IMPROVING THE QUALITY OF CROP RESIDUES BY THE REDUCTION OF ASH CONTENT AND INORGANIC CONSTITUENTS

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Abstract

Fuel pellet producers in Canada have started to consider alternative feedstocks that include agricultural crop residues. Yet, the higher ash content and inorganic constituents of crop residues can impose problems on the equipment, the quality of products, and the environment due to air emission.

In this study, mechanical size fractionation in combination with leaching was conducted to improve the quality of crop residues by reducing the ash content to target value of 6% db following the applicable standard. Experimental results of mechanical size fractionation suggest that the finest fraction of ground crop residues had much higher ash contents than the coarser fractions. Results also indicate that size fractionation can reduce the need for leaching as ash removal technique, and it is most effective for corn stover when compared to canola straw and wheat straw. For the leaching tests, the leaching performance is affected by the leaching conditions whereas particle size can have some impact. Under the same leaching conditions, non-fractionated ground crop residues with larger average particle size had higher ash removal efficiency than the finest fraction of crop residues. Among the three species of crop residues, canola straw was found to have the best leaching performance, regardless of whether mechanical size fractionation was used prior to leaching. Canola straw had the highest ash removal efficiencies, $K_2O$ removal efficiency (greater than 90%) and $SiO_2$ removal efficiency (more than 50%). The results also demonstrate that the effect of leaching temperature on $K_2O$ removal efficiency is negligible while $SiO_2$ removal efficiency increases significantly as water temperature increases from 25 to 45 °C upon leaching for 12 h.

A preliminary cost analysis was performed to estimate the total production cost (TPC) of agro-pellets based on different process designs with respect to the ash removal techniques. TPC for the base case of pellet production without ash removal pretreatment was estimated to be
US$102/dry tonne (dt) pellets, and it would increase by 30% to US$133/dt for Option 1 (pretreatment by mechanical size fraction plus water leaching) and increase by 66% to US$169/dt for Option 2 (pretreatment by water leaching only).
Lay Summary

Biomass has been utilized globally as a renewable low-carbon energy; nevertheless, its ash content and inorganic constituents can be harmful to the equipment, the products and the environment. This research project aims at improving the quality of agricultural crop residues (canola straw, wheat straw and corn stover) by reducing the ash content using a combination of mechanical size fractionation and leaching. Mechanical size fractionation was found to be effective in reducing the need for leaching as a further ash removal technique, but water leaching was observed to be more effective for ash removal. For leaching tests, canola straw was found to have the highest ash removal efficiencies. A preliminary cost analysis was performed to estimate the total production cost (TPC) of agro-pellets. The TPC would be increased by 30-66% for the two options with ash removal pretreatment with respect to the base case of pellet production without ash removal pretreatment.
Preface

The research work presented in this thesis was completed under the supervision of Dr. Anthony Lau. The author, Yige Peng, conducted literature review, developed the experimental design, assembled the equipment for the combined biomass pretreatment methods of mechanical size fractionation and water leaching, and subsequently collected and analyzed the experimental data. The author also performed a preliminary cost analysis for the production of pellets with and without using ash removal techniques for the raw materials. This dissertation represents original, unpublished and independent work by the author. A manuscript is being prepared for submission to journal for peer review and publication.
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To my family
Chapter 1 Background, Research Rationale and Objectives

1.1 Introduction

Energy production and consumption can have a crucial effect on the progress made by a country during its development. The major energy that currently fuels human life and society are obtained from fossil fuels such as coal, oil and natural gas. However, the use of fossil fuel in the long run is not sustainable or environmentally benign. The extensive use of fossil fuel is gradually depleting these resources; besides, air has imposed adverse environmental impacts including air pollution and climate change (Uihlein and Schebek, 2009; Lynd and Wang, 2003). As potential low-carbon renewable energy source from agriculture, forestry and the organic fraction of municipal solid waste, biomass is being increasingly utilized to replenish the declining fossil fuel supply.

Canada and the US possess abundant lignocellulosic waste biomass. These wastes can be used as renewable resources for conversion into heat and power, biofuels and other products using a variety of technologies. Ideally, biomass that meets both quantity and quality criteria must be available to a conversion facility year round at a competitive price. A broad assessment of biomass resources for bioenergy production was provided in the DOE report (USDOE, 2016) which includes resource analysis and optimization, as well as environmental sustainability analysis of some agricultural and forestry biomass production scenarios.

1.2 Literature review
1.2.1 Renewables and biomass

As shown in Fig.1-1, world energy consumption is projected to keep increasing between now and 2040 for all types of fuels other than coal. Meanwhile, renewable energy is the fastest-growing energy source (EIA, 2017), and the ongoing search for alternative and sustainable sources of energy is focused on renewable energy. Renewables are obtained from natural resources that can be replenished over a period of time. These include solar energy, wind energy, hydropower, geothermal energy, biomass and tidal energy (Stelt et al., 2011; NRCan, 2017).

The composition of biomass varies among different types of biomass, and it is closely related to fuel performance. Composition includes the three major components (cellulose, hemicellulose and lignin) along with smaller amounts of extractives and ash content (Yang et al., 2006). The calorific value of biomass is mainly dependent on its volatile matter (VM), fixed carbon (FC) and ash contents. Biomass with higher VM, higher FC and lower ash contents is eco-friendly and preferable for energy conversion processes. Ultimate analysis for straw and other crop residues in Ontario is indicated in Table 1-1 (Clarke and Preto, 2011; Tumuluru et al., 2011).
Table 1-1. Ultimate analysis of biomass in Ontario (on dr basis for straw/residue part)  
(Clarke and Preto, 2011; Tumuluru et al., 2011)

<table>
<thead>
<tr>
<th>Biomass Type</th>
<th>MJ/kg</th>
<th>BTU/lb</th>
<th>Ash</th>
<th>Carbon</th>
<th>Hydrogen</th>
<th>Nitrogen</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfalfa residue</td>
<td>17</td>
<td>7,435</td>
<td>9.1</td>
<td>45.9</td>
<td>5.2</td>
<td>2.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Barley straw</td>
<td>17</td>
<td>7,480</td>
<td>5.9</td>
<td>46.9</td>
<td>5.3</td>
<td>0.7</td>
<td>0.1</td>
</tr>
<tr>
<td>Corn cobs</td>
<td>18</td>
<td>7,927</td>
<td>1.5</td>
<td>48.1</td>
<td>6.0</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Corn stover</td>
<td>19</td>
<td>7,960</td>
<td>5.1</td>
<td>43.7</td>
<td>6.1</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Flax straw</td>
<td>18</td>
<td>7,810</td>
<td>3.7</td>
<td>48.2</td>
<td>5.6</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>18</td>
<td>7,710</td>
<td>7.7</td>
<td>43.4</td>
<td>6.0</td>
<td>0.8</td>
<td>0.1</td>
</tr>
</tbody>
</table>

As combustion feedstock, the high volatility and high reactivity are good attributes of biomass (Demirbas, 2004). Biomass accounts for part of renewable power capacity, biofuel or biodiesel production and contributed to transportation fuel around the world in 2016 (Sawin et al., 2013; Demirbas, 2001). The utilization of waste biomass such as forest-origin residues and agricultural residues can help to mitigate greenhouse gas emissions and reduce waste on condition that the removal of these residues from the harvest area is properly managed following sustainable principles (LePori and Soltes, 1985).

Traditionally, the raw materials for producing solid biofuel such as pellets are mill residues such as sawdust, planer shavings and wood chips. Due to the dwindling supply of sawmill residues in Canada, pellet producers have started to consider alternative forms of biomass residues. The large volume availability of logging residues that consist of tree branches, tops of trunks, and stumps after forest logging and thinning operations can become a major source of feedstock. A review of agricultural crop residue supply in Canada has shown that when correctly managed, waste
herbaceous biomass can potentially be a sustainable low-carbon fuel (Li et al., 2012). Partial residue removal is the management of choice as excessive crop residue removal can degrade the long-term productive capacity of soil resources (Muth et al., 2013; Sanscartier et al., 2014).

1.2.2 Pelletization

In the industry, biomass needs to be processed and handled in an efficient manner. However, biomass resources are difficult to handle, transport, store, and utilize in their original form due to their high moisture or ash content, low bulk density, and irregular shape and sizes (Kaliyan et al., 2009). One major limitation on biomass utilization is a processing capacity of less than 5000 tonnes of biomass per day due to the challenges of transporting and storing low-density lignocellulosic biomass (Kim and Dale, 2015). In general, the low density and high moisture content of biomass makes collection and transportation of these residues inefficient and costly. For instance, delivery cost was estimated at 35-50% of the total cost of biofuel production (Kumar et al., 2006). Collection and transportation can be influenced by factors such as collection method, geographic location of biomass as well as the types and quality of biomass. A potential solution to improve the efficiency of collection and transportation is to implement biomass densification via pelletization.

Pelletization is a suitable and established technique for upgrading raw biomass to consistent and high quality feedstock with uniform shape or size for making biofuel and bioproducts in order to meet specifications of the conversion facilities, and safe and economical handling and storage (Zhijia et al., 2013). Pelletization of biomass reduces its handling costs and results in a homogeneous fuel with relatively consistent moisture content and particle size. The bulk density of lignocellulosic biomass in its original form is usually quite low and the moisture content ranges from 10-70% (wet basis) (Mani et al., 2006). The bulk density of densified biomass pellets typically reaches 600-800 kg/m³ while the moisture content decreases to less than 10%
(Kurian et al., 2013; Stephen et al., 2010; Sultana and Kumar, 2011). Densified pellets can be shipped over long distances to domestic and international markets due to their enhanced mobility. Pellets are primarily utilized as solid biofuel for residential and industrial heating and power generation.

The use and production of pellets were projected to have an upward trend (Sikkema et al., 2011). Global pellet markets have experienced significant growth in the past decade. In 2016, global pellet production went up by 6% reaching 29 million tons. Europe and Northern America accounted for some 58% and 32% of global pellet production respectively and accounted for 81% and 8% of global pellet consumption respectively. In recent years, the importation of pellets from outside Europe has increased (Jensen et al., 2011). Consumption of wood pellets in Asia has increased by 17% (Food and Agriculture Organization of the United Nations, 2016). Canada produced more than 3 million tons of wood pellets in 2016, about 85% of which was exported to European countries (e.g. UK, The Netherlands, Sweden, Denmark) and 15% to Asia (Natural Resources Canada, 2016). The province of British Columbia is the nation's leader in wood pellets production, exporting 2 million tons of pellets annually. In British Columbia, softwoods are the most prominent tree type that is regarded as the primary feedstock source (including the beetle-killed pine) for pellet manufacturing (Axelson et al., 2010).

While wood pellets have been produced commercially in places around the world, there is some production of agro-pellets (i.e. agricultural biomass-based pellets). In western Canada, the most concentrated source of field-based agricultural residues is the straw from crops such as wheat and barley (Kumar et al., 2002). When some agricultural crops are threshed, straw is one kind of byproduct. Most of them are laid back on the field and left to rot while a small quantity can be collected and used as bedding or feed supplement. Sultana et al. found that while production cost
of straw pellet is lower than wood pellet, the maturity of technology for straw pellet production is also lower (Sultana and Kumar, 2012).

During the pelletization process, the biomass chips are mechanically ground to a smaller particle size and dried to reduce their moisture content before being compressed to form pellets. The conditions of the pelletization process as well as the biomass feedstock have influence on the quality of the pellets. Woody biomass has been the primary choice of lignocellulosic feedstock for industrial pellet manufacturing. Wood pellets do not only originate from sawdust and wood shavings (sawmill by-products), as pellets can also be produced from the tops and branches of trees (Andersson et al., 2006). Densification of agricultural residues in the form of pellets or briquettes has also been investigated to enhance the transportation, handling and storage of biomass materials (Theeraratthananoon et al., 2011). They investigated the physical properties of pellets made from sorghum stalk, corn stover, wheat straw, and big bluestem as well as the effect of moisture content and hammer mill screen size on bulk density.

1.2.3 Impacts of ash content and inorganic constituents

Ash is used as a general term to describe the non-combustible inorganic content in fuels. The initial deformation temperature (IDT) of ash must be greater than 900°C. Ash in waste biomass is generally in the form of structural ash bound in the plant cell walls or entrained ash.

Structural or authigenic ash is a kind of nutrient deposit inside the plant fibers. Structural ash is formed in biomass and introduced via uptake or transportation of mineral within the plant from surrounding water and soil during its growth as well as generated after the plants’ death through evaporation and precipitation (Kozlowski et al., 1997; Vassilev et al., 2012). Plants are known to
require 16 elements on earth for proper growth and development. These elements are categorized as macronutrients and micronutrients. The macronutrients include (C, H, O, N, P, K, Ca, Mg, S) while micronutrients include (Cu, Fe, Mn, Zn, Mo, Cl, B). The amount of macronutrients in plants is greater than 1000 mg/kg whereas the amount of micronutrients is less than 100 mg/kg (Pilon-Smits et al., 2009). C, H, O are derived in plants from the atmosphere, soil, and water whereas the remaining elements are supplied either from soil minerals or organic and inorganic fertilizers (Pradha, 2015). Phosphorus is a major part of the components of genetic information, RNA and DNA. Potassium acts as enzyme activator and promotes metabolism. Calcium assists in the formation of cell wall and it is an activator of several enzyme systems in protein synthesis. Magnesium is involved in photosynthesis (Tucker, 1999).

Entrained or detrital ash is fixed in biomass (e.g. tree limbs) or on the surface of biomass resulting from soil and sand contamination during biomass handling which includes harvesting, storage, and other processing (Vassilev et al., 2012). Furthermore, the separated limbs, leaves and barks are left on the ground during the delimming and debarking process. Hence, the contamination by soil particles is unavoidable during the collection of the forest residues.

There are two main groups of elements in ash: minor elements and major elements (Lu et al., 2014). According to EN 15297 (for solid biofuels), the major inorganic elements in coal include Al, Ca, Fe, Mg, P, K, Si, Na and Ti, whereas the minor inorganic elements include As, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V and Zn. However, heavy metals are usually absent or present in negligible concentration within biomass.

During biomass thermochemical conversion processes such as combustion, gasification and pyrolysis, the presence of inorganic compounds of ash from certain types of biomass is harmful. The afore-mentioned major and minor ash-forming elements in biomass are not converted into
fuels and the deposit of these inorganic elements can cause slagging, fouling and corrosion problems in reactors, furnaces, heat exchangers and other downstream equipment. Substantial cost is required to repair the furnace under these conditions or to treat the emission of particulate matter.

Slagging, with a glass layer rich in Fe$_2$O$_3$ and K$_2$O, is a process formed by the melting of the deposits of ash and other inorganic compounds within the furnace, in areas directly exposed to flame radiation (such as furnace walls and super-heaters) due to the melting of the inorganic compounds (Kostakis, 2011). Thus, slagging takes place in the hottest parts of the furnace. Fouling occurs when the temperature of hot gases and suspended fly ash cools down and the vaporized inorganic compounds deposit on the surfaces of the combustion furnace. Interaction of the deposit layers with the furnace’s metal surfaces accelerates corrosion. Moreover, the suspension of the fly ash in the flue gas stream reduces the convective heat transfer to the heating surface, thereby decreasing the combustion efficiency (Benson, 1992).

With the increasing demand of energy fuel, crop residues are considered to be potential fuels for power generation. However, the fuel quality of herbaceous species was much lower compared to wood due to higher ash content and high percentage of Si, K and Na (Olanders et al., 1995). Higher contents of some ash elements (e.g. Si, K, and Na) can decrease the temperature of ash melting (and increase the possibility of slagging and fouling (Vassilev et al., 2013; Khan et al., 2009; Jenkins et al., 1998). As ash content increases, the heating value of biomass decreases since ash reduces the combustible compounds in biomass. Ash can also affect the properties of the pyrolytic products such as bio-oil, activated carbon and carbon fibers (Livingston et al., 2006; Liu et al., 2011).
This issue has been studied by a number of researchers. Olanders et al. (1995) investigated the sintering and melting behaviors of the ashes from bark and wood chips and straw fuels by sequential heating in a laboratory furnace. Turn et al. (1998) studied the retention of inorganic elements in the bed when banagrass fuels were gasified in a bench-scale fluidized bed. Arvelakis et al. (2001) found that the ash content of wheat straw and olive residue led to severe ash-related problems during conversion process such as uneconomical operation of fluidized bed reactors and even shut-down of the plant. Davidsson et al. (2002) investigated the effectiveness of water and acid leaching methods for wheat straw and wood waste by comparing alkali metal release during pyrolysis of untreated and treated biomass samples. In addition, sintering of ash component during combustion of straw pellets has yet to be overcome.

Other problematic inorganic elements include N, S and Cl. The nitrogen content of biomass varies from 0.2% to more than 1%. Fuel-bound nitrogen will contribute significantly to nitrogen oxides (NO\textsubscript{x}) formation during biomass combustion. As for sulfur content, most biomass fuels have values below 0.2% and a few have 0.5 - 0.7%. Sulfur content should be responsible for the emission of sulfur oxides (SO\textsubscript{x}) and particulate matter (PM). In addition, high chloride concentrations (> 1,000 µg/g) can be found in some kinds of biomass such as stovers and corn cobs, and this can cause increased ash fouling during biomass combustion. High chloride concentration in boiler tubes should also be responsible for the formation of hydrochloric acid, which results in corrosion and possible leakage problem for equipment (Clarke et al., 2011).

Ash content has financial impact during the transportation of biomass from the harvesting site to the conversion plant. Tentative cost of transporting woody biomass using different transportation systems such as trucks and railway has been calculated (Tahvanainen and Anttila, 2011). More financial cost will be wasted on transportation of higher amount of ash in biomass.
1.2.4 Factors in the supply chain that affect ash content

Several factors in the supply chain have been proven to influence the ash and primary elements’ content in biomass. Different types of biomass require different growing and storage conditions, which heavily impact the ash level. Warm-season grasses (e.g. big bluestem) and annuals (e.g. corn) have lower level of ash as compared to cool-season grasses (e.g. orchard grass and perennial ryegrass) (Arvelakis et al., 2003; Ray et al., 2017). Besides, some overwintering biomass such as switchgrass can help to reduce ash levels.

Water uptake directly affects the amount of silicon and other inorganic elements in herbaceous biomass (Lu et al., 2014). More specifically, it accounts for the fact that the ash level of non-woody biomass is higher than the woody biomass. C3 plants (e.g. wheat, reed canary grass) have a higher yield potential in cold climates and need more water uptake to achieve a similar productivity as compared to C4 plants (e.g. Douglas fir, poplar, switchgrass). Hence, C3 plants have a higher ash level due to deposition of Si and other inorganic constituents in plant biomass through more uptake of water (Bakker et al., 2005). Similarly, the utilization of fertilizers also plays an important role in the amount of ash content in virgin biomass, particularly in regard to elements such as K, P and Cl.

Soil type, conditions and composition affect the ash levels of biomass. For instance, lower overall ash and potassium contents are found in switchgrass grown on sandy soils vs. clay soils (Elbersen et al., 2002). The differences in ash content among the soil types can be largely explained by the level of soluble silica. Specifically, the higher soluble silica content in clay soils will result in higher ash content in crops grown on clay soils.
The ash composition of a plant varies among different plant fractions. For example, Werkelin et al. (2005) determined total ash in different botanical fractions of spruce, pine, birch and aspen, and concluded that ash content varied significantly among fractions. The ash content in the wood tissues was 0.2–0.7%, including both the stem- and branch-wood samples. Foliage contained the highest ash content, at 2.4 – 7.7%, whereas ash content in the bark tissues was 1.9 - 6.4% and roughly 10 times higher than the corresponding wood tissues.

Literature review indicates that several methods can be used to reduce the ash content of collected waste biomass. Firstly, selection of biomass type can be considered as one method. Secondly, the ash levels of biomass can be lowered by changing the growing conditions for crops on sandy soils instead of clay soils. Thirdly, ash and other elements can be minimized by leaving the cut biomass in the field to in purpose of loss of biomass components with higher ash level (i.e., leaves) (Lokare et al., 2006). Finally, field collection of wood or crop residues with removal of soil particles can minimize soil pickup, improve the quality of biomass feedstock and increase its energy potential during thermochemical conversion (Pradhan, 2015). Notwithstanding these methods, structural ash remains a main component in waste biomass.

1.2.5 Biomass pretreatment techniques for ash removal

Researchers have explored various types of technologies to reduce ash content and other inorganic constituents in the biomass prior to their utilization in the conversion processes (Clarke et al., 2011). The methods utilized can be classified as mechanical (physical) and chemical pretreatment techniques. Mechanical pretreatment techniques consist of mechanical size fractionation and blending. Chemical pretreatment techniques include leaching by water, acid or chelating agent.
**Mechanical pretreatment techniques**

**Mechanical size fractionation**

Mechanical size fractionation is a process that combines milling and sieving. Milling is the reduction of particle size by chipping or grinding in order to make material handling easier and increase the surface area (Harmsen et al., 2010). The development of biomass milling technology has caught attention since 1993 (Asplund et al., 1993; Brockway et al., 1993). Sieving is based exclusively upon particle size and shape and takes advantage of the fact that different fractions of the biomass will tend to break into different-sized pieces during size reduction, providing a basis for separation of the milled biomass. Selective ash separation is possible because the different anatomical fractions have different ash contents and compositions. Sieves with small openings can allow fine soil particles adhering to biomass to pass through via vibration, while capturing larger organic particles (Hu et al., 2017).

Papatheofanous et al. (1998) used milling and sieving equipment to separate wheat straw into two major fractions: a chip fraction and a meal fraction. The chip fraction is made up by straw or stem internodes, richer in lignocellulose and lower in ash, whereas the meal fraction with smaller particle size consists of ground crop leaves, nodes and husks.

Researchers have separated particles into various fractions before conducting leaching experiment, with an aim to enhance the ash removal efficiency. Liu and Bi (2011) demonstrated that sieving could remove 33% of the ash from pine bark while only removing 24% of the organic material, and for switchgrass, the corresponding values were 16% and 11%. Thus, ash content in the meal fraction is generally much higher and easier to be broken down to fine particles. Huang et al. (2017) determined the ash content in the fine fraction of birch and reed canary grass (with particle size of less than 0.25 mm) to be 2-3 times higher than that of the
coarse fraction (with particle size of larger than 0.5 mm). Earlier, Arvelakis et al. (2002) studied the effect of fractionation and leaching on ash composition of wheat straw, olive residue and corn cob. They found that, out of two fractions (particle size < 1 mm and > 1mm), the ash content in the coarse fraction (size > 1 mm) is much lower than original samples, but most of main elements including K, Cl, and S that are responsible for problematic ash thermal behavior remained in the coarse fraction. Size-reduced corn stover was used in studies on chemical pretreatment, but the effect of mechanical size fractionation was not quantified (Wyman et al., 2005; Chang et al., 2012).

Subsequently, Lacey et al. (2016) studied ash removal from corn stover by separating the anatomical fractions (cobs, husk, leaves, sheaths, internodes and nodes). For particle size reduction, each of the anatomical fractions was ground through a hammer mill until it passed through an ASTM E-11 19.1 mm (0.75 inch) sieve. Each of the ground fractions was further separated into seven size fractions by (9.5, 6.0, 2.0, 0.6, 0.425, 0.15 mm) sieves and the pan (< 0.15 mm). They suggested that the removal of silica deposits embedded in the tissue as Si-complexes may require physical and chemical disruption of the tissue structure. Moreover, they concluded that the need for more expensive ash reduction treatments (such as leaching) can be minimized.

**Blending**

Blending has been utilized by industries (e.g. coal and animal feed) to alter/improve the quality of feedstock. Different grades of coal are blended to meet emission targets and minimize ash production. Blending animal feed is helpful to meet some nutritional requirements (Ray et al., 2017). As for biofuel and bioproduct industry, blending high-quality biomass with low-quality biomass could be a good way to meet quantity and quality specifications of biomass feedstock at a lower cost.
Lignocellulosic materials such as wood residues with high lignin content and higher heating value can help to improve the strength and durability of pellets and briquettes derived from wheat straw, increase the calorific value and decrease the ash content (Lu et al., 2014). They also investigated the optimum weight ratio for blending sawdust and paper pulp to produce briquettes from wood residues. Thompson et al. (2017) examined the interdependencies of cost, supply, and quality among raw feedstocks and investigated a method that upgrades low-cost and low-quality feedstocks by blending feedstock. And it meets ash specifications suitable – to reduce total ash to below the preferred 0.9% target for fast pyrolysis at the lowest possible cost. Lokare et al. (2006) proved that total deposition rates of fuel (straw or grain screenings) mixed with other fuels (e.g., sawdust and sunflower shells) decreased by approximately half when comparing with pure fuels (straw and grain screening).

**Chemical pretreatment techniques for ash removal**

**Water leaching**

Water leaching has been used as a pre-treatment method to reduce inorganic constituents in biomass in order to improve the combustion quality of fuel (Jenkins et al., 1996; Turn et al., 1997; Arvelakis et al., 2003). The effectiveness of the leaching process depends on material characteristics, particle size distribution and treatment conditions, such as water-to-biomass ratio (w/w), leaching temperature, and leaching duration (Liu et al., 2011).

Water leaching can efficiently reduce the water-soluble inorganic elements (e.g. K, Na, Ca, Cl, S, and Mg) and improve the quality of the remaining ash (Dayton et al., 1999). The impact of washing is minimal on the higher heating value (HHV) and further reduces the tendency of fouling and slagging (Gudka et al., 2015).
Jenkins et al. (1996) tested different ways of applying water (spraying, flushing, soaking and rain-wash) and concluded that the soaking method had the best results, as compared to other methods. Natural rain wash can be seen as the simplest and most inexpensive method of water leaching but it is poorly controlled, suffers from weather condition and may cause potential increase in ash content due to losses of organic matter and plant matter (Jenkins et al., 2003). Arvelakis et al. (2001) suggested using deionized water after a low removal efficiency of 44% was found for K upon washing wheat straw with tap water.

Water washing method has also been developed for enhancing some inorganic constituents' removal efficiency. In order to solve problems caused by potassium, such as the deactivation of selective catalytic reduction (SCR) catalysts applied for NO reduction and deterioration of the fly ash quality, Jensen et al. (2001) investigated a multistep washing process based on pyrolysis and char wash. Biomass sample such as straw was first pyrolyzed at moderate temperatures at which potassium is retained in the char. The second step was to extract K and residual Cl from char by water leaching. Obviously, less pyrolyzed material needs to be washed and the quantity of water needed in the second process of washing was relatively smaller during multistep washing compared to the single one step about direct water washing. Pyrolysis gas, a byproduct generated in the prior process of mild pyrolysis, can be burned as a fuel directly for maximizing the utilization of resources. In addition, the char generated in the first pyrolysis step is smaller so that it is much easier to mill than biomass (Livingston et al., 2006).

**Leaching with chemicals**

Water leaching is an effective method of removal of problematic elements in biomass but it is not effective for substantial removal of the water-insoluble metals. Therefore, the use of dilute acid for
leaching has been studied to remove both the water-soluble and water-insoluble inorganic elements.

The acids that have been generally selected include hydrochloric acid (HCl), nitric acid (HNO₃), sulfuric acid (H₂SO₄) and acetic acid (CH₃COOH). HCl, HNO₃, H₂SO₄ have strong acidity but potentially introduce undesirable Cl, N and S into the treated biomass after pretreatment process. On the contrary, acetic acid has a mild acidity and it only contains C, H and O elements, which have no adverse effect on ambient environment and the treated biomass.

Jiang et al. (2013) compared the efficacies of leaching samples of 10 ml/g ratio with six different agents at 5 wt.% solutions (HCl, HNO₃, H₂SO₄, CH₃COOH, H₃PO₄ and deionized water). They found that chemical leaching is effective in reducing the ash content and minerals. However, the structure of samples after acid leaching seemed to be eroded and became fuzzy, and the visible particles adhered on the surface were much fewer, especially for strong acid leaching. Hence, acid leaching has more notable impact on physicochemical structure of biomass comparing to water and weak acid leaching.

Werkelin et al. (2010) applied chemical fractionation analysis to woody biomass (spruce, pine, birch and aspen). Ion chromatography found the water-soluble elements Cl, P, and S present as Cl⁻, PO₄³⁻, and SO₄²⁻ respectively as shown in Fig. 1-2. Leaching was conducted in water, NH₄Ac (aq), and HCl (aq) sequentially. They made the following observations: all of Cl and most of K, Na, and P in the samples were water-soluble (blue zone in Fig. 1-3); most of Mg and Mn, and some of Ca were removed after NH₄Ac (aq) (yellow zone); most of Ca was leached out in HCl (aq) (red zone); but most of Si and S remained insoluble (grey zone).
Fig. 1-2. Ash-forming elements and their chemical forms in woody biomass fuels
The dashed lines apply to only certain fuel types (+ means bark and forest residue of pine; * means bark and forest residue of all four species). The dotted line applies to fuel impurities, of which the amounts may vary and for which the solubility is unknown (but typically insoluble). (Werkelin et al. 2010)

An improper choice of acid can hydrolyze hemicellulose and cellulose into smaller molecules, which may have negative impact on the biomass and its products (Das et al., 1997). An acid leaching process of biomass ash with degrading lignin content can also adversely influence the conversion process and increase waste disposal costs. Thus, leachate from the pretreatment process must be treated before discharging to the ambient environment.

Recent studies suggested that alternative solvents such as chelating agents that have been commonly used for removing inorganic ions in soil remediation are effective in disrupting and removing the water-insoluble elements in biomass, while retaining its high carbon content (without degrading hemicellulose, cellulose, and lignin). For instance, Edmunds et al (2017) found that ethylenediaminetetraacetic acid (EDTA) nearly completed extraction of alkali and alkaline earth metals such as K, Ca, and Mg, and high removal of S and Si of switchgrass by
using a microwave-assisted extraction method. Besides, nitrilotriacetic acid (NTA) and ethylenediaminopropandioic acid (EDDM) are biodegradable comparing to EDTA. Pyrolytic acid was also recently used as an alternative solvent for removing ash from waste biomass (Oudenhoven et al., 2016), and this organic acid is preferred over mineral acids.

1.3 Research rationale and objectives

Most of the previous studies by researchers on the reduction of ash content and the inorganic constituents from lignocellulosic waste biomass have applied mechanical size fractionation before conducting leaching experiment. However, the whole range of resulting particle sizes was subject to leaching, and the effectiveness of size fractionation on ash removal efficiency has not been separately quantified.

Besides, literature review reveals that allowable ash content has not been used as the major criteria for assessing the effectiveness of ash removal techniques. There is an existing standard (CEN, 2014) for the quality of fuel pellets derived from non-woody biomass feedstock such as cereal straw, whereby the allowable ash content of 6% dry-basis (db) is higher than that specified at 3% db for utility-grade wood pellets (CEN Standard: EN 14961-2) used for power and heat generation.

The overall goal of this thesis research is to improve the quality of agricultural crop residues by reducing the ash content to target values (allowable by applicable standards) using a combination of two pretreatment methods - mechanical size fractionation and leaching. It is desirable to minimize the need for water leaching and subsequent drying of the leached biomass for further processing into agro-pellets.

The specific objectives are:
• To assess the effectiveness of mechanical size fractionation in combination with the leaching technique to reduce the ash content and inorganic constituents from agricultural crop residues;
• To compare the effectiveness of leaching alone versus the combined method for ash removal;
• To perform a preliminary cost analysis of the ash removal techniques with respect to the production of agro-pellets
Chapter 2 Experimental Study of Ash Removal from Agricultural Crop Residues

2.1 Methodology and experimental design

2.1.1 Characterization of waste biomass

Three species of agricultural crop residues that were selected for investigation include canola straw, wheat straw, and corn stover as shown in Fig. 2-1. The waste biomass was collected from rural areas near London ON, Canada and dirt was removed before delivery to UBC. Various properties (moisture content, ash content and element composition) of the biomass were measured before the pretreatment tests for ash removal were performed in order to assess the effectiveness of the pretreatment methods under different conditions.

![Fig. 2-1. Corn stover (left), wheat straw (middle) and canola straw (right)](image)

Ash content and moisture content measurements

Ash content is a measure of the mineral matter and other inorganic constituents in the biomass sample. It is the most significant indicator that determines the effectiveness of the pretreatment methods. Moisture content was measured by drying the biomass sample in a convection oven (Thermo precision laboratory Model 130 DM). It is necessary to measure moisture content since ash content is expressed on dry basis.
Ash content was determined according to the National Renewable Energy Laboratory Standard Method NREL/TP-510-42622 (Sluiter et al., 2005), which is substantially similar to ASTM Standard E1755-01 (2003). The dried biomass sample was ignited in a program furnace (ThermoFisher Lindberg/Blue M™ Moldatherm™ Box Furnaces). The temperature of the program furnace is ramped from ambient temperature to 105 °C for 30 min and held for 12 min, then increased to 250 °C for 15 min and held for 30 min, and further ramped to 575 °C for 17 min and held for 3 h. The sample is cooled to 105 °C for 24 h before it is removed from the furnace and cooled to room temperature inside a glass desiccator. Finally, the sample is placed in the muffle furnace again at 575 °C and allowed to ash to constant weight. Constant weight is defined as less than ±0.3 mg change in weight after re-heating the crucible for 1 h.

**Elemental composition analysis**

The fusion behavior of ash is correlated with the slagging problem, which can be measured by the ash fusion test or analyzing the chemical composition of ash. The ratio of basic oxides (CaO, MgO, Fe$_2$O$_3$, Na$_2$O and K$_2$O) to acidic oxides (SiO$_2$, TiO$_2$ and Al$_2$O$_3$) present in ash has been a widely used index for the ash fusion behavior and fouling tendency of ash (Deng et al., 2013). This ratio is widely used in the industry to help establish the fuel specifications and for the purpose of plant operation and boiler design (Melissari et al., 2014.)

Biomass sample were sent to SGS Laboratory Inc. in Burnaby, BC for the analysis of the elemental composition of ash. Preliminary sample preparation required acid digestion of the biomass inside an oven. Thereafter, the sample was analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), whereby the ICP source converts the atoms of the elements in the sample to ions, and the ions are separated and detected by mass spectrometer.
2.1.2 Experimental method

The experimental method involves several series of tests that included mechanical size fractionation and leaching treatment. Fig. 2-2 illustrates the experimental procedure. Initially, crop residues were ground by hammer mill to facilitate characterization for moisture content, ash content and element composition. A grinder was then used for size reduction of the feedstock. The materials were sequentially milled to a particle size smaller than 3.175 mm (1/8”). Then, mechanical fractionation test was conducted, whereby the materials were separated into various size fractions. Through mechanical size fractionation, it will be possible to determine the percentage of original waste biomass that needs to go through further ash removal by leaching, so that the final ash content can meet with the target (allowable) ash content set by the international standard. Subsequently, leaching test was conducted on two sets of samples: 1) the ground biomass without mechanical fractionation; and 2) the fraction of ground biomass with the highest ash content (that does not meet the target level) after mechanical fractionation. More details about the experiment are described below. All of the tests in the experiment were performed in replicates.
Test Series I - mechanical fractionation

This series of test was performed after taking the raw samples for initial measurements of the biomass properties. During mechanical fractionation, the sample was sequentially ground to a particle size smaller than 3.175 mm using a hammer mill (Glenmills 10 HMBL; Fig. A1) with 3.175 mm screen according to previous studies (Lu et al. 2014; Theerarattananoona et al. 2011; Mani et al. 2004). An air suction system was attached to the hammer mill to remove and store the ground biomass temporarily before the milled biomass was fed to a vibratory screen shaker (Test-Master, Model W.S. Tyler RX-29; Fig. B2). The device consists of a series of sieves with different mesh sizes (>2, 1.4-2, 1-1.4, 0.5-1, 0.25-0.5, <0.25 mm). The materials were sieved to separate the fine residues and coarse residues after 10 min operation. The finest fraction of particles was collected in a pan. All samples were stored in sealed sampling bags at room temperature for analysis of physical and chemical properties. The size fractions and the ash
content of each size fraction are expected to be different from those observed by Lacey et al. (2016) using a 19.1 mm sieve. Hence, the amount of fractionated biomass going to the next stage of ash reduction treatment (leaching) is also expected to be different.

**Test Series II - leaching**

Water was used as the solvent in this series of test, with an aim to determine the extents of removal of the water-soluble elements vs. the water-insoluble elements in the biomass sample. Water temperature, leaching time and water-to-biomass ratio are the main factors in the washing process. The effectiveness of leaching depends on the particle size of the biomass, the type of material and the operational conditions of pretreatment (Yuan et al., 2011).

<table>
<thead>
<tr>
<th>Table 2-1. Leaching conditions for preliminary experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction</td>
</tr>
<tr>
<td>Water-to-biomass ratio (w/w)</td>
</tr>
<tr>
<td>Temperature, °C</td>
</tr>
<tr>
<td>Leaching time, hr</td>
</tr>
</tbody>
</table>

In order to narrow down the levels of each major factor chosen for the leaching test, preliminary tests were performed for ground canola straw as a typical type of crop residues. Table 2-1 shows an orthogonal experimental design, which consists of two levels of water temperature (25 and 45°C), five levels of leaching time (0.25, 1, 3, 12, and 24 h) and three levels of water-to-biomass ratio (30, 60 and 90). For each test, a fixed amount of biomass (10 g) were submerged and soaked in water in a 1 L beaker. Six beakers were placed in a water bath for conducting simultaneous tests with different combinations of the parameters. The experimental setup is shown in Fig. 2-3.
**Liquid/solids separation and moisture content measurement**

The solution was filtered out after leaching. Leached samples were then washed with ultrapure water three times before oven drying and measurement of ash content and element composition. For the leaching experiment, changes in electrical conductivity (EC) and pH of the leachate were measured by EC meter and pH meter, respectively. After washing, the biomass sample and the solution were separated using a filtration unit (glass funnel and beaker flask connected to the vacuum pump). The solids were recovered from the filter paper placed on top of the funnel. Leached samples were washed with ultrapure water to a constant pH value. The sum of the filtrate and the residue was used to determine the total dry mass recovered.

**2.2 Results and discussion**

Prior to mechanical fractionation, the materials were sequentially milled to a particle size smaller than 3.175 mm (1/8”). Some of the particles were actually found to be smaller than 1 mm. This follows the findings by Arvelakis et al (2003) from their study on agricultural residues. Data was analyzed for the three species of agricultural residues with different pretreatment methods.

**2.2.1 Mechanical size fractionation**

After mechanical size fractionation, data processing and analysis aims at illustrating the variation of ash content with respect to the particle size distribution. Ash contents and moisture contents of the raw crop residues are presented in Table 2-2. The ash contents of ground crop residues
(canola straw, corn stover, wheat straw) are (7.3±0.3%, 5.5±0.8%, 6.0 ±0.15% db) respectively, and the corresponding moisture contents are (9.1±0.3%, 8.3±0.2%, 7.6±0.1% wb) respectively. The ash contents of these materials are not very high since the dirt was removed after collection from the field. Moreover, the materials were air-dried before delivery to UBC.

<table>
<thead>
<tr>
<th></th>
<th>Ash content, % db</th>
<th>Moisture content, % wb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canola straw</td>
<td>7.3 ± 0.3</td>
<td>9.1 ± 0.3</td>
</tr>
<tr>
<td>Corn stover</td>
<td>5.5 ± 0.8</td>
<td>8.3 ± 0.2</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>6.0 ± 0.15</td>
<td>7.6 ± 0.1</td>
</tr>
</tbody>
</table>

As shown in Fig. 2-4, the finest fraction of ground canola straw, corn stover and wheat straw after mechanical size fractionation had the largest ash content, at 15.4±0.94%, 22.4±1.1% and 9.6±0.25%db, respectively. Fig. 2-5 shows the mass fraction of crop residues with respect to particle sizes ranging from <0.25 mm to >2 mm. Both canola straw and wheat straw has about 12% of particles (vs. 5% for corn stover) in the finest fraction. The weight percent of ash (wt%) with respect to particle sizes was also calculated knowing the mass of ash in each particle size range, as shown in Fig. 2-6.

Ash content increases with a decrease in particle size for all three types of crop residues. This could be attributed to two main reasons. Firstly, different plant tissues have different ash contents. The outer layer of crop residue is harder than the inner layer and thus more difficult to be milled into small size particles. Moreover, the outer layer of crop residue contains less inorganic constituents because the majority of soluble elements there can be washed off by rain. Hence, the coarser fractions of crop residues have lower ash contents. Secondly, entrained ash can result from soil and sand contamination during biomass harvesting, handling and storage, and the entrained ash tends to go into the small particle size fraction when milling raw biomass.
According to CEN Standard “EN ISO 17225-6:2014 Solid biofuels - Fuel specifications and classes - Part 6: Graded non-woody pellets” (CEN, 2014), the allowable ash content of non-woody pellets is 6% db. As seen in Figs. 2-4 and 2-5, for both canola straw and wheat straw, 32% of the fractionated materials (with particle size < 0.5 mm) had ash content that exceeds this limit. Whereas, for corn stover, only 5% of the fractionated materials (with particle size < 0.25 mm) had ash content that exceeds 6%. These are the materials that need to use other techniques to further remove ash in order to achieve the target ash content of 6% db. Thus, mechanical size fractionation is more effective for ash removal for corn stover as compared to canola straw and wheat straw. Since the original canola straw having an ash content of ash content of 7.3% is above the target of 6%, it is necessary to use other techniques to further remove ash from the canola straw.

The results of size fractionation are somewhat different from those observed by Lacey et al. (2016) as the size of the sieve used along with the grinding process was different (3.175 mm sieve in this study vs. 19.1 mm sieve used by Lacey et al.). It shall be noted that, if the target ash content were to be 3% rather than 6% (which makes it on par with the pellet quality standard for wood pellets), then for canola straw 100% of the fractionated biomass would need ash removal techniques beyond mechanical size fractionation because all fractions had ash content ranging from 4.8 to 15.4% db. This is also applicable to wheat straw since all fractions had ash content ranging from 3.5 to 9.6% db.
Fig. 2-4. Ash content of crop residues with respect to different particle sizes

Fig. 2-5. Mass fraction of crop residues with respect to different particle sizes
As shown in Table 2-3, Si, Ca and K are the main components of ash found in the biomass. Thus, the mode of their occurrence in the biomass structure is of great importance for removal. When compared to ground canola straw, ground corn stover and wheat straw had much higher SiO$_2$ contents by about 10 times. Fractionated corn stover and wheat straw (particle size < 0.25 mm) also had higher SiO$_2$ contents by about 3 times compared to fractionated canola straw. Corn stover and wheat straw had much lower CaO contents than canola straw. As for potassium, the K$_2$O content of ground canola straw and wheat straw was about 5 times greater, whereas the K$_2$O content of fractionated canola straw and wheat straw were about 8 times greater, when compared to corn stover.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>K$_2$O</th>
<th>MgO</th>
<th>P$_2$O$_5$</th>
<th>Na$_2$O</th>
<th>Fe$_2$O$_3$</th>
<th>Al$_2$O$_3$</th>
<th>TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground canola straw</td>
<td>5.4</td>
<td>31.1</td>
<td>26.8</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>0.4</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Ground corn stover</td>
<td>62.3</td>
<td>8.4</td>
<td>5.4</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
<td>4.1</td>
<td>9.6</td>
<td>0.7</td>
</tr>
<tr>
<td>Ground wheat straw</td>
<td>59.2</td>
<td>5.8</td>
<td>23.3</td>
<td>1.4</td>
<td>1.4</td>
<td>1.4</td>
<td>0.3</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Fractionated canola straw*</td>
<td>22.3</td>
<td>27.0</td>
<td>15.7</td>
<td>3.2</td>
<td>3.2</td>
<td>3.2</td>
<td>1.3</td>
<td>4.0</td>
<td>0.8</td>
</tr>
<tr>
<td>Fractionated corn stover</td>
<td>71.7</td>
<td>3.3</td>
<td>1.7</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>4.5</td>
<td>7.9</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Fig. 2-6. Weight percent of ash (wt%) with respect to different particle sizes

> 2 mm  1.4 - 2 mm  1 - 1.4 mm  0.5 - 1 mm  0.25 - 0.5 mm  < 0.25 mm
2.2.2 Preliminary leaching test

Determination of leaching conditions

Leaching test was performed on the finest fraction of the fractionated crop residues that has the highest ash content. The results of 30 experimental treatments for ground canola straw are summarized in Table 2-4. Under the same leaching time and temperature, a lower water-to-biomass ratio of 30:1 was able to attain a satisfactory and in fact the best performance (i.e. achieving the lowest ash content for the leached sample) vs. larger water-to-biomass ratio of 60:1 and 90:1. Leaching time of 0.25 h and 1 h were found to be less effective. Ash contents of leached canola straw samples were lower at 45 °C vs. 25 °C except for the longest leaching time of 24 h.

Although the original corn stover and wheat straw had ash content very close to the target of 6% db, the SiO\textsubscript{2} content of corn stover and wheat straw are much higher at 62-72% of ash and 59-69% of ash, respectively than canola straw (at 5-22% of ash). Therefore, it is desirable to conduct leaching experiment using all three species of crop residues in the follow-up series of experiment. The water-to-biomass ratio was set as 30:1, and the experimental treatments involve two leaching temperatures (25, 45 °C) and three leaching times (3, 12, 24 h). The advantage of using a lower water-to-sample ratio is the saving in water consumption.
Table 2-4. Experimental design and results of preliminary leaching test using canola straw

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Leaching time, h</th>
<th>Water-to-biomass ratio (w/w)</th>
<th>Ash content, % db</th>
<th>Ash removal efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Leaching temperature 25 °C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.25</td>
<td>30</td>
<td>3.98</td>
<td>43.5</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>60</td>
<td>4.04</td>
<td>42.7</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
<td>90</td>
<td>4.90</td>
<td>30.7</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>30</td>
<td>3.54</td>
<td>49.6</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>60</td>
<td>3.74</td>
<td>47.2</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>90</td>
<td>4.41</td>
<td>37.8</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
<td>30</td>
<td>2.49</td>
<td>66.2</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
<td>60</td>
<td>2.62</td>
<td>64.8</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
<td>90</td>
<td>2.82</td>
<td>61.9</td>
</tr>
<tr>
<td>10</td>
<td>12</td>
<td>30</td>
<td>2.30</td>
<td>68.9</td>
</tr>
<tr>
<td>11</td>
<td>12</td>
<td>60</td>
<td>2.35</td>
<td>68.1</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>90</td>
<td>2.66</td>
<td>63.9</td>
</tr>
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<td>24</td>
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<td>24</td>
<td>90</td>
<td>2.52</td>
<td>66.4</td>
</tr>
</tbody>
</table>
Ash color

The ash of untreated canola straw sample was initially dark grey, and the color of ash from the leached samples was visibly different. The canola straw samples leached for 3 h and 0.25 h at 45 °C had ash contents of 2.5 and 4.0% db respectively and the color of the ash colors appeared to be nearly white and light grey, respectively. The samples leached for 1 h at 45 °C had 3.54% ash content and its ash had an intermediate color between light grey and white. These observations suggest that the darkness of ash color could be a good indicator of leaching effectiveness for the same species of crop residue.

![Fig. 2-7. Ash colors of canola straw leached at 45°C (Leaching hour: left -3 h, middle-1 h, right-0.25 h)](image)

2.2.3 Water leaching

In this section, results are presented for water leaching tests using ground crop residues with and without mechanical size fractionation as the raw materials. Moreover, only the finest particle fraction (size < 0.25 mm) with an ash content exceeding the allowable level needs to go through this ash removal technique.

Ash color

For the unleached canola straw and wheat straw samples, the ash appeared grey dark. After the leaching experiments, their ash turned to a nearly white color, and it became even whiter for
longer leaching times. By comparison, the ash of unleached corn stover was initially brownish yellow and became lighter after the leaching experiments, as displayed in Fig. 2-8.

![Fig. 2-8. Ash color of samples leached at 25 °C for 3 h (left: canola straw, middle: corn stover, right: wheat straw)](image)

**Ash content after leaching**

The ash contents before and after water leaching are illustrated in Fig. 2-9. As previously stated, the ash contents of unleached ground canola straw, corn stover and wheat straw are 7.3±0.3%, 5.54±0.78% and 6.0±0.15% db respectively. Whereas, the ash contents of unleached finest fraction of canola straw, corn stover and wheat straw are 15.4±0.94%, 22.4±1.1% and 9.6±0.25% db, respectively.

![Fig. 2-9. Ash contents before and after water leaching](image)
Ground crop residues without fractionation

For canola straw, the ash content was sharply reduced from 7.3% to 2.87% db after leaching for 3 h at 25 °C. Thus the target ash content is achieved, though longer leaching times (12 h and 24 h) and higher temperature (45 °C) could lead to even lower ash content (~ 2.36% db). For corn stover, the ash content was reduced from 5.54% to 4.0% db when leaching for 3 h at 25 °C. Again, the target ash content is achieved, though the final ash contents could improve somewhat to 3.3% db with leaching times (3 h, 12 h) and increased temperature at 45 °C. For wheat straw, the ash content was reduced from 6% to ~ 4.2% db for both temperatures and all three leaching times, and the target ash content was achieved.

Finest fraction of ground crop residues with mechanical size fractionation

The best leaching conditions vary among the species of crop residues. For canola straw, the ash content was reduced from 15.4% to (7.16-8.14% db) when leaching for 3 h, 12 h and 24 h at 25 °C. At a higher temperature of 45 °C, the final ash content was improved to (6.36-6.79% db) with the same leaching times. However, for corn stover, the ash content was reduced from 22.4% to (17-18% db) regardless of leaching temperature and leaching time. The final ash content does not meet the target ash content. Similar findings were obtained for wheat straw, since the ash content was reduced from 9.6% to a rather narrow range of (7.48-8.25% db) regardless of leaching temperature and leaching time, and the final ash content does not meet the target ash content. Apparently, particle size has significant impact on the leaching performance. Under the same leaching condition, ground crop residues with larger average particle size have better leaching performance than the finest fraction of crop residues with particle size less than 0.25 mm.
**Ash removal efficiency**

The loss in biomass dry matter after leaching needs to be taken into consideration when estimating the ash removal efficiencies. The ash removal efficiency $\eta$, in %, may be calculated as follows:

$$\eta = 1 - \frac{M_f A_f}{M_i A_i}$$

where $M_i$ and $M_f$ are the dry mass of the samples, and $A_i$ and $A_f$ are the ash content of the samples before and after leaching, respectively.

![Fig. 2-10. Ash removal efficiency due to water leaching](image)

Fig. 2-10 depicts the ash removal efficiencies by water leaching under the two water temperatures (25 and 45 °C), and three leaching times (3, 12 and 24 h).

For the ground crop residues without fractionation, the ash removal efficiency of ground canola straw (65.4-73.3%) is much higher when compared to (35.3-53.6%) and (34.5-51.3%) for ground corn stover and ground wheat straw, respectively. At 25 °C, ash removal efficiency for canola straw has no significant change when leaching time is increased from 12h to 24h, but more
significant change from ~35% to ~50% was observed for wheat straw and corn stover. At 45 °C, all three species of crop residues exhibit little change in ash removal efficiency as leaching time is increased from 12h to 24h.

As for the finest fraction of ground crop residues with mechanical size fractionation, canola straw has the highest ash removal efficiency (55.6-71.0%) while corn stover and wheat straw have similar leaching performance with ash removal efficiency of (33.3-51.4%) and (28.1-48.0%), respectively. At 25 °C, ash removal efficiency for canola straw has no significant change when leaching time is increased from 12h to 24h, but more significant change was observed for wheat straw (from 30% to 40%) and corn stover (from 35% to 50%). At 45 °C, ash removal efficiency for canola straw again has no significant change when leaching time is increased from 12h to 24h, but ash removal efficiency for wheat straw and corn stover actually experienced a rather large drop from 45-50% to ~30%.

Overall, Fig. 2-10 illustrates that particle size has significant impact on the leaching performance. Under the same leaching condition, ground crop residues with larger average particle size have better leaching performance than fractionated crop residues having particle size smaller than 0.25 mm.

Based on the experimental data obtained under leaching conditions of (25 °C, 12h), the resulting total ash content of finest canola straw, corn stover and wheat straw were reduced to 5.4, 5.2 and 5.3% respectively after mechanical size fractionation followed by water leaching of the finest fraction of particles. By comparison, for the ground crop residues without size fractionation, the resulting total ash contents of canola straw, corn stover and wheat straw after leaching were reduced from (7.3, 5.5, 6.0% db) to (2.7, 3.9, 4.2% db), respectively. These values are based on the ash removal efficiency for each species of the crop residues. The resulting ash contents for the
leached and fractionated crop residues are higher than the ash contents of leached crop residues without fractionation since for the former case, it is not necessary for some of the fractionated biomass to go through the leaching process. Nevertheless, the ash contents of the materials involved in all experimental treatments are reduced to below the target value of 6% db.

**Removal efficiency of elements**

In order to determine the effectiveness of using water as solvent to remove different elements from the biomass, the removal efficiency of an individual element or constituent $\eta_e$, in %, is defined as

$$\eta_e = 1 - \frac{M_f A_f X_{i_f}}{M_i A_i X_{i_i}}$$

where $M_i$ and $M_f$ are the dry mass of the samples, $A_i$ and $A_f$ are the ash content of the samples, and $X_{i_i}$ and $X_{i_f}$ are the wt% of an individual element ($i$) in the ash before and after leaching, respectively.

Silicon is the second most abundant element in the earth’s crust so that all plants grown in soil will contain some Si in their tissues. Plant roots assimilate silicon in the form of silicic acid Si(OH)$_4$ (Marschner 2011). The solubility of amorphous silica in water involves an equilibrium between the solid phase and a monomeric form of silica in solution, presumably Si(OH)$_4$ (Alexander et al., 1954). Therefore, removal of silicon by water leaching can be represented by the removal efficiency of SiO$_2$ from biomass ash.

Potassium and calcium are taken up in the form of $K^+$ ion and $Ca^{2+}$ ion by the roots of biomass (Marschner 2011). When biomass is being washed in water, the cations of the alkali earth group are able to interact with the anions of carboxylic acids and other weak acids to form partially dissociated complexes (Joseph, 1946).
Fig. 2-11 demonstrates the effect of leaching time and water temperature on the removal efficiencies of the major elements Ca, Mg, K, Na and Si in corn stover alone. Firstly, 12 h leaching time results in significantly higher removal efficiencies of K and Na compared to 3 h leaching time at the same temperature of 25 °C. Secondly, 45 °C water temperature leads to significantly higher removal efficiencies of K, Na, Ca, Mg and Si compared to 25 °C for the same leaching time of 12 h.

Fig. 2-12(abc) shows the removal efficiencies of Si, Ca and K when the various types of biomass materials were subject to water leaching under two conditions (12h, 25 °C) and (12h, 45 °C).

The SiO₂ removal efficiencies for wheat straw, corn stover, and canola straw range from 14.9–34.4%, 32.3–48.0%, and 53.7–75.5%, respectively. Only canola straw had more than 50% SiO₂ removal efficiency. The difficulty of removing SiO₂ by water leaching indicates that SiO₂ is highly insoluble and stable refractory in biomass ash. According to Deng et al. (2013), the removal efficiency of SiO₂ probably reflects the bonding strength between amorphous silica and biomass matrix. Our results show that wheat straw has the lowest SiO₂ removal efficiency,
suggesting that the bonding strength in wheat straw could be the strongest among the three species of crop residues.

For all six types of biomass materials, SiO$_2$ removal efficiency increases significantly with an increase in water temperature from 25 to 45 °C upon leaching for 12 h (Fig.2-12a). At a higher temperature, the solubility of amorphous silica in water becomes higher; besides, more hemicellulose and cellulose would be released from the biomass matrix into water (He et al., 2009).
A large amount of potassium is removed from the fuels after water leaching (Fig. 12b). The K$_2$O removal efficiencies of all samples are greater than 80%, except for corn stover. Canola straw has somewhat higher K$_2$O removal efficiency (93-96%) compared to wheat straw (84-93%). By comparison, corn stover has significantly lower K$_2$O removal efficiency (ground residue: 77.5-81.6%; finest residue: 60.2-66.1%). Nevertheless, the effect of temperature on K$_2$O removal efficiency is negligible.

Canola straw has higher CaO removal efficiencies (44-61%) when compared to wheat straw (about 30%) and corn stover (40-50%). The finest (ground and fractionated) materials did better than the ground materials without fractionation (Fig. 12c). The CaO removal efficiencies increase with increasing water temperature for canola straw and corn stover, but this trend is not applicable to wheat straw. It is likely that more Ca$^{2+}$ ions that form complexes with organic acid anions will break away from the biomass matrix when water temperature rises.

These results are then compared to those reported in the literature that are pertinent to the removal efficiencies of several major elements from wheat straw by water leaching at 25-30 °C. Deng et al (2013) used 3 h soaking time and water-to-sample ratio of 80 in their experiment, and
achieved 90% removal efficiency of K but only 23% removal efficiency of Si. Dayton et al (1999) applied a longer soaking time of 24 h and water-to-sample ratio of 100; the (K, Na, Ca and Si) removal efficiencies were (84%, 83%, 37% and 13%), respectively. Jenkins et al (1996) used 24 h as soaking time along with a water-to-sample ratio of 70; the K and Na removal efficiencies were 67-68%, while the weight percent of Ca and Si in ash actually increased. In this study, water leaching is found to be less effective for Ca and Si (average 40% and 15%) as compared to K and Na (average 88-89%), and these findings are in line with observations made by other researchers. Liu et al (2011) observed a substantial reduction of soluble metal salts after water leaching on pine barks and switchgrass. Turn et al. (1997) reported ash reduction by 45%, and reduction in the elements (Cl, K, P, Mg, Na, S) by (98, 90, 72, 68, 68, and 55%) in their study of water leaching for fine banagrass.

**Properties of leachate**

At the beginning, electrical conductivity (EC) value measured is 0 µs/cm for ultrapure water without any biomass added. As illustrated in Fig. 2-13(a), the change in EC of leachate was 58-71, 9-15, 21-27 µs/cm for ground canola straw, corn stover and wheat straw. The change in EC of leachate for the finest fraction of ground canola straw, corn stover and wheat straw was 81-102, 10-16, 22-32 µs/cm respectively as Fig. 2-13(b).

EC is directly related to the concentrations of inorganic cations and anions (Chu et al., 1994). Thus, the high EC of leachate reflects the highly soluble salt contents. Based on the results for both the ground canola straw and the finest fraction of canola straw, a positive correlation is observed between ash removal efficiency and change in EC during water leaching.
The pH of leachates was in the range of (5.5-6.2, 4.7-6.2, 5.3-7.4) for ground canola straw, corn stover, and wheat straw. The values are slightly different, being in the range of (6.1-6.9, 5.3-7.0, 6.0-7.5) for the finest fraction of ground canola straw, corn stover, and wheat straw, respectively.

The color of the leachate varied from light yellow to dark yellow and could be attributed to the soluble salt contents and the oxidation of the ferrous ion (Fe$^{2+}$) to ferric form (Fe$^{3+}$). A small quantity of ferric form (Fe$^{3+}$) can form ferric hydroxide colloids and fulvic complexes, which contribute to the brownish color of leachate and the increase in suspended solids (Chian and DeWalle 1976). Though Fe was not present in significant amount in all samples, its contribution to color change is obvious.

2.3 Summary

In this chapter, the reduction of ash and the inorganic constituents in canola straw, wheat straw and corn stover was done by the mechanical size fractionation and water leaching methods. The following conclusions can be drawn:
1. After mechanical size fractionation, the finest fraction of ground crop residues (particle size < 0.25 mm) had much higher ash contents than the coarser fractions, at 15.4%, 22% and 9.6% db, respectively for canola straw, corn stover and wheat straw.

2. For both canola straw and wheat straw, 32 wt% of the fractionated materials had ash content that exceeds the allowable ash content of 6% db for fuel pellets made from non-woody biomass feedstock in accordance with the CEN Standard. Whereas, for corn stover, only 5 wt% of the fractionated materials had ash content that exceeds 6%. Hence, mechanical size fractionation can effectively reduce the need for leaching as a further ash removal technique, and it is most effective for corn stover.

3. Based on the results of preliminary experiments that involve two leaching temperatures (25, 45 °C), a lower water-to-biomass ratio (w/w) of 30:1 led to better leaching performance than ratios of 60:1 and 90:1, and shorter leaching time of (0.25 and 1 h) were found to be less effective than (3, 12 and 24 h). These operating conditions were then used in further water leaching tests that include all three species of crop residues.

4. For the water leaching tests, ground crop residues with and without mechanical size fractionation were used as the raw materials. Water leaching was applied to the finest particle fraction with ash content that exceeds the allowable level. Canola straw was found to have the best leaching performance and highest ash removal efficiencies when compared to corn stover and wheat straw, regardless of whether mechanical size fractionation was used for ash removal prior to leaching.
5. Particle size appears to have significant impact on the leaching performance. Under the same leaching conditions, non-fractionated ground crop residues (with larger average particle size) had higher ash removal efficiency than the finest fraction of fractionated crop residues.

6. Leaching time of 3 h or 12 h at a leaching temperature of 25 °C were found to be sufficient for effective ash removal for canola straw. Longer leaching time of 24 h would improve the ash removal efficiency for corn stover and wheat straw.

7. Under the leaching condition of (25 °C, 12h), the resulting ash content of canola straw, corn stover and wheat straw are 5.4, 5.2 and 5.3% db after mechanical size fractionation followed by water leaching of the finest fraction of particles, and the corresponding values are 2.7, 3.9 and 4.2% db, respectively for the materials without size fractionation prior to leaching. This means, the leaching technique is more effective than size fractionation for ash removal though the ash contents of the materials involved in all experimental treatments are reduced to below the target value of 6 % db.

8. Canola straw has somewhat higher K₂O removal efficiency (greater than 90%) compared to wheat straw, whereas corn stover has lower K₂O removal efficiency (65-80%), and the effect of leaching temperature on K₂O removal efficiency is negligible.

9. Among the three species of crop residues, only canola straw had more than 50% SiO₂ removal efficiency, whereas wheat straw has the lowest SiO₂ removal efficiency (below 35%). SiO₂ removal efficiency increases significantly with an increase in water temperature from 25 to 45 °C upon leaching for 12 h.
10. Positive correlation is observed between ash removal efficiency and change in EC value. Both ground canola straw with and without mechanical size fractionation have the highest ash removal efficiencies among their sample sets, and their leachates have the highest EC values.
Chapter 3 Preliminary Cost Analysis for Agro-pellet Production with Pretreatment of Crop Residues

3.1 Introduction

A preliminary cost analysis was performed to estimate the total production cost of agro-pellets with the pretreatment of crop residues to remove ash and the inorganic constituents. Following upon the experimental work done in Chapter 2, two options of pretreatment were considered in the analysis. Option 1 is pertinent to the removal of ash and inorganic constituents from the biomass using mechanical size fractionation and followed by water leaching. Option 2 is pertinent to ash removal using water leaching alone. The specific objective is to estimate and compare the total production cost of both options to that of pellet production without pretreatment for ash removal.

3.2 Methodology of cost estimation

Initially, the life cycle costs of making pellets from crop residues were estimated, following the guideline VDI 2067 (VDI 2067, 1983) and The Pellet Handbook (Obernberger and Thek, 2010). Data were extracted from open literature as well as website information provided by pellet manufacturers and equipment suppliers. Moreover, the data and information reported in two previous studies (Sultana et al. 2010 and Thompson et al. 2017) that are relevant to crop residues were adapted to the cost estimation in this study and in particular, for comparison purposes.

Sultana et al. (2010) estimated the life cycle cost (in 2008 USD) of producing agri-pellets in Western Canada. They divided the total cost incurred from straw (wheat, barley, or oats) harvesting to pellet production into three main components – field cost, transportation cost, and pellet production cost. Field cost includes the costs associated with harvesting and collection, bale wrapping, on-field storage, farmer’s premium payment, and nutrient replacement (fertilizers that need to be spread over the crop for replacing the nutrients removed from the soil when straw
is harvested). The cost of transportation cost (by truck) is made up of fixed cost for loading and unloading, and variable cost that covers wages, fuel and maintenance. Pellet production cost includes capital investment and operating cost (labour, energy, maintenance, consumables).

Thompson et al. (2017) investigated how the interdependent parameters of cost, supply and quality of biomass feedstock (logging residues, construction and demolition waste, corn stover, switchgrass) affect the biomass blends required by depots and/or biorefineries. Feedstock cost was considered to have three parts – farmgate price, feedstock logistics, and process costs for quality upgrading. The farmgate price is the sum of harvest and collection cost, on-field storage/queuing, delivery from the field to the farmer gate, and payment to grower. Feedstock logistics cost involves transportation, size reduction/grinding, drying, screening, and pelleting. Quality upgrading cost refers to the cost of leaching the biomass by dilute acid.

3.2.1 Process flow

Typical conversion of crop residues into pellets consists of four major unit operations: drying, grinding (size reduction), pelleting, and cooling as shown in Fig. 3-1(a). In addition, the process flow for Option 1 consists of the following major unit operations: grinding, mechanical size fractionation, leaching, filtering, drying of the unleached and leached biomass, pelleting, and cooling as shown in Fig. 3-1(b). The process flow for Option 2 is illustrated in Fig. 3-2(c).
This preliminary cost analysis is based on the use of canola straw as the raw materials to produce agro-pellets as solid biofuel. For Option 1, hammer mill equipped with a 3.175 mm screen is used to grind the raw biomass into suitable sizes for pelletization. The finest fraction of biomass
after screening is sent to the water-leaching unit for ash removal. Leaching will take place at 25°C and for 12 h duration as the removal of ash and the inorganic constituents was found to be effective under these operating conditions, as reported in Section 2.2.3 (Chapter 2). Both the leached biomass and unleached biomass will then enter the drying unit. Subsequently, the dried biomass (with 10% moisture content, wb) is compacted in the pellet mill to form pellets with specific size (such as 6 mm in diameter and 12-24 mm in length) (ISO 17225, 2014). Pellets that exit the pellet mill are fragile and hot, with temperature ranging from 70-90°C due to friction generated during the pre-heating and extrusion of pellets. A cooler is used to reduce the temperature of pellets before passing them over a screen to have fines removed. Pellets can then be stored in enclosed storage areas.

### 3.2.2 Pellet production cost

The total production cost (TPC) of pellets ($/tonne) is made up of the capital cost and the operating cost. Pellet production capacity of 6 dry tonnes (dt)/hr (or, 43,200 dt/yr) was assumed for this study, following the study made by Sultana et al. (2010) for straw. Capital cost includes the costs associated with capital investment (mainly purchased and installed equipment, building construction, and land use). Operating cost mainly includes the cost of raw materials, utility, labor, and maintenance. The plant is assumed to operate on the basis of 3 shifts/d, 24 h/d and 300 d/yr, thus the plant’s on-stream factor is 0.83. The general framework conditions for the base case (pellet production without pretreatment) are shown in Table 3-1.
### Table 3-1. General framework conditions for the cost analysis

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<th>Value</th>
<th>Unit</th>
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</tr>
<tr>
<td>Working days</td>
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<tr>
<td>Production capacity (pellets)</td>
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</tr>
<tr>
<td>Operating hours</td>
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<td>h/yr</td>
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<td>Plant on-stream factor</td>
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<td></td>
</tr>
<tr>
<td>Plant life &lt;sup&gt;a&lt;/sup&gt;</td>
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<td>yr</td>
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<td>Electricity price &lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.07</td>
<td>$/kWh</td>
</tr>
<tr>
<td>Other costs (insurance, administration, etc.)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.8</td>
<td>%</td>
</tr>
<tr>
<td>Interest rate</td>
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<td>%</td>
</tr>
<tr>
<td>Inflation rate</td>
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<td>%</td>
</tr>
<tr>
<td>Material loss during pelleting</td>
<td>5</td>
<td>%</td>
</tr>
</tbody>
</table>

<sup>a</sup> Plant life for the pellet plant is assumed based on other biomass-processing facilities. Kumar et al. (2003) and Sarkar et al. (2009) assumed similar number.

<sup>b</sup> https://www.statista.com/statistics/263492/electricity-prices-in-selected-countries/

<sup>c</sup> Average value over 10 years (Kumar et al. 2003 and Sarkar et al. 2009)

**Capital investment**

Capital cost includes investments in equipment, infrastructure, construction, and planning for the plant (equipment for grinding, pelletization, cooling, storage, leaching and drying; miscellaneous equipment, building construction, and land use). The purchase and installation costs of various equipment for the pellet mill as shown in Table 3-2 are taken from the literature (Sokhansanj et al., 2010; Mani et al., 2006; Perry and Green, 1999; Stanley and Walas, 1990) and websites.

For Option 1, leaching is applied to process about 2 tonnes/h (or 48 tonnes/d) of biomass, which represents the finest fraction of particles (< 0.25 mm) after mechanical size fractionation. Following the experimental work in Chapter 2, a water-to-biomass ratio (w/w) of 30 was used to estimate the size (capacity) of each vessel and hence the number of vessels required for the leaching operation. A similar procedure is used for Option 2 where the leaching is applied to process 6 tonnes/hr (or 144 tonnes/d) of biomass. Tanks for filtering and storage purposes are
included in the capital cost estimation. The cost of steel tank with capacity over 20 m$^3$ is assumed to be $126/m^3$.

The “capital recovery factor, CRF” is used to convert the capital cost of each device into an annualized capital cost, in $/yr.

\[
CRF = \frac{(1 + i)^N i}{(1 + i)^N - 1}
\]

where $i$ is the interest rate per annum (assumed to be 6%) and $N$ is utilization period of each piece of equipment.

The annualized capital cost is calculated by multiplying the capital recovery factor (CRF) with the investment cost, and it is further converted to the unit capital cost, in $/dt pellets, knowing the annual production capacity of pellets.

\[
Annualized \ capital \ cost = CRF \times Total \ Capital \ Investment \\
= CRF \times (Purchase \ Cost + Installation \ Cost)
\]

**Operating cost**

Operating cost consists mainly of the field and transportation costs for the crop residues, as well as the utility cost, labour cost and maintenance cost associated with pellet production and quality upgrading (pretreatment for ash removal). Since the loss of materials during pellet production is typically around 5% (Sultana et al., 2010), the actual mass of feedstock input to the pellet mill is about 45,500 tonnes.

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1 [www.Alibaba.com](http://www.Alibaba.com) and wxxlkj.1688.com
Field and transportation costs

Grain harvesting and stalk collection are to take place at the same time, and no tillage as part of sustainable residues management is considered for estimating the availability of straw. On-field storage of round bales (typically 500 kg weight each) will be in an open structure (under a roof) in order to avoid large dry matter loss over an extended time period (due to exposure to precipitation or higher ambient temperature), and this is less expensive than an enclosed storage structure. A premium should be paid to the farmers to encourage participation in biomass collection and ensure a constant supply of biomass throughout the year (Campbell, 2007).

Transportation is an important component of logistics for waste biomass utilization project as the low energy density of the bulky raw materials could lead to high transportation cost. In this study, the biomass feedstock is assumed to be transported from in-field storage to pellet plant by trucks. Sultana et al. (2010) suggested that the size of the pellet plant determines the area (assumed to be circular) from which the biomass is drawn. Thus, the transportation distance is proportional to the square root of the plant capacity and they derived a quantitative relationship between transportation cost and pellet plant capacity.

Utility cost

Utility cost accounts for the consumption of electricity, natural gas and water during the pellet production process.

**Electricity** Electricity is a significant component of pellet production cost since all pellet plant equipment needs power. Among all the equipment used for agro-pellet production, the pellet mill consumes the most power (~35% of total), followed by the dryer (~20% of total) (Sultana et al., 2010). The horsepower needed is determined by the feedstock species, particle size, pellet size,
moisture level and so on. It is assumed that an extra 100% of electricity is used for screen shaker during pretreatment with mechanical size fractionation (Option 1) compared to Option 2 (only use screen shaker to screen the agro-pellets with qualified size). The electricity price is assumed to be $0.07/kWh.

Natural gas According to the experimental results of mechanical size fractionation (Chapter 2), 32% of the fractionated canola straw (with particle size less than 0.5 mm) or about 2 tonnes/h biomass needs to go through the leaching process (25 °C temperature and 12 h duration) for effective ash removal. Measurements indicated that the leached biomass had a moisture content of 80% (wb). Thus, based on an annual requirement of 45,500 tonnes canola straw, the amount of water in fractionated canola straw that needs to be removed via drying the biomass from 80% to 10% (wb) moisture content will be 11,200 tonnes for Option 1. For Option 2, where ash removal is done by leaching only, the corresponding amount of water removed from 45,500 tonnes canola straw will be 31,850 tonnes.

Natural gas is commonly used as the fuel for the dryer to reduce the biomass moisture content and as the boiler fuel to produce steam. The energy requirement for drying depends on the type of dryer, fuel characteristics and drying medium. Typically, 3.0-3.8 MJ energy is required to evaporate 1 kg of water from wood (Kumar et al., 2017). Drying straw may need somewhat less energy when compared to woody biomass because of differences in their structure. In this study, an energy requirement of 3.0 MJ/kg water removed from canola straw was assumed. Hence, for Option 1, 30560 GJ/yr of natural gas is required for drying the leached biomass. At a 2018 natural gas rate of $3.8/GJ (C$5.1/GJ, $1=C$1.33) for large commercial users (FortisBC)², the unit natural gas cost is calculated to be $2.7/dt and $8.5/dt pellets for Option 1 and Option 2.

respectively. The original moisture content of canola straw is assumed to be 10%, so drying is not required prior to the grinding operation.

**Water**  The procedure for estimating the water cost is similar to that used for estimating the size of the vessel for leaching purposes. For Option 1, leaching at 25 °C and 12 h duration is applied to process about 2 dt/h (or 48 dt/d) of biomass, and a water-to-biomass ratio (w/w) of 30 was used to calculate the amount of water required. Likewise, for Option 2, the amount of water required was calculated in the same way.

The water rental rate for industrial use in BC is $1.69/m³ (C$2.25/m³) according to the BC Water Sustainability Act\(^3\). It is assumed that tap water is used for the leaching operation.

**Labor cost**

Labor cost includes the cost of personnel in production, marketing and administration in the agro-pellet production plant.

**Maintenance cost**

Equipment maintenance costs are calculated for each unit of the pellet plant, taking the different wear and useful life into consideration. The maintenance cost of each piece of equipment is assumed to be 2% of the equipment purchase cost, except for the hammer mill and pellet mill which are much higher at 18% and 10% of the equipment purchase cost, respectively (Thek and Obernberger, 2004).

---

**Total production cost**

After the capital cost and operating cost are estimated, the annualize capital cost, in $/yr and the operating cost, in $/yr was summed to arrive at the Total Production Cost (TPC) according to the following equation:

\[
\text{Total Production Cost, } $/\text{dt} = \frac{\text{Annualized capital cost} + \text{Annual operating cost (}}$/\text{yr})}{\text{Annual production capacity (dt/yr)}}
\]

**3.3 Results and discussion**

**3.3.1 Capital cost**

Table 3-2 shows the purchase and installation costs for the equipment involved in pellet production (without pretreatment of raw materials). The unit capital cost sums up to $5.79/dt pellets. As expected, the pellet mill and the dryer constitute 67% of the unit capital cost.

Similarly, the unit capital costs associated with Option 1 and Option 2 are calculated and shown in Table 3-2. Option 1 has a unit capital cost of $6.69/dt and Option 2 has a unit capital cost of $8.48/dt. Thus, pretreating the raw materials with mechanical size fractionation followed by leaching (Option 1) will add 12% to the capital cost associated with pellet production, whereas pretreating the raw materials with leaching alone (Option 2) will add almost 30% to the capital cost.

**3.3.2 Operating cost**

*Field and transportation costs*

As indicted in Table 3-3, the field cost and transportation costs are estimated to be $40.5/dt and $28.7/dt, respectively. In previous study, field cost was estimated to be $34/dt for wheat straw (harvesting and collection: $10/dt, on-field storage: $6.3/dt; nutrient replacement: $12.6/dt, farmer’s premium: $5.5/tonne) (Sultana et al., 2010; Wang et al., 2017). Transportation cost was
estimated to be $25/dt (based on 45,000 dt/yr pellet plant capacity and the correlation developed by Sultana et al. 2010 for wheat straw). These costs are assumed to be similar for canola straw in this study. Comparison was made with two studies in this aspect. In their simulation analysis of the logistics of corn stover supply, Wang et al. (2017) reported a total cost of $70/dt (or C$82/dt) for delivery of corn stover (without densification by pelleting) to a small-scale 63,000 dt/yr capacity biorefinery, which includes field cost, transportation cost and cost of storage in a depot. Whereas, Thompson et al. (2017) suggested that the farmgate cost (harvest and collection cost), storage cost as well as transportation and handling cost associated with a 63,500 dt/yr corn stover depot would be around $62/dt. Thus, the estimated cost in this study is in line with the relevant literature based on an average annual inflation rate of 2%.

Utility cost

For the base case (pellet production without pretreatment of raw materials), the electrical energy cost amounts to approximately $11.5/dt (Sultana et al. 2010). When pretreatment is applied, additional power requirement for Option 1 is small (less than 1% of total). Table 3-4 shows the components of the utility cost for Option 1 and Option 2. For electricity consumption, the electricity costs are essentially the same for both options (~$11 dt). Since Option 2 has greater natural gas consumption for drying, the natural gas cost for Option 2 ($9.4/dt) is about three times that for Option 1 ($3.0/dt). Water cost shows the largest difference between the two options; the water cost for Option 2 ($50.8/dt) is substantially higher (by three times) than that for Option 1 ($16.9/dt). Thus, Option 2 has a total utility cost of $70.7/dt which is double the utility cost of $31.1/dt for Option 1.
**Labor cost**

Based on the literature (primarily Campbell 2007), four permanent employees (secretary, general manager, financial manager and supervisor) and 6-9 hourly wage employees would be required for the pellet plant with a production capacity of 43,200 dry tonnes per year. Three additional hourly-wage workers are required for operating the leaching and mechanical size fractionation equipment. Therefore, the unit labor cost for pellet production without pretreatment is estimated to be $13.8/dt, whereas that for Option 1 and Option 2 are estimated to be $23.8/dt and $18.8/dt, respectively. More details about the estimation of labor cost can be found in Appendix C2.

### 3.3.3 Total production cost

The total production cost (TPC) of agro-pellets as summarized in Table 3-5 indicates that TPC for the case of pellet production without pretreatment would be USD102/dt. The TPC will be increased by 30% to USD132.6/dt for Option 1 (pretreatment by mechanical size fraction plus water leaching), and increased by 66% to USD169.1/dt for Option 2 (pretreatment by water leaching only).

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Purchase Cost ($)</th>
<th>Installation Cost ($)</th>
<th>Expected Life (yr)</th>
<th>Capital recovery factor</th>
<th>Annualized capital cost ($/yr)</th>
<th>Unit capital cost ($/dt)</th>
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<tbody>
<tr>
<td>Hammer mill</td>
<td>79,169</td>
<td>31,667</td>
<td>10</td>
<td>0.1359</td>
<td>15,063</td>
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<td>0.1359</td>
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<td>0.16</td>
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<tr>
<td>Rotary drum dryer</td>
<td>461,818</td>
<td>277,091</td>
<td>15</td>
<td>0.103</td>
<td>76,108</td>
<td>1.76</td>
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<tr>
<td>Pellet mill</td>
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<td>10</td>
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<td>1.97</td>
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<tr>
<td>Pellet cooler</td>
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<td>31,667</td>
<td>15</td>
<td>0.103</td>
<td>7,611</td>
<td>0.18</td>
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</tbody>
</table>

57
Summary of capital cost

(Option 1 – pretreatment with mechanical size fractionation + leaching)

<table>
<thead>
<tr>
<th>Item</th>
<th>Option 1</th>
<th>Option 2</th>
<th>Base case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaching and filtering</td>
<td>136,080</td>
<td>408,240</td>
<td>38,766</td>
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<tr>
<td>Total</td>
<td>$1.57M</td>
<td>$1.8 M</td>
<td>288,640</td>
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</table>

Summary of capital cost

(Option 2 – pretreatment with leaching only)

<table>
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<th>Item</th>
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</thead>
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<tr>
<td>Leaching and filtering</td>
<td>136,080</td>
<td>408,240</td>
<td>38,766</td>
</tr>
<tr>
<td>Total</td>
<td>$1.57M</td>
<td>$1.8 M</td>
<td>288,640</td>
</tr>
</tbody>
</table>

Table 3-3. Unit operating cost for agro-pellet production ($/dt)

<table>
<thead>
<tr>
<th>Item</th>
<th>Option 1</th>
<th>Option 2</th>
<th>Base case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field cost</td>
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<td>40.5</td>
<td>40.5</td>
</tr>
<tr>
<td>Transportation cost</td>
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<td>28.7</td>
<td>28.7</td>
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<tr>
<td>Utility cost</td>
<td>31.1</td>
<td>70.7</td>
<td>11.5</td>
</tr>
<tr>
<td>Labor cost</td>
<td>23.8</td>
<td>18.8</td>
<td>13.8</td>
</tr>
<tr>
<td>Maintenance cost</td>
<td>1.76</td>
<td>1.89</td>
<td>1.7</td>
</tr>
<tr>
<td>Total</td>
<td><strong>125.9</strong></td>
<td><strong>160.6</strong></td>
<td><strong>96.2</strong></td>
</tr>
<tr>
<td></td>
<td>Option 1</td>
<td>Option 2</td>
<td></td>
</tr>
<tr>
<td>--------------------------</td>
<td>----------</td>
<td>----------</td>
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</tr>
<tr>
<td>Electricity cost</td>
<td>11.5</td>
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</tr>
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<td>Natural gas cost</td>
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<td>Water cost</td>
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</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>31.1</strong></td>
<td><strong>70.7</strong></td>
<td></td>
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</table>

Table 3-5. Total production cost (TPC) of agro-pellets ($/dt)

<table>
<thead>
<tr>
<th></th>
<th>Option 1</th>
<th>Option 2</th>
<th>Base case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit capital cost</td>
<td>6.69</td>
<td>8.48</td>
<td>5.79</td>
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<tr>
<td>Unit operating cost</td>
<td>125.9</td>
<td>160.6</td>
<td>96.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>132.6</strong></td>
<td><strong>169.1</strong></td>
<td><strong>102.0</strong></td>
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</tbody>
</table>

### 3.4 Summary

1. The total production cost (TPC) for the base case of pellet production without pretreatment to remove ash was estimated to be US102/dry tonne pellets. The unit operating cost represents 94% of the TPC, whereas unit capital cost accounts for the remaining 6%. Field cost and transportation cost constitute a significant part of the operating cost at 69%.

2. The TPC will be increased by 30% to USD133/dt for Option 1 (pretreatment by mechanical size fraction plus water leaching), and increased by 66% to USD169/dt for Option 2 (pretreatment by water leaching only).

3. Unit capital cost increases from $5.8/dt (base case) to $6.7/dt for Option 1 and $8.5/dt for Option 2. Hence, capital cost remains being a smaller portion of the TPC for both options.
4. Increase in operating cost is the main reason for the substantial increase in TPC for Option 1 and Option 2 vs. the base case (without pretreatment). In turn, this is due to the higher labor cost induced by more workers for conducting leaching unit and the higher utility cost induced by a large water-to-biomass ratio (w/w) of 30:1. Besides, if water-to-biomass ratio could be reduced to 20:1 or lower, the water cost can at least drop from $16.9/dt to $10.83/dt and from $50.8/dt to $33.83/dt, respectively for Option 1 and Option 2. Due to the dominance by utility cost, field and transportation costs make up 54% and 42% of the operating cost for Option 1 and Option 2, respectively and become a less significant component of the operating cost.
Chapter 4. Overall Conclusion and Recommendations for Future Work

4.1 Overall conclusion

In this study, a combination of two pretreatment methods - mechanical size fractionation and leaching was conducted to improve the quality of agricultural crop residues (canola straw, wheat straw and corn stover) by reducing the ash content to the allowable (target) value of 6% db following the applicable standard (CEN: EN ISO 17225-6). The preliminary cost analysis of agro-pellet production with ash removal technology was performed on the basis of the experimental results.

Study of the mechanical size fractionation process can help to delineate the range of biomass particle sizes having the smallest and largest amount of harmful inorganic elements after fractionation. The results suggest that after size fractionation, the finest fraction of ground crop residues (particle size < 0.25 mm) had much higher ash contents than the coarser fractions. Results also indicate that size fractionation can reduce the need for leaching as a further ash removal technique, and it is most effective for corn stover when compared to canola straw and wheat straw.

Results of the leaching tests after mechanical fractionation suggest that the leaching operating conditions and particle size can have significant impact on the leaching performance. Shorter leaching time of (0.25 and 1 h) and higher water-to-biomass ratio (60:1 and 90:1) were found to be less effective. Under the same leaching conditions, non-fractionated ground crop residues with larger average particle size had higher ash removal efficiency than the finest fraction of fractionated crop residues. Among the three species of crop residues, canola straw was found to have the best leaching performance, regardless of whether mechanical size fractionation was used for ash removal prior to leaching. Canola straw had the highest ash removal efficiencies,
K₂O removal efficiency (greater than 90%) and SiO₂ removal efficiency (more than 50%). The results also demonstrate that the effect of leaching temperature on K₂O removal efficiency is negligible while SiO₂ removal efficiency increases significantly with water temperature increasing from 25 to 45 °C upon leaching for 12 h. Moreover, positive correlation is observed between ash removal efficiency and change in electrical conductivity (EC) value.

A preliminary cost analysis was performed to estimate the total production cost of agro-pellets based on different process designs with respect to the ash removal techniques. The total production cost (TPC) for the base case of pellet production without ash removal pretreatment was estimated to be US$102/dry tonne pellets. The TPC would be increased by 30% to US$133/dt for Option 1 (pretreatment by mechanical size fraction plus water leaching) and increased by 66% to US$169/dt for Option 2 (pretreatment by water leaching only). Capital cost remains to be a minor portion of the TPC (approximately 5%) for the base case and both options. Rather, an increase in operating cost is the main reason for the substantial increase in TPC for Option 1 and Option 2 vs. the base case. In turn, this is due mainly to the higher utility cost induced by a large water-to-biomass ratio (w/w) of 30:1, and the somewhat higher labor cost for operating the leaching unit. If the water-to-biomass ratio could be reduced to 20:1 or lower, the water cost can at least drop from $16.9/dt to $11.3/dt and from $50.8/dt to $35.4/dt, respectively for Option 1 and Option 2.

4.2 Recommendations for future work

Future research work that can build upon the findings in this thesis project are listed below.

1. Water leaching conditions: investigate lower water-to-biomass ratio (w/w) such as 20:1 and assess the cost-effectiveness of ash removal via water leaching.
2. Investigate the feasibility of using river water for leaching if the farms are located closer to river and the leaching operation can be carried out on-site. However, the study shall include the collection of sufficient river water samples in order to carry out a thorough analysis of the water quality. In this regard, the focus will be on the concentrations of the AAEMs (alkali and alkaline earth metals) and other elements (if any are present) that may hinder the leaching process.

3. Obtain crop residues that have higher content (10-15% db) of structural ash (rather than ash in entrained soil which can be readily removed) in order to assess the effectiveness of mechanical size fractionation technique and water leaching technique more fully.

4. Use scanning electron microscope (SEM) to help determine if and how the structure of wheat straw can affect silicon removal as results show that wheat straw has the lowest SiO₂ removal efficiency, suggesting that the bonding strength in wheat straw could be the strongest among the three species of crop residues.

5. Conduct tests under different experimental conditions and do more elemental composition analysis after the ash removal tests in order to obtain a larger set of data for the removal of the key elements from ash (Silicon and AAEM – alkali and alkaline earth metals). Then, investigate if it is necessary to use other solvents such as biodegradable chelating agents to removal the highly water-insoluble elements (in particular, silicon).

6. Consider the option of mixing the crop residues with sawdust to further reduce the ash content after mechanical size fractionation and water leaching. This will also improve the binding properties of the raw materials and hence the durability of the pellets made primarily
from crop residues. Depending on the availability and price of sawdust in a region, the blending with sawdust could also help reducing the cost associated with ash removal.

7. Perform techno-economic assessment that includes the analysis of costs, benefits, and profitability indicator (such as net present value) with an aim to determine the most cost-effective strategy for ash removal during waste biomass preprocessing.
References


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Appendices
## Appendix A

### Table A-1. Results of water leaching tests for the three species of crop residues

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Leaching temperature, °C</th>
<th>Leaching time, h</th>
<th>EC, (10 µs/cm)</th>
<th>Ash content (% db)</th>
<th>Ash removal efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canola straw &lt; 0.25 mm</td>
<td>25</td>
<td>3</td>
<td>8.63</td>
<td>8.14</td>
<td>55.6</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>12</td>
<td>8.87</td>
<td>7.25</td>
<td>64.9</td>
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<tr>
<td></td>
<td>25</td>
<td>24</td>
<td>10.23</td>
<td>7.16</td>
<td>69.6</td>
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<td></td>
<td>45</td>
<td>3</td>
<td>9.03</td>
<td>6.79</td>
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<td></td>
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<td>8.10</td>
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<td></td>
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<td>24</td>
<td>9.57</td>
<td>6.36</td>
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<td>Corn stover &lt; 0.25 mm</td>
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<td>17.03</td>
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<td></td>
<td>25</td>
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<td>Ground wheat straw</td>
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<td>4.23</td>
<td>39.3</td>
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</tr>
</tbody>
</table>
Appendix B

B1. Experimental equipment

Fig. B-1. Glenmills 10 HMBL hammer mill

Fig. B-2. Test-Master screen shaker (W.S. Tyler RX-29)
B2. Removal efficiencies of elements

(a) Si removal efficiency, %

(b) Ca removal efficiency, %

(c) K removal efficiency, %
Fig. B-3 (a-i). Removal efficiencies of (Si, Ca, K, Mg, P, Na, Fe, Al, Ti) after leaching
Appendix C

C1. Capacity adjustment factor

The equipment costs are estimated for various capacities by using the capacity adjustment factor. The power function is commonly used for adjusting the cost of equipment from one capacity to another, using the following equation

\[ Cost_2 = Cost_1 \times \left( \frac{Capacity_2}{Capacity_1} \right)^n \]

where \( n \) is the capacity adjustment factor related to the production capacity of the equipment, as measured by flow rate or heat duty. The values of \( n \) for different equipment range from 0.33 to 1.0 (Sarkar et al., 2009), typically in the range of 0.6 to 0.7. In our case, the costs for most equipment items are estimated based on their size in the present design. It is assumed that the overall plant capacity adjustment factor is 0.65 for estimating the cost of pellet processing equipment (Mani et al., 2006; Spath et al., 2005). Thus, capital cost will increase by 0.65% as the plant capacity increase by 1%.
C2. Data for cost analysis

Table C-1. Power requirement and electricity cost

<table>
<thead>
<tr>
<th>Electric power</th>
<th>Electricity consumption, MWh/yr</th>
<th>Electric power cost, $/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>demand, kW</td>
<td></td>
<td></td>
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<tr>
<td>Hammer mill</td>
<td>75</td>
<td>540</td>
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<tr>
<td>Screening</td>
<td>5</td>
<td>36</td>
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<tr>
<td>Rotary drum dryer</td>
<td>120</td>
<td>864</td>
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<td>Pellet mill</td>
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<tr>
<td>Pellet cooler</td>
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<tr>
<td>Miscellaneous equipment</td>
<td>40</td>
<td>288</td>
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<tr>
<td>Lighting and heating</td>
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<td>806</td>
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Data source: https://www.alibaba.com; Sultana et al., 2010; Campbell, 2007; Obernberger I and Thek G, 2010.

Table C-2. Employee and administrative costs

<table>
<thead>
<tr>
<th>Number of hourly-wage employee</th>
<th>Option 1</th>
<th>Option 2</th>
<th>Hourly rate</th>
<th>Salary</th>
<th>Unit</th>
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<tbody>
<tr>
<td>Maintenance &lt;sup&gt;b&lt;/sup&gt;</td>
<td>1</td>
<td>1</td>
<td>34</td>
<td>50,000</td>
<td>$/year</td>
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<tr>
<td>Leaching &lt;sup&gt;c&lt;/sup&gt;</td>
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<td>6</td>
<td>30</td>
<td>70,000</td>
<td>$/year</td>
</tr>
<tr>
<td>Loading and unloading &lt;sup&gt;d&lt;/sup&gt;</td>
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<td>2</td>
<td>28</td>
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<td>Number of permanent employee</td>
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<td>Marketing</td>
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<td>$/year</td>
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<td>70,000</td>
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<td>$/year</td>
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<td>$/year</td>
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<td>Supervisor</td>
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<td>60,000</td>
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<td>$/year</td>
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<td>Specific labor cost</td>
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<td>18.8</td>
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<td>$/dt</td>
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</table>

Data source: Sultana et al., 2010;
https://www.glassdoor.ca/Salaries/vancouver-pellet-plant-salary-SRCH_IL.0,9 IM972 KO10,22.htm

<sup>b</sup> On-call, assumed maintenance worker works for 10 h every month (120 h per year).
Assumed three plant operators and three workers for pretreatment work for 7200 h every year and each one work for 2400 h due to three shift operation.

Assumed two plant operators work for 8 h every day (2400 h per year).

<table>
<thead>
<tr>
<th>Table C-3. Maintenance cost</th>
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</thead>
<tbody>
<tr>
<td>Maintenance cost, $/yr</td>
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<tr>
<td>Hammer mill</td>
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<td>Screening</td>
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<td>Rotary drum dryer</td>
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<td>Pellet mill</td>
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<tr>
<td>Pellet cooler</td>
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<tr>
<td>Storage bin</td>
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<tr>
<td>Leaching and filtering (Option 1)</td>
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<td>Leaching and filtering (Option 2)</td>
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<tr>
<td>Option 1</td>
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<td>Option 2</td>
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