# A Fast Estimation of Activation Energy of Low Density Polyethylene (LDPE)

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## Abstract

A dynamic experimental study of thermal decomposition of low density polyethylene has been carried out with two different heating rates .As usual , we can determine the activation energy of any polymer using( 3 - 6 ) TGA experiment as minimum , but in this work , we estimate the activation energy of LDPE using two of TGA experiments only.

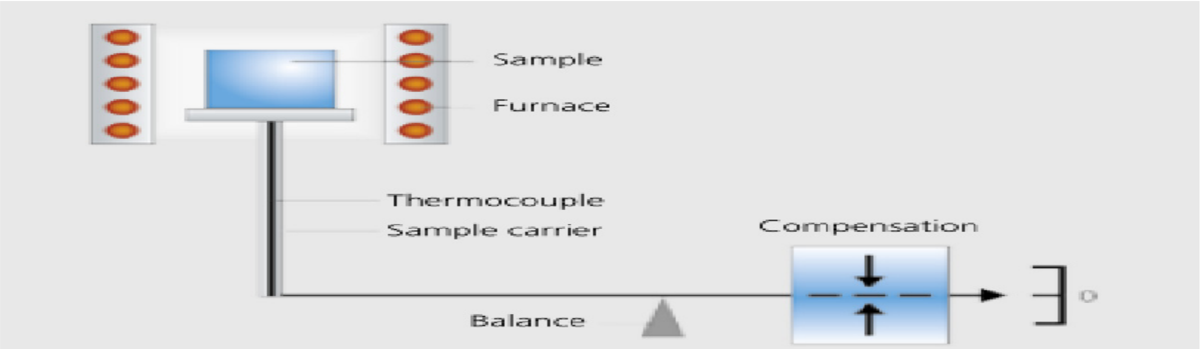
**Key words** : Low density polyethylene (LDPE), activation energy ,thermal decomposition and thermogravimetric analysis .

# Introduction

The determination of activation energy of a polymer is very useful since its used to predict
the kind of a polymer using the thermo gravimetric analysis (TGA) which is the one of the members of the family of thermal analysis techniques used to characterize a wide variety of materials.
There have recently appeared several publications which describe some methods of estimation activation energy for the thermal decomposition of polymers using two methods : Flynn -Wal l-Ozawa (FWO) and Kissinger - Akahira – Sunose (KAS) [1-6] .
These methods are time - consuming and involve curve fitting , a prior knowledge of reaction order and type of kinetic process in addition to using between (3-6) curves of thermo-gram of polymer degradation with different heating rates [7,8].
In present work , we can overcome some of these objections and estimate the activation energy of low density polyethylene using only a two curves of thermogravimetry with two different heating rates ,so we can get a rapid estimation of activation energy for any polymer.

# Experimental

We cut two samples of the same water pipe which is made of low density polyethylene and characterize them by thermogravimetric teqnique, where this polymer is heated from temp. (approx. 23 $^{o}$C) to 600 $^{o}$C, the weight of samples is loss with time /temperature .
These samples with weight (30 - 35 mg) are heated with heating rate (5 $^{o}$C/min ) for the first sample and (9 $^{o}$C / min ) for the second. In (TGA) a thermo balance is used to measure the mass change of a sample as a function of temperature or time .



The thermal decomposition of polymer is generally assumed to be as in eq.(1)
A( solid ) → B( volatiles ) + C( solid ) ----------------(1 ) [ 4 ]
The rate of polymer degradation is generally assumed to be proportional to the concentration of reactants which is defined as
$r = - d\alpha/ dt$ -----------------------------( 2 ) [9 ]
Where : $d\alpha /dt$ is the rate of mass loss
$\alpha$ is the fraction of material reacted
We may write

$$- \int_{\alpha_o}^{\alpha} d\alpha / \alpha^{n} \approx \int_{0}^{T} \frac{A}{\beta} e^{-E/RT} \, dT \quad \text{----------------(3) [4,10]}$$

So we can write

$$-\int_{\alpha_o}^{\alpha} d\alpha/\alpha^n \approx \frac{A}{\beta}\left(\frac{RT^2}{E}\right)e^{-E/RT} \text{ ------------------ } (4)$$

Where : A is the exponential factor ( $sec^{-1}$ )
$\beta$ is the heating rate
R is the universal gas constant ( 8.314 J/mole .$^{o}$K)
T is the absolute temperature ($^{o}$K )

Utilizing two thermo grams for the same material possessing different heating rates ( $\beta$ ) we can write

$$A/\beta_1(RT_1^2/E)e^{-E/RT_1} = A/\beta_2(RT_2^2/E)e^{-E/RT_2} \text{ ----------------}(5)$$

Or $$\ln[\frac{\beta_2}{\beta_1}(\frac{T_1}{T_2})^2] = \frac{E}{R}(\frac{1}{T_1}-\frac{1}{T_2}) \text{ ---------------------}(6)$$

So $$E = \frac{2.303R\log[\frac{\beta_2}{\beta_1}(\frac{T_1}{T_2})^2]}{(\frac{1}{T_1}-\frac{1}{T_2})} \text{ ----------------------(7}$$

Where E is the activation energy of a polymer.

## Results and Discussion

Displayed in figures 1 and 2 are the TGA results generated on the LDPE at an applied heating rate $\beta_1$ ( 5 $^{o}$C/min ) and $\beta_2$ (9 $^{o}$C/min ) respectively , these plots show the mass loss as a function of temperature . To get the conversion levels in weight , we must take the percent of mass loss as a function of temperature as in figures 3 and 4 , where the conversion level 20% is at 80 of weight% and the decomposition temperatures $T_1$ is 435 $^{o}$C for the first sample at heating rate 5 $^{o}$C/min as in (figure 3) and $T_2$ is 448 $^{o}$C/min for the second sample at heating rate 9 $^{o}$C/min as in (figure 4) then all the decomposition temperatures ($T_1$ and $T_2$ ) are fixed at any conversion levels as in table 1 , where the decomposition temperatures are pushed to higher with the increase of the heating rate and the conversion rate ,which agreed with [5].

From TGA results and using equation 7 , the activation energy of LDPE can be established as in table 2 , where the activation energy is changed with temperature . In figure (5) , we can see that the activation energy began to be constant at conversion rate 30% so this conversion level is very suitable to get the value of activation energy in our work .

The activation energy of LDPE is (215 – 221 KJ/ mol) using the friedman , Kissinger - Akahira –Sunose and Flynn - Wall- Ozawa [2,11] but in our study the activation energy of LDPE is a bout 227 KJ / mole , because the activation energy is influenced by estimation method and the operating condition [12].

## Conclusion

1- The value of activation energy depends on conversion levels.
2-The decomposition temperatures increase with the increase of the heating rate.
3- The advantage of this method is to consume relatively little time.
4- The conversion level 30% is suitable to estimate the activation energy .
5- We can estimate the activation energy of any polymer using two curves of TGA only.

6- As future work , we can use this method to predict the kind or the grade of a polymer in some applications that we do not know the kind of polymers that are made.

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**Table No.(1): The decomposition temperatures at different conversion levels at two heating rates for (LDPE)**

| Conversion levels % | Rate 5 ( $^{o}$C.min$^{-1}$) | | Rate 9 ( $^{o}$C.min$^{-1}$ ) | |
|---|---|---|---|---|
| | $T_1$ ($^{o}$C ) | $T_1$ ($^{o}$ K ) | $T_2$ ( $^{o}$C ) | $T_2$ ($^{o}$K ) |
| 20 | 435 | 708 | 448 | 721 |
| 30 | 453 | 726 | 462 | 735 |
| 40 | 459 | 732 | 470 | 743 |
| 50 | 462 | 735 | 475 | 748 |
| 60 | 470 | 743 | 486 | 759 |

**Table No.(2): The values of activation energies at different conversions levels of (LDPE )**

| Conversion levels % | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|
| Activation energy (KJ. mol$^{-1}$) | 179.81 | 227.10 | 228.56 | 193.9 | 160.19 |

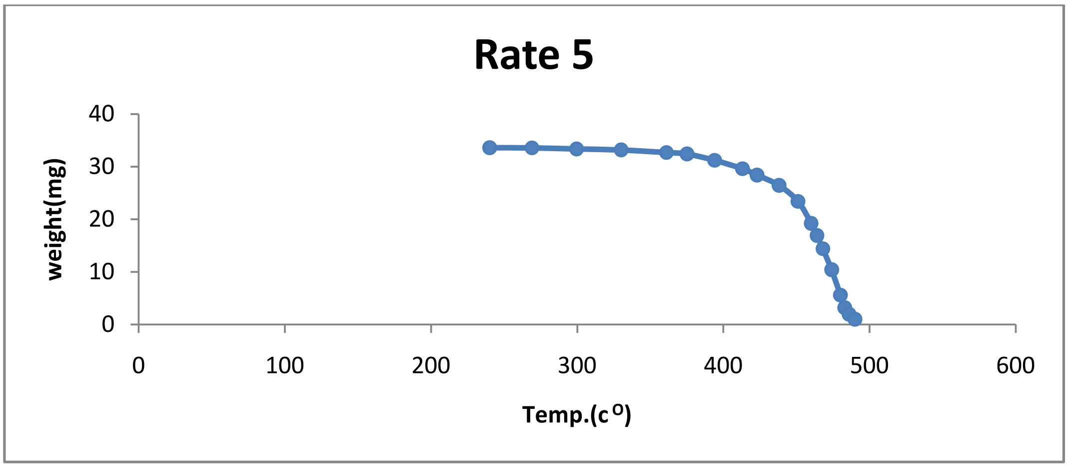

Figure1.Low density polyethylene decomposition with heating rate 5c$^{0}$/min .

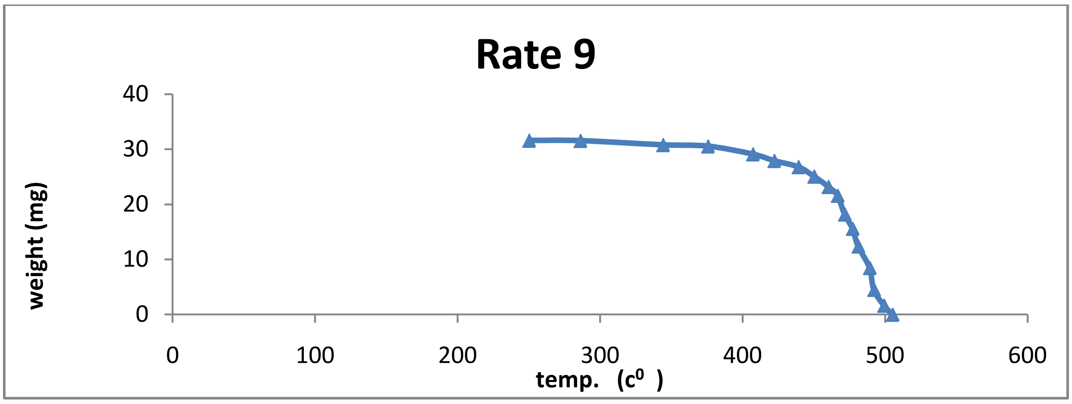

Figure 2.Low density polyethylene decomposition with heating rate 9 c$^{o}$/min .

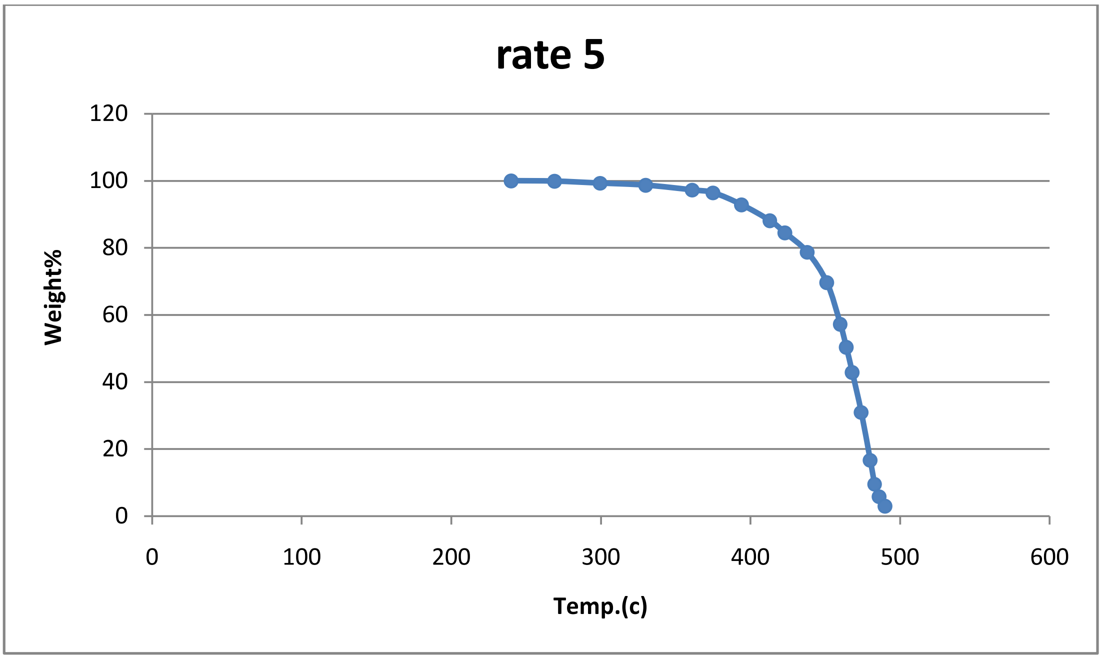

Figure 3.the percentage decomposition with different conversion levels at heating rate 5 c$^{0}$/min .

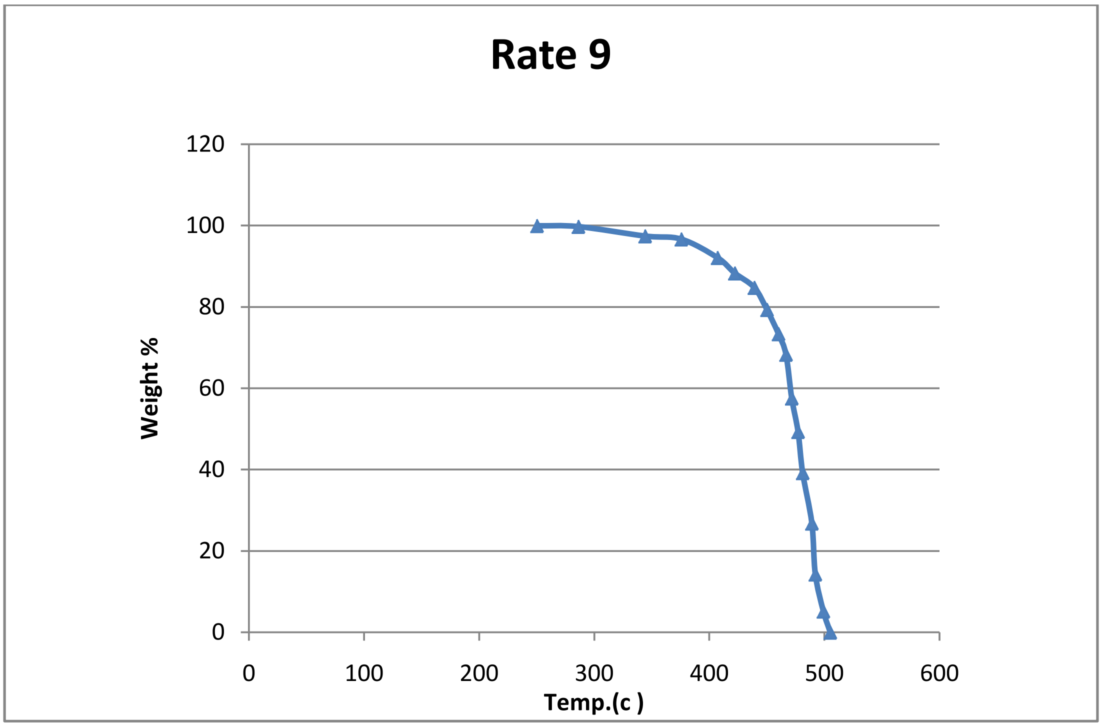

Figure 4. the percentage decomposition with different conversion levels at heating rate 9c°/min .

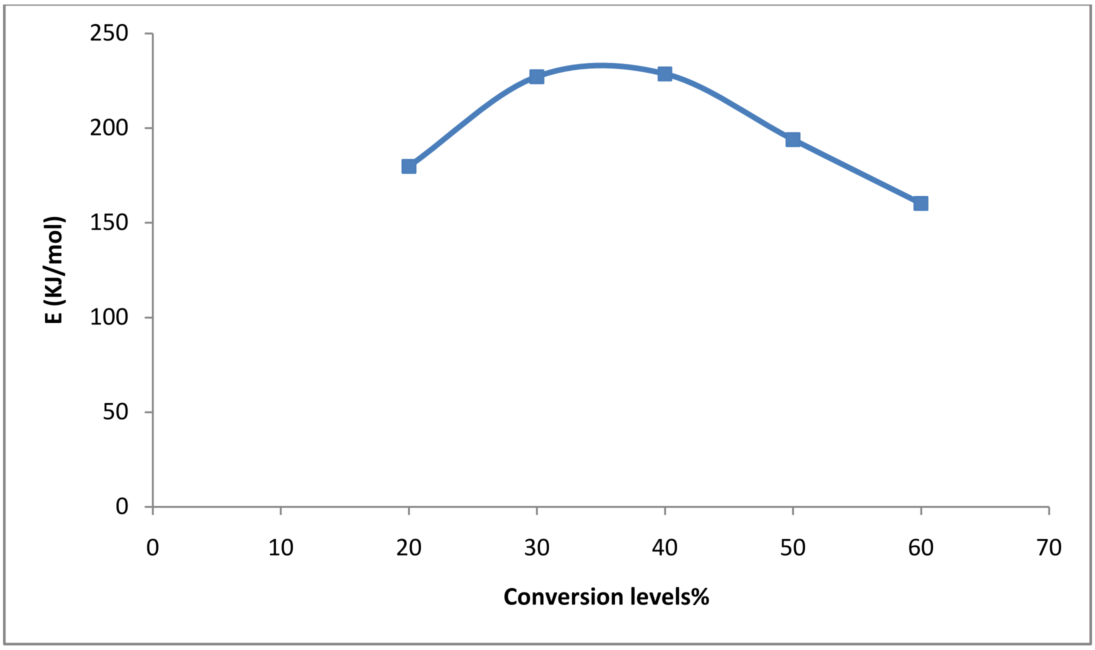

Figure 5.the relation of activation energy with different conversion levels .

# الحساب السريع لطاقة التنشيط للبولي أثيلين واطئ الكثافة(LDPE)

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## الخلاصة

درست ديناميكية التحلل الحراري للبولي أثيلين واطئ الكثافة بشكل عملي باستخدام أثنين من معدلات التسخين المختلفة . عادة نستطيع أن نحسب طاقة التنشيط لأي بوليمر باستخدام ما بين ثلاث إلى ست تجارب للتحليل الحراري الوزني (TGA ) حدا أدنى ولكن في هذا البحث تمكنا من حساب طاقة التنشيط للبولي أثيلين واطئ الكثافة باستخدام اثنين من هذه التجارب .

**الكلمات المفتاحية:البولي أثيلين واطئ الكثافة (LDPE) ،طاقة التنشيط ، التحلل الحراري ، التحليل الحراري الوزني.**