Feasibility of Improving Biomass Combustion through Extraction of Nutrients

CENNATEK BIOANALYTICAL SERVICES

The Future Looks Greener

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ization of technologies that will accelerate
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Executive Summary

The use of fossil fuels as the primary source of energy is the most significant contributor to Green House Gas (GHG) emissions. GHG induced global warming, and all the negative environmental impacts associated with climate change have been widely accepted among experts in the scientific community for more than two decades. In more recent years a slowly growing number of business and political leaders around the world have also accepted the overwhelming body of evidence presented by the scientific community. Various plans and programs have been launched to mitigate GHG emissions and address the potential environmental, social and economical impacts of climate change.

Biomass is a renewable energy source that can substitute some of the world's energy demands currently supplied by fossil fuels. Biomass combustion in particular can be used to offset coal in electricity generation. Ontario as a province, and North America as a region has tremendous biomass production capacity. Agricultural residues such as corn stover, soybean stover, wheat straw, barley straw and other residual products from current food production can be processed into a solid fuel for heat and electricity generation. Energy crops such as miscanthus, switchgrass, willow and poplar hybrids are currently being studied as feedstocks for various forms of biofuels.

Biomass, especially in the form of agricultural residues is not an ideal fuel for combustion. This report examines the technical and economic feasibility of employing pre-treatment processes that can improve the combustion properties of biomass.

High concentrations of inorganic nutrients have the most significant negative impact on biomass combustion properties. These nutrients are found in higher concentrations in agricultural residues and energy crops, than in typical forestry products. The nutrients of most significant concern are the alkali metals (Potassium and Sodium), alkaline earth metals (Magnesium and Calcium), Chlorine (Cl), and Silica (Si). Alkali metals in particular form euctectic mixtures of silicates that have half the melting temperature of silica. The presence of these nutrients in biomass significantly lowers the ash fusion temperature of the fuel.

At typical combustion temperatures these nutrients cause the formation of deposits, slags, and fouling. As a result of these formations the thermal conversion efficiency of the power generating plant is significantly lowered. Furthermore, costly retrofitting would be required for any existing power generating station to mitigate the negative impacts of these problematic formations. Nitrogen (N), Sulphur (S) and Chlorine (Cl) contribute to air pollution, and Cl in particular causes corrosion. The nutrient content of various forms of biomass can vary significantly based on the environment, the soil type, soil quality, and agricultural practices employed.

Most of the nutrients of concern are water soluble and can be removed through leaching, a simple and inexpensive liquid extraction process. Field leaching has been shown to be effective in removing nutrients however, field leaching is uncontrollable, results in organic matter yield loss, and poses a significant practical challenges to supply dependability. A good example of this has been the current spring of 2011, where in many regions of Southwest Ontario it has been an unusually wet spring. As a result, many farmers have been unable to get in their fields to seed their crops let alone be able to harvest the residues from their fall crops that have been left-out to leach over winter. In a spring like this, if a biomass pelletization or torrefaction facility were to depend on field leached biomass, it would find itself short of feedstock. The plant would have to pull agricultural residues from much farther distances to meet its production needs increasing production costs, and reducing margins.

An industrial leaching process can provide consistent quality of biomass. The nutrient extraction process is more effective in reducing the nutrient content, does not lead to yield loss or contamination, and eliminates the practical challenges associated with field leaching. Several methods of leaching have been reported in literature. The most effective process consists of immersing the biomass in water with aggressive agitation for short periods of time (less than one hour) followed by using a mechanical dewatering (pressing) process to further remove excess leachate. Typical mechanical dewatering units are able to reduce the moisture content of biomass to about 50% moisture. Additional drying will be required to prepare the biomass for further processing (pelletizaiton). Previous research on leaching process has reported removal of 90-100% of Cl, 91% of K, 86% of S, 61% of Mg, and 57% of N.

More than 90% of the silicon found in plants are in the form of insoluble amorphous silica (SiO_2). Therefore, leaching does not result in significant reductions in the Si content. Alternative methods for Si removal are required to lower the ash content of biomass and improve the energy density of the fuel as measured by the Higher Heating Value (HHV). Although Silica is not soluble in water it is soluble in basic solutions thus one possible method for silica removal is the use of chemical pulping processes. The problem with chemical pulping processes such as the Kraft process is that the basic solutions also dissolve lignin, thus reducing the yield and energy density of the biomass. One possible method that could overcome this problem is the application of a chemi-mechanical desilication process developed by Dr. Chute as described in U.S Patent 7,364,640. The process which was developed at Alberta Innovates was developed for the purpose of producing paper from wheat straw. This process is more cost-effective for use in paper production from agricultural residue when compared with traditional chemical pulping processes, but it is much more costly than using an electrostatic separation process.

Electrostatic separation is the most technically and economically feasible approach for extraction of silica from green biomass. Tribo-electrostatic separation has been extensively researched by Dr. Stencel at the University of Kentucky. He holds several patents on this technology. There are no published information on the use of this technology for silica extraction from agricultural products. The most similar application to silica removal is coal beneficiation where inorganic constituents of coal are separated to reduce its ash content. Dr. Stencel has founded a company called Tribo Flow Separations (TFS) that has commercially installed various tribo-electrostatic separation plants as large as 200,000 tonnes/yr.

Reverse Osmosis is a highly effective means of concentrating nutrients in the leachate to produce a liquid fertilizer. The production of a liquid fertilizer from the nutrients removed in the leaching step is an effective means of generating additional revenues for the conversion facility.

The inclusion of the nutrient recovery process, in particular the leaching process improves the overall economics of biomass combustion. An economic evaluation of the entire process including pelletization was carried out in the study. The evaluation consisted of producing financial data on 21 different case scenarios using a model developed by CENNATEK.

Based on an average feedstock price of $100/DMT, a pelletization plant would have to sell pellets at $150/DMT. At this sales price considering an operating cost of $7.50/MWh and 8% return for the power generating station the cost of the electricity generated would be approximately $136/MWh.

The inclusion of the nutrient removal and recovery pre-treatment process as outlined in this report will lower the sale price of the pellet to less than $130/DMT. This combined with the higher energy density of the produced pellets, and the higher thermal efficiencies expected for the power generation will result in the lowering of the cost of electricity generation to $84/MWh.

Integrating the pre-treatment process with pelletization will reduce the cost of pellets for power generating stations by 38%. Natural gas is currently viewed as the preferred fossil fuel to coal. Based on current spot market prices the cost of electricity generation using natural is $51.57/MWh. Thus, the proposed process is closing the gap in cost between a renewable energy in the form of biomass and a fossil fuel such as natural gas.

Lab-scale experiments conducted for this report confirm the viability of nutrient recovery through leaching and reverse osmosis. The results of experiments using Tribo-electrostatic separation indicate that silica can be separated from other components of biomass, however further process development and optimization required to confirm technical and economic feasibility.

This report recommends continued investigation into the technical feasibility of the proposed biomass pre-treatment process, including further lab-scale optimization, modeling and scale-up, and the building of a pilot-scale plant to demonstrate the technical and economical potential of the proposed pre-treatment process.

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Nomenclature

Al	Aluminum
$Al(OH)_2$	Aluminum Hydroxide
$AlPO_4$	Aluminum Phosphate
Al_2O_3	Aluminum Oxide (Alumina)
A_{tot}	Total Membrane Area (m^2)
ATP	Adenosine triphosphate
B	Boron
BL	Black Liquor
bu	Bushel
C4	Carbon Fixation Mechanism
Ca	Calcium
Ca^+	Calcium Ion
$CaCO_3$	Calcium Carbonate (Limestone)
$CaHPO_4$	Dicalcium Phosphate
CaO	Calcium Oxide
$Ca_5(OH)(PO_4)_2$	Hydropatite
$Ca_3(PO_4)_2$	Tricalcium Phosphate
CAM	Crassulacean Acid Metabolism
Cd	Cadmium
C_f	Concentration in Feed (ppm)
Cl	Chlorine
Cl^-	Chloride Ion
Co	Cobalt
CO	Carbon Monoxide
CO_2	Carbon Dioxide
$Cost_{inv}$	Investment Cost per Unit Area of Membrane
C_p	Concentration in Permeate (ppm)
Cr	Chromium
Cr_2O_3	Chromium Oxide
CSTR	Continuous Stirred-Tank Reactor
Cu	Copper
Cu^{2+}	Copper Ion
DMT	Dry Metric Tonnes

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DNA	Deoxyribonucleic Acid
EBITDA	Earnings Before Interest, Taxes, Depreciation & Amortization
EC	Electrical Conductivity
ECN	Energy Research Centre of Netherlands
ED	Electrodialysis
EDX	Energy Dispersive X-ray Spectroscopy
eV	Electron Volt
Fe	Iron
Fe_2O_3	Ferric Oxide
$Fe(OH)_2$	Ferrous Hydroxide
$Fe(OH)_3.xH_2O$	Ferric Hydroxide
$Fe_2(PO_4)_2.8H_2O$	Vivianite
$FePO_4.2H_2O$	Strengite
FTB	Fluidized Bed Tribocharger
GFD	Gallon per Square Foot per Day
GHG	Greenhouse Gas Emissions
H_2O	Water
ha	Hectare
HCl	Hydrochloric Acid
$(HFO)[Fe_2O_3.xH_2O]$	Hydrous Ferric Oxide
HHV	Higher Heating Value (MJ/kg or BTU/lb)
$H_2PO_4^-$	Dihydrogen Phosphate Ion
H_3PO_4	Phosphoric Acid
HSO_3^-	Bisulfite Ion
H_2SO_3	Sulphurous Acid
H_2SO_4	Sulphuric Acid
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
IRR	Internal Rate of Return
J	Permeate Flux ($L.m^{-2}.hr^{-1}$)
J_o	Corrected Permeate Flux ($L.m^{-2}.hr^{-1}$)
K	Potassium
K^+	Potassium Ion
KCl	Potassium Chloride (Sylvite)
K_2CO_3	Potassium Carbonate
KH_2PO_4	Potassium Phosphate
K_2O	Potassium Oxide
K_2SO_4	Potassium Sulphate

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kDa	kilo Dalton
$KMgPO_4$	Potassium, Magnesium, Phosphate struvite
KMP	Potassium, Magnesium, Phosphate struvite
kV	Kilovolts
kWh	Kilowatt Hour
m•	Mass Flow Rate (g/s)
MAP	Magnesium, Ammonium, Phosphate Struvite
MCC	Cooking Liquor
Mg	Magnesium
Mg^{2+}	Magnesium Ion
$MgCl_2$	Magnesium Chloride
$MgCl_2.6H_2O$	Magnesium Chloride Hexahydrate
$MgCO_3$	Magnesium Carbonate
$MgNH_4PO_4.6H_2O$	Magnesium, Ammonium, Phosphate Struvite
MgO	Magnesium Oxide
$Mg(OH)_2$	Magnesium Hydroxide
MGD	Millions of Gallons per Day
mM	Millimolar
Mn	Manganese
Mo	Molybdenum
MW	Megawatt
MWh	Megawatt Hour
N	Nitrogen
N_2	Nitrogen Gas
Na	Sodium
Na^+	Sodium Ion
NaH_2PO_4	Monosodium Phosphate
$Na_2HPO_4.12H_2O$	Disodium Hydrogen Phosphate
NaOCl	Sodium Hypochlorite
NaOH	Sodium Hydroxide
Na_2CO_3	Sodium Carbonate
Na_2O	Sodium Oxide
Na_2S	Sodium Sulphide
NH_4^+	Ammonium Ion
NH_4Cl	Ammonium Chloride
Ni	Nickel
NO_3^-	Nitrate Ion

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NO_x	Nitrogen Oxide Gases (NO, NO_2)
NPV	Net Present Value
NREL	National Renewable Energy Laboratory
O	Oxygen
O_2	Oxygen Gas
OPG	Ontario Power Generation
P	Phosphorous
P_2O_5	Phosphorous Pentoxide
PO_4^{3-}	Phosphate Ion
PG_i	Inlet Gauge Pressure (bar)
PG_o	Outlet Gauge Pressure (bar)
PGW	Pressure Ground Wood Pulp
PVC	Polyvinyl Chloride
RM	Rotameter
RMP	Refiner Mechanical Pump
RNA	Ribonucleic Acid
RO	Reverse Osmosis
rpm	Rotations Per Minute
RTS	Rotary Tribo Electrostatic Separation
S	Sulphur
SEM	Scanning Electron Microscope
SGW	Stone Ground Wood Pulp
Si	Silicon
SiO_2	Silica
SO_3	Sulphur Trioxide
SO_3^{2-}	Sulfite Ion
SO_4^{-}	Sulphate Ion
SO_x	Sulphur Oxide
SRC	Short Rotation Coppices
T	Temperature (°C)
TDS	Total Dissolved Solids
TFS	Tribo Flow Separation
Ti	Titanium
TiO_2	Titanium Dioxide
TMP	Thermal Mechanical Pump
TMP	Transmembrane Pressure (bar)
TOC	Total Organic Carbon

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UF	Ultrafiltration
V1,V2,V3	Solenoid Valves
VR	Volume Reduction
w/v	Mass Concentration
w/w	Mass Fraction
XPS	X-ray Photoelectron Spectroscopy
XRF	X-ray Fluorescence
Zn	Zinc
Zn^{2+}	Zinc Ion
€	Euro
$\gamma\text{-}Fe_2O_3$	Magemite
ρ	Density (g/cm^3)
μ	Viscosity (Pa.s)
\$M	Millions of Dollars

Nomenclature

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Chapter 1
Agricultural Biomass as a Combustion Fuel

Around the globe environmental concerns around Greenhouse Gas (GHG) emissions coupled with health concerns related to air quality and pollution have led to regulations aimed at moving away from electricity generation from coal-fired plants. The Ontario Power Generation (OPG) has been legislated to cease the use of coal by the end of 2014. OPG currently has four thermal power generation stations with total generation capacity of 4,227MW, operating on coal power. There is a potential for substituting a significant portion of the current coal capacity with agricultural biomass in the form of energy crops and crop residue produced in Ontario. The use of agricultural residues or purpose grown energy crops leads to bioremediation of land on a local level, as well as minimizing the effects that are associated with open burning, wild land fires, landfilling, soil erosion and drain water management (Dayton et al., 1999; Jensen, 2001).

In recent years, there have also been significant advancements in the commercialization of biomass processing technologies related to the production of second generation ethanol (cellulosic ethanol), biodiesel, bio-oil (pyrolysis/gasification) and other industrial applications of biomass. Many of these technologies aim to use similar agricultural residues or purpose grown energy crops as those under consideration for combustion. Given the large area of arable land and agricultural production capacity in Ontario, the emerging biofuel markets and bio-based economic sector translate into a great opportunity for the agricultural community in Ontario and Canada.

Biomass, especially in the form of agricultural residues in its raw form is not an ideal fuel for thermal conversion processes (i.e. direct combustion, co-firing, gasification, or pyrolysis). Technologies that could be applied to remove undesirable elements from biomass prior to their use in thermal conversion processes are significant because these constituents often contribute to adverse impacts on the reactors, furnaces, heat exchangers, turbines, emission control devices, and other equipment. Fouling, slagging, agglomeration of bed media and corrosion are the most problematic of these impacts.

In this chapter, the most common biomass nutrients are described. The impact of the presence of these nutrients on combustion processes are detailed. Finally, a number of energy crops and agricultural residues currently under consideration in Ontario as combustion fuel are described. Detailed data on the combustion properties of these biomass are also provided.

1.1 Biomass Nutrients

For plants to grow and thrive, a collection of nutrients in the form of inorganic elements are needed. **Figure 1-1**, provides an illustration of the various nutrients essential to plant growth.
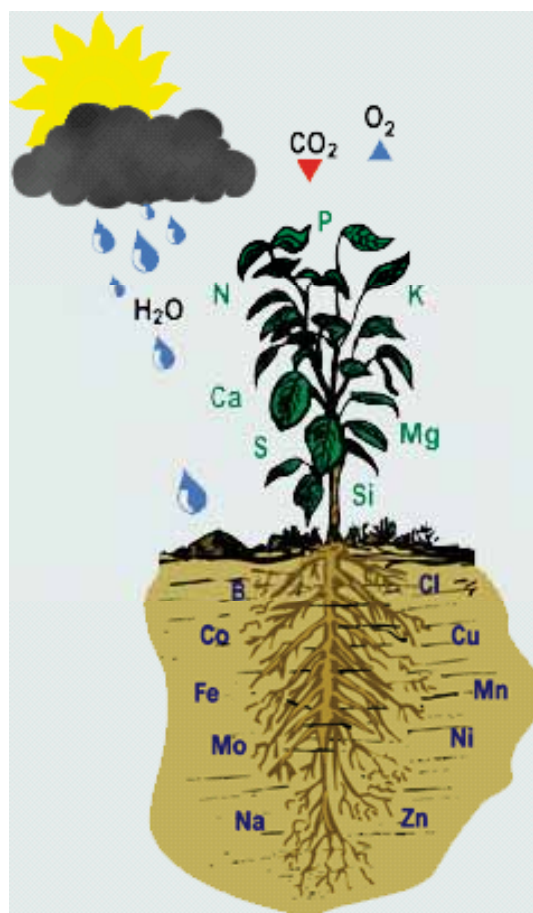
Figure 1-1 Biomass Nutrients (gleeson-11biology.pbworks.com)

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Plant nutrients are divided into three main categories:

- Primary Macronutrients
- Secondary Macronutrients
- Micronutrients

1.1.1 Primary Micronutrients

Macronutrients differ from other nutrients (i.e. micronutrients) due to the relatively larger quantities of these nutrients that are required by the plant to grow. Primary among these macronutrients are Nitrogen (N), Potassium (K) and phosphorous (P), which are the three nutrients that are required in the greatest quantity.

Nitrogen: Nitrogen (N) is considered the most important nutrient for plant growth (Khan et al., 2009). It is taken up from soil in two inorganic forms, ammonium (NH_4^+) and nitrate (NO_3^-) Ammonium ions are incorporated into organic compounds in the roots, while the nitrate ions are more mobile within the plant and can travel to the xylem and vacuoles. In order for the nitrogen to be incorporated into various organic structures needed for the more essential functions in plant growth, the nitrate needs to be reduced into ammonia (NH_3^+) form through dentrification.

For ammonium or ammonia to be used in the plant, they next need to be assimilated into various organic structures before they become toxic to the plants. The nitrogen is assimilated by the amino acid glutamate, which in turn forms the amide glutamine. The nitrogen that is organically bound in the glutamate and glutamine can then be used to produce other organic components like other amides, ureides, amino acids, amines, peptides and proteins. Aside from proteins, these nitrogen containing organic compounds can also form nucleic acids, coenzymes, membrane constituents and secondary products used in processes such as photosynthesis and production of carbohydrates. The nitrogen content of healthy plant varies between 2-5% of the total dry weight (Marschner, 1995).

Phosphorous: Phosphorous has many important functions in plants. Generally taken up from the soil in the form of a dihydrogen phosphate ion ($H_2PO_4^-$), phosphorous is used in many organic structures involved in photosynthesis, respiration, energy storage and transfer, cell division and enlargement. Specifically it is a component of ATP, which is needed to convert light energy to chemical energy during photosynthesis. It is also used to modify the activity of various enzymes by the process of phosphorylation, a main component of the DNA and RNA of plants, and in the phospholipids of biomembranes. Phosphorous can either remain as inorganic phosphate, in the form of a phosphate ester (in DNA and RNA) or attached to another phosphate ion by an energy-rich pyrophosphate bond (in ATP or phospholipids). The main fraction of phosphorous is in inorganic form in highly vacuolated tissue. The amount of phosphorous needed in healthy plant ranges from 0.3-0.5% dry weight (Marschner, 1995).

Potassium: Potassium (K) is essential for water balance regulation in living organisms (Steenari et al., 2009). The main role of potassium is to help regulate osmotic pressure through the opening and closing of stomata by means of a potassium ion pump. **Figure 1-2**, provides a Scanning Electron Microscope (SEM) image of a plant stomata that is open (left) and closed (right). **Figure 1-3**, provides a schematic description of the function of Potassium (K^+) is stomatal function.
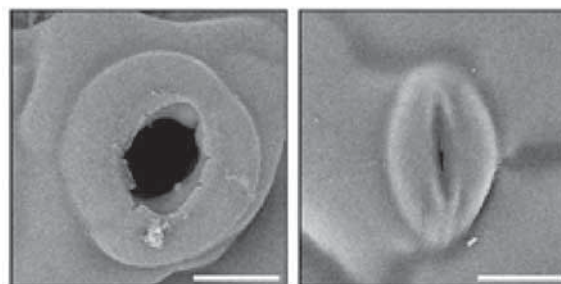
Figure 1-2 SEM image of stomata (sciencemag.org)

Since the osmotic pressure effects water uptake by a plant, potassium helps reduce water loss and increases drought tolerance.

Potassium has other important functions, including activating enzymes used in photosynthesis and respiration. In photosynthesis it helps in the formation of a chlorophyll precursor, and is also essential in protein synthesis. Potassium ions are not metabolized, and generally only form weak complexes that are readily exchangeable. As a result, potassium remains in the form of a potassium ion (K^+), and is highly mobile throughout the plant. This includes movement be-
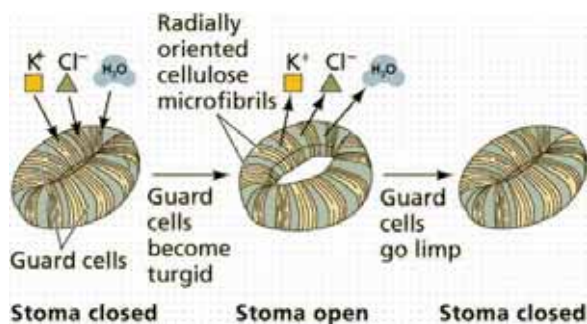
Figure 1-3 Potassium and stomatal function (catage.org.lb)

tween individual cells, between tissue, and long-distance transport. The potassium ions are highly soluble in water and are therefore susceptible to leaching. The amount of potassium found in a plant is generally 1 - 5% of the total dry weight (Bakker, 2000; Marschner, 1995).

1.1.2 Secondary Macronutrients

Secondary macronutrients consist of sulphur (S), magnesium (Mg) and calcium (Ca). These three nutrients are also required in large quantities, but not to the degree of the primary macronutrients.

Sulphur: Sulphur (S) is considered to be the most important of the secondary macronutrients. It is generally taken up by the plants in the roots in the form of a sulphate ion (SO_4^-). Once in the plant, the majority of sulphate is reduced for incorporation into various organic structures. These organic structures include amino acids, proteins and enzymes, and the function of the sulphur is closely related to the functions of these organic structures. The amount of sulphur present in plants is generally 0.1-0.5% of the dry weight (Bakker, 2000; Marschner, 1995).

Magnesium: The main functions of magnesium in plants involve bonding or interaction with other compounds. It can form an ionic bond with strongly nucleophilic ligands such as phosphoryl groups, as well as functioning as a bridging element or helping in the formation of complexes of varying stabilities.

It is used in photosynthesis as a component of chlorophyll, as well as forming ternary complexes with enzymes in processes that require enzymes and substrate to have a precise geometry. **Figure 1-4** depicts Magnesium as the central element in chlorophyll.

Finally, a large portion of magnesium is used in the regulation of cellular pH and the balance between cations and anions.

In terms of the forms of magnesium present, between 6 and 25% is in chlorophyll, 5-10% is in phosphate form, and the final 60-90% as a soluble form in water. The amount of magnesium contained in a plant is between 0.15-0.35% of the total dry weight (Marschner, 1995).
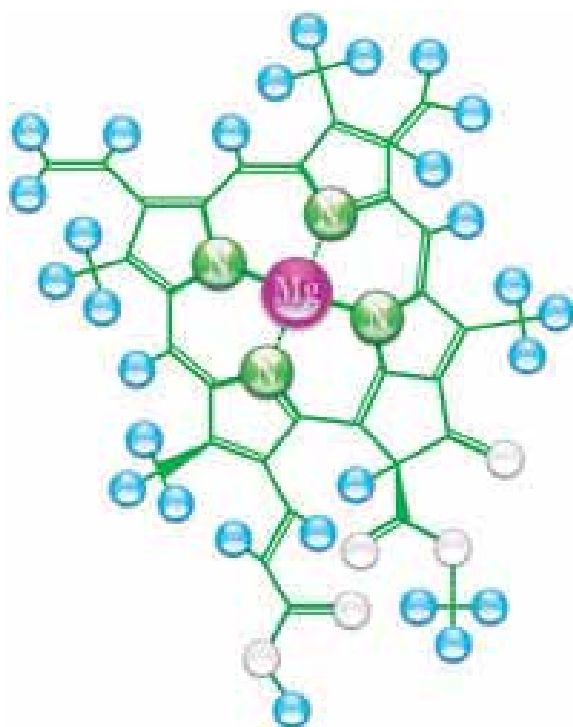
Figure 1-4 Magnesium is the central element in chlorophyll (ancient-minerals.com)

Calcium: The main function of calcium in plants is to serve as a structural component of macromolecules, due to its capacity for providing stable intermolecular linkages in cell walls and at the plasma membrane. Other areas of calcium concentration include vacuoles and the endoplasmic reticulum. Calcium is present in several forms, including water soluble (Ca^{2+}), or as a pectate, phosphate, oxalate or residue. Typical amounts of calcium can range from as low as 0.1% to greater than 5% of the dry weight (Marschner, 1995).

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Silicon: Silicon, in the form of silica or silicon dioxide, is another nutrient in plants that is considered a macronutrient. Silicon is a very important element in biology and it is significant to the metabolism of plants, especially grasses. Typically, living plants contain silicon in three basic forms:

i. Insoluble amorphous silica (SiO_2) (about 90%),

ii. Silicate ion (about 0.5% to 8%), and

iii. Colloidal acid (about 0% to 3.3%).

Silica gives structure to the plant. It is the largest mineral component of perennial grasses. Grass species and their water uptake influence the silica content. Biomass absorb silica when they uptake water. The uptake of more water results in more silica content. For example, warm-season grasses (e.g. switchgrass) have low water uptake therefore, their silica content is half as much as crops with high water uptake such as, cool-season grasses (e.g. canary grass).

Soil type also influences the silica content of biomass. For example grasses which grow in high silica content soil such as, clay have a higher concentration of silica. When agricultural residues are harvested after over wintering soil contamination contributes to further increasing the silica content of crop residues. Typically, grass inflorescence contains five times more and leaves contain three times more the silica content of stems. Grass inflorescences refers to group of flowers growing from a common stem of the grass often in a characteristic arrangement.

This amorphous silica is found in epidermal cells of the

Figure 1-5 Phytolith (Opaline Silica) (Geoarchelogie et mediation scientifique)

plants in dumb-bell shaped cells called opal phytolith (**Figure 1-5**) or silica phytolith (Lanning et al; Farone et al, 1997).

Phytoliths exist in abundance in grasses, including rice, wild rice, maize and wheat. Silica is an inert compound and does not react with many compounds. It is insoluble in water but it can be dissolved in hot, concentrated alkali or fused hydroxide. Silica is also dissolved in hydrofluoric acid (Lanning et al.). **Figure 1-6** provides images of various phytoliths found in grass.
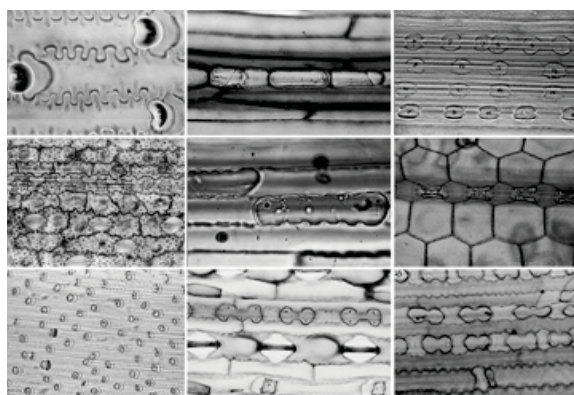
Figure 1-6 Silica Bodies (Phytoliths) in grass (pliths.jpg)

1.1.3 Micronutrients

Micronutrients also have important functions in plant growth and development, however, these nutrients are generally required in smaller quantities relative to the macronutrients (i.e. <0.01% dry weight). Micronutrients include elemnts such as: Chlorine (Cl), Boron (B), Copper (Cu), Iron (Fe), Manganese (Mn), Molybdenum (Mo), and Zinc (Zn). Of these various micronutrients, chlorine is the nutrient of most concern in biomass combustion.

Chlorine: Chlorine acts much like potassium in plants, being taken up by plants and existing as a chloride ion (Cl⁻). It can also be loosely bound and readily exchangeable, and is highly mobile throughout the plant. Its main function is to also play an essential role in the opening and closing of stomata, allowing for an electrochemical equilibrium between its negative anion and the positive cation of potassium. Existing as an ion, chlorine is also readily soluble in water, and generally accounts for 0.2-2% of the plants dry weight (Bakker, 2000).

Additional Beneficial Nutrient: An additional nutrient that is sometimes present in certain plants is sodium (Na). It is classified as a beneficial mineral nutrient, but is only essential for a small number of species, and in some cases can be detrimental to growth. Sodium is not present in large quantities or essential for plant growth in many plants. Species that are characterized by the C4 and CAM photosynthetic pathways and/or halophyte species experience growth enhancement with sodium uptake. Sodium ions (Na^+) can also in some instances replace potassium ions (K^+) without any negative effect on growth, and is therefore also mainly in the form of a soluble ion in plants (Marschner, 1995).

1.2 Effects of Nutrients on Combustion

High quantities of alkali metals like potassium (K) and to a lesser extent sodium (Na), alkaline earth metals like calcium (Ca) and magnesium (Mg), and other inorganic compounds such as chlorine (Cl), sulphur (S), nitrogen (N) and silicon (Si) all contribute to problems during combustion in a variety of ways.

In general, a measurement to predict whether fouling or slagging will occur in a boiler is based on the amount of volatile alkali (i.e. K and Na) in the biomass in units of kg/GJ. For feedstocks with a volatile alkali content greater than 0.34 kg/GJ, fouling or slagging is almost certain to occur due to the lowering of the ash fusion temperature. Virtually all untreated biomass fall within this range (Miles and Miles, 1995; Turn et al., 1997).

In this section detailed descriptions are provided on how nutrients adversely impact the reactors, furnaces, heat exchangers, turbines, and emission control devices used in typical thermal power generation units.

1.2.1 Formation of Deposits

The combustion of biomass in boilers that use stoker-fired grate furnaces, suspension units or fluidized beds causes rapid formation of deposits on interior fireside surfaces (**Figure 1-7**). These deposits are generally comprised of alkali metals and alkaline earth metals in the form of chlorides, sulphates, carbonates and complex silicates. Potassium in ash ends up in various forms (KCl, K_2SO_4 and K_2CO_3) that have low melting temperatures, increasing the potential of deposit formation (Steenari et al., 2009).

Figure 1-7 Formation of Deposits on Boiler Tubes (Boiler Fouling & Deposits)

Some general problems associated with the formation of these deposits include (Vamvuka et al., 2008):

- Slowing down the rate of heat transfer due to their low thermal conductivity and high reflectivity;
- Bridging across tube bundles and causing an increase in combustion side pressure drop, leading to either a reduction in flow through the convection pass or an increase in the fan work needed to maintain the flow;
- Accelerated corrosion of tube metal; and
- General increase in the costs associated with generating power as low quality fuels reduces plant efficiency, capacity and availability.

In furnaces that use fluidized beds, the presence of deposits would also lead to agglomeration of the fluidized bed media. Sodium and Potassium are the main contributors to agglomeration in fluidized bed reactors. Sand from the bed material react with these elements to create a eutectic mixture of silicates. A eutectic mixture is a mixture of substances that melt and solidify at a single temperature that is lower than the melting points of the separate constituents or of any other mixture of the substances. These silicates reduce the melting temperature of silica by half, leading to melt-induced agglomeration. The more common form of agglomeration in fluidized beds is known as coating-induced agglomeration. Thin layers of agglomerates, consisting of potassium silicates, calcium-silica mixtures and magnesium stick to other coated bed

particles (Mettanant et al., 2009).

Sintering also plays a role in fluidized bed agglomeration, where silica content and high heating value (HHV) are important (Mettanant et al., 2009).

While potassium and sodium contribute to agglomeration, calcium reduces agglomeration tendency. Therefore, agglomeration propensity is expressed by a Ca/(Na+K) ratio (Mettanant et al., 2009).

1.2.2   Formation of Slags

Slags are a specific form of deposit formation. The formation of slags mainly occur when potassium and silica contained in the biomass react in the presence of chlorine at common furnace temperatures (800-900°C or higher).

The reaction of potassium and silica produce heavily sintered and fused glassy deposits known as slag or clinker (**Figure 1-8**). Specifically, potassium sulphates and chlorides were found to condense on upper furnace walls, while convection tubes became coated with alkali chlorides, carbonates and sulphates mixed with silica, alumina and complex silicates (Mettanant et al., 2009, Miles and Miles, 1995; Turn et al., 1998).

Formation of these slags in the furnace and on the grates can hinder fuel feeding, combustion, ash removal and ash handling. Generally any alkali species contained in the biomass ash will reduce the ash melting temperature which can be measured and quantified by the ash fusion temperature.

Figure 1-8 Boiler Slag (Geo-sites)

Ash fusion temperatures give an indication of the softening and melting behavior of fuel ash. The fusion temperatures are significant for predicting whether the ash will perform properly in the process for which the fuel was chosen (ASTM D1857). Thus, the ash fusion temperature is widely cited in fuel specifications. Fusion temperatures are typically measured at the following four defined points:

i.   Initial deformation temperature (IT): Temperature at which the point of the cone begins to round;

ii. Softening or spherical temperature (ST): Temperature at which the base of the cone is equal to its height;

iii. Hemispherical temperature (HT): Temperature at which the base of the cone is twice its height; and

iv. Fluid temperature (FT): Temperature at which the cone has spread to a fused mass no more than 1.6 mm in height.

Any liquid components of slag present can lead to further accumulation through the capture of fly ash on its surfaces by inertial impaction and sticking.

1.2.3   Fouling

Fouling is defined as the formation of undesired deposits on heat transfer surfaces, which increase the resistance to fluid flow, resulting in higher pressure drop and reduced heat transfer. Fouling generally causes the performance of heat exchangers to degrade over time. Like other deposit formations discussed, potassium, chlorine, silicon and sulphur are mostly associated with fouling problems, with calcium, magnesium and phosphorous also contributing.

The fouling of heat exchangers is of great importance as it is a critical limitation in their design and operation in biomass combustion processes. A heat exchanger tube that begins clean and clear of deposits will very quickly develop a layer of condensed alkali salt after biomass is initially fired in the boiler. As the biomass continues to burn, the deposit layer in the tubes will continue to increase through a combination of inertial impaction, homogeneous and heterogeneous chemical reactions and thermophoresis. The deposit layer will eventually form an aerodynamic wedge on the upstream surface of the tube, reducing the efficiency (Dayton, 1999).

1.2.4   Other Negative Impacts of Biomass Nutrients

Nitrogen, another macronutrient present in biomass significantly increases Nitrogen oxides (NO_x) such as nitrogen dioxide (NO_2) and nitric oxide (NO) emissions and the formation of acidic gases. These compounds play an important role in the atmospheric reactions that create harmful particulate matter, ground-level ozone (smog) and acid rain. As an air pollutant NO_x emissions are regulated in Ontario.

Increased amounts of sulphur and chlorine can lead to increased emissions of SO_x, HCl, aerosols, dioxins and furans, all of which are air pollutants contributing to smog, acid rain, and human health problems (Tonn et al., 2010; Prochnow et al., 2009).

Chlorine and sulphur are also key contributors to corrosion and metal wastage. Corrosion on heat exchanger surfaces is considered to be one of the most important limitations to the use of biomass in combustion. Types of corrosion include: pitting (point), inter-granular, crevice, selective and uneven (Pisa et al., 2009)

If biomass containing appreciable amounts of amorphous silica is burned in the range of 900-1000°C, the silica can convert to crystalline silica, posing a respiratory health hazard (LeBlond et al., 2010).

Alkali species can also contribute to catalyst deactivation in certain catalytic reduction systems used to reduce NO_x emissions, thus increasing the cost of the emission reduction systems required to meet emissions standards (Jenkins et al., 2003).

The adverse effects of biomass combustion described above can have an impact on all components in the combustion process, including reactors, furnaces, heat exchangers, turbines, emission control devices and other equipment. Previous researchers have recommended designing special boilers that run at lower temperatures (<830°C) for biomass combustion. This approach will help to mitigate the formation of fouling and slagging in the boilers, however, it does not address all of the concerns described. More importantly, this approach requires extensive renovations to existing thermal power generation facilities to faciliate biomass combustion (Dayton, 1999; Miles and Miles, 1995).

1.3   Sources of Agricultural Biomass

There are many sources of agriculture based biomass currently under consideration across Ontario for use in thermal conversion processes. The combustion properties of these various sources of biomass vary significantly due to variations in the quantity of undesirable nutrients in the feedstock.

Agricultural Biomass can be broadly grouped into two categories:

   i.   Energy Crops
   ii. Agricultural Residues

1.3.1   Energy Crops

Energy crops are plants purposely grown to produce some form of energy. Ideal attributes of an energy crop are low cost, low maintenance, high yielding, low moisture content, greater energy content, good fuel characteristics, and no environmental risks (Oo, 2009).

Herbaceous energy corps are perennial grasses such as miscanthus, and switchgrass. These grasses are usually harvested on a yearly basis. They re-grow from their roots, and do not require replanting for 15 years or more. Short rotation coppices (SRC) such as poplar and willow are considered woody biomass, and typically have better combustion properties in comparison with the herbaceous grasses. SRCs are harvested on a 2-5 year cycle. They re-grow by producing new shoots from rootstock that remains in the ground after harvesting (Oo, 2009).

Miscanthus, switchgrass, willow and hybrid poplar are considered as the leading species of plants for use as energy crops in Ontario. These plants and their combustion properties are discussed in further detail in this section.

Table 1-1 provides a summary of the combustion properties for Miscanthus, Switchgrass, Willow and Poplar.   Climate, geographic location, soil constituency, water quality, harvest time and harvesting method all contribute to the combustion properties of any agricultural product. Thus, reported data on combustion properties typically vary widely from study to study. For this reason, the Phyllis database provided by the Energy Research Centre of the Netherlands (ECN) was used. The database contains information on the composition of biomass and waste. Phyllis enables users to obtain the average composition of any combination of groups and/or subgroups.

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Table 1-1   Summary of Combustion Properties of Energy Crops (ECN Phyllis)

Parameters	Miscanthus	Switchgrass	Willow	Poplar
Proximate Analysis				
Moisture (wt%)	50	12	60	50
Ash (wt%)	1.5	4	1.1	2.5
Volatile (wt%)	82	74	85	85
Fixed Carbon (wt%)	6	10		
Ultimate Analysis (wt%)				
Carbon	48	48	48	50.2
Hydrogen	6	6	6	6
Nitrogen	0.5	1.5	0.6	0.6
Sulfur	0.1	0.1	0.06	0.02
Oxygen	43.9	41.4	44.4	40.4
Elemental Ash Composition (Ash %)				
SiO_2	39	24.3	16.8	5.9
Al_2O_3	1.6	1.4	3	0.8
TiO_2	<0.05	<0.05	0.1	0.3
Fe_2O_3	1.1	0.9	0.9	1.4
CaO	8.6	22.5	34.9	49.9
MgO	5.9	9.4	2.5	18.4
Na_2O	2.2	0.5	3	0.1
K_2O	30.4	14.2	12.2	9.6
P_2O_5	6.3	25.5	10.4	1.3
SO_3	4.9	0.6	1.7	2
HHV Dry Basis (MJ/kg)	19.6	18.6	19.3	19.0
Cl (wt%)	0.05	0.02		
Ash Fusion Temp (°C)	1090	1016	1380	1350

Miscanthus

Miscanthus (**Figure 1-9**) is a large perennial grass that produces cane-like stems. Possessing the efficient C4 photosynthetic pathway, with relatively low nutrient requirement and good water use efficiency, miscanthus grass can grow to heights of more than 3.5 m in one season. Miscanthus is planted in spring, and once planted can remain in the ground and be productive for at least 15-20 years (Oo, 2009).

Figure 1-9 Miscanthus (University of Illinois)

First year growth is insufficient to be economically worth harvesting. The crop can be harvested from the second year onwards, however, the crop normally takes three years to reach a mature yield (DEFRA, 2007).

Miscanthus is a genus of about 15 species of perennial grasses native to subtropical and tropical regions of Africa and southern Asia, with one species (M. sinensis) extending north into temperate eastern Asia. Miscanthus x giganteus, the sterile hybrid between M. sinensis and M. sacchariflorus, has been at the center of the research and field trials, extensively in Europe and recently in North America, due to the fact that M. sacchariflorus types are well adapted for warmer climates, and M. sinensis can provide genetic resources for cooler regions (Clifton-Brown and Lewandowski, 2000).

Miscanthus is currently grown as a fuel crop, as it pro-vides an annual harvest, is relatively easy to cultivate/harvest and gives a reasonable high dry-matter yield (LeBlond et al., 2010). On a gross margin basis, Miscanthus compares favourably and can compete with conventional agricultural systems such as cattle rearing, sugar beet, winter wheat and spring barley (Prochnow et al., 2009).

Miscanthus is established by planting pieces of the root called rhizomes, which are usually collected from "nursery fields" where miscanthus has already been established. Rhizomatous grasses retain a large proportion of the nutrients in the rhizomes, and little in the biomass, so nitrogen and nutrient requirements are very low. **Figure 1-10** is a picture of a Miscanthus x giganteus rhizome.

Figure 1-10   Miscanthus x giganteus Rhizome (Oo, 2009)

Miscanthus ash showed clear sintering tendencies at temperatures as low as 600°C, compared with reed canary grass and willow (the latter of which was inert up to 900 °C). Ash sintering as mentioned in section 1.2 (pg 5 -6) leads to deposit formation, bed agglomeration and potentially slag formation or fouling. This may be due to the combination of relatively high silica content in miscanthus together with potassium and fluxing agents (material that helps to melt or sinter) such as iron (Hallgren and Oskarsson, 1998). The silica content in ash from Miscanthus has been reported as high as 70% (LeBlond et al., 2010).

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Switchgrass

Switchgrass, Panicum virgatum, is a perennial warm season grass native to North America. Once established, it can be harvested on an annual basis, and will remain productive for an indefinite period. Switchgrass generally reaches full yield capacity after three years, but the crop can be harvested starting from the second year. The normal height of switch grass is 1.5 - 2.5 m, depending on the region (Sokhansanj et al., 2009).

Its permanent root system can extend over 3 m into the ground and coupled with its large temporary root system it can improve soil quality through erosion control, soil stabilization, increased water infiltration and nutrient-holding capacity (Qin et al., 2006).

Like miscanthus, it processes the C4 photosynthetic pathway, offering low nutrient requirement and efficient water use. Switchgrass varieties are classified into two broad categories: lowland and upland. Lowland ecotypes historically developed under floodplain conditions, while upland ecotypes developed under drier upland sites. Higher yields have been achieved with some lowland varieties, however, lowland varieties are more susceptible to winter kill. Cave-in-Rock is the most widely planted variety for northeastern North America, and produced the greatest yield among the switchgrass varieties tested (Kludze et al., 2010). **Figure 1-11** is a photo of switchgrass.

Figure 1-11   Switchgrass (Michigan Sportsman)

Harvest timing of grasses plays an important role in nutrient management and fuel characteristics of energy crops. Summer harvested switchgrass can have high chlorine, potassium, sulphur and nitrogen. Over-wintering allows these nutrients to trans-locate into the root systems or to be leached by rainfall (Oo, 2009). The production of switchgrass on clay soils has also been found to lead to three to four times higher ash content due to the higher uptake of silica in these soils. Sandy soils, which have less monosilicic acid, produce feedstocks with lower ash content (Ogden et al., 2010).

Willow Short Rotation Coppice

Willow is a short rotation coppice (SRC), which is widely used as an energy crop in Europe. Willow is usually densely planted and harvested every three years. This SRC is a woody, perennial crop, the rootstock or stools remaining in the ground after harvest with new shoots emerging the following spring. Willow SRC can grow up to 6 m with 5-6 cm diameter stems before it is harvested. A plantation could be viable for up to 30 years before re-planting becomes necessary. Willow clones have several characteristics that make them attractive including the potential for high and consistent biomass production in short time periods, ease of vegetative propagation from dormant hardwood cuttings, a broad genetic base, ease of breeding, and the ability to resprout after multiple harvests. Willow can also provide environmental co-benefits, such as soil and water remediation, and providing wildlife habitat (McKenny et al., 2011).

The "osier", a shrub willow, is parental stock to the majority of willow varieties planted as an energy crop. Selection of willow varieties is region and site-specific. There are over 120 species of shrub willow worldwide, and there have been rapid improvements and developments of willow varieties in recent years in search for higher yields and greater pest and disease resistance. Two willow clones which have good performance in the regions similar to Ontario are Salix dasyclados, studied by Kopp and Abrahamson, 2001 in New York, and Salix viminalis, investigated by Labreque and Teodorescu, 2003 in Quebec. Usually a mix of four to five varieties are planted in a field to enhance structural and functional diversity, reduce the impact of pests and diseases and lower the potential for widespread crop failures (Oo, 2009).

The establishment of SRC plantations has more in common with agricultural or horticultural crops than forestry. Ground preparation is carried out using conventional agricultural machinery and methods. Generally, willow is planted by simply pushing cuttings, approximately 20 cm long and 1 cm in diameter, into the soil, usually 15,000 cuttings/ha at commercial sites. Shoots and roots quickly develop from these cuttings. Typically two or three shoots sprout from each cutting and grow between 2-4 m in the first growing season. During the winter after planting, the stems are usually coppiced (cut back to ground level) to encourage the growth of multiple stems.

The major disadvantage of willow SRC in comparison with the herbaceous grasses is the higher establishment cost due to requirement of planting cuttings, which need to be stored at -2 to -4°C, and utilization of specialized equipment (Prochnow et al., 2009).

Weed control is very critical during the first year of establishment and is often a significant portion of total establishment cost. Willow, in comparison with poplar, has a broader genetic base, offering more selection of varieties to suit different climate and soil conditions.

Willow SRC biomass offers lower overall ash content, lower silica, lower potassium and higher calcium ashes and higher ash fusion temperature in comparison with herbaceous grasses. Moisture content of willow can be as high as 60%. The cut-and-bundle harvester cuts the willow stems and collects them in the bundle 2.5m long. The bundles can be stacked on headlands to reduce moisture content (Oo, 2009). **Figure 1-12** is a picture of willow being harvested.

Figure 1-12   Harvesting of Willow SRC (Canadian Biomass)

Hybrid Poplar Short Rotation Coppice

Hybrid poplars are among the fastest-growing trees in North America and are well suited for the production of bioenergy, fiber, and other biobased products. Like willow, poplar grown as a SRC plantation constitute densely planted high-yielding varieties harvested on a 3 year cycle following coppice of the first establishment year's growth. Poplar grows to the tree form, whereas willow grows with multiple stems of equal size (Oo, 2009).

There are a large number of hybrid poplar species commercially available, and scientists continue to crossbreed hybrids to create trees that will grow faster, are more drought tolerant, and insect resistant. Common hybrid poplar are crosses developed from P. deltoids, P. trichocarpa, P. balsamifera, and P. nigra. As with the willow, selection of hybrid poplar varieties are site-specific and mixed types are usually used in a field to make the SRC more rust and disease tolerant (Oo, 2009).

The density of planting has generally been lower than that for willow at 10-12,000 cuttings/ha. The cuttings are 20-25 cm long and must have an apical bud within 1 cm of the top of the cutting. This means that poplar cannot be planted using step planters, as the cuttings have to be manually processed to ensure the presence of the apical bud. Establishment cost for hybrid poplar is more than willow. The removal of poplar SRC at the end of its life is also more problematic than willow making willow the preferable biomass species over poplar as an energy crop (DEFRA, 2002). Hybrid poplar and willow have similar fuel characteristics.

1.3.2   Agricultural Residues

Compared to purpose grown energy crops many agricultural residues have significantly poorer combustion properties. Typical agricultural residues such as corn stover and cob, soybean stover or straw, wheat straw, and barley straw have higher ash content, chlorine, potassium, magnesium, nitrogen, sulphur, aluminum, calcium, manganese and silica. Agricultural residues also suffer from a lower higher heating value (HHV).

Corn stover, corn cob, soybean stover, wheat straw, and barley straw are considered as potential agricultural residues of interest. These plants and their combustion properties are discussed in further detail in this

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section. **Table 1-2** provides a summary of the combustion properties for corn straw and cob, soybean stover, wheat straw, and barley straw. The Phyllis database from the Energy Research Centre of the Netherlands (ECN) was once again used to obtain average values for the combustion properties. For more details on the database refer back to section 1.3.1 (p. 8).

Table 1-2   Summary of Combustion Properties of Agricultrual Residues (ECN Phyllis)

Parameters	Corn Straw	Corn Cob	Soybean Stover	Wheat Straw	Barley Straw
Proximate Analysis					
Moisture (wt%)	34 - 50	28 - 38.5	6.5-10	6.5 - 10	6.5 - 10
Ash (wt%)	4	1.2	6	6.2	5.5
Volatile (wt%)	78.6	80.6	75.3	69.4	72.1
Fixed Carbon (wt%)	20.6	17.4	19.7	21.5	18.5
Ultimate Analysis (wt%)					
Carbon	46.9	47.8	44.3	44.3	44.3
Hydrogen	5.5	5.6	6	5.3	6
Nitrogen	0.6	0.4	0.7	0.6	0.7
Sulfur	0.04	0.1	0.1	0.1	0.1
Oxygen	41.5	44.2	45.7	39.8	45.7
Elemental Ash Composition (Ash %)					
SiO_2	33.8	40.3		51.5	50.8
Al_2O_3	0.5	0		0.8	0.2
TiO_2	0	0		0.1	0.1
Fe_2O_3	0.6	4.1		0.4	0.1
CaO	6.7	1.3		6.6	8.1
MgO	3.6	2.5		1.7	1.8
Na_2O	0.4	1.2		1.9	1.0
K_2O	30.3	2.0		17.1	18.5
P_2O_5	5.7	8.7		2.1	3.8
SO_3	1.9	6.9		3.7	2.5
HHV Dry Basis (MJ/kg)	18.47	17.89		17.82	17.96
Cl (wt%)	0.16			1.9	0.5
Ash Fusion Temp (^{o}C)	1408		1148	1228	

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Corn Stover

Corn leads all other crops in value and volume of production in Ontario. Corn stems resemble bamboo canes and are conventionally 2-3 m in height with leaves like broad flags, generally 50-100 cm long and 5-10 cm wide. The plant grows about 3mm a day. The corn grains grow on the corn cob. When corn is harvested in the fall (**Figure 1-13**), the corn ears are removed from the stalk. Corn stover consisting of long leaves and tall stalk of the plant is the residual material. The corn grain is gleaned from the corn cob by the combines and the cob is returned to the field.

Figure 1-13   Corn stover at harvest (Recharge)

Soybean Straw

Soybean is a species of legume native to China, where it has been cultivated as a source of dietary protein and oil for thousands of years. The plant was introduced to North America in the mid-18th century and since then the cultivation of soybeans has grown enormously. The height of the plant varies from 20 cm up to 2 m. The leaves fall before the seeds are mature. The stalk of the soybean plant is the available residual material at the time of harvest. The harvesting practice is to cut the soybean plant during harvest of the beans with return of stalk to the fields.

Wheat Straw

Wheat grains grow on multi seed heads at the top of stalks. The stalks are cut above the ground during the grain harvest and are left in the field to dry. The wheat plant has long, slender leaves, and stems that are hollow in most varieties. Though grown under a wide range of climates and soils, wheat is best adapted to temperate regions with rainfall between 30 and 90cm. Winter and spring wheat are the two major types of the crop. Winter wheat has a higher grain yield than the spring wheat. Winter wheat is typically planted after harvesting soybean or corn in the fall. Winter wheat is harvested in July, while spring wheat is planted in March and typically harvested in the fall.

Barley Straw

Barley is a cereal grain derived from the annual grass Hordeum vulgare. Barley grows on hollow, cylindrical stems, which become the barley straw. The stems are cut above the ground during the kernel harvest and are left in field to dry prior to straw baling.

1.4   Biomass Pretreatment

In this chapter, the various macro and micro nutrients found in biomass were reviewed. Many of these nutrients that are essential to biomass growth are also highly undesirable in thermal conversion processes. In particular, when direct combustion is considered, the presence of these undesirable nutrients make it difficult to use biomass. A review of typical agricultural biomass properties indicates that agricultural residues as well as herbaceous energy crops have higher quantities of these undesirable nutrients than desired. The most effective method to overcome the challenges posed by these nutrients is to extract them through pretreatment processes prior to combustion.

Reduction of alkali metals, chlorine, sulphur, and silica will lead to the following improvements:

- Decreases in the concentrations of both gas and particle-phase alkali species in the furnace;
- Decreases in the rate of condensation and chemical reactions;
- Decreases in the amount of liquid formation in particles, therefore reducing the rate of deposit accumulation through particle impaction;
- Decrease corrosion of contact surfaces;
- Decrease in ash content, corresponding to a higher heating value; and
- An increase in ash fusion temperatures, allowing biomass fuel to be used in conventional boilers.

Furthermore, there is both environmental and economical drivers to the recovery of the extracted nu-

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trients. Silica in various forms is a commodity of commercial value that can be a net revenue generator if extracted and further processed.

The potential reduction of soil nutrients by removal of agricultural residue from the field has been a cause for concern within the farming community. Soil nutrient depletion is also a cause for concern with energy crop cultivation, where almost all of the above ground plant is harvested. Many researchers across Ontario, and other regions of the world have undertaken projects attempting to examine the impact energy crops or agricultural residue harvesting has on soil nutrients and organic matter. According to Ted Cowan and the Ontario Federation of Agriculture on average the removal of corn stover from a farm can result in approximately 69 kg/hectare (62 lbs/acre) reduction of Nitrogen, 28 kg/hectare (25 lbs/acre) reduction of Phosphorous and 121 kg/hectare (108 lb/acre) of Potassium (assuming corn yield of 10 tonnes/hectar or 161 bu/acre).

In the subsequent chapters of this report a number of approaches and technologies that could be applied to remove and potentially recover nutrients from biomass are further examined.

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Chapter 2
Biomass Nutrient Extraction Methods

The majority of inorganic constituents in biomass, with the exception of silica, are water soluble. As a result, extensive research has examined various methods of extraction using water to remove the unwanted portions of the biomass prior to combustion. The following sections explore various methods of leaching, the most popular and effective extraction method, as well as some alternative methods that can potentially be applied to nutrient removal from biomass.

Leaching is an extraction process by which material is removed from a solid by means of dissolving them away. The two main mechanisms of leaching in plants are referred to as passive mechanisms, the first being leaching from damaged plant tissue and the second leaching from the outer surface of intact leaf tissue.

More active mechanisms for leaching, such as leaching of solutes that are excreted to external surfaces by plants, are of lesser importance ecologically and do no significantly affect the overall leaching rates (Bakker, 2000). Along with the various inorganic nutrients that are desired to be removed, leaching can also remove free sugars, pectic substances, sugar alcohols, amino acids and organic acids. Leaching can be divided into two main subcategories, field leaching and industrial leaching.

2.1 Field Leaching

Field leaching refers to natural leaching of plant material remaining in or on the ground from a combination of rain, dew, mist and fog. Instead of harvesting the biomass in late summer/early fall, the biomass is left in the field into the fall or over winter and harvested in early spring the following year. The various forms of precipitation (such as rain, snow, and snow melt) over the few months leach-out the nutrients in the biomass, allowing for direct recycling back into the soil.

Delaying harvest until spring increases opportunity to field leach. This leads to (Prochnow et al., 2009; Sokhansanj et al., 2009):

- Reduction of moisture content;
- Reduction of ash content;
- Reduction of Nitrogen (N), Sulphur (S), Potassium (K), and Chlorine (Cl);

- Reduction of ash fusion temperature,
- Reduction in slagging and fouling; and
- Increase in energy content.

All of the fuel improvements described are not directly associated with the leaching process when crops are over wintered. Other contributing factors include (Prochnow et al., 2009):

- Decrease in leaves which generally have higher nutrient content;
- Nutrient translocation and storage to below ground parts of the plant;

The various advantages and disadvantages of field leaching are listed below (Prochnow et al., 2009).

Advantages of Field Leaching:

- Beneficial impacts of direct nutrient recycling back into the soil;
- Inexpensive, no need for equipment; and
- Reduction in fertilization costs.

Disadvantages of Field Leaching:

- Poorly controlled: susceptible to weather variability and risk of contamination from soil;
- Degradation of fuel quality due to organic matter loss;
- Unpredictable scheduling of operations for subsequent crops;
- In some cases, the amount of nitrogen in the biomass does not decrease;
- Biomass yield loss. Prochnow et al. (2009), reported losses of 20% for switchgrass, 34% for miscanthus;
- Ash content initially decreases as compared to unleached samples, but can increase again if left in the field too long (due to microbial induced decomposition removing organic matter at a rate faster than inorganic material extraction by leaching (Hadders and Olsson, 1997; Jenkins, 1997; Jenkins, 2003).

2.1.1 Reported Data on Field Leaching

There have been several research studies performed on field leached biomass to determine the extent of

nutrient removal.

A study in Germany explored the feasibility of using semi-natural grassland native grasses as a combustion fuel. Field leaching between the months of June-October did not show any significant reduction in nutrients other than potassium. It was concluded that this type of biomass was a more problematic fuel than most herbaceous biomass sources (Tonn et al., 2009).

In another recent study conducted at Purdue University, Ogden et al. (2010), investigated the effects of field leaching on switchgrass in relation to harvest time. Samples were harvested between maturity (July) and November, with changes in moisture, ash content and mineral content observed. While chlorine was not measured, the greatest reduction was again with potassium (66%). Other significant reductions were only reported in nitrogen (50%) and ash content (37%). A limited decrease in sulphur (9%) and increases in phosphorous, sodium and calcium were also determined.

It was concluded that field leaching (along with translocation) did reduce the content of some of the fouling and slagging causing nutrients, but not to a degree that would significantly decrease fouling and slagging tendencies (Ogden et al., 2010)

A similar study on switchgrass conducted in Greece also determined that potassium was the only nutrient to have any significant reduction between the early and late harvest. It was concluded that an industrial leaching pretreatment would further improve the reduction in the other nutrient values (Vamvuka et al., 2010).

To date some of the most extensive research into various forms of leaching has been carried-out by researchers from the University of California Davis (Yu et al., 2010, Thy et al., 2010, Turn et al., 2003, Bakker, 2000, Dayton et al., 1999, Turn et al., 1997, Jenkins et al., 1997, and Jenkins et al., 1996).

In a study on field leaching Jenkins (1996) examined the effect of leaving rice straw to field leach in two separate trials. In the first set of trials, the straw was harvested in the fall and was subject to approximately 65 mm of rainfall. The second trial had the rice straw remain over the winter season and harvested in the early spring, with an exposure of 254 mm of precipitation. The samples leached in the fall showed a significant decrease in the alkali metals potassium and sodium (82% and 91% respectively), as well as in chlorine (92%). Decreases were also measured in phosphorous

(78%), magnesium (31%) and sulphur (33%). Levels of nitrogen and calcium showed no decrease, indicating that they were inert with respect to field leaching/washing.

In terms of ash content, there was a decrease of approximately 8% in the field leached sample as compared to an unleached sample. A correlation between ash content and higher heating value has been established in literature for most types of biomass. **Figure 2-1** provides a plot for this empirical correlation between HHV and ash content. As would be expected, reduction in ash content leads to an increase in heating value, a trend that is confirmed with the rice straw analyzed in this study. An 8% reduction in ash content corresponded to an increase in heating value of 2-4% (Jenkins et al., 1996).

The samples that were leached over the winter season showed similar results, albeit with slightly smaller
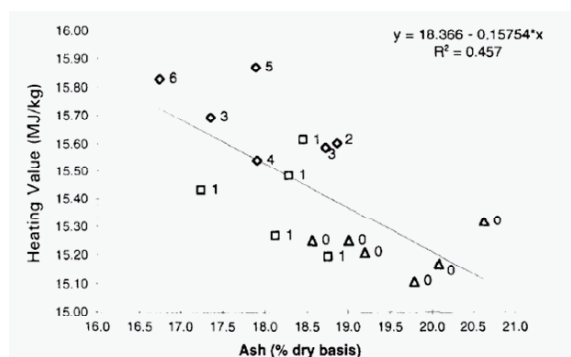
Figure 2-1 Plot of HHV vs. Ash Content (Jenkins et al., 1996)

reductions. Potassium, sodium and chlorine again had the greatest reduction in concentrations, but at 78%, 73% and 92% respectively. Reductions in phosphorous (38%), sulphur (18%) and magnesium (2%) were also much lower when compared to the fall leached samples, and there was also similarly no decrease in the amount of nitrogen and calcium. The ash content was reduced by 4%, with a corresponding increase in the heating value of 2% (Jenkins et al., 1997). The results indicate that the longer time spent in the field may have caused further decomposition of organic matter, without significantly increasing the absolute quantity of nutrient leached. Thus resulting in the over-wintered samples having higher concentration of nutrients.

Several studies were conducted in Sweden, where reed canary grass (Phalaris arundinacea L.) was selected as a potential biomass to be used in energy production due to its high yield, good quality and sustainabley (Landstrom, 1996, Hadders and Olsson, 1997). In order to improve the fuel characteristics of the grass, the biomass was kept in the field over winter and harvested in the early spring to take advantage of field leaching of nutrients.

Overall, it can be stated that field leaching is highly effective in removing large amounts of potassium and chlorine from biomass, while the removal of other inorganic constituents is more variable A summary of selected reported field leaching data is provided in **Table 2-1**.

Table 2-1   Summary of Results for Various Field Leaching Studies

Percent Reduction in the Percentage of Each Nutrient Through Field Leaching (%)					
	Rice Straw	Rice Straw	Reed Canary Grass	Reed Canary Grass	Barley Straw
Harvest Time	Fall	Spring	Spring	Spring	N/A
Phosphorous (P)	78	38	37	62	84
Potassium (K)	82	78	78	78	N/A
Nitrogen (N)	-15	-25	23	34	90
Chlorine (Cl)	92	92	81	84	N/A
Magnesium (Mg)	31	2	60	62	5
Calcium (Ca)	-23	-28	N/A	43	N/A
Sodium (Na)	91	73	N/A	0	N/A
Sulphur (S)	33	18	N/A	47	N/A
Ash	8	4	22	13	N/A
HHV	2 - 4	2	N/A	-1.7	N/A
Reference	Jenkins et al., 1996	Jenkins et al., 1997	Landstrom et al., 1996	Burvall, 1997	Sander, 1997

Note: Negative values denote relative increase in concentration of a given parameter as a percentage of overall biomass

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2.2   Industrial Leaching

Industrial leaching refers to the extraction of nutrients and other components using an aqueous solution in a reactor under controlled conditions and time. Industrial leaching has the technical advantages of controllability resulting in consistent product quality, as well as decreased reaction times and decreased chance of contamination or loss of material in comparison with field leaching. A controlled, industrial water leaching process would represent additional capital and operating costs. However, if the leaching can effectively reduce the alkali metals in the biomass, large-scale leaching prior to combustion may be economically feasible in industrial conversion systems. The reduction in the alkali compounds would mean savings in maintenance costs, and allow the heating equipment to be durable for longer periods (Khan et al., 2009, Maciejewska et al., 2006). Combining industrial leaching with torrefaction and pelletization is considered an interesting option for biomass pretreatment in the co-firing of herbaceous biomass (Dai et al., 2008).

The preferred solvent for extraction of nutrients from biomass is water. Acid leaching has been investigated for use in biomass, but water is the preferred choice due to its relative low cost, nontoxic nature and the fact that it is generally readily available. The overall rate of extraction during leaching depends on a few factors, namely the rate of diffusion of the solvent (water) into the mass of solid to be leached (biomass), the rate of diffusion of solute (the inorganic nutrient) into the solvent, and the diffusion rate of the extracted solution out of the solid (Bakker, 2000).

Many mechanisms for leaching inorganic constituents from biomass are taken from principles used in the commercial process of extracting sugar from sugarcane. In both cases, a soluble product (sugar or nutrients) are extracted from an agricultural crop, while the remaining solid biomass is used for combustion in a boiler system.

The three most common types of industrial leaching of biomass are immersion leaching, immersion leaching with agitation, and spray percolation or pouring of water. Based on the research completed to date, immersion leaching with agitation consistently produces the most efficient removal of nutrients when compared to the other methods examined.

2.2.1   Immersion Leaching

Immersion leaching involves submerging the entire biomass sample within water and submitting it to either a batch or continuous flow of water. Immersion leaching has been investigated with and without agitation. Some of the most promising results have been achieved by the addition of pressing both before and after a leaching process where agitation has been employed to improve diffusion of solute to the solution (water).

Recent work by Yu et al. (2010), at the University of California (UC) Davis explored the effectiveness of immersion leaching with agitation on food industry residues from biomass sources, specifically sugar beet pulp. Leaching times of 30 minutes and two hours were tested, at water to biomass ratios of 20 and 50 L/kg. Results indicated that the leachate contained 70-86% of the potassium, 70-82% of the sodium and 64-76% of the chlorine. The ash content of the biomass was reduced by 55-68%. The amount of potassium and chlorine leached out increased with an increase in the water to biomass ratio, as well as a slight increase with the longer residence times.

The group from UC Davis also studied the effect of leaching a wheat straw feedstock prior to combustion in a fluidized bed reactor and its effect on agglomeration problems in the bed material. The results showed that the leached biomass did not have sylvite (i.e. KCl) in its ash. This suggested that the leaching process effectively removed the majority of the salt in the wheat straw, indicating that leaching strongly restricts agglomeration (Thy et al., 2010).

In China, a study by Deng et al. (2010), on the leaching/washing of wheat straw at different reaction temperatures was conducted. It was shown that leaching effectively removed significant amounts of potassium, sodium, chlorine and sulphur, leading to an increase in ash fusion temperatures. Increasing the temperature of the leached water did not dramatically increase leaching efficiency, confirming that water used for industrial leaching does not require the added energy and cost for heating.

A European research team (Giuntoli et al., 2009) examined the effect of leaching on the combustion characteristics of several agricultural residues available in local regions. One study looked at immersion leaching without agitation using wheat straw, peach stones and

olive residue as the biomass feedstocks for pyrolysis. Water to biomass ratios of between 67:1 and 89:1 were used. Residence times of 23-24 hours were examined.

The focus of the study was to determine the effect that leaching had on the pyrolysis reaction temperature, the pyrolysis reaction rate, and the release of volatiles from the process. Although all three residues showed a decrease in potassium (31-63% reduction), sodium (71-99% reduction) and chlorine (44-100% reduction), only the leached wheat straw and olive residues showed improvements in the reaction parameters listed above. It is believed that the large quantities of chlorine found in wheat straw and olive residue was the main contributing factor to the observable improvement found between the treated and untreated samples of these two feedstocks (Giuntoli et al., 2009).

In a pair of studies conducted by Arvelakis (Arvelakis, et al., 2005 & Arvelakis et al., 2003), the leaching of peach stones and olive oil residue was also examined with a focus on their use as feedstock for a fluidized bed gasification system.

The peach stones were immersed with no agitation at a water to biomass ratio of 15:1 for 8 hours at room temperature. There were relatively lower reductions in the levels of potassium (45%) and chlorine (61%), while aluminum (96%), iron (84%) and sodium (76%) showed larger reductions in the leached material. The nutrient reductions observed translated to a longer operating period for the gasifier before any agglomeration was observed. The olive oil residues (including kernels, pulp, leaves and limbs) also resulted in significant nutrient reductions for sodium (98%), chlorine (97.9%), aluminum (79%), magnesium (75%) and potassium (65%). The ash content of the gasification fuel was reduced by 40-60% and a slight increase in the calorific value was observed. Six fold increase in operating time prior to bed agglomeration was observed when the fulidized bed gasifier opertated on the treated fuel versus the untreated (not leached) (Arvelakis et al., 2005, Arvelakis et al., 2003).

A German study also examined the use of immersion leaching without agitation on two olive oil residues (olive kernels and olive tree wood) but this time using hot water. Leaching procedures were conducted at 80°C for 2 hours, at a water to biomass ratio of

120:1. Large amounts of potassium (89-92%), sodium (82-96%) and chlorine (75-98%) were removed after leaching, but little to no reductions were reported for calcium, magnesium, aluminum and iron. The study focused on the effects of leaching and other pretreatments on reducing problems in fluidized bed combustors, and it was concluded that the reduction in the alkali metals and chlorine would reduce the propensity for slagging, fouling and agglomeration (Vamvuka et al., 2008; Vamvuka et al., 2004).

Turn et al. (2003), used a press-leach-press approach on two sugarcane fibre feedstocks (whole cane and stripped cane). For the pressing step, the biomass was fed through a Cuba mill (consisting of three rollers) four times to remove liquids and reduce the moisture content. In their study they examined three approaches:

i. No treatment;

ii. Milling only; and

iii. Milling-leaching-milling

Water to biomass ratio of 10:1 was used to leach with 1 minute agitation and dripping time of 5 minutes. Potassium levels decreased by 86-91%, chlorine by nearly 100%, 82-86% for sulphur and 27-57% for nitrogen. The results indicated that each step in the process was responsible for a portion of the reduction in the various inorganic elements (Turn et al., 2003).

Dr. Bryan Jenkins from the University of California Davis (Dayton et al., 1999, Jenkins et al., 1997, and Jenkins et al., 1996) led a number of extensive studies into different types of industrial leaching, including immersion leaching. The first study was done concurrently with the fall field leaching samples of rice straw. This study examined the effect of immersion leaching on both rice straw and wheat straw. Whole samples of rice and wheat straw (100 grams) were submerged in 7 L of distilled water (water to biomass ratio of 70:1) for a period of 24 hours. The leached rice straw had a significant reduction in potassium (83%), sodium (91%) and chlorine (92%), almost identical to the results of field leaching. Also similar, were the reductions in phosphorous (86%), sulphur (33%) and ash content (8%). Unlike the field leached samples however, the immersion leaching had an increased reduction in magnesium (57% vs. 31%), and some reductions in nitrogen content (8% reduction vs. No reduction) (Jenkins et al., 1996).

Leached wheat straw samples also had significant re-

ductions in potassium (84%), sodium (84%) and chlorine (90%), as well as in sulphur (77%). Magnesium (53%), calcium (37%) and nitrogen (6%) had smaller reductions, while the phosphorous content did not decrease.

Significant decrease in ash content of the wheat straw was observed in this study. The researchers observed a remarkable 49.5% reduction in the percentage of ash compared to the untreated wheat straw. The results of leaching with cold water have been found to be similar to results of chemical fractionation assays that remove certain elements from solid samples. In the fractionation method, water at 90°C is used, along with ammonium acetate and HCl. These results would again indicate that heating of the water would not improve leaching, thereby reducing the energy and cost needed to heat the water (Jenkins et al., 1997).

The effects of leaching on the ash fusion temperatures were also analyzed for both rice and wheat straw samples (detailed description of ash fusion and its significance to biomass combustion provided in section 1.2.2, page 6). Untreated rice straw showed evidence of sintering at 800°C, and began to fuse at around 1200°C. Leached rice straw on the other hand didn't begin to sinter up to 1200°C, and showed no evidence of fusing up to the maximum temperature tested (1650°C). Untreated wheat straw completely fused into to a hard, glassy slag at temperatures between 800 and 850°C. Leached wheat straw showed an improvement, with sintering not beginning until a little over 1000°C (Jenkins et al., 1996).

The difference in fusibility improvement between the two biomass types has to do with the differences in ash composition. Even though the wheat straw showed a much more significant decrease in ash content in the leached samples, the concentrations of alkali species is still sufficient to cause a reduction in melting temperatures when compared to the leached rice straw.

Finally, the elemental composition of the resulting leachate solution was analyzed to determine how much of the various constituents are present for potential recycling. The rice straw leachate contained high concentrations of bicarbonate, potassium and chlorine ions, with lower amounts of sodium, magnesium and calcium (concentrations of phosphorous and nitrogen compounds were not measured). Wheat straw leachate contained much higher concentrations of potassium, sodium and chlorine ions, with comparable levels of magnesium, calcium and bicarbonate ions. The results appear consistent with the initial concentrations of the various ions in the biomass .

In two follow up studies (Jenkins et al., 1997; Dayton et al., 1999) similar significant reductions in potassium, sodium, chlorine and phosphorus were observed, along with a slight increase in the reduction of nitrogen. In one of these studies, the leached and unleached rice straw samples were tested for their effect on a pilot-scale combustion process. Samples were sent to a Multifuel Combustor (MFC) in California. The MFC is an entrained flow combustor in which milled fuel is pneumatically injected into and burned (at 900°C) in an air stream of an electrically heated downflow tube furnace of 15 cm internal diameter and 4.3 m length. The unleached straw began to rapidly form deposits on the furnace wall, leading to a clogging of the furnace and an early termination of the test.

Analysis of the deposits indicated a potash glass matrix surrounding nodules of silica, demonstrating how the fuel ash transforms to a molten glass by the reaction between potassium and silica at typical furnace temperatures. With the leached straw, only very light wall deposits appeared that were almost immediately blown off by the furnace flow. Samples collected at the exhaust consisted of loose, friable aggregates having almost no sintering. Microscopic inspection showed no fusion of the ash particles, and no significant deposits were collected on deposition probes over two hours. The results show a clear improvement in combustion characteristics for leached biomass over untreated biomass on an industrial scale (Jenkins et al., 1997).

Garland and Mackowiak (1990), produced a study for NASA, looking at the use of water soluble fractions (i.e. leachate) of wheat straw as a plant nutrient source. The wheat straw samples were cut into 25mm sections and submerged in water at a 5% w/v biomass to water ratio for a period of 96 hours. The results indicate a 78% reduction in potassium, a 58% reduction in phosphorous, a 70% reduction in magnesium and a 51% decrease in calcium. Nitrogen and chlorine values were not measured. Analysis of the leachate indicated that 40% of the total composition was inorganic, with the remaining 60% consisting of organic matter. The inorganic composition indicated relatively large amounts of nitrate, phosphate and potassium in the leachate (5, 2.92 and 12.7 mM concentration respectively). It was

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also concluded that two forms of pretreatment, drying and size reduction of the biomass prior to leaching, increased the leaching rate (Garland and Mackowiak, 1990).

Turn et al. (1997) and Dayton et al. (1999) also performed immersion leaching tests with agitation on banagrass (Pennisetum purpureum), a fast-growing tropical grass that is considered a potential dedicated energy crop feedstock for combustion. The leaching process applied mirrored the process used to remove sugars from sugarcane. The biomass first underwent size reduction. Next, the samples are dewatered using a hydraulic press to reduce the moisture content prior to leaching. The leaching process consisted of placing the solid biomass into a basket lined with a stainless steel mesh screen and submerged into a container with enough water to achieve an 8.3:1 water to biomass ratio. The biomass was agitated by hand for three minutes, followed by the removal of the basket from the water and allowing the leach water to drip into the water container for ten minutes. The samples were then pressed again prior to analysis. Three processes were tested with respect to nutrient removal and the results analyzed in two separate studies: forage chopped and pressed without leaching; forage chopped, pressed, leached and pressed; milled, pressed, leached and pressed.

The results show that pressing the biomass without any subsequent leaching does not remove large portions of inorganic nutrients, with potassium, chlorine, nitrogen, sulphur and magnesium only being reduced between 15-50%, while there is little to no decrease in amounts of phosphorous, calcium and sodium. Forage chopped biomass that underwent the pressing-leaching-pressing method showed improved reductions for all nutrients (between 26 and 84% reduction), with the exception of phosphorous and calcium (no decrease). Ash content also decreased by 32%, with a corresponding increase of 3% in the heating value (Turn et al., 1997; Dayton et al., 1999).

The milled biomass samples subjected to the same press-leach-press process produced the best results. Potassium levels decreased by an average of 80%, with relatively larger decreases in chlorine (98%), magnesium (61%), sulphur (50%) nitrogen (48%) and sodium (53%). An appreciable amount of phosphorous was removed (between 41 and 60%) where none was removed in the other two methods tested. Reductions in ash content and increases in the heating value were similar to the forage chopped samples. The results indicate that the combination of dewatering, greater size reduction and leaching remove the most inorganic constituents from the biomass. **Figure 2-2** indicates the fraction of the initial elemental mass in the banagrass that has been removed in the first press, second press, and leaching step for the milled sample process.
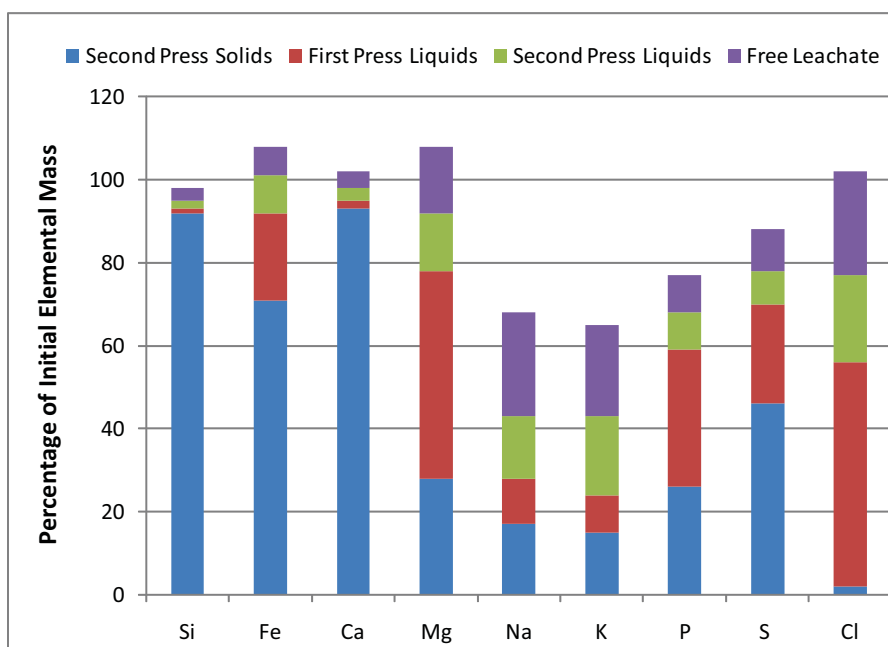
Figure 2-2 Banagrass Leaching Subject to Pressing, leaching and pressing (Turn et al., 1997)

The figure confirms that both presses and the immersion leaching all have a part in the reduction of inorganic ions from the biomass (Turn et al., 1997; Dayton et al., 1999).

Another study by the UC Davis group examined various reaction parameters and their effect on the reduction of potassium, chlorine and ash, and the effect on ash fusion characteristics. The first set of tests looked at the effect of residence time on rice straw immersed in water (with no agitation) at a water to biomass ratio of 120:1. As the residence time increased from 1 minute to 60 minutes, there was an increasing trend in the reduction of potassium, chlorine and ash, as well as in improvement in ash fusion temperatures. One noteworthy result was that for each residence time, the amount of leached chlorine removed is larger than the amount of leached potassium, and that there is a linear relationship between the values reported by the researchers (Bakker, 2000).

A second set of tests examined the effect of the water to biomass ratio on potassium and chlorine removal during immersion leaching with agitation. Water to biomass ratios of 20:1, 30:1 and 40:1 were tested, with the immersed biomass (both uncut and milled) agitated for 10 minutes. The results show that with an increased ratio, a larger amount of potassium and chlorine was removed. Milled samples also showed an increased reduction in potassium and chlorine when compared to the whole samples. Finally, it was shown that immersion leaching with agitation improves the extraction of the elements when compared to the immersion leaching tests without agitation. After 10 minutes, the reduction of potassium and chlorine (73 and 91% respectively for ratio of 40 L/kg) were much higher when compared to reductions in the non-agitated immersion leaching for the same amount of time with a much larger ratio of 120 L/kg (37% and 53% reduction for potassium and chlorine) (Bakker, 2000).

Two other studies examined immersion leaching with agitation. Christensen (1985) leached samples of barley straw (5 cm length samples) in cold water at a water to biomass ratio of 20 L/kg. Samples were agitated by hand at the beginning of the method, left for 30 minutes, then agitated again and left for 18 hours. After 4 consecutive immersions, potassium had the highest reduction (87%), while the other nutrients measured (phosphorous, nitrogen, calcium and magnesium) had reductions between 20 and 59% (chlorine and sulphur

were not measured). Ash content decreased by only 2.6% (from an original value of 4.5%) (Christensen, 1985).

The second study examined the leaching of wet corn stover using a stirred tank reactor for immersion leaching with agitation. The biomass was placed in a jar filled with water (at a water to biomass ratio of 4:1 w/w) and was agitated with an overhead stirrer between 10-30 rpm. The study focused on concentrating the resulting leachate using ultrafiltration, and therefore did not report the change in composition between the untreated and leached biomass. Analysis of the leachate confirmed that appreciable ion concentrations of potassium (384.6 mg/L) and chlorine (57.1 mg/L) were present, along with lower amounts of sodium (5 mg/L) and phosphate ions (3.7 mg/L) (Colyar, 2008).

In summary when examining all of the various studies conducted on immersion leaching of various forms of biomass it can be concluded that immersion with agitation of biomass increases the effectiveness of the leaching.

2.2.2   Spraying or Pouring of Water

Another common method investigated as an industrial leaching process involves the spraying or pouring of the water onto a layer of biomass on some type of porous surface (i.e. steel mesh) and allowing the leachate to drip through.

The UC Davis research group also investigated the pouring technique on different types of biomass. One study subjected milled samples of switchgrass, wheat straw and a wood fuel blend (a collection of ponderosa pine and Douglas fir chips) to a pouring leaching technique. The process consisted of placing 50 grams of the milled sample on a paper element filter and pouring increments of 500 mL of water for a total water to biomass ratio of 120:1. The switchgrass sample showed a significant reduction in several inorganic nutrients, including potassium (84%), chlorine (100%), phosphorous (87%), sulphur (63%) and nitrogen (45%). Reductions were also shown for magnesium (43%) and sodium (35%), but not calcium (no decrease) (Dayton, et al., 1999).

The leached wheat straw sample had similarly large reductions in potassium (84%), chlorine (90%), sodium (83%) and sulphur (77%). The wheat straw samples

also showed reasonable reduction in calcium (37%), but a relatively low decrease in phosphorous (15%).

The wood fuel samples also had large reductions in potassium and chlorine, as well as a relatively significant decrease in nitrogen (75%). However there was no decrease in the amount of sulphur, as well as a small decrease in sodium (17%) and phosphorous (46%) (Dayton et al., 1999).

In a separate study, the group explored the spraying of water using a nozzle on samples of rice straw. In this method, a 30mm thick bed of rice straw (uncut) was placed on an expanded steel mesh, with tap water uniformly sprayed over the bed for one minute. The leached biomass did not show any significant decrease in inorganic nutrients compared to the other methods tested, with a 49% reduction in chlorine, 38% reduction in potassium and 39% reduction in phosphorous. The poor results were attributed to the short spraying time and possibility of not all biomass coming in contact with the water (Jenkins, 1996).

Small scale combustion experiments of leached biomass samples were conducted to once again verify an improvement in combustion characteristics. Apart from benefits to ash fusion temperatures and decreased deposits, it was also shown that the removal of alkali metals and chlorine corresponds to a removal of HCl and alkali metal vapours released during combustion. In addition, the removal of alkali metals reduced the amount of time required for char burnout, an indication that less char and therefore less CO gas released (Dayton et al., 1999).

Based on the literature to date all methods, given enough time and water, can effectively remove large amounts of potassium and chlorine, with varying results for the other nutrients of interest. To minimize time and water requirements however, it has been shown that immersion leaching with agitation can remove significant amounts of most nutrients in shorter amounts of time and lower water requirements when compared (directly or indirectly) with immersion leaching and spraying/pouring of water. While significant work has been done on olive oil resiudes, banagrass and rice straw, more data is required for other energy crops (switchgrass, miscanthus, etc.) and agricultural residues (corn cob, corn stover, etc.) to get a more definitive conclusion on the benefits of immersion leaching with agitation.

2.3   Drip Irrigation

In this process biomass is placed in a packed bed column to which water and bacteria is added. The bacteria is used to decompose the biomass. The column consists of a drip irrigation system at the top and a filter and sub-drain on the bottom. Periodically the leachate is recirculated from the drain to the irrigation system with a pump. After sufficient time, the leachate is removed and placed in a second container, while fresh leachate is added to the first column for the next run. The leachate in the second container is concentrated by heating. The resulting concentrated solution is used as a liquid fertilizer (Samani, 2010).

The process could be used to remove N, P, K, Ca, Mg, Fe, Mn, Zn and is currently applied industrially to porudce liquid fertilizers. The process is suitable for use in producing liquid fertilizer from bio-solids, however, given that the process results in the decomposition of the biomass it is not suitable for producing a biofuel.

2.4   Steam Distillation

In this process the biomass is pressed (hot or cold), followed by steam distillation and centrifuge to separate the liquid fertilizer solution. Biomass sources include pine needles, coconut fatty acids, extracts from cottonseed, rice husk, castor seed, linseed, citrus peel and lemongrass (Agrogreen Canada, 2010). The nutrients extracted include: P, K, N. The process is currently industrially applied to produce liquid fertilizer by Agrogreen Canada from pine needles. The process suitability is undetermined for agricultural residues and energy crops commonly considered for combustion fuel.

2.5   Technical Gaps in Reported Literature

There are several technical gaps in current literature concerning industrial leaching techniques. The high water to solid ratios used in most investigations are not scalable to throughputs that would be common in large industrial sized units. Furthermore, there is very little to no data reported for pilot or industrial scale projects, as well as a lack of scale-up and modelling research. Integration of an industrial leaching process with other extraction and recovery processes has been limited to a few studies examining the recovery of nutrients and water through a reverse osmosis process (Colyar, 2008; Jenkins et al., 2003), with no reported processes combining leaching with silica extraction.

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For leaching processes that include some form of agitation, little research into mixing parameters has been conducted to optimize the process to potentially reduce process residence times. Finally, there is very little economic data reported for an industrial-scale leaching process. As part of a doctoral thesis (Bakker, 2000), an economic feasibility study was conducted, but was limited in scope.

Chapter 3
Methods for Extraction of Biomass Silica

3.1   Introduction

Silicon is the eighth most common element in the universe, and the most common metalloid. In nature, Silicon is typically found in various forms of silica (SiO_2) or silicates. As described in detail in Chapter 1 (pages 3-4) silicon (Si) plays a very important role in biology. Plants contain silicon in three basic forms: Insoluble amorphous silica (SiO_2) (more than 90%), silicate ions and colloidal silicic acid. Silica is the largest mineral component of perennial grasses and provides structure to plants. The uptake of more water results in more silica content in the plant, thus warm-season grasses (switchgrass & miscanthus) have lower silica content in comparison with cool-season grasses (canary grass) that require more uptake of water. Soil type and condition also has an influence on the concentration of silicon in the plant.

Silicon contributes to a number of problems associated with biomass combustion including:

i.   Formation of deposits that slow down the rate of heat transfer; cause bridging across tube bundles; accelerate corrosion; and generally increase costs associated with generating power;

ii. Formation of slags resulting from reaction of potassium and silica to produce heavily sintered and fused glassy deposits (also known as clinkers);

iii. Fouling resulting form accumulation of Si, K, Cl, and S on solid surfaces; and

iv. High ash content.

Given the many negative attributes of biomass combustion associated with the silicon content of plants, early adopters of biomass combustion have chosen the utilization of plant species with low Si content. Wood-based residues have been particularly attractive sources of biomass for both heat and electricity generation around the world with a multitude of industrial applications.

Field leaching has been effectively applied in various studies to reduce the overall nutrient content of particular energy crops and agricultural residues. Although, leaching can improve the combustion quality of biomass by reducing various water-soluble nutrients, it has minimal effect on the Si concentration. Silica which

contributes to more than 90% of the Si composition of biomass is soluble in basic solutions and as a result does not leach-out with water or acidic solutions like most other biomass nutrients. Therefore, alternative methods are required for the extraction of Silicon from most agricultural residues and energy crops to enable their use in thermal conversion processes.

Silicon extraction can also provide a revenue stream that would make the process economically favourable. There are a wide range of industrial applications for silicon. It is the principal component of semiconductors, microchips, and integrated circuits (**Figure 3-1**) found in virtually every electronic device.
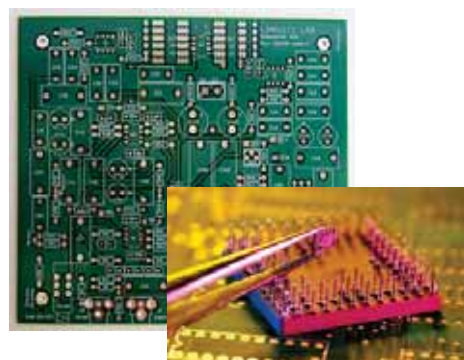
Figure 3-1 Integrated Circuit Board & Chip (Digital Circuit)

The largest application of metallurgical grade silicon, representing about 55% of world consumption, is in the manufacture of aluminium-silicon alloys to produce cast parts, mainly for the automotive industry. Silicon is an important constituent of electrical steel, modifying its resistivity and ferromagnetic properties.

The second largest application of silicon (about 40% of world consumption) is as a raw material in the production of silicones, compounds containing silicon-oxygen and silicon-carbon bonds that have the capability to act as bonding intermediates between glass and organic compounds, and to form polymers with useful properties such as impermeability to water, flexibility and resistance to chemical attack. Silicones are used in waterproofing treatments, molding compounds and mold-release agents, mechanical seals, high tempera-

ture greases and waxes, caulking compounds and even in applications as diverse as breast implants, contact lenses, explosives and pyrotechnics (Koch & Clement, 2007). **Figure 3-2** is a collage of silicone products.

Currently (as of March 2011) silicon metal 4-4-1 (98.5% min Si, 0.4% Fe, 0.4%, Al, 0.1% Ca) and Silicon metal 5-5-3 (98.5% min Si, 0.5% Fe, 0.3% Al, 0.3% Ca) are trading at $2600, and $2500 USD per metric ton on global markets (metal-pages.com).

Figure 3-2 Various Silicone Products

3.2 Pulping Process for Extraction of Silica

It is a well known fact that silica (SiO_2) can be dissolved in hot base or fused hydroxides. The most common method used to extract silica involves dissolving it in a strong base such as sodium hydroxide.

Pulping processes can be broadly divided into two large categories: chemical pulping and mechanical pulping. Chemical pulping involves using chemical reactions to solubilize lignin and produce individual fibers or pulp from lignocellulosic raw materials. The main types of chemical pulping processes are the Kraft process, and Sulfite process. Mechanical pulping process as well as both of these chemical pulping processes can be applied to extract silica from biomass. A brief description of the pulping processes are provided in the following two subsections.

3.2.1   The Kraft Process

The Kraft process was invented by Carl F. Dahl in 1879. to whom U.S Patent 296,935 was issued in 1884. The first pulping mill using this technology was established in Sweden in 1890 (Biermann, 1993). Today, the Kraft

process is the most common chemical pulping process. The process entails treatment of wood chips with a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), known as white liquor that break ligno-cellulosic bonds in plants (Gullichsen & Fogelholm, 2000). In the process wood chips are cooked in high pressure vessels called digesters at an elevated temperature of 180°C for several hours in the presence of white liquor. Under these specific conditions, the lignin that links the cellulosic fibres, breaks and dissolves in the liquor along with the mineral contents and the hemicellulose. The resulting liquor is called black liquor with a pH of 13 to 14. Cellulose fibres in this process are separated as brown pulp and are sent for further processing to get high quality paper. Various methods such as, ultrafiltration membranes, lime and carbon dioxide are employed to separate lignin from silica to varying degrees. **Figure 3-3** below provides a simplified schematic of a typical commercial pulp and paper plant employing the   Kraft process.
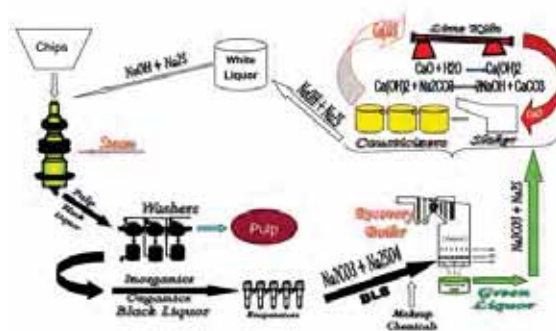
Figure 3-3 Kraft Process (AQuinde Pulping Consulting Inc.)

3.2.2   Sulfite Process

The sulfite process produces wood pulp which is almost pure cellulose fibers by using various sulfites (SO_3^{2-}), or bisulfites (HSO_3^-) to extract lignin from wood chips in large digesters. The first pulp mill using the sulfite process was built in Sweden in 1874 and used magnesium as a counter ion. Calcium became the standard counter ion until the 1950s. The invention of the recovery boiler by G.H. Tomlinson in the early 1930s allowed pulp mills employing the Kraft process to recycle almost all of their pulping chemicals. This, along with the ability of the Kraft process to accept a wider variety of types of wood and produce stronger fibers made the Kraft process the dominant pulping process

starting in the 1940s. Sulfite pulping now account for less than 10% of the total chemical pulp production and the number of sulfite mills continues to decrease (Biermann, 1993).

Sulfite pulp is used to make fine paper, tissue, glassine and to add strength to newsprint. A special grade of bleached sulfite pulp known as "dissolving pulp" is the raw material for a wide variety of cellulose derivatives, for example rayon, cellophane, cellulose acetate and methylcellulose. Rayon is a reconstituted cellulose fiber used to make many fabrics (Gullichsen & Fogelholm, 2000).

Sulfite pulping is carried out between pH 1.5 and 5, depending on the counterion and the ratio of base to sulfurous acid. The pulp is in contact with the pulping chemicals for 4 to 14 hours and at temperatures ranging from 130 to 160°C depending on the chemicals used (Sjöström, E., 1993) .

The spent cooking liquor from sulfite pulping is usually called brown liquor, but the terms red liquor, thick liquor and sulfite liquor are also used (compared to black liquor in the Kraft process). Pulp washers, using countercurrent flow, remove the spent cooking chemicals and degraded lignin and hemicellulose. The extracted brown liquor is concentrated, in multiple effect evaporators. The concentrated brown liquor can be burned in the recovery boiler to generate steam and recover the inorganic chemicals for reuse in the pulping process or it can be neutralized to recover the useful byproducts of pulping (Sjöström, E., 1993).

3.2.3 Mechanical Pulping Process

The use of wood to make pulp for paper began with the development of mechanical pulping in Germany by F.G. Keller in the 1840s. The earliest mills used sandstone grinding rollers to break up small wood logs called "bolts", but the use of natural stone ended in the 1940s with the introduction of manufactured stones with embedded silicon carbide or aluminum oxide. The pulp made by this process is known as "stone groundwood" pulp (SGW). If the wood is ground in a pressurized, sealed grinder the pulp is classified as "pressure groundwood" (PGW) pulp (Biermann, 1993).

Most modern mills use chips rather than logs and ridged metal discs called refiner plates instead of grindstones. If the chips are just ground up with the plates, the pulp is called "refiner mechanical" pulp (RMP), if

the chips are steamed while being refined the pulp is called "thermomechanical" pulp (TMP). Steam treatment significantly reduces the total energy needed to make the pulp and decreases the damage (cutting) to fibers. Mechanical pulp mills use large amounts of energy, mostly electricity to power motors which turn the grinders. A rough estimate of the electrical energy needed is 10,000 MJ/tonne of pulp (2,750 kWh per tonne) (Biermann, 1993).

Mechanical pulping seems to be more suitable for raw materials with higher silica content, particularly wheat and rice straws, since the silica is not dissolved to the same extent as for chemical pulps and will for the most part remain with the fibers throughout the pulping and bleaching process. Mechanical pulping also generates a minimal volume of effluent, thus reducing the environmental impact (Chute et al. 2008).

Mechanical pulping generally results in pulp of lower quality resulting from significant amounts of lignin left with the mechanical pulp. This results in a weaker pulp that is more difficult to bleach to high brightness than its chemical pulp counterpart (Chute et al., 2008). When applying this process for treating biomass for combustion it is important to leave significant quantity of lignin with the pulp, given that lignin is a major contributor to the heating value of the fuel. Thus, what is a disadvantage to mechanical pulping for paper production is a very important advantage to mechanical pulping for silica removal from biomass intended to be feedstock for thermal conversion processes such as direct combustion.

A number of researchers have investigated chemical and mechanical processes which are similar in essence to the pulping processes described above in order to recover various value-added product streams from biomass including Silica.

3.3   Chemi-mechanical Desilication of Non-Wood Plants (U.S Pat. 7,364,640)

Of all the reported patents and research work that has been carried out on the removal of silica from biomass using techniques similar to the pulping processes, U.S Patent 7,364,640 is the most promising. In this section this important patent by Chute et al., 2008 will be described in detail. In U.S. patent 7,364,640 (Chute et al., 2008) a chemi-mechanical desilication process for non-wood plant materials is described. Chemi-mechanical

pulping (CMP) treats raw material with weak solutions of pulping chemicals such as sulfur dioxide, sodium sulfite, sodium bisulfite or sodium hydrosulfite, followed by mechanical defibration (Chute et al., 2008).

The purpose of the patent is to address the "growing interest in using nonwood plant fiber sources, such as wheat straw, flax and hemp, for pulping and papermaking" (Chute et al., 2008). "As wood fiber shortages are predicted in the future, nonwood plants are believed to be a sustainable fiber source to potentially supplement the use of wood fibers in paper applications. Market forces and legal requirements may stimulate the production of paper that contains nonwood plant fibers, as exemplified by experience with recycled fibers" (Chute et al., 2008).

One of the problems associated with the chemical pulping of nonwood plants is the difficulty in recovering the cooking chemicals from the spent cooking liquor ("black liquor"), caused by the relatively high levels of silica found in most nonwood plant fibers, as compared to wood. During alkaline cooking of nonwood plant fibers, this silica is dissolved and is subsequently removed from the fibers via the black liquor stream, which is sent to the chemical recovery system for conversion into fresh cooking liquor. The silica-laden liquor causes scaling and fouling in evaporators, concentrators and the recovery boilers, resulting in inefficient operation and increased downtime for cleanouts (Chute et al., 2008).

The inability to recover cooking chemicals from silica-laden black liquor results in increased operating cost and effluent treatment system loading. On the other hand, conventional mechanical pulping processes are limited in the quality of pulp that can be produced due to the fact that significant amounts of lignin are left with the pulp (Chute et al., 2008).

In U.S. Pat. No. 6,183,598 (Myreen, 2001), a process for recovering alkali and heat energy from black liquor containing high quantities of silicate ions produced from chemical pulping of nonwood plants is disclosed. Recovery of the sodium hydroxide using lime is usually impeded by the formation of calcium silicate, which makes recycling of the lime difficult or impossible. The solution proposed in this patent is to treat the black liquor with carbon dioxide (soda) to precipitate silica and lignin. The solids are then removed and the remaining black liquor is evaporated and burnt to generate heat and a sodium carbonate melt, from which carbon dioxide is formed. The carbon dioxide is then reused to treat the black liquor (Chute et al., 2008).

However, the drawback to the process proposed by Myreen (U.S. Pat. No. 6,183,598) is that with the precipitation of lignin, there may also be a loss of some inorganics that will limit the potential recovery efficiency. Furthermore, the proposed process is energy intensive because of the heat lost by precipitation of some lignin, which would otherwise be burnt in the recovery boiler to generate steam (Chute et al., 2008).

Other methods for removing silicate from black liquor have been proposed. In U.S. Patent 4,056,356 (Mudler et al., 1985) a continuous process for removing silica from spent pulping liquors (black liquors) which have been obtained by the alkaline digestion of annual plants is disclosed (Mudler et al., 1985). In this process the spent liquor is pre-concentrated and contacted with the flue gas containing CO_2. The precipitated silica is removed from the treated liquor by sedimentation or centrifugation; then washed with water. The silicon is precipitated as a mixture of silica and calcium silicate by adding lime. Solid and liquid phases are separated from each other and the resulting residue is burnt out to obtain, if desired, a molten material, which is cooled and then granulated (Mudler et al., 1985 & Myreen, 2001).

The process patented by Mudler et al., 1985 was installed at the RAKATA company's mill in Egypt, however never worked satisfactorily (Myreen, 2001). The reason for this is that, in order to convert a sufficient portion of the silicate into crystalline and hence separable form, the pH must be decreased to a point that a portion of the lignin in the black liquor will be converted into a gelatinous phase and that makes the separation of the silica and the gelatinous lignin from the liquor very difficult. Removal of lignin form the liquor will also decrease its calorific value, so it will not be high enough to allow it to be burnt in steam boilers developed for liquor combustion (Myreen, 2001).

A number of other variation of the patent by Mudler and Myreen have been proposed for separation of silicates from black liquor, all of which have similar drawbacks as the ones identified.

In the desilication process descibed by Chute et al. (U.S. Pat No. 7,364,640), baled plant material is brought

into the process. The bale breaker separates the bales into manageable pieces by particle size reduction (forage cutter, disc chipper, or tub grinder) followed by a screening stage (rotary drum screen, vibrating screen, or roll type screen). The material is then pulped at low consistency, for example between about 0.5% and about 6% solids, under mild alkaline conditions (pH 7-11) using a Tornado Pulper™ (Bolton-Emerson Americas Inc.). In the pulper, the particle size is reduced and the removal of the silica-rich components of the straw begins (Chute et al., 2008).

Material that passes forward through the pulper is processed in a junk cyclone to remove large tramp material such as rocks and metal prior to refining. The plant material is then refined at low consistency in a refiner, where the mechanical liberation of the epidermis and nodes is substantially completed. After refining, material is passed through a sidehill screen, where water is removed from the fiberized suspension along with the epidermis and nodal material. The size of the liberated epidermal material is such that it is able to pass through the sidehill screen with the filtrate (Chute et al., 2008).

Further dewatering occurs in a press, which may be a screw press, belt filter press, or similar dewatering device. The pH and temperature of the pulper may be controlled to conditions optimum for the removal of silica. The preferred conditions are a temperature between 50°C and 90°C, and a pH of between 7 and 12. As used herein, "silica" refers to both silica found in the epidermis and nodal material, which may be mechanically liberated and removed, and silica that may be solubilized under the preferred process conditions.

The filtrate of both the sidehill screen and dewatering press will be rich in silica. It passes to a filtrate tank and may then be pH-adjusted to precipitate soluble silicate ions, and then processed in a hydrocyclone system to remove suspended solids and the precipitated silica. The lean filtrate may then be reused as dilution to the pulper and low consistency refiner, with make-up water coming from the aforementioned sources.

Surplus water in this loop may be directed to the effluent treatment system for further treatment. Treatment may include settling or flotation for suspended solids removal, and aerobic or anaerobic treatment for removal of dissolved and colloidal organic materials, or combination of these treatments.

The precipitated silica may itself be a useful or valuable product and may be used in other industrial applications or processes. This ability to recover and reuse the silica may enhance the economics of a non-wood fiber processing facility (Chute et al., 2008).

The low operating temperatures, and mild alkalinity required in the desilication process proposed by Chute et al., as described in U.S. Pat. No. 7,364,640, makes it a promising approach to silica removal in other applications besides pulping. The technical and economic feasibility of the process as a pre-treatment to production of high quality biomass pellet require further investigation.

3.4 Strong Acid Hydrolysis of Cellulosic & Hemicellulosic Material (U.S. Pat. No. 5,597,714)

In U.S. patent 5,597,714 (Farone et al, 1997), a process for acid hydrolysis of cellulose and hemicellulose is described. The process was developed for the purpose of recovering sugars from biomass using concentrated acid hydrolysis. The patent described the process for rice straw, which is very high in silica content.

In one embodiment of the patent, rice straw was first washed with water to remove the dirt and contamination and then dried to a moisture content of 10%. The cellulose and hemicellulose were first partially hydrolysed in a decrystallization stage. In this stage the rice straw was added slowly to 77% by weight of sulphuric acid (H_2SO_4) and maintained at temperatures below 60°C producing a gelatinous mixture.

After the crystallization stage, the concentrated acid in the gelatinous mixture is diluted to about 20% to 30%. The mixture is hydrolyzed at 100°C for 60 minutes and filter-pressed to obtain a liquid fraction containing sugars and acid and a solid fraction. The solid fraction is treated with a second stage of acid hydrolysis to ensure effective hydrolysis. The sugars are separated from acid to be used for production of ethanol whereas lignin-silica cake is further processed for silica extraction.

The pressed solid remaining from both the first and second hydrolysis is treated by 5% -10% NaOH solution in order to extract silicic acid. The mixture is then heated to a temperature of 80°C for about 90 minutes. The cake was pressed and washed with water. The total

liquid extracted was found to have a pH above 12. This liquid can be treated with concentrated HCl to reduce the pH to about 10 producing a light fluffy precipitate. The precipitate is separated by filtration and treated with 11% solution of NaOCl to produce essentially pure silica gel. Alternative acid precipitation processes are described and can be implemented to produce zeolites. The pressed cake that was left behind after NaOH treatment was dried to moisture content of less than 10%. This cake was shown to have a fuel value of 20.0 GJ/kg (8600 BTU/lb) and very low ash content. **Figure 3-4** is a schematic of the described process.

U.S Patent 5,597,714 describes a pathway for the production of three value-added product streams from agricultural residues and energy crops including:

i. Sugars for further conversion to ethanol;

ii. Silica based products; and

iii. High quality combustion fuel

BlueFire Ethanol has licensed the above patented technology from Arkenol Fuels and is currently the only ethanol producer that the author could confirm employing concentrated acid hydrolysis process for cellulosic ethanol production.

3.5   Ultrafiltration of Black Liquor

Ultrafilitration (UF) is a cross-flow separation process for the removal of high molecular weight substances, colloidal material, and organic and inorganic polymeric molecules. The liquid stream to be treated flows tangentially along the membrane surface producing two streams. The stream that flows through the membrane is called permeate or filtrate whereas the stream that is retained is called concentrate or retentate.

The UF membranes do not collect particles but acts as the barrier to fractionate them according to the molecular weight The porosity of UF membranes lies in the range of 0.1 to 0.001 microns. UF membranes are able to retain particle size of 1,000 to 1,000,000 molecular weight. Therefore, organic and inorganic
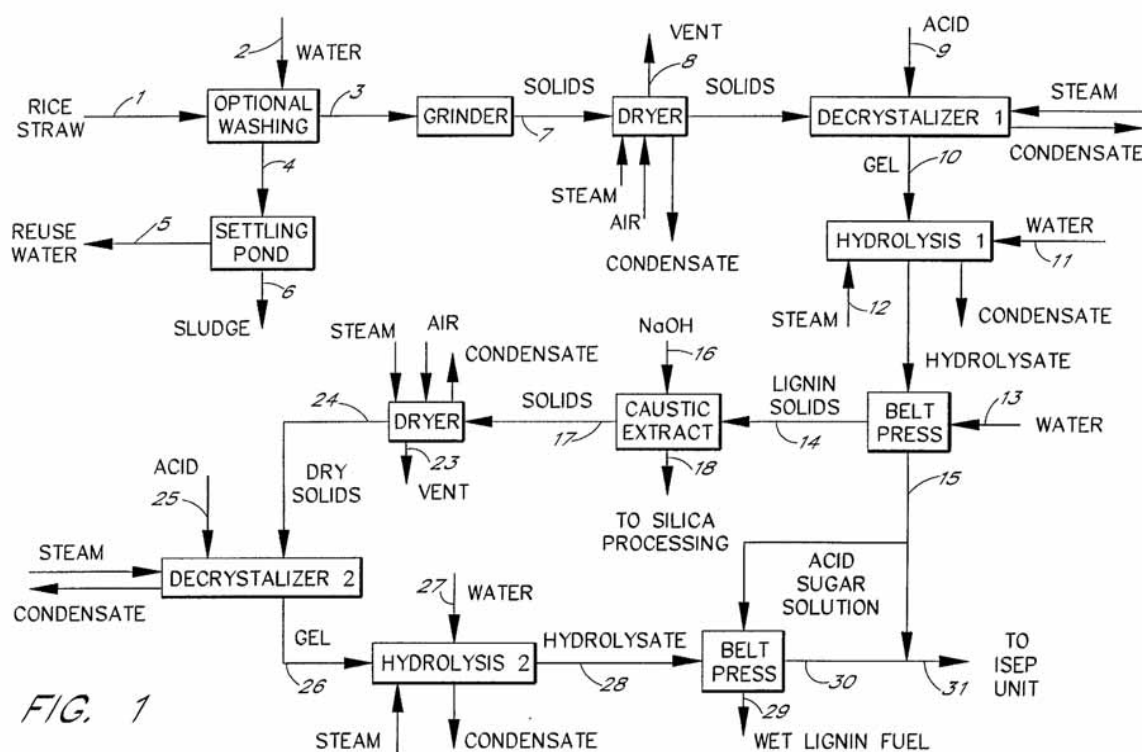
Figure 3-4 Schematic of the Process Described in U.S Pat. No. 5,597,714

molecules with low molecular weights such as sodium, calcium, magnesium chloride and sulphates are not retained by UF membrane. The osmotic differential pressure across the UF membranes is minimal because it can achieve removal of only high molecular weight particles. Hence, UF membranes require low pressure to achieve high flux rates. Generally, the flux rates of UF membranes vary between 50 and 200 Gallon per square foot per day (GFD). However, it is possible to accomplish extremely high flux rates by using UF membranes (appliedmembranes.com & millipore.com).

UF membranes are used in purification of drinking water, wastewater treatment for water reuse and reclamation, as well as in many industrial applications such as power, pharmaceutical, biotechnology and semiconductor industries (gewater.com).

UF membrane modules are available as plate-and-frame, spiral-wound and tubular configurations. The configuration selected depends upon the application, the type and concentration of the species to be retained. Open configuration such as plate-and-frame and tubular are used to concentrate solutions. The optimum system design of the configurations takes into consideration the flow velocity, pressure drop, power consumption, membrane fouling and module cost.

Various materials are used for UF membranes in which polysulphone and cellulose acetate are most commonly used. Ceramic UF membranes are used in instances where high chemical and physical stability are required (www.gewater.com). **Figure 3-5** shows samples of polymeric and ceramic UF membranes.

In U.S. Pat. No. 5,735,196 (Lucas et al., 1998) a process for the production of lignin fuel, ethanol, cellulose, silica/silicates and cellulose derivatives from plant biomass is disclosed. The process involves a series of physical and chemical treatments of high silica content plants to produce ethanol, lignin, a high protein animal feed supplement, and silica.

The first step in the process is to reduce the size of the plant material using a hammermill or ballmill to between 40 and 60 mesh. The reduced size plant material is then fed into a counter current extractor. An acidic solution, preferably carbonic acid, is added to the biomass at a temperature between 40°C and 60°C for 60 minutes to hydrolyze hemicellulose. The liquid stream from the first counter-current extractor con-
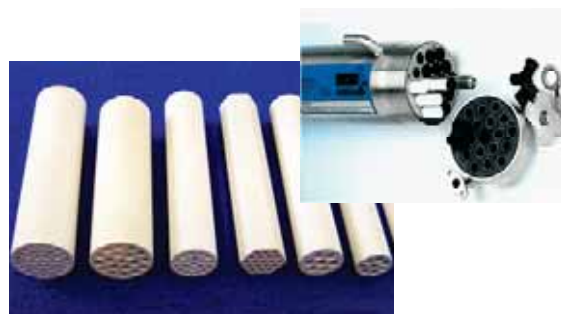
Figure 3-5 Polymeric & Ceramic UF Membranes

tains xylose (and other C5 sugars), soluble salts such as sodium and calcium salts and soluble protein and polypeptides. This solvent stream is sent directly to a fermentation unit containing organisms that convert 5-Carbon sugars into ethanol (Lucas et al., 1998).

The solids from the first counter-current extractors were filter pressed to a moisture content of about 25%. A strong caustic solution of 50% NaOH was added and the mixture was maintained at 50°C for 120 minutes. The strong base dissolved lignin and silica. The mixture of lignin and caustic silicate is fed to an ultrafiltration unit with a polysufone membrane cast on the outside of a hollow cermaic core (Lucas et al., 1998).

The mixture was passed over the membrane at a pressure, varying between 150 psig and 300 psig. The flow rate of the feed was maintained at 5 to 6 GPM (18.9 to 22.7 L/min). The lignin was concentrated to 38% to 42% total solids. The lignin thus obtained was washed to a pH between 7.0 and 6.5 preferably, 6.7. The lignin with adjusted pH is then dried and grounded to a powder form. The sodium silicate solution passed through the polysulfone UF membrane and was sent to the bleeder system. The bled sodium silicate was packaged for sale. The solid leaving the second counter-current extractor consisted of cellulose which was centrifuged and sent to the sacchrification system. A partial sacchrification of cellulose was done using a weak sulfuric or hydrochloric acid. Cellulose was converted to glucose monomer by addition of hydrolytic sacchrification enzyme. Fermentation of glucose was done by genetically engineered bacteria which gave an ethanol concentration between 3% and 5% while the stillage was analyzed to be high protein animal feed (Lucas et al., 1998).

The process described in the above patent provides a good example of how ultrafiltration could be em-

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ployed in a biomass pretreatment process to separate dissolved silica from lignin in black liquor.

Wallberg (2003a), investigated the performance of three tubular polymeric membranes with cut off of 4kDa (ES404, made of polyethersulphone), 8kDa (PU608 made of poysulphone) and 20kDa (PU120 made of polysulphone) to retain lignin from black liquor. The membranes were manufactured by PCI Membranes System Ltd., UK. The black liquor used for the experiments was removed before the evaporation process without any alterations to the pH. The pH of black liquor was found to be between 13 and 14. The temperature was kept at 60°C throughout the experiments. Two types of experiments were performed. The first series of experiment studied the retention of lignin by the UF of different cut-offs while the second, series of experiment studied the effect of diafiltration on the purity of lignin.

Diafiltration is a membrane based separation that is used to reduce, remove or exchange salts and other small molecule contaminant from a process liquid or dispersion. In batch diafiltration, the process fluid is typically diluted by a factor of two using "clean" liquid, brought back to the original concentration by filtration, and the whole process repeated several times to achieve the required concentration contaminant. In continuous diafiltration the "clean" liquid is added at the same rate as the permeate flow.

In the retention experiments, two ES404, one PU608 and one PU120 were mounted in series. Reproducibility check was performed by two ES404 membranes. In the beginning of the experiment, permeate valves were used to keep the transmembrane pressure (TMP) low and then increased from 100kPa to 700kPa, increasing temperature every 30 minutes. The average transmembrane pressure was calculated by subtracting the average pressure at inlet and outlet at permeate side from the average pressure at inlet and outlet at feed side.

The second series of experiment performed diafiltration of black liquor by using four PU608 membranes. This experiment was done to reduce the ash-generating substances in the lignin fraction. In the diafiltration, deionized water was added to the retentate which was then ultrafiltered to achieve selective removal of species having low molecular weights. Diafiltration was done in both batch and continuous operations. In this

experiment, permeate valves were open throughout the experiment. The initial average transmembrane pressure was 560kPa and at the end of experiment increased to 640kPa. This experiment showed the lignin content to be 80%, 67% and 45% for the membrane cut-off of 4kDa, 8kDa and 20kDa respectively. The retention of sodium and sulphur was found to be insignificant regardless of membrane cut-off. Purity of lignin was achieved with the diafiltration.

In another study (Wallberg & Jonsson, 2003b) the retention of lignin was investigated by using two ceramic membranes with cut-offs of 5kDa and 15kDa. The membranes were manufactured by Orelis, France. **Figure 3-6** provides a scheamtic of the UF separation of lignin.
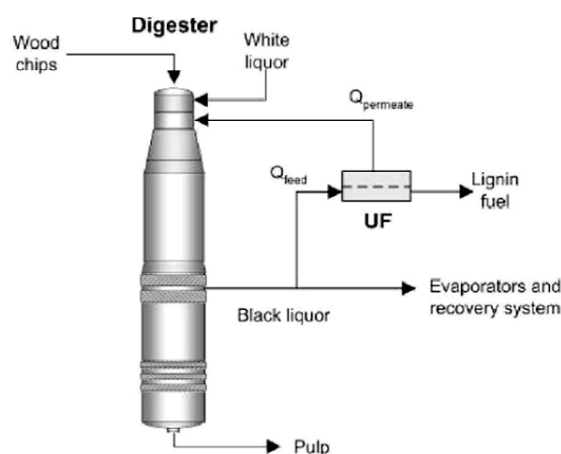
Figure 3-6 UF Separation of Lignin (Wallberg, 2003b)

The temperature was kept to 90°C through out the experiments. The 5kDa membrane reduced the volume of black liquor to 80% whereas the 15kDa membrane reduced the volume to 90%. The difference in the permeability of two membranes resulted in the lower average flux during concentration of black liquor for 5kDa as compared to15kDa. The average flux value for 5kDa was found to be 45 L/m²h, when the transmembrane pressure was 400kPa and circulation velocity was 3.6 m/s whereas, the average flux of 15kDa membrane was found to be 95 L/m²h, when the tranmembrane pressure was 100kPa and circulation velocity was 4.5 m/s. There was a marked difference in the lignin reten-

tion of two membranes. The lignin retained by 5kDa was 66% while 15kDa retained 28% of the lignin. The retention of monovalent ions such as Na, K and S ions was negligible while the majority of multivalent ions such as Fe, Mg, Mg & Ca passed through both 5kDa and 15kDa membranes (Wallberg & Jonsson, 2003b).

In yet another study (Wallberg et al., 2003c) the researchers investigated the separation of lignin from black liquor produced by the Kraft process using tubular ceramic membrane made up of Al_2O_3-TiO_2. The membranes were manufactured by Orelis, France and had a cut-off of 15kDa. The black liquor was taken before the evaporation unit with a pH of 13-14 which was not adjusted. The effect of different temperature on lignin recovery was studied. The temperatures taken into consideration were, 60°C, 75°C and 90°C at different pressure. The fluxes were found to be 90, 110 & 130 L/m²h at 60°C, 75°C and 90°C, when the trans-membrane pressure was kept at 100kPa. The lignin retention was found to be between 30% and 40%. Minimal retention of monovalent ions was observed, however, almost all the multivalent ions such as Ca, Mg, Mn & Fe were retained.

The last of the series of ultrafiltration studies of interest (Wallberg, 2006) investigated lignin recovery using ceramic membrane with cut-offs of 5kDa and 15kDa at a temperature of 145°C and transmembrane pressure of 400kPa. The cooking liquor was taken from between pre-impregnation and digester process. No cooling, adjustment of pH and pre-filtration was implemented prior to the experiments. The results showed that the flux was higher for both membrane cut-offs. The flux for 15kDa membrane was 100 L/m²h and it retained 20% of the lignin whereas the flux of 5kDa membrane was 50 L/m²h and it retained 30% lignin.

3.6   Sodium Carbonate - Lime Method

In U.S. Patent Application Publication No. US 2006/0225852 A1 (Pekarovic, et al., 2006) a simple and economical method for removing silica from cellulosic material is disclosed. The biomass deemed suitable for this method was high silica containing non-wood biomass.

According to this process the biomass is first cut into pieces between 10 mm to 30 mm and screened to reduce the content of silica by 50%. Steam is then used to moisturize and preheat the shredded biomass to

facilitate impregnation. Dilute solution of sodium carbonate (Na_2CO_3) is used to leach the silica out of the biomass. The ratio of impregnation liquid to biomass was in the range of 1:2.5 to 1:20 depending upon the type of biomass. The ratio was kept as small as possible while maintaining a good impregnation. The impregnation was performed for 30 to 60 minutes at a temperature of 70°C to 100°C at atmospheric pressure. The silica containing impregnation black liquor was separated from the raw material using filtration. The soild mass was at least partially desilicated. The silica containing impregnation black liquor was causticized using calcium oxide (quick lime) to precipitate silica-enriched calcium carbonate, and separating the precipitated silica enriched calcium carbonate from the causticized impregnation liquor. It is claimed that the process can remove up to 100% of the silica contained in the biomass by this method prior to any conventional pulping methods (Pekarovic, et al., 2006).

The patent application claims that this process is a simple and economical method of removing silica from biomass in comparison with prior art. Further investigation into the technical and economical merits of this process are recommended.

3.7   Electrostatic Separation of Silica

Electrostatics is the branch of science that studies the behaviour of static or slow moving electric charges. Electrostatics has been used to give positive or negative charge to particles by creating an electron imbalance on the surfaces that causes a build up of charge. The principle of electrostatics has been successfully applied to operate photocopiers (Xerox process), powder coating, and separate materials, such as minerals, metals, plastics, and particulates from flue gases. Electrostatic separation process have also been shown to have encouraging results in coal beneficiation (described in detail in section 3.7.2).

3.7.1   Mechanisms of Particle Charging

There are three major mechanisms for imparting electrostatic charge onto particles before they are separated in high-intensity electric fields, including:

i.   Corona Charging;

ii. Induction Charging;

iii. Tribo Charging

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Corona charging (Figure 3-7): This process involves charging of particles by ion bombardment. In this mechanism, the potential between the two electrodes is increased by high voltage that ionizes an otherwise non-conductive stream of gas. The charged ions in turn transfer this charge to the surface of particles they come in contact with. The charge given to the particles is influenced by the particle size, its dielectric constant (work function), the field intensity and the concentration of ions in the gaseous medium (Kelly & Spottiswood, 1989a & b). Corona charging is an effective solution for separating insulating materials from conductive materials such as metals from plastics (Tilmatine et al., 2009, Iuga et al., 2011) and fly ash from coal particles (Das et al., 2010).

Dascalescu et al., 2010 and Hermey et al., 2009, investigated corona charging for the separation of different layers of wheat bran, to produce fractions rich in the different bran layers, such as pericarp-rich fractions (rich in fiber) or aleuronerich fractions (rich in vitamins, minerals and antioxidant compounds). A belt-type corona electrostatic separator was used for this purpose. The influence of particle size (0.3 mm and 0.5 mm) on the separation efficiency was investigated and it was found that the smaller the particles, the higher the specific charge, due to the greater number of particles/charging device collisions. It was expected that the difference in the electric conductivity of different layers might be adequate to exploit their electrostatic separation. However, as most of the wheat bran tissues had similar conductivities, the corona charger was not efficient for separating the different layers (Dascalescu
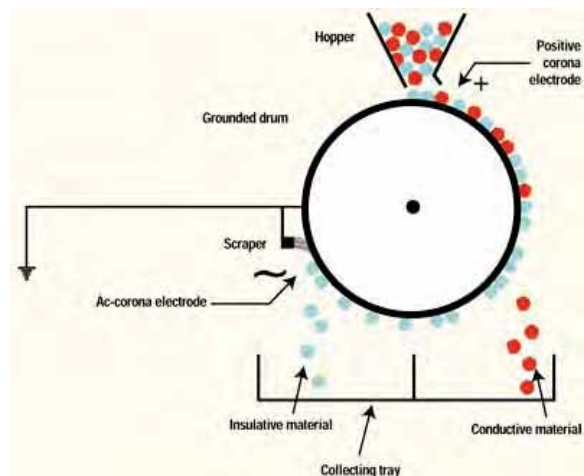
Figure 3-7 Corona Charging Separator (ce-mag)

et al., 2010 and Hermey et al., 2009)

Induction Charging: In this process, initially uncharged particles in an electric field acquire an electric charge from the field. When the conductive charged particle comes in contact with a conductive surface, it conducts a charge of one polarity to the surface. The particle is then left with a net charge which is opposite to its previous charge. On assuming similar charge as the surface, the particle is then repelled by the surface. If the surface is grounded, then the other electrode with an opposite charge attracts the particle (Kelly & Spottiswood, 1989a & b).

Tribo Charging (Figure 3-8): This process involves imparting charge on the surface of particles or materials by means of contact or friction against other dissimilar particles or material such as walls of containers, pipes and/or other processing devices. Electrons in a material occupy lowest states unless heated or activated by other means. When two materials of different work functions come in contact some electrons acquire high energy states (excited state) and there is transfer of electrons from one surface to another until the energy of electrons is equalized at the interface of both the materials.
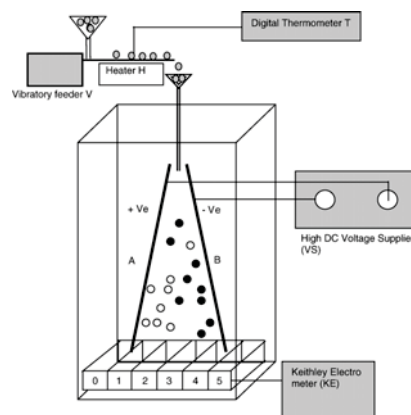
Figure 3-8 Tribo Charging Separator (Dwari and Rao, 2006)

The transfer of charge depends upon the work function of the particles, which is the minimum energy required to remove electrons from the surface of a material. The material with higher affinity for the electrons or higher work function gains electrons and therefore charges negatively. The material with low affinity for electrons or lower work function loses electrons and

therefore charges positively. For example, when copper which has a work function (electron affinity) of 4.38eV comes in contact with silica which has a work function of 5.4eV, it gives electrons to silica and therefore silica gains a negative charge. However, when copper comes in contact with carbon which has a work function of 4.0eV, carbon gives up electrons and acquires a positive charge. Hence, in order to give opposite charge to two components, a material of work function value intermediate to the work function values of the components to be separated is chosen as the contact material used in the tribocharger.

Once the particles are tribocharged relative to their work functions, they are made to fall through an electric field which deflects the particles according to the magnitude and type of charge on them. Materials or particles can be tribocharged when there is a contact between two conductors (metals) or when a conductor and non-conductor come in contact or when two non-conductors come in contact. The contacts or friction may be created through a fluidized bed, a vibrating bed or a pneumatically conveyed stream of particles (Dwari & Rao, 2006; Dwari & Rao, 2009)

3.7.2   Coal Beneficiation

In the mining industry beneficiation is defined as a variety of processes that can be employed to improve the chemical or physical properties of an ore so that the mineral of interest can be recovered with better profitability. With respect to coal mining, beneficiation is typically processes used to separate the inorganic constituents of coal (ash forming content and minerals) from the organic components of coal that provide heating value.

The removal of ash producing inorganic constituents of biomass, in particular silica (which does not readily dissolve in water) has similar technical challenges as coal beneficiation. Much like removal of nutrients from biomass, the purpose for coal beneficiation is to produce a higher quality fuel for combustion out of low quality coal. Electrostatic separation has been shown to work in coal beneficiation, and thus may also be applicable to removing silica from biomass. In this section the use of electrostatic separation for coal beneficiation is described.

In geological terms, coal is a sedimentary rock containing a mixture of constituents, mostly of biomass origin. When the biomass decays under water, in the

absence of oxygen, the carbon content increases resulting in peat production. The formation of peat is the first step in formation of coal. With increasing depth of burial and increasing temperature, peat deposits are gradually changed to lignite. With increasing time and higher temperatures, these low-rank (lignite) coals are gradually converted to sub-bituminous and bituminous coal.

Macerals are the various microscopically recognizable, individual organic constituents of coal with characteristic physical and chemical properties. Macerals are the coalified plant remains preserved in coal and other rocks that change progressively, both chemically and physically, as the rank of coal is increased. Coal rank is a measure of a coal's degree of metamorphism based on decreasing volatile matter and increasing carbon
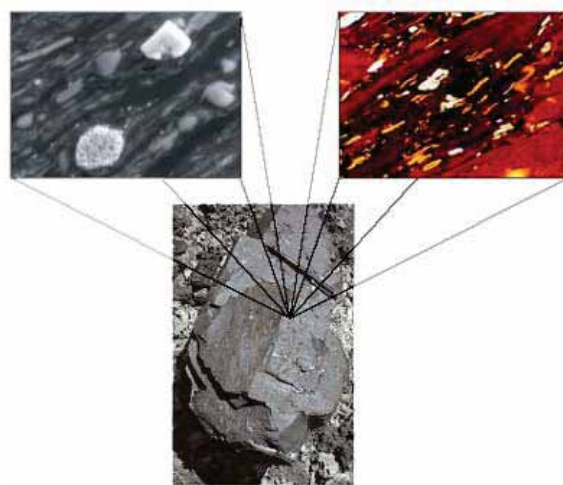
Figure 3-9 Macerals in Coal (usgs.gov)

content from lignite (lowest rank) to anthracite (highest rank).

Figure 3-9 provides microscopic images taken from a chunk of Texas sub-bituminous coal in the field. Top-left enlargement is an example of a scanning photomicrograph showing minerals in coal. The bright-white, oval-shaped fragment is a pyrite framboid; the bright-white triangular fragment is zircon; each fragment is about 10 microns wide. The light-colored, equant blebs are quartz grains. They are set in a light-gray matrix consisting of coal macerals and a variety of clay minerals. Top-right enlargement is an example of a transmitted-light photomicrograph showing various

coal macerals such as: vitrinite (dark reddish orange); liptinite (yellow and light orange); and inertinite, and minerals (black). View is about 200 micrometers wide. Each of the three main types of macreals identified in the image are further described below:

Vitrinite: A shiny, glass-like material that is considered to be composed of cellular plant material such as roots, bark, plant stems and tree trunks. Vitrinite contains the highest content of oxygen and organic sulphur of all macerals. Vitrinite macerals when observed under the microscope show a boxlike, cellular structure, often with oblong voids and cavities which are likely the remains of plant stems. They have a high calorific value (24 - 28 MJ/kg) and a large proportion of volatile matter (24 - 30%). Vitrinite often occurs interbanded or interlaminated with inertinite and can be recognised as bright bands (Dow, 1977). **Figure 3-10** is an SEM image of vitrinite.
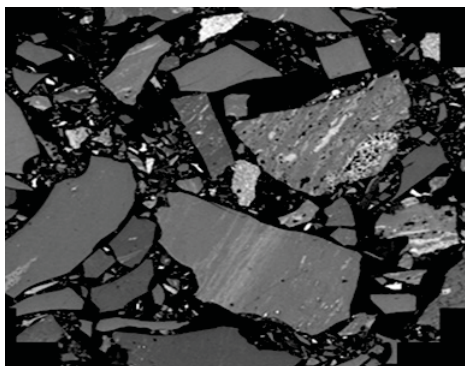
Figure 3-10   Vitrinite Reflectance for coal ranking (zeiss.com)

Liptinite: These macerals are considered to be produced from decayed leaf matter, spores, pollen and algal matter. Resins and plant waxes can also be part of liptinite macerals. Lipitinite consists of aliphatic structures with comparatively high hydrogen and low oxygen contents. Liptinite macerals tend to retain their original plant form, thus resembling plant fossils. These are hydrogen rich and have the highest calorific values of all coal macerals (Taylor et al., 1988).

Inertinite: This maceral is carbon rich and greatly resembles graphite. Inertinite is considered to be the equivalent of charcoal and degraded plant material. It is highly oxidised in nature and may be said to be burnt. A large portion of South Africa's coal reserves consist of inertinite (Coal Macerals Tutorial).

Dwari & Rao (2009) used a fluidized bed triboelectrostatic separator consisting of internal baffles to give opposite charges to the maceral (organic) and mineral (inorganic or ash forming content) particles of pulverized coal samples. The maceral and mineral particles acquired a positive and negative charge respectively on the basis of their work function. The two were then separated by negatively and positively charged electrodes. This research was successful in reducing the ash content in the coal samples examined from 43% to 18%.

The apparatus is comprised of fluidized bed tribocharger (FTB) with internal baffles made of copper. The apparatus also included a copper made cyclone discharging system and two electrodes in the form of two oppositely charged copper plates diverging progressively from top to bottom. The charge to the electrode was provided by a high DC voltage supply source and the plates were encased in a rectangular box. Six collecting bins in the form of Faraday cups were placed in such a way that Bin 1 was closest to negative electrode whereas Bin 6 was closest to positive electrode. The experimental set-up also included a nitrogen gas cylinder to fluidize the particles and a Keithley electrometer to measure the magnitude of the charge acquired by the particles. **Figure 3-11** provide a schematic depiction of a fluidized bed tribocharger by Dwari & Rao, 2009.
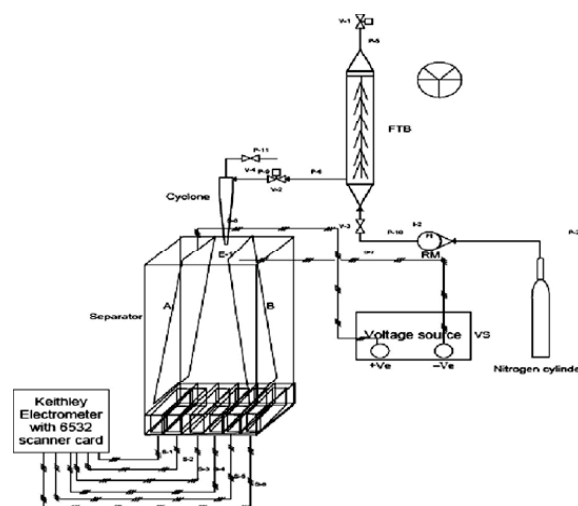
Figure 3-11   Fluidized Bed Tribocharge (FTB) (Dwari & Rao, 2009)

The pipes used to transport the charged particles from the FTB to the box containing electrodes were also made of copper to facilitate ample tribocharging. The experiment was done at voltages of 10kV, 15kV and 20kV to see the effect of applied voltage on particle separation. Effect of time and flow rate of nitrogen for fluidization and size and weight of the particle was also studied.

The coal sample used was prepared by screening it to less than 300μm with D90 of 234 μm and a mean diameter of 86μm. The coal sample consisted of 5.8% moisture, 23.5% volatile matter, 43.2% ash and 33.3% fixed carbon.

The process resulted in 70% of the mineral content collected in bins close to positive electrode whereas 20% collected at bins close to negative electrode. The optimum conditions to separate coal from its ash content were found to be at an applied voltage of 10kV with a tribocharging time of 60s at a gas flow enough to effect particle fluidization. The optimum condition was successful in reducing the ash content from 43% to 18% at a yield of 30%. At a higher yield of 67%, the ash content was reduced to 33%.

Given the low yields experienced in this experiment, the process necessitated the recycling of particles to achieve better separation results and higher yields. It is also possible to treat fine coal material with the vapours of acidic and/or basic organic solvents in the fluidised bed tribocharger for altering the surface energetic structure of particles and thereby enlarging the work function difference between the surfaces.

Bada et al (2010) used a rotary tribo electrostatic separator developed at The University of Kentucky for separation of coal maceral (organic) from its mineral content. The apparatus consisted of a cylindrical charging chamber where the components of coal were given a charge. The chamber consisted of an octogonal rotary charger held at a certain potential which enhanced the charge generation by keeping the particles in friction.

The apparatus also included Particle Separation Zone with a negative electrode (plate R) and a positive electrode (plate L). These electrodes separated the particles by attracting the oppositely charged particles whereas the uncharged particles fell in between the two electrodes. The splitter incorporated in the apparatus was used to keep the three streams separate.

Two streams at the far end consisted of positive or negative charge while the centre stream consisted of uncharged particles. The particles of these streams were collected by three bins through the air cyclone. **Figure 3-12** provides a schematic of the rotary tribo electrostatic separator investigated by Bada et al., 2010.
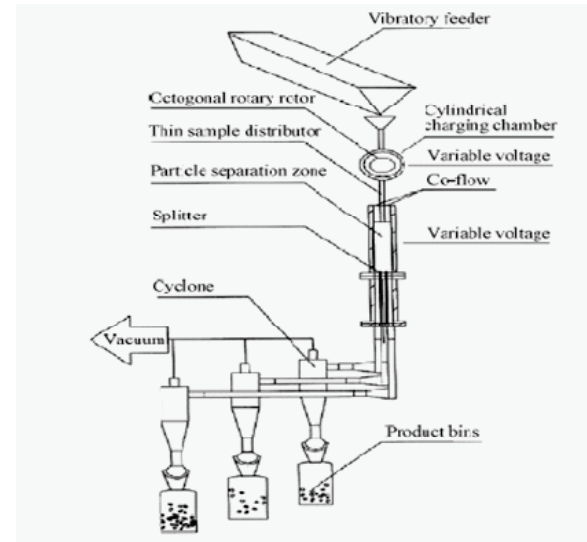
Figure 3-12   Rotary Tribo Electrostatic Separator (Bada et al., 2010)

Single stage and two stage separation was studied in this research with two types of sample with particle sizes of less than 177μm. A Majuba coal sample consisted of 43.69% fixed carbon, 30.10% ash, 23.01% volatile matter and 3.19% moisture contents. A Koorfontein coal sample comprised of 52.35% fixed carbon, 24.04% volatile matter, 20.58% ash and 3.03% moisture. The experiment was performed at applied voltage of 10kV, 15kV and 20kV and a feed rate of 12 to 24 g/min.

It was found that the RTS technique was effective in reducing the ash content of the cleaned coal. The results were that at 10kV lower mineral content and coal yield were observed than 20 kV. The higher feed rate examined improved ash reduction. As expected, the two staged separation proved to be more efficient than single stage. The results of their study is summarized in **Table 3-1** (next page).

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Table 3-1 Summary of Beneficiation Results from Bada et al. (2010)

Coal Sample	Calorific Value	Ash (%)
Majuba Feed	20.15	30.22
Majuba After Single Pass	25.67	14.67
Majuba After Second Pass	27.4	10.76
Koorfontein Feed	24.53	21.36
Koorfontein After Single Pass	25.82	12.92
Koorfontein After Second Pass	28.30	11.11

In a number of earlier studies Dawari & Rao (2006) designed a simple triboelectrostatic separator which was tested to investigate the type of charge acquired by the inorganic and organic constituents of coal against various tribocharging mediums. The inorganic constituents studied were, quartz (silica), kaolinite, illite, geothite, siderite and pyrite. The different contact materials used as tribocharging medium included: perspex (2.7eV), brass (4.28 eV), copper (4.38 eV), aluminium, PVC (4.85 eV), and Teflon (5.75eV).

The experimental set-up was essentially comprised of a vibrator feeder with a hopper and a plate at the top of the vibratory feeder. The plate acted as the tribocharging medium. The set-up also included a heater and a thermometer to observe the effect of the temperature. A funnel shaped pipe was positioned between the tribocharging medium and separation chamber to allow the charged particles to enter the separation section. The separation section was comprised of a rectangular perspex box with dimensions of 1 × 0.52 × 0.52 m fitted with positive and negative electrodes, each having a length 0.84m and breadth 0.43m. The coal sample comprised of coal particles with a D90 of 238μm, and a mean diameter of 88.9μm. The feed rate was kept slow in order to facilitate the sliding of only single layer of the particles over the plate. The particles were charged by vibratory plate and then were allowed to fall between the electrodes.

The effect of temperature on tribocharging was observed by maintaining the temperatures of the plate at different setpoints between 18°C to 78°C. The effect

of electrode voltage on separation was also investigated at 10kV, 15kV and 20kV.
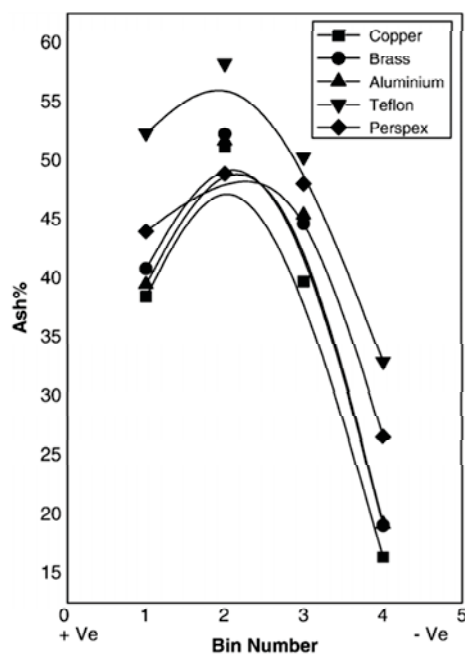
Figure 3-13 Effect of contact medium on separation efficiency (Dawari & Rao, 2006)

Figure 3-13 depicts the ash content of coal collected in each of the bins for different contact materials. As the figure shows Copper was the most effective medium for coal beneficiation since it results in lowest ash content in Bin #4 indicating the highest separation efficiency for the ash content. It was also found that as the temperature was increased, the magnitude of the charge acquired by the particles also increased. Increase in temperature caused more electrons to be in excited state in the outermost orbit resulting in higher electron transfer from material of low work function to high work function. However, separation of inorganic and organic components was adversely affected by increase in temperature. The lowest inorganic (ash) content was achieved at a tribocharger temperature of 18°C.

In U.S Pat. No. 5,938,041, Stencel et al. (1999a) invented a triboelectrostatic device based on pneumatic stream principles. The triboelectrostatic separation apparatus proposed consisted of: a separator with an inlet (20), a separation chamber (26), first and second

electrodes (28) & (30), a variable voltage source for applying respective positive and negative voltage potentials to the electrodes, a pair of separated particle outlets (34) & (36) and a curtain gas flow generation system (40). The curtain gas flow generation system includes a source of curtain gas at positive pressure, a metering valve (44) for matching curtain gas flow velocity to particle flow velocity and flow straighteners (46) & (48) for eliminating eddy currents. Figure 3-14 provides a schematic diagram of the pneumatic tribo-electrostatic separator (Stencel et al., 1999a)
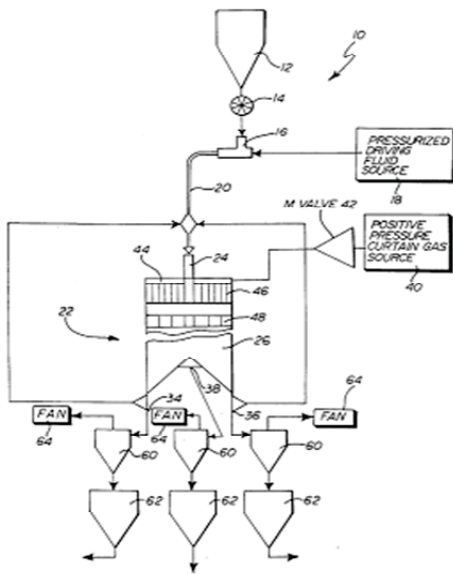
Figure 3-14   Pneumatic Triboelectrostatic Separator (Stencel, et al., 1999a)

This particular design was successful in reducing the unburned carbon content from the fly ash to about 60% to 80%. The inventors claim numerous benefits to the proposed invention, including:

i. The curtain gas flow longitudinally along the electrodes facilitates for the particles that are drawn electrostatically to the electrodes to be swept smoothly towards the associated discharge outlet and collected with high purities achieved; and

ii. Matching the velocity of curtain gas flow to the particles in the driving fluid minimizes turbulence at the interface of the two streams and results in enhanced particle separation efficiency.

In another earlier patent by Stencel et al., 1998 (U.S. Pat. No. 5,755,333), a method and apparatus for tribo-electric-centrifugal separation is disclosed. The process proposed employs both centrifugal and electrostatic forces to separate the desired particles. Stencel et al. claim that the combined process will provide an additive effect on particle separation, thereby achieving enhanced separation efficiency (Stencel et al., 1998).

The design was applied to separate unburned carbon from fly ash which resulted in reduction of unburned carbon from 10% to 5% and the concentration of the carbon in the carbon stream was increased to 34%. Given that the results were obtained from a single pass of material through the process, Stencel et al. 1998 claim that by recycling one or both of the streams of particles multiple times through the process further enhanced separation can be achieved. Figure 3-15 provides a schematic diagram of the triboelectrostatic-centrifugal separator (Stencel et al., 1998).
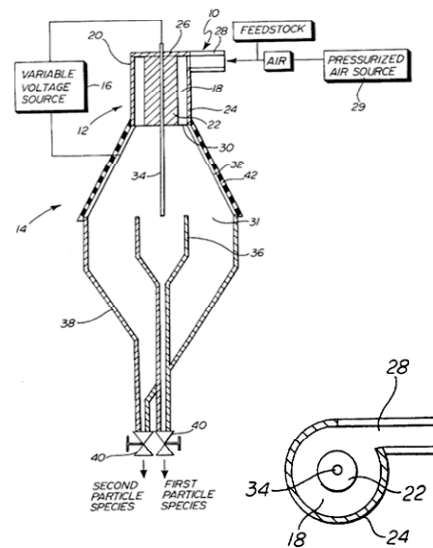
Figure 3-15   Triboelectric-Centrifugal Separator (Stencel et al, 1998)

The inventors claimed that the triboelectric-centrifugal separator has numerous benefits compared to conventional tribo charging separators, including:

i. By harnessing both centrifugal and electrostatic forces, enhances particle separation of two species of particles with different dielectric constants

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and specific gravities can be achieved; and

ii. Method and apparatus proposed can be operated in either batch or continuous mode.

In two subsequent patents, U.S. Pat. Nos. 6,323,451 (Stencel et al., 2001) and 6,498,313 (Stencel et al., 2002) John Stencel and his research team at the University of Kentucky Research Foundation disclose further advancements to their original tribo-electrostatic separation system design based on pneumatic principals.

In U.S Pat. No. 6,498,313 Stencel et al. disclose an electrostatic particle separation system, and related method for separating a particle mixture into two constituent species. The system includes: a distributor for differentially tribocharging the particle species forming the mixture and supplying the charged mixture to a multitude of electrostatic separation cells. Each cell includes at least one separator having an inlet, a separation chamber, a collector, and a transition outlet. The length of the electric field zone in the cells is adjustable. Charged particles drawn from the particle mixture in the electric field zone are carried by a curtain gas flow to the collector. Flow straighteners are used for both the particle mixture flow and the curtain gas flow to reduce the turbulence in the separation chamber and improve separation efficiency. The collector includes a discharge outlet for discharging the selected charged particles to a first collection bin. The transition outlet receives the remaining particle flow and delviers it to a second collection bin for recovery or onto a second separator for a second pass.

There has been a single report published in 2011 that examines the use of triboelectrostatic separation on biomass. Hemery et al. (2011) published a study investigating the separation of wheat bran layers into purified fractions using the tribo-electrification technique. To separate the fractions of wheat bran, the different layers of wheat bran should acquire charges of opposite signs to allow the particles to be separated in an electric field. Two separation experiments were performed, with the bran undergoing one or three successive grindings at ambient temperature. It was observed that the aleurone intracellular compounds were not concentrated in one fraction in particular. More purified fractions that were rich in aleurone (i.e. rich in minerals, vitamins), and rich in the most outer layers (i.e. rich in fibers), were obtained by electrostatic separation when the starting material was more

finely ground or more dissociated (i.e. after three successive grindings). Three fractions named 'negative', 'middle', and 'positive' were obtained, with yields of 15.9%, 33.7%, and 41.3%, respectively (with 9% loss observed). Fibre rich particles of pericarp were more abundant in the fractions of negatively charged particles, and aleurone cell walls (b-glucans, ferulic acid) and loose protein-containing material from aleurone and endosperm were more abundant in the positively charged particles. These two separated fractions underwent second and third separation steps to further purify the fractions. Yields of 34.1% and 12.6% of the starting material were obtained for the positively and negatively charged fractions, respectively, after the third step separation. Indeed, 26.3% aleurone cell walls in the positively charged fractions were quantified after one separation step, 32.3% after two steps, and (to a lesser extent) 34.0% after three successive separation steps. The outer pericarp content in the negatively charged fractions was found 40.6% after the first separation step, 48.4% after the second step, and (in a lesser extent) 48.8% after the third steps.

During tribocharging and separation, the main factors that determine the particle trajectories are the polarity and the magnitude of the charge acquired by the particles. The electrical properties of particles are altered by chemical adsorption on the surface of the particles. Haifeng et al., 2010 investigated the effect of chemical conditioning on the surface properties of coal/minerals and consequently on the efficiency of coal triboelectrostatic separation. The chemicals tested included starch, lignin, kerosene, ethanol, acetic acid, salicylic acid, sodium oleate, Sodium Hexametaphosphate (SH), sodium silicate, Sodium Dodecylbenzenesulfonate (SDBS), Sodium Bicarbonate (SB) and ammonia. Salicylic acid was the optimal additive to enhance the triboelectrification performance of coal samples. Starch, lignin and sodium oleate were effective additives that increased the charge magnitude of pyrite. An addition of two or more kinds of chemicals was recommended to improve the efficiency of the electrostatic separation by increasing the magnitude of charge difference between the coal and minerals.

3.8   Technical Gaps in Reported Literature

For the separation of silica using an electrostatic process, there is no reported data in literature that uses

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a biomass feedstock. The closest application reported involves the separation of silica from the ash of rice hulls, but is not applicable to the proposed pretreatment process as the biomass needs to be burnt prior to separation. In terms of other processes reported in literature, coal beneficiation is a close approximation of the proposed process as the ultimate goal of obtaining a higher quality fuel through the separation of silica is the same. However, data on this process is also limited and the majority of the data obtained for this report was through direct communication with an expert in the field (John Stencel). As a result, there are large gaps in the electrostatic separation of silica from biomass that require further investigation. This includes fundamental lab-scale research to test and optimize various parameters, modelling and scale-up research for an industrial scale separation process, and economic data for an industrial-scale process.

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Chapter 4
Methods for Nutrient Recovery

4.1. Introduction

Thus far in this report the focus of the research has been to investigate various technologies that could be employed to extract undesirable nutrients from agricultural based biomass. The primary objective of investigating these processes was to determine the technical feasibility of employing these pretreatment processes to produce higher quality combustion fuel from agricultural residues and energy crops. In this section a number of technologies will be examined for their feasibility in recovering the extracted nutrients for recycling back to the soil and/or producing a marketable final product.

The significance of being able to recover and recycle nutrient is both environmental as well as economical. The potential reduction of soil nutrients by removal of

agricultural residue from the field has been a cause for concern within the farming community. The three main nutrients of concern are: Nitrogen (N), Phosphorous (P), and Potassium (K). However other nutrients such as Magnesium (Mg), Sodium (Na), Sulphur (S) and Calcium (Ca) also play a role.

For instance according to data from the Ontario Federation of Agriculture (OFA) the removal of corn stover from a farm can result in approximately 62 lb/acre (69.4 kg/ha) reduction of Nitrogen, 25 lb/acre (28 kg/ha) reduction of Phosphorous and 108 lb/acre (121 kg/ha) of Potassium (assuming corn yield of 161 bu/acre). **Table 4-1** provides approximate quantities of nutrients depleted by removal of various crops. The concern is not limited to agricultural residues. Energy crops can also contribute to soil nutrient and organic matter depletion. These crops are intended to be harvested

Table 4-1   Approximate pounds of nutrients depleted by removal of crops (lbs/tonne of crop removed)

Crop	Nitrogen (N)	Phosphorous (P_2O_5)	Potassium (K_2O)
Blue Grass	35.0	12.0	35.0
Bermuda Grass	50.0	12.0	47.0
Brome Grass	40.0	12.0	44.0
Fescue	42.0	14.0	47.0
Lespedeza	48.0	15.0	45.0
Miscanthus (Caslin et al., 2010)	13.2	1.5	11.0
Orchard Grass	45.0	14.0	55.0
Poplar (Lodhiyal & Lodhiyal, 1997)	12.7	1.4	6.9
Red Clover	56.0	12.5	45.0
Reed Canary Grass (Beale, 1997)	51.2	7.9	55
Sorghum Sudan	40.0	15.0	55.0
Sweet Clover	44.0	11.0	44.0
Switchgrass (Lemus et al., 2009)	10.0	1.9	13.6
Timothy	36.0	13.5	56.0
Willow (Jug, 1999)	14.5	2.4	6.8

Non-sited crops adapted from OFA reported data

in their entirety from the field. Furthermore, given the high cost of establishment there is great effort towards increasing the yield of these crops which can also impact soil nutrient.

This chapter investigates the most suitable processing technologies for nutrient recovery from water-based solutions. The extraction of these nutrients using water has been described in detail in Chapter 2. Extensive studies have been performed on nutrient recovery (mostly nitrogen and phosphorus) from aquatic systems (mainly wastewater), and various processes have been proposed. The literature review indicates that membrane separation and chemical precipitation facilitated by struvite formation are the two most promising methods that can be used to recover nitrogen, phosphorus, and potassium from aquatic systems.

4.2   Economics of Fertilizer Usage

Canadian farmers spend approximately $2 billion per year on fertilizers, and this represents about 10% of their operating expenses (Korol, 2002). Farmers in Ontario spend over $300 million a year on fertilizers consuming approximately 740,000 tonnes of fertilizer. **Table 4-2** provides a summary of fertilizer usage in Canada as of the 2007 census.

Table 4-2   Fertilizer consumption in Ontario and Canada (Canadian Fertilizer Institute, 2011; Korol, 2002)

Year	Total Fertilizer (t)		Total Cost (000$)	
	Ontario	Canada	Ontario	Canada
2006	686,158	4,920,955	428,490	2,926,218
2005	625,307	5,055,102	338,424	2,605,190
2004	745,307	5,385,035	310,312	2,134,787
2002	740,597	5,025,706	308,324	1,992,330
2001	754,132	5,029,607	334,046	2,254,070
2000	730,289	5,254,305	334,046	1,998,870
1999	778,035	5,181,856	282,850	1,882,070
1998	802,274	5,342,001	291,544	1,972,970
1997	714,232	5,130,207	283,215	1,975,710
1996	754,369	4,829,045	288,821	2,007,490

Nitrogen fertilizer consumption is the highest, accounting for around sixty percent of the nutrients consumed in the world. Twenty-four percent of fertilizer consumption is attributed to phosphates, while potash makes up sixteen percent of the total global consumption. The ratio of nutrient consumed globally (NPK) is 3.8: 1.5: 1 (Korol & Larivière, 1998).

4.3   Nutrient Recovery by Reverse Osmosis

Reverse osmosis (RO) is a membrane-based filtration technique used to separate dissolved solutes from a solution. Reverse osmosis offers the finest membrane filtration operation rejecting most dissolved solutes, such as ions, as well as suspended solids. Reverse osmosis is a pressure driven operation, with the pressure providing a driving potential to force solvent (most applications involve water-based solutions, which is also the focus of this work) to permeate through the membrane while other dissolved species are retained by the membrane (Kucera, 2010). **Figure 4-1** is a picture of a typical RO wastewater treatment plant.

Figure 4-1 Reverse osmosis wastewater treatment Plant, Kuwait

RO can be used to either purify water or to concentrate and recover dissolved solutes in the feed water (known as dewatering). The most common applications of RO include desalination of seawater and brackish water for potable use, waste treatment for the recovery of process materials such as metals for the metal finishing industries, and water reclamation of municipal and industrial wastewaters (Kucera, 2010).

4.3.1 Reverse Osmosis Process Description

Reverse osmosis (RO) membranes can be operated in a dead-end or a cross-flow mode. Dead-end systems are used only for small-scale and laboratory applications. Most medium and large scale filtration processes are carried out in the cross-flow operation mode. The main advantage of cross-flow operation is the minimization of solute accumulation near the membrane surface. The cross-flow arrangement also facilitates recirculation of retentate stream to the feed tank followed by its mixing with fresh feed (Baker, 2004; Kucera, 2010). **Figure 4-2** depicts cross-flow and dead-end mode membrane separation mechanisms.
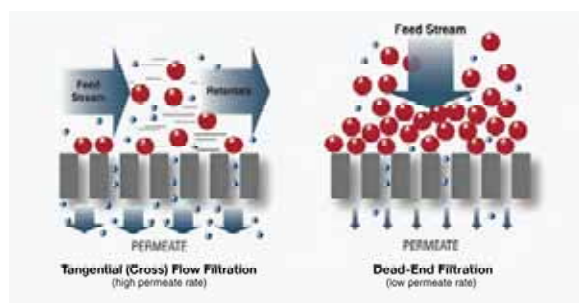
Figure 4-2 Cross-flow mode (left) and dead-end mode (right)

The most common cross-flow devices are flat sheet tangential flow modules, tubular modules, spiral wound modules, and hollow fiber modules. Spiral-wound (**Figure 4-3**) and hollow fiber membrane (**Figure 4-4**) modules are the most widely used membrane devices because they allow a high membrane surface area to volume ratio. Spiral wound membrane modules include some advantages over hollow fibers; spiral wound membranes are easy to replace and can be manufactured from a wide variety of materials (Baker, 2004; Kucera, 2010).

1 Permeate
2 Feed
3 Spacer
4 Membrane envelop
5 Retentate
6 Permeate collecting tube
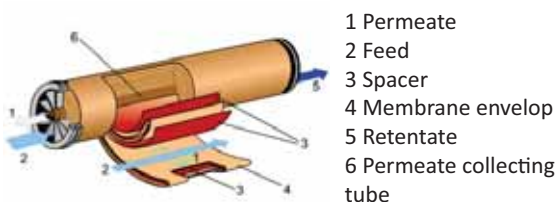
Figure 4-3 Spiral Wound Membrane Module

Spiral wound membrane modules consist of multiple membrane envelopes. A membrane envelope is made up of two membranes with a porous spacer between them. The membrane envelope is connected to a perforated permeate collecting tube. The spacers together with the membrane envelopes are wound spirally around the permeate collecting tube. The feed solution arrives at the front face of the module and flows axially between the envelopes. In the envelopes the water flows spirally towards the permeate collecting tube and exits the module in an axial direction. Hollow fiber modules usually consist of a bundle of fibers with a diameter range of 0.25 to 2.5 mm which can be set up either in a U-shape or in a straight-through configuration (Baker, 2004; Kucera, 2010).

Membrane separation processes such as reverse osmosis can recover the NPK as well as some other particulate and soluble mineral compounds. The rejected stream from the membrane (retentate) becomes rich in minerals and components that cannot pass through the membrane while permeate stream becomes free of these components (Kucera, 2010).
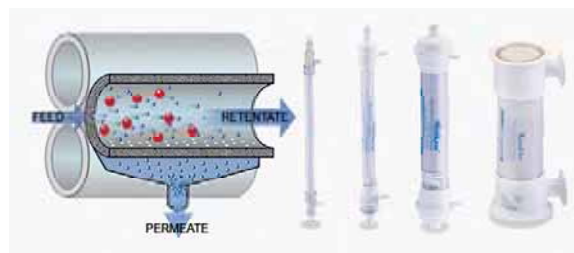
Figure 4-4 Hollow Fiber Membrane Modules

4.3.2 Research in Nutrient Recovery by Reverse Osmosis

Nutrient recovery from aquatic systems using RO membranes have been widely cited in literature. Kurama et al. (2001) evaluated the performance of RO membrane on ion recovery, most importantly ammonia, calcium, and chlorine, from wastewater plant effluent. Results showed that RO can effectively separate ammonia, calcium, and chlorine by 97%, 99%, and 99%, respectively. The possibility of nutrient recovery from an anaerobically treated black water (concentrated stream of decenteralized wastewater) using RO technology was investigated by Voorthuizen et al. (2005). Black water was found to be rich in nitrogen

(as ammonium) and phosphate. Results showed rejections for ammonium between 80–90% and phosphate above 90%.

Bilstad (1995) investigated the feasibility of RO to separate nitrogen from domestic wastewater with tubular and spiral wound membrane modules. Nitrogen separation efficiency of 95% was observed with both membrane modules. It was also found that spiral wound membranes could not operate efficiently with suspended solids and therefore upstream pretreatment such as pre-filters were needed to remove suspended solids. Since tubular membrane modules provide much less membrane surface area than that of spiral wound modules, tubular membranes were considered unrealistic for high volume feed flow such as domestic effluents.

Reverse osmosis has been also been applied to separate heavy metals from industrial wastewater in order to recover valuable metals and prevent environmental degradation. Application of RO technology was investigated by Qadis and Moussa (2004) for treatment of wastewater containing copper (Cu^{2+}) and cadmium (Cd^{2+}). High removal efficiency was achieved by the RO process, as 98% of the copper and 99% of the cadmium was recovered.

The effectiveness of the RO membrane technology in treating wastewater containing mixed heavy metals was also tested. The result showed that the RO membrane was able to reduce initial cadmium concentrations of 500ppm in wastewater to 3ppm with removal efficiency equal to 99.4%. Padilla and Tavani (1999) used spiral wound RO membranes to separate chromium (III) from the tanning wastewater. Results showed that the RO membrane was able to reject chromium by at least 98% but to a lesser extent sodium, chloride, and sulfate. Ozaki et al. (2002) presented the feasibility of using an ultra-low pressure, aromatic polyamide RO membrane to separate heavy metals (copper, nickel and chromium (VI)) from synthetic wastewater and wastewater from the heavy metal industry. The study revealed rejection of heavy metals greater than 95%.

Reverse osmosis has also been tested for nutrient recovery from biomass. Jenkins et al. (2003) performed water leaching of rice straw with a subsequent RO filtration of the leachate. Rice straw was submerged in deionized water for 24 hours at room temperature without agitation (10 kg biomass/350L). A spiral

wound module consisting of a low-pressure thin film composite membrane (2.42 m^2) was used to filter the leachate. The RO membrane rejected greater than
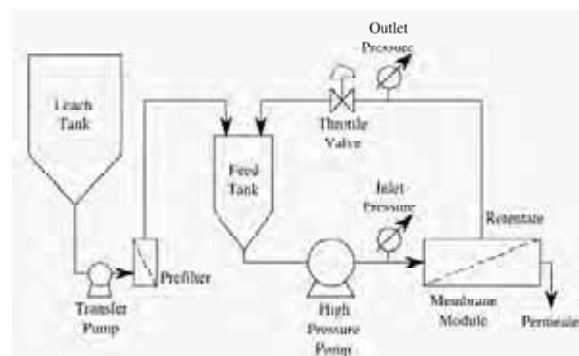
Figure 4-5 Nutrient Recovery Plant Proposed by Jenkins (Jenkins et al., 2003)

90% of the ions in the leachate at 90% permeate recovery. **Figure 4-5** provides a scheamtic of the nutrient recovery plant proposed by Bryan Jenkins (Jenkins et al., 2003)

Colyar (2005) filtered the leachate of corn stover using a sequential membrane set-up of ultrafiltration and RO. 100% of the total suspended solids and 10-20% of the soluble TOC (total organic carbon) in the leachate was separated by the UF membrane. High rejection (>70%) of phosphate, potassium, chloride and total organic carbon species was obtained with the RO membrane.

A combination of reverse osmosis (RO) and electrodialysis (ED) was tested by Mondor et al. (2008) to produce a concentrated nitrogen fertilizer from liquid swine manure. The ED concentrate was passed through RO membranes as an attempt to further concentrate nitrogen by the use of high pressures which would overcome the osmotic forces experienced during ED. A maximum ammonia concentration of 13 g/L was achieved. The permeate contained 8.6% of the initial ammonia and alkalinity as CaCO3, while the concentrate retained 66.6% of the ammonia and 62.9% of the alkalinity.

4.4   Nutrient Recovery by Chemical Precipitation

Ammonium, magnesium, and phosphorus can be

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chemically recovered from a solution by a struvite formation process. In the struvite formation process, ammonium reacts with magnesium and phosphorus to form a struvite (MAP). Generally, struvite production only recovers nitrogen and phosphorous in a nutrient-rich solution, to the detriment of potassium. However, if no nitrogen is present in solution, potassium can react with magnesium to produce potassium magnesium phosphate struvite (KMP). Since struvite has a low solubility constant (pKs), its insoluble form can be easily formed and simply separated from the water phase. The struvite can be removed from the liquid solution using solid separation processes, such as sedimentation, filtration, and membrane separation (Metcalf and Eddy, 2003).

The stoichiometry of the struvite reaction is:

$$Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O => MgNH_4PO_4.6H_2O + 2H^+$$
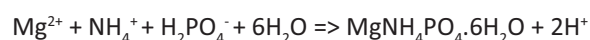
To the authors' knowledge, magnesium struvite formation is the only practical chemical method that can recover ammonium by forming a low soluble struvite. In most other chemical processes such as the breakpoint chlorination process, ammonium is converted to N_2 (g). Various chemical reaction processes have been known to chemically precipitate and recover potassium and phosphorus. In chemical processes, phosphorus reacts with metal salts or lime forming precipitates. **Table 4- 3** provides a list of possible precipitates that can be formed.

Selective precipitation or crystallization of potassium can be achieved by the addition of chemical agents, such as dipycrylamine, sodium bismuth thiosulfate, or calcium perchlorate (Gurbuz et al., 1996). The chemical process however, is expensive since these chemicals cannot be recovered efficiently during the process. Potassium can also be chemically separated from water by adding sodium pentaborate (Gurbuz et al 1996). Potassium is crystallized as potassium pentaborate octa hydrate (Liberti et al., 1984; Wilsenach et al., 2007). Another possible method of potassium recycling is with the use of clinopitlolite, a natural zeolite. It is worth mentioning that in chemical addition processes, separation of precipitated components from liquid controls the recovery efficiency.

A question raised here is which chemical should be used to precipitate PKN. Most have yet to progress beyond demonstration projects and no plans were iden-

tified for further development. Furthermore, some of these chemical precipitators could pollute soil and ground water and, therefore, are not recommended to be used as fertilizers. The only practical chemical method is magnesium struvite formation because all of the chemical components are needed for plant growth. From an economic point of view, two or more available components are precipitated by the addition of magnesium.

Table 4-3 Possible Precipitates Formed During Phosphate Removal

Cation	Percipitate
Al(III)	Aluminium Phosphate[$AlPO_4$]
	Aluminum hydroxide[$Al(OH)_2$], hydrous aluminum oxide[$Al_2O_2.xH_2O$]
Fe(II)	Vivianite [$Fe_2(PO_4)_2.8H_2O$]
	Ferrous hydroxide [$Fe(OH)_2$]
Fe(III)	Strengite [$FePO_4.2H_2$)]
	Ferric hydroxide [$Fe(OH)_3$], hydrous ferric oxide (HFO) [$Fe_2O_3 \bullet xH_2O$]
	magemite [$\gamma\text{-}Fe_2O_3$]
Ca(II)	Tricalcium phosphate [$Ca_3(PO_4)_2$]
	Hydroapatite [$Ca_5(OH)(PO_4)_2$]
	Dicalcium phosphate [$CaHPO_4$]
	Calcium carbonate [$CaCO_3$]
Mg(II)	Struvite [$MgNH_4PO_4 \bullet 6H_2O$]

4.4.1 Nutrient Recovery by Struvite Formation

With leaching being the more likely method for soluble nutrient extraction from biomass, nutrient recovery methods should focus on nutrient uptake from aqueous solutions. A proven method in literature is the production of struvite. Struvite is a crystalline substance consisting of magnesium, ammonium and phosphorus in equal molar concentrations ($MgNH_4PO_4 \bullet 6H_2O$).

The recovered struvite acts as a slow-release fertilizer (Bridger et al., 1961; Schuiling and Andrade, 1998; Nelson, 2000; Li and Zhao 2003; Uysal et al., 2010;

Yetilmezsoy and Sapci-Zengi, 2009). While only slightly soluble in water and soil solutions, struvite is a highly effective source of P, N and Mg for plants through foliar and soil application. The release of nutrients is enhanced by a biological nitrification mechanism, with the nutrients being released at a controlled rate over an extended period of time. When properly granulated, it can be applied to soil at rates greatly exceeding those of conventional fertilizers without danger of burning plant roots (Yetilmezsoy and Spaci-Zengi, 2009; Booker et al. 1999). Struvite crystallization and recovery have been achieved in many types of aqueous solutions, including calf manure (Schuiling and Andrade, 1998), coke manufacturing wastewater (Zdybiewska and Kula, 1991), leather tanning wastewater (Tunay et al., 1997), swine wastewater (Nelson, 2000; Song et al., 2011; Ye et al., 2010), anaerobic digester sidestreams (Uysal et al., 2010; Zhang et al., 2010), municipal landfill leachates (Di Iaconi et al., 2011; Di Iaconi et al., 2010), and semiconductor wastewater (Kim et al., 2009; Warmadewanthi and Liu, 2009).

Magnesium ammonium phosphate (MAP) struvite is a naturally occurring crystal, when the combined concentrations of Mg^{2+}, NH^{4+} and PO_4^{3-} exceed its solubility limit. As struvite has a low solubility constant pKs between 12.60 (Stumm and Morgan, 1996) and 13.26 (Ohlinger et al., 1998), its insoluble form can be easily formed and simply separated from the water phase. Controlled MAP crystallization can be used to remove nutrients such as nitrogen and phosphorus from wastewaters. However, the success of the MAP process depends on two main factors: the molar ratio of Mg:N:P and the pH value in the reactor (Ye et al., 2010, Munch and Barr, 2001). In most cases, magnesium deficiency in wastewater allows it to be added to remove all available nutrients such as phosphorus and/or ammonium-nitrogen in the water phase. Three types of magnesium, MgO, $Mg(OH)_2$ and $MgCl_2$, are generally used in the MAP/KMP process. Compared to $Mg(OH)_2$, $MgCl_2$ is more widely used because it dissociates faster than $Mg(OH)_2$ and results in shorter reaction time.

Both MgO and $Mg(OH)_2$ raise the pH and can come close to the ideal pH of 8 or 9 depending on the dosage. The use of $MgCl_2$ with a base (typically caustic soda (NaOH)), allows the pH to be raised to the ideal level. In a report prepared by Cayuga County Soil & Water Conservation District (Hotaling, 2006), little difference in struvite formation was found between the two reagents and no trends could be discerned in the amount of phosphate versus the amount of magnesium added. If the MAP process is applied to remove ammonium-nitrogen only, phosphate forms of H_3PO_4 or $NaHPO_4$ are usually needed (Siegrist, 1996; Schulze-Rettmer, 1991). As for the required alkaline condition of an elevated pH in the MAP system, it can be achieved by alkaline addition or pre-aeration (Battistoni et al. 1998). Fujimoto et al. (1991) has demonstrated that addition of NaOH is more effective than addition of lime or $Mg(OH)_2$.

Despite such attractive agronomic properties, struvite is not widely used in the fertilizer industry owing to its high cost of production from raw chemicals. Since magnesium tends to be low relative to concentrations of ammonia and phosphate in agriculture leachates and wastewaters, the cost of adding magnesium salts is a major economic constraint to application of struvite crystallization for nutrient recovery. One potential solution is the use of low-cost materials containing magnesium such as seawater (Kumashiro et al., 2001), magnesite minerals (Gunay et al., 2008), byproducts generated in the production of magnesium oxide (Quintana et al., 2008) and pyrolysate of magnesite (Huang et al., 2010). Kumashiro et al. (2001) have demonstrated the use of seawater as a source of Mg^{2+} for struvite crystallization at a pilot scale. Another natural source of Mg^{2+} ions that would be more suitable than seawater in inland areas is bittern, the salt produced by evaporation of seawater. This byproduct of salt production contains mostly magnesium chloride with smaller amounts of other inorganic compounds. Its Mg^{2+} content is approximately 32 g/l, 27 times that of seawater.

Struvite production recovers not only nitrogen and phosphorous but also potassium. If no nitrogen is present in solution, potassium can react with magnesium to produce potassium magnesium phosphate struvite. A practice of recovering phosphate as struvite from urine and animal manure was performed by Wilsenach et. al (2007) and Schuiling and Anrade (1999). Magnesium ammonium phosphate (MAP) as well as potassium magnesium phosphate (KMP) were two forms of struvite that were precipitated. Wilsenach et. al also found that addition of MgO provides sufficient alkalinity for struvite precipitation in nitrified urine.

Ostara Nutrient Recovery Technologies Inc., a company based in Vancouver B.C., has been producing commercial fertilizers through the magnesium struvite

formation process. Ostara´s process (**Figure 4-6**) involves the recovery of ammonia and phosphate from nutrient rich fluids, specifically from nearby wastewater treatment plants. Using a fluidized bed reactor technology, the nutrients are recycled into struvite using magnesium. Some other full-scale struvite processes and designs exist in the Netherlands (Crysta-

lactor, two installations), in Japan (Unitika-Phosnix, four installations), in Italy (RIM-NUT IonExchange), in Austalia (Sydney Water Boar) and south Africa (CSIR Proces). These commercial plants treat industrial and municipal wastewater.
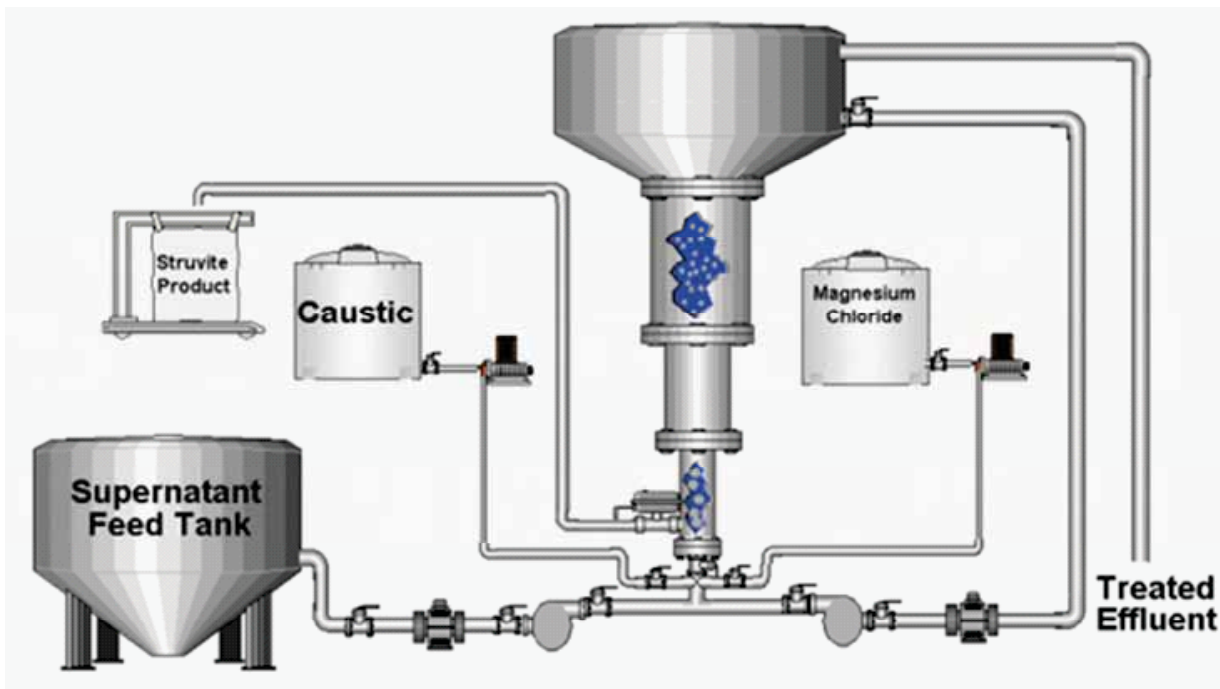
Figure 4-6 Magnesium struvite plan (ostara.com)

4.5   Technical Gaps in Reported Literature

Reverse osmosis is the most widely reported and used process examined in this report. It is used in various water treatment processes and is available in various small-scale and large-scale applications. In terms of applications involving nutrient recovery from biomass leachate however, there is only a few studies available in literature (Colyar, 2008; Jenkins et al., 2003). Although there are some gaps in this specific application, there is a lot of economic, scale-up and optimization data using reverse osmosis for other applications (i.e. desalination) that allows the data to be confidently used as a basis for a nutrient recovery method from biomass leachate. Specific technical gaps that still need to be addressed include the solute reten-

tion time of nutrients in biomass leachate, the presence of nutrients in the permeate and retentate, and membrane fouling behaviour during the filtration of leachate. Furthermore, there is no optimization studies on the effects of operating conditions such as TMP, pH, temperature and membrane material on the recovery of nutrients.   As a result it is important for further lab-scale research into the recovery of nutrients from biomass leachate to be conducted to reduce the specific gaps in this application.

Chapter 5
Economic Evaluation of Proposed Pre-treatment Processes

In chapters one through four various approaches for the removal and recovery of nutrients from biomass were investigated. A thorough search of the published literature has uncovered very little data on an economic evaluation of biomass nutrient recovery. The limited publicly available economic data on biomass leaching, reverse osmosis, magnesium struvite, and electrostatic separation of silica are presented and discussed in the subsequent sections of this chapter. **All financial figures reported are in USD**.

Furthermore, for a complete economic evaluation of the pre-treatment process all of the individual conversion steps required in the process need to be considered. The literature review did not find any publications that had considered the entire nutrient removal and recovery process. In recognition of this gap, the authors of this report have developed their own financial models, and economic evaluation of the complete conversion process based on integration of some of the published data with CENNATEK's own commercial knowledge, and assumptions.

5.1 Published Economic Data on Biomass Leaching

The economic evaluation of nutrient recovery from biomass through an industrial leaching process has been limited to data provided by a dissertation published by Bakker (2000). In his dissertation, a design for an industrial scale leaching facility to be located in California was considered.

In general, when designing an industrial scale leaching facility, several factors that may inhibit the feasibility of the process include:

- Water requirement
- Cost and energy for size reduction;
- Residence time required in the reactor;
- Dewatering of the leached biomass; and
- Treatment and disposal of the leachate.

Figure 5-1, below provides a schematic for Bakker's (2000) leaching design.
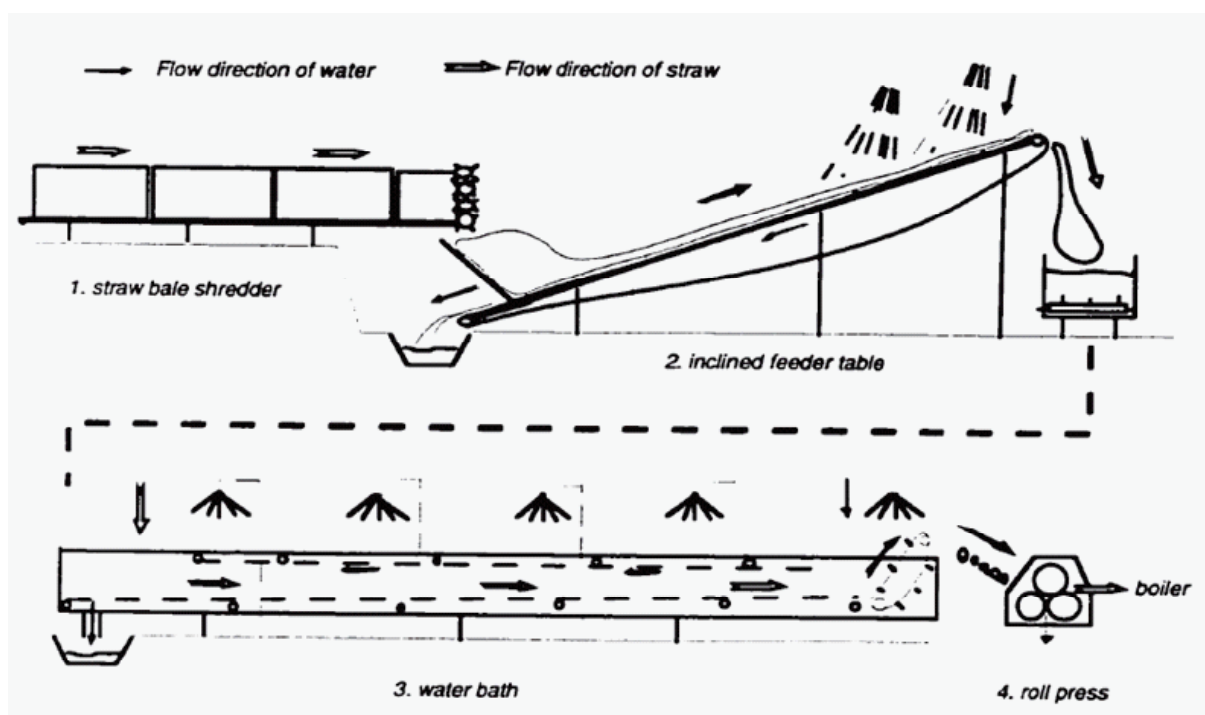
Figure 5-1 Schematic for an Industrial-Scale Leaching Facility (Bakker, 2000)

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The following assumptions for the facility design were used by Bakker (2000):

Capacity: Leached straw was proposed to replace 25% of the total capacity for a 25MW power plant, equivalent to 135 tonnes of straw per day on a dry weight basis. Assumptions include a higher heating value of 16 MJ/kg for the straw with 20% conversion efficiency.

Delivery and handling of Biomass: A straw biomass would generally be delivered in large bales. Size reduction by a hammermill was found to lead to extensive dust emissions, loss of fuel, and clogging of straw in augers, screens and chutes, therefore a forage shredder was used for size reduction.

Dewatering: After leaching, biomass generally has a moisture content between 80-85%. In order to improve the heating value, the moisture content needs to be reduced by a dewatering step. Air drying of the biomass would be more time consuming, and additionally the residual moisture of the biomass after leaching has nutrients and air drying will redeposit these nutrients on the surface of the biomass as opposed to a physical dewatering step that will squeeze out the nutrient rich water (Bakker, 2000).

Combustion: In his design, Bakker considered a small 25MW plant that would receive bales of straw and have the leaching facility located at the generation site. Thus, his design did not consider pelletization, and did not require any additional operations. The dewatered biomass (approx. 50% moisture) would be used directly as fuel at this facility.

The system designed by Bakker had four main subsections (**Figure 5-1**):

i. Bale Shredding: A forage shredder was used which has the added advantages of lower power requirements when compared to hammermills, a higher capacity, and an automatic method of feeding the bales. The capacity of a forage shredder is typically up to 30 metric tons per hour.

ii. Feed Section: The material was fed into a water bath using an inclined feeder table with water spraying on top of the biomass to increase the moisture content of the bales and initiate the leaching process. The inclined feeder table is similar to ones used in the cleaning of sugar cane prior to milling. The feeder table is equipped with a chain with rake-type teeth to transport the straw along. Water is sprayed from the top of the table down, allowing it to percolate through all of the biomass. The leachate from this initial leaching is collected in a trough at the bottom of the feeder, while the wet straw is dropped at the top of the table into the washing bath.

iii. Water Bath Immersion: The straw is submerged using a horizontal drag chain that is itself immersed under the water in a rectangular bath. The spent wash water (i.e. leachate) can be removed at the same side of the bath where the straw enters, while the leached straw is removed at the opposite end where fresh water is added. Additional water sprays are mounted above to apply water on the top layer of the straw bed that may float to the surface. The residence time of the straw in the bath is estimated to be between 10 and 30 min. for secondary extraction through immersion; and

iv. Dewatering Section: A roll press for physical dewatering of the leached biomass was proposed. The system would reduce the moisture content of the leached straw from 80% down to about 50% by mechanical dewatering. A roll press that is used in sugar cane factories was recommended. A typical setup is three rollers assembled in a triangle, with the roller on top pressing against the two bottom rollers with the assistance of a hydraulic pressure system (Bakker, 2000). It should be noted that a 50% moisture content is very high for pelletization. Thus an additional biomass drying system that is coupled with a heat recovery system would be required for pelletization to reduce the moisture to around 15%. Common types of biomass dryers include:

- Rotary Dryers;
- Flash Dryers;
- Disk Dryers;
- Cascade Dryers; and
- Superheated Steam Dryers

Based on lab-scale experiments, a water to biomass ratio of 10:1 was determined to be sufficient for leaching biomass. A 135 tonne/day capacity would translate to 1350 m^3/day of water consumption. To improve the economics of the process and reduce its environmental impacts, large portions of the water discharge is recovered through reverse osmosis and recycled back into the system.

The total capital cost of the proposed system was estimated at approximately $750K (**Table 5-1**). The total marginal costs on a material basis, expressed in $/tonne of biomass (dry basis) was determined for the proposed 135 tonne/day leaching facility, and is summarized in **Table 5-2** (Bakker, 2000).

Table 5-1   Capital Costs of Leaching (Bakker, 2000)

Components	Power Req. (kW)	Capital Cost (USD $)
Straw Bale Shredder	67	25,500
Inclined Feeder System	37	100,000
Water Bath System	22	125,000
Mechanical Dewatering	52	350,000
Pumps	15	20,000
Foundation & Flooring		62,050
Contingency (10%)		68,255
Totals	**193**	**$ 750,805**

The total marginal cost was determined to be $17.88/tonne, assuming an economic life of 10 years. It is speculated that the costs could be decreased if a larger fraction of leached straw is used in the combustion process (over the proposed 25%) or if a larger overall capacity is used. For example a facility at twice the capacity (i.e. 50 MW) shows an incremental cost of only $15.59/tonne.

Bakker's dissertation made the following assumptions to conclude that the process was not economically feasible:

- HHV of 16 MJ/kg;
- Plant efficiency of 20%, 889 kWh/ton generated;
- Feedstock cost of $25/tonne at plant gate;
- Additional electricity production costs of $6.50/tonne of biomass used; and
- Electricity sale price of $0.04/kWh.

Based on the above assumptions the revenue generated from sales of electricity was estimated at $13/tonne of biomass. As this is below the $17.88/tonne

reported marginal cost of the leaching facility, the process would not be viable.

However, there are several aspects of Bakker's evaluation that require revisions to current conditions in Ontario. For example changing the selling price of electricity from $0.04/kWh to $0.06/kWh would increase the revenues generated by the process to over $19/tonne combined with improved conversion efficiency of the plant these changes can have an appreciable effect on the process economics, allowing the economical viability of an industrial-scale leaching facility.

Another important consideration that will have significant impact on the economics of the process is the value of the nutrients removed. Bakker (2000) investigated leaching as a stand-alone process and did not include any revenues generated from the recovery of the nutrients in the leachate. The nutrients in the leachate can be concentrated through reverse osmosis to produce a liquid fertilizer that can generate significant returns. In Section 5.5 of this report a much more comprehensive economic evaluation is provided which builds on the basic capital and operating costs reported by Bakker.

Table 5-2 Summary of Incremental Costs (Bakker, 2000)

Components	Amount (USD/tonne)
Capital Recovery Cost	$2.13
Electricity (at $0.04/kWh)	1.38
Labour Cost (at $18/hr)	4.27
Water Cost (at 0.045/m³)	0.54
Maintenance Cost (10% of capital)	1.90
Thermal Drying Cost (50% moisture)	1.78
RO Treatment of Leachate	5.88
Totals	**17.88**

5.2   Published Economic Data on Tribo-electrostatic Separation of Silica

There has been no single published data on the technical or economic evaluation of the use of electrostatic separation technologies to the extraction of silica from biomass. Stencel (1999b) reported the only economic

evaluation of a triboelectrostatic separator for coal beneficiation (Details on coal beneficiation provided in section 3.7.2). The pilot plant was a 2 tonne/hr standalone system. The total capital cost for the pilot unit was estimated at $167,400 (USD). In his economic evaluation of the process, Stencel (1999b) assumed a 20 tonne/hr plant for the calculations of his labour and marginal costs. The following assumptions were made:

- Labour cost of $20/hr (USD); and
- Electricity cost of $0.07/kWh (USD).

Based on the above assumptions and a 15% contingency the report estimated the total marginal cost of the standalone pilot plant to be $3.00/tonne (USD) (Stencel, 1999b).

In direct communiqués between CENNATEK researchers and Dr. John Stencel, data was collected on industrial scale electrostatic separation processes. Dr. Stencel is the current president of Tribo Flow Separations (TFS) an American based company that sells, manufactures, and installs turn-key, industrial scale triboelectric processing plants based on Dr. Stencel's patented technology. According to Dr. Stencel, in their plant design they have electrostatic separation cells with nominal throughputs of 1 tonne/hr. For commercial systems, they install eight of these cells in a transportable module which has a design throughput of 50,000 tonne/yr. TFS along with its exclusive engineering, plant design, manufacturing and construction company Apex Bulk Technologies have designed plants as large as 200,000 tonne/yr and as small as 15,000 tonne/yr. According to Dr. Stencel these plants have operating costs ranging from $12-$16/tonne (USD). This range for the operating costs are based on data from a 100,000 tonne per year plant operating in Colorado during the 2003-2008 period processing combustion fly ash. This cost does not take into account the cost of size reduction of the feedstock. The capital cost for a 200,000 tonne/yr plant would be about $1.2 Million (USD).

5.3 Published Economic Evaluation on Reverse Osmosis Recovery

Dr. Bryan Jenkins who has been an active researcher of nutrient extraction through leaching at the University of California, Davis conducted the only published economic evaluation (uncovered through this investigation) on the use of Reverse Osmosis (RO) in the

recovery of nutrients from the leachate. Jenkins et al. (2003) estimated the cost of RO processing for a leaching facility handling 50,000 tonne/year of biomass and generating 1,900 m³/day of leachate. The marginal cost of the process was estimated at $0.671/m³ (USD) of leachate. Marginal cost of $0.719/m³ (USD) leachate for a facility processing approximately 25,000 tonne/yr of biomass.

In additions to this study, there is a large body of economic data on the use of Reverse Osmosis in desalination. There are about 250 desalination plants in the U.S of appreciable sizes. Almost half of them (114) are in Florida, 33 in California, and 38 in Texas. The vast majority of these desalination facilities use reverse osmosis to remove salt from seawater. The capital cost of membrane modules for reverse osmosis depends on the plant capacity and varies between $500 to $1000 per module. These membranes have production rates of 50-100 m³/day (El-Dessouky and Ettouney, 2002). **Table 5-3** provides some figures on the capital cost of RO desalination plants published by various researchers.

Table 5-3 Capital cost for reverse osmosis process

Capacity (m³/day)	Capital ($)	Reference
50	0.25-0.38	Khalifa (2011)
30,000	21-45M	Banat (2007)
110,000	200M	Tuas Seawater Desalination Plant (2005)
30,000	28M	Ionics Freshwater Ltd (2000)
15,000	14.5M	Leitner (1991)
36,000	80.9M	Leitner (1991)
56,800	65.3M	Leitner (1991)
32,000	53.3M	Wade (1993)

The unit product (marginal) cost of RO process depends on the capacity. **Table 5-4** provides a summary of some of the published data on the marginal cost of various RO desalintation plants. The Ashkelon sea-

water reverse osmosis plant in Israel with a capacity of 330,000 m³ per day producing around 13% of the country's domestic consumer demand has claimed to produce low price desalinated water ($0.52/m³).

Table 5-4   Unit product cost for reverse osmosis process

Capacity (m³/day)	Cost ($/m³)	Reference
50 (Iraq)	1.8-2.4	Khalifa (2011)
330,000 (Israel)	0.52	Ashkelon (2008)
30,000	0.62-0.68	Banat (2007)
110,000 (Singapore)	0.48	Tuas (2005)
45,420	0.68	Ebensperger (2005)
113,562	0.54	Ebensperger (2005)
3,800 (Persian Gulf)	1.41	Leitner (1987)
11,400 (Persian Gulf)	1.25	Leitner (1987)
18,900 (Persian Gulf)	1.19	Leitner (1987)
37,900 (Persian Gulf)	1.11	Leitner (1987)
23,000 (Persian Gulf)	1.31	Leitner (1989)
100	2.37	Darwish (1990)
15,000 (Las Palmas)	1.18	Leitner (1991)
36,000 (Malta)	1.62	Leitner (1991)
56,800 (Saudi Arabia)	0.59	Leitner (1991)
112,000 (California)	0.86	Hess (1992)
32,000 (Persian Gulf)	1.39	Wade (1993)

5.4   Published Economic Data on Magnesium Struvite Recovery

There were three studies that reported economic data on struvite formations. The first two studies performed by Celen and Turker (2001) and Turker and Celen (2006) looked at applying struvite formation to anaerobic digestion. In these studies phosphate and magnesium was added to the available ammonia in

the wastewater to form the magnesium struvite. The cost of recovered ammonia as struvite was calculated as $0.36/kg and $7.7/kg for nutrient recycle and non-recycle modes, respectively. The cost is equivalent to $0.026/kg MAP and $0.57/kg MAP, respectively. The most significant contributor to the marginal cost was the addition of phosphate.

In the third study, an economic evaluation of nutrient removal from piggery wastewater using a struvite precipitation technique was performed by Huang et al., 2011. In this assessment, the manpower cost was not taken into account. In this study the marginal cost associated with the process was between $10.3/m³ and $4.9/m³ of wastewater depending on the source of Magnesium and Phosphate used.

The high cost associated with this process in comparison with reverse osmosis makes it a less attractive option for this project. Furthermore, early lab results conducted by CENNATEK on leachate samples indicate that the leachate produced does not have a sufficiently high enough nutrient content to effectively apply this process. Based on these two reasons Magnesium Struvite will not be considered in the economic evaluation of the process conducted by CENNATEK, the details of which are provided in the subsequent sections of this chapter.

5.5   Economic Evaluation of Pretreatment Processes

Figure 5.2 provides a simplified process flow diagram (PFD). The overall process considered for the economic evaluation consists of the following specific components:

- Receiving which would include weighting stations, quality testing of bales, bar coding and storage of biomass bales. The purpose of bar coding is to identify and tag bales with the source material for further processing. An important part of the process will be to control the "recipe" of source material used to ensure consistent quality of output product;
- Size reduction of biomass to increase leaching efficiency;
- Leaching to remove water soluble nutrients;
- Reverse Osmosis to concentrate nutrients in leachate to produce a liquid fertilizer for local ap-

plication and recycle water to process;

- Mechanical Dewatering to reduce moisture content to approximately 50%, and thermal drying (rotating drum dryer) to achieve <1% moisture for electrostatic separation;

- Electrostatic separation to produce a 20% silica rich biomass stream (75% of the overall silica content would be in this stream); and 80% product stream of low silica content for pellet production (25% or of initial silica will remain in this stream);

- Combined heat and power generation to burn the

residual biomass in the silica rich stream and produce an ash for silica purification. This step dramatically reduces the cost of chemicals required to purify the silica, and provides additional electricity that could be sold and heat that could be used in the drying stage;

- Silica Purification to produce high purity silica (>98.5% Purity) to be sold from the CHP ash;

- Pelletization to densify the biomass for sale as a high quality combustion fuel

Inputs:
1.Biomass feedstock
2.Water
3.Chemicals
4.Natural gas
5.Electricity

Outputs:
1.Pellet
2.Silica
3.Liquid fertilizer
4.Electricity
5.Heat
6. Calcium carbonate
7. Effluent
8.Waste heat

Recieving → Storage → Chopping (Tub grinder) → Milling → Leaching → Drying → Electrostatic Separation → Pelletization; Reverse Osmosis; Electrostatic Separation → CHP → Silica Purification
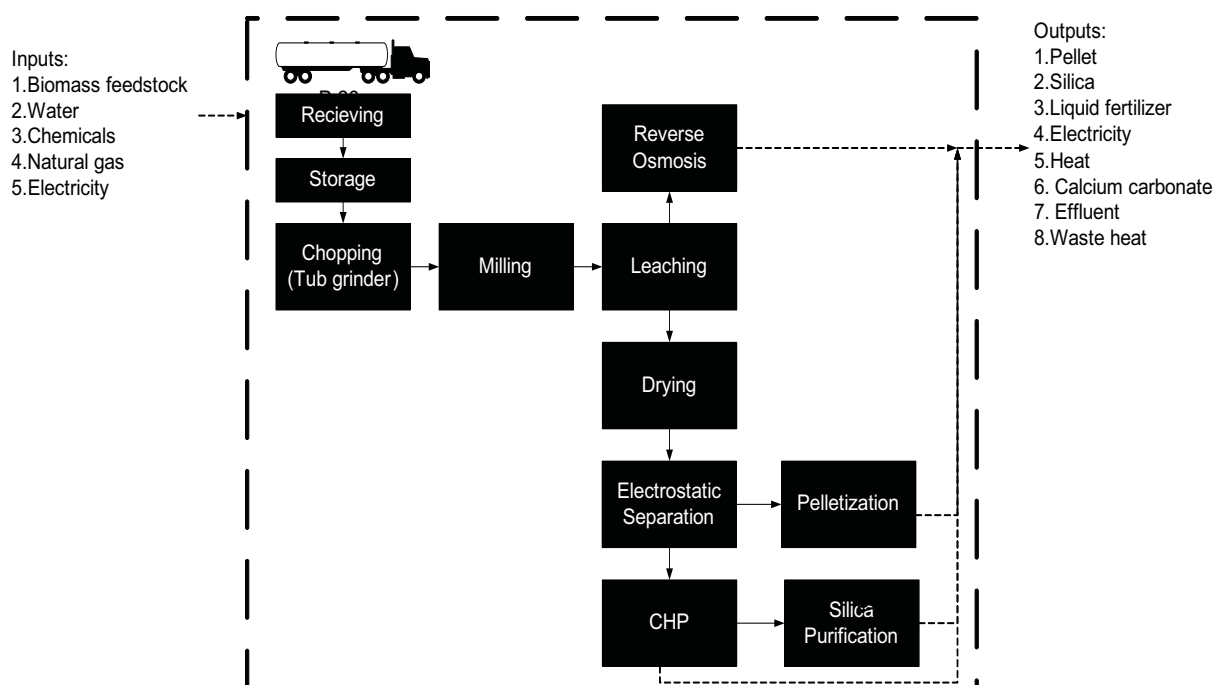
Figure 5-2 Process Flow Diagram of Pretreatment Process

The following general assumptions for the overall process were made for the economic evaluation:

- The biomass feed will consist of a blend of energy crops and agricultural residues with the following nutrient concentrations (by weight percent): N 1.6%, P 0.4%, K 1.6%, Ca 0.12%, Mg 0.06%, and Si 2.0;

- Production capacity of the processing facility will be 200,000 DMT/yr equating to a 30 DMT/hr processing rate;

- The cost of biomass feedstock at processors gate (including transportation from farm to processing

facility) is assumed to be $100/tonne an average of $80/tonne for agricultural residues and $120/tonne for energy crops;

- Electricity costs are assumed to be $0.095/kWh (Current costs in Ontario);

- The investor will own the whole process and is in control of all revenues and costs associated with the process (i.e. no partners or selling off of individual units); and

- Operating hours per year are estimated at 7692 operating hours per year, representing a downtime of approximately 12%

5.5.1 Leaching

The following assumptions were made for the economic evaluation of the leaching step:

- Processing costs used were based on a dissertation by Bakker (2000) looking at an industrial leaching process of 50,000 tonnes/day;

- An inflation rate of 26.7% was used for the years 2000-2011 (Bank of Canada);

- Labour rate of $12/hr for a nutrient removal operator, 24 hours a day, 365 days a year;

- Electricity cost of $0.095/kWh (estimated current rate in Ontario);

- Maintenance costs are assumed to be 5% of capital costs (Bakker, 2000);

- Additional drying costs (to reduce moisture from 50% to <5% for subsequent electrostatic separation and pelletization is sourced from the heat generated by the onsite CHP;

- Capital costs for the dryer (rotary dryer) estimated at $2,400,000 (Ted Cowan, 2011);

Based on the above assumptions the capital cost for the leaching process was calculated at **$6,200,000** and the marginal cost for a 200,000 DMT/yr plant was calculated at **$4.00/tonne**.

5.5.2 Reverse Osmosis

The following assumptions were made for the economic evaluation of the reverse osmosis process:

- The following nutrient recovery percentages were assumed based on lab work conducted by CENNATEK: N 55%, P 80%, K 90%, Ca 10%, Mg 55%;

- The following fertilizers costs were used:

    a. N: $1239.13/tonne ($570/tonne for 46-0-0)

    b. P: (P_2O_5): $1176.67/tonne ($638/tonne for 23-12-18)

    c. K: (K_2O): $1176.67/tonne

    d. Mg: (MgO): $239.13/tonne ($110/tonne for 46% MgO)

    e. Ca: ($CaCO_3$): $365.63/tonne ($117/tonne, 32% $CaCO_3$);

- A water to biomass ratio of 12:1 is used for the leaching process;

- The leaching process is a continuous process discharging 10% of the leachate produced and recycling 90% back into the leaching process;

- 99% of the water is removed and recovered in the RO process; and

- The operating costs are estimated at $1.01/m³ of water to be removed (CENNATEK, 2011).

Based on the above assumptions the capital cost for the reverse osmosis was calculated at **$840,000** and the marginal cost for a 200,000 DMT/yr plant was calculated at **$1.20/tonne**. Total revenues that would be generated from the sales of the nutrient rich retentate is $44.01/tonne of biomass processed equating to $8.8 Million USD annually. In calculating this we multiply the amount of nutrient expected to be recovered per tonne of biomass processed by the sales price assumed for each of the nutrients.

5.5.3 Silica Extraction using Electrostatic Separation

In this step, the silica in the biomass is separated from the remaining biomass material through electrostatic separation. The silica-rich portion (~20% of the original biomass) is burned as fuel in a combined heat and power (CHP) unit to produce heat and electricity. The heat produced is used in biomass drying and other internal operations. Silica is purified from the resulting ash using a base-acid extraction. The produced silica will have 98.5% purity and will be an important by-product and revenue generator in the economic model.

The following assumptions were made for the economic evaluation of the electrostatic separation of silica:

- The operating costs of $12/tonne were based on conversations with John Stencel (TFS). The estimated cost is based on a 100,000 tonne/year electrostatic separation used to separate carbonaceous material from fly ash (Stencel, 2011)

- The separation efficiency of silica from biomass is estimated at 75% based on conversations with John Stencel (Stencel, 2011)

- It is assumed that 80% of the original 200,000 DMT/year of biomass will be separated by the electrostatic process and sent for pelletization and subsequent combustion. The remaining 20% of the

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original biomass, considered "silica-rich" is sent for purification.

Based on the above assumptions the capital cost for the electrostatic separator is **$1.1 Million USD** and the marginal cost for a 200,000 DMT/yr plant was calculated at **$12.00/tonne**.

The following assumptions were made in regards to the purification of silica, combined with heat and electricity generation using a CHP process:

- 20% of the original 200,000 DMT/year biomass separated in the electrostatic separation step, considered rich in silica, is burned to produce heat and electricity in a CHP process. The resulting ash goes through a base solubilisation and precipitation process to produce a purified silica product for sale;

- The amount of ash is estimated to be 10% of the original 40,000 tonne per year of silica-rich biomass (4000 tonne/year). Assuming 75% separation efficiency, the silica rich stream will produce 3000 tonne/year of purified silica for sale;

- The sale price of silica ($2500/tonne) is based on current market value;

- The operating costs for the silica purification process are taken from an industrial scale process design in India (IPSIT, 2011);

- The capacity of the India process was 1825 tonne/year, thus linear adjustment for costs were used to estimate a 3600 tonne/year facility;

- Amount of NaOH needed to solubilise the silica in ash based on the stoichiometric amount needed x 1.5 and a mass ratio of NaOH to silica of 4/3;

- 90% of the NaOH is recovered and reused;

- Carbon dioxide is used to precipitate the solubilised silica, forming a purified silica product.

- Cost of NaOH is $337/tonne based on current market values;

- Cost of Calcium hydroxide is $177/tonne based on current market values;

- Calcium hydroxide is needed to recover the NaOH, as well as producing another by-product for resale, calcium carbonate;

- Thermal energy for silica purification provided by the heat generated from CHP;

- Labour costs are for one operator, $12/hour, 365 days a year, 24 hours a day;

- The HHV of the silica-rich biomass was assumed to be 18.2 MJ/kg (7811 BTU/lb);

- The thermal efficiency of the electricity generation was 15%, and the thermal efficiency of the heat production was 65% (80% total efficiency)

- The capital and operating costs of the CHP was based on similar-sized CHP systems (NREL, 2000).

- The revenues from electricity sales was based on two scenarios:

  i. Peak power sale at $0.16/kWh; and

  ii. Feed-in-tariff (FIT) sale at $0.122/kWh.

- Use of a MW battery adds an additional $1,000,000 in capital costs (Ted Cowan, 2011)

Based on the above assumptions the capital cost for the silica purification plant was **$1.7 Million USD** and the marginal cost for a 200,000 DMT/yr plant was calculated at **$8.00/tonne**. The capital cost for the CHP plant estimated at **$10.2 Million USD** without a 1MW battery and **$11.2 Million USD** with a 1MW battery. The marginal cost associated with the operations of the CHP for a 200,000 DMT/yr plant was calculated at **$2.88/tonne**.

Total revenues that would be generated from the sales of the silica is $37.50/tonne of biomass processed equating to $7.5 Million USD annually.

Total revenues that would be generated from the sales of the electricity generated by the CHP under the FIT program would be $18.10/tonne of biomass processed equating to $3.7 Million USD annually and $23.74/tonne selling at peak demand equating to $4.7 Million USD annually.

5.5.4 Pelletization

The following assumptions were made for the economic evaluation of the pelletization of biomass:

- Capital and operating costs for a 200,000 DMT/yr pelletization unit determined by CENNATEK;

- Biomass drying accounted for in leaching step;

- Power plant efficiency of 33% assumed for the pellets produced since nutrient removal produces high quality combustion fuel;

- The pellets being sold to the end user represent

80% of original input (160,000 DMT/year)

- The HHV of the biomass with nutrients removed is estimated at 20.5 MJ/kg (8840 BTU/lb);

- Operating Costs of the combustion process are assumed to be $0.0075/kWh based on current values found in literature for a coal-powered system

- Four different sales prices were used for the produced pellets in the economic evaluation including: $110/tonne, $130/tonne, $150/tonne and $170/tonne

Based on the above assumptions the capital cost for the pelletization plant was **$21.6 Million USD** and the marginal cost for a 200,000 tonne/yr plant was calculated at **$12.70/tonne**.

5.5.5 Additional Capital & Operating Costs

The following additional capital costs were taken into account for the economic evaluation:

- Land: Cost estimated at $10,000/acre, with 20 acres required

- Building: Costs estimated at $30/square foot, total size of 150,000 square feet

- Receiving: Baled biomass received by truck and inventory tracking using a barcode system costs estimated at $45,000

- Storage: Up to 6 months storage capacity estimated at $250,000 for 3 acres (Ted Cowan, 2011)

- Tub grinder: For initial breaking of bales prior to further milling in leaching process estimated at $500,000 (Ted Cowan, 2011)

The following additional operating costs were taken into account for the economic evaluation:

- Labour Costs:
  a. General Manager: $40/hr, $84,480/year
  b. Procurement: $25/hr, $52,800/year
  c. Accounting/Admin: $20/hr, $42,240/year
  d. Logistics Manager: $20/hr, $42,240/year
  e. Shipping/Receiving: $12/hr, $25,344/year
  f. Shift Supervisors (4x): $17/hr, $148,920/year
  g. Feed Operators (4x): $12/hr, $105,120/year

- Other Operating Costs:
  a. Waste Disposal: Estimated at 2% of feed general and 3% of feed as fly ash from the CHP disposed at $90/tonne including transport
  b. Insurance: Estimated at $240,000/year
  c. Professional Services: Estimated at $60,000/yr
  d. R&D: Estimated at $200,000/year
  e. Office Expenses: Estimated at $90,000/year
  f. Travel: Estimate at $80,000/year

Table 5-5 provides a summary of all of the capital and marginal costs associated with each step of the entire process based on a 200,000 DMT/yr process.

Table 5-5 Summary of Capital Costs

Process	Capital ($ USD)	Marginal ($ USD/tonne)	Reference
Biomass Feedstock		$100.00	
Land/Building	$4,700,000		CENNATEK, 2011
Receiving & Storage	$295,000		CENNATEK, 2011
Tub Grinder	$500,000		Ted Cowan, 2011
Leaching Process	$6,200,000	$4.00	Bakker, 2000 (adjusted)
Reverse Osmosis Process	$840,000	$1.20	CENNATEK, 2011
Electrostatic Separation	$1,130,000	$12.00	Stencel, 2011
Silica Purification	$1,690,000	$7.97	IPSIT, 2011
CHP (Inc. 1MW Battery)	$11,161,000	$2.88	NREL, 2000
Pelletization Process	$21,628,000	$12.70	CENNATEK, 2011
Additional Operating Costs		$10.36	CENNATEK, 2011
Total Costs	**$48,144,000**	**$151.11**	

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5.5.6 Scenarios Considered for the economic evaluation

Various scenarios were chosen to determine the overall revenue, operating costs, capital costs, EBITDA (Earnings Before Interest, Taxes, Depreciation, and Amortization), internal rate of return (IRR), and net present value (NPV) of investment. The following assumptions were made in the calculations:

- Financial model based on 10 year operating life
- Annual inflation rate of 3% per year assumed on all revenues, cost of feedstock and labour

- Annual inflation rate of 2% assumed on all other operating costs
- A sustaining capital cost begins in year 5, increasing from 2% of the capital cost to 5% in year 8 and continuing at 5% until year 10
- Net Present Value (NPV) calculated at 12% discount rate

Financial data on a total of 21 scenarios were calculated using the financial model. **Table 5-6** provides details on the different conditions considered for all of the scenarios investigated.

Table 5-6   Various Scenarios Used for Economic Evaluation

	Process Considered	Recycled Leaching Water (%)	CHP Electricity Sales Price ($/kwh)	Thermal Efficiency of Final Pellets Produced (%)	Pellet Price $/tonne
Scenario 1	leaching + RO + silica extraction + silica purification + CHP + pelletization	90%	$0.16	33%	110
Scenario 2					130
Scenario 3					150
Scenario 4					170
Scenario 5	leaching + RO + silica extraction + silica purification + CHP + pelletization	70%	$0.12	27.5%	110
Scenario 6					130
Scenario 7					150
Scenario 8					170
Scenario 9	leaching + RO + pelletization	90%	NO CHP	27.5%	110
Scenario 10					130
Scenario 11					150
Scenario 12					170
Scenario 13	leaching + RO + pelletization	70%	NO CHP	26%	110
Scenario 14					130
Scenario 15					150
Scenario 16					170
Scenario 17	pelletization	NO LEACHING	NO CHP	22%	110
Scenario 18					130
Scenario 19					150
Scenario 20					170
Scenario 21	leaching + RO + silica extraction + silica purification + pelletization	90%	CHP BY THIRD PARTY	33%	110

Table 5-7   Summary of Financial Data Generated for the 21 Scenarios Considered

SCENARIO	PELLET SALE PRICE ($USD)	Capital Cost ($M USD)	MARGINAL COST ($/DMT)	EBITDA 10YR ($M USD)	NET CASH FLOW 10YR ($M USD)	10YR IRR (%)	NPV (10YR) (12% DISC.) ($M USD)	POWER GENERATION ($/MWh)
1	110	58.56	170	102.50	43.94	13.98%	0.91	72.58
2	130	58.56	170	137.35	78.79	22.70%	18.79	84.31
3	150	58.56	170	172.20	113.64	30.52%	36.68	96.03
4	170	58.56	170	207.05	148.49	37.84%	54.56	107.76
5	110	59.43	173	96.06	36.62	11.61%	(3.64)	87.10
6	130	59.43	173	130.91	71.47	20.39%	14.25	101.17
7	150	59.43	173	165.76	106.32	28.19%	32.13	115.24
8	170	59.43	173	200.61	141.17	35.44%	50.02	129.31
9	110	39.67	141	58.33	18.65	9.13%	(5.52)	88.75
10	130	39.67	141	101.89	62.22	25.31%	16.83	103.08
11	150	39.67	141	145.45	105.78	38.92%	39.19	117.42
12	170	39.67	141	189.02	149.34	51.56%	61.54	131.75
13	110	41.78	144	53.07	11.29	5.54%	(10.09)	92.97
14	130	41.78	144	96.63	54.85	21.91%	12.27	107.99
15	150	41.78	144	140.20	98.41	35.24%	34.62	123.01
16	170	41.78	144	183.76	141.98	47.46%	56.98	138.03
17	110	32.50	137	(33.54)	(66.04)	0%	(46.57)	102.76
18	130	32.50	137	10.02	(22.48)	0%	(24.22)	119.36
19	150	32.50	137	53.59	21.09	11.85%	(1.86)	135.96
20	170	32.50	137	97.15	64.65	30.18%	20.49	152.56
21	130	44.72	164	115.33	70.61	25.07%	18.79	84.31

1. For calculating the power generation costs a fixed cost of $7.50/MWh was used for the operating cost of the power plant (not including fuel). Furthermore an 8% return rate was added to the total production cost for the power generation plant.

2. Capital cost includes capital infusion of 2, 3, 4, 5, 5, and 5 percent of initial investment in years 5, 6, 7, 8, 9, and 10 respectively

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Table 5-7 on page 59 provides a summary of the financial data that was generated by applying the model discussed in this chapter. As the table indicates a 12% discount rate was used to calculate the Net Present Value (NPV). From a project financing and capital budgeting perspective this is a conservative discount rate that was chosen to reflect the perceived technical and financial risks of the project to investors. Discount rates as low as 5% could be justifiable in current market conditions for a 10yr project that is assessed to be a low risk investment. Using the 12% discount rate as the benchmark for our NPV calculations we have introduced a 7% risk premium for potential investors. As a minimum requirement of economic viability the NPV calculated should be positive. Based on Table 5-7, scenarios 5, 9, 13, 17, 18 and 19 are not economically viable as the NPV calcluated for them is a negative number.

The Internal Rate of Return (IRR) is another good indication of the economic viability of the investment. The higher the IRR the more profitable the investment. However, high IRR and NPV values calculated are primarily a function of the sales price of the processed biomass pellets to a power generator. In the financial data presented pellet pricing of $110/DMT, $130/DMT, $150/DMT and $170/DMT were used. Higher pellet sales prices will translate to higher power production costs. Therefore, in determining the most suitable sale price for the biomass it is important to balance the profitability of the project with increase power production costs.

In terms of power generation costs natural gas is currently a very low cost alternative to coal. Given that current natural gas prices are $4.50 per million BTUs (CNN Money, June 2011) the comparative cost of power generation through biomass combustion (which is predominantly a function of the fuel cost) cannot be exuberantly higher. To calculate the cost of power generation from natural gas in $/MWh it was assumed that an additional $7.50/MWh in marginal cost (not including the fuel cost) would be required to account for production costs. The same 8% return rate on the total production cost used in the financial models was also used. Assuming that the thermal efficiency of the plant on natural gas is 35%, the cost of power generation using natural gas is estimated at **$51.57/MWh**.

None of the 21 scenarios investigated had power generation costs that were nearly as low as the $51.57/

MWh calculated for natural gas based on current spot pricing. The lowest power generation cost was calculated for **scenario 1 at $72.58/MWh**. The low cost of power generation from natural gas drives the economic evaluation of any biomass project to the lowest sale price which can be achieved by the biomass processor and still attract investment.

Higher perceived risks leads investors to have higher IRR expectations for their investments. Considering both sides of this equation a minimum IRR of 15% is assumed as sufficient over the 10yr life of the investment to make the project attractive. **Figure 5-3** plots the IRR for the different scenarios at different pellet sales prices. As the figure indicates based on a desired IRR target of 15% the most suitable sale price for the pellets produced is between $110/DMT and $130/DMT.
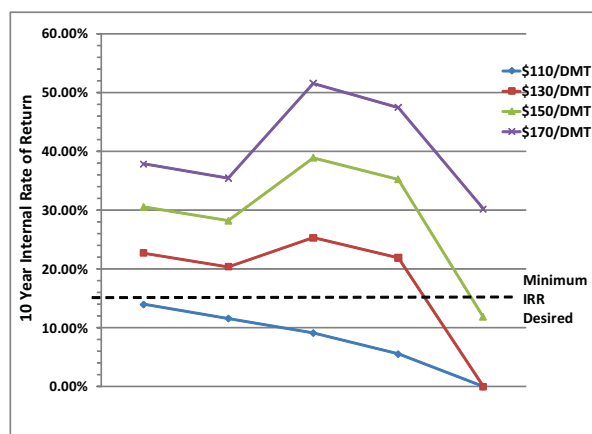
Figure 5-3 Plot of IRR at different scenarios and pellet pricing

This analysis of the financial data produced establishes the $130/DMT pellet sale price as the most suitable one modelled. Slightly lower pricing may be established for some of the scenarios.

Another very important feature of the economic evaluation is that if only pelletization is considered by the processor a minimum pellet price of just over $150/DMT is required to have a positive NPV and a roughly 12% IRR. Thus, the nutrient removal and recovery process has positive impacts on fuel quality, soil quality, and the economics of biomass combustion. The reasoning for the improved economics is the additional revenue streams created by the sales of the nutrients in the form of fertilizer, silica, lime, and electricity by

the pellet producer through the use of a CHP unit. Each of these product streams help improve the overall returns, however the most important in all aspects is the removal and recovery of the water soluble nutrients, and their sale as fertilizer.

Figure 5-4 provides the NPV calculated for all six scenarios considered where the pellet sale price was set at $130/DMT. The only negative NPV value is associated with doing pelletization only where at a feedstock cost of $100/DMT, the NPV is -$24.22 Million USD. As the figure indicates the best NPV values are achieved when either the full process is undertaken (scenario 2) or scenario 21.
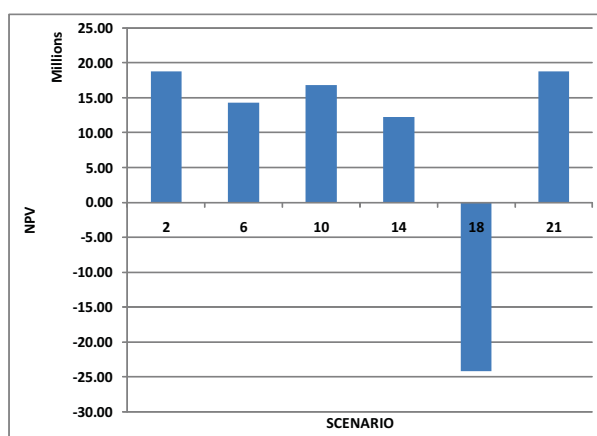
Figure 5-4   NPV for Scenarios at $130/DMT

Scenario 21 is a unique situation where the CHP requirement for the silica purification process is handled by a third party. Under this scenario the silica rich biomass would be sold in loose form to the CHP operator at $30/DMT. The heat generated by the CHP would be provided free of charge as process heat back to the primary biomass processor. This limits the location of the CHP unit to a very close proximity to the processing plant if not onsite. The ash produced is also provided back from the CHP operator for further silica purification. The electricity generated can be sold by the CHP operator. The purpose of including this scenario was to externalize the $11.16 Million USD cost of the CHP unit and reduce the initial investment demand. As the IRR and NPV values indicate so long as the silica rich biomass can be sold at a minimum price of $30/DMT the overall NPV and IRR values are maintained while reducing initial capital investment. Assuming a

$16/MWh sale pricing (peak pricing) for the electricity generated the NPV for the CHP operator (12% discount rate) would be $2,223,761 over the 10yr life of the asset and the IRR will be 18.37%. The silica extraction and purification process when combined with the CHP unit doesn't improve the NPV significantly from $16.83 Million in scenario 10 (where it is not included) to $18.79 Million in scenario 2 (where it is included). Furthermore, the IRR actually reduces from 25.3% to 22.7% over the ten year life of the asset. The silica extraction and purification steps add an additional $2.82 Million USD to the initial investment while the CHP unit adds an additional $11.61 Million USD.

The most significant economic impact of the silica extraction and purification process is on the cost of power production by the end-user of the biomass. By removing 75% of the silica in the biomass a higher quality fuel with improved energy density is produced, and higher thermal efficiencies are expected. In scenario 10 where the silica is left in the biomass a thermal efficiency of 27.5% is assumed, whereas in scenario 2 the thermal efficiency is assumed to reach 33%. This improved thermal efficiency results in the cost of power production in scenario 2 to be $84.31/MWh in comparison to $103.08/MWh for scenario 10.

In conclusion when evaluating the overall process based on both technical and economical merits the best overall scenario investigated is scenario 2 or scenario 21 if external investor used for the CHP unit. A sample calculation spreadsheet for scenario 2 is provided as a fold-out insert at the end of this chapter.

Chapter 6

Experimental Results on Nutrient Removal and Recovery

Chapter 6 of this report details the results obtained from **preliminary** lab-scale experiments performed on the most promising methods described. These experiments are being carried-out in order to validate the results given in literature. A further goal of these experiments is to develop and integrate an industrial scale process that combines the various extraction and recovery methods into a single, cohesive process. Lab-scale experiments included various types of leaching for nutrient extraction, an electrostatic separation method to extract silica, and both reverse osmosis and magnesium struvite precipitation for nutrient recovery.

The experimental work and the corresponding process development carried out by the research team is an ongoing project that extends beyond the timeframe provided for preparing this report. As a result, the data reported in this chapter are those obtained from initial experiments and do not reflect the final results for this project. Nevertheless, some valuable conclusions have been drawn from these experiments. Recommendation for further future work are also provided.

6.1 Water Soluble Nutrient Extraction Experiments

Chapter 2 of the literature review focused on various methods of extracting water soluble nutrients in order to improve the combustion properties of biomass. CENNATEK carried out a number of lab-scale experiments in order to develop a process that could be used at an industrial scale for liquid extraction of these water soluble nutrients.

6.1.1 Materials & Methods

Biomass Samples

Various biomass feedstocks for lab-scale leaching experiments were obtained from local producers including: two energy crops and one agricultural residue. Miscanthus bedding was obtained from Dean Tiessen (New Energy Farms, Leamington, Ontario), a bale of switchgrass from Don Nott (Nott Farms, Clin-

ton, Ontario) and a bale of soybean straw from Paul Wettlaufer (Wettlaufer Family Farm, Ayton, Ontario). All three biomass samples were harvested in the fall and allowed to field dry over the winter months prior to collection. Switchgrass was left lying in swaths or windrows, while soybean straw was left to field dry with netting to partially prevent precipitation from affecting the biomass quality.

Preparation of Biomass Prior to Leaching

Prior to the two immersion leaching methods (described below), each biomass was passed through a Wiley knife mill for size reduction. The reduction in particle size increased the available surface area of the biomass, allowing for a greater contact area between the water and nutrients in the biomass. In addition, the reduced particle size increased the rate of extraction by decreasing the path of diffusion, which is a key factor in the overall rate of extraction. The particle size attained by the knife mill was <2.0mm. Biomass with moisture content above 10% could cause clogging in the knife mill due to build up between the knives. If the moisture content of the raw biomass was above 50%, a drying step was applied prior to milling. For the pour/spray leaching method, the biomass was broken down to lengths of a few centimeters, similar to forage chopping on a larger scale.

6.1.2 Leaching Procedure

Leaching was carried out using distilled water at a specified ratio of water to biomass. In order for this process to be industrially feasible the water to biomass ratio must be kept to a minimum. For this set of experiments water to solid ratios of 8:1 and 12:1 were deemed adequate. Similarly, one would expect that the longer the biomass is processed the more nutrients are recovered, however there are capital and operating cost implications with increased residence time, thus shorter residence times are better for industrial scale applications. For this reason in the initial set of experiments residence times of 30 minutes and one hour were used. There were three approaches to leaching investigated:

   i.   Immersion with agitation,

ii. Immersion without agitation, and

iii. Pouring/spraying method.

In the first step, the appropriate amount of distilled water and biomass were measured and mixed according to the desired ratios. The mixture was then agitated with a Phipps & Birds PB-700 Jar tester apparatus at a rate of 300 rpm for the appropriate residence time. After the immersion leaching was complete, the sample was first filtered using vacuum filtration to separate the water (now leachate) from the solid biomass. The wet biomass was then further dewatered using a lab-scale potato ricer press to extract more leachate and to further reduce the moisture content. The biomass was then dried using an infrared moisture analyzer (Denver Instrument IR-35) prior to analytical testing.

The immersion without agitation method was setup in a similar manner to the immersion with agitation method. The biomass was weighed with a specific ratio to water, and manually stirred to allow full submersion within the distilled water. The sample was then left to leach with no agitation for the specified residence time prior to filtration, pressing and drying.

The third leaching method tested was the pour/spray method. This involved placing the raw, chopped biomass along a steel mesh with a collection basin underneath. The distilled water was placed in a spray bottle and sprayed over the biomass over two intervals, with a lag of ten minutes between sprays. The total amount of water sprayed on the biomass maintained the same water to biomass ratios of 8:1 and 12:1 as used in the immersion leaching methods. The lag between sprayings allowed the leachate to run off the biomass and get retained in the collection basin. The same period of time was used after the final spray before collecting the leachate. The steel mesh diameter was 2.0mm, which caused a small amount of biomass material to be collected in the basin. As a result, the leachate was filtered to remove the solid biomass prior to drying and further analysis.

Additional Parameters Tested

Miscanthus was tested using different values of pH of distilled water. These tests were performed under controlled conditions, with a water to biomass ratio of 12:1 using the immersion with agitation method and a residence time of one hour. A total of six tests were completed at various pH levels, ranging from pH 4-9.

The average pH of the distilled water used in the current research was 6.33. To lower the pH, a 1% sulphuric acid solution was added to the water. The volume of sulphuric acid was recorded and used to calculate the amount of sulphur present in the distilled water after adjusting the pH. This was taken into account when interpreting the sulphur content of the leached biomass & leachate. To increase the pH, a solution of 5% sodium hydroxide was used. Similarly, the volume was recorded and the sodium content within the increased pH water was calculated when interpreting the results.

Lower residence times of 5, 10, 15 and 20 minutes were tested using milled miscanthus and switchgrass. These parameters were tested to determine if a lower residence time for leaching would significantly affect the extraction efficiency of nutrients from the biomass. Tests were run using the same method described for immersion leaching with agitation, using a water to biomass ratio of 12:1.

Finally the effect of multi-cycle leaching was determined in order to determine the effect of recycling leachate for use in a subsequent leaching process. A miscanthus sample underwent immersion leaching with agitation for one hour at a water to biomass ratio of 12:1. After the run, the leachate was filtered and pressed and reused with fresh biomass for a subsequent run under the same conditions. The process was repeated four times, with no fresh water added to the recycled leachate.

Analytical

Solid biomass samples underwent standard characterization testing for use in thermal processes. The tests (summarized in **Table 6-1**) include: proximate and ultimate analysis, calorific value (or HHV), chlorine, elemental ash composition and ash fusion temperatures. The resulting leachate was also measured for nutrient content using an ICP-OES (Inductively coupled plasma-optical emission spectrometry) and for chlorine.

6.1.3 Nutrient Extraction Results

Analysis of Biomass Samples as Received

The three biomass samples (miscanthus, switchgrass, and soybean straw) were analyzed prior to leaching. The results are shown in **Tables 6-2 and 6-3**.

As mentioned in the materials and methods section,

all three biomass samples used in this study were subject to varying amounts of field drying/field leaching.

Table 6-1   Summary of ASTM Test Methods for Analysis of Biomass Samples

Analysis	ASTM Test Method
Proximate Analysis	
Moisture Content (wt. %)	E871
Ash Content (% DMT)	E1755
Ultimate Analysis (% DMT)	
Carbon, Hydrogen, Nitrogen	D5373
Sulfur	D4239
Oxygen	E870
Chlorine	D4208
Calorific Value (HHV)	E711
Elemental Ash Composition	D6349
Ash Fusion Temperatures (°C)	D1857

This explains the relatively low moisture content values of 7-12% on the as-received samples. Ash content values also indicate that some field leaching has occurred, as the calculated values were all lower when compared to typical ash content values for miscanthus (4%), switchgrass (5%) and soybean straw (7.5%) found in literature at harvest (Kludze et al., 2010).

Leaching Results – Immersion with Agitation

Reduction in Nutrients and Recovery in Leachate

Based on the literature review, immersion leaching with agitation provides the most efficient nutrient extraction when compared to other industrial leaching processes. Thus the experimental work carried out primarily focused on immersion leaching with agitation.

Figures 6.1 to 6.3 summarize the amount of various nutrients removed from the biomass and recovered in the leachate for miscanthus, switchgrass and soybean straw.

As these figures indicate, the extraction of nutrients varies between the biomass feedstocks. The nutrients that were most readily extracted into the water/

leachate for the two energy crops were phosphorous, and potassium. Soybean straw leachate also indicated a relatively large extraction of potassium, but had a lower phosphorous recovery and higher magnesium recovery. In addition to the nutrients in the above figures, chlorine recovery in the leachate and nitrogen and sulphur reduction in the leached biomass was also determined due to their importance in fuel quality improvement and/or use in fertilizer. Virtually all of the chlorine present in the biomass processed at 12:1 water to biomass ration and one hour residence time was recovered for both miscanthus and switchgrass. Approximately 89% of the chlorine in soybean straw was recovered in the leachate.

Reductions in sulphur ranged from 29% for miscanthus, 40% for soybean straw and 54% for switchgrass, with similar extractions for both water to biomass ratios tested. For nitrogen, the initial amount in the untreated miscanthus was 0.09% and 0.28%, respectively. Nitrogen values for all post-leached samples were under the detection limit (~0.05 wt. %) for the nitrogen analyzer used. This is an indication that there was an appreciable amount of nitrogen removed from the two energy crops through leaching, but an accurate value could not be determined.

In terms of relative nutrient extraction efficiencies, the obtained results are in good agreement with results reported in literature (Bakker, 2000; Dayton et al., 1999; Turn et al., 1997; Jenkins et al., 1997). The more readily extracted nutrients were chlorine, potassium, phosphorous and sodium, while extraction of nitrogen, sulphur, magnesium and calcium were variable and ranged from less than 5% to 50% extraction.

One difference between the obtained results and results obtained in literature to make note of is the actual amount of nutrients extracted. While the amount of chlorine extraction is common, the reductions in potassium and phosphorous reported for the more efficient immersion leaching with agitation processes is higher than the results from the current lab-scale experiments. Potassium and phosphorous reductions of 75-90% have been reported, while the maximum phosphorous and potassium reductions in the current work is between 35 and 60% (with lower reductions for phosphorous in soybean straw).

There are several explanations for the difference in extraction efficiencies. As mentioned previously, the biomass samples used in the current study were

Table 6-2   Characteristics of Untreated Biomass Feedstocks

Parameters	Miscanthus	Switchgrass	Soybean Straw
Proximate Analysis			
Moisture (wt%)	12.64	9.56	7.43
Ash (wt% dry matter)	2.66	1.96	2.79
Ultimate Analysis (% dry matter)			
Carbon	46.99	49.32	43.08
Hydrogen	5.94	5.89	5.64
Nitrogen	0.09	0.28	0.70
Sulfur	0.01	0.02	0.02
Oxygen	44.31	42.53	47.77
Ash Fusion ($^{\circ}$C)			
Initial Deformation Temperature	916	1227	>1538
Softening Temperature	1022	1238	>1538
Hemispherical Temperature	1224	1250	>1538
Fluid Temperature	1317	1265	>1538
Chlorine (wt% dry matter)	0.14	0.10	0.12
Calorific Value (MJ/kg)	19.12	18.43	17.67
Calorific Value (BTU/lb)	8222	7927	7598

Table 6-3   Elemental Ash Analysis of Untreated Biomass Feedstocks

Parameters	Miscanthus	Switchgrass	Soybean Straw
Elemental Oxide	Elemental Ash Composition (% of Ash)		
SiO_2	61.25	51.69	13.55
P_2O_5	6.75	5.97	8.72
Al_2O_3	0.59	0.98	2.08
Fe_2O3	0.37	0.65	1.05
MnO	0.30	0.05	0.08
MgO	3.66	9.37	21.50
CaO	6.13	22.67	43.26
K_2O	19.48	8.01	8.74
Na_2O	1.40	0.51	0.87
TiO_2	0.02	0.06	0.10
Cr_2O_3	0.06	0.04	0.05
Total	100.00	100.00	100.00
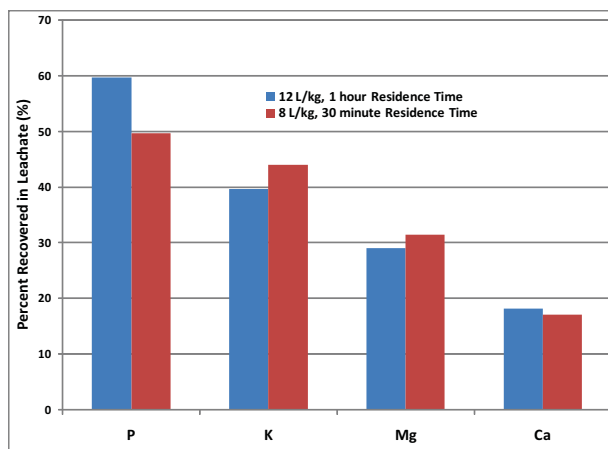
Figure 6-1 Percent Recovery of Selected Nutrients in Leachate for Miscanthus following Immersion Leaching with Agitation

subject to varying levels of drying in the field over winter, leading to a certain amount of nutrients being field leached into the soil prior to collection. With some of the more readily leachable portions of nutrients already removed prior to the experiments the extraction efficiency of the remaining nutrients would tend to be lower. For example, phosphorous is present in biomass materials in a variety of forms, both organic and inorganic. The more leachable inorganic forms of phosphorous would be more easily removed during field leaching, while the remaining organic phosphorous would only be leached out with a more vigorous process and time. Another reason for the discrepancy in removal efficiencies is the water
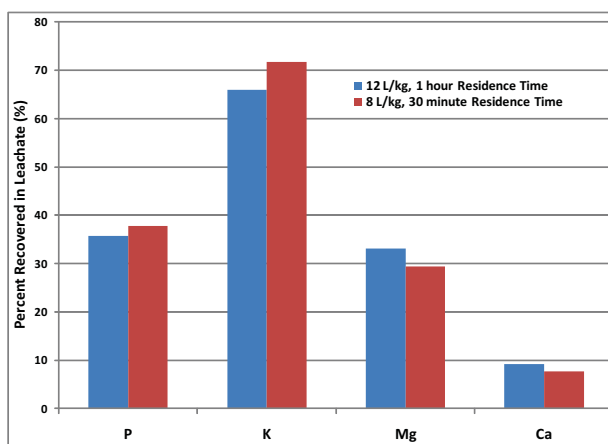
Figure 6-2 Percent Recovery of Selected Nutrients in Leachate for Switchgrass following Immersion Leaching with Agitation

to biomass ratios used in literature, the residence times used, or a combination of both factors. The vast majority of researchers used very large water to biomass ratios, ranging from 20 to 120:1. Combined with longer residence times ranging from two hours to two days, this allowed for longer contact times and more water to interact with the biomass, leading to more leaching of nutrients. When considering a scale-up of an industrial leaching process, it is not practical to use the larger water to biomass ratios and residence times due to size and time constraints. For example,
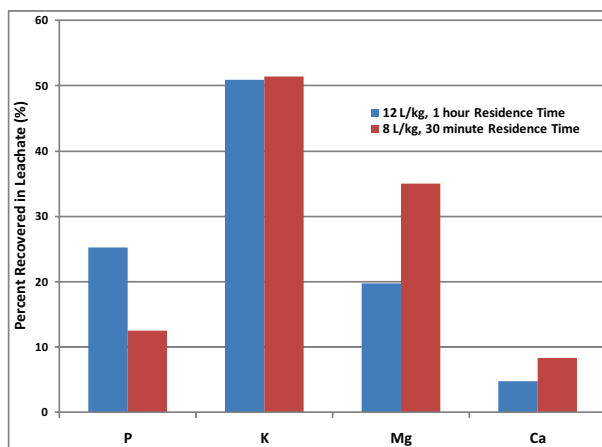
Figure 6-3 Percent Recovery of Selected Nutrients in Leachate for Soybean Straw following Immersion Leaching with Agitation

a 100,000 DMT/year biomass leaching facility would require anywhere from 2 million to 12 million litres of water/year requiring larger reactors and pumps translating to higher costs. Similarly a process that requires 24 hours of residence time will require very large reactors to facilitate the liquid extraction process leading to significantly higher capital and operating costs.

Researchers that used similar ratios and shorter residence times to the current research (Turn et al., 2003; Turn et al., 1997) also included a pre-leaching and post-leaching pressing of solids to retrieve more leachate and to reduce the moisture content prior to further processing and/or pelletization. The pressing carried out in the preliminary experiments reduced the moisture content of the biomass after leaching from 85-90% to between 69-79% thus leaving 15-20% more nutrient rich leachate with the biomass. In order to further mechanically dewater the biomass and obtain more nutrients in the leachate a press that would more closely mimic an industrial scale dewatering system

(i.e. screw, roller or filter press) should be used.

Figures 6.1 – 6.3 also show an interesting trend when comparing the two water to biomass ratios used in the current research. Aside from the phosphorous recovery in the soybean straw, the trials using 8:1 water to biomass ratio at half and hour of residence time had nutrient recovery percentages that were very similar to the samples exposed to 12:1 water to biomass ratio at one hour of residence time. These results, combined with the fact that no other test parameters were altered, indicate that for most nutrients of interest a lower water to biomass ratio of 8:1 is sufficient.

Effect on Combustion Characteristics

The effect of the immersion with agitation leaching process on ash content, calorific value and ash fusion temperatures was determined for the three biomass feedstocks. **Table 6-4** provides the percent difference after leaching with a water to biomass ratio of 12:1 and one hour residence time, and with a water to biomass ratio of 8:1 and 30 minute residence time.

As with the nutrient recovery results, these results show a difference when comparing the two energy crops to the agricultural residue. Both miscanthus and switchgrass showed a significant decrease in ash content after the leaching process, with switchgrass having a reduction between 6 and almost 27%, while miscanthus showed a significant reduction between 60 and 87% for the two leaching methods performed. Switchgrass showed a corresponding increase in calorific value (1.11 to 5.52%), while miscanthus showed only a slight increase in calorific value following leaching. The decrease in ash content and corresponding increase in calorific value is in general agreement with trends shown in literature, which show a linear relationship between a decrease in ash content and an increase in calorific value (see **Figure 2-1**). In terms of ash fusion temperature, miscanthus showed a significant improvement in the initial deformation and softening temperatures for both ratios tested, while the hemispherical and fluid temperatures were lower than the untreated sample for the 12:1 sample. Switchgrass showed a slight improvement for all four ash fusion temperatures for the 12:1 sample, while the 8:1 sample showed an increase in the fluid temperature only. These results can again be partially attributable to the fact that the untreated biomass already underwent some field leaching and subsequently already displayed improved ash fusion temperatures when compared to a freshly harvested sample.

The results for soybean straw showed no significant change in ash content after leaching. In terms of the

ash fusion temperatures, the untreated soybean straw produced a high quality ash as no deformation was observed to the upper limit of the ash fusion furnace equipment used (1538°C). The leached samples also showed no deformations up to the same temperature, indicating that there was at a minimum no decrease in the ash fusion characteristics.

Leaching results – Immersion without Agitation and Pouring/Spraying

Immersion leaching without agitation and a pouring/spraying method were tested at similar water to biomass ratios (and in the case of immersion without agitation, similar residence times) to compare nutrient extraction efficiencies with the results obtained from the trials on immersion with agitation. The percent reduction in the amount of sulphur in the biomass after leaching (see **Figure 6-4**) was chosen as a basis of comparison. The results indicate that for all biomass feedstocks tested, the reduction in sulphur with immersion leaching with agitation (for both water to biomass ratios tested) is larger (significantly so in the case of switchgrass and soybean straw) when compared with the two other leaching techniques. The discrepancy between agitation immersion leaching and the pour/spray method is largely due to the biomass in the pour/spray method being forage chopped only and not further reduced in size through milling. With less surface area for the water to come in contact with the biomass, as well as reduced contact time between the water and biomass, a significantly larger amount of water would need to be sprayed in order to achieve a similar reduction in nutrients.
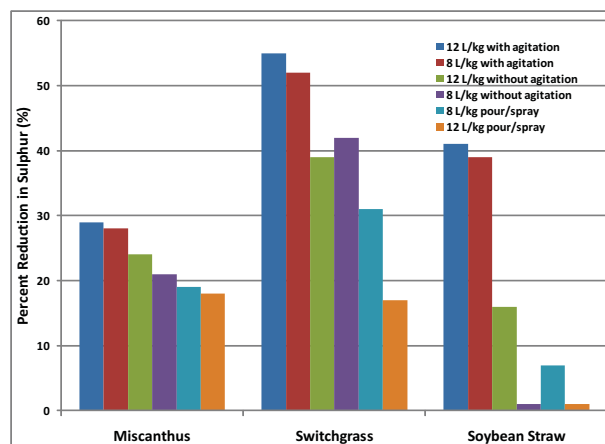
Figure 6-4 Percent Reduction in Sulphur in Biomass Following Several Leaching Techniques

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Table 6-4   Percent difference in ash content, calorific value and ash fusion temperature values after immersion leaching with agitation for various biomass feedstocks

	Untreated	12 L/kg, 1 hour	% Difference	8 L/kg, 30 minutes	% Difference
Miscanthus					
Ash content (wt. % dry)	2.66	0.34	-87.22	1.08	-59.40
Calorific Value (BTU/lb)	8012	8083	0.89	8088	0.95
Ash Fusion Temperature (°C)					
Initial Deformation	916	1199	30.90	1038	13.32
Softening	1022	1202	17.61	1324	29.55
Hemispherical	1224	1208	-1.31	1364	11.44
Fluid	1317	1212	-7.97	1396	6.00
Swtichgrass					
Ash content (wt. % dry)	1.96	1.84	-6.12	1.44	-26.53
Calorific Value (BTU/lb)	7927	8015	1.11	8365	5.52
Ash Fusion Temperature (°C)					
Initial Deformation	1227	1230	0.24	1193	-2.77
Softening	1238	1258	1.62	1208	-2.42
Hemispherical	1250	1259	0.72	1224	-2.08
Fluid	1265	1268	0.24	1294	2.29
Soybean Straw					
Ash content (wt. % dry)	2.79	2.79	0.00	N/A	N/A
Calorific Value (BTU/lb)	7598	7972	4.92	7936	4.44
Ash Fusion Temperature (°C)					
Initial Deformation	>1538	>1538	0.00	>1538	0.00
Softening	>1538	>1538	0.00	>1538	0.00
Hemispherical	>1538	>1538	0.00	>1538	0.00
Fluid	>1538	>1538	0.00	>1538	0.00

For the immersion leaching without agitation, it is clear from these results that the presence of the agitation improves the contact between the biomass and the water. Visually, it can be observed that when there is no agitation applied to the leaching process the majority of the biomass floats in the water.

Recycling of the Leachate

The effect of recycling the leachate as water for further nutrient extraction was examined. Leachate from the first stage of extraction was reused (as opposed to fresh water) to leach fresh biomass in a subsequent

leaching process. **Table 6-5** summarizes the concentration of various elements/nutrients removed and recovered in the leachate after the first, third and fourth cycle using Miscanthus as the biomass feedstock.

The results indicate that with each cycling of the leachate, there is a linear increase in the amount of each nutrient present in the leachate (with only chlorine showing a decrease after the fourth cycle). These results are very promising, as it shows that leachate can effectively be recycled without any loss of leaching

efficiency. This represents an improvement to the process when applied on an industrial scale. The ability to recycle the leachate reduces the amount of fresh water required for the overall process. When combined with a reverse osmosis nutrient recovery system (as discussed in Section 5.3), the amount of fresh water required can be reduced up to ten-fold, depending on the number of times the leachate can be recycled before an observed plateau or loss in nutrient recovery in the leachate occurs. Further optimization is required to determine the maximum number of cycles that are feasible.

Table 6-5   Concentration of Nutrients Recovered in Multi-Cycle Leaching of Miscanthus

Element	Cycle 1 (ppm)	Cycle 3 (ppm)	Cycle 4 (ppm)
K	142.3	391.3	650.8
P	39.0	119.6	176.7
Mg	14.2	45.8	69.4
Ca	17.6	52.0	73.2
Na	6.4	31.2	63.9
Cl	265.5	1173.0	803.6

Effect of pH

Water used for an industrial leaching process would generally be taken from local water sources (rivers, wells, etc.). As they can exhibit differences in water quality due to the presence of contaminants, tests were conducted using water with different pH levels (ph 4-9) to determine if there would be any significant effect on leaching results.

Figure 6-5 indicates the relative change in sulphur, chlorine, calorific value and ash content between the parameter measured at a given pH (i.e. between 4 and 9) and the parameter measured at pH 6. A pH of 6 was chosen as the reference value as the distilled water used in the lab-scale leaching methods (pH 6.33) was closest to this value.

For sulphur there exists a clear trend from more acidic (lower pH values than seven) resulting in improved removal to more basic (higher pH values than seven) resulting in lower sulphur removal.

For chlorine pH has no effect on its removal within the

ranges examined. The chlorine found in biomass is almost entirely inorganic and very water soluble leading to very high recovery rates through a liquid extraction process.

As expected the calorific value reduces when leaching is conducted with more acidic solutions (pH 4 and 5). This is because at lower pH acid hydrolysis of the organic matter begins to occur leading to decomposition of the organic matter and thus reduced calorific values. Therefore it is important to ensure that the water used in the liquid extraction process maintains a pH of 6 or higher.

Finally, for the ash content the most interesting trend has been observed. At pH levels below 6 the ash content is much higher than the pH at 6 due to acid hydrolysis of organic matter. Most of the water soluble nutrients have higher solubilities at lower pH (higher acidity levels). In fact acid digestion is a common analytical technique that is used to dissolve these elements into a solution as a preparation step for determining their concentrations. However, organic Si is not
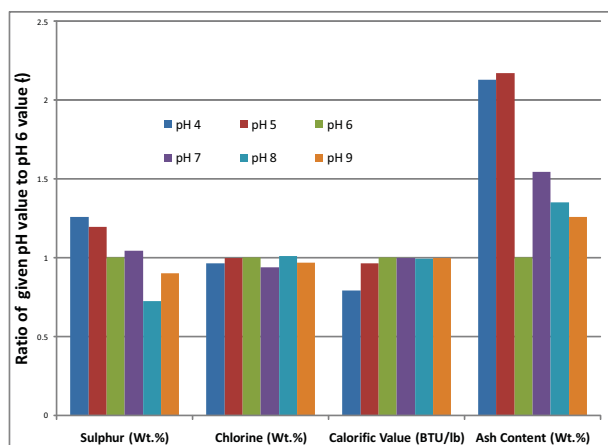
Figure 6-5 Relative change in sulphur, chlorine, calorific value and ash content of miscanthus between samples at different pH values and at pH 6

readily acid soluble. Silica is the largest constituent of the ash content and is only soluble in very basic solutions (high pH). As acid hydrolysis dissolves some of the organic matter in the biomass the ash content of the biomass increases due to the increased percentage of Silica that remains in the biomass. Thus, the advantages gained by the higher solubility of the other nutrient is offset by acid hydrolysis of the organic matter that results in a lower heating value for the biomass and higher ash contents.

On the other hand as the solution approaches neutral at pH7, the solubility of nutrients such as K, Na, Mg, and Ca reduces resulting in higher ash contents. Further increases in the pH into basic solution results in increased dissolution of the Silica and reduced dissolution of all other nutrients discussed. Given that Silica is the largest constituent of the ash, the ash content once again gets lower as pH is raised from 7 to 8 and 9 due to more Silica being dissolved. This trend is expected to reverse or flatten out as the pH is raised higher initiating breakdown of lignin.

The overall conclusion is that the most ideal pH for the liquid extraction of water soluble nutrients is to have the solution slightly acidic at pH levels around 6. In practice this is great given that most natural water supplies are found at slightly acidic pH levels around 6, which would mean that very little tampering with pH would be required.

Effect of Residence Time

Based on the literature review of leaching processes to remove nutrients, the residence time for immersion leaching ranged from a few minutes to several hours. On an industrial scale, residence times of a few hours to a few days are not practical due to size limitations for leaching reactors. As a result, residence times of
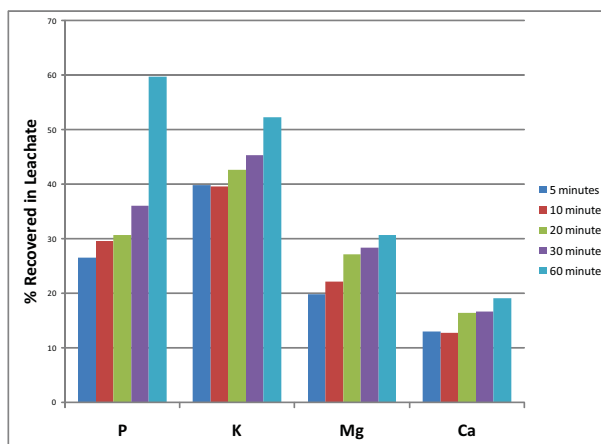
Figure 6-6 Amount of nutrients recovered in leachate at various residence times

30 minutes and 1 hour were tested as described in sections 6.1.2. To determine if lower residence times were able to remove similar amount of nutrients from the biomass, residence times of 5, 10 and 20 minutes were examined using the immersion leaching with agitation process for miscanthus and switchgrass. **Figure 6-6** shows the amount of various nutrients recovered in the leachate (as a percentage of the initial amount in the biomass) for residence times ranging from 5 to 60 minutes.

Results for switchgrass showed similar incremental increases in nutrient recovery in the leachate with increased residence times, with an average increase of 19% in leachate nutrient content from 10 minutes to 60 minutes.

The results show that as expected increases in leaching residence time lead to a corresponding increase in the amount of nutrients extracted and released into the leachate. As discussed previously, the rate of nutrient extraction in immersion leaching with agitation is dependent on the contact area and the contact time

between the water and biomass. Three ways to improve the nutrient extraction is through biomass size reduction, increased residence time, increased water and increased agitation. For these experiments, the water to biomass ratio, biomass size and agitation rate were kept constant, making the residence time the key factor in the amount of nutrients extracted.

In order to achieve a similar leaching efficiency with shorter residence times, the alternative is to further reduce the size of the biomass and/or increase the rate of agitation. Further reduction in biomass particle size may be limited due to limits of industrial-scale mills for biomass and the cost of further size reductions. Increasing contact through more aggressive agitation should be a better method of increasing extraction efficiency.

6.1.4   Conclusions and Recommendations

Lab-scale leaching experiments based on immersion and pouring/spraying methods reported in literature were conducted, with the following conclusions drawn from the results:

- Immersion leaching with agitation is a more effective leaching process when compared to immersion leaching without agitation and pouring/spraying of water.

- Chlorine, potassium, phosphorous and sodium are the most readily leached nutrients, while removal of nitrogen, magnesium, calcium and sulphur are variable and depend on the type of biomass feedstock.

- A water to biomass ratio of 8:1 to 12:1 is sufficient to extract nutrients at a residence time of 30 minutes to 1 hour.

- Biomass that has undergone field leaching can have further nutrients removed using an industrial leaching process.

- Leaching further reduces the ash content of energy crops after field leaching, but the effect on the calorific value and ash fusion temperatures is variable.

- Recycled leachate showed no decrease in extraction efficiency after four cycles of use. The recycling of leachate results in a lower demand of fresh water required for an industrial-scale leaching process.

- Nutrient extraction for producing a combustion fuel is sensitive to pH. The optimal pH for the leach-

ing process is a slightly acidic solution with a pH of about 6.

- Varying the residence time from five minutes to 60 minutes showed an incremental increase in the amount of nutrients removed. In order to reduce the residence time without the corresponding loss in nutrient recovery, a further decrease in particle size and/or an increase in agitation speed should be applied.

Based on the above results and conclusions from the current lab-scale work, the following are recommendations for further optimization and potential scale-up to an industrial-scale process:

- Experiments with freshly harvested biomass in the fall to compare the extraction efficiency with field leached biomass.

- Experiments with better dewatering of biomass following the leaching process capable of reducing the moisture content to approximately 50%.

- An optimization study to determine the maximum number of cycles that leachate can be recycled before the nutrient extraction efficiency is reduced, as well as a comparison of different biomass feedstocks.

- An optimization study to determine the effects of biomass particle size and rate of agitation on immersion leaching with agitation at lower residence times.

- For scale-up to an industrial-sized process, a further investigation into additional equipment and logistics needed. Additional steps in the process may include a pre-spraying step prior to immersion leaching to remove any dirt and/or contaminants from the received biomass, conveyors from the various steps in the process, and an additional drying unit to further reduce the moisture content of the leached biomass.

- In addition to the above recommendation, a further investigation into how the leaching process would incorporate into a larger process that would also include silica extraction, nutrient recovery methods and pelletization.

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6.2 Electrostatic Separation of Silica from Biomass

6.2.1 Introduction

The principle of electrostatics has been successfully applied to separate various materials based on differences in their tribo-charging characteristics. An electrostatic separation process has been shown to have encouraging results in coal beneficiation. This technology has also been used at an industrial scale to remove carbon from fly ash.

The aim of this work was to evaluate the potential of using tribo-electric separation as a process to remove silica from biomass. Silica contributes to a number of problems associated with biomass combustion including deposit formation, slag formation, and high ash content. Little information has been published into the physical and chemical properties of biomass that are related to the separation purities that can be attained using dry triboelectrostatic separation.

6.2.2 Experimental procedure

Electrostatic separation of silica was performed for a number of biomass feedstocks, including switchgrass, miscanthus, and soybean straw. The biomass was milled using various size reduction equipment including a knife mill (Wiley No. 4), a ball mill (Retsch PM 200) and a mill grinder (Strand Mill Lab Grinder, Model # S101DS) and was sieved into different size fractions in order to investigate the effect of particle size on the separation efficiency.

Copper, with a work function value intermediate to the work function values of silica and carbonaceous components, was chosen as the contact material used in the tribo-charger. This assures that silica and carbonaceous particles obtain opposite charges and can be separated.

A schematic depiction of the tribo-electrostatic experimental set-up used is provided in **Figure 6-7**. A copper plate was placed on top of the vibrating feeder plate to act as a tribo-charging medium. Tribo-charging of the particles was conducted in the vibratory feeder for one hour prior to release. After the one hour, the particles were dropped into a copper funnel leading to a separation chamber (Plexiglas box). The feed rate was slow enough that only a single layer of particles

was allowed to exit the tribo-charger at one time. The rectangular Plexiglas chamber had dimensions of 12×12×18 cm. The chamber contained two copper electrodes of length 14 cm and width 5 cm connected to a positive and a negative high voltage DC supply. The copper plates were fixed within the box with insulating Teflon screws. The top and bottom gaps of the plates were maintained at 7.5 and 32.5 cm, respectively. There were four collection bins of 12×3×2 cm bellow the electrode plates to collect the material after passing through the electric field. Bins were labelled 1 to 4 in which bins 1 and 4 were closest to the positive and negative electrodes, respectively. Prior to the triboelectrostatic separation tests, the biomass samples were evaluated for their ash content. After the triboelectrostatic separation, samples were collected from the four bins and were again subjected to ash content analysis in order to investigate the performance of the electrostatic separator.
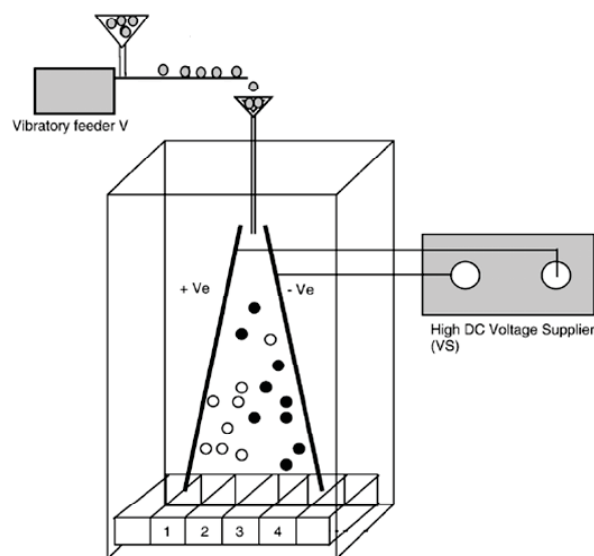
Figure 6-7 Tribo-electrostatic separator (Adapted from: Dwari and Rao, 2006)

6.2.3 Results and discussions

Triboelectrostatic separation

Figure 6-8 shows the ash content of particles collected from bins 1-4 after a one-stage separation. In these experiments, particles were tribo-charged for one hour in the copper tribo-charger. After tribo-charging, the

Switchgrass 0.15-0.25 mm

Swtichgrass 0.25-0.589 mm

Miscanthus 0.15-0.25 mm

Miscanthus 0.25-0.589 mm

Soybean 0.15-0.25 mm

Soybean 0.25-0.589 mm
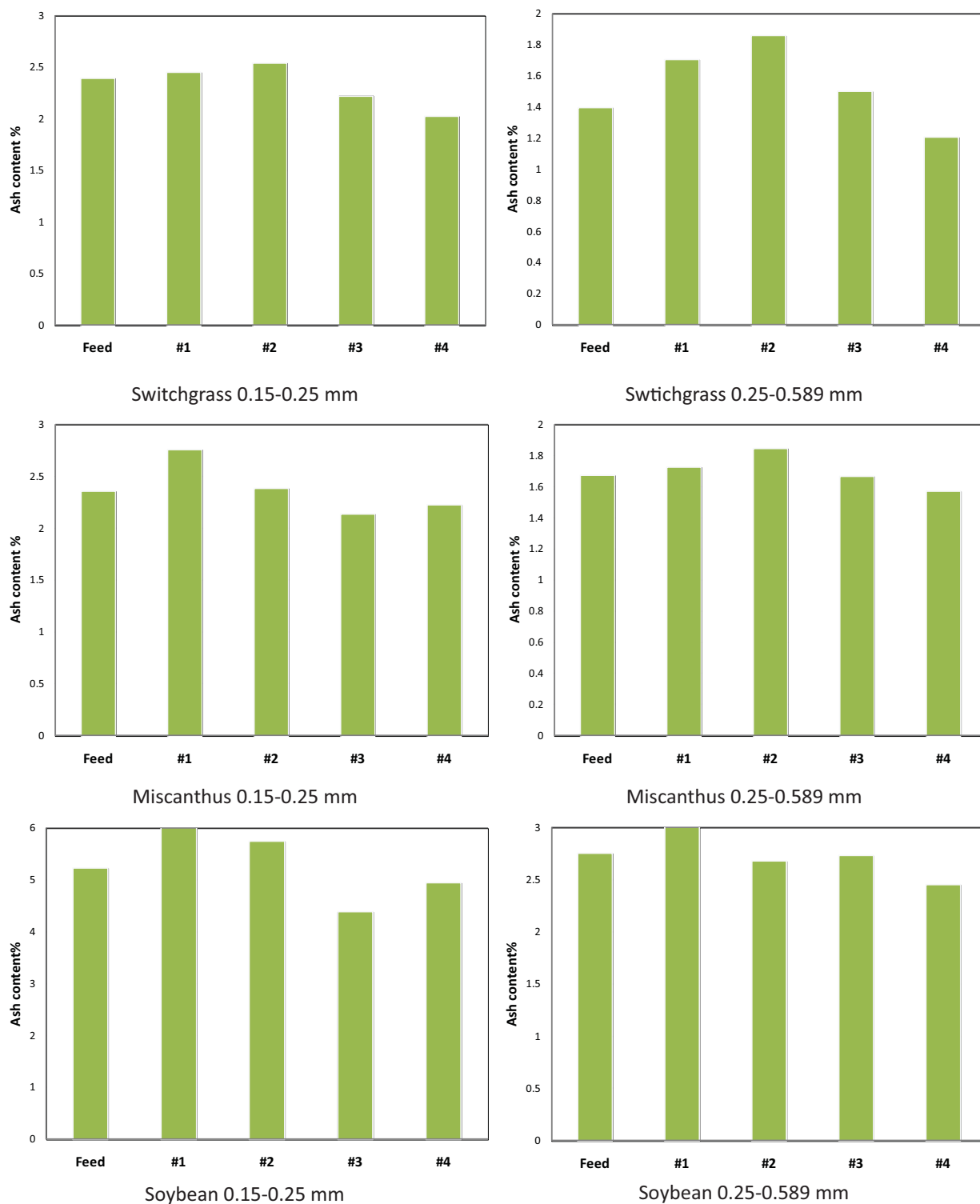
Figure 6-8 Triboelectrostatic Separation Results Based on Ash Content in Feed and Bins 1-4

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particles were allowed to fall freely between the two electrode plates. The applied voltage was kept constant at +15 and -15 kV.

It can be observed from most of the figures that low ash biomass particles were recovered at the bins closest to the negative electrode (bins 3 and 4) whereas high ash biomass particles were collected at the bins closest to the positive electrode (bins 1 and 2). This behaviour is explained by studying the electrophysical properties of silica as the major component in the biomass ash. Silica has a work function of 5.4 eV, while copper has a work function of 4.38 eV. When silica comes in contact with copper, the copper gives an electron to the silica and therefore the silica gains a negative charge. Alternatively, when copper comes in contact with carbonaceous material, which has a work function of 4.0 eV, the carbonaceous material gives up an electron to the copper and acquires a positive charge. As a result, positively charged carbonaceous particles and negatively charged silica-rich particles were attracted by the negative and positive electrodes, respectively.

Recovering high ash content particles at the bins closer to the positive electrode confirmed the fact that these particles contained more silica than those collected from the bins closer to the negative electrode. The results also showed that the ash content of particles were not significantly different from each other, nor from that of the feed. Although the charge polarity of silica and carbonaceous particles were different,

material was close to that of copper, charge exchange between these materials was very low. Therefore, carbonaceous particles obtained a small amount of positive charge when they came into contact with the copper. Once these slightly positively charged particles were introduced to the separation chamber, they were electrostatically induced by the positive and negative high voltage electrical field. As a result, these uncharged particles became polarized so that the side of the particles away from the electric field developed the same charge as the electrical field. Depending on how the charges (positive and negative) are distributed on the surface of the polarized particles, as well as the orientation of these particles while falling down between the electrodes, the particles deviated towards either the positive or negative electrodes.

This scenario explained the existence of carbonaceous particles in all of the bins and not only in bin 4. Induction of particles occurred at the entrance of the separator because the electrical field was the highest in the separator chamber due to its design; the positive and negative electrodes were only 7.5 cm apart at the top of the separator.

Table 6-6 shows the maximum ash content reduction obtained for two particle size cuts of each biomass after one separation stage, along with the percent recovery. These results once again illustrate that carbonaceous particles were positively charged relative to the silica rich particles and accordingly the low ash biomass par-

Table 6-6   % Ash content reduction of biomass

Biomass/Size (mm)	% Ash reduction	% Recovery	Bin #
Switchgrass 0.15-0.25	15.44	11.95	4
Switchgrass 0.25-0.589	13.46	27.61	4
Miscanthus 0.15-0.25	9.54	19	3
Miscanthus 0.25-0.589	6.12	10.62	4
Soybean 0.15-0.25	16.07	8.29	3
Soybean 0.25-0.589	10.85	41.97	4

poor separation of these two groups of particles was observed. One reason for the observed low efficiency of the process was the existence of no charge or slightly positively charged carbonaceous particles. Since the work function of carbonaceous

ticles were collected at the negative electrode (bins 3 and 4). At similar operating conditions, results showed that ash content reduction of biomass after one stage of separation could vary from 6%-16% depending on the biomass type and the particle size. The percent

recovery of the particles with the lowest ash content varied from 8% to 42%. Particles with the lowest ash content were observed in bin 4 for all three biomass feedstocks when the particle size was 0.25-0.589 mm. When the particle size decreased to 0.15-0.25 mm, the lowest ash content particles were found in bin 3 for miscanthus and soybean. The reason for this result has not yet been well understood. Ash content reduction was found to be higher for all the biomass with a smaller particle size. This indicates that a better separation of silica from carbonaceous particles is achieved when the biomass particle size was smaller.

Another important result was that sieving the milled biomass into different particle size fractions could affect the distribution of high/low ash content particles. **Table 6-7** shows that smaller particles have a higher ash content due to a larger fraction of silica in the particles. Silica forms the basis of the protective shell of plants which are more brittle than other parts of the plant and therefore can easily be ground to a smaller particle size. It should not be concluded, however, that size reduction increases the ash content of biomass.

Figure 6-9 Effect of various size reduction equipment on the particle size distribution of Miscanthus

2.66%, and 2.79% ash, respectively. Ultimate analysis of the various biomass obtained by X-ray Fluorescence XRF method showed that only 51.69%, 61.25%, and 13.55% of the ash in switchgrass, miscanthus, and soybean straw, respectively, is silica. Results are shown

Table 6-7   Effect of Particle Size on Ash Content

Particle size (mm)	Switchgrass	Miscanthus	Soybean
<0.106	3.91	5.66	11.49
0.106-0.15	3.70	2.48	7.90
0.15-0.25	2.40	2.12	5.23
0.25-0.589	1.59	1.73	2.75
0.589-1	0.94	N/A	2.43
Feed	2.66	1.96	3.00

The effect of various size reduction equipment on the particle size distribution of miscanthus was investigated and the results shown in **Figure 6-9**. Little difference in the size distribution pattern was observed between the size reduction equipment tested.

Biomass characteristics

Some properties expected to play a more important role in the electrostatic separation of various elements from biomass include ash mineralogy and surface segregation of elemental species. Proximate analysis of the various biomass feedstocks showed that miscanthus, switchgrass, and soybean straw contain 1.96%,

in **Table 6-3**. Calcium oxide (CaO), Magnesium oxide (MgO), and Potassium oxide (K_2O) were the next most available components in the ash. **Table 6-8** compares the work function of these components with the work function of copper. It can be seen that silica is the only component in ash with a higher work function than that of copper. This means that silica would be the only component that can acquire a net negative charge. The other components obtain positive charges, the magnitude of which depends on the work function difference between each component and copper. This data indicates that measuring the ash content of the separated samples is not enough to judge if the efficiency of silica removal was low because of the existence of other

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Table 6-8 Work function of Various Components in Biomass

Component	Work function (eV)
Copper (Cu)	4.38
Carbon (C)	4
Silica (SiO$_2$)	5.4
Calcium oxide (CaO)	1.76
Magnesium oxide (MgO)	3.1-4.3

minerals in the ash. Therefore, XRF analysis should be performed on the separated samples to quantify the silica separation.

6.2.4 Conclusions and Recommendations

The results obtained in this work showed that low ash biomass particles were recovered at the bin closest to the negative electrode, whereas high ash biomass particles were collected at the bins closest to the positive electrode. The results also showed that carbonaceous particles could be electrostatically induced by the positive and negative high voltage electrical field resulting in charge polarization of the particles. Depending on the charge distribution on the surface of the polarized particles and the orientation of these particles while falling down between the electrodes, the particles could deviate toward either the positive or negative electrode. As a result, carbonaceous particles could distribute in all of the bins, which lowers the separation efficiency. To avoid the induction of particles, two strategies are recommended in future work:

- Modifying the separator set-up by increasing the distance between the electrode plates at the top of the separator.

- Optimizing the applied voltage in order to obtain a high purity product with a high recovery value. Because the electric field intensity in the separation zone controls the extent to which positive and negative particles are defected toward the electrodes, experiments should be performed at various voltages.

Clear separation cannot occur unless silica and other mineral inclusions are physically liberated from the carbonaceous matrix. Therefore, each biomass sample should be analyzed using X-ray photoelectron spectroscopy (XPS) to determine the mineral surface composition. This analysis would help to determine the particle size required to detach silica from the carbonaceous matrix.

Results illustrated that the collected biomass after one separation stage has low purity and recovery. Therefore, two or more electrostatic stages are recommended to further improve the separation quality.

Another reason for not achieving good separation could be due to the agglomeration of fine particles. The interparticle forces responsible for agglomeration are primarily of Coulombic nature and are between negatively charged silica and positively charged carbonaceous particles. As a result, the charge on the particles is neutralized and particle clusters form. One way to partially alleviate this problem is to conduct the separation by spraying the particles through a nozzle in a dilute mode, i.e. low particle loading.

Some other recommendations to further improve the separation quality include:

- Measuring the charge density of particles after tribo-charging using an electrometer. This would help to find the most appropriate material to be used in the tribo charger.

- Investigating the effect of moisture content on the tribo-charging of particles and consequently on the separation efficiency.

6.3 Nutrient Recovery from Leachate by Reverse Osmosis

This experimental study investigated the feasibility of Reverse Osmosis to recover water from the leachate produced in the industrial leaching process described above. The concentrate stream achieved through this process is expected to be rich in nutrients such as Nitrogen (N), Phosphorous (P) and Potassium (K), which can be utilized as a liquid fertilizer.

Reverse Osmosis (RO) is a proven technology for effective water recovery and concentration of dissolved solutes. RO has been deemed as the most economical technology for ion recovery from feed water containing over 50,000 ppm of total dissolved solids (TDS). Various studies have found RO to achieve 95% rejection of total nitrogen (Bilstad, 1995), over 90% rejection of phosphate and 90-96% of potassium (Jenkins, 2003). Currently, this technology is being successfully implemented at an industrial scale for desalination of seawater and water reclamation from wastewater. Furthermore, the success of RO has generated significant interest in the area of ion recovery and active research and development of this technology is being carried out to make this process even more efficient (Lee, 2011).

6.3.1 Materials and Methods

Experimental Set-Up

This lab-scale study involved a batch crossflow filtration set-up. The Process Flow Diagram is provided in **Figure 6-10**.

The experimental set-up consisted of a glass beaker for the concentrate/feed tank. A low-pressure nylon tube was used to draw feed from the concentrate/feed tank to the diaphragm feed pump. The pump then supplied a high-pressure feed to the membrane cell through a high-pressure hose. A pressure gage was installed before the membrane cell to read the Gage Pressure of feed entering the membrane cell or Inlet Gage Pressure (PG_i).

A lab-scale CF042 crossflow cell was used as a membrane cell (see **Figure 6-11**). The CF042 crossflow cell is comprised of two components. The rectangular piece of TF (Thin Film) Composite polyamide RO membrane was placed at the base of the cell. The membrane was manufactured by KOCH Membrane Systems. The

metal membrane support consisted of a permeate carrier. The two components were then secured together by means of stainless steel studs and hand nuts. The feed entered the cell from the base of the cell into the membrane cavity where it flowed tangentially across the membrane surface.
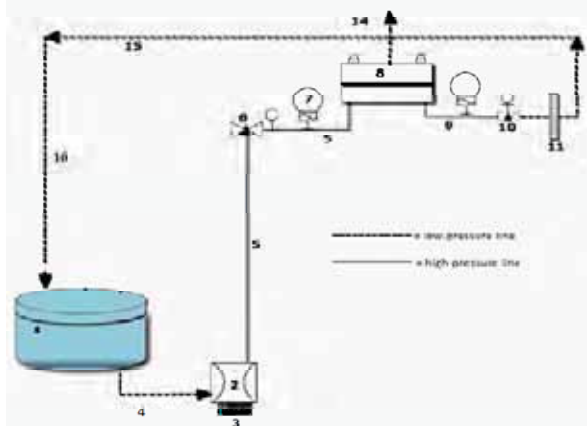
Item	Description
1	Concentrate Feed Tank
2	Diaphragm Feed Pump (Hydracell Pump)
3	Variable Flow Device (VFD)
4	Low Pressure Tube
5	High Pressure Hose, 7/16" OD, 5/16" ID, Ends 3/8", 1/4"
6	Needle Valve with 3/8" Tee for Bypass
7	Pressure Gage (0-1500 psi)
8	CF042 Cross Flow Cell (Delrin, 316 SS, PTFE, or Acrylic)
9	1/4" FNPT Rigid Tubing, assembled with Concentrate Control Valve #10
10	Concentrate Control Valve 1/4" inlet, 3/8" Outlet
11	Site Read Flowmeter/Rotameter
12	Permeate Collection Vessel
13	Digital Scale for Measuring Permeate
14	1/8" Nylon Permeate Tubing
15	3/8" Nylon Tubing
16	Low Pressure Tube

Figure 6-10   Process Flow Diagram

The portion of feed permeating through the RO membrane flowed out of the cell by means of the permeate carrier. Permeate was collected into another glass beaker which was placed on a balance to measure the weight of permeate being accumulated. The portion of the feed rejected by the membrane flowed out of the cell as a concentrate stream. The concentrate stream was recycled back to the concentrate/feed tank by means of a rigid tube. A pressure gage was installed to measure the Gage Pressure of the concentrate stream leaving the membrane cell or Outlet Gage Pressure (PG_o). The system hold-up of this set-up was 230 mL.

Figure 6-11   Sterlitech CF042 Cell

6.3.2   Procedure

A set of various biomass leachates were tested experimentally to study the effectiveness of RO for water recovery. The leachate was prepared with a water to biomass ratio of 12:1 (as described in section 6.1.2) This leachate was vacuum filtered with a 1.5 µm filter paper before running the RO trial. Miscanthus–L4 was a fourth cycled leachate. In this case, miscanthus was first leached with water by the above mentioned method to attain leachate 1. A fresh batch of miscanthus was then leached with leachate 1 to achieve leachate 2. The process was repeated until leachate 4 was achieved. This leachate 4 was then filtered with 1.5 µm filter paper before the RO trial. **Table 6-9** has

tabulated the feed sizes and various biomass feedstocks used.

Each RO Trial consisted of 3 steps. The first step involved running clean DI water through the membrane at a set of different Transmembrane Pressures (TMP). Temperature was kept at 25±3^{0}C. Time was measured to collect 1 g of permeate at each specific TMP to calculate Mass Flow Rate (m•) of permeate at that specific TMP. The flux in this step is called the clean water flux. This step determined the resistance offered by membrane material.

Table 6-9   Feed Types and Sizes

Biomass Leachate		
Feed Type	**Code**	**Feed Size (mL)**
Soybean	SB	2000
Miscanthus	MS	1000
Switchgrass	SG	2000
Miscanthus - L4	MS-L4	960

The second step involved running the specific feed (i.e. the biomass leachate). Initial pH and Electrical Conductivity (EC) was recorded. TMP throughout the run was kept at 10±3 bars. The TMP fluctuated near the end of the experiment due to formation of bubbles. An extensive explanation of this phenomenon is provided in the Conclusion and Recommendation section (Section 6.3.4). Temperature was maintained between 25±3 ^{0}C. Permeate mass after every half hour was recorded in order to calculate the Mass Flow Rate. Permeate samples were also drawn at an hourly increment. Elemental analysis of some of the permeate samples were carried out to evaluate the performance of RO for nutrient rejection. The pH and EC of each permeate sample were also recorded. After a certain time, fouling was expected in this step as particles from the feed may accumulate on the membrane surface forming a cake. Furthermore, some smaller particles may block the membrane pores. Fouling decreases the permeate flux, therefore observing the permeate flux with respect to time gave an understanding of the resistance exhibited by the membrane due to fouling. This step was run until the maximum water recovery was achieved from the feed to obtain a concentrated solution or retentate at the end. The retentate was an-

alyzed for pH and EC. Elemental analysis of the retentate was done to find the concentration of nutrients.

The third step was similar to the first step and involved running the clean DI water through the membrane at a set of various TMP. Some accumulated and trapped particles were dislodged in this process giving the estimation of irreversible fouling of the membrane.

The modified form of Darcy's law for pressure driven membrane operations was used to calculate the resistance exhibited by the membrane in each step. Some significant parameters used in the calculations are tabulated in **Table 6-10**. Transmembrane pressure (TMP) was calculated by taking the average of the Inlet and Outlet Gage Pressures. Permeate Flux (J) is the volume flowing through the membrane per unit area per unit time. Permeate Flux (J) was calculated with the help of Mass Flow Rate and was adjusted (J_o) for temperature by the following equation provided by Jenkins et al (2003):

$$J_o = J/1.03^{(T-25)}$$

Table 6-10 Significant Parameters for Calculations

Significant Parameter	Value	Units
Effective Membrane Area	42	cm^2
System Hold-up Volume	230	mL
TMP	10±3	bar
Temperature	25±3	^0C
Density of water (ρ)	0.997130	$g.cm^{-3}$
Viscosity of water (μ)	0.000891	Pa.s

6.3.3 Results and Discussion

Permeate Flux vs. Time

Permeate flux characterizes the performance of RO. The trend of permeate flux was studied during the four RO trials with a plot of Permeate Flux vs. Time shown in **Figure 6-12**. The membrane experienced fouling with time which decreased the permeate flux. Fouling however increased the % Rejection as small particles deposit inside the pores of the membranes and decrease the pore size. Furthermore, accumulation of particles on the membrane formed a layer. This layer of particles trapped the incoming particles and thus, facilitated their rejection. As can be seen in **Figure 6-12**, the general trend in four RO trials showed a sharp initial decrease in permeate flux.
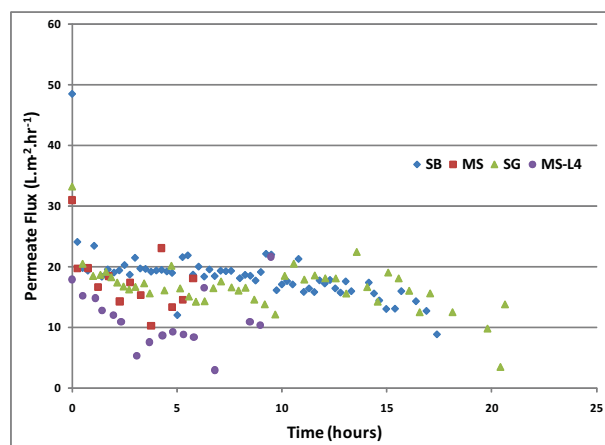
Figure 6-12   Permeate Flux vs. Time

The flux then remained steady for a certain period of time before declining again. In this experimental study, some fluctuations in TMP were observed due to limitations associated with the implemented lab equipment and more importantly, due to excessive foaming near the end of the experiment. A sudden increase in permeate flux was seen during foaming. The increase in permeate resulted in a decrease in the % Rejection of the nutrient for that period of time. The behaviour of permeate flux in each of the feed types is described below.

The vacuum filtered Soybean (SB) feed was yellowish brown in color and had a feed size of 2000 mL. The permeate flux (see **Figure 6-12**) sharply declined from 48 $L.m^{-2}.hr^{-1}$ to 20 $L.m^{-2}.hr^{-1}$ in the first half hour due to initial deposition of particles on the membrane surface. It remained steady at approximately 20 $L.m^{-2}.hr^{-1}$ for nine hours showing slight variation due to fluctuations in TMP. Permeate color within this period was a very pale yellow. After approximately 9.5 hours, the flux decreased to 16 $L.m^{-2}.hr^{-1}$, indicating additional fouling. The permeate at this time was observed to be transparent as more particles were entrapped in the cake formed on the membrane surface, thus increasing the % Rejection. The flux remained at a steady state between the 10th and 15th hour. After a run of 15 hours, the flux began to decline until the end of the experiment.

Miscanthus (MS) feed was light brown in color and had a lower feed size of 1000 mL. The permeate flux of the feed decreased from 31 $L.m^{-2}.hr^{-1}$ to 20 $L.m^{-2}.hr^{-1}$ within the first half hour, before decreasing almost linearly from 19 $L.m^{-2}.hr^{-1}$ to 13 $L.m^{-2}.hr^{-1}$ in the next five hours. Within this period however, some fluctuations were witnessed due to variation in TMP. The clarity of permeate collected during this period increased with respect to time. After six hours, the decrease in volume caused excessive foaming in the tubes. The bubbles scoured the particle build-up on the membrane surface, decreasing the % Rejection and increasing the flux.

Switchgrass (SG) leachate of volume 2000 mL began as a dark brown fluid. The flux dropped from an initial value of 33 $L.m^{-2}\ hr^{-1}$ to 20 $L.m^{-2}.hr^{-1}$ in the first half hour. The fouling increased slowly and uniformly for the next ten hours, with the flux showing a slow decreasing trend as shown in **Figure 6-12**. The filtration rate was slower as compared to SB and MS. This was, however, also instrumental in achieving more transparent permeate because of more fouling. The leachate flow was mostly smooth for the first 4.5 hours. Approaching the fifth hour TMP increased, slightly increasing the flux. The TMP was set back to 10 bars, at which point the flux slowly declined again due to accumulation of particles on the membrane. The flux was again steady between 10th and 15th hour and then declined slowly until the end of the experiment.

Miscanthus-L4 (MS-L4) has been prepared after recycling of the initial leachate three times. The elemental analysis showed MS-L4 contained approximately four times more nutrients than leachate 1, as shown in **Table 6-5**. The feed volume of 960 mL was the lowest among all the feeds. The permeate flux decreased from 18 $L.m^{-2}\ hr^{-1}$ to 15 $L.m^{-2}\ hr^{-1}$ in the first half hour, decreasing almost linearly for the next 2.5 hours showing low but uniform fouling. The flux was the lowest as compared to other feed types, which was expected due to the high nutrient content. After running for three hours, the flux reduced to 5 $L.m^{-2}\ hr^{-1}$. The transparency of permeate increased progressively during this period. However, since the feed volume was too low, bubbles started forming which slowly flushed some of the cake formed on the membrane surface and increased the flux while decreasing the % Rejection slightly. Just after six hours, the foaming increased and the agitated bubbles on the membrane's surface scraped the particles from the membrane's surface to

increase the flux to approximately 17 $L.m^{-2}\ hr^{-1}$. However, constant deposition of the particles on the membrane from the nutrient enriched feed quickly formed another layer and thus, the flux was steady once again at approximately 10 $L.m^{-2}\ hr^{-1}$ for the next two hours. After this time, bubbles started disturbing the layer on the membrane again and thus, deteriorated the % Rejection.

Percent Rejection

ICP testing for elemental analysis was done on the feed and permeate to calculate the % Rejection of various nutrients. Permeate samples after six hours were analyzed for all four feed types and the % Rejection was calculated by the following formula:

% Rejection= $(1 - C_p/C_f) \times 100$

Where: C_p= Concentration in permeate (ppm)

C_f= Concentration in feed (ppm)

The % Rejection of various nutrients of importance in the four RO trials after six hours is summarized in
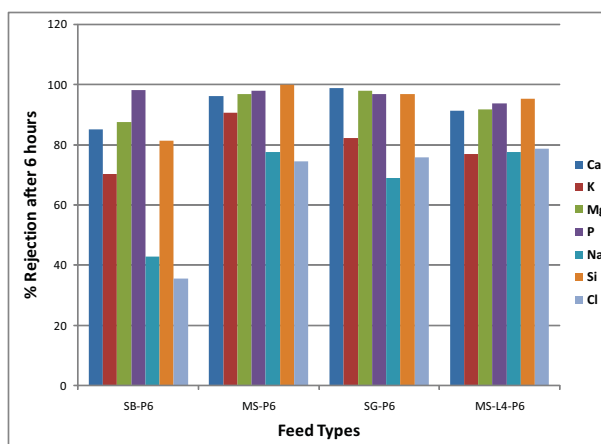
Figure 6-13   % Rejection of Nutrients for various feed types after 6 hours

Figure 6-13. Calcium (Ca), Magnesium (Mg), Phosphorous (P) and Silica (Si) showed a % Rejection between 80% and 99% in all four types of biomass feed. % Rejection for Sodium (Na) and Chlorine (Cl) was found to be between 70% and 80% in the case of MS, SG and MS-L4 while, SB after six hours showed less than 50% Rejection for Na and Cl.

Generally SB showed less % Rejection after six hours as compared to the other feed types. This is also supported by the relatively larger permeate flux values during the first ten hours as discussed previously.

These results could be due to the piece of RO membrane used for this particular run. When using flat sheet membranes, the quality of the membrane is not necessarily consistent as different portions of the sheet may have flaws and therefore can behave differently. However, after ten hours due to the formation of a particle layer on the membrane surface, SB showed decreasing flux (see **Figure 6-12**). A permeate sample for SB collected after ten hours was analyzed. Marked improvement in % Rejection was obtained in case of Na (89% Rejection at 10th hour as opposed to 43% achieved at 6th hour) and Cl (55% at 10th hour as opposed to 36% at the 6th hour) as shown in **Figure 6-14**.

Figure 6-14   % Rejection for feed types during smooth flow

MS showed a consistent trend of slowly decreasing flux in the first six hours and reasonably smooth flow during the remainder of the experiment, which can be depicted by the superior % Rejection it exhibited after six hours (see **Figure 6-13**).
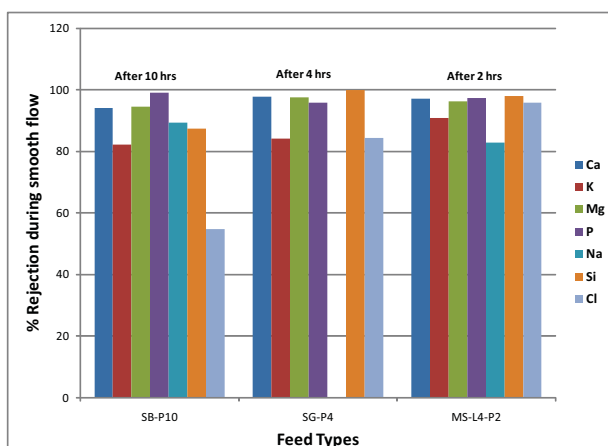
SG showed nearly undisturbed flow in the first five hours of the run. During this time, flux decreased slowly while % Rejection increased with decreasing flux. A permeate sample after four hours for SG showed notably better results especially in the case of Cl which was 84% after four hours. Due to disturbances in the flow caused by TMP fluctuations, it reduced to 76% at the sixth hour (see **Figures 6-13 and 6-14**). Na concentra-

tion has been omitted in **Figure 6-14** as it was found to be incorrect due to experimental error.

Similarly, MS-L4 showed a smooth flow during the first three hours with minimum TMP fluctuations and permeate flux was found to decrease almost linearly. As a result, a permeate sample after two hours was tested. Remarkably better results were shown, with a % Rejection above 95% for Ca, K, Mg, P, Si and Cl and 83% for Na.

Percent Water Recovery

Table 6-11 shows the % Water Recovery achieved after six hours. Generally, the water recovery at six hours was found to be between 40% and 45% for most feed types. For SG, the % Water Recovery at six hours was 35% due to the high fouling observed during the filtration. The quality of permeate for SG was found to be significantly better than the permeate samples achieved from other feed types.

A 90-95% water recovery with the lab equipment used is possible by running the RO trial for 15 to 20 hours depending upon the feed type and feed size. An inadequate membrane area of 0.0042 m^2 provided by the flat sheet membrane in the experimental set-up contributed to the longer time required for sufficient water recovery. Furthermore, excessive foaming experienced at the end of the experiment due to a continuous decrease in volume of the concentrate/feed in the crossflow filtration system limited the course of the experiment and consequently the % Water Recovery.

Table 6-11 % Water Recovery after six hours

Feed	% Water Recovery
SB-P6	43
MS-P6	46
SG-P6	36
MS-L4-P6	40

6.3.4   Conclusions and Recommendations

This experimental study found Reverse Osmosis to be a very effective technology to recover water from the biomass leachate. By removing the nutrients, the process increased the nutrient concentrations in the re-

tentate which can be utilized as a liquid fertilizer. Some fouling was exhibited in RO trials which aided the rejection of nutrients. However, excessive fouling of the membrane was not encountered even after running the apparatus for a long period of time.

The apparatus used in this study had limitations. The RO unit incorporated a flat sheet membrane instead of spiral membranes. Spiral membranes are used for industrial and pilot-plant scale processes. They are high performing and incorporate a significantly larger membrane area than the flat sheet membranes. A comprehensive discussion on spiral membranes has been provided in the literature review in Chapter 4. Furthermore, due to time constraints and insufficient membrane area (0.0042 m^2) available for filtration, the selected feed sizes were low and ranged from 1000 mL to 2000 mL, out of which 230 mL was held-up by the system. Undisturbed smooth flow was desired. However, as the volume of concentrate/feed decreased, the pump began to suck air into the tube. Suction of air resulted in foaming in the tubes and in the concentrate/feed tank, which agitated the flow of the fluid. This turbulence in the flow resulted in fluctuation of TMP. Very high TMP caused leakage in the membrane cell. On several occasions, the two fastened components of the cell nearly burst. The rigid pipe carrying the concentrate stream back to the feed did burst in two instances. Bubbles increased the shear rate on the membrane surface and disturbed the solid build-up on the surface. Excessive foaming restricted the length of the experiment and therefore were unable to run the RO trial until the desired % water recovery. Some TMP fluctuations were also observed due to derangement of feed tubing during the experiment.

The effect of foaming on the efficiency of the system was also studied. The respective permeate samples from when the flow in the system was smooth without any foaming and the permeate flux was displaying a consistent trend were also analyzed for each of the RO trials. The results showed even better % Rejection in this scenario. Hence, with better membranes, such as spiral membranes, we expect superior nutrient rejection and % water recovery. For future research, it is strongly recommended to utilize a spiral membrane module to further study and optimize the RO process implemented for the water recovery and nutrients concentration from biomass leachate.

6.4 Nutrient Recovery by Magnesium Struvite Precipitation

This experimental study has also investigated the viability of a Struvite formation process to produce Magnesium Struvite (MAP) or Potassium Magnesium Phosphate Struvite (KMP) from the biomass leachate and utilized as a slow-release solid fertilizer. A detailed literature review of this technology has been included in Chapter 4.

This technology has been effectively implemented for wastewater. Magnesium, preferably in the form of $MgCl_2$, is added to the nutrient enriched wastewater. Ammonium reacts with magnesium and phosphorous to form struvite (MAP). In the absence of ammonium, potassium reacts with magnesium and phosphorous to form potassium magnesium phosphate struvite (KMP). The struvite thus obtained is filtered and can be directly utilized as an effective fertilizer. As mentioned in Chapter 4, Ostara Nutrient Recovery Technologies Inc., a Canadian company located in Vancouver B.C., has been successfully producing commercial fertilizers through the magnesium struvite formation process from wastewater.

6.4.1 Materials and Methods

Increasing the pH is expected to facilitate formation of struvite from the dissolved magnesium, nitrogen or potassium and phosphorous in the leachate. Depending upon whether nitrogen or potassium present in the leachate, struvite formation can either be MAP or KMP.

The stoichiometry of MAP is given by:

$$Mg^{2+} + NH_4^+ + H_2PO_4^- + 6H_2O => MgNH_4PO_4.6H_2O + 2H^+$$
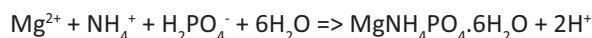
The stoichiometry of KMP is given by:

$$K^+ + Mg^{2+} + HPO_4^{2-} => KMgPO_4 + H^+$$
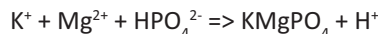
Three process methodologies were adopted to experimentally test the Magnesium Struvite process as a means to chemically precipitate N or K and P out of the leachate in order to derive a fertilizer. Process I and II have been conducted with Standards while Process III involved switchgrass leachate prepared at a ratio of 12 L/kg and immersed with agitation for one hour at room temperature. The leachate was then filtered and pressed.

For the standards used in Process I and Process II, the compounds selected for Mg, N, P and K sources were Magnesium Chloride Hexahydrate ($MgCl_2.6H_2O$), Ammonium Chloride (NH_4Cl) and Potassium Phosphate (KH_2PO_4) respectively. The mass ratio of NH_4Cl, KH_2PO_4 and $MgCl_2.6H_2O$ was taken to be 1:2.5:3.8 in one litre of water for all the samples in both Process I and II. Struvite formation requires equal molar ratios. The implemented ratio reflected the 0.1 M concentrations of N, P, Mg and K in the selected compounds. The room temperature was 20^0C in all three processes. The initial pH was 4 for the NH_4Cl, KH_2PO_4, $MgCl_2.6H_2O$ and water mixture in Process II. Flowcharts for the three processes are given in **Figure 6-15**.

nesium struvite when formed was in the form of white powder. The resulting solution was vacuum-filtered using a fine (0.7-1.5μm) filter paper. The solids were then oven dried at a temperature of 105^0C until the weight of the solids achieved was constant. The solids were analyzed for elemental analysis by SEM and the liquid was analyzed by ICP.

In Process II, Ammonium Chloride (NH_4Cl), Potassium Phosphate (KH_2PO_4) and Magnesium Chloride Hexahydrate ($MgCl_2.6H_2O$) were added in the water to form a transparent solution. The initial pH was measured to be 4. The pH was then increased by adding NaOH
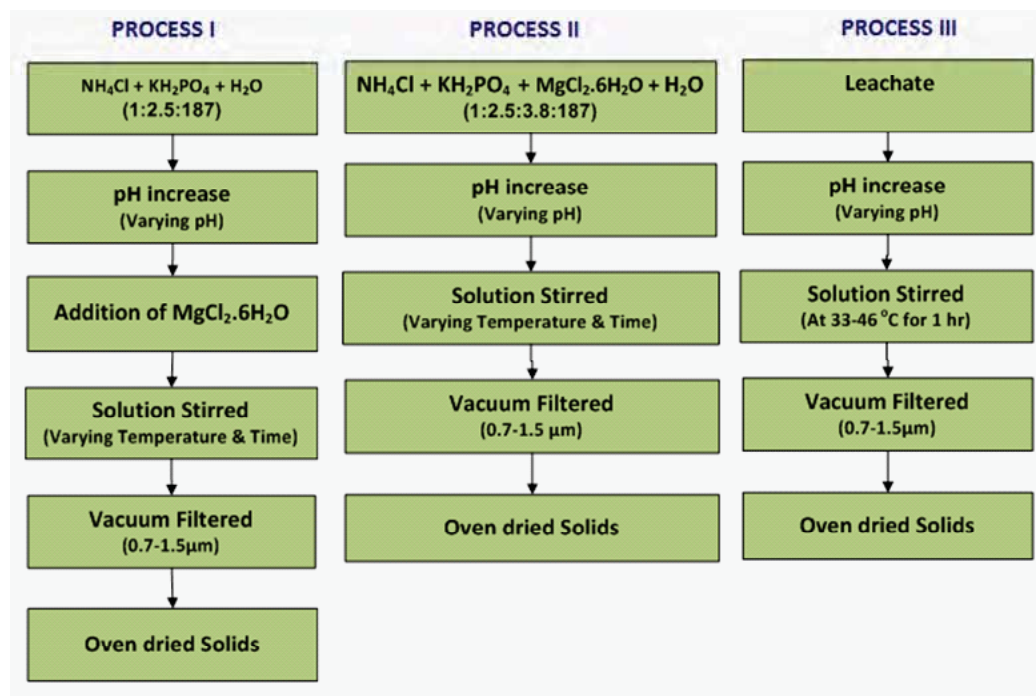

Figure 6-15   Flowcharts for Magnesium Struvite Processes in Current Work

In Process I, Ammonium Chloride (NH_4Cl) and Potassium Phosphate (KH_2PO_4) were added in water to form a clear solution. By adding 10% NaOH, the pH of the solution was then raised to the desired level (from 5.5 to 8.5) depending upon the operating condition of the sample. See **Table 6-12** for various operating conditions selected for each sample. Magnesium Chloride Hexahydrate ($MgCl_2.6H_2O$) was then added to the solution. The mixture was stirred continuously by magnetic stir bar for the required time and temperature as per the operating conditions listed in **Table 6-12**. The mag-

or maintained at its initial value depending upon the sample. The values of pH, temperature and the time stirred for each sample is given in **Table 6-12**. The solution was vacuum-filtered and oven dried.

In Process III, switchgrass leachate was pre-filtered by 0.15 μm filter paper for both Sample 12 and Sample 13. The pH was increased to 8.5 and 9.0 in Sample 12 and Sample 13 respectively. The mixture was then stirred for one hour at a temperature between 34^0C and 40^0C. The solutions were then vacuum-filtered and the solids were dried in the oven.

Table 6-12 Operating Conditions of Different Processes

		Operating Conditions			
Process - I (Standard)					
Sample ID	Feed Size (mL)	pH	Temperature (°C)	Time Stirred (hr)	Dried Solids (g/L)
Sample 4	500	8.50	20	1	6.40
Sample 5	500	8.50	33-45	1	6.76
Sample 8	250	7.00	20	1	3.76
Sample 9	250	6.50	20	1	1.68
Sample 10	250	6.00	20	1	1.88
Sample 11	250	5.50	20	1	None
Process - II (Standard)					
Sample ID	Feed Size (mL)	pH	Temperature (°C)	Time Stirred (hr)	Dried Solids (g/L)
Sample 1	1000	9.00	20	1	12.44
Sample 2	500	4.00	20	1	None
Sample 3	400	4.00	34-46	1	None
Sample 6	500	8.50	20	2	12.56
Process - III (Leachate)					
Sample ID	Feed Size (mL)	pH	Temperature (°C)	Time Stirred (hr)	Dried Solids (g/L)
Sample 12	1000	8.50	34-40	1	0.03
Sample 13	1000	9.00	34-40	1	0.10

6.4.2 Results and Discussion

Physical Analysis

In Process I, slightly more precipitate was obtained in Sample 5 as compared to Sample 4. This suggests that temperature favourably affected the precipitation of the solids to some extent. However, the difference was not found to be significant (see **Table 6-12**). Additionally, as the pH was increased, more precipitate was formed. It can be seen from **Table 6-12** that the samples with a high pH of 8.5 formed significantly more precipitate. Hence, pH was a very important consideration in achieving large amounts of precipitate. In Sample 10 at pH 6.0, no precipitate was witnessed

initially and hence the sample was not immediately filtered to separate solids. However, after a few days some solids were observed in the same solution. The sample during that period remained unstirred and was kept at room temperature. These solids were then filtered out of the solution. On drying the solids, it was found that although the pH in Sample 10 was lower (6.0) as opposed to Sample 9 (6.5), the weight of the solids achieved was slightly higher. This may be because of the longer residence time of Sample 10 as it was allowed to sit for a few days to form precipitate. Sample 11 at a pH of 5.5 however, showed no signs of precipitation even after a few days and the solution remained clear.

The addition of $MgCl_2.6H_2O$ resulted in a decrease of the overall pH of the solution. In Samples 4 and 5, the addition of $MgCl_2.6H_2O$ resulted in a reduction of pH
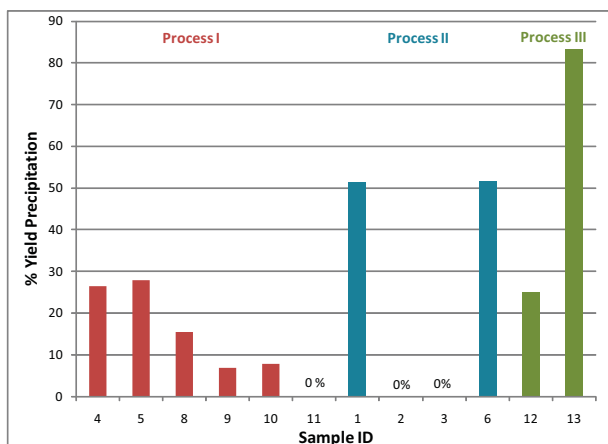
Figure 6-16   % Yield Precipitation Achieved in Process I, Process II & Process III

value from 8.5 to 5.6. Assuming that an amount of 0.1 M of Mg, N and P would form 0.1 M of Magnesium Struvite, % Yield Precipitation was calculated with respect to the predicted struvite formation (see **Figure 6-16**, Process I).

In Process II, the pH values of Sample 2 and Sample 3 were maintained at their initial value of 4. The temperature of Sample 3 was kept between 34-46^{0}C while in Sample 2, room temperature was adopted to investigate the effect of temperature on precipitation at initial pH value. No precipitate formation was witnessed in either of the samples. The solutions remained transparent even after few days. In Sample 6 at a pH of 8.5 however, a significant amount of precipitate was achieved when the sample was stirred for two hours at room temperature. Similarly, a large amount of precipitation was also achieved in Sample 1 with a high pH of 9 when the sample was stirred for one hour at room temperature. However, the amount was slightly less than the amount achieved in Sample 6, most likely due to the shorter residence time. % Yield Precipitation was calculated with the same method as implemented for Process I. See **Figure 6-16** for the % Yield Precipitation of Process II.

As can be seen by **Table 6-12** and **Figure 6-16**, Process II yielded more (almost double) precipitation than Process I for similar conditions. The reason for this is

the overall pH of $MgCl_2.6H_2O$, NH_4Cl and KH_2PO_4 solution was higher in Process II (8.5) than in Process I where it reduced from 8.5 to 5.6 due to the addition of $MgCl_2.6H_2O$ in the NH_4Cl and KH_2PO_4 solution.

In Process III, switchgrass leachate was tested to form struvite. Both the leachate samples, Sample 12 and Sample 13 yielded very small amounts of precipitate which encrusted the surface of the filter paper upon drying (see **Table 6-12** for the weight of dried precipitates obtained). The compositional analysis of untreated Switchgrass biomass (**Table 6-3**) showed the amount of P_2O_5 to be equal to 0.117 wt. %. The molar concentration of phosphorous (P) (0.00165 mol) in 100 g of untreated switchgrass was calculated to be lower than nitrogen (N) (0.02 mol), magnesium (Mg) (0.0045 mol) and potassium (K) (0.003 mol). The elemental analysis of leachate showed the concentration of P to be equal to 0.0152 g/L which is also lower than K (0.0716 g/L) and Mg (0.0305 g/L). The concentration of N was not available. The % Yield Precipitation was thus calculated assuming that the amount of P was lowest in the leachate based on the amounts of Mg, P, N, and K found in untreated switchgrass. Since struvite formation requires equal molar ratios, P was considered to be the limiting factor. Since nitrogen present in the biomass was greater than the amount of potassium, the formation of MAP over KMP was predicted. The maximum amount of MAP formed was calculated with respect to molar ratio of P which was calculated to be 4.91×10^{-4} mol/L from the concentration of P (0.0152 g/L) obtained from the elemental analysis of leachate. The molecular weight of MAP is 242.26 g/mol, therefore the predicted maximum struvite was calculated to be 0.12 g/L. **Figure 6-16**, Process III gives the % Yield Precipitation produced from the switchgrass leachate. The % Yield Precipitation showed good precipitation (83%) for Sample 13 at pH of 9. The amount of nutrients (N, P, Mg and K) available in biomass is very low. Furthermore, with the leaching process not achieving 100% removal of these nutrients, the amount of nutrients available in the leachate to form significant amounts of precipitate is insufficient. Therefore, although the process is efficient, the amount of nutrients available in the leachate is insufficient to form adequate amounts of MAP.

SEM/EDX Analysis of Precipitations

SEM/EDX analysis was conducted on dried solids from Process I and II to determine the wt. % of N, Mg, P and

K. Due to very low quantity of precipitates obtained from Process III, SEM/EDX analysis of the precipitates achieved from the leachate could not be completed.

**Figure 6-17** shows the wt. % of N, Mg, P and K obtained through SEM/EDX Analysis of the samples obtained from Process I. From the results it can be deduced that
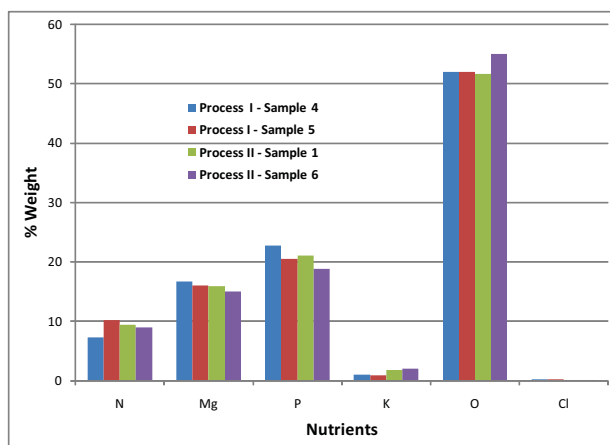
Figure 6-17   N, Mg, P and K in Precipitate achieved from Process I and Process II

the struvite produced was MAP as a very low quantity of K can be seen in the precipitate. An ICP analysis of the filtered solution further revealed that 65% of the K remained in the liquid, thus confirming the MAP formation. This proves that a solution with equal molar amounts of N and K is more liable to form MAP with Mg and P at increased pH rather than KMP.
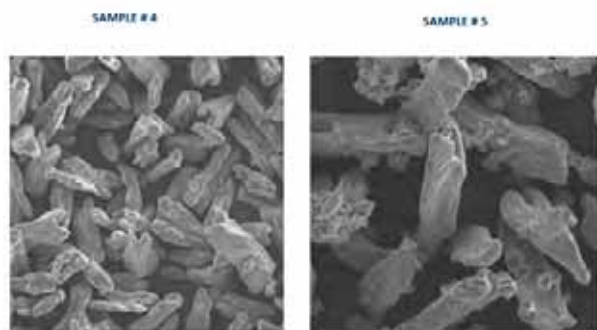
Figure 6-18   Process I - SEM Image of Sample 4 & Sample 5

In Process I, Sample 4 was run at room temperature while Sample 5 was run at a temperature of 33-45^{0}C (see **Table 6-12**). The results of both these samples
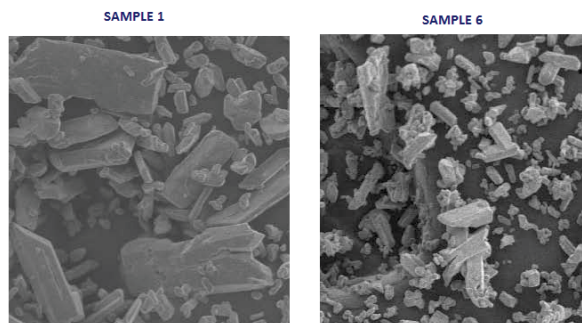
Figure 6-19   Process II - SEM Image of Sample 1 & Sample 6

indicate that the wt. % composition of the formed precipitates did not vary significantly with an increase in temperature. An image of Sample 4 and Sample 5 taken using the SEM is shown in **Figure 6-18**.

The MAP produced in Process I, was found to have approximately 10% nitrogen, 20% phosphorus and 16% magnesium (by weight). A significant portion (50%) of the precipitate was found to be composed of oxygen. Some trace amounts of chlorine (0.2 wt. %) was also found. In Process II, Sample 1 was prepared at pH 9 and stirred at room temperature for one hour while Sample 6 was prepared at pH of 8.5 and stirred at room temperature for two hours. The amount of precipitate obtained from Process II was almost twice of that obtained from Process I. However, the wt. % composition of the two precipitates was found to be similar as can be seen from **Figure 6-17**.

The precipitate produced was MAP as very low K content by weight was found in the precipitate. Furthermore, the struvite was comprised of approximately 9% nitrogen, 20% phosphorous and 15% magnesium (by weight). Oxygen (O) accounted for 50-55 % of the total weight, while the amount of chlorine (Cl) was negligible (0.1% by weight). An image of Sample 1 and Sample 6 taken by SEM is shown in **Figure 6-19**.

6.4.3   *Conclusions and Recommendations*

This experimental study found the Magnesium Struvite formation process to be an inadequate method to precipitate N and P from the first cycle leachate due to low amounts of nutrients available in the biomass for this process. The amount of precipitate produced with Switchgrass leachate was too low to perform a SEM/EDX analysis to investigate the % wt composition. Depending upon the nutrient concentration of the

leachate, the addition of magnesium or phosphorous may be a requirement for struvite formation, which translates into additional costs. Another concern is that only P, Mg, N and/or K can be retrieved through this process, leaving the other nutrients remaining in solution. In most cases, MAP would be formed prior to KMP, as struvite is more readily formed with N than with K.

Although the Magnesium Struvite process showed inferior results with the first cycle leachate due to low nutrient content, the elemental analysis presented in **Table 6-5** showed that the fourth-cycled leachate contained over four times more nutrients than the leachate obtained after the first cycle. Hence, the Magnesium Struvite process may produce more favourable results with a multi-cycle leachate process that would lead to more nutrients available for struvite formation. Further investigation is recommended to test a nutrient enriched multi-cycle leachate at a high pH of 9.5 to 10.5 in order to evaluate the feasibility of this process. As needed, the addition of Mg in the form of $Mg(OH)_2$ will facilitate the increase of pH to a desired level while achieving the required Mg concentration. This technology can also be applied in conjunction with the RO process to recover MAP as a slow release fertilizer from the retentate achieved through the RO process.

Chapter 7
Conclusions and Recommendations

It is widely accepted among researchers and experts in the scientific community that Greenhouse Gas (GHG) emissions resulting from the use of fossil fuels by humans is having negative and detrimental effects on our environment. Many jurisdictions, and countries around the world have adopted various regulations and measures to promote the use of alternative energy as one of several approaches to reducing GHG emissions. In Ontario, the Provincial government has passed legislation to cease the use of coal in power generation by the end of 2014. The Ontario Power Generation (OPG) currently has four coal-powered thermal generation stations with a total capacity of 4227MW.

There is a potential for substituting a significant portion of the current coal capacity with agricultural biomass in the form of energy crops and crop residue produced in Ontario. Furthermore, recent developments in commercialization of biomass processing technologies related to the production of second generation ethanol (cellulosic ethanol), biodiesel, bio-oil (pyrolysis/gasification) and other industrial applications of biomass provide additional opportunities for production of combustion fuels as a co-product of these processes. Many of these technologies aim to use similar agricultural residues or purpose grown energy crops as those under consideration for combustion. Given the large area of arable land and agricultural production capacity in Ontario, the emerging biofuel markets and bio-based economic sector translate into a great opportunity for the agricultural community in Ontario and Canada.

Biomass, especially in the form of agricultural residues in its raw form is not an ideal fuel for thermal conversion processes (i.e. direct combustion, co-firing, gasification, or pyrolysis). This report examined various processing technologies that could be employed to improve the combustion properties of agricultural based biomass. Detailed description of a number of potential processes were provided. An assessment was made on the technical feasibility of employing the technologies to:

- Produce a higher quality combustion fuel from biomass through the extraction of undesirable elements such as: Alkali metals, Alkaline earth metals, Cl and Si prior to densification;

- Recover and market the extracted Si; and

- Recover plant nutrients, most importantly: Nitrogen (N), Phosphorus (P), and Potassium (K), from the biomass, and process into a suitable fertilizer.

In this chapter the results of this investigation are summarized, conclusions are detailed and recommendation are made on a section by section basis.

7.1.1 Biomass Nutrients

There are three categories of nutrients found in plants, which are generally divided by the concentration of the nutrients in the plant. Primary Macronutrients consisting of Nitrogen (N), Phosphorous (P), and Potassium (K) are the most prevalent nutrients found in most plants. Secondary Macronutrients consisting of Calcium (Ca), Magnesium (Mg) and Sulphur (S) are also found in large quantities in biomass, however they are not as essential to plant growth as the primary. Silicon (Si) is also considered as a Macronutrient due to the relatively large quantities of it found in plants. Silicon is primarily found as insoluble amorphous silica and provides structure to plants. Micronutrients consisting of Chlorine (Cl), Boron (B), Copper (Cu), Iron (Fe), Manganese (Mn), Molybdenum (Mo), Zinc (Zn) and Sodium (Na). Micronutrients also have important functions in plants however they are required in much lower quantities than the macronutrients listed.

7.1.2   Effects of Nutrients on Combustion

The nutrients in biomass have a number of negative impacts on the combustion process including:

Formation of deposits: Alkali metals (predominately K and Na in biomass) and alkaline earth metals (predominately Mg and Ca in biomass) cause rapid formation of deposits. These deposits are in the form of chlorides, sulphates, carbonates and complex silicates. Formation of deposits negatively impacts the combustion process by: i) Slowing down the rate of heat transfer; ii) Bridging across tube bundles and causing an increase in combustion side pressure drop; iii) Accelerating corrosion of tube metal; and iv) reducing plant efficiency and capacity.

Agglomeration of bed media: Alkali metals form a eutectic mixture of silicates that have half the melting temperature of silica causing melt-induced agglomera-

tion.

Formation of slags: Clinkers (slags) are a specific form of deposit formation occurring when Potassium (K) and Silica (SiO_2) react to produce heavily sintered and fused glassy deposits. Formation of these slags in the furnace and on the grates can hinder fuel feeding, combustion, ash removal and ash handling. The quantity of volatile alkali (K and Na) is a good indicator for predicting whether fouling or slagging will occur in a boiler. If the quantity of volatile alkali is greater than 0.34kg/GJ of energy produced by the biomass, fouling and/or slagging is almost certain to occur. Another good indicator for all deposit formation is the ash fusion temperature of the fuel.

Fouling: When deposit formation occurs on heat transfer surfaces it is known as fouling. The fouling of heat exchanges increase resistance to fluid flow resulting in higher pressure drop and reduced heat transfer efficiency.

Pollution: Nitrogen, Sulphur (S) and Chlorine (Cl) contribute to smog, and acid rain and having negative impact on human health and air quality.

Corrosion and metal wastage: Cl and S, also contribute to corrosion and metal wastage and are particularly a cause for concern in the heat exchangers.

The litany of negative impacts associated with the nutrient content of biomass is the primary technical limitation to the use of agricultural residue and energy crops as fuels in combustion. These forms of biomass in particular have higher average concentrations of nutrients when compared with wood-based sources of biomass.

7.1.3 Sources of Agricultural Biomass

Energy Crops: These plants are purpose grown to produce some form of energy. In Ontario, miscanthus, switchgrass, poplar and willow are the four species that have attracted the most interest, and are deemed as most suitable for large-scale production. Miscanthus is currently grown as a fuel crop in Europe and other regions of the world. The concentration of the various nutrients in all forms of agricultural products is highly variable and is a function of location, climate, soil type, soil quality, and agricultural practices. As such it is very difficult to compare nutrient contents of the various forms based on the crop species. Some researchers have reported higher levels of silica in miscanthus where ash sintering tendencies were ob-

served at temperatures as low as 600°C.

Switchgrass has also been reported to have good yields, however most studies show lower production in terms of DMT/ha for switchgrass than miscanthus. Studies have reported higher ash content found in switchgrass that is grown in clay soils versus sandy soils. Willow and poplar are short rotation coppice (SRC) that are harvested every three years. In general, the nutrient contents in these crops is lower than the herbaceous grasses. The drawback to these crops is the higher production costs ($/kg) associated with SRC establishment and harvesting when compared to herbaceous grasses.

Agricultural Residues: The after-harvest residue of various forms of crops currently left behind in the field are broadly referred to as residues. In comparison with energy crops, many of the agricultural residue under consideration have higher nutrient contents and thus poorer combustion properties. Typical agricultural residues such as corn stover, soybean stover, wheat straw, and barley have higher ash content, chlorine, potassium, magnesium, nitrogen, sulphur, calcium, and silica contents that would be expected in energy crops.

7.2.1 Field Leaching

Leaching is an extraction process by which material is removed from a solid by means of dissolving them away. Field leaching refers to natural leaching of plant material remaining in or on the ground over winter from a combination of rain, dew, mist and fog. Field leaching can remove several nutrients that would improve the fuel quality of the biomass (reported values of up to 92% reduction in chlorine, 91% sodium, 82% potassium and 78% phosphorous).

Despite its effectiveness, field leaching is not recommended as a means of improving fuel quality for combustion processes at an industrial scale. There is no practical control of the process due to weather variability and changes in conditions, leading to inconsistency in the quality of the final biomass fuel. The unpredictable nature of the weather cannot guarantee a steady supply of feedstock for any given year. Other disadvantages include biomass yield losses, possible contamination, and degradation of fuel quality due to losses in organic matter. As a result, it is recommended that a pre-treatment process be employed as a part of the pelletization or torrefaction process to remove nutrients and produce a consistent and controllable fuel.

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7.2.2 Industrial Leaching

Industrial leaching refers to the extraction of nutrients and other components using an aqueous solution in a reactor under controlled conditions and time. This method of nutrient removal is recommended for an industrial scale process as it has the technical advantages of controllability resulting in consistent product quality, as well as decreased reaction times and decreased chance of contamination or loss of material in comparison with field leaching.

Several methods of industrial leaching have been reported in literature, including immersion leaching with agitation, immersion leaching without agitation and spraying/pouring of water. Immersion leaching with agitation is recommended as it consistently produces the most efficient removal of nutrients when compared to other methods. Specifically, a press-leach-press method of sufficiently milled biomass, involving a mechanical dewatering of the biomass both before and after an immersion leaching process with agitation step was found to remove significant portions of nutrients (up to ~100% of chlorine, 91% of potassium, 86% of sulphur, 61% magnesium and 57% nitrogen). Each step in the process was responsible for a portion of the nutrients removed.

7.2.3 Drip Irrigation

In this process biomass is placed in a packed bed column consisting of a drip irrigation system and filter to which water and bacteria is added. Periodically the leachate is recirculated to the irrigation system, after which the leachate is removed and placed in a second container where it is concentrated by heating to produce a liquid fertilizer. The process results in the decomposition of the biomass by the bacteria and is not suitable for this application.

7.2.4 Steam Distillation

In this process the biomass is pressed (hot or cold), followed by steam distillation and centrifuge to separate the liquid fertilizer solution containing various nutrients. The process is currently industrially applied to produce liquid fertilizer from pine needles. The process suitability is undetermined for agricultural residues and energy crops commonly considered for combustion fuel, and further experimentation is therefore required.

7.2.5 Technical Gaps in Reported Literature

There are several technical gaps in current literature concerning industrial leaching techniques. The high water to solid ratios used in many reported studies are not scalable to throughputs common for large industrial sized units. There is very little to no data reported for pilot or industrial scale projects, scale-up and modelling research. Integration of an industrial leaching process with other extraction and recovery processes has been limited to a couple of studies examining the recovery of nutrients and water through a reverse osmosis process with no reported processes combining leaching with silica extraction.

For leaching processes that include agitation, little research into process optimization has been conducted to potentially reduce process residence times. Finally, there is very little economic data reported for an industrial-scale leaching process.

7.3.1 Extraction of Biomass Silica

Plants contain silicon in three basic forms, with more than 90% in the form of insoluble amorphous silica (SiO_2). Silica is the largest mineral component of perennial grasses and provides structure to plants. It contributes to a number of problems associated with biomass combustion, including the formation of deposits, slags and a high ash content.

Silica extraction is therefore important as it can improve the fuel quality of biomass, as well as provide a revenue stream to make the overall process economically favourable. There are a wide range of industrial applications for silicon, and current market prices for high purity silicon are around $2500 USD per metric ton.

7.3.2 Pulping Processes for Extraction of Silica

Although silica is not soluble in water it is soluble in basic solutions thus one possible method for silica removal is the use of chemical pulping processes. Pulping processes for the removal of silica can be divided into two main categories: chemical pulping and mechanical pulping. Chemical pulping, heavily used in the pulp and paper industry, involves the use of basic solutions (NaOH and Na_2S for the Kraft process and various sulfites and bisulfites for the Sulfite Process) to solubilize the lignin and mineral contents (including silica) into a liquor. Mechanical pulping involves the use of stones or metal to grind material to produce a

pulp. Mechanical pulping on its own cannot be used for Silica extraction given that thee are no means of separating the silica from the pulp. Chemical pulping on its own is also not suitable because it results in the dissolution of a significant percentage of the lignin in the biomass thus reducing the heating value of the feedstock.

7.3.3   Chemi-mechanical Desilication of Non-Wood Plants

US patent 7,364,640 provides a promising chemi-mechanical desilication process similar in essence to the pulping process. The process combines the attributes of both chemical and mechanical pulping and is the most promising pulping process for this application. The low operating temperatures and mild alkalinity required are its main advantages, however further investigation is required into the technical and economic feasibility as a pretreatment process. The process involves the treatment of raw material with a weak basic solution to dissolve and remove a portion of the silica, followed by a mechanical liberation of the remaining silica found in the epidermis and nodal material. The soluble silica is pH adjusted to form a precipitate, with it and the suspended solids separated from the solution using a hydrocyclone.

7.3.4   Strong Acid Hydrolysis of Cellulosic & Hemicellulosic Material

US Patent 5,597,714 described a concentrated acid hydrolysis process to hydrolyze cellulose and hemicellulose from biomass for the purpose of recovering sugars. In the process, a silica-rich biomass feedstock was acid hydrolyzed using sulphuric acid and filter pressed to obtain a liquid fraction containing the sugars a solid cake containing lignin and silica. The silica is extracted using a dilute base solution, with the resulting liquid treated with acid to produce a precipitate than can be treated to produce an essentially pure silica gel. The process is not considered more economically and technically viable for fuel production alone.

7.3.5   Ultrafiltration of Black Liquor

Ultrafilitration (UF) is a cross-flow separation process for the removal of high molecular weight substances, colloidal material, and organic and inorganic polymeric molecules. The liquid stream flows tangentially along the membrane surface producing two streams, the permeate and retentate. The UF membrane acts as a barrier to fractionate particles according to their mo-

lecular weight.

The majority of ultrafiltration methods described in literature (including diafiltration) dealt with the separation of lignin from black liquor, with various amounts of lignin being retained in the membrane while other materials (including silica) would pass through. Ultrafilitration is a potential method to separate dissolved silica from lignin if a base extraction of silica is used as opposed to an electrostatic separation method.

7.3.6 Sodium Carbonate - Lime Method

US Patent Application No. US 2006/0225852 A1 describes a method for removing silica from cellulosic materials from non-wood biomass with a high silica content. The biomass is first cut into pieces between 10 and 30 mm and screened to reduce the content of silica by 50%. The shredded biomass is then moistened and preheated with steam, allowing for the biomass to be impregnated with a dilute solution of sodium carbonate to leach silica from the biomass. The resulting silica-rich liquor is filtered and causticized with calcium oxide to precipitate calcium carbonate enriched with silica. Further investigation into the technical and economic merits of the process are recommended.

7.3.7 Electrostatic Separation of Silica

Electrostatic separation involves the imparting of a positive or negative charge to particles to separate various constituents based on their work function. Three mechanisms for impacting an electrostatic charge onto particles were researched (Corona, Induction and Tribo-charging), with tribo-charging showing the most promise for silica extraction from biomass.

In the triboelectrostatic separation technique, particles with higher affinity for electrons or higher work function gains electron and therefore charges negatively. The material with low affinity for electrons or low work function loses electrons and therefore charges positively. A key factor for this separation technique is to give opposite charge to the components needed to be separated. Hence, a material of work function value intermediate to the work function values of two components should be chosen as the contact material.

Coal beneficiation was identified as the reported process most similar to the proposed silica extraction form biomass process. In coal beneficiation, inorganic constituents of coal (ash forming content and minerals) are separated from the organic components of

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coal that provide heating value. The removal of ash producing inorganic constituents of biomass, in particular silica (which does not readily dissolve in water) has similar technical challenges as coal beneficiation. Much like removal of nutrients from biomass, the purpose for coal beneficiation is to produce a higher quality fuel for combustion out of low quality coal. Electrostatic separation has been shown to work in coal beneficiation, and thus may also be applicable to removing silica from biomass.

7.3.8 Technical Gaps in Reported Literature

There is no reported data in literature on electrostatic separation that uses a biomass feedstock, with the closest reported application involving the separation of silica from the ash of rice hulls. In terms of other processes reported in literature, coal beneficiation is a close approximation of the proposed process however, data on this process is also limited and the majority of the data was obtained through direct communication with an expert in the field (John Stencel). As a result, there are large gaps in the electrostatic separation of silica from biomass that require further investigation.

7.4.1 Methods for Nutrient Recovery

The significance of being able to recover and recycle nutrients is both environmental and economical. The potential reduction of soil nutrients by the removal of agricultural residue from the field has been a cause for concern within the farming community. The three main nutrients of concern are: Nitrogen (N), Phosphorous (P), and Potassium (K). However other nutrients such as Magnesium (Mg), Sodium (Na), Sulphur (S) and Calcium (Ca) also play a role.

The most suitable processing technologies for nutrient recovery from water-based solutions (after nutrient extraction using leaching) are through membrane separation (using reverse osmosis) and chemical precipitation facilitated by struvite formation.

7.4.2 Economics of Fertilizer Usage

Canadian farmers spend approximately $2 billion per year on fertilizers, representing about 10% of total operating expenses. Farmers in Ontario spend over $300 million a year on fertilizers consuming approximately 740,000 tonnes of fertilizers. As a result, there is a significant need to recover the nutrients from the biomass material to offset the total operating costs on farm.

7.4.3 Nutrient Recovery by Reverse Osmosis

Reverse osmosis is the recommended method of nutrient recovery compared to chemical precipitation through struvite based on technical and economic feasibility. Reverse osmosis is a membrane-based filtration process used to separate dissolved solutes from a solution. The RO process is well established and has been applied to nutrient recovery in wastewater, heavy metal separation from wastewater and desalination of seawater. Reported data on nutrient recovery from biomass leachate has been limited, with 90% rejection of nutrient ions and a 90% permeate recovery.

7.4.4 Nutrient Recovery by Chemical Precipitation

Ammonium, magnesium, and phosphorus (along with potassium in nitrogen is not present) can be recovered from a solution by the chemical precipitation of struvite. Struvite has a low solubility constant (pKs), allowing for its insoluble form to be easily formed and separated from the water phase. The struvite can be sold as a slow-release solid fertilizer, and has been developed commercially with a nutrient-rich wastewater as a feedstock. The leachate from the nutrient extraction process does not have a high enough concentration of nutrients to make this process economically viable.

7.4.5 Technical Gaps in Reported Literature

While reverse osmosis is the most widely reported and used process examined in this report, there are only a few studies available in literature on the application of nutrient recovery from biomass. There is a lot of economic, scale-up and optimization data using reverse osmosis for other applications (i.e. desalination) that can be confidently transferred to nutrient recovery from biomass leachate.

Specific technical gaps that still need to be addressed include the solute retention time of nutrients in biomass leachate, the presence of nutrients in the permeate and retentate, and membrane fouling behaviour during the filtration of leachate. Furthermore, there is no optimization studies on the effects of operating conditions such as TMP, pH, temperature and membrane material on the recovery of nutrients. As a result it is important for further lab-scale research into the recovery of nutrients from biomass leachate to be conducted to reduce the specific gaps in this application.

7.5.1 Published Economic Data on Biomass Leaching

The economic evaluation of nutrient recovery from biomass through an industrial leaching process has been limited to data provided by a dissertation published by Bakker (2000). For a 135 metric tons/day process, capital costs of $750,805 and an incremental cost of $17.88/ton were determined. The evaluation concluded that the process was not viable, but several factors require revisions to current conditions. These include a higher conversion efficiency of the plant, a higher selling price for electricity, and the added revenue from the removed nutrients as a fertilizer.

7.5.2 Published Economic Data on Triboelectrostatic Separation of Silica

There has been no single published data on the technical or economic evaluation of the use of electrostatic separation technologies for the extraction of silica from biomass. For an triboelectrostatic separator used for coal beneficiation, a 2 tonne/hr standalone system had estimated capital costs of $167,400 USD and a marginal cost of $3/tonne USD.

In direct communiqués between CENNATEK researchers and Dr. John Stencel, data was collected on industrial scale electrostatic separation processes. Dr. Stencel is the current president of Tribo Flow Separations (TFS) an American based company that sells, manufactures, and installs turn-key, industrial scale triboelectric processing plants based on Dr. Stencel's patented technology. According to Dr. Stencel a 100,000 ton per year plant would have operating costs ranging from $12-$16/tonne (USD), with the cost not taking into account the cost of size reduction of the feedstock. The capital cost for a 200,000 tonne/yr plant would be about $1.2 Million (USD).

7.5.3 Published Economic Data on Reverse Osmosis Recovery

There is only one published economic evaluation (uncovered through this investigation) on the use of Reverse Osmosis (RO) in the recovery of nutrients from biomass leachate. The marginal costs for a facility handling 50,000 tonne/year of biomass and generating 1,900 m^3/day of leachate was estimated at $0.671/$m^3$ (USD) of leachate. Marginal cost of $0.719/$m^3$ (USD) leachate was estimated for a facility processing approximately 25,000 tonne/yr of biomass.

In additions to this study, there is a large body of eco-

nomic data on the use of Reverse Osmosis in desalination. The capital cost of membrane modules for reverse osmosis depends on the plant capacity and varies between $500 to $1000 per module with production rates of 50-100 m^3/day per module. The marginal cost of these RO processes depends on the capacity, and range from $0.48-$2.40/m^3 USD.

7.5.4 Published Economic Data on Magnesium Struvite Recovery

There were three studies that reported economic data on struvite formations, with two looking at applying struvite formation to anaerobic digestion and one from piggery wastewater. In the first two studies, phosphate and magnesium was added to the available ammonia in the wastewater to form the magnesium struvite. The reported cost was equivalent to $0.026/kg MAP - $0.57/kg MAP, respectively. The most significant contributor to the marginal cost was the addition of phosphate. In the third study, the marginal cost associated with the process was between $10.3/$m^3$ and $4.9/$m^3$ of wastewater depending on the source of Magnesium and Phosphate used, and did not take into account the cost of manpower.

The high cost associated with this process in comparison with reverse osmosis makes it a less attractive option for this project. Furthermore, early lab results conducted by CENNATEK on leachate samples indicate that the leachate produced does not have a sufficiently high enough nutrient content to effectively apply this process. Based on these two reasons Magnesium Struvite was not considered in the economic evaluation of the process conducted by CENNATEK, the details of which are provided in the subsequent sections of this chapter.

7.5.5 Economic Evaluation of Pretreatment Processes

An economic evaluation of the biomass pretreatment process included the following components:

- Receiving,
- Size reduction,
- Leaching (water soluble nutrient removal),
- Reverse osmosis (nutrient recovery),
- Mechanical dewatering,
- Thermal drying,
- Electrostatic separation (silica extraction),
- Combined heat and power (CHP) system,
- Silica purification, and
- Pelletization.

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The main sources of revenue generation include:

- Biomass pellets,
- Purified silica,
- Liquid fertilizer
- Electricity from the CHP, and
- Calcium carbonate from silica purification

Based on the assumptions and data provided in Section 5.5, an economic evaluation of a 200,000 DMT/year production facility with a 10 year operating life was conducted. Total capital costs of $48,144,000 and total marginal costs of $151.11 USD/tonne were determined.

Twenty-one different scenarios were investigated using a financial model developed in this study. The model assumed:

- Ten year operating life for the plant;

- NPV calculated at 12% discount rate;

- Annual inflation rate of 3% on all sales, costs of feedstock and labour;

- Annual inflation rate of 2% assumed on all other operating costs; and

- Sustaining capital cost begins in year 5, increasing from 2% of the capital cost to 5% in years 5, 6, 7 and 8 and continuing at 5% until year 10.

The model was used to calculate revenues, operating costs, capital costs, EBITDA (Earnings Before Interest, Taxes, Depreciation and Amortization), internal rate of return (IRR) and net present value (NPV) for the twenty-one scenarios.

Based on the financial models, assuming a feedstock cost of $100/DMT it was determined that a pellet sale price of $130/DMT would provide the appropriate IRR and NPV to be economically sustainable. The cost of electricity generation would be $84.31/MWh at a pellet feedstock price of $130/DMT. This is much lower cost than wind or solar energy which are currently the most widely deployed alternative energy technologies in Ontario.

Given that currently there are no economic costs associated with GHG emissions in Canada, and no cap and trade program for carbon, the cost of electricity generation by fossil fuels are still significantly lower than green energy. Natural gas is deemed to be the most competitive fossil fuel considered as an alternative to coal. Based on current spot market prices the cost of electricity generation by natural gas was calculated to be $51.57/MWh, which is considerably lower than the $84.31/MWh calculated for biomass pellets in this study.

The most significant financial data generated by this study is that the inclusion of the nutrient recovery processes described lower the final cost of pellets, by providing alternate revenue streams. If biomass was processed by a stand-alone pelletization plant a minimum selling price of roughly $150/DMT is required to make the process attractive to investment.

Thus, the nutrient removal and recovery process has an overall positive impact on fuel quality, soil quality, and the economics of biomass combustion.

7.6.1 Water Soluble Nutrient Extraction Experiments

Lab-scale leaching experiments based on immersion and pouring/spraying methods reported in literature were conducted, with the following conclusions:

- Immersion leaching with agitation is a more effective leaching process when compared to immersion leaching without agitation and pouring/spraying of water.

- Chlorine, potassium, phosphorous and sodium are the most readily leached nutrients, while removal of nitrogen, magnesium, calcium and sulphur are variable and depend on the type of biomass feedstock.

- A water to biomass ratio of 8:1 to 12:1 is sufficient to extract nutrients at a residence time of 30 minutes to 1 hour.

- Biomass that has undergone field leaching can have further nutrients removed using an industrial leaching process.

- Leaching further reduces the ash content of energy crops after field leaching, but the effect on the calorific value and ash fusion temperatures is variable.

- Recycled leachate showed no decrease in extraction efficiency after four cycles of use. The recycling of leachate results in a lower demand of fresh water required for an industrial-scale leaching process.

- Nutrient extraction for producing a combustion fuel is sensitive to pH. The optimal pH for the leach-

ing process is a slightly acidic solution with a pH of about 6.

- Varying the residence time from five minutes to 60 minutes showed an incremental increase in the amount of nutrients removed. In order to reduce the residence time without the corresponding loss in nutrient recovery, a further decrease in particle size and/or an increase in agitation speed should be applied.

Based on the above results and conclusions from the current lab-scale work, the following are recommendations for further optimization and potential scale-up to an industrial-scale process:

- Experiments with freshly harvested biomass in the fall to compare the extraction efficiency with field leached biomass.

- Experiments with better dewatering of biomass following the leaching process capable of reducing the moisture content to approximately 50%.

- An optimization study to determine the maximum number of cycles that leachate can be recycled before the nutrient extraction efficiency is reduced, as well as a comparison of different biomass feedstocks.

- An optimization study to determine the effects of biomass particle size and rate of agitation on immersion leaching with agitation at lower residence times.

- For scale-up to an industrial-sized process, a further investigation into additional equipment and logistics is needed. Additional steps in the process may include a pre-spraying step prior to immersion leaching to remove any dirt and/or contaminants from the received biomass, conveyors from the various steps in the process, and an additional drying unit to further reduce the moisture content of the leached biomass.

In addition to the above recommendation, a further investigation into how the leaching process would incorporate into a larger process that would also include silica extraction, nutrient recovery methods and pelletization.

7.6.2 Electrostatic Separation of Silica from Biomass

The results obtained in this work showed that low ash biomass particles were recovered at the bin closest to the negative electrode, whereas high ash biomass particles were collected at the bins closest to the positive electrode. The results also showed that carbonaceous particles could be electrostatically induced by the positive and negative high voltage electrical field resulting in charge polarization of the particles. Depending on the charge distribution on the surface of the polarized particles and the orientation of these particles while falling down between the electrodes, the particles could deviate toward either the positive or negative electrode. As a result, carbonaceous particles could distribute in all of the bins, which lowers the separation efficiency. To avoid the induction of particles, two strategies are recommended in future work: Modifying the separator set-up by increasing the distance between the electrode plates at the top of the separator and optimizing the applied voltage in order to obtain a high purity product with a high recovery value. Because the electric field intensity in the separation zone controls the extent to which positive and negative particles are defected toward the electrodes, experiments should be performed at various voltages.

Clear separation cannot occur unless silica and other mineral inclusions are physically liberated from the carbonaceous matrix. Therefore, each biomass sample should be analyzed using X-ray photoelectron spectroscopy (XPS) to determine the mineral surface composition. This analysis would help to determine the particle size required to detach silica from the carbonaceous matrix.

The results illustrated that the collected biomass after one separation stage has low purity and recovery. Therefore, two or more electrostatic stages are recommended to further improve the separation quality.

Another reason for not achieving good separation could be due to the agglomeration of fine particles. The interparticle forces responsible for agglomeration are primarily of Coulombic nature and are between negatively charged silica and positively charged carbonaceous particles. As a result, the charge on the particles is neutralized and particle clusters form. One way to partially alleviate this problem is to conduct the separation by spraying the particles through a nozzle in a dilute mode, i.e. low particle loading. However there is a limit of solid concentration in the gas below which the cost of separation becomes economically prohibitive.

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Some other recommendations to further improve the separation quality include measuring the charge density of particles after tribo-charging using an electrometer. This would help to find the most appropriate material to be used in the tribo charger. Investigating the effect of moisture content on the tribo-charging of particles and consequently on the separation efficiency is also recommended.

7.6.3 Nutrient Recovery from Leachate by Reverse Osmosis

The lab-scale experiments conducted found Reverse Osmosis to be a very effective technology to recover water from the biomass leachate. By removing the nutrients, the process increased the nutrient concentrations in the retentate which can be utilized as a liquid fertilizer. Some fouling was exhibited in RO trials which aided the rejection of nutrients. However, excessive fouling of the membrane was not encountered even after running the apparatus for a long period of time.

The apparatus used had limitations. The RO unit incorporated a flat sheet membrane instead of spiral membranes. Spiral membranes are used for industrial and pilot-plant scale processes. They are high performing and incorporate a significantly larger membrane area than the flat sheet membranes. Furthermore, due to time constraints and insufficient membrane area (0.0042 m^2) available for filtration, the selected feed sizes were low and ranged from 1000 mL to 2000 mL, out of which 230 mL was held-up by the system. Undisturbed smooth flow was desired. However, as the volume of concentrate/feed decreased, the pump began to suck air into the tube. Suction of air resulted in foaming in the tubes and in the concentrate/feed tank, which agitated the flow of the fluid. This turbulence in the flow resulted in fluctuation of TMP. Very high TMP caused leakage in the membrane cell. On several occasions, the two fastened components of the cell nearly burst. The rigid pipe carrying the concentrate stream back to the feed did burst in two instances. Bubbles increased the shear rate on the membrane surface and disturbed the solid build-up on the surface. Excessive foaming restricted the length of the experiment and therefore were unable to run the RO trial until the desired % water recovery. Some TMP fluctuations were also observed due to derangement of feed tubing during the experiment.

The effect of foaming on the efficiency of the system was also studied. The respective permeate samples from when the flow in the system was smooth without any foaming and the permeate flux was displaying a consistent trend were also analyzed for each of the RO trials. The results showed even better percent rejection in this scenario. Hence, with better membranes, such as spiral membranes, we expect superior nutrient rejection and percent water recovery. For future research, it is strongly recommended to utilize a spiral membrane module to further study and optimize the RO process implemented for the water recovery and nutrients concentration from biomass leachate.

7.6.4 Nutrient Recovery by Magnesium Struvtie Precipitation

This experimental study found the Magnesium Struvite formation process to be an inadequate method to precipitate N and P from the first cycle leachate due to low amounts of nutrients available in the biomass for this process.

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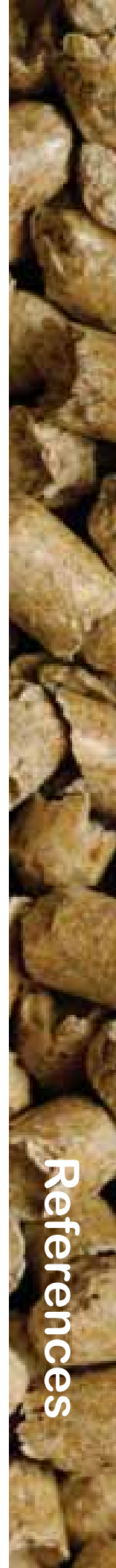
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