KINETICS OF PYROLYSIS OF CIGARETTE BUTTS

N. Y. SELEM [1], N. F. AL HOSENY[2], AND EL-S. M. H. EL-ZAHED[2]

ABSTRACT

Cigarette butts are considered a hazardous waste that can be potentially used as a source of energy. In this work, butts were ground to pass 60 mesh screen, dried and subjected to pyrolysis in a thermal analysis apparatus, under nitrogen flow, at four heating rates: 5, 10, 15 and 20 K.min^{-1}. The TG curves showed a substantial loss in mass followed by formation of biochar. The kinetics of char formation were investigated using four methods, namely the Kissinger and FWO methods, as non – model methods, a multiple regression technique that allowed determining the apparent order of reaction, and the Coats - Redfern model method which disclosed the reaction mechanism as being diffusion controlled. The values of activation energies obtained by the different methods were comparable ranging from about 164 to 196 kJ.mol^{-1}. Determination of the calorific values of butts and the produced char yielded values of 17200 kJ.kg^{-1} and 27450 kJ.kg^{-1} respectively.

KEYWORDS: Cigarette butts, Pyrolysis, Kinetics, Activation energy, Kinetics of pyrolysis

1.   INTRODUCTION

The global energy shortage has led to seek new energy sources satisfying both economic and environmental criteria. Agricultural wastes have been widely researched as a potential source of energy, either as a source of biochar [1] or as source of energy by direct combustion [2]. A lot of such wastes have been investigated in that respect such as citrus peels [3, 4], banana peels [5], rice straw [6], date kernels [7] and bagasse [8]. Some vegetable wastes have also been used in promoting the formation of pores in clay bricks. In a comprehensive review, Abdul Kadir et al [9 – 11] incorporated cigarette butts with clay to prepare bricks by molding, drying and firing at 1050 °C.

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[1] Lecturer, Chemical Engineering Department, Higher Technological Institute, 10th of Ramadan City, Cairo, Egypt, nora.abdelftah@hti.edu.eg

[2] Lecturer, Chemical Engineering Department, Higher Technological Institute, 10th of Ramadan City, Cairo, Egypt.

Increasing the butts' content resulted in increased water absorption and thermal conductivity but its effect on compressive strength was deleterious as it decreased from 25.6 MPa to 3 MPa as the percent waste was increased from 0 to 7.5% by weight.. The thermal conductivity was also found to decrease with increased percentage butt addition reaching a minimum value at 5% addition. These results were however different from those obtained by Sarani [12], using similar preparation conditions, as the values of thermal conductivity fluctuated about a mean value of about 0.85 $W.m^{-1}K^{-1}$ from 0 to 5% addition. However, the maximum recommended addition of butts in clay bricks, in order to prevent the emission of obnoxious gases, was recommended to be 1% by Mohajerani et al [13]. More recently, Kurmus et al [14] prepared clay – butts samples pressed at 240 kPa and fired at 1050 °C for 3 hours that resulted in a compressive strength of 27 MPa at 2% addition.

Pyrolysis of cigarette butts, as potential source of energy was carried out by Soltani et al [15]. They obtained a biochar at 250 °C and showed that more than 80% of the used butts were devolatilized below 130 °C. They also characterized cigarette butts using EDX analysis and found them to have a carbon content of about 11%. Also, Blankenship et al [16] have proved that biochar produced from cigarette butts pyrolysis possesses an extremely elevated surface area that makes it an excellent candidate for hydrogen storage. On the other hand, it is worth noticing that Benaventi et al [17] were able to isolate cellulose acetate from cigarette butts and determine the optimum conditions for that process.

It is worth mentioning however, that no literature was found to date, dealing with the kinetics of the pyrolysis process, which is the very subject of that work.

2.   RAW MATERIALS AND TECHNIQUES

The raw material used consists of cigarette butts which were shredded to pass 60 mesh screen (250 µm). The resulting material was dried overnight in a drying oven at 100°C then subjected to thermal analysis under a constant flow of nitrogen (20 ml.min^{-1}). The thermal analysis equipment was of TGA-50H – Shimadzu type that

could be operated at heating rates ranging from 2 to 50 K.min^{-1}. TGA and DTG data were retrieved as both spreadsheets and curves. The four chosen heating rates were 5, 10, 15 and 20 K.min^{-1}.

The determination of the calorific value was carried out in a bomb calorimeter. This apparatus consists of water jacketed stainless steel container in which one gram of the sample is placed and electrically heated until it ignites. Heat is transmitted through the steel walls to the water in the jacket. The elevation in water temperature is calibrated so as to provide the heat of combustion. The apparatus used is a PARR 6000 series type.

The calculation of activation energy from thermogravimetric data was carried out using two non – model methods, namely, Kissinger method [18, 19] and Flynn – Wall – Ozawa (FWO) iso-conversional method [20, 21]. The conversion (α) at any decomposition step is calculated from:

$$\alpha = \frac{m_0 - m}{m_f - m_0} \qquad (1)$$

Where m_0 is the initial mass, m is the mass at any time during the reaction and m_f is the final mass remaining after the reaction has ended.

The Kissinger method relies on the application of the following equation [18]:

$$\ln \frac{\beta}{T_p^2} = -\frac{E}{RT_p} + \ln -[\frac{R}{E} g(\alpha)] \qquad (2)$$

Where, T_P is the DTG peak temperature (K), β is the heating rate (K.min^{-1}), E is the activation energy (kJ.mol^{-1}) and $g(\alpha) = kt$ is the function relating conversion to time.

If a plot is performed between $\ln \frac{\beta}{T_p^2}$ and $\frac{1}{T}$, the slope of the straight line obtained is $-\frac{E}{R}$ from which the activation energy can be deduced.

The Flynn – Wall – Ozawa (FWO) method is based on the following equation [20]:

$$\log \beta = \log \frac{A.f(\alpha)}{\frac{d\alpha}{dT}} - \frac{0.456E}{RT} \qquad (3)$$

Since α is held constant, the first term in the RHS is constant and a plot of log β against $\frac{1}{T}$ should produce a straight line of slope $= -\frac{0.456E}{R}$

A simple multi-regression method was also used that allows determining the apparent order of reaction as well as the activation energy [22]. It relies on writing the general rate equation in the form:

$$-\frac{dm}{dt} = A \times e^{\frac{-E}{RT}} \times (1-\alpha)^n \qquad (4)$$

Where, $-\frac{dm}{dt}$ is obtained from DTG readings, A is the pre-exponential factor and n is an apparent order of reaction. This can be linearized in the form:

$$\ln(-\frac{dm}{dt}) = n \times \ln(1-\alpha) - \frac{E}{RT} + \ln A \qquad (5)$$

Using simple multiple regression, it is possible to determine both n and E. Finally, the determination of the most probable mechanism of reaction was carried out using the Coats – Redfern method which also allowed calculating the activation energy [23, 24]. This method relies on choosing a suitable kinetic function $g(\alpha)$ defined by the relation: $g(\alpha) = kt$ from the set of functions outlined by Khawam et al [25].

In this method, the relation between conversion and temperature takes the form:

$$\ln\frac{g(\alpha)}{T^2} = -\frac{E}{RT} + f(\beta) \qquad (6)$$

Where, $f(\beta)$ is a function of heating rate.

The plot performed between $\ln\frac{g(\alpha)}{T^2}$ against $\frac{1}{T}$ for different heating rates should produce a straight line of slope = (-E/R)

3. RESULTS AND DISCUSSION

3.1 TG – DTG Curves

Figure 1 shows the TG – DTG trace for the pyrolysis of cigarette butts at a heating rate of K.min⁻¹. The curves obtained at the three other heating rates were similar in nature although the devolatilization temperatures were different. In Fig. 1, two DTG peaks appear: The first, starting at 100 °C (373K) and ending slightly above

200 °C (473K), corresponds to volatilization of moisture and accounts for about 10% mass loss.
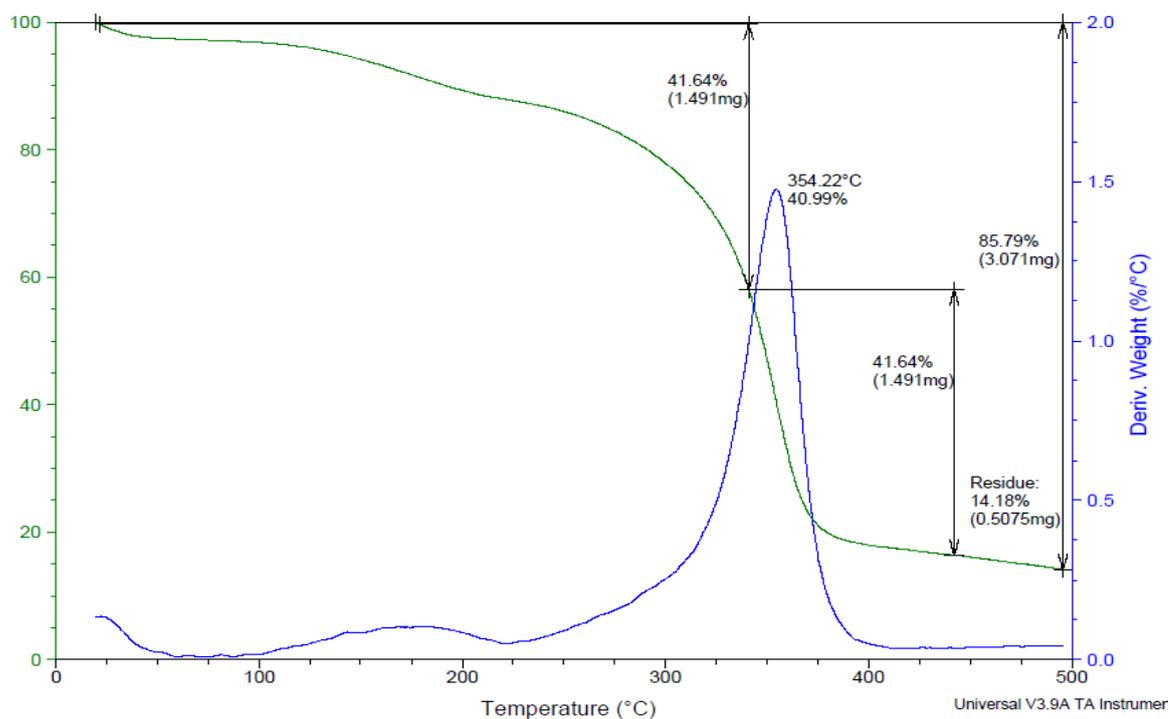

Fig. 1. TG – DTG curves for the pyrolysis of cigarette butts at heating rate = 10 K.min^{-1}.

The second peak, associated with the loss of the organic portion, starts at about 220 °C (393 K) ending at 400 °C (673 K). At the end of that step biochar is formed. The total loss at 500°C in mass amounts to about 85%.

It was possible to evaluate the conversion as function of temperature at the four chosen heating rates using Eq. (1). The results are shown in Fig. 2 where it appears that all four curves are similar in shape except that there is a shift towards higher decomposition temperatures at higher heating rates.
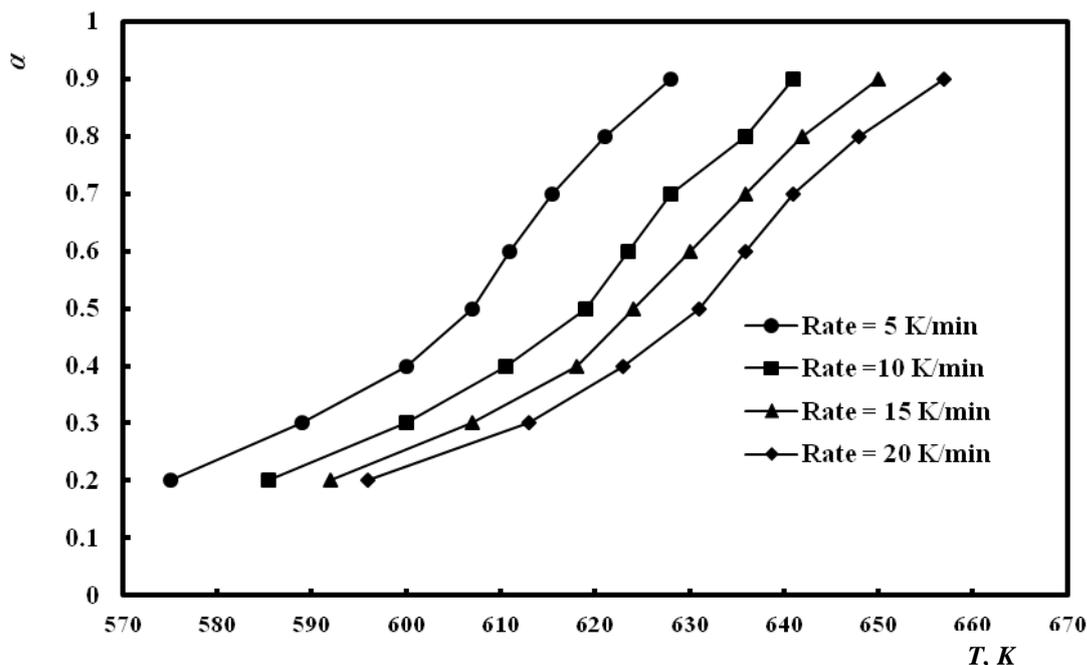
Fig. 2. Effect of heating rate on conversion – temperature curves.

3.2 Kinetics of Pyrolysis

3.2.1 Application of Kissinger method

The Kissinger method was first applied by plotting $\ln \dfrac{\beta}{T_p^2}$ against $\dfrac{1}{T}$ to obtain the straight line shown in Fig. 3. The numerical value of the slope (E/R) = 23616 corresponds to an activation energy of 196 kJ.mol^{-1}.

3.2.2 Application of the FWO method

The FWO method was used where selected values of conversion (α) were chosen and the corresponding temperatures (T K) at each heating rate (β) determined. Log β was plotted against $\dfrac{1}{T}$ as shown in Fig. 4. In principle, more or less parallel straight lines should result of slope $= \dfrac{-0.4567E}{R}$, from which the value of activation energy can be deduced.
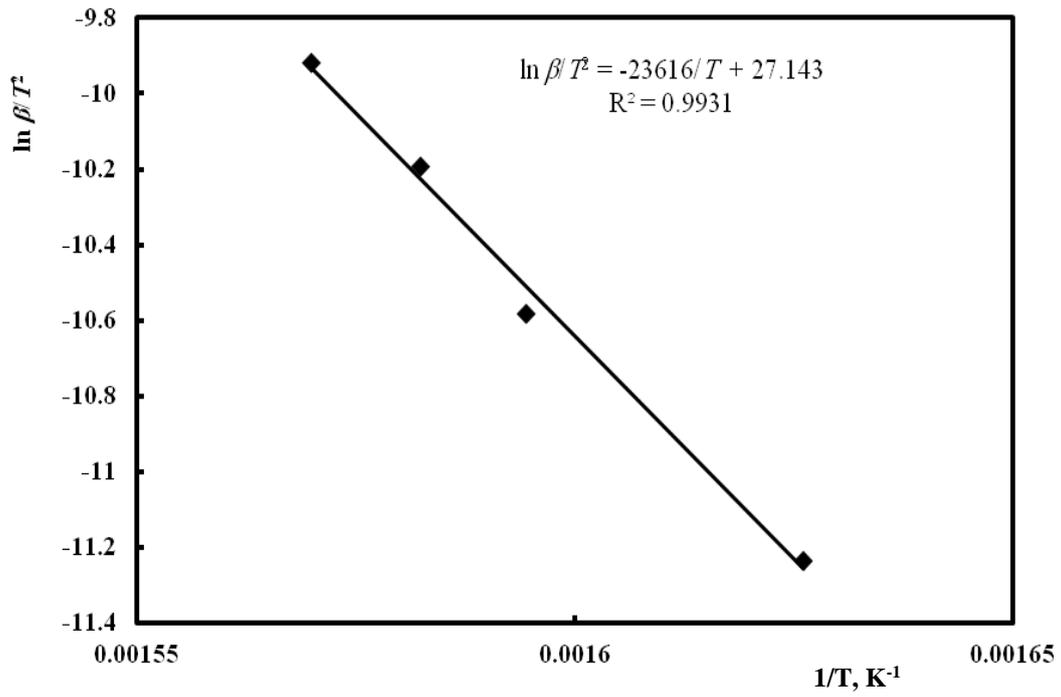
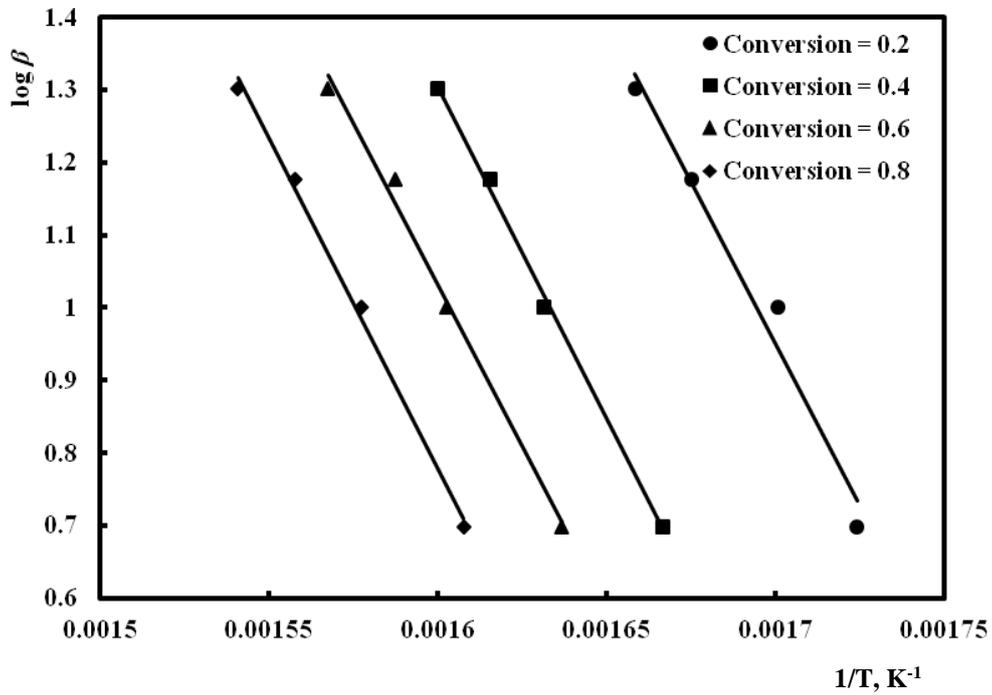Fig. 3. Kissinger plot for butt fibers pyrolysis.

Fig. 4. FWO plots for the pyrolysis of cigarette butts.

Figure 4 illustrates the lines obtained at conversions = 0.2, 0.4, 0.6 and 0.8 while Table 1 reveals the activation energies obtained at each heating rate. As can be seen, their values are close enough to assume that activation energy did not depend on conversion. The average value of activation energy is about 164 kJ.mol^{-1}.

Table 1. Values of activation energy calculated by the FWO method.

A	0.2	0.4	0.6	0.8
E, kJ.mol^{-1}	162.60	166.25	161.92	165.14

3.2.3 Application of the regression method

The multiple regression method was applied where Eq. (3) was used and a simple linear regression carried out to relate $\ln \dfrac{-dm}{dt}$ to $\ln(1-\alpha)$ and $\dfrac{1}{T}$.

The values of the apparent order of reaction (n) and activation energy (E) obtained at the different heating rates are compiled in Table 2. The average value of n = 0.93 and that of E = 166.2 kJ.mol^{-1}.

Table 2. Values of n and E obtained by the multiple regression method.

β, K.min^{-1}	5	10	15	20
N	0.85	0.91	1.09	0.88
E, kJ.mol^{-1}	145.3	178.0	182.2	159.3

3.2.4 Application of the Coats – Redfern method

The Coats – Redfern method was applied where the most suitable form of $g(\alpha)$ was found to be that of the diffusion-controlled model for cylindrical symmetry following the expression [25]:

$$g(\alpha) = \alpha + (1-\alpha) \times \ln(1-\alpha) \tag{7}$$

The use of that model for cylindrical particles agrees well with the fibrous nature of waste.

Figure 5 shows the plots of $\ln \dfrac{g(\alpha)}{T^2}$ against $\dfrac{1}{T}$ for different heating rates from which the slopes $\dfrac{-E}{R}$ were determined.
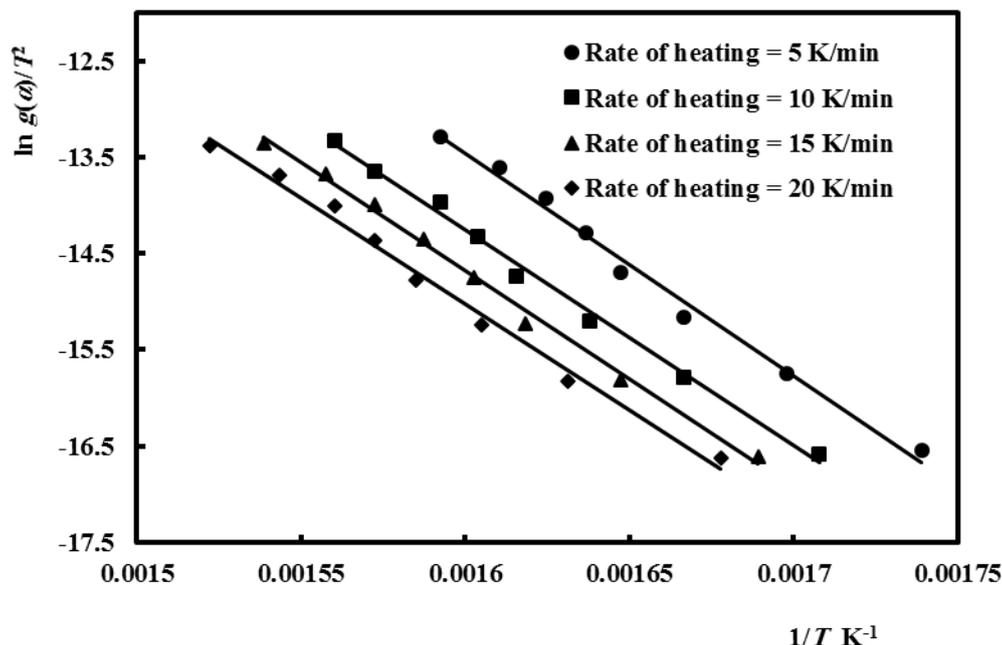

Fig. 5. Coats - Redfern plots for the pyrolysis of cigarette butts.

The values of activation energies obtained at different rates are tabulated below in Table 3 and yielded an average value of activation energy $=186.9$ kJ.mol^{-1}.

Table 3. Values of activation energy calculated by the Coats - Redfern method

β, K.min^{-1}	5	10	15	20
E, kJ.mol^{-1}	191.68	186.17	186.79	182.97

3.3 Determination of Calorific Value

Following the formation of biochar, a sample of 120 g cigarette butts was heated in a horizontal tube furnace under nitrogen flow to 400°C, soaked for 15 minutes, then cooled down to room temperature. The biochar formed was placed in the bomb calorimeter and its heating value was determined. Its value was found to be 27450 kJ.kg^{-1}. On the other hand, direct determination of the calorific value of

cigarette butts waste showed it to have a calorific value of 17200 kJ.kg^{-1}, a value close to that obtained by Kurmus et al [15] (16530 kJ.kg^{-1}), but higher than that recently reported by Mohajerani et al [26].

4. CONCLUSIONS

Seen as a potential source of energy, cigarette butts were subjected to thermal analysis under nitrogen flow. The thermogravimetric curves obtained at four different heating rates (5, 10, 15 and 20 K.min^{-1}) showed the occurrence of one major peak at the end of which biochar is formed, the temperatures of its formation increasing with increased heating rate. Four different methods were applied to determine the activation energy of that step, namely, the Kissinger and the FWO methods as non – model methods, a multiple regression method that can yield the apparent order of reaction and the Coats – Redfern method.

The values of activation energy obtained by the different methods showed comparable agreement, except for a moderately higher value obtained by the Kissinger method, Table 4.

Table 4. Comparison of the values of E obtained by different methods.

Method	Kissinger	FWO	C – R	Regression
Mechanism and order of reaction	N.D.	N.D.	Diffusion	$n = 0.93$
Average E, kJ.mol^{-1}	196	164	166.9	166.2

Determination of the calorific value of butts using a bomb calorimeter produced a value of 17200 kJ.kg^{-1} and that of biochar obtained from their pyrolysis was 27450 kJ.kg^{-1}.

It is worth mentioning that the establishment of an economic assessment regarding the pyrolysis of cigarette butts to produce biochar on a semi-industrial or industrial level is recommended. Such study is expected to yield positive results since the raw materials are almost priceless. The main problem is the method to be adopted to collect enough butts to justify a positive return.

DECLARATION OF CONFLICT OF INTERESTS

The authors have declared no conflict of interests.

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حركية التحليل الحراري لأعقاب السجائر

يتعرض هذا البحث إلى دراسة إعادة استخدام أعقاب السجائر والتي تعد من النفايات الخطرة كمصدر للطاقة. حيث تم طحنها وتجفيفها وتعريضها للتحلل الحراري في جهاز تحليل حراري تحت تدفق غاز النيتروجين بأربعة معدلات تسخين مختلفة ($5, 10, 15, 20$ K.min^{-1}) وقد أظهرت منحنيات التحلل الحراري خسارة كبيرة في الكتلة متبوعة بتكوين الفحم الحيوي. تم فحص حركية تكوين الفحم الحيوي باستخدام أربع طرق مختلفة (Regression, C – R, FWO, and Kissinger) لتحديد طاقه التنشيط لهذه الخطوة وأظهرت النتائج تقاربا في القيم، باستثناء القيمة الأعلى التي تم الحصول عليها بواسطة طريقة كيسنجر (Kissinger) وهي ١٩٦ كيلوجول / مول. كذلك تم تحديد القيمة الحرارية لأعقاب السجائر بواسطه (Bomb calorimeter) وهي ١٧٢٠٠ و ٢٧٤٥٠ كيلوجول / كيلوجرام باستخدام التحليل الحراري.