MAKING IT WORK

Is Supercritical Water the Green Future of Chemical Processing?

Industry stands to gain significant benefits and new opportunities

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INCREASING CONCERNS about atmospheric carbon dioxide levels are spurring a rapidly growing emphasis worldwide on sustainability and circular economies (i.e., the use of renewable materials and recycling to minimize waste and resource depletion). To reduce CO_2 emissions, commercial passenger aircraft already are flying on biodiesel fuel derived from renewable plant sources converted by standard chemical processing.

This quest for sustainability is prompting a move to develop matching greener nonconventional processing systems — with those based on water in a supercritical state especially attractive. This special form of ordinary water, first discovered in 1822, has remarkable solvent and heat transport properties. However, chemical engineers in industry largely have ignored it until recently. The situation now is changing with the appearance of two books.

Yizhak Marcus' small (201-page) volume "Supercritical Water: A Green Solvent: Properties and Uses," published in 2012 by John Wiley & Sons, provides all the basic data about supercritical water needed by chemical processors and explains how this amazing plasma-like material is created when ordinary water is heated above 374°C. In this condition, its solvent power resembles that of acetone.

A more recent (2014) and detailed text is Gerd Brunner's "Hydrothermal and Supercritical Water Processes," published by Elsevier, Amsterdam.

The energy content of supercritical water enables selectively breaking down the chemical bonds in many structures exposed to it to yield smaller fragments. Such thermal breakages normally create highly reactive free radicals that can combine to form valueless char. However, the presence of supercritical water prevents the production of such char because hydrogen atoms from the water molecules can react with and stabilize the free radicals as small molecules. This is an important difference from purely thermal breakdown that some companies have tried to exploit but with only limited success.

In addition, supercritical water's higher temperature (400°C versus 100°C) increases the rate of chemical processing vastly — by about one billionfold.

This means chemical processing in supercritical water media takes only a few seconds instead of hours. The short duration, in turn, demands equipment capable of continuous operation with a small reaction zone that maintains the supercriticality of water.

Standard commercial extruders for plastics most readily can meet these simultaneous requirements of temperature and time. Such units routinely can withstand internal pressures of up to 20,000 psi and usually come with electric heating bands around the conveying barrel. There are many extruder manufacturers both in the U.S. and worldwide.

The complete chemical processing cost of passing material though a 10-t/d unit runs less than 5¢/lb. The yield is about 100% or higher.

POTENTIAL FOR INDUSTRY

All these benefits of supercritical water constitute opportunities for the chemical industry of the future. Most low-value wastes consist of large-molecular-weight entities that supercritical water readily can break down into small higher-value pieces.

Biomass processing is especially attractive because supercritical water can convert undried nonfood cellulosic polysaccharides to constituent fermentable sugars in less than one second. The more-than-200 companies in the U.S. now striving to synthesize bioethanol from corn will have to shift to nonfood starting materials in the near future.

A relatively new U.S. company, Renmatix, King of Prussia, Pa., www.renmatix.com, commercially produces a variety of products from fermentable sugars derived from the reaction of nonfood biomass with supercritical water via its Plantrose process. (For more on the Renmatix process, see "Biomass Processor Banishes Bottleneck," http://bit.ly/2olNRYZ.)

Another comparatively new company focusing on chemical processing with supercritical water is Licella Holdings, North Sydney, Australia, www.licella.com.au, which has received Australian government funding as a bridge to a lower carbon future. Licella states that converting wood wastes to biocrude via its catalytic hydrothermal reactor (Cat-HTR) technology is its first goal. In 2016, the firm entered into a joint venture with Canfor Pulp, Vancouver, B.C., to construct a large biorefinery at Canfor's Prince George, B.C., pulp and paper mill. Licella also sees its process as a way to tackle the environmental problems posed by end-of-life plastics and, in 2017, established a joint venture with Armstrong Chemicals, Cheltenham, U.K., to build a commercial-scale plant at Wilton, U.K., to convert waste plastics to usable chemicals. In August of this year, Neste, Helsinki, a leading producer of renewable diesel, signed on to collaborate on investigating the use of liquefied waste plastic as a feedstock for refineries.

Chemical processors should keep in mind an observation made in June 2018's *National Geographic*: most of the plastic produced since 1950 still is with us and that 8 million metric tons per year end up polluting the sea. Supercritical water could convert this widely distributed plastic waste to a high-cetane low-sulfur oil.

Contact with supercritical water also enables economic upgrading of crude oil itself with greater selectivity to lower molecular sizes. The Green Research Group at the Massachusetts Institute of Technology (MIT), Cambridge, Mass., has a broad energy program involving breakdown of heavy Saudi Arabian crude. The group relatively recently published a paper on its experimental approach, "Supercritical Water Treatment of Crude Oil and Hexylbenzene: An Experimental and Mechanistic Study on Alkylbenzene Decomposition," *Energy & Fuels* (2015), that demonstrates the difficulties that all chemical processors initially must face in studying a new supercritical water opportunity. The MIT group used a small sealed pressure vessel that was lowered into a heated sand bath at 450°C and held there for some minutes before withdrawal (Figure 1).

Figure 1. Pressure vessel is immersed in a 450°C sand bath for several minutes. *Source: MIT Energy Initiative, © Stuart Darsch.*

This immersion technique is a relatively simple way of establishing a rough value of the benefits that supercritical water processing of a material offers. However, practical feasibility inevitably will require continuous operation. The needed equipment probably should be based upon a commercial extruder to contain the high pressure of supercritical water and simultaneously to manage, with computer controls, the very brief reaction periods employed. U.S. Patents 9,932,285 and 9.932,532, issued on April 3,, 2018, describe such continuous supercritical-water chemical processing equipment.

The opportunities extend beyond upgrading of waste materials and feedstocks. For example, brief exposure to supercritical water can make animal feed, e.g., for piglets, more digestible.

So, we can confidently conclude that the continuing greening of the chemical industry certainly will involve a form of water elegantly discovered almost 200 years ago by a French engineer. ●

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