

## KINETICS OF WEIGHT LOSS BY THERMAL DECOMPOSITION OF XYLAN AND LIGNIN. INFLUENCE OF EXPERIMENTAL CONDITIONS

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### ABSTRACT

The kinetics of weight loss in the thermal decomposition of xylan and lignin in a nitrogen environment have been studied thermogravimetrically. The data from this study are analysed in the light of previous conclusions obtained with cellulose. The results from isothermal and dynamic experiments at different heating rates are related by using the results of dynamic experiments with low heating rates ( $1.5^{\circ}\text{C min}^{-1}$ ) as a reference.

### NOTATION

$A_S$	pyrolysable weight fraction at a given temperature, dry basis
$C_p$	specific heat of solid
$H$	weight percentage of material pyrolysed at $150^{\circ}\text{C}$
$\Delta H_{r2}$	heat of reaction for thermal decomposition of the solid
$k_S$	kinetic coefficient for thermal decomposition of the solid
$k_{S_i}$	kinetic coefficient for thermal decomposition of the solid, obtained from isothermal experiments
$k_{S_{1.5}}$	kinetic coefficient for thermal decomposition of the solid, obtained from dynamic experiments at $\beta = 1.5^{\circ}\text{C min}^{-1}$
$k_{S_\beta}$	kinetic coefficient for thermal decomposition of the solid, obtained from dynamic experiments
$n$	order of reaction with respect to the solid
$t$	time
$t_i$	time at which the isothermal period starts
$t_1$	time at which the temperature $T_{f_1}$ is reached
$t_2$	time at which the temperature $T_{f_2}$ is reached
$t_3$	time at which the temperature $T_{f_3}$ is reached
$T$	solid temperature
$T_f$	oven temperature

$T_{f_1}$	oven temperature at the end of the first interval
$T_{f_2}$	oven temperature at the end of the second interval
$T_{f_3}$	oven temperature at the end of the third interval
$T_i$	temperature of isothermal pyrolysis
$W$	weight of solid after $t$ seconds of reaction time
$W_{OS}$	initial weight of solid, dry basis
$W_\infty$	final weight of solid for a given temperature, at the end of the pyrolysis process
$X_S$	conversion of solid, dry basis
$X_{S_i}$	conversion of solid at the start of the isothermal period, dry basis
$\beta$	heating rate

## INTRODUCTION

The rate of weight loss of lignocellulosic waste materials by thermal decomposition is strongly influenced by the physical and chemical characteristics of the material in question.

Obtaining kinetic expressions for the thermal decomposition of lignocellulosic waste materials directly is often difficult, as each of their main constituents (hemicellulose, cellulose and lignin) undergoes decomposition at a different rate. Therefore, knowledge of the thermal decomposition kinetics of the main constituents can serve as a guide when trying to predict the thermochemical behaviour of a given lignocellulosic material of known composition.

In previous works [1,2], Bilbao and co-workers have reported on studies of the kinetics of the thermal decomposition of cellulose in a nitrogen atmosphere using thermogravimetric methods. The findings of these works are useful in establishing the influence of different operating variables, and in selecting an appropriate range of experimental conditions. In the present work, new results are presented for xylan (which has been used as a representative of hemicellulosic materials) and lignin.

## EXPERIMENTAL

Weight losses for these materials were measured in a nitrogen atmosphere using a Perkin-Elmer TGS-2 thermobalance. Xylan was supplied by the Sigma Chemical Company, while the lignin used came from the Department of Chemical Engineering, Málaga, Spain.

Conclusions from the previous work with cellulose led to the selection of two basic types of experiment.

(i) Isothermal experiments, which are started with a low heating rate until the desired temperature is reached. This temperature is then kept constant

throughout the pyrolysis process. The use of a low heating rate ensures that no temperature gap exists between the solid and its surroundings.

(ii) Dynamic experiments, in which there is no constant temperature period. Instead, a constant heating rate is maintained throughout the experiment.

The influence of weight loss at temperatures below 150°C (which is mainly due to moisture evaporation) on the conversion values observed [1] was taken into account by referring all conversion values to a dry basis. Thus, conversion was defined as

$$X_S = \frac{W_{OS} - W}{W_{OS}} \quad (1)$$

## RESULTS AND DISCUSSION

### *Isothermal experiments*

As stated above, isothermal experiments were carried out with a low preheating rate (1.5°C min<sup>-1</sup>) in order to minimize external heat transfer resistances, thus ensuring that the temperature measured when the isothermal period was started did actually correspond to the true sample temperature.

Experiments were carried out at temperatures ranging from 200 to 300°C for xylan, and from 275 to 400°C for lignin. Continuing to higher temperatures with the heating rate used would bring about the reaction of most of the solid during the preheating period, and consequently very few data would be obtained in the isothermal period of the experiment.

The pyrolysable fraction  $A_S$  can be determined at different temperatures from isothermal experiments.  $A_S$  is defined as

$$A_S = \frac{W_{OS} - W_\infty}{W_{OS}} \quad (2)$$

Figure 1 shows the values of  $A_S$  obtained at different temperatures for xylan and lignin. Higher values can be observed for the former.

The weight loss was referred to the initial sample weight (on a dry basis), according to the equation

$$-\frac{1}{W_{OS}} \frac{dW}{dt} = k_S \left( \frac{W - W_\infty}{W_{OS}} \right)^n \quad (3)$$

From eqns. (1), (2) and (3) we can write

$$\frac{dX_S}{dt} = k_S (A_S - X_S)^n \quad (4)$$

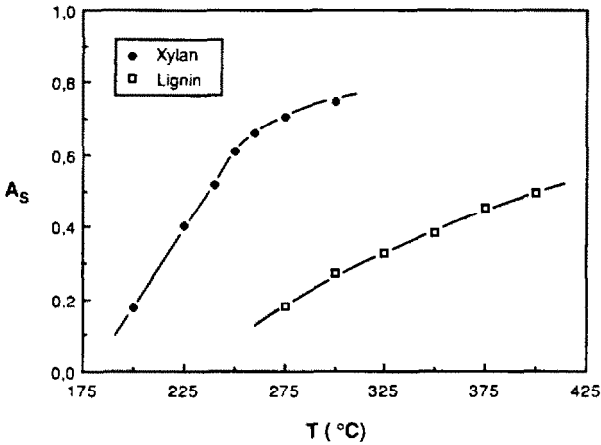


Fig. 1. Values of  $A_S$  vs. temperature for xylan and lignin.

This equation can be linearized. For the isothermal experiments we can write

$$\log \frac{dX_S}{dt} = \log k_{S_i} + n \log(A_S - X_S) \quad (5)$$

from which the value of the reaction order can be determined.

For xylan,  $n$  was found to be equal to 1 at temperatures below  $250^\circ\text{C}$ . At higher temperatures, values of  $n$  higher than 1 were obtained, which could be indicative of the decomposition of other constituents (present as impurities in the xylan samples used) at these temperatures. However, given the fact that most of the decomposition of hemicelluloses takes place at low temperatures, the results obtained at  $T < 250^\circ\text{C}$  are the ones to be considered when comparing data from xylan and from lignocellulosic materials. The value of  $n$  found for lignin was equal to 1 in the temperature range studied.

Thus, for  $n = 1$ , eqn. (4) becomes

$$\frac{dX_S}{dt} = k_{S_i}(A_S - X_S) \quad (6)$$

which can be written as

$$\ln(A_S - X_S) = \ln(A_S - X_{S_i}) + k_{S_i}t_i - k_{S_i}t \quad (7)$$

From eqn. (7) the values of the kinetic constant can be obtained using data from isothermal experiments.

The values of the kinetic constants for the thermal decomposition of xylan and lignin are shown in Tables 1 and 2 respectively. The conversion ranges investigated are also indicated.

TABLE 1

Kinetic constants obtained in isothermal experiments with xylan

Experiment	$T_i$ ( $^{\circ}\text{C}$ )	$X_S$	$k_{S_i}$ ( $\text{min}^{-1}$ )
XI-8	200	0.0402–0.1351	0.00518
XI-7	225	0.0797–0.3504	0.00799
XI-12	240	0.1460–0.4745	0.01121
XI-6	250	0.2174–0.3696	0.01922
		0.3696–0.5652	0.00959
		0.2174–0.5652	0.01092
XI-11	260	0.3376–0.4872	0.02189
		0.4872–0.6047	0.00990
		0.3376–0.6047	0.01187
XI-9	275	0.4451–0.5518	0.02415
		0.5518–0.6799	0.01052
		0.4451–0.6799	0.01218
XI-10	300	0.6019–0.6388	0.02479
		0.6388–0.7285	0.01364
		0.6019–0.7285	0.01441

*Dynamic experiments*

Isothermal experiments with low preheating rates are not useful for the study of pyrolysis at higher temperatures, because the temperatures are reached at high values of solid conversion, so few kinetic data are obtained. This difficulty is overcome by the use of dynamic experiments, with heating rates of  $\beta = 1.5\text{--}80^{\circ}\text{C min}^{-1}$ .

The values of the kinetic constant  $k_{S\beta}$  for each temperature and heating rate were obtained by taking  $n = 1$  in eqn. (4) and using the experimental values  $dX_S/dt$  and  $(A_S - X_S)$ .

Previous work carried out with cellulose [1,2] has indicated that the use of low heating rates minimizes the gap between the temperature of the solid  $T$

TABLE 2

Kinetic constants obtained in isothermal experiments with lignin

Experiment	$T_i$ ( $^{\circ}\text{C}$ )	$X_S$	$k_{S_i}$ ( $\text{min}^{-1}$ )
LI-4	275	0.0835–0.1643	0.01515
LI-1	300	0.1410–0.2031	0.02222
		0.2134–0.2588	0.01253
LI-2	325	0.2189–0.2606	0.03111
		0.2670–0.3189	0.01293
LI-3	350	0.2838–0.3669	0.01164
LI-6	375	0.3361–0.4308	0.01140
LI-5	400	0.3891–0.4744	0.01137

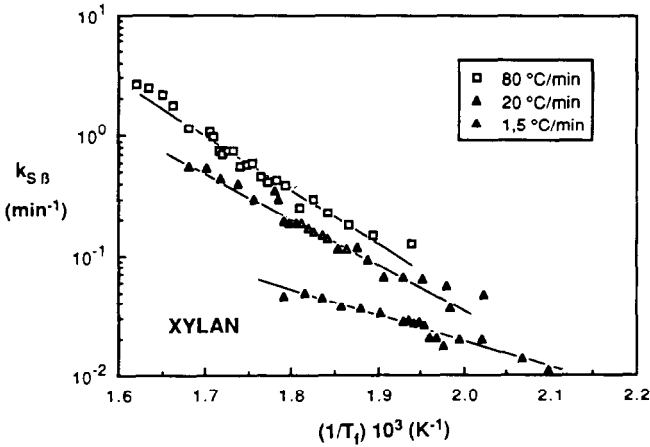


Fig. 2. Values of  $k_{S\beta}$  vs.  $1/T_f$  for xylan.

and the temperature measured in the thermogravimetric system  $T_f$ . A heating rate of  $\beta = 1.5^\circ\text{C min}^{-1}$  was used in this work, in order to ensure that the temperature gap was negligible. The values of  $k_{S\beta}$  obtained can be described by the following expressions

$$\text{Xylan: } k_{S_{1.5}} (\text{min}^{-1}) = 590 \exp(-10200/RT) \quad T \leq 280^\circ\text{C} \quad (8)$$

$$\text{Lignin: } k_{S_{1.5}} (\text{min}^{-1}) = 1.55 \times 10^5 \exp(-17750/RT) \quad T \leq 325^\circ\text{C} \quad (9)$$

Obtaining kinetic data at temperatures higher than those indicated for eqns. (8) and (9) requires the use of higher values of  $\beta$ . Figures 2 and 3 show the values of  $k_{S\beta}$  found for xylan and lignin as a function of  $1/T_f$ , using different heating rates. It can be observed that, for a given temperature of

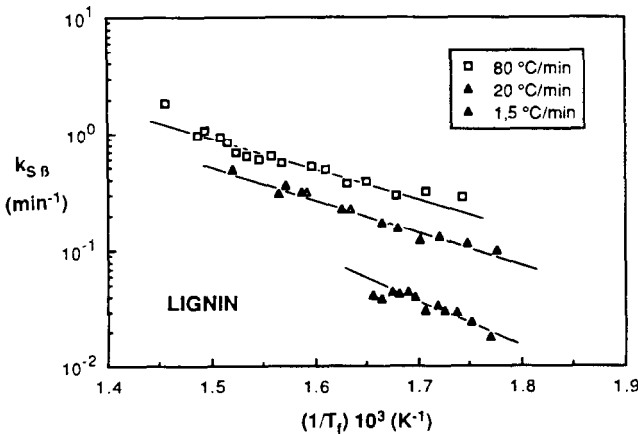


Fig. 3. Values of  $k_{S\beta}$  vs.  $1/T_f$  for lignin.

TABLE 3

Values of  $T_{f_1}$ ,  $T_{f_2}$  and  $T_{f_3}$  for xylan

Experiment	$\beta$ ( $^{\circ}\text{C min}^{-1}$ )	$T_{f_1}$ ( $^{\circ}\text{C}$ )	$t_1$ (min)	$T_{f_2}$ ( $^{\circ}\text{C}$ )	$t_2$ (min)	$T_{f_3}$ ( $^{\circ}\text{C}$ )	$t_3$ (min)
XC-1	80	71	0.45	133	1.225	217	2.275
XC-2	40	60	0.625	99	1.60	207	4.30
XC-3	20	53	0.90	127	4.60	191	7.80
XC-5	10	48	1.30	101.5	6.65	188	15.30
XC-7	5	41	1.20	96	12.20	182	29.40
XC-4	2.5	41.5	2.60	93.5	23.40	168.5	53.40
XC-6	1.5	40.1	3.40	86.6	34.40	166.4	87.60

the thermogravimetric system, an increase in the heating rate gives rise to an increase in the kinetic constant obtained.

These results differ from those obtained with cellulose [1], for which increased values of  $\beta$  gave rise to lower values of  $k_{S\beta}$ , for the same temperature of the system. This previous observation was explained in terms of the temperature gap between the solid and the oven for high heating rates. This temperature gap was accounted for by the use of a mathematical model which allowed prediction of the solid temperature as a function of the oven temperature and the heating rate employed [2].

The same model has been applied to the results obtained with xylan and lignin. The model considers three temperature intervals before reaching the temperature at which the main decomposition takes place. The values of  $T_{f_1}$ ,  $T_{f_2}$  and  $T_{f_3}$  obtained experimentally for xylan and lignin are shown in Tables 3 and 4.

It can be observed that as  $\beta$  is increased,  $T_f$  also increases, i.e. a higher temperature of the system is needed to obtain the same temperature in the solid. These results seem to indicate the existence of a temperature gap when high values of  $\beta$  are used. Therefore, the difference with respect to the behaviour observed with cellulose should lie in the fourth temperature

TABLE 4

Values of  $T_{f_1}$ ,  $T_{f_2}$  and  $T_{f_3}$  for lignin

Experiment	$\beta$ ( $^{\circ}\text{C min}^{-1}$ )	$T_{f_1}$ ( $^{\circ}\text{C}$ )	$t_1$ (min)	$T_{f_2}$ ( $^{\circ}\text{C}$ )	$t_2$ (min)	$T_{f_3}$ ( $^{\circ}\text{C}$ )	$t_3$ (min)
L-2	80	73	0.475	157	1.525	245	2.625
L-3	40	70	0.875	170	3.375	211	4.400
L-6	20	70	1.750	128	4.650	192	7.850
L-5	10	47	1.200	101	6.600	176	14.100
L-4	5	45	2	85	10	158	24.600
L-7	1.5	50.6	10.400	—	—	152.3	78.200

interval, i.e. should be related to the thermal decomposition of the material and the associated heat of reaction.

Different authors agree on classifying the thermal decomposition of hemicelluloses and lignin among exothermic processes [3–7], while considering the decomposition of cellulose to be endothermic [4,8]. This means that in experiments carried out with xylan and lignin, the actual temperature of the sample could be equal to or even higher than  $T_f$ . Therefore, equal or even higher values of the kinetic constant could be obtained as  $\beta$  increases, i.e. when the effect of the heat of reaction  $\Delta H_{r2}$  is more important [2]

$$\frac{dT}{dt} = \frac{B}{1 - X_S} (T_f - T) + \frac{(-\Delta H_{r2})}{C_p} \frac{1}{1 - X_S} \frac{dX_S}{dt} \quad (10)$$

which describes the fourth interval.

The above equation was solved numerically for different values of  $\Delta H_{r2}$ . For each of these values the temperature of the solid can be calculated, given the temperature of the system and the heating rate  $\beta$ .

Once the values of  $T$  for a given  $T_f$  have been obtained the appropriate calculations can be carried out in order to obtain the corresponding kinetic constants.

From the graphs of  $\log k_{S\beta}$  vs.  $1/T$  for different values of  $\beta$ , it was found that taking  $\Delta H_{r2} = -362 \text{ cal g}^{-1}$  led to very similar values of the kinetic constant for the same temperature, whatever the value of  $\beta$ , especially in the region of high temperatures, as shown in Fig. 4. However, in the region of low temperatures, where there is a marked influence of temperature on  $A_S$ , the differences among the kinetic constants obtained are noticeable, higher values of  $k_{S\beta}$  being obtained as  $\beta$  is increased.

Few quantitative data are available for the heat of reaction in the thermal decomposition of lignin. The value of  $\Delta H_{r2} = -192 \text{ cal g}^{-1}$  was selected

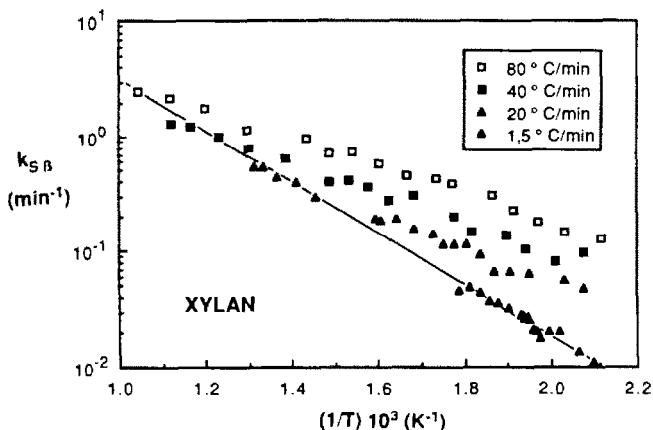


Fig. 4. Values of  $k_{S\beta}$  vs.  $1/T$  for xylan.



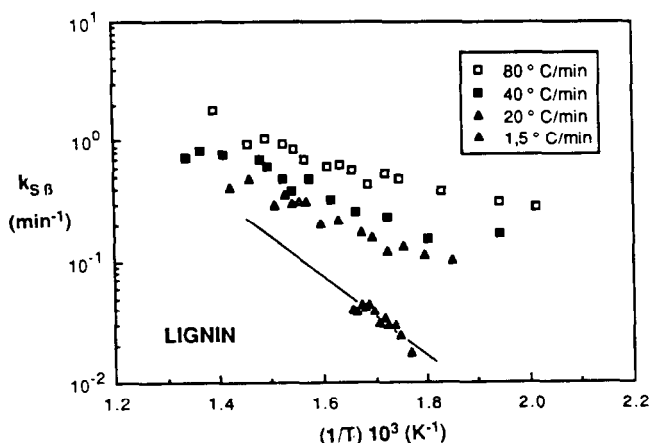


Fig. 5. Values of  $k_{S\beta}$  vs.  $1/T$  for lignin.

from among those given by Tinney [7]. This value was used in eqn. (10) for the calculation of  $T$  for a given  $T_f$ .

The kinetic constants could then be calculated for the corresponding solid temperatures. Figure 5 shows the plot of  $\log k_{S\beta}$  vs.  $1/T$ . It can be seen that at high temperatures similar values of the kinetic constants are obtained at the same temperature for different heating rates, but the same does not hold at low temperatures.

The behaviour at low temperatures cannot be explained purely in terms of a temperature gap, since none of the  $\Delta H_{r2}$  values used yielded similar results for the kinetic constants when evaluated at the solid temperature.

Besides, it must be noticed that in dynamic experiments the values of  $dX_S/dt$  are obtained from conversion data which depend not only on time but also on temperature, since both  $k_{S\beta}$  and  $A_S$  are temperature dependent. Therefore, if we consider

$$X_S = f(t, T) \quad (11)$$

then we can write

$$\left( \frac{dX_S}{dt} \right)_\beta = \left( \frac{\partial X_S}{\partial t} \right)_T + \left( \frac{\partial X_S}{\partial T} \right)_t \frac{dT}{dt} \quad (12)$$

where  $dT/dt = \beta$ .

There is no agreement in the literature about the use of the term  $(\partial X_S/\partial T)_t$ . Thus, while for some authors [9–12] this term has no logical meaning and it is therefore acceptable to use kinetic expressions obtained under isothermal conditions in non-isothermal calculations, others [13,14] have found that Arrhenius-type parameters obtained in isothermal and non-isothermal experiments are different.

The values of  $(\partial X_S/\partial t)_T$  must be calculated for a given temperature. In a first approach, it seems logical to make these calculations using the results

from isothermal experiments. Thus we can write

$$\left(\frac{\partial X_S}{\partial t}\right)_T = k_{S_1}(A_S - X_S) \quad (13)$$

However, as mentioned above, there are important restrictions in the temperature range that can be explored using isothermal experiments. Therefore, we propose as an alternative the use of the values of the kinetic coefficients obtained in dynamic experiments performed with a low heating rate (e.g.  $1.5^\circ \text{C min}^{-1}$ ).

In this case, eqn. (12) becomes

$$\left(\frac{dX_S}{dt}\right)_\beta = k_{S_{1.5}}(A_S - X_S) + \left(\frac{\partial X_S}{\partial T}\right)_t(\beta - 1.5) \quad (14)$$

The value of  $(\partial X_S/\partial T)_t$  was determined from experimental data at different heating rates using the expression

$$\left(\frac{\partial X_S}{\partial T}\right)_t = \frac{\left(\frac{dX_S}{dt}\right)_\beta - k_{S_{1.5}}(A_S - X_S)}{\beta - 1.5} \quad (15)$$

where  $k_{S_{1.5}}$  can be obtained from eqns. (8) and (9). The evolution of  $A_S$  is shown in Fig. 1 as a function of the solid temperature.

An average value of 0.0017 has been found for  $(\partial X_S/\partial T)_t$  from experiments carried out with xylan and lignin. Thus, the following equation can be used for dynamic experiments

$$\left(\frac{dX_S}{dt}\right)_\beta = k_{S_{1.5}}(A_S - X_S) + 0.0017(\beta - 1.5) \quad (16)$$

This equation yields the value of  $dX_S/dt$ , given  $k_{S_{1.5}}$ ,  $A_S$  and  $\beta$ . A comparison of the values thus obtained with the experimental results can be used as a test of eqn. (16). Figures 6 and 7 show this comparison for xylan and lignin respectively. Although the data show some dispersion, the fitting can be considered as satisfactory.

From eqn. (16), it follows that the term  $0.0017(\beta - 1.5)$  is a constant for a given heating rate. The influence of this term on  $dX_S/dt$  becomes stronger as  $k_{S_{1.5}}(A_S - X_S)$  decreases, i.e. at lower temperatures. Thus, the term  $0.0017(\beta - 1.5)$  is useful in correcting the results obtained at low temperatures, and has a weak effect on the rates calculated at high temperatures.

Kinetic constants for different temperatures and heating rates can be obtained using

$$k_{S_\beta} = \frac{k_{S_{1.5}}(A_S - X_S)_T + 0.0017(\beta - 1.5)}{(A_S - X_S)_{T_t}} \quad (18)$$

which uses the experimental values of  $k_{S_{1.5}}$  and  $A_S$ .

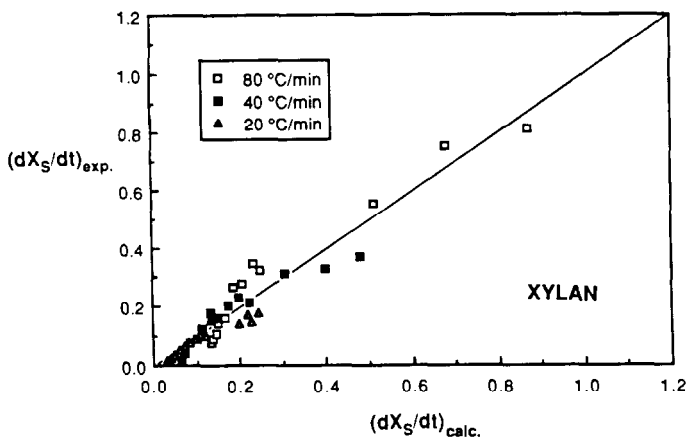


Fig. 6. Experimental and calculated values of  $dX_S/dt$  for xylan.

It is interesting to relate the results from isothermal experiments to those obtained with  $\beta = 1.5^\circ\text{C min}^{-1}$ . This can be done using eqn. (12). The study was carried out for the main temperature interval in the thermal decomposition of xylan and lignin, for which  $n = 1$ . Substitution of eqn. (13) into eqn. (12) yields

$$\left(\frac{dX_S}{dt}\right)_\beta = k_{S_i}(A_S - X_S) + \left(\frac{\partial X_S}{\partial T}\right)_i \beta \quad (18)$$

where  $\beta = 1.5^\circ\text{C min}^{-1}$ . The values of  $k_{S_i}$  for xylan were calculated using the whole range of conversions, whereas for lignin only those within the temperature interval  $275\text{--}325^\circ\text{C}$  were considered.

For the temperature interval studied, the values of  $(\partial X_S/\partial t)_T$  calculated were 0.0012 for xylan and 0.00075 for lignin.

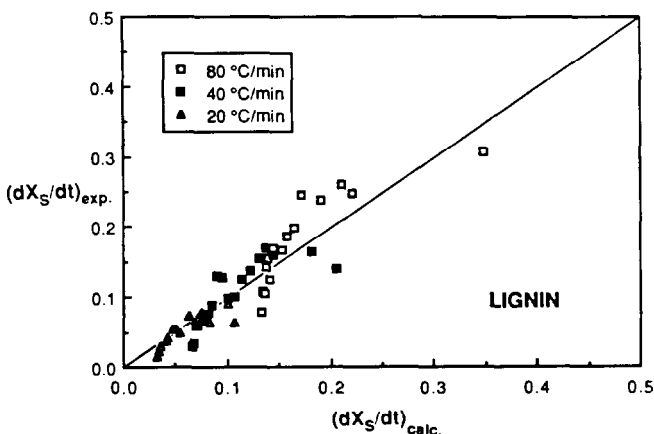


Fig. 7. Experimental and calculated values of  $dX_S/dt$  for lignin.

From the above, it is possible to relate the results obtained in dynamic and isothermal experiments using the following expressions

$$\text{Xylan: } \left( \frac{dX_S}{dt} \right)_{1.5} = k_{S_{1.5}} (A_S - X_S) = k_{S_1} (A_S - X_S) + 0.0012 \times 1.5 \quad (19)$$

$$\text{Lignin: } \left( \frac{dX_S}{dt} \right)_{1.5} = k_{S_{1.5}} (A_S - X_S) = k_{S_1} (A_S - X_S) + 0.00075 \times 1.5 \quad (20)$$

In conclusion, results obtained in isothermal experiments and in dynamic experiments with different values of  $\beta$  can be related using as a reference results obtained using  $\beta = 1.5^\circ \text{C min}^{-1}$ .

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