

## A Manual Kinetic Study For Pyrolysis of Scrap Tires By Use of TG Technique

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### Abstract

The kinetic study of pyrolysis involved the use of a homemade thermogravimetric analysis (TG) system and showed that the reaction is first order at high temperature range (390- 450) °c.

The reaction rate constant has been increased with temperature (0.15903- 0.9183) min<sup>-1</sup> at the same range of temperature above according to Arrhenius model equation modeled Bovier and Gelus, which can be used to estimate the kinetic parameters .the activation energy of reaction is found to be 1.33 kcal/mol. , whereas the frequency factor is equal to 1x 10<sup>-8</sup> l/mol. sec.

From comparison between theoretical and experimental conversion due to the same model above it could be seen that there is a good agreement between theoretical and experimental results and higher temperatures (390-450) °c but become worse of low temperatures (200-350) °c.

### الموديل الرياضي لدراسة حركية التكسير الحراري للاطارات المستهلكة باستخدام تقنية TG

الخلاصة

دراسة الحركية لعملية التكسير تتضمن استخدام منظومة وزنية - حرارية مصممة يدويا (TG) حيث اثبتت هذه الدراسة بان تفاعل التكسير من الدرجة الاولى عند درجات الحرارة العالية (390 -450) °م. ثابت معدل التفاعل ( K ) يزداد مع درجة الحرارة ( min<sup>-1</sup> ) 0.9183 - 0.15903 ) بتطبيق موديل ارينيوس المدرس من قبل العالمين Bouvier , Gelus من اجل حساب ثوابت التفاعل . حيث وجد ان طاقة التنشيط بهذا التفاعل هي 1.33 kcal / mol فبينما معامل التردد هو 1 x 10<sup>-8</sup> l / mol. Sec. من المقارنة بين نتائج التحول النظرية والعملية للموديل المذكور اعلاه اثبتت تقارب جيد ومقبول بين النتائج النظرية والعملية عند درجات الحرارة العالية لكنه يصبح اسوء عند درجات الحرارة الواطئة (200 - 350) °C.

**Keywords:** pyrolysis scrap tires, model, and TG technique.

### Introduction

Pyrolysis of a solid is a typical irreversible chemical reaction. The Stoichiometric equation for such a reaction is given by. [1, 2]

Where: A, B and C are the original



solid, final solid residue, and volatile matter, and a, b, and c are

the coefficient of stoichiometric equation, receptively. The decomposition rate of solid can be represented by the general rate equation

$$\frac{dx}{dt} = k f(x) \dots\dots\dots(2)$$

Where x = is the fraction of solid decomposed at time (t), f(x) is a function of (x) depending on the reaction

mechanism, and (k) is the rate constant given by Arrhenius equation as:

$$k = A_0 \exp\left(-\frac{E}{RT}\right) \dots\dots\dots(3)$$

Where: A = frequency factor,  
E = activation energy, R = is the universal gas constant (8.314 J/mol\*K), and T = is the absolute temperature. For a linear heating rate, say  $\beta$ .  $k \text{ min}^{-1}$  the following relationship holds

$$\beta = \frac{dT}{dt} \dots\dots\dots(4)$$

Combining equations (2), (3) and (4) and integrating between the initial temperature  $T_0$ , and any final temperature T, and conversion between  $x_0$  and x respectively the results is :

$$\int_{x_0}^x \frac{dx}{f(x)} = \frac{A_0}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \dots (5)$$

The right hand side of equation (5) is not analytically integrable. Use is made of the Coates-Redfern approximation [3] where:

$$\int \exp\left(-\frac{E}{RT}\right) dT \approx \frac{RT^2}{E} \left(1 - \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right) \dots(6)$$

This is used for  $f(x) = (1-x)^n$ , where (n) is the reaction order to obtain initial estimate for the Arrhenius constant.

**1- first-Order Decomposition Model**

This model is simple has a history of successful utilization for condensed phase substance and is useful in engineering calculations. In this model the rate of formation of product (i) in yield (Vi) at rime (t) is given by the expression [4]:

$$\frac{dV_i}{dt} = (V_i^* - V_i) k_{oi} \exp\left(-\frac{E_i}{RT_i}\right) \dots(7)$$

Where  $k_{oi}$  and  $E_i$  are respectively the pre-exponential factor and apparent activation energy for component (i). The quantity  $(v_i^*)$  is the ultimately attainable yield product (i), i.e. the yield at high temperature and long residence time. Best fit values for the kinetic parameters  $k_{oi}$ ,  $E_i$  and  $V_i^*$ . I.e. those the minimize the sum of squared errors between calculated and observed yield  $V_i(T)$ , measured in non-isothermal experiments to different peak temperature T, and the overall duration t, with corresponding values, calculated using measured laboratory time-temperature, histories, a non-linear least squares regression code, and the integrated form of equation (2):

$$\ln\left[\frac{V_i^* - V_i(T)}{V_i^*}\right] = -\int k_{oi} \exp\left(-\frac{E_i}{RT}\right) dt \dots(8)$$

**2. Heterogeneous Character of Diffusion Process Model**

As both temperature and time are conversion deterring factors in non-isothermal conditions of thermogravimetric analysis, starting with the simplest law of formal kinetics for the time dependent of the conversion degree, x

- 1- for the temperature dependence of the reaction rate constant, k,[5,6]

- 2- It is easy to understand that the steepness of TG / DTG. curves

is rather determined by the activation energy (E), of the process.[5,6]

$$f(x) = (1-x)^n \dots\dots\dots(9)$$

$$f(x) = k t \dots\dots\dots(10)$$

$$k = A \exp\left(-\frac{E}{RT}\right) = \frac{d \log k}{dT} = E \frac{1}{2.303RT^2} \dots(11)$$

$$\frac{dx}{dt} = k(T) f(x) g(x, T) h(\sum x_i) \dots(12)$$

$$\frac{dx}{dt} = k(T) f(x) \dots\dots\dots(13)$$

Conversion-temperature cross terms g (x, T) are assumed ineffective and all physical factors which may influence the heterogeneous process, like sample size and shape, as well as surrounding atmosphere and pressure are eliminated due to the constancy of chosen reaction conditions.[5,6]

$$\beta = \frac{dT}{dt} \dots \dots \dots (14)$$

Rearrange equation (2-14) get:

$$\frac{dx}{dt} = \left[ \frac{k(T)}{\beta} \right] f(x) \dots\dots\dots(15)$$

Assume:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \dots\dots\dots(16)$$

And the conversion in simple case:

$$f(x) = (1-x)^n \dots\dots\dots(9)$$

Although for heterogeneous solid-gas reaction also more complicated expression are encountered.

$$\frac{dx}{dt} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) (1-x)^n \dots(17)$$

$$f(x) = \int_0^x \frac{dx}{(1-x)^n} \dots\dots\dots(18)$$

Only trial and error method can be recommended to approximate (n) for best fit of experimental data. For temperature Integral equation:

$$I_T \int_{T_i}^T \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dt \dots\dots\dots(19)$$

The following approximate solution can be used if the ratio (E / RT) > 15. Conditions fulfilled by majority of degradation process.

$$\log f(x) = \log \frac{AE}{R} - \log \beta - 2.315 - 0.457 \left(\frac{E}{R}\right) T^{-1} \dots(20)$$

For different heating rate and constant transformation degree (iso-x) this equation could be written as

$$-\frac{d \log \beta}{dT^{-1}} = 0.457 \left(\frac{E}{R}\right) \dots\dots\dots(21)$$

This type of heating however is up to now not applied in (TG) kinetic estimation can consider variable heating rate and generally the trend of conversion dependence of activation energy is preserved ever if absolute values of activation energy are quite different. [5]

### 3. Kinetic of Tire Pyrolysis (Isothermally Model)

Accounting for experimental conditions (sample geometry, physical properties of N<sub>2</sub>, temperature) the Biot number (Bi) is between (0.1 – 0.15), meaning that heat resistance in the gas film only. Then the rubber sample can be assumed isothermal at any time but its temperature at time (t) is, Tt increases and is given by. [7, 6, 8-10]

$$\frac{T_t - T_g}{T_0 - T_g} = \exp\left(-\frac{h t}{L \rho_s C_s}\right) \dots\dots(22)$$

Where  $T_0$ ,  $T_g$  are the initial temperature of the rubber sample and the temperature of the flowing gas, respectively,  $h$ , is the film resistance at the surface of the sample,  $L$ , the characteristic length of the sample (vol./sur.),  $\rho_s$ , the density of the sample and  $C_s$ , the specific heat of the sample. For the above equation constant pyrolysis temperature, and first-order behavior especially above 466 °C so, the sigmoidal curves can be modelled [80] assume that the coordinates of the inflection point are  $x_i$ ,  $t_i$ , then for  $0 < x < x_i$

for  $T_0 < T < T(t_i)$ :

$$x = \exp(-k(T)t) \dots\dots\dots(23)$$

And for  $x_i < x < 1$

$$T = T_g \dots \dots \dots (24)$$

$$x = 1 - (1 - x_i) \exp[-k(t - t_i)] \dots(25)$$

The rate constant,  $k$ , was identified using Rosenbrock algorithm (derivative-free algorithm); then temperature dependence of the rate constant,  $k$  (in  $\text{min}^{-1}$ ) can be modelled through the Arrhenius equation:

$$k = \exp\left(20.8 - \frac{15.100}{T}\right) \dots(26)$$

$$\frac{dx}{dt} = k(1 - x) \dots\dots\dots(27)$$

**Experimental**

This was a homemade system to suit the study of weight losses from bulky sample of the scarp tire pieces. The pyrolysis system under nitrogen was employed as a

basis of the TG – system. The connections at the top of the tube reactor were removed and the scrap tire sample (1.35 - 2.06) gm was placed in a stainless steel basket (20mm length and 15mm o.d.). The basket was hanged to the bottom of a semi microbalance by a 100cm stainless steel wire. The system is shown in Fig. (1), the general arrangement of equipment indicated. Heating was carried out under nitrogen gas flow rate (0.2, 0.35, 0.5)  $\text{m}^3/\text{hr}$ , temperature was measured at the two specified points a long the reactor at (5, 1, and 0.5 min) intervals depending on the rate of temperature increase, at the same time weight losses was recorded in order to investigate the isothermal model studied by Bouvier, and the evaluation of kinetic parameters. TG-DTG-Tt-curves were studied due to the conditions above.

**Result and discussion**

**1. TG - DTG Curves Investigations**

For a detailed understanding of the pyrolysis process, the scrap tires samples were subjected to a programmed temperature increase and the weight was continuously recorded for different particle size and nitrogen flow rates. A homemade thermogravimetric (TG) system was designed to allow the study of thermal decomposition of relatively large samples (few grams) because the standard TG instruments deal with milligram samples [15]. The design of sample holder was a basket form which allows the nitrogen gas to flow through the sample particles,

i.e. similar to the pyrolysis conditions. Such a configuration drives the decomposition volatile products to move upwards with upwards with the gas flow. The weight values recorded were plotted versus the corresponding temperature and the resultant curves are shown in Figs. (2 – 7).

The derivative of weight loss with respect to temperature- (DTG) was calculated from the relation:

$$\frac{\Delta W}{\Delta T} = \frac{W_2 - W_1}{T_2 - T_1} \dots (28)$$

And plotted against the average temperature  $(T_1 + T_2) / 2$ . The resultant curves were superimposed on the TG curves and also shown in Figs. 8 - 13. Thus, typical Tg and DTG curves could be obtained.

It can be seen that scrap tires decomposition commences above 300 °c and the flow rate of the inert gas has appreciable effect on the mode of the thermal decomposition. The overall weight loss of scrap tires depends on the particle sizes and the flow rate. The data are summarized in Table 1.

The higher the flow rate of N<sub>2</sub> the higher will be the temperature range of the decomposition. The widest temperature range for the thermal decomposition was noticed for the 10 mm sample and 0.2 m<sup>3</sup> / hr flow of N<sub>2</sub>. However the slow flow of N<sub>2</sub> allows the distinction of several steps starting from 315 °C loosing about 2.5 % which can be the volatilization of the oils required during the processing of tires and a second step starting at

328 °C with a loss of further 15 % and the final step at 350 °C loosing 26 % of the weight. The last two steps may be related to the decomposition of polybutadiene and polystyrene respectively [15]. The effect of size of the particles was typical to that reported by Mosques [1] where he studied also the effect of shape of the sample particles.

The higher flow rate of N<sub>2</sub> causes the over lap of the decomposition patterns and the differential curves indicated lower number of steps (DTG peaks). Slight evidence may be drawn from the DTG curves that the process occurs in one clear step for low and optimum gas flow rate (0.2, and 0.35) m<sup>3</sup>/hr at temperature 330, and 353 °C. And three steps in the case of high gas flow rate 0.5 m<sup>3</sup>/hr at 360, 375 and 390 °C, for large particle size pieces (10 mm). At these temperatures the extent of weight loss was 20 % and 65 % at (0.2 and 0.35 m<sup>3</sup>/hr), but the losses were 15 %, 45 % and 70 % at high gas flow rate (0.5 m<sup>3</sup>/hr), as shown in Figures (2, 3, 4, 8, 9, 10).

For small particle size scrap tires the DTG curves indicated only a single decomposition step ( peak ) at low and optimum nitrogen flow rate ( 0.2 and 0.35 m<sup>3</sup>/hr ) at 363, 33 °C. Two peaks appeared at high gas flow rate (0.5 m<sup>3</sup>/hr) in temperature range (365 - 385) °C. The weight losses were 45 %, 45 % and (35 - 75) % at temperatures above as shown in Figures (5, 6, 7, 11, 12, and 13).

Beyond ( 400 - 420 ) °C temperature ranges, the residual material represented only 45 %, 30 %, 25 %, 20 %, 2 % and 7 % of the original samples that will be tested above,, then it could be concluded that complete decomposition occurs for small particle size with gas flow rate range ( 0.35 - 0.5 ) m<sup>3</sup>/hr [ 1 ]. Also this result clearly indicates that the pyrolysis was limited by conductive heat transfer at higher temperature, for larger samples [7].

## 2. Evaluation of Experimental Kinetic Parameters

Fig. 14 shows the relationship between logarithmic rate constant values versus reciprocal temperature to aid the calculation of both the activation energy (E<sub>a</sub>) and frequency factor (A) of the decomposition is (1.33 kcal / mol. K) and (1 x 10<sup>-8</sup>). This value of ( E<sub>a</sub> ) was less than obtained by LUCCHESI in 1983 that is ( 5.9 kcal / mol. K ) at temperature range (400 - 700) °C [15]. The values rate constant (k) were determined from the temperature distribution equation modeled by Bouvier in 1987 at temperature range (375-525) °C [2]. Experimental curves show sigmoidal profiles particularly at optimum operating conditions (10 mm, and 0.35 m<sup>3</sup>/hr) and over range of nitrogen flow rate (0.35 - 0.5) m<sup>3</sup>/hr, as shown in Figures ( 15 - 20 ), this results is in agreement with that published by Bouvier in 1987 [7]. Also these experimental curves show first-order behavior, especially above the inflection point at (332-409) °C temperature range.

A comparison between the theoretical and experimental conversion ratio were shown in Figures (15 - 20). Good points is agreement with experimental points is noted at temperature range ( 332 - 409 ) °C Below these temperatures the agreement becomes worse, due to the negligible or non-effective pyrolysis reaction at low temperature [7]. These studied also proved that a practical temperature gives complete pyrolysis was above 450 °C which is in agreement with Bouvier [7].

## Conclusions:

1. A Thermogravimetric technique was used to investigate the comparison between theoretical and experimental conversion ratio.

$$X_{\text{theo.}} = 1 - \exp^{-kt}$$

2. The reaction is first order at high temperatures when the pyrolysis occurred at (390-450) °C .noting that this research studied a range of diameter (2 & 10 mm), while both Bouvier and Gelus were studied only one type of diameter of ( 5mm).

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Table (1) The Data of TG-DTG Curves

Flow rate m <sup>3</sup> / hr	% Total weight loss		Decomposition range° c	
	10 mm	2 mm	10 mm	2 mm
0.20	55	76	330 - 450	350 - 420
0.35	68	98	337 - 406	357 - 420
0.5	73	93	356 - 418	357 - 428

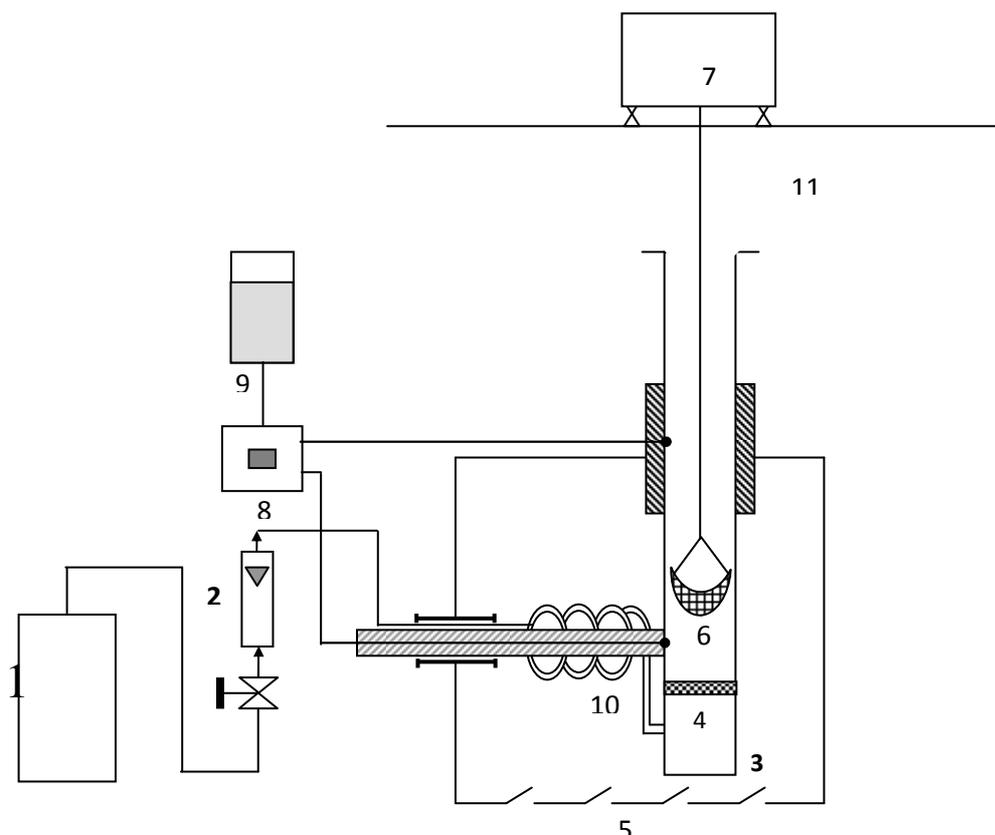


Figure (1) Experimental apparatus for kinetic studies.

- 1- Gas source with regulator .2- gas Rota meter. 3- Stainless steel reactor. 4- Gas distributor. 5- Electrical furnace. 6- Stainless steel basket. 7- Sensitive balance. 8- Selector switch. 9- Digital thermometer. 10- Stainless steel coil. 11- Stainless steel wire.

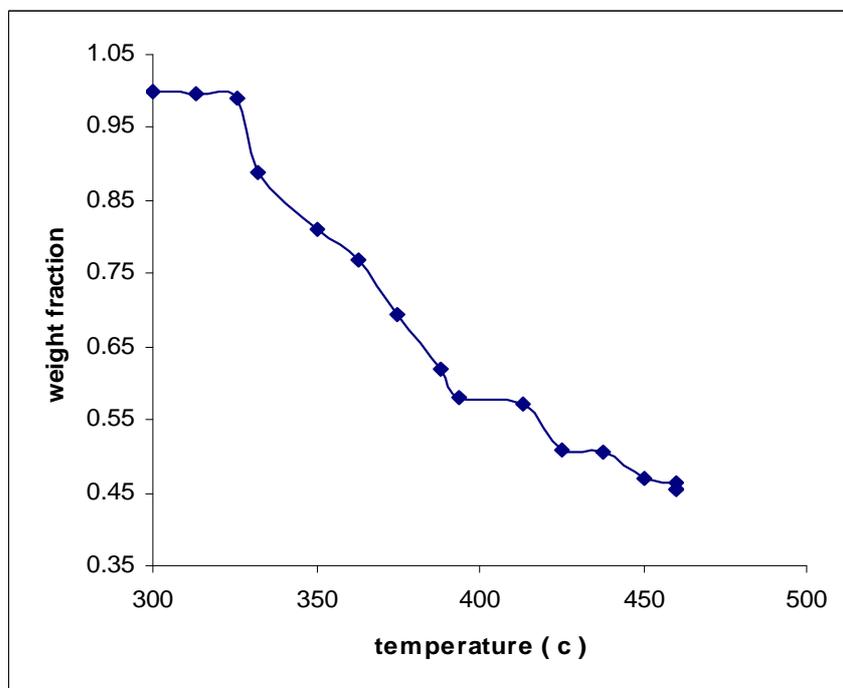


Figure (2) TG -curve for sample (10 mm, 0.2 m<sup>3</sup>/hr).

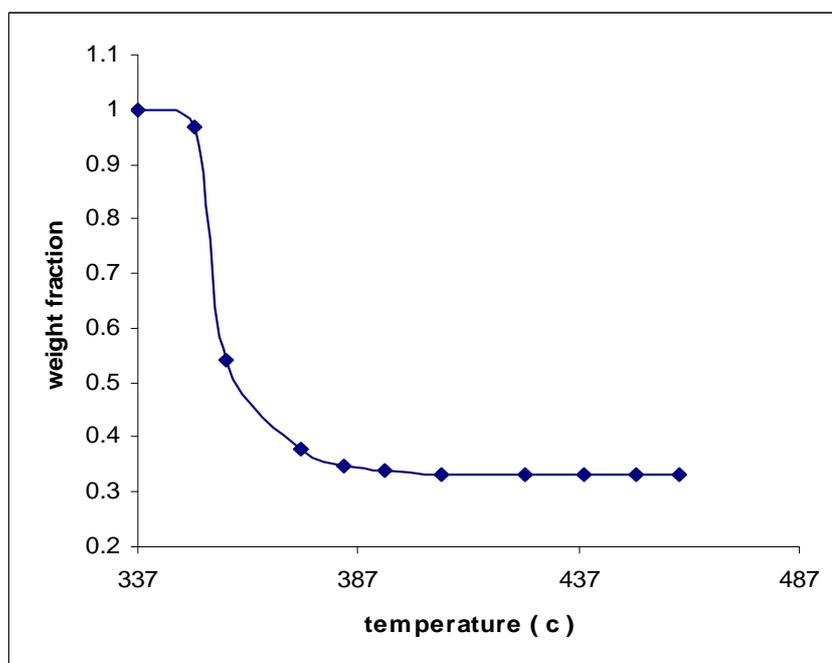


Figure (3) TG-curve for sample (10 mm, 0.35 m<sup>3</sup>/hr).

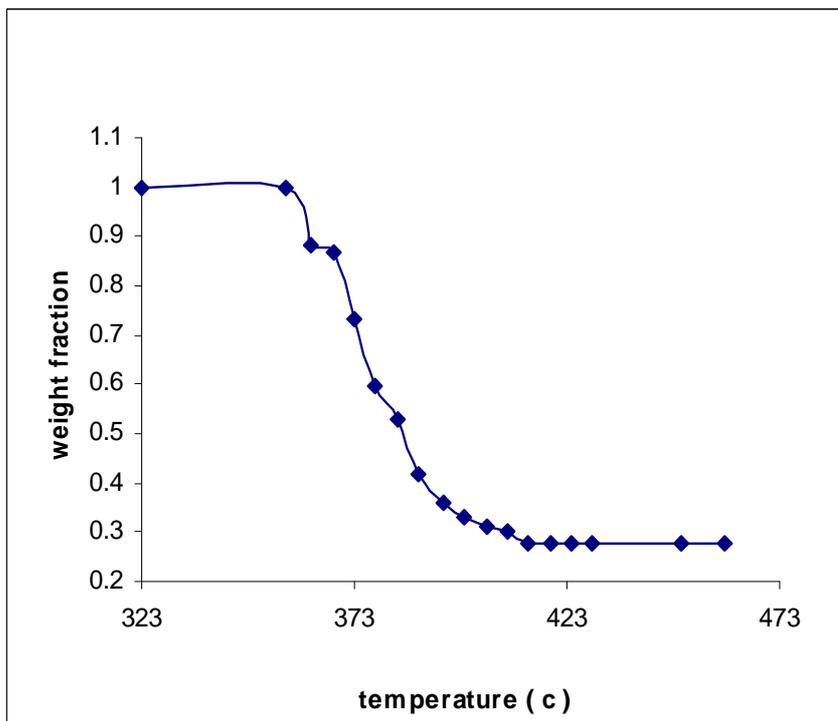


Figure (4) TG-curve for sample (10 mm, 0.5 m<sup>3</sup>/hr).

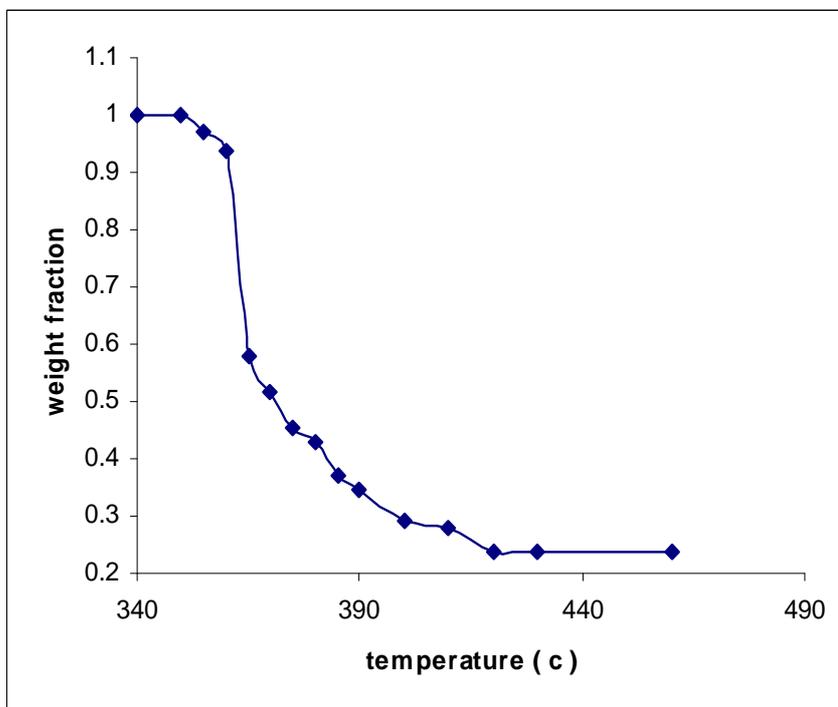


Figure (5) TG-curve for sample (2 mm, 0.2 m<sup>3</sup>/hr).

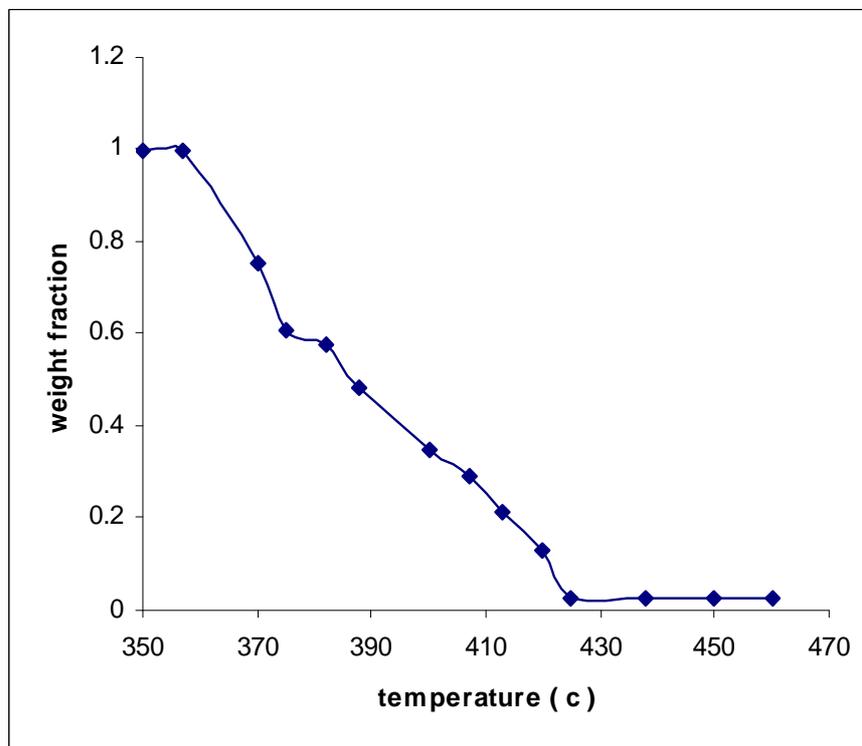


Figure (6) TG-curve for sample (2 mm, 0.35 m<sup>3</sup>/hr).

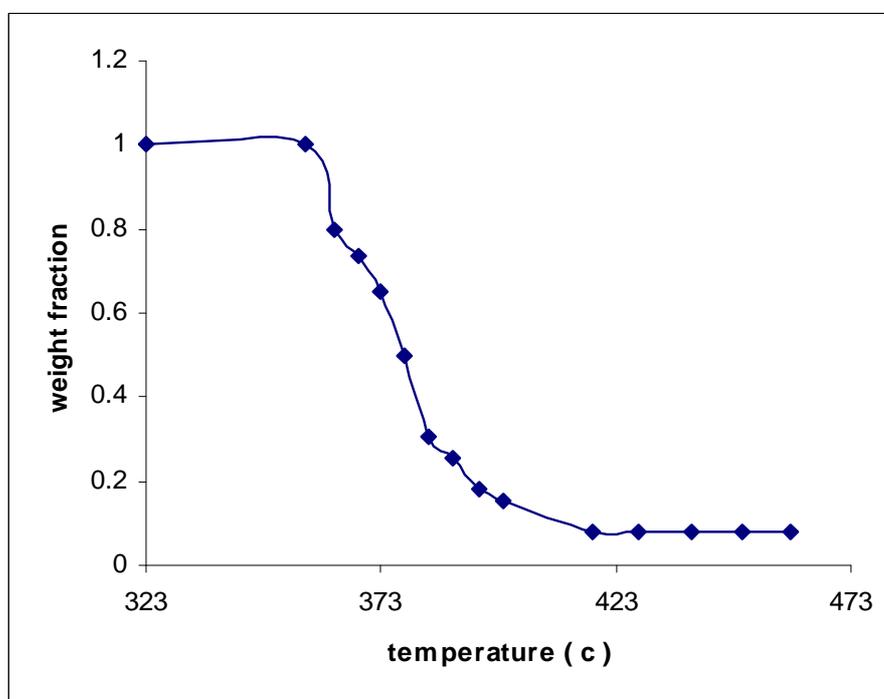


Figure (7) TG-curve for sample (2 mm, 0.5 m<sup>3</sup>/hr).

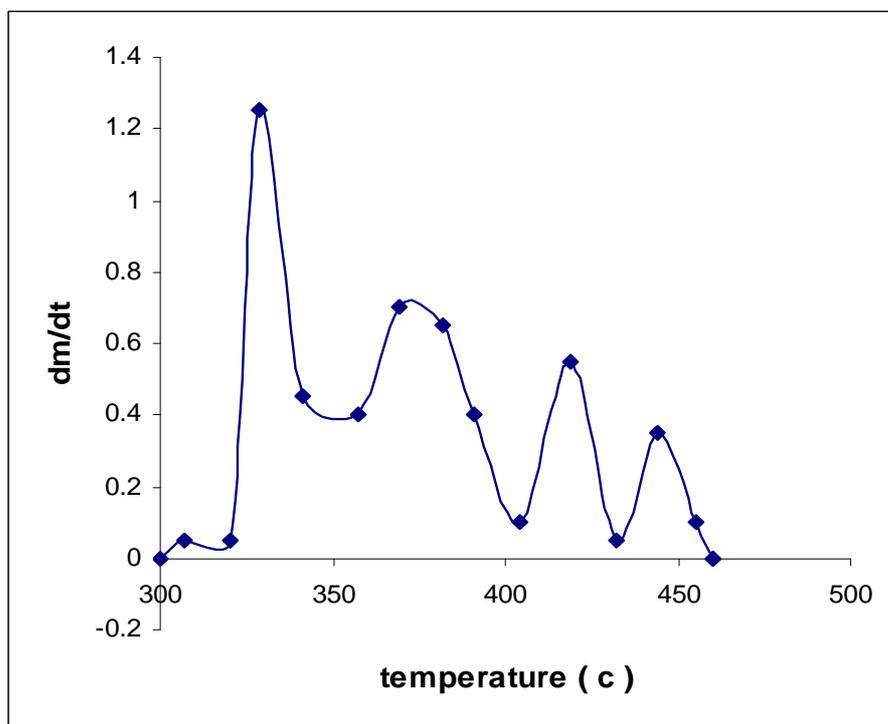


Figure (8) DTG-curve for sample (10 mm, 0.2 m<sup>3</sup>/hr).

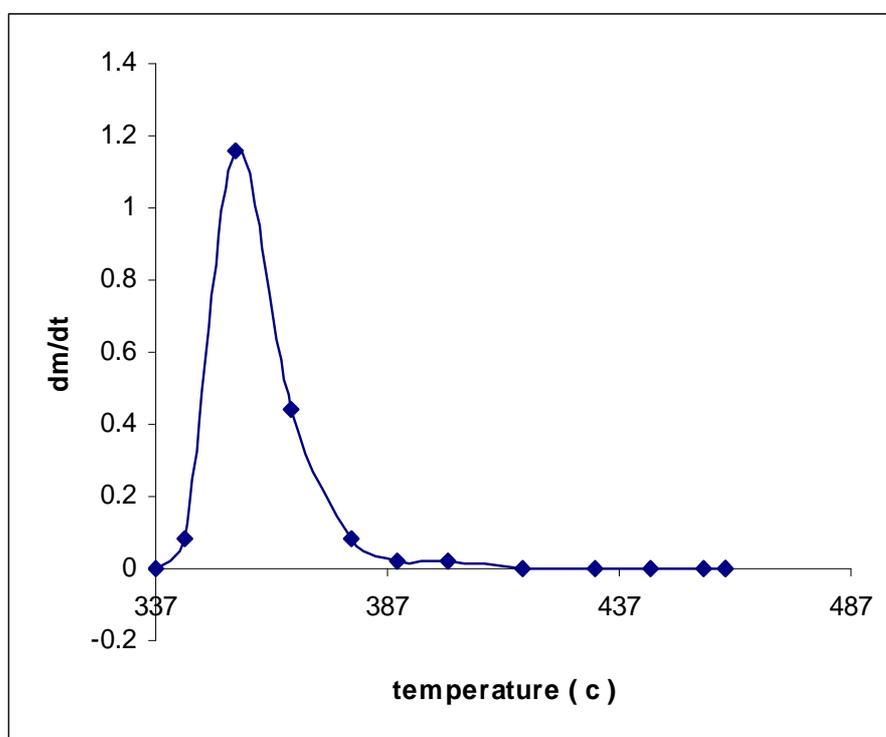


Figure (9) DTG-curve for sample (10 mm, 0.35 m<sup>3</sup>/hr).

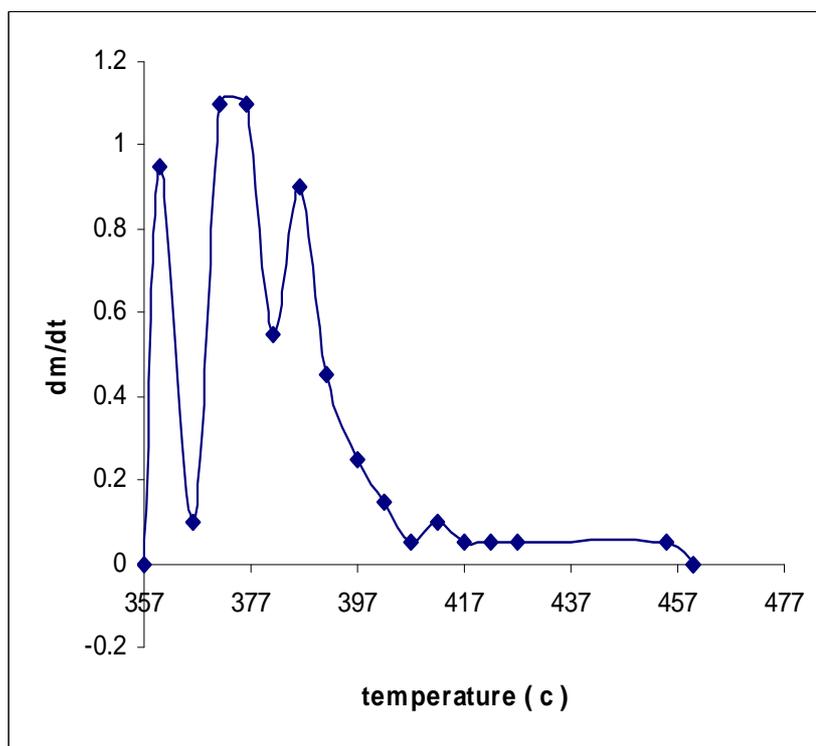


Figure (10) DTG-curve for sample (10 mm, 0.5 m<sup>3</sup>/hr).

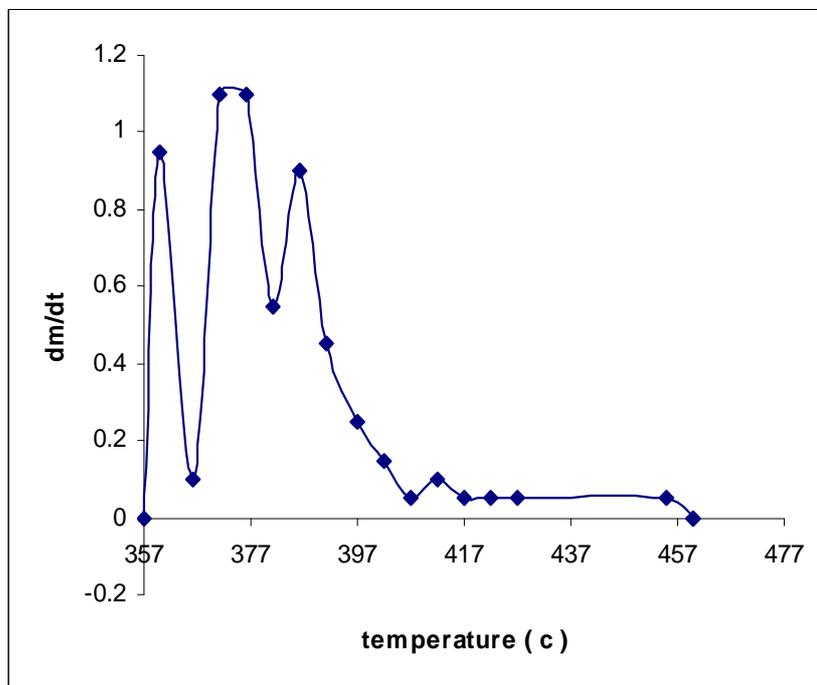


Figure (11) DTG-curve for sample (2 mm, 0.2 m<sup>3</sup>/hr).

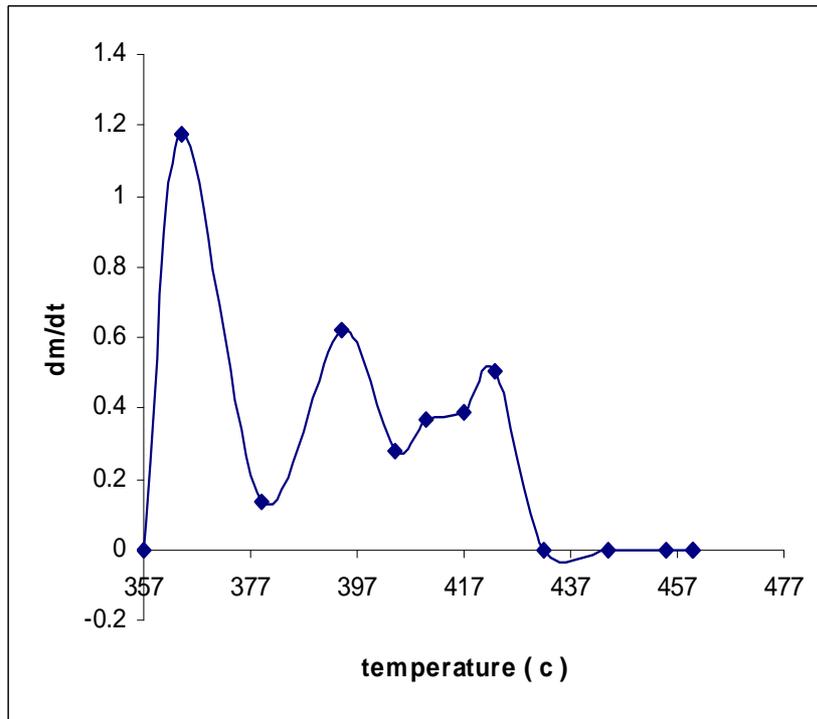


Figure (12) DTG-curve for sample (2 mm, 0.35 m<sup>3</sup>/hr).

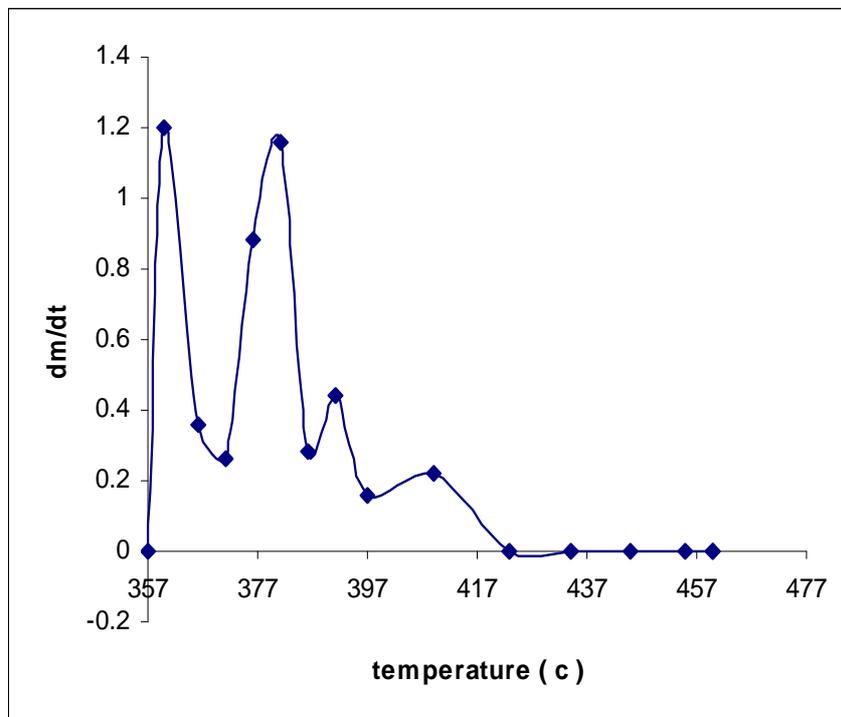


Figure (13) DTG-curve for sample (2 mm, 0.5 m<sup>3</sup>/hr).

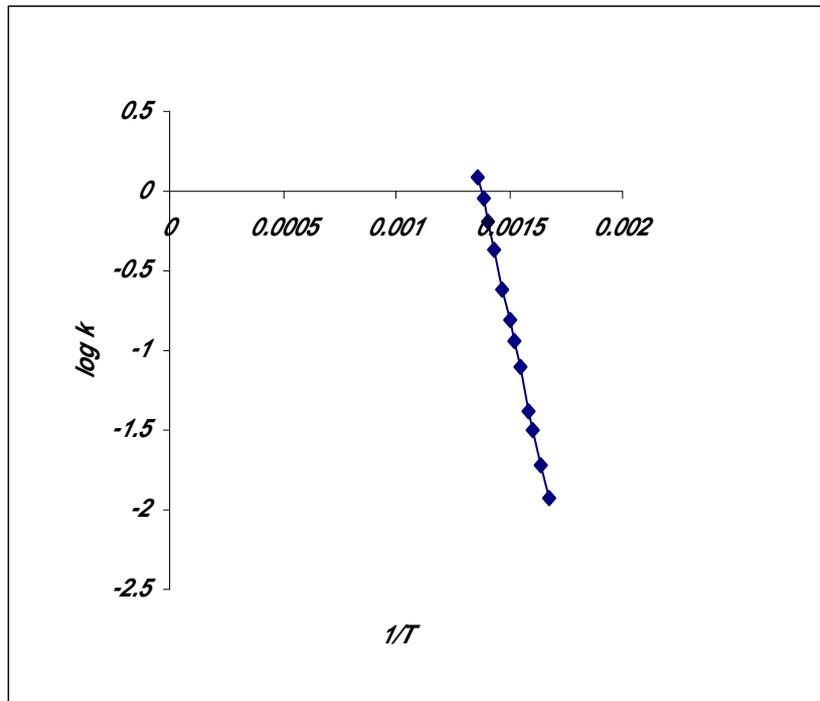


Figure (14) relation between rate constant vs. temperature.

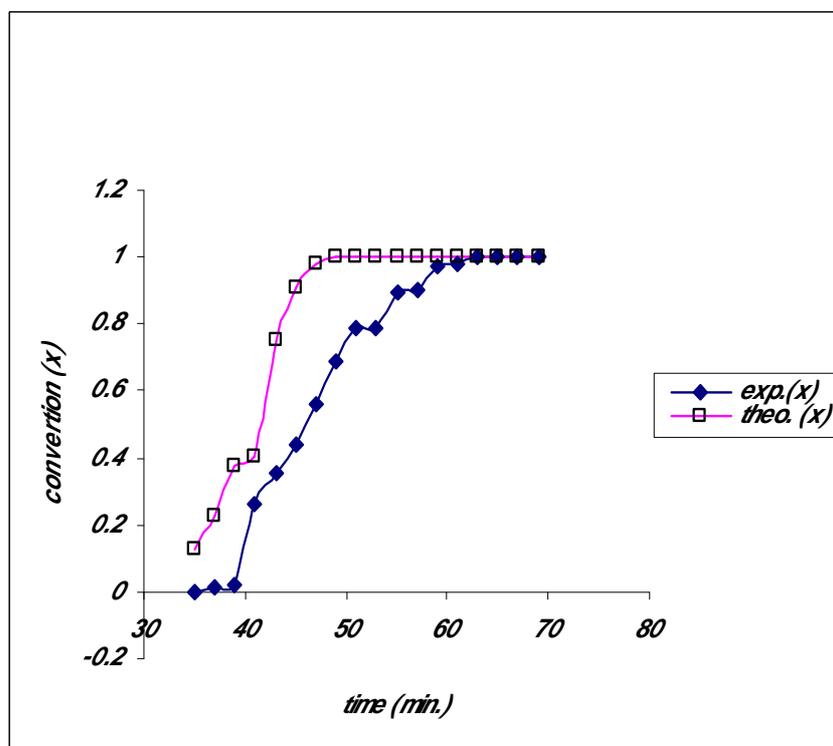


Figure (15) comparison between theoretical and experimental conversion ratio for sample (10mm, 0.2 m3/hr).

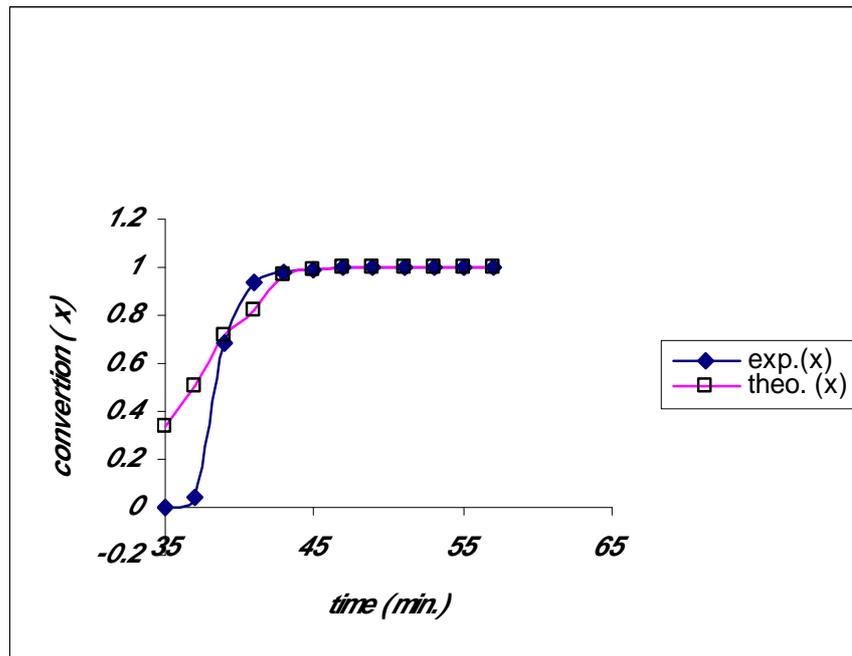


Figure (16) comparison between theoretical and experimental conversion ratio for sample (10mm, 0.35 m3/hr).

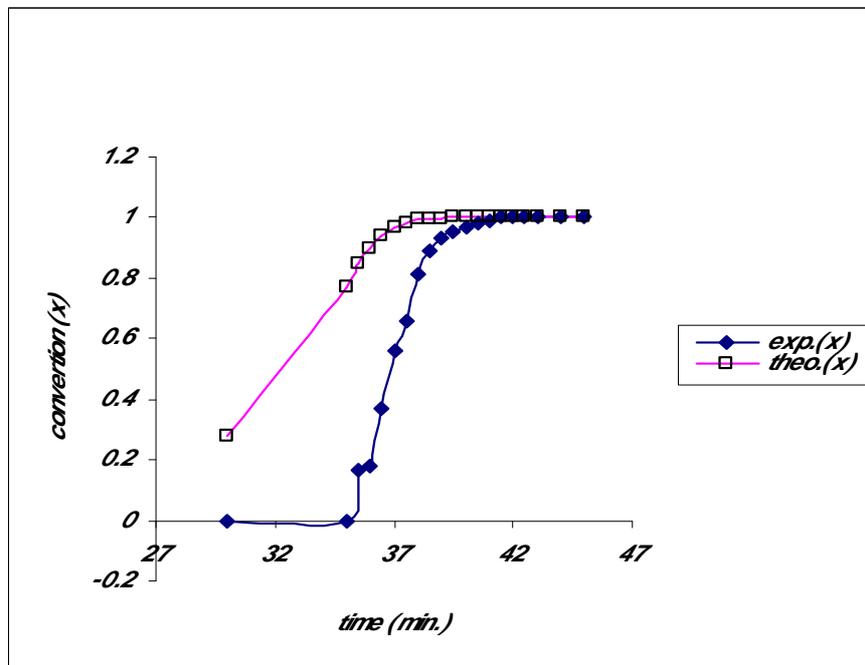


Figure (17) comparison between theoretical and experimental conversion ratio for sample (10mm, 0.5 m3/hr)

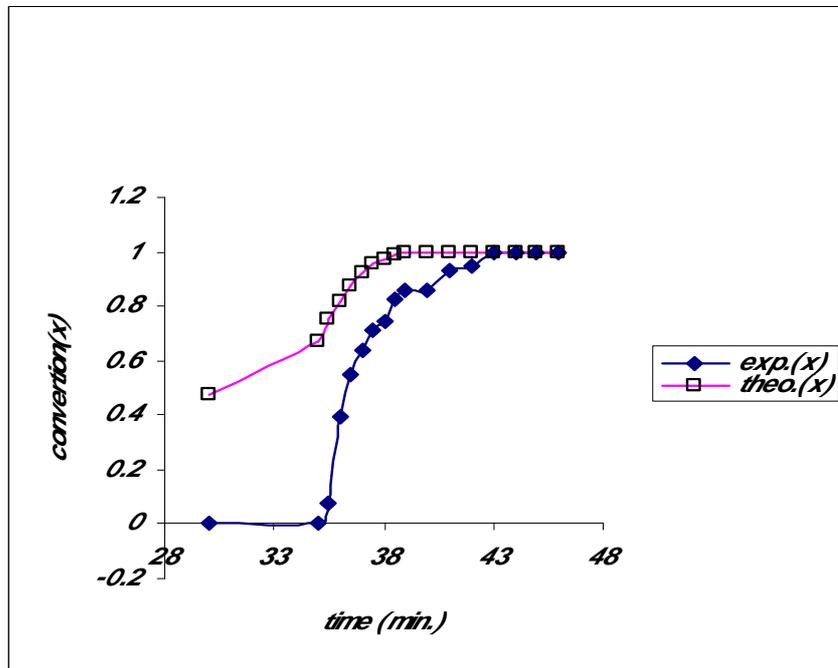


Figure (18) comparison between theoretical and experimental conversion ratio for sample (2mm, 0.2 m3/hr)

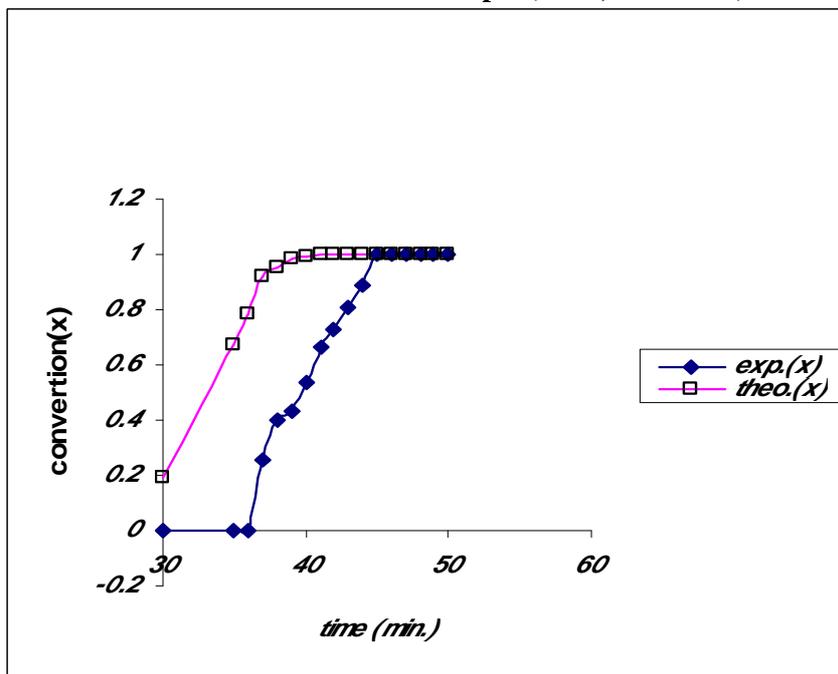


Figure (19) comparison between theoretical and experimental conversion ratio for sample (2mm, 0.35 m<sup>3</sup>/hr)

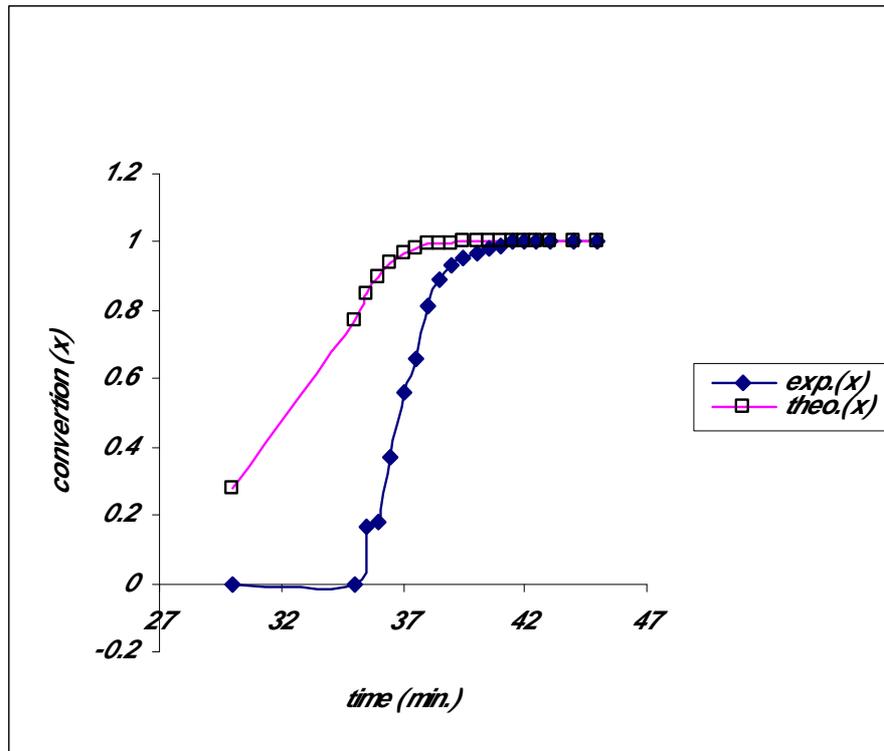


Figure (20) comparison between theoretical and experimental conversion ratio for sample (2mm, 0.5 m<sup>3</sup>/hr)