Intrinsic kinetics of isothermal xylan degradation in inert atmosphere

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Abstract

Thermal degradation of thin layers of milled, commercial xylan is made to occur under controlled sample temperature, by proper variation in the intensity of the applied radiative heat flux. The process consists of fast sample heating (40–70 K s⁻¹) to the desired temperature, which is then maintained until complete conversion. A continuous helium flow avoids extra-particle secondary reactions of primary volatile products and establishes an inert reaction environment. Time-weight loss curves are determined for reaction temperatures in the range 473–613 K, where the ratio between the conversion and the heating times is very large (1000–100) and the weight loss during the heating period is small (0–16%). The isothermal weight loss curves are well interpreted by a two-stage mechanism. The first, fast stage takes into account the competitive formation of volatiles and a solid intermediate. The second, slow stage takes place for temperatures above 523 K and describes the competitive formation of char and volatiles from the degradation of the reaction intermediate. The kinetic data for the two stages are: \( A_1 = 3.62 \times 10^2 \text{ s}^{-1}, E_1 = 18.3 \text{ kcal mol}^{-1} \) and \( A_2 = 3.83 \times 10^2 \text{ s}^{-1}, E_2 = 13.1 \text{ kcal mol}^{-1} \). The final solid char yields vary with the reaction temperature from 68 to 10%, and most of the volatiles are released in the course of the first reaction stage. © 1997 Elsevier Science B.V.

Keywords: Thermal degradation; Xylan; Kinetics

1. Introduction

Detailed transport models have been recently proposed [1–6] of physical and chemical processes of cellulosic material pyrolysis, to improve design and operation...
of chemical reactors for thermochemical biomass conversion. In general, the design of pyrolysis units is dependent upon the knowledge of the residence times required for complete conversion of the biomass particle feed. The residence time is, in its turn, the result of heat, mass and momentum transfer and solid degradation rate in the reacting environment. Of course, this can be predicted only if the chemical kinetics are known. Two different approaches [7] have been proposed, the first describes biomass as a single homogeneous fuel while the second takes into account the contributions from the three main biomass components, that is, cellulose, hemicellulose and lignin. For both cases, the knowledge of the degradation kinetics of biomass components is thus an important step for the understanding of the chemical behavior of complex fuels.

Hemicelluloses constitute 20–35% of the weight of most woods [8]. They include several components such as xylose and mannose, which are the prevalent monomers for hardwoods and softwoods, respectively, glucose, galactose, arabinose and other polysaccharides [8]. Compared to cellulose, few studies have been carried out on the pyrolysis of hemicelluloses, which are the least stable among wood components. In some cases xylan polysaccharides and model compounds have been considered and it has been shown that degradation takes place in the temperature range 473–573 K or even lower [9]. For high temperatures, xylan pyrolysis products are mainly volatiles with solid char yields variable from about 20 to 10%, depending on the heating rate [11, 12].

A summary of the main static (isothermal) and dynamic (variable temperature) studies on hemicelluloses (essentially xylan) pyrolysis, classified in terms of one-step and multi-step reaction mechanisms, is presented in Table 1 and Table 2. Isothermal experiments have been carried out by TGA techniques [10, 13, 14], an open oven [15] and a tube furnace [16]. Dynamic studies have also been conducted through TGA techniques at tube reactors [10, 12, 14, 17, 18, 20] with heating rates from 1.5 to 80 K min⁻¹ and temperatures in the range 468–993 K.

The simplest models are a one-step global reaction [10, 12, 14, 15, 18]. Evaluation of the Arrhenius factor through one-step (isothermal) kinetics shows comparable values for the data reported in [10, 14], whereas those obtained through data [15] are much higher. It is plausible that this behavior is due to the different experimental conditions and, more precisely, to possible oxidation processes in [15]. Comparable reaction rates are also observed under dynamic conditions [12, 14], for comparable heating rates. However, the activation energies decrease and the pre-exponential factors increase with the heating rate in one case [12], whereas the opposite trend is seen in the other [14]. Though one-step mechanisms are useful to describe the global solid degradation rate, they cannot be applied to predict product distribution from chemical reactor simulation, as the assumption of a constant ratio of char to volatile yields is assumed.

Some studies on the thermal degradation of xylan and related model compounds have shown the existence of a two-step decomposition mechanism [9–11, 13, 20]. 'Cleavage of the glycosidic group, polymerization of the glycosyl units, decomposition of the sugar moiety within a narrow range of temperature' was postulated in [11]. Mass spectrometric [20] and DTA [9, 13] curves also appear to confirm the
<table>
<thead>
<tr>
<th>Reactor</th>
<th>Sample</th>
<th>Heating rates</th>
<th>Temperature</th>
<th>Kinetics mechanism and data</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass bulb in an oil bath or an electric oven</td>
<td>Hemicellulose isolated from Douglas fir sawdust (40–60 μm)</td>
<td>Isothermal</td>
<td>383–493 K</td>
<td>$E = 26.7$ kcal mol$^{-1}$ $A = 2.16 \times 10^{12}$ min$^{-1}$</td>
<td>Stamm (1956) [15]</td>
</tr>
<tr>
<td>TGA/DTA under vacuum</td>
<td>200 mg potassium xylan (30–50 μm)</td>
<td>Isothermal</td>
<td>488–523 K</td>
<td>$E = 30 \pm 2$ kcal mol$^{-1}$ $A = 1.32 \times 10^{11}$ min$^{-1}$</td>
<td>Ramiah (1970) [10]</td>
</tr>
<tr>
<td>TGA/DTA under vacuum</td>
<td>Kinetics as difference from wood (40 mg cedar sapwood)</td>
<td>5 k min$^{-1}$</td>
<td>513–523 K</td>
<td>$E = 28.5$ kcal mol$^{-1}$ $A = 2.9 \times 10^{10}$ min$^{-1}$</td>
<td>Hirata (1974) [17]</td>
</tr>
<tr>
<td>Ceramic tube + gas detector</td>
<td>Kinetics as difference from wood (0.7 g fir and 0.79 g beech)</td>
<td>Up to 833 K</td>
<td>30 K min$^{-1}$</td>
<td>$E = 29.6$ kcal mol$^{-1}$ $A = 8.67 \times 10^{10}$ min$^{-1}$</td>
<td>Min (1977) [18]</td>
</tr>
<tr>
<td>TGA</td>
<td>2–4 mg of commercial xylan</td>
<td>1.5 K min$^{-1}$</td>
<td>473–673 K</td>
<td>$E = 10.2$ kcal mol$^{-1}$ $A = 590$ min$^{-1}$</td>
<td>Bilbao et al. (1989) [14]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 K min$^{-1}$</td>
<td></td>
<td>$E = 17.2$ kcal mol$^{-1}$ $A = 1.2 \times 10^{6}$ min$^{-1}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>80 K min$^{-1}$</td>
<td></td>
<td>$E = 20.6$ kcal mol$^{-1}$ $A = 4.6 \times 10^{7}$ min$^{-1}$</td>
<td></td>
</tr>
</tbody>
</table>
Table 1 (continued)
One-step global reaction mechanisms of hemicellulose degradation

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Sample</th>
<th>Heating rates</th>
<th>Temperature</th>
<th>Kinetics mechanism and data</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA/DTA</td>
<td>20 mg of commercial xylan</td>
<td>5 K min⁻¹</td>
<td>Up to 993 K</td>
<td>( E = 61.8 \text{ kcal mol}^{-1} )( A = 1.12 \times 10^{24} \text{ min}^{-1} )</td>
<td>William and Besler (1993) [12]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20 K min⁻¹</td>
<td></td>
<td>( E = 61.4 \text{ kcal mol}^{-1} )( A = 1.6 \times 10^{24} \text{ min}^{-1} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>40 K min⁻¹</td>
<td></td>
<td>( E = 46.3 \text{ kcal mol}^{-1} )( A = 1.76 \times 10^{17} \text{ min}^{-1} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>80 K min⁻¹</td>
<td></td>
<td>( E = 29.8 \text{ kcal mol}^{-1} )( A = 9.66 \times 10^{10} \text{ min}^{-1} )</td>
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*Estimated in this study.*
existence of two consecutive steps. As shown in Table 2, estimations of kinetic data for mechanisms based on two consecutive reactions of xylan pyrolysis have also been proposed in [9,13]. Again, these models can predict the global solid degradation rate, but no information can be obtained on the dependence of product yields on reaction temperature.

Table 2
Multi-step reaction mechanisms of hemicellulose degradation

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Sample</th>
<th>Heating rates</th>
<th>Temperature</th>
<th>Kinetics mechanism and data</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA/DTA</td>
<td>50 mg xylan (from beechwood holocellulose)</td>
<td>isothermal</td>
<td>477 - 494 K</td>
<td>( E = 278 \text{ kcal/mol} ) ( A = 5 \times 10^{18} \text{ exp}^{-1} ) (1)</td>
<td>Shimazu and Teranaka (1969)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>461 - 498 K</td>
<td>498 - 538 K</td>
<td>( E = 219 \text{ kcal/mol} ) ( A = 6 \times 10^{16} \text{ exp}^{-1} ) (2)</td>
<td>(13)</td>
</tr>
<tr>
<td>TGA/DTA under vacuum</td>
<td>200 mg potassium xylan (30 - 50 µm)</td>
<td>4 K/min</td>
<td>377 - 494 K</td>
<td>( E = 258 \text{ kcal/mol} ) ( A = 7 \times 10^{15} \text{ exp}^{-1} ) (3)</td>
<td>Ramanaiah (1970)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>398 - 538 K</td>
<td>( E = 7 \times 10^{15} \text{ kcal/mol} ) ( A = 1 \times 10^{16} \text{ exp}^{-1} ) (4)</td>
<td>(10)</td>
</tr>
<tr>
<td>TGA</td>
<td>sawdust 200 mg (3 - 0.85 mm)</td>
<td>3.20.60 K/min</td>
<td>up to 973 K</td>
<td>( E = 1732 \text{ kcal/mol} ) ( A = 1.9 \times 10^{16} \text{ exp}^{-1} ) (5)</td>
<td>Kostopoulos et al. (1989)</td>
</tr>
<tr>
<td></td>
<td>tube furnace</td>
<td>isothermal</td>
<td>373, 623, 673, 773, 873, 973 K</td>
<td>( E = 476 \text{ kcal/mol} ) ( A = 6 \times 10^{16} \text{ exp}^{-1} ) (6)</td>
<td>(10)</td>
</tr>
<tr>
<td></td>
<td>sawdust 150 mg (0.1 - 0.85 mm)</td>
<td>473 K/min</td>
<td>up to 973 K</td>
<td>( E = 412 \text{ kcal/mol} ) ( A = 1 \times 10^{16} \text{ exp}^{-1} ) (7)</td>
<td>(10)</td>
</tr>
<tr>
<td>TGA</td>
<td>kinetics as difference from wood (100 mg of wild cherry wood)</td>
<td>1.7 K/min</td>
<td>373 K/min</td>
<td>( E = 460 \text{ kcal/mol} ) ( A = 1.5 \times 10^{15} \text{ exp}^{-1} ) (8)</td>
<td>Ward and Bratlow (1983)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.1 K/min</td>
<td>373 K/min</td>
<td>( E = 516 \text{ kcal/mol} ) ( A = 1.2 \times 10^{15} \text{ exp}^{-1} ) (9)</td>
<td>(19)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.1 K/min</td>
<td>473 K/min</td>
<td>( E = 599 \text{ kcal/mol} ) ( A = 1.2 \times 10^{15} \text{ exp}^{-1} ) (10)</td>
<td>(19)</td>
</tr>
<tr>
<td>TGA/DTA</td>
<td>1.2 mg xylan from beech sawdust</td>
<td>10 K/min</td>
<td>up to 623 K</td>
<td>( E = 439 \text{ kcal/mol} ) ( A = 0.5 \times 10^{15} \text{ exp}^{-1} ) (11)</td>
<td>Vanhegge et al. (1988)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80 K/min</td>
<td>623 K/min</td>
<td>( E = 459 \text{ kcal/mol} ) ( A = 7.9 \times 10^{14} \text{ exp}^{-1} ) (12)</td>
<td>(9)</td>
</tr>
</tbody>
</table>
Multi-step reaction mechanisms have also been presented in [16,19]. The kinetic scheme proposed in [16] for xylan pyrolysis includes a zero-order stage, presumably describing a sort of depolymerization process, followed by two reactions for the formation of volatiles and a solid charred residual, through 1.5 order Arrhenius reactions. These two reactions are not truly competitive because the two activation energies are equal. Thus, this model again predicts a solid char yield not dependent on temperature. Three consecutive steps are considered in [19] for the kinetics of hemicelluloses pyrolysis, derived as the difference between those of wood and the other two components (lignin and cellulose). Again, a constant ratio between total volatile and char yield is assumed.

In all cases, kinetic data have been estimated assuming that the temperature of the sample is the same as that of the heating system and that no temperature gradients are established through the sample. Apart from [9,14], rather large amounts of powdered sample have been degraded and it is unlikely that the above assumptions are valid. Antal [8,21,22] pointed out that these conditions are difficult to achieve, and that heat transfer limitations may cause large errors in the evaluation of the intrinsic kinetics of solid degradation.

Other limitations are usually encountered in both the dynamic and the static investigations on hemicelluloses degradation currently available. The main drawback of the dynamic analyses is that the heating rate, which highly affect the reaction process, are much slower that those usually achieved in chemical reactors (gasification and pyrolysis). Therefore, the degradation kinetics may not be valid for conditions different from those under which they have been derived. In the static analyses two different methodologies are followed to attain the isothermal stage, that is very slow heating rates (1.5–2.5 K min\(^{-1}\)) to avoid intra-particle temperature gradients [13,14], or the sample holder is introduced in a pre-heated reactor in order to keep short the first dynamic stage [16]. However, in the first case, the weight loss is not negligible in the heating stage and the subsequent interpretation of the data may be lacking of an important part of the whole process. In the second case, the results may be seriously affected by heat transfer limitation.

Finally, a question may arise as to how the degradation process of the same material, under similar conditions, can be described either by a one-step global reaction or by a multi-step mechanism. An answer to this question is given in [9]. It is shown that the time derivate of the solid weight fraction as a function of the temperature exhibits a double peak, which is well fitted by a two-step, consecutive reaction scheme (deviations 1.3–1.7%). Furthermore, it is noted that the DTG curves can also be fitted by a one-step reaction, but the deviation becomes rather large (10%). Small deviations (1.2%) are, on the contrary, observed when the one-reaction scheme is applied to fit the TGA curves, where the variation in the slope is much less evident. This may explain why in several cases one-step kinetics appear to describe the kinetics of xylan degradation quite well.

In this study a new experimental system is used to investigate the kinetics of xylan pyrolysis under controlled sample temperature and reduced heat transfer limitations. A short heating period and the absence of spatial temperature gradients allow isothermal weight loss curves to be measured. These are used to formulate a
two-stage mechanism, constituted by four independent reactions, and to estimate kinetic data, without assumptions on pyrolysis product distribution.

2. The experimental system

An experimental system has been designed and constructed to investigate solid pyrolysis under reduced limitations of heat and mass transport, so that information on the chemical kinetics (semi-global mechanisms and data) can be obtained. The system allows for the continuous monitoring of the sample temperature and weight and for the collection of final products, here lumped into three main classes: solid char, liquid tar and gas. The system combines some characteristics of the pyrolysis tube used in previous experiments (for instance, [23]) and the fast TGA system presented in [24]. Fig. 1 schematically represents the main characteristics of the experimental apparatus. It consists of (1) a radiant heating chamber; (2) a quartz reactor; (3) a PID temperature controller; (4) an inert gas feeding system (to reduce the activity of secondary reactions of volatile products evolved from primary degradation); (5) an acquisition data set (PC and related accessories); (6) a precision balance and (7) a collection system for condensable and non-condensible products of solid pyrolysis.
The heating system is a radiant chamber (research), whose heating elements are tubular quartz infrared lamps with a tungsten wire filament that emits radiant energy in proportion to the applied voltage. Four elliptical, polished aluminum reflectors focus the high-density infrared energy, emitted by the lamps, onto a cylindrically shaped target area (maximum reactor heating rate $750 \text{ K s}^{-1}$). To avoid interaction between the volatile pyrolysis products and the lamps, a quartz tube, transparent to infrared radiation, is located inside the furnace and used as a reaction chamber. A powdered solid sample is exposed to thermal radiation by means of a 325 stainless steel mesh basket. The temperature is continuously recorded by a chromel-alumel thermocouple (0.1 mm bead). It is worth observing that the sample is located at the center of the radiant chamber and is radiatively heated on both the upper side and the bottom side, this in contact with the sample holder (Fig. 1(B)). Therefore, the half-thickness of the sample layer is the characteristic size for the problem. Aluminum supports directly connect the sample holder to a precision balance (Mettler-Toledo AT400 with 0.1 mg accuracy and time constant equal to 0.2–0.4 s). The time lags of the measuring devices are much shorter than the characteristic process times only for system heating rates below $100 \text{ K s}^{-1}$. Thus, though the system can reach much faster heating rates, these are not accomplished in the course of the experiments. Also, at very high heating rates, intra-particle gradients of temperature may become large and obscure the intrinsic kinetics of sample degradation. The radiant heater is made to work according to two modalities, here indicated as A and B, which correspond to the emission of a constant flux and to the attainment of certain temperature with an assigned rate, respectively.

The modality A, which is the easier, also corresponds to a constant temperature of the emitters and is similar to the classical TGA approach. It has been shown [6,22] that, with this procedure, significant temperature differences between the reactor and the sample cannot be avoided. In other words, the reaction process occurs at temperatures which are not known and cannot be controlled, due to sample thermal capacity and reaction energetics. The modality B can be implemented to impose a certain time evolution of a temperature, which can be that of the emitters or the specimen, by varying the intensity of the radiant flux. In this study, the controlled variable is the temperature of the sample surface, while the manipulated variable is the electric voltage applied to the furnace. This approach is chosen with the scope of minimizing the differences between the temperature of the furnace (lamps) and the sample, and to work under conditions of known, controlled sample temperature.

Preliminary tests have been conducted for cellulose to determine the conditions which allow for a negligible activity of secondary intra-particle reactions of primary tars and for the absence of temperature spatial gradients. The char yield has been determined as a function of the sample thickness for temperatures in the range 573–623 K. As expected, it decreases as the sample is made thinner, because of successively larger primary reaction temperatures, which favor volatile formation, and successively shorter residence times of intra-particle tar residence times, which reduce the activity of secondary charring reactions. Then, as these effects become
negligible, constant char yields are attained, corresponding to sample thicknesses varying from 140 μm (low temperature) to 120 μm (high temperature). Given the comparable values of physical properties, it is assumed that hemicelluloses behave in a similar way. Therefore, samples 100 μm thick are used in the degradation tests (half-thickness r = 50 μm).

3. Isothermal weight loss curves

Thermal degradation of commercial xylan, obtained from oat spelt (Sigma, Aldrich), has been carried out according to modality B, by varying the final temperature of the sample in the range 473–613 K. Prior to pyrolysis, xylan powder has been milled (particle sizes of about 50 μm) and dried (10 h at temperature of 388 K). A continuous helium flow equal to 800 cm³ min⁻¹, at ambient temperature, has been applied.

The initial time history of sample temperature, for different set points (final sample temperatures), obtained through a proper selection of control parameters, is reported in Fig. 2. It can be seen that, after the first stage of linear increase, a constant temperature (Tᵣ) is more slowly attained and maintained for the whole duration of the process. The sample heating rates, during the stage of linear increase, vary from about 40 to 70 K s⁻¹, as the reaction temperature is increased.

![Fig. 2. Temperature of the sample as function of time for the initial stage of the process.](image)

![Fig. 3. Weight loss curves of xylan for different sample temperatures.](image)
After this stage, a slower increase is observed, resulting from the need to avoid any temperature deviation from the set points. These conditions result in global sample heating rates, during the dynamic stage, varying from about 27 to 36 K s$^{-1}$.

The weight loss curves, for the different final temperatures of the sample, are reported in Fig. 3. As expected, the conversion process becomes successively faster and the final solid char yields decrease as the reaction temperature is increased. However, as shown in Fig. 4, the ratio between the conversion time (no variation in the final solid charred residual) and the sample heating time, $t_h$, defined as the time needed to achieve the final temperature, is always high (1000-100) and the weight fraction for $t = t_h$ is only slightly lower than 1 (1-0.84). Therefore, these data can be analyzed through an isothermal model.

4. Reaction mechanism and kinetic data

The theory here developed is based on the assumption that conversion occurs under pure kinetic control and that semi-global reaction mechanisms can be applied. In agreement with previous studies [9-11,13,20], the weight loss curves are interpreted through a two-stage mechanism:
where the A is xylan and B the intermediate reaction product, that is, a solid with a reduced degree of polymerization. Both in the first and the second stage a competitive volatile and solid (B or char) formation is taken into account. Information on the volatile composition can be found in \([11,20]\). The model equations can be expressed as:

\[
\frac{dM_A}{dt} = -K_1 M_A \\
\frac{dM_B}{dt} = K_B M_A - K_2 M_B \\
\frac{dM_{V1}}{dt} = K_{V1} M_A
\]

(\(a1 - a4\))

Fig. 6. Ratios \(\tau^*/\tau_h\) and \(\tau^{**}/\tau^*\) as functions of the reaction temperature.

Fig. 7. (A) Maximum values of the reaction intermediate mass fraction of species B and final mass fraction of solid char as functions of the reaction temperature. (B) Final mass fraction of volatiles, generated in the first and second stage of the reaction process, as functions of the reaction temperature.
\[
\frac{dM_{v2}}{dt} = K_{v2} M_B
\]
\[
\frac{dM_C}{dt} = K_C M_B
\]

where \( M_i \) (i = A, B, V1, V2, C) is the mass of chemical species,
\[
K_1 = K_B + K_{V1}, \quad K_2 = K_{v2} + K_C
\]

and the reaction rates are first-order in the mass of pyrolyzable material:
\[
K_i = A_i e^{-E_i/(RT)}, \quad i = A, B, V1, V2, C
\]

Integration of Eqs. (1)-(5) with conditions [25]:
\[
M_A(0) = M_0, \quad M_B(0) = M_{v1}(0) = M_{v2}(0) = M_C(0) = 0, W(0) = M_0
\]
\[
M_{v1}(\infty) = M_{v1}, \quad M_{v2}(\infty) = M_{v2}, \quad M_C(\infty) = M_C, \quad W_\infty = M_C
\]

\((M_0 \text{ is the initial sample mass})\) gives:
\[
M_A = M_0 e^{-K_1 t}
\]
\[
M_{v1} = \frac{K_{v1} M_0}{K_1} (1 - e^{-K_1 t})
\]
\[
M_B = \frac{K_B M_0}{K_1 - K_2} (e^{-K_2 t} - e^{-K_1 t})
\]
\[
M_{v2} = \frac{K_{v2} K_B M_0}{(K_1 - K_2) K_1 K_2} (K_1 - K_2 - K_1 e^{-K_2 t} + K_2 e^{-K_1 t})
\]
\[
M_C = \frac{K_C K_B M_0}{(K_1 - K_2) K_1 K_2} (K_1 - K_2 - K_1 e^{-K_2 t} + K_2 e^{-K_1 t})
\]

where \( W \) is the solid residual, that is:
\[
W = M_A + M_B + M_C
\]

Final product yields can be evaluated through Eqs. (9), (11) and (12) as:
\[
M_{v1\infty} = \frac{K_{v1} M_0}{K_1}
\]
\[
M_{v2\infty} = \frac{K_{v2} K_B M_0}{(K_1 - K_2)}
\]
\[
M_{C\infty} = \frac{K_C K_B M_0}{K_1 K_2}
\]

Combination of Eqs. (8), (10), (12), (13) and (16) gives an expression for the solid residual, \( W \), as function of the two stages of the reaction mechanism, that is:
\[
\frac{W - M_{C\infty}}{M_0} = \lambda_1 e^{-K_1 t} + \lambda_2 e^{-K_2 t}
\]
where

\[ \lambda_1 = \frac{(K_1 - K_2)K_2 - K_BK_1 + K_CK_B}{K_1(K_1 - K_2)}, \quad \lambda_2 = \frac{K_1K_2K_B - K_1K_CK_B}{K_1K_2(K_1 - K_2)} \]  

Eq. (17) represents the solid residue as two independent exponentials and cannot be solved, unless the time evolution of one of the two volatile products is known. However, the plots of the ln of Eq. (17) (Fig. 5) indicate the existence of two highly different slopes and of a demarcation time, \( t^* \), between the first and the second stage for \( T_r > 543 \) K (lower temperatures give rise to a one-stage process). Therefore, it appears plausible to assume that the first stage goes to completion for \( 0 < t \leq t^* \) (the second step is not active during this time period). Then, for \( t^* < t \leq t_c \), only the second stage takes place (\( t^{**} = t_c - t^* \) is the time needed for the completion of the second stage). Consequently, the time \( t^* \) can be used to evaluate the maximum value of the reaction intermediate mass \( M_B^{**} \), formed as a consequence of the first reaction stage, and the kinetic data for the two stages estimated.

Some information on the process dynamics can be obtained from Fig. 6, which reports the ratio between the characteristic time of the first reaction stage, \( t^* \), and the heating time, \( t_h \), and that between the two reaction time, \( t^{**} \) (II) and \( t^* \) (I), as functions of the temperature. The first stage is much faster (by a factor of about 20) than the second, but its duration is always significantly longer than the heating time.
Fig. 10. Arrhenius plot: $K_1$ and $K_2$ as function of $1/T_r$.

Fig. 11. Arrhenius plot: $K_{V1}$, $K_{R}$, $K_C$ and $K_{V2}$ as function of $1/T_r$.

(by factors of 10−5), so that, not only the global degradation process (Fig. 4), but also the first reaction stage can be considered isothermal. Furthermore, though the duration of both stages decreases with temperature, their ratio remains almost constant.

Fig. 7(A) and (B) show the product yields for the two reaction stages as functions of the reaction temperature, that is, the maximum or the final solid residual (B or char) and volatile yields (mass fractions), respectively. At low temperatures, the

Fig. 12. Comparison between model predictions (dashed lines) and experimental measurements (symbols) of the nondimensional solid weight $(W - M_{C,\infty})/M_0$. 
yields of species B coincide with those of char and attain a maximum value of about 70% (with respect to the initial sample weight). As the reaction temperature is increased, yields of both solid phase species decrease (while the volatile yields increase) and, as expected, char yields are significantly lower. In particular, at the highest temperature, the final char yield is about 10%. A large fraction of volatiles is released in the initial faster step of the conversion process. Furthermore, for $T_r \geq 513$ K, the contributions vary from about 45% (I) against 25% (II) to 63% (I) against 28.5% (II).

The equations for volatile species ($M_{v1}$, $M_{v2}$) can be integrated over the two time intervals $0 - t^*$ and $t^* - t_*$ to get the global rates of the first and the second stage, $K_1$ and $K_2$. For the first stage it can be easily obtained:

$$M_{v1} = M_0 - W$$
$$M_{v1,*} = M_0 - M_{B*}$$

Combination of Eqs. (9), (14) and (18) gives:

$$1 - \frac{M_0 - W}{M_0 - M_{B*}} = e^{-K_1t}$$

or, through the logarithm:

$$\ln \left(1 - \frac{M_0 - W}{M_0 - M_{B*}}\right) = \ln (P_1) = -K_1t$$

For the second stage it can be easily obtained:

$$M_{v2} = M_{B*} - W$$
$$M_{v2,*} = M_{B*} - M_{C*}$$

Integration of Eq. (4) over the second time interval leads to:

$$M_{v2} = \frac{K_{v2}M_{B*}}{K_2}(1 - e^{-K_2(t_* - t^*)}) = M_{v2,*}(1 - e^{-K_2(t_* - t^*)})$$

Finally, combination of Eqs. (21) and (22) gives:

$$1 - \frac{M_{B*} - W}{M_{B*} - M_{C*}} = \ln (P_2) = -K_2(t - t^*)$$

or, through the logarithm:

$$\ln \left(1 - \frac{M_{B*} - W}{M_{B*} - M_{C*}}\right) = \ln (P_2) = -K_2(t - t^*)$$

It should be noted that all the variables appearing in the definitions of the nondimensional solid weights, $P_1$ and $P_2$, are known. Therefore, $\ln (P_1)$ and $\ln (P_2)$ can be plotted as functions of time (Fig. 8, Fig. 9) for the different temperatures investigated. The plots result into two sets of straight lines, whose slopes are $K_1$ and $K_2$, respectively, for the different temperatures. Arrhenius plots (Fig. 10) are then used to get activation energies and pre-exponential factors for the two reaction stages. The set of data determined are: $E_1 = 18.3$ kcal mol$^{-1}$, $A_1 = 3.62 \times 10^4$ s$^{-1}$ and $E_2 = 13.1$ kcal mol$^{-1}$, $A_2 = 3.83 \times 10^2$ s$^{-1}$. The standard deviations for the two stages are equal to 6 (I) and 3% (II).
Finally, Eqs. (6), (14) and (22), given the final values of the volatiles yields (Eq. (18), Eq. (21)), can be used to get the reaction constants $K_{V_1}$, $K_{V_2}$, $K_{B}$, $K_{C}$ for the different temperatures. Again the Arrhenius plots, reported in Fig. 11, allow the kinetic data for the four reactions of the semi-global reaction mechanism here proposed to be determined. The results are: $A = 1.74 \times 10^4 \text{ s}^{-1}$, $E = 15.82 \text{ kcal mol}^{-1}$ ($K_{B}$); $A = 3.31 \times 10^5 \text{ s}^{-1}$, $E = 21.864 \text{ kcal mol}^{-1}$ ($K_{V_1}$); $A = 3.43 \times 10^2 \text{ s}^{-1}$, $E = 13.47 \text{ kcal mol}^{-1}$ ($K_{C}$); $A = 58.7 \text{ s}^{-1}$, $E = 12.57 \text{ kcal mol}^{-1}$ ($K_{V_2}$).

The prediction of the weight loss, according to Eq. (17), where the reaction constants $K_{V_1}$, $K_{V_2}$, $K_{B}$, $K_{C}$ are obtained through the kinetic data estimated in Fig. 10 and Fig. 11, are compared with experimental data in Fig. 12. It can be seen that for the higher temperatures there is a close agreement between the theory here proposed and the experimental data, while small deviations are seen for the lower temperatures. This indicates that the description of xylan pyrolysis through a two-stage, consecutive mechanism is valid.

5. Conclusions

Isothermal weight loss curves, obtained under reduced heat and mass transfer limitations, have been measured and used to investigate the intrinsic chemical kinetics of xylan pyrolysis in the temperature range 473–613 K. According to previous analyses [9–12,20], the process appears to be two-stage. The first stage is very fast and is characterized by a high volatile release and the formation of a solid product. For reaction temperatures equal to or greater than 543 K, again in agreement with the analysis given in [9], further degradation of the solid product is observed, which gives rise to a solid charred residual and further volatile formation. A mathematical formulation of the problem, which assumes two consecutive reaction steps, has been proposed and the kinetic data for the four reaction steps have been determined. Compared to previous analyses, based on a constant ratio between the solid char and the volatile yields, this model does not assume any link among the rates of product formation. Therefore, it can be integrated in more complex kinetic schemes and coupled to the equations of transport phenomena to simulate the dynamics of chemical reactors and, in particular, the variations in product distribution, as the reaction conditions are varied.

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