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Kinetic study of the thermal degradation of alkaline straw black liquor in nitrogen atmosphere

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Abstract

The kinetics of solid weight loss in the pyrolysis of straw black liquor solids at low temperature ($<500\,^{\circ}$C) has been studied by thermogravimetric techniques in nitrogen atmosphere. Isothermal and dynamic experiments have been performed.

Assuming a first order for the thermal decomposition rate of the solid at a given temperature, the instantaneous kinetic constant for the same temperature diminishes as the reaction proceeds. This could be due mainly to the heterogeneity of straw black liquor solids. Both, the pre-exponential factor and the activation energy of the Arrhenius law, seem to vary linearly with the solid conversion.

Keywords: Pyrolysis; Thermogravimetric studies; Lignocellulosic solid

1. Introduction

Black liquor (BL) is the residue from the cooking of wood, straw or other fibrous plants in the production of pulp and paper. Lignin, hemicellulose, other carbohydrates and inorganic compounds dissolve and form part of the black liquor. Recovery of the chemicals used, as well as of the energy contained in the organics, is important for the economics of the paper mill.

Nowadays the recovery cycle is based on the black liquor burning producing steam and a slag. Approximately 35% of the total energy requirement in the pulp and paper industry comes from black liquor combustion [1]. However this process presents some disadvantages such as low energy efficiency and operational problems. These problems increase particularly when black liquor proceeds from cereal straw, which explains the importance of studying the possible implementation of alternative technologies [2]. Black liquor gasification is generating particularly high expectations because the development of combined-cycle co-generation can provide more electrical power relative to steam in pulp mills [3].

Pyrolysis is also a potential process for using black liquor as a source of fuel production, but it is also important as an initial stage of gasification and combustion processes. For example, the properties and yield of pyrolytic products (char, tar and gas) determine the energy requirements and the optimal operating conditions for gasifying black liquor char. If the gas yield is increased to the detriment of the char yield during black liquor pyrolysis, black liquor char gasification would be more energy efficient, because char gasification reactions require more energy and are slower than black liquor pyrolytic reactions [4]. In addition, tar production has been identified as a problem for low temperature gasification of kraft black liquor because tar is a non-desirable product in industrial processes [5]. The tar yield greatly depends on pyrolysis reactions. A good knowledge of BL pyrolytic behavior is required for the design of new gasifiers and combustors. Thus, the study of black liquor pyrolysis is important from the scientific and industrial points of view. There are few papers to be found on this subject in the literature, and most of the available data deals with kraft wood BL. Some previous works have studied the composition of the gas resulting from kraft wood BL pyrolysis as a function of residence time in the reactor, temperature, pressure and heating rate [1,3,5,6,7]. Other authors have determined the behavior of the organic components of kraft wood black liquor during their devolatilization by means of thermogravimetric studies [8]. Another widely studied phenomenon is BL swelling: during its pyrolysis the volume of a liquid droplet can increase up to thirty times [9]. Studies performed with laboratory-produced BL show that its composition has a

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great influence on swelling [10]. In another research work [11] it was found that hemicelluloses, such as xylan, have a great influence on swelling (even small amounts leading to a noticeable increase in the volume), and that aliphatic carboxylic acids are the main source of the volatile release needed for the swelling [12,13], whereas the effect of lignin in pyrolysis is to delay this release of volatiles. The studies cited have been performed with kraft BL. A study performed with the straw BL used in this paper [14] shows that this BL swells more than kraft BL. Both BL types show that the volume of the swelling is bigger in pyrolysis than in combustion atmospheres.

If there is, relative to other biomass residues, little data on kraft wood BL pyrolysis, information about the pyrolysis of soda straw black liquor is still more limited. Puértolas et al. [15] evaluated the influence of a previous oxidation stage at low temperature on the surface area of the resulting char from straw BL pyrolysis. More recently, Gea et al. [16] performed a thermogravimetric study to determine the influence of the temperature (500–900 °C), heating rate (5–30 °C/min) and the concentration of CO (0–40 vol.%) in inert atmospheres on the solid conversion and the devolatilization rate during the pyrolysis of this type of straw BL. However, virtually no data is available about kinetic equations relating to straw BL. Since straw and wood BL are different types of liquors (the differences have already been reported in detail elsewhere [16]), both liquors can behave very differently in the same recovery boiler under the same operating conditions [17]. Therefore, a specific study of each type of liquor is required to characterize their behavior during pyrolytic reactions and to determine each kinetic equation.

The thermal decomposition of straw black liquor seems to take place in two different steps [16]. The first is at temperatures below 550 °C, where the decomposition of the organic matter of the BL mainly occurs, while the second is at temperatures higher than 600 °C, where the decomposition of alkaline carbonates, which form part of the inorganic fraction of black liquor, can take place. To begin with, it is easier to study both steps separately. A previous work about the thermal decomposition of straw BL [16] was performed at high temperatures (higher than 500 °C). The present work studies the thermal degradation of straw BL at low temperatures (lower than 500 °C). The reason for using these low temperatures is to make sure that the weight loss is due to organic material decomposition [18]. Both works can be considered as complementary.

2. Experimental

The black liquor used in this study was supplied by a Spanish paper mill where cereal straw is cooked with soda as the only chemical.

The straw black liquor, as produced, has a solid content ranging between 5 and 10% in weight. Before being used in the thermogravimetric system, it is carefully dried in an oven at 105 °C until completely dry. The black liquor solids (BLS) obtained are crushed and sieved to a particle diameter smaller than 150 μm. The ultimate analysis of the BLS, obtained in a CHNS Carlo Erba elemental analyzer (mod. EA 1108), is shown in Table 1, as well as the content of Cl, K, Na and Si. The ash content of BLS is 22.2%. The organic composition is (wt.% dry basis) alkali lignin: 25.2%, hemicellulose: 9.7%, carboxilyc acids: 39.3%.

The thermogravimetric study was performed in a Cahn Instruments TG-131. A nitrogen flow rate of 150 Ncm^3/min was set with a mass flow controller in order to purge the reaction chamber. Around 15 mg of BLS were evenly placed on the sample pan. These conditions were chosen, after some previous experiments performed, in order to avoid any external and extraparticular mass transfer limitations.

Two kinds of experiment were performed: isothermal and dynamic.

In the isothermal experiments the sample was heated at a constant heating rate of 5 °C/min up to the final temperature, which was maintained for long enough (up to 48 h) to assure complete decomposition. Experiments were performed from 200 to 500 °C, although only the data obtained up to 300 °C have been used to calculate the kinetics, as at higher temperatures the sample is almost completely decomposed when the final temperature is reached.

In the dynamic experiments, the BLS was heated at different heating rates ranging from 1 to 75 °C/min, up to a temperature of 500 °C. Higher temperatures can lead to volatilization of part of the inorganic content of the BLS.

Experiment reproducibility was checked with dynamic experiments. Calcium oxalate monohydrate was used to check balance reproducibility under experimental conditions similar to the ones used for BLS. The variation in final conversion was found to be 1.08%, where as the variation in final conversion for BLS was 1.41% (for three runs in each case), so it was considered that experimental reproducibility was good.

3. Results

The results obtained are shown here as solid conversion values, X_s, defined as the ratio between the solid weight loss

Table 1
Elemental composition of straw BLS

Elements	% in weight
C	39.05
H	4.54
N	1.00
S	0.78
Cl	3.50
K	4.10
Na	8.83
Si	0.23
Others	37.97

at a given time (ΔW) and the initial dry and ash free weight (W_0), calculated by subtracting the ash from the initial sample weight. As the study was performed at low temperatures, it is assumed that the weight loss observed is due only to organic material decomposition:

$$X_s = \frac{\Delta W}{W_0} \tag{1}$$

3.1. Isothermal experiments

The X_s values obtained in nitrogen atmosphere are shown in Fig. 1.

It can be observed that the different conversion curves show two sections. In the first, the X_s increases sharply due to the initial heating of the sample. Subsequently, the X_s increases asymptotically to a final value.It is considered that the solid conversion variation during pyrolysis can be represented by a power-law equation [19]:

$$\frac{dX_s}{dt} = k(A_s - X_s)^n \tag{2}$$

where A_s is the maximum conversion attainable at a given temperature for a lignocellulosic solid in the reaction atmosphere, and n is the reaction order. Under pyrolysis conditions A_s is always smaller than 1, and its value at different temperatures was calculated as the final X_s for each isothermal experiment. Fig. 2 shows the values obtained up to 500 °C.

It has been found that $n = 1$ for other materials such as cellulose and pine sawdust [19] as well as for a kraft BL [7].

Assuming also a first order decomposition for the straw BLS, it is possible to numerically calculate an instantaneous value of the kinetic constant from the value of the slope of the curves shown in Fig. 1 (dX_s/dt) and Eq. (2). The values of the instantaneous kinetic constant obtained for the isothermal experiment performed at 225 °C are shown versus X_s in Fig. 3. It can be observed that the apparent instantaneous first order kinetic constant k decreases as the decomposition proceeds, showing that the decomposition rate for BLS depends not only on the pyrolysis temperature but also on the composition of the solid present at a given time, which depends on X_s. Similar curves result from the data obtained at the other temperatures tested.

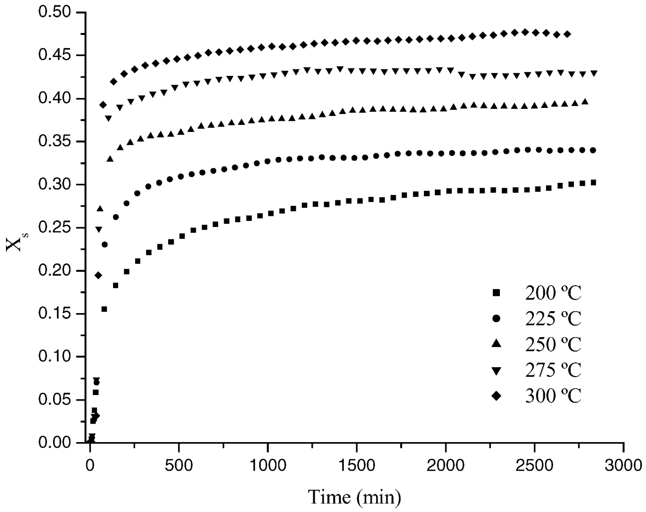

Fig. 1. X_s vs. time. Isothermal experiments.

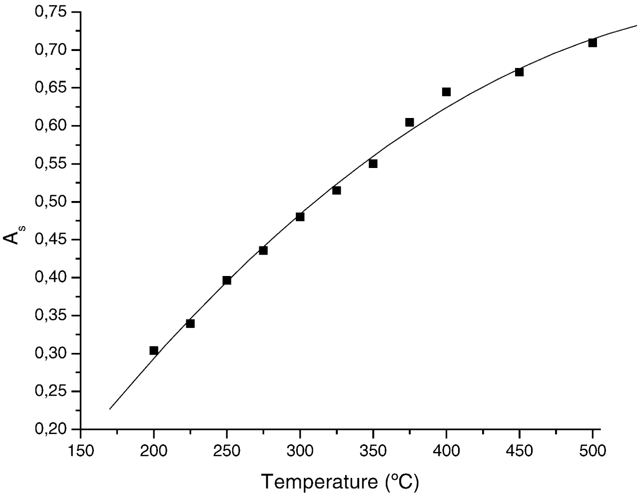

Fig. 2. A_s vs. temperature.

The decrease observed in the kinetic constant could be due to the heterogeneity of straw BLS: more reactive compounds (with a higher k) could decompose earlier and, as the reaction proceeds, less reactive compounds (with a lower k) would be left in the solid residue, without one specific compound predominating during the isothermal period.

The heterogeneity of straw BLS causes that its thermal decomposition takes place through a complex series of chemical reactions, which makes it an extremely difficult task to establish a mechanism for the pyrolysis. For this reason, and in order to keep the model for the decomposition simple, it has been assumed that the effect of the material heterogene-

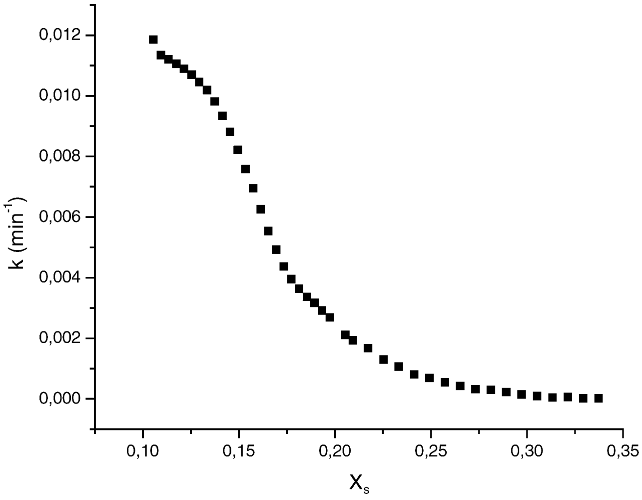

Fig. 3. Instantaneous k calculated vs. X_s. Isothermal experiment ($T = 225$ °C, $n = 1$).

ity on the observed kinetic constant is to change the value of both the pre-exponential factor and the activation energy in the Arrhenius law expression, and that the relationship between these parameters and X_s is a linear one, so that the dependence of the kinetic constant on temperature and conversion could be written as in Eq. (3):

$$k = (P_1 + P_2 X_s)e^{-(P_3+P_4X_s)/T} \tag{3}$$

By means of a non-linear algorithm, the k values obtained from Eq. (2) (assuming $n = 1$) at the different temperatures tested were fitted to Eq. (3). The parameters calculated are $P_1 = 4.8 \times 10^{11}\ \text{min}^{-1}$, $P_2 = -1.11 \times 10^{12}\ \text{min}^{-1}$, $P_3 = 17820\ \text{K}$, $P_4 = 6510\ \text{K}$. With the parameters obtained, the pre-exponential factor decreases with the solid conversion while the activation energy increases. Both effects cause the kinetic constant calculated to decrease as the reaction proceeds. The fitting curves obtained are shown together with the experimental k values in Fig. 4.

As can be seen, the fitting curve approaches the experimental values reasonably well, with a correlation coefficient of 0.927.

In order to confirm that the pyrolysis of straw BLS at low temperatures can be properly described by Eq. (3), dynamic experiments were performed in nitrogen atmosphere.

3.2. Dynamic experiments

Dynamic experiments of thermal decomposition of BLS in a nitrogen atmosphere were performed. The BLS was heated at different heating rates (1, 5, 10, 20, 40, 50, 60 and 75 °C/min) up to a temperature of 500 °C. X_s curves versus temperature are shown in Figs. 5 and 6.

In a first stage the results of X_s obtained experimentally have been compared with those calculated using Eqs. (2) and (3) with $n = 1$. For this calculation, Eq. (2) has been numerically integrated using the Simpson method. The initial conditions considered for the integration were $T_i = 200\ °\text{C}$, $X_i = X_{\text{exp}}$. T_i is the temperature at which thermal decomposition of BLS is considered to begin and X_{exp} is the solid conversion experimentally obtained at $T = T_i$. The temperature variation over time is governed by the heating rate at which the experiment was carried out (T (°C) $= 200\ °\text{C} + \beta t$). Data of X_s were calculated up to a solid conversion of approximately 0.45.

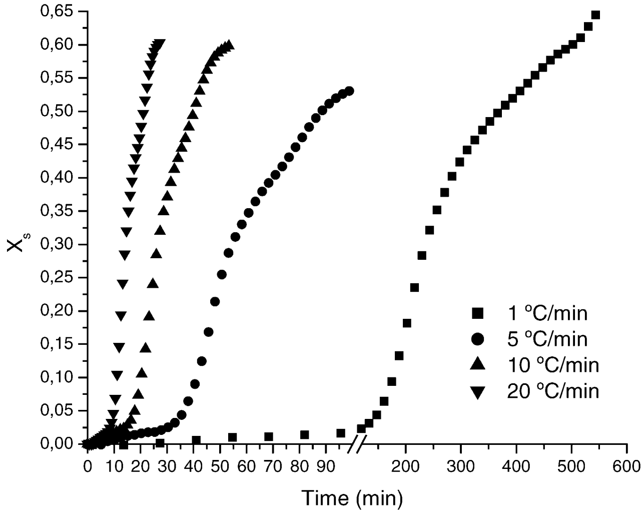

Fig. 5. Results of dynamic experiments for 1, 5, 10 and 20 °C/min.

The values of X_s calculated at heating rates from 1 to 75 °C/min are represented versus the experimentally obtained in Fig. 7.

It can be observed that for the data obtained at 1, 5 and 10 °C/min, the agreement between the calculated and the experimental data is quite good, with a linear regression coefficient of 0.976 (1 °C/min), 0.974 (5 °C/min) and 0.961 (10 °C/min). However, the higher the increase in the heating rate, the greater the deviation between calculated and experimental results.

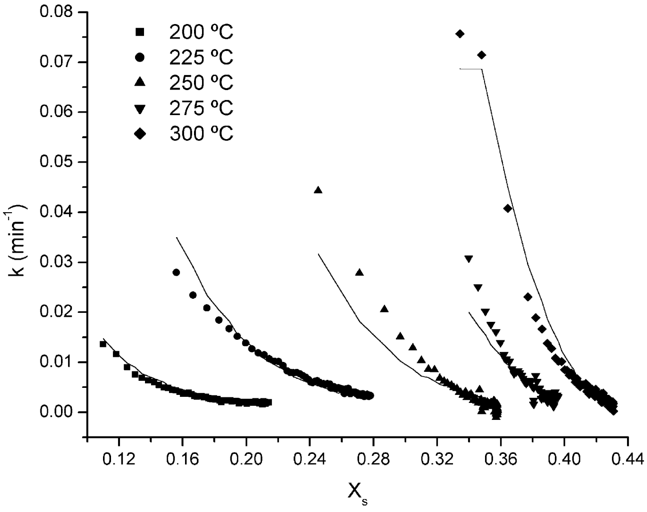

Fig. 4. Fitting curve obtained from isothermal experiments.

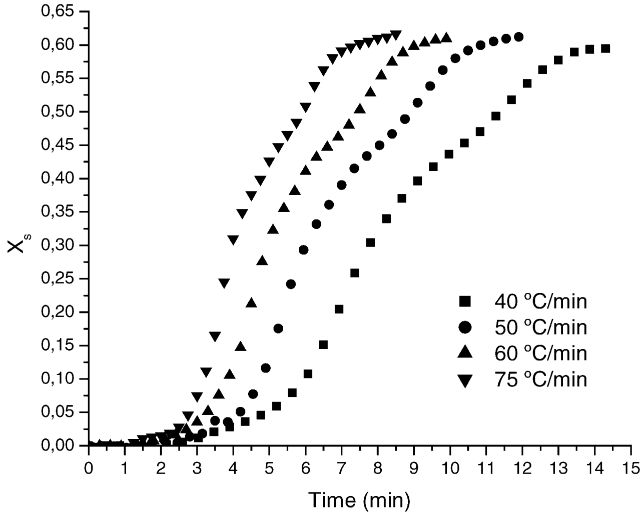

Fig. 6. Results of dynamic experiments for 40, 50, 60 and 75 °C/min.

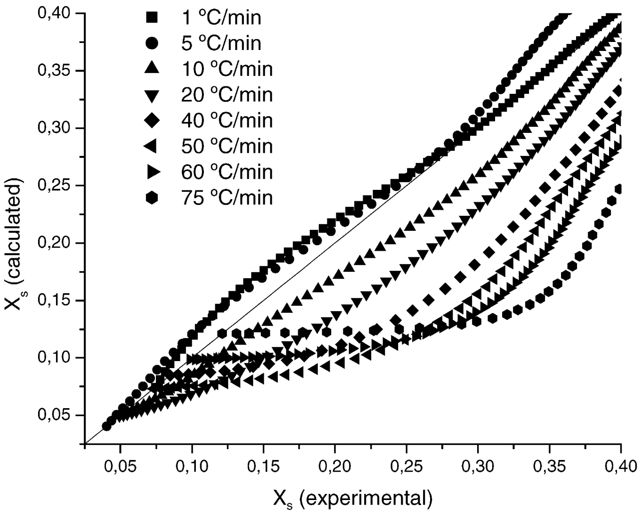

Fig. 7. X_s calculated vs. X_s experimental.

As pointed out in a previous research work [20] with different materials, for dynamic experiments solid conversion is a function of time and temperature. The heating rate must therefore be taken into account when relating isothermal to dynamic experiments. Thus it can be considered that:

$$X_s = f(t, T) \tag{4}$$

and

$$\left(\frac{dX_s}{dt}\right)_\beta = \left(\frac{\partial X_s}{\partial t}\right)_T + \left(\frac{\partial X_s}{\partial T}\right)_t \frac{dT}{dt} \tag{5}$$

where $dT/dt = \beta$, the heating rate of the dynamic experiment.

The values of $(\partial X_s/\partial t)_T$ correspond to the calculated with isothermal experiments and they must be calculated for a given time. Eq. (5) can thus be written as:

$$\left(\frac{dX_s}{dt}\right)_\beta = (P_1 + P_2 X_s) e^{-(P_3+P_4X_s)/T}(A_s - X_s) + \left(\frac{\partial X_s}{\partial T}\right)_t \beta \tag{6}$$

This equation is valid only up to the time when $X_s = A_s$ and for not very high values of β.

The data from the dynamic experiments carried out at 20 and 60 °C/min were used to calculate a value of $(\partial X_s/\partial T)_t$, in order to minimize the difference between the calculated and experimental values of X_s. This value was found to be 0.0023.

Integrating numerically Eq. (6) with this value of $(\partial X_s/\partial T)_t$ for the heating rates higher than 10 °C/min, new values are calculated for X_s. These new values are shown in Fig. 8.

It can be observed in Fig. 8 that the calculated values of X_s are in much better agreement with the experimental data with the heating rate factor added, $(\partial X_s/\partial T)_t$. The values of the linear regression coefficient were 0.976 (20 °C/min), 0.990 (40 °C/min), 0.980 (50 °C/min), 0.948 (60 °C/min), 0.825 (75 °C/min). The regression coefficients calculated show that the agreement between the calculated and experimental data is good for heating rates of up to 60 °C/min. For the highest heating rate tested, the mechanism of the thermal decomposition does not seem to follow Eq. (6).

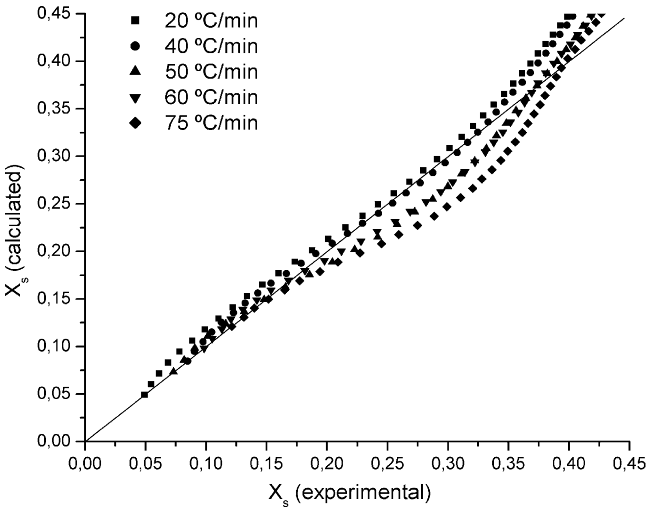

Fig. 8. X_s calculated with $(\partial X_s/\partial T)_t = 0.0023$ vs. X_s experimental.

4. Conclusions

The pyrolysis of black liquor at low temperatures has been studied by thermogravimetric techniques (isothermal and dynamic experiments)in a nitrogen atmosphere. The objective of keeping the temperature lower than 500 °C is to assure that the solid weight loss can be ascribed only to organic compound decomposition.

It has been found that, for isothermal experiments and assuming a first order decomposition for BLS pyrolysis, the kinetic constant observed changes as the BLS decomposes, which could be due to a change in the chemical composition of whatever material is decomposing. In order to fit the data, it has been assumed that both the pre-exponential factor and the activation energy of the kinetic constant have a linear dependency on the solid conversion X_s.

For dynamic experiments the kinetic equation for the decomposition of BLS can be integrated, giving a good agreement between the calculated values of X_s and the values obtained experimentally for the heating rates of 1, 5 and 10 °C/min. As has been found in previous works, the weight loss at higher heating rates also depends on the heating rate of the experiment. A value of 0.0023 was found for the factor $(\partial X_s/\partial T)_t$. Using this factor, a good agreement between calculated and experimental values of X_s is obtained for heating rates up to 60 °C/min. Values of X_s calculated for higher heating rates do not show such a good correlation. This could be due to a change in the pyrolysis mechanism.

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