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Separations Landscape for the Production of Biofuels

On August 1, 2012, The National Petroleum Council (NPC) in approving its report, *Advancing Technology for America's Transportation Future*, also approved the making available of certain materials used in the study process, including detailed, specific subject matter papers prepared or used by the study's Task Groups and/or Subgroups. These Topic Papers were working documents that were part of the analyses that led to development of the summary results presented in the report's Executive Summary and Chapters.

These Topic Papers represent the views and conclusions of the authors. The National Petroleum Council has not endorsed or approved the statements and conclusions contained in these documents, but approved the publication of these materials as part of the study process.

The NPC believes that these papers will be of interest to the readers of the report and will help them better understand the results. These materials are being made available in the interest of transparency.

Separations Landscape for the Production of BioFuels

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Summary

This report summarises in a general form BioSeparations technologies as they apply to biofuels. The report is divided into two parts. In part 1, we discuss the broad landscape of separation techniques that are relevant to the biofuel production. Part 2 is devoted to case studies on separation options identified for selected possible development projects.

The technology landscaping is focussed on three areas namely: the selective separation of organics from water, solid-liquid separations and solid handling, and lipid removal from within the algae cell structure. Furthermore, some special consideration is given the current state and needs in separations as related to thermo-catalytically derived fuels from bio-mass. Lastly, an in depth study of adsorptive separations for biofuels is presented as an example of the state of the art in one specific field

Distillation/Evporation is most commonly used for the recovery of biofuel components from water these days. It is energy intensive, suffers from limited selectivity, and is not amenable for temperature-sensitive materials. So clearly alternatives are necessary as we expand the biofuel and biofeedstock slates. Several techniques were identified that have potential to improve the energy efficiency of conventional distillation methods as well as overcome some of the other limitations. These are: membranes, adsorption based processes, and extraction based separations.

Aggregation of suspended solids and separation of the aggregates are key steps in the case of solid separations from water. Aggregation techniques using chemical, electrochemical or physical methods were explored in the present study. The resulting aggregates can be separated further by microfiltration or rotary vacuum filtration. VSEP technology is a promising dewatering technique that could be applied for treating biomass slurries. The technique uses a membrane, but the chances of fouling is overcome by adding shear to the membrane surface through torsional vibrations.

The currently available lysis techniques for algae use thermal and/or mechanical methods. Future technologies in this area aim at arrangements that consume less energy such as supercritical, chemical, surface activity based separations. The emulsion breaking technologies used for produced fluids (crude-water emulsions) is one example that can be exploited in this area.

Ethanol-water separation was one of the cases we have considered for in-depth discussion. In ethanol dehydration, there are technologies by companies such as Sulzer, Vaperma, and Mitsui that offer energy efficient alternatives. Hybrid line-ups involving distillation as a primary unit followed by a membrane unit are also evaluated in this report. Based on the analysis, a hybrid line-up that shows promising energy efficiency involves traditional distillation as the first step (in a single column) producing ca. 90 wt% ethanol. The vapour distillate from distillation unit is then fed to a pervaporation unit to produce anhydrous ethanol (above 99.5 wt %).

The pharmaceutical industry is one of the major beneficiaries of novel bio-separation technologies. It is followed by the food, water treatment and mining industries. These industries, especially the food and pharmaceutical, have a different cost-value proposition in comparison with the bio*fuel* industry. This is a challenge for the biofuel industry to address, while adopting such technologies. Also, many of these novel separation technologies are system (molecule) specific and vary in terms of their separation and recovery efficiencies. This, on the one hand suggests the absence of a single solution for all separation challenges,

but on the other hand, gives an opportunity for designing hybrids involving novel and/or conventional technologies.

Nature has for the most part explored elegant processes for the separations it has needed to carry out. As an example, movement of triglycerides from the intestine to the blood stream is done by several steps to ensure that the flow is only in one direction. Tri glycerides will not pass directly from the intestine thru the cell membranes to the blood stream and this also means that triglycerides in the blood will not leak back out to the intestine and be lost. Nature has designed catalysts (enzymes) in the intestine that converts triglycerides to monoglycerides and fatty acids. . Nature selected these types of couplings of reactions with separations, we have not for the most part because energy has been cheap enough the brute force has normally won. It is entirely plausible that in the future such couplings could be developed for industrial processes and provide a significant advantage in the manufacture of biofuels at commercial scale.

This report also will discuss briefly the separations technologies that will be required in existing refining processes to incorporate biofuels as a blending stock. Two examples here are the reduction of oxygenates in hydrocarbon streams from biomass (biodiesel, esters, pyrolysis oils, etc) to preserve heat content, cetane number, and other fuel properties, and the need to provide biomolecules as blend compononents that do not harm hydrophobicity or vapor pressure. The applications of reactive separations to the former in the form of Hydroprocessing/distillation hybrids are explored. The latter appears amenable to adsorptive separation methods

Finally, the report will also address some of the opportunities presented by the fields of nanotechnology and biomimicry to develop novel separation techniques for biomolecules from complex matrices

In the end though, the separations technologies that need to be addressed with great emphasis to help make biofuels a viable source of alternative energy, are those that densify the energy avialble in the biomass in a fast and effective manner. The separation of air, water, refractory materiasl, and other non energy components from the biomass before the manufacture of the biofuels is actually the critical development issue in the whole landscape. The very elegant and complex separations solutions required in the manufacture of biofuels are not the pain point in terms of the economics and sustainability of the processes; it is the energy densification step that unequivocally controls the outcomes.

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3. Challenges for BioSeparations . Separations forThenochemically derived Biofuels and Separations the way Nature does them

1. Introduction

1.1 Background

This report on BioSeparations is part of a larger effort which constitutes the National Petroleum Council's response to the Secretary of Energy's request for advice on U.S. fuel-vehicle prospects through 2050 for passenger, truck, air, rail and waterborne transport. To respond to the Secretary's request, the Council:

- Examined demand projections to 2050 for passenger, truck, air, rail and waterborne transport;
- Focused on opportunities to reduce costs and GHG emissions for light duty passenger and heavy duty truck transport since they account for approximately 80% of the GHG emissions from the U.S. transportation sector;
- Considered technical and non-technical challenges, including supply chain and infrastructure needs, to commercialize advanced fuel-vehicle systems by 2050 using hydrocarbon liquids, biofuels, natural gas, electricity, and hydrogen;
- Considered performance characteristics for potential light- and heavy-duty fuel-vehicle portfolios, such as cost of driving and fuel savings under various conditions including differing oil prices;
- Assessed GHG emission characteristics of potential fuel-vehicle systems and portfolios and methods to further reduce 2050 GHG emissions; and
- Considered the implications to energy security.

One of the findings of the broader NPC study (as detailed in the Executive Summary of that report) is: ***Advances in twelve priority technologies are essential if all alternative fuel-vehicle options considered are to achieve wide scale commercial adoption by 2050***

*More than 250 hurdles to wide scale commercial adoption of alternative fuel-vehicle systems are discussed in this report. Through a peer review process that included prominent academic and industry experts, the twelve priority technology advances shown in the table below were identified as necessary to enable each fuel-vehicle system to achieve economic competitiveness by 2050. The study did not estimate the R&D and implementation cost required to enable these advancements, but achieving them yields the most value for wide scale commercial adoption.*Five of these priority technologies relate to biofuels, namely:

Biotechnology to increase biomass production, Biomass logistics and densification, Biochemical hydrolysis for biofuel production, Improved sugar fermentation processes, Pyrolysis oil re*fining*

The report herein addresses the Landscape of Separations Technology in the area of Biofuels.

1.2 Objectives of the BioSeparations study

The success of biotechnology for bulk fuel manufacturing heavily depends on the engineering solutions in the downstream processes. This means that separation and purification steps have a crucial role in the commercial development of the process. The key factors that determine the choice of separation strategy include process throughput, particle size of the product and the impurities and the desired end-product concentration.

The objectives of this study were to identify relevant technical publications and patents in the area and produce the following:

- Summary of technologies/concepts relevant to different focus areas
- Preliminary assessment of the viability of the identified separation processes
- Specific comments/recommendations pertaining to individual processes

2. Landscaping Study on BioSeparations

2.1 Methodology

Over a period of several months in 2011(a BioSeparations landscaping study was conducted in by a team of engineers & researchers from different delivery groups with periodical review by the domain expert-Chief Scientist (Jose Bravo) and with input from other colleagues in Houston. Literature information (patents, journals, company websites, etc) for this study came from

- Third party searches performed by EVS (Delhi, India) and Avalon (Mumbai, India)
- Web-based literature search by Shell staff

Each EVS and Avalon search started with active guidance from STI in the form of ToR including scope, source and prescribed output summary format. This also included follow-up conversation with (third-party) search teams to highlight the focus and expectations from these searches. These 3rd parties used a combination of databases (listed below) and public domain information for their searches

- ➢ Sciencedirect
- ➢ ACS
- ➢ Interscience Wiley
- ➢ Scopus
- ➢ Ingentaconnect
- ➢ Informaworld
- ➢ Micropatent
- ➢ PubMed
- ➢ Thomasregister.net
- ➢ Dogpile.com
- ➢ Scirus.com

Also, peer views of BioSeparation challenges and solutions were obtained via the Circle of Experts service, offered by EVS. An external expert (CTO, Kreido BioFuels) was interviewed by EVS staff to get feedback on current & future technology trends in our focus areas including opinion on solutions for some of the toughest BioSeparation challenges (Appendix B). All exchange of information between EVS and this expert was non-confidential in nature. This expert's valuable comments validated the study team's view of promising technologies and supported many of the recommendations made by the STI team.

Towards the end of the study, the identified technologies/concepts were shared with the stakeholders (Biodomain project leads, internal Separation experts) to get their comments/feedback.

2.2 Study Exclusions

- Focus area # 2 was restricted to the removal of bulk solids (non-colloidal systems). This meant that the separation issues relevant to fermentation broth and downstream steps were excluded. Solids handling aspect was excluded from focus area # 2 due to the broad nature of the subject.
- Focus area # 2 was expanded to include the specific challenges of solid-liquid separation in the algal context
- Focus area # 4 dealt with cell rupture (removal of lipid from cells) only and it did not cover cell extraction (recovery of lipid from non-lipid components).

During the landscaping exercise, a conscious effort was made to not exclude any exploratory idea/process of promise. However, domain knowledge and judgement was exercised to exclude literature that targeted process gains at the expense of CAPEX and OPEX.

The technologies identified to be of interest in different focus areas are summarized in Appendix C. Some of them apply to more than one area. Detailed discussion is presented under various focus areas:

2.3 Results and Discussion

2.3.1 Separating organics from water

The separation of organic molecules from water appears in a biofuels manufacturing process in three areas: separation of the products, recovery of valuable bi-products, and effluent water treatment. For example, in the case of cellulosic ethanol production, the desired concentration of the product, ethanol, is about 5-10% wt in the fermentation broth. Getting the fuel grade ethanol (> 99.5 % purity) is a challenge and conventionally, an energy intensive azeotropic distillation set up is used to achieve this. Acetic acid is another molecule that is generated in many of the processes for the bio-fuel production and its concentrations are typically of the order of a percent. This means, we need to look for energy efficient solutions to achieve economical recovery of such molecules.

Three main classes of techniques for the separation of organic molecules from water were identified as promising in the study. Although, the maturity levels of these are different, each of them has the potential to replace (at least partly) the conventional distillation. The three classes are membrane-based, adsorption-based and extraction-based separation technologies.

2.3.1.1 Membrane based techniques

Pervaporation is one of the most promising alternatives for the separation of ethanol from water [1]. Membrane processes are generally energy efficient, simple to operate technologies with fewer environmental impacts. In pervaporation, the permeation of certain molecules is coupled with evaporation. There are two categories of membranes. The first category of pervaporation is to use hydrophilic membranes to separate out water (already concentrated by, say, a distillation). Polyvinyl alcohol based membranes are very popular in this category. The second category separates out organic molecules from water. In the case of ethanol recovery from dilute solutions, an organophilic membrane could be used [2]. Membranes based on polydimethylsiloxane fall under this [3]. Membrane distillation technologies are available for degassing of liquids as well as for selective separation of ethanol from water. Biopolar membrane electrodialysis is a promising technology for separation of organic acids like lactic acid from water. Some of the active players in membrane-based technologies include, Sulzer, Vaperma, Membrane Technology Research Inc., Mitsui Kuhni[1], Grace[2], Mitsui Engineering and COMETAS[3].

2.3.1.2 Adsorption based techniques

Adsorbents are traditionally used to selectively adsorb organic compounds from solvents like water in pharmaceutical and water treatment industries. A high surface area adsorbent is used in this case to bond (physically) the target molecules. The molecules are then separated from the adsorbent by desorption. Different types of adsorbents are reported in the literature.

2.3.1.2.1 Adsorption using zeolites

This is by far the most matured separation technique based on adsorption. For example, in ethanol recovery from the fermentation broth, zeolites are used for the final drying of ethanol

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[1] existing NDA, petraction

[2] Existing non analysis agreement with Shell

[3] Ceramics for biofuel, NDA with Shell

(from ca. 92 wt% to ca. 99 wt %)[4]. Zeolites are molecular sieves that are permeable to water, but not to ethanol.

2.3.1.2.2 Adsorption using Resins

In this case the adsorbent is a polymer gel with a highly porous structure. The nature of the polymer and the adsorbing media are key in determining the efficiency of separation. For example, polymeric adsorbents exhibiting non-polar or hydrophobic behaviour can adsorb organic species from polar solvents such as water. Example, AMBERLITE™ XAD™1180N (Rohm Haas) is a polymeric adsorbent for the selective separation of large organic molecules from aqueous solutions or polar solvents. Apart from Rohm Haas other players in this area include BASF, Arkema, and DuPont.

2.3.1.2.3 Adsorption using Salt bed

This is a technology that shows promise, but yet to developed for bioseparation applications. In this case water-organic mixture is passed through a $Mg_3(PO4)_2$ bed and the organic adsorbs on bed and is later recovered in vapour form by heating the bed. One advantage of this technology is that it can produce products with high purity. But, the maturity level of this process is still in the Discovery phase of evolution. GlobeLive International AB is an active player in this field in this technique.

2.3.1.3 Extraction based techniques

In liquid-liquid extraction, the separation of the dissolved component in the feed solution is achieved based on the distribution of the same in added solvent. The solvent that now contains the useful component has to be insoluble in the feed solution. The separated solvent containing the extract is then distilled to recover the component from the solvent.
When a supercritical fluid such as CO_2 is used as the solvent, the final removal of the fuel component becomes more efficient as it involves depressurising the system to remove gaseous CO_2. This technology is not well proven at commercial scale and some of the active players are Food/Pharma Industries, GXL: Georgia Institute of Technology and VITO

2.3.1.4 Hybrids and other techniques

Hybrid separation techniques are increasingly being explored. Most of them are based on the philosophy of improving the efficiency of conventional separation techniques by incorporating the strengths of novel techniques. For example, distillation can be combined with novel separation technologies such as membrane distillation or pervaporation to yield an energy efficient process. Membrane solvent extraction (MSE) is another example of a hybrid system, where, the solute is selectively extracted through a separating polymeric membrane from a feed solvent phase to extracting liquid phase where the solute has less solubility than in the feed phase.

Extractive distillation combines the advantages of extraction and distillation. The principle is explained like this: the effectiveness of distillation of a mixture of 1 and 2 depends on the relative volatility of the component 1 with respect to the component 2. When the relative volatility becomes close to unity, the separation of 1 from 2 becomes extremely difficult. In extractive distillation, a suitable extractant is added to the mixture (of 1 and 2) so that the new molecule changes the relative volatility in favour of 1. This means 1 can be collected at the top of the distillation column easily. One novel variant of this technique is the use of ionic liquids (IL) as an extractant. In the distillation of the ethanol-water azeotrope addition of IL improves the relative volatility of ethanol thereby its separation at the top becomes energy efficient. Some of the active players in IL are: DuPont, BASF, Merck and Ohio State University. This technology is very new and is not proven beyond the lab scales.

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[4] See chapter 4, section on the cellulosic ethanol process

Dephlegmation is a partial condenser with one vapour output and one liquid output. Dephelgmation unit is normally placed intermediate between hydrophobic pervaporation and hydrophilic pervaporation membrane system to get a purity of 99 % ethanol with separation of 35 % to 85 % obtained in the Dephelgmation unit. Dephlegmation is a promising technique for separation of ethanol from water but one of the major drawbacks is its low recovery. Some of the players are Membrane Technology and research [3], Air products and chemical Inc, Chart Ind. Etc.

Use of Hydrogels is a novel separation technique that can be used to concentrate solutes, separate water or separate solids such as lignin. Hydrogels swell to about 30 times its dry weight in water at 25°C and its volume collapses by a factor of approximately 10 from 25 to 35 °C. Temperature sensitive hydrogels made out of Poly (hydrogel *N-isopropylacrylamide*) is one example in this category. Some of the active players are Auburn University and University of Minnesota.

The conventional technologies that are widely practiced in the bioseparations areas include, ordinary distillation, aseotropic distillation using entrainer, multiple effect evaporation, extractive distillation, liquid-liquid extraction-fermentation hybrid, Zeolites molecular sieve adsorption and Nanofiltration. A good review of these technologies is given by Huang et al., 2008 [4].

Appendix D gives a summary of different techniques, their maturity levels and with specific remarks.

2.3.2 Solids-liquid separation with reduced water consumption

Two aspects that deal with the two stages of solid-liquid separations are considered here. They are techniques that accelerate the aggregation of solid particles in the system and techniques that efficiently remove the aggregates from the liquid.

2.3.2.1 Techniques for aggregation

The conventional way of accelerating the aggregation is to use a centrifuge. Usage of externally added agents like, thickeners, coagulants/flocculants is another way to step up the aggregation. Second way of achieving the same is to make use of the inherent nature of the solid, like, the charge / zeta potential. An example of this strategy is used in electro-dewatering. The technique uses electro-osmosis energy to concentrate the sludge. The technology is commercialized for pulp and paper industries and for wastewater treatments (Electrotech Technologies), but not for the bioprocessing industry Osmotic dehydration is another technique that comes close to its electro-counterpart and is widely used for the partial removal of water from plant tissues by immersion in a hypertonic (osmotic) solution. The technology developed for food industry but yet to be proven in biofuels manufacturing.

Sedimentation is a common solid liquid separation technique used in the industry. It has several limitations like higher residence time, requirement of a significant density difference etc. Bokela Inc. has developed a sedimentor for washing suspended solids. The sedimentor is novel in the manner that combined benefits of displacement and dilution washing is used and this reduces water demand significantly.

Once the material is reasonably aggregated, several separation strategies are employed to achieve the final removal of the solids. Some of them are listed below

2.3.2.2 Techniques for Separations

2.3.2.2.1 Microfiltration

Microfiltration is a low-pressure (10-100 psig) process for separating larger size solutes from aqueous solutions by means of a semi-permeable membrane. The applications of microfiltration are in wastewater treatment plants and in wine filtration. This is one technique that has the potential to be used in the fermentation broth clarification (removal of suspended solids and liquid). Some of active players are Koch membranes and applied membrane Inc.

VSEP is a technique developed by NEWLOGIC, which reduces the fouling by adding shear to the membrane surface through torsional vibrations; as a result, this increase in the shear eliminates the stagnant boundary layer that exists with the more traditional membrane systems. This is a promising dewatering technique for biomass slurries. This technique is also demonstrated for ethanol production process. Some of the vendors are: New logic, Dunhill group, Lund University, Membraflow and GTI.

2.3.2.2.2 Rotary vacuum filtration

Rotary vacuum filtration is a conventional technology widely used for solid liquid separations. One of the drawbacks of this process is its high-energy consumption. Several vendors available in the market are Metso, FL Smidth, Dorr Oliver and Alstom.

Simulated moving bed is a method in process chromatography that enables substance mixtures to be continuously separated and extracted in two fractions. Some of the challenges are scalability and solvent specificity. The technology is already commercialized in pharmaceuticals, food industry, biochemistry and petrochemical (xylene/toluene separations). Flow Spek proves technology for this chromatography-based technique. Pervaporation, Hydrogel, Membrane Solvent Extraction and Dephlegmation techniques are already covered under FA#1. So, they are not discussed in this section.

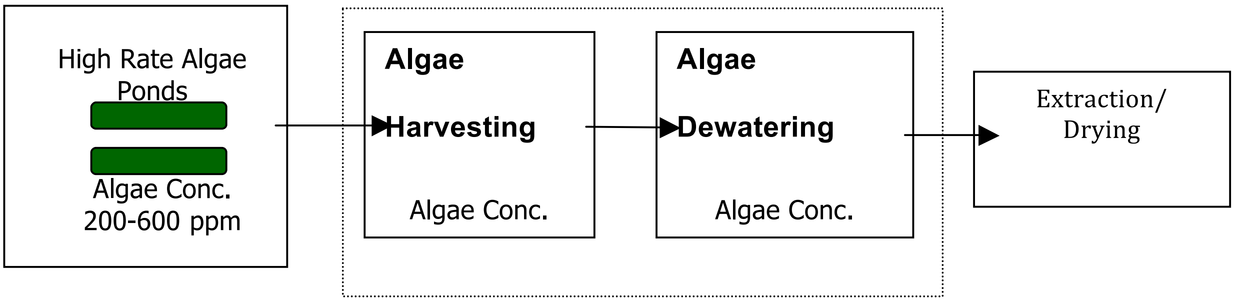
As mentioned before, hybrid techniques are possible to effectively capitalise the strengths of conventional and novel technologies. Several hybrid combinations of more than one technique are also possible such as rotary vacuum filtration coupled with membrane process, rotary vacuum filter coupled with membrane and solvent extraction process.

Some commonly employed systems are Screw-press (Huber), filtration system (Bokela), Resin systems (ProMetic), Electro-filtration (Elcotech) and Centrifugal Systems (Milieu-Nomics). Several technologies under development are sophisticated nanotechnology systems, Centrifugal adsorption technology and Ultrasound based technologies.

Appendix E gives a summary of different techniques for these focus area, their maturity levels and with specific remarks.

2.3.3 Solid – liquid separation - Algae

2.3.3.1 Harvesting



The term an alga harvesting refers to the concentration of a fairly diluted (200 ppm to 600 ppm) algae suspension until a slurry or paste containing 1% to 10% TSS or more is obtained. Sometimes a dewatering step is needed to further concentrate the algae to 10 to 25% or more. Harvesting and dewatering of algae requires one or more solid-liquid separation steps.

Recovery of algal-biomass is a challenge because of the smaller size (3–30 μm diameter) of the algal cells, their negatively charged surfaces and in some cases their mobility form stable suspension. Dilute culture broths (<1000 ppm) necessitate the need of a suitable harvesting method that must be able to process large volumes of algal streams. The selection criteria for a suitable harvesting method include acceptable level of water in the product, type of algae species and end use of the final product. Low-cost filtration techniques are presently applicable only for harvesting fairly large microalgae. Small microalgae should be flocculated into larger bodies that can be harvested by flotation, filtration or gravitational sedimentation techniques. Addition of chemicals/alkali to algal culture in order to induce flocculation is a routine procedure in wastewater treatment industry. We have focused on several novel flocculation techniques at D1-D3 stages of development: Several flocculation-based techniques used for the harvesting of the algae from ponds are discussed below:

2.3.3.1.1 Ultrasound Flocculation

The low intensity ultrasound improves coagulating effect and dewatering ability of the algae biomass [5]. There are several vendors that provide ultrasound technologies like Hielscher Ultrasonics GmbH, Advance Sonics Processing Systems and Sonix®. It has been demonstrated that use of ultrasound along with addition of flocculants can reduce requirement of flocculants and also enhance dewatering ability of the algal-biomass.

2.3.3.1.2 Bioflocculation

Addition of bioflocculants (chitosan, sodium alginate, xanthan gum etc.) or microorganisms capable of producing it can achieve flocculation of algae. Bioflocculation is a naturally occurring phenomenon in activated sludge wastewater treatment but yet to be developed for algae system.

2.3.3.1.3 Autoflocculation

Autoflocculation (spontaneous flocculation) in algal cultures is associated with increase of culture pH levels, due to CO_2 consumption by the algal photosynthetic activity, sunlight availability, nutrient limitation, extracellular polymer production, longer residence time etc. So, by controlling process conditions one can achieve flocculation and gravity settling of the flocs without adding any harsh chemicals and recovering them. NREL has already demonstrated this technique (mentioned as bioflocculation in the report) for their ‘Biodiesel from Algae’ report [6]. The autoflocculation technique is the potential technique for the harvesting of the algae.

2.3.3.1.4 Electroflocculation

Flocculation and coagulation is also achieved by passage of a mild electric current through algae water. Several issues associated with electroflocculation are poor life of electrodes and clogging and flogging of them. There are several suppliers for this technology like Electropure Australia, TreaTec21, and University of Tsukuha City. This technique is demonstrated for wastewater treatment plants.

Appendix F gives comparison of these flocculation techniques based on several parameters like potential for scalability, capex, opex, etc.

2.3.3.2 Dewatering

The recovery of the flocculated microalgae from water is achieved by either flotation or gravity sedimentation. The choice of sedimentation or flotation methods depends on the density difference between the algae cell and the growth medium. For oil-filled micro algae with small density, flotation technologies should be preferred. Several flotation technologies are given in the literature.

2.3.3.2.1 Flotation

2.3.3.2.1.1 Dissolved air flotation

Dissolved air flotation is a widely adopted technology in solid-liquid separations with vendors available in the market like DAF Environmental, DAF Corporation, AJM Envornmental Services Pty Ltd. In DAF, the bubbles generated when the pressure of the air-saturated feed is reduced are very small (0 - 100 µm). While such bubbles are very effective in collecting flocs and small particles, they also have correspondingly small terminal velocities, leading to relatively large equipment sizes.

2.3.3.2.1.2 Induced-air flotation

Induced-air flotation overcomes this difficulty and is widely used for the removal of fine particulates from industrial wastewaters. Induced air flotation does not require any blower/compressor thus reducing energy consumption of the process. A faster rise velocity is achieved meaning smaller footprints and lower capital costs. There exist many suppliers, which provide IAF technologies like Armatec Environmental Ltd, Xstrata Technology, OJF Technology Pty Ltd, University of Canterbury, and University of Newcastle.

Use of surfactants enhances flotation by creating a chemically active film around air bubbles, which strongly attaches to the flocculated solids algae cells to the bubble achieving high rate and efficient flotation. All these flotation techniques are developed for wastewater treatment processes, which also involve removal of algae from water. Several other flotation techniques like cavitation air flotation (provided by Filtration Solutions Pty Ltd and HydroCal Inc USA mainly for food industry and paint and tannery industry) and centrifugal air flotation (provided by Clean WaterTech). CleanWaterTech, USA has also developed a hybrid centrifugal flotation dissolved air flotation system termed the Gas Energy Mixing (GEM) system. It incorporates all advantages of the centrifugal flotation and dissolved air flotation. With over 20 patents in the field of flotation and flocculation, the company is the leader of the flotation and flocculation systems through its GEM System.

Appendix G gives comparison of these flotation techniques based on several parameters like potential for scalability, capex, opex, etc.

2.3.3.2.2 Centrifugation

Centrifugation is one of the widely practiced dewatering techniques for further concentration of harvested algae slurry. There are many commercially available prototypes for concentration of algae. ‘US centrifuge’ has supplied centrifuge for harvesting of algae to “Live Fuels Inc., USA). Centrifuges are less promising and energy intensive for harvesting step, as it requires handling of large quantities of dilute algae-water suspension. One can explore use of centrifuge for the removal of the algal slurry. To separate small sized microalgae centrifuges need to be operated at higher rpm thus, increasing energy demand.

There are several other dewatering techniques available in other industries like extruder based dewatering systems like Contipress®, Ultrafine coal dewqatering extruder. There are several other novel filtration based dewatering techniques like Masko zoll and VSEP. VSEP is a novel membrane separation technology developed by New Logic Research Inc. USA, which has many applications in chemical industry, wastewater treatment, pulp and paper industry etc.

2.3.4 Algae Cell Lysis

Algae cell disruption is needed to release the contents of the cell (intracellular lipids) into the surrounding medium, which can be then extracted for further conversion. The selection of the methods may depend on criteria such as susceptibility of cells to disruption (type of algae strain), product stability (degradation/denaturation), ease of extraction from the cell debris, speed of method, cost of method etc. The non-lipids fraction (proteins, phospholipids, nucleic acids, carbohydrates) of the algae cells which typically could be 30%-80% of the dry cell weight can be used as animal/fish meal or for some other applications. So, recovery of these non-lipid matters and use of it for various applications can also affect economics of the process [7]. Some cell disruption techniques have been commercialized in other industries like food, pharmaceutical and for sludge disintegration in wastewater treatment.

2.3.4.1 Mechanical Cell Disruption

2.3.4.1.1 Homogenizers

High-pressure homogenizers are typically used in food, biotechnology and pharmaceutical industries. There are many vendors, which provide lab scale to pilot scale homogenizers for e.g. Microfluidics Inc. [8], Thermo Scientific [9] (French Press), GEA Process Engineering Inc. [10], Alfa Laval [11] etc. Homogenizers operate at higher pressure so they are associated with higher energy consumption. Some algae which are difficult to break requires more passes through homogenizers leading to high energy consumption and degradation of the intracellular products due to increase in the temperature or due to shear.

2.3.4.1.2 Shear centrifuge

Lysatec GmbH [12], Germany provides mechanical shear centrifuge techniques for wastewater sludge disintegration. They have done comparative studies of various method used for WW sludge disintegration in terms of energy consumption and observed that shear centrifuge is associated with lower energy consumption but the cell disruption achieved is only 40% (figure 4.1).

Figure 4.1: Comparison of energy consumption of various techniques for waste water sludge disintegration rate

2.3.4.1.3 Ultrasonic

Several algae companies such as Origin oil Inc. [13] and Petrosun Inc. [14] have patented ultrasonic cell disruption techniques for algal lysis. Origin Oil Inc. uses a hybrid technology combining advantage of microwave and ultrasound both. Algae cells are first subjected to microwave to weaken cell walls and then ultrasound to completely break algae cells. Ultrasonic technology is also used for sludge disintegration in WWTP, food and pharmaceutical industry. One of the issues here is the possibility of denaturation/degradation of intracellular products as the results of the ultrasound. There are several other vendors like Hielscher Ultrasonics GmbH [15], Elbe AUE™ [16] Advance Sonics Processing Systems [17], and Eimco's sonolyzer™ [18], Prosonix [19]. The main barrier to the successful commercialization is its high energy consumption and scale up. The typical power consumption estimated by Hielscher Ultrasonics GmbH is given in table 4.1.

Table 4.1: Typical power consumption for sonication

Flow Rate (m^3/hr)	Power (kW)
10	100
100	1000

2.3.4.1.4 Electromechanic

Center for Electromechanics at University of Texas in collaboration with Organic fuel Inc. has developed electromagnetic (EM) [20] cell disruption technique for algae. Cell disruption is achieved due to elongation and breaking of the cell membranes in the direction of electric field. Though, this technology is not fully developed yet it seems to be more promising as it does not require any addition of chemicals and has a smaller hardware footprint.

2.3.4.1.5 Pulsed Electric Field

Pulsed Electric field (PEF) is similar to EM, which has applications in sterilization in industrial processes. In PEF processing, a pulsed high voltage electric field (30-50 kv/cm) is applied and this enlarges the pores of the cell membranes (electroporation) releasing intracellular products. Diversified Technologies [21] provides PEF technology for sterilization in food.

2.3.4.2 Non-mechanical Cell Disruption

2.3.4.2.1 CO2 super critical fluid

CO_2 based cell disruption techniques include super critical CO_2 cell disruption and CO_2 based "CELLRUPTOR" technology. Super critical conditions help to create cell disruption. This technology is practiced in food and pharmaceutical industry but scalability of the process at large scale is still an issue due to requirement of high-pressure reactors and energy needed to create super critical conditions. Supercritical Fluid Technologies Inc. provide SCF technology for different sectors [22]. Global Green solutions Inc. [23] is planning to use SCF technology for algae lipid extraction.

Ecosolids Inc. [24] has developed a CO2 based "Cellruptor" technology for WWTP. This technique may not be applicable to Algae lysis as it involves pH of 12-13 and temperature in the range of 60C to 80C at high pressure. These harsh conditions may lead to the degradation of the intracellular products.

2.3.4.3 Lytic enzymes or virus

Enzymes such as cellulase or glycoproteinase, structured enzyme arrays or a viral agent can be used to digest cell wall, weaken it and make algae cells permeable to release intracellular products. This is a very gentle process of lysing cells, but the cost of enzymes/virus could be an important factor for consideration. This technology can be coupled with some other technology to make the cell lyses more efficient for e.g. enzymes can be used to weaken the cell walls first and then some other technique like ultrasound can be used to finally break the cells releasing intracellular products Hielscher Inc. [15]. A techno economic evaluation is required to see the feasibility of such a hybrid system.

2.3.4.3.1 Chemical

Chemicals (alkyl pyridinium salts, boron compounds, bleaches, high pH buffers) are the basic ingredients of most commercially available algicides. When cell lysis occurs these ‘cocktails’ containing different and optimized systems facilitates as extractants to the cell contents. There could be some potential for IP if we can identify the cocktail specific for our algal strain but due to cost, recycle and non-selectivity of the chemical reaction this route does not look promising.

2.3.4.3.2 Surfactants

Surfactants can be used for algae cell lysis but this process has several drawbacks such as cost and recovery of surfactants, formation of emulsion of surfactants with lipids and other cellular products etc. Hence this route is not promising for algae lysis.

2.3.4.3.3 Aqueous biphasic systems ABS

Aqueous biphasic systems (ABS) or aqueous two-phase systems are clean alternatives for traditional organic-water solvent extraction systems. This technique is typically used in enzyme separations and chemical downstream processing but not demonstrated for algae cell lysis.

Combination of more than one technique for efficient cell lysis is worth looking at as it can strike a balance between the CAPEX/OPEX issues with improvement in the cell lysis. Some examples for hybrid techniques are Microwave assisted ultrasound extraction [13], HFPR®TM Technology (Combined effect of centrifugal force, compression, and shear leading to microcavitation), combined electric field and ultrasound therapy [25], Ultrasound assisted supercritical fluid extraction [26], and Ultrasound assisted enzymatic extraction [15]

Appendix H gives comparison of various techniques in terms of their scale up potential.

3. Challenges for BioSeparations

***NOTE** THE MAJORITY OF THIS MATERIAL WAS PRODUCED BY PROF DAN SHANTZ OF TAMU IN RESPONSE TO AN INITIATIVE FROM THE NATIONAL SCIENCE FOUNDATION and by Tom Binder of ADM in a series of emails*

CHALLENGES FOR THERMO-CATLYTIC DERIVED BIOFUELS

Synopsis

An NSF sponsored workshop was held April 4 – 5 2011 to review the current status of biofuel production from thermo-catalytic processes and to identify key separations challenges that hinder increased production of biofuels. Approximately 20 scientists from academia, industry, national laboratories and federal funding agencies were in attendance. The attendees agreed that separations play a critical role in biofuel production and that fundamental research, including the identification of transformative approaches, is needed to generate separation technologies that will enable larger-scale production. What follows is a concise summary of the specific separations challenges that currently exist in thermo-catalytic biofuels production and an associated set of recommendations for fundamental research themes required to meet them.

Challenges

The workshop attendees organized the separations challenges within these four stages of thermo-catalytic biofuel production.

- Feedstock treatment prior to conversion
- The conversion unit
- Product clean up and conditioning
- Product upgrading and fuel synthesis

Interestingly, some of the key challenges represent general separations problems that would enable biofuels production while others are truly unique to this field.

Feedstock treatment prior to conversion

Two major challenges were identified at this stage. The first was developing means to increase both the ‘energy density’ and ‘bulk density’ of the raw biomass prior to transporting it to the conversion unit. The second was to remove undesired water and inorganic contaminants (e.g. salts, metals) prior to thermal or catalytic conversion. These two challenges may be linked; for example, low energy, preferably non-thermal routes to water removal are relevant to both. The removal of trace inorganic impurities prior to conversion is a challenge not unique to biomass (e.g. coal).

Biomass conversion unit

The workshop identified several challenges that will require true transformative technologies. These include

- The ability to generate high-purity low cost oxygen at small scale that could be co-fed to high temperature reactors to, for instance, inhibit tar formation
- The ability to remove impurities including water, CO, CO_2, nitrogen-containing compounds, sulfur compounds, and acids at the elevated temperatures (500 °C and above) currently used in thermal and catalytic conversion of biomass (e.g. pyrolysis)
- A renewable low-cost source of hydrogen
- The ability to separate ranges of oxygenates in the vapor phase at the operating conditions of current high temperature biomass conversion units

The first two points would benefit many industrial sectors but would dramatically improve the efficiency of subsequent downstream processing. The third point is actually a grand societal challenge that would impact many fields. The fourth point is a problem unique to biofuels processing.

Reactor product clean up and conversion

Ideally separations of converted biomass could be performed at the elevated temperatures used in current conversion schemes. In the absence of that, the ability to perform separations in the condensed phase would also be desirable. Three major needs, all unique to biofuel production were identified in the area of low (below 200 °C) temperature/condensed phase processing of bio-oils.

- Understanding the chemical changes that take place in bio oils upon condensation
- Improved mixture material property prediction
- The ability to separate oxygenates at reduced temperatures more effectively

Product upgrading and fuel synthesis

This point, while important, was deemed to be beyond the scope of this report, as the major needs are all of a chemical transformation nature; i.e. catalysis, not separations, is the critical need.

Recommendations

Efficient and scalable solutions, in terms of materials and processes, do not currently exist for most of the challenges listed above. Many of them represent highly interdisciplinary problems, in that basic science in the area of thermodynamics and fluid mechanics is necessary in order to design the successful separation. Several basic research themes were identified to address the specific separations challenges outlined above. These research themes include:

- The basic chemistry of oxygenated compounds and its impact on reactivity/transport / equilibrium fluid structure
- The interactions between oxygenated compounds and interfaces (e.g. emulsions, oxygenate-solid interactions)
- Molecular-level modeling of oxygenated compounds
- High-quality experimental thermodynamic and transport data of oxygenates
- Robust and scalable multi-functional materials or hybrid materials to achieve separations. These materials will need to be both thermally and chemically robust.
- Integrated reaction/separation schemes
- Separations of components from highly dilute mixtures, containing chemically similar (and dilute) species
- Non-thermal water separations
- Design schemes for three-phase separations

COUPLED BIIREACTIOUNS AND SEPARATIONS. THE WAY NATURE DOES IT

Nature has for the most part explored much more elegant processes for the separations it has needed to carry out. As an example, movement of triglycerides from the intestine to the blood stream is done by several steps to ensure that the flow is only in one direction. Tri glycerides will not pass directly from the intestine thru the cell membranes to the blood stream and this also means that triglycerides in the blood will not leak back out to the intestine and be lost. Nature has designed catalysts (enzymes) in the intestine that converts triglycerides to monoglycerides and fatty acids. The cells lining the intestine have special carriers (affinity adsorbents) that bind with monoglycerides and fatty acids allowing them to enter these cells. Inside these cells triglycerides are resynthesized and then transported

again by special carriers into the blood stream. This allows for unidirectional flow of the oil into our system. For the most part nature has designed all of its pathways for conversion and separations by coupling specific chemical reactions with affinity separations.
If we were to consider acetic acid would it be possible to set up an extraction system coupled with an acetic fermentation at pH 6 using hexanol which would extract a small portion of the acetic acid with an esterification reaction with the hexanol in the organic phase to produce the acetate ester of hexanol. Using a selective membrane and a very hydrophobic solvent like hexane transporting the ester to a hydrogenation zone to convert the ester to ethanol and decanol which is recycled. Is this a better lower energy intensive process than we would currently use in industry. It would allow coupling of low concentration fermentations with a conversion process to drive the equilibriums. Nature has been very elegant at these types of couplings of reactions with separations, we have not for the most part because energy has been cheap enough the brute force has normally won.

Here are the links to three articles touching on the needs for future separations especially the need to develop less energy intensive processes than distillation and crystallization. The problem with the low energy processes is that they are at present not as selective as distillation with many theoretical plates. Developing these other processes along with affinity supports, selective reactions and fine tuning solvent properties have large potentials. As indicated earlier, we have the basic methods of separation listed in the white paper but do not describe the need for research to do them in much more elegant manners. The first link is a good review of our needs.
http://www1.eere.energy.gov/manufacturing/industries_technologies/imf/pdfs/separationsreport.pdf
http://onlinelibrary.wiley.com/doi/10.1002/9783527628698.hgc045/abstract
http://www.ncbi.nlm.nih.gov/pubmed/20565064

4. Examples of Separation challenges of Bio-domain projects

In this section, we summarise study recommendations of four specific separation challenges of biodomain projects. They are ethanol water separation, removal of acetic acid from pre-treated stream, reduction of ash content of biomass and novel water treatment techniques for the recovery of algae oil. The basis of initiating such studies was initiated by series of engagement sessions with biodomain projects. The summary of the engagement sessions and detailed reports of each of the cases are given in Appendix H-L

4.1 Alternative techniques for ethanol-water separation

Conventionally recovery of ethanol from fermentation broth is done by a combination of distillation and molecular sieve units. Here, we explored alternate energy efficient options for recovering fuel grade ethanol. The selection of a suitable option is arrived at based on two criteria viz. lower energy requirement and maturity of the process for commercialisation. Based on these criteria membrane pervaporation systems are found to offer promise because of its energy efficiency. Stand-alone membrane systems will have the risks of membrane fouling and frequent maintenance because the upfront unit has to handle a large volume of the fermentation broth with high solids content. Hence, hybrid line-ups involving distillation as a primary unit followed by a membrane unit are evaluated in this report. Based on this analysis, the following line-up is found to have promising energy efficiency

- The traditional distillation as the first step (in a single column) producing ca 90 wt% ethanol.
- The vapour distillate from distillation unit is being fed to a pervaporation unit to produce anhydrous ethanol (above 99.5 wt %).

Recommendation: To go for a CAPEX and reliability analysis of membrane units from different vendors such as Mitsui, Vaperma and Sulzer

4.2 Removal of Acetic acid inhibitant from biomass hydrolysate

Acetic acid, a fermentation inhibiting molecule, is formed during the pre-treatment of lignocellulosic materials. Removal of this molecule becomes very critical when high solid concentrations are handled during pretreatment and enzymatic hydrolysis. There are many techniques reported such as electro dialysis, emulsion liquid membrane, Microbial Fuel Cell, inhibitor metabolizing microbes, non-sterile fermentation and in-situ conversion to others products to reduce the inhibition level but most of them are still in the exploratory stage.

Here, we arrived at a promising scheme which comprises of a flash column that makes use of the energy available with pretreated stream (high pressure and temperature) to flash off the acetic acid/furfural along with aqueous phase. The cellulose fibers along with lignin will be removed from the bottom of the vessel. The condensed aqueous phase will be feed to an ion exchange column or extraction unit or a membrane unit to recover acetic acid and furfural. Depending on the end use, further purification of the acetic acid or furfural can be carried out

4.3 Ash reduction from biomass

Washing methods are simple techniques for reducing K, Na and Chlorides from crushed biomass. The machinery and scaling up issues are well established. Washing/leaching of the biomass is a better method for the removal of alkali metal compounds from a nutrient recycling point of view. For energy crops containing high amount (ca. 70wt %) of initial moisture content, washing and drying steps impart relatively smaller additional energy load.

The main disadvantages of washing process are its water consumption and cost of drying. This holds especially true for feedstock such as wheat and rice straw, agricultural wastes available with relatively low moisture contents (< 10 wt %). In such cases, washing will increase the moisture content to higher levels (> 75 wt %) and "re-drying" is not a right strategy from an energy efficiency point of view. Leaching is known to reduce Na, K and Cl, but not other metal compounds. This means we need to know what all elements and in what quantities need to be removed before proceeding to the densification process.
Avenues for integrating of washing and drying steps in the post-harvest operations (until the energy densification step) are to be looked at.

If the preferred choice of energy densification is torrefaction, it makes sense to adopt technologies such as torwash, which couples washings with the rest of the process. The maturity of the process and scale up issues are largely unknown.
On the other hand, if the preferred densification process is pyrolysis, then washing is an option to consider.
It is important to note that the techniques reported in the literature are mainly for wheat and rice straw. The suitability of these processes (especially washing) for palm oil residue (empty fruit bunch and fronds) needs to be found out.

5. Conclusions and Way forward

The separation landscaping study for biofuel applications was done with following four focus areas. They are:

- Recovery of organics from large volume of water (hereafter referred as FA # 1)
- Solid/liquid separation & Solids Handling (hereafter referred as FA # 2)
- Minimized use of water for transport, heat-transfer and solvency (hereafter referred as FA # 3)
- Lipid removal from within cell structures (hereafter referred as FA # 4)

Based on the study, it is found that

- Many of the bio-separation technologies are mainly developed for pharmaceutical, food, and water treatment and mining industry.
- The maturity levels for separation techniques for biofuel applications are mainly at D1, D2 levels
- Hybrid systems involving membrane based techniques (such as pervaporation) and traditional techniques (distillation) offer good promise in the removal of organics from water, particularly, in the case of ethanol separation from the dilute fermentation broth
- Autoflocculation needs to be looked at closely as a potential algae harvesting technique
- Supercritical systems hold out a lot of promise but high OPEX could be an obstacle in the commercialization of the process at higher scale.
- VSEP technology is a promising dewatering technique that could be applied for treating biomass slurries. The technique uses a membrane, but the chances of fouling is overcome by adding shear to the membrane surface through torsional vibrations.

The main results are tabulated as given below:

Technology	**FA#1**	**FA#2**	**FA#3**	**FA#4**	**Industry status**	
					Biodomain	Other
Membrane Distillation	x					D4 (food, beverage)
ED w/ Ionic Liquid	x		x		D1	D1 (gas-gas separation)
Supercritical extraction	x		x	x	D1	D4 (food, pharma, WWT)
Resin (polymeric) adsorption	x					D4 (water treatment, pharmal)
Salt bed solvent extraction	x			x	D1 (ethanol-water)	D3 (water purification)
Simulated Moving Bed Chromotography						D4 (pharma, food, petrochemical)
Hydrogels		x		x		
VSEP					D4 (ethanol-water)	
Electroosmotic Dewatering		x				D2 (mining)
Osmotic dehydration		x				D4 (food)
Electrodialysis	x					D4 (organic acid synthesis in food industry)
Ultrasonic Flocculation		x			D1	
Bio Flocculation						D4 (waste water

						treatment)
Auto Flocculation						D2 (waste water treatment)
Electro Flocculation					D1	
Induced Air Flotation		x			D1	D4 (waste water treatment, mining)
Suspended Air Flotation					D1	D4 (waste water treatment, mining
Dissolved Air Flotation					D1	D1 (waste water treatment)
Perevaporation	x		x		D4 (ethanol water)	D4
Membrane solvent extraction	x		x		D1	D4
Dephlegmation	x		x		D2	
Electromechanic Disruption				x	D1	
Pulsed Electric Field				x	D1	D4 (food, WWT)
Ultrasonics		x		x	D1	D4 (food industry)
Shear centrifuge				x		D4 (WWT)
Enzyme, Surfactant, Chemical assisted Extraction				x	D1	
Homogenizer				x		D4 (food, pharma)

Many of the bio-separation technologies are mainly developed for pharmaceutical, food, and water treatment and mining industry. This means the maturity levels in the area of biofuel production is still in the early phases. The difference lies in the scale of operation and in the cost-value proposition of biofuel industry. This gives challenges to the biofuel industry, while adopting these technologies.

One thing that is important to note here that many of these novel separation technologies are system (molecule) specific and also vary in terms of separation efficiencies. On the one hand this reflects that there is no single solution to all separation challenges, but on the other hand gives an opportunity for designing hybrid technologies for separations. Hybrid technologies are combination of the different novel technologies with and without the conventional techniques of separations.

The replacement of MSU with a membrane unit is still a short-term improvement in the ethanol-water separation. Long-term solution to this challenge can be achieved by developing ideas that offer better energy efficiency to the entire ethanol-water separation process (including solids separation). Co-development of processes with companies such as MTR (pervaporation and dephlegmation technology) or TransIonics (extraction based technology) could be one way to achieve this.

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Appendix A. Preliminary template for documenting the results of the literature search

Chromatographic Separation of Hydrolysis Acids and Sugars

ARKENOL

Technology[1]

An integrated, full-scale commercial process plant consists of five basic unit operations:

1. Feedstock preparation;
2. Decrystallization/Hydrolysis Reaction Vessel;
3. Solids/Liquid Filtration;
4. ***Separation of the acid and sugars using Chromatography***
5. Fermentation of the sugars; and,
6. Product purification.

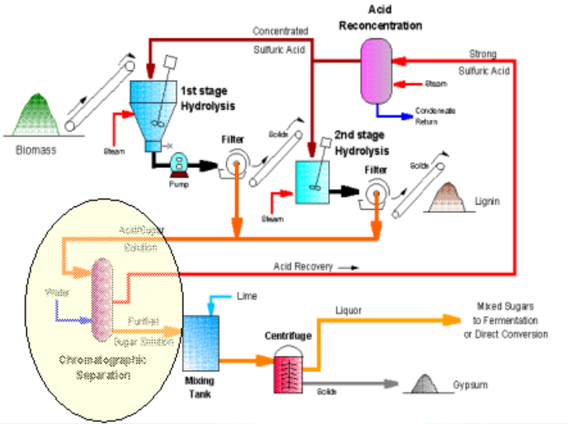
Founded: 1992 as an affiliate of **ARK** Energy Location: Mission Viejo, CA

Technology: patented Private

Process scale: pilot plant

Special alliances: JGC, licensed technology to BlueFire Ethanol

Vendors supplying te4chnology ?????



Source 1- Company Website

Chromatographic Separation of Hydrolysis Acids and Sugars

Patents[2]

Patent #5,820,687 (1998) *Method of separating acids and sugars using ion resin separation*

- **Abstract** A economically viable method for producing sugars using concentrated acid hydrolysis of biomass containing cellulose and hemicellulose is disclosed. The cellulose and hemicellulose in the biomass is first decrystallized and then hydrolyzed to produce a hydrolysate containing both sugars and acid. Silica present in the biomass can then be removed for further processing. The remaining solids are then subjected to a second decrystallization and hydrolyzation to optimize the sugar yields. An improved method for separating the sugars from the acid in the hydrolysate is also disclosed. The resulting sugar stream can then be fermented, using an improved method which allows both hexose and pentose sugars to be fermented simultaneously.
- Inventors:
- **Farone; William A.** (Irvine, CA)**, Cuzens; John E.** (Santa Ana, CA)
- Assignee:
- **Arkenol, Inc.** (Las Vegas, NV)

- Appl. No.:
- **08/664,184**Filed:
- **June 13, 1996**

Source 1: Company Website 2: US Patent and Trademark Office

Appendix B. Interview Notes

B.1 General Questions

Question 1: Which is the most promising Bioseparation technique that has the potential to replace distillation/molecular sieve combination, thereby reducing energy consumption in concentrating cellulosic ethanol (from 5% to 95%)?

Answer- According to the expert, the membrane technology has the potential to replace existing techniques. Although the membrane technology is not completely developed and may take a few years to develop, still it is the most promising technology to go beyond distillation (which is energy intensive) and the molecular sieve technology.

His recommendation: According to the Expert, Vaperma - a Canadian company focused on membrane products for biofuels sector, has a highly promising Bioseparation technology. He attended one of Vaperma's recent seminars and was impressed with its membrane offerings (thermoplastic membranes).

Regardless of the source of the Ethanol production, which could be cellulosic or from sugars, the mixture is always in the form of an azeotrope—comprising 96% ethanol and 4% water. Vaperma's membrane technology is a promising technology for this kind of separation—azeotropic membrane separation.

Question 1a: Can membranes be used to cater to bulk of volumes?

Answer- Yes

His recommendation: Vaperma has the technology that can be used on bulk scale. It has a prototype in Canada which is not yet proven but has a lot of potential.

Question 1b: Apart from membranes, what are the other known techniques?

Answer: Azeotropic distillation, molecular sieve, and double distillation (existing technologies)

Comments: Prior to Azeotropic distillation and molecular sieve, people used hydrocarbon or cyclohexane/benzene to do double distillation. This technique is successful; however, it consumes a considerable amount of energy and can only be used in petroleum refineries, which capitalize on their crude.

Which companies/technologies in your view are best poised to solve BioSeparation problems?

Answer - Following are the key players**:**
Delta-T (US based)
Vaperma
Lurgi/Air liquide (New owner of Lurgi – very strong in membranes)

Question 2a: Are you aware of any other biotech industry engaged in Bioseparation?

Answer: Pharmaceuticals industry

Comments: The pharmaceuticals industry has been using membranes for a long time and it is more sensitive toward using membranes. One of the problems faced by this industry is that there is a costly need for prefiltration prior to membrane receiving solid, liquid or colloidal fluids. Most of the membrane failure in this industry were not due to the membrane per se, but because the materials were not processed adequately before reaching the surface of the membrane. He mentioned that a stronger sense of pretreatment is necessary for the successful use of membranes. A company should spend extra money in pretreatment processes to protect the membrane surface.

Question 2b: Please mention some membrane manufacturers for the pharmaceutical sector.

Answer: Following are the key players:
General Electric
PALL
Sartorius
Insight: Japanese manufacturers are trying to capture the membrane market but they have not been successful. US players are leading the market followed by Europeans.

Question 3: Which universities/research groups in your view are active or have a proven track record in finding economic solutions for Bioseparation issues?

Answer: Following are the prominent universities (historically):
University of California, Los Angeles (UCLA)
MIT
Dartmouth
Texas A&M has contributed a lot in membranes for separating water from oil (the expert finds their technologies very effective).

Research groups:
Department of Energy – National Renewable Energy Laboratory (DOE-NREL)
He feels that the research group at Vaperma is the first one to do a good job in this area (membranes).

Question 4: Are there separation techniques in other industries, such as paper or mining industry, which can be employed in Biodomain?

Answer: Semiconductor industry

Comments: The pulp and paper industry has never been using membrane technology but the semiconductor industry uses it to separate water from solids/dissolved solids (going right up to reverse osmosis techniques). They also have some technologies to separate acids. More information about other membrane companies can be obtained from SEMI (which is a semiconductor industry trade association) website. The website also provides contacts to membrane providers.

Pharmaceutical companies have a reluctance to change technology because of stringent regulations and quality control (as they have to revalidate their plants). However, the semiconductor industry is willing to try new membranes (data trials or demonstration trials); whereas the pharma does not, because the process/plant has to be reauthorized from the government, which is a long and painful process.

Question 5: Are there other improvements (such as process/feedstock improvements) that could be done to reduce the complexity & cost of Bioseparation?

Answer: Yes, by installing biodigestors to produce methane (recycling of waste streams)

Comments: Most chemical company or process companies are trying to find out ways to convert their waste material to save energy that will come under biodigestors or bioreactors. The cost of Bioseperation can be reduced, if there is a way to recirculate the waste stream to make gas, such as methane.

Question 6: In terms of process changes, do you have some thing to add?

Answer: By using computer control process systems and prefiltration prior to using membranes

Comments: The most important process changes are the introduction of PLC and computer driven control systems having sensors to detect pressure changes. Now we have input and out put points linked to the PLC or **computer control process systems, which can help improve performance.**

Prefiltration is very important and effective in reducing costs but is often ignored in the design of the plant or the fittings of the plant.

Question 7: Are there any advanced/emerging washing equipment (as used in solvent extraction) which have the potential to drastically reduce water consumption?

Answer: The best way to do that is to use supercritical extraction.

Comments: This technology takes a hydrocarbon solvent material (CO_2/butane etc.), heats it, and uses it as a separation media. The solvent is taken at a very high temperature and pressure and forced through the material to be separated. This technology is very effectively used for the extraction of oils from seeds in biodiesel industry but the set up or plant should be able to handle high pressures and temperatures. This technology is not common as it needs pumps which can generate very high-pressure.

Crown iron works, a biodiesel company uses this technology for extracting oils from rapeseed, sunflower, and canola.

Question 8: Are there any new economic techniques to deal with separation of azeotropic mixtures?

Answer: Nothing beyond the standard and established techniques

The double distillation, **Pressure Swing Adsorption** (**PSA**), zeolites (molecular sieves), and membranes are all being used.

Standard molecular sieves from Delta-T/ICM

Question 8a: Are u aware of any commercialization attempts with membrane and zeolites (w.r.t Azeotropic separation)?

Answer: Yes, This can be seen in petroleum refining where membranes are used to separate oil and water.

Question 8b: What would be the ideal technique for azeotropic separation?

Answer: Membranes offer a promising method for azeotropic separation.

Comments: From an engineering point of view, if one can not take any risks, the standard molecular sieves from Delta-T/ICM would be recommended. If a modern plant is needed with a willingness to absorb some risk (not 100% guaranteed), then membrane technology would be preferred. I would recommend Vaperma and their membrane for Bioseparation.

Question 9: What are your views on the advancements in technologies such as ultrafiltration, nanofiltration, and microfiltration?

Answer: Reverse osmosis is the finest separation known today because the separation is of an ionic level. Ultrafiltration, nanofiltration, and microfiltration are the three areas where most of the research is being conducted. The **cellulose acetate technology** in reverse osmosis is now replaced by **nylon type** technology. So, primarily, we have **polyether sulphone membrane** and **Teflon membrane** as the latest developments for water separation.

Question 10: What are the challenges in employing ultrafiltration, nanofiltration and microfiltration to Bioseparation involving colloidal systems?

Answer: The biggest problem we face with these three techniques (ultrafiltration, nanofiltration, and microfiltration) is while dealing with molecules above the atomic sizes but below the size of 1 micron. Around the 0.1 micron sizes, the separation is actually a liquid-liquid separation.

For example, to separate two acids (ionic liquids) the membranes with **the right pore size** have to be selected and also be **compatible with the chemistry** of the liquids. Following are some of the key challenges with membranes used in ultrafiltration, nanofiltration, and microfiltration:
Adaptability of the membrane with the chemistry of acids
Operability at high temperature, for example, ceramic membranes
Energy/pressure considerations – to push the fluids through the membranes
Viscosity of the liquid that is to be separated which needs energy consumption for their movement through the column.

B.2 Solid-Liquid Separation

Question 11: What are the most promising emerging Bioseparation techniques for Solid-liquid separation?

Answer- For solid-liquid separation, centrifuges is the established technology. Beyond the centrifuges, there are hydro cyclones, especially the emerging 'high G force hydro cyclones', where the solid stream is separated (or concentrated) from the liquid stream.

Membrane separation - When it comes to solids above the size of 0.1 microns, we can also use microfiltration (dead-end filtration), where we put the liquid solid through the membranes and then the membrane is backwashed.

Backwash Filtration: Use of a media for separating solid and liquid is suggested with computer assistance to sense the pressure increase across the surface of the membrane. Then to remove the solids, reverse the flow and push a clean fluid in a direction opposite the flow of the solid. Finally, there is a valve actuation or a valve system that disposes the solid in a disposal stream. The backwash filtration is also an effective method for solid-liquid separation.

Question 11a: Are u aware of electro osmotic dewatering? Do you think that is a promising technique for solid-liquid separation?

Answer: Electrodialysis/Electrophoresis is a process of separation done by using electrical charges. These are mostly used in biopharma and physical laboratory works and not at manufacturing and production scales.

Question 11b: Are you aware of Vibration Shear Enhanced Process (VSEP)?

Answer: Kreido uses a shear field technology to rupture cells or break down the cellular structure using microwave technology or ultrasonics. There are biodiesel technologies using both microwaves and ultrasonics technology.

Question 11c: Do you think these technologies are promising while dealing with the large-scale Bioseparation?

Answer: Microwaves or ultrasonics are unproven technologies. These technologies do not have large commercial applications. The problem faced by both ultrasonics and the use of microwave energies is the need of electrical inputs which is at times very costly. In laboratory works, we can afford the energy to support that kind of separation work but it’s not possible to scale it up to a pilot scale with this kind of electrical demands.

Question 11d: What is the potential of Ultrasonic dehydration in Bioseparation?

Answer: At commercial scales, the cost of the electricity for ultrasonic techniques is too high.

Question 11e: What is your view on the hybrid processes for solid-liquid separation? Which process do you think is most interesting and is a potential breakthrough?

Answer: If we can engineer a plant, which uses a normal filtration system with a low energy cost followed by a more developed technology, it can be really effective. In other words, if we can have 90% of the separation done using a normal molecular sieve, then the final purity can be enhanced by using new technologies.
Algal Harvesting

Question 12: What are the most promising emerging Bioseparation techniques in this domain?

Answer: Supercritical CO_2 extraction

Comments: The use of a supercritical solvent for algal cell extraction is the most promising technology so far. The current technology to separate the algae uses an expeller to provide a physical or mechanical separation. In the last few years, using a supercritical solvent has emerged as a way forward to separate lipids. This technique enables us to separate lipids/oils from membranes, proteins, carbohydrates, and wax materials. This technology is very cost effective since we may use waste CO_2 from a power plant (or any other waste source) to grow the algae and as a solvent in the extraction. Further, it can be scaled up to cater to the biofuel/biodiesel industry.

Kreido has a rupturing device that pushes algal cells through a spinning tube-in-tube with a sieve, such that the membrane is broken up and the contents, such as proteins and the lipids, are separated up from the structures of the membrane cell.

Question 12b: How would you rate supercritical extraction with the flocculation technique presently being used for this purpose?

Answer: Supercritical extraction for algae is not a proven technology and there are no commercial plants using this technology. This technology has been proven in laboratory and small scale plants but not at a large volume plants for making biodiesel form algae. Algal cell flocculation is a proven technology.

There were no particular comments on the different types of flocculation—electro-flocculation, auto-flocculation, and bio-flocculation, etc.

Question 12c: Other than the supercritical CO_2 extraction, do you think there is any other technology which holds the key to future?

Answer: Carrying out supercritical extraction at reduced pressure and temperature

Comments: A recent development in the supercritical extraction of lipids by CO_2 revealed that we do not need to take the CO_2 to a supercritical state for the purposes of extraction. It was found that high temperature and high pressure CO2 (below the supercritical state) could still dissolve the lipids. The CO2 could be removed by vacuum distillation. However, how much CO2 was being generated was not quantified, since CO2 was not being recovered.

The challenge in these processes is to completely recover $CO_{2.}$ It is very important to find a low cost way to recover CO_2 because the discharge of CO_2 to the atmosphere is regulated and it will not be possible to vent the CO2 to the atmosphere in the future.

Question 13a: What is your view of the hybrid processes as applied to algal cell separation? Which process do you think are most interesting and potential breakthroughs?

Any conventional technology, such as flocculation, followed by more exotic/unproven technologies to get the desired purities. In fact, most of the processes being used presently are hybrid processes including several steps.

He did not know about the Dephlegmation technology.

B.3 Algal Cell Extraction

Question 14: What are the most promising emerging Bioseparation techniques for algal cell extraction?

Answer: One of the most advanced techniques is the Spinning Tube-in-Tube STT^{TM} process used by Solazyme.

Comments: Algal cells are grown in a ratio of 1 cell for 1000 parts of water. The cost of separation of the alga from the water is the biggest bottleneck. Conventionally, a screen is used to collect the algal cells from the water and add the algal cells into a stream of solvent (hydrocarbon or a salt water system to rupture the cells). The biggest problem is the high volume of water relative to the volume of the cells.

Solazyme is a company, which has come up with a really good solution. Solazyme has modified algae to grow in the dark in fermentation tanks (anaerobically), sustained by sugar, rather than photosynthetically (in the open). Therefore, they have highly concentrated algal cell system and don’t have the problem of separating high volume of water from algal cells as encountered with photosynthetically raised algae.

A big problem with photosynthesis is that one needs a lot of surface area.

Question 14a: Can you name the most active companies engaged in algal cell extraction?

Answer: Solazyme and Kreido are the two companies using advanced algal cell extraction technologies. Kreido has a reactor that can be used to separate cells, and rupture the algal cells to recover lipids.

Question 14b: Do you have an idea about the following (i) Electro mechanical cell disruption (ii) Pulsed electric fields (iii) ultrasonic disruption (iv) enzyme/surfactant assisted extraction (v) CO_2 – based supercritical extraction for algae cell extraction?

Answer- All of the above are laboratory techniques and are unproven at the commercial scale. Currently, there are no algae separation technologies, which are proven on full commercial scale. Most of the algae companies have been able to extract in 20L-100L, but not a million liters or 10 million liters.

Question 14c: Which technique do you think is close to commercialization?

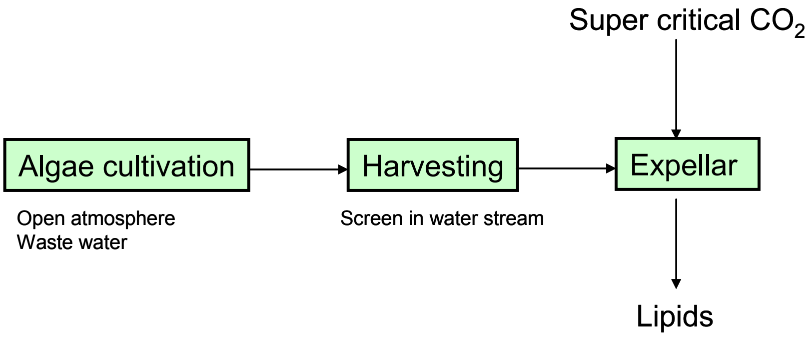
Answer: The only technique close to commercialization is supercritical CO_2 extraction.

Comments – The Expert mentioned that his choice of an algae extraction process/plant would be as follows:

A way to grow the algae on high volumes without a lot of water
Rupture the cells in an expeller and extraction of lipids with supercritical CO2 solvent

The ideal situation for algae growth is low quality water with a lot of nutrients (from waste water), and a lot of sunshine. Hence, the design would entail an open system (open to atmosphere) with circulating water, screens to separate the algae from water (to get a concentrated algal system), then use expeller to rupture the cell wall and followed by supercritical solvent extraction to extract lipids. The waste material could also be processed to separate proteins.

General design for a prototype alga extraction system



B.4 Minimized use of water for solvency, heat-transfer and transport

Question 15: What are the most promising ways to achieve minimized use of water?

Answer: There are two ways to reduce/minimize use of solvents.
Standard design using heat exchanger and jacketed reactors (or steam).

Heat transfer material called Paratherm. I have also designed plants where the boiler are fired on natural gas and the heat transfer is not done by water or steam, but by an oil that has a high heat constant and carries a lot of heat energy relative to steam.

Question 15a: Can you comment upon usage of Hydrogels?

Answer: Yes, they are based on the above principles. They can be used to exothermically pull heat from a reactor or use a boiler system to provide the heat.

Recovery of acids from dilute solutions

Question 16: What is the most promising way for recovery of organic acids?

Answer: Acid resistant membranes like PVDF or pure PTFE type membrane are quite promising. Gore-Tex PTFE membranes can be used to separate organic acids like acetic & formic acid.

Question 16a: How would compare membranes separation with supercritical fluids? Do u think membrane separation is better?

Answer: Membranes are better in certain conditions

Comments- The problem with using supercritical with acids is that most of the acids can be aggressive on the metals. When the temperature in increased, the likelihood of acid being very aggressive on the metals increases. Further, using exotic alloys would be very costly.

Hence, using a plastic or thermoplastic material (azure membrane or ceramic membrane) is a better option. Materials like PTFE or PVDF can be designed to (in a thermoplastic range) cater to separation of acids. We have used this for Hydrofluoric acid and hydrochloric acid and some other organic acids.

Question 16b: How about using gas expanded liquids?

Use of Ionic liquids is another emerging area. Michael Gonzalez at EPA is working on ionic liquids and would be the right person to contact for ionic liquids separation and recovery.

B.5 Concluding remarks

Most of these new technologies work well in the laboratory. However, the pilot tests often prove that while the technology is good at smaller scale, building a large scale commercial plant is often very costly. Hence, Engineers are reluctant to experiment with these new technologies, unless there is a governmental/organizational push.

Appendix C. Bioseparation Landscaping Study Results Summary

Technology	**FA#1**	**FA#2**	**FA#3**	**FA#4**	**Industry status**	
					Biodomain	Other
Membrane Distillation	x					D4 (food, beverage)
ED w/ Ionic Liquid	x		x		D1	D1 (gas-gas separation)
Supercritical extraction	x		x	x	D1	D4 (food, pharma, WWT)
Resin (polymeric) adsorption	x					D4 (water treatment, pharmaceautical)
Salt bed solvent extraction	x			x	D1 (ethanol-water separation)	D3 (water purification)
Simulated Moving Bed Chromotography						D4 (pharma, food, petrochemical)
Hydrogels		x		x		
VSEP					D4 (ethanol-water separation)	
Electroosmotic Dewatering		x				D2 (mining)
Osmotic dehydration		x				D4 (food)
Electrodialysis	x					D4 (organic acid synthesis in food industry)
Ultrasonic Flocculation		x			D1	
Bio Flocculation						D4 (waste water treatment)
Auto Flocculation						D2 (waste water treatment)
Electro Flocculation					D1	
Induced Air Flotation		x			D1	D4 (waste water treatment, mining)
Suspended Air Flotation					D1	D4 (waste water treatment, mining
Dissolved Air Flotation					D1	D1 (waste water treatment)
Perevaporation	x		x		D4 (ethanol water separation)	D4
Membrane solvent extraction	x		x		D1	D4
Dephlegmation	x		x		D2	
Electromechanic Disruption				x	D1	
Pulsed Electric Field				x	D1	D4 (food, WWT)
Ultrasonics		x		x	D1	D4 (food industry)
Shear centrifuge				x		D4 (WWT)
Enzyme, Surfactant, Chemical assisted Extraction				x	D1	
Homogenizer				x		D4 (food, pharma)

Appendix D: Summary of techniques for FA#1 (separation of organics from water)

Name of the technique	**Mechanism**	**Scale of Development**	**Remarks**
Resin separation	Use of adsorbent resins for selective separation	D3-D4	Widely using waste water and pharma industry
Pervaporation	Selective permeation through membrane	D2-D4	Potential technique for ethanol/water
Membrane distillation	Membrane separation depending upon difference in vapour pressures	D3	Higher CAPEX
Membrane solvent extraction	Selective extraction through membrane with use of solvents	D1-D3	Solvent recycling
Hydrogel	T sensitive hydrogels swells 30 time in water	D2	Gel lifetime and regeneration
Dephlegmation	Partial condensation to get two phases V and L	D2	Thermodynamically more efficient
Supercritical extraction	Use of supercritical solvents (CO2) for extraction	D1	High pressure requirement, practised in food and pharma
Salt bed	L-L separation by use of salts as adsorbents	D1	Early stage of development
Extractive distillation (Ionic liquids)	Extractive distillation with use of ionic liquids as solvents	D1	ILs are expensive and limited supply
Electro-dialysis	Main actions- Electro acidification, on the anionic side, and electro-alkalinization, on the cationic side	D1 (D2 in biotechnology)	Effective in separation of organic acids produced by fermentation
Hybrid technologies	Combination of two (or more) processes that offer complimenting synergies	D3	Additional CAPEX and OPEX, could be better than individual technique in performance
Conventional techniques	(azeotropic/extractive) distillation, extraction, nano filtration, mol. sieves	D4	Already in use, but needs improvement for better economics

Appendix D. Summary of techniques for FA#2 (Solids-liquid separation with reduced water consumption

Name of the technique	Mechanism	Scale of Development	Remarks
Conventional	e.g. Thickners, sieves, coagulants, flocculants, centrifugal decanters	D4	Already in use, but needs improvement for better economics
Sedimentation	Use of gravity for settling of solids	D4	Widely used
Microfiltration	low pressure (10-100 psig) process for separating larger size solutes from aqueous solutions by membranes	D4	Used in WW and beverage ind, life of membrane?
Rot. Vaccum Filter	Use of vacuum for transport of liquid across filter	D4	High throughput but energy intensive
Hybrid technologies	Combination of two (or more) processes that offer complimenting synergies	D3	Additional CAPEX and OPEX, could be better than individual technique in performance
VSEP	Reduction in fouling by adding shear to the membrane surface through torsional vibration	D3-D4	Potential method for prevention of clogging/fouling
Osmotic Dehydration	partial removal of water from plant tissues by immersion in a osmotic solution	D3-D4	Energy efficient and deployed in food, pulp & paper industry
Electro-Dewatering	lectro-osmosis and mechanical energy to remove water from the sludge	D2-D3	High energy consumption and commercialized for pulp and paper and water industry
Hydrogel	Main actions- Electro acidification, on the anionic side, and electro-alkalinization, on the cationic side	D2-D3	Effective in separation of organic acids produced by fermentation
Moving Bed Chromatography	Process chromatography that enables substance mixtures to be continuously separated and extracted in two fractions	D2	Used in pharma, food and biochem applications, scalibility?

Appendix E. Comparison of flocculation based techniques for harvesting of algae

+++ - High, ++ Medium, + Low

Flocculation based Harvesting Techniques for Algae

Name of the Technique	Space requirement	External aids	Status of development	CAPEX (Relative order of magnitude)	OPEX (Relative order of magnitude)	Residence time	Scalability	Remarks
Ultrasonic flocculation	+	+, Not required. (Only Sonication required)	Bench	++	++	+	+	Major issue is technology development
Bioflocculation	+	+ (only micro-organisms/bioflocculants)	Pilot	+	++	++	++	Unfamiliarity with industrial use of microorganisms or products directly derived from them
Autoflocculation	++	Not required (Only adjustment of culture media/conditions is done to achieve autoflocculation with sep. eff. > 90%)	Pilot	+	+	+++ (<24 hr settling time)	+++	Residence time requirement can be high and is dependent on type of algae
Electroflocculation	+	+, Not Required (Only electrodes and electricity is required)	Pilot	++	+ , (0.3 kWh/m3)	+	+	Shorter life of electrodes and Chlorine generation in salt waters could pose problems.

Appendix F. Comparison of flotation based techniques for harvesting of algae

+++ - High, ++ Medium, + Low

Flotation based Harvesting Techniques for Algae

Name of the Technique	Space requirement	External aids	Status of development	CAPEX (Relative order of magnitude)	OPEX (Relative order of magnitude)	Residence time	Scalability	Remarks
Induced air Flotation/Jet Flotation	++	++ (flocculant)	Semicommercial	++	++	++	+++	Can handle green Algae/blue green Algae, microalgae, Requires flocculant
Suspended Air Flotation	+	+ (flocculant), + (Surfactant) (Can be flocculant free)	Pilot	+	+	++	++	Toxicology and contamination of water due to surfactants
Dissolved Air Flotation	+++	+++ (flocculants)	Semicommercial	+++	+++(Blowers or commpressors are required)	+++	+++	Highly energy intensive though can remove most types of algae

Appendix G. Appendix H:Comparison of various cell lysis techniques for algae

Name of the technique	**Mechanism**	**Scale of Development**	**Scale up Potential**	**Remarks**
Electromagnetic cell disruption	Electric field induced elongation of cells	D2	Medium	Demonstrated for Algae
Pulsed Electric Field (PEF) Cell Disruption	High electric field pulses for cell lysis	D1	Medium	Poor life of electrode and Temperature rise
CO2 based Cell Disruption Techniques	Supercritical CO2 as a solvent for algae cells	D2	Medium	Higher CAPEX
Mechanical Shear Centrifuge	Mechanical shear force in centrifuge	D2	Medium	Poor cell lysis (~40%) reported for WWTP sludge
Surfactant for Algal Oil Recovery	Surfactants for cell lysis	D1	Low	Not demonstrated for algae
Lytic Enzymes/Virus	Lytic enzymes induced disruption of cells	D1	Medium	It has to be coupled with other lysis technique
Homogenizers	Compression and sudden de-compression burst cells	D3	High	High power requirement and heat generation
Ultrasonic Cell Disruption	Cell lysis by sonic cavitation	D2	Medium	Protein damage, genration of heat and free radicals
Chemical Algal Oil Recovery (cAOR)	several chemicals induce cell death and lysis	D1	Low	Degradation of intracellular products, cost and recovery of chemicals
Aqueous Biphasic Systems (ABS)	Use of polymer & chaotropes/kosmotropes for extraction of proteins	D1 (D4 in biotechnology)	Medium	Cost and recovery of chemicals and unexplored for algae oil recovery

Appendix H. Specific separation challenges of typical biodomain projects

H.1 Cellulosic Ethanol Projects

Main challenge in the project is that the ethanol broth is very dilute (ca. 5%) and the conventional distillation is not energy efficient. The project is open to ideas that are energy efficient, at the same time, with good maturity levels in order to substitute the conventional distillation techniques for the ethanol recovery from water.
Second challenge is the solid-liquid separation. There are four solid-liquid separations in the process. They are

1) Adjusting the solid content before liquefaction
2) Separation of lignin and un-reacted cellulose before fermentation
3) Removal of yeast (after fermentation) for recycling
4) Final separation of the solids from the bottom of the distillation (water treatment)

The challenge is to accelerate the settling of the solids and then the removal of the same in an energy efficient manner.

H.2 Sugar to Hydrocarbons Projects

The process envisages the separation of organic molecules from water. This is important from a molecule recovery of point of view and from the wastewater treatment point of view. Separation of acetone from water is one example. Sugar concentration (feedstock) is another challenge and options are being looked at currently. Another separation challenge in the project is the separation of large quantities of CO_2 (ca. 80%) from the off gas steam (containing H_2 and lights). Separation of CO_2 is important here, as it improves the quality of H_2 that needs to be recycled in the process.

H.3 Pre-treatment Projects

Solid handling challenges are very similar to what is described in section 4.1. Additionally the project is looking at low water pre-treatment options. This means feed sugar concentrations and thereby more concentration of certain bi-products that are harmful to the microorganisms. One such molecule is acetic acid, which is poisonous to the yeast above 1% in concentrations. So effective separations of acetic acids is important in this context (before the stream reaches the fermentor).
Second challenge in the pre-treatment is the corrosion on the units caused by chlorides present in the biomass feedstock. Removal of chlorides is an important challenge that needs to be addressed in an energy efficient way.

H.4 Algae projects

At the moment heat is used to disrupt the algae cells and the pressing or extrusion to remove water. Some experiments are done to use dimethyl ether (DME) as the extractant to for the algae oil. There is a potential challenge to look at from the separation point of view and that is the separation of proteins from the process water stream.

H.5 Biomass gasification project

The presence of alkali metals has a significant impact on the efficiency of the gasification process.

Appendix I. Alternative techniques for ethanol-water separation

I.1 Introduction

In the conventional fuel grade ethanol production, the ethanol-water separation is done in three or more stages. In the first stage, the beer mash (containing about 85 wt% water, 10 wt% ethanol and 5 wt% solids) is sent to a stripping column (distillation column) and the distillate is collected as ca 40 wt% ethanol. The bottom products are solids, water and minor quantities of ethanol. The first distillate, in the form of vapour, is then fed to a second distillation column (rectification column). The distillate of this unit is typically ca 90 wt% ethanol. This stream is then dried to anhydrous ethanol (purity more than 99.5 wt %) using a molecular sieve unit (MSU). Conventionally, crystalline zeolites are used to adsorb water and the dried ethanol is collected at the bottom.

The other promising separation techniques to consider are pervaporation, extraction, and dephlegmation. This report presents an overall comparison of these different processes and a specific evaluation of a hybrid line-up having distillation and pervaporation.

I.2 Evaluation

The evaluation of the processes is done based on the following two criteria

1. Energy requirement
2. Maturity of the process for commercialisation

I.2.1 Distillation and MSU line-up

The molecular sieve needs regeneration when it becomes saturated with water. The regeneration is done by passing a part of the product (anhydrous ethanol) through the zeolite bed. The ethanol, now diluted by the water present in the molecular sieves, is then mixed with the feed stream of the rectifier. This means that even in the case of MSU, it is the distillation that dries the ethanol. Therefore, MSU, while avoiding the more energy intensive azeotropic distillation conditions, still consumes considerable amount of energy.

I.2.2 Extraction based techniques

Trans Ionics has developed an extraction based ethanol separation system. Here, the stream from the fermentation tank (heated to a higher temperature) is extracted by a non-volatile solvent (such as vegetable oil). In one configuration, the stream is made in contact with the extractant by vaporising the feed and passing the vapour through a venturi nozzle, where the extractant serves as the working fluid. In the second configuration, the ethanol water stream is contacted with a non-porous membrane and the permeate (ethanol) is driven forward by a vacuum created by a venturi nozzle, with the extractant as the working fluid. The extracted ethanol extracted is then flashed off and the resulting ethanol solution (ca 95 %wt) is then dried by a molecular sieve unit.

Replacement of distillation unit by extraction unit is a good idea, but it is in the developing stage. Large energy savings of such a process is also not very obvious since the feed has to be vaporised and ethanol has to be again separated from the extractant. Moreover, the process has the energy disadvantage of having MSU as the drying unit.

I.2.3 Membrane based techniques

Membrane units have emerged as an alternative technology to replace different stages of the conventional line-up such as

i) a substitute for MSU
ii) a substitute for the rectification and MSU units and
iii) a stand-alone system

Some of the major players developing these membrane based technologies for ethanol separation are 1) Mitsui & Co., 2) Sulzer Chemtech-Kuhni, 3) Vaperma Inc., 4) Membrane Technology Research Inc. (MTR) and 5) Whitefox. A list of key players with more details is attached as an excel sheet in Appendix 1.

I.2.4 Pervaporation units in combination with Dephlegmator

MTR has developed a separation process consisting of pervaporation units and a Dephlegmator (US Patent 6755975). The stripping column in conventional line-up is replaced by a pervaporation unit (having hydrophobic membrane such as silicon rubber). The permeate will have ethanol concentration of 30-40 wt% ethanol. This permeate is sent to a Dephlegmator unit replacing the rectification unit. Dephlegmator is similar to a reflux condenser, equivalent to four to six theoretical stages of equilibrium operation. The permeate vapour enters the bottom of the dephlegmator. At the top, the vapour is partially condensed and the condensate trickles down in counter-current manner. The vapour enriched with 90-95 wt% ethanol is collected at the top. Further dehydration is done by a hydrophilic pervaporation unit.

MTR claims that these hybrid line-ups work efficiently at small-scale operations. For large scale operations, replacing stripper with membrane may be energetically attractive. But there are risks of fouling, maintenance and the need for large membrane surface due to the large volume and solid content of fermentation broth. Dephlegmation is also not a matured process. Considering these pitfalls, completely replacing distillation is not an attractive option, at least in the short term, for large-scale operations.

I.2.5 Replacing Rectification and MSU with Pervaporation units

A case study proposed by Vaperma to replace rectification unit with a pervaporation unit is considered here for evaluation.

The below process scheme with conventional distillation and MSU is considered as the base case by Vaperma. The feed rate for the stripping column is 184300 kg/h with 9 wt% ethanol. The ethanol concentration at the end of the stripping section is ca 42 %wt and at the end of the rectification section is ca 93 %wt. The distillate rate at the end of the stripping section is 38643 kg/h. The final product rate is 20833 l/h.

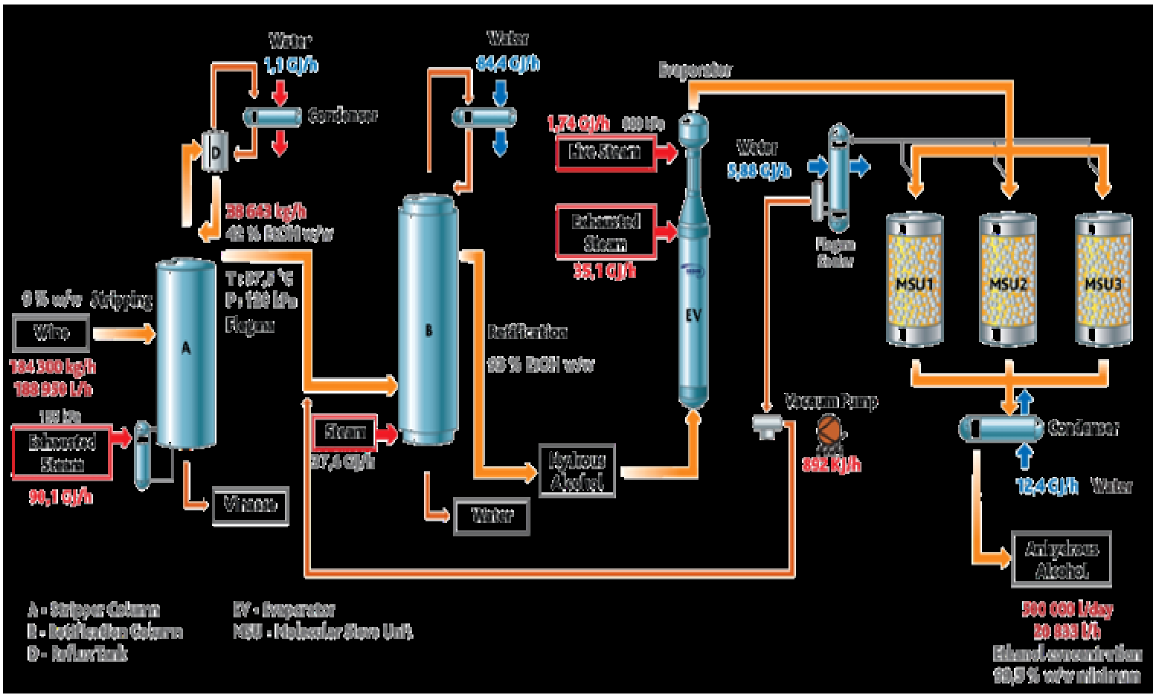


Fig. 1 Sugar Cane to Ethanol Process: Beer enters the stripper, A, then goes to a rectifier, B and then an evaporator C before it goes for final drying up in MSU units (source: Vaperma presentation).

In the above described line up, the steam requirement of ca 165.2 GJ/hr was calculated with the below split up for different units
Stripper - 90.1 GJ/h
Rectifier – 37.4 GJ/h
Evaporator – 36.84 GJ/h
Vacuum pump – 0.892 GJ/h

I.2.6 Vaperma’s alternative line-up with two membrane units

One of the alternative line-ups that Vaperma has put forward is to use two membrane units replacing the rectification section and a MSU unit producing the anhydrous ethanol from ca 40 wt% ethanol feed. Vaperma claims that this hybrid line up gives a net saving of ca. 70 GJ/hr steam.

I.2.7 Our simulation for Vaperma’s base case

We tried to simulate Vaperma’s base case ethanol plant. The distillation unit has separate stripping and rectification columns. First, the stripping column was simulated using Aspen and results are shown in Table 1.

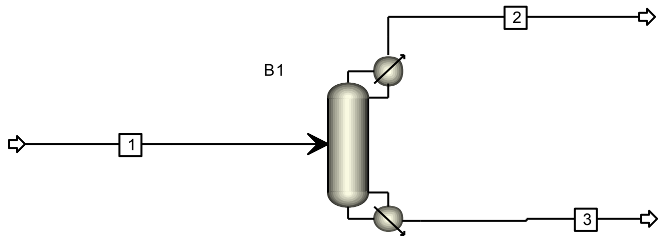


Table 1. Vaperma’s base case stripper simulation results

Feed T	Feed (kg/h)	Feed Conc	Reflux ratio	D rate (kg/h)	Stages	Feed stage	Condenser duty GJ/h	Reboiler duty GJ/h	Product ethanol wt%	Tray efficiency
75	184300	9%	0.013	38643	30	20	-1.10	**90.55**	**42.9**	75%

Table 1 shows that the reboiler duty and the product concentration are similar to that of Vaperma’s simulation results. In the Vaperma’s base case, the stripper was followed by a rectifier (with steam stripping). The liquid stream from the rectifier was passed through a vaporiser before feeding to a MSU unit.

The order of these operations raised the following questions:

1. Why is it necessary to have two separate distillation columns? Can’t stripping and rectification be combined in a single column?
2. Why is steam used in the rectification column when the stripper reboiler itself is sufficient to supply heat?
3. Why is it required to have an evaporator between the rectifier and the drying unit? What happens if the vapour distillate is taken from the rectification column directly to the MSU unit?

2.3.2.3 Our Proposed Alternative design for Distillation part

To answer these questions, we have simulated by combining stripping and rectification in a single column. The single column simulation results are given in Table 2.

Table 2. Stripper and rectifier combined column simulation results

Feed T °C	Feed (kg/h)	Feed Conc	Reflux ratio	D rate (kg/h)	Stages	Feed stage	Condenser duty GJ/h	Reboiler duty GJ/h	Product ethanol wt%	Tray efficiency
75	184300	9%	3.0	17835	30	20	-50.37	**92.95**	**93**	75%

From Table 2, it can be seen that the reboiler duty of the single column is very close to that of the stripping column of the Vaperma’s base case. At the same time, the concentration of the distillate achieved is as high as 93 %wt. Thus, a rectifier and stripper combined in a single column can save the energy and CAPEX of the first membrane unit of Vaperma’s hybrid line up. We also propose to take vapour distillate from this column to the final drying unit.

I.2.8 Vaperma's Final Drying line up

For further dehydration, the claims of Vaperma are convincing that using a membrane unit consumes lesser energy compared to an MSU unit. According to their calculation, the energy consumption of membrane system is about one tenth that of the MSU unit. It is also reported that the investments of pervaporation units and MSUs are similar. This means substitution of MSU with membrane is a valuable proposition.

As far as process maturity is considered, membranes are still in demonstration stage. But, the replacement of MSU alone with a membrane unit is a feasible and viable proposition. In such a configuration, the volume of feed handled by the membrane unit is only one tenth of the feed that enters the primary distillation unit, which reduces the scale up risk of the membrane unit.

I.3 Conclusion

Hybrid line-up involving distillation as a primary unit followed by a membrane unit is found to be an energy efficient option for producing fuel grade ethanol from dilute fermentation broth. The configuration is presented below

- Stripping and rectification combined in a single distillation column to produce ca 90 wt% ethanol from the fermentation broth feed
- The vapour distillate from the column is fed to a pervaporation unit instead of a MSU to produce anhydrous ethanol (above 99.5 wt %).

I.4 Recommendations:

The above proposition to combine stripper and rectification to a single column and replace MSU with a membrane unit offers promise for ethanol water separation. However, we recommend to do a CAPEX and reliability analysis for membrane units supplied by major vendors such as Mitsui, Vaperma and Sulzer.

The replacement of MSU with a membrane unit is still a short-term improvement in the ethanol-water separation. Long-term solution to this challenge can be achieved by developing ideas that offer better energy efficiency to the entire ethanol-water separation process (including solids separation). Co-development of processes with companies such as MTR (pervaporation and dephlegmation technology) or TransIonics (extraction based technology) could be one way to achieve this.

Attachment

ethanol_water_tech
nobgies_new.xls

Appendix J. Removal of Acetic acid inhibitant from biomass hydrolysate – A review and Recommendations

J.1 Introduction

The major challenge in cellulosic ethanol production is the product isolation since ethanol is formed at low concentration during the fermentation. One of the ways to overcome this problem is to have high sugar concentration in the fermenter. This can be achieved by having high cellulose concentration in the enzymatic hydrolysis step to produce high sugar concentration and Simultaneous Saccharification and Co-fermentation (SSCF) of the concentrated biomass feedstock. In SSCF enzyme and microbial inhibition by high sugar concentration is avoided by maintaining a threshold sugar concentration. It also helps to convert both C5 and C6 sugars into ethanol. Thus increasing the solid content of the feed biomass leads to better throughput and sugar concentration in the fermenter.

Conversion of lignocellulosic materials into digestible oligosaccharides is done by a pretreatment process. Pre-treatment process loosens the cellulose and hemi-cellulose from the lignin structure. Particularly during mild acid or hot water pre-treatment, the hemi-cellulose part of the biomass goes into the aqueous hydrolysate. During this process, many inhibitors such as lignin degradation products (phenolic compounds), hemi-cellulose degradation products (such as furfural and HMF) are formed. The acetyl group of hemicellulose is hydrolyzed into acetic acid. When the acetic acid concentration goes above 1 wt%, it becomes toxic to the subsequent enzymatic hydrolysis process and as well for sugar fermenting yeast. This is the case particularly when we use high solid concentration in pretreatment stream. The protonated form of acetic acid can pass through the cell membrane and destabilize the electro-neutrality of the cell and ultimately leading to cell lysis.

Thus removal of fermentation inhibitor molecules such as acetic acid, furfural and phenols is very important and also forms the subject of this report. Several techniques to remove acetic acid have been reported such as electro dialysis, emulsion liquid membrane, Microbial Fuel Cell, inhibitor metabolizing microbes, non-sterile fermentation (patent from Inbicon) and in-situ conversion but most of them are still in the exploratory stage. These techniques are briefly described in Appendix 1. This report describes an energetically promising scheme for removing the inhibitors from biomass stream which has undergone mild acid/steam explosion pretreatment.

J.2 Proposed scheme for acetic acid/furfural removal from biomass hydrolysate

First, the scheme for acetic acid/furfural removal is outlined with an Aspen model. Following that the literature information available on those specific techniques is briefly dscribed.

In this process, mild acid pre-treatment is carried out at high pressure (10-15 bar) and temperature (~200°C). We propose to make use of this energy, to flash off the inhibiting components like acetic acid and furfural in a flash drum. This flashed vapors containing acid, acetic acid and furfural can be condensed in a condenser. We propose the following options to further treat this condensate to recover the acetic acid and furfural:

1. Ion exchange resin column
2. Extraction unit
3. Membrane unit

Figure 1. shows the schematic of the proposed scheme.

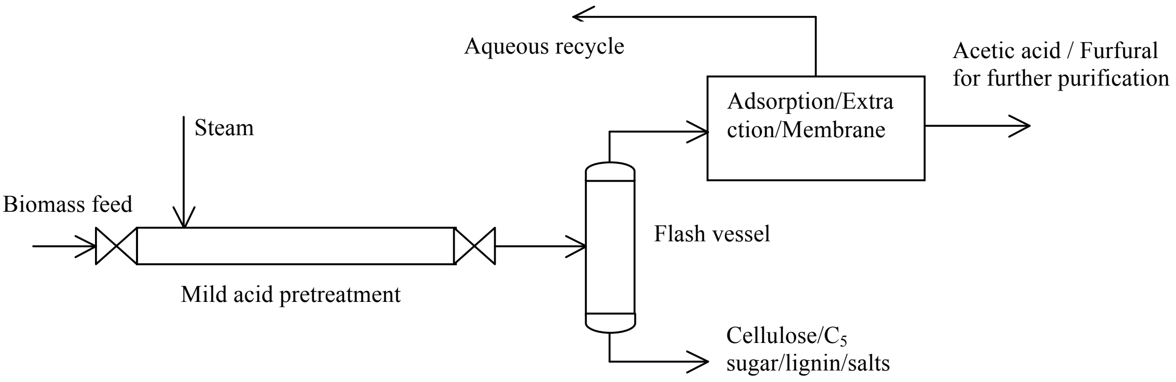


Figure 1. Proposed scheme for recovery of acetic acid/furfural from pretreated biomass hydrolysate

We have done an Aspen modeling to simulate the flash vessel condition. For the simulation, the feed biomass is considered to enter the flash vessel at 200°C and 15 bar pressure after the mild acid pretreatment. The feed and vapor composition of the flash vessel obtained from the simulation is shown in the below Table.

Table 1. Simulation results of flash drum with feed materials of 70% aqueous phase (water + sulphuric acid) and 30% solid phase.

Property	Feed 1	Top vapor stream 1	Bottom stream 1
Temperature K	473.15	374.1	374.1
Pressure atm	14.8	0.99	0.99
Water (kg/h)	57750	32514.3	19985.7
H2SO4 (kg/h)	583.3	0	583.3
Furfural (kg/h)	150	128.5	21.5
Xylose (kg/h)	5940	0	5940
Acetic acid (kg/h)	750	375.3	374.7
Cellulose (kg/h)	10000	0	10000
Hemicellulose (kg/h)	660	0	660
Lignin (kg/h)	7500	0	7500

From the above Table, it can be seen that almost 50% of the feed acetic acid and 85.7% of feed furfural goes to with top vapor stream. Further separation of these inhibitors from the vapor stream can be carried out by either adsorption or extraction or membrane techniques. Thus the inhibitor concentration in the bottom stream can be reduced significantly within a threshold limit. This simulation analysis forms the basis our proposal to have a flash vessel followed by adsorption/extraction/membrane units.

As an exploratory approach, to improve degree of the acetic acid separation, we introduced steam to the same above stream before entering the flash vessel and after pretreatment. For various amount of steam introduction, simulation was performed. The results are shown in the below table.

Table 2. Simulation results of flash drum with feed materials of 80% aqueous phase (water + sulphuric acid) and 20% solid phase.

Property	Feed 2	Top vapor stream 2	Bottom stream 2
Temperature K	473.1	374.3	374.3
Pressure atm	14.8	0.99	0.99
Water (kg/h)	94166.7	32514.3	19985.7
H2SO4 (kg/h)	583.3	0	583.3
Furfural (kg/h)	150	141.5	8.5
Xylose (kg/h)	5940	0	5940
Acetic acid (kg/h)	750	561	1
Cellulose (kg/h)	10000	0	10000
Hemicellulose (kg/h)	660	0	660
Lignin (kg/h)	7500	0	7500

Table 3. Simulation results of flash drum with feed materials of 90% aqueous phase (water + sulphuric acid) and 10% solid phase.

Property	Feed 3	Top vapor stream 3	Bottom stream 3
Temperature K	473.1	376.5	376.5
Pressure atm	14.8	0.99	0.99
Water (kg/h)	219166.7	211585.8	7580.9
H2SO4 (kg/h)	583.3	0	583.3
Furfural (kg/h)	150	147.9	2.1
Xylose (kg/h)	5940	0	5940
Acetic acid (kg/h)	750	713.7	36.3
Cellulose (kg/h)	10000	0	10000
Hemicellulose (kg/h)	660	0	660
Lignin (kg/h)	7500	0	7500

In all the above cases, we can observe that when steam is introduced before flash drum, degree of acetic acid and furfural separation increases. At the same time, the water quantity in the solid stream also goes down which is the desired condition for high solid content hydrolysis. But, the concentration of acetic acid and furfural in the top vapor stream decrease to a very low value. Then it may need energy intensive separation process for further purification of acetic acid/furfural from the above stream.

J.3 Examples of application of flashing specific to biomass pretreatment

The concept of flash drum is a well known technique to remove the volatiles making use of the pressure and temperature available with the stream. A process that is quite similar to steam stripping is reported in the patent US 6743928 [1] for the separation of furfural. In this case, the liquid stream is heated by introducing steam in the reactor and a particular pressure is maintained. Once the stream achieves the desired temperature, the reactor is gradually depressurized to remove the more volatile components.

SunOpta has filed a patent [2] for removing acetic acid from biomass hydrolysate. SunOpta is specialized in steam explosion pretreatment of lignocellulosic materials. The current patent claims that after the high temperature and pressure pretreatment, the feedstock is introduced to a cyclone separator operating under vacuum. The difference in the pressure removes the volatile inhibiting agents from the solids. Thus pretreated solids are subjected to enzymatic hydrolysis under vacuum. The following fermentation step is also carried out under vacuum.

These examples form the basis of our proposal to have a flash vessel after pretreatment.

J.4 Removal of inhibitors using adsorption (ion exchange) resins

Ion exchange is a robust and matured technique used in large scale water treatment plants. To remove acidic molecules like acetic acid from sugar hydrolysate, weak basic anionic resins are considered to be a promising candidate [3]. The adsorption mechanism is more like an ion pair formation as opposed to a pure ion exchange. This means that the adsorption capacity may not be as large as that achieved by a strong base resins. There are no reports about using strong base resins for removing acetic acid. Strong base resins are suspected to catalyze reactions of sugars. Hence, acetic acid removal over week base resins is considered to be a more robust separation method to reduce acidic molecules. Novozymes has filed a patent [4] which claims to use weak base anionic resins to remove inhibiting molecules especially acidic ones. Mancilha and Nazmul Karim [5] reported that almost 100% acetic acid could be removed from corn stover hydrolysate for xylitol fermentation using Purolite a 103 S resin.

J.4.1 Membranes

Ranil Wickramasinghe and Grzenia used a cellulose membrane with strong base anion ($R\text{-}CH2\text{-}N^+\text{-}(CH_3)_3$) as surface functional group to remove acetic acid from biomass hydrolysate [6]. They compared the performance of a weak base anionic resin with this membrane to remove acetic acid. They found that the acetic acid capacity of ion exchange membrane is more than that of the resin. Pervaporation technique is also being studied as the separation technique to concentrate dilute acetic acid solutions. Zeolite membranes are one class of membranes reported in the literature. While these techniques hold an advantage in terms of energy consumption, the lower maturity level, especially while handling large quantities of dilute streams is a clear disadvantage.

J.4.2 Solvent Extraction

For extraction of acetic acid from aqueous solution, ethyl acetate and MTBE are considered as potential extractants [7]. Further purification of acetic acid is done by a distillation unit. Tri-octyl phosphine oxide (TOPO) as a fatty acid carrier is also tested to increase the distribution coefficient of acetic acid [8]. Hong and Hong used tri-n-octylamine dissolved in n-octanol to selectively extract acetic acid from aqueous mixture of succinic and acetic acid at pH 5.1 [9]. Grzenia et al. reported a hollow fibre-based liquid extraction to remove acetic acid from lignocellulosic hydrolysate after pre-treatment with dilute sulphuric acid [10]. They observed a 50:50 mixture of Alamine 336, a tertiary amine, in octanol could take up to 60% of the acetic acid. Based on this knowledge, we recommend developing our own extraction scheme suitable for our application by conducting experiments.

J.4.3 Conclusions and Recommendations

Many of the separation techniques reported so far to remove acetic acid from biomass hydrolysate are in the exploratory stage. We propose a scheme to separate acetic acid/furfural from biomass hydrolysate. It comprises of a flash vessel which makes use of the energy available with the pretreated stream (high pressure and temperature) to flash off the acetic acid/furfural. The cellulose fibers along with lignin will be removed from the bottom of the flash drum. The condensed aqueous phase from top will be feed to a secondary purification step such as an ion exchange column or extraction unit or a membrane unit to recover acetic acid and furfural. Depending on the end use, further purification of acetic acid or furfural from secondary purification step can be carried out. Based on the open knowledge and preliminary Aspen simulation, we consider that the above proposed scheme can offer promise in terms of robustness, maturity and energy efficiency.

We also recommend having experimental support making use of Bioseparation team expertise for studying different ion exchange resins, extractants specific for process. This will help to come up with a suitable process for inhibitors recovery.

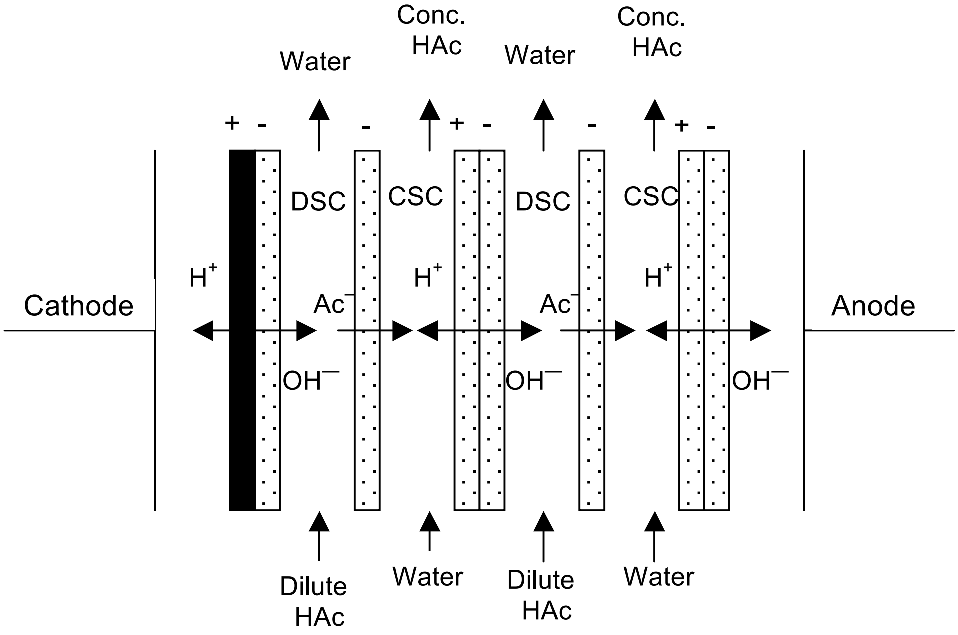
J.5 Literature Review on Different Technologies Reported for Acetic acid Removal

J.5.1 Over liming

Conventionally after mild acid pretreatment (with low solid content), over liming is done by adding lime to the hydrolysate to increase the pH to a value in the range of 9-11. Overliming the hydrolysate has been effective as a detoxification process due to partial removal of toxic inhibitors, such as furfural and 5-hydroxymethylfurfural, although the whole mechanism is not well understood. During overliming, sulphuric acid and acetic acid are removed from the initial hydrolysate by adding lime to adjust the pH and precipitation as gypsum. However, it was observed that the concentrations of acetic acid before and after the detoxifying treatment were not significant altered [11, 12, and 13]. They also report that overliming did change the acetic acid concentration significantly. Moreover, the potential drawback is sugar degradation due to hydroxide –catalyzed degradation reactions [14].

J.5.2 Electrodialysis

Electrodialysis is used to remove acetic acid from wastewater stream. Yu et al from Tsinghua University report a bipolar Electrodialysis (EDB) technique for the separation of dilute acetic acid [15, 16]. The principle of is depicted in the diagram below



Dilute acetic acid solution is introduced in the space between the anion-exchange side of the bipolar membrane and the anion-exchange membrane (Dilute Solution Chamber, DSC). When an electric field is introduced, acetate ions are transported to the space between the anion-exchange membrane and the cation-exchange side of the bipolar membrane (Concentrated Solution Chamber, CSC). In the CSC, the acetate ions combine with protons generated by the bipolar membrane to produce acetic acid. When the concentration of acetic acid reaches about ca. 30%, the concentration solution is withdrawn for further purification. Due to the cost of the instrument, large scale operation seems to be a major challenge [17].

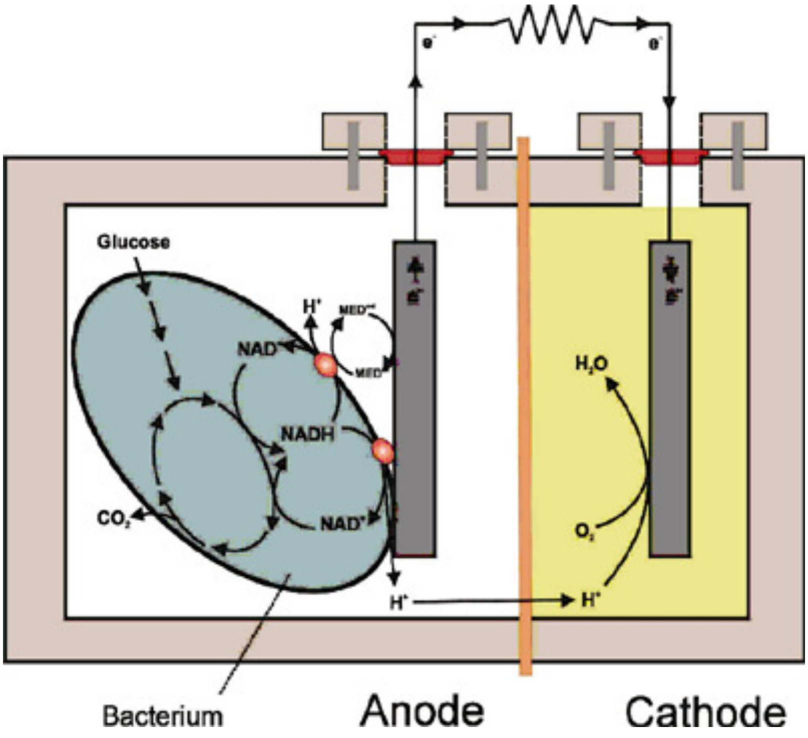
J.5.3 Emulsion Liquid Membranes (ELM)

In this case, water in oil emulsion in water (W/O/W) is created in an appropriate reactor, the water – oil interface being the membrane here. O'Brien and Senske reported the application of such systems for the removal of acetic acid and propionic acid from aqueous solutions [18]. The composition of the "membrane" is 96 % of middle distillate paraffinic solvent and 4% non-ionic surfactant. The emulsion was made by blending the oil + surfactant with an internal reagent (5 M NaOH or KOH). The feed is then added to the emulsion and a mixer speed of about 500 rpm was maintained.

J.5.4 Microbial fuel cell

Borole et al. investigated using a MFC to remove inhibitory products generated during the pretreatment of lignocellulosic materials [19]. A MFC consists of an anode, a cathode, a proton or cation exchange membrane and an electrical circuit.

The bacteria live in the anode and convert a substrate such as acetate and glucose into CO2, protons and electrons. Under aerobic conditions, bacteria use oxygen or nitrate as a final electron acceptor to produce water. However, in the anode of a MFC, no oxygen is present and bacteria need to switch from their natural electron acceptor to an insoluble acceptor, such as the MFC anode. Due to the ability of bacteria to transfer electrons to an insoluble electron acceptor, we can use a MFC to collect the electrons originating from the microbial metabolism. The electron transfer can occur either via membrane-associated components, soluble electron shuttles or nano-wires. The electrons then flow through an electrical circuit with a load or a resistor to the cathode.



The potential difference (Volt) between the anode and the cathode, together with the flow of electrons (Ampere) results in the generation of electrical power (Watt). The protons flow through the proton or cation exchange membrane to the cathode. At the cathode, an electron acceptor is chemically reduced. Ideally, oxygen is reduced to water.

J.5.5 Inhibitor metabolizing microbes

Schneider isolated a mutant Saccharomyces cerevisia which can grow on acetic acid but not on sugars [20]. This mutant yeast was used to remove acetic acid from hardwood-spent sulfite liquor.

J.5.6 Non-sterile fermentation

Inbicon has patented a non-sterile ethanol fermentation process by making use of the inhibitor produced in pretreatment step [21]. The concentration of the "cock tail" of inhibitors is controlled in the fermentation mixture in such a way that inhibits contaminating bacterial growth (esp. lactic acid bacteria) while having no effect on ethanol yeast. The optimization of inhibitor level is achieved by controlling the water/biomass ration before or after pretreatment.

J.5.7 References

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Appendix K. Ash Reduction from Biomass

K.1 Introduction

Two kinds of energy densification strategies are commonly employed for the conditioning the biomass feedstock for gasification. One is to do the biomass pyrolysis and to use the resulting oil in a Shell Gasification Process (SGP) type operation. The pyrolysis process is relatively simple and the resulting oil is easier to transport through pipes. The main disadvantages of pyrolysis oil are: high reactivity of the oil, causing lack of stability on storage and high acidity, causing corrosion to the pipes and storage vessels. Torrefaction is an alternative method, which converts the biomass to a peat like material that can be (co) fired in a Shell Coal Gasification Process (SCGP). Torrefaction degrades the fibrous components of the biomass, producing a hydrophobic material, which is easier to grind.

Pyrolysis oil is made from biomass by heating the feed in the absence of oxygen at ca. 500 °C with a vapour residence time of ca. 1 s. The volatiles thus produced are condensed to produce a micro-emulsion of a pyrolytic lignin in an aqueous solution of holocellulose, stabilised by monomeric lignin products. For the pyrolysis oil route, there are four challenges limiting suitability of the process viz. fuel quality, phase separation, stability and fouling of the unit. It is further reported that the alkali metals (especially Na, K) present in the feed affect catalytic cracking of the volatiles, causing degradation of the oil also increase the amount of water in the product. These result in both yield loss and phase separation of the oil.

In the case of torrefied pellets, the presence of alkali metals poses a different challenge. Gasification of such pellets lead to the rapid formation of deposits on the walls of the furnace and on the grates. This hinders feeding, combustion and ash removal. The composition of these deposit shows that they are composed of alkali and alkaline earth metal chlorides, sulphate, carbonates and complex silicates.

It is clear from the above statements that the presence of alkali metals has a significant impact on the efficiency of the gasification process. The present report focuses on the different strategies reported for reducing the alkali metal compounds, especially potassium, from the biomass. They are:

1) Simple washing (leaching) of the biomass with water or with dilute acids
2) Hydrothermal pre-treatment
3) Torwash
4) Charwash

The first two can be classified under pre-treatment; the third is an 'in situ' treatment and the fourth, a post treatment (not included in this report).

There are several factors that affect the choice of a pre-treatment technique. Some of them are listed below

- Type of biomass and its ash content, e.g. what straw, palm oil residue, switch grass
- Moisture content of biomass
- Availability of water for pre-treatment
- CAPEX and OPEX for pre-treatment
- Effectiveness of the technique for ash removal
- Improvements obtained in the quality of pyrolysis products (gas, oil, char)

K.2 Biomass Washing/Leaching

Leaching provides a technical solution to the use of biomass in the existing facilities without the need to incorporate new technology, such as gasifiers (which also benefit from the removal of alkali metals and halogens). Leaching has proven to be a very effective method for removing alkali metals and chlorine from biomass.

Fahmi et al. studied the effect of washing of switch grass and a low lignin grass (*Festuca arundinacea*) and showed that the washing step (at 25 °C for 2 h in de-ionised water) improved the quality of the pyrolysis gas. The relevant results are summarised as below:

Feed Analysis

	Switch grass		*Festuca arundinacea*	
	Before washing	After washing	Before washing	After washing
Elemental (%) C	44.77	47.14	42.22	45.2
H	5.79	6.08	5.64	5.98
N	0.31	0.07	1.5	0.87
O	49.13	46.71	50.65	47.95
Total Elemental	100	100	100	100
Al. Metal (ppm) Ca	6173	5409	4334	3209
K	717	78	24,026	1605
Mg	542	422	1136	757
Na	158	32	1346	47
Tot. Al. Metal (ppm)	7589	6945	35653	8436
Ash (%)	4.3	3.4	7.3	4.4

Product Mass Balance [Yields] (mf wt %)

	Switch grass		*Festuca arundinacea*	
	Before washing	After washing	Before washing	After washing
Char	24.7	20.2	33.8	19.9
Organics	51.5	55.2	30.8	41.7
Gas	7.9	10.54	15.4	21.6
Water in Feed	12.4	11.9	16.4	8.7
Closure (%)	96.5	97.8	96.5	91.9

TGA analysis on dry mass basis

Oil Analysis (mf wt %)

	Switch grass		*Festuca arundinacea*	
	Before washing	After washing	Before washing	After washing
HHV (MJ/Kg)	16.4	16	16.7	21.7
LHV(MJ/Kg)	14.8	14.5	14.5	19.7
Viscosity, cp @40 °C	34.2	33.3	10.9	13.5
Aged viscosity, cp @40 °C	57.6	52.1	12.8	18.3
Homogeneity	Single phase	Single phase	Phase separated [a]	Single phase

TGA analysis on dry mass basis

[a] Phase separation 3 months after analysis

Lee et al report similar results on the effect of washing (rice straw cut and soaked in a tank for 2 days, then dried at 60 °C) of the rice straw. The bio-oil yield was increased by ca. 7 %

after the washing step and it was attributed mainly to the reduction of K (from 25261 ppm to 12355 ppm). It was demonstrated that chlorides and potassium could be washed out at 50-60°C. It has been claimed that the energy losses caused by washing, drying and the leaching of organic matter make out approx. 8% of the calorific value of the straw.

Leaving the agricultural residue in the field to natural precipitation can also reduce the alkali metal content. It has been known for a long time that the straw that has been lying in the field and has been exposed to rain has a reduced content of corrosive matters, chlorides and potassium. This means that in comparison with the "yellow" straw, the "grey" one is more lenient to the boiler, since part of the matter that corrodes boiler wall and tubes has now been removed. Grey straw also has a somewhat higher calorific value than the yellow.

Davidsson et al. have used a surface ionisation technique to determine the effect of washing (with water and with 1M acetic acid) of wheat straw. The surface ionisation is a highly sensitive measurement technique to look at the release of alkali metals from the sample[5]. The technique also reveals the presence of two types of bonding of the metal compounds to the biomass structure – organically bound and inorganically bound metals - and the their effects on the washing efficiently. The results show there are two temperature regions, 300 – 400 °C and > 800 °C, where alkali metal ions are released. Washing is effective in reducing the inorganically bound metals (> 800 °C) very significantly (ca. 70 % by water washing and ca. 90 % by acid washing). The removal of the organically bound alkali metals stayed at ca. 30 % for water washing and ca. 70 % for the acid washing.

Turn et al reports (1997) that washing method suits better to herbaceous species (devoted energy crops) because the initial moisture content of the feedstock is very high (ca. 70%). The additional steps required in the feed preparation of such systems are a crushing and a leaching step before the regular milling step. The calculated incremental cost of the process was ca. 1.4 $ per tonne of the dry biomass.

The following section summarises the advantages and disadvantages of biomass washing strategies to reduce the alkali metal contents in the feedstock.

Pros:

- Reduction in S, N, O, K content of biomass. Leaching could mitigate the undesirable effects of biomass ash in thermal systems
- Increased generation of CO and other hydrocarbon gases because of the lower content of alkali metals in the biomass. Without increasing reaction temperature, the product gases can obtain higher caloric values, giving them greater potential for use in fuel applications.
- Higher scalability as no extra equipment except washing unit is required
- Applications where leaching can be integrated into an existing process might be beneficial and feasible (e.g. sugarcane bagasse).
- Wastewater containing inorganic nutrients like K, Cl, and S can be used in fertilizer preparation or for irrigation.

Cons:

- Treatment time
- Large quantities of water required for leaching
- Higher energy consumption

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[5] The sample is placed in a crucible and heated at a constant rate of 20°C/min. Vaporises compounds are transported by a N2 gas flow towards the surface ionisation detector (hot Pt filament at 1230 °C). The alkali compounds are decomposed at the Pt surface and K+ and Na+ ions are emitted and are detected. The ions are then differed to an ion collector and the current o the collector is measured by an electrometer.

- Reduction of conversion efficiency due to higher fuel moisture content

K.3 Pre-pyrolysis Followed by Washing/Leaching

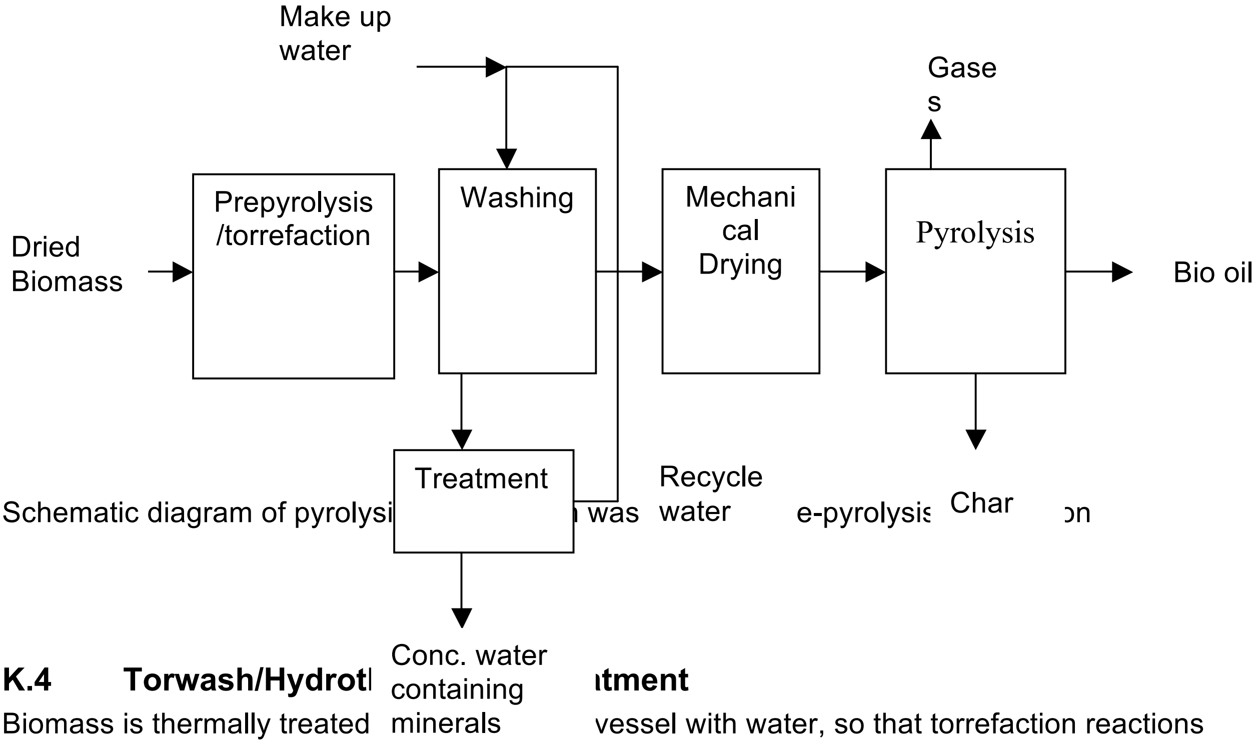
The pre-pyrolysis or partial pyrolysis provides a methodology aiming at the removal of the harmful ash constituents from the biomass, such as alkali metals, chlorine and sulphur, prior to its thermochemical conversion. The patent application, WO 2009/003920 (filed by Emmanouil Koukios), claims a pre-pyrolysis technology in which the biomass such as wheat straw and olive kernel were heated at 250 °C for 1 hr and were then leached by water for 4 hr at a solid/water ratio of 90 g/ yielding a low moisture content and hydrophobic material with reduced alkali metals and chlorine contents. This patent application, however, has a lot of commonalities with an earlier patent granted to FI-PRO Limited (EP 0588 833 B1). The patent claims a method of heating the biomass at ca. 200 °C to undergo partial pyrolysis and a subsequent washing to remove salts. The treatment removes chlorides almost completely. Alkali and sulphur removal efficiencies of, respectively, 50 - 70% and 45 - 65% were also achieved.

Pros:

- Easy drying of the hydrophobic biomass after pre-pyrolysis
- Wastewater containing inorganic nutrients like K, sulphates, carbonates can be used in fertilizer preparation or for irrigation.
- Complete removal of chlorides

Cons:

- Poor removal of K as compared to direct biomass leaching
- CAPEX intensive; pre-pyrolysis and washing means two additional units before the normal pyrolysis / torrefaction process



Schematic diagram of pyrolysi was e-pyrolysis on

K.4 Torwash/Hydrot tment

Biomass is thermally treated vessel with water, so that torrefaction reactions take place in liquid water at ture. The advantage is that the drying afterwards does not require thermal energy, but only mechanical energy. Drying before torrefaction is also not needed here. As the result of torrefaction, water is only physically bound and can be removed by mechanical means. Torwash is suitable for upgrading wet and fibrous biomass that cannot be dried by simply compressing it because the biomass is springy and water is mainly bound chemically and biologically. In Torwash, the torrefaction reactions release ions that immediately dissolve in water and are taken along when the water is removed mechanically. In this way, biomass can be converted into a fuel that is until now unattractive because of problems with corrosion and agglomeration due to the high salt/mineral content.

Pros:

- Removal of minerals during process
- Drying before torrefaction is not required.

Cons:

- Energy consumption in heating large quantities of water containing biomass at elevated T and P
- Scalability

Active Players: INBICON, ECN

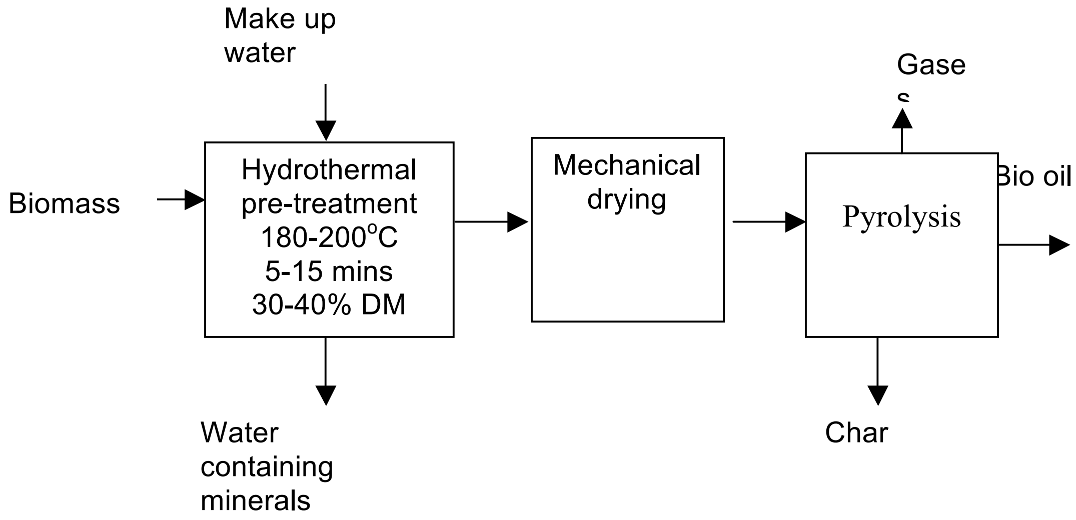


Figure 4: Schematic diagram of pyrolysis process with hydrothermal pre-treatment

K.5 Concluding Remarks

Washing methods are simple techniques for reducing K, Na and Chlorides from crushed biomass. The machinery and scaling up issues are well established. Washing/leaching of the biomass is a better method for the removal of alkali metal compounds from a nutrient recycling point of view. For energy crops containing high amount (ca. 70wt %) of initial moisture content, washing and drying steps impart relatively smaller additional energy load. The main disadvantages of washing process are its water consumption and cost of drying. This holds especially true for feedstock such as wheat and rice straw, agricultural wastes available with relatively low moisture contents (< 10 wt %). In such cases, washing will increase the moisture content to higher levels (> 75 wt %) and “re-drying” is not a right strategy from an energy efficiency point of view. Leaching is known to reduce Na, K and Cl, but not other metal compounds. This means we need to know what all elements and in what quantities need to be removed before proceeding to the densification process.

Avenues for integrating of washing and drying steps in the post-harvest operations (until the energy densification step) are to be looked at.

If the preferred choice of energy densification is torrefaction, it makes sense to adopt technologies such as torwash, which couples washings with the rest of the process. The maturity of the process and scale up issues are largely unknown.

On the other hand, if the preferred densification process is pyrolysis, then washing is an option to consider.

It is important to note that the techniques reported in the literature are mainly for wheat and rice straw. The suitability of these processes (especially washing) for palm oil residue (empty fruit bunch and fronds) needs to be found out.

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Appendix L. De-oiling techniques for water

L.1 Introduction

An overview of the various techniques used in the de-oiling of water is given in attachment 3. In general, the first step in the water treatment process is when the water is passed through a weir and the phase separated oil overflows. Note that in the beginning of the oil production, the fluid is almost 100 % oil and by the end of the lifetime, it becomes almost 100 % water. This means the design of the water treatment unit takes care of extreme situations. Skimmer or a plate interceptor is a basic unit at the first stage. The unit is essentially a tank where the oil droplets coalesce at the oil/water interface and overflow. In plate pack interceptors, the use of parallel or corrugated plates allows droplets to coalesce easily by hitting on the same. This unit can separate 100 % droplets above 150 μm, dependent on the specific gravity and temperature. The technology is well established. A case study from NATCO is given in the reference as an attachment (1). In the case of plate interceptors, for droplets with size larger than 35-40 µm, complete removal is reported. A useful SPE paper on oil-water separation using Performax® coalescer (NATCO) is attached as attachment 2.

L.2 Hydrocyclones

Since the skimmer technique depends on the normal coalescence of oil, there are limitations. If the feed has a significant amount of oil phase in the form of small droplets (in the order of 10 μm or less), efficient removal by a skimmer becomes difficult. Some of the strategies to deal with these systems are to install chemical coalescing agents, membranes, media filers, hydrocyclones or centrifuges. In these cases, energy efficiency, cost and maturity of the technology become important. Hydrocyclones are very popular in oil removal from production water. They achieve good separations of oil droplets with sizes greater than 15-30 μm. Centrifuges typically remove droplets over 3 μm with good efficiency.

The hydrocyclone for de-oiling of water was developed in 1980 by Colman and Thew. Hydrocyclones enhance the separation of *insoluble* oil droplets by achieving movement of the same in the continuous water medium. This movement is given by Stoke’s law as given by

$$v_s = \frac{g(\rho_c - \rho_d)D^2}{18\mu} \qquad (1)$$

where, v_s is the terminal velocity achieved by the oil drop travelling to coalesce, g is the acceleration field created by the flow (vortex flow in a hydrocyclone), ρ_c and ρ_d are, respectively, the densities of the continuous (water) and dispersed (oil) phases, D is the diameter of the drop and μ is the viscosity of the continuous phase. The main action of the apparatus is to achieve high centrifugal acceleration (g) to the produced water (to be de-oiled). The multiphase feed is fed tangentially at a high velocity into the upper swirl chamber, which causes the flow to spin in a vortex flow pattern. The vortex creates a high acceleration pattern (2000-3000 g for de-oiling hydrocyclones) that forces the oil to migrate to the center of the cyclone. The heavier phase in the primary vortex flows out through the underflow and lighter (at the center) reverses direction and leaver through the overflow.

From equation 1, it can be seen that velocity or the rate of coalescence heavily depends on the diameter of the droplets. Now, any idea that makes the diameter of the drop to grow will in turn makes the velocity faster and the drop reaches the oil core before being carried out with the water in the underflow. The fact is well captured in the figure given below, where the removal efficiency of the oil droplets is plotted against the droplet size.

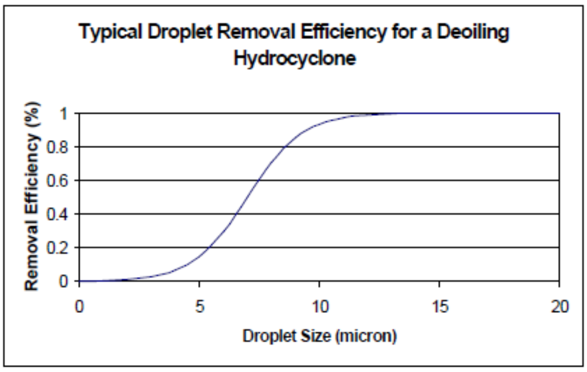

Fig 2 – Typical Deoiling Hydrocyclone Cut Size Curve

L.3 Enhancement of hydrocyclone performance

Looking at the relation (Eq. 1) and the graph, it can be seen that even a small change in oil drop size can potentially improve the recovery. One strategy to achieve bigger drop size of the dispersed oil phase is by passing through a hydrophobic media (such as array of fibers made of hydrophobic materials - polypropylene, polyurethane). The improved coalescence process happens in the following steps

1) **Droplet Contact**: The oil dispersed in water is passed through a hydrophobic (oleophilic) media of a suitable form (fiber, particles, foam) offering (necessary) resistance to the flow.
2) **Droplet capture:** The force of adhesion binds the smaller oil droplets to the media
3) **Droplet growth:** Coalescence of small oil droplets on the surface of the media; media progressively retaining more and more oils
4) **Droplet disengagement**: Bigger drops getting stripped off from the media

The feed will now have oil droplets with enriched drop sizes that can be fed to a hydrocyclone for the oil water removal.

In the second page of the attachment 3, we have listed some process intensification techniques based on this phenomena. Three such techniques are selected for further analysis. They are

Mare's tail (Opus Plus Inc.)
Torr (ProSep Inc.)
PECT-F (Cyclotech Ltd)

A comparison between three technologies is given in attachment 4.

1 OffshoreWestAfricaProject_Skimmer.pdf

2) 00011562_plate_interceptor.pdf

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3) techniques_Adsorptic

Technologies.xls

4)

Report distribution

Appendix E. Comparison of flocculation based techniques for harvesting of algae

+++ - High, ++ Medium, + Low

Flocculation based Harvesting Techniques for Algae

Name of the Technique	Space requirement	External aids	Status of development	CAPEX (Relative order of magnitude)	OPEX (Relative order of magnitude)	Residence time	Scalability	Remarks
Ultrasonic flocculation	+	+, Not required. (Only Sonication required)	Bench	++	++	+	+	Major issue is technology development
Bioflocculation	+	+ (only micro-organisms/bioflocculants)	Pilot	+	++	++	++	Unfamiliarity with industrial use of microorganisms or products directly derived from them
Autoflocculation	++	Not required (Only adjustment of culture media/conditions is done to achieve autoflocculation with sep. eff. > 90%)	Pilot	+	+	+++ (<24 hr settling time)	+++	Residence time requirement can be high and is dependent on type of algae
Electroflocculation	+	+, Not Required (Only electrodes and electricity is required)	Pilot	++	+ , (0.3 kWh/m3)	+	+	Shorter life of electrodes and Chlorine generation in salt waters could pose problems.

Appendix F. Comparison of flotation based techniques for harvesting of algae

+++ - High, ++ Medium, + Low

Flotation based Harvesting Techniques for Algae

Name of the Technique	Space requirement	External aids	Status of development	CAPEX (Relative order of magnitude)	OPEX (Relative order of magnitude)	Residence time	Scalability	Remarks
Induced air Flotation/Jet Flotation	++	++ (flocculant)	Semicommercial	++	++	++	+++	Can handle green Algae/blue green Algae, microalgae, Requires flocculant
Suspended Air Flotation	+	+ (flocculant), + (Surfactant) (Can be flocculant free)	Pilot	+	+	++	++	Toxicology and contamination of water due to surfactants
Dissolved Air Flotation	+++	+++ (flocculants)	Semicommercial	+++	+++(Blowers or commpressors are required)	+++	+++	Highly energy intensive though can remove most types of algae

Appendix G. Appendix H:Comparison of various cell lysis techniques for algae

Name of the technique	Mechanism	Scale of Development	Scale up Potential	Remarks
Electromagnetic cell disruption	Electric field induced elongation of cells	D2	Medium	Demonstrated for Algae
Pulsed Electric Field (PEF) Cell Disruption	High electric field pulses for cell lysis	D1	Medium	Poor life of electrode and Temperature rise
CO2 based Cell Disruption Techniques	Supercritical CO2 as a solvent for algae cells	D2	Medium	Higher CAPEX
Mechanical Shear Centrifuge	Mechanical shear force in centrifuge	D2	Medium	Poor cell lysis (~40%) reported for WWTP sludge
Surfactant for Algal Oil Recovery	Surfactants for cell lysis	D1	Low	Not demonstrated for algae
Lytic Enzymes/Virus	Lytic enzymes induced disruption of cells	D1	Medium	It has to be coupled with other lysis technique
Homogenizers	Compression and sudden de-compression burst cells	D3	High	High power requirement and heat generation
Ultrasonic Cell Disruption	Cell lysis by sonic cavitation	D2	Medium	Protein damage, genration of heat and free radicals
Chemical Algal Oil Recovery (cAOR)	several chemicals induce cell death and lysis	D1	Low	Degradation of intracellular products, cost and recovery of chemicals
Aqueous Biphasic Systems (ABS)	Use of polymer & chaotropes/kosmotropes for extraction of proteins	D1 (D4 in biotechnology)	Medium	Cost and recovery of chemicals and unexplored for algae oil recovery

Appendix H. Specific separation challenges of typical biodomain projects

H.1 Cellulosic Ethanol Projects

Main challenge in the project is that the ethanol broth is very dilute (ca. 5%) and the conventional distillation is not energy efficient. The project is open to ideas that are energy efficient, at the same time, with good maturity levels in order to substitute the conventional distillation techniques for the ethanol recovery from water.
Second challenge is the solid-liquid separation. There are four solid-liquid separations in the process. They are

1) Adjusting the solid content before liquefaction
2) Separation of lignin and un-reacted cellulose before fermentation
3) Removal of yeast (after fermentation) for recycling
4) Final separation of the solids from the bottom of the distillation (water treatment)

The challenge is to accelerate the settling of the solids and then the removal of the same in an energy efficient manner.

H.2 Sugar to Hydrocarbons Projects

The process envisages the separation of organic molecules from water. This is important from a molecule recovery of point of view and from the wastewater treatment point of view. Separation of acetone from water is one example. Sugar concentration (feedstock) is another challenge and options are being looked at currently. Another separation challenge in the project is the separation of large quantities of CO_2 (ca. 80%) from the off gas steam (containing H_2 and lights). Separation of CO_2 is important here, as it improves the quality of H_2 that needs to be recycled in the process.

H.3 Pre-treatment Projects

Solid handling challenges are very similar to what is described in section 4.1. Additionally the project is looking at low water pre-treatment options. This means feed sugar concentrations and thereby more concentration of certain bi-products that are harmful to the microorganisms. One such molecule is acetic acid, which is poisonous to the yeast above 1% in concentrations. So effective separations of acetic acids is important in this context (before the stream reaches the fermentor).
Second challenge in the pre-treatment is the corrosion on the units caused by chlorides present in the biomass feedstock. Removal of chlorides is an important challenge that needs to be addressed in an energy efficient way.

H.4 Algae projects

At the moment heat is used to disrupt the algae cells and the pressing or extrusion to remove water. Some experiments are done to use dimethyl ether (DME) as the extractant to for the algae oil. There is a potential challenge to look at from the separation point of view and that is the separation of proteins from the process water stream.

H.5 Biomass gasification project

The presence of alkali metals has a significant impact on the efficiency of the gasification process.

Appendix I. Alternative techniques for ethanol-water separation

I.1 Introduction

In the conventional fuel grade ethanol production, the ethanol-water separation is done in three or more stages. In the first stage, the beer mash (containing about 85 wt% water, 10 wt% ethanol and 5 wt% solids) is sent to a stripping column (distillation column) and the distillate is collected as ca 40 wt% ethanol. The bottom products are solids, water and minor quantities of ethanol. The first distillate, in the form of vapour, is then fed to a second distillation column (rectification column). The distillate of this unit is typically ca 90 wt% ethanol. This stream is then dried to anhydrous ethanol (purity more than 99.5 wt %) using a molecular sieve unit (MSU). Conventionally, crystalline zeolites are used to adsorb water and the dried ethanol is collected at the bottom.

The other promising separation techniques to consider are pervaporation, extraction, and dephlegmation. This report presents an overall comparison of these different processes and a specific evaluation of a hybrid line-up having distillation and pervaporation.

I.2 Evaluation

The evaluation of the processes is done based on the following two criteria

1. Energy requirement
2. Maturity of the process for commercialisation

I.2.1 Distillation and MSU line-up

The molecular sieve needs regeneration when it becomes saturated with water. The regeneration is done by passing a part of the product (anhydrous ethanol) through the zeolite bed. The ethanol, now diluted by the water present in the molecular sieves, is then mixed with the feed stream of the rectifier. This means that even in the case of MSU, it is the distillation that dries the ethanol. Therefore, MSU, while avoiding the more energy intensive azeotropic distillation conditions, still consumes considerable amount of energy.

I.2.2 Extraction based techniques

Trans Ionics has developed an extraction based ethanol separation system. Here, the stream from the fermentation tank (heated to a higher temperature) is extracted by a non-volatile solvent (such as vegetable oil). In one configuration, the stream is made in contact with the extractant by vaporising the feed and passing the vapour through a venturi nozzle, where the extractant serves as the working fluid. In the second configuration, the ethanol water stream is contacted with a non-porous membrane and the permeate (ethanol) is driven forward by a vacuum created by a venturi nozzle, with the extractant as the working fluid. The extracted ethanol extracted is then flashed off and the resulting ethanol solution (ca 95 %wt) is then dried by a molecular sieve unit.

Replacement of distillation unit by extraction unit is a good idea, but it is in the developing stage. Large energy savings of such a process is also not very obvious since the feed has to be vaporised and ethanol has to be again separated from the extractant. Moreover, the process has the energy disadvantage of having MSU as the drying unit.

I.2.3 Membrane based techniques

Membrane units have emerged as an alternative technology to replace different stages of the conventional line-up such as

i) a substitute for MSU
ii) a substitute for the rectification and MSU units and
iii) a stand-alone system

Some of the major players developing these membrane based technologies for ethanol separation are 1) Mitsui & Co., 2) Sulzer Chemtech-Kuhni, 3) Vaperma Inc., 4) Membrane Technology Research Inc. (MTR) and 5) Whitefox. A list of key players with more details is attached as an excel sheet in Appendix 1.

I.2.4 Pervaporation units in combination with Dephlegmator

MTR has developed a separation process consisting of pervaporation units and a Dephlegmator (US Patent 6755975). The stripping column in conventional line-up is replaced by a pervaporation unit (having hydrophobic membrane such as silicon rubber). The permeate will have ethanol concentration of 30-40 wt% ethanol. This permeate is sent to a Dephlegmator unit replacing the rectification unit. Dephlegmator is similar to a reflux condenser, equivalent to four to six theoretical stages of equilibrium operation. The permeate vapour enters the bottom of the dephlegmator. At the top, the vapour is partially condensed and the condensate trickles down in counter-current manner. The vapour enriched with 90-95 wt% ethanol is collected at the top. Further dehydration is done by a hydrophilic pervaporation unit.

MTR claims that these hybrid line-ups work efficiently at small-scale operations. For large scale operations, replacing stripper with membrane may be energetically attractive. But there are risks of fouling, maintenance and the need for large membrane surface due to the large volume and solid content of fermentation broth. Dephlegmation is also not a matured process. Considering these pitfalls, completely replacing distillation is not an attractive option, at least in the short term, for large-scale operations.

I.2.5 Replacing Rectification and MSU with Pervaporation units

A case study proposed by Vaperma to replace rectification unit with a pervaporation unit is considered here for evaluation.

The below process scheme with conventional distillation and MSU is considered as the base case by Vaperma. The feed rate for the stripping column is 184300 kg/h with 9 wt% ethanol. The ethanol concentration at the end of the stripping section is ca 42 %wt and at the end of the rectification section is ca 93 %wt. The distillate rate at the end of the stripping section is 38643 kg/h. The final product rate is 20833 l/h.

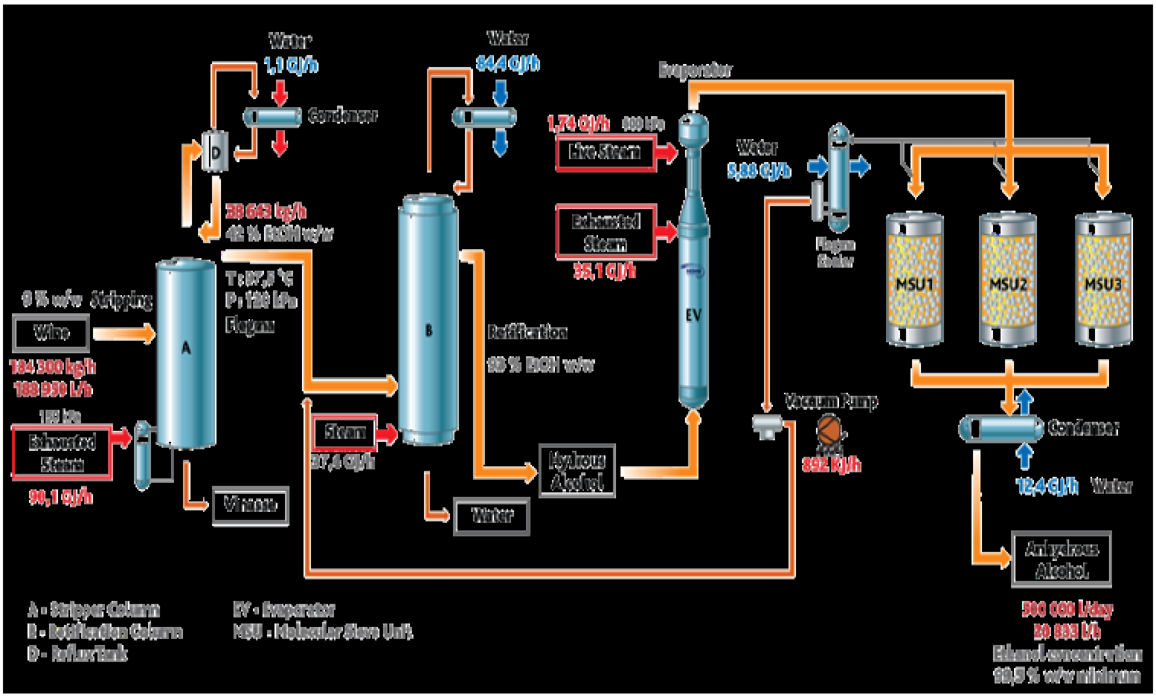


Fig. 1 Sugar Cane to Ethanol Process: Beer enters the stripper, A, then goes to a rectifier, B and then an evaporator C before it goes for final drying up in MSU units (source: Vaperma presentation).

In the above described line up, the steam requirement of ca 165.2 GJ/hr was calculated with the below split up for different units
Stripper - 90.1 GJ/h
Rectifier – 37.4 GJ/h
Evaporator – 36.84 GJ/h
Vacuum pump – 0.892 GJ/h

I.2.6 Vaperma’s alternative line-up with two membrane units

One of the alternative line-ups that Vaperma has put forward is to use two membrane units replacing the rectification section and a MSU unit producing the anhydrous ethanol from ca 40 wt% ethanol feed. Vaperma claims that this hybrid line up gives a net saving of ca. 70 GJ/hr steam.

I.2.7 Our simulation for Vaperma's base case

We tried to simulate Vaperma's base case ethanol plant. The distillation unit has separate stripping and rectification columns. First, the stripping column was simulated using Aspen and results are shown in Table 1.

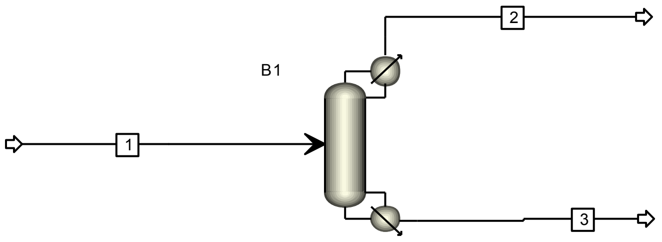


Table 1. Vaperma's base case stripper simulation results

Feed T	Feed (kg/h)	Feed Conc	Reflux ratio	D rate (kg/h)	Stages	Feed stage	Condenser duty GJ/h	Reboiler duty GJ/h	Product ethanol wt%	Tray efficiency
75	184300	9%	0.013	38643	30	20	-1.10	**90.55**	**42.9**	75%

Table 1 shows that the reboiler duty and the product concentration are similar to that of Vaperma's simulation results. In the Vaperma's base case, the stripper was followed by a rectifier (with steam stripping). The liquid stream from the rectifier was passed through a vaporiser before feeding to a MSU unit.

The order of these operations raised the following questions:

1. Why is it necessary to have two separate distillation columns? Can't stripping and rectification be combined in a single column?
2. Why is steam used in the rectification column when the stripper reboiler itself is sufficient to supply heat?
3. Why is it required to have an evaporator between the rectifier and the drying unit? What happens if the vapour distillate is taken from the rectification column directly to the MSU unit?

2.3.2.3 Our Proposed Alternative design for Distillation part

To answer these questions, we have simulated by combining stripping and rectification in a single column. The single column simulation results are given in Table 2.

Table 2. Stripper and rectifier combined column simulation results

Feed T °C	Feed (kg/h)	Feed Conc	Reflux ratio	D rate (kg/h)	Stages	Feed stage	Condenser duty GJ/h	Reboiler duty GJ/h	Product ethanol wt%	Tray efficiency
75	184300	9%	3.0	17835	30	20	-50.37	**92.95**	**93**	75%

From Table 2, it can be seen that the reboiler duty of the single column is very close to that of the stripping column of the Vaperma's base case. At the same time, the concentration of the distillate achieved is as high as 93 %wt. Thus, a rectifier and stripper combined in a single column can save the energy and CAPEX of the first membrane unit of Vaperma's hybrid line up. We also propose to take vapour distillate from this column to the final drying unit.

I.2.8 Vaperma’s Final Drying line up

For further dehydration, the claims of Vaperma are convincing that using a membrane unit consumes lesser energy compared to an MSU unit. According to their calculation, the energy consumption of membrane system is about one tenth that of the MSU unit. It is also reported that the investments of pervaporation units and MSUs are similar. This means substitution of MSU with membrane is a valuable proposition.
As far as process maturity is considered, membranes are still in demonstration stage. But, the replacement of MSU alone with a membrane unit is a feasible and viable proposition. In such a configuration, the volume of feed handled by the membrane unit is only one tenth of the feed that enters the primary distillation unit, which reduces the scale up risk of the membrane unit.

I.3 Conclusion

Hybrid line-up involving distillation as a primary unit followed by a membrane unit is found to be an energy efficient option for producing fuel grade ethanol from dilute fermentation broth. The configuration is presented below

- Stripping and rectification combined in a single distillation column to produce ca 90 wt% ethanol from the fermentation broth feed
- The vapour distillate from the column is fed to a pervaporation unit instead of a MSU to produce anhydrous ethanol (above 99.5 wt %).

I.4 Recommendations:

The above proposition to combine stripper and rectification to a single column and replace MSU with a membrane unit offers promise for ethanol water separation. However, we recommend to do a CAPEX and reliability analysis for membrane units supplied by major vendors such as Mitsui, Vaperma and Sulzer.

The replacement of MSU with a membrane unit is still a short-term improvement in the ethanol-water separation. Long-term solution to this challenge can be achieved by developing ideas that offer better energy efficiency to the entire ethanol-water separation process (including solids separation). Co-development of processes with companies such as MTR (pervaporation and dephlegmation technology) or TransIonics (extraction based technology) could be one way to achieve this.

Attachment

ethanol_water_tech
nobgies_new.xls

Appendix J. Removal of Acetic acid inhibitant from biomass hydrolysate – A review and Recommendations

J.1 Introduction

The major challenge in cellulosic ethanol production is the product isolation since ethanol is formed at low concentration during the fermentation. One of the ways to overcome this problem is to have high sugar concentration in the fermenter. This can be achieved by having high cellulose concentration in the enzymatic hydrolysis step to produce high sugar concentration and Simultaneous Saccharification and Co-fermentation (SSCF) of the concentrated biomass feedstock. In SSCF enzyme and microbial inhibition by high sugar concentration is avoided by maintaining a threshold sugar concentration. It also helps to convert both C5 and C6 sugars into ethanol. Thus increasing the solid content of the feed biomass leads to better throughput and sugar concentration in the fermenter.

Conversion of lignocellulosic materials into digestible oligosaccharides is done by a pretreatment process. Pre-treatment process loosens the cellulose and hemi-cellulose from the lignin structure. Particularly during mild acid or hot water pre-treatment, the hemi-cellulose part of the biomass goes into the aqueous hydrolysate. During this process, many inhibitors such as lignin degradation products (phenolic compounds), hemi-cellulose degradation products (such as furfural and HMF) are formed. The acetyl group of hemicellulose is hydrolyzed into acetic acid. When the acetic acid concentration goes above 1 wt%, it becomes toxic to the subsequent enzymatic hydrolysis process and as well for sugar fermenting yeast. This is the case particularly when we use high solid concentration in pretreatment stream. The protonated form of acetic acid can pass through the cell membrane and destabilize the electro-neutrality of the cell and ultimately leading to cell lysis.

Thus removal of fermentation inhibitor molecules such as acetic acid, furfural and phenols is very important and also forms the subject of this report. Several techniques to remove acetic acid have been reported such as electro dialysis, emulsion liquid membrane, Microbial Fuel Cell, inhibitor metabolizing microbes, non-sterile fermentation (patent from Inbicon) and in-situ conversion but most of them are still in the exploratory stage. These techniques are briefly described in Appendix 1. This report describes an energetically promising scheme for removing the inhibitors from biomass stream which has undergone mild acid/steam explosion pretreatment.

J.2 Proposed scheme for acetic acid/furfural removal from biomass hydrolysate

First, the scheme for acetic acid/furfural removal is outlined with an Aspen model. Following that the literature information available on those specific techniques is briefly dscribed.

In this process, mild acid pre-treatment is carried out at high pressure (10-15 bar) and temperature (~200°C). We propose to make use of this energy, to flash off the inhibiting components like acetic acid and furfural in a flash drum. This flashed vapors containing acid, acetic acid and furfural can be condensed in a condenser. We propose the following options to further treat this condensate to recover the acetic acid and furfural:

1. Ion exchange resin column
2. Extraction unit
3. Membrane unit

Figure 1. shows the schematic of the proposed scheme.

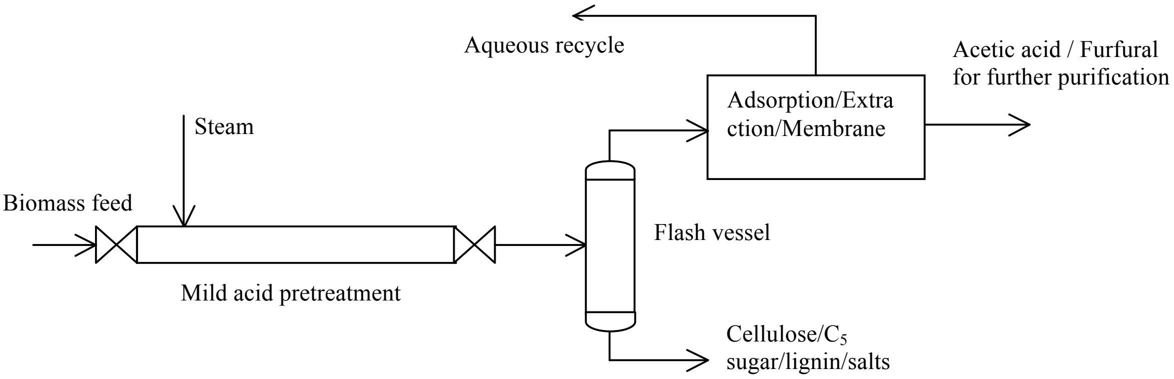


Figure 1. Proposed scheme for recovery of acetic acid/furfural from pretreated biomass hydrolysate

We have done an Aspen modeling to simulate the flash vessel condition. For the simulation, the feed biomass is considered to enter the flash vessel at 200°C and 15 bar pressure after the mild acid pretreatment. The feed and vapor composition of the flash vessel obtained from the simulation is shown in the below Table.

Table 1. Simulation results of flash drum with feed materials of 70% aqueous phase (water + sulphuric acid) and 30% solid phase.

Property	Feed 1	Top vapor stream 1	Bottom stream 1
Temperature K	473.15	374.1	374.1
Pressure atm	14.8	0.99	0.99
Water (kg/h)	57750	32514.3	19985.7
H_2SO_4 (kg/h)	583.3	0	583.3
Furfural (kg/h)	150	128.5	21.5
Xylose (kg/h)	5940	0	5940
Acetic acid (kg/h)	750	375.3	374.7
Cellulose (kg/h)	10000	0	10000
Hemicellulose (kg/h)	660	0	660
Lignin (kg/h)	7500	0	7500

From the above Table, it can be seen that almost 50% of the feed acetic acid and 85.7% of feed furfural goes to with top vapor stream. Further separation of these inhibitors from the vapor stream can be carried out by either adsorption or extraction or membrane techniques. Thus the inhibitor concentration in the bottom stream can be reduced significantly within a threshold limit. This simulation analysis forms the basis our proposal to have a flash vessel followed by adsorption/extraction/membrane units.

As an exploratory approach, to improve degree of the acetic acid separation, we introduced steam to the same above stream before entering the flash vessel and after pretreatment. For various amount of steam introduction, simulation was performed. The results are shown in the below table.

Table 2. Simulation results of flash drum with feed materials of 80% aqueous phase (water + sulphuric acid) and 20% solid phase.

Property	Feed 2	Top vapor stream 2	Bottom stream 2
Temperature K	473.1	374.3	374.3
Pressure atm	14.8	0.99	0.99
Water (kg/h)	94166.7	32514.3	19985.7
H2SO4 (kg/h)	583.3	0	583.3
Furfural (kg/h)	150	141.5	8.5
Xylose (kg/h)	5940	0	5940
Acetic acid (kg/h)	750	561	1
Cellulose (kg/h)	10000	0	10000
Hemicellulose (kg/h)	660	0	660
Lignin (kg/h)	7500	0	7500

Table 3. Simulation results of flash drum with feed materials of 90% aqueous phase (water + sulphuric acid) and 10% solid phase.

Property	Feed 3	Top vapor stream 3	Bottom stream 3
Temperature K	473.1	376.5	376.5
Pressure atm	14.8	0.99	0.99
Water (kg/h)	219166.7	211585.8	7580.9
H2SO4 (kg/h)	583.3	0	583.3
Furfural (kg/h)	150	147.9	2.1
Xylose (kg/h)	5940	0	5940
Acetic acid (kg/h)	750	713.7	36.3
Cellulose (kg/h)	10000	0	10000
Hemicellulose (kg/h)	660	0	660
Lignin (kg/h)	7500	0	7500

In all the above cases, we can observe that when steam is introduced before flash drum, degree of acetic acid and furfural separation increases. At the same time, the water quantity in the solid stream also goes down which is the desired condition for high solid content hydrolysis. But, the concentration of acetic acid and furfural in the top vapor stream decrease to a very low value. Then it may need energy intensive separation process for further purification of acetic acid/furfural from the above stream.

J.3 Examples of application of flashing specific to biomass pretreatment

The concept of flash drum is a well known technique to remove the volatiles making use of the pressure and temperature available with the stream. A process that is quite similar to steam stripping is reported in the patent US 6743928 [1] for the separation of furfural. In this case, the liquid stream is heated by introducing steam in the reactor and a particular pressure is maintained. Once the stream achieves the desired temperature, the reactor is gradually depressurized to remove the more volatile components.

SunOpta has filed a patent [2] for removing acetic acid from biomass hydrolysate. SunOpta is specialized in steam explosion pretreatment of lignocellulosic materials. The current patent claims that after the high temperature and pressure pretreatment, the feedstock is introduced to a cyclone separator operating under vacuum. The difference in the pressure removes the volatile inhibiting agents from the solids. Thus pretreated solids are subjected to enzymatic hydrolysis under vacuum. The following fermentation step is also carried out under vacuum.

These examples form the basis of our proposal to have a flash vessel after pretreatment.

J.4 Removal of inhibitors using adsorption (ion exchange) resins

Ion exchange is a robust and matured technique used in large scale water treatment plants. To remove acidic molecules like acetic acid from sugar hydrolysate, weak basic anionic resins are considered to be a promising candidate [3]. The adsorption mechanism is more like an ion pair formation as opposed to a pure ion exchange. This means that the adsorption capacity may not be as large as that achieved by a strong base resins. There are no reports about using strong base resins for removing acetic acid. Strong base resins are suspected to catalyze reactions of sugars. Hence, acetic acid removal over week base resins is considered to be a more robust separation method to reduce acidic molecules. Novozymes has filed a patent [4] which claims to use weak base anionic resins to remove inhibiting molecules especially acidic ones. Mancilha and Nazmul Karim [5] reported that almost 100% acetic acid could be removed from corn stover hydrolysate for xylitol fermentation using Purolite a 103 S resin.

J.4.1 Membranes

Ranil Wickramasinghe and Grzenia used a cellulose membrane with strong base anion ($R\text{-}CH2\text{-}N^{+}\text{-}(CH_3)_3$) as surface functional group to remove acetic acid from biomass hydrolysate [6]. They compared the performance of a weak base anionic resin with this membrane to remove acetic acid. They found that the acetic acid capacity of ion exchange membrane is more than that of the resin. Pervaporation technique is also being studied as the separation technique to concentrate dilute acetic acid solutions. Zeolite membranes are one class of membranes reported in the literature. While these techniques hold an advantage in terms of energy consumption, the lower maturity level, especially while handling large quantities of dilute streams is a clear disadvantage.

J.4.2 Solvent Extraction

For extraction of acetic acid from aqueous solution, ethyl acetate and MTBE are considered as potential extractants [7]. Further purification of acetic acid is done by a distillation unit. Tri-octyl phosphine oxide (TOPO) as a fatty acid carrier is also tested to increase the distribution coefficient of acetic acid [8]. Hong and Hong used tri-n-octylamine dissolved in n-octanol to selectively extract acetic acid from aqueous mixture of succinic and acetic acid at pH 5.1 [9]. Grzenia et al. reported a hollow fibre-based liquid extraction to remove acetic acid from lignocellulosic hydrolysate after pre-treatment with dilute sulphuric acid [10]. They observed a 50:50 mixture of Alamine 336, a tertiary amine, in octanol could take up to 60% of the acetic acid. Based on this knowledge, we recommend developing our own extraction scheme suitable for our application by conducting experiments.

J.4.3 Conclusions and Recommendations

Many of the separation techniques reported so far to remove acetic acid from biomass hydrolysate are in the exploratory stage. We propose a scheme to separate acetic acid/furfural from biomass hydrolysate. It comprises of a flash vessel which makes use of the energy available with the pretreated stream (high pressure and temperature) to flash off the acetic acid/furfural. The cellulose fibers along with lignin will be removed from the bottom of the flash drum. The condensed aqueous phase from top will be feed to a secondary purification step such as an ion exchange column or extraction unit or a membrane unit to recover acetic acid and furfural. Depending on the end use, further purification of acetic acid or furfural from secondary purification step can be carried out. Based on the open knowledge and preliminary Aspen simulation, we consider that the above proposed scheme can offer promise in terms of robustness, maturity and energy efficiency.

We also recommend having experimental support making use of Bioseparation team expertise for studying different ion exchange resins, extractants specific for process. This will help to come up with a suitable process for inhibitors recovery.

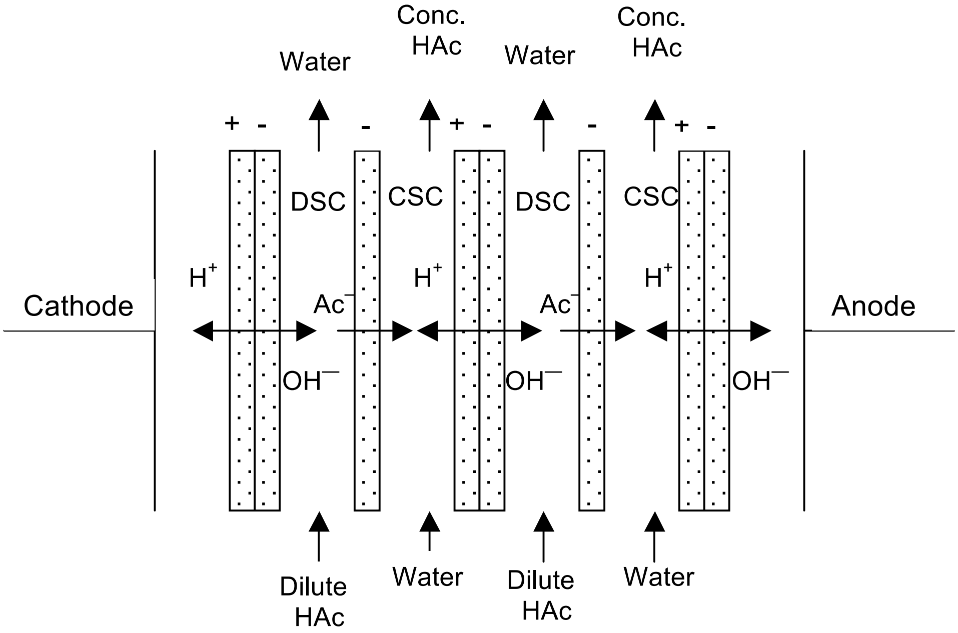
J.5 Literature Review on Different Technologies Reported for Acetic acid Removal

J.5.1 Over liming

Conventionally after mild acid pretreatment (with low solid content), over liming is done by adding lime to the hydrolysate to increase the pH to a value in the range of 9-11. Overliming the hydrolysate has been effective as a detoxification process due to partial removal of toxic inhibitors, such as furfural and 5-hydroxymethylfurfural, although the whole mechanism is not well understood. During overliming, sulphuric acid and acetic acid are removed from the initial hydrolysate by adding lime to adjust the pH and precipitation as gypsum. However, it was observed that the concentrations of acetic acid before and after the detoxifying treatment were not significant altered [11, 12, and 13]. They also report that overliming did change the acetic acid concentration significantly. Moreover, the potential drawback is sugar degradation due to hydroxide –catalyzed degradation reactions [14].

J.5.2 Electrodialysis

Electrodialysis is used to remove acetic acid from wastewater stream. Yu et al from Tsinghua University report a bipolar Electrodialysis (EDB) technique for the separation of dilute acetic acid [15, 16]. The principle of is depicted in the diagram below



Dilute acetic acid solution is introduced in the space between the anion-exchange side of the bipolar membrane and the anion-exchange membrane (Dilute Solution Chamber, DSC). When an electric field is introduced, acetate ions are transported to the space between the anion-exchange membrane and the cation-exchange side of the bipolar membrane (Concentrated Solution Chamber, CSC). In the CSC, the acetate ions combine with protons generated by the bipolar membrane to produce acetic acid. When the concentration of acetic acid reaches about ca. 30%, the concentration solution is withdrawn for further purification. Due to the cost of the instrument, large scale operation seems to be a major challenge [17].

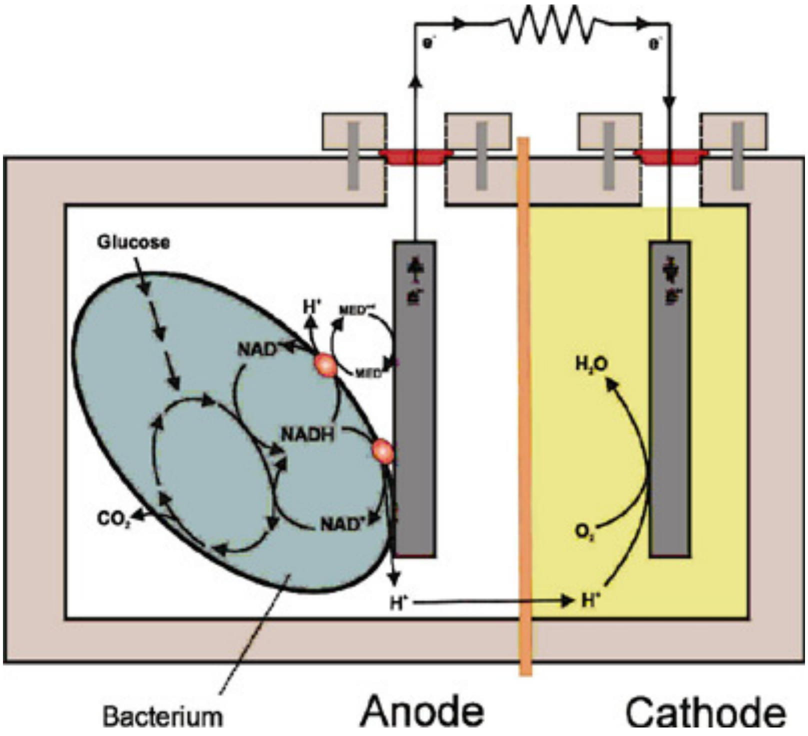
J.5.3 Emulsion Liquid Membranes (ELM)

In this case, water in oil emulsion in water (W/O/W) is created in an appropriate reactor, the water – oil interface being the membrane here. O'Brien and Senske reported the application of such systems for the removal of acetic acid and propionic acid from aqueous solutions [18]. The composition of the "membrane" is 96 % of middle distillate paraffinic solvent and 4% non-ionic surfactant. The emulsion was made by blending the oil + surfactant with an internal reagent (5 M NaOH or KOH). The feed is then added to the emulsion and a mixer speed of about 500 rpm was maintained.

J.5.4 Microbial fuel cell

Borole et al. investigated using a MFC to remove inhibitory products generated during the pretreatment of lignocellulosic materials [19]. A MFC consists of an anode, a cathode, a proton or cation exchange membrane and an electrical circuit.

The bacteria live in the anode and convert a substrate such as acetate and glucose into CO2, protons and electrons. Under aerobic conditions, bacteria use oxygen or nitrate as a final electron acceptor to produce water. However, in the anode of a MFC, no oxygen is present and bacteria need to switch from their natural electron acceptor to an insoluble acceptor, such as the MFC anode. Due to the ability of bacteria to transfer electrons to an insoluble electron acceptor, we can use a MFC to collect the electrons originating from the microbial metabolism. The electron transfer can occur either via membrane-associated components, soluble electron shuttles or nano-wires. The electrons then flow through an electrical circuit with a load or a resistor to the cathode.



The potential difference (Volt) between the anode and the cathode, together with the flow of electrons (Ampere) results in the generation of electrical power (Watt). The protons flow through the proton or cation exchange membrane to the cathode. At the cathode, an electron acceptor is chemically reduced. Ideally, oxygen is reduced to water.

J.5.5 Inhibitor metabolizing microbes

Schneider isolated a mutant Saccharomyces cerevisia which can grow on acetic acid but not on sugars [20]. This mutant yeast was used to remove acetic acid from hardwood-spent sulfite liquor.

J.5.6 Non-sterile fermentation

Inbicon has patented a non-sterile ethanol fermentation process by making use of the inhibitor produced in pretreatment step [21]. The concentration of the "cock tail" of inhibitors is controlled in the fermentation mixture in such a way that inhibits contaminating bacterial growth (esp. lactic acid bacteria) while having no effect on ethanol yeast. The optimization of inhibitor level is achieved by controlling the water/biomass ration before or after pretreatment.

J.5.7 References

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Appendix K. Ash Reduction from Biomass

K.1 Introduction

Two kinds of energy densification strategies are commonly employed for the conditioning the biomass feedstock for gasification. One is to do the biomass pyrolysis and to use the resulting oil in a Shell Gasification Process (SGP) type operation. The pyrolysis process is relatively simple and the resulting oil is easier to transport through pipes. The main disadvantages of pyrolysis oil are: high reactivity of the oil, causing lack of stability on storage and high acidity, causing corrosion to the pipes and storage vessels. Torrefaction is an alternative method, which converts the biomass to a peat like material that can be (co) fired in a Shell Coal Gasification Process (SCGP). Torrefaction degrades the fibrous components of the biomass, producing a hydrophobic material, which is easier to grind.

Pyrolysis oil is made from biomass by heating the feed in the absence of oxygen at ca. 500 °C with a vapour residence time of ca. 1 s. The volatiles thus produced are condensed to produce a micro-emulsion of a pyrolytic lignin in an aqueous solution of holocellulose, stabilised by monomeric lignin products. For the pyrolysis oil route, there are four challenges limiting suitability of the process viz. fuel quality, phase separation, stability and fouling of the unit. It is further reported that the alkali metals (especially Na, K) present in the feed affect catalytic cracking of the volatiles, causing degradation of the oil also increase the amount of water in the product. These result in both yield loss and phase separation of the oil.

In the case of torrefied pellets, the presence of alkali metals poses a different challenge. Gasification of such pellets lead to the rapid formation of deposits on the walls of the furnace and on the grates. This hinders feeding, combustion and ash removal. The composition of these deposit shows that they are composed of alkali and alkaline earth metal chlorides, sulphate, carbonates and complex silicates.

It is clear from the above statements that the presence of alkali metals has a significant impact on the efficiency of the gasification process. The present report focuses on the different strategies reported for reducing the alkali metal compounds, especially potassium, from the biomass. They are:

1) Simple washing (leaching) of the biomass with water or with dilute acids
2) Hydrothermal pre-treatment
3) Torwash
4) Charwash

The first two can be classified under pre-treatment; the third is an ‘in situ’ treatment and the fourth, a post treatment (not included in this report).

There are several factors that affect the choice of a pre-treatment technique. Some of them are listed below

- Type of biomass and its ash content, e.g. what straw, palm oil residue, switch grass
- Moisture content of biomass
- Availability of water for pre-treatment
- CAPEX and OPEX for pre-treatment
- Effectiveness of the technique for ash removal
- Improvements obtained in the quality of pyrolysis products (gas, oil, char)

K.2 Biomass Washing/Leaching

Leaching provides a technical solution to the use of biomass in the existing facilities without the need to incorporate new technology, such as gasifiers (which also benefit from the removal of alkali metals and halogens). Leaching has proven to be a very effective method for removing alkali metals and chlorine from biomass.

Fahmi et al. studied the effect of washing of switch grass and a low lignin grass (*Festuca arundinacea*) and showed that the washing step (at 25 °C for 2 h in de-ionised water) improved the quality of the pyrolysis gas. The relevant results are summarised as below:

Feed Analysis

	Switch grass		*Festuca arundinacea*	
	Before washing	After washing	Before washing	After washing
Elemental (%) C	44.77	47.14	42.22	45.2
H	5.79	6.08	5.64	5.98
N	0.31	0.07	1.5	0.87
O	49.13	46.71	50.65	47.95
Total Elemental	100	100	100	100
Al. Metal (ppm) Ca	6173	5409	4334	3209
K	717	78	24,026	1605
Mg	542	422	1136	757
Na	158	32	1346	47
Tot. Al. Metal (ppm)	7589	6945	35653	8436
Ash (%)	4.3	3.4	7.3	4.4

Product Mass Balance [Yields] (mf wt %)

	Switch grass		*Festuca arundinacea*	
	Before washing	After washing	Before washing	After washing
Char	24.7	20.2	33.8	19.9
Organics	51.5	55.2	30.8	41.7
Gas	7.9	10.54	15.4	21.6
Water in Feed	12.4	11.9	16.4	8.7
Closure (%)	96.5	97.8	96.5	91.9

TGA analysis on dry mass basis

Oil Analysis (mf wt %)

	Switch grass		*Festuca arundinacea*	
	Before washing	After washing	Before washing	After washing
HHV (MJ/Kg)	16.4	16	16.7	21.7
LHV(MJ/Kg)	14.8	14.5	14.5	19.7
Viscosity, cp @40 °C	34.2	33.3	10.9	13.5
Aged viscosity, cp @40 °C	57.6	52.1	12.8	18.3
Homogeneity	Single phase	Single phase	Phase separated [a]	Single phase

TGA analysis on dry mass basis

[a] Phase separation 3 months after analysis

Lee et al report similar results on the effect of washing (rice straw cut and soaked in a tank for 2 days, then dried at 60 °C) of the rice straw. The bio-oil yield was increased by ca. 7 %

after the washing step and it was attributed mainly to the reduction of K (from 25261 ppm to 12355 ppm). It was demonstrated that chlorides and potassium could be washed out at 50-60°C. It has been claimed that the energy losses caused by washing, drying and the leaching of organic matter make out approx. 8% of the calorific value of the straw.

Leaving the agricultural residue in the field to natural precipitation can also reduce the alkali metal content. It has been known for a long time that the straw that has been lying in the field and has been exposed to rain has a reduced content of corrosive matters, chlorides and potassium. This means that in comparison with the “yellow” straw, the “grey” one is more lenient to the boiler, since part of the matter that corrodes boiler wall and tubes has now been removed. Grey straw also has a somewhat higher calorific value than the yellow.

Davidsson et al. have used a surface ionisation technique to determine the effect of washing (with water and with 1M acetic acid) of wheat straw. The surface ionisation is a highly sensitive measurement technique to look at the release of alkali metals from the sample[5]. The technique also reveals the presence of two types of bonding of the metal compounds to the biomass structure – organically bound and inorganically bound metals - and the their effects on the washing efficiently. The results show there are two temperature regions, 300 – 400 °C and > 800 °C, where alkali metal ions are released. Washing is effective in reducing the inorganically bound metals (> 800 °C) very significantly (ca. 70 % by water washing and ca. 90 % by acid washing). The removal of the organically bound alkali metals stayed at ca. 30 % for water washing and ca. 70 % for the acid washing.

Turn et al reports (1997) that washing method suits better to herbaceous species (devoted energy crops) because the initial moisture content of the feedstock is very high (ca. 70%). The additional steps required in the feed preparation of such systems are a crushing and a leaching step before the regular milling step. The calculated incremental cost of the process was ca. 1.4 $ per tonne of the dry biomass.

The following section summarises the advantages and disadvantages of biomass washing strategies to reduce the alkali metal contents in the feedstock.

Pros:

- Reduction in S, N, O, K content of biomass. Leaching could mitigate the undesirable effects of biomass ash in thermal systems
- Increased generation of CO and other hydrocarbon gases because of the lower content of alkali metals in the biomass. Without increasing reaction temperature, the product gases can obtain higher caloric values, giving them greater potential for use in fuel applications.
- Higher scalability as no extra equipment except washing unit is required
- Applications where leaching can be integrated into an existing process might be beneficial and feasible (e.g. sugarcane bagasse).
- Wastewater containing inorganic nutrients like K, Cl, and S can be used in fertilizer preparation or for irrigation.

Cons:

- Treatment time
- Large quantities of water required for leaching
- Higher energy consumption

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[5] The sample is placed in a crucible and heated at a constant rate of 20°C/min. Vaporises compounds are transported by a N2 gas flow towards the surface ionisation detector (hot Pt filament at 1230 °C). The alkali compounds are decomposed at the Pt surface and K+ and Na+ ions are emitted and are detected. The ions are then differed to an ion collector and the current o the collector is measured by an electrometer.

- Reduction of conversion efficiency due to higher fuel moisture content

K.3 Pre-pyrolysis Followed by Washing/Leaching

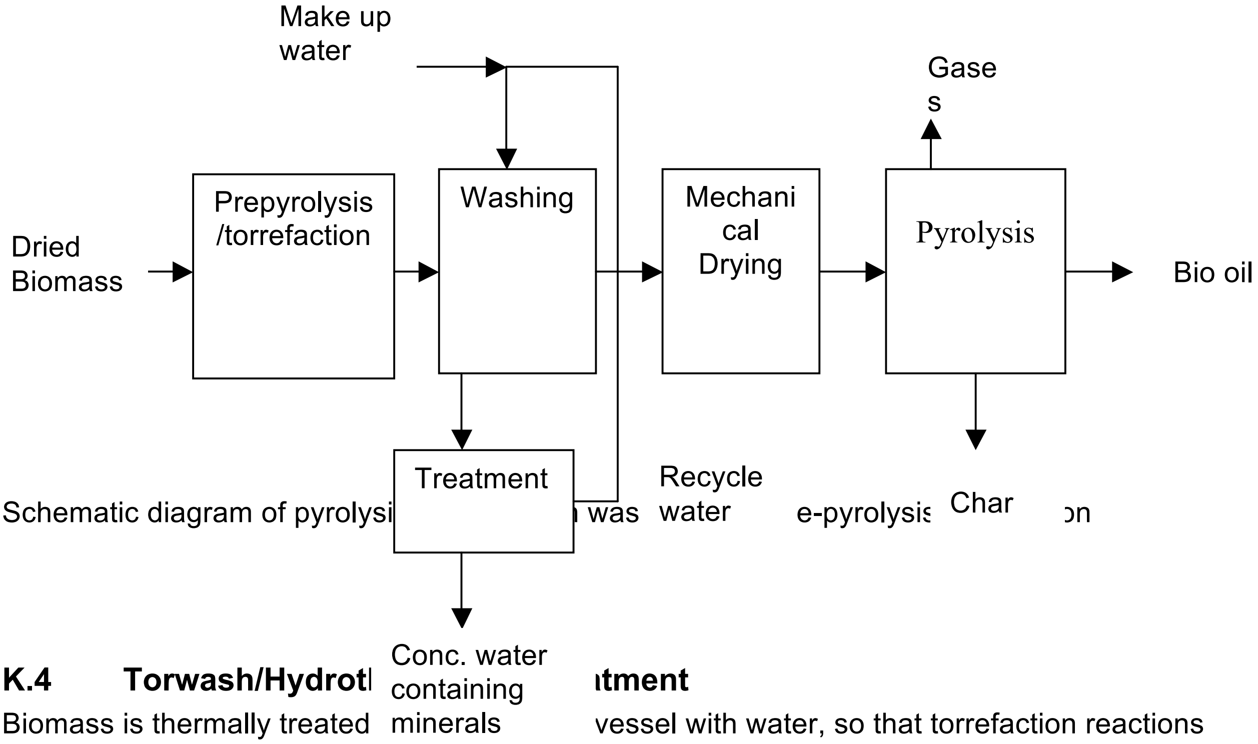
The pre-pyrolysis or partial pyrolysis provides a methodology aiming at the removal of the harmful ash constituents from the biomass, such as alkali metals, chlorine and sulphur, prior to its thermochemical conversion. The patent application, WO 2009/003920 (filed by Emmanouil Koukios), claims a pre-pyrolysis technology in which the biomass such as wheat straw and olive kernel were heated at 250 °C for 1 hr and were then leached by water for 4 hr at a solid/water ratio of 90 g/ yielding a low moisture content and hydrophobic material with reduced alkali metals and chlorine contents. This patent application, however, has a lot of commonalities with an earlier patent granted to FI-PRO Limited (EP 0588 833 B1). The patent claims a method of heating the biomass at ca. 200 °C to undergo partial pyrolysis and a subsequent washing to remove salts. The treatment removes chlorides almost completely. Alkali and sulphur removal efficiencies of, respectively, 50 - 70% and 45 - 65% were also achieved.

Pros:

- Easy drying of the hydrophobic biomass after pre-pyrolysis
- Wastewater containing inorganic nutrients like K, sulphates, carbonates can be used in fertilizer preparation or for irrigation.
- Complete removal of chlorides

Cons:

- Poor removal of K as compared to direct biomass leaching
- CAPEX intensive; pre-pyrolysis and washing means two additional units before the normal pyrolysis / torrefaction process



Schematic diagram of pyrolysi was e-pyrolysi on

K.4 Torwash/Hydrot tment

Biomass is thermally treated vessel with water, so that torrefaction reactions take place in liquid water at ture. The advantage is that the drying afterwards does not require thermal energy, but only mechanical energy. Drying before torrefaction is also not needed here. As the result of torrefaction, water is only physically bound and can be removed by mechanical means. Torwash is suitable for upgrading wet and fibrous biomass that cannot be dried by simply compressing it because the biomass is springy and water is mainly bound chemically and biologically. In Torwash, the torrefaction reactions release ions that immediately dissolve in water and are taken along when the water is removed mechanically. In this way, biomass can be converted into a fuel that is until now unattractive because of problems with corrosion and agglomeration due to the high salt/mineral content.

Pros:

- Removal of minerals during process
- Drying before torrefaction is not required.

Cons:

- Energy consumption in heating large quantities of water containing biomass at elevated T and P
- Scalability

Active Players: INBICON, ECN

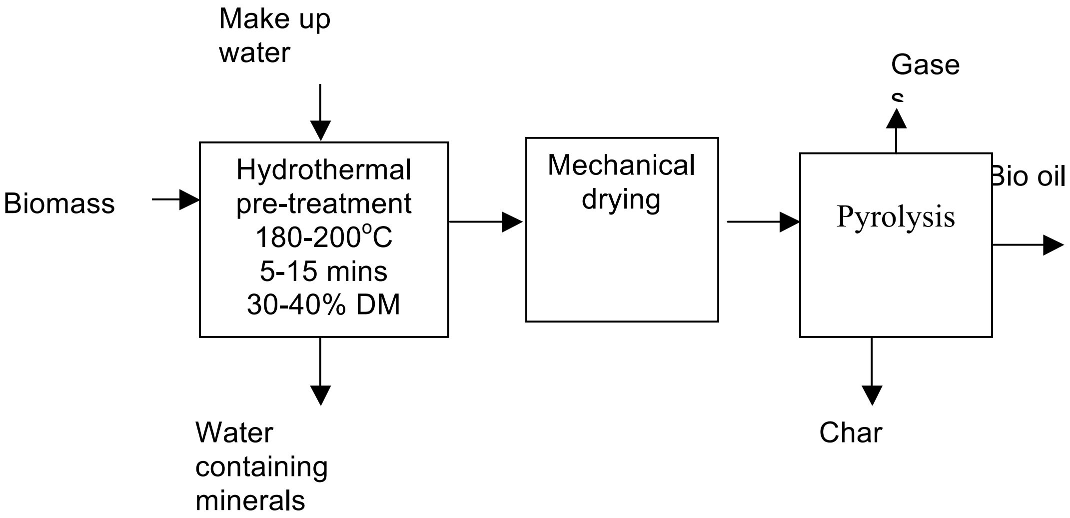


Figure 4: Schematic diagram of pyrolysis process with hydrothermal pre-treatment

K.5 Concluding Remarks

Washing methods are simple techniques for reducing K, Na and Chlorides from crushed biomass. The machinery and scaling up issues are well established. Washing/leaching of the biomass is a better method for the removal of alkali metal compounds from a nutrient recycling point of view. For energy crops containing high amount (ca. 70wt %) of initial moisture content, washing and drying steps impart relatively smaller additional energy load. The main disadvantages of washing process are its water consumption and cost of drying. This holds especially true for feedstock such as wheat and rice straw, agricultural wastes available with relatively low moisture contents (< 10 wt %). In such cases, washing will increase the moisture content to higher levels (> 75 wt %) and “re-drying” is not a right strategy from an energy efficiency point of view. Leaching is known to reduce Na, K and Cl, but not other metal compounds. This means we need to know what all elements and in what quantities need to be removed before proceeding to the densification process.

Avenues for integrating of washing and drying steps in the post-harvest operations (until the energy densification step) are to be looked at.
If the preferred choice of energy densification is torrefaction, it makes sense to adopt technologies such as torwash, which couples washings with the rest of the process. The maturity of the process and scale up issues are largely unknown.
On the other hand, if the preferred densification process is pyrolysis, then washing is an option to consider.
It is important to note that the techniques reported in the literature are mainly for wheat and rice straw. The suitability of these processes (especially washing) for palm oil residue (empty fruit bunch and fronds) needs to be found out.

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Appendix L. De-oiling techniques for water

L.1 Introduction

An overview of the various techniques used in the de-oiling of water is given in attachment 3. In general, the first step in the water treatment process is when the water is passed through a weir and the phase separated oil overflows. Note that in the beginning of the oil production, the fluid is almost 100 % oil and by the end of the lifetime, it becomes almost 100 % water. This means the design of the water treatment unit takes care of extreme situations. Skimmer or a plate interceptor is a basic unit at the first stage. The unit is essentially a tank where the oil droplets coalesce at the oil/water interface and overflow. In plate pack interceptors, the use of parallel or corrugated plates allows droplets to coalesce easily by hitting on the same. This unit can separate 100 % droplets above 150 μm, dependent on the specific gravity and temperature. The technology is well established. A case study from NATCO is given in the reference as an attachment (1). In the case of plate interceptors, for droplets with size larger than 35-40 µm, complete removal is reported. A useful SPE paper on oil-water separation using Performax® coalescer (NATCO) is attached as attachment 2.

L.2 Hydrocyclones

Since the skimmer technique depends on the normal coalescence of oil, there are limitations. If the feed has a significant amount of oil phase in the form of small droplets (in the order of 10 μm or less), efficient removal by a skimmer becomes difficult. Some of the strategies to deal with these systems are to install chemical coalescing agents, membranes, media filers, hydrocyclones or centrifuges. In these cases, energy efficiency, cost and maturity of the technology become important. Hydrocyclones are very popular in oil removal from production water. They achieve good separations of oil droplets with sizes greater than 15-30 μm. Centrifuges typically remove droplets over 3 μm with good efficiency.

The hydrocyclone for de-oiling of water was developed in 1980 by Colman and Thew. Hydrocyclones enhance the separation of *insoluble* oil droplets by achieving movement of the same in the continuous water medium. This movement is given by Stoke's law as given by

$$v_s = \frac{g(\rho_c - \rho_d)D^2}{18\mu} \tag{1}$$

where, v_s is the terminal velocity achieved by the oil drop travelling to coalesce, g is the acceleration field created by the flow (vortex flow in a hydrocyclone), ρ_c and ρ_d are, respectively, the densities of the continuous (water) and dispersed (oil) phases, D is the diameter of the drop and μ is the viscosity of the continuous phase. The main action of the apparatus is to achieve high centrifugal acceleration (g) to the produced water (to be de-oiled). The multiphase feed is fed tangentially at a high velocity into the upper swirl chamber, which causes the flow to spin in a vortex flow pattern. The vortex creates a high acceleration pattern (2000-3000 g for de-oiling hydrocyclones) that forces the oil to migrate to the center of the cyclone. The heavier phase in the primary vortex flows out through the underflow and lighter (at the center) reverses direction and leaver through the overflow.

From equation 1, it can be seen that velocity or the rate of coalescence heavily depends on the diameter of the droplets. Now, any idea that makes the diameter of the drop to grow will in turn makes the velocity faster and the drop reaches the oil core before being carried out with the water in the underflow. The fact is well captured in the figure given below, where the removal efficiency of the oil droplets is plotted against the droplet size.

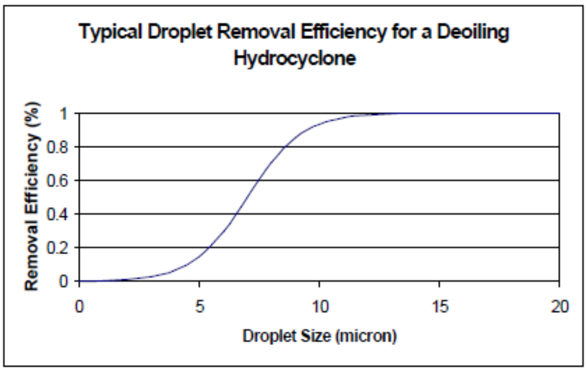

Fig 2 – Typical Deoiling Hydrocyclone Cut Size Curve

L.3 Enhancement of hydrocyclone performance

Looking at the relation (Eq. 1) and the graph, it can be seen that even a small change in oil drop size can potentially improve the recovery. One strategy to achieve bigger drop size of the dispersed oil phase is by passing through a hydrophobic media (such as array of fibers made of hydrophobic materials - polypropylene, polyurethane). The improved coalescence process happens in the following steps

1) **Droplet Contact**: The oil dispersed in water is passed through a hydrophobic (oleophilic) media of a suitable form (fiber, particles, foam) offering (necessary) resistance to the flow.
2) **Droplet capture:** The force of adhesion binds the smaller oil droplets to the media
3) **Droplet growth:** Coalescence of small oil droplets on the surface of the media; media progressively retaining more and more oils
4) **Droplet disengagement**: Bigger drops getting stripped off from the media

The feed will now have oil droplets with enriched drop sizes that can be fed to a hydrocyclone for the oil water removal.

In the second page of the attachment 3, we have listed some process intensification techniques based on this phenomena. Three such techniques are selected for further analysis. They are

Mare's tail (Opus Plus Inc.)
Torr (ProSep Inc.)
PECT-F (Cyclotech Ltd)

A comparison between three technologies is given in attachment 4.

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