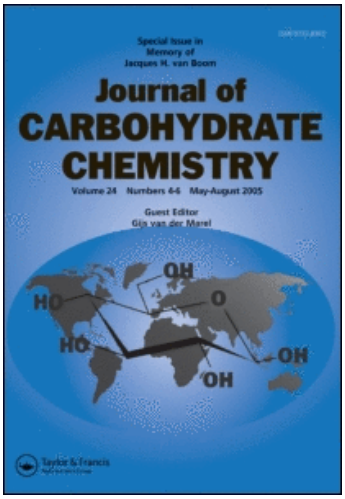

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Hydrothermolysis of Cellulose Under Static and Dynamic Conditions at High Temperatures

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To cite this Article Schwald, W. and Bobleter, O.(1989) 'Hydrothermolysis of Cellulose Under Static and Dynamic Conditions at High Temperatures', Journal of Carbohydrate Chemistry, 8: 4, 565 — 578
To link to this Article: DOI: 10.1080/07328308908048017
URL: http://dx.doi.org/10.1080/07328308908048017

J. CARBOHYDRATE CHEMISTRY, 8(4), 565-578 (1989)

HYDROTHERMOLYSIS OF CELLULOSE UNDER STATIC AND DYNAMIC CONDITIONS AT HIGH TEMPERATURES

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Received January 20, 1988 - Final Form February 27, 1989

ABSTRACT

Cellulose (cotton) was hydrolyzed under high temperature conditions without any addition of acidic or alkaline catalysts. Kinetic parameters of this hydrothermal process were established in batch experiments at temperatures ranging from 200 - 300°C. The degradation of cellulose followed a first-order reaction kinetic with an activation energy of 129 kJ mol^{-1}. Relatively small concentrations of monomeric sugars were detected in the reaction solutions due to the rapid decomposition into furfurals under static conditions. In dynamic experiments, cellulose was hydrolyzed at various percolation rates. Several reaction products were analyzed quantitatively. Application of optimized parameters allowed almost complete solubilization of cellulose, with more than 60 % of the initial material recovered as sugars.

INTRODUCTION

Hydrothermolysis is known as an autohydrolytic process for the conversion of lignocellulosic materials

into soluble products of different molecular weight.[1-3] As an alternative to processes based on acidic or alkaline catalysis[4-6] the reaction under hydrothermal conditions uses only pure water at elevated temperatures. The required temperature and the reaction time depend on the objective and the plant material which is investigated.

Generally, a direct conversion of cellulose into glucose in one step can only be accomplished at relatively high temperatures. Lignocellulosic biomass, such as aspenwood, birchwood or wheat straw is, preferably, hydrolyzed in two steps,[7,8] whereby in the first step the hemicelluloses and the easily hydrolyzable lignin are removed at temperatures between 180-220°C. The resulting water-soluble fraction contains oligo- and polymeric hydrolysis products of hemicellulose, as well as low-molecular weight degradation products derived from lignin.[9] Subsequent enzymatic or acidic treatment of the remaining cellulosic fraction allows the conversion of the insoluble residue into glucose. It was shown that at temperatures between 260 - 270° C also hydrothermal treatment gives saccharification yields (approx. 50 % glucose) comparable to acid catalysis.[10] However, these results are based on the main fraction, and therefore not representative for the total conversion of the starting material. Moreover, a further increase of the amount of sugars formed during the reaction is desired.

With respect to the results of Saeman[11] and Fagan et al.,[12] who described the temperature dependance of acid hydrolysis of cellulose, an increase in reaction temperature is expected to result in improved saccharification yields obtained after hydrothermolysis. They have shown that, in equation I, the reaction rate constant k_1 (hydrolysis of cellulose) is affected more by increasing temperatures, than is k_2 (decomposition of glucose).

$$\text{Cellulose} \xrightarrow{k_1} \text{Glucose} \xrightarrow{k_2} \text{Decomposition products} \qquad \text{(I)}$$

Therefore, in the present work, we have investigated the hydrothermal degradation of cellulose over a wide range of temperatures up to 300°C. Kinetic parameters were established from studying the hydrolysis reaction under static conditions (batch experiments). For dynamic experiments a hydrothermolysis apparatus was constructed, which allowed operation at pressures required for the high temperature treatment. Reaction parameters were varied, in order to optimize the saccharification yields for this percolysis process. The course of reaction was studied by analyzing a number of hydrolysis and degradation products.

RESULTS AND DISCUSSION

The course of reaction for the hydrothermal degradation of cellulose (cotton) is shown in Fig. 1. As can be seen the reaction follows a first-order kinetic. In contrast to earlier studies[14], the calculation of reaction rate constants k_1 for the hydrolysis of cellulose resulted in considerably lower values. However, the observed difference was to be expected, due to modifications in the experimental set-up. Whereas the studies in[14] were carried out in glass ampules, the results described here were obtained by using stainless steel autoclaves. Thus, any catalytic effect caused by the glass wall (increased alkalinity in the solution) could be avoided. Another difference was that, in the present study, cotton cellulose was treated hydrothermally, rather than cellulose from oat plants, which were grown under a $^{14}CO_2$-containing atmosphere, where consequently radiation induced crosslinking occurs.[14] Evaluation of the Arrhenius-plot shown in Fig. 2 results in an activation energy of

$$E_a = 129.1 \ \text{kJ} \times \text{mol}^{-1} \qquad \text{(II)}$$

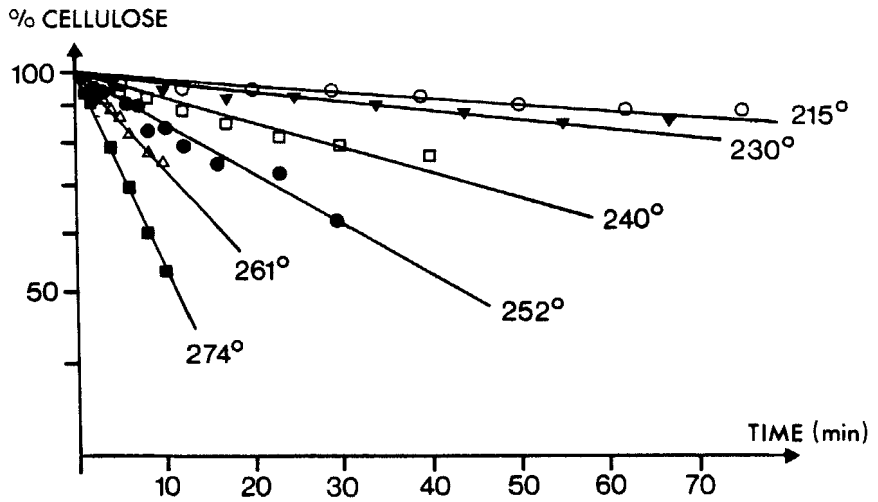

Fig.1: Hydrothermal degradation of cellulose; percentage of original cellulose as a function of time and temperature (°C).

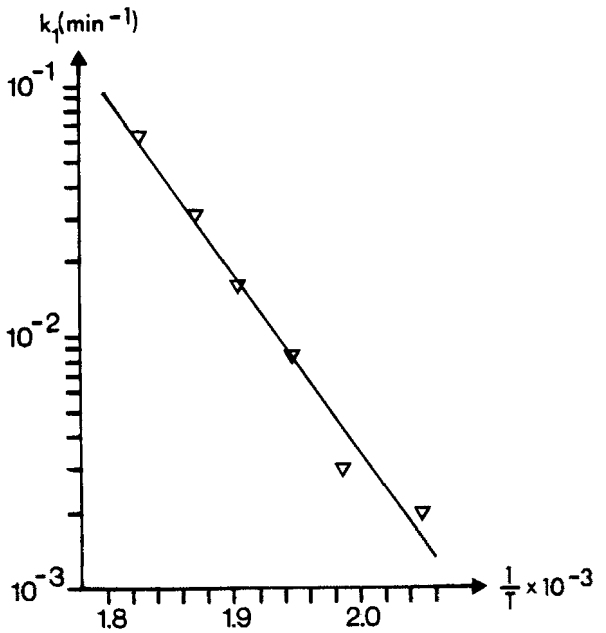

Fig.2: Arrhenius-plot of the hydrolysis of cellulose under hydrothermal conditions.

Surprisingly, the value for this heterogenous reaction is comparable with the activation energy obtained after hydrothermal degradation of cellobiose in a homogenous system.[15] A similar E_a-value (133 kJ x mol^{-1}) was obtained for the hydrolysis of cellobiose under acidic conditions.[16] E_a-values for the acid catalyzed hydrolysis of cellulosic substrates at temperatures between 170 and 240 °C are reported to be ca. 180 kJ x mol^{-1}.[17,18] In comparison to the activation energy for the high temperature hydrothermal degradation of cellulose these values are considerably higher. The fact that the E_a-values for both, the homogeneous and the heterogeneous hydrothermal reactions are virtually identical, suggests that at temperatures between 200 and 300° C the hydrogen bonds are weakened to such an extent that the cellulose under the given conditions shows the reaction behaviour of a dissolved carbohydrate.

When the experimentally determined k_1-values are used together with the reaction rate constants k_2 for the degradation of glucose, which are reported by Bobleter and Pape,[19] the glucose build up $(G)_t$ can be calculated according to equation III,

$$(G)_t = (C)_o \frac{k_1}{k_2 - k_1} \mu (e^{-k_1 t} - e^{-k_2 t}) \qquad \text{(III)}$$

where $(G)_t$ represents the concentration of glucose at the time t and $(C)_o$ the initial amount of cellulose. The concentration of glucose at t = 0 is zero and μ is the stoichiometric factor that corrects for the weight increase, when cellulose is converted into glucose. The corresponding curves for glucose production and degradation are shown in Fig. 3. It is apparent that under isothermal batch condiditons up to 4 % of the initial cellulose should be recovered as glucose. The actual glucose concentrations,

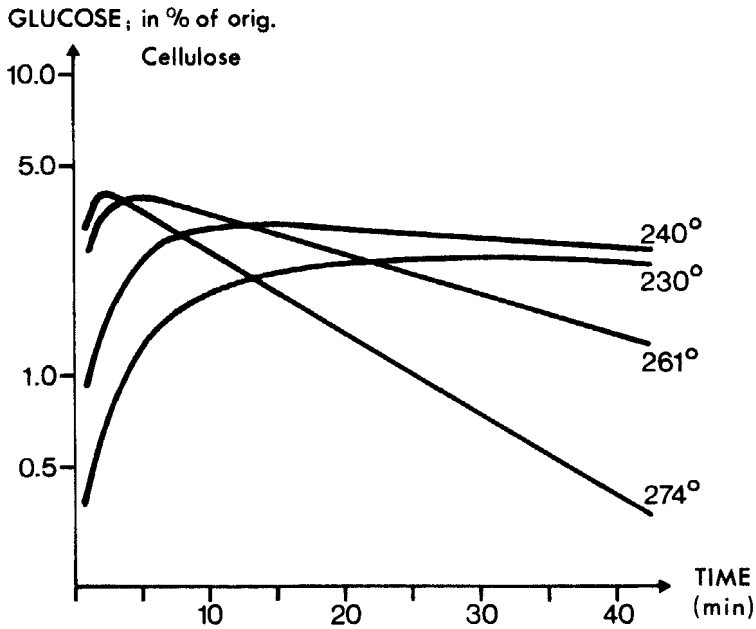

Fig.3: Calculated curves for the formation of glucose from hydrothermolysis of cellulose as a function of time and temperature (°C) according to equation III.

however, found in the corresponding reaction mixtures were substantially lower. This can be explained by the fact, that under the given conditions isomerization products of glucose are formed according to the Lobry-de-Bruyn-Alberda-van-Ekenstein-rearrangement. Similar to earlier studies[15] a considerable amount of fructose, but no mannose, could be detected in the respective solutions. Especially at the reaction temperatures of 230 and 240°C, the concentration of fructose accounted for ca. 50 % of the glucose, present in the solution. At higher temperatures and prolonged reaction times the fast decomposition of both, glucose and fructose, is reflected in relatively high concentrations of HMF and, to a lesser extent, furfural.

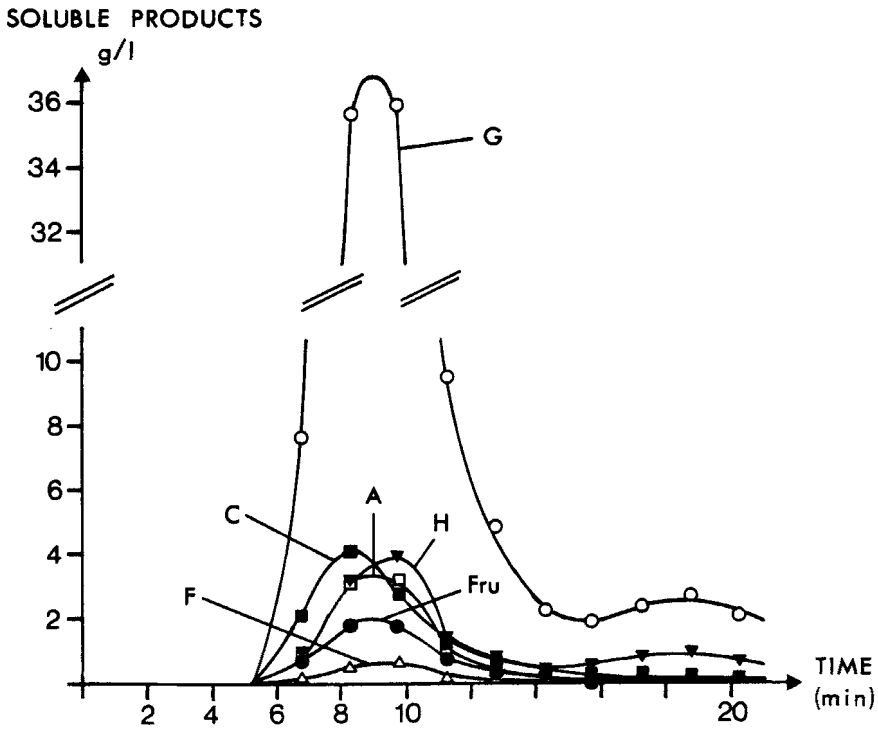

Fig.4: Elution curves for the hydrothermolysis of cellulose under dynamic conditions at 295°C with a percolation rate of 12.5 ml/min;
G...glucose, C...cellobiose, Fru...fructose,
A...anhydro-glucose, H...HMF, F...furfural.

In order to avoid the rapid decomposition of the glucose formed from cellulose, the reaction products, mainly monomeric and some oligomeric sugars, have to be removed from the reaction zone quickly. After a number of preliminary experiments with the newly constructed hydrothermolysis apparatus, and based on the kinetic parameters described above, the reaction temperature was increased even further. At 295°C a series of percolysis experiments was performed with flow-rates ranging from 5.0 - 15.0 ml/min. This corresponds roughly to a 0.5 - 1.5-fold

exchange of the reaction volume per minute. A typical elution profile for the hydrothermal degradation of cellulose is shown in Fig. 4.

Under the given conditions (flow-rate = 12.5 ml/min) the percentage of glucose obtained in the main fraction (based on the solids content) exceeded 60 %. The concentration of glucose in the same fraction reached 3.6 %. Although at lower flow-rates substantially higher glucose concentrations can be achieved (i.e. more than 7.6 % glucose at a flow-rate of 5.0 ml/min), Table 1 shows, that at the same time the over-all solubilization of cellulose decreased markedly. As a result, more than 20 % of the initial material remains insoluble and is, in part, converted into tarry products. However, at flow-rates higher than 10 ml/min the cellulose is hydrolyzed almost quantitatively, with ca. 90 % being recovered as soluble products. The difference is lost due to the formation of volatile compounds, such as furfural and organic acids. Of these soluble products close to 80 % have been identified in this study. The distribution of various characterized substances is shown in Fig. 5. It is apparent that the formation of glucose reaches a maximum at a flow-rate of ca. 12.5 ml/min. While glucose accounts for ca. 50 % of the starting material, (somewhat less than in the main fraction alone) cellobiose and the reversion products fructose and anhydro-glucose[20] add another 13 % to the potentially available sugars. Interestingly enough, the amount of HMF remains virtually unchanged with increasing flow-rate.

The integral curves for the production of glucose at the various flow-rates are shown in Fig. 6. The steep slope of these curves indicates that the major part of the cellulose is hydrolyzed within a relatively short time. It should be noted that the total amount of glucose decreases when the reaction vessel is percolated with the highest flow-rate of ca. 15 ml/min. However, the apparent loss in potential glucose is compensated by an increased amount of cellobiose and higher oligomers. This points to the fact,

TABLE 1

Mass Balance and Maximum Concentrations after Hydrothermal Degradation of Cellulose under High Temperature Percolysis Conditions (295°C) as a Function of the Flow-rate

Flow-rate (ml/min)	Water solubles		Insoluble residue	Losses	max. Solids[a)]	max. Glucose[a)]
	Total	Identified				
	in % of orig. Cellulose				in mg/ml	
5.7	67.6	47.8	21.7	10.7	149.7	77.9
7.6	71.0	52.6	16.5	12.5	132.7	77.8
10.1	86.9	64.9	5.4	7.7	83.1	43.3
12.9	88.5	68.8	2.4	9.1	60.2	35.9
15.6	87.0	67.9	2.0	11.0	48.6	28.3

[a)] Concentration of the fraction collected at the elution peak maximum

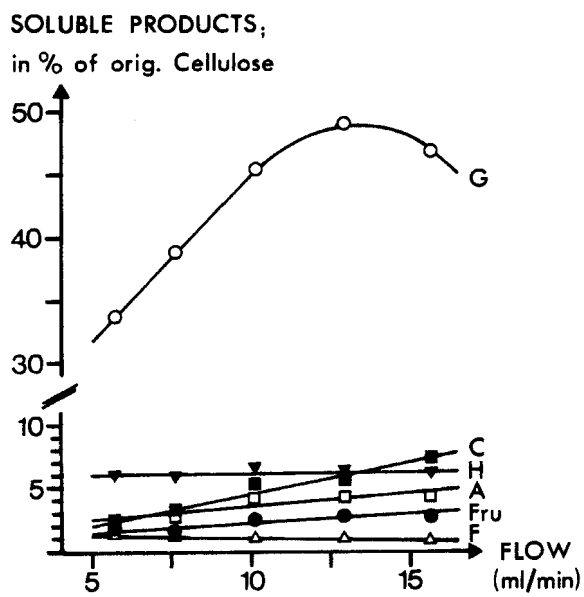

Fig.5: Hydrothermolysis of cellulose at 295°C; distribution of reaction products in percent of the original cellulose as a function of the percolation rate; product identification...same as in Fig.4.

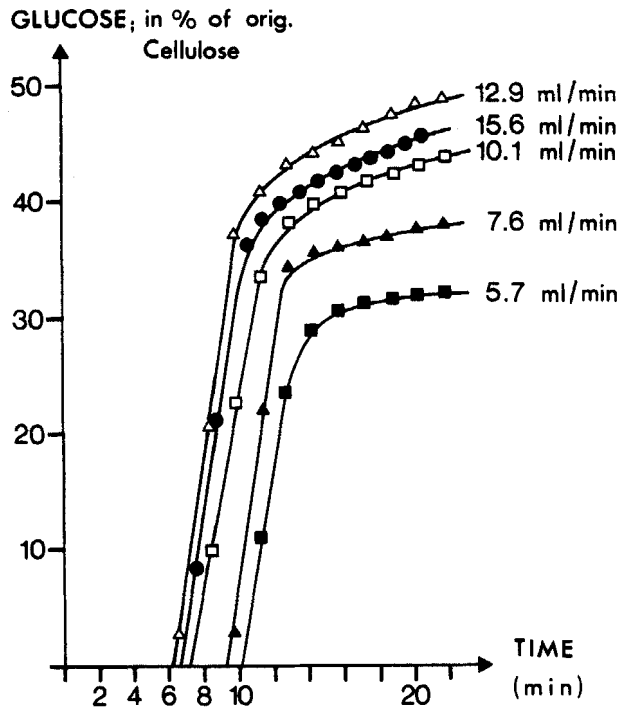

Fig.6: Integral curves for the formation of glucose by hydrothermal degradation of cellulose at 295°C as a function of the percolation rate.

that due to the high liquid velocity the residence time inside the reaction vessel is too short to allow complete hydrolysis of the oligomers which are formed in the first place. The situation is clearly reflected in the relative concentrations of glucose and cellobiose. Whereas at a flow-rate of only 5 ml/min the ratio of glucose : cellobiose in the main fraction is 25.8, the corresponding ratio of the 15 ml/min-experiment is merely 7.3. Although the cellodextrins with higher molecular weight than cellobiose could not be determined quantitatively, the low ratio at 15 ml/min implies that under these conditions a considerable amount of higher oligomers is present in the reaction solutions.

It is concluded that under optimized conditions hydrothermolysis at high temperatures allows saccharification of cellulose with total sugar yields exceeding 60 % of the initial material. The evaluation of the kinetic parameters indicates that hydrothermolysis of cellulose exhibits a reaction mechanism which is distinctively different from that of acid hydrolysis.

EXPERIMENTAL

Materials. Air-dry cotton cellulose with a moisture content of 5% (oven-dry basis) was used for hydrolysis experiments under static conditions. Cotton cellulose from fabric clippings were used for hydrothermolysis in percolation experiments.

Batch Experiments. Cellulose was placed into small stainless steel autoclaves (180 x 8 mm I.D.). Destilled water was added to give a final concentration of 10 mg/ml. The autoclaves were kept in a metallic bath at temperatures between 200 and 300°C for a predetermined period of time. The reaction was then quenched immediately in a mixture of ice/water. The reaction solution was recovered by filtration through a sintered glass funnel. The solid residue was washed for several times, dried at 105°C and then weighed.

Percolation Experiments. Semi-continuous hydrothermolysis was carried out in an apparatus, shown in Fig. 7. Water without any additives is delivered by a high-pressure pump, through a preheating unit into an electrically heated reaction vessel with a reaction volume of 11 cm^3. The cellulose, which was placed inside the vessel, is hydrolyzed by the action of hot water and the reaction products are eluted continuously. After passing a cooling unit and a control valve the reaction solution is collected and fractionated. The control valve has to be adjusted

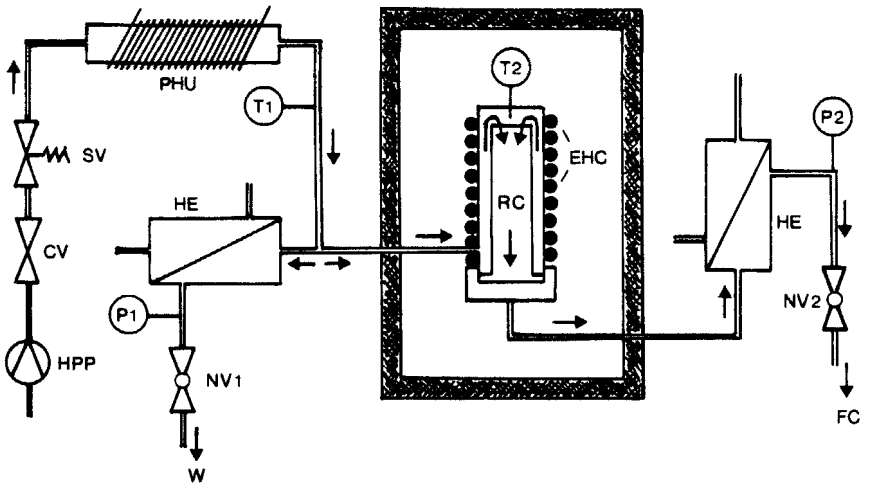

Fig.7: Flow-sheet and reaction vessel of the hydrothermolysis apparatus;
HPP...high pressure pump, CV...check valve, SV... safety valve, PHU...preheating unit, T...thermocouples, P...manometers, EH...heat exchangers, RC...reaction cell, EHC...electrical heating coils, NV...metering valves, W...waste, FC...fraction collector.

such, that the pressure inside the system exceeds the saturation pressure at a given temperature.

Analysis. Quantification of reaction products was performed by HPLC. Carbohydrates were separated on an HPX-87P-column (Bio-Rad Labs, California, USA) with water as eluent.[13] A refractive index detector was used for monitoring the substances. Decomposition products (5-hydroxymethylfurfural (HMF) and furfural) were separated on a reversed-phase column (Nucleosil 5 C_{18}, Machery, Nagel & Co., Düren F.R.G.) with methanol/water (35 : 65, v/v) as eluent. For identification a UV-detector was operated at 254 nm.

ACKNOWLEDGEMENT

The authors wish to thank Ms. B. Hämmerle for skillful technical assistance.

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