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Research is Fundamental

Using the logo RIF, a public service announcement once proclaimed "Reading Is Fundamental." When it comes to this month's cover topic of sustainability, we can also say RIF, here meaning "Research Is Fundamental."

A major threat to our sustainability is global climate change. Unfortunately, we are a long way from understanding the complex relationships between CO_2 emissions and atmospheric CO_2 concentrations and the resulting environmental effects.

That's where Biosphere 2 plays an important role. Built in the 1980s as an experiment to see if eight people could live in a sealed self-sustaining environment, today Biosphere 2 is a giant living laboratory for Earth systems research, specifically CO_2 in the atmosphere. Scientists there are studying the effects of increased CO_2 in various biomes (or land types), such as a rainforest, ocean, forest and desert.

Biosphere is unique in its ability to isolate an environment of interest and monitor and control such parameters as temperature, humidity, airflow and CO_2 levels. Chemical engineer John Persson is responsible for that instrumentation and control system. You can read about him and his job in the Profile on p. 96.

The project that I found most interesting when I toured the facility a few months ago takes place in the intensive forestry biome (IFB). It is aimed at answering the question "Can the release of CO_2 emissions be offset by responsible forestry practices such as planting and harvesting trees?" The IFB is partitioned into three fully instrumented compartments in which cottonwood trees (chosen for their incredibly fast growth rate, up to a meter a month) have been planted. In one section, CO_2 concentrations are maintained at current atmospheric levels, in another at double today's levels (which is what is expected at the end of this century), and in the third at triple the current levels. Light, humidity, temperature and CO_2 concentration throughout the day, as well as leaf photosynthesis and soil respiration, are measured, and an overall carbon balance is calculated. The researchers have found that carbon uptake (*i.e.*, photosynthesis) increases with increasing CO_2 concentration. In the first year of the study, there were significant differences in above-ground biomass production among the three bays — the higher the CO_2 level, the more biomass. In the second and third years, the differences in biomass production were not as great, although carbon uptake still varied significantly from one bay to another. This leads me to believe that the cottonwood tree might be one important component of a CO_2 control strategy. But a great deal more research is needed to make this a reality. (The results of a related research project being conducted in the IFB are discussed in R&D Update on p. 18.)

Biosphere is currently managed by Columbia Univ. Unfortunately, Columbia has announced that while it will continue its management activities until its contract expires in 2010, it is considering discontinuing its financial support. Given the importance of the work being done at Biosphere, it is my hope that if that happens, other universities and industrial partners will step forward to enable its research — which is so fundamental to our sustainability — to continue.

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A Supercritical Solution for Hydrogenation

Pilot trials of Härröd Research's (Gothenburg, Sweden; www.harrod-research.se) supercritical single-phase hydrogenation (SSPH) process are underway at a newly commissioned facility at the firm's site. The technology is currently being demonstrated for hydrogenation of fatty acid methyl esters (FAME) to fatty acid alcohols (FAOs), but can also be used with many other organic compounds, fats, oils and polymers. "In all cases, SSPH improves product quality to levels impossible to reach with traditional multiphase processes, while cutting operating costs in half," says Magnus Härröd, the company's president. "For example, during partial hydrogenation of FAME, it is desirable to minimize the trans-fatty acid concentration when half of the C=C bonds has been hydrogenated. At these conditions, we have reached trans-fatty acid content below 1%, while with traditional multiphase processes the lowest trans-fatty acid content reached is about 30%."

During pilot tests, 40 kg/h of propane (78 mol% of feed) were mixed with hydrogen (20 mol%) and FAME (2 mol%, 15 wt.%) and brought to supercritical conditions prior to entering a copper-catalyst-filled (100-μm pellets) fixed-bed reactor operating at 230°C and 150 bar. "The restricting factors in conventional hydrogenation are how to get hydrogen to the catalyst surface through a liquid and how to control the excess heat released during the reaction," Härröd points out. "Key to our success is the introduction of a solvent (*e.g.*, propane) in the reaction zone, which creates a homogeneous supercritical phase that minimizes the transport resistance of hydrogen, achieving reaction times in the order of seconds with conversion levels in excess of 98%," he says, adding that in multiphase hydrogenation to FAOs, conversions higher than 90–95% result in the formation of unwanted alkanes.

The reactor effluent contains 10 kg/h of FAO, 1 kg/h of methanol, propane and hydrogen. Pressure is reduced in a flash separator and propane, methanol and hydrogen exit overhead, while the FAO leaves from the bottom. Propane and hydrogen are distilled from the methanol, and are recompressed and mixed with fresh hydrogen and FAME. The productivity of a reactor using the single-phase technology is typically 100 times higher than the traditional gas/liquid technology, enabling smaller reactors to be used.

The pilot plant at Härröd Research for hydrogenation at supercritical single-phase conditions.

Through R.C. Costello & Associates, Inc. (Redondo Beach, CA; www.rccostello.com), the technology will be licensed to U.S. customers. Härröd Research will be the licensor to European and all other customers. Härröd Research has applied for patents in 27 countries (WO9601304) and has already received several patents, including one in the U.S. (No. 5,962,711).

Process Tomography Validates CFD Model

Radial-flow packed beds offer several advantages over traditional vertical columns, such as larger mean cross-sectional areas and reduced travel distances for flow. However, there are some design difficulties that need to be overcome, including uniform flow-distribution at the inlet and low-pressure drops through the catalytic bed.

Recently, Synetix (now a part of Johnson Matthey; Billingham, UK; www.synetix.com), a specialist in catalysis, designed a radial-flow reactor in which the outer annulus is packed with large, high-void inert particles, and the main part of the reactor is packed with a catalyst. Making assumptions about bed porosity to account for the changes in void between packed and unpacked zones, and for the different diameters of the packed material, a computational fluid dynamics (CFD) model was generated. The model indicated that the new design had substantial radial flow through the main part of the reactor.

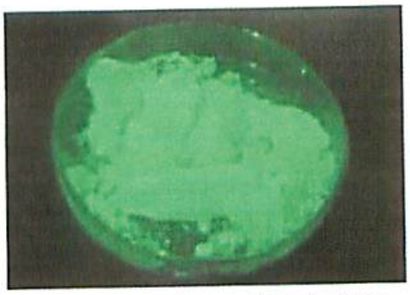
However, the firm wanted to validate the model — not an easy thing to do because of the non-uniform porosity. Enter electrical-resistance tomography (ERT), a novel technology for visualizing the contents of the vessel without disturbing the flow. ERT uses multiple electrodes arranged around the periphery of the process vessel in such a way that they are in contact with the process fluid, but do not disturb the process flow pattern. A small AC current is then applied between one of the electrode pairs and voltage measurements are made between the remaining electrode pairs. A 16-electrode sensor delivers over 100 independent measurements in about 25 ms. An image-reconstruction algorithm is used to generate images of the flow distribution.

To validate the CFD model results, Synetix, with help from Industrial Tomography Systems (ITS; Manchester, U.K.; www.itoms.com), built a physical model of the proposed new reactor with an internal diameter of 914 mm and a cylindrical flow-collector with a height of 1,000 mm (located in the center of the reactor). The reactor was packed to a height equal to the top of the collector. The outer annulus was packed with 10-mm-dia. inert particles, while the main part of the reactor was filled with 3-mm-dia. catalyst particles. A flow distributor was located above the packed bed reactor to provide a uniform flow of water over the cross-sectional area. The flow was expected to enter the vessel across the entire cross-section of the vessel, proceed down near the wall of the vessel, then radially inward through the bed of 3-mm particles, and finally out in a downward direction via an axial collector.

Natural Gas Hydrate — A Viable GTL Alternative

NKK Corp. (Tokyo, Japan; www.nkk.co.jp) is paving the way for low-cost transport and storage of natural gas from remote fields that complements liquefied natural gas (LNG)-based systems. The company's continuous production process for natural gas hydrate (NGH) has been successfully demonstrated at the laboratory scale and an application for a worldwide patent (No. PCT/JP02/12496) has been submitted.

"LNG requires handling at cryogenic temperatures (–162°C) and incurs high equipment costs, which makes the development of the many smaller gas fields, such as those in Southeast Asia and Oceania regions economically unfeasible," says Kazuo Kohda, NKK Corp.'s chief researcher, at the energy plant systems lab. "While gas-to-liquids technology has its distinct applications for use in making clean liquefied fuels, NGH can be used in the whole application field currently served by natural gas," says Kohda.



The highest temperature at which natural gas hydrate (NGH) can exist under atmospheric pressure is about –80°C. If NGH is placed under atmospheric pressure and at room temperature, its surface decomposes (during an endothermic process) and discharges gas, leaving only water on the surface. The water cools and forms a layer of ice on the NGH, thereby preventing further decomposition. This phenomenon is called the self-preservation effect, and makes it possible to keep the NGH at –20 to –10°C at atmospheric pressure over a long period of time.

NGH, also known as methane hydrate, consists of a cage-like structure made of water molecules that can store about 150 Nm^3 (N stands for normal conditions, *i.e.*, 0°C and 1 atm) of natural gas in 1 m3 of space. In the case of the hydrate in natural and untreated state, the temperature must be below 10°C at 7 MPa, below 0°C at 2.5 MPa, and below –78°C at 1 atm. In contrast, if the stabilization process is applied, thereby taking advantage of the hydrate's self-preservation effect (photo), it enables the hydrate to exist stably at –10 to –20°C and 1 atm. Further, NGH can be transported and stored at these conditions, enabling use of much simpler facilities and reduced cooling requirements.

The gas molecules are "held" as the result of a physicochemical process that effects a molecular dynamic action between water molecules and gas molecules. Although different from NGH, the similar physicochemical process also works in hydrogen-storing alloys or metal hydrides, in which a large volume of hydrogen (exceeding the same volume of liquid hydrogen), typically 700 to 1,000 Nm^3, can be held.

Conventionally, NGH is produced by bringing natural gas into contact with water in a stirred-tank reactor or a spray-tower reactor, typically operating under low-temperature, high-pressure conditions, usually 5°C and 50 atm. Any CO_2 or H_2S in the source gas must be removed prior to NGH production. In the case of methane, about 410 MJ of reaction heat are generated when 1 m^3 of NGH is formed. "The key to industrial mass-production is to the efficiency with which this reaction can be performed and the reaction heat removed," says Kohda.

NKK increases gas/liquid contact surface by using a static mixer, placed upstream of a 3.5-L tubular reactor, designed for microbubble generation. Water and natural gas are supplied to the mixer so that 1–10-µm-dia. gas bubbles are distributed in the water. "The hydrate production rate, 4.5 kg/h, is six times higher than with conventional stirring and about 50 times higher than with water spraying," says Kohda. Further, NGH conversion is almost 100% vs. 1% obtained by water spraying. To effectively remove the reaction heat, NKK uses a pipe-type heat exchanger, such as a double-pipe or shell-and-tube configuration. "Unlike conventional cooling devices that cool from outside of a pressure vessel, use of the heat exchanger achieves a 50 times or greater overall heat transfer coefficient," says Kohda.

The Japan National Oil Corp. (Tokyo; www.jnoc.go.jp) has selected the NKK technology for one of its funded research projects. NKK is using the grant to construct a benchmark experimental facility where it plans to produce 400 kg/h of NGH using a water flowrate of 14 L/min, pressure of 5–8 MPa, *in-situ* methane flowrate of 14 L/min, and reaction temperature of 2–8°C. The cooling system will use a double-pipe heat exchanger cooled by ethylene glycol, and will have a cooling capacity of 66 kW. These tests will be completed by the end of 2003. Pilot plant construction and demonstration tests will be the focus of the next several years, with the ultimate goal being commercialization of the technology. Kohda says that since NKK's process uses compact equipment, it would have lower capital and operating costs than conventional systems.

Prior to packing the vessel, an 8 × 16 electrode tomographic sensor array was installed around the perimeter of the packed bed. Each set of 16 electrodes made up a measurement plane (for a total of eight). This was connected to ITS's P2000 ERT system, which was in turn connected to a PC for control and data storage. Experiments were performed using water as the background fluid (instead of gas, since ERT requires a fluid that conducts electricity) and a sodium chloride solution as the conductivity tracer injected into the inlet feed to determine the flow pattern and the residence time within the reactor.

Combining the results for all eight measurement planes, Synetix validated the CFD model. "This graphic evidence allows our engineers to confirm to potential customers that their full-size catalytic process works as claimed," says Hugh Stitt, Synetix team leader for this project.