SEMICONTINUOUS HYDROLYSIS OF DEFATTED PRESSED PALM FIBER IN SUBCRITICAL WATER

Fiorella P. Cardenas-Toro, Tania Forster-Carneiro, M. Angela A. Meireles*

LASEFI/DEA (School of Food Engineering)
UNICAMP (University of Campinas)
Rua Monteiro Lobato, 80; Campinas, São Paulo, Brazil

Email: meireles@fea.unicamp.br

Abstract. The use of biomass has been receiving considerable attention in recent years because it can be used as an alternative to fossil fuels. Hydrolysis of lignocellulosic biomass produces mono- and oligosaccharides, valuable products in chemical industry. The subcritical water hydrolysis has the advantage of use of non-toxic solvents, short conversion times and low residue generation. For sugar production optimization, an understanding of the reaction behavior is needed. The objective of this work was the study of hydrolysis of defatted pressed palm fiber with subcritical water, using a non-isothermic semicontinuous unit equipped with a 50 cm^3 reaction vessel. Defatted pressed palm fiber was obtained after supercritical extraction with CO_2 at 328 K and 20 MPa. The reactions were performed at inlet temperatures of 423 K, 523 K, 673 K; pressures of 15 and 25 MPa; solvent:solid ratios (S:F) of 120 cm^3: 1 g wet weight and 240 cm^3: 1 g wet weight; and residence times of 1.25, 2.5 and 5 minutes. The reaction was evaluated in function of total reducing sugar yield, biomass conversion, and pH. Total sugar yield rate (g glucose/100 g carbohydrate) increased up from 423 K (2-7%) to 523 K (8-15%), and decreased at 673 K (10-12%) for all conditions of pressure, solvent:solid ratio and residence time. Biomass conversion (40- 90%) increased with temperature indicating the formation of by-products. Therefore, optimal conditions were obtained at 523 K, 15 MPa, S:F of 120 cm^3:1 g wet weight and 2.5 min. The influence of pressure was not significant.

Keywords: subcritical hydrolysis, defatted pressed palm fiber, semicontinuous process.

1. Introduction

Biomass consists mainly of agricultural, forestry, animal and industrial residues. These residues are source of cellulose, hemicellulose and lignin, which can be transformed into higher value-added products, such as intermediates for the chemical industry or the production of second generation ethanol. The principal problem of biomass conversion is the lignocellulosic cell wall which is resistant to chemical and enzymatic treatment. In addition, some residues can provide bioactives such as antioxidants and vitamins that are of great interests for food, cosmetic and pharmaceutical industry [1-4].

Conventional techniques, such as acid, base and enzymatic hydrolysis present some disadvantages as later neutralization stages in acid hydrolysis and prolonged reaction times in case of enzymatic hydrolysis. The development of efficient, economic and renewable alternatives is necessary for industrial applications. The use of supercritical technology offers the advantage of change of properties with temperature and pressure, which promotes the selectivity of chemical reactions without producing waste into the environment, so it is considered as a green technology [5-7].

Water is considered to be in the subcritical state when the temperature is between 423 K and 647 K and pressure is higher than its vapor saturate pressure. The physical and chemical properties for subcritical water

differ from those at ambient condition. Ion product increases and dielectric constant decreases, causing water ready to ionize hydrogen and hydroxide ions, thus promoting hydrolysis reactions and solubilizing non-polar compounds and polar gases. These variations influence the kinetics and selectivity of chemical reactions within a network, and in many cases is considered as catalyst [8,9].

Studies on sub- and supercritical hydrolysis of model compounds such as cellulose and hemicellulose have been carried out in order to have a better understanding of reaction pathway. These studies demonstrated that cellulose and hemicellulose can be converted into oligosaccharides, monosaccharides and glucose degradation products. For these model compounds exist a competition between polysaccharide hydrolysis rate and product degradation rate. In addition, a rapid conversion of polysaccharides from lignocellulosic materials in semi-continuous or continuous systems will permit high saccharides production and low degradation products [10-13].

In Brazil, the principal agroindustrial residues are soy, wheat, corn stalks, sugarcane bagasse, corn cob, pressed palm fiber, coconut, among others. All of them contain high amounts of lignocellulosic materials. The palm oil industry produces an estimated amount of 123,000 ton of residues per year, which are burned as fuel for energy production. These residues contain oils rich in alpha and beta carotenes, precursors of vitamin A and large amounts of carbohydrate. The separation of this oil and the conversion of carbohydrates, cellulose and hemicellulose, into value-added products are an alternative of less pollutant utilization [4,8].

In this work, a study of semicontinuous non-isothermic hydrolysis of defatted pressed palm fiber with subcritical water have been proposed in order to evaluate the suitable conditions for production of total reducing sugar. Experiments were performed to investigate the effect of water inlet temperature (423 K, 523 K, 673 K), pressure (15, 25 MPa), solvent:solid ratio (120 cm^3:1 g wet weight, 240 cm^3:1 g wet weight) and residence time (1.25 min, 2.5 min, 5 min) on saccharides production and carbohydrate conversion.

2. Materials and methods

2.1 Materials

Pressed palm fiber was provided by Agropalma Company, Pará-Brazil. The raw material was dried at 313 K for 24 hours in an oven, comminuted using a knife mill (Marconi, model A340, series 0204244, São Paulo, Brazil), and classified using an agitator (Bertel, São Paulo-Brazil). Particle size larger than 80 mesh were stored at 268 K for supercritical fluid extraction experiment.

Supercritical fluid extraction with CO_2 was done in a Speed SFE unit (Applied Separations Inc., Model 7071, Allentown, USA) with extraction cell of 290 cm^3; the extraction procedure was similar to that described by Albuquerque and Meireles [14]. The defatted pressed palm fiber was obtained at 328 K and 20 MPa with CO_2 (99% of purity, White Martins, São Paulo, Brazil). This material was maintained at 268 K. Distilled water was used in all experiments.

2.2 Hydrolysis Equipment

The schematic unit for semi-continuous hydrolysis of defatted pressed palm fiber in subcritical water is given in Figure 1.

The equipment is composed by a liquid high-pressure pump (Thar Technologies, SFE-2×5LF-2-FMC model, Pittsburgh, EUA) for water pumping, a stainless steel heating coil (Autic, 6m x 1/8" i.d., Campinas,Brazil) for inlet water heating, a stainless steel electric heating reactor with capacity of 50 cm^3 (Autic, Campinas,Brazil) and metal-to-metal fit to allow using temperatures up to 673 K, a temperature controller (Autic, Campinas,Brazil), a condenser connected with a thermostatic bath at 298 K (Marconi, model MA-184, Piracicaba, Brazil) to guarantee a rapid cooling of hidrolizates after reaction. The equipment also contains block valves, micrometric valve, thermocouples and manometers [13].

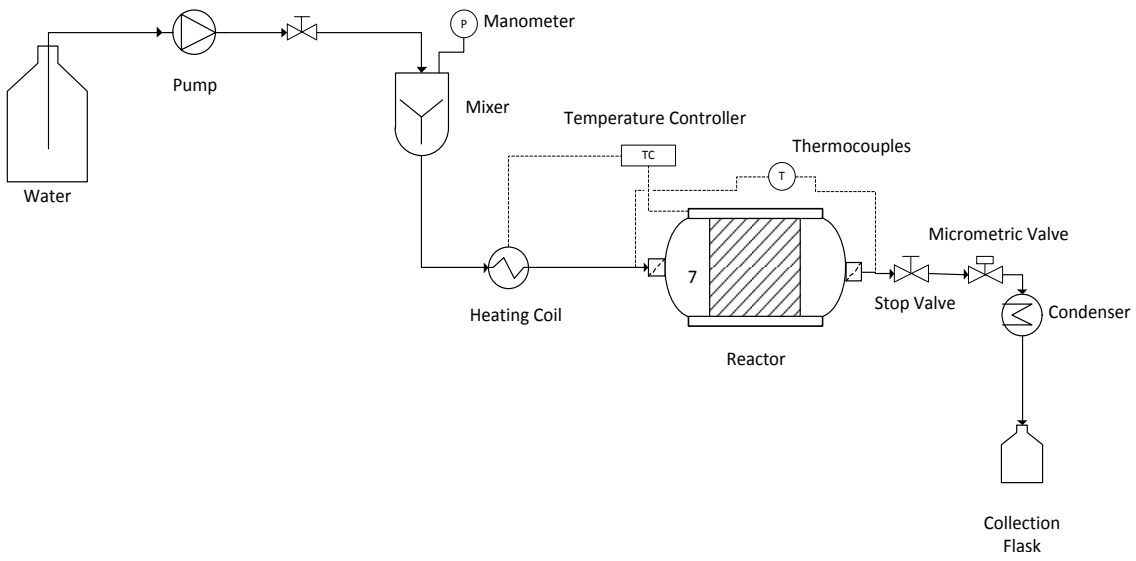


Figure 1. Scheme of the subcritical water hydrolysis unit.

2.3 Experimental procedure

Defatted pressed palm fiber (2.5 g or 5 g) was added into the reactor prior its connection to the unit system. Water was pumped in order to pressurize the system. After the pressurization, water pump was stopped, stop valve was closed and heating of coil and reactor was turned on. The coil was preheated to water inlet temperature of 423 K, 523 K and 673 K while the reactor was pre-heated to 373 K. After the temperatures reached the objective temperature, dynamic process was started by pumping water at a specific flow rate (10, 20 and 40 cm^3/min) through the system to keep residence times of 1.25 min, 2.5 min and 5 min. At the same time, reactor temperature was changed to set process temperature, causing a temperature profile. The average temperature profile between inlet and outlet temperature of reactor was recorded. Pressure (15, 25 MPa) was regulated with valves and maintained constant during the hydrolysis. The solution was cooled rapidly at 298 K and collected in a sample flask. One hydrolysis sample was collected for each experiment at a set time of 15, 30 and 60 minutes (for water flow rate of 10, 20 and 40 cm^3 /min) in order to maintain constant the solvent:solid ratio of 120 cm^3:1 g wet weight and 240 cm^3:1 g wet weight.

The experimental design of subcritical hydrolysis under various conditions is showed in Table 1.

Table 1. Experimental design of subcritical hydrolysis of defatted pressed palm fiber

N°	Inlet temperature (K) Ti	Pressure (MPa)	Solvent : solid ratio (cm^3:g wet weight)	Residence time (min)
1	423	15	120:1	2.5
2	523	15	120:1	2.5
3	423	25	120:1	2.5
4	523	25	120:1	2.5
5	673	25	120:1	2.5
6	423	15	240:1	2.5
7	523	15	240:1	2.5
8	423	25	240:1	2.5
9	523	25	240:1	2.5
10	673	25	240:1	2.5
11	423	25	240:1	5.0
12	523	25	240:1	5.0
13	423	25	240:1	1.25
14	523	25	240:1	1.25

2.4 Analysis of hydrolyzate products and residue

Yield. Hydrolyzate products were evaluated in function of total reducing sugars (TRS) using Somogyi - Nelson methodology [15]. A volume of 1 cm^3 diluted solution was reacted with 1 cm^3 of HCl 0.2 N in a boiling water bath for 5 min. Solution was cooled and 1 cm^3 of NaOH 0.2 N was added for neutralization. Then, 1 cm^3 of hydrolyzed solution was taken and mixed with 2 cm^3 of SN_1 reagent in a boiling water bath for 15 min. After that, solution was cooled and 2 cm^3 of SN_2 was added. Volume up to 25 cm^3 was made with distilled water. Its absorbance was measured in a spectrophotometer (Femto, model 800 XI, São Paulo-Brazil) at 730 nm and glucose was used as a standard. The quantity of carbohydrate presented in the raw material was considered to be 80% as determined by França [4]. TRS yield was calculated using Equation 1.

$$\text{Yield}\left(\frac{\text{g glucose}}{100\text{g carbohydrate}}\right) = \frac{\text{Concentration}_{TRS}\left(\frac{\text{g glucose}}{\text{L hydrolyzate}}\right)*\text{Vol.}_{\text{hydrolyzate}}(\text{L})}{\text{defatted pressed palm fiber weight (g)x 0.8}} \text{ x } 100 \quad (1)$$

Conversion. The residue was dried at 353 K until constant weight. The conversion of defatted pressed palm fiber (dppf) at the studied reaction conditions were calculated with Equation 2.

$$\text{Conversion}\left(\frac{\text{g}}{100\text{g initial dppf}}\right) = \frac{\text{initial dppf weight (g)} - \text{residue (g)}}{\text{initial dppf weight (g)}} \text{ x } 100 \quad (2)$$

pH. The hydrolyzate solution pH was analyzed using a potentiometer to check the change of pH after reaction.

3. Results and discussion

3.1 Equipment performance

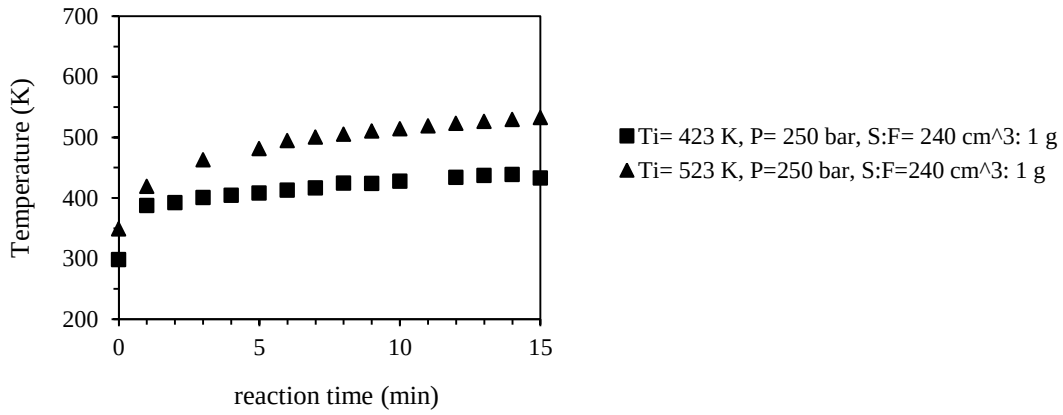
This system was designed to work with temperatures up to 673 K and pressures up to 40 MPa. As reaction rate is highly dependent on temperature, average temperature profiles inside reactor were constructed for each condition in order to assure that equipment performance had reproducibility. Figure 2 shows average temperature profile for 423 K. 523 K and 673 K.; pressure of 15 MPa, 25 MPa, solvent: solid ratio of 120 cm^3: 1 g wet weight, 240 cm^3: 1 g wet weight and residence time of 1.25, 2.5 and 5 min. The profiles of temperature showed the logarithmic increment until set temperature of 423 K and 523 K. However, in the experiment at 673 K, average temperature inside reactor did not reached the target temperature, keeping a constant temperature of 633 K at the end of the process. These results suggested that the temperature profiles showed a similar tendency in all operation conditions. It suggested that heating of reactor is not influenced by pressure, solvent: solid ratio or residence time, which showed analogous reaction rates.

3.2 Yield

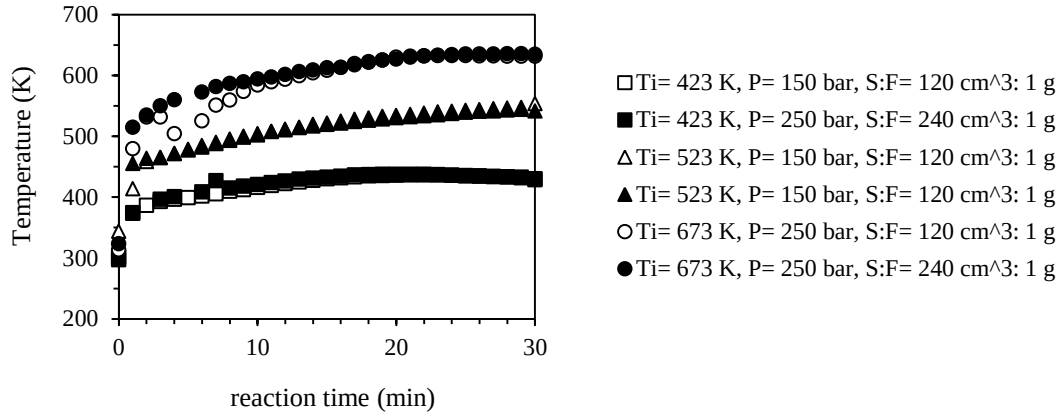
Figure 3 shows the variation of total reducing sugar yield with water inlet temperature, Ti, for residence times of 1.25, 2.5 and 5 min and different operational conditions. The effect of hydrolysis temperature was investigated at inlet temperature of 423 K, 523 K and 673 K.

The results showed an increasing trend in TRS yield of 423 K (2–7%), 523 K (8-15%) until 673 K (10-12%). These results propose that when temperature increases from 423 K to 523 K hydrolysis rate of polysaccharide (cellulose and hemicellulose) increases. On the other hand, when temperature increases from 523 K to 673 K, near supercritical conditions, a competition between hydrolysis rate and glucose degradation rate gives a reduction in total reducing sugar yield. In addition, total reducing sugar formation was promoted by high residence times (2.5 and 5 min), suggesting that water flow rate of 20 or 10 cm^3 /min permits an adequate contact between water and defatted pressed palm fiber. Respect at effect of pressure and solvent:solid ratio on TRS yield the results was not significant for the studied conditions. The best operational conditions were temperature of 523 K, pressure of 15 MPa, S:F ratio of 120 cm^3: 1 g wet weight and residence time of 2.5 min.

a) 1.25 min



b) 2.5 min



c) 5 min

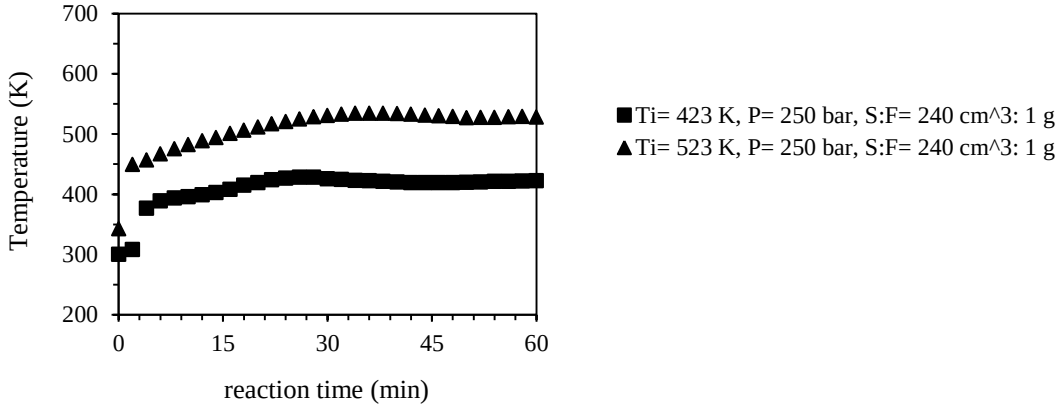


Figure 2. Average temperature profile for residence time of a) 1.25 min, b) 2.5 min and c) 5 min at different reaction conditions

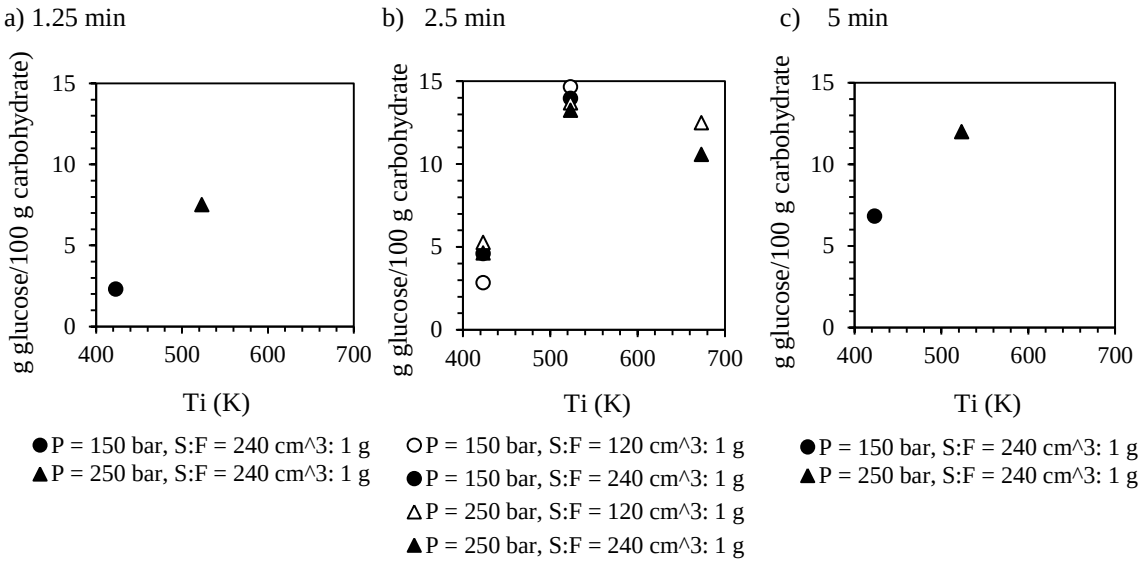


Figure 3. Total reducing sugar yield of hydrolyzate fractions for subcritical hydrolysis of defatted pressed palm fiber for residence time of a) 1.25 min, b) 2.5 min and c) 5 min

3.3 Conversion

Figure 4 showed the effect of temperature on carbohydrate conversion for operational conditions select. The results suggested that the temperature influenced carbohydrate conversion. The use of highest temperature resulted in highest conversion of defatted pressed palm fiber (90 – 95% at 673 K). The influence of pressure, solvent: solid ratio and residence time was not significant on conversion.

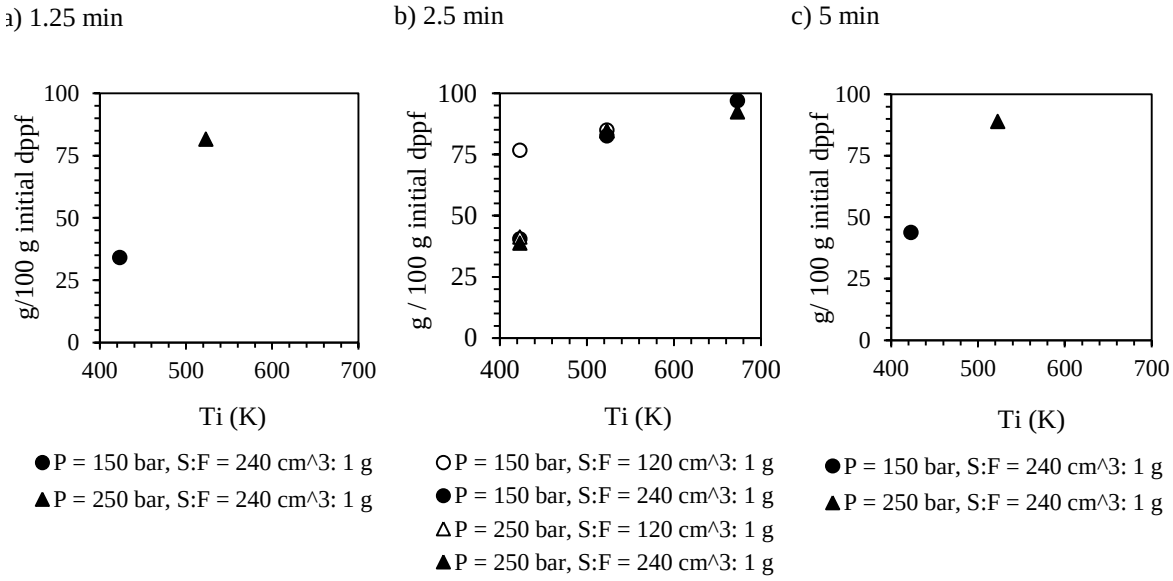


Figure 4. Defatted pressed palm fiber conversion for residence time of a) 1.25 min, b) 2.5 min and c) 5 min

3.4 pH

The values of pH of hydrolyzed solutions ranged between 3 and 5. The lowest values of pH were related at temperatures of 673 K due the presence of higher concentrations of sugars formed.

4. Conclusion

The subcritical hydrolysis of defatted pressed palm fiber was carried out in a non-isothermic semicontinuous equipment. Evaluated parameters were water inlet temperature of 423 K, 523 K and 673 K, pressure of 15 and 25 MPa, solvent: solid ratio of 120 cm^3: 1 g wet weight and 240 cm^3: 1 g wet weight, and residence times of 1.25, 2.5 and 5 min. The effects of temperature and residence time were significant; while effects of pressure and solvent: solid ratio had no significant influence on sugar formation. The optimal conditions were founded at 523 K, 15 MPa, S:F of 120 cm^3: 1 g wet weight and 2.5 min with total reducing sugar yield of 15 g glucose /100 g carbohydrate. The highest conversion was founded at 673 K. pH values decreased in subcritical regions, favoring the hydrolysis reaction mechanism.

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