

COMMENT

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ANEK SUWANNAPHOOM



Refineries use huge amounts of thermal energy to process crude oil.

Seven chemical separations to change the world

Purifying mixtures without using heat would lower global energy use, emissions and pollution — and open up new routes to resources, say **David S. Sholl** and **Ryan P. Lively**.

Most industrial chemists spend their days separating the components of large quantities of chemical mixtures into pure or purer forms. The processes involved, such as distillation, account for 10–15% of the world's energy consumption^{1,2}.

Methods to purify chemicals that are more energy efficient could, if applied to the US petroleum, chemical and paper manufacturing sectors alone, save 100 million tonnes of carbon dioxide emissions and US\$4 billion in energy costs annually³ (see 'Cutting costs').

Other methods would enable new sources of materials to be exploited, by extracting metals from seawater, for example.

Unfortunately, alternatives to distillation, such as separating molecules according to their chemical properties or size, are underdeveloped or expensive to scale up. Engineers in industry and academia need to develop better and cheaper membranes and other ways to separate mixtures of chemicals that do not rely on heat.

Here, we highlight seven chemical

separation processes that, if improved, would reap great global benefits. Our list is not exhaustive; almost all commercial chemicals arise from a separation process that could be improved.

SEVEN SEPARATIONS

Hydrocarbons from crude oil. The main ingredients for manufacturing fossil fuels, plastics and polymers are hydrocarbons. Each day, refineries around the world process around 90 million barrels of crude ▶

► oil — roughly 2 litres for every person on the planet. Most do so using atmospheric distillation, which consumes about 230 gigawatts (GW) globally³, equivalent to the total energy consumption of the United Kingdom in 2014 or about half that of Texas. In a typical refinery, 200,000 barrels per day of crude oil are heated in 50-metre-tall columns to liberate thousands of compounds according to their boiling points. Light gases emerge at the cool top (at around 20 °C); progressively heavier fluids leave at lower and hotter points (up to 400 °C).

Finding an alternative to distillation is difficult because crude oil contains many complex molecules,

some with high viscosities, and myriad contaminants, including sulfur compounds and metals such as mercury and nickel. It is feasible in principle to separate hydrocarbons according to their molecular properties, such as chemical affinity or molecular size. Membrane-based separation methods, or other non-thermal ones, can be an order of magnitude more energy efficient than heat-driven separations that use distillation. But little research has been done.

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Uranium from seawater. Nuclear power will be crucial for future low-carbon energy generation. Although the trajectory of the nuclear industry is uncertain, at current consumption rates, known geological reserves of uranium (4.5 million tonnes) may last a century⁴. More than 4 billion tonnes of uranium exist in seawater at part-per-billion levels.

Scientists have sought ways to separate uranium from seawater⁴ for decades. There are materials capable of capturing uranium, such as porous polymers containing amidoxime groups. But these molecular ‘cages’ also capture other metals, including vanadium, cobalt and nickel.

Chemists need to develop processes to remove these metals while purifying and concentrating uranium from seawater. In 1999–2001, Japanese teams captured around 350 grams of uranium using an adsorbent fabric⁴. Starting up a new nuclear power plant requires hundreds of tonnes of uranium fuel, so the scale of these processes would need to be vastly increased. In particular, efforts to reduce costs for adsorbent materials are needed.

Similar technologies could capture other valuable metals⁴, such as lithium, which is used in batteries. The quantity of lithium

dissolved in the oceans is ten times larger than that in known land-based resources; the limited size of the latter may become a long-term barrier to energy storage.

Alkenes from alkanes. Manufacturing plastics such as polyethene and polypropene requires alkenes — hydrocarbons such as ethene and propene, also known as olefins. Global annual production of ethene and propene exceeds 200 million tonnes, about 30 kilograms for each person on the planet. The industrial separation of ethene from ethane typically relies on high-pressure cryogenic distillation at temperatures as low as –160 °C. Purification of propene and ethene alone accounts for 0.3% of global energy use, roughly equivalent to Singapore’s annual energy consumption.

As with crude oil, finding separation systems that do not require changes from one phase to another could reduce by a factor of ten the energy intensity of the process (energy used per unit volume or weight of product), and offset carbon emissions by a similar amount⁵. For example, porous carbon membranes are being developed that can separate gaseous alkenes and alkanes (also called paraffins) at room temperature and at mild pressures (less than 10 bar)⁶. But these cannot yet produce the more than 99.9% pure alkenes needed for chemicals manufacturing.

In the short term, ‘hybrid’ separation techniques might help — membranes can be used for bulk separation and cryogenic distillation for ‘polishing’ the product. Such approaches would reduce the energy intensity of alkene production by a factor of 2 or 3, until membranes become good enough to replace distillation entirely. A major hurdle is scaling up the membranes — industry might require surface areas of up to 1 million square metres. Deployment on this scale will require new manufacturing methods as well as advances in materials’ properties.

Greenhouse gases from dilute emissions. Anthropogenic emissions of CO₂ and other hydrocarbons, such as methane released from refineries and wells, are key contributors to global climate change. It is expensive and technically difficult to capture these gases from dilute sources such as power plants, refinery exhausts and air.

Liquids such as monoethanolamine react readily with CO₂, but because heat must be applied to remove CO₂ from the resulting liquid, the process is not economically viable for power plants. If the approach was applied to every power station in the United States, CO₂ capture could cost 30% of the country’s growth in gross domestic product each year⁷. Cheaper methods for capturing CO₂ and hydrocarbon emissions with minimal energy costs need to be developed.

A complicating factor is deciding what to do with the purified product. CO₂ could be used in a crude-oil production method known as enhanced oil recovery, or in vertical farming and as chemical and biorefinery feedstocks. But human activities emit so much of the gas⁸ that in practice much of it will need to be stored long term in underground reservoirs, raising other issues.

Rare-earth metals from ores. The 15 lanthanide metals, or rare-earth elements, are used in magnets, in renewable-energy technologies and as catalysts in petroleum refining. Compact fluorescent lamps use europium and terbium, for example, and catalytic converters rely on cerium. Producing rare earths economically is a problem of separation, not availability. Despite their name, most of the elements are much more plentiful in Earth’s crust than gold, silver, platinum and mercury. Unfortunately, rare earths are found in trace quantities in ores and are often mixed together because they are chemically similar.

Separation of rare earths from ores



High-capacity (HiCap) polymers can separate metals such as uranium from solution.

requires mechanical approaches (such as magnetic and electrostatic separation) and chemical processing (such as froth flotation). These are inefficient: they must contend with the complex compositions of mined ores, use large volumes of chemicals, and produce lots of waste and radioactive by-products. Improvements are sorely needed.

The recycling of rare earths from discarded products is increasing. Bespoke processes could be designed because the chemical and physical compositions of the products are well defined. A variety of metallurgical and gas-phase extraction methods have been explored, but recycled rare earths are not yet part of most supply chains^{9,10}. Research is needed to reduce the ecological impact of key items containing rare earths over their whole life cycle.

Benzene derivatives from each other. The supply chains of many polymers, plastics, fibres, solvents and fuel additives depend on benzene, a cyclic hydrocarbon, as well as on its derivatives such as toluene, ethylbenzene and the xylene isomers. These molecules are separated in distillation columns, with combined global energy costs of about 50 GW, enough to power roughly 40 million homes.

The isomers of xylene are molecules with slight structural differences from each other that lead to different chemical properties. One isomer, para-xylene (or *p*-xylene), is most desirable for producing polymers such as polyethylene terephthalate (PET) and polyester; more than 8 kilograms of *p*-xylene is produced per capita each year in the United States. The similar size and boiling points of the various xylene isomers make them difficult to separate by conventional methods such as distillation.

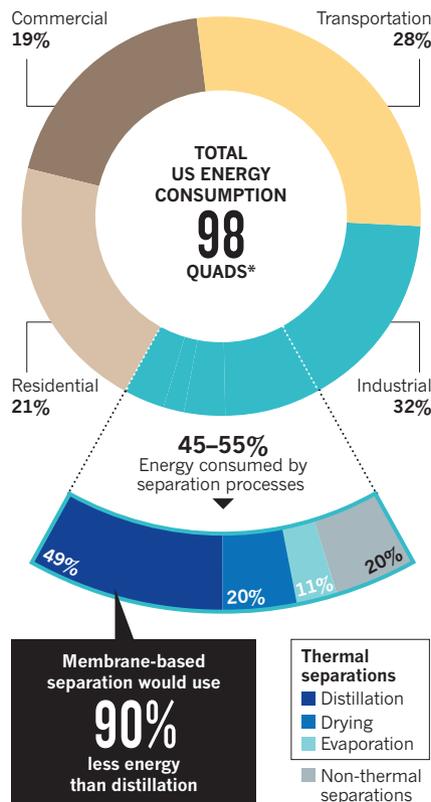
Advances in membranes or sorbents could reduce the energy intensity of these processes. As for other industrial-scale chemical processes, implementing alternative technologies for separating benzene derivatives will require that their viability be proved on successively larger scales before commercial implementation. Constructing a chemical plant can cost US\$1 billion or more, so investors want to be sure that a technology will function before building new infrastructure.

Trace contaminants from water. Desalination — whether through distillation or membrane filtration — is energy and capital intensive, making it unfeasible in many dry areas. Distillation is not the answer: thermodynamics defines the minimum amount of energy needed to generate potable water from seawater, and distillation uses 50 times more energy than this fundamental limit.

Reverse-osmosis filtration, a process that applies pressure across a membrane to salty water to produce pure water, requires only

CUTTING COSTS

Chemical separations account for about half of US industrial energy use and 10–15% of the nation's total energy consumption. Developing alternatives that don't use heat could make 80% of these separations 10 times more energy efficient.



*A quad is a unit of energy equal to 10^{15} British Thermal Units (1 BTU is about 0.0003 kilowatt-hours).

25% more energy than the thermodynamic limit⁵. But reverse-osmosis membranes process water at limited rates, requiring large, costly plants to produce a sufficient flow. Reverse osmosis of seawater is already done on commercial scales in the Middle East and Australia. But the practical difficulties of handling more-polluted water — including corrosion, biofilm formation, scaling and particulate deposition — mean that expensive pretreatment systems are also needed.

Developing membranes that are more productive and resistant to fouling would drive down the operating and capital costs of desalination systems to the point that the technique is commercially viable for even highly polluted water sources.

NEXT STEPS

Academic researchers and policymakers should focus on the following issues.

First, researchers and engineers must consider realistic chemical mixtures. Most academic studies focus on single chemicals and infer the behaviour of mixtures using this information. This approach risks missing phenomena that occur only in

chemical blends, and ignores the role of trace contaminants. Academics and leaders in industrial research and development should establish proxy mixtures for common separations that include the main chemical components and common contaminants.

Second, the economics and sustainability of any separation technology need to be evaluated in the context of a whole chemical process. Performance metrics such as cost per kilogram of product and energy use per kilogram should be used. The lifetime and replacement costs of components such as membrane modules or sorbent materials need to be factored in.

Third, serious consideration must be given early in technology development to the scale at which deployment is required. Physical infrastructure such as academic and industrially operated test beds will be needed to take new technologies from the lab to pilot scales so that any perceived risk can be reduced. Managing this will require academia, government agencies and industry partners to collaborate.

Fourth, current training of chemical engineers and chemists in separations often places heavy emphasis on distillation. Exposure to other operations — such as adsorption, crystallization and membranes — is crucial to develop a work force that is able to implement the full spectrum of separations technologies that the future will require. ■

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1. Oak Ridge National Laboratory. *Materials for Separation Technologies: Energy and Emission Reduction Opportunities* (2005).
2. Humphrey, J. & Keller, G. E. *Separation Process Technology* (McGraw-Hill, 1997).
3. US Dept. Energy Advanced Manufacturing Office. *Bandwidth Study on Energy Use and Potential Energy Saving Opportunities in U.S. Petroleum Refining* (US Dept. Energy, 2015).
4. Kim, J. *et al. Sep. Sci. Technol.* **48**, 367–387 (2013).
5. Koros W. J. & Lively, R. P. *AIChE J.* **58**, 2624–2633 (2012).
6. Xu, L. *et al. J. Membr. Sci.* **423–424**, 314–323 (2012).
7. Interagency Working Group on Social Cost of Carbon (US Govt.). *Social Cost of Carbon for Regulatory Impact Analysis* (2013).
8. Song, C. *Catal. Today* **115**, 2–32 (2006).
9. Jordens, A., Cheng, Y. P. & Waters, K. E. *Miner. Eng.* **41**, 97–114 (2013).
10. Massari, S. & Ruberti, M. *Resour. Policy* **38**, 36–43 (2013).

CORRECTION

The graphic 'The dirty ten' in the Comment 'Three steps to a green shipping industry' (Z. Wan *et al. Nature* **530**, 275–277; 2016) gave the wrong unit for PM_{2.5} concentrations. It should have been $\mu\text{g per m}^3$, not mg per m^3 .

CORRECTION

The Comment 'Seven chemical separations to change the world' (D. S. Sholl and R. P. Lively *Nature* **532**, 435–437; 2016) gave the incorrect units for atmospheric distillation. It should have read 230GW globally.