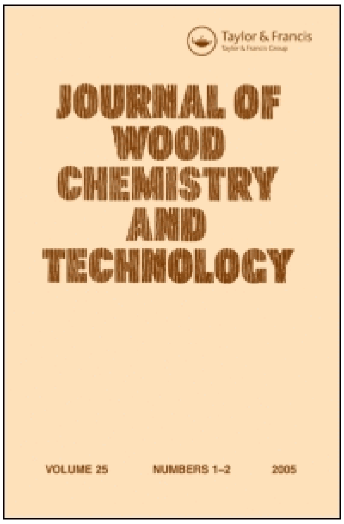

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TWO-STAGE STEAM PRETREATMENT OF WILLOW FOR INCREASED PENTOSE YIELD

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ABSTRACT

A two-stage procedure for pretreatment of fast-growing willow with steam has been investigated. The first stage was performed at temperatures in the range 180°C to 220°C for times between 6 and 10 minutes while the second stage was performed at 220°C for 10 minutes.

The fibrous material was washed between the two stages to remove the pentosans and thus increase the pentose yield. The pretreatment was assessed in terms of glucose yield and xylose yield in the subsequent enzymatic hydrolysis.

The maximum yields, around 70% for both glucose and xylose, were obtained for a pretreatment temperature of 200°C in the first stage. The major part of the xylose was found in the first rinsing water while almost all the glucose was recovered from the final fibrous material.

The glucose yield was increased to above 80% when wet material (30% ODM) was used in the first stage. This required a modification of the steam pretreatment unit, allowing for condensate removal during steaming. The results are very promising but further investigations are needed to optimize the process.

INTRODUCTION

The costs of raw material and enzyme are major contributors in the economics of bioconversion of lignocellulosic materials to ethanol[1]. It is consequently necessary to convert as much as possible of the cellulose and hemicellulose to fermentable sugars. Steam treatment of the raw material has, in several investigations[2-4], been shown to substantially increase the enzymatic digestibility of the cellulose.

Steam pretreatment of willow was investigated in a previous study[5] to find the optimum temperature and time regarding the glucose yield. Pretreatment at 220°C for 10 to 15 minutes was found to give the highest glucose yield, about 80%, based on the raw material. The xylose yield was below 15% but increased at lower temperatures. At 180°C the xylose yield from the fibrous product was about 20% and a small but non negligible amount of oligosaccharides was detected in the rinsing water.

In this study a two-stage steam pretreatment procedure was adopted. The first pretreatment step was performed at a temperature around 200°C and the second at a higher temperature. A wide range of pretreatment conditions has been investigated to optimize both the glucose and xylose yields. The pretreated substrates and rinsing waters were assessed in terms of enzymatic hydrolysis.

EQUIPMENT

Most of the pretreatment experiments were performed with a steam explosion unit consisting of a boiler, a vertically mounted steel cylinder, equipped with three air-activated ball valves, and a cyclone. The maximum pressure in the boiler is 40 bar, which is equivalent to saturated steam at 250°C. A maximum of 100 g ODM can be charged into the pressure vessel. The equipment has been described in more detail elsewhere[5].

The equipment was modified to better handle the condensation inside the pretreatment vessel when using wet material in the second pretreatment stage. The new vessel is a larger cylinder of inner diameter 0.1 m and volume 2.4 L. It is equipped with an inner cylinder which is perforated to separate the condensate from the fibrous material. The condensate is withdrawn from a steam trap. A schematic flow-sheet is shown in Figure 1.

MATERIALS

The raw material was a fast-growing willow, Salix caprea (Q082), which was ground and fractioned. The fraction between 1.0 and 3.15 mm was dried to 94% ODM at room temperature and then stored at 5°C. The composition of the final material is shown in Table 1. The analyses were performed at the Swedish University of Agricultural Sciences in Ultuna[6].

The enzyme preparation used in the hydrolysis was a 1.25:1 mixture of Celluclast 2L, a cellulase from Trichoderma reesei, and Novozyme 188, a cellobiase from Aspergillus niger (both generously supplied by NOVO A/S, Denmark). The specific activity of the Celluclast was 59 FPU/g enzyme solution[7]. The β-glucosidase activity of the cellobiase was 45 μmole p-nitrophenol/g min using p-nitrophenol-β-D-glucopyranoside as substrate[8].

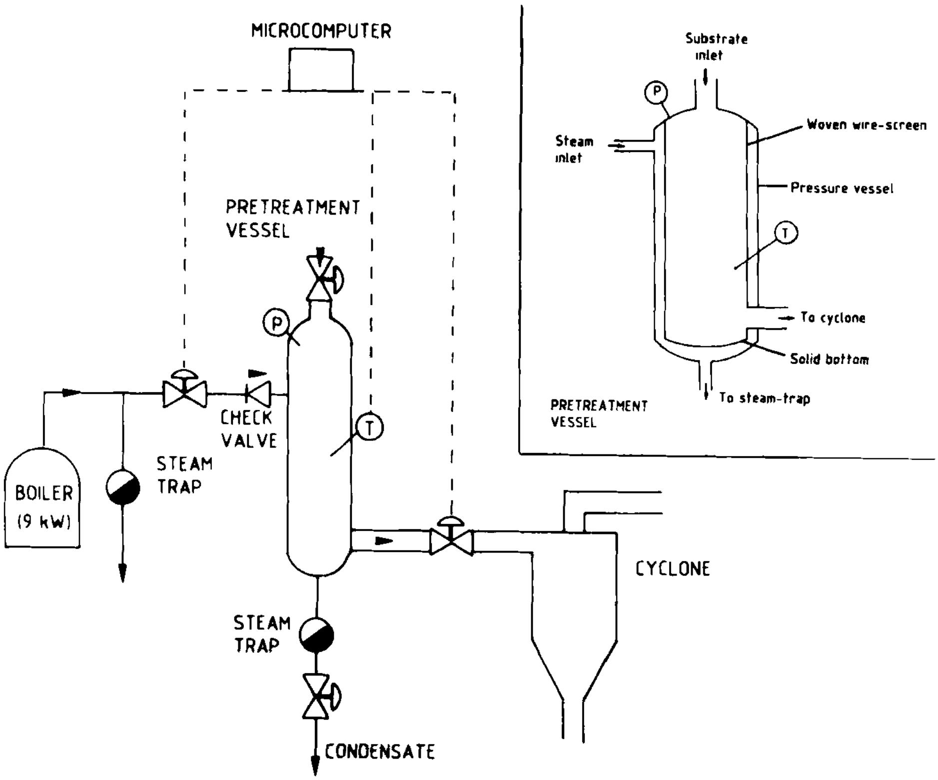

FIGURE 1 Steam pretreatment unit

METHODS

The pretreatment was performed in two stages. A series of experiments was performed where the temperature in the first stage was varied between 180 and 220°C while the second stage was performed at 220°C. The pretreatment time was 10 minutes in the second stage while it was varied between 6 and 10 minutes in the first stage. 200g ODM raw material (94% ODM) were first pretreated at the selected temperature and time. Due to the size of the pressure cell, the pretreatment was carried out in three con-

TABLE 1

Composition of Willow (%ODM) Harvested in 1985 and 1986

	1985	1986
Extractives	7.9	4.9
Klason lignin	21.1	20.7
Cellulose	33.7	36.8
Hemicellulose	24.3	23.0
Raw protein*	≈5-6	≈5-6
Ash*	≈3	≈3

*Estimated from analyses on similar willow

secutive runs, with 1/3 of the material in each, without emptying the cyclone between runs. The pretreated material was washed with 1 L water and then filtered.

The wet solids were recharged into the pretreatment vessel and treated at a higher temperature. The final product was thoroughly washed with four volumes of water of which the first volume was saved and the rest discarded.

The pretreatment was assessed in terms of enzymatic hydrolysis which was performed in stirred vessels at 40°C. In all the hydrolysis experiments a total amount of 200 g solution was used, including 4.55 g of the enzyme mixture. The amount of enzyme was chosen to give an enzyme activity/g ODM comparable to our previous work[5] in which Celluclast from a different batch (76 FPU/g solution) was used.

In the hydrolysis of the solid product, an amount corresponding to 20 g ODM was immersed in 100 g of a 0.1 M sodium citrate buffer solution (pH = 4.8), the enzyme was added and the total weight was adjusted to 200 g by adding water.

The filtrates were also hydrolysed using 200 g of a mixture consisting of 95.45 g filtrate, 4.55 g enzyme mixture and 100 g of 0.1 M sodium citrate buffer solution (pH = 4.8).

Samples of about 2 g were withdrawn from the hydrolysis after 24, 48, 72 and 96 hours. The samples were analysed for glucose, xylose and cellobiose with HPLC using a Bio-Rad Aminex HPX 87H column at 60°C and water as eluant at a rate of 0.4 ml/min.

RESULTS AND DISCUSSION

In a previous study pretreatment of willow at 220°C for 10 minutes led to the highest enzymatic digestibility of the cellulose part. The glucose yield was 80-85% based on the original raw material. At these conditions the xylose (pentose) yield was below 15%. This gives an unacceptable loss of hemicellulose, mainly due to byproduct formation. Table 2 shows the degradation of hemicellulose at different temperatures. The results are obtained from analyses of the unwashed pretreated material.

To increase the pentose yield pretreatment in two stages was investigated. The intention was to remove the major part of the pentose fraction in the first stage, which is performed at a lower temperature, while the hexoses are obtained from the second stage, at 220°C, as in the previous study. Similar results were obtained for all pretreatment times and the following results are for treatment times of 10 minutes.

TABLE 2

Amount of Xylose, Based on % of Original Raw Material, Available After Pretreatment.

Pretreatment Conditions	Xylose Available, %
200°C, 20 min	81
220°C, 10 min	49
235°C, 6 min	14

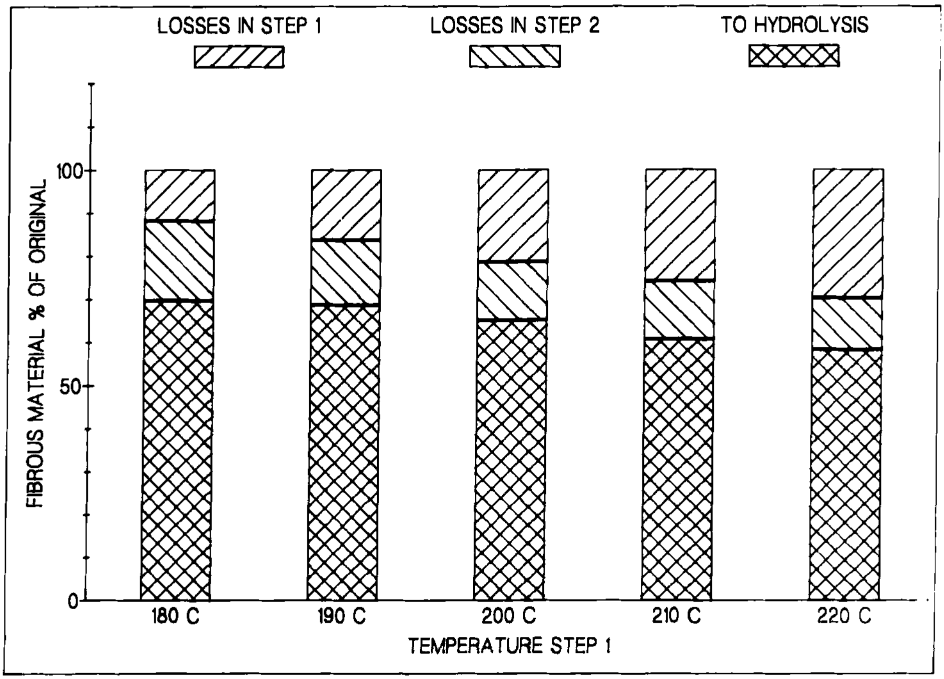

FIGURE 2 Mass balance for fibrous material

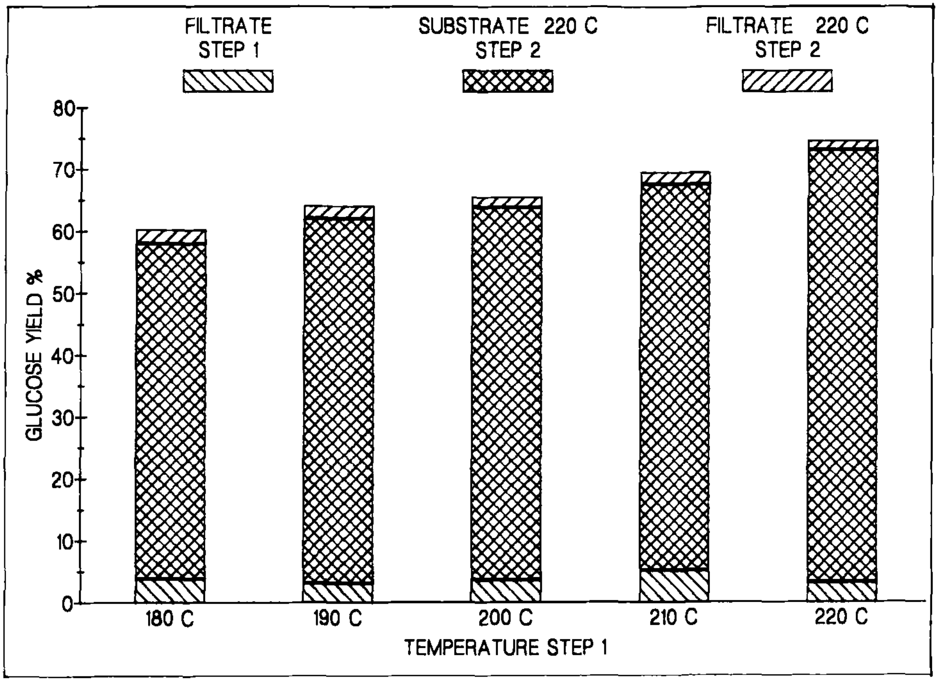

FIGURE 3 Glucose yield

Figure 2 shows the mass balance of fibrous material for the two pretreatment stages. The reduction in fibrous material is mainly due to solubilisation of the extractives and the pentosans. At higher temperatures some degradation of the hemicellulose to byproducts occurs, as can be seen in Table 2. The amount of fibrous material remaining after the two stages decreases with increasing temperature.

Figure 3 shows the glucose yield, based on the original raw material. The amount of glucose in the filtrates from steps 1 and 2 is low and almost constant in all the experiments. The total

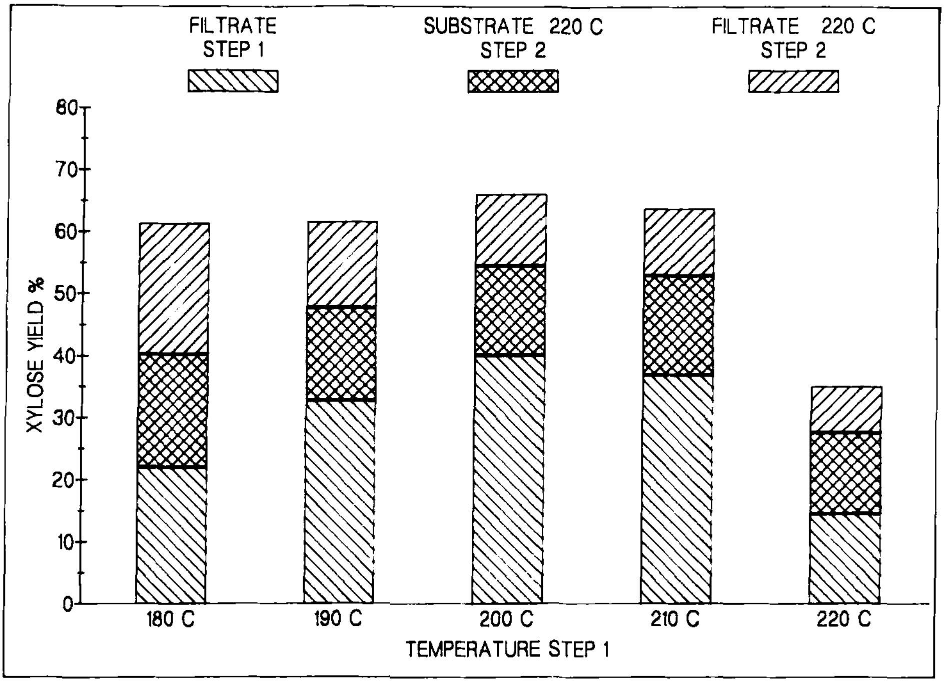

FIGURE 4 Xylose yield

amount of glucose, of which the main part is obtained from the fibrous material, increases with increasing temperature. The maximum glucose yield, 75%, is reached when both the pretreatment stages are performed at 220°C. It is however lower compared with the yield in the previous investigation where only one pretreatment stage was performed at 220°C.

A reason for this could be that the solid material in the second stage is more wet, 35% ODM as compared with the original raw material which holds 94% ODM.

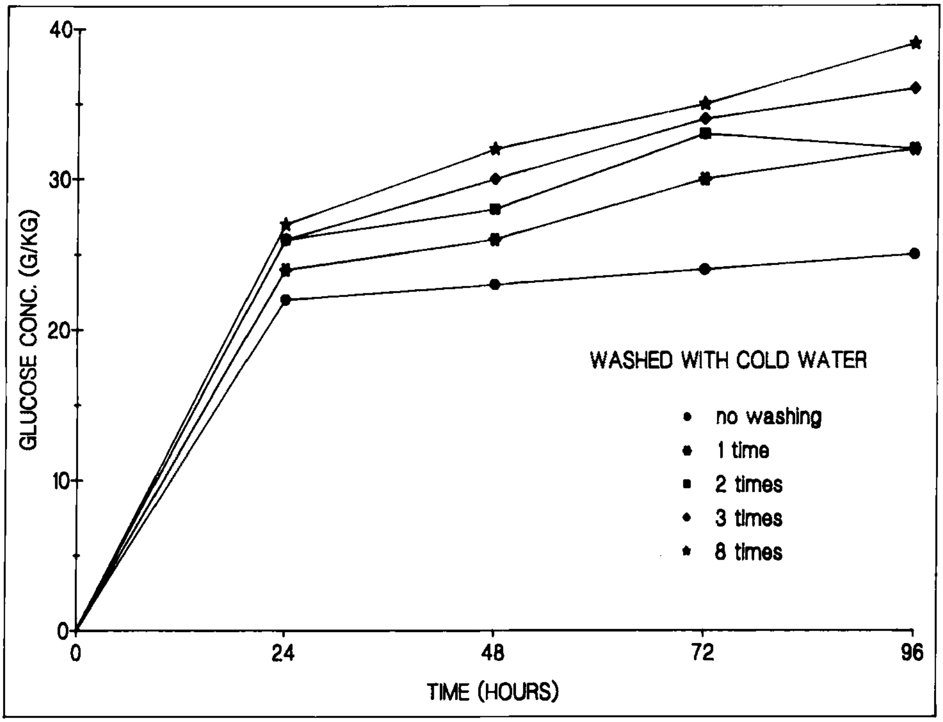

FIGURE 5 Hydrolysis curves for willow washed with cold water
Pretreated at 220°C, 10 min

The xylose yield, also based on the original raw material, is shown in Figure 4. The total amount of xylose increases slightly with increasing temperature to a maximum of 67% at 200°C and then decreases. At 220°C it has dropped considerably to about 35%. At 200°C more than 60% of the recovered xylose is in the first rinsing water.

Some preliminary runs in the modified steam pretreatment equipment were also performed. The main difference compared with

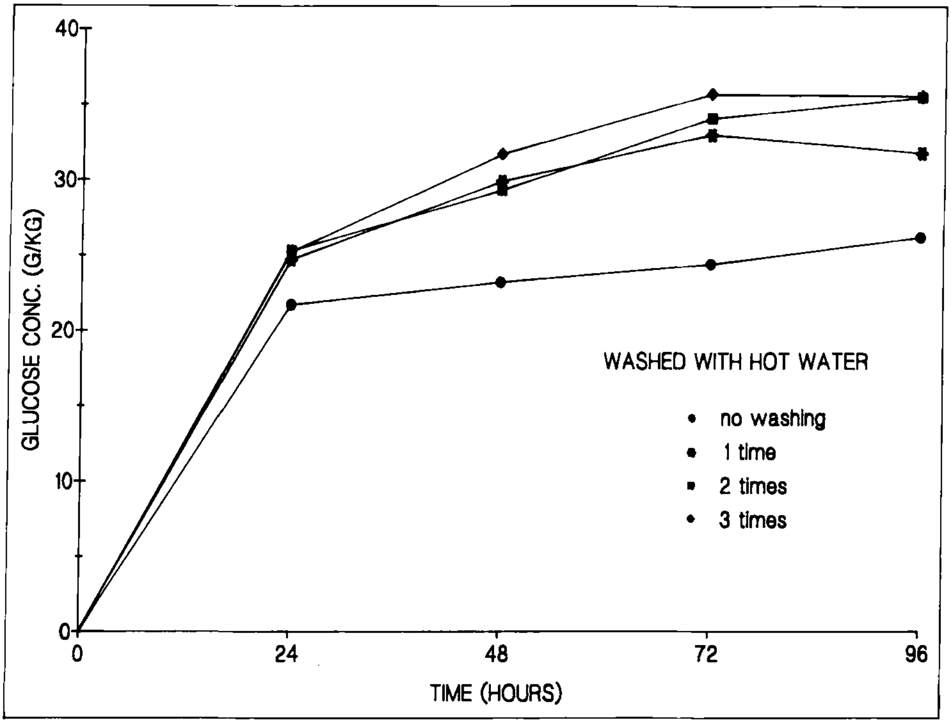

FIGURE 6 Hydrolysis curves for willow washed with hot water. Pretreated at 220°C, 10 min.

the previous equipment is the continuous removal of the condensate formed during the pretreatment. The preliminary results indicate that the glucose yield was increased to above 80%, and up to almost 90% when wet material (30% ODM) was used in the first pretreatment step. On the other hand, the maximum xylose yield decreased from 67% to about 54%.

All the hydrolyses described above were performed with the same amount of enzyme, i.e. 0.76 FPU/g solution, to evaluate the maximum achievable amount of xylose and glucose. In terms of

TABLE 3

Amount of Glucose and Xylose Obtained from the Hydrolysis. Based on 100 g Raw Material

S = Fibrous substrate W1: Wash water from stage 1
W2: Wash water from stage 2

Hydrolysis of	Glucose (g)	Xylose (g)
S	31.9	1.2
W1	0.9	3.6
W2	0.9	1.6
S+W1	32.4	4.3
S+W2	32.0	2.5

FPU/g sugar produced the enzyme concentration is much higher in the rinsing water hydrolysis, about 190 FPU/g sugar, compared with 15 FPU/g for the substrate hydrolysis. In a commercial process the rinsing water would have to be hydrolysed together with the substrate thus reducing the enzyme consumption.

Previous results indicate that hydrolysing the substrate from the second stage without washing it reduces the yield. Figures 5 and 6 show the influence of washing, using cold water and hot water respectively, on the hydrolysis of willow pretreated in one stage at 220°C[5]. The reduction of the hydrolysis rate when washing is omitted could be due to some inhibitory substances or to the change in structure of the fibrous material when physically removing the soluble hemicellulosesaccharides.

Some experiments using a mixture of the rinsing waters and the substrate were also performed using the same enzyme concentration (0.76 FPU/g solution). The results, which are shown in Table 3, indicate that it is possible to hydrolyse the rinsing water together with the substrate. The total amount of sugars from the combined hydrolysis is only slightly less than from the separate hydrolyses. This is somewhat contradictory to the results shown in Figures 5 and 6. The new results are obtained with material from the new pretreatment equipment and thus a certain continuous washing during the steaming is obtained due to the condensate removal.

The results are very promising but more research is needed to optimize the two-stage pretreatment. Different pretreatment conditions will be investigated in future work on improving the yields. Further studies to examine the effect of the rinsing water in more detail are also required.

ACKNOWLEDGEMENTS

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REFERENCES

1. G. Zacchi, K. Skoog and B. Hahn-Hägerdal, "Economic evaluation of the enzymatic hydrolysis of phenol pretreated wheat straw", To be published in Biotech. Bioeng.

2. P. Foody, "Optimization of steam explosion pretreatment", Final report to DOE (USA) Contract ACO-2-79 ET 23050.

3. T.F.P. Schultz, et al, Ind. Eng. Chem., Prod. Res. Dev. 22 (2), 344 (1983)

4. H. Mamers and D.N.J. Menz, Appita, 37 (8), 644 (1984)

5. G. Zacchi and M. Galbe, Biotech Bioeng Symp No 17, 97 (1986)

6. O. Theander and P. Åman, Swedish J. Agric. Res., 8, 189 (1978)

7. M. Mandels, R. Andreotti and C. Roche, Biotech. Bioeng. Symp. No 6, 21 (1976)

8. B. Hägerdal, H. Harris and E.K. Pye, Biotech. Bioeng. 21, 345 (1979)