ABSTRACT

This research addressed the separation and concentration of organics from the product mixture obtained during the Oxidative Hydrothermal Dissolution (OHD) process. The product mixture consists predominantly of water with small amounts of dissolved organics and inorganics from coal. This process solubilizes coal to produce low-molecular weight organic acids such as benzene, di, tri and tetra carboxylic acids, and aliphatic carboxylic acids etc., which are widely used as chemical feedstock. These chemicals present in the product aqueous stream may prove to have a significant impact in chemicals industry if they are successfully and selectively concentrated and isolated. There is little information on the separation of the products and their low concentration has been proven to be a challenge.

The innovative process design combined reverse osmosis and electrodialysis for the effective separation of pure water, inorganic salts and organic acids as three different fractions. The overarching goal of this research was to evaluate the effect of process variables on the separation of OHD products and the feasibility of the process for the aforementioned separation. The specific objectives were a) to evaluate the effect of process variables and feed composition on reverse osmosis separation efficiency, b) to evaluate the effect of process variables and feed composition on electrodialysis process efficiency, c) to integrate the two processes and develop engineering data to optimize the two processes working in tandem to separate the products of OHD and d) to design the overall separation process capable of processing 1 gallon a day output from the OHD process. The results showed that the use of reverse osmosis with commercially available components was effective in concentrating single and multicomponent solutions by removing pure water at permeate flow rates of 1 L/min. In addition, tests with OHD liquor were also successful. The ED system tests showed that single components and multi-component systems could be separated and fractionated using the differences in the ionic mobilities. A process design that would be readily integrated into the OHD process was also developed.
EXECUTIVE SUMMARY

This research addressed the critical issue of the separation and concentration of organics from the products obtained during the Oxidative Hydrothermal Dissolution (OHD) of coal. The OHD product consists predominantly of water with small amounts of dissolved organics and inorganics from coal. OHD process solubilizes coal to produce low-molecular weight organic acids such as benzene, di, tri and tetra carboxylic acids, and aliphatic carboxylic acids etc., which are widely used as chemical feedstocks. These chemicals present in the product aqueous stream may prove to have a significant impact in chemicals industry if they are successfully and selectively concentrated and isolated. There is little information on the separation of the products and their low concentration has been proven to be a challenge. One of the possible processes for the recovery of water and the concentration of the products is flash evaporation. While seemingly a feasible option, flash evaporation may lead to the loss of valuable products and the water itself may not be clean enough for reuse. In the completed research, two mature technologies - reverse osmosis and electrodialysis - were used in tandem for the separation of water, organics and inorganics. The organics were concentrated and high purity water was recovered using reverse osmosis. However, the presence of organics and inorganics limited the degree of concentration to reduce the fouling of the membranes. Thus, electrodialysis was used to separate the salts and the organic fractions.

Hydrothermal treatment with and without hydrogen have been reported for some time. Hydrothermal treatment in the presence of an oxidizing agent that results in liquefaction is referred to as the Oxidative Hydrothermal Dissolution. However all these studies focused on the production of acetic acid although some researchers (not reported here) have also evaluated the production of lactic acids. Kinney and Friedman and Frank and his co-workers demonstrated that polycarboxylic acids could be produced by the oxidation of coal. The research by Frank et al showed that the coal could be solubilized by hydrogen peroxide or by gaseous oxygen at 270 °C and 900 psig. Roughly one third of the products obtained were water soluble aromatic carboxylic acids. Oxidative Hydrothermal Dissolution or OHD was coined by SIUC researchers Drs. Anderson and Crelling, who developed the novel continuous coal conversion technology with support from the Illinois Clean Coal Institute. This process has opened new avenues for coal utilization beyond the power and transportation sectors and can now be seen as a clean and relatively abundant replacement for petroleum-derived raw chemical feedstocks. The product is an aqueous solution containing low-molecular weight organic acids(acetic acid, polycarboxylic acids, hydroxylated and methoxylated benzoic acids, benzene di- tri- and tetra carboxylic acids, hydroxylated or methoxylated coumaric acid, aliphatic keto-acids and aliphatic dicarboxylic acids), which are widely used as useful chemical precursors and are biodegradable. One key bottleneck for the commercialization of the process is the separation and isolation of inorganics/water/organics. That was the focus of this research which was be conducted with simulated solutions using single, dual and multiple species to understand the separation mechanism and evaluation of separation performance as well as with OHD liquor.

In summary, this research resulted in a hybrid approach for the separation and concentration of organics from product mixture from the Oxidative Hydrothermal
Dissolution (OHD) process. The ultimate outcome of the project was a process design that would be readily integrated into the OHD process. In the project, two mature technologies – reverse osmosis and electrodialysis - were used for the separation of water, organics and inorganics. High purity water was recovered using reverse osmosis while electrodialysis removed the inorganics and thereby produced a concentrated stream of organics while keeping the osmotic pressure relatively low. Since the exact nature and composition of the organics in the OHD product stream is unknown, it was difficult to predict and design an exact process. What is known is that the product stream is an aqueous solution containing low-molecular weight organic acids (acetic acid, polycarboxylic acids, hydroxylated and methoxylated benzoic acids, benzene di- tri- and tetra carboxylic acids, hydroxylated or methoxylated coumaric acid, aliphatic keto-acids and aliphatic dicarboxylic acids depending on the source of the feed to the OHD. The PI evaluated low concentrations (<0.01 – 5 wt. %) of representative organic compounds in each class compounds and total inorganics (comprising of the chlorides of aluminum, calcium, magnesium and sodium at a total loading of less than 10 % of total organics) for reverse osmosis experiments. Similarly, the PI used similar organic and inorganic constituents but at levels that are concentrated at least 10 to 20 times as the feed to the RO unit to conduct the electrodialysis experiments. Once a good fundamental understanding of the process variables for each kind of aqueous solution was obtained, the two processes were integrated and experiments were run in tandem to evaluate the process variables to maximize yields, recoveries and selectivities. As can be seen from the discussion, the research itself is innovative even though the technologies have been quite well developed for other purposes. Owing to the technical risk inherent in the development of any novel scheme, this research was mainly conducted to provide data on the laboratory based separation performance of individual units as well as the integrated unit and use the data to design the RO and ED units for different scales. A follow up collaboration with Thermaquatica Inc. to obtain actual OHD samples was initiated and the feasibility for the OHD process was partially demonstrated.
OBJECTIVES

The overarching goal of this proposed research was to evaluate the effect of process variables on the separation of OHD products and the feasibility of the process for the aforementioned separation. The ultimate outcome of the project was the development of a process design that would be readily integrated into the OHD process. The specific objectives were a) to evaluate the effect of process variables and feed composition on reverse osmosis separation efficiency, b) to evaluate the effect of process variables and feed composition on electrodialysis process efficiency, c) to integrate the two processes and develop engineering data to optimize the two processes working in tandem to separate the products of OHD and d) to design the overall separation process capable of processing 1 gallon a day output from the OHD process. These objectives were achieved by conducting the following tasks.

Task 1. Materials Acquisition.

Chemicals were acquired. New chemicals were acquired based on consultations with Thermaquatica. The reverse osmosis system components were purchased and set up. A 5 cell electrodialysis system was purchased. Additional membranes were purchased from other vendors.

Task 2. Reverse Osmosis.

Single component systems were evaluated. The salt rejection, permeate flow rates and solvent recovery were found to be favorable. The rejected water was very pure with little or no dissolved ions. Multi stage, single pass operation was compared with the single stage system with recycle. In general it was observed that the chosen membrane allowed ~1 L/min of permeate at 150 psig irrespective of the mode of operation. Nonetheless, the size of the RO system with recycle is expected to have a smaller footprint. Based on the current data, it was seen that at a recycle ratio of 1, the single stage with recycle would have a six times lower footprint as compared to that of the single pass, multistage system. In addition, it was estimated that the solvent recovery would be higher for the same sized modules. Finally some OHD liquors were also processed successfully.

Task 3. Electrodialysis.

Single solute, dual solute and multi-solute systems were evaluated. It was observed that the electrodialysis can separate solutes based on their mobility in the membranes and applied charge. Very low power consumption was observed. It was also found the use of methanol on the concentrate side is also feasible.

Task 4. Integrated Reverse Osmosis/Electrodialysis System.

A two solute system was evaluated in which the solution was first concentrated using reverse osmosis and then separated using electrodialysis. Although the process was observed to be feasible, it was found that the feed concentration is of great importance to the efficacy of the electrodialysis system. Thus careful evaluation of the effect of
Task 5. Scaled up Design of the Hybrid Process.

A scaled up design for accommodating 1000 gal/hr was designed.

INTRODUCTION AND BACKGROUND

Hydrothermal chemistry is basically the reactions taking place in the presence of aqueous medium under high pressures and temperatures. Hydrothermal processing can be divided into three main regions, liquefaction, catalytic gasification, and high-temperature gasification, depending on the processing temperature and pressure. Hydrothermal conversion via liquefaction pathways occurs generally between about 200 and 370 °C, with pressures between about 4 and 20 MPa, sufficient to keep the water in a liquid state. At near-critical temperatures up to about 500 °C, effective reforming and gasification generally requires catalytic enhancement to achieve reasonable rates and selectivity. At higher temperatures above 500 °C, homogeneous gasification and thermolysis often occur. Such reactions have a prominent place in the formation of fossil fuels. Fossil fuels have been the key driver for the industrial revolution and the rapid economic and technological growth seen since the 1700s. However, fossil fuels are deemed non-renewable due to the long time it requires for its formation. Nonetheless, in the near term, fossil fuels will continue to play a prominent role in both the developed and developing countries. Unabated and inefficient use of these resources will definitely render the growth unsustainable not only due to the rapid depletion of the said resources but also due to the release of pollutants into the air and water necessary for human life. In order to place fossil fuels like coal as a part of the sustainable development, one needs to reduce emissions from their usage by pre and post utility treatments and extend its availability by improving efficiency. Even though coal has a dominant (over 50 %) share in the electricity market, it is deemed “too dirty”. Thus for a fossil fuel like coal to be a part of the sustainable future, new processes like the oxidative hydrothermal dissolution (OHD) patented by Drs. Anderson and Crelling finds niche areas for the use of coal.

OHD process solubilizes the entire coal – both the organics and inorganics - to produce water soluble products including simple acids such as acetic acid, polycarboxylic acids, hydroxylated and methoxylated benzoic acids, benzene di- tri- and tetra carboxylic acids, hydroxylated or methoxylated coumaric acid, aliphatic keto-acids and aliphatic dicarboxylic acids, etc., that could be used to sustain the need for important chemicals. Organic acids include carboxylic acids, phenols, sulfonic acids, mercapto-compounds, and phosphonic acids. They have been widely used in a variety of human activity and consumption including foods, beverages, pharmaceuticals, cosmetics, detergents, plastics, resins, and other biochemical or chemical products. The primary aim of this proposed research is the separation of organic fraction from OHD of coal, namely acetic acid, polycarboxylic acids, hydroxylated and methoxylated benzoic acids, benzene di- tri- and tetra carboxylic acids, hydroxylated or methoxylated coumaric acid, aliphatic keto-acids, and aliphatic dicarboxylic acids. The following just shows the wide impact acetic acid – one of the carboxylic acids produced by OHD- has in our daily lives. Today acetic acid
acetic acid is one of the most important industrial organic acids and is consumed worldwide, with the US share being nearly 50%. The global demand of acetic acid is around 6.5 million tonnes per year (Mt/a), of which approximately 5Mt/a manufactured from petrochemical feedstock or from biological sources. The primary product from acetic acid is vinyl acetate monomer that is polymerized to PVAc for end uses such as for vinyl plastics, adhesives, textile finishes and latex paints. In addition a significant portion of the acetic acid production is supplied for acetic anhydride (for cellulose acetate and pharmaceuticals and plasticizers production and ester industries) and ester production. In households diluted acetic acid is often used in descaling agents. In the food industry acetic acid is used under the food additive as an acidity regulator. Thus, OHD technology has poised coal to compete with petrochemical feedstock for this chemicals market. The EIA outlook shows that in the near terms coal demand in the power sector will increase. Similar sentiments are also shared by energy companies such as ExxonMobil. However, these sources also forecast that after this initial increase in coal demand, it will see a gradual decline with natural gas steadily gaining power sector market share from coal. New technologies may come and reverse the economic and environmental reality that was used to make these forecasts. Nonetheless, having alternatives that would act as hedges ensuring the future of coal would be a prudent choice. It is in this future that OHD has a very vital role. An inexpensive and green technology that can produce chemical precursors from coal would allow coal to compete in markets where petrochemical feedstock had the monopoly.

One key issue for the deployment of OHD technology is the use of high amounts of water, resulting in very dilute products and the loss of significant amount of fresh water if it is not properly recovered. In addition, it is expected that some dissolved inorganics may also be present. One of the possible processes for the recovery of water and the concentration of the products is flash evaporation. While seemingly a feasible option, flash evaporation may lead to the loss of valuable products and the water itself may not be clean enough for reuse.

The primary goal of this research was the separation of polycarboxylic acids from the OHD product stream. The carboxyl functional group that characterizes the carboxylic acids is unusual in that it is composed of two functional groups; the carboxyl group is made up of a hydroxyl group bonded to a carbonyl group. It is often written in condensed form as \(-\text{CO}_2\text{H}\) or \(-\text{COOH}\). No matter their source, they require concentration and separation. Traditional techniques include precipitation and acidification, solvent extraction, crystallization, distillation, ion-exchange, and adsorption. However, it becomes difficult for them to meet the requirements of modern chemistry, which is characterized by “design for the environment” and “green chemistry”. In addition to the pressures of green technology and sustainability, there are issues with dilute streams such as those found in OHD products. Precipitation and acidification are have serious issues with sludge disposal—\(\text{CaSO}_4\) sludge. Solvent extraction has to overcome the hurdle of undesirable distribution coefficients, in addition to the safe disposal spent hazardous solvents. Thus, many researchers following this technique have resorted to an advancement of the technique called “reactive extraction”. Reactive extraction reduces the need for solvent but only to a certain degree. High costs due to chemical usage, meeting waste discharge criteria and most importantly, low yield, renders crystallization
unfavorable for this purpose. Distillation is uncompetitive due to high-energy consumption and in some cases will cause the use of thermal energy results in product transformation, such as the polymerization of lactic acid. As for ion-exchange, a significant amount of acid, base and water are needed to regenerate the ion-exchange resins. Furthermore, salt formation cannot be avoided because the acid’s anion and the base’s cation have no other outlets. Adsorption has issues such as short lifetime of adsorbents, low capacity and additional filtration. Finally, none of the above techniques would prove economical for low concentration streams. Thus, the techniques that could compete economically and provide high and selective recoveries, low waste generation and low energy consumption is needed.

Membrane technologies have been proving their advance in the fields of separation and purification. Figure 1 shows schematics of two types of membrane processes considered in this research – pressure driven and electric field driven. As seen in the Figure, reverse osmosis (RO) is a pressure driven process with the highest separation efficiency of the smallest molecules. RO is independent of the charge on the species in most cases. On the other hand, electrodialysis (ED), being electric field driven, is strongly related to the charge on the species. Both RO and ED are membrane technologies that have attracted much attention from the academia and industry due to its diversity, sophisticated functions, and technological compatibility. When it comes to the separation and production of organic acids, either RO or ED may be a competitive technology. ED has its advantages because of its predominance in simultaneous supply of H\(^+\) and OH\(^-\)/alkoxide ions without salt introduction or discharge, salt conversion, technological symbiosis, and resource utilization. However, at low concentrations, ED would require a significantly large stack. In addition, the issue of water recovery from the OHD product stream would remain. RO could separate relatively pure water for reuse while increasing the concentration for ED. RO has its advantages at low osmotic pressures if it were to be used alone. However, the process would just recover pure water. If the retentate was recycled, it would keep increasing the concentration of the ions in the feed. The rapid increase in osmotic pressure will quickly exceed the feasible limits of pressure in a practical system. ED would however aid in the removal of the electrolytes and thus increase the useful life of RO. Thus, neither would compete well by itself in the current scenario. However, together, ED and RO would prove to be an extremely competitive technology for the extraction of polycarboxylic acids from OHD product stream. The following describe each process in more details.

Reverse osmosis\(^1\) (RO) is used on large scale desalination of seawater for human consumption. RO has also been shown to be an effective method for retention and concentration of DOM from fresh waters. Essentially RO is a deionization technique. A significant fraction\(^2\) (on the order of 90% or more) of organic fractions from OHD may be recovered by RO with little physical or chemical alteration. Unfortunately, RO membranes also very effectively retain and concentrate the salts and minerals, so any attempt to simply apply RO directly to a given aqueous mixture of inorganics and organics could lead to rapid co-concentration of both organic components and inorganic salts in the feed side as nearly pure water is removed by RO. The rapid increase in osmotic pressure will quickly exceed the feasible limits of pressure in a practical system. Electrodialysis (ED) is a well-established method for removal of electrolytes from
aqueous solutions. ED and RO have been used together to remove inorganic ions and concentrate dissolved organic carbon/matter from freshwaters resulting in extremely pure dissolved organic matter samples with constituents including carboxyl-rich alicyclic molecules, hetero polysaccharides, and aromatic compounds.

Figure 1: Schematic illustration of pressure driven and electric field driven membrane processes.

A process combining ED and RO has also been investigated some time ago with the goal of efficient seawater desalination, but not with the target of recovery and concentration of DOM from seawater. This combination may prove to be useful for the recovery of organics and the separation of water (for reuse) and inorganics from the OHD product stream. Figure 2 shows the simplistic schematic of the original process.

Figure 2: Simplistic Schematic of the Original Process Flow Diagram.
REVERSE OSMOSIS: Osmosis is the phenomenon in which water from dilute salt solution moves to a concentrated salt solution through a semi-permeable membrane. Thus, in this case, the membrane is selective to water and not the salt. As a result of this movement of water, the height of concentrated solution may rise, resulting in a height difference between the dilute and concentrated solution. As it rises, the concentrated solution may reach a height at which the pressure exerted by the column of fluid may be high enough to prevent the further flow of water through the semi-permeable membrane. The pressure exerted by this column is called the osmotic pressure. So if one was to exert a pressure higher than this osmotic pressure on the concentrated solution, water could then move across the same semi-permeable membrane to the dilute solution. It should be noted here that since it is the same semi-permeable membrane, salt would not permeate through although water would. Thus reverse osmosis works at typically high pressures. Figure 3 shows a reverse osmosis module and its principle.

The permeate flux and salt rejection are the two key performance metrics for reverse osmosis. From an economic standpoint, recovery and feed flow rates are also important criteria. The permeate flux and salt rejection are dependent on parameters such as pressure, temperature, recovery and feed salt concentration. Table 1 shows the relative effects of each of these parameters on the two performance criteria.

Figure 3. Reverse Osmosis Process.
Table 1. Factors affecting Reverse Osmosis Performance.

<table>
<thead>
<tr>
<th></th>
<th>Permeate Flux</th>
<th>Salt Rejection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Temperature</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Recovery</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Feed Salt Concentration</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

ELECTRODIALYSIS: Electrodialysis differs from pressure-driven membrane processes by using an electric potential gradient to drive the material separation. This type of separation is useful only in cases targeted towards the separation of charged particles. In the case of electrodialysis wherein ionic species – cations and anions- are separated, the use of a porous permeable membrane is sufficient for the separation and concentration of the species in each chamber. However, the possibilities are expanded if ion-exchange membranes such as a cation exchange membrane and an anion exchange membrane are used. The ion exchange membranes prevent the ions to migrate to the electrodes thereby preventing any electrochemical reactions. Now the process can be used to concentrate process streams, separate ionic species from non-ionic species, or recover or extract charged solutes from waste streams. In the past century, ED kept evolving and improving to meet new demands. At the present, this ED family comprises conventional electrodialysis (CED), electrometathesis (EMT), electrophotone substitution (EIS), electrophotone injection-extraction (EIIE), electrophotone-electrodialysis (EED), electrohydrolysis with bipolar membranes (EDBM), electrodeionization (EDI), and two-phase electrodialysis (TPED\textsuperscript{19-22}). Each of these processes can be adapted for the recovery of organic acids.

No matter what method is used, there are four basic elements to electrodialysis process, namely, direct current supply, electrodes (cathode and anode), ion exchange membranes (anion exchange, cation exchange and bipolar) and electrolyte. Figures 4a and 4b show the two options to demineralize or concentrate organic acids. The efficiency of demineralization or concentration mainly depends on the counter ion competence which increases the ion quantity and mobility. When one is trying to demineralize, it is better to acidify such that the organic anions can exist in the form of acid molecules and stay in the feed while the inorganic anions migrate across the membrane. In the case of concentrating the organic acids and salts, the opposite measures can be taken to improve the efficiency. For separation of the organic acid mixtures, the differences in ionization degree, ion mobility, molar concentration and molecular dimensions should be considered. The process parameters of concern are the current density and cell resistance while the process metrics are separation efficiency, yields and run time before electrodialysis reversal (EDR) is applied to descale the membranes. Even though conventional ED is the first priority to demineralize the organic acids, electroelectrodialysis (EED) with the help of low amounts of organic solvents may be used as an alternate if conventional technique has issues of implementation in the research.
Figure 4: Conventional Electrodialysis for (a) Demineralization or (b) concentration of organic acids or salts. MX: organic acid or salt, NY: inorganic salt, z: inert substance or low concentration inorganic salt.
EXPERIMENTAL PROCEDURES

This research will address the hybrid approach for the separation and concentration of organics from product mixture produced by the Oxidative Hydrothermal Dissolution (OHD) process of coal. The use of the hybrid process will produce three different streams — water, organics and inorganics. The overarching goal of this proposed research is to evaluate the effect of process variables on the separation of OHD products and the feasibility of the process for the aforementioned separation. The ultimate outcome of the project would be an OHD product separation process design that would be readily integrated into the OHD process. The project expected outcomes were that the organics will be concentrated to over 90% with less than 1% inorganics along with over 90% water recovery. This was achieved by this five task project. The approach and sequencing of the five tasks are shown in Figure 5.

![Figure 5. Schematic of the Research Approach.](image)

MATERIALS: Acetic acid and representative organic compounds in the following classes, polycarboxylic acids, hydroxylated and methoxylated benzoic acids, benzene di-tri- and tetra carboxylic acids, hydroxylated or methoxylated coumaric acid, aliphatic keto-acids and aliphatic dicarboxylic acids, were obtained. Inorganic salts of aluminum, calcium, magnesium and sodium were purchased. The chemicals are listed in Table 2. In consultation with Dr. Anderson, specific chemicals such as parahydroxybenzoic acid and vanillic acid were also purchased. RO system membrane, pressure vessel, pump, and motor were acquired. All accessories for the RO system were also acquired. The parts (Figure 6) were acquired from MidwestRO while the accessories were obtained from McMaster Carr. A 5 cell ED system was obtained from PcCell, GMBH (Figure 7). The
ion exchange membranes were obtained from Selemion, PcCell and Neosepta. However, the exact membranes used are not disclosed herein.

REVERSE OSMOSIS: The acquired RO components were integrated. The 0.5 hp pump was used to supply the pressure and recirculation flow for RO. All tubing and fittings for the RO system were made of stainless steel. The feed-side pressure tested for RO was in the range of 0–225 PSIG. The specific conductivity of the permeate was measured. Evaluation of low concentrations (<0.01 – 5 wt. %) of representative organic compounds in each class compounds and total in organics (comprising of the chlorides of aluminum, calcium, magnesium and sodium at a total loading of less than 10 % of total organics) was planned. The effect of feed concentration, pressure, and recovery on the permeate flux and salt rejection was evaluated. The final concentration of the dissolved material in the retentate was measured with the help of Dr. Ken Anderson. Experiments were also conducted on actual OHD liquor the design of the concentrator section was modified. Single pass RO performance was compared to recycle mode.

Table 2. Chemicals tested.

<table>
<thead>
<tr>
<th>Chemicals Tested</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic Acid</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Hexanoic Acid</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Terephthalic Acid</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Trimesic Acid</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Calcium Chloride</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Iron Chloride</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Sodium Sulfate</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Methoxybenzoic Acid</td>
<td>Alfa-Aesar</td>
</tr>
<tr>
<td>Hydroxycinnamic Acid</td>
<td>Alfa-Aesar</td>
</tr>
</tbody>
</table>

Figure 6. RO components a) vessel, b) membrane, c) pump, d) motor.
ELECTRODIALYSIS: Strongly basic anion exchange membrane sets and a strongly acidic cation exchange membrane sets with low resistivity were acquired. A two chamber electrodialysis cell equipped with a rectifier, centrifugal pump (seal less), and continuous data acquisition for temperatures, flowrates, pH, specific conductivities, tank levels, and electrodialysis current and voltage was purchased from PCCELL (PCCell GmbH, Heusweiler, Germany). 5 cell stacks were used in this study. The membrane sizes used were 110 mm X 110 mm. The active membrane area was 64 cm$^2$/ membrane. The processing length of the cell is 80 mm and the cell thickness is 0.5 mm. Up to 20 cell pairs can be used in this system. The anode to be used is a Pt/Ir coated titanium while the cathode is a V4A steel. The electrodes are housed in a propylene chamber. In the event of membrane clogging, electrodialysis reversal can be employed in this system. Electrodialysis experiments will be performed under constant current density conditions (i.e. the voltage will be monitored and recorded). Steps will be taken to ensure that neither the limiting current density nor the maximum voltage per cell are exceeded or even approached. The limiting current density is a function of the conductivity and thus the composition of the feed. The effects of feed conditions and applied current density on the separation efficiency (organics recovery, organics concentration) were evaluated.

The two processes were integrated. The feasibility of the hybrid process was demonstrated using synthetic solutions. The effect of process parameters and feed conditions on the integrated setup was planned. In addition, the sequencing of the ED and RO units was also planned. The aim is to be able to operate at least 1 gallon per min feed rate such that the organics will be concentrated to over 90% with less than 1% inorganics along with over 90% water recovery. Finally, the hybrid system design was scaled for 1000 gallon per hour feed flow rates. The data from the integrated system studies was used for the overall design. A preliminary cost estimate calculations were also performed.

DATA ANALYSIS: Most of the data was analyzed based on the conductivity. The instrument was calibrated for various single component systems. The evaluation was conducted in both water and methanol as solvents. As a check, some dual component systems were analyzed to evaluate if the conductivity was simply an additive function of individual components. Permeate flow and retentate flows were measured by the use of a

**Figure 7.** Electrodialysis system: left) Bench Electrodialysis Pump Unit (with Accessories), right) ED Cell Unit
measuring cylinder and a stopwatch. Assuming steady state flow, the feed flow rate was reconstituted. Salt rejection was calculated by the following

\[
Salt \ Rejection = \frac{\text{Retentate Flowrate} \times \text{Salt Concentration}_{\text{retentate}}}{\text{Feed Flowrate} \times \text{Salt Concentration}_{\text{feed}}}
\]

RESULTS AND DISCUSSION

Since one of the major measurement tools was conductivity, the calibration curves of various single solute concentrations as a function of conductivity are shown in Figure 8 on the following page. The calibration curves are clearly found to be non-linear. Therefore several linear segments were utilized for data reduction. However, the best fitting curves are provided in this report. Table 3 contains the summary of the best fitting non-linear equations for the various solutes studied. As mentioned earlier, the RO and ED systems were evaluated separately. The RO studies are discussed first.

Table 3. Summary of concentration – conductivity relations.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Sodium Chloride</th>
<th>Trimesic Acid</th>
<th>Benzoic Acid</th>
<th>3,5 Dihydroxybenzoic Acid</th>
<th>Parahydroxybenzoic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0.1362 \times x^{1.0094})</td>
<td>(1.5 \times 10^{-3} \times x^{2.004})</td>
<td>(1.284 \times 10^{-6} \times x^{3.387})</td>
<td>(1.227 \times 10^{-5} \times x^{1.086})</td>
<td>(3.623 \times 10^{-4} \times x^{2.346})</td>
</tr>
<tr>
<td>R^2</td>
<td>0.999</td>
<td>0.999</td>
<td>0.991</td>
<td>0.999</td>
<td>0.994</td>
</tr>
</tbody>
</table>

REVERSE OSMOSIS: Preliminary experiments were conducted to test the permeate rate. This was necessary to maximize the volume of water recovered. The initial tests show that the water is permeating the membrane at a satisfactory rate (>900 mL/min) under current conditions (200 psi feed pressure), indicating there is no current need for a higher pressure system. Table 4 contains the data on the results from these studies. Four stages were used wherein the retentate from a previous stage was fed to the subsequent stage.

Table 4. Tap Water experiments with RO.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Feed µS/cm</th>
<th>Permeate µS/cm</th>
<th>Retentate µS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage 1</td>
<td>246</td>
<td>8.7</td>
<td>377</td>
</tr>
<tr>
<td>Stage 2</td>
<td>377</td>
<td>4.1</td>
<td>549</td>
</tr>
<tr>
<td>Stage 3</td>
<td>549</td>
<td>5.8</td>
<td>693</td>
</tr>
<tr>
<td>Stage 4</td>
<td>693</td>
<td>9.3</td>
<td>938</td>
</tr>
</tbody>
</table>
The second set of tests with sodium chloride (feed – 4.9 g/L) was conducted to ensure good permeate flow and separation. Experiments were conducted at 0, 50, 100 and 150 psig. Negligible permeate flow was observed for experiments at 0 and 50 psig. The separation efficiency is evaluated during the test by evaluating the conductivity in the feed, retentate and permeate. The performance was evaluated by the conductivity changes in the streams. Negligible conductivity is observed in the permeate. Figure 9 shows the multistage RO tests. Figure 10 and 11 summarizes the findings of the NaCl tests at 100 psig and 150 psig. The solvent recovery was doubled when the feed pressure was increased from 100 to 150 psig. Nearly 100 % salt rejection was observed at every stage.
Figure 9. Multi Stage RO system. F-feed, P-permeate, R-retentate.

Figure 10. Performance of reverse osmosis of 4.9 g/L NaCl solution. Applied pressure = 100 psig.
Figure 11. Permeate Yield, Retentate Yield, Salt Rejection and Retentate concentrations for experiments with a starting feed of 4.9 g/L NaCl and 150 psi.

Tests were also successfully conducted with trimesic acid and benzoic acid. Figures 12 and 13 contain similar data as Figure 11 for these two compounds, respectively. Initial feed concentration for trimesic acid was 0.6 g/L and 0.15 g/L for benzoic acid tests. The system was maintained at 150 psi. Very high salt rejection (>95 %) and permeate recovery (>80 %) were obtained after six stages for the trimesic acid. The metrics for the benzoic acid was even better after only four stages.
Figure 12. Permeate Yield, Retentate Yield, Salt Rejection and Retentate concentrations for experiments with a starting feed of 0.6 g/L trimesic acid and 150 psi.

A follow up meeting was held after the midpoint presentation. The following suggestions were made by Thermaquatica in consultation with the ICCI:

- A new list of surrogate chemicals and identified.
- Vanillic and parahydroxybenzoic acids were identified as the vital compounds to be extracted.
- The use of esters of the component acids was suggested since they can be more easily separated downstream.
- The use of up to 2% acetic acid to improve component solubility.
- The main objective for the initial RO stages would be to completely remove water. This could be achieved by concentrating in the initial stages followed by dilution with methanol or butanol in subsequent RO stages to completely dehydrate the mixture.
- The initial studies were to be conducted using parahydroxy benzoate to determine the feasibility of this approach.
Figure 13. Permeate Yield, Retentate Yield, Salt Rejection and Retentate concentrations for experiments with a starting feed of 0.15 g/L benzoic acid and 150 psi.

Based on discussions, steps were taken to concentrate para-hydroxybenzoic acid followed by dilution with methanol to maximize the elimination of water. Two hydrometers were purchased and the concentration of methanol in water vs the density calibration was performed (Figure 14). The calibration curve correlated well with the literature available values.
Figure 14. Calibration curves of specific gravity of solution as a function of methanol content in water.

A baseline RO run with 50:50 water:methanol feed was conducted. The data showed that both water and methanol were permeable through the membrane and thus the RO did not allow for significant partitioning. 50g/L parahydroxybenzoic acid (pHb) in 50:50 water:methanol mixture was tested in the RO system. While the parahydroxybenzoic was found to concentrate in the retentate, methanol was still observed to permeate. One of the issues of using 50 g/L was that precipitates occurred during the RO tests and were found to settle at the end of each stage. To overcome this issue, the pHb amount was reduced to 10 g/L or 1% solution. In addition, the retentate was recycled. It should be noted that The RO system retains approximately 1.5-2 L of the fluid. Figure 15 shows the concentration change in the retentate and permeate as a function of time.

Figure 15. Permeate and Retentate concentration of parahydroxybenzoic acid in 50% aqueous methanol solution as a function of time in the reverse osmosis process.
At the end of 14 minutes, it was observed that 66.7% of the solvent was recovered. In addition, it was observed that the salt rejection was nearly 82%. Please note that this data is based on the assumption that methanol separation does not take place and thus the calibration based on conductivity in a 50/50 methanol:water solvent is valid. After concentrating the p-hydroxybenzoic acid, the volume of the retentate was doubled by adding methanol and the RO system was run again for four more minutes. 52.5% of the solvent was rejected. If there is no separation of methanol and water through the RO membrane, then 84.2% of the water has been rejected at the cost of the addition of 1.7 times the volume of methanol as compared to the water. To summarize, with a total time of 18 minutes of run and the addition of 1.7 times of methanol, the water content in the retentate was decreased from 50% to 25%. A simple dilution would have reduced the concentration of water to only 37.5%. However, staging the dilution and concentration resulted in higher decrease in water content. The concentration of pHb in the final retentate was 2.18% that doubled from the initial feed of 1%. The same analysis was carried out in conjunction with hydrometer readings and it was found that the methanol was concentrated from the 50% mixture to nearly 70.35% in the retentate and was concentrated further to 99.23%. Thus, in the presence of a solute and recycling to concentrate the solute, there is significant concentration effect for water resulting in less than 1% in the retentate. Further experiments need to be conducted with more sophisticated analysis to evaluate this water recovery effect. When considering this new data, the concentration of pHb in the retentate was found to increase from 1% to 2.29% which is closer to the no loss to permeate curve and the overall salt rejection was found to be 95.42%.

Armed with the above data, one set of test were conducted with an OHD liquor sample which was diluted by two times by the addition of methanol. Two stages were conducted as a single pass and then three stages were conducted as recycle. In between each stage the retentate was diluted with methanol to double the feed volume. While there was significant reduction in volume, the hydrometer readings were inconclusive with respect to the separation of methanol and water. Both the permeate and retentate density were found to decrease. Thus the use of methanol with staged separation was not tested further due to obvious drawbacks of large amount of methanol requirement as well as insufficient evidence of water rejection for subsequent esterification.

Based on Dr. Anderson’s suggestion, we also evaluated the effect of acetic acid in the solution. As seen in Figure 16, there is some amount of concentration of the acetic acid but some of the acetic acid from the 2% solution is clearly permeating across the membrane.
Based on the above information, a process flow sheet for the concentration of the OHD product stream has been envisioned and presented in Figure 17. All the stages would be conducted in recycle mode, although the exact recycle ratio would depend on the product characteristics. A high pressure module operating at 1000 psig would be first used to recover the solvent as well as small molecules. The second concentrating stage treating the retentate would be operated anywhere between 200 – 750 psig, depending on the product stream composition and the ability to recover some work due to pressure difference from the 1000 psig stream. The retentate from both the concentration stages would be treated at a lower pressure (>150 psig) to scrub the smaller molecules from the water and recover pure water as the final permeate.

Several experiments were also conducted with OHD liquors produced from coals of various sources. Both multi stage single pass and single stage with recycle modes were evaluated. Figures 18 and 20 show that irrespective of the mode, roughly 1 L/min of clean water is produced. In 8 single pass stages roughly 71.8 % water was recovered and the organics were concentrated from 530 ppm to 1940 ppm in 10 minutes. When single stage recycle (Figure 20) was used 80.5 % water was recovered and the carbon content...
was concentrated from 804 ppm to 2015 ppm in 11.21 min. Figures 19 and 20 are the corresponding images of the concentrated streams obtained from the two modes.

Figure 18. Data of multi stage, single pass RO operation conducted on OHD product. F-feed, P-permeate, R-retentate.

Figure 19. Product image at each stage for the multi stage RO system.
Another OHD product was concentrated with the RO. The initial raw data on the conductivity and flow rates are provide in Table 5. The results showed roughly 1 L/min of permeate is recovered. More than 90% rejection of clean water was achieved. Figure 21 is the image of several retentate samples arranged in increasing retention time from left to right. The permeate (clean water) had a low conductivity (lower than tap water) and the dissolved organics were less than the lowest calibrated amount of 25 ppm. The total dissolved carbon tests were conducted in the Geology Department at SIUC.

**ELECTRODIALYSIS:** Similar to the RO studies preliminary evaluation of the system using aqueous NaCl solution was conducted. Two experiments were conducted in which the concentrate solvent used was water and methanol (Figure 22). The increase in concentration in the concentrate for both systems is observed. The near complete removal of NaCl to the concentrate required 60 minute residence times at feed and concentrate solvent flow rates of 40 gal/hr. In both cases, 1.6 Whr were expended.
Table 5. Single stage with recycle RO operation on another OHD product.

<table>
<thead>
<tr>
<th>Check</th>
<th>Time (s)</th>
<th>Volume (mL)</th>
<th>Cond (μS/cm)</th>
<th>Flow (mL/min)</th>
<th>Volume (mL)</th>
<th>Cond (μS/cm)</th>
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<td>26800</td>
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<td>833.33</td>
<td>27500</td>
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</tr>
</tbody>
</table>

Figure 21. Product image at various times for the single stage with recycle RO operation on another OHD product.
Two single component studies were conducted. In the first test, 0.6 g/L of trimesic acid (Figure 23) was evaluated while in the second test 10 g/L of 3, 5 dihydroxybenzoic acid (Figure 24) was evaluated. The time for complete removal of the two acids were 25 min and 60 min respectively. The energy cost for the operation with trimesic acid was 0.13 Whr while that for removing 10 g/L of 3,5 dihydroxybenzoic acid was 0.69 Whr.

One dual component test was conducted using 0.6 g/L of trimesic acid and 5 g/L of NaCl. Figure 25 shows the changes in conductivity as a function of time.

Figure 22. Evolution of concentration in the two streams during electrodialysis of NaCl solution.

Figure 23. Evolution of concentration in the two streams during electrodialysis of trimesic acid solution.
Figure 22. Evolution of concentration in the two streams during electrodialysis of 3,5 dihydroxybenzoic acid solution.

Figure 25. Evolution of concentration in the two streams during electrodialysis of trimesic acid and NaCl solution.
Multicomponent studies were conducted in the electrodialysis system. Four compounds were used. In order to concentrate the components, the concentrate solvent was kept at $1/3$rd the volume of the diluate solvent. In addition, tests were conducted with water only concentrate, methanol only concentrate, water only concentrate but fresh concentrate being added every 30 minutes, water only concentrate for the first 30 minutes followed by fresh additions of methanol only concentrate every 30 minutes for the remainder of the test. Figure 2 is an example of one such test. The curves in Figure 26 show the changes in conductivity as a function of time and Figure 27 shows the conductivity evolution of the concentrate in each stage.

![Graph showing conductivity changes](image)

**Figure 26.** Evolution of concentration in the two streams during electrodialysis of a multicomponent solution.
Figure 27. Evolution of concentration in the concentrate stream during electrodialysis of a multicomponent solution elucidating various stages of fresh solvent addition (water only in the first stage).

The data on these tests (Figure 28) show that the components can be separated based on both ionic mobilities as well as the molecular size of the components (and the two are somewhat related). The data are being withheld by the PI as proprietary information. It should be noted that the PI had conceptualized the system as off-the-shelf technology solutions to facilitate the commercialization of the OHD process and as such the system components can be obtained off-the-shelf. The IP of the PI is the system design, component purposes and the data. The total energy requirement was 3.65 Whr.

Figure 28. Concentrate composition during various stages of the operation showing separation of the components (H-hexanoic acid, PHB- parahydroxybenzoic acid, DHB-3,5 dihydroxybenzoic acid).
Another experiment was conducted with 5 g/L of parahydroxybenzoic acid, 1 g/L of trimesic acid, 0.5 g/L of benzoic acid, 1 g/L of 2,6 dihydroxybenzoic acid and 0.25 g/L of NaCl. The experiment was conducted in three stages of 60 minutes each. Fresh concentrate solvent (water) was added prior to each stage. There is an initial sharp rise in conductivity (Figure 29) of the concentrate in the 1st stage due to the initial removal of NaCl. Thereafter the remainder of the curves were nearly parallel to each other indicating the removal of the organic species. A total energy requirement of 1.05 Whrs was required for this process. The two systems were integrated and experiment on a dual component system wherein a solution containing 1.9 L of trimesic acid and 3.75 g/L of sodium chloride was first concentrated in the RO system followed by ED separation. Figure 30 contains the information of this test. The data show that nearly 50 % of clean water was first rejected and then it was found that 41.3 % of trimesic acid was recovered in the first hr. It should be noted that the concentrate solvent was water. The energy requirement for the ED phase was 0.3225 Whr. The pumping cost of the RO system was not calculated.

![Figure 29. Evolution of concentration in the two streams during electrodialysis of multisolute solution containing 2,6 dihydroxybenzoic acid, trimesic acid, benzoic acid and parahydroxybenzoic acid along with NaCl.](image)

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Figure 30. Integrated RO/ED test with two components: trimesic acid and NaCl.

Based on the data obtained from the studies conducted in this research, a conceptual design has been completed for processing 1000 gals of OHD product. Please note that only the ED costs have been included. In addition, the RO system shown for the concentration effect is actually the RO system shown in Figure 31. Barring the RO pumping costs, the total power requirement is expected to be 1.14 kWhr.
Figure 31. Scaled Up design to operate at 1000 gal/min of OHD liquor.
CONCLUSIONS AND RECOMMENDATIONS

The project goals were successfully achieved and the following conclusions can be made:

1. Membrane processes are suitable to separate organic and inorganic components.
2. RO is an efficient concentration operation.
3. Combining RO and ED can both reject water for reuse as well as separate various components.
4. Over 90% solute rejection and 90% water recovery was achieved by both multistage or retentate recycle approaches.
5. Single stage with recycle will reduce the required RO footprint.
6. ED can separate components based on ionic mobility and molecular size.
7. The suggested design includes the possibility of
   a. Separating clean water.
   b. Separating inorganic salts.
   c. Separating small sized organic ions.
   d. Separating larger sized organic ions.

The following recommendations are made:

1. Higher pressure RO system needs to be evaluated on OHD product to quantify the permeation of smaller molecules.
2. The exact effect of solute composition on the methanol water partitioning across the RO membrane needs to be evaluated.
3. The relationship of the solute concentration on the ED system efficacy needs to be evaluated.
4. Actual OHD liquor tests on the ED system and the combined RO/ED system needs to be evaluated.
5. Optimized RO/ED needs to be evaluated for any given feed composition and concentrations.
REFERENCES


6. Kinney, C. Friedman, W. JACS, 74, 57-61, 1952


10. Personal communication with Dr. Ken Anderson.


DISCLAIMER STATEMENT

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