Optimization and Scale-up of Liquid Nutrient Extraction and Recovery Process



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lick Runich

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Executive Summary

In "Feasibility of Improving Biomass Combustion through Extraction of Nutrients", a report submitted by CENNATEK to the Ontario Federation of Agriculture in 2011, it was concluded that the quality of solid biomass fuel for combustion can be improved through the extraction of water-soluble nutrients in a pretreatment liquid extraction process. The main issues related with the use of biomass in typical combustion equipment, including the formation of slags and deposits, fouling and corrosion are greatly reduced with the removal of ~90% of potassium, chlorine and sodium. Along with a significant removal of phosphorous and some removal of nitrogen, calcium and magnesium, the resulting liquid extract contains the necessary macronutrients and micronutrients to be used as a liquid fertilizer following additional refining. A literature review conducted as part of the report also concluded that the alternative process of field leaching is a passive process that is inadequate in providing high-quality biomass fuel pellets. Significant amounts of nutrients remain in the biomass as compared to a liquid extraction process.

A liquid nutrient extraction process developed by CENNATEK has been optimized to extract and recycle nutrients from biomass prior to thermal conversion processes. Various reaction parameters associated with the liquid extraction process were optimized in a scaled-down, bench-scale version of the proposed large-scale extraction reactor. Agitation rate of 3500 RPM, residence time of 30 minutes, water-to-biomass ratio of 10-12:1 and recycling of 80% of the liquid extract were determined as optimal operating guidelines to ensure that the process is both economically and technically feasible on a commercial scale.

Silica extraction would be unnecessary from a fuel quality perspective. A triboelectrostatic separation technique based on technologies developed for similar extraction applications provided inconclusive results on its ability to extract silica from biomass. This was due to the inability to completely separate silica from the remainder of biomass material. The removal of water-soluble nutrients using the liquid extraction process reduces the negative effects that silica has on equipment used in thermochemical processes. Silica forms eutectic mixtures with other nutrients that lead to the formation of deposits. Without the other nutrients Silica remains as the main constituent of the ash; however, its presence does not lead to slagging, fouling, or clinker formation.

Nutrients extracted from biomass during the liquid extraction process are in forms suitable for use in commercial liquid fertilizers, but require further refining. The three primary nutrients in fertilizers, nitrogen, phosphorous and potassium (NPK) are in the forms of NH_{4}^{+} and NO_{3}^{-} ions (for N), phosphate ions for (P) and potassium ions (for K). However, nutrient levels in the liquid extract are relatively low and need concentrating by the removal of water and clean-up to remove suspended solids. The refining process is broken down into three steps. Primary refining involves the removal of 99.9% of suspended solids greater than 4 microns in size. Secondary refining incorporates a reverse osmosis (RO) process to remove 50% of the water from the nutrients. In the tertiary refining step, the remaining water is evaporated to remove 95% or more of the total water.

The current and future liquid fertilizer market is sufficient enough to allow for the introduction of fertilizer produced from the liquid extraction process. Market trends indicate a steady increase in fertilizer usage and demand globally.

The proposed liquid extraction process can be scaled up to a commercial scale process. A commercial scale process would include: inputs of biomass (in the form of agricultural residues), water, natural gas and electricity. The two outputs are a high quality biomass fuel pellet for use in thermochemical conversion and other processes, and a line of commercial liquid fertilizers. The main components of the process consist of receiving and storage, size reduction, the liquid nutrient extraction reactor, biomass dewatering and drying, a three-step liquid fertilizer refining process, and pellet mill. The total reactor volume is 35 m³.

A financial model based on the commercial-scale liquid extraction process indicates an economically feasible system. The process would ideally be located at an existing pellet mill, allowing for leveraging of existing infrastructure and logistics and reducing the capital costs. The total capital cost for a 6 ton/hour process is approximately \$1 million (\$1,017,677). Revenues from the two products will amount to \$10.75 million/year, with 44.6% of revenues from the sale of biomass fuel pellets and 55.4% from the sale of liquid fertilizers. The EBITDA (Earnings before interest, taxes,



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depreciation and amortization) for the process was determined to be \$1,812,948/year.

Gasification is an alternative thermochemical conversion process to combustion in both fixed bed and fluidized bed configurations. Fixed bed gasifiers, both in downdraft and updraft setups, are more suitable for small to medium sized applications for their simple and reliable design. Fluidized bed gasifiers, owing to superior mass and heat transfer characteristics, are more suitable for large scale applications. The most important reaction parameter in terms of increasing the product gas yield is temperature, while catalysts can be used to modify the composition of the product gas to meet the requirements of the end user.

An economic evaluation of two biomass gasification scenarios indicated that the cost per MWh of electricity produced (\$180.00 and \$119.20/MWh) were not viable compared to scenarios involving biomass combustion. The two scenarios were a direct heated gasifier for a 0.5 MW generator and an indirect heated gasifier for a 3 MW generator. The most economical scenarios involving biomass combustion from CEN-NATEK's previous report submitted to the OFA were between \$72.58 and \$102.76/MWh. There is therefore no economical advantage to using a biomass gasification process over a biomass combustion process when electricity production is the objective.

Liquid extraction of nutrients would be a beneficial pretreatment process prior to gasification without any negative effects on the overall process. The liquid extraction process would improve the quality of biomass going into a gasifier by removing undesirable water-soluble nutrients and reducing the chance of slag formation. The particle size reduction required for the extraction process (i.e. < 2mm) would not have any negative effects on the gasification process.

Torrefaction is a thermochemical conversion process that can also be used as a pretreatment process for gasification or combustion. Fluidized beds, moving beds and multiple heating zone reactors are the most promising reactor configurations, based on a comparison of available technologies. As with gasification, temperature is the most important reaction parameter for the torrefaction process. Changes in temperature affect the mass yield of the torrified biomass, along with improvements in calorific value, grindability, energy density, fixed carbon and ash content. Residence time and feedstock type are the next two important reaction parameters.

Torrefaction can improve several problems related to the use of biomass for thermochemical processes; however, the process is not yet commercially viable. Reported improvements in the quality of biomass after torrefaction include improved hydrophobicity, reduction in oxygen content, increase in calorific value, improved grindability, increased energy and bulk density, and more thermal stability. These improvements have not been verified on a long-term, large scale system, with further testing required to confirm the viability on a commercial scale.

Liquid extraction of nutrients would be a beneficial co-pretreatment process with torrefaction, and does not negatively affect the torrefaction process. One issue that cannot be improved through the use of torrefaction is the presence of nutrients causing deposits in conversion equipment. As the liquid extraction process is designed to extract these nutrients, the combination of torrefaction and the extraction process can theoretically address all issues related to the use of biomass as a fuel. The size reduction required for the liquid extraction process would not result in any issues during the torrefaction process.



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Nomenclature

Al	Aluminum
Al ₂ O ₃	Aluminum Oxide (Alumina)
В	Boron
Ва	Barium
BaSO ₄	Barium Sulphate
С	Carbon
C ₂ O ₄ ²⁻	Oxalate Ion
Са	Calcium
CaO	Calcium Oxide
CaSO ₄	Calcium Sulphate
CFIA	Canadian Food Inspection Agency
CH ₂	Long-Chain Hydrocarbon Precursor (Methylene)
CH₃OH	Methanol
CH_4	Methane
Cl	Chlorine
Cl	Chloride Ion
СО	Carbon Monoxide
CO ₂	Carbon Dioxide
Cr ₂ O ₃	Chromium Oxide
D _A	Blade Diameter
DMT	Dry Metric Tonnes
D _T	Reactor Diameter
E	Height of the Agitator from the Bottom of the Reactor
EBITDA	Earnings Before Interest, Taxes, Depreciation & Amortization
eV	Electron Volt
Fe	Iron
Fe ₂ O ₃	Ferric Oxide
FIT	Feed-in-Tarriff
н	Reactor Height
H ₂	Hydrogen gas
H ₂ O	Water
HCO ₃ -	Bicarbonate Ion
HHV	Higher Heating Value (GJ/ton, MJ/kg or BTU/lb)
J	Width of Baffles



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К	Potassium
K⁺	Potassium Ion
KCI	Potassium Chloride
КОН	Potassium Hydroxide
K ₂ O	Potassium Oxide
KSP	Solubility Product Constant
kWh	Kilowatt Hour
L	Agitator Blade Length
LHV	Lower Heating Value (GJ/ton, MJ/kg or BTU/lb)
Mg	Magnesium
MgO	Magnesium Oxide
Mn	Manganese
MnO	Manganese Oxide
Мо	Molybdenum
MW	Megawatt
MWh	Megawatt Hour
Ν	Nitrogen
Na	Sodium
Na ₂ O	Sodium Oxide
NH_4^+	Ammonium Ion
Ni	Nickel
NO ₃ ⁻	Nitrate Ion
NO _x	Nitrogen Oxide Gases (NO, NO ₂)
0	Oxygen
0 ₂	Oxygen Gas
OFA	Ontario Federation of Agriculture
Р	Phosphorous
P_2O_5	Phosphorous Pentoxide
PAH	Polycyclic Aromatic Hydrocarbon
PFD	Process Flow Diagram
PO ₄ ³⁻	Phosphate Ion
RO	Reverse Osmosis
RPM	Rotations Per Minute
S	Sulphur
SiO ₂	Silica
SO ₄	Sulphate Ion
TDS	Total Dissolved Solids



Nomenclature

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TiO ₂	Titanium Dioxide
VFD	Variable Frequency Drive
W	Agitation Blade Width
Zn	Zinc
Zn ²⁺	Zinc Ion



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Chapter 1 Nutrient Extraction Testing and Analysis

The report, "Feasibility of Improving Biomass Combustion through Extraction of Nutrients", submitted by CENNATEK to the Ontario Federation of Agriculture in June, 2011 outlined ways to improve the quality of biomass fuels used for combustion through the extraction of undesirable nutrients. Given the nutrients of concern are water soluble, with the exception of silica, it was determined through an extensive literature review that methods of extraction using water were the most promising. The process of field leaching, in which harvesting of crops are delayed in order for the natural removal of nutrients from the biomass back into the land, has been suggested. However, the report determined (and was confirmed by a study conducted by the University of Guelph) that field leaching does not guarantee improvement in biomass guality, and could also lead to undesirable tradeoffs such as increased loss of plant matter and/or an increase in total ash content (Kludze et al., 2011). The use of industrial methods to remove water-soluble nutrients in a controlled manner eliminates the challenges present in field leaching. Preliminary lab-scale experiments of these methods were also conducted as part of the first report, where three types of water-based nutrient extraction methods were compared (immersion extraction, immersion extraction with agitation and pouring/ spraying of water). Based on the results obtained, immersion extraction with agitation was determined to be the most effective process in terms of nutrient extraction and improvement of biomass combustion characteristics.

In order to produce an economically feasible largescale liquid extraction process, it was concluded that two reaction parameters, the water-to-biomass ratio and the residence time, need to be reduced while maintaining the same extraction efficiencies. The rate at which nutrients are extracted is dependent on the contact area, rate of diffusion, and contact time between the biomass and water. Apart from increasing the residence time or amount of water, nutrient extraction can be improved through a decrease in the size of biomass particles and by an increase in the rate of agitation. The report recommended that with the current limits to biomass size reduction that can be achieved by large-scale mills, increasing the rate of agitation would be the most effective method of improving nutrient extraction.

Experimental work based on this and other recommendations continued beyond the completion of the first report in order to more fully develop a larger-scale process that is both technically and economically feasible. Further recommendations from the first report pertaining to the liquid extraction of nutrients included:

- Experiments with freshly harvested biomass
- Incorporating effective dewatering of biomass post-extraction to reduce the moisture content of the biomass to approximately 50%
- Investigating the affect of particle size
- Determining the maximum number of times the liquid extract can be recycled without significant loss in extraction efficiency
- Further investigation into equipment and logistics for an industrial-scale process, including incorporation into a larger system including nutrient recovery, pelletization, etc.

The data presented in this chapter further examines the affect of several reaction parameters on the liquid extraction process, using a reactor design developed by CENNATEK that represents a scaled-down version of a proposed commercial-scale reactor.

1.1 Materials and Methods

1.1.1 Materials

Miscanthus was used as a feedstock for the benchscale nutrient extraction experiments. The miscanthus was harvested in early September from a test plot located at the University of Western Ontario Research Park in Sarnia Ontario. The combination of an early fall harvest and immediate removal from the field ensured that there was minimal field leaching and loss of nutrients prior to extraction. Prior to size reduction, the miscanthus was oven-dried at low temperatures to reduce the moisture content and ensure effective milling. The moisture content was less than 10% after the drying step, at which point the size reduction was performed using a Wiley knife mill. In order to investigate the effect of particle size on nutrient extraction efficiency, the miscanthus was milled to <2.0mm and < 4.0mm using different sized screens. The reduction in particle size increases 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 resulted in an increased rate of extraction by decreasing the path of diffusion, which is a key factor in the overall rate of extraction.

1.1.2 Extraction Procedure

Nutrient extraction was carried out using milli-Q water (resistivity > 18.5 M Ω -cm) at a specified ratio of water to biomass. Based on the preliminary results and the literature review, various water to biomass ratios of 8:1, 12:1, and 15:1 were tested. Biomass was immersed in water in a ten litre reactor and agitated at room temperature for 20 and 80 minutes residence time. The mixture was agitated with a 1 hp motor with a variable frequency drive (VFD) at a rate of 1500, 2500, and 3500 RPM for the appropriate residence time. The reactor was one compartment of a multi-sectional commercial scale reactor which was scaled down by approximately 330:1 ratio by volume. The lab scale reactor was 0.5m tall with 0.16m hydraulic diameter. The effect of blade configuration on the extraction efficiency was investigated using two dispersion blades with and without a hydrofoil impeller. The mixture was then filtered to produce the liquid extract. The wet biomass was then further dewatered using a 10 ton hydraulic press to extract more liquid extract and to further reduce the moisture content. A portion of the biomass was then dried using an infrared moisture analyzer (Denver Instrument IR-35) prior to analytical testing.

1.1.3 Analytical

Solid biomass samples underwent standard solid biomass characterization testing for use in thermal processes. Standard tests (summarized in Table 1.1) include selected proximate and ultimate analysis, calorific (or higher heating) value, chlorine, elemental ash composition and ash fusion temperatures.

1.2 Results and discussion

1.2.1 Analysis of Biomass Samples as Received

The biomass samples (miscanthus) were analyzed prior to leaching for moisture and ash content (proximate analysis), CHN (ultimate analysis), chlorine, higher heating value (HHV), ash fusion temperatures and elemental ash composition. The results are shown in Tables 1.2 and 1.3.

The miscanthus was stored indoors after harvesting to

Table 1-1Summary of ASTM Test Methodsfor 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
Chlorine	D4208
Calorific Value (HHV)	E711
Elemental Ash Composition	D6349
Ash Fusion Temperatures (°F)	D1857

dry prior to analysis to prevent any field leaching of nutrients prior to liquid extraction. The nutrient content present in the miscanthus used in these experiments was lower than typical values found in practice. The land where the miscanthus was grown was not farmed for at least 30 years, and no fertilizer inputs or weed control were added to the crop. As a result, the yields were low, and do not represent the nutrient content of typical miscanthus which is purposely grown with standard inputs to increase biomass yield.

The reaction parameters of importance in the liquid nutrient extraction process included the rate of agitation, residence time, the water to biomass ratio, and the particle size. The effects of varying these parameters on several biomass parameters are summarized and discussed in the following sections. In addition, the process of recycling the liquid extract for use in subsequent extractions in order to reduce fresh water requirements was also analysed.

1.2.2 Effect of Extraction and Pressing Procedure on Biomass and Liquid Extract

The experiments carried out in Chapter 6 of "Feasibility of Improving Biomass Combustion through Extraction of Nutrients" did not incorporate an effective dewatering step after liquid extraction. The current experimental setup included a two-step dewatering process



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Table 1-2Analysis of Harvested MiscanthusPrior to Extraction

Parameters	Miscanthus	
Proximate Analysis		
Moisture Content (wt. %)	6.5	
Ash Content (wt% DM)	3.31 ±0.35	
Ultimate Analysis (wt% DM)		
Carbon	46.22±1.63	
Hydrogen	5.68±0.19	
Nitrogen	0.63±0.05	
Ash Fusion (°F)		
Initial Deformation Temperature	897	
Softening Temperature	1813	
Hemispherical Temperature	2130	
Fluid Temperature	2224	
Chlorine (wt% DM)	0.061±0.000	
Gross Calorific Value (GJ/ton)	19.3±0.1	
Gross Calorific Value (BTU/lb)	8300±42	

Table 1-3ElementalAshAnalysisofHar-vested Biomass Prior to Extraction

Parameters	Miscanthus
Elemental Oxide	Elemental Ash Composition (% of Ash)
SiO ₂	56.68
P ₂ O ₅	5.65
Al ₂ O ₃	<0.01
Fe ₂ O ₃	0.14
MnO	0.04
MgO	3.84
CaO	8.04
K ₂ O	25.03
Na ₂ O	0.58
TiO ₂	0.01
Cr ₂ O ₃	0.01
Total	100.00

(filtering and use of a hydraulic press) to reduce the moisture content of the treated biomass and to further extract any remaining water soluble nutrients into the liquid extract. Table 1.4 summarizes the average reduction in moisture content after the two dewatering steps, along with the amount of liquid extract removed in each step. As the table indicates, the moisture content of the biomass after pressing is 48%, a moisture content that is more consistent with industrial-sized dewatering systems. In terms of water recovery in the extract, approximately 90% of the fresh water is captured, with losses due to experimental error and handling of the mixture.

Table 1-4Effect of Dewatering Process onBiomass and Liquid Extract

Dewatering Step	Average Moisture Content of Biomass (%)
Prior to Liquid Extraction	6.5
After Initial Filtering of Solids	79.0
After Hydraulic Press	48.0
Dewatering Step	Amount of Liquid Extract (L)
Prior to Liquid Extraction (Fresh Water Added)	8.4
After Initial Filtering of Solids	
and Hydraulic Press	5.36
and Hydraulic Press After Hydraulic Press	2.20

1.2.3 Effect of Agitation Rate

Experiments conducted in the previous report had a fixed agitation rate of 700 RPM. To further improve the extraction efficiency, much higher agitation rates were applied to the extraction, ranging from 1500 to 3500 RPM. A set number of blades were used to ensure uniform mixing and extraction within the reactor.

The first set of experiments examined the effect that agitation rate has on the reduction of ash content. With water-soluble nutrients being a significant portion of the inorganic components of ash, the liquid



extraction of biomass should result in a decrease in the overall ash content. While the agitation rate was varied, the residence time was kept constant at 80 minutes, the water to biomass ratio at 15:1, and the particle size reduction to less than 2 mm. The changes in ash content are shown in Figure 1.1:



Figure 1-1 Effect of Agitation Rate on Ash Content

As the above figure indicates, there is a significant reduction in ash content for all treated samples (1.67-2.73%) when compared to the untreated sample (3.31%), with a percent reduction ranging from 18 to 49.5%. The largest reduction in ash content occurred with the highest agitation rate of 3500 RPM, indicating that increased agitation does improve the extraction efficiency. This is further confirmed when looking at the effect of increased agitation rate on the calorific value of treated biomass. The reduction in watersoluble nutrients contained in the biomass leads to a relative increase in the amount of energy-rich carbon remaining. This would be quantitatively shown with a corresponding increase in the calorific value, which measures the amount of energy produced per pound of biomass. As shown in Figure 1.2, the calorific value of the untreated miscanthus (8300 BTU/lb) steadily increased in the treated miscanthus at 1500 RPM (8452 BTU/lb) to 3500 RPM (8584 BTU/lb), representing a percent increase of 1.8 to 3.4%. Due to the experimental error, results in Figure 1.1 shows that biomass ash content at 2500 RPM is larger than the ash content for biomass at 1500 RPM. Results in Figure 1.2, however, confirm that the higher the agitation rate, the higher the extraction efficiency. Carbon content of untreated and treated biomass was measured to support the ash content and calorific value data. Carbon content increased by 10% and 11% from the untreated sample by increasing the agitation rate to 2500 and 3500 RPM respectively, confirming the calorific value results.

From the data obtained on the untreated miscanthus sample, silica accounts for approximately 57% of the ash content, or 1.87% of the original 3.31%. As a result, it is expected that there is a limit to a decrease in the ash content and subsequent increase in calorific value since the majority of silica remains. Therefore, the decrease in ash content shown with 3500 RPM is not expected to further decrease with any additional increase in the agitation rate.



Figure 1-2 Effect of Agitation Rate on Calorific Value

The specific amount of individual nutrients removed from the biomass was determined to indicate subsequent improvements in the burning characteristics of the treated biomass, as well as determining the amounts in the liquid extract to be used for a potential fertilizer product. The percent reduction of the main nutrients of interest, looking at agitation rates of 2500 and 3500 RPM, are summarized in Table 1.5.

The largest reductions were in phosphorous, potassium, chlorine and sodium (>86%) at 3500 RPM. These



Optimization and Scale-up of Liquid Nutrient Extraction and Recovery Process values are a marked improvement in the reductions found in the field dried miscanthus in the first report by CENNATEK (Chapter 6, pages 64-66 of "Feasibility of Improving Biomass Combustion through Extraction of Nutrients"). This confirmed that the use of freshly harvested biomass that had not been subject to any field leaching would result in larger reductions in nutrients that are more consistent with results found in literature. In terms of agitation rate, there is a clear improvement in the extraction efficiency at 3500 RPM as compared to 2500 RPM, with increases in reduction from 10% for potassium up to 42% for calcium. This further confirms that the best results are clearly with the highest agitation rate of 3500 RPM.

Table 1-5Effect of Agitation Rate on Nutri-ent Removal

Nutrient	% Reduction in Treated Miscanthus (3500 RPM)	% Reduction in Treated Miscanthus (2500 RPM)
Phosphorous	87.5%	76.4%
Potassium	86.5%	80.7%
Nitrogen	16.6%	20.5%
Calcium	57.7%	33.6%
Magnesium	76.9%	57.8%
Sodium	87.8%	70.1%
Chlorine	95.2%	91.9%

Table 1.6 compares the reduction in elemental ash composition of the miscanthus treated with the liquid nutrient extraction process, and average reduction values from various biomass feedstocks that have undergone field leaching. The results indicate that there are consistently greater reductions in nutrient content following the proposed liquid extraction process as compared to field leaching. Coupled with the additional disadvantages associated with field leaching (e.g. loss of overall yield), it is clear that the proposed process is preferred over the practice of field leaching for the removal of nutrients from biomass prior to thermal conversion.

To quantitatively verify the improvement in combustion characteristics of the treated biomass, the ash fusion temperatures were determined for the untreated and treated miscanthus samples. As shown in Table

Table 1-6Reductions in Nutrients afterLiquid Nutrient Extraction and Field Leach-ing

Nutrient	% Reduction af- ter Liquid Nutri- ent Extraction	Average % Re- duction after Field Leaching
Phosphorous	87.5%	53.8%
Potassium	86.5%	79.0%
Nitrogen	16.6%	4.25%
Calcium	57.7%	None
Magnesium	76.9%	38.8%
Sodium	87.8%	54.7%
Chlorine	95.2%	87.3%

(Sources: Burvall, 1997; Jenkins et al., 1997; Jenkins et al., 1996; Landstrom et al., 1996)

1.7, there is a significant improvement in the ash fusion temperatures for all treated samples as compared to the untreated biomass. The initial deformation temperature increased by a dramatic 161-200% compared to the untreated sample. Such a significant improvement in the initial deformation temperature is important as any deformation is an indication of the potential formation of slags or other deposits. Therefore, the use of a high agitation rate represents a vast improvement in the combustion properties of the treated biomass. There is a slight improvement in the ash fusion temperatures at the highest agitation rate of 3500 RPM; however, all three agitation rates produce a significant improvement over the untreated sample. This is due to the fact that even at the lower agitation rate, the amount of alkali and alkaline earth metals (e.g. potassium, sodium, magnesium) removed from the biomass is enough to improve the ash fusion characteristics.

The analysis described above was conducted on samples of miscanthus that were reduced to less than 2 mm size. The analyses were repeated on samples of miscanthus reduced to less than 4 mm size to determine the effect of particle size on extraction efficiency. The results indicated that there was no significant improvement in calorific value and ash content compared to the untreated sample, indicating that the biomass would need to be further reduced in size to less than 2 mm in order to achieve improved nutrient extraction.



Ash Fusion Tempera- ture (°F)	Untreated Miscanthus	Treated Miscanthus 3500 RPM	Treated Miscanthus 2500 RPM	Treated Miscanthus 1500 RPM
Initial Deformation	897	2542	2699	2344
Softening	1813	2801	2766	2628
Hemispherical	2130	>2825	2800	2800
Fluid	2224	> 2825	> 2825	>2825

Table 1-7 Effect of Agitation Rate on Ash Fusion Temperatures

Based on the above data, there is a clear indication that the greatest improvement in biomass combustion properties and the removal of nutrients for use in liquid fertilizer occurred with the highest agitation rate of 3500 RPM. As expected, the increased agitation allows for better mixing and contact between the water and biomass, allowing for more extraction of watersoluble nutrients.

1.2.4 Effect of Residence Time

The residence time of water and biomass in the reactor needs to be minimized in order for the size of the reactor to be feasible on a large scale. Based on literature and previous work completed by CENNATEK, a residence time below two hours would be required to design an appropriate-sized reactor. For the current set of experiments, two residence times of 20 and 80 minutes were used to determine an appropriate value based on extraction efficiency. For the experiments comparing the two residence times, the water to biomass ratio was kept constant at 15:1, the particle size to less than 2 mm, and all three agitation rates were used.

Figure 1.3 shows the effect of residence time on the ash content of treated biomass compared to untreated biomass. While the ash content is reduced as the residence time is increased for the lowest agitation rate, there is no significant improvement in ash content reduction when increasing the residence time from 20 to 80 minutes at 2500 and 3500 RPM. To compare these results, the effect of residence time on the calorific value of treated biomass is shown in Figure 1.4. Factoring in the standard deviation, there is only a slight increase in calorific value from 20 to 80 minutes for the 1500 RPM sample. For the 2500 RPM sample,

there is an increase in calorific value, indicating that the longer residence time may be beneficial at these conditions.



Figure 1-3 Effect of Residence Time on Ash Content

For the 3500 RPM sample, however, the improvement in calorific value is essentially equal for both 20 and 80 minute residence times. This result indicates that at the highest agitation rate, already determined to be ideal rate in the previous section (1.2.3), similar results can be obtained at the lower residence time as the increased mixing and contact time allows for the extraction of nutrients in a reduced amount of time.

The amount of nutrients removed at the different residence times are summarized in Table 1.8. The



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Figure 1-4 Effect of Residence Time on Calorific Value

Table 1-8Effect of Residence Time on Nutri-ent Removal

Nutrient	Percent Reduc- tion in Treated Miscanthus (80 minute Res- idence Time)	Percent Reduc- tion in Treated Miscanthus (20 minute Resi- dence Time)
Phosphorous	87.5%	83.6%
Potassium	89.6%	86.5%
Nitrogen	16.6%	21.3%
Calcium	57.7%	54.2%
Magnesium	76.9%	72.4%
Sodium	87.8%	86.5%
Chlorine	95.2%	96.1%

results, both at an agitation rate of 3500 RPM, indicate that there is generally only a slight decrease in the amount of nutrients removed at 20 minutes compared to 80 minutes, confirming the calorific value data at the highest agitation rate of 3500 RPM. Further confirmation is indicated in Table 1.9, summarizing the effect of residence time on ash fusion temperatures at the 3500 RPM agitation rate. The improvements in all four ash fusion temperatures for both the 20 minute and 80 minute residence times compared to the untreated sample are nearly identical. From these cumulative results, it can be concluded that at the highest agitation rate of 3500 RPM, there is negligible differences in nutrient extraction and the corresponding improvement in combustion characteristics at residence times ranging from 20 to 80 minutes. This range of residence times allows for an appropriately sized reactor on a pilot scale to be economically feasible.

1.2.5 Effect of Water-Biomass Ratio

Like the residence time, the water to biomass ratio also needs to be kept low in order to be feasible on a pilot or industrial scale. Ratios of 8, 12 and 15:1 were chosen based on preliminary experiments conducted in the initial CENNATEK report. For these set of experiments, the agitation rate was kept at 3500 RPM, the residence time at 80 minutes and the biomass particle size at less than 2 mm.

Figure 1.5 shows the effect of liquid extraction at various water to biomass ratios on the ash content. All three ratios used produced significant reductions in ash content compared to the untreated sample, with an average percent reduction of 47%. The reduction using the 8:1 ratio is slightly less than the higher two ratios, but not to a significant degree. Conversely, the effect of the water to biomass ratio on the calorific value of treated biomass shows a steady increase in calorific value as the ratio is increased (Figure 1.6).

The percent increase in calorific value as compared to the untreated sample increases from 1.6% for the 8:1 ratio up to 3.42% for the 15:1 ratio. The carbon content in the treated biomass confirms the trend in calorific value, with a steady increase in carbon content as the ratio increases.

Table 1.10 indicates the effect of different water-tobiomass ratios on the extraction of nutrients. At a ratio of 8:1, the reductions in nutrients are on average 10% lower than at the 15:1 ratio. The increased amount of water allows for a larger difference in concentration between the biomass and the liquid, which could enhance the diffusion of nutrients into the lower concentrated liquid. However, significantly larger amounts of water used in previously reported literature are not required as the amount of nutrients removed at a 10-15:1 ratio is sufficient.



Ash Fusion Temperature (°F)	Untreated Miscanthus	Treated Miscanthus 80 minutes	Treated Miscanthus 20 minutes
Initial Deformation	897	2542	2486
Softening	1813	2801	2797
Hemispherical	2130	>2825	> 2825
Fluid	2224	> 2825	> 2825
4.00 3.50 3.00 2.50 1.50 1.50 0.50 0.00		8700 - 8500 - 8500 - 8800 - 8800 - 8800 - 8800 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 -	
Untreated 8 12 Water to Biomass Ratio	15 o (-)	8000 - 0 8 Water-Bio	12 15 mass Ratio (-)

Table 1-9 Effect of Residence Time on Ash Fusion Temperatures

Figure 1-5 Effect of Water-Biomass Ratio on Ash Content

The ash fusion temperatures of the treated biomass at ratios of 12:1 and 15:1 are again both significantly increased when compared to the untreated biomass (Table 1.11). The fluid temperatures for both treated samples are above the temperature limit of the ash fusion furnace, while the initial three temperatures show a slight improvement for the 15:1 ratio sample.

These results indicate that an 8:1 water to biomass ratio is not sufficient compared to higher ratios in terms of nutrient extraction and improvements in treated biomass. The 15:1 ratio provided the best results in terms of calorific value, nutrient extraction and ash fusion, while the reduction in ash content was similar for both 12:1 and 15:1. When determining the most effective water to biomass ratio for a larger-scale process, the effect of a higher ratio on the design and size Figure 1-6 Effect of Water-Biomass Ratio on Calorific Value

Table 1-10 Effect of Water-Biomass Ratio on Nutrient Removal

Nutrient	Percent Reduc- tion in Treated Miscanthus (15:1 Ratio)	Percent Reduc- tion in Treated Miscanthus (8:1 Ratio)
Phosphorous	87.5%	80.2%
Potassium	89.6%	81.0%
Nitrogen	16.6%	13.6%
Calcium	57.7%	54.9%
Magnesium	76.9%	73.3%
Sodium	87.8%	69.6%
Chlorine	95.2%	89.4%



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Ash Fusion Temperature (°F)	Untreated Miscanthus	Treated Miscanthus 15:1 ratio	Treated Miscanthus 8:1 ratio	
Initial Deformation	897	2542	1888	
Softening	1813	2801	2684	
Hemispherical	2130	>2825	2797	
Fluid	2224	>2825	>2825	

Table 1-11 Effect of Water-Biomass Ratio on Ash Fusion Temperatures

of the reactor has to be taken into account. As will be shown in the economic model, a ratio of 15:1 is not economically feasible due to the large amounts of water that would need to be removed or evaporated from the liquid extract to produce a commercially viable fertilizer. As a result, a water-to-biomass ratio between 10 and 12:1 would be most effective and feasible in the extraction of nutrients.

1.2.6 Recycling of Extract

The previous report examined the possibility of recycling the nutrient-rich liquid extract and reusing it in a subsequent run rather than fresh water. This recycling would further reduce the amount of fresh water required for the process, with only a fraction of the total amount required in make-up water to account for any losses from the previous extraction. Further experiments were performed to determine the number of times the liquid extract could be recycled without any significant loss in extraction efficiency. For this set of experiments, a water to biomass ratio of 15:1 and an agitation rate of 3500 RPM were used for each run. After the liquid extract has been filtered and pressed out of the biomass, it is reused in the subsequent run with a small amount of fresh water to ensure that the ratio is kept at 15:1. The experiment was repeated 15 times.

For each experiment, approximately 3.37 litres of liquid (i.e. water and recycled extract) are required. An average of 3.05 litres of extract was collected from each run, representing 90% of the total liquid required. Figure 1.7 shows the extraction efficiency of selected nutrients as a ratio of the amount extracted from the initial run. The results show that the extraction efficiency remains 80% or above the original extraction efficiency until the fifth run only. The reason for the



Figure 1-7 Ratio of Nutrients Extracted from Recycled Runs Compared to First Extraction

reduction in extraction efficiency is due to the removal of nutrients from the treated biomass into the liquid extract. After the first run, the nutrients removed from the treated biomass are mechanically pressed to remove approximately 50% of extracted nutrients in the liquid. The remaining 50% of the extracted nutrients remain in the wet biomass. Upon drying, these remaining nutrients would redeposit onto the surface of the biomass. The recycled liquid extract used to extract further nutrients from fresh untreated biomass would cause the overall concentration of nutrients in the extract to increase. Since only 50% of this more concentrated liquid extract is removed using mechanical dewatering, more nutrients will end up redepositing on the treated biomass. As a result, the calculated extraction efficiency is reduced in subsequent recycle



runs, as indicated in Figure 1.7. Therefore, if all of the extract is recycled back into the system, the liquid extract after the fifth run would need to be removed, further processed and fresh water used for the subsequent run.

In order to use the recycled liquid extract in subsequent runs without any significant loss in extraction efficiency, it is proposed that 80% of the liquid extract is to be recycled back to the reactor while the remaining 20% is immediately sent for further processing into a liquid fertilizer product. The addition of more fresh water to make up the difference allows for less concentration of nutrients in the liquid, allowing the extract to be recycled continuously without a loss of efficiency. Based on calculations, if less than 85% of the extract is recycled back to the reactor, the saturation concentration achieved after 5 runs when the entire liquid extract is recycled is never reached. A final value of 80% was chosen to include a safety margin below the 85% value.

1.2.7 Silica Extraction

The only significant nutrient present in biomass that is not water soluble is silica. In the previous report, a literature review on potential methods of removing silica from biomass was performed, with a triboelectric separation process showing the most promise. In this process, the biomass particles are given a surface charge through contact against other dissimilar particles. Depending of the work function of the particles, either a positive or negative charge would be imparted on the particles. A specific example involves using copper as the dissimilar particle. Silica has a larger work function (5.4 eV) than copper (4.38 eV), while carbon has a lower work function (4.0 eV). This would cause silica to have a negative charge and carbon a positive charge. The charged particles would then come in contact with an electric field, where the particles would be separated based on their different charges.

Some initial lab-scale testing on the triboelectric separation of biomass particles to remove silica were inconclusive. The silica present in the biomass was unable to be completely separated from the carbonaceous matrix, resulting in incomplete separation. In order to possibly remove the silica form the carbon, the biomass would need to be reduced in size significantly, a process that becomes more cost and energy intensive without any guarantee of separation. Tribo Flow Separations, a company based out of Kentucky with several patents relating to triboelectric separation of materials, was contacted. TFS had not previously tested raw biomass for the separation of silica and was not sure of the success of the proposed method.

Research has shown that the negative effects that silica has on the combustion properties of biomass occur when it interacts with other nutrients of concern, namely potassium, sodium and chlorine. With large amounts of these nutrients removed using the proposed liquid extraction process, the presence of the silica remaining in the biomass would not cause any significant issues (deposits, slags, etc.) with the combustion equipment. The initial economic evaluation developed by CENNATEK in the first report concluded that the inclusion of silica separation and purification to produce a silica by-product and additional heat and electricity was required in order to make the overall process more economically viable. However, a new economic model presented in this report concludes that a process that does not incorporate silica extraction or purification and includes two main product streams (liquid fertilizer and treated biomass) can be economically viable. Due to the unproven nature of the silica extraction process and the increased energy costs related to further particle size reduction, it was concluded that silica extraction is not necessary in the nutrient extraction process to be economical..

1.3 Conclusions

Bench-scale experiments were conducted on freshly harvested miscanthus samples based on conclusions and recommendations from preliminary experiments conducted in the previous report by CENNATEK for the OFA. The following conclusions were drawn from the results of the current experimental work:

- Various reaction parameters were investigated and values that are economically and technically feasible on a commercial scale were confirmed for the liquid nutrient extraction process. A preferred method would incorporate the following parameter values :
 - Agitation Rate 3500 RPM Lower agitation rates are sufficient for improvements in the combustion properties of the treated biomass, but the 3500 RPM is required for slight improvements and the maximum nutrient removal for the liquid fertilizer.



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- Residence Time Experiments indicated only a slight reduction in efficiency between 20 and 80 minute residence times when using the highest agitation rate. In order to maximize efficiency while keeping the reactor size small to maintain economic feasibility, a residence time of 30 minutes was chosen.
- Water to Biomass Ratio Of the three biomass ratios tested, 8:1 was not a sufficient ratio, while ratios of 12 and 15:1 produced appropriate reductions in nutrient content. While the 15:1 ratio had the best results experimentally, the resulting size of reactor required is not economical based on financial models. Therefore, a ratio of 10 or 12:1 is appropriate to ensure sufficient nutrient extraction while maintaining economic feasibility.
- The liquid extract could be recycled up to five times with less than 20% reduction in extraction efficiency when the entire extract is recycled. Recycling 80% of the extract would allow the extract to be recycled on a continuous basis without loss of extraction efficiency due to the additional makeup water. This reduces the amount of total fresh water needed for the process.
- The use of freshly harvested biomass, as opposed to biomass that has been subject to field leaching, allows for an increased extraction of nutrients in the proposed liquid extraction process.
- Sufficient dewatering of the biomass following the liquid extraction process was achieved, with reductions in moisture content to less than 50%, values that are consistent with industrial scale dewatering equipment.
- The extraction of silica using a triboelectric separation technique is an unproven technology. The removal of the water-soluble nutrients reduces the negative effects of silica on thermochemical processes.
- The economic feasibility of the process without silica extraction and purification negates the need for silica extraction in this process until the technology is further proven.



Chapter 2 Nutrient Recovery and Fertilizer Production

The focus of the research in Chapter 1 was to optimize the nutrient extraction from agricultural-based biomass in order to produce a high quality solid biomass fuel. The primary objective of optimizing the extraction process was to make the process economical. An equally important objective to make the overall process economically feasible is the integration of a nutrient recovery system to take the nutrient rich liquid extract and refine it to produce a liquid fertilizer from a natural source. The recovered nutrients in the form of liquid fertilizer can then be reused and recycled back into the soil for agricultural purposes. This chapter investigates the nature of the nutrients in the extract stream, government regulations, and the market for an all-natural liquid fertilizer.

2.1 Nutrients in Fertilizer

Three primary nutrients in fertilizer are symbolized by the letters N-P-K (for nitrogen, phosphorus and potassium). Most fertilizers are marked with the percentages of each of these three nutrients. Nitrogen 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⁺) and nitrate (NO⁻). 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. Most of the nitrogen taken up by plants is from the soil in the forms of NO₃⁻. Amino acids and proteins in the plant can only be built from NH⁺ so NO⁻₂ is reduced. Phosphorus in the form of ions is necessary for the growth of healthy root systems, as well as being an integral component in the process of photosynthesis. Plants absorb phosphate ions from the soil then bind the phosphate into organic compounds. The presence of potassium in fertilizer reduces loss of water from the leaves, and helps the plant to tolerate dry growing conditions. Potassium is taken up by the plant in the form of K⁺ ions. Potassium in the plant exists as an ion and does not form any organic compounds.

2.2 Nutrient Forms in Liquid Extract

Chemical fractionation analysis was performed by Johan Werkelin et al. (2010) to analyse the form and concentration of water extractable nutrients from woody biomass. The extraction process included drying of

the biomass at 105°C for two hours, size reduction to 1 mm, mixing with water at a water to biomass ratio between 6 and 10, and stirring at 65 RPM for 24 hours. The process extracted most of the K (75%), P (65%), and Na (65%), some of the Mg (40%), Mn (25%), and Ca (25%), and a small fraction of the Al (10%) and Fe (5%). They showed that 83% of the phosphorous in the leachate is in the form of the phosphate ion PO_4^{3-} . The anions PO_4^{3-} , SO_4^{2-} , Cl⁻, and $C_2O_4^{2-}$ are present as water soluble salts with the metal ion K⁺ in the biomass. No NO₃⁻ was detected in the extracted liquid. The NH_{4}^{+} was compared with the nitrogen (N) content of the solid, untreated sample. The water leached ammonium $(NH_{,+})$ constituted only 0.1-1.4% of the total Nitrogen in the original biomass sample. Based on this information, it can be concluded that the extracted NPK in the liquid extract are all in forms that can be directly absorbed by the plant without any additional conversion.

2.3 Fertilizer Regulations in Canada

In Canada, the process of registering a product as a fertilizer is under the jurisdiction of the Canadian Food Inspection Agency, or CFIA. Under the Fertilizers Regulations Act, any fertilizer sold or imported into Canada has to:

- Be Registered as Prescribed
- Conform to Prescribed Standards
- Packaged and Labelled as Prescribed

Fertilizers can be registered in three categories including Fertilizer-Pesticide, Micronutrients, and Low Analysis Farm Fertilizer. Pesticide-free fertilizers can be registered as either Micronutrients or Low Analysis Farm fertilizer. Fertilizers containing micronutrients that have less than 24% combined NPK (chemical based), or less than 18% combined NPK (animal or vegetable based), require registration as a low analysis farm fertilizer.

The registration application requires a guaranteed analysis of the proposed fertilizer and three copies of a label intended for the fertilizer.

Guaranteed analysis is a set of standard test methods



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developed by the Association of Official Agricultural Chemists (AOAC) to determine the amount of various nutrients in a fertilizer. The N-P-K values present on fertilizer labels represent the minimum amount of total nitrogen, the available phosphoric acid (P₂O₂) and soluble potash (K₂O) expressed as a weight percent. In addition, the minimum amount of calcium, magnesium and sulphur is expressed in percent elemental basis. Other lesser plant nutrients, including boron, manganese, zinc, iron, copper, chloride and molybdenum are also included on a percent elemental basis. Finally, if a fertilizer contains more than 25% of the nitrogen in a water-insoluble form from plant or animal origin or other source of slowly available nitrogen, the minimum amount of water-insoluble nitrogen is also expressed in weight percent.

The label contained on any package of fertilizer requires the following information:

- Name and address of the manufacturer
- Brand of fertilizer (if any)
- Name of the Fertilizer
- Registration number (where applicable)
- Guaranteed analysis
- Directions for use (if containing pesticide or lesser plant nutrients)
- Weight of the fertilizer
- A cautionary statement if the fertilizer contains boron, copper, manganese, molybdenum or zinc
- Lot number (unless the fertilizer is a custom formula)

The following list of information should also be provided for the assessment of by-products fertilizers beside the guaranteed analysis and product label:

- Identify and describe in general terms the industrial or manufacturing process from which the product and each constituent by-product material are derived. A flow-chart diagram of this process would also be helpful.
- Include a description of feedstock for the process, any chemicals or materials added throughout the pathway of the process, and any transformations these undergo as a result of the process.

- Provide scientific reports on the effectiveness of the product, on the human, plant, animal or environmental safety.
- Identify whether this material is currently being used in agirculture, or any other uses to which the material is being put.

2.3.1 Canada Organic

On June 30, 2009 the Canadian government implemented the Organic Products Regulation to regulate organic certification in Canada for organic products. The regulations require mandatory certification to the revised Canadian Organic Standards for agricultural products represented as organic in import, export and inter-provincial trade, or that bear the federal organic agricultural product logo.

Organic certification of fertilizers can be achieved through Accredited Certification Bodies (CBs). CBs are accredited by Conformity Verification Bodies (CVBs), who are under the agreement with Canadian Food Inspection Agency (CFIA) to access and recommend CBs.



Figure 2-1 Canada Organic Logo (http:// www.cog.ca)

The application for organic certification includes the following information:



- Composition and percentage of organic products contained in a multi-ingredient product.
- Substances used in production and processing of the end product and the manner used.
- Detailed production, processing and control methods.

All products wishing to bear the organic logo (Figure 2.1) must first be certified according to the Organic Products Regulations. To qualify for this logo, products need to have an organic content that is greater than 95%. Certified organic multi-ingredient product that contains less than 95% organic contents can use the words Organic Ingredients, subject to certain limitations in wordings as specified by the Organic Product Regulation.

2.4 Refining of Liquid Extract

Results from the analysis in Chapter 1 suggest a water to biomass ratio of 10 or 12:1 is optimal to extract nutrients from biomass in the extraction reactor. Due to the large ratio of water to biomass and an initial low amount of nutrients present in most biomass sources, the nutrient concentration in the liquid extract leaving the process is generally low. The nutrient concentration in the liquid extract also depends on the biomass feedstock used in the process; however, most nutrient content values in typical agricultural residues and energy crops are insufficient as is for use in a liquid fertilizer. In order to increase the nutrient concentration in the liquid extract stream to achieve higher NPK ratios, various strategies and refining technologies were considered to be used in the process.

The initial strategy, explained in detail and optimized in Chapter 1, was the recycling of the liquid extract. Eighty percent of the liquid leaving the extraction reactor is mixed with fresh water and used in the subsequent run. This strategy lowers the water consumption by 80% and allows the use of the same liquid extract to extract fresh biomass. The remaining 20% of the liquid is treated through multiple stages in order to remove any suspended solids and 95% of the water to concentrate the nutrients in solution. Treatment of the liquid is essential in order to reach a standard nutrient concentration that can be sold in the market as a liquid fertilizer. The primary treatment process involves the removal of suspended solids from the liquid. 99.9% of suspended solids larger than 4 µm are removed in this stage. The second stage of refining involves the use of a reverse osmosis (RO) process to concentrate the liquid. The feasibility of using RO to recover nutrients from the liquid extract stream and to recycle water back to the extraction reactor was initially investigated in the first report submitted by CENNATEK to the Ontario Federation of Agriculture. Reverse osmosis was found to be a proven technology for the effective water recovery and concentration of dissolved solutes. Experimental and simulation results obtained, however, revealed that only 50% of the water can be removed from the liquid extract using reverse osmosis.

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). The retained nutrients therefore build up on the membrane surface and reduce the efficiency of the RO system. After removing approximately 50% of the water, the nutrient concentration on the membrane surface increases. As a result, some nutrients begin to lose their solubility and start building a rigid layer on the membrane surface.

RO membranes readily foul with precipitated metals, including iron, manganese, and aluminum. Soluble iron and manganese (and cobalt present in some bisulphite solutions used for dechlorination) are also a problem for RO membranes. Silica, as insoluble silicates and as soluble or "reactive" silica, can also cause problems for an RO system. Insoluble silicates form when silica precipitates. When iron and aluminum are present, silicates of these metals can form quickly and at silica concentrations less than saturation. Saturation of soluble silica is a function of temperature and pH (Kucera, 2010). Silica is more soluble at higher temperature and at pH below 7.0 and above 7.8. Soluble silica often limits the recovery of an RO system because of the potential for scaling and the difficulty in removing silica scale from membranes. Reverse osmosis filtration of the biomass liquid extract was simulated and results are shown in Table 2.1. The results show that at 50% water removal from the liquid extract, the silica concentration reaches 92% of the saturation concentration. Silica loses its solubility when its concentration reaches the saturation concentration and precipitates on the membrane surface. Therefore, the membrane is expected to foul by silica at water removal levels higher than 50%. Maintaining the water removal lev-



Optimization and Scale-up of Liquid Nutrient Extraction and Recovery Process Table 2-1 Simulation Results of Reverse Osmosis of Liquid Extract. (Feed flow rate: 100 gpm, Permeate flow rate: 50 gpm; Permeate recovery: 50%; Feed pressure: 268 psi; Temperature: 25 °C)

	FEED	PERMEATE	CONCENTRATE
ION		mg/L	
Са	581	6.241	1155
Mg	353	3.792	702
Na	74	3.77	144
К	4590	291.19	8888
Ва	9.4	0.1	18.7
HCO3	249	20.6	478
SO4	26	0.3	51.7
Cl	6040	280.4	11800
В	2.8	2.6	2.98
SiO ₂	70	1.35	138.6
TDS	11995.8	610	23381
рН	5	3.96	5.11
Osmotic pressure (Psi)	109.8		214
CaSO ₄ /KSP*100	1%		2%
SiO ₂ saturation:	52%		92%
BaSO ₄ /KSP*100			2152%

els at 50% will minimize fouling but some cleaning of membranes would be required. The frequency of cleaning is process dependent and would need to be determined experimentally in the large-scale system. The most common type of problem that RO membranes experience is calcium carbonate scaling. Simulation results, however, show that calcium carbonate concentration is only 2% of the saturation concentration. Therefore, it is less likely that the membrane fouls because of calcium carbonate. The other metal of concern for membrane fouling is barium that is not readily soluble and is the least soluble of all alkalineearth sulphates. Simulation results confirm this fact and shows that Barium Sulphate (BaSO₄) concentration in the concentrate stream is over the saturation concentration. Therefore, it is expected that barium sulphate will precipitate on the membrane wall and easily foul the membrane.

For all the reasons mentioned above, it appears that RO can be used to remove only 50% of water from the liquid extract and therefore other refining steps are required to further concentrate the liquid. For this purpose, a tertiary refining step was proposed to evaporate excess water until the desired nutrient concentration is obtained in the concentrate liquid extract. The excess heat used in the tertiary refining step is used to dry the treated biomass leaving the reactor, improving the overall economic feasibility of the process.



2.5 Liquid Fertilizer Market

All indicators and analysts predict a general upwards trend for both demand and pricing of fertilizers (Figures 2.2 and 2.3). In particular, there is strong growth in demand predicted for organic fertilizers. There are also social trends related to sourcing locally, creating jobs and economic opportunities in rural communities across Ontario, Canada, and the U.S.



Figure 2-2 Midwest Fertilizer Price Index (Jan 2003-2010)

The nutrients that are necessary for plant growth come to farmers fields from a variety of sources around the world. As a result, fertilizer production and use are subject to many global economic factors including commodity prices, transportation costs, the cost and availability of natural resources, and the value of the U.S. dollar. While North America is a major fertilizer producing region, demand is also significant. Current pricing of liquid starter fertilizers fluctuate between \$1.35/L to more than \$10.00/L depending on the volumes purchased and markets (consumer retail pricing vs. agricultural wholesale pricing).





A recently published report in April, 2011 by the Freedonia Group projects that the world demand for fertilizers will increase at an annual rate of 3.8% from 345 Million tonnes per year to 415 million tonnes per year in 2014. Multi-nutrient & organic type fertilizers will grow the fastest but still constitute a small segment of the overall market. According to a presentation by Roger Larson, President of the Canadian Fertilizer Institute to the House of Commons Standing Committee on Agriculture and Agri-Food, Canadian farmers spend about \$2.7 billion on fertilizer per year. In the U.S liquid fertilizer constitute 23 million tonnes per year or 40% of the overall market (~60 million tonnes/yr). Of the liquid starter fertilizer consumed in the United States, 5.1 million tonnes or 23% of the demand is in the great lakes regions of Wisconsin, Michigan, Ohio, Indiana and Illinois. There are 7 million acres of certified organic farms in the U.S and this market is growing at 12% Compound Annual Growth Rate. A proposed commercial plant processing 6 tonnes/hour of biomass will generate approximately 6,900 tonnes/yr of liquid starter fertilizer translating to just over 0.13% of the demand in the Great Lakes Region of the U.S. Adding the local demand in Southwestern Ontario, the production capacity of the plant will be less than 0.1% of the regional demand (Great Lakes Region). Ten plants the size of the one proposed will make-up less than 1% of the regional demand.

The produced liquid fertilizer from the liquid extraction process would enter the fertilizer market as liquid starter fertilizers with various NPK concentrations (e.g. 5-10-5, 4-5-5). All products will also have additional quantities of micronutrients. The produced liquid fertilizers have the advantage of having a spectrum of additional nutrients to the NPK, including: Ca, B, Cl, Fe, Mg, Mn, Mo, Na, Ni, S, and Zn. There are also social advantages associated with being able to position these products as bio-based fertilizer that is predominately produced through the recycling of nutrients. Initial markets for the liquid fertilizer would include cash crop farmers, greenhouse operators, landscaping, lawn-care and domestic floral markets in Southwestern Ontario.

2.6 Conclusions

Recovering nutrients from the liquid extract produced by an extraction reactor is an important section in the overall economic viability of the process. Further refining of the liquid extract is required to produce a liq-



uid fertilizer suitable for agricultural use. Regulations for fertilizer registration and the potential market of the produced liquid fertilizer were also examined.

- The desired nutrients in fertilizer are in the form of NH₄⁺ and NO₃⁻ ions (for nitrogen), phosphate ions (for phosphorous) and potassium ions (for potassium) for use (if containing pesticide or lesser plant nutrients)
- All of the valuable nutrients present in the liquid extract are in forms that can be readily absorbed into plants
- Fertilizer that is produced or imported into Canada require registration with the CFIA, with registration including a minimum guaranteed analysis and proper labels to be used with the fertilizer
- Fertilizers can be registered in three categories including fertilizer-pesticide, micronutrients, and low analysis farm fertilizer.
- Fertilizers in Canada that wish to be considered organic must be certified according to the Organic Products Regulations. To qualify, products need to have an organic content that is greater than 95%. Certified organic multi-ingredient products that contain less than 95% organic contents can use the words Organic Ingredients, subject to certain limitations.
- The concentration of nutrients present in the liquid following the nutrient extraction process are low and requires further refining and concentration to achieve appropriate levels for a commercial liquid fertilizer. The refining steps include:
 - Primary Refining Removal of 99.9% of suspended solids larger than 4 microns
 - Secondary Refining Reverse osmosis to remove 50% of the water in the extract
 - Tertiary Refining Evaporation to remove 95% of the initial water from the solution
- Reverse osmosis, due to fouling on the membrane because of certain nutrients present in the solution, is not sufficient to remove the required 95% of water
- A proposed commercial scale process based on the liquid nutrient extraction and recovery process developed by CENNATEK can produce approximately 6,900 tonnes of liquid fertilizer to the market

- Current market trends indicate a steady increase in fertilizer growth and demand for North America and worldwide.
- Fertilizer demand in the Great Lakes region is sufficient that the amount produced by the proposed plant will account for less than 0.1% of the regional demand



Chapter 3 Scale-Up and Financial Model

3.1 Liquid Extraction Process Flow Diagram

A scaled-up liquid extraction process was designed based on the results obtained from bench-scale testing outlined in Chapter 1. Figure 3.1 provides a process flow diagram (PFD) of the liquid nutrient extraction process outlining the inputs and outputs to the system and the various steps within the process. The overall process considered for the economic evaluation consists of the following specific components, with combiomass;

- Biomass dryer to reduce moisture content of biomass to 15% prior to pelletizing;
- Fertilizer refining units to concentrate nutrients in the liquid extract to produce a liquid fertilizer and recycle water to the extraction reactor;
- Fibre pellet mill;

Biomass bales are received at 15% moisture content



Figure 3-1 Process Flow Diagram (PFD) of the Liquid Nutrient Extraction Process

ponents outside of the main black box associated with equipment already present at an existing pellet mill:

- Receiving which would include weighing stations and storage of biomass bales;
- Size reduction of biomass to increase liquid extraction efficiency;
- Extraction reactor to remove water soluble nutrients;
- · Dewatering units to reduce moisture content of

and stored at the storage facility. On-site storage will be minimized to about 1000-3000 tonnes of material depending on operational capacity. On farm storage of bales under tarp, plastic wrapped, or unwrapped is expected to reduce moisture content to 15% at the facility gate. Regularly scheduled pick-ups of the feedstock from the producers would be conducted to maintain an inventory of approximately 3000 tonnes of feedstock at any given time when operating at full capacity. This amount equates to roughly 4 weeks of operation. The biomass is milled to reduce its size to 2mm using



hapter



Optimization and Scale-up of Liquid Nutrient Extraction and Recovery Process a size reduction unit. Milled biomass is conveyed into the nutrient extraction reactor to remove the nutrients. The treated biomass is passed through the dewatering units to separate water from biomass and to reduce the moisture content of biomass. Eighty percent of the liquid squeezed from the biomass in the dewatering stages is mixed with fresh water and is recycled to the nutrient extraction reactor. The other 20% of liquid is passed through fertilizer refining steps to remove 95% of the water. The concentrated liquid leaving the refining stages is pumped out to a mixing tank for final formulation into a number of liquid fertilizer concentrations for agricultural and horticultural applications. The expected labour requirement for the process is a minimum of one person to feed material to the process and monitor operations. Depending on the degree of automation that is integrated to the process, a second employee may be required.

3.2 Scale-up sizing and calculations

One important design feature for the extraction process is an effective agitation of the liquid-solid mixtures. Agitation of liquid-solid mixtures can be achieved with a variety of impeller designs, but efficiency and power requirements depend on several factors. The mixing and consequently the extraction efficiencies are controlled through these factors, which include:

- 1. The mixer type, diameter and configuration;
- 2. Operating speeds;
- 3. Diameter and height of the mixing tank;
- Physical properties of the mixture (i.e. specific gravity of solid and liquid as well as the vis cosity of the mixture);
- 5. Solids concentration in the reactor; and
- 6. Solids settling velocity.

The technical performance and economics of various designs need to be experimentally determined in order to make a good, cost-effective selection of the device in a process application. Generally there are three directions in which an impeller can move surrounding mixture: upwards, downwards, and radially outwards. The performance of mixers also involves high flow operation or high shear operation. Many mixing processes utilize a combination of two; however, there are some which can have only high flow or high shear.

Multiple impellers are commonly used in industry for mixing in tall slender tanks (height>2*diameter), where a single impeller may be insufficient to agitate all parts of the tank contents. Dual impeller systems comprised of different impeller designs operating together have been found to be efficient in mixing slurries (A. Kayode Coker, 2007). During mixing of fluids, it is essential to avoid solid body rotation and a large central vortex. When solid body rotation occurs, the liquid-solid contact reduces substantially as the fluid rotates as if it were a single mass. Centrifugal force of the fluid causes a central surface vortex being thrown outward by the impeller. Entrainment of air results if the vortex reaches an impeller, resulting in reduced mixing of the fluids. This situation can be averted by installing baffles on the vessel walls, which impede rotational flow without interfering with radial or longitudinal flow. Mounting the impellers in angular offcentre position or designing a non-symmetrical reactor would also prevent vortex formation. Geometric properties for standard agitation systems (shown in Figure 3.2) are as follows:

- Type of blade
- Reactor height (H): reactor height should equal the reactor diameter ($D_{_T}$) for a single blade design $H{=}D_{_T}$
- Number of impellers (blades) and shaft: multiple blade configuration is recommended if H >D_T
- Position of the blade: height of the agitator from the bottom of the reactor (E)=blade diameter (D_{a})
- Number of baffles: 4-6 (depending on the reactor size)
- Width of baffles (J): $J=1/12 D_{T}-1/8 D_{T}$
- Blade size to reactor size: $D_{A}/D_{T}=0.3-0.6$

The following factors have to be considered for a liquid extraction reactor design:

- H/D_T = 1
- L/D_A = 1/4
- W/D_A = 1/5
- E/D_A = 1





Figure 3-2 Standard Tank Configuration showing a Flat Six Blade Turbine Impeller (A. Kayode Coker, 2007)

Where:

D_^ =agitator diameter

H =liquid height

 D_{τ} =tank diameter

E =height of the agitator from the bottom of the tank

L =agitator blade length

W =agitator blade width.

The above considerations and empirical data from bench-scale experiments were used to develop the design of the liquid extraction reactor. In order to verify the efficiency of the reactor, a scaled-down cross-section of the reactor was built and tested on a bench-scale. As mentioned in Chapter 1, the scaleddown version had a 330:1 ratio in volume comparison to the original design. This ratio translates to about a 7:1 ratio in any given dimension of the reactor. The scaled-down reactor segment maintained geometric similarity to the large-scale design all corresponding dimensions of the smaller system having the same ratios as the large-scale design.

For effective scale-up analysis, kinematic similarity is required in the reactor. Kinematic similarity is achieved when all corresponding points in the smallscale and large-scale designs of the reactor have the same velocity ratios and move in the same direction between the new system and the model. Dynamic similarity requires geometric and kinematic similarity in addition to force ratios at corresponding points being equal, involving properties of gravitation, surface tension, viscosity, and inertia. With proper and careful application of this principle, scale-up from test model to large-scale systems is often feasible and quite successful (Couper J.R 2010).

Other considerations that played an important role in the design of the liquid extraction reactor included: construction, transportation, assembly, spatial consideration (height of typical farm buildings), loads on structural supports, overall weight, and materials. Extensive consultations were carried-out with numerous component vendors, machine shops and engineering consultants to develop practical limits, and basic guideline frameworks for the reactor design.

Once the reactor design and capacity was finalized and validated through empirical data from the scaleddown reactor, the remaining unit operations upstream and downstream of the extraction reactor were sized and quotations received from several vendors. The end result of the design effort has been the development of a six oven-dried metric ton per hour process to remove nutrients from agricultural residues and produce a high quality biomass fibre and liquid fertilizer product.

3.3 Liquid Extraction Process Capital Cost

The total capital cost of adding a liquid extraction process to a pellet mill with a capacity of 6DMT/hr is estimated at \$1,017,600. Table 3.1 provides the breakdown of these costs, along with power requirements.

Controls & Electrical: PLC controllers and a small central control station are required with level indicators and other measurement inputs used to monitor and control the process. All equipment will require to be wired to the central switchgear and will need electrical



Optimization and Scale-up of Liquid Nutrient Extraction and Recovery Process

CAPEX FOR 6 TPH LIQUID EXTRACTION PRO- CESS	PRICE	Max Hp	Max kWatt
1. Biomass Size Reduction Unit (1)	\$ 65,000.00	75	56
2. Material Conveyors (3)	\$ 35,776.00	8	6
3. Pumps (3)	\$ 9,100.00	22.5	17
4. Nutrient Extraction Reactor (1)	\$ 230,000.00	521	389
5. Preliminary Dewatering Unit (1)	\$ 26,801.00	4	3
6. Secondary Dewatering Unit (1)	\$ 100,000.00	20	15
7. Primary Fertilizer Refiner (1)	\$ 80,000.00	55	41
8. Secondary Fertilizer Refiner (1)	\$ 118,000.00	30	22
9. Tertiary Fertilizer Refiner (1)	\$ 100,000.00		
10. Liquid Storage (3)	\$ 10,000.00		
11. Controls & Electrical	\$ 48,000.00		
12. Piping & Structural Support	\$ 25,000.00		
13. Site Preparation, Installation & Assembly	\$ 60,000.00		
14. Engineering	\$ 50,000.00		
15. Capital Contingency	\$ 60,000.00		
TOTAL CAPEX	\$ 1,017,677	735.50	548.46

Table 3-1 Capital cost breakdown for the Liquid Extraction process

engineering stamps and ESA approvals.

Piping & Structural Support: The compact design of the reactor and process requires a level of elevation that would need structural supports. Piping will also be required to move fluids through the various stages of the process.

Site Preparation, Installation & Assembly: The reactor requires on-site assembly, and many of the components require mechanical installation that needs millwrights and custom fabrication of pieces.

Engineering: The Engineering consists of detailed electrical engineering for the plant, as well as structural engineering for construction of supports, mechanical drawings and schematics for piping, and installation of the unit, and assembly of the reactor.

Contingency: Given the firm pricing received on most

components and minimal custom, a low contingency amount of \$60,000 has been factored into the capital cost of the project.

The \$1,017,677 in estimated capital cost does not include the biomass dryer and pellet mill required to convert the fibres into fuel pellets. It is assumed that the unit will be an add-on to existing pelleting, briquetting, torrefaction, gasification, or heat and electricity generation processes. Locating the liquid extraction process at an existing facility would also create other synergies in relation to material storage and handling, leading to further reductions in capital costs. The treated biomass fibres can also be used for a variety of other applications, including animal bedding, kitty litter, or combined with a small scale combined heat and power (CHP) unit (<50MW) to produce electricity for sale to the grid and heat for internal usage. CHP's, especially in Northern Europe, are currently using agricultural biomass grown locally as fuels without densification. The process would provide these facilities with fertilizer that lowers their input costs, and a better quality fuel that will increase their efficiency and lower their overall maintenance and operations costs. Under the CHP model in Ontario, pelletization of the fuel would also not be required and the sale of the electricity would occur under the FIT program. The FIT (or Feed-in Tariff) program is "North America's first comprehensive guaranteed pricing structure for renewable electricity production. It offers stable prices under long-term contracts for energy generated from renewable sources, including biomass" (http://www. fit.powerauthority.on.ca). The program was established in 2009, and offers current rates of electricity generated from biomass of 13.8¢/kWh for processes <10 MW and 13.0¢/kWh for processes >10MW.

3.4 Financial Model Assumptions

For the purpose of developing the financial model, and analyzing the economics of our scaled-up process we applied the technology to an existing pellet mill, where

Table 3-2Processing Assumptions for Developing a Financial Model for the Liquid ExtractionProcess

Capacity and Production Assumptions			
Capacity Required	43,200	ODMT/yr	
Feedstock Moisture Content (At Facility Gate)	15%		
Green Capacity	50,824	GMT/yr	
Unit Gross Hourly Capacity	5.8	ODMT/hr	A1
Operating Hours Per Year	7446	hr/yr	A2
Production Losses (Due to dirt, fines and nutrient losses)	15%		
Initial Cost of Biomass (At Facility Gate)	70	\$/GMT	
Energy Production Assumptions			
Net Pellet Production	36,720	DMT/yr	
Moisture Content of Pellet	8%		
Gross Pellet Production (At 8% Moisture)	39,913	MT/yr	
Heat Content of Delivered Pellets	19.7	MJ/kg	B1
Ash Content of Delivered Pellets	1.5%		B2
Initial Cost of Pellet	120	\$/MT	
Liquid Fertilizer Production Assumptions			
Net Liquid Fertilizer Production	4,060,753	L/yr	C1
Net Liquid Fertilizer Production	4,935	t/yr	
Liquid Fertilizer Nutrient Level	5-10-5 and 4-4-5 plus		
Liquid Fertilizer Pricing Assumptions	1.35 and 2.75	\$/L	C2
Operating Cost Assumptions			
Electricity Cost	0.07	\$/kWh	
Natural Gas Cost	4.52	\$/MMBTU	
Waste Disposal (dirt, foreign debris assumed at 3% of weight)	70	\$/ton	



Optimization and Scale-up of Liquid Nutrient Extraction and Recovery Process the monthly depreciation costs of the pellet mill was assumed \$12,000 (\$144K in annual depreciation for a 6 TPH pellet mill). All maintenance and operations costs associated with the mill were included in the operating costs of the process. Table 3.2 provides details for other assumptions used to develop a financial model for the process.

Notes from Table 3-2:

A1: Based on lab data that show 30 min and 10:1 water to biomass ratio in the reactor sufficient to achieve desired levels of nutrient extraction.

A2: Operating hours based on 24hrs/day, 7 days/week operation with 15% downtime for equipment maintenance.

B1: Higher Heating Value (HHV) based on an average improvement of 3% in HHV values of raw biomass due to the nutrient extraction process.

B2: Ash content based on Silica content of about 1.5% and substantiated through lab trials

C1: Formulation developed based on nutrient content and marketability to agricultural industry and retail horticulture

C2: It is assumed that after three years of operations we will ramp up to 15% of the product marketed to retail home and garden suppliers at \$2.75/L, the remaining 85% of the production capacity is conservatively priced for agricultural industry based on current market pricing of \$1.35/L.

3.5 Financial Model Results

Based on the above assumptions, the results of the financial model for the proposed 6 TPH process are summarized in Table 3.3.

3.6 Conclusion

In conclusion, the liquid extraction process consists of a number of unit operations that have been integrated to achieve the desired process outputs. Detailed design and scale-up work was carried out on the nutrient extraction reactor and each of the unit operations required to feed material to the reactor and produce biomass pellet fuel and liquid fertilizer product. The scaled-up model for the nutrient extraction reactor will process 6 TPH of feed material with a total reactor

Table 3-3Financial Model for a 6TPH LiquidExtraction Process Applied to a Pellet Mill

Income Statement	Year End Totals
Operating Paraneters	
Inputs (ODMT)	43,200
Biomass Pellets Produced (8% moisture)	39,913
Fertilizer Produced (L)	
5-15-5 Starter (85% of nutrients)	3,721,370
4-4-5 Home & Garden (15% of nutrients)	339,382
Income	
Pellet Sales (\$120/t)	\$4,789,565
5-15-5 Liquid Fertilizer Sales (\$1.35/L)	\$5,023,850
4-4-5 Liquid Fertilizer Sales (\$2.75/L)	\$933,302
TOTAL INCOME	\$10,746,717
TOTAL OPERATING EXPENSES	\$8,933,768
EBITDA	\$1,812,948

volume of 35m³. To achieve this the nutrient extraction will take place at 10:1 water to biomass ratio with 30 minute residence time in the reactor. Bench-scale results using a scaled-down version of the reactor have shown that this amount of time and water should be sufficient to achieve adequate nutrient extraction.

The total capital cost for the 6 TPH system, minus the pellet mill, was estimated at just over \$1 Million (\$1,017,677). For the financial models it was assumed that the liquid extraction process will be used by an existing biomass pellet mill capable of processing 6 TPH of biomass pellets. Under this scenario, the combined pelleting and nutrient extraction process would generate \$10.75 Million/yr in revenues (44.6% of the revenues from the sale of fuel pellets and 55.4% from the sale of liquid fertilizer). The EBITDA (Earnings before interest, taxes, depreciation and amortization) for this process would be \$1,812,948 per year.



Chapter 4 Gasification and Torrefaction Literature Review

Energy sources derived from biomass and biomass waste have the potential to become the largest and most sustainable energy feedstock worldwide. Recent statistics indicate that over 220 billion dry tonnes of renewable resources are available worldwide in primary production. Only 5% of the energy that can be derived from these resources would account for about half of the world's primary energy demand. By 2007 however, energy from biomass accounted for only 10% of the 470 EJ of world primary energy demand, the majority of which came from non-commercial biomass sources. The potential for energy from biomass sources could reach up to 400 EJ/yr by the year 2050, or 25% of the world's primary energy demand. This would be accomplished with the use of agricultural residues and the growing of perennial energy crops such as miscanthus and switchgrass (Balat and Kirtay, 2010).

To produce energy in the form of electricity and/or heat, biomass undergoes one of several thermochemical processes that release the energy present within the lignocellulosic material of the biomass. Apart from combustion, the main thermochemical processes available for biomass include torrefaction, pyrolysis and gasification. A brief description of each process is given below:

Torrefaction

Torrefaction is defined as a thermochemical process or treatment of biomass generally in the range of 200-300°C. It is generally viewed as a pretreatment of biomass prior to further thermochemcial conversion processes (pyrolysis, gasification, combustion). The main motivations for a torrefaction pretreatment is to reduce the moisture content to near hydrophobic conditions, increase the energy density, improve the grindability and to produce a more uniform quality product (Prins et al., 2006).

Pyrolysis

Pyrolysis, along with combustion and gasification, are currently the three most common thermochemcial conversion methods for biomass. The reaction involves the conversion of biomass to various products in the absence of oxygen (Wang et al., 2008). The main desired product from the pyrolysis reaction is liquid tar, also referred to as bio-oil, while solid char and a mixture of gases with a high heating value are also produced at lower quantities (Arena et al., 2010). The reactions occur in the range of 200 to 900°C, with a decrease in tar formation and corresponding increase in gases with increasing temperature (Carpenter et al., 2010; Wei et al., 2011). Limited uses and a difficulty in the downstream processing of bio-oil have to date restricted wide application of pyrolysis technologies (Wang et al., 2008).

Combustion

Combustion has traditionally been the most common thermochemical conversion processes to produce heat and electricity from biomass (Wang et al., 2008). In conventional combustion-based systems, biomass is burned in the presence of air to generate a hot flue gas. This gas is then either used directly to provide heat or fed into a boiler to generate steam. Combustion equipment generally run at temperatures in the 800-900°C range or higher, depending on the type of combustor used. The main advantages of a combustion system are its proven, simple and low-cost technology, and the flexibility to use biomass of various moisture content and particle sizes. When compared to other thermochemical conversion processes, the greater possibility of NO_v, CO and particulate emissions, as well as a relatively inefficient conversion process of 20-30% to power generation, is seen as the main weaknesses of the technology (Peterson and Haase, 2009).

Gasification

Gasification is a thermal treatment that generally occurs in a temperature range between 600 and 1000°C. It is defined as a thermal decomposition in the presence of a gasifying agent, resulting in a gas mixture mainly composed of hydrogen, carbon monoxide, carbon dioxide and methane along with char and tar residues (Corujo et al., 2010). The higher reaction temperatures in gasification lead to an increased proportion of the gaseous products and smaller amounts of the char and tar. The entire reaction generally involves an initial pyrolysis reaction followed by combustion to provide heat for the endothermic pyrolysis reactions. Gasification has several environmental advantages over straight combustion reactions. The fuel



Optimization and Scale-up of Liquid Nutrient Extraction and Recovery Process gas produced from gasification is lower in both volume and temperature than products from a full combustion. This allows for an increased opportunity to clean and condition the fuel gas prior to subsequent use. In addition, the combustion of a gaseous fuel as opposed to a solid fuel can be more accurately controlled, allowing for a reduction in overall emissions (i.e. NO_x) (Stevens, 2001).

The previous report prepared by CENNATEK focused on the combustion of biomass following the proposed nutrient extraction pretreatment process. The following chapter reviews the gasification and torrefaction processes as alternatives for the treated biomass. The review includes the important reaction parameters and reactor configurations, any potential effects of a proposed liquid nutrient extraction pretreatment process on these processes, and an economic evaluation of two biomass gasification processes for comparison with combustion conversion processes also covered in the initial CENNATEK report for the OFA.

4.1 Gasification

The main product of gasification is a mixture of gases that can be used to generate heat and electricity, or further cleaned to synthesize hydrogen, a variety of liquid fuels and chemicals. The amount, composition and end-use are dependent on several factors, including reactor type, temperature, residence time and feedstock.

4.1.1 Gasification Process

The gasification process is composed of four main stages: drying, pyrolysis, oxidation and reduction. In the drying stage, water in the form of moisture is driven off the biomass and converted to steam by the heat generated from the higher-temperature zones. Pyrolysis begins above 200°C, producing solid char, liquid tar and a mixture of gases. Oxygen is then introduced, through air or a pure oxygen stream, at a temperature range of 700-1000°C. The carbon present in the biomass reacts with the oxygen to produce carbon dioxide, while hydrogen present in the biomass reacts to produce steam and heat. These reactions are exothermic in nature, causing the temperature to quickly rise to 1200°C. At this point, the amount of oxygen becomes insufficient, and the final reduction reactions occur between the hot gases and the remaining char. These endothermic reactions reduce the overall temperature of the reactor, and produce a gaseous mixture primarily containing carbon monoxide, hydrogen, methane and carbon dioxide. The overall gasification reaction can be summarized using the following equation (Balat and Kirtay, 2010):

Biomass + O_2 (or H_2O) --> CO, CO_2 , H_2O , H_2 , CH_4 + other hydrocarbons + tar + char + ash

4.1.2 Common Gasification Reactors

While other designs have been researched with varying degrees of success, the most widely used reactors for gasification are fixed beds, either updraft or downdraft, and fluidized beds, either bubbling, circulating or entrained.

Fixed Beds

Fixed bed gasifiers have a stationary reaction zone supported by a grate with the biomass fed into the top of the reactor. Fixed beds are generally considered for small to medium sized applications up to a few megawatts and are air-blown to produce low-energy gases. At larger scales, bridging of the feedstock due to uneven gas flow and the inability to achieve uniform heat and mass transfer without mixing are the main problems encountered. Other technical issues include a long residence time, and low efficiency and productivity. However, simple and reliable designs based on a fixed bed design can be used to economically gasify wet biomass on a small-scale (Wang et al., 2008). As mentioned, fixed beds can be designed in a downdraft or updraft configuration, with the resulting product gases varying significantly in composition (Stevens, 2001).

Downdraft Fixed Bed Gasifier

For downdraft fixed beds, the oxidizing air or oxygen stream travels down co-currently with the biomass flow. The gasification reactions occur at the bottom of the reactor in hot and shallow area that is composed of a layer of charcoal, as seen in Figure 4.1.

The majority of tars produced are broken down by thermal cracking as they pass the high temperature zone, with the resulting gaseous product exiting the reactor from the bottom. As a result, one advantage to the downdraft fixed bed gasifiers setup is it generally has the lowest amount of tar remaining in the product prior to further gas cleanup. In addition, the







Figure 4-1 Downdraft Fixed Bed Gasifier (http://www.greenstone.org)

absence of mixing or turbulence in the bed allows for relatively low levels of particulates to be passed with the product gas. Some alkali vapours, however, can still be contained in the gas phase and would need to be removed after exiting the reactor.

Updraft Fixed Bed Gasifier

As the name implies, an updraft fixed bed gasifier has the air or oxygen stream passing upward through the reactor, counter-currently to the flow of the biomass feed (see Figure 4.2). Heat in the raw gas is transferred to the biomass as the gas passes upwards, with the biomass going through the stages of drying, pyrolysis and gasification.

The exiting product gas is at a relatively lower temperature as compared to the downdraft fixed bed gasifier, leading to higher amounts of tar. This is due to the tar vapours that are formed during the pyrolysis step being swept upward in the reactor along with the product gas. Like the downdraft fixed bed, the lack of mixing and turbulence lead to low particulate levels as compared to fluidized beds.

Fluidized Beds

As mentioned, fluidized bed gasifiers (Figure 4.3) can be bubbling, circulating or entrained beds. The gas



Figure 4-2 Updraft Fixed bed Gasifier (http://www.greenstone.org)

used to fluidize the bed material, which consists of an inert material and 1-3% (by weight) of the biomass, includes air, oxygen, steam, recycled product gases, or a combination thereof. The turbulence provided by fluidization leads to effective mixing between the gas and solids, along with a more efficient heat transfer when compared to fixed beds. The improved mixing and heat transfer characteristics allows for fluidized bed gasifiers to be sized for medium to large-scale facilities (Wang et al., 2008).

The required heat needed for the endothermic gasification reactions can be derived through the partial oxidation of the air or oxygen (i.e. direct heating), or through the use of heat exchangers, preheated bed material, or other external sources (i.e. indirect heating). The resulting product gas is released at relatively high temperatures, leading to tars exiting with the product gas at levels in between those for downdraft and updraft fixed beds (Michel et al., 2011). The amount of particulates in the exit gas, in the form of



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Figure 4-3 Fluidized Bed Gasifier (http://www.fao.org)

ash and fines from the bed material, are increased due to the turbulence in the reactor. However the majority of the particulates can be removed through the use of cyclonic filters at the exit of the gasifier.

Comparison of Gasification Reactor Configurations

Table 4.1 summarizes the various advantages and disadvantages for the three gasification reactor configurations described above. The proper choice of gasifier is dependent on the end use, with fixed beds being more suitable for small and medium-sized applications, while a fluidized bed reactor would be better suited for large-scale applications due to better mixing and heat transfer.

4.1.3 Important Parameters

The distribution and yield of products from a gasification reaction are dependent on several factors. Apart from the different reactor configurations, reaction parameters such as residence time, temperature and pressure, gasifying agent and method of gas cleanup and use of catalyst are important. As for the biomass feedstock being used, the type of feedstock, moisture content, particle size and elemental content also play important roles in the resulting products.

Temperature and Pressure

The temperature at which gasification occurs has a significant effect on the product yield and composition (Michel et al., 2011; Stevens, 2001). Previous research looking at the effect of temperature found that the amount of gas produced increased with increasing temperature, while the amounts of char and liquids decreased for fluidized beds (Feng et al., 2011; Kitzler et al., 2011; Michel et al., 2011; Smolinski et al., 2010; Stevens, 2001). Higher temperatures also lead to hydrogen to carbon monoxide ratios of about 2, which is favourable for the production of high quality syngas for the synthesis of liquid fuels and chemicals (Michel et al., 2011). Feng et al. (2011) showed that increasing the temperature from 700 to 900°C lead to



Reactor Configuration	Amount of Tar Exiting Reactor	Amount of Particulates Exiting Re- actor	Residence Time	Advantages	Applica- tions
Downdraft Fixed Bed	Low	Low	High	•Simple and Reliable •Can gasify	Small to Me- dium Sized Gasifiers
Updraft Fixed Bed	High	Low	High	wet bio- mass	Small to Me- dium Sized Gasifiers
Fluidized Bed	Medium	High	Low	 Efficient Heat and Mass Trans- fer Excellent Mixing 	Medium to Large Sized Gasifiers

Table 4-1 Comparison of Gasification Reactor Configurations

an increase in dry gas yield, a significant increase in hydrogen yield, and a reduction in char and tar formation. The one disadvantage to increased temperature for electricity generation applications was a decrease in the lower heating value. This is due to the reduction in methane and other hydrocarbons, which have higher heating values compared to the other product gases beneficial for syngas production (Stevens, 2001). Kitzler et al. (2011) found a temperature of 850°C to be optimal for electricity generation in a pressurized gasification reaction of pelletized woody biomass due to the maximum production of methane. Conversely, Smolinski et al. (2010) reported that for steam gasification of selected energy crops, an increase in calorific value was observed with an increase in temperature (maximum 900°C). The increase in hydrogen yield in the product gas was given as the reason for increased calorific value. A summary of the change in product gas composition with temperature is shown in Table 4.2

The use of a pressurized gasification reactor has also been evaluated. The main advantage to this type of reactor is that in many applications, syngas would need to be compressed prior to its use. Producing a gas that is already pressurized would reduce the sometimes costly compression steps downstream of the gasifier. Another application of pressurized gasification is the use of supercritical water as a reaction medium. There are many potential advantages to the use of supercritical water (i.e. temperatures greater than 374°C and pressures greater than 22 MPa). There is no heat loss due to having no phase change, low char and tar formation, the ability to produce a hydrogen-rich gas with low amounts of carbon monoxide, and the ability to gasify wet biomass. However, pressurized reactors have the main disadvantage of increased costs, and to date the process is not commercially viable (Kong et al., 2008; Wang et al., 2008).

Gasifying Agent

As mentioned, the types of gases used to gasify the biomass include air, oxygen, steam, recycled product gas or a combination of the above. When using air, the nitrogen present dilutes the product gas, resulting in a low-energy gas with a heating value of 2.5-8 MJ/ Nm³. Air is therefore used in systems where the heat content of the fuel gas is not critical, such as co-firing heating systems and several types of electricity generation systems. Using pure oxygen eliminates the nitrogen dilution, resulting in a medium-energy product



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		Product Gas Composition (% Volume)				
Biomass Feedstock	Temperature (°C)	Methane	Hydrogen	Carbon Dioxide	Carbon Monoxide	
Miscanthus	650	4	52	33	11	
Miscanthus	700	2	59	31	8	
Miscanthus	800	2	63	27	8	
Miscanthus	815	9	42	23	26	
Miscanthus	860	8	46	23	24	
Miscanthus	880	8	46	22	24	
Miscanthus	900	2	65	25	8	
Pine Sawdust	900	4	47	32	16	

Table 4-2 Effect of Temperature on Product Gas Composition

(Michel et al., 2011; Feng et al., 2011; Smolinski et al., 2010)

gas with an average heating value of 10-20 MJ/Nm³. The majority of current designs use oxygen, either in air or on its own, as an oxidizing agent used to generate the heat required for the subsequent endothermic gasification reactions.

In the absence of oxygen, steam can also be used as a gasifying agent to produce a medium-energy product gas through pyrolytic gasification. However, the lack of oxygen as an oxidizing agent requires the process to have an external or indirect heating supply for the endothermic gasification reactions (Figure 4.4). Alternatively, air or oxygen can be combined with the steam to provide the necessary heat through partial combustion. Heating values for steam gasification are similar to oxygen-fed gasification, with average values of 10-15 MJ/Nm³. Carbon dioxide has also been evaluated as a gasifying agent that would require an indirect heating source and has shown some initial promise (Wang et al., 2008).

Gas Cleanup/Conditioning and Use of Catalysts

Gas cleanup and conditioning refers to the removal or conversion of char, tar and other contaminants to obtain a cleaner product gas and/or to change the composition of the product gas. There are five main types of contaminants: particulates, alkali compounds, tars, nitrogen-containing compounds and sulphur. These impurities can interfere with downstream processes or components and can also lead to emission problems. Particulates are solid material that remains entrained in the product gas, and primarily consists of inorganic ash, unconverted biomass or char, and in the case of a fluidized bed reactor, solid material from the bed. Char can undergo devolatilization reactions and become less reactive than fresh biomass, while the presence of unconverted biomass contributes to low conversion efficiencies overall. Alkali compounds are components of particulate matter that contain high alkali content (e.g. potassium). As with the combustion of biomass, the presence of alkali compounds can have a significant negative effect in the gasification reactor (sintering, agglomeration, corrosion, defluidization) as well as in downstream equipment (Wang et al., 2008).





Figure 4-4 Example of Gasifier with Indirect Heating (http://www.ecn.nl)

Equipment generally used to remove particulates includes cyclones (to remove coarser particles), barrier filters, electrostatic filters and wet scrubbers (to remove fine particles) (Wei et al., 2011; Stevens, 2001).

The term tar is a generic term for a wide range of oxygenated organic compounds that are produced during the partial reaction of the biomass feedstock. During the reaction, biomass is dehydrated and then volatilizes as it is decomposed. This volatilized material can then either further decompose to produce gas or further dehydrate, condense and polymerize to produce tars (Stevens, 2001). There are four main types of tar formation during gasification: primary products from lignocellulosic material (e.g. furfural), secondary products (e.g. phenolics), alkyl tertiary products (e.g. methyl derivatives of aromatic compounds) and condensed tertiary products (e.g. condensed PAH's). The composition is dependent on the temperature and residence time, changing from primary to tertiary products as the reaction temperature increases and is generally difficult to remove. Problems associated with tar formation are similar to problems with particulates and include condensing on cooler components (leading to plugging and fouling) as well as the formation of char and coke in further dehydration reactions (Michel et al., 2011; Balat and Kirtay, 2010; Stevens, 2001).

While there are both physical methods (cooling the product gas to condense the tars into droplets and

then removed using particulate removal technologies) and thermal methods (thermal cracking at temperatures greater than 1200°C) to remove tars, the use of catalysts are most frequently used during or after the gasification process to both remove tars at lower temperatures as well as improving the final composition and yield of the gaseous products (Bulushev and Ross, 2011; Michel et al., 2011; Stevens, 2001). The types of catalysts used can be broken down into two categories, catalysts that are used in the gasification reactor to reduce the amount of tar formation, and catalysts that are used downstream in a secondary reactor primarily for hydrocarbon and methane reforming. The main reaction for tar reduction, as well as adjustment of the hydrogen to carbon monoxide ratio, is the water-gas shift reaction:

 $CO + H_2O --> CO_2 + H_2$

For reforming reactions, methane or other hydrocarbons are converted to hydrogen and carbon monoxide by reacting with steam in the presence of a proper catalyst according to the following equation:

 $C_nH_m + nH_2O \leftrightarrow nCO + (m/2 + n)H_2$

The choice of specific catalysts is based on the type of gasifier and the type of biomass being used. The main criteria for the choice of catalysts are summarized in Table 4.3.

Catalysts employed in the main reactor are typically

Table 4-3Main Criteria for Choice of Cata-lysts for Gas Cleanup

Effective in the Removal of Tars
Capable of Reforming Methane
Able to Provide a Suitable Ratio of Hydro-
gen to Carbon Monoxide
Resistant to Deactivation
Easily Regenerated
Inexpensive

(Sutton et al., 2001)

natural minerals such as olivine and dolomite, which have the advantage of low cost, high attrition resistance and their ability to decompose tar, as well as alkaline metal oxides (Kitzler et al., 2011; Michel et al.,



2011; Balat and Kirtay, 2010; Stevens, 2001). For hydrocarbon and methane reforming, nickel-based catalysts have been widely used, either on their own or combined with other metals such as molybdenum and cobalt, while precious metals such as platinum, ruthenium, rhodium and palladium have also been shown to effectively catalyze reforming reactions (Ronkkonen et al., 2011). Metal-based catalysts are mounted on supports such as silica, alumina and zeolites, with zeolites found to maintain catalyst activity the longest (Stevens, 2001).

Nitrogen containing compounds are primarily ammonia and come from the protein and other nitrogen components in biomass. Their presence can lead to the formation of NO_v gases, which have strict emission regulations. While the amount of NO_v is not generally high in gasifiers, total emissions need to be taken into account. NO, can generally be destroyed using similar catalysts for tar cracking, as well as the use of wet scrubbers. Sulphur is generally not a problem due to the low amounts present in most biomass feedstocks, but low levels may still be a problem for applications that produce high quality syngas where the presence of sulphur could have an effect on certain types of catalysts or fuel cells. Removal methods include the use of wet scrubbers, conversion to hydrogen sulphide or adsorption to metal oxide pellets (Stevens, 2001).

4.1.4 Commercially Available Processes

The use of gasification to produce heat, power and other products from biomass has steadily increased in recent years. Systems employing close-coupled biomass gasification-boiler systems, in which the produced gas is fed into a boiler to produce steam for combined heat and power, are more viable and commercially available. Two-stage gasification systems that involve gas cleanup/conditioning after gasification and prior to use in an engine or turbine are more in the developmental and demonstration stage (Peterson and Haase, 2009). Table 4.4 lists a variety of commercially available biomass gasification processes, mainly for CHP applications, involving a variety of reactor types, feedstocks and gasifying agents.

4.1.5 *Effect of Nutrient Extraction Pretreatment on Gasification*

The removal of nutrients using a liquid extraction process was initially designed with the end use of the treated biomass as a solid fuel feedstock for combustion to produce heat and/or electricity. The following section examines the effects that the nutrient extraction pretreatment method would have on the gasification process and to ensure that it is an effective pretreatment method for alternative thermal conversion processes.

The main purpose of the nutrient extraction pretreatment is to reduce the amount of water soluble nutrients due to their negative effects on the combustion process, namely the formation of deposits, slags, fouling and corrosion on reactors and other equipment used in combustion. The presence of these nutrients would also have similar effects on gasification equipment, mainly due to the presence of alkali metals. Potassium present in the biomass vaporizes to form KOH and KCl, which can react with chlorine and sulphur to form sulphates and with silica to form silicates. The resulting eutectic mixtures can then either form deposits in the gasification reactor (due to the resulting ash having melting temperatures below 700°C), or vaporize and exit with the product gas. Condensation of these vaporized solids would then begin at around 650°C with deposition occurring on cooler surfaces of downstream equipment such as heat exchangers and turbine blades. The deposits in the gasification reactor either stick to reactor walls or leave sticky deposits on the surface of bed particles, leading to bed sinterization and defluidization.

Overall the presence of nutrients is less of a problem in gasification systems when compared to combustion systems, but their presence must still be addressed to avoid unwanted problems. The proposed end-use of the gas also plays a factor in the importance of removing the nutrient material. Boiler systems can incorporate a cooling of the product gas and a physical removal of bulk particles where the presence of ash deposition is not a significant issue, while gas turbines require a relatively cleaner fuel gas since they operate at high rotational speeds where any type of deposition would cause an imbalance and failure. In addition, non-deposition issues such as the corrosion of metal surfaces and the inactivation of catalysts used in gas conditioning are also important considerations when dealing with the presence of the eutectic mixtures in the product gas.

To reduce the specific problems related to ash deposition within the reactor, two suggested pretreatments





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Company name	Location	Type of Gasifier	Feedstock	Power (MW _e)	Gasifying Agent
Cratech	USA (Texas)	Fluidized Bed	Wood, other solid fuels	5-100 MW	Air/oxygen/ steam
Thermogenics	USA (New Mexico)	Fixed bed, down- draft	Many	0.6-60 MW	Air
Nexterra	Canada (BC)	Fixed bed, updraft	Wood, other solid fuels	2-42 MW	Air/oxygen/ steam
Diversified Energy	USA (Arizona)	Molten metal bed	Any carbon source	10-40 MW	Steam/oxy- gen
Chiptec	USA (Vermont)	Fixed Bed	Wood	0.44 - 37 MW	Air
Frontline bioenergy	USA (Iowa)	Bubbling Fluidized Bed	Wood, other solid fuels	29 MW	Air/oxygen
Primenergy	USA (Okla- homa)	Fixed bed, updraft	Wood, other solid fuels	Up to 12.8 MW	Air
PRM Energy	USA (Arkansas)	Fixed bed, updraft	Wood, other solid fuels	0.9-11 MW	Air
Entimos	Finland	Moving Grate	Biomass, wood, residues	1-7 MW	Air
AESI	USA (Kansas)	Moving Grate	Wood, Ag byprod- ucts, densified fuel	0.17-5.8 MW	Air
Carbona Corporation	USA (California)	Bubbling Fluidized Bed	Woodchips, twigs, residues	5.5 MW	Air
Bijendra Heavy Elec- tricals	India	Circulating updraft fluidized bed	Biomass, waste, etc.	Up to 4 MW	Air/Steam
Babcock & Wilcox Volund	Denmark	Fixed bed, updraft	Woodchips	3.5 MW	Air
Xylowatt	Belgium	Co-current fixed bed	Wood, agricultural residues	0.3-1.5 MW	Air
BioSynergi	Denmark	Unknown	Woodchips	0.25-1 MW	Air
ECN	Netherlands	Circulating fluid- ized bed	Wood residues	0.8 MW	Air (indirect)
Community Power Corporation	USA (Colorado)	Fixed bed, down- draft	Wood, other solid fuels	0.25-0.75 MW	Air
Thompson Spaven	United King- dom	Fixed bed, down- draft	Biomass	Up to 0.5 MW	Air
ThermoChem Recov- ery International	USA (Maryland)	Fluidized Bed	Biomass, liquid	N/A	Steam

Table 4-4 List of Selected Commercially Available Biomass Gasification Systems



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are a liquid extraction method similar to the proposed method and mechanical fractionation. While mechanical fractionation can reduce up to 50% of the total ash from biomass, the elemental content of the remaining ash remains unchanged and can still cause problems in the reactor and further downstream (Wang et al., 2008). Standard leaching extraction methods are reported to have low extraction efficiencies for certain biomass feedstock (i.e. wheat straw) due to the complex structure of the straw limiting the extraction of nutrients. Our proposed method, which incorporates size-reduction and high-agitation mixing in the liquid extraction process, reduces this potential problem.

Another key factor in the liquid extraction process that may have an effect on the gasification process is the size reduction of the biomass feedstock. The reduction of biomass prior to liquid extraction improves the extraction efficiency by increasing contact area between the biomass and liquid. Biomass feedstocks for gasification reactions can be fed as-is (at different sizes) or in a pelletized form. Therefore the effect of biomass particle size on both gasification and pelletization processes were researched to determine the optimal size range.

Two studies in literature examined the effect of biomass particle size on the gasification reaction using non-densified biomass. Rapagna and Latif (1997) examined the influence of both temperature and particle size on steam gasification of almond shells in a fluidized bed reactor. Several particle sizes, ranging from 287 microns to 1090 microns, were used along with alumina particles for the fluidized bed material. In terms of gas yield, a decrease was observed as the particle size increased, with the effect less significant as the gasification temperature increased from 600 to 800°C. The reduction in yield with increased particle size was speculated to be a result of the increase in the effective thermal conductivity, which in turn is due to the increase of radiation contribution to heat transfer. The effect of particle size on the product gas composition was also examined. Again, the amount of each individual gas decreased with an increase in particle size and became negligible with increased temperature. The effect of particle size on heat transfer was used to explain the decrease in the individual gases. As the particle size increases, the heat transfer resistance also increases, leading to a lowering of the temperature inside the particle at which devolatilisation occurs. At this point, estimated at a particle size of 1 mm, the reaction is controlled by heat transfer rather than kinetics. The reduced change in gas compositions with increased temperature is related to the fact that the molar concentrations of the individual gases are linked together by the equilibrium in the water-gas shift reaction at these conditions. Finally, the effect of particle size on char and tar formation was examined. The smallest particle size of 287 microns produced negligible amounts of char and tars for all temperatures tested, while medium sized particles (533-747 microns) had large amounts of residual solids at lower temperatures but only 2-3% by weight at higher temperatures. Larger particles also showed a decrease in residual solid content with increased temperature, but even at the highest temperature evaluated had the residual solids account for 20% of the total product. It was concluded that extra and/or intra-particle thermal resistances have a significant effect on particles greater than 1 mm and should be taken into account when designing a gasifier.

A more recent study also examined the effect of particle size on both gas yield and gas composition for an externally heated fixed bed reactor using pine sawdust as a feedstock and a calcined dolomite catalyst. Four size ranges (< 125 microns, 125-149 microns, 149-177 microns and 177-250 microns) were examined at reaction temperatures ranging from 700-900°C. Unlike the previous study, an increase in particle size lead to an increase in gas yield. However, the reason for the increase was due to a decrease in the biomass feeding rate due to the larger size, leading to increased gas residence time and allowing for more complete gasification. However, the increase in yield was not significant. In terms of the effect on gas composition, the amount of hydrogen and carbon monoxide increased as the particle size decreases, while the amount of carbon dioxide and methane decreased. It was concluded that as particle size decreased, reactions are mainly controlled by pyrolysis and gasification processes, while reactions are controlled by gas diffusion processes as the particle size increases. As a result, smaller particle sizes are more advantageous to the production of high quality syngas (i.e. more hydrogen and carbon monoxide). Other published research used a specific biomass particle size in their gasification experiments, ranging from 130 to 600 microns.

For the pelletization of biomass, the majority of studies indicate that biomass fed into a pelletizer should be below 3 mm for best results. However, there have





been few studies that determined the minimum or optimum size within this range. Stelte et al. (2011) looked at the effect of particle size of beech woody biomass on the pelletizing pressure, with a defined trend of increasing pressure with decreasing particle size from 2.8 mm to less than 0.5 mm. The trend was a result of increased surface area of contact between the biomass and the walls of the pelletizer with decreased particle size, leading to a greater amount of friction. Chaiyaomporn and Chavalparit (2010) examined the effect of particle size on the percent of biomass pelletized and found that a mixture of particles less than 2 mm performed best compared to particles in the range of 0.5-1 mm and less than 0.5 mm. Based on these results, the size reduction of biomass should be limited to include particles in the range of 2-3 mm or less. The proposed extraction process uses mills that reduce the particle size to less than 2 mm prior to the extraction process. It is therefore concluded that the effect of size reduction required in a liquid extraction process does not negatively affect the efficiency of the biomass gasification process.

4.1.6 Economic Evaluation

Gasification is one alternative biomass thermal conversion process to combustion. In the previous report completed by CENNATEK, an economic evaluation of several scenarios involving the combustion of treated biomass (using the liquid extraction process) to produce electricity was conducted. Various biomass pellet selling prices were used to determine the cost of power generation using biomass combustion. This report examines two case studies of power generation from gasification, using a biomass feedstock, to compare the economic viability of these processes versus standard combustion processes. The first case involves a direct heated gasifier (using air as the gasifying agent) to produce electricity for a 0.5 MW generator, while the second case involves the use of an indirect heated gasifier (using steam as the gasifying agent) to produce electricity for a 3 MW generator.

4.1.6.1 Direct Heated Gasifier

Wei et al (2011) evaluated the use of syngas produced from biomass gasification to produce electricity for a micro-scale (i.e. 0.5 MW or less) generator. The generation station scenario was based in the state of Mississippi, using syngas produced from a downdraft, fixed-bed gasifier using air as the gasifying agent. The following conditions were used for the given process scenario:

- All potential hurdles to the gasification technology have been overcome and the process has reached commercially mature levels
- Calculations are on a "before income tax" basis
- Electricity capacity of 0.5 MW
- Biomass feedstock wood chips (LHV of 18.7 MJ/ kg, 1% ash content, <20% moisture content)
- No transport costs, as biomass is available on-site or within 32 km
- Minimal construction required

The gasification facility (Figure 4.5) is divided into four main sections: Feedstock preparation (size reduction and drying), Gasification, Syngas cleaning (cyclone, heat exchanger, filter set) and Electricity Generation (gas tank, engine and generator). The engine is started with conventional fuel (gasoline or diesel) before being replaced with the syngas.

The model used to determine capital and operating costs consisted of 14 principal equations. The capital costs include equipment, installation, construction, property tax and insurance, while the operating costs are divided into variable costs (feedstock, tax, utilities, labour, waste treatment, maintenance) and fixed costs (insurance, depreciation, overhead, general expenses). Assumptions for the model are given below:

- Facility life of 20 years
- Straight line depreciation
- 4% Interest Rate
- 1 shift/day 52 weeks/year, 5 days/week, 8 hours/ day for a total of 2080 hours
- 0.6 operators required for one shift at a rate of \$18.5/hour
- Biomass to Electricity efficiency of 25% (70% if heat generated used for heating)
- Cost of electricity \$0.0718/kWh
- Cost of biomass feedstock \$35/ton

The various costs associated with the model are summarized in Table 4.5.

Based on the electricity capacity, the number of working hours and the efficiency of the power facil-





Figure 4-5 Layout of Proposed Direct Heated Gasification Process (Wei et al., 2011)

ity, the model estimated an annual electricity yield of 910,000 kWh. With total annual production costs of \$164,377.91, the final unit cost of electricity production was estimated at \$0.18/kWh or \$180/MWh.

4.1.6.2 Indirect Heated Gasifier

Cattolica et al. (2009) examined the use of syngas produced from an indirectly-heated gasifier to produce electricity for a 3 MW generating station. The analysis was based on construction of the generating station at an existing landfill, Miramar Landfill in San Diego County California, where 1.4 million tons of waste are processed and disposed annually. The proposed process incorporates an indirectly heated fluidized bed process that includes two separate reactors for gasification (i.e. the endothermic reaction) and oxidation (i.e. the exothermic reaction). In this design (Figure 4.6), dried biomass comes into contact with steam and hot fluidized sand in the gasification reactor to produce gas and char. The char and fluidized sand then flow to the second oxidation reactor where the char is burned with air to produce exhaust gas and heated sand. The heated sand then returns to the gasification reactor to provide the energy for gasification. The produced gas is cooled and filtered before passing through a enginegenerator set to produce electricity.

The following conditions and assumptions were used for the proposed process:

- Electricity capacity of 3 MW_e
- Feedstock mixture of pre-chipped biomass residues found in the landfill that have been processed average moisture content of 30%, ash content of 5% and an HHV of 7000 BTU/lb
- Cost of processed biomass feedstock \$15/ton
- Natural Gas cost of \$11.00/MMBTU
- 24/7 operations
- Construction period of 9 months for all capital equipment
- 20 year project life
- Inflation rate of 2.1%
- Land lease cost of \$100,000/year
- Sale of waste heat for increased revenue is assumed to be zero

The capital costs for the gasification and gas cleanup equipment were estimated at \$6 million with no detailed breakdown of costs provided. The equipment included in the process is summarized in Table 4.6. The cost of the engine-generator set was set at \$750/





Table 4-5	Capital	and	Operating	Costs	for
Proposed	0.5 MW	Pow	er Plant		

Capital Costs	Amount (US Dol- lars annually)
Equipment	\$31,149.61
Building	\$8,186.02
Installation	\$7,791.51
Property Insurance	\$2,334.17
Auxiliaries	\$2,334.17
Overhead	\$1,167.08
Interest	\$29,522.27
Equity Recovery	\$12,295.47
Total Annual Capital Costs	\$94,780.30

Operating Costs	Amount (US Dol- lars annually)
Feedstock	\$24,492.31
Electricity	\$4,290.26
Labour	\$26,563.47
Waste Treatment	\$279.44
Maintenance	\$2,367.04
Contingency	\$5,802.54
General Expenses	\$5,802.54
Total Annual Operating Costs	\$69.597.61
Total Annual Cost	\$164,377.91

kW, equating to a total capital cost of approximately \$8,275,000.

The various operating costs, summarized in Table 4.7, were broken down as a percentage of the total operating costs (not including cost of feedstock), with no specific dollar amounts given for each.

Based on the determined capital and operating costs, a model was used to calculate the annual cost per MWh of electricity produced, which for the Miramar Landfill Site was \$119.20/MWh. With the selling of electricity expected to be only \$98.40/MWh in California based on a Feed-in Tariff system, the net present value of the process would be -\$2.7 million. In order to potentially reduce production costs, two other scenarios were ex-



Figure 4-6 Layout of Proposed Indirect Heated Gasification system (Cattolica et al., 2009)

Table 4-6Capital Costs and Equipment forProposed 3 MW Gasification Process

Capital Equipment	Cost
1 Gasification Reactor	
1 Oxidation Reactor	
1 Biomass Drier	
4 Heat Exchangers	\$6,000,000
2 Flash Drums	
1 Evaporative Cooling Tower	
2 Filters	
Engine-Generator Set	\$750/kW
Total Capital Costs	\$8,275,000

amined; location at a Marine Corp Air Station adjacent to the landfill, and a generic site with optimized parameters in order to obtain a positive net present value. Use of the Air Station resulted in a higher product cost (\$124.63/MWh), while the optimized generic site was able to sell the produced electricity at the feed-in rate of \$98.40/MWh while maintaining a positive NPV. In order to reach this value, however, feedstock costs were assumed to be only \$2/ton, and land lease costs at \$30,000/year (as opposed to \$100,000/year). Current Ontario FIT (Feed-in Tariff) prices for processes producing less than 10 MW of power from biomass



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Operating Cost	Percentage of Total Operating Costs (%)
Labour	42
Maintenance	15
Equipment Lease	11
Land Lease	9
Environmental	6
Other Direct Costs	5
Utilities	5
Consumables	3
Disposal	2
Insurance	2

equates to \$138/MWh. As a result, the proposed gasification system would have an improved ability to have a positive net present value. However, the costs are still higher as compared to biomass combustion systems, as detailed in the next section.

4.1.6.3 Comparison of Gasification and Combustion Scenarios

Table 4.8 compares the annual cost per MWh of electricity produced for the above two scenarios with several scenarios involving the combustion of biomass as determined in the previous report completed by CEN-NATEK.

The data shows that the two gasification systems examined have higher costs compared to combustion scenarios with a biomass feedstock cost of \$110/ton. The costs for biomass feedstock in the gasification scenarios (\$35 and \$15/ton) were much lower when compared to the anticipated costs of biomass feedstock used in the combustion scenarios. It is clear that the use of a gasification system versus a combustion system to produce electricity does not represent any significant advantage based on the associated capital and operating costs. Alternative uses for the gasification process, including the production of syngas as a replacement for natural gas in areas where no natural gas pipelines exist, may be more economical based on the capital and operating requirements. Table 4-8Annualized Cost of Electricity forProposed Gasification and Combustion Processes

Thermal Conversion Method	Details	Cost of Produced Electricity (\$/MWh)
Combustion	Scenario 1 from previous report (includes nutrient extraction, nutri- ent recovery, silica extraction and pu- rification, pelletiza- tion)	\$72.58
Combustion	Scenario 9 from previous report (includes nutrient extraction, nutrient recovery and pel- letization)	\$88.75
Combustion	Scenario 17 from previous report (includes pelletiza- tion only)	\$102.76
Gasification	Direct-Heated, 0.5 MW	\$180.00
Gasification	Indirect-Heated, 3	\$119.20

4.1.7 Alternative Products from Gasification Processes

There are many additional products and uses besides electricity that can be produced using the gaseous mixture resulting from a biomass gasification reaction.

4.1.7.1 Hydrogen

Hydrogen can be produced from biomass using both thermochemical processes such as gasification and biological processes such as biophotolysis and dark fermentation, although thermochemical processes are more efficient and have lower production costs (Balat and Kirtay, 2010). As mentioned, the use of catalysts for gas cleaning and conditioning strongly influences the composition of the final gas. Gasification followed by water reforming of methane to hydrogen



and carbon monoxide and a water-gas shift reaction of carbon monoxide to hydrogen and carbon dioxide would increase the amount of hydrogen produced. Subsequent adsorption of carbon dioxide using an adsorbent would lead to a purified hydrogen gas, while the remaining syngas can be further processed. While current yields of hydrogen from biomass are relatively low and the cost of producing hydrogen from gasification is relatively high, long-term modelling scenarios predict that hydrogen production from biomass gasification will be competitive with hydrogen from fossil fuel sources with CO2 capture and storage technologies (Balat and Kirtay, 2010).

4.1.7.2 Liquid Fuels

Another popular alternative for syngas produced from the gasification of biomass is in the synthesis of liquid fuels. The Fischer-Tropsch reaction is used to produce hydrocarbons of variable chain length from carbon monoxide and hydrogen using the following reaction:

Where $-CH_2$ - is a precursor for long-chain hydrocarbons that are alternatives to diesel, gasoline and kerosene produced from petroleum sources. A hydrogen to carbon monoxide ratio of 2:1 is ideal for Fischer-Tropsch reactions, indicating that steam reforming and water-gas shift reactions are necessary to produce the proper ratio (Bulushev and Ross, 2011). The removal of carbon dioxide and contaminants prior to Fischer-Tropsch synthesis is important as they can lower the activity of catalysts typically used in the reaction (e.g. cobalt) (Wang et al., 2008).

Methanol and Dimethyl ether are two other liquid fuels that can be synthesized from syngas. They represent clean liquid fuels that can be used as substitutes for gasoline and diesel fuels, while methanol is also widely used as a reactant in the production of biodiesel. Methanol is produced from syngas through the hydrogenation of carbon monoxide and/or carbon dioxide using the following reactions:

Dimethyl ether is then synthesized by further dehydration of methanol. Typical catalysts for methanol production as copper, alumina and zinc oxide, while dimethyl ether production use a silica-alumina catalyst (Wang et al., 2008). Like Fischer-Tropsch synthesis, a 2:1 hydrogen to carbon monoxide ratio is favourable and is best optimized through the water-gas shift and steam reforming reactions (Bulushev and Ross, 2011; Michel et al., 2011).

4.1.7.3 Bio-based Products through Syngas Fermentation

Syngas produced from biomass gasification can be further processed through a biological fermentation process to produce several bio-based products including organic acids, polyesters and alcohols. Several types of bacteria have been examined that use syngas as a source of carbon and energy to produce liquid fuels (butanol and ethanol), hydrogen and polyesters. Unlike the other synthesis reactions described above, these biological conversions do not require a specific carbon monoxide to hydrogen ratio or high temperature and pressure processes. However, low growth rates and mass transfer limitations and product inhibition are some of the problems associated with largescale production (Bulushev and Ross, 2011; Wang et al., 2008).

4.2 Torrefaction

4.2.1 Torrefaction Technology

Torrefaction is a thermochemical process that is considered a thermal pretreatment technology. The process generally occurs in the range of 200-300°C, with the main objective being the removal of oxygen while maintaining a solid product. Also referred to as slow or mild pyrolysis, the removal of oxygen is accomplished by the removal of moisture and low weight organic volatile components while also depolymerising and partially decomposing hemicellulose.

When using biomass that has not been subjected to a torrefaction (or other) pretreatment process, several problems associated with their use in thermochemcial conversion processes can occur (Chen et al., 2011; van der Stelt et al., 2011; Pimchuai et al., 2010; Deng et al., 2009; Bridgeman et al., 2008; Prins et al., 2006):

- Biomass has high moisture content and is hygroscopic in nature, therefore having a tendency to absorb moisture after it has been dried;
- The high oxygen content and low calorific value



Optimization and Scale-up of Liquid Nutrient Extraction and Recovery Process does not make it an ideal fuel for combustion or for co-firing with coal;

- Difficulty in grindability as compared to coal;
- Low energy density;
- Low bulk density;
- Biomass is thermally unstable, potentially leading to formation of condensable tars in gasification processes;
- Lack of uniformity in feedstock.

The resulting changes to the biomass after torrefaction reportedly address the majority of the problems listed above to various extents. The depolymerisation of the hemicellulose removes hydroxyl (OH) groups. This fact, along with the formation of unsaturated structures, decreases the locations for hydrogen bonding to occur. Increased locations for hydrogen bonding are the main cause of biomass absorbing moisture; therefore the torrified biomass is more hydrophobic (Basu, 2011; Chen et al., 2011; Pimchuai et al., 2010).

The reduction of oxygen lowers the O/C (oxygen/carbon) ratio of the biomass, as seen in the Van Krevelen diagram (Figure 4.7). The diagram shows the elemental composition of a feedstock based on their values of hydrogen, oxygen and carbon. As oxygen and hydrogen (shown as ratios to carbon) are reduced in the torrefaction process, biomass begins to approach coal in composition, allowing for easier co-combustion with coal (van der Stelt et al., 2011; Couhert et al., 2009). The relatively larger reduction in oxygen and hydrogen (compared to the energy-rich carbon) also leads to an increase in calorific value approaching values for coal (20-24 MJ/kg). Energy density is also increased with torrified biomass. While roughly 30% of the initial weight is lost, only 10% of the energy content is lost, leading to a more energy dense product on a mass basis (Bridgeman et al., 2010; Uslu et al., 2008).

Torrified biomass is also more porous than raw biomass, therefore causing more fragility as mechanical strength is lost (Uslu et al., 2008). This improves the grindability of biomass, allowing it to be pulverized and co-fired with coal in the same facility. The improved grindability also significantly reduces the electricity/ energy requirements for the size reduction of biomass, with estimates indicating an energy reduction of 50-85% for torrified wood versus raw wood (Chen and Kuo, 2010; Pimchuai et al., 2010; Bridgeman et al., 2008; Prins et al., 2006). The main application for torrified biomass is as a renewable fuel for combustion, gasification or pyrolysis. Feedstocks with lower O/C ratios and more hydrophobicity generally improve gasification efficiencies and better quality syngas (van der Stelt et al., 2011; Prins et al., 2006).



Figure 4-7 Van Krevelen Diagram (http:// www.handbook.ifrf.net)

There are several steps in the torrefaction process as the reaction temperature is slowly increased, as summarised in Table 4.9 (Basu, 2011; van der Stelt et al., 2011).

4.2.2 Common Torrefaction Reactors and Status of Commercial Processes

With torrefaction technologies still in the developmental stage, a wide variety of reactor configurations have been proposed and tested on a demonstration scale. They various technologies can be broadly divided into two main categories, with heating to the system applied either directly or indirectly.

4.2.2.1 Direct Heating Torrefaction Technologies

Direct heat torrefaction processes represent the majority of available technologies with six configurations: fluidized bed, moving bed, microwave, vibrating belt, multiple heating zone and screw conveyors/augers.

Fluidized Bed





Step	Name	Temperature Range	Description
1	Initial Heating	< 100°C	Initial drying of the biomass, moisture evaporating near end of stage
2	Pre-Drying	100°C	Free water in biomass is evaporated at near constant tem- perature – greatest amount of energy requirements
3	Post-Drying and Imme- diate Heating	100°C - 200°C	Physically bound water released, resistance against mass and heat transfer within particles
4	Torrefaction	200°C – up to 300°C, cooled to 200°C	Process of Torrefaction occurs
5	Solids Cooling	Cooled from 200°C to Final Temperature	Generally cooled to room temperature, waste energy pro- duce

Table 4-9 Steps in Torrefaction Process

As with several applications employing fluidized bed technology, a bed of particles is fluidized using a gas or liquid to give the particles fluid-like properties. General advantages of fluidized beds include high heat and mass transfer rates and excellent mixing. For torrefaction, Topell, a Dutch company, has developed the Torbed fluidized bed (Figure 4.8). It consists of a cylindrical reactor chamber with a rotating flow of process gas entraining the biomass feedstock. Typical gas velocities are between 50-80 m/s, with a residence time of 90-300 seconds, and a temperature of 280°C. The turbulent environment within the reactor allows for quick heat and mass transfer, and the ability to process a wide range of particle sizes. The Torbed does not require additional bed material outside of the biomass feed, and there are no moving parts. The main disadvantages are high attrition rates and loss of fine materials, lack of plug flow and a slow temperature response.

Moving Bed

Moving bed reactors pass hot gases through a moving bed of biomass material to transfer the required



Figure 4-8 Fluidized Bed Torrifer from Topell (http://www.topellenergy.com)



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heat from the gas to the biomass. Several companies have developed a moving bed torrefaction process, including Thermya in France. In their TORSPYD reactor (Figure 4.9), hot gas flows up a column while crushed biomass flows down, with the temperature gradient within the reactor causing the biomass to lose moisture and volatile matter. Advantages to this process include high heat transfer rates, uniform product quality, the ability to use different feedstocks, and an accurate control of temperature. The main disadvantages are channelling of the gas, fouling within the reactor, pressure drop limitations for smaller particles, and lack of scalability.

Microwave

In this process, electromagnetic radiation in the range of 300 MHz to 300 GHz make polar molecules within



Figure 4-9 TORSPYD Moving Bed Torrifer (http://www.torspyd.com)

the biomass rotate in a microwave, leading to friction and heating of the biomass material. Rotawave, a company based in England, has developed a microwave torrefaction process called the Targeted Intelligent Energy System. It incorporates multiple electromagnetic frequencies simultaneously within a ceramic phase separation drum to maximize heat and mass transfer. Advantages include easy control of residence time, the ability to torrify large particles and the ability to torrify/pyrolyse in a wide range of conversion. The main disadvantage is the difficulty in uniform heating, with the interior of the biomass becoming overheated while the exterior is not. Proven scalability to industrial scale is also an issue.

Vibrating Belt

A vibrating belt is used to carry biomass through a heated reactor full of inert gas. This allows for all the biomass to have a uniform residence time within the reactor. It is a proven technology that allows for a wide variety of biomass particle sizes. However, the process requires several mechanical parts, heat and mass transfer rates are low, uniform heating is difficult and scalability is limited.

Multiple Heating Zone

As the name implies, this process involves the heating of biomass as it is slowly transferred to multiple heating zones within a reactor. Wyssmont in the US markets a multiple heating zone torrifier consisting of a stack of rotating circular trays. Biomass enters at the top tray and after one revolution is transferred to the next tray, where it is again mixed before transferred to the next tray, and so on. Advantages of this setup include the use of any heating source (e.g. gas, steam, electricity), the ability to operate as other process in combination with torrefaction (e.g. dryer, cooler, humidifier, agglomerator), provides the lowest moisture content compared to other processes, along with the best temperature control. The main disadvantages include sealing problems and fouling in the internal moving parts.

Screw Conveyors/Augers

Screw conveyors or augers involve the movement of biomass with the use of a conveyor through an environment of hot gases. Direct heated conveyors, including the Spirajoule from France, use a heated coreless screw where direct contact between the electrically



heated screw (in conjunction with steam injection) and the biomass. Advantages to this method include low power requirements, low capital and operating costs and very good heat transfer. The main disadvantage is that due to the shape of the reactor, larger particles are not well suited for the process.

4.2.2.2 Indirect Heating Torrefaction Reactions

Two indirect heating reactors have been proposed for the torrefaction process: A rotary drum and an indirectly heated screw conveyor.

Rotating Drum

In this configuration, biomass is tumbled around in a cylindrical drum dryer with heat supplied by hot inert gases (Figure 4.10). Torrcoal in the US offers a rotating drum where biomass is torrified in the absence of air. Flammable gases supply heat during start up, with the process self-sustaining afterwards at a temperature range of 280-310°C. Advantages include the reduction of chlorine and sulphur in the biomass, a reduction in moisture to below 5%, the ability to torrify large biomass particles and easy modification to either direct or indirect heating modes. Difficulties include temperature control, low heat transfer rates, large physical footprint and unproven scalability.

Biomass Torrefaction drum

Figure 4-10 Rotating Drum Torrifier (http://www.tfe.umu.se)

Screw Conveyor/Auger

Unlike the direct heated screw conveyor process, the indirect method uses steam and combustion gases to heat the conveyor chamber through the wall. Similar advantages to the direct method include low power requirements and low operating costs, along with the combustion of volatile organic carbons and hydrocarbons to generate a large portion of the required process heat. The main disadvantages are low heat transfer rates and areas of local hot spots

4.2.2.3 Comparison of Torrefaction Reactor Configu*rations*

A comparison of the various torrefaction reactor configurations was conducted, looking at 12 criteria: Proven technology, high heat and mass transfer, handling feedstock types, temperature control, residence time control, scalability, heat integration, plug flow, uniform heating of materials, wide range of particle sizes, no internal moving parts and scaling problems. For each of these criteria, a score between 0 and 2 was given. The results are summarized in Table 4.10. Based on these results, direct heated reactor configurations with high heat and mass transfer rates represent the most promising methods for torrefaction . Currently, Ontario Power Generation and other electricity generators have retained Natural Resources Canada's CanmetENERGY to further evaluate available torrefaction technologies, with a completion date set for 2014.

Table 4-10 Comparison of Torrefaction Re-
actor Configurations (Basu, 2011)

Reactor Configuration	Cumulative Ranking (based on 12 crite- ria)
Moving Bed	19
Fluidized Bed	18
Multiple Heating Zone	18
Rotary Drum	17
Screw Conveyor (Indirect Heated)	13
Microwave	12

4.2.3 Important Parameters

Apart from the reactor configurations described above, the main parameters that affect the quality of torrefac-



4.2.3.1 Temperature

The temperature at which torrefaction occurs has the most significant impact on the torrified biomass. As a result, there has been extensive research in recent years looking at varying the temperature and the corresponding effect on the overall process. The most general trend observed universally from all research is that an increase in temperature leads to a corresponding increase in mass loss. Bridgeman et al. (2008) found that the mass loss for two energy crops (willow, reed canary grass) and one agricultural residue (wheat straw) was negligible at lower temperatures (230°C) but increased to 27-38% at higher temperatures (290°C). Similar decreases in mass yield were observed for other biomass feedstocks, including woody biomass (loblolly pine, eucalyptus, bamboo, banyan,

maritime pine and pedunculate oak), woody residue (sawdust, eucalyptus bark, oil palm bunches, fibre and kernel shells), energy crops (miscanthus) and agricultural residues (rice straw, rice husks, rape stalk, peanut husks, bagasse, coconut shells, cotton stalk and wheat straw) (Almeida et al., 2011; Chen et al., 2011; Pierre et al., 2011; Chen et al., 2011; Rousset et al., 2011; Uemura et al., 2011; Wang et al., 2011; Bridgeman et al., 2010; Chen and Kuo, 2010; Pimchuai et al., 2010; Yan et al., 2010; Deng et al., 2009). The majority of mass loss is due to the breakdown of hemicellulose, the most reactive of the biomass components, while a corresponding increase in liquids and non-condensable gases also occurs (Yan et al., 2010; Deng et al., 2009; Bridgeman et al., 2008). Table 4.11 summarizes the effect of temperature on several types of biomass feedstocks.

In addition to loss in mass yield, there are also several improvements to torrified biomass with increased

Biomass Feedstock	Temperature (°C)	Mass Yield (%)	Reference
Wheat Straw	230	91%	Bridgeman et al., 2008
	250	83%	
	270	72%	
	290	55%	
Rice Straw	200	60%	Deng et al., 2009
	250	40%	
	300	37%	
Bagasse	250	61%	Pimchuai et al., 2010
	270	57%	
	300	41%	
Bamboo	220	91%	Rousset et al., 2011
	250	76%	
	280	57%	

Table 4-11 Effect of Temperature on Mass Loss in Torrefaction Process



temperature. The calorific or higher heating value (HHV) increases with increased temperature with values in some cases approaching those of lignite, a lower quality coal (26-28 MJ/kg). Improvements in HHV values are much faster with increases in temperature as opposed to increases of residence time, but these increases cannot keep up with the corresponding loss in mass (e.g. a 40% increase in HHV for wood torrified at 280°C, with a corresponding 50% loss in mass). As a result, there is an overall decrease in total energy yield (Almeida et al., 2011; Chen et al., 2011(1); Chen et al., 2011(2); Pierre et al., 2011; Rousset et al., 2011; Wang et al., 2011; Bridgeman et al., 2010; Pimchuai et al., 2010; Yan et al., 2010; Deng et al., 2009; Prins et al., 2006). Increasing temperature also leads to improved grindability properties, leading to decreases in storage and transportation costs, as well as reduced energy required for biomass milling (Chen et al., 2011(2); Wang et al., 2011; Bridgeman et al., 2010; Sadaka and Negi, 2009). Further increases are also observed for energy density, fixed carbon and ash content, while the amount of volatile matter decreases. For example, torrified woody biomass would retain 70% of the original mass while retaining over 90% of the energy content, an increase of 1.3 for energy densification (Almeida et al., 2011; Wang et al., 2011; van der Stelt et al., 2011; Bridgeman et al., 2010; Pimchuai et al., 2010).

Some studies have recommended specific temperatures in order to balance the improvements in calorific value and grindability with the loss in mass yield. Chen and Kuo studied the effect of temperature on four types of biomass: bamboo, willow, coconut shells and Ficus benjamina L. wood. It was found that at 240°C there was a significant reduction in hemicellulose content with minimal effects of cellulose and lignin. Increasing the temperature to 275°C leads to an increased mass loss and decomposition of cellulose and lignin along with hemicellulose. Therefore, a torrefaction temperature of 240°C was recommended. Chen et al. (2011) looked at the effects of temperature and residence time on Lauan wood chips. The greatest increase in calorific values was at 280°C, but with an accompanying mass loss of 50%. It was found that grindability was improved at a temperature of 250°C and a time of 1 hour. A temperature of 250°C was therefore recommended to improve the calorific value to a certain extent while maintaining improved grindability characteristics and reduced mass loss.

4.2.3.2 Residence Time

After temperature, residence time is the second most important factor in the torrefaction process. Similar advantages (increased HHV, energy density, improved grindability) and disadvantages (increased mass loss, decreased energy yield, etc.) occur with increased residence time, but at a lesser extent when compared to temperature. Residence times between 15 minutes and 5 hours have been researched, with varying recommendations for an optimum time. Chen et al. (2011) concluded that torrefaction beyond 30 minutes would not have a significant effect on the process due to negligible mass loss after this time with sawdust, a result not consistent with other research that shows increased mass loss with increased time. Chen et al (2011) found that a minimum of one hour residence time was required to increase the heating value and improved grindability while at the same time avoiding too much mass loss, while Repellin (2010) found that increasing the residence time from 5 minutes to 60 minutes lead to an increased mass loss of only 10%. Determining the minimum or optimum residence time is important for industrial applications of torrefaction, as reduction in necessary residence time reduces the size of reactor and the overall capital cost. In addition, the use of the torrified product also plays a role. Shorter residence times lead to more brittle biomass, ideal for co-firing with coal, while longer residence times may be required for applications requiring a higher heating value (Basu, 2011).

4.2.3.3 Feedstock Type

The type of biomass feedstock being used for torrefaction also plays an important factor, mainly due to the differences in lignocellulosic content. Bridgeman et al. (2008) found that the greatest mass loss occurred for herbaceous-type biomass (wheat straw and reed canary grass) as opposed to woody biomass (willow) due to the presence of higher amounts of hemicelluloses in herbaceous biomass, the most reactive component of lignocellulosic material in the range of temperatures used for torrefaction (hemicelluloses begins to devolatilize at 200°C while cellulose doesn't begin to decompose until 250°C and not significantly until greater than 300°C). The same research group also found similar differences with greater mass loss in miscanthus compared to willow (Bridgeman et al., 2010). Deng et al. (2009) concluded that the type of feedstock plays an important factor in the torrefaction



Optimization and Scale-up of Liquid Nutrient Extraction and Recovery Process process due to the differences in volatile matter between different biomass.

4.2.4 Effect of Nutrient Extraction Pretreatment on Torrefaction

As mentioned in the previous section, the removal of nutrients by a liquid extraction process was designed as a pretreatment for solid biomass prior to combustion or other thermochemical processes. In many cases, torrefaction is also seen as a pretreatment process to improve certain characteristics of biomass prior to further thermochemical processes. This section examines the effects that a liquid extraction method would have on the torrefaction process. It will be determined if liquid extraction can be used as a beneficial co-pretreatment process, and to ensure that it does not have any detrimental effects on torrefaction.

Again, the main purpose of the liquid extraction process is to reduce the amount of water soluble nutrients in the biomass due to their negative effects on thermochemical processes and equipment. Based on published research, the presence of these nutrients in biomass does not have any direct effect on the torrefaction process. The majority of problems relating to the presence of nutrients occurs at higher temperatures typical of combustion or gasification, where nutrients vaporize and form new compounds that lead to deposits, slag formation and fouling. At temperatures of 200-300°C the water-soluble nutrients are for the most part unchanged and remain in the torrified biomass (Basu, 2011).

While the presence of nutrients not having any detrimental effect on torrefaction can be seen as an advantage, the fact that the nutrients remain after torrefaction mean that they can still cause the same problems when used in further thermal conversion processes like combustion or gasification. The list of problems associated with the use of biomass for thermochemical conversion that torrefaction can improve (Section 4.2.1) does not include any issues related to the presence of nutrients. Based on this information, there would be a benefit to using a liquid extraction process with torrefaction as a co-pretreatment due to the combined improvements in the transportation, handling, storage and use of the biomass fuel in further thermal conversion processes.

As indicated in the previous section, one of the main

process considerations in a liquid extraction process is the reduction in biomass particle size and the potential effect that this size reduction may have on downstream processing. Biomass is typically placed into torrefaction reactors as chips, chopped biomass or milled biomass to various sizes. There have been only a few studies examining particle size on torrefaction, with no clear consensus on the effect. One study looked at poplar biomass in cylinder form with varying diameters ranging from 4.76 to 25.4 mm (with a constant length of 65 mm). It was found that the change in size has no significant effect on mass yields. A similar study looked at wood chips made out of willow at various diameter ranges (0-10, 10-30 and 30-50 mm) with again no significant difference in the solid mass yields observed (Basu et al., 2011). Bridgeman et al. (2010) looked at two particle size ranges for willow (< 10 mm and >20 mm) and miscanthus (<4 mm and >10 mm). Changes in particle size did not affect the proximate and ultimate analysis of the torrified biomass, and it was determined that particle size was the least significant parameter after temperature and residence time.

Prins et al., (2006) examined the effect of particle size on the torrefaction of willow based on a kinetic model of the process. The Biot number and Pyrolysis number were determined in order to maximize heat transfer and minimize residence time, with a preferred Biot number near 1 and a Pyrolysis number greater than 1. This research indicated that a particle size around 2 mm was chosen as an ideal particle size for torrefaction. Based on these preliminary results, the particle size of biomass exiting the liquid extraction pretreatment process (~2mm) would not cause any negative effects on the torrefaction process. Smaller particles heat faster and therefore torrify more quickly, while one potential safety issue is the increased explosivity hazard with finer-sized particles (Basu et al., 2011). Further research is required to confirm if particle size has no significant affect, or that small particle sizes in the 2 mm range (the preferred size for the liquid extraction process) are preferred.

4.3 Conclusions

Gasification and Torrefaction were reviewed as alternative thermochemical conversion technologies to combustion following pretreatment of a biomass feedstock using a liquid extraction process. The following conclusions were drawn:





Gasification

- Fixed Bed Gasifiers, both downdraft and updraft, are suitable for small to medium sized applications due to simple and reliable designs, but encounter problems with larger scale processes due to low heat and mass transfer efficiency.
- Fluidized Bed Gasifiers, with superior mass and heat transfer due to increased mixing, are more suitable for larger scale applications.
- Temperature is the most important reaction parameter in terms of increased gas yield, while the use of catalysts can modify the composition of the product gas according to the end use.
- Gasification units in which product gas is fed directly into a boiler to produce steam are more commercially viable compared to two-stage systems that include cleaning or conditioning of the product gas (i.e. into syngas)
- A liquid extraction process would improve the biomass feedstock going into a gasifier by removing undesirable nutrients and reducing the chance of slag formation. The particle size reduction required for the extraction process would not have any negative effects on the gasification process.
- An economic evaluation of two biomass gasification scenarios indicate that the cost per MWh of electricity produced is not economically viable compared to scenarios involving biomass combustion, unless it involves recycling materials with associated tipping fees.

Torrefaction

- Of the many reactor configurations proposed for torrefaction, the most effective technologies to date include the fluidized bed, moving bed and the multiple heating zone reactors.
- Torrefaction can reportedly improve several problems related to the use of biomass for thermochemical processes, including hydrophobicity, grindability and low energy density
- Temperature is the most important reaction parameter in terms of mass loss, energy densification, and improved grindability
- A liquid extraction pretreatment process can exist as a co-pretreatment process along with torrefaction, as torrefaction cannot remove nutrients



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from the biomass. As with gasification, the liquid extraction process and the resulting particle size reduction to 2mm would not negatively affect the biomass going into the torrefaction reactor, regardless of the reactor configuration used.

The process of torrefaction is not yet commercially viable on a large scale, with further large-scale and long-term testing required to confirm the reported improvements in biomass quality.

Chapter 5 Conclusions

The extraction of water-soluble nutrients from biomass prior to combustion or other thermochemical conversion processes has been found to significantly improve the quality of the biomass and reduce the problems associated with their use in various combustion equipment (Rahbari, 2011). Significant reductions in the most problematic nutrients, namely potassium, chlorine, and sodium, greatly reduce the formation of slags and other deposits. In addition, the nutrients that are removed in the liquid extract can be further refined to produce a liquid fertilizer for use in agricultural applications. The initial report produced by CENNATEK for the Ontario Federation of Agriculture examined various methods of nutrient extraction and recovery, as well as examining the economic feasibility of the process on a larger scale through a preliminary economic evaluation. It was found that field leaching, the process of leaving biomass in the field over the winter season to leach nutrients directly into the soil, was not an effective method to produce high quality biomass fuel. Many of the nutrients of concern remain in significant quantities following field leaching, along with additional issues relating to losses in plant matter and increases in ash content. It was concluded that a water-based liquid nutrient extraction process using immersion with agitation allowed for a more controlled and effective method of nutrient extraction to produce a high quality biomass fuel. In addition, a nutrient recovery process involving reverse osmosis produces a liquid fertilizer product. As a result, the liquid extraction process not only effectively removes nutrients from the biomass, it also generates additional revenue from the liquid fertilizer product to make the overall extraction process economically feasible. An additional step involving the extraction and purification of silica was also evaluated to determine its feasibility in the overall process. It was recommended that additional experiments be conducted on the liquid extraction process to confirm the initial conclusions and further evaluate the technical and economic feasibility of the process.

This report focused on completing additional benchscale experiments, optimizing various reaction parameters in order to fully develop a technical and economical feasibility assessment of a commercialscale process. The addition of a silica extraction and purification method was evaluated, along with various methods of nutrient recovery and refining to produce a marketable liquid fertilizer. A refined economic model was developed to establish the feasibility of the process on a commercial-scale. The effect of the liquid nutrient extraction pretreatment on gasification and torrefaction, was also examined.

Based on bench-scale experimentation and optimization of the nutrient extraction reactor design carriedout by CENNATEK the following operating conditions were found to be most suitable for the nutrient extraction process (Table 5-1):

Table 5-1OptimalOperatingParametersfor the Nutrient Extraction Reactor

Operating Parameter	Optimal Value
Agitation Rate	3500 RPM
Residence Time	30 minutes
Water to Biomass Ratio (L/kg)	10-12:1
Number of cycles liquid extract to be recycled	5

5.1.1 Effect of Extraction and Pressing on Biomass and Liquid Extract

A combination of filtering and mechanical pressing allowed for sufficient dewatering of the biomass following the liquid extraction process. Reduction in moisture content to less than 50% was achieved, which is consistent with industrial scale dewatering equipment. The amount of liquid extract recovered as a percentage of fresh water used in the extraction process is approximately 90%.

5.1.2 Effect of Agitation Rate on Nutrient Extraction

Agitation rates of 1500, 2500, and 3500 RPM were examined for their effect on nutrient extraction. All three of the agitation rates examined were higher than those applied in the experimental data provided in our previous report (Rahbari, 2011). The results indicated that all three agitation rates were sufficient in removing enough of the water soluble nutrients to improve the combustion properties of the treated biomass, as indicated in the improvement in ash fusion tempera-



tures. However, the highest agitation rate of 3500 RPM is required for additional improvements in the reduction of ash content, increase in calorific value, and the extraction of larger quantities of nutrients. This allows for the maximum nutrient removal in the extract to be used as a liquid fertilizer. Additional increases in the agitation rate would not have any further improvement in ash content as there is a limit to the amount due to the presence on insoluble silica remaining in the biomass.

5.1.3 Effect of Residence Time on Nutrient Extraction

Two residence times, 20 and 80 minutes, were analyzed to determine the effect of residence time on the nutrient extraction efficiency. Residence time needs to be minimized in order to keep the reactor at a size that is economically feasible. Experiments indicated only a slight reduction in efficiency between 20 and 80 minute residence times when using the highest agitation rate. Residence times of 20 to 40 minutes are expected to be sufficient for the nutrient extraction reactor.

5.1.4 Effect of Water to Biomass Ratio on Nutrient Extraction

The water to biomass ratio is another reaction parameter that needs to be minimized in order for the overall process to be economically feasible. Three ratios, 8:1, 12:1 and 15:1 were used in the lab-scale experiments. Of the three biomass ratios tested, 8:1 was not a sufficient ratio, while ratios of 12 and 15:1 produced appropriate reductions in nutrient content. The 15:1 ratio had the best results experimentally, however, the resulting volume of biomass that could be treated in the reactor would be significantly lower. This reduction in the treatment throughput cannot be justified by the improved nutrient extraction. Therefore, the results indicate that the optimal water to biomass ratio for the extraction reactor is between 10 to 12:1. It is better to increase the agitation rate at lower water to biomass ratio to achieve increased nutrient extraction rather than keeping the agitation rate lower and increasing the amount of water used.

5.1.5 Recycling of Liquid Extract

The liquid extract could be recycled up to five times with less than 20% reduction in extraction efficiency when the entire extract is recycled. This is due to the extract becoming more concentrated with nutrients and causing more of these nutrients to redeposit on the treated biomass after drying. Recycling 80% of the extract would allow the extract to be recycled on a continuous basis without loss of extraction efficiency due to the additional makeup water. This reduces the amount of total fresh water needed for the process.

5.1.6 Silica Extraction

The extraction and purification of silica using a triboelectric separation technique was initially included in the overall extraction process to produce additional value added products (purified silica, by-products and CHP). However, initial lab-scale testing was inconclusive and talks with a company with several patents related to triboelectric separation have concluded that its use with raw biomass is still an unproven technology. The removal of the water-soluble nutrients reduces the negative effects that silica has on thermochemical processes, and a new economic model indicates the process is feasible without any silica extraction.

5.2.1 Nutrients in Fertilizer and Liquid Extract

The three primary nutrients in fertilizer for plants, nitrogen, phosphorous and potassium (NPK) are in the form of NH_4^+ and NO_3^- ions (for nitrogen), phosphate ions (for phosphorous) and potassium ions (for potassium). The nutrients present in the liquid extract from the proposed liquid nutrient extraction process are in similar forms and can be readily absorbed into plants without any additional conversion.

5.2.2 Fertilizer/Organic Regulations in Canada

Fertilizer that is produced or imported into Canada require registration with the Canadian Food Inspection Agency (CFIA), with registration including a minimum guaranteed analysis and proper labels to be used with the fertilizer. Fertilizers can be registered in three categories including a fertilizer-pesticide, micronutrients, and low analysis farm fertilizer. Fertilizers that wish to be considered organic in Canada must be certified according to the Organic Products Regulations. To qualify, products need to have an organic content that is greater than 95%. Certified organic multi-ingredient products that contain less than 95% organic contents can use the words Organic Ingredients, subject to certain limitations.



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5.2.3 Refining of Liquid Extract

The concentration of nutrients present in the liquid following the nutrient extraction process are low and requires further refining and concentrating to achieve appropriate levels for a commercial liquid fertilizer. The refining steps include:

- Primary Refining Removal of 99.9% of suspended solids larger than 4 microns
- Secondary Refining Reverse osmosis to remove 50% of the water in the extract - Due to fouling on the RO membrane because of certain nutrients present in the solution, it is not feasible to remove more than 50% of the water from the liquid extract.
- Tertiary Refining Evaporation to remove 95% of the initial water from the solution.
- 5.2.4 Liquid Fertilizer Market

Current market trends indicate a steady increase in fertilizer growth and demand for North America and worldwide. Fertilizer demand in the Great Lakes region alone is more than five million tonnes/year in the United States. This demand is sufficient enough that the amount produced by a commercial plant processing 40,000 tonnes/year of biomass will account for less than 0.1% of the regional demand.

5.3.1 Commercial Scale Liquid Extraction Process

A commercial-scale liquid nutrient extraction process would be based on the promising results obtained in bench-scale experiments. A proposed 6 TPH process would have inputs of biomass, water, natural gas and electricity, and outputs of treated biomass pellets and liquid fertilizer. The main components of the process include receiving, storage, size reduction, a nutrient extraction reactor, biomass dewatering and drying, liquid fertilizer refining and a pellet mill.

5.3.2 Scale-up of Liquid Extraction Process

Detailed design and scale-up work was carried out on the nutrient extraction reactor and each of the unit operations required to feed material to the reactor and produce biomass pellet fuel and liquid fertilizer product. The scaled-up model for the nutrient extraction reactor will process 6 TPH of feed material with a total reactor volume of 35m³. To achieve this throughput the nutrient extraction will take place at 10:1 water to biomass ratio with 30 minute residence time in the reactor. Bench-scale results using a scaled-down version of the reactor have shown that this amount of time and water should be sufficient to achieve adequate nutrient extraction.

5.3.3 Commercial-Scale Financial Model

The total capital cost for the 6 TPH system was estimated at just over \$1 Million (\$1,017,677). For the financial models it was assumed that the liquid extraction process will be used by an existing biomass pellet mill capable of processing 5-6 TPH of biomass pellets. Under this scenario, the combined pelleting and nutrient extraction process would generate \$10.75 Million/ yr in revenues (44.6% of the revenues would be from the sale of fuel pellets and 55.4% from the sale of liquid fertilizer). The EBITDA (Earnings before interest, taxes, depreciation and amortization) for this process would be \$1,812,948 per year.

5.4.1 Gasification

A literature review was conducted on gasification and torrefaction as alternative thermochemical extraction process. The literature review examined the processes, the important parameters, and the status of commercially available reactor configurations. In addition, economic evaluation for two gasification scenarios were summarized and compared to similar scenarios involving combustion in the previous report. Finally, any effects from a liquid extraction process were determined for both gasification and torrefaction. For gasification, the following conclusions were drawn concerning the overall process and economics:

- Fixed Bed Gasifiers, both downdraft and updraft, are suitable for small to medium sized applications due to simple and reliable designs, but encounter problems with larger scale processes due to low heat and mass transfer efficiency;
- Fluidized Bed Gasifiers, with superior mass and heat transfer due to increased mixing, are more suitable for larger scale applications.
- Temperature is the most important reaction parameter in terms of increased gas yield, while the use of catalysts can modify the composition of the product gas according to the end use;
- Gasification units in which product gas is fed directly into a boiler to produce steam are more

commercially viable compared to two-stage systems that include cleaning or conditioning of the product gas (i.e. into syngas);

 An economic evaluation of two biomass gasification scenarios indicate that the cost per MWh of electricity produced (\$119.20 and \$180/MWh) is not economically viable compared to scenarios involving biomass combustion.

5.4.2 Effect of Liquid Extraction Pretreatment on Gasification

A liquid extraction pretreatment process would improve the biomass feedstock going into a gasifier by removing undesirable nutrients and reducing the change of slag formation. While the improvements are not as dramatic when compared to a combustion process, their presence must still be addressed to avoid any unwanted problems. Based on experiments conducted in literature, the particle size reduction required for the extraction process would not have any negative effects on the gasification process. Therefore, a liquid extraction process would be a beneficial pretreatment process for gasification systems.

5.4.3 Torrefaction

For the torrefaction process, the following conclusions were drawn based on the literature review :

- Of the many reactor configurations proposed for torrefaction, the most effective technologies to date include the fluidized bed, moving bed and the multiple heating zone reactors;
- Torrefaction can reportedly improve several problems related to the use of biomass for thermochemical processes, including hydrophobicity, grindability and low energy density;
- Temperature is the most important reaction parameter in terms of mass loss, energy densification, and improved grindability;
- The process of torrefaction is not yet commercially viable on a large scale, with further large-scale and long-term testing required to confirm the reported improvements in biomass quality.

5.4.4 Effect of Liquid Extraction Pretreatment on Torrefaction

Torrefaction claims to improve several issues with biomass for use in thermochemical conversion processes. One issue, however, that is not addressed is the removal of undesirable nutrients from the biomass. As a result, a liquid extraction process can exist as a co-pretreatment process along with torrefaction. As with gasification, the liquid extraction process and the resulting particle size reduction would not negatively affect the biomass going into the torrefaction reactor.



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