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Continuous recycle membrane reactor for enzymatic hydrolysis of dual modified potato starch

Joanna Sulej-Chojnacka*, Emilia Konował, Krystyna Prochaska

[a]*Institute of Chemical Technology and Engineering, Poznan University of Technology, pl M. Skłodowskiej-Curie 2, 60-965 Poznań, Poland. Tel.: +48 061 6653601; Fax.: +48 061 6652852; email: joanna.sulej@op.pl, krystyna.prochaska@put.poznan.pl*

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ABSTRACT

The chemically modified starches, and their hydrolysates were developed with broad application in the food, paper and textile industries because of their capacities for emulsifying various colloidal emulsions. One of the methods of making starch hydrolysates is conducting an enzymatic reaction in a continuous recycle membrane reactor (CRMR). The introduction of the membrane reactor makes it possible to conduct the enzymatic hydrolysis process more economically by reusage of enzymes to increase the reaction yield, shorten the reaction time and reduce costs. The aim of the present research was selection of optimal work conditions for enzymatic hydrolysis of dual modified potato starch in a CRMR with an outer ultrafiltration (UF) module (CRMR). Two different variants of courses of the hydrolysis process were investigated. Materials for investigations were dual modified potato starches (by oxidation and acetylation), with the various content of acetyl groups. BAN 480 L, which contains amylase of bacterial origin, was used as an enzymatic preparation. The measure of hydrolysis productivity was a change of dry substance (DS) in the filtrate fraction, while the measure of its efficiency was the obtained degree equivalent (DE) of hydrolyzed derivative.

Keywords: Enzymatic hydrolysis; Dual modified starches; Continuous recycle membrane reactor; Fouling

1. Introduction

Enzymatic bioconversion processes are of increasing use in the production and transformation of raw materials. Important applications have been developed in the fields of food industries, fine chemical synthesis and even for environmental purposes [1]. One of the methods of making starch hydrolysates is conducting a continuous enzymatic reaction in a continuous recycle membrane reactor (CRMR) and separating all the hydrolysis products at the same time. Traditionally reactions are carried out in a classical batch reactor at controlled temperature. At the end of the reaction the enzyme is inactivated before recovering the final product [1]. The membrane with a resolving pore diameter ensures not only retention of the enzyme in a reaction mixture but also isolation of all the expected hydrolysis products from the mixture.

Unlike the tank reactor, the membrane reactor makes it possible to conduct the enzymatic hydrolysis process more economically way by increasing the reaction yield, shortening the reaction time and reducing costs as a result of reuse of enzymes. This reactor is environmentally friendly as well, because of the pure products and their stabilized qualities [1–5]. This kind of reactor has already been proposed for the

*Corresponding author

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production of glucose, maltose or maltotetrose from soluble, gelatinized or liquefied starch [2,5].

The correct selection of the ultrafiltration (UF) membrane is an essential condition for the effective enzyme separation during the process, whereas the isolation of the desirable product requires suitable parameters of the isolating module, like a suitable transmembrane pressure and the velocity of the flow flux.

The major problems in the application of the membrane reactor for enzymatic hydrolysis are large decreases in permeate flux due to fouling [6–8]. Starch preparations used in the research are characterized by high viscosity. There is a potential risk of blocking the membrane, especially at the beginning of the hydrolysis process. The restricted permeability of the membrane grows over the course of time and is connected with the chemical composition of the mixture.

According to this, the CRMR which is used in this research, was equipped with the extra circulation named 'bypass' [9]. It enabled the periodic process of hydrolysis (at the beginning of the process until the viscosity level of the preparations goes down) without simultaneous separation of the product.

Furthermore, CRMR has been stated with two filtration units, which made the separation of the hydrolysis products possible on two different membranes with dissimilar pore diameters and helped to eliminate the membrane blockage during the hydrolysis, without discontinuing the process.

Many kinds of chemically modified starches, particularly their hydrolysates, have been developed with broad application not only in food, but also in the paper and textile industries, it is because of their capacities for emulsifying various colloidal emulsions [10,11]. Not only does the enzymatic hydrolysis of starch preparations decrease the molecular mass of the derivative but it also changes the physical and chemical properties remarkably, mainly viscosity of the solutions.

The purpose of the described research is to find working conditions for the CRMR, with the outer module UF, suitable for enzymatic hydrolysis of double modified starches and the estimation on the influence of the type of derivative modifications on the hydrolysis effectiveness and the separation process of the obtained hydrolysates.

2. Materials and methods

Materials for investigation were modified potato starch produced by Department of Food Concentrates and Starch Products in Poznan, Institute of Agricultural and Food Biotechnology. Double modified starches were obtained by the acetylation process of commercial oxidized potato starches: ''pudding powder'' (P), ''gel-forming food starch'' (G) and ''LUBOX'' (L). As a result of reaction for starches, P and G obtained products, which included 0.5% and 2.5% acetyl groups as a result for starch L product contents of 3% of acetyl group.

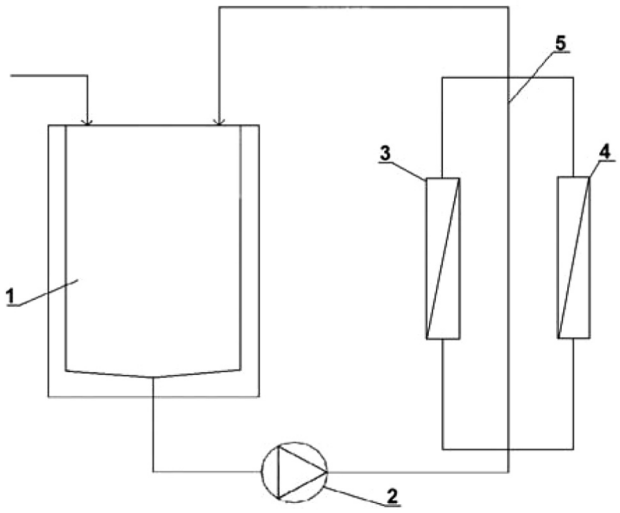

Fig. 1. Schematic diagram of system studied. 1 – reaction vessel; 2 – rotary lobe pump; 3, 4 – ultrafiltration module; 5 – bypass.

These studies were carried out using BAN 480 L, kindly provided by Novozymes (Denmark). BAN 480 L contain α-amylase obtained from selected strains of bacteria *Bacillius amyloliquefaciens* with activity of 480 KNU/g.

Processes of hydrolysis were performed on the CRMR which consisted of a reaction vessel of a 5 L capacity made of acid and basic resistant steel, an outer ultrafiltration (UF) module with two ceramic membranes and a rotary lobe pump. A schematic diagram of the applied system is given in Fig. 1. For these studies a tubular ceramic membrane (Tami Industries) was used. Ceramic membranes were preferred to organic barriers because they have better endurance at high viscosities, temperatures, pressures and acid and basic washing, thus allowing improved working and regeneration of the system [8]. The membrane was characterized by the following parameters: the length 250 mm, three channels, the total surface 0.0083 m^2 and the molecular weight cut off 50, 15 and 8 kDa.

The hydrolysis processes were carried out at a constant temperature of 60°C, and pH of 6.5. These are the conditions in which α-amylase shows the activity. The membrane filtrations were performed at a

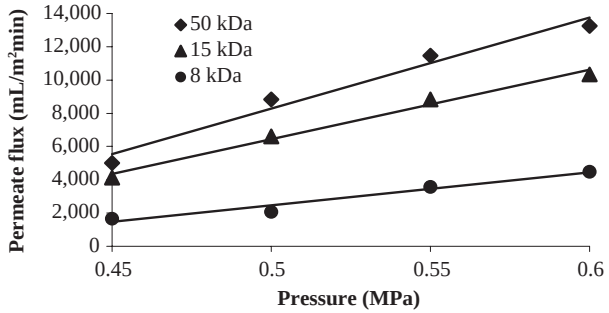

Fig. 2. Dependence of pure water flux on transmembrane pressure for membranes with cut off 8, 15 and 50 kDa.

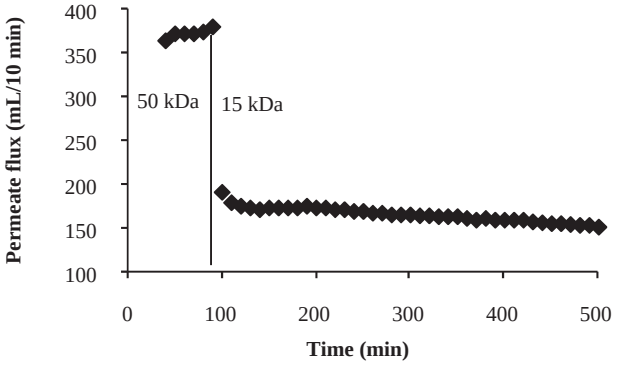

Fig. 4. Time dependence of permeate flux for hydrolysis on membrane module 50/15 kDa.

transmembrane pressure of 0.5 MPa. Initial solution was prepared by heating starch solution (of 5% for (P) starch and of 10% for (G) and (L) starch) at temperature of 90°C and simultaneously stirring. After cooling the starch solution from 90°C to 60°C, the enzyme BAN 480 L with the concentration of 0.33 mL/kg dry starch was added.

The hydrolysis processes lasted for 180 min. Two different variants of courses of hydrolysis process were investigated. According to variant I, for the first 30 min of hydrolysis, the process was led without any simultaneous separation of products. The reaction mixture has been circulating in a reactor only through the 'bypass.' Then, for the next 150 min, it progressed in the filtering system with two different membranes. For the next 60 min, the ultrafiltration processes were carried out on the membrane with a higher cut off of 50 or 15 kDa, and the following 90 min on the membrane with lower cut off of 15 or 8 kDa. In variant II the membrane reactor was used in the classic setup. A weighed amount of pretreated substrate was placed in the reactor and an enzyme solution was then added to the final volume

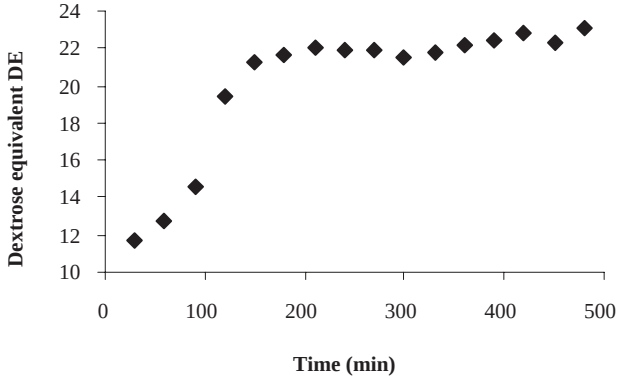

Fig. 3. Time dependence of DE of components in permeate during enzymatic hydrolysis of P 0.5% Ac starch (15 and 50 kDa membranes).

(during hydrolysis, performed according to variant II,) the whole reaction mixture was led to directly to on the ultrafiltration module, without using the bypass. The first 60 min of the ultrafiltration processes were progressed on the membrane with a higher cut off of 50 or 15 kDa, and the following 120 min on the membrane with a lower cut off of 15 or 8 kDa. At the same time, hydrolysis and separation processes were carried out.

The permeate flux was measured every 10 min as an indicator of the effectiveness of the separation process. The filtrate and retentate fractions were taken to determine the efficiency of hydrolysis by estimation of content of dry substance (DS) according to PN-EN ISO 1666:2000; PN-78/A-74701 and the amounts of reducing groups in the permeate fractions. Dextrose equivalents (DE) were determined by the modified Schooal-Roenbogen method (PN-EN ISO 5377-2001).

3. Results and discussion

The hydrodynamic parameters for each of the membranes used in separating modules (i.e. 50, 15 and 8 kDa) were studied before the start of the ultrafiltration process. The change in volume of the flux of deionized water in the time on the transmembrane pressure was studied. Obtained results were presented in Fig. 2. As it can be seen, the membrane with cut off of 8 kDa gives an almost three times smaller filtrate flux in comparison to the membrane with cut off of 15 kDa and four times smaller in comparison to the membrane with cut off of 50 kDa.

To ensure the stability of the system, several long-time (8 h) hydrolysis were carried out (Fig. 3). Results for one of them are presented in Figs. 2 and 4. These data confirm earlier presumption of/about pointless of long time hydrolysis longer than 3 h.

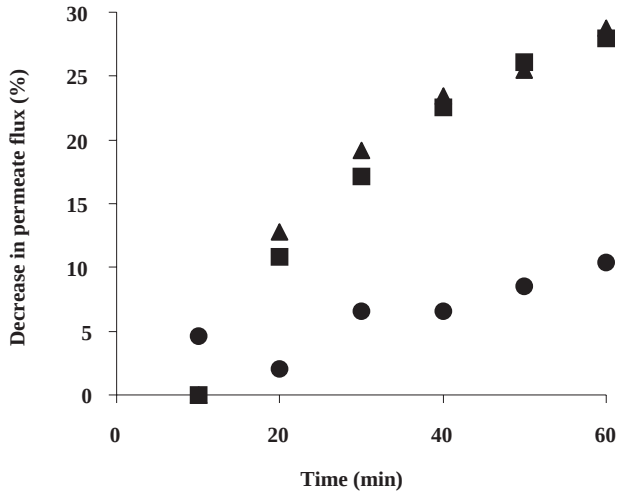

Fig. 5. Change of permeate flux of pudding 2.5% Ac modified starch during first 60 min of separation process for 15 kDa membrane: 15 kDa (▲), 15/8 kDa (■), 50/15 kDa (●).

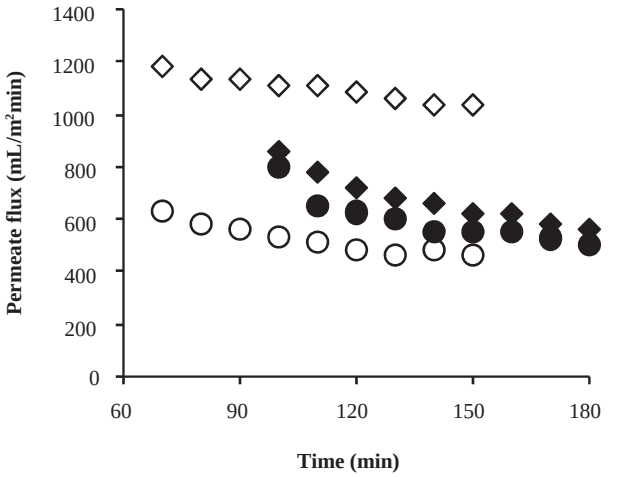

Fig. 7. Time dependence of permeate flux for hydrolysis on second module (8 kDa membrane). Variant I: ▲ 2,5% P, ● 3% L, Variant II: Δ 2,5% P, ○ 3% L.

The results obtained during the long-time process of the hydrolysis prove that the system reaches the steady-state already after 180 min. After this time (180 min), the value of DE and permeate flux are constant and they do not change with time. With regards to economical aspects there is no point in continuing the process for more than 3 h to get the final products.

At the beginning of the hydrolysis process the viscosity of the starch in reaction temperature gruel is relatively high. Taking into account the quality of the obtained maltodextrines (DE < 25), membrane with cut-off of 15 kDa is a strategic one. Unfortunately, the application of this membrane caused significant membrane fouling, and in some cases, the flux was reduced to 30% after the first 60 min of membrane filtration (Fig. 5). The use of the 50 kDa membrane for the first 60 min of the separation process brings about a reduction in the fouling of the membrane working after the 50 kDa membrane. The highest decrease in the permeate flux follows during the first 60 min of separation process, after this time the flux is stable.

Changes in the permeate flux over time (Figs. 6 and 7) show unequivocal differences in the efficiency of the separation process, dependent on the method of hydrolysis and the type of modification of starch preparation used in this process. The reduction of separation efficiency, observed after 90 min in case variant I and after 60 min in case variant II, was connected with a change of membrane module. According to variant I, a drop of permeate flux is noticeable in all analyzed systems, however, the oxidation level of

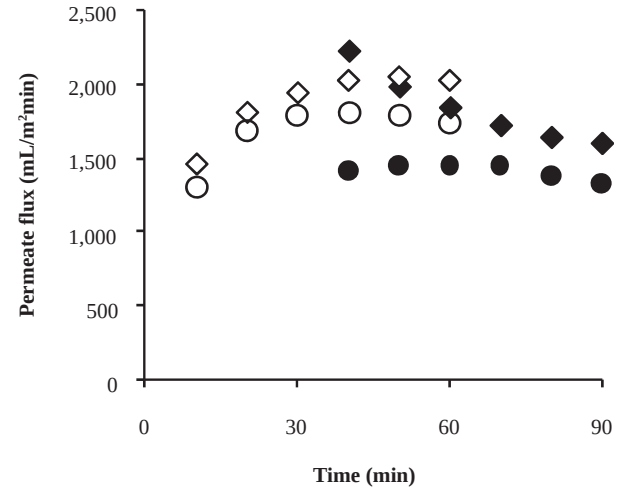

Fig. 6. Time dependence of permeate flux for hydrolysis on first module (15 kDa membrane). Variant I: ▲ 2,5% P, ● 3% L, Variant II: △ 2,5% P, ○ 3% L.

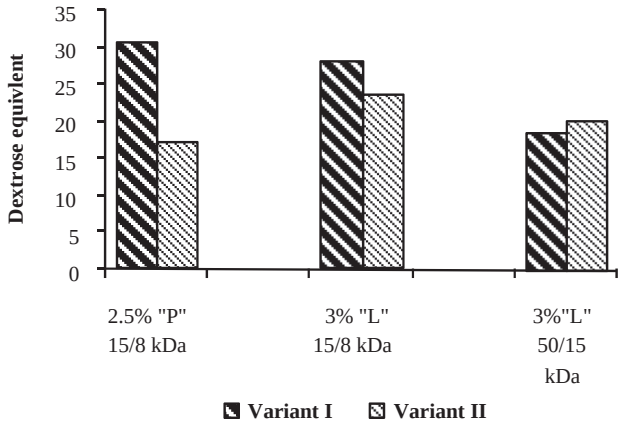

Fig. 8. Dextrose equivalent of hydrolysis products after 150 min of process.

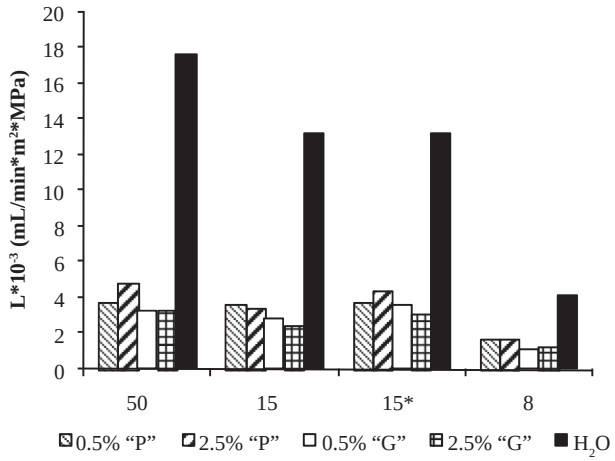

Fig. 9. Permeability of membrane.

hydrolyzed starch preparation was the decisive parameter for the separation deficiency. During the hydrolysis carried out by variant II, the permeate flux and low molecular weight products grew rapidly at the beginning of the process (membrane 15 kDa), until a stable state was reached.

On the basis of the results depicted in Fig. 8, it can be seen that the method of the hydrolysis has the significant influence on the value DE that is on the efficiency of the process. The dextrose equivalent of the hydrolyzed derivative obtained in the case of the CRMR according to variant I is higher, with the exception of one case, in which measured values of DE values differ insignificantly. The dextrose equivalent also depends on the type of dual modified starch.

The membrane permeability during the hydrolysis process of starch and the membrane permeability for deionized water are compared in Fig. 9. It was observed that the obtained products of hydrolysis significantly reduce the permeability of membranes, independently of the type of modification of starch used in the hydrolysis process.

During the separation process of products of enzymatic hydrolysis products, the value of the permeability of the membrane was reduced almost four times as compared to that for pure water.

4. Conclusion

The membrane reactor with an external separation module of UF type enables an effective hydrolysis process of doubly modified starch preparations. Considering high viscosity of hydrolyzed derivatives in the initial stage of the process, it is necessary to switch off the separation unit, which increases the efficiency, it means that there is a higher saccharification level in the obtained hydrolysates. The hydrolysis progress depends on the type of starch modification. The system is stable after 180 min of hydrolysis Independently of the cut off of the membrane. The separated products of the hydrolysis decrease the permeability of the used membrane.

Acknowledgment

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