Chitin depolymerization in sub and supercritical water by ultrafast reactors

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Chitin [β-1,4-poly(n-acetyl-D-glucosamine)] is the second most abundant biopolymer after cellulose, and it is produced by crustaceans, mollusks, insects, and fungi. Chitin has high interest as a biocompatible and biodegradable material, but also as a source of biologically active oligosaccharides and nanoparticles.

The recalcitrant structure of chitin makes traditional processes use harsh acidic conditions to generate these products. In this work, the use of water at high temperature (270 to 400ºC) and pressure (20MPa) was studied to produce oligosaccharides and nanoparticles. The physicochemical properties of water (density, viscosity, diffusivity, ionic product, and dielectric constant) change dramatically below and above of the critical point (374 °C and 22 MPa) providing a tunable reaction medium, remarkably at subcritical medium (SubCW) ionic reactions are promoted due to the high ionic product while the low the concentration of [H+] and [OH-] at supercritical conditions (SCW) favor radical reactions. Furthermore, control on residence time is critical in such conditions: according to literature, formation of solid (char) and liquid (5-hidroxy methyl furfural) degradation compounds have even prevailed working in batch-type systems even at short times up to 1 minute [3]. In this work, residence times as short as 0.1 to 8 s are explored thanks to a Press-Tech group designed facility working in continuous mode: heating and cooling down are achieved almost instantaneously by mixing an aqueous suspension of chitin (Stellar Biosol flakes) at room temperature with hot pressurized water in “T” piece just before the micro-reactor (1.2-25 mL) and, afterwards, is cooled down by a sudden expansion valve at the outlet.

Results spotlight the stability of chitin at low temperatures, as shown in Figure 1, a maximum of 32% of solubilization was achieved at 270 and 300ºC. Solid recovery decreased dramatically when increasing processing temperature. Regarding particle size distribution (PSD) of this product, two behaviors can be distinguished: a

monomodal distribution with mean particle size of 10 microns is achieved at temperatures below 350ºC (at this temperature only residence time below 1.3 results in such PSD). At conditions above these ones, nanoparticles size distribution is achieved.

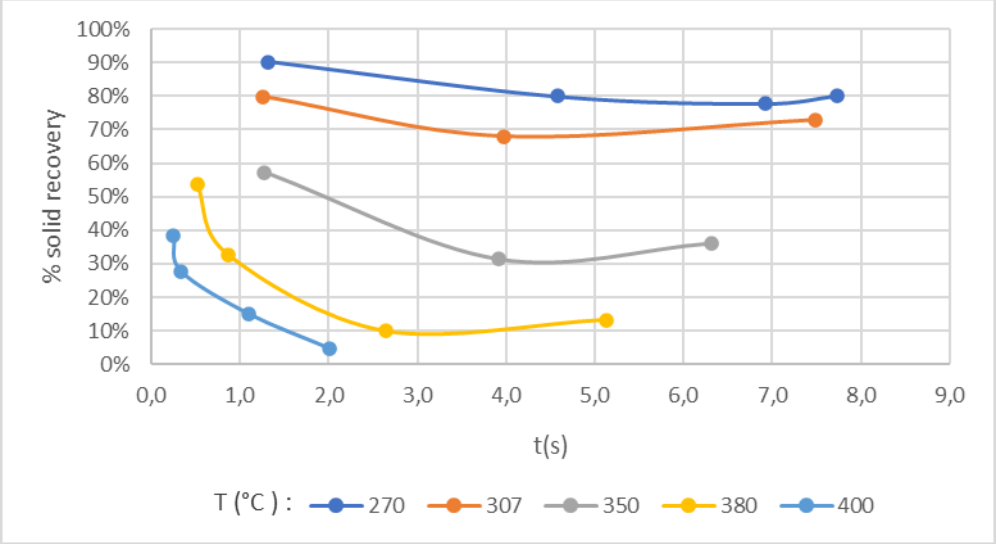

Figure 1. Solid recovery percentage vary processing residencia time and temperature.

Liquid fraction was analyzed by HPLC for the identification of chitooligosaccharides and degradation compounds. At low temperature and residence time, almost pure oligosaccharides are produced, while degradation compounds increase sharply as temperature increased rather than residence time. The main degradation compounds are glycolaldehyde, formic acid and acetic acid. At 400ºC and 0.3 s, 42% of the initial chitin is transformed into oligomers, 30% to degradation compounds and the remaining solids show almost the same acetylation degree as the raw material, by FT-IR analysis. In conclusion, the ultrafast reaction technology at sub and supercritical conditions allows producing simultaneously chitin nanoparticles, and oligomers with relatively high yields (up to 40% from the initial material of each product), However, the minimization of degradation products is still challenging despite the strict control of reaction time.