

ESTIMATION OF KINETIC PARAMETERS FROM THERMOGRAVIMETRIC ANALYSIS

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Abstract

Activation energy is the crucial factor in deciding the reactor volume in the thermochemical conversion of biomass. Thermogravimetric analysis (TGA) records the weight loss of the samples with respect to temperature in the different heating environments. Arrhenius parameters, k_0 , and E , determine thermal degradation of substances from TGA data for assumed order of reaction by trial-and-error method. The proposed method is based on dividing the entire degradation process into various zones akin to Differential Thermo Gram (DTG) data. The combined effect of temperature and weight in deciding the rate curve has been explained for different shapes. For each zone, the rate constant is determined by assuming the orders from 0.5 to 3 in steps of 0.5. The order of reaction gives the importance of concentration of reactions during the reaction. Whichever order gives the best fit in Arrhenius plot that is the best order. The corresponding Arrhenius parameters are taken. This gives the importance of the reactants in the zone. This method has been demonstrated successfully for the determination of k_0 , E , and n for the auto-gasification of poultry litter at a heating rate of 5°C/min in a static nitrogen medium. It has been observed that higher order of reaction has been observed in the temperature range of 34-160°C, 265-325°C and 325-435°C, mostly endothermic nature of the combustion substances.

Keywords: Arrhenius parameters, Activation energy, Order of reaction, Rate constant, TGA.

1. Introduction

Thermogravimetric analysis (TGA) is widely used for studying the effect of heating on the thermal degradation of chemicals. The weight fraction yet to be converted at any heating rate, and the environment is recorded at regular intervals of time or temperature. The derivative thermogram (DTG) is also obtained from TGA data. For elucidating the kinetics and mechanism of thermal degradation, it is necessary to determine the reaction rate constant (k) and order of the reaction (n). Further, the dependency of the rate constant on temperature should be established by the Arrhenius equation. Arrhenius frequency factor (k_0) and activation energy (E) are to be evaluated.

Accurate determination of these kinetic parameters (k_0 , E , and n) would result in elucidating the correct mechanism for understanding the proper course of the reaction. Further, these parameters enable the design of commercial reactors to be very reliable.

The kinetic parameters are estimated presently by dividing the entire temperature range into several zones and assuming the reaction order. These zones may represent various thermal degradation stages. For example, in biomass gasification, these zones represent drying, devolatilization, and gasification. The constituents of biomass are broadly grouped as moisture, hemicellulose, cellulose, lignin and ash. Devolatilization represents the thermal degradation of hemicellulose, cellulose and lignin at different temperature ranges. Char is the product of gasification [1, 2]. During the gasification, char is converted into gaseous fuel. Each thermal degradation stage occurs at different temperature ranges, drying up to 120°C, devolatilization between 200°C and 375°C and gasification above 375°C.

The order of the reaction is mostly assumed to be one and the constants E and k_0 are determined by trial and error for each zone [3]. The prediction of weight yet to be converted at any time or temperature is also very cumbersome.

In this study, an alternative approach is proposed to overcome uncertainties in determining kinetic parameters within previous studies. This could enable an accurate measurement of the reaction rate constant to be achieved [4].

Based on the TGA studies, many models have been developed and verified. Table 1 lists those models. These models relate the weight loss at different temperatures in nitrogen medium [5]. Even though kinetics of degradation due to temperature at various heating rates with N_2 /air purging have been reported.

Table 1. List of models.

Model No.	Method of Analysis	The equations of determining of kinetic parameters (for $n=1$)
1	Agrawal and Sivasubramanian [6]	$\ln \left[\frac{-\ln(1-x)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(\frac{1-2(RT/E)}{(1-5(RT/E)^2)} \right) \right] - \frac{E}{RT}$
2	Coats and Redfern [7]	$\ln \left[\frac{-\ln(1-x)}{T^2} \right] = \ln \left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{\beta E} \right) \right] - \frac{E}{RT}$
3	Lapuerta Magin et al. [8]	$(1-x) = \exp \left[\frac{-ART^2 \exp(-E/RT)}{\beta E} \right]$
4	Piloyan and Novikova [9]	$\ln \left(\frac{\omega}{T^2} \right) = \ln \frac{AR}{\beta E} - \frac{E}{RT}$

2. Proposed Method Development

Depending upon the substances' thermal degradation characteristics, a different constituent of the substances degrades in different temperature ranges. The identification of these ranges is essential. It is impossible to determine the number of zones and the corresponding temperature ranges using TGA data alone. However, DTG data derived from TGA data could be used for this purpose. The TGA setup is given in Fig. 1.

On heating, each substance degrades differently depending upon its constituents. TGA shows a continuous reduction in total weight with increasing temperature or time. Therefore, DTG derived from TGA data gives the rate of reaction concerning temperature or time and picturizes the effect of temperature or time and weight yet to be converted at the rate. Therefore, understanding of DTG data would become essential for the elucidation of the kinetics of thermal degradation. Temperature or time affects the rate of degradation in several ways. Most commonly occurring relationships between weight yet to be converted and the rate is shown in Fig. 1.

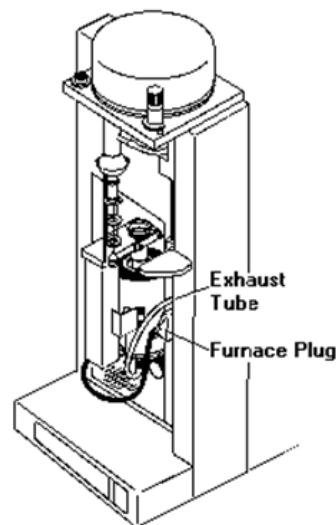


Fig. 1. TGA setup.

Depending upon the number of different compounds present in the degrading substance, one or all the above relationships may be observed.

The rate of reaction ($-r_d$) is given by

$$-r_d = kM_{avg}^n \quad (1)$$

The reaction rate constant varies exponentially with temperature and is related by the Arrhenius equation as follows:

$$k = k_0 e^{-E/RT} \quad (2)$$

The non-isothermal rate of reaction is obtained by combining Eqs. (1) and (2)

$$-r_d = k_0 e^{-E/RT} M_{avg}^n \quad (3)$$

At time $t = 0$, the weight of a particular compound yet to be converted is the highest and temperature is the least. As time progresses, temperature increases due to heating at a constant heating rate and weight yet to be converted decreases due to degradation. The rate constant k increases exponentially with temperature. The reduction in weight due to degradation tries to pull down the rate while increasing temperature pulls up the rate constant k exponentially.

The resultant rate increases for some time. At some point of time, the continuous depletion in the weight outweighs the benefit of higher temperatures (and k) and the resultant rate decreases to a minimum. This results in the shape of rate vs. weight, as shown in Fig. 2(a).

The rate of reaction is constant irrespective of weight and temperature. As explained for Fig. 2(a), k increases exponentially with temperature and weight decreases with the progress of the reaction. However, the product of k and weight balances out the variation in such a way to maintain the rate of reaction constant (Fig. 2(b)).

The rate of reaction decreases with weight. As time progresses, weight decreases while temperature increases. An exponential rise in k values due to an increased temperature outweighs the effect of a reduction in weight and maintains a steady decrease in rate values with weight as shown in Fig. 2(c).

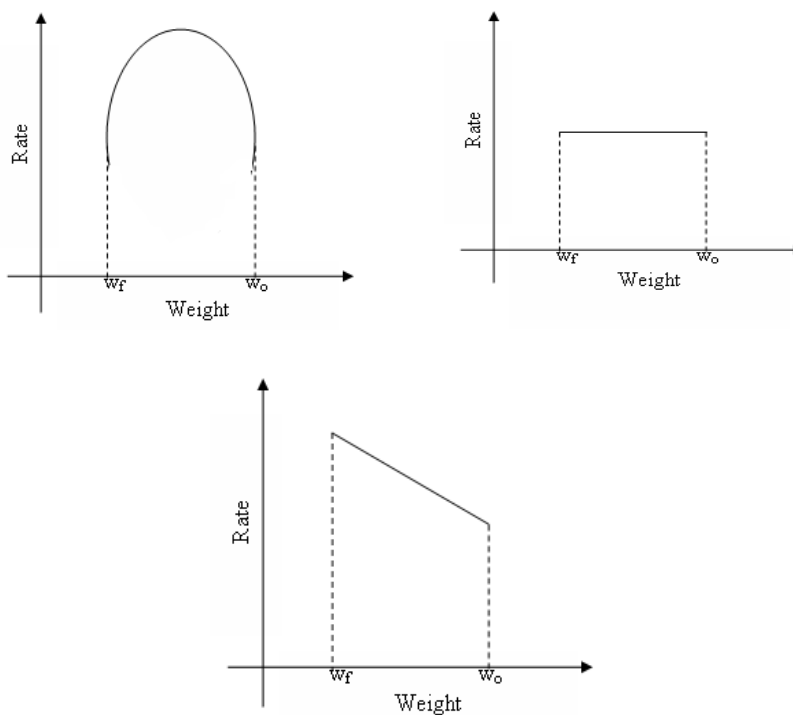


Fig. 2. Shapes of rate vs. weight relationship.

However, it is to be kept in mind that in all the above cases, while weight decreasing with time (temperature), k keeps on increasing with temperature (time). The order of reaction ' n ' plays a crucial role in maintaining these variations and retaining the relationship. It is essential that the effect of temperature on k must be well defined by the Arrhenius equation [10].

Therefore, the following steps for estimating the correct order are followed:

- For the various values of $n = 0.5, 1, 1.5, 2, 2.5,$ and 3 determine rate constant k using $-rd$ and M_{avg} in Eq. (1). The above range of ' n ' values has been chosen by many authors to elucidate the kinetics.
- Relate k and temperature using Arrhenius Eq. (2).
- For whichever order, the best fit for Arrhenius Equation is obtained, which is the reaction's order.

The proposed model simplifies the model which is used for prediction of rate constant and activation energy prescribed in Table 1. TGA records weight loss for every minute. From this data average weight yet to be converted has been arrived.

3. Demonstration of Model

The proposed method is demonstrated for the determination of kinetic parameters for the auto gasification of poultry litter at a heating rate of $5^{\circ}\text{C}/\text{min}$ in a static nitrogen medium. The authors [11] collected poultry litter from nearby poultry farms dry it and made a fine powder. Several trials runs have been made in TGA $5^{\circ}\text{C}/\text{min}$ in a static nitrogen medium. Sample of 10mg has been taken for every trial run. TGA has the balance Sensitivity of $10\ \mu\text{g}$ ($10^{-2}\ \text{mg}$), balance Accuracy of better than 0.1% , Weighing Precision of up to $10\ \text{ppm}$. Figure 3 shows the TGA and DTG plot obtained. for the poultry litter with $5^{\circ}\text{C}/\text{min}$ in static nitrogen medium.

Poultry litter contains moisture, hemi cellulose, cellulose, lignin, fixed carbon and ash [12, 13]. Upon heating, these compounds, except ash undergo degradation at different temperature levels [14, 15]. A close observation of the DTG plot indicates several zones of degradation, each representing a compound. The negative values of derivative Weight % ($\%/ \text{min}$) are shown in Fig. 3. However, positive are taken for analysis [16, 17].

Table 2 gives ranges of temperature, the weight of individual compounds and the type of degradation. Explanations similar to Figs. 2(a)-2(c) can be offered to various zones.

The rate constants k , for the range of temperature in each zone are calculated for assumed orders of $0.5, 1, 1.5, 2, 2.5$ and 3 by using Eq. (3). The rate constant and the corresponding temperature for each order were related using Arrhenius equation Eq. 2. The Arrhenius constants were determined for each zone. Table 3 gives the values of k_0, E for different ' n ' for each zone along with regression coefficients. The best values of kinetic parameters for which the regression coefficient is the highest can be obtained from the table. These values are given in bold types in Table 3.

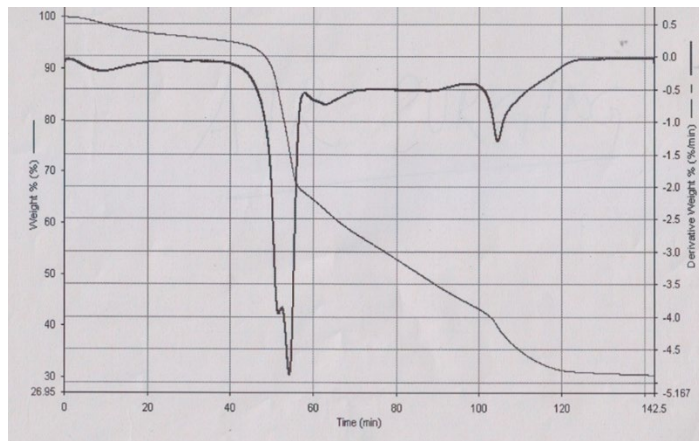


Table 2. Ranges of temperature and weight.

Zone	Time Range, min		Temperature range, °C		Probable component	Total Weight of Component (mg)	Type of degradation
	From	To	From	To			
1	0	26	34	160	Moisture	0.1033	Fig. 2(a)
2	26	32	160	190	Volatiles	0.0053	Fig. 2(b)
3	32	41	190	240	Hemi Cellulose	0.0527	Fig. 2(a)
4	41	47	240	265	Cellulose	0.1634	Fig. 2(a)
5	47	59	265	325	Lignin	0.1013	Fig. 2(a)
6	59	80	325	435	Volatiles	0.1255	Fig. 2(b)
7	80	101	435	545	Char	0.1048	Fig. 2(a)

Table 3. Values of Arrhenius parameters for various orders.

S. No.	Zone	Temperature Range °C	Order	E/R	k_{do}	Reg. Coeff. R^2
			n	kJ/mole K	min ⁻¹	
1	1	34-160	3	24.5897	3.71352E+12	0.8703
			2.5	19.6904	5445198238	0.867
			2	14.7916	7984398.436	0.8603
			1.5	9.8923	11704.16453	0.8428
			1	4.9934	17.16204055	0.7653
			0.5	0.0942	0.025165029	0.0024
2	2	160-190	3	148.8438	1.32754E+49	0.8839
			2.5	125.1936	5.88023E+40	0.8841
			2	101.5476	2.61765E+32	0.8842
			1.5	77.8974	1.16528E+24	0.8845
			1	54.2514	5.18217E+15	0.8846
			0.5	30.6016	23068993.47	0.8831
3	3	190-240	3	117.7260	3.20173E+33	0.8379
			2.5	105.0378	2.40135E+29	0.8537
			2	92.3496	1.80E+25	0.8709
			1.5	79.6656	1.35217E+21	0.8938
			1	66.9774	1.01415E+17	0.9228
			0.5	54.2934	7.61393E+12	0.9583
4	4	240-265	3	266.6958	1.07982E+67	0.9255
			2.5	218.4084	4.66648E+54	0.927
			2	170.1168	2.03079E+42	0.9294
			1.5	121.8294	8.80247E+29	0.9335

			1	73.5378	3.81543E+17	0.9423
			0.5	25.2487	165379.8122	0.9685
			3	163.7832	5.19536E+38	0.8506
			2.5	133.7448	2.02559E+31	0.845
5	5	265-325	2	103.7064	7.90537E+23	0.8362
			1.5	73.6722	3.08527E+16	0.8199
			1	43.6338	1202898623	0.7804
			0.5	13.5937	49.36294295	0.571
			3	64.2264	2.8275E+13	0.909
			2.5	53.9952	83323795034	0.9072
6	6	325-435	2	43.7598	245301837.5	0.9044
			1.5	33.5278	722158.5557	0.8998
			1	23.2945	2125.580031	0.8906
			0.5	13.0607	6.258246287	0.8644
			3	202.7844	5.84804E+34	0.9583
			2.5	161.7294	2.65436E+27	0.9624
7	7	435-540	2	120.6744	1.20599E+20	0.9683
			1.5	79.6194	5.47931E+12	0.9762
			1	38.5644	248948.1697	0.9634
			0.5	2.4906	0.011303985	0.0329

*Best values are shown in bold types

4. Summary and Conclusion

The existing procedure for the determination of kinetic parameters such as k_0 , E and n for thermal degradation of substance is very cumbersome. It does not give a clear picture of the degradation process. Even though TGA and DTG data are being used to elucidate of kinetics and mechanism, generally, the parameters k_0 and E are determined for an assumed order without justifying the assumption.

The proposed method eliminates these misgivings by dividing the degradation process in the entire range of time (or temperature) into various zones akin to DTG data. The combined effect of temperature and weight in deciding the rate curve has been explained for different shapes. For each shape of curve occurring in each zone, the rate constants are determined by assuming orders from 0.5 to 3 in steps of 0.5. Whichever order gives the best fit in the Arrhenius plot, that is the order of reaction and the corresponding k_0 and E values are taken. The proposed method has been demonstrated with several trials and proved that it elucidates the kinetic parameters for the auto gasification of poultry litter at a heating rate of 5°C/min in static nitrogen medium.

The zones with the temperature range of 34-160°C, 265-325°C and 325-435°C records the higher order of reaction due to the endothermic in nature of reaction and the concentration of reactants is dominates. The remaining regions mostly the order of reaction is with the range of 1. The above findings will be very much useful for the design of combustor/gasifier.

Nomenclatures

E	Activation Energy, kJ/mole
k	Reaction rate constant, min^{-1}
k_0	Arrhenius frequency factor, min^{-1}
M	Weight of component yet to be converted, gram
n	Order of the reaction
$-rd$	Rate of reaction, gram/min

R	Gas constant, kJ/mole K
T	Temperature, °C or K
w	Total weight yet to be converted in a particular zone at any time, grams
w_f	Total weight yet to be converted at the end of the zone, grams
W_o	Initial weight of biomass
W_t	Weight of biomass at any time 't'
W_∞	Weight of biomass at the completion of degradation
x	Fractional conversion
ω	The decomposed fraction of solid at any time 't'
β	Heating rate
Abbreviations	
DTG	Differential Thermo Gram
TGA	Thermogravimetric Analysis

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