CRITICAL NATIONAL NEED IDEA

Critical National Need Idea Title: Cost effective separations of liquid phase materials for biofuels, biochemicals and water

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Cost effective separations of liquid phase materials for biofuels, biochemicals and water

National Needs in Cost-effective Separation Technologies for Producing Clean Biofuels and Biochemicals

A key enabling technology for hydrocarbon processing is gas phase fractional distillation which has the ability to resolve or separate similar molecules. The ability to start with a complex material such as crude oil and cost effectively fractionate it into components for further processing has been a key part of the growth of the hydrocarbons industry. There is no analogous liquid phase approach for the cost effective separation of large bioactive organic molecules or for the separation of the complex mixtures present in bio-based raw materials.

The polar nature of many bio-materials means that more energy is required to vaporize them and the molecules often do not have the thermal stability to survive the approach. Another related problem is encountered with organism based synthesis approaches. In general organisms tend to produce the desired product at low concentrations. In addition, the products are dissolved in a high energy of vaporization solvent, water. Thus a key problem plaguing the development of bio-based materials as replacements for hydrocarbon based materials is the development of technology that can be cost effectively used to produce pure and dry materials.

An example of the energy aspect of the problem is from the ethanol production process where the bulk of the energy required to operate the plant is used for water removal from the organism produced ethanol. As a recent, 2006, process economics analysis by Dale and Tyner at Purdue indicate the highest operating expense after the corn feedstock is energy. First, there is the distillation and drying of the ethanol and then the dehydration and recovery of the byproduct distillers dry grain and solubles, DDGS. They point out that the average dry mill process consumed 36,000 Btu's of thermal energy per gallon of product and the largest percent (32%) was for distillation though water removal from drying of the DDGS and evaporation of thin stillage used over half of the energy. The separation section is also one of the major capital cost areas.

Considering that there is capacity for the production of 6 billion gallon of ethanol and a national intent to make more, a more energy efficient separation process would have a significant impact on our overall energy usage and carbon dioxide emissions. In addition, given the scale of energy use, some in the industry are moving away from natural gas to lower cost coal for their energy source. Coal fired boilers while more cost effective will probably not have the scale to justify new high technology approaches for carbon dioxide capture which will make the carbon dioxide emission issue worse.

A corollary problem as pointed out by Aden at NREL is the high water usage associated with the high energy usage. It is estimated that in 2005 the average ethanol plant used 3-4 gallons of water per gallon of ethanol produced, much of it in the energy production section for cooling tower and boiler system operation to support water removal from the products.

The good news for ethanol production is that yeast produces a relatively high concentration of ethanol and that the traditional distillation methods will work. The same cannot be said for many of the new biopharmaceuticals. Many of the new proteins that are being developed are produced at low concentrations and the molecules do not have the thermal stability for distillations.

At a recent conference on “Accelerating Innovation in 21st Century Biosciences: Identifying the Measurement Standards and Technological Challenges” organized by NIST, the Manufacturing Plenary lecture demonstrated the problem. In his presentation Thomas showed a representative process flow chart for the production of a new biotherapeutic. The flow sheet had two rows of unit operation pictured indicating all the processing steps. The first step was the organism based production and then the rest of the steps were required for concentration and cleanup of the active. In the breakout section it was stated that what was needed was new ways for process cleanup and there was general agreement that cleanup was the holy grail for this new generation of biomaterials. No more was said about it as it was not really an analysis problem and the group did not know how else it could be achieved.

Cost effective methods for preparing the sugar feeds for organism growth systems will become more important as cellulose and hemicellulose are hydrolyzed to produce the simple sugar feeds. As the larger biopolymers are decomposed to their subunits it is important to be able to remove unwanted byproducts of the reaction and other impurities present in the feed. An intermediate separation process can be very important as often the extraneous molecules that are present can be toxic to the organism.

The sugars recovered from biomass can be fermented to many useful chemicals (lactic acid), food ingredients (monosodium glutamate, xylitol), enzymes, pharmaceuticals, and nutraceuticals. Costs of recovery of these compounds from fermentation broths, however, are quite high because of low concentrations in the crude broths.

Another area that would benefit from better separation technology would be the processing of seed oils into biodiesel and jet fuels. The raw materials oils have various impurities that can cause foaming and other problems throughout the process. As a side light several of these impurities are expected to have value as nutraceuticals if they can be cost effectively separated. In addition, several reaction impurities can cause problems in cold weather operation such that cost effective separations would be of a benefit for better product performance.

Finally, at a conference on microreaction technology held at the Center for Process Analytical Chemistry, CPAC, the attendees agreed that the whole microreaction technology area would benefit from better separation technology. A liquid separation technology with high resolving power for large molecules or high-value fine chemicals would be quite useful for the continuous separation of the output of microreactors. The current approach is to continuously make the material and then collect it for some batch separation technique such as extraction or recrystallization. Microreactors operate at high concentrations and tend to have high yields compared to batch but there are no real separation methods currently in use that are well matched to their output rates when used for the production of large molecules. There is a major concern that by having to collect product and reactants into a batch receiver for later separation, there is time for potential unwanted side reactions to occur.

National Needs in Cost Effective Separation Technologies for Producing Clean Water

Sources of drinking water and water for irrigation are increasingly contaminated by municipal and industrial wastes. Low levels of contaminants such as pesticides, herbicides, disposed drugs, toxic chemicals, and heavy metals in water have long term harmful effects on human health. Cost effective separations technologies are needed to remove the undesirable impurities from drinking water and waste water.

Technology Developments Needed to Reduce Costs of Liquid Phase Separations

Three technology areas need to be further developed and for maximum effectiveness integrated to provide reasonable cost solutions to the liquid separation problems stated above. By incorporating the latest technology developments into a new generation of operating devices a significant improvement in current liquid separation practices should be attainable which would lower cost, save energy and improve quality.

The first separation technology which would improve the processing of water soluble materials would be the commercialization of the new generation of ceramic membranes. At the CPAC meeting a class of new organic modified ceramic membranes was shown to have the flux and stability to enable the cost effective separations of water from most organic molecules including alcohols. The second needed advance which was also described at the meeting was the next generation of simulated moving bed chromatograph, SMB, for the separation of complex mixtures. The third technology that is needed was discussed at the meeting as well and that is the utilization of high efficiency high throughput heat exchangers that are manufactured using microscale designs.

Ceramic Membranes

Ceramic membranes have several useful features which make them quite useful for biomaterial separation and dewatering. A key feature for long term operation is the ability to apply a back pressure cleaning pulse to combat fouling. In addition in the extreme case they can usually be taken off line and refired for more extensive cleaning. While they have high fluxes, it is important to get to even higher fluxes to enable cost effective operation as they are more expensive than other approaches. Fortunately, the new materials allow operation at higher pressures, and temperatures with no significant loss of selectivity and yet with the needed significant improvements in flux.

To extend these materials to the full range of organic separations the pore size of these new materials needs to be extended to lower sizes for even greater selectivity in dealing with biomaterial processing especially ethanol. The expansion of the pH range of operation would enable even more separations without the need for pre-adjustment of the pH. In addition larger scale testing and finally production at scale needs to occur to make them more available to use in commercial applications.

Simulated Moving Bed Technologies

Adsorption technologies are most effective for recovery of target compounds from dilute solutions. Simulated moving bed chromatography is an efficient continuous adsorption process. A well designed SMB process can increase adsorbent utilization and decrease solvent/eluent consumption by an order of magnitude compared to conventional batch chromatography. It has been commercially practiced for some time and is the method of choice for the continuous separation of high fructose corn syrup and production of enantiomeric pharmaceuticals. While the method is very cost efficient to operate, even at very large scale, it is very difficult to implement. The problem is that there are many variables that need to be optimized for efficient operation. New research has shown that the system can now be modeled to enable separations to be achieved in less than a month. In addition it is expected that additional analytical tools can be used to shorten the time further and enable longer term stable operation. These advances need to be implemented in new systems for commercial use to occur.

Also, to expand the technology to other classes of separations it will be important to design develop and test additional packing materials for new classes of separations. The models demonstrate that all of the standard mechanisms for separations that are found in high performance liquid chromatography are valid in the technique which means that most classes of compound can be separated.

A major fraction of the cost for SMB is due to adsorbents. Effective low cost adsorbents is a key to reducing overall SMB separation cost.

High Efficient Heat Exchange

Finally, work as reported by IMM in Germany has shown that high volume heat exchangers incorporating microscale design concepts can operate at very high efficiencies. This is important as heat integration of this new generation of separation systems will further optimize operation. For example, the new generation of membranes operates at pressure in the 100-200 degree centigrade range for the required high fluxes. To achieve energy efficient operation it will be important to heat exchange the products with the incoming liquids.

Just to demonstrate the point one discussion at the CPAC meeting was to remind the attendees that by using high quality heat exchange, distillation could be as energy effective as membranes since heat of condensation and heat of vaporization are equal in magnitude. As stated above many biomolecules cannot take high temperatures but to the extent temperature can be used it is important to do it as energy efficiently as possible.

However, it is expected that for many of the pharmaceutical applications as well as for organism based fuel production a combination of techniques will need to be used for best optimization of the separation system. For example it is expected that the membranes will be used as an integral part of the SMB systems to concentrate the incoming stream for separation. It is also expected that the recycling of the SMB solvent that is used for the separation could be cleaned with a membrane. Also as mentioned the cleanup of the solvent will probably best be done at temperature which means that good quality heat exchange should be built into the system as well.

<u>Relevance for NIST TIP Program</u>

Thus it is expected that with some additional lab based development to advance the above techniques, they can be integrated into commercially viable units that can solve many of the liquid separation problems for the biofuels, biomaterials, biopharma and bioactive molecule production areas. The development of the needed technology will save the industries energy, time and money while improving the quality of the produced products. The problem with getting this done is that the research needed is mostly development and outside the range of research supported by the individual agencies. NSF has a small Separations Program with an annual budget about $ 1.5 million. The NSF Separations program is focused on fundamental discoveries, not engineering or technology development. NIH is focused on research on diseases and medical treatments. Many companies in the biofuels/biorefinery area are start-up companies or medium-sized companies. They cannot afford costly development of separation technologies. Since the separations technology to be developed would be expected to enable many of the supported research areas to be much more effective, this seems to indicate that the envisioned research would be a good fit for a NIST TIP program.

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