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Studies of kinetic on thermal decomposition of mesoporous carbon of gelatin by thermogravimetric technique

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ABSTRACT: The kinetic of thermal decomposition of mesoporous carbon of gelatin were studied using thermogravimetric technique at 25-1400 °C. The mesoporous carbon of gelatin prepared by nanocasting method using SBA-15 as hard template and gelatin as source of carbon The decomposition of the mesoporous carbon of gelatin samples proceeds via a two stage reaction, first stage are dehydration involving loss of water molecules and the last stage are carbonization. The investigation decomposition process conclude that stability of mesoporous carbon of gelatin at high temperature (1000-1400) due to the uniformity of pore size and shape of carbon framework. The kinetic analysis from decomposition reactions of mesoporous carbon of gelatin sample were discussed using integral method by Freeman Carroll and Coats and Redfem, The activation energy, order of reaction and parameter factor of mesoporous carbon of gelatin were calculated by various method and the results were discussed. The result of calculating data showed that the characteristics of activation parameter of mesoporous carbon of gelatin determined by Coats and Redfem method were substantially higher than calculated Freeman Carroll.

KEYWORDS: thermal decomposition, mesoporous carbon of gelatin, kinetic, isothermal.

1 INTRODUCTION

Mesoporous carbon of gelatin is the one kind of ordered mesocarbon based biomaterials which have high of carbon content and good properties such as thermal stability, inert, large pore size, high surface ares and pore volume [1-2]. The unique of properties proposed mesoporous carbon of gelatin to be a good material in the various reaction which involve the giant molecule such as adsorption dye or catalyst. The mechanism during synthesis can determined by kinetics of mass loss of mesoporous carbon of gelatin. The global kinetics of the pyrolisis as the represent of thermal degradation are the key to determined the steps of mechanistic of weight loss of mesoporous carbon during carbononization.

The kinetic of thermal decomposition reaction has been widely studied by thermogravimetry (TG) method. The theory about mass-loss which is equivalent to a large of isothermal mass-loss curve is used during determination [3-4]. The Data of thermogravimetry are only narrowly definitive. The motion of kinetic analysis can lead only to trivial kinetic parameter for mass-loss under a particular set of experimental condition. The advantages of thermogravimetry such as comparable, extend over wider temperature, proportional, give exact quantitative analysis and can be used to analyzed material which for some reason can't be analyzes by other instrument [5-7]. The experimental factors were influence the kinetic of TG method such as heating rate, particle size, sample mass and holder design. The thermal decomposition data generated from TG can be analysed and manipulated to obtain kinetic parameters. The kinetics of thermally of solid material can obtain thermal stability information of material which is the best information of many applications such as adsorption and catalytic.

MATHEMATICAL METHODE

In the case of dehydration and carbonization process, the kinetic calculation from thermogravimetric data have foundation based on the formal kinetic equation [8-9] :

$$\frac{dx}{dt} = -kx^n \qquad (1)$$

$$-\,dx = dw \qquad (1.a)$$

$$-\int_{x_0}^{x} dx = \int_0^w dw \qquad (1.b)$$

$$-(x - x_0) \quad = w - 0 \qquad (1.c)$$

$$at\ t_\infty; \quad -(x_\infty - x_0) = w_\infty \qquad (1.d)$$

$$so, \quad (m_0 - m_\infty) \ = w_\infty \qquad (1.e)$$

By substitution Eq 2d to (2.a) , the obtain equation is:

$$\int_{m_0}^{m} \frac{-dx}{m_0 - m_\infty} = \int_0^w \frac{dw}{w_\infty} \qquad (1.f)$$

$$\int_{m_0}^{m} -dx = \frac{m_0 - m_\infty}{w_\infty} \int_0^w dw \qquad (1.g)$$

$$-\int_{m}^{m_\infty} dx = \int_{w}^{w_\infty} \frac{m_0 - m_\infty}{w_\infty} dw \qquad (1.h)$$

$$-(m_\infty - m) = \frac{m_0 - m_\infty}{w_\infty}(w_\infty - w) \qquad (1.i)$$

$$\frac{m - m_\infty}{w_\infty - w} = \frac{(m_0 - m_\infty)}{w_\infty} \qquad (1.j)$$

Where x is the mass sample of species undergoing reaction, n is the order of reaction and the kinetic constant (k) can be expressed by an Arrhenius law from the temperature dependence is expressed by equation of Arrhenius [10-12] :

$$k \ = Ae^{-E/RT} \qquad (2)$$

Where A is the preexponential factor, E is activation energy and R is the gas law constant.

Is it usual to express the rate of weight loss as a function of the ratio m_o/W~ (usually called 'weight fraction', or 'mass fraction', the relationship of X to mass-loss, w, is given by the equation

$$\frac{dx}{dw} = -{}^{(m_0 - m_\infty)}/_{w\infty} \qquad (3)$$

Where mo is the initial mass of the sample and $w_\sim$ is the maximum mass-loss. The integration of both side of Eq (3) obtained the equation below

$$\frac{x}{w_\infty - w} = \frac{(m_0 - m_\infty)}{w_\infty} \qquad (4)$$

As our based assumption, if $m_0 - m_\infty = \mathrm{m}$

So, dx= dm

Freeman and Carrol obtained the equation (5) by substitution of Eq 2 and 4 into Eq 1 as the first step and by differentiation of the result form as the second step [7-8].

$$\frac{-\left(\frac{E}{2.3R)}\right)\Delta(\frac{1}{T})}{(\Delta \log W_r)} = -\,n + \frac{\Delta \log^{dw}/_{dt}}{(\Delta \log W_r)} \qquad (5)$$

where $W_r = w_{c-}w$, wc is weigth loss maximum and w is weight loss of total reaction at time t. The plot of $\frac{\Delta \log^{dw}/_{dt}}{(\Delta \log W_r)}$ versus $\frac{10^3\Delta(\frac{1}{T})}{(\Delta \log W_r)}$ produce the slope as activation energy and intercept as order of reaction.

$$\log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.3RT} \qquad (6)$$

Where α is the fraction of sample that decomposed at time t, a is heating rate. The Coats and Redfern express the equation (6) by transposition Eg 3 and 4 as the first step and by integration the result form as last step [9-10]. The activation energy obtained from the slope of straight line from the plot between $\log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\}$ versus 1/T where *n*=1 .

Moreover, the kinetic thermal thermogravimetric analysis of mesoporous carbon of gelatin used viarious mathemathical methods are never reported before. Based on the above consideration, the authors undertaken, this paper primarily focuses on the study of kinetic of the thermal decomposition of mesoporous carbon of gelatin. The synthesis and characterization of mesoporous carbon of gelatin has been reported in our previous paper [1-2] In the present study, the kinetics of the thermal decomposition mesoporous carbon of gelatin were studied using different various theoretical method. The correlation among theoretical method were discussed. The thermal stability of the product were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results of Kinetic analysis of data of thermogravimetric sample of mesoporous carbon of gelatin were discussed.

2 EXPERIMENTAL SECTION

2.1 MESOPOROUS CARBON OF GELATIN EXTRACTION

Mesoporous carbon material was synthesized by using SBA-15 mesoporous material as a silica template (particle size 0,1 µm, pore diameter 7-8 nm, surface area 550 m^2/g, pore volume 1,0 cm^3/g) and gelatin as the carbon source which prepared in our previously wor[ ]. In a typical synthesis of mesoporous carbon, 1 g of template (mesoporous silica material) was added to a solution obtained by dissolving 1 g of gelatin and 0.32 g of H_2SO_4 in 16 g of water, and keeping the mixture in an oven for 7 h at 110 °C. Subsequently, the oven temperature was raised to 150 °C for 7 h. In order to obtain fully polymerized and carbonized gelatin inside the pores of the silica template, 0,5 g of gelatin, 0.11 g of H_2SO_4 and 5 g of water were again added to the pre-treated sample and the mixture was subjected to the thermal treatment described above. The template–polymer composites were then pyrolyzed in a nitrogen flow at 900 °C and kept under these conditions for 3 h to carbonize the polymer. The mesoporous carbon was recovered after dissolution of the silica framework in NaOH 2 M at temperature of 70°C, by filtration, washed several times with ethanol, and dried at 120 °C produced the mesoporous carbon of gelatin sample.

2.2 CHARACTERIZATION

TG analysis was carried out simultaneously with DTA measurements using a Setaram TG– DTA 92 apparatus under dry air, flowing at a constant rate. The heating rates were 5 K/min. DSC measurements were performed with a Perkin Elmer 7 or a Pyris 1 apparatus, between 253 and 333 K at a heating rate of 5 or 10 K/min, under nitrogen flow. Since the thermal response is mainly due to 8CB, for comparison the curves were normalized to its amount in the corre- sponding composit. Differential scanning calorimetry (DSC) analyses were carried out on a Netzsch DSC 204 calorimeter (Netzsch, Germany). Samples of about 6 mg weight were placed in an aluminum pan with a pierced lid, placed in a DSC oven, and heated from 25 to 1400 °C at a heating rate of 5°C/min. The measurements were conducted under a nitrogen atmosphere. An empty pan was used as a reference.

3 RESULT AND DISCUSSION

The results of the DTA-TG of mesoporous carbon of gelatin (MCGe) in flowing nitrogen showed in Fig.1. MCGe starts to lose water at temperatures slightly above room temperature (35-120 °C) to produce the anhydrous mesoporous carbon of gelatin at about 320°C. The results show how the peaks in the DTA correspond closely to the weight changes observed on the TG trace. The broad endothermic dehydration clearly shows one minima in air at about 120°C. The TG curve, however, shows that dehydration proceeds in two steps, the first stage represent the loss of water molecules for temperature range at 50-280°C and the last stage was carbonization represent the los of monoxide and dioxide carbon molecules for temperature range at 900- 1200°C. Nothing weight loss of any molecul at 320-900 °C means the frame work of anhydrous mesoporous carbon of gelatin was stabil due to completely pore filing by nanocasting strategy followed by pyrolitic step at 900 °C. In addition, mesoporous carbon of gelatin show the high thermal stability at 1200-1400 °C with the total weight loss up to 20% means the uniformity and the regular structure of carbon can minimize carbonization effect as one of destruction process.

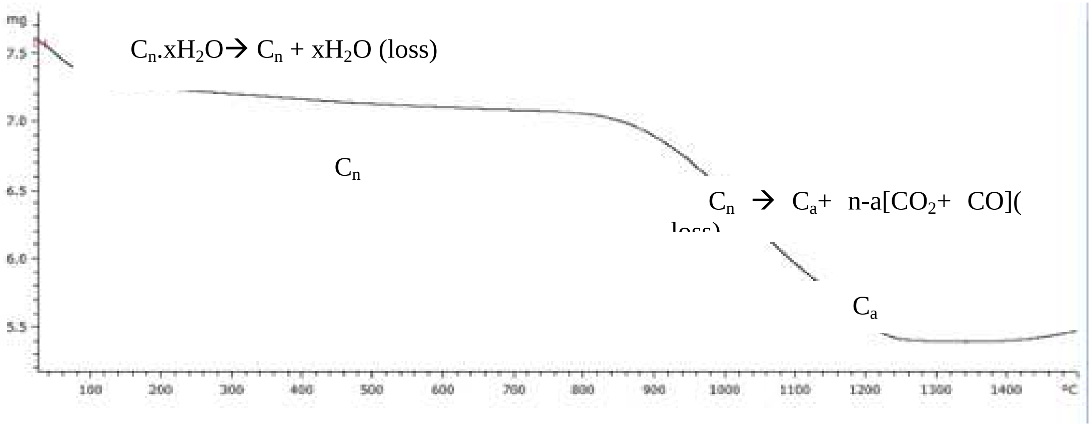


Fig 1. DTA Profile of mesoporous carbon of gelatin

Fig 1 showed the structural organization and rearragenment type in general DTA curve peaks analysis theory. Mesoporous carbon of gelatin at temperature 9001-1200 °C showing the structural organization of carbon followed by weight loss of carbon oxide. At the end, mesoporous carbon showing the rearrangement step at 1200-1400 °C represent the pre-grafitization process.

The DTA curves reveal that dehydration may involve decomposition in stages: incongruent melting and evaporation of liquid water [9-10]. The TG curves showed that the decomposition of th he anhydrous mesoporous carbon of gelatin proceeds in one step with the expected loss in weight to break chain of from mesoporous carbon of gelatin and with the simultaneous loss of acetone and carbon dioxide. In nitrogen, the DTA curve showed a dented endothermic peak at about 320 °C, which indicates that the main mesoporous carbon of gelatin decomposition occurs in at least two stages. The two-stage decomposition of the anhydrous mesoporous carbon of gelatin may indicate at least partially, as in the chain of mesoporous carbon of gelatin, the presence of an intermediate mixed acetate-oxide vapor occurs on contact with the oxygen, with the consequent marked exothermal activity. The endothermal salt. In air, however, decomposition of the acetone decomposition at about 300 and 320°C. is overshadowed by the exothermal reaction giving two well-defined steps in the DTA and with peak temperatures

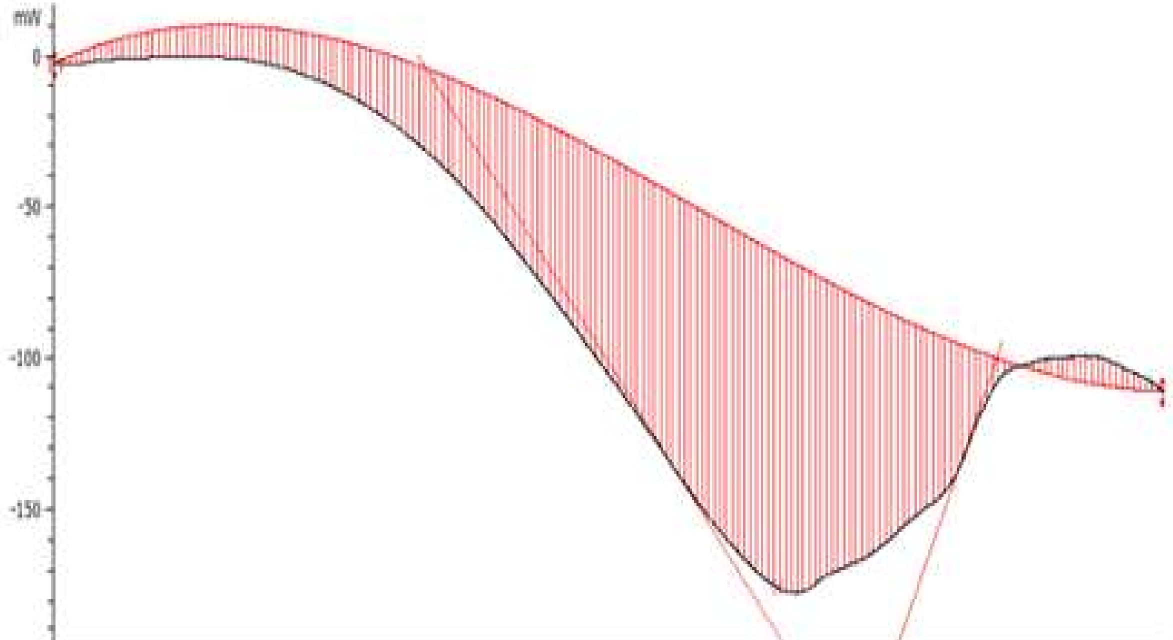


Fig 2. The crystalinity profile by Extrapolating curve of DTA from mesoporous carbon of gelatin

The quantitative analysis of material to obtain the crystalinity information was describe in previous literature [11-18]. The information about the decomposition from manganese(II) oxalate dihydrate and manganese(II), oxalate trihydrate, sodium oxalate, potassium metaperiodate potassium bromated obtained by ΔH data [18-22]. Table 1 was used to identify the uniformity of mesoporous carbon of gelatin during decomposisition. The high crystalinity and peak height of heat flow (table 1 and Fig 2) represent that the amorphous mesoporous carbon of gelatin have the regular morphology closely with the crystal material. The ΔH data reperesent the tha phase transition hydrous carbon to anhydrous carbon followed by the pure carbon formation.

Tabel 1. The output data of Cristalinity from DTA DSC measurement of mesoporous sample of gelatin

Parameter	Value
Crystalinity	$4.58\mathrm{x}10^6$ %
Integral	$-352.29\mathrm{x}10^3$ mJ
Integral normalized	$-45.75\mathrm{x}10^3$ J/g
ΔH	1 J/g
Onset	518,74 °C
Peak Height	110,46 mW
Peak	977.59 °C
Extrapolarization peak	1084.20 °C
End set	1272.01 °C
Peak width	510.07 °C
Right limit	1497.66 °C
Left limit	36.07
Heating rate	10 °C/ min

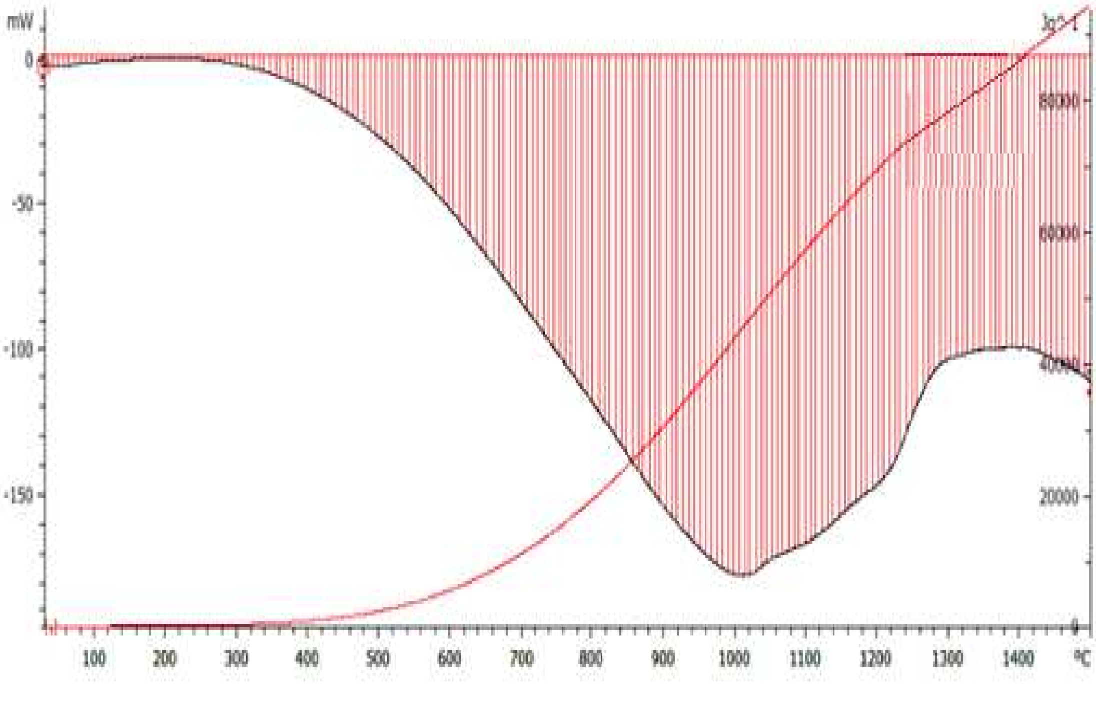


Fig 3. DTA enthalpy and heat flow profile of mesoporous carbon of gelatin

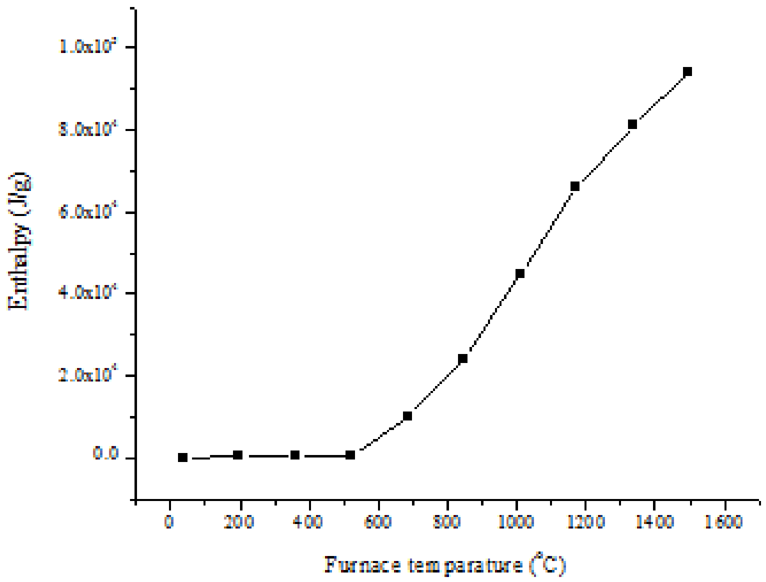
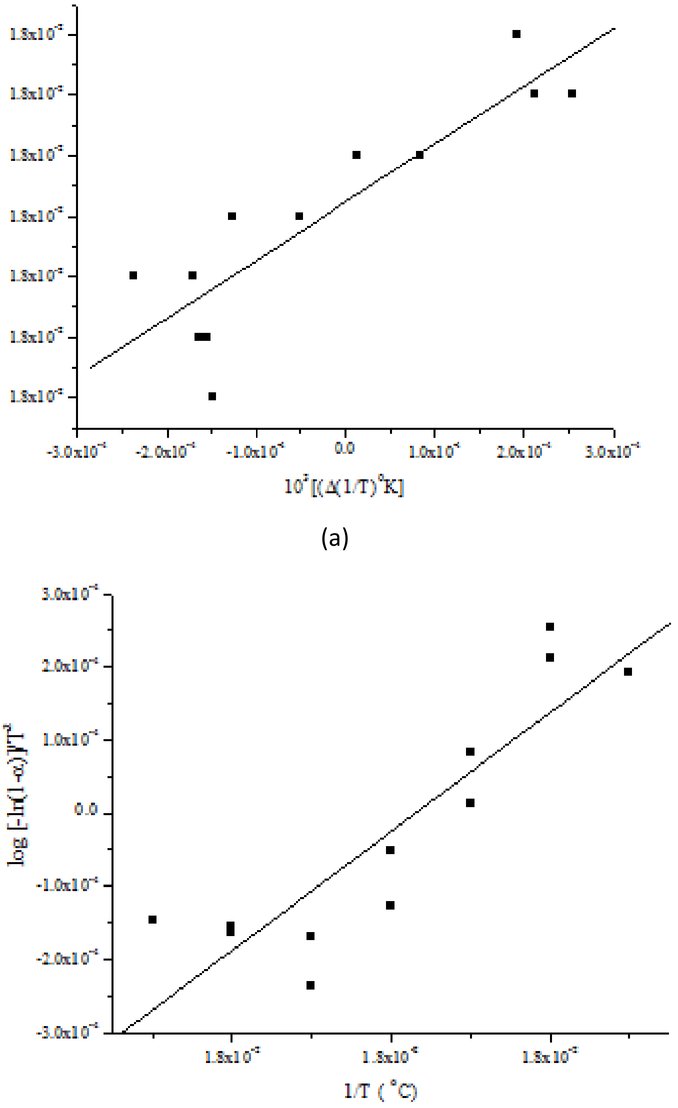


Fig 4. Enthalpy Profile of mesoporous carbon of gelatin

Fig 3 showed the enthalpy and heat flow profile of mesoporous carbon of gelatin The net area of the endothermic peak in the 320-1300 °C temperature range should be directly related to the volatile matter content of carbon. Fig showed the three region of endotermic reaction were observed, first stage as dehydration peak in the range 25-200 °C, second stage very abroad endothermic peaks that spans the range from 350-1350 °C and endothermic peak at temperature >> 1400C. the broad reaction from 350-1350 °C probably correspond to pyrolytic fragmentation of the carbon skeletal structure in sample and pre reaarengement structure at >>1400 °C. Fig 4 showed the the enthalpy of mesoporous carbon at the different furnace temperature. The average enthalpy at each temperature heating is 70,07 KJ/g. The result conclude that the increasing temperature influence to increasing the enthalpy of regular material.

Table 2. Kinetic parameters of mesoporous carbon of gelatin sample by Freeman Carroll and Coats and Redfern

Methode	T(C)	E (KJ/mol)	n	A(min^{-1})
Freeman &Carroll	100-300	2.03	1.00	5.36 x10^{5}
	300-600	10.22	1.01	1.19x10^{4}
	600-900	45.34	1.34	1.32X10^{4}
	900-1200	58.55	0.75	5.05 x10^{5}
	1200-1490	80.75	2.05	5.45 x10^{5}
Coats and Refern	100-300	2.50	1.00	5.40 x10^{5}
	300-600	11.22	1.11	1.30x10^{4}
	600-900	48.34	1.40	1.40X10^{4}
	900-1200	59.55	0.80	5.40 x10^{5}
	1200-1490	85.75	2.10	5.45 x10^{5}



(a)

(b)

Fig 5. Data calculated by using (a) Freeman Carol and (b) Coat and Redfern method from mesoporous carbon of gelatin sample

The Fig 5 and table 2 showed the calculating result and the plot by freeman carrol and coats redfern method. Both of the plot showed good linearity. The result of both method showed the close value of kinetic parameter. Fig 5 showed the comparison of the kinetic result calculated by different method for a system to the dehydration and carbonization of mesoporous carbon of gelatin. From these calculation it was found that the deviation of computed value of E did not differ by more than 10%. In general observation, the value of E, n and A from Coats and Redfern was higher than Freeman Carrol method due to the different way to describe the fundament equation of kinetic. However, all the correlation coefficient value of kinetic parameter from both method were close each other.

4 CONCLUSION

The kinetic of thermal decomposition of mesoporous carbon of gelatin were investigated using thermogravimetric technique at 25-1400 °C. The mesoporous carbon of gelatin synthesis by using SBA-15 as hard template and gelatin as source of carbo. The decomposition of the mesoporous carbon of gelatin samples proceeds via a two stage reaction , dehydration involving and carbonization. The uniformity of pore size and shape of carbon framework increase the effect of decomposition due to the high stability of mesoporous carbon of gelatin. The kinetic parameter analysis to determined activation energy, order of reaction and parameter factor calculate by Freeman Carroll and Coats and Redfem. The kinetic parameter obtained fromMesoposrous carbon of gelatin with value E=70.07KJ/g , n=1, A=5.5 $10^{5.}$ The result of calculating data showed that the characteristics of activation parameter of mesoporous carbon of gelatin determined by Coats and Redfem method were substantially higher than calculated from Freeman and Carroll

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