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# KINETICS OF THE THERMAL DECOMPOSITION OF EGYPTIAN COTTON STALKS, CORN STALKS, AND RICE STRAW

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## ABSTRACT

A kinetic study of three Egyptian agricultural wastes has been conducted at a heating rate of 5$^o$C/min using thermogravimetric analysis TGA. The kinetic parameters (order of reaction, activation energy, and frequency factor) have been determined from the TGA experiment measurements. The kinetic results indicate that the thermal degradation is a first order reaction. The activation energies (25.7 - 26.2 - 26.1) kJ/mol and the pre-exponential factors (5.86E-3, 6.95E-3, and 6.95E-3) were attained for cotton stalks, corn stalks, and rice straw, respectively. These activation energy values are considered low, which specify the ease of gasification of these three types of the agricultural wastes.

**Keywords:** kinetics, agricultural wastes, thermogravimetric analysis, activation energy.

## INTRODUCTION

Tremendous amounts of agricultural wastes accumulate seasonally in Egypt (El-Haggar, 1998). These agricultural wastes encompass Cotton stalks, corn stalks, and rice straw. Typically 52% of the Egyptian agricultural wastes is burnt on the fields, while the remaining is used as a fertilizer and animal food (El-Mashad, *et al.*, 2003). Thus large fraction of the Egyptian agricultural wastes is still not treated in the perfect way, as these wastes can be an energy source shall the embedded energy is extracted efficiently.

To extract the embedded energy of these agricultural wastes, different technologies can be applied. For instance, combustion processes can release the heat content of the agricultural wastes (Tora and Dahliquest, 2015); fermentation is a biological process that can convert the embedded energy content into fuels (El-Zanati *et al.*, 2006); biodiesel production is a chemical conversion process that can convert the biomass into diesel (Tora, *et al.*, 2015); pyrolysis and gasification are thermochemical conversion processes release the heat content with producing high heating value oil and gaseous mixtures, respectively (Chen, *et al.,* 2015).

Gasification is an efficient technology converting the agricultural wastes into gaseous mixture. Nevertheless, it's a complex process taking place in different stages (Puig-Arnavat, *et al.*, 2010). The process in endothermic at the beginning, and then becomes exothermic in the remaining of the process. Activation energy of the reaction is a criterion defining the gasification effectiveness and thermochemical decomposition readiness. Thermal decomposition of each agricultural waste can be evaluated by the value of the reaction activation energy and the reaction rate constant (Huang, *et al*, 2015).

Accordingly, the objective of this work is to determine the kinetic parameters (reaction order, activation energy, pre-exponential factor) of the thermal decomposition of three types of agricultural wastes: cotton stalks, corn stalks, and rice straw. These kinetics parameters are elaborated from the measurements of thermogravimetric analysis at 5$^o$C/min.

## EXPERIMENTAL PROCEDURE

### Materials preparation and characterization

Rice straw, corn stalks and cotton stalks were the Egyptian agricultural wastes used in this study. The samples were crushed and then sieved and classified to fractions. The average particle size (0.825 mm) was used in all the experiments. The proximate and ultimate analysis (Heggo, 2012) of these agricultural wastes are reported in Tables (1-2).

**Table-1.** Proximate analysis of biomass samples (wt%).

| Biomass type | % Moisture content | % Total volatile matter | % Fixed carbon | % Ash |
|---|---|---|---|---|
| Cotton stalk | 8.9 | 81.24 | 14.48 | 4.28 |
| Rice straw | 8.04 | 69.24 | 16.7 | 14.42 |
| Corn stalk | 7.96 | 76.6 | 19.12 | 4.27 |

**Table-2.** Elemental analysis of biomass samples (wt%).

| Biomass type | C % | O % | H % | N % | S % |
|---|---|---|---|---|---|
| Cotton stalk | 44.8 | 43.8 | 5.8 | 1.09 | 0.57 |
| Rice straw | 33.86 | 39.18 | 4.5 | 1.045 | 0.945 |
| Corn stalk | 40.3 | 46.93 | 4.2 | 2.3 | Nil |

The molecular formulas of the biomass wastes based on the ultimate analysis were estimated as cotton stalks, $CH_{1.4}O_{0.66}$, corn stalks, $CH_{1.5}O_{0.74}$ rice straw, $CH_{1.3}O_{0.65}$ and saw dust CH1.65 $O_{0.66}$. From both molecular formulas it was concluded that there is no considerable difference in the elemental composition of the biomass residues.

The higher heating value for selected biomass in our project was estimated based on the ultimate analysis by using the following formula;

Higher Heating value (kJ/kg) = 349.1C+1178.3H+100.5S-103.4O-15.1N-21.1ASH. The results are reported in Table-4.

**Table-3.** Heating value of the studied biomasses.

| Biomass | Molecular formula | HHV (kJ/kg) |
|---|---|---|
| Cotton stalks | $CH_{1.4}O_{0.66}$ | 3.06 |
| Corn stalks | $CH_{1.5}O_{0.74}$ | 3.24 |
| Rice straw | $CH_{1.3}O_{0.65}$ | 2.95 |

**Thermogravimetric analysis**

Thermogravimetric analysis (also called thermal gravim analysis) measures the weight loss as the material is heated. The measurement determines the thermal stability of the biomass and its volatile content (Singh, *et al.*, 2013) (Ali, *et al.*, 2014). The onset of the decomposition occurs at a specific temperature depending on the type of the biomass, particularly its cellulosic and lignin content (Sittisun, *et al.*, 2015).

Thermogravimetric analysis TGA was conducted on three types of agricultural wastes at a heating rate of 5°C/min; the final heating temperature was 550°C under nitrogen atmosphere. The measurements attained from the TGA are used to determine the kinetic parameters of the thermochemical degradation.

**KINETIC ANALYSIS**

Taking into account the TGA results and the observed weight loss over a wide temperature range, kinetic parameters (the activation energy $E$ and the reaction rate constant $k$) were estimated for cotton stalks, corn stalks, and rice straw. Elaborating the kinetic parameters of biomass thermal decomposition using TGA is an evident method giving acceptable results (Sun, *et al.*, 2012) (Mohd Din, *et al.*, 2005) (Aboulkas and El Harfi, 2008).

The reaction order was assumed to be first order and the parameters were estimated according to Coats and Redfern equation (Coats and Redfern, 1964) as;

$$da/dt = k(1-a)^n \quad (1)$$

$$k = k_o e^{-E/R.T} \quad (2)$$

$$a = (w - w_f)/(w_o - w_f) \quad (3)$$

where $a$ is the percentage of the products of the volatile products in time, $k$ is the Arrhenius rate constant; $w_o$ and $w_f$ are the initial and ultimate yield of the volatile products during reaction, $n$ is the reaction order, $k_o$ is pre-exponential factor ($s^{-1}$), and $E$ is the activation energy (*kJ/mol*). The kinetic study was conducted in the non isothermal area of the TGA curves and the temperature ranged from 200 to 500° C.

The reaction order ($n$) is determined via comparing the TG experiment measurements and the model predictions; the accepted reaction order is the one provided a straight line. Elaborating the reaction order is implemented via integrating Equation (1) with considering Equation (2) and Equation (3); the integration is done one time for the first- order reaction and results in Equation (4).

$$Ln[-Ln(1-\alpha)/T^2] = Ln[(k_o.R)/(E.dT/dt)] - E/(R.T) \quad (4)$$

For a constant value of the heating rate ($dT/dt$= 5°C/min), the plot of $Ln[-Ln(1-\alpha)/T^2]$ vs. $[-1/T^2]$ should be a straight line. The kinetic parameters for each agricultural waste can be calculated as the slope of the plotted line defines the value of the activation energy ($E$) and the intercept elaborates the pre-exponential factor ($k_o$).

**RESULTS AND DISCUSSIONS**

The results of the thermogravimetric analysis for three Egyptian agricultural wastes (cotton stalk, corn stalk, and rice straw) are listed in Table 4-6. These measurements have been used to determine the reaction kinetic parameters of each type of the investigated agricultural biomasses.

**Cotton stalk**

The results of the thermal degradation of cotton stalks at 5°C/min are given in Table-4; the weight losses against the temperature degrees are measured. The decomposition started at a temperature typically 200°C, and the decomposition rate was low till a temperature of 300°C. After, higher thermal decomposition was observed. Nevertheless, at temperatures higher than 500°C, trivial decomposition occurred.

**Table-4.** TGA results for cotton stalk.

| T °C | Wt % |
|---|---|
| 200 | 91.8 |
| 250 | 87.65 |
| 300 | 72.97 |
| 350 | 47.08 |
| 400 | 42.26 |
| 450 | 38.8 |
| 500 | 35.82 |
| 550 | 33.45 |

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For the case of first- order reaction assumption, Eq. 4 has been plotted, and a straight line with regression square root coefficient of 0.93 was attained. Therefore, the assumption of a first- order reaction is proved herein. The slope of the line indicates that the activation energy of cotton stalk decomposition is 25.7 kJ/mol. Also, the intercept elaborates the value of the pre-exponnetial factor ($k_o$) and its value is 0.00586 $s^{-1}$.

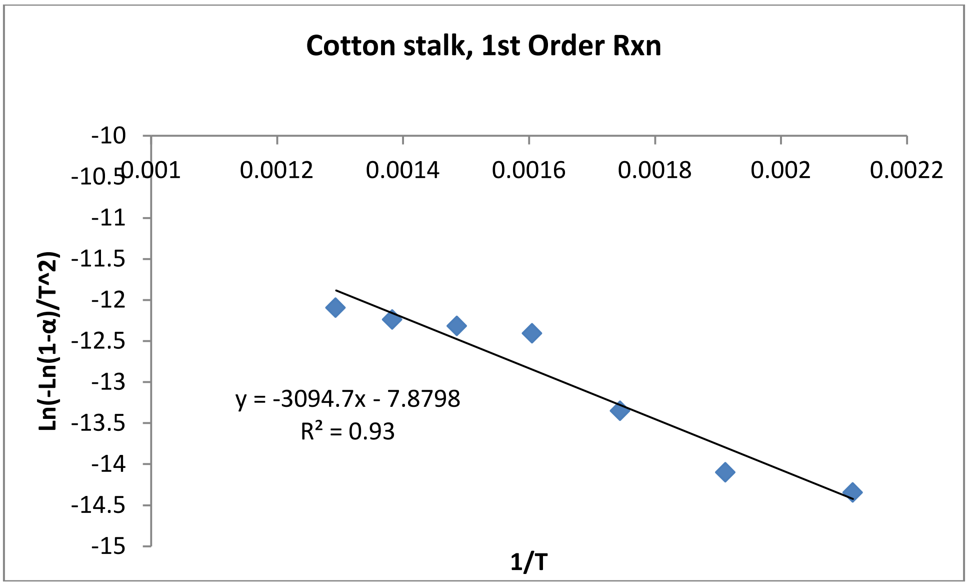


**Figure-1.** Order of the decomposition reaction of cotton stalk.

**Table-5.** Kinetic parameters of cotton stalk thermal decompostion reaction.

| *n* | *E (kJ/mol)* | $k_o(s^{-1})$ | $R^2$ |
|---|---|---|---|
| 1 | 25.7 | 5.86E-3 | 0.93 |

**Corn stalks**

For corn stalks, the weight losses at different temperatures degrees obtained from TG measurements were reported in Table-6. It appears that the rapid thermal decomposition starts when the temperature became above 300°C. Significant decomposition occurs till a temperature of 400°C.

This means the end of the significant decomposition of corn stalks occurs at a temperature lower than that of the cotton stalk (500°C). Also, the thermal decomposition of corn stalk is faster than that of the cotton stalk. That observation is augmented as considering the residual of the biomass: 27% at 550°C in case of cotton stalk, 33% at 550°C in case of cotton stalk. Accordingly, corn stalks may be a better gasification feedstock than the cotton stalks, in terms of the decomposition rate and the residual fraction.

**Table-6.** Weight loss of corn stalks.

| T °C | Wt % |
|---|---|
| 200 | 91.4 |
| 250 | 83.86 |
| 300 | 69.62 |
| 350 | 39.71 |
| 400 | 35.16 |
| 450 | 32.16 |
| 500 | 29.51 |
| 550 | 27.39 |

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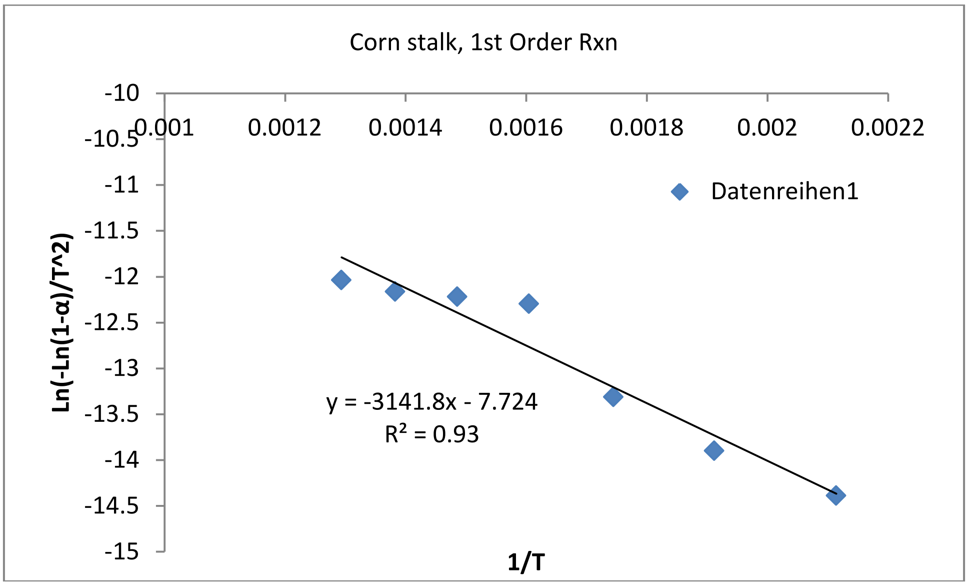


**Figure-2.** Order of the thermal decomposition reaction of corn stalk.

**Table-7.** Kinetic parameters of corn stalk thermal decomposition.

| ***n*** | ***E (kJ/mol)*** | $k_o$ ($s^{-1}$) | $R^2$ |
|---|---|---|---|
| 1 | 26.1 | 6.95E-3 | 0.93 |

From the slope of the straight line represented in Figure-2, the activation energy was elaborated to be 26.1 kJ/mol, which is slightly higher than that of the cotton stalk. The frequency factor equals 0.00695 $s^{-1}$.

**Rice straw**

The TG measurements are listed in Table-8 whereby it is observed that the decomposition is slightly faster than that in case of corn stalk. Moreover, the residuals are less than in the above two cases. The activation energy is similar to the value of corn stalk.

**Table-8.** TG measurements of rice straw.

| **T** (°C) | **Wt** % |
|---|---|
| 200 | 91.69 |
| 250 | 87.52 |
| 300 | 71.13 |
| 350 | 35.45 |
| 400 | 30.28 |
| 450 | 27.04 |
| 500 | 24.72 |
| 550 | 22.94 |

Plotting Equation (4) that assumes a first order reaction gives a straight line as represented in Figure-9. From the slope of the line, the activation energy is determined to be 26.1 kJ/mol. The intercept elaborates the frequency factor value of 0.00695 $s^{-1}$.

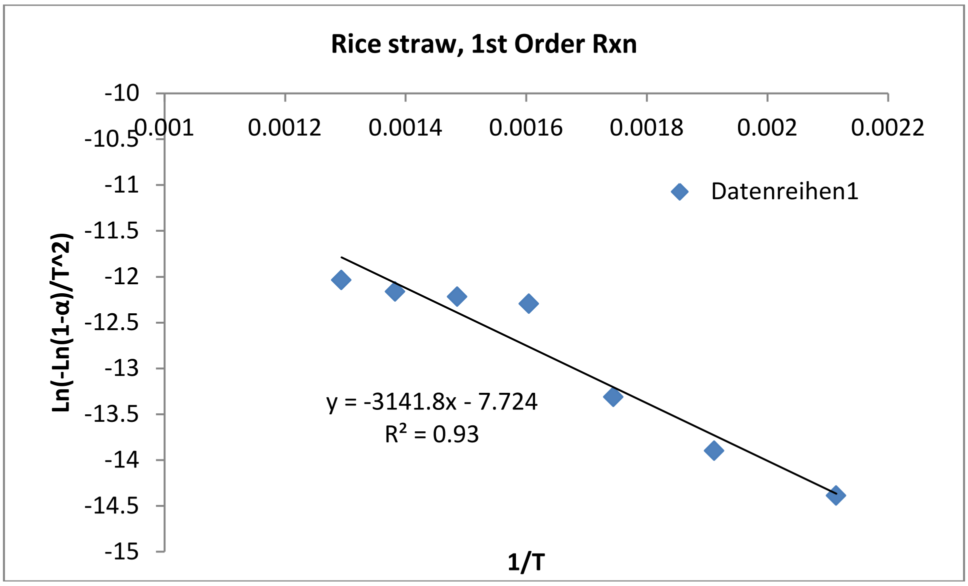


**Figure-3.** Order of the thermal decomposition reaction of the rice straw.

**Table-9.** Results of the kinetic analysis of rice straw thermal decomposition.

| *n* | *E (kJ/mol)* | $k_o(s^{-1})$ | $R^2$ |
|---|---|---|---|
| 1 | 26.1 | 6.95E-3 | 0.93 |

The value of the activation energy is an important indication of the gasification process effectiveness. Ease of gasification entails low activation energy. The kinetic analysis using the TG measurements results that the thermal decomposition of the studied agricultural wastes needs low activation energies.

## CONCLUSIONS

The results of thermogravemtric analysis TG for three types of Egyptian agricultural wastes have been investigated via a kinetic study. The thermal decomposition appears to follow the first order reaction mechanism. The attained kinetic parameters, particularly the activation energies, indicate that relatively high activation energy is needed to gasify these agricultural wastes. That may be attributed to the low heating rate (5°C/min). On the other side, the heating values of these agricultural wastes are reasonably high. Accordingly, Egyptian cotton stalks, corn stalk and rice straw can be appropriate energy source via gasification process provided that high heating rates are used.

The decomposition rate of Corn stalks is higher than that of cotton stalk; also the residual is lower when corn stalk was used as the feedstock. Furthermore, the activation energy of corn stalks decomposition is lower. Consequently, corn stalks may be a preferred feedstock for the gasification processes.

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## REFERENCES

[1] El-Haggar S.M. 1998. Recycling of solid waste in Greater Cairo. in Ain Shams 1st Conference on Engineering and Environment, Cairo, Egypt.

[2] El-Mashad H.M., Loon W.K.P., Zeeman G., Bot G.P. and Lettinga G. 2003. Reuse potential of agricultural wastes in semi-arid regions: Egypt as a case study. Reviews in Environmental Science and Biotechnology. 2(1): 53-66.

[3] Tora E. A. and Dahliquest E. 2015. CFD Ansys - Fluent Simulation of Prevention of Dioxins Formation via Controlling Homogeneous Mass and Heat Transfer within Circulated Fluidized Bed Combustor. Energy Procedia. 75: 130-136.

[4] El-Zanati E., Abdel-Hakim E., El- Ardi O. and Fahmy M. 2006. Modeling and Simulation of Butanol Separation from Aqueous Solutions Using Pervaporation. Journal of Membrane Science. 280: 278-283.

[5] Tora E., AbdelKader I., El Diwani G. and Hawash S. 2015. A multivivariate regression model for estimation of biodiesel production from Jatropha seeds. Research Journal of Pharmaceutical, Biological and Chemical Sciences. 6(6): 1598-1604.

[6] Chen D., Zhang H., Liu D. and Chen Y. 2015. Effect of torrefaction temperature on biomass pyrolysis

using TGA and py-GC/MS. Asia-Pacific Energy Equipment Engineering Research Conference, 2015 AP3ER. pp. 253-256.

[7] Puig-Arnavat M., Bruno J.C. and Coronas A. 2010. Review and analysis of biomass gasification models. Renewable and Sustainable Energy Reviews. 14: 2841-2851.

[8] Huang S., Wu Q., Zhou D. and Huang R. 2015. Thermal decomposition properties of materials from different parts of corn stalk. Bio Resources. 10(1): 2020-2030.

[9] Singh R.K., Biswal B. and Sachin K. 2013. Determination of activation energy from pyrolysis of paper cup waste using thermogravimetric analysis. Research Journal of Recent Sciences. 2: 177-182.

[10] Ali N., Saleem M., Kamil M., Shahzad K. and Chughtai A. 2014. ThermoGravimetric study of Pakistani cotton and maize stalk using iso-conversional technique. Life Science Journal. 11(8): 382-387.

[11] Heggo D.A.M. 2012. Production of Hydrogen- rich gas from thermal gasification of biomass. MSc. Thesis, Cairo University, Egypt.

[12] Sittisun P., Tippayawong N. and Wattanasiriwech D. 2015. Thermal degradation characteristics and kinetics of oxy combustion of corn residues. Advances in Materials Science and Engineering. 2015: 1-7.

[13] Sun W.G., Zhao H., Yan H. X., Sun B.B. Dong S.S., Zhang W. and Qin S. 2012. The pyrolysis characteristics and kinetics of Jerusalem artichoke stalk using thermogravimetric analysis. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 34(7): 626-635.

[14] Mohd Din A.Z., Hameed B. H. and Ahmad A.L. 2005. Pyrolysis kinetics of oil palm solid wastes. 18: 57-66.

[15] Aboulkas A. and El harfi K. 2008. Study of the kinetic and mechanisms of thermal decomposition of Moroccan therfaya oil shale and its kerogen. Oil Shale. 25(4): 426-443.

[16] Coats A. W. and Redfern J.P. 1964. Kinetic parameters from thermogravimetric data. Nature. 201: 68-69.