

XYLITOL RECOVERY FROM SYNTHETIC SOLUTIONS AND FERMENTED HEMICELLULOSE HYDROLYZATES

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Preliminary xylitol separation tests were carried out using both xylitol-xylose synthetic solutions and fermented hardwood hemicellulose hydrolyzate. Xylitol was recovered by a crystallization methodology consisting of dilute solutions evaporation up to supersaturation, supersaturated solutions cooling, separation of crystals by centrifugation, and final filtration. Besides, xylitol solubility limits were estimated at different crystallization temperatures. Product yields and crystal purity were calculated and crystallization kinetics were investigated.

1. INTRODUCTION

Xylitol is a polyol with some interesting properties which make it an important product for food industry. It has similar sweetness as sucrose, is non-cariogenic, tolerated by diabetics and, because of its negative heat of dissolution, used as a part of the coating of pharmaceutical products (Parajó *et al.*, 1998). Nowadays, xylitol is synthesized by hydrogenation of xylose but the solution produced by this process requires expensive purification and separation steps to obtain pure xylitol. It can alternatively be produced by biotechnological methods based on fermentation of agro-industrial residues, which could potentially compete with the traditional chemical way. *Pachysolen tannophilus*, *Debaryomyces hansenii* and *Candida guilliermondii* showed good performances as xylitol producers (Converti *et al.*, 1999). Xylitol recovery is the hardest step of the whole fermentation process because of the low product concentration as well as the complex composition of the fermentation broth. The literature on polyol recovery from fermented broths is quite poor owing to the innovating characteristics of the process. Gurgel *et al.* (1995) suggests very long process time (about one week) but did not report completely the operative conditions. This study aims at setting up a xylitol recovery methodology from fermented and purified broths. For this purpose, the best conditions to separate xylitol were determined combining low pressure evaporation and cooling. Preliminary experiments were carried out under conditions able to prevent the crystallization of xylose, which is present at relatively high concentrations in fermented solutions. Tests were performed on synthetic solutions to optimize the recovery efficiency and on hardwood hemicellulose hydrolyzate to point out the possible influence of compounds dissolved in the fermented broths.

2. MATERIALS AND METHODS

Experiments were performed in a bench-scale system composed of a rotavapor, a crystallization unit, a centrifuge, and a vacuum filtration system. *Debaryomyces hansenii* (NRRL Y 7426) was used for preliminary fermentations of hemicellulose hydrolyzate, which were performed in a 3 l-working volume fermentor. To avoid any possible organic compounds degradation and to prevent any liquid loss, at the beginning of each experiment the solution was concentrated in rotavapor at low pressure ($1.6 \cdot 10^4$ Pa), low temperature (30÷50°C), and slow rotational speed (45÷50 rpm). After concentration, xylitol-xylose solutions were subjected to crystallization in a simple crystallization unit. It consisted in 25 ml glass test-tubes submerged into an ethylene glycol bath and mechanically stirred. As soon as the crystallization temperature was reached, finely ground commercial xylitol was added, up to 1.0 g/l, to favour the nucleation of xylitol crystals. After crystallization, the solutions were subjected to centrifugation. Xylitol crystals were separated by vacuum filtration, re-dissolved in water and analyzed by HPLC.

3. RESULTS AND DISCUSSION

The experimental study was subdivided in three subsequent phases. Preliminary crystallization tests were carried out at two different levels of starting xylitol (270 and 360 g/l) and xylose (93 and 116 g/l) and two different temperatures (-10 and -15°C) to point out the temperature-concentration limit under which the crystallization phenomenon did not occur or a sudden and fast crystal and ice mixture became visible. Crystallization experiments were then carried out using xylitol-xylose solutions at a xylitol concentration beyond the solubility limit, which was determined through preliminary assays. Two different starting xylitol concentrations (582 and 730 g/l) were tested at three different temperatures (-10, -5 and 0°C) to determine the best crystallization conditions and to recovery the product as pure as possible. A final crystallization test was performed using hardwood hemicellulose hydrolyzate.

3.1. Evaporation tests

The low pressure evaporation process allowed to concentrate the solutions, with a concentration similar to those obtained by fermentation (30 g/l xylose and 90 g/l xylitol), up to very high levels, thus simplifying the subsequent crystallization process and making it as profitable as possible.

3.2. Crystallization tests and kinetics

The whole tests were carried out at atmospheric pressure and maintaining constant the selected temperature during each experiment. Because of xylitol solubility reduction due to the simultaneous presence of xylose or by-products in the solutions, previous data referring to temperatures higher than 0°C and to pure xylitol solutions (De Faveri, 2001) are of scarce significance for the purposes of the present work.

As a general rule, a decrease in temperature and an increase in concentration both favoured the crystallization, while a generalized growth in xylose concentration, observed during the starting phases of these tests, was likely due to the volume

reduction consequent to xylitol precipitation. As shown in more detail forward, the highest crystallization yield (0.56) was obtained at 730 g/l xylitol and -5°C . This test was performed at particularly high supersaturation ratio (1.25) with respect to the industrial practice, because of the lack of information in the literature about xylitol solubility in binary mixtures with xylose. On the contrary, the experiment at -10°C and 730 g/l did not give satisfactory results because at such high concentration and low temperature solid precipitation was too fast.

Final xylitol concentrations detected at the end of crystallization tests on synthetic solutions were utilized to obtain the xylitol solubility curves at different concentrations shown in Figure 1. These curves give useful preliminary information to build up a mathematical model able to describe the dependency of crystallization efficiency on mixture concentration.

Table 1 lists the values of the total crystallization yield (Y_c), defined as the ratio of the total mass separated by precipitation to the starting mass of xylitol in the solution, of the purity degree (PD), calculated as the ratio of xylitol to total mass of the recovered precipitate, and of the xylitol yield (Y_{xyl}), expressed as the total crystallization yield multiplied by the purity degree. These results on the whole show a satisfactory total crystallization yield and excellent purity degree, close to 1.00. As previously mentioned, the best results were obtained at 730 g/l xylitol and -5°C : under these conditions most of xylose kept in the solution, whereas about 50% xylitol was recovered. Finally, although the presence of additional solutes imposed to perform test n°6 on hemicellulose hydrolyzate at quite lower xylitol concentration (470 g/l), yields and purity degree comparable to those on synthetic solutions were obtained.

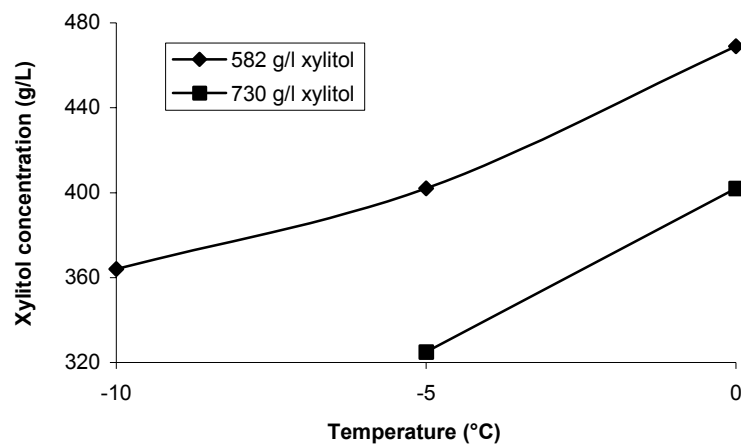


Fig.1: Xylitol solubility curves in the simultaneous presence of xylose

Table 1: Results of crystallization tests X_{yt_e} = Xylitol concentration after concentration; X_{yt_c} = Xylitol concentration after crystallization

Test	T (°C)	X_{yt_e} (g/l)	X_{yt_c} (g/l)	Y_c	PD	Y_{xyt}
1	- 10	582	363	0.41	0.92	0.38
2	- 5	582	402	0.31	1.00	0.31
3	0	582	468	0.20	0.98	0.20
4	- 5	730	324	0.56	1.00	0.56
5	0	730	402	0.48	0.93	0.45
6	-10	470	345	0.29	0.92	0.27

According to the methodology reported by Bravi and Mazzarotta (1998), crystallization kinetics, for starting limpid solutions, can be described by a supersaturation function:

$$r = k (X_r - X_r^*)^m \quad (1)$$

where X_r is the actual solution concentration, X_r^* the saturation concentration at a given temperature, k a kinetic constant and m the growth rate order. Eq. (1) may not be applied to ternary systems, since the driving force for the crystal growth can not be defined properly. However it can be adopted as an assumption of simplification. This rate can also be expressed as:

$$r = -b \frac{dX_r}{dt} \quad (2)$$

where b is a proportionality parameter depending on temperature. Combining Eqs. (1) and (2):

$$\frac{dX_r}{dt} = -k' (X_r - X_r^*)^m \quad (3)$$

where k' is the crystallization kinetic constant. Since our solutions held two compounds at relatively high concentrations, the actual concentration X_r is given by the sum of the concentrations of both components and the term $(X_r - X_r^*)$ becomes:

$$X_r - X_r^* = X_{yt} + X_{yl} - (X_{yt} + X_{yl})^* \quad (4)$$

Because xylose concentration kept almost constant during crystallization, Eq. (4) becomes:

$$X_r - X_r^* = X_{yt} - X_{yt}^* \quad (5)$$

where only xylitol concentration appears.

According to this model, the experimental results were correlated well with the second growth rate order ($m = 2$). This result is in good agreement with those reported in the literature for solutions of different organic compounds, which satisfied crystallization kinetics with order ranging from 1.18 to 2.64 (Bravi *et al.*, 1998). Plotting in Figure 2 the crystallization results, the values listed in Table 2 were calculated for the crystallization kinetic constant, k' .

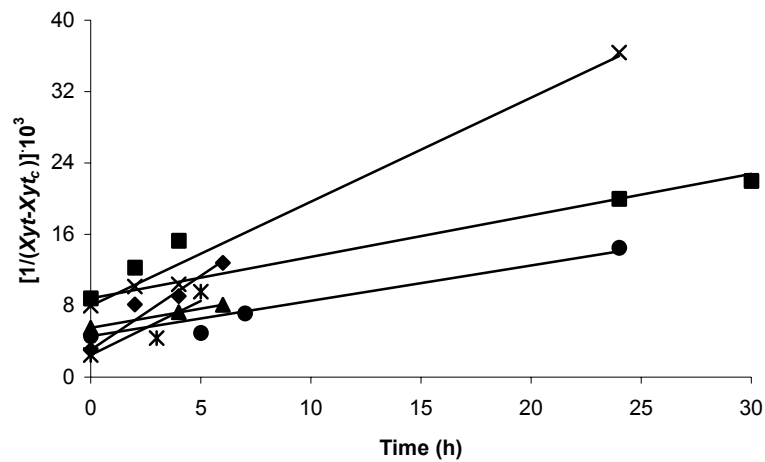


Fig. 2. Results of xylitol crystallization tests plotted according to second order kinetics. (●) Test n°1; (▲) Test n°2; (■) Test n°3; (*) Test n°4; (◆) Test n°5; (×) Test n°6.

The highest values of the second order kinetic constant were obtained with tests n°4 and n°5 because the large amount of dissolved compounds remarkably increased xylitol crystallization rate. In particular, test n°6, performed on hemicellulose hydrolyzate, gave better results than tests on synthetic solutions with even higher starting xylitol concentrations (tests n°1, n°2 and n°3). In fact, organic compounds present in fermented hemicellulose hydrolyzate (xylose, arabinose, arabitol, mannose, mannitol, etc.) lowered the whole broth solubility, thus aiding xylitol crystallization.

Table 2 Second order kinetic constants estimated for xylitol crystallization

Test	X_{yt_e} (g/l)	T (°C)	K' ($l\ g^{-1}\ h^{-1}$)	r^2
1	582	-10	0.396	0.955
2	582	-5	0.428	0.999
3	582	0	0.465	0.760
4	729	-5	1.213	0.851
5	729	0	1.650	0.928
6	470	-10	1.165	0.991

Finally, it is noteworthy the fact that our crystallization experiments lasted quite shorter times than those reported in the literature for an analogous system (Gurgel *et al.*, 1995).

4. CONCLUSIONS

The data collected in this work on xylitol recovery from fermented broth are encouraging: yield even exceeded 0.50 and crystal purity degree was always > 0.90 . The best results were obtained with quite concentrated solutions (730 g/l) at relatively high temperature (about -5°C). The experimental results allowed us to approximately evaluate the crystallization kinetics as function of supersaturation and total solute concentration. Crystallization tests followed second order kinetics. Further studies are planned to confirm the validity of the proposed kinetic model as well as to clarify the influence of xylose concentration on the general economy of the process. In fact, since total xylitol and xylose concentration must be equal to the solubility threshold and xylose concentration keeps almost constant during crystallization -provided it does not exceed the saturation curve-, xylitol concentration decreases as that of xylose increases. According to the present results, which are far to be exhaustive, it is possible to conclude that xylitol separation by crystallization from fermented hemicellulose hydrolyzate is feasible.

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