CHEMICAL ENGINEERING TRANSACTIONS

VOL. 99, 2023

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Sauro Pierucci, Flavio Manenti

ISBN 978-88-95608-98-3; **ISSN** 2283-9216

DOI: 10.3303/CET2399061

Regression Models Analysis for the Degradation of Polystyrene Waste by Thermogravimetric Data

Arantxa M. Gonzalez-Aguilar, M. Celeste Santiago-Zavala, Zivoni D. Mosqueda-Huerta, José M. Riesco-Ávila*

Mechanical Engineering Department, Engineering Division, Campus Irapuato-Salamanca, University of Guanajuato, Guanajuato 37320, Mexico.
riesco@ugto.mx

Plastics are known for their beneficial properties, such as lightness, strength, and low cost, and they are used in different applications such as construction, electronics, and packaging. However, plastics do not degrade naturally, accumulating in soils and affecting the environment. Recycling techniques have been developed to minimize plastic waste; chemical recycling through pyrolysis has been cataloged as an effective method for transforming plastic waste into high-value products in the chemical and petrochemical industry. Previous studies of feedstock degradation through thermogravimetry analysis (TGA) have been essential to estimate the optimal temperature ranges to evaluate the pyrolysis process. The present work aims to study regression models to estimate the temperature degradation of polystyrene (PS) through thermogravimetry data, which can be applied before the pyrolysis process. In addition, this work compares linear and polynomial regression models to estimate the best-fitting model and to determine the maximum temperature of degradation of PS by different heating rates. Relative errors were calculated by comparing them with experimental values from the literature not included in the models. As a result, a polynomial model of a fourth-order obtained a better fit with an r^2=70.45 % compared to the linear models, where the best fit was obtained with r^2= 69.71 %. However, a higher relative error was obtained, with the polynomial models being the lowest, 7.35 and 0.50 % for 15 and 60 °C min^{-1}; for the linear models, 7.05 and 0.39 % were obtained for heating rates of 15 and 60 °C min^{-1}, respectively.

1. Introduction

Polymers are versatile and have been successfully implemented for over three decades due to their physicochemical properties, such as lightweight, high durability, thermal insulation, flexibility, and low production cost (Maafa, 2021). Pyrolysis is considered an attractive method for recycling plastic waste since it transforms it directly into useful energy and valuable products for the petrochemical industry because plastics mainly derive from petroleum (Jeswani et al., 2021). Temperature is the most critical parameter in matter degradation because it governs the chemical reaction. Some studies indicated that the pyrolysis process at low temperatures improved the production of liquid with long hydrocarbon chains (Klaimy et al., 2021). In contrast, others reported that high reaction temperatures favored gasification and allowed secondary reactions inside the reactor, reducing the obtaining of solid fractions (López et al., 2011).

The influence of temperature in the pyrolysis process of PS has been studied by Verma et al. (2021), who experimented with ranges between 400 to 700 °C and heating rates from 5 to 25 °C min^{-1}; regarding heating rate, the results showed that the liquid yield increased as the heating rate increased; however, high rates decreased the yield. Another study where they analyzed the influence of the heating rate in the EPS pyrolysis process was that of Gonzalez-Aguilar et al. (2022), where they evaluated rates between 4 to 40 °C min^{-1}, they demonstrated a curved effect in obtaining liquid as output response; rates higher than 4 °C min^{-1} but lower than 12 °C min^{-1} were the ones that yielded higher.

On the other hand, TGA is a commonly used technique to consider the degradation trend in terms of different pyrolysis process parameters, such as temperature and heating rate (Verma et al., 2021). It is a necessary tool to determine optimal parameters before performing the pyrolysis process.

Paper Received: 22 January 2023; Revised: 5 March 2023; Accepted: 20 April 2023
Please cite this article as: Gonzalez-Aguilar A.M., Santiago-Zavala M.C., Mosqueda-Huerta Z.D., Riesco-Avila J.M., 2023, Regression Models Analysis for the Degradation of Polystyrene Waste by Thermogravimetric Data, Chemical Engineering Transactions, 99, 361-366 DOI:10.3303/CET2399061

TGA analysis must be carried out for different heating rates, which is costly since, in addition to the purchase of the experimental apparatus, it is necessary to use an inert gas with the highest quality.
The present research aims to estimate a model that relates the heating rate and the maximum degradation temperature (Tmax) of PS waste to be applied in the PS pyrolysis process. Linear and polynomial models were developed, and an analysis of their fitting and error with experimental data excluded was addressed.

2. Methodology

2.1 Data

Polystyrene is one of the polymers found in 1930, made through a polymerization process with additives, and it can be found in solid or foam states (Maafa, 2021). PS represents a high carbon content plastic; virgin PS can contain at least 91.23 wt.% and when it is discarded, the carbon content decreases up to 87.40 wt.% (Park et al., 2020; Van der Westhuizen et al., 2022).
The data to be studied were obtained from different works of thermal and catalytic pyrolysis of virgin PS and its waste in the literature and is shown in Table 1, where authors described that PS feedstock was supplied from Sigma Aldrich and Nanometer-Micro Technology Co. or recollected from local markets; XPS distributor was not defined. In order not to consider the influence of other factors, such as inert gas and its flow rate in the determination of maximum temperature, the data collected are results of experiments under nitrogen as inert gas and at a flow rate of 100 mL min^{-1} and were complemented by studies with flows not reported.

Table 1. TGA data considerations

Parameter	Unit	Value
Inert gas	-	Nitrogen
Flow rate	mL min^{-1}	100
Heating rate	°C min^{-1}	5 – 80
Feedstock	-	PS/XPS

(Ding et al., 2019; Inayat et al., 2021; Li et al., 2020; Nisar et al., 2019)

2.2 Methods

GetData 2.26 software (Sarov, Russia) was used for recollecting the data from graphics in the literature with a risk of bias of ±2%. As a first stage, a visual representation through box plots (25-75% quartiles) describing the mean (±95% confidence intervals), and outliers were analyzed to compare the distributions and observe the influence of heating rate on maximum degradation temperature degradation in PS pyrolysis. The statistical analysis was performed using OriginPro 2022 software.
This paper compares linear and polynomial regression models to estimate the best-fitting model to determine the maximum temperature of degradation of PS by different heating rates. The regression analysis was obtained using Statgraphics Centurion XIV software with α=0.05 %. Finally, the maximum degradation temperature of two exclusion points was calculated to evaluate the resulting models; their relative errors were compared with those found in the literature using eq.(1).

$$Relative\ error\ (\%) = \frac{(calculated - experimented)}{experimented} * 100 \qquad (1)$$

3. Results

3.1 Influence of heating rate in Tmax degradation on PS TGA

Figure 1 visualizes the box plots of the data collected from the literature to visualize the distribution of the different heating rates and the maximum degradation temperature of PS by TGA.
The mean temperatures range from 401 to 466 °C for 5 and 80 °C min^{-1}, respectively. Despite the wide scatter of the data collected, it can be observed that the mean maximum degradation temperature increases as the heating rate increases; this trend is fulfilled except for 50 °C min^{-1}, where the temperature decreases to 447 °C. Outlier points are presented for the heating rates of 5, 10, and 20 °C min^{-1}; these resulted from TGA data obtained from PS waste and where the nitrogen flux is not specified. However, they were considered in the study to extend the experimental data collection.

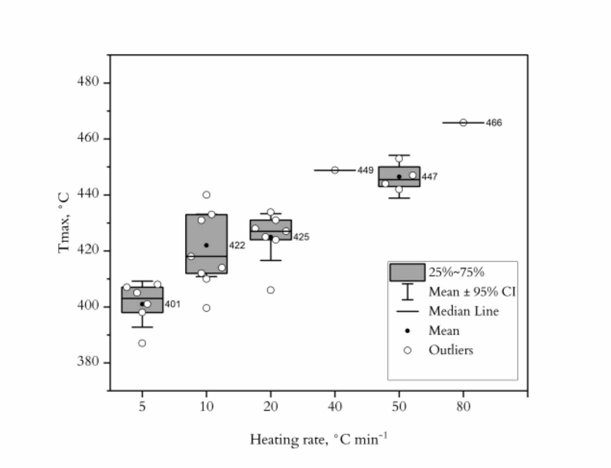

Figure 1: Effect of heating rate on the maximum temperature of degradation on PS TGA. *Data's risk of bias ±2%*

Table 2 details the results of the ten main linear fits that estimate the behavior of the analyzed data and the formulas that describe them. It is observed that a maximum fit of r^2= 69.71 % was obtained with a square-Y log-X model and a correlation of 0.83 with a confidence interval of 95 %. The minimum fit reported is the linear type, with 63.40 %.

Table 2. Linear models to estimate maximum degradation temperature (T_{max}) on PS TGA.

Model	Correlation	r^2	Formula
Square-Y Log-X	0.8349	69.71%	$T_{max} = \sqrt{136169 + 16479 * \ln(h)}$
Logarithmic-X	0.8323	69.28%	$T_{max} = 372.477 + 19.3109 * \ln(h)$
Square Root-Y Log-X	0.8308	69.03%	$T_{max} = (19.3382 + 0.467702 * \ln(h))^2$
Square-Y Square Root-X	0.8303	68.94%	$T_{max} = \sqrt{149650 + 7363.75 * \sqrt{h}}$
Multiplicative	0.8292	68.76%	$T_{max} = \exp(5.92779 + 0.453272 * \ln(h))$
Square Root-X	0.8239	67.88%	$T_{max} = 388.439 + 8.58961 * \sqrt{h}$
Double Square Root	0.8205	67.33%	$T_{max} = (19.7268 + 0.20756 * \sqrt{h})^2$
Logarithmic-Y Square Root-X	0.8171	66.76%	$T_{max} = \exp(5.96564 + 0.0200695 * \sqrt{h})$
Square-Y	0.8059	64.95%	$T_{max} = \sqrt{165929 + 696.189 * h}$
Linear	0.7962	63.40%	$T_{max} = 407.501 + 0.808584 * h$

h: heating rate °C min^{-1}.

Figure 2 visualizes the fit of all the linear models studied with the data collected. Additionally, a lack of fit test was performed to determine if the selected model adequately describes the observed data or if a more complicated model is needed. The results showed a minimum lack of fit of 0.06 corresponding to the linear model and a maximum of 0.35 for the multiplicative model; a p-value=0 was obtained for all models being less than 0.05. Therefore, the models were adequate for the observed data with a confidence level of 95 %.

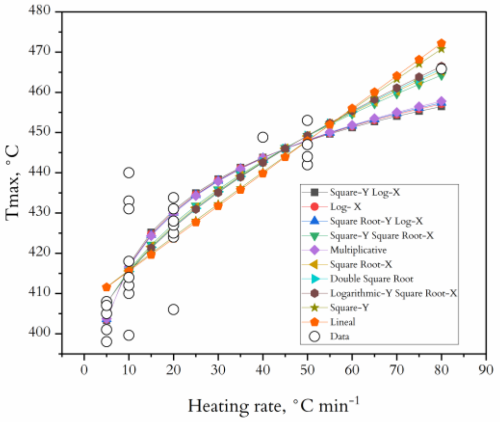

Figure 2: Linear fitting to estimate T_{max} degradation on PS TGA. Data's risk of bias ±2%

On the other hand, a study was carried out using normality tests to determine whether the residuals resulting from the linear model with the best fit (Square-Y Log-X) can be adequately modeled with a normal distribution. The tests performed were chi-square, Shapiro-Wilk W statistic, z-value for skewness, and z-value for kurtosis. The chi-square test divides the range of residuals into 15 equally probable classes and compares the number of observations in each class with the expected number of observations; the Shapiro-Wilk test is based on the comparison of the quartiles of the normal distribution fitted to the data. On the other hand, the standardized skewness test looks for a lack of symmetry in the data. Finally, the standardized kurtosis test looks for whether the shape of the distribution is flatter or sharper than the normal distribution (Statgraphics, 2007).

Figure 3 shows the histogram of the residuals resulting from the Square-Y Log-X model. The normality tests showed that the smallest p-value was 0.249, corresponding to the chi-square test being major than 0.05; therefore, the residuals come from a normal distribution with 95 % confidence.

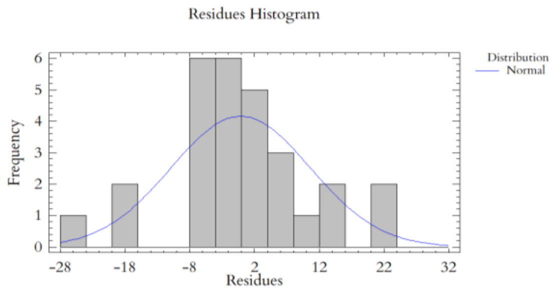

Figure 3: Residues histogram from the best-fitting linear model.

Table 3 shows the results of the polynomial models estimating the maximum degradation temperature of PS using TGA data. The best fit was obtained with the fourth-order model with an r^2=70.46. On the other hand, to determine if the polynomial order is appropriate, the p-value is shown for all cases; it is observed that all are greater than 0.05. Therefore, the models are not statistically significant with a confidence level of 95 %; thus, it is considered to reduce the order resulting in linear models.

Table 3. Polynomial models to estimate maximum degradation temperature (T_{max}) on PS TGA.

Model	Formula	r^2	p-value
2nd Order	$T_{max} = 394.337 + 2.5699 * h - 0.0468546 * h^2 + 0.000324754 * h^3$	65.85	0.1322
3rd Order	$T_{max} = 394.337 + 2.5699 * h - 0.0468546 * h^2 + 0.000324754 * h^3$	68.13	0.1691
4th Order	$T_{max} = 376.466 + 6.8262 * h - 0.31882 * h^2 + 0.00610133 * h^3 - 0.0000376172 * h^4$	70.46	0.1913

h: heating rate °C min^{-1}.

Figure 4 plots the polynomial models on the collected data. The calculated maximum degradation temperatures showed outlier residuals for the polynomial models. For all models, there was a difference of 24.2 °C for a heating rate of 10 °C min^{-1} between the predicted and experimental. Additionally, for the third order model, there was an outlier residual of 23.59 °C for 20 °C min^{-1}, while for the second order, there was an additional outlier residual of 21.94 °C for a heating rate of 5 °C min^{-1}.

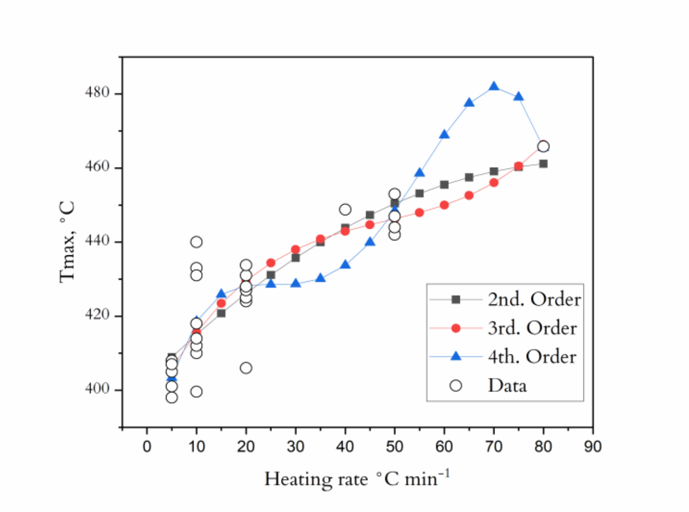

Figure 4: Polynomial fitting to estimate T_{max} degradation on PS TGA. Data's risk of bias ±2%

Finally, to evaluate the developed models, the maximum degradation temperature was calculated for 15 and 60 °C min^{-1} and compared with experimental values found in the literature; the results are shown in Table 4.

Table 4. Maximum degradation temperature predicted vs. experimental.

Reference	(Nisar et al., 2019)	(Li et al., 2020)
Heating rate, °C min^{-1}	15	60
Experimental value, °C	392.20	457.80
Model	Relative error, %	
Linear fitting		
Square-Y log-X	8.47	1.43
Log-X	8.36	1.37
Square Root-Y Log-X	8.31	1.33
Square-Y Square Root-X	7.68	0.69
Multiplicative	8.25	1.30
Square Root-X	7.58	0.62
Double Square Root	7.53	0.58
Logarithmic-Y Square Root-X	7.48	0.53
Square-Y	7.13	0.45
Linear	7.05	0.39
Polynomial fitting		
2nd Order	7.35	0.50
3rd Order	8.02	1.70
4th Order	8.64	2.42

The results showed that for both heating rates, the linear model was the one that predicted closer values, resulting in a relative error of 7.05 and 0.39 % for 15 and 60 °C min^{-1}, respectively. It is observed that although the polynomial model of order four was found to have a better overall fit, in this case, it resulted in higher relative errors than those predicted by the linear model.

Finally, if Square-Y Log-X and Linear models are considered to calculate the maximum degradation temperature, the results will indicate that the higher the heating rate, the degradation temperature will increase. However, it is essential to consider other factors that may influence the pyrolysis process, such as reactor type or residence time. The results of the present investigation serve as a preliminary consideration to address the pyrolysis process of polystyrene.

4. Conclusions

The poor disposal of plastic waste and the lack of recycling result in a large amount of waste affecting the environment. The pyrolysis process has proven to be an effective method that reduces plastic waste and converts it into high-value products in the chemical industry. This process is based on the thermal degradation of plastics under an inert atmosphere. Thermogravimetric analyses help estimate the maximum degradation temperature, initial and final temperatures and, thus, obtain ideal operating ranges to be applied in the pyrolysis process.

In the present study, a statistical analysis was developed to determine by regression, linear and polynomial models describing the behavior of the maximum degradation temperature of polystyrene at different heating rates; the models were developed based on experimental data obtained from the literature. Low fittings were obtained, which can be attributed to different factors such as the preparation method of the polymer, particle size, polymer molecular weight, operation conditions of the TGA apparatus, and the mathematical treatment of thermogravimetric data. However, the results showed that a linear model is the best fit, obtaining a fit of r^2=69.71 % with a Square-Y Log-X model. Although the fourth-order polynomial model shows a slightly better fit of r^2= 70.46%, this model yielded higher relative errors when compared to experimental data excluded from the development of the models. In addition, the Linear model showed relative errors lower than those predicted by the polynomial models, obtaining an error of 7.05% and 0.39% when a heating rate of 15 and 60 °C min^{-1} were evaluated, respectively. For both types of models, the lack of tests showed that the models are adequate for the observed data, and the residuals of the best linear fit present a normal distribution for a confidence interval of 95 %.

References

Ding L., Zhao J., Pan Y., Guan J., Jiang J., Wang Q., 2019, Insights into Pyrolysis of Nano-Polystyrene Particles: Thermochemical Behaviors and Kinetics Analysis, Journal of Thermal Science, 28, 763-771.

Gonzalez-Aguilar A. M., Cabrera-Madera V. P., Vera-Rozo J. R., Riesco-Ávila J. M., 2022, Effects of Heating Rate and Temperature on the Thermal Pyrolysis of Expanded Polystyrene Post-Industrial Waste, Polymers, 14, 4957.

Inayat A., Klemencova K., Grycová B., Sokolava B., Lestinský P., 2021, Thermo-catalytic pyrolysis of polystyrene in batch and semi-batch reactors: A comparative study, Waste Management & Research, 39, 260–269.

Jeswani H., Krüger C., Russ M., Horlacher M., Antony F., Hann S., Azapagic A., 2021, Life cycle environmental impacts of chemical recycling via pyrolysis of mixed plastic waste in comparison with mechanical recycling and energy recovery, Science of the Total Environment, 769, 144483.

Klaimy S., Lamonier J.-F., Casseta M., Heymans S., Duquesne S., 2021, Recycling of plastic waste using flash pyrolysis – Effect of mixture composition, Polymer Degradation & Stability, 187, 109540.

Li A., Zhang W., Zhang J., Ding Y., Zhou R., 2020, Pyrolysis Kinetic Properties of Thermal Insulation Waste Extruded Polystyrene by Multiple Thermal Analysis Methods, Materials, 13, 5595.

López A., De Marco I., Caballero B. M., Laresgoiti M. F., Adrados A., 2011, Influence of time and temperature on pyrolysis of plastic wastes in a semi-batch reactor, Chemical Engineering Journal, 173, 62–71.

Maafa I. M., 2021, Pyrolysis of Polystyrene Waste: A Review, Polymers, 13(225).

Nisar J., Ali G., Shah A., Iqbal M., Ali Khan R., Sirajuddin Anwar F., Ullah R., Akhter M. S., 2019, Fuel production from waste polystyrene via pyrolysis: Kinetics and products distribution, Waste Management, 88, 236–247.

Park K.-B., Jeong Y.-S., Guzelciftci B., Kim J.-S., 2020, Two-stage pyrolysis of polystyrene: Pyrolysis oil as a source of fuels or benzene, toluene, ethylbenzene, and xylenes, Applied Energy, 259, 114240.

Statgraphics, 2007, Probability Distributions, StatPoint, Inc.

Van der Westhuizen S., Collard F.-X., Görgens J., 2022, Pyrolysis of waste polystyrene into transportation fuel: Effect of contamination on oil yield and production at pilot scale, Journal of Analytical and Applied Pyrolysis, 161.

Verma A., Sharma S., Pramanik H., 2021, Pyrolysis of waste expanded polystyrene and reduction of styrene via in-situ multiphase pyrolysis of product oil for the production of fuel range hydrocarbons, Waste Management, 120, 330–339.