

The Sudden Expansion Reactor for Hydrothermal Upgrading of Biomass

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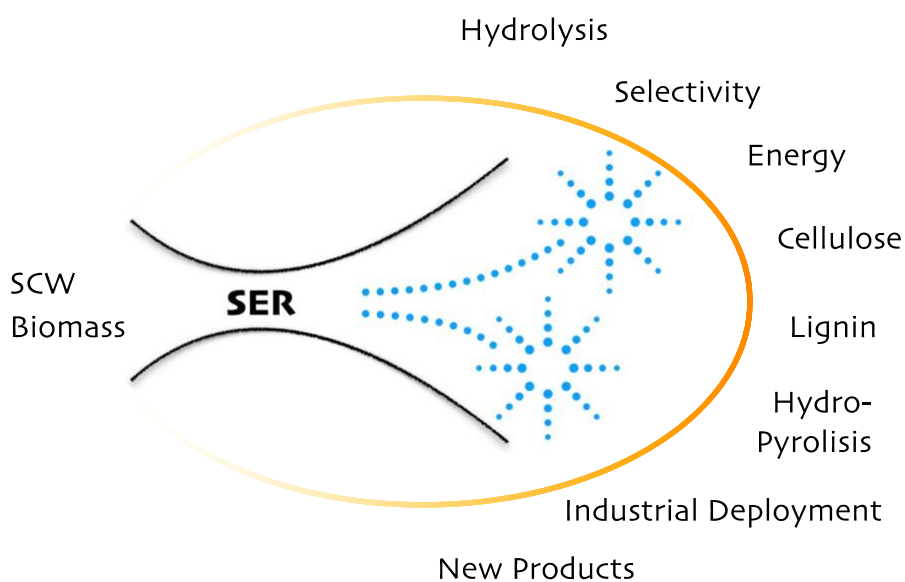
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Abstract

It was back in 2009 when the scientists at the University of Valladolid, Spain, opened a new research program about Supercritical Water Hydrolysis (SCW) of Biomass. The team got inspired by previous publications of Dr. Sasaki about cellulose hydrolysis in supercritical water [1]. The fact that cellulose seemed to swell and partially solubilize in SCW made it a very promising technology to produce cellulosic sugars. This behavior opened the door for intensifying the process of cellulose hydrolysis, converting cubic meters reactors (enzymatic or acidic) to just liters reactors. It was our goal to employ that concept while maximizing the sugars yields and product concentration. This was the *genesis* of the Sudden Expansion Reactor (SER) [2]. The main goal for the development was to achieve the highest rates of heating, reaction, and cooling. In that way, the reactions can be accelerated to intensify the process while keeping high yields. This device was achieved by linking a biomass-SCW mixer, a tubular – plug flow – reactor, and a let-down valve. Special attention should be paid to the mixer (short reaction times require very efficient mixing) and the let-down valve (the valve should be able to reduce the pressure and handle solids at the same time). With this device, we were able to execute reactions with reaction times as low as 0.1 seconds at 400 Celsius and 250 bars. More noticeably, this device was able to drop the reaction temperature from ~400 Celsius to ~100 Celsius almost instantaneously (Joule-Thompson effect). This invention allowed many advances in the field, which will be briefly described next. Also, few opportunities to further progress the technology will be presented.

The SER was deeply studied for cellulose and biomass hydrolysis [3–5]. One finding was the optimization of cellulose hydrolysis reaction over glucose and oligosaccharides degradation. That optimization at very low reaction times was translated into cellulose hydrolysis yields higher than ~80%. That behavior was also seen for cellulose in lignocellulosic biomass, at lower yields though, around ~70%. In the later years, the SER was employed to partially hydrolyze cellulose and produce micro size particles [6]. Those particles are still in development for its best application. SER was also employed for glucose conversion into aldehydes and lignin depolymerization [3,4]. In this case, the reaction times are usually larger, in the order of seconds. Very



interestingly, the products profile of the hydrolysis to those components is very similar to the ones obtained from pyrolysis. It becomes then very interesting to evaluate if the water as reaction medium is offering any medium benefit or if it is only an “energy carrier”. At industrial scale, the company Renmatix is the pioneer in the use of SCW to hydrolyze biomass. The company counts with more than 100 patents, which protects the technology [7]. The author spent 6 years as scientist applying the process intensification concepts of SCW hydrolysis.

Although the technology has been developed deeply, few aspects should still be addressed to fully deploy the technology at efficient and integrated products: (1) Refining: the SH product consists of a mix of mono and oligosaccharides and byproducts. This should be converted to glucose in an efficient and clean way; (2) Since the SER allows extremely low reaction time, could it be used for more labile carbohydrates, like starch or gums? (3) The water and energy demand for this technology is high. It is then very important to develop water recycling systems as well as energy integration loops. Few opportunities were already evaluated for energy integration employing gas turbines. What about Supercritical Water Oxidation?

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REFERENCES

- [1] M. Sasaki, B. Kabyemela, R. Malaluan, et. al. Cellulose hydrolysis in subcritical and supercritical water, *J. Supercrit. Fluids*. 13 (1998) 261–268.
- [2] D. Cantero, M. Dolores Bermejo, M. Jose Cocero, High glucose selectivity in pressurized water hydrolysis of cellulose using ultra-fast reactors, *Bioresour. Technol.* 135 (2013) 697–703.
- [3] D. Cantero, Intensification of cellulose hydrolysis process by supercritical water: Obtaining of added value products, University of Valladolid, 2014. <http://uvadoc.uva.es/handle/10324/5374> (accessed April 27, 2019).
- [4] N. Abad-Fernández, E. Pérez, Á. Martín, M.J. Cocero, Kraft lignin depolymerisation in sub- and supercritical water using ultrafast continuous reactors. Optimization and reaction kinetics, *J. Supercrit. Fluids*. 165 (2020) 104940.
- [5] C.M. Martínez, T. Adamovic, D.A. Cantero, M.J. Cocero, Ultrafast hydrolysis of inulin in supercritical water: Fructooligosaccharides reaction pathway and Jerusalem artichoke valorization, *Ind. Crops Prod.* 133 (2019) 72–78.
- [6] J. Buffiere, N. Abad, P. Ahvenainen, J. Dou, M.J. Cocero, H. Sixta, Tailoring the Structure and Morphology of Low-Molecular-Weight Cellulose Produced during Supercritical Water Hydrolysis, *ACS Sustain. Chem. Eng.* 6 (2018) 16959–16967.
- [7] Renmatix. <https://renmatix.com/plantrose-process/> (accessed January 27, 2022).