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Analysis of reaction kinetics of carton packaging pyrolysis

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Abstract

The post-consumption carton packaging has been recycled using different process. Pyrolysis can be a promising technology to be used for recovering the aluminum from polyethylene and generating products with high heating value. In this research paper, a kinetic study on pyrolysis reactions was performed in order to estimate the global activation energy using methods of Starink, Kissinger and Kissinger-Akahira-Sunose. Therefore, for both samples of carton packaging and its pure components, dynamic thermogravimetric analyses (TGA) were carried out. The results show that Starink, Kissinger and Kissinger-Akahira-Sunose methods applied to carton packaging, cardboard and polyethylene can be satisfactorily used for estimating the global activation energy and showed similar results between each other.

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Keywords: Pyrolysis; carton packaging; thermogravimetric analysis

1. Introduction

A modern solid waste commonly found in urban areas is the post-consumption carton packaging, composed of 75% paper, 20% polyethylene and 5% aluminum. Recycling is one of the alternatives for recovering the long-life packaging. The recycling starts in the paper industry where recycling fibers can

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be recovered by repulping process. The polyethylene and aluminum separated in a hydropulper can be recovered in three different ways: energy generation from paraffinic oil, recovery of aluminum in pyrolysis ovens, recovery of polyethylene and aluminum by plasma technology, and the processing of the mixtures of polyethylene and metal to obtain high-end plastic lumber products [1]. Among these technologies, pyrolysis is considered to be a good alternative either to separate aluminum from polyethylene or to generate products with high heating value. Most of the current interest associated with pyrolysis is focused on the environmental issue, since these processes represent attractive ways of utilizing agricultural and forestry residues, as well as a major part of the components in municipal solid wastes.

Many studies have been concentrated on pyrolysis reaction, for example: biodegradable products [2], urban waste [3] and residues from agriculture [4,5,6], but only few have done on carton packaging pyrolysis and extend their research to estimate reaction activation energy using kinetic models reported by Literature [7]. Korkmaz et al. [8] studied the pyrolysis reaction of carton packaging in a fixed bed reactor, quantifying the yield of pyrolysis products (coal, liquid and gas). Wu and Chang [7] used data obtained by thermogravimetric analysis (TGA) and Friedman kinetic model to estimate the activation energy of carton packaging pyrolysis reaction and its pure components.

Thus, this research aims to use the kinetic models proposed by Kissinger [9], Starink [10] and Kissinger-Akahira-Sunose [11] to calculate the global activation energy of pyrolysis reaction of carton packaging and its pure components, using data obtained from TGA.

Nomenclature

E_a	activation energy ($\text{kJ}\cdot\text{mol}^{-1}$)
k	rate constant (s^{-1})
k_0	pre-exponential factor (s^{-1})
m	mass of solid at a given instant of time (mg)
m_0	initial mass of solid (mg)
m_∞	residual mass of solid (mg)
R	universal gas constant ($\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
r^2	correlation coefficient
T	temperature (K)
T_0	initial temperature (K)
T_{max}	higher peak temperature on DTG curve (K)
t	time (s)
X	conversion
β	heating rate ($^{\circ}\text{C}\cdot\text{min}^{-1}$)

2. Methodology

2.1. Thermogravimetric analysis

The data were obtained using a thermogravimetric analyzer, TGA-60 (Shimadzu). Table 1 presents operating conditions and sample characteristics used in this research and those reported in the literature.

Table 1. Operating conditions, physical properties and kinetic models used.

References	Operating conditions, physical properties and models
Present research	<ul style="list-style-type: none"> - N₂: 50 mL min⁻¹ - Particle diameter: < 1 mm - Density: carton packaging (1.3234g.cm⁻³), cardboard (1.4893g.cm⁻³) and polyethylene (0.9414g.cm⁻³) - Heating rates: 5, 10, 20 and 50 °C min⁻¹ - Kinetic model: Kissinger [9], Starink [10] and Kissinger-Akahira-Sunose [11]
Wu and Chang [7]	<ul style="list-style-type: none"> - N₂: 50 mL min⁻¹ - Particle diameter: < 1 mm - The same properties of this present research - Heating rates: 5.2, 12.8 and 21.8 K min⁻¹ - Kinetic model: Friedman [12]
Paik and Kar [13]	<ul style="list-style-type: none"> - N₂: 200mL min⁻¹ - Particle diameter: ~20, ~10, ~1µm and < 500 nm - Heating rates: 5, 10 and 15 °C/min⁻¹ - Kinetic models: Friedman [12], Freeman–Carroll [14], Kissinger [15], Kim–Park [16] and Flynn–Wall [15]
Volker and Rieckman [17]	<ul style="list-style-type: none"> - He: 1.7 L h⁻¹ - Density: 400 and 550 kg m⁻³ - Heating rates: 0.14, 3, 41 and 105 K min⁻¹ - Kinetic model: not isoconversional

2.2. Kinetic model

The conversion of solids (X) to gases and volatiles, that is, so-called devolatilization, can be expressed as:

$$X = \frac{m_0 - m}{m_0 - m_\infty} \quad (1)$$

where m is the solid mass for a given time, m_∞ is the residual mass of solid and m_0 is the initial mass of solid.

Considering that the thermal degradation of solid material is carried out by thermogravimetry with a linear increase in the temperature ($T = T_0 + \beta t$), the rate of conversion can be defined as:

$$\frac{dX}{dt} = f(X) \times K(T) \quad (2)$$

where f is the conversion function, K is a reaction rate constant, β (dT/dt) is the heating rate and T_0 is the initial temperature.

The dependence of reaction rate constant with temperature can be described by the Arrhenius equation:

$$K(T) = k_0 e^{\frac{-E_a}{RT}} \quad (3)$$

where E_a is the activation energy, R is the ideal gas constant, k_0 is the pre-exponential factor and T is the temperature of the sample.

Based on equations (1), (2) and (3), the expression for degree of solid transformation as function of temperature can be calculated:

$$\frac{dX}{f(X)} = \frac{k_0}{\beta} e^{\frac{-E_a}{RT}} dT \quad (4)$$

By integrating the equation (4) from T_0 (corresponding to X_0) to temperature inflection (T) (corresponding to X), the following equation is obtained:

$$g(X) = \int_{X_0}^X \frac{dX}{f(X)} = \frac{k_0}{\beta} \int_{T_0}^T e^{\frac{-E_a}{RT}} dT \quad (5)$$

Because of the complexity of the pyrolysis reaction, the form of the function $f(X)$ can be simplified assuming that the reaction follows a first order kinetics:

$$f(X) = (1 - X) \quad (6)$$

The isoconversional kinetic methods proposed by Starink [10] and Kissinger-Akahira-Sunose (K-A-S) [11] follow the same considerations physicochemical and mathematical and differ in the approximation method integration of equation (5). The method proposed by Kissinger [9] uses the technique of integration by parts. This method is based on the displacement of the higher temperature peak with an increase in the rate of heating. Thus, the value of the activation energy is obtained by simple linear regression, where $\ln(\beta/T_{max}^2)$ is plotted against $1/T_{max}$ for a series of experiments at different heating rates. T_{max} is the higher peak temperature on DTG curve.

Table 2 shows the equations resulting from integration of equation (5) according with each method used to determine the activation energy.

Table 2. Equations of the isoconversional methods

Method	Equation
Kissinger	$\ln\left[\beta/T_{max}^2\right] = \left[\ln\left[k_0 R/T\right] - \ln g(X)\right] - [E_a/R][1/T_{max}]$ (7)
K-A-S	$\ln\left[\beta/T_x^2\right] = \ln\left[\left[k_0 R\right]/\left[E_a \times g(X)\right]\right] - [E_a/R][1/T_x]$ (8)
Starink	$\ln\left[\beta/T_x^{1.8}\right] = -A[E_a/RT_x] + C_2$; with $A = 1.007 - 1.2 \times 10^{-5} E_a$ (9)

Calculation of activation energy for each method shown in Table 2 is based on the linear regression model, where the slope of the straight obtained allows us to estimate the activation energy. The data are plotted in Figures 2, 3 and 4 according to the information contained in the equations (7), (8) and (9).

3. Results and discussions

3.1. Thermogravimetric tests

Fig.1 shows the curves of the rate of mass loss (DTG) in dynamic tests, as a function of temperature and heating rate, for carton packaging (a), cardboard (b) and polyethylene (c). The DTG curves show that, in general, there are three separate steps of carton packaging devolatilization. At low temperatures (up to 100°C), the first step is characterized by the significant moisture loss. The second step can be perfectly correlated with the cardboard devolatilization, which occurs at temperatures ranging from 300 to 420°C. Then, it can be associated the third step with the polyethylene devolatilization, occurring in the range of 400 to 550°C.

In addition, a devolatilization step is also observed in Fig.1 (a) and (b), at temperature range of 500 to 600°C. This may be probably indexed to either the dye used in manufacturing of both the carton packaging and cardboard. Moreover, it can be noted in Fig.1 that there is a displacement of the main peaks of mass loss to the higher temperatures as heating rate is increased. These probably are due to a change in the decomposition mechanism.

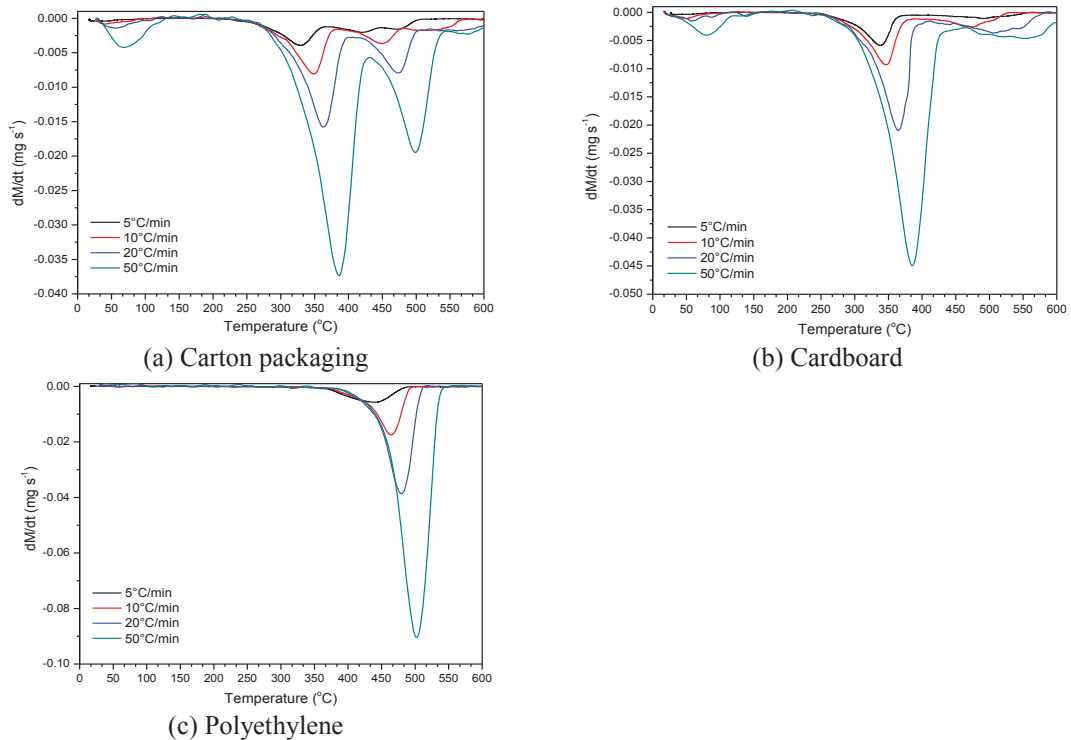


Fig. 1. Rate of mass loss (DTG) as function of reaction temperature and heating rate.

3.2. Activation energy using isoconversional kinetic models

In a conversion range from 10 to 70%, Fig. 2, 3 and 4 show the linear regression of Kissinger-Akahira-Sunose (K-A-S) and Starink methods for pyrolysis reaction of carton packaging, cardboard and polyethylene, respectively.

In Fig. 2 and 3, it is possible to observe that the lines from linear fit are approximately parallel in the range 20-50% conversion for pyrolysis reaction of carton packaging and cardboard. The parallelism of these lines denotes a similar kinetic behavior, indicating that probably the same reaction mechanism is achieved. However, at 10% conversion, the non-parallelism of the line can be associated with moisture loss, which characterizes a process with different mechanism as compared with those attained at 20-50% conversion. In addition, the non-parallelism of the lines at 60 and 70% conversion indicates that there are changes in reaction mechanisms at higher temperatures [18]. Distinct reaction mechanisms show different values for activation energy.

For polyethylene, Fig4 shows that the lines are not approximately parallel, suggesting that there are distinct mechanisms for each conversion process. Consequently, this leads to different values of activation energies for each conversion analyzed.

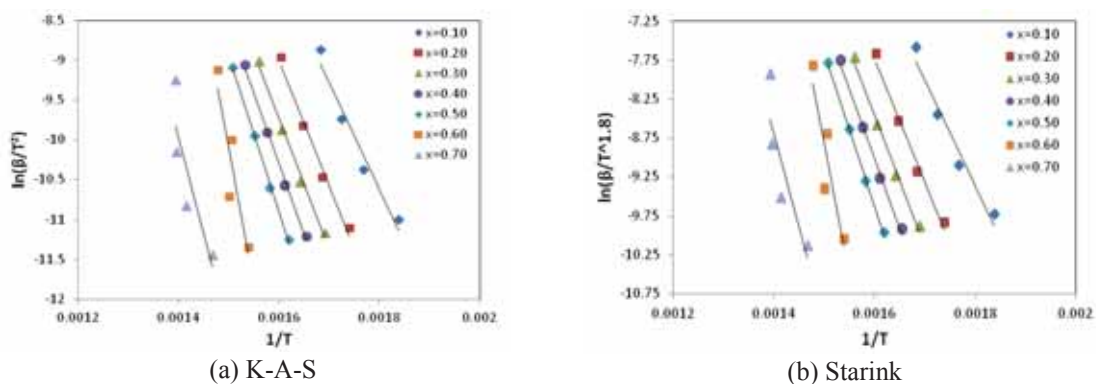


Fig. 2. Linear regression of K-A-S (a) and Starink (b) methods for pyrolysis reaction of carton packaging.

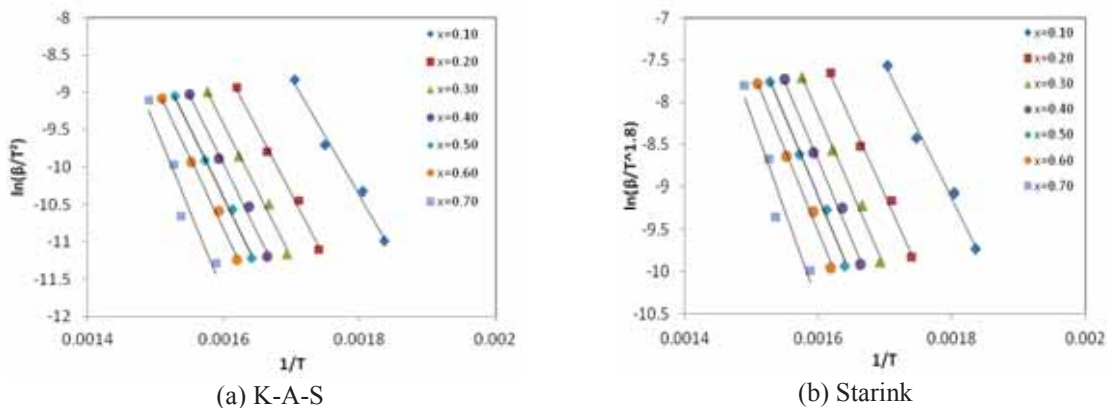


Fig. 3. Linear regression of K-A-S (a) and Starink (b) methods for pyrolysis reaction of cardboard.

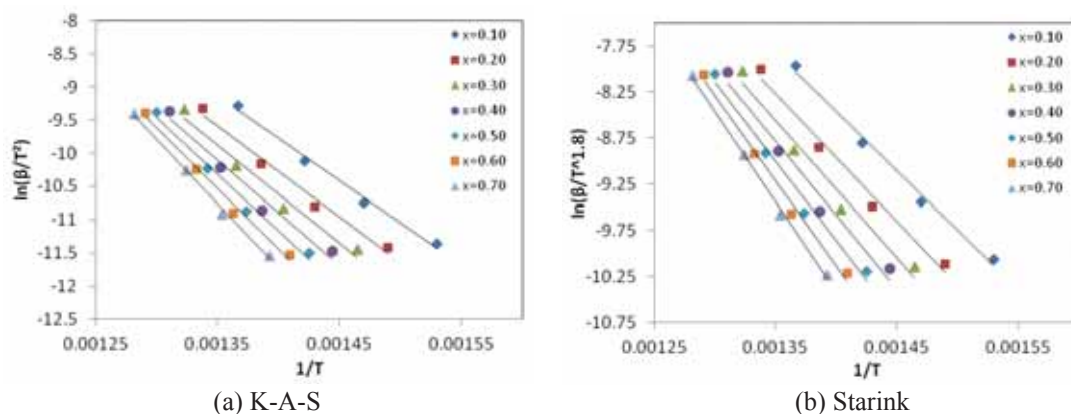


Fig. 4. Linear regression of K-A-S (a) and Starink (b) methods for pyrolysis reaction of polyethylene.

Table 3 shows the activation energy for each conversion value, calculated by K-A-S and Starink methods for pyrolysis of carton packaging, cardboard and polyethylene. The values of correlation coefficients (r^2) and root-mean-square error (RMSE) of linear fits showed in Table 3 are reasonably satisfactory for the estimates of activation energy ($0.75 \leq r^2 \leq 1.00$ and $0.03 \leq \text{RMSE} \leq 0.41$).

The Kissinger method also shows a good fit with the experimental data ($r^2 = 0.99$ for carton packaging, $r^2 = 0.99$ for cardboard and $r^2 = 0.98$ for polyethylene). The values for the activation energy calculated by this model were $121.42 \text{ kJ}\cdot\text{mol}^{-1}$, $144.89 \text{ kJ}\cdot\text{mol}^{-1}$ and $155.15 \text{ kJ}\cdot\text{mol}^{-1}$, respectively, for pyrolysis of carton packaging, cardboard and polyethylene. By comparing the methods used, it can be stated that methods of K-A-S and Starink present similar results; however, Kissinger method shows slightly different values. Such a difference can be attributed to the changes of integration method of equation 5 used by authors.

Table 4 shows the results of global activation energies obtained by Literature. Comparing the results obtained in this study to those of Paik and Kar [13], Volker and Rieckmann [17] and Wu and Chang [7] it is observed that activation energies are in the same order of magnitude, even considering either different methods, operating conditions or material physical properties used (see Table 1).

Table 3. Activation energies for pyrolysis reaction of carton packaging, cardboard and polyethylene, calculated by K-A-S and Starink methods.

CARTON PACKAGING						
X	K-A-S			Starink		
	Ea (kJ.mol ⁻¹)	r ²	RMSE	Ea (kJ.mol ⁻¹)	r ²	RMSE
0.1	112.04	0.96	0.16	112.34	0.96	0.16
0.2	129.91	0.98	0.10	130.19	0.98	0.10
0.3	137.24	0.99	0.07	137.52	0.99	0.07
0.4	146.31	0.99	0.06	146.58	1.00	0.06
0.5	162.38	1.00	0.03	162.62	1.00	0.03
0.6	280.00	0.81	0.36	280.07	0.81	0.36
0.7	197.93	0.75	0.41	198.16	0.75	0.41
Mean	166.54			166.78		
CI (95%)	113.88-219.21			114.19-219.38		
SD	56.94			56.87		
CARDBOARD						
X	K-A-S			Starink		
	Ea (kJ.mol ⁻¹)	r ²	RMSE	Ea (kJ.mol ⁻¹)	r ²	RMSE
0.1	130.18	0.99	0.09	130.40	0.99	0.09
0.2	143.32	0.99	0.07	143.54	0.99	0.07
0.3	149.19	0.99	0.07	149.42	0.99	0.07
0.4	153.45	0.99	0.07	153.69	0.99	0.07
0.5	156.52	1.00	0.05	156.76	1.00	0.05
0.6	159.00	0.99	0.06	159.24	0.99	0.06
0.7	182.59	0.93	0.21	182.79	0.93	0.21
Mean	153.46			153.69		
CI (95%)	138.59-168.34			138.82-168.56		
SD	16.08			16.08		
POLYETHYLENE						
X	K-A-S			Starink		
	Ea (kJ.mol ⁻¹)	r ²	RMSE	Ea (kJ.mol ⁻¹)	r ²	RMSE
0.1	105.55	0.99	0.07	106.08	0.99	0.07
0.2	114.05	0.98	0.10	114.59	0.98	0.10
0.3	122.12	0.97	0.13	122.64	0.97	0.13
0.4	131.45	0.97	0.13	131.95	0.97	0.13
0.5	141.32	0.98	0.11	141.79	0.98	0.11
0.6	151.50	0.99	0.08	151.94	0.99	0.08
0.7	161.42	1.00	0.05	161.85	1.00	0.05
Mean	132.49			132.98		
CI (95%)	113.80-151.18			114.33-151.63		
SD	20.21			20.17		

Table 4. Activation energy from data obtained by Literature.

References	Wu and Chang [7], for carton packaging	Paik and Kar [13], for polyethylene	Volker and Rieckmann [17], for cardboard
Ea (kJ.mol ⁻¹)	150.0	232.5	244.0

4. Conclusion

Based on analysis established in this research the following conclusions can be drawn:

- The carton packaging pyrolysis follows three steps characterized by moisture loss, cardboard and polyethylene devolatilization, respectively.
- The comparison between the methods of K-A-S and Starink applied to carton packaging, cardboard and polyethylene shows similar results for global activation energy. The Kissinger method applied to carton packaging and cardboard presents the lowest Ea values; whereas for polyethylene shows the highest Ea value.
- Based on the results of an overall statistical analysis of t-test distribution, a low RMSE value and a highly significant correlation coefficient comparing the models to the experimental data, it can be stated that all models analyzed can be used satisfactorily for estimating the activation energy of pyrolysis reactions of carton packaging, cardboard and polyethylene.

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