

# GREEN REVO

Chemical manufacturing today consumes ca 10% of energy produced globally, according to one estimate from the International Energy Agency. Downstream processes – for example, separations and purifications after reactions take place – consume over 40% of the total energy used by the chemical industry, says Andrzej Stankiewicz, a professor of process intensification at Delft University of Technology in the Netherlands. Material efficiency is also poor – in fine chemicals manufacturing, 5t to 50t of byproduct is generated for every ton of product. In pharmaceuticals manufacturing that number rises to 25t to over 100t.

These glaring inefficiencies in chemical manufacturing can be blamed on a flawed design principle: that one process should take place in one vessel. A stirred-tank mixes reactants, a column separates a mixture of products, a distillation tower purifies individual chemicals. Reagents and intermediates travel from one vessel to another and another; for a chemical synthesis with 20 steps, that means 20 pieces of equipment occupying space, consuming energy and generating waste.

Chemical engineers are trained to design and build plants using such standard unit operations, says Bill Grieco, CEO of the Rapid Advancement in Process Intensification Deployment (RAPID) manufacturing institute, run by the American Institute of Chemical Engineers. 'Those things still apply, but what process intensification really does is it allows us to step away a little bit from that traditional unit operations view and instead think about the transformations that are going on in the process,' he says.

Through the invention of new equipment and integration of chemical processes, process intensification promises to shrink not only the energy requirements of the chemical industry,

*Innovations in reactors and processes promise to make the chemical industry smaller, safer and more efficient, XiaoZhi Lim reports*

but also its spatial and material footprint. 'It's all about efficiency,' says Kamelia Boodhoo, a chemical engineer at Newcastle University, UK. A knock-on effect of having smaller operations overall is safety, she says.

Stankiewicz agrees, pointing to two of the worst chemical explosions in history. Spaced 80 years apart, the 1921 explosion at BASF's plant in Oppau, Germany, and 2001 explosion at the AZF fertiliser factory in Toulouse, France, were remarkably similar: in both, hundreds of tonnes of ammonium nitrate were stored onsite. 'Size really matters, the smaller inventory you have, the less consequences there are if something goes wrong,' he says.

While slow to catch on, interest in process intensification has picked up in recent years. In Europe, Stankiewicz leads the European Process Intensification Centre (EUROPIC), founded in 2009. Its American counterpart, RAPID, arrived later in 2016. Increasingly, industry and government agencies like the US Department of Energy, which funds RAPID projects, are recognising process intensification as a viable strategy to reduce energy consumption increase yields while cutting capital and operating costs, Grieco says.

### Organising principles

One of the first examples of process intensification was built as long ago as 1980, says Stankiewicz. At that time, Eastman Chemical in Kingsport, Tennessee, piloted a new way to make methyl acetate, an industrial solvent for glues and paints. Called reactive distillation, the new process integrated five separate reaction and purification processes into one, all taking place



**A Croda unit for making an emulsion in a UK company**

NITECH SOLUTIONS

# UTION

## Nanomaterials manufacturing

Besides chemicals and pharmaceuticals, process intensification can be extended for manufacturing other materials. In the past two decades, many new advanced, nanostructured materials have appeared for improving electric vehicle batteries or solar cells, says Ruud van Ommen, a process engineer at Delft University of Technology, the Netherlands. 'But quite often, it's not clear, when these materials first come out of the lab, how to produce them at a large scale,' he explains.

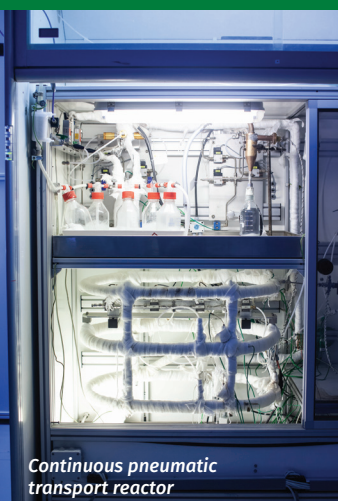
Van Ommen's approach combines a technique widely used in the semiconductor industry called atomic layer deposition with a specialised reactor called a fluidised bed. In semiconductor manufacturing, atomic layer deposition places atom-thick layers of materials one at a time onto silicon wafers. In a fluidised bed reactor, a gas or a liquid is forced through a bed of solid powders, wafting them up into the reactor. By combining the two, van Ommen can precisely coat fine particles and powders with one-atom-thick layers of materials, instead of wafers.

This could be used, for example, to coat powders on pharmaceuticals, such that they dissolve more slowly and have a longer shelf life, van Ommen says. His spin-off company Delft Intensified Materials Production is now operating a pilot that produces about 10kg/hour of coated powders.

Other than adding to the process intensification toolbox, the process industry faces a grand challenge in coming years – one of sustainability, Stankiewicz says. 'It is evident that in the long-term, renewable electricity must become the primary energy source for processes,' he says.

For that, not only do engineers have to start considering electrically-driven reaction techniques such as microwave or induction heating, but also electrically-driven separation techniques, for example, via a charged membrane. Electrification also brings an additional challenge of having to cope with fluctuating electricity supply, says van Ommen. But that could become an opportunity to use chemical manufacturing to store electricity, by ramping up production when there is excess renewable electricity and down when there is too little.

'This is really a sort of an industrial revolution to make manufacturing greener,' says Ni.



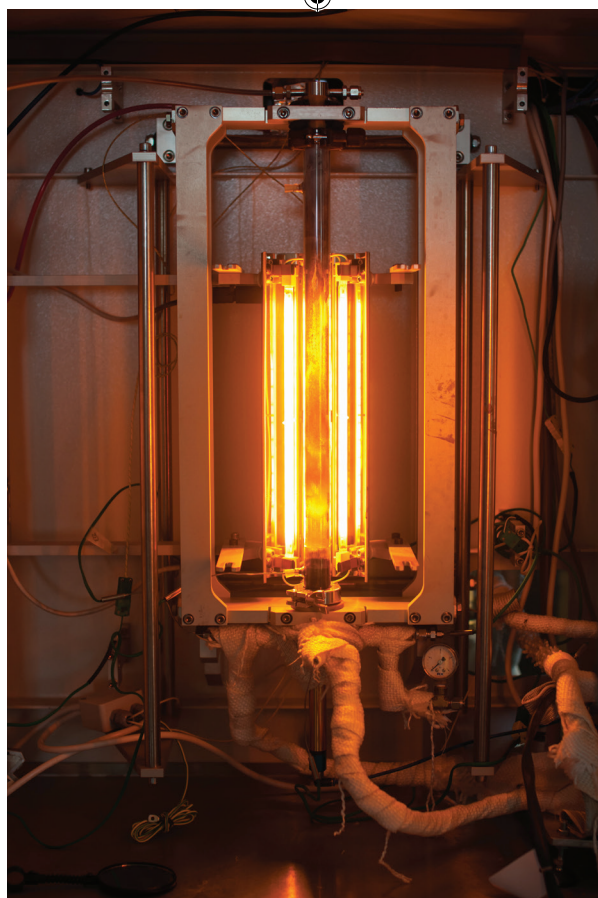
Continuous pneumatic transport reactor

## PROCESS TECHNOLOGY

in an 80m tower. The intensified method shrank Eastman's energy requirements for methyl acetate synthesis by 80%.

'This is kind of the seminal example of process intensification,' says Grieco. But that was an isolated example, and for many years, process intensification suffered from disorganisation, says Stankiewicz. For one thing, no one agreed on what it meant. The European Roadmap for Process Intensification defined it as simply anything that raised process efficiency by a factor of two or more. Others demanded a performance boost by at least an order of magnitude. For years, one almost had to go with a 'gut feeling', Stankiewicz says. 'When you see something that brings huge improvements, then it is process intensification.'

Other limitations, particularly in equipment design and manufacturing capabilities, also slowed the advent of process intensification. Nowadays, reactors can be designed with the aid of computers and even artificial intelligence, Grieco says. More importantly, advanced manufacturing techniques available today like 3D printing can turn a complicated equipment design into reality.



A key problem that process intensification addresses is mixing, particularly in large reactors. 'Once you go big, it's very difficult to stir,' says Xiong-Wei Ni, a chemical engineering professor at Heriot-Watt University in Edinburgh, UK. A chemical reaction that takes ten minutes to complete in a laboratory setting might need several hours at full scale. As a reaction goes from a laboratory-scale flask to a stirred-tank at pilot or at full scale,

Fluidised bed lab-scale reactor

concentration and temperature gradients and side reactions appear, he explains. 'This is why, in a chemical plant, one seventh of the inventory is for reaction, and six sevenths is for separation,' he says. To Ni, the challenge lies in designing an environment that provides consistent reactant mixing regardless of scale.

### Reaction and separation

In 2009, Stankiewicz with his colleague Tom Van Gerven attempted to thematically organise the principles of process intensification (*Ind. Eng. Chem. Res.*, doi: 10.1021/ie801501y). For instance, a way to intensify a process is to combine operations, such as a reaction with a separation, like Eastman's reactive distillation tower. But there are other, more nuanced ways as well. One can structure the space in which reactants collide, and in doing so, maximise the effectiveness of those collisions. An intensified process could also minimise the temperature gradients within equipment through small-scale or localised mixing, such that the molecules have the same processing experience.

Flow processes are usually prized for enabling continuous

## Boost for bio-based chemicals

As bio-based chemicals move to take on traditional chemical manufacturing from fossil fuels, they face staggering barriers to entry. Bio-based feedstocks like crop residues, for example, are usually distributed, a poor fit for existing logistics as chemical manufacturing tends to be centralised. Bio-based feedstocks also contain a lot of water, aggravating the problem of having to transport them to one location. So, even though the idea of shifting to bio-based feedstocks has been around for years, building a centralised biorefinery remains cost-ineffective, Grieco says.

'I personally feel that modular processing and intensified processes are going to be one of the keys to unlocking bio-based chemicals manufacturing,' he says.

At Southern Research in Alabama, US, chemical engineer Amit Goyal is developing a new process that manufactures acrylonitrile from non-food biomass. Acrylonitrile is an important commodity chemical used to make carbon fibres, acrylic fibres and ABS plastics, with some

several million tonnes produced annually. Traditional acrylonitrile plants have 100,000 to 250,000t/year of capacity, and can come with a price tag of hundreds of millions of dollars, Goyal says.

Goyal estimates that Southern Research's process, which is flexible enough to consume several different types of woody biomass or crop residue, could be scaled up to a commercial operation with as low as 5000t/year capacity for \$15-20m. Once at that scale, 'it will be mostly a carbon copy,' he says. Such small, modular plants could be distributed across the US or around the world, wherever biomass or second-generation sugars are available locally, making it a better fit for bio-based feedstocks, he says.

For a start-up company trying to bring a new product to market, the availability of a small, modular manufacturing unit means they could synthesise large enough quantities for formulators to sample without having to pay a huge capital cost upfront.

With support from RAPID, Christoph

Krumm, co-founder of start-up Sironix Renewables, is now working to figure out how to manufacture environmental-friendly biosurfactant products that he developed during his PhD. Bio-based chemicals have a different chemistry than petrochemicals, as they contain a lot more oxygen, Krumm says. 'Inherently, you're working with a different reaction than you normally would with petrochemicals.' The higher oxygen content means that water management in the reactor becomes a big issue, he explains, because water could deactivate catalysts or generate side reactions like hydrolysis.

Krumm is working on a kilogram-scale catalytic reactive distillation tower to make his biosurfactants. The manufacturing consists of three processes, which all take place in the tower. Beds containing catalysts are strategically located along the tower, and reactants enter from both top and bottom ends, consuming or releasing water vapour at each bed where reactions take place.



Reactive distillation apparatus used for the RAPID project at Sironix HQ in Seattle

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Ni's research group. This reactor comprises of a long winding tube, with stationary orifices placed periodically within it. As reactants flow through it, they oscillate, taking two steps forward and one step back. Along the way, the combination of orifices and fluid oscillation generates eddies, which help the reactants mix uniformly. In 2004, Ni formed a spin-off company, NiTech Solutions, based in Edinburgh, to commercialise this oscillatory baffled reactor. Since then, it has been used for over 70 types of chemical reactions, including transesterification, hydrogenation and polymerisation, Ni says.

NiTech Solutions also commercialised a related piece of equipment, the continuous oscillatory baffled crystalliser. Like the reactor, the crystalliser is also a long, winding tube, but with temperature zones set up along it. In 2009, Ni demonstrated a continuous crystallisation of one of AstraZeneca's active pharmaceutical ingredients (APIs) that took just 12 minutes to complete. In contrast, AstraZeneca's existing crystallisation process took 9 hours 40 minutes. (Org. Process Res. Dev., doi: 10.1021/op900237x). Since then, the crystalliser has been adopted by many pharmaceutical, agrochemical and chemical companies for over 40 chemical compounds and 25 APIs. More recently, Ni has demonstrated the reactive crystallisation of paracetamol in one continuous process (Org. Process Res. Dev., doi: 10.1021/acs.oprd.8b00446).

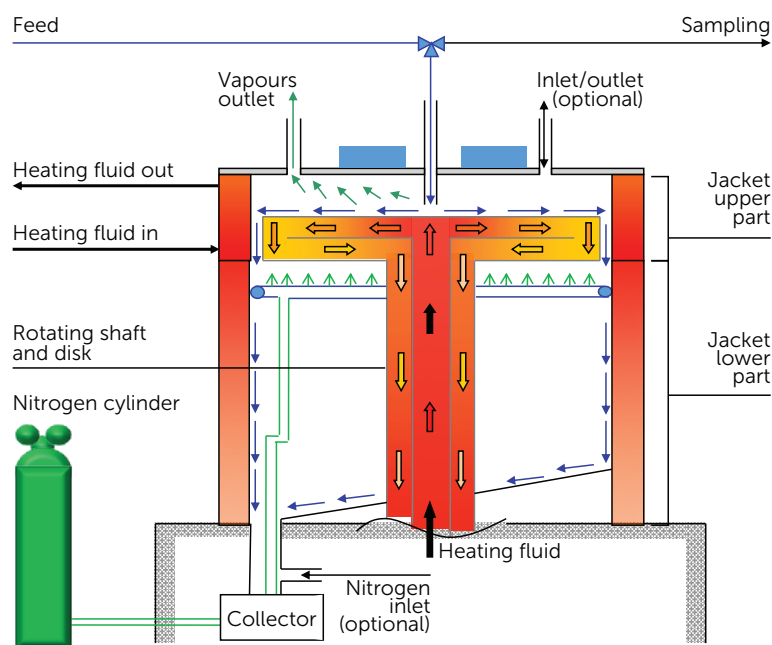
Boodhoo is working on another novel flow technique called the spinning disc reactor. Reactions take place in a thin film just several microns thick on the surface of the disc. The rapidly spinning motion creates waves on the film's surface, generating huge surface area while enhancing heat and mass transfer; typically, reactants spend just a few seconds on the disc, she says. This reactor is very useful for strongly exothermic reactions that take place very quickly, especially if it reduces or even eliminates the need for cryogenic cooling. Boodhoo has used the spinning disc reactor to perform a number of chemical reactions, including ortho-lithiation, a key reaction in pharmaceuticals manufacturing (Org. Process Res. Dev., doi: 10.1021/acs.oprd.7b00142).

Schematic of a spinning disk reactor

manufacturing, but batch processes continue to dominate, especially in fine chemicals and pharmaceuticals manufacturing. Operations at specialty chemicals company Lubrizol, for example, are almost entirely batch-type, says chemical

engineer Cliff Kowall. He has been tasked with finding opportunities to convert batch processes at Lubrizol into flow ones, a form of process intensification.

A novel flow technique is the oscillatory baffled reactor from



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