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Quantitative Studies on Furfural and Organic Acid Formation during Hydrothermal, Acidic and Alkaline Degradation of *D*-Xylose

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Summary. Chromatographic analysis of the degradation of *D*-xylose either in plain water or aqueous sulfuric acid at temperatures ranging from 180 – 220°C gave up to 50 mol% of furfural. Activation energies did not differ significantly between reactions in plain water (E_a = 119.4 kJ/mol), 0.001 *M* H_2SO_4 (E_a = 120.6 kJ/mol), 0.01 *M* H_2SO_4 (E_a = 130.8 kJ/mol), and 0.1 *M* H_2SO_4 (E_a = 120.7 kJ/mol). However, under alkaline conditions the activation energy was only 63.7 kJ/mol, indicating a different reaction mechanism. Isotachophoretic analyses revealed the formation of pyruvic, formic, glycolic, lactic, and acetic acid. While the relative yields of these acids ranged from 0.8 to 7% under hydrothermal and acidic conditions, 10 – 23% were obtained in alkaline degradation.

Keywords. *D*-xylose; Furfural; Organic acids; Isotachophoresis.

Quantitative Studien zur Bildung von Furfural und organischen Säuren während des hydrothermalen, sauren und alkalischen Abbaues von *D*-Xylose

Zusammenfassung. Die chromatographische Analyse des Abbaues von *D*-Xylose in reinem Wasser und Schwefelsäure bei Temperaturen von 180 – 220°C ergab die Bildung von bis zu 50 mol% Furfural. In bezug auf die Aktivierungsenergie zeigten sich keine signifikanten Unterschiede zwischen dem Abbau von *D*-Xylose in reinem Wasser (E_a = 119.4 kJ/mol), 0.001 *M* H_2SO_4 (E_a = 120.6 kJ/mol), 0.01 *M* H_2SO_4 (E_a = 130.8 kJ/mol), and 0.1 *M* H_2SO_4 (E_a = 120.7 kJ/mol). Unter alkalischen Bedingungen hingegen betrug die Aktivierungsenergie nur 63.7 kJ/mol. Dies weist auf einen unterschiedlichen Reaktionsmechanismus hin. Ferner konnte mittels Isotachophorese die Bildung von Brenztraubensäure, Ameisensäure, Glycolsäure, Milchsäure und Essigsäure nachgewiesen werden. Während sich die relativen Ausbeuten in Wasser und Schwefelsäure zwischen 0.8 und 7% bewegten, betrugen sie unter alkalischen Bedingungen 10 bis 23%.

Introduction

As the production of energy carriers and chemical raw materials from biomass matter, e.g. straw and wood, is gaining importance, mechanistic studies on the formation of biomass degradation products attract increasing interest [1 – 2]. In addition to enzymatic [3], alkaline [4 – 5] and acidic hydrolysis [6 – 8], both hydrothermal [9 – 12] and organosolv [13 – 14] processes have been applied for

the utilization of biomass. Both of these processes permit the gradual and temperature-dependent degradation of biomass. Specifically, at approx. 200°C hemicellulose and a considerable part of the lignin components are dissolved, at 280°C the cellulose part is degraded to a large extent with formation of monomeric carbohydrates, and above 300°C the residual lignin can be transformed into soluble compounds, such as phenols. In the hydrothermal process, lignocellulosic materials are decomposed only in water at elevated temperature and pressure. In the organosolv process, organic solvents, such as methanol and ethanol, are added to water to increase delignification.

A previous study has already shown that the *pH*-value decreases during hydrothermolysis of biomass under both dynamic and static conditions [10]. The extent of the *pH*-shift depended on the temperature of degradation. In a subsequent study [15], the formation of organic acids during hydrothermolysis and organosolv degradation of wheat straw was evaluated quantitatively by means of isotachophoresis and ion chromatography. A comparison of data obtained showed no significant qualitative or quantitative difference in the acid composition. However, in several experiments it was found that the formation of organic acids preceded the elution of hemicellulose. Moreover an increase in temperature from 190°C to 225°C resulted in tripling of the maximum amounts of acetic acid formed.

In order to elucidate further the reaction mechanisms underlying the degradation of biomass under hydrothermal, acidic and alkaline conditions, high-performance liquid chromatography and isotachophoresis were used in this study to evaluate quantitatively the formation of furfural and organic acids during the degradation of xylose in different solvents at temperatures ranging from 180 – 220°C.

Materials and Methods

Degradation of D(+)Xylose

D(+)Xylose (Merck, Art. 8689, Darmstadt, FRG) was dissolved in H_2O, 1 *M* H_2SO_4, 0.1 *M* H_2SO_4, 0.01 *M* H_2SO_4 and 0.001 *M* H_2SO_4, respectively, at a concentration of 10 mg/ml. Three to five milliliters of each of the solutions in stainless steel autoclaves (170 × 7 mm I.D.) were kept in an oil bath at 180°C to 220°C for 2 to 55 minutes. The heating-up period found to be approximately 60 seconds was deducted from the total reaction time. Reactions were quenched by submerging the autoclaves in a mixture of ice and water. For evaluating the degradation of *D*(+)xylose under alkaline conditions, solutions containing 14.8 mg each of xylose per ml of 0.1 *N* NaOH were treated at 61°C and 79°C for 4 to 19 minutes.

High-Performance Liquid Chromatography

The liquid chromatographic system, used for the analysis of xylose and furfural, consisted of a pump (Beckman, Model 112, Berkeley, CA, USA), a sample injection valve (Beckman, Model 210) with a 20-µl loop, a column oven (Shimadzu, Model CTO-2A, Kyoto, Japan), a differential refractive index detector (Bio-Rad, Model 1770, Richmond, CA, USA) and a Shimadzu C-R3A integration system. A pre-packed Aminex HPX-87 H strong cation-exchange resin column (300 × 7.8 mm I.D., Bio-Rad) served as stationary phase. The eluant was 0.01 *M* H_2SO_4. The analyses were carried out at a flow-rate of 0.8 ml/min and at a temperature of 85°C. No sample pretreatment was required.

Ultrafiltration

Due to the small volumes injected in capillary isotachophoresis, the fine particles dispersed in most biomass degradation samples may cause a considerable reduction in accuracy of analysis. Therefore,

all samples were purified by ultrafiltration, using the disposable micropartition system Centricon 10 (cut-off: 10 000 Dalton, Amicon, Danvers, MA, USA) which allows the recovery of organic acids with an efficiency of almost 100% [15]. The ultrafiltrates were obtained by centrifugation in a fixed angle rotor (Heraeus, Hanau, FRG) at 1 500 × *g* for 15 minutes at room-temperature.

Isotachophoresis

Isotachophoretic analyses of organic acids were carried out on an LKB 2127 Tachophor (LKB-Producter AB, Bromma, Sweden), equipped with a 250-mm Teflon capillary of an internal diameter of 0.5 mm. The running electrolytes were chosen on the basis of a recent evaluation of the impacts of *pH*-value and concentration of electrolytes on relative mobilities and molar flow-rates of organic acids [16]. The leading electrolyte system contained 5 m*M* of hydrochloric acid (Merck, Art. 9970), adjusted to *pH* 3.50 by the addition of β-alanine (Merck, Art. 1008). Triton X-100 (Serva 37238, Heidelberg, FRG) was added to the leading electrolyte to sharpen zone boundaries by depressing electroendosmosis. The final electrolyte contained 5 m*M* of propionic acid (P 1386, Sigma, St. Louis, MO, USA).

Standards and samples were injected by means of 10 µl-Hamilton syringes (701 N, Hamilton Bonaduz AG, Switzerland) through the inlet membrane into the leading electrolyte. All reference substances, which were purchased from Fluka (Buchs, Switzerland) and Sigma (St. Louis, MO, USA), were of the highest possible purity and dissolved in doubly distilled water. Separations were started at a current of 210 µA, which was gradually reduced to 60 µA, when separated zones could be detected on account of their conductivity and differential of conductivity. All analyses were performed at 20°C.

Results and Discussion

Formation of Furfural

In Fig. 1, the results of the hydrothermal degradation of *D*-xylose as well as the formation of furfural in relation to the initial amount of *D*-xylose are plotted as a function of time and temperature in a range of 180 to 220°C. Figure 2 shows the

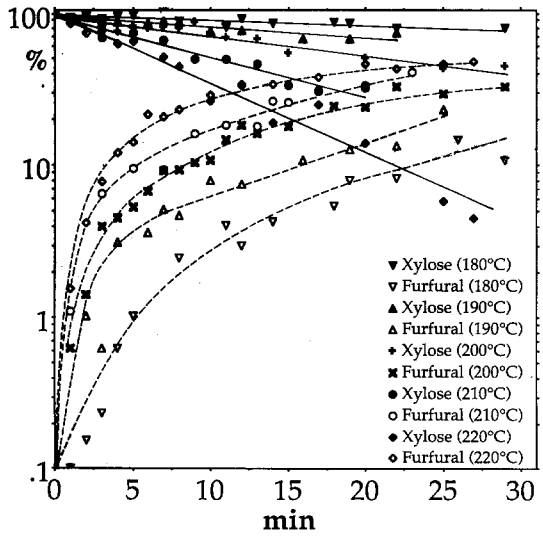


Fig. 1. Rates of hydrolysis of *D*-xylose in plain water and formation of furfural in mol % at temperatures ranging from 180 – 220°C

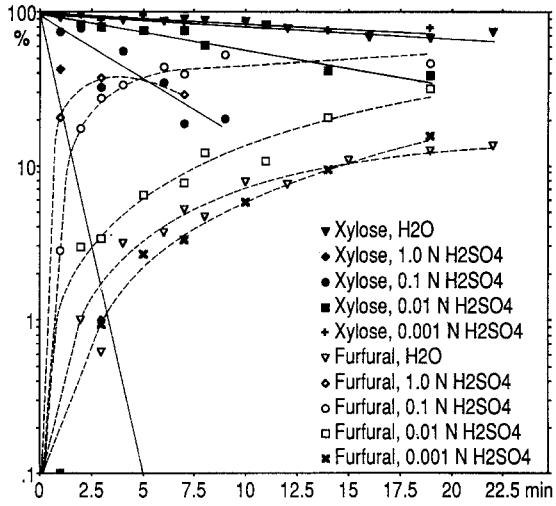


Fig. 2. Effect of the concentration of sulfuric acid on the hydrothermal degradation of xylose to furfural in mol % at 190°C

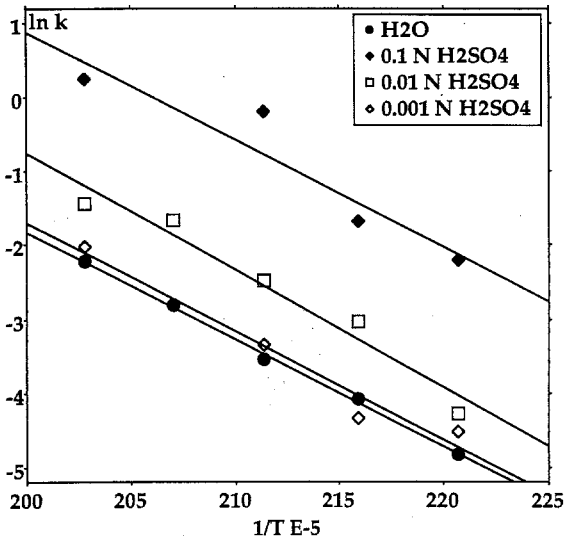


Fig. 3. Arrhenius plot of the measured rate constants

Table 1. Activation energies and impact factors for the hydrolysis of xylose

Medium	E_a [kJ/mol]	A
H_2O	119.4	$4.83 \cdot 10^{11}$
0.001 N H_2SO_4	120.6	$7.15 \cdot 10^{11}$
0.01 N H_2SO_4	130.8	$2.20 \cdot 10^{11}$
0.1 N H_2SO_4	120.7	$9.98 \cdot 10^{11}$
0.1 N NaOH	63.7	$3.45 \cdot 10^{8}$

influence of the concentration of sulfuric acid on the degradation of *D*-xylose at 200°C. In the presence of 1 *M* H_2SO_4, *D*-xylose was degraded completely within 5 minutes. Because of the paucity of data points obtained at this concentration, it was not included in the determination of rate constants. In the temperature range investigated, hydrolysis of *D*-xylose follows first order kinetics. The solid lines in the Arrhenius diagram (Fig. 3) were obtained by linear regression analysis. Acti-

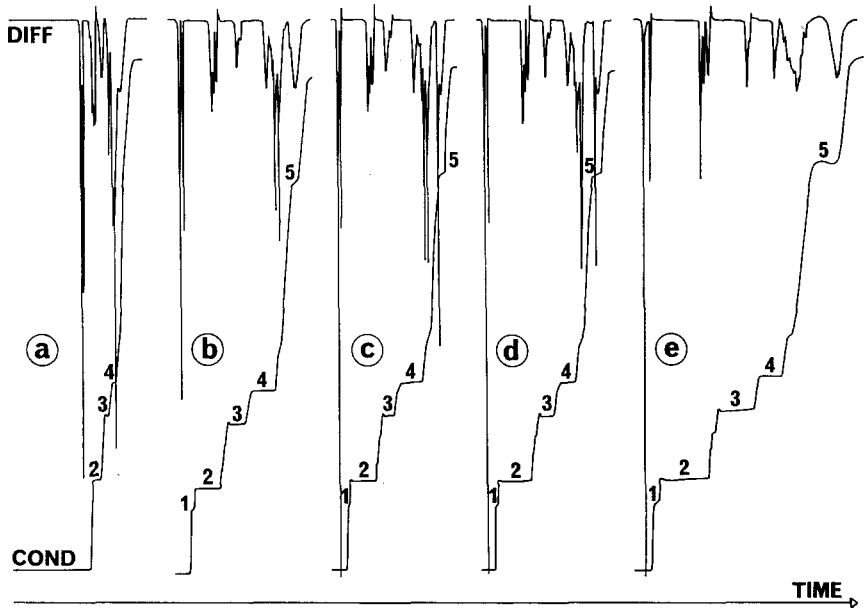


Fig. 4. Isotachopherograms of hydrothermal degradation samples of *D*-xylose obtained after 4 min (a), 6 min (b), 9 min (c), 14 min (d), and 19 min (e) of reaction at 220°C. Leading electrolyte: 0.005 *M* HCl, β-alanine, 0.1% Triton X-100, *pH* 3.50. Terminating electrolyte: 0.005 *M* propionic acid. Detection current: 60 μA; temperature: 20°C; chart speed: 0.2 mm/sec; sample volumes: 7 μl. Zone identification: 1 = pyruvic acid, 2 = formic acid, 3 = glycolic acid, 4 = lactic acid, 5 = acetic acid

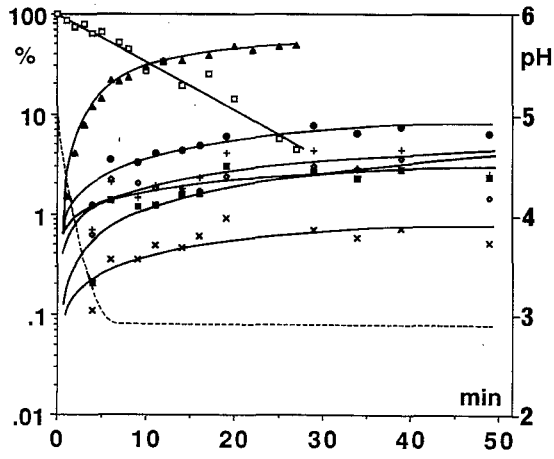


Fig. 5. Relative yields of organic acids (*w*/*w*) obtained from the hydrothermal degradation of *D*-xylose at 220°C: xylose (□), furfural (▲), pyruvic acid (×), formic acid (●), glycolic acid (+), lactic acid (◇), acetic acid (■), *pH* (---)

vation energies were calculated from the slope of the regression lines. Whereas there were no significant differences between the activation energies of the hydrolysis of *D*-xylose in plain water or sulfuric acid, approximately only half the activation energy was required under alkaline conditions (Table 1). In these cases, no furfural was formed.

Formation of Organic Acids

The formation of organic acids during degradation of *D*-xylose was determined quantitatively by isotachophoresis. Figure 4 shows isotachopherograms of five fractions obtained at 220°C in plain water, which consisted of pyruvic, formic, glycolic, lactic, and acetic acid, identified by the injection of an additional small amount of proper reference samples.

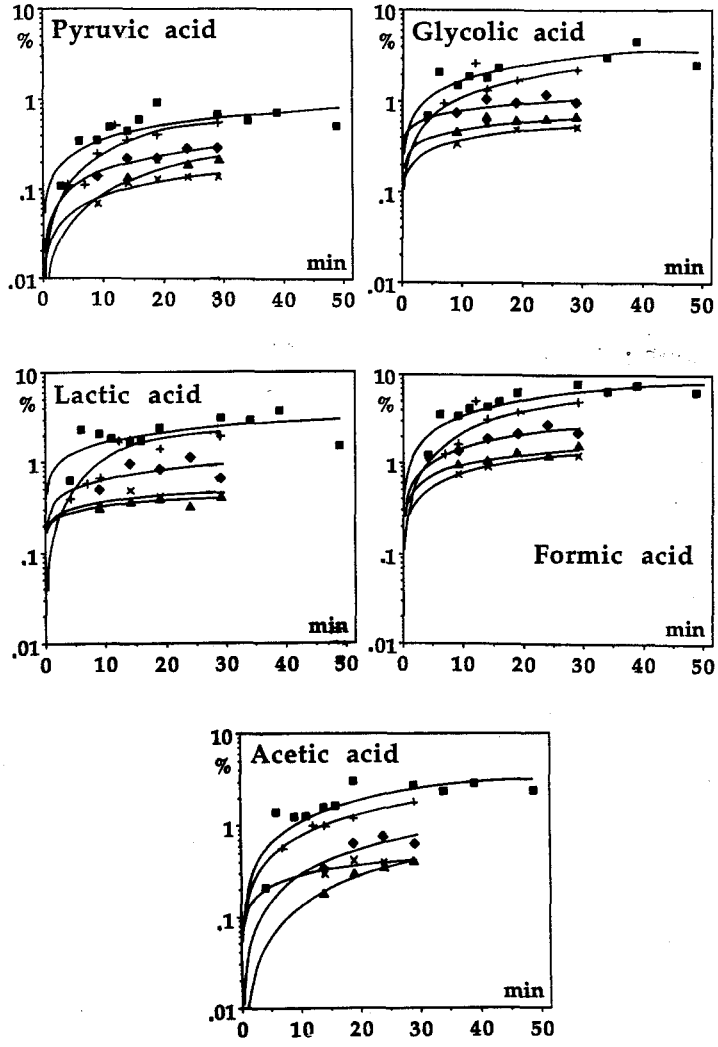


Fig. 6. Effect of degradation temperature on relative yields (*w*/*w*) of pyruvic, glycolic, lactic, formic, and acetic acid obtained from hydrothermolysis of *D*-xylose: 180°C (▲), 190°C (×), 200°C (◆), 210°C (+), and 220°C (■)

As shown in Fig. 5, the *pH*-value decreased rapidly from 5.1 to 2.9. This result partly from the organic acids formed, amounting to 15–20% of the xylose degradation products. At 220°C the relative yields of formic, glycolic, lactic, acetic, and pyruvic acid were approx. 7%, 4%, 3%, 2.5%, and 0.8%, respectively. As shown in Fig. 6, these yields increased with increasing temperature.

In comparison to the hydrolysis of *D*-xylose in plain water, in 0.01 *M* or 0.001 *M* H_2SO_4 less glycolic and lactic acid was formed, while the yields of formic and acetic acid increased (Fig. 7). Only small differences were found with respect to the formation of pyruvic acid.

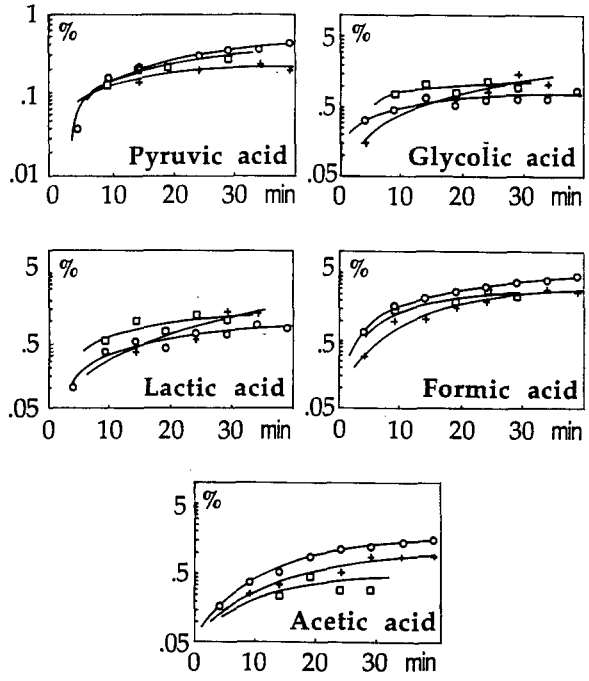


Fig. 7. Comparison of relative yields of organic acids (*w/w*) obtained from the degradation of *D*-xylose at 200°C in plain water (□), 0.01 *M* H_2SO_4 (○), and 0.001 *M* H_2SO_4 (+)

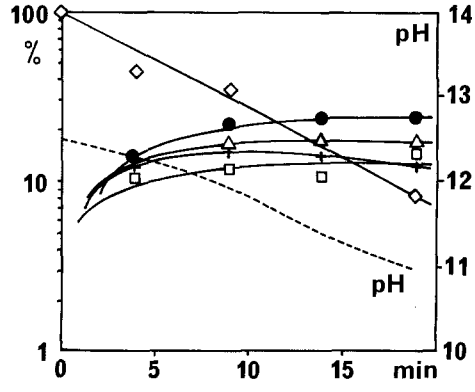


Fig. 8. Relative yields of organic acids (*w/w*) obtained from the degradation of *D*-xylose in 0.1 *M* NaOH at 79°C: xylose (◇), formic acid (+), glycolic acid (△), lactic acid (□), acetic acid (●), *pH* (---)

Under alkaline conditions the relative yields of formic, glycolic, lactic, and acetic acid, ranging from 10 to 23%, were significantly higher than those obtained under acidic or hydrothermal conditions. Among the acidic compounds formed only formic, glycolic, lactic, and acetic acid were determined quantitatively (Fig. 8). Whereas the *pH*-value decreased from 12.5 to 12.3 at an incubation temperature of 61°C, at 79°C it dropped to approx. 11.

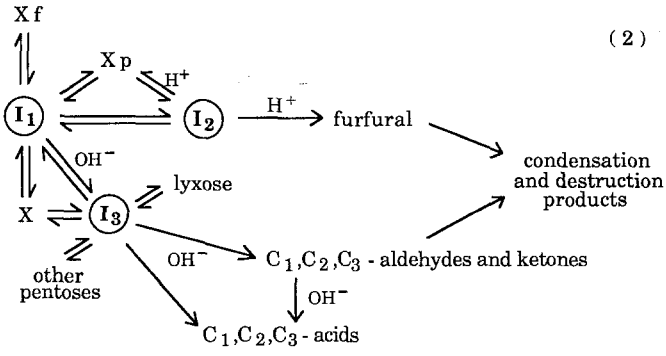
Reaction Kinetics

Root and coworkers [17] describe the degradation of xylose and the formation of furfural as follows:

$$\text{xylose} \rightarrow (\text{intermediates}) \rightarrow \text{furfural} \rightarrow \text{destruction products} \quad (1)$$
$$\downarrow \qquad\qquad \downarrow$$
$$\text{condensation products}$$

This equation is generally accepted as an overall description of the process. In subsequent studies, however, a more detailed reaction mechanism was outlined. Moreover, a comparison of the results obtained from the degradation of pentoses with those of hexoses [5, 8, 11, 18, 19] provides additional information for an interpretation of the complex degradation pathway.

Based on publications directly concerned with the degradation of pentoses [7, 17, 20–22] and our own data, the degradation of xylose may be described as follows:



(2)

In Eq. (2), the intermediate I_1 is responsible for the equilibrium between acyclic xylose (X), xylofuranose (Xf) and xylopyranose (Xp). For the second intermediate (I_2), Antal and coworkers [21] proposed a protonated xylopyanose compound. Intermediate I_3 governs the Lobry de Bryn-Alberta van Ekenstein rearrangement, leading to lyxose and other pentoses. Furthermore, it is assumed that the fission of the C_5-chain originates from this intermediate, resulting in the formation of aldehydes, ketones and organic acids. By equation 2, several results can be explained:

1. In relatively acidic solutions and under continuous removal of furfural over 90% of xylose can be transformed into furfural (method of xylane determination).
2. At high temperatures (200–250°C) the generally alkali catalyzed Lobry de Bruyn-Alberta van Ekenstein rearrangement proceeds even in neutral or low acidic media.
3. Under alkaline conditions very high yields of acids are obtained and this pathway may also lead to the formation of 3-deoxy-glycosuloses [23].

4. Equation 2 is in agreement with the more detailed kinetic evaluation of the formation of furfural, aldehydes and ketons as described by Antal et al. [21] in neutral and acidic media.

The degradation of xylose (X) follows a first order mechanism:

$$\frac{d[X]}{dt} = k_1 [X]. \tag{3}$$

After prolonged reaction times of 20 – 30 minutes in plain water at temperatures of 180 – 220°C nearly 50 mol% of the consumed xylose are transformed into furfural (Fig. 1). During the first period of the reaction, the relative yield of furfural is markedly lower, indicating that the concentrations of the intermediates increase somewhat during the reaction. Reaction rates, determined in the presence of sulfuric acid at concentrations of 0.001 *M* and lower, did not differ from those in plain water. Only at considerably higher sulfuric acid concentrations reaction rate constants become approximately proportional to the content of acid (Fig. 2). This is in good agreement with the results of previous experiments [24] of the hydrolysis of cellobiose.

The activation energy (E_a) and the impact factor (A) of the overall xylose degradation reaction were calculated according to

$$k_1 = Ae^{-Ea/RT}. \tag{4}$$

From Table 1 it can be concluded that activation energies are essentially identical for both hydrothermal and low acidic conditions (119 and 121 kJ/mol, respectively) and deviate only insignificantly at higher acid concentrations (131 and 121 kJ/mol, respectively). These values are in good agreement with those obtained by other investigators [6, 8, 17, 20], ranging from 114 to 141 kJ/mol under similar conditions. Moreover, the significant difference in activation energy values (approx. 60 kJ/mol) found for the hydrothermal and acidic conditions on the one hand and the alkaline procedure on the other hand proves that the latter does not follow the acid catalyzed pathway.

The hypothesis that a second molecule, probably the proposed protonated xylopyranose intermediate, is involved in the dehydration of xylose to form 2-furaldehyde is further supported by the observed impact factors.

Finally, the somewhat delayed formation of organic acids compared to the rate of the consumption of xylose indicates that, as in the formation of furfural, an intermediate (I_3) may be involved in the reactions described.

References

[1] Wase D. A., Foster C. F. (1984) Biomass **4**: 127
[2] Graneli W. (1984) Biomass **4**: 183
[3] Hörmeyer H., Schwald W., Bonn G., Bobleter O. (1988) Holzforschung **42**: 95
[4] De Brujin J. M. (1986) Monosaccharides in Alkaline Medium: Isomerisation, Degradation, Oligomerisation, CSM TH Delft
[5] Bonn G., Binder H., Leonhard H., Bobleter O. (1985) Monatsh. Chem. **116**: 961
[6] Brennan A., Hoagland W., Schell D. (1986) Biotechn. Bioengin. Symp. **17**: 53
[7] Sproull R., Bienkowski P., Tsao G. (1985) Biotechn. Bioengin. Symp. **15**: 561
[8] Baugh K., McCarty P. (1988) Biotechn. and Bioengin. **31**: 50
[9] Bobleter O., Pape G. (1986) Austrian Patent 263661

[10] Bobleter O., Binder H. (1980) Holzforschung **34**: 48
[11] Bobleter O., Bonn G. (1983) Carbohydr. Reg. **124**: 185
[12] Bonn G., Concin R., Bobleter O. (1983) Wood Sci. Technol. **17**: 195
[13] Moeller M. B., Isbell R. E. (1982) Report No. TVA, OP/ED & T-82/42, Tennessee Valley Authority
[14] Bonn G., Hörmeyer H. F., Bobleter O. (1987) Wood Sci. Technol. **21**: 179
[15] Bonn G., Oefner P. J., Bobleter O. (1988) Fres. Z. Anal. Chem. **331**: 46
[16] Oefner P., Häfele R., Bonn G., Bartsch G. (1990) J. Chromatogr. **516**: 251
[17] Root D. F., Saeman J. F., Harris J. F., Neill W. K. (1959) Forest Prod. J. **9**: 158
[18] Kallury R. K. M. R., Ambidge C., Tidwell T. T., Boocock D. G. B., Agblevor F. A., Stewart D. J. (1986) Carbohydr. Res. **158**: 253
[19] Antal M. J., Mok W. S. L., Richards G. N. (1990) Carbohydr. Res. **199**: 91
[20] Conner A. H., Lorenz L. F. (1986) Wood Fibre Sci. **18**: 248
[21] Antal M. J., Leesomboon T., Mok W. S., Richards G. N. (1991) Carbohydr. Res. **217**: 71
[22] Feather M. S., Harris J. F. (1973) Adv. Carbohydr. Chem. Biochem. **29**: 161
[23] Feather M. S. (1970) Tetrahedron Letters **48**: 4143
[24] Bobleter O., Schwald W., Concin R., Binder H. (1986) J. Carbohydr. Chem. 5: 387

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