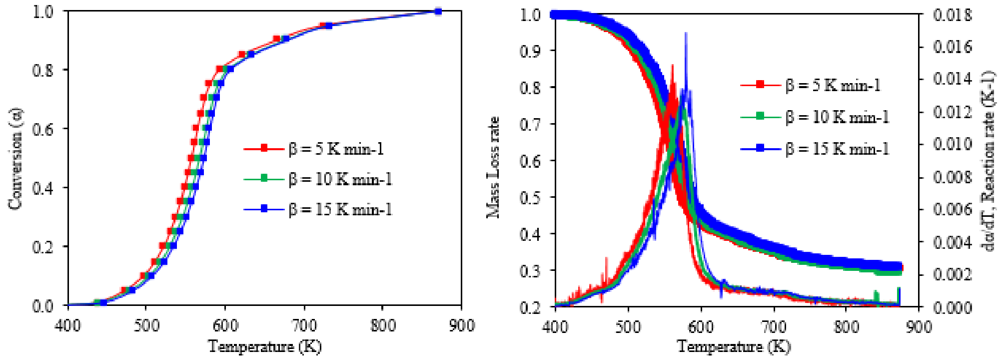

Fig. 2 Variation of conversion (α) and rate of decomposition ($d\alpha/dT$) with temperature during pyrolysis of rice straw sample at multiple heating rates.

3.2 Prediction of experimental TGA data

AIC scores help to identify the better reaction model for pyrolysis study. Lower AIC scores for a reaction model, more correct is the model representing the system. Therefore, the kinetic triples as shown in Table 3 obtained by GA method employed in the present study are used in simulation to calculate the AIC scores for all 14 models considered. For rice straw used, that the AIC scores is minimum for 3D Diffusion model. The Avarami-Erofe'ev nucleation models also show encouraging scores. Thus, the pyrolysis kinetic Eq. was simulated using optimized kinetics triplet for the 3D diffusion reaction model to prediction of the experimental TGA data.

Table 3: Average of kinetic parameters for rice straw

Kinetic models	Differential form *f(α)*	Integral form *g(α)*	*E*, (kJ mol^{-1})	ln *A*, (min^{-1})	AIC score
Nucleation models					
Power Law (P2)	$2\alpha^{(1/2)}$	$\alpha^{(1/2)}$	204.983	45.509	-13,051.971
Power Law (P3)	$3\alpha^{(2/3)}$	$\alpha^{(1/3)}$	204.874	45.727	-6,566.156
Avarami-Erofe'ev (A2)	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$	205.123	44.918	-35,720.241
Avarami-Erofe'ev (A3)	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$	204.968	45.239	-31,287.948
Geometrical contract models					
Contracting area (R2)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$	205.121	45.434	-7,699.234
Contracting volume (R3)	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$	205.046	45.968	116.871
Diffusion models					
1D Diffusion (D1)	$1/2\alpha$	α^2	204.795	45.639	-46,989.821
2D Diffusion (D2)	$[-\ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha)]+\alpha$	204.534	46.056	-9,902.993
3D Diffusion-Jander (D3)	$3(1-\alpha)^{2/3}/2(1-(1-\alpha)^{1/3}$	$[1-(1-\alpha)^{1/3}]^2$	205.516	47.252	-65,733.737
Ginstling-Brounshtein (D4)	$3/2((1-\alpha)^{-1/3}-1)$	$1-(2\alpha/3)-(1-\alpha)^{2/3}$	204.789	46.668	-9,315.629
Reaction-order models					
Zero-order (F0)	1	α	205.251	45.377	-13,979.749
First-order (F1)	$(1-\alpha)$	$-\ln(1-\alpha)$	205.073	44.596	-24,990.604
Second-order (F2)	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$	205.308	42.103	-27,781.789
Third-order (F3)	$(1-\alpha)^3$	$0.5[(1-\alpha)^{-2}-1]$	205.127	43.023	-29,234.627

Fig. 4 shows prediction of the experimental TGA data by 3D diffusion for different heating rates. It is observed from the Fig. that 3D diffusion model successfully predicted the experimental TGA data particularly for rice straw samples.

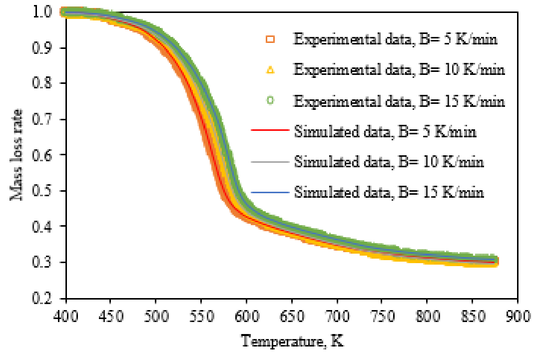

Fig. 4 Comparison between simulated and experimental mass loss during non-isothermal pyrolysis of rice straw at three different heating rates for 3D Diffusion model.

4. Conclusion

Pyrolysis studied of rice straw are conducted at several different heating rates: 5, 10 and 15 K min^{-1} to evaluate the kinetic triplet parameters (activation energy, *E*; pre-exponential factor, *A* and reaction model, $f(\alpha)$). The constant pattern behavior of TG curves for all different heating rates possibly suggests existence of similar reaction mechanism. We have approximated the whole process of pyrolysis as multi-step and accordingly found out the globally optimum overall kinetics parameters employing genetic algorithm and using 14 different decomposition models. The suitability of the models is tested using the AIC score.

Results show that 3D diffusion model is the best suited one and is also predicted the experimental TGA data successfully. However, the Avarami-Erofe'ev nucleation models also shows good AIC score and well predicted the experimental TGA data.

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