Bubble Reactions to Improve Sustainability

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There are two upcoming technologies that, together, have the potential to improve many ways by which we process microorganisms, raw materials and waste. When fully developed and implemented, they should reduce our costs and/or usage of energy, fossil fuels, water and many industrial chemicals by substantial amounts, as well as reducing emissions and global warming.

Introduction

The first of these technologies is the fluidic oscillator (FO) technology invented at Sheffield. This has already been shown capable of generating dense clouds of nearly monodisperse nano/microbubbles with regular spacing, at extremely low energy costs. This is due to the fact that the FO is a no-moving part, bistable amplifier capable of generating oscillatory flow that results in a longer lifetime concomitant with greater reliability. The FO can inject a continuous flow of bubbles to suffuse the liquid in any size of container, under almost any pressure. Most gases or gas mixtures can be used under a wide range of operating conditions. The additional capability to tailor the FO to make it purpose-built for specific operations makes this a versatile technology.

Such simple and elegant technology has an impressively wide range of applications. It can:

- Remove water and other volatiles selectively from their parent liquor, virtually without heating them – Isothermal distillation [3]
- Provide efficient froth flotation separations [4, 5]
- Improve transport phenomena, such as permeating liquids with gases, exchanging the gases within liquids, and improving the processes of aeration, oxygenation, ozonisation, and carbonation [6-8]
- Improve the operation of plasma microreactors [9]
- Generate bubbles that, by their controlled decavitation under gravitational pressure in a drillhole reactor, can cause a wide variety of desirable physical and chemical reactions to occur, at energy costs considerably less than current industrial methods.

The second technology [35] is a suite of technologies grouped under the general heading of Winwick Drillhole Reactor (WDR) technology. Typically, these combine one or more of the effects of: explosive cavitation (bubble formation), adiabatics, catalytics, gravitic pressure changes in deep boreholes, heat exchanges, and the remarkable energetics of decavitating bubbles to produce desirable physicochemical changes in materials at very low energy cost, at any required scale, and with minimal pollution or risk. Of these processes, decavitation is the key one, as it has been shown that, as a bubble disappears under increasing pressure, its destruction causes a spike in highly-localised temperature of up to 5,000^{0}C, together with a microshockwave and two stabbing microjets [36]. These form the basis of sonochemistry that uses acoustic/ultrasonic/hydrodynamic decavitation, but the method described here does not require sonochemistry's typically high-energy inputs. The conditions are more than adequate to cause chemical reactions with high energy level barriers to occur, whilst often inhibiting destructive back reactions, thereby improving yields. Moreover, as passive pressure in a pipe-within-a-pipe WDR is almost a free resource, even supercritical conditions and extractions are economical to achieve and are designed to scale well. Furthermore, WDR processes are cost-effective continuous ones that can readily be combined with efficient heat exchanges and with centrifugal separation by means of helical vanes and offtakes.

Scientific debate

There is yet minimal debate on these novel formation technologies, though considerable on both microbubbles and sonochemistry.

Processes and prospective applications

As there are potentially hundreds of applications of the two technologies, only the more prominent are listed here. The FO ones are listed first, then those that shade through into principally Winwick ones. They are:

- Lubrication of the hulls of marine vessels to reduce water resistance and fuel usage, or to improve speed. The same technology can be used to provide in-pipeline surge protection and to reduce turbulence, hammer, and wall friction. However, the FO bubble densities applied in both instances must, and can, be orders of magnitude greater than those used in *Maritech* [2, 34, 48-50]
- Increasing ocean albedo (reflectiveness) via long-lasting bubbles [50]
- Concentrating solutes and slurries by dewatering, virtually without raising their temperature (isothermal distillation). It can thus be used to concentrate fragrances, fruit juices, milk, sugar cane/beet/maple syrup, whey, and other slurries, some of which might otherwise clog filters and membranes, or require high evaporative energy input due to latent heat costs [3]. It can be used to reduce packaging, transport and disposal costs.
- Reactive distillation involving the removal of water during transesterification.
- Breaking the azeotrope barrier [10] and adding economical options for volatile organic separation and desalination processes
- Increasing the heat carrying capacity of water or other volatiles for geothermal heat pumps
- Airlift loop bioreactor work has been performed at laboratory, pilot and industrial scale, including for improved aeration, algal growth, enhanced mass transfer, etc. This can be extrapolated to fermentation and enhanced oil recovery [2, 7, 8, 11-13]
- Water disinfection/purification/sterilisation/treatment [14], with ship ballast water being an early target
- Aeration or oxygenation of sewage, wastewater, in aquaculture, or with algal blooms [2, 6, 8]
- Improving froth flotation, micro-algal flotation, protein and emulsion separation [4, 5, 16-19], foam-

mediated concentration, algal separation [20], and helping in biofuel upgrading and bioprocessing

- Surface cleaning of objects such as silicon wafers, foodstuffs [21] and automobiles [22]
- Provision of uniformly distributed catalysis sites engenders the ability to act as nucleation sites for crystals and other formulations – including smooth, high-volume, low-calorie, flavoursome ice-cream and chocolate made with nanobubble emulsions [15]
- 'Oxygation' of subterranean irrigation water, thereby helping with plant growth and soil biome improvement
- Aiding plasma microreactor reactions, including disinfection, oxidation, ozonisation and organics' removal
- Rapid blood oxygenation [23], theranostics (drug delivery and diagnostics), as well as sensors for the body [24-33]
- Winwick Cell Rupture (WCR) of tough, slippery algae and other cellular material. Cell lysis.
- Fibre Release (WFR) of diverse components from lignocellulosic material
- Lipid Esterification (WLE) [43]
- Ammonia Synthesis (WAS) [51-55]
- Syngas Synthesis (WSS) [35, 46]
- Methanol Synthesis (WMS) [39, 40]
- Hydrothermal Liquefaction (WHL) [35, 46, 47]
- Hydrothermal Carbonization (WHC) [42]
- Supercritical eXtraction (WSX) [41]
- Sub/supercritical Conversion (WSC) [35, 37, 44-47]

Triple bottom line aspects

Many of the listed applications of the two, broad technologies have triple bottom line effects TBD. Several of the applications are currently undergoing industrial evaluation. Together, these two technologies might provide much of the basis for the development of a sustainable biorefinery industry.

The two applications selected for practical consideration here are: isothermal distillation and ammonia synthesis. Both employ FO microbubbles.

DESALINATION / PHASE SEPARATION BY ISOTHERMAL DISTILLATION

The extraction of purified water from saline, waste, polluted or mine water can be achieved economically, provided there is a local source of hot waste or solar-heated (to >80^{0}C) gas. Most sources of parasitic hot gas can be used. Cycloning can be used to remove particulates in the gas prior to microbubbling, whilst this removes solubles from the gas, thereby remediating both [4,5].

Hot FO microbubbles are bubbled into a shallow body of wastewater/liquid of interest. There, they extract vapour from the liquid (dewatering), virtually isothermally using thermochemical potential. The key operational parameters are tuneable bubble size and inlet gas temperature. This leads to extremely effective separations with substantially reduced energetics. Co-products, such as salt, concentrated heavy metals or acids, may then be recovered from the thickened residuum. A simple undergraduate case study on using microbubbles to improve water-use efficiencies in shale-gas fracking won the BP Ultimate Field Challenge –March 2015 [56, 57]. It showed an increase in water and thermal recovery efficiencies in comparison to traditional desalination, coupled with the possibility of quick uptake of the technology industrially. The method has advantages over traditional methods of water purification as it requires no: high pressures/ temperatures; fragile cloggable membranes; chemicals; or high capital costs.

AMMONIA SYNTHESIS VIA DECAVITATION IN A DRILLHOLE REACTOR

Nitrogenous fertilizer made from ammonia sustains much of our agriculture, but is produced unsustainably. The Haber-Bosch process currently used to produce ammonia by combining nitrogen and hydrogen requires expensive: high pressures (150-250atm), high temperatures (300-550^{0}C), and inefficient cooling between multiple passes http://en.wikipedia.org/wiki/Haber_process. References 51-55 indicate that bubble decavitation can generate ammonia. Both economically and sustainably, the WAS method uses a variant of sonochemistry to: generate the required changing process pressures; include the catalysts in its carrier liquid; and use the energetics of decavitating microbubbles to provide spiking temperatures for the conversion; whilst improving the yield because the produced ammonia is immediately cooled and removed from the reactants by dissolution in the carrier. The ammonia gas may then be removed from the carrier and catalysts by isothermal distillation, prior to their recycling. Sustainability may further be increased by the production of hydrogen from biomass using the WSS process, rather than from natural gas.

Issues for further consideration

The generation of FO microbubbles and plasma microreactions have been proven at laboratory scale and in some industrial pilots. Sub- and supercritical reactions, some in drillhole reactors, have been used at industrial scale to remediate hazardous waste and to produce syngas. What is now required is a concerted effort to see which, and how industrially viable, are the applications that can be derived from the initiating work described here.

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