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## Starch gelatinization and hydrolysis in the apparatus with *Couette-Taylor* flow

### Introduction

During the hydrolysis starch is transformed into useful, added-value biochemicals used in many industries. Starch hydrolysis could be divided into a number of individual processes [1]: gelatinization (preparation to proper hydrolysis), liquefaction, dextrinization, and saccharification. One of the problems, encountered during starch gelatinization is the rapid increase of the fluid viscosity. An example how this problem could be overcome is simultaneous gelatinization and hydrolysis of concentrated starch slurries in extruders (continuous reactor), which was discussed e.g. in [2]. Another example is an application of a coiled heater to starch gelatinization [3]. The flow in coiled heaters is characterized by the presence of *Dean* vortices when axial flow is sufficiently high. According to the authors, presence of these vortices improves heat transfer condition and cause more uniform heating of aqueous starch suspension.

In this work, it was investigating the application of the continuous *Couette-Taylor* flow (CTF) reactor to simultaneous starch gelatinization and hydrolysis. In such an apparatus reacting mixture flows through the annular space between two concentric cylinders, with the inner cylinder rotating (rotor) and the outer one being stationary. *Couette-Taylor* flow possesses some unique characteristics, which arise from the hydrodynamic flow instabilities (emerging above the critical value of rotor rotation frequency  $\omega_c$  in the form of *Taylor* vortices) combined with the axial flow. The shear stress generated by the rotor rotation are expected to reduce the apparent viscosity of the working fluid (because of its non-Newtonian rheological properties) causing also a reduction of the flow resistance. Moreover, the existence of the vortices may also improve the performance of the apparatus, as it was aforementioned. Additionally, in the CTF reactor the appearance of the vortices depends rather on the rotor rotation frequency than on the value of the axial flow. This gives quite wide freedom in the controlling of the reactant residence time in the apparatus. Hence, the CTF reactor seems to be more flexible when compared to the coiled heater.

In this paper, there is presented a preliminary investigation on gelatinization and enzymatic hydrolysis of starch in the apparatus with *Couette-Taylor* flow.

### Computer simulation of starch gelatinization

Our study into starch gelatinization was conducted by numerical simulations of the process using *Fluent 6.2.16*. The results of that investigation were already presented in [4]. There were considered two apparatus: smaller one with  $R_1 = 0.0125$  m (rotor radius) and  $R_2 = 0.0175$  m (outer cylinder radius), and bigger one with  $R_1 = 0.025$  m and  $R_2 = 0.03$  m. The length of the apparatus was  $L = 0.4$  m. Because of extremely high viscosity of fluid, laminar flow without vortices or with axially symmetric *Taylor* vortices was expected for investigation flow conditions. Hence, the simulation were carried out in 2D geometry (the grid cell number 50000). Since there was only a preliminary investigation, the studies were limited to a state after gelatinization, when the viscosity of the fluid was the highest. Therefore, these results represent kind of an extreme situation. It was assumed that the rheological properties of gelatinized starch could be described by *Herschel-Balkley* model [5]:

$$\tau = 11.8 + 13.92\dot{\gamma}^{-0.39} \quad (1)$$

where  $\tau$  is a shear stress and  $\dot{\gamma}$  is a shear rate. The kinetic of starch gelatinization was taken from a paper [6], where a first-order reaction of

starch gelatinization was assumed. Our study was performed for laminar regime flow with or without *Taylor* vortices.

Further computer simulation was conducted using *Comsol* software. There was an attempt of implementation of the model of starch gelatinization presented in the paper [3]. This model allows tracing the change of the starch slurry rheological properties during the process of gelatinization.

### Results of computer simulations

The results of *Fluent* simulation showed that the presence of *Taylor* vortices in the flow caused intensification of heat transfer from the heat jacket to the reacting mixture. Because of this also the process of starch gelatinization was faster for the flow with vortices. Furthermore, rotor rotation caused a reduction of apparent viscosity of the reacting mixture and a reduction of axial pressure drop. However, higher reduction of these parameters was achieved for the bigger apparatus. On the contrary, degree of starch conversion into gelatinized starch was not influenced by the size of apparatus.

These results might suggest that the bigger apparatus is better for starch gelatinization. This conclusion is also supported by the fact that *Taylor* vortex regime flow occurs for smaller value of  $\omega_c$  in the bigger apparatus than in the smaller one. Moreover, in the bigger apparatus, there is a higher value of the productivity for the same reactant residence time in the apparatus, hence lower value of energy consumption (per unit of product) may be expected.

The results of *Comsol* simulation suggested a flow pattern in CTF apparatus during starch gelatinization: in the inlet part of the apparatus there is a flow regime of laminar *Taylor* vortex, which farther turns into laminar flow without vortices. It is connected to the increasing value of apparent viscosity during starch gelatinization.

### Experimental investigation of starch gelatinization and hydrolysis

Starch hydrolysis experiments were carried out in a continuous *Couette-Taylor* apparatus with the water heat jacket. The length of the apparatus was 0.3 m; the radius of inner and outer cylinder was  $R_1 = 0.0125$  and  $R_2 = 0.0175$  m, respectively. The operating parameters are presented in the tab. 1. The experiments were carried out without addition of enzyme (gelatinization alone) and with addition of enzyme (for  $u = 0.018$  cm/s). In the second case, enzyme was introduced through the nozzle at the distance of 5 cm from the reactor inlet. In order to check the heat transfer performance of the apparatus, temperature was measured at the distance of 0.05, 0.15 and 0.25 m from the apparatus inlet (in the middle of the gap between cylinders).

Tab. 1. Conditions of experiments

Inlet ungelatinised starch concentration [g/l]	25; 50; 150
Inlet axial velocity of starch slurries $u$ [cm/s]	0.0088-0.0057
Enzyme volumetric flow rate $u_e$ [ml/h]	0.1-0.3
Inlet temperature [°C]	25
Inlet pH	5.9-6
Temperature of the water in heat jacket $T_{hj}$ [°C]	85, 90
Rotor rotation frequency $\omega$ [1/s]	0.10-97.8
Termamyl 120L (enzyme), Starch from wheat (Wako)	

The sample of the reacting mixture was taken at the outflow of the apparatus. In order to stop the process of hydrolysis they were cooled immediately to about 0°C and their pH was reduced to 2 with addition of HCl. The sample was centrifuged at 2000 g for at least 30 min (to separate solid from liquid phase). The reactants concentration in the liquid phase of the sample was estimated using spectrophotometer (by measurement light absorbance) [5]: 1. The content of starch was measured using aqueous solution of I<sub>2</sub> (0.15%), and KI (0.5%); 2. The content of reducing sugars was measured using DSN method (aqueous solution of 10g/l 3,5-dinitrosalicylate, 16g/l NaOH and 300 g/l potassium sodium tartrate 4-hydrate). The solid phase (if observed) was freeze-dried and weighed.

### Results of experiments

The distribution of the reacting mixture temperature along the apparatus is shown in fig. 1. The temperature inside of the apparatus achieved quickly the value of the heat jacket temperature for  $\omega \geq 11 \text{ s}^{-1}$ . Moreover, heat intensification was visible when compared to  $\omega = 0 \text{ s}^{-1}$ . It suggests indirectly a presence of *Taylor* vortices (at least in the first inlet part of the apparatus) in the flow for  $\omega \geq 11 \text{ s}^{-1}$ . This conclusion is also supported by comparison to results of computer calculation of heat transfer in the CTF apparatus presented in fig. 1. The calculation was conducted assuming that liquid in the apparatus has water properties, hence close to the properties of starch suspension before gelatinisation (i.e. at the inlet part of the apparatus).

The results of some studies of starch gelatinization are presented in the fig. 2. In this figure, there is shown light (630 nm) absorbance of samples (mixed with aqueous solution of I<sub>2</sub> and KI) taken at the outlet of the apparatus. A high value of light absorbance denotes high starch concentration in liquid phase, hence high degree of starch gelatinization. As it is visible the process of starch gelatinisation in the CTF apparatus depended more strongly on axial fluid flow rather than on rotational speed of the rotor. However, degree of gelatinisation increased with increasing value of  $\omega$  and decreasing value of axial flow. Additionally, the temperature of the process influenced significantly starch gelatinization. The degree of gelatinization seemed to increase with temperature when other operating parameters are kept constant.

The results of the investigation on starch hydrolysis are shown in the fig. 3. Quite significant degree of the starch hydrolysis was achieved using a small amount of enzyme (about 6.6  $\mu\text{l}$  of enzyme per 1 g of starch). Moreover, in the fig. 3, reducing sugars ( $C_{rs}$ ) and starch ( $C_{sk}$ ) concentration at the outlet of the apparatus (after hydrolysis) were presented as a function of rotor rotation frequency. The decreasing value of  $C_{rs}$  with increasing  $\omega$  (mechanical energy) could be explained probably by enzyme deactivation. Similar results were noticed in the literature [2], where application of extruder to starch hydrolysis was studied.

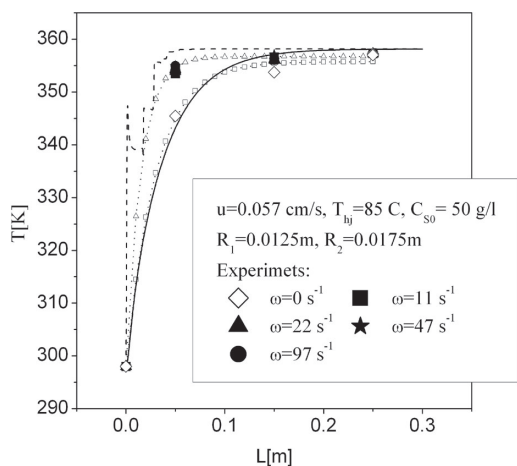


Fig. 1. Distribution of the reacting mixture temperature along the apparatus. Experiments: dash line with white squares –  $\omega = 0 \text{ s}^{-1}$ ; dash line with white triangles –  $\omega \geq 11 \text{ s}^{-1}$ . *Fluent 12.1* Computer calculation assuming that liquid has water properties: solid line –  $\omega = 0$  or  $0.1 \text{ s}^{-1}$  (flow without *Taylor* vortices); dash line –  $\omega = 10 \text{ s}^{-1}$  (flow with *Taylor* vortices)

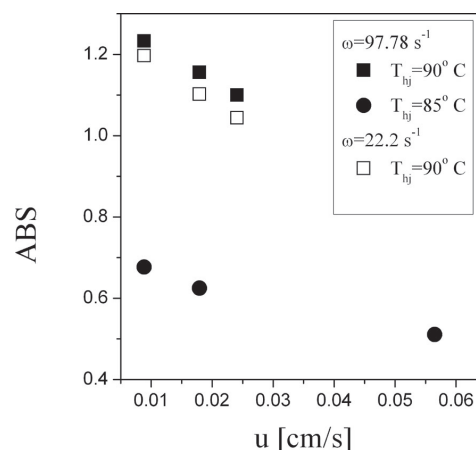


Fig. 2. Light absorbance in outlet liquid phase – experiments without addition of enzyme (gelatinization)

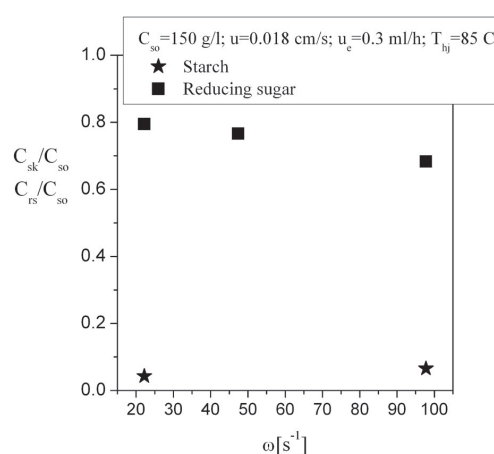


Fig. 3. Concentration of the starch and reducing sugar in outlet fluid ( $C_{so}$  – inlet starch concentration) – experiments without addition of enzyme

### Summary

- The laminar flow regime with *Taylor* vortices in the inlet part of apparatus seems to exist during starch gelatinization in the CTF reactor.
- Enlargement of apparatus seems to be advantageous for the process.
- The presence of these vortices intensifies heat transfer and in such a way process of starch gelatinization and hydrolysis. Moreover, improves reactants mixing, and prevents from separation of starch and water.
- Starch gelatinization depends more strongly on axial flow and temperature rather than on rotor rotation frequency. Nevertheless, the degree of starch gelatinization increase with increasing value of  $\omega$ .
- Significant starch conversion was achieved with quite small amount of enzyme. However, rotation may cause enzyme deactivation. It suggests that the best operating conditions are for the value of the rotor rotation frequency just about  $\omega_c$ .

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*This study has been carried out within the financial support of the Japan Society for the Promotion of Science.*