Development of a Binder from Hydrolyzed Specified Risk Materials for Pelletization of Torrefied Wood

by

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Abstract

Torrefaction is a thermal pretreatment of woody biomass in a temperature range of 200-300 °C without air or oxygen, which leads to a heating value for the woody biomass that is closer to that of coal, and also improves hydrophobicity. Torrefied wood pellets could improve co-firing rate with coal in coal-fired power plants or be used as substitute for coal. However, a densification technique like pelletization is needed to increase the bulk density of torrefied wood to decrease costs associated with handling, transportation, and storage. It is difficult to pelletize torrefied wood because the natural binder for wood pellets, lignin, undergoes structural changes during torrefaction. Therefore, an external binder is needed.

The objective of this research was to develop a protein-based binder from specified risk materials (SRM) that could be used for pelletization of torrefied wood. SRM are a proteinaceous by-product from cattle tissues where prions are most likely to concentrate. About 300,000 tonnes of SRM are landfilled or incinerated annually in North America[1, 2]. As an alternative, SRM can be thermally hydrolyzed, allowing peptides recovery. Prior to using peptides as a binder for pelletization of torrefied wood, several challenges need to be addressed: a suitable binding strength of the peptides must be achieved, chlorine and salts must be removed, and an industrially relevant method for drying SRM hydrolysates must be developed. During this study, the freeze-drying step currently used for processing of SRM hydrolysates at laboratory scale was replaced with spray drying, a much more industrially feasible drying option. The available carboxylic and primary amine groups were estimated and found to be statistically similar to those of peptides obtained from freeze drying. Chlorine in freeze-dried and spray dried peptides was assessed at 1.8 % and 1.3 %, respectively. A washing step was then introduced before thermal hydrolysis to reduce the chlorine content in resulting peptides. It was found that the prewashing step could reduce chlorine levels to 0.436 %, and could also lower levels of some salts.

The use of unmodified peptides did not improve the durability of torrefied wood pellets at a 0-2 % binder level. This clearly indicated the necessity to improve the binding strength of peptides by proper chemical modification and/or chemical crosslinking. Polyamidoamine epichlorohydrin (PAE) was chosen as a crosslinker, as previous work in the Bressler lab showed that peptides-PAE was a successful plywood adhesive. At 1 % peptides-PAE (25 % PAE) binder level and 28 % moisture, the durability of torrefied wood pellets was 81.7 ± 2.0 %. An increase of peptides-PAE (25 % PAE) to 2 % significantly improved the durability to 88.6 ± 1.0 %. Increasing the PAE percentage from 23 % to 25 % did not improve the durability of pellets. However, under the same pelletization conditions, the peptides-PAE binder resulted in pellets of much higher durability than that of the control sodium lignosulphonate. The lowest moisture content using the pilot scale pelletizer in this research for pelletization was 27-28 %. This was too high from the industrial perspective as cracks or pores could be created in pellets during drying and moisture removal, which could result in pellets with low durability. In order to lower the moisture content for pelletization, a different single pellet press pelletization system was used. It was found that the durability of single pellets with 3 % peptides (prewashed & spray dried)-PAE (33 % PAE) was significantly better than that of pellets without binder, at 10 % moisture content.

This research showed that using of peptides-PAE as a binder could improve durability of resulting torrefied wood pellets. Additionally it demonstrated that spray drying could replace freeze drying and be adapted into SRM hydrolysates processing protocol, washing SRM before thermal hydrolysis could reduce chlorine content of resulting peptides, and moisture content for pelletization could be lowered to 10 % using a single pellet press.

Preface

This project was continuum of proof of concept experiments. The bulk of the research was done independently by Chengyong Zhu, and no part of the main thesis has been published (both appendices have been previously published). Dr. David C. Bressler, Dr. Michael Chae, Dr. Birendra Adhikari, and Chengyong Zhu contributed to the experimental design and data evaluation. Drs. Chae and Bressler also helped with thesis editing.

The thermal hydrolysis of specified risk materials (SRM) was done in the Bressler lab with the help of Dr. Birendra Adhikari (postdoctoral researcher). Dr. Adhikari also helped by developing the spray drier protocol for drying SRM hydrolysates. The CHNS elemental analysis of peptides was done in the Analytical and Instrumentation Laboratory of the Chemistry Department, University of Alberta. The chlorine content of peptides was analyzed by the Natural Resources Analytical Laboratory, Department of Renewable Resources, University of Alberta. The main metals content of peptides was assessed in the Canadian Centre for Isotopic Microanalysis, Department of Earth and Atmospheric Sciences, University of Alberta. The pilot scale pelletization of torrefied wood was done at the Bio-processing Innovation Center, Alberta Agriculture and Forestry with the help of Dr. Jianbo Lu and technician Zhixiong Zhang. The single pelletization of torrefied wood was a collaboration work with Dr. Shahabaddine Sokhansanj, University of British Columbia.

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List of Abbreviations

SRM: Specified risk materials

CFIA: Canadian Food Inspection Agency

PAE: Polyamidoamine epichlorohydrin

LLDPE: Linear low-density polyethylene

BSE: Bovine Spongiform Encephalopathy

PFI: Pellet Fuel Institute

ISO/DIS: International Organization for Standardization /Draft International Standard

SDS-PAGE: Sodium dodecyl sulfate polyacrylamide gel electrophoresis

SDS: Sodium dodecyl sulfate

SEC-HPLC: Size exclusion high performance liquid chromatography

FTIR: Fourier-transformed infrared spectroscopy

OPA: O-phthalaldehyde

TNBSA: 2, 4, 6 -Trinitrobenzenesulfonic acid

1 Introduction

1.1 Research background

Electricity plays a pivotal role in our modern society. Currently, electricity generated from coal remains a major fraction of the electrical grid. According to World Coal Association, coal accounts for 37 % electricity generation globally[3]. However, electricity from coal-fired facilities results in significant greenhouse gas emissions, which negatively impacts global warming. There are many initiatives and efforts around the world to reduce greenhouse gas emissions. For example, the EU set ambitious targets for 2030: a minimum 40 % cut in greenhouse gas emissions compared to 1990 and a minimum 27 % of total energy consumption must come from renewable sources[4]. In Alberta, Canada, the government plans to phase out all pollution from coal-fired electricity and have 30 % of electricity coming from renewable sources by 2030[5].

Presently, woody biomass is gaining importance and popularity for power generation around the world. This is because energy from woody biomass is considered carbon neutral[6]. It can significantly reduce net carbon emissions and negative environmental impacts when woody biomass displaces coal or other fossil fuels[6]. However, woody biomass is characterized as having a low bulk density, low calorific value, high moisture content, and a hygroscopic nature, which results in difficulties in collecting, handling, transportation, and storage[7]. In addition, when woody biomass is co-fired with coal, density differences between the two materials could cause difficulties during feeding into the boiler and thus reduce burning efficiency[8].

One method to overcome the low bulk density of woody biomass is to densify it through pelletization. Densification can increase the bulk density of woody biomass from 150-200 kg/m^3 to 600-800 kg/m^3 and reduce costs associated with handling, transportation, and storage[9].

Wood pellets are mainly used for co-firing in coal-fired power plants as well as for domestic and district heating[10]. It is estimated that the annual production of wood pellets will reach 10 million metric tons by 2020[11].

During co-firing with coal, a relatively low blending rate (about 5-10 %) of pellets is currently employed[10] because of the lower heating value of traditional wood pellets compared with that of coal. In addition, traditional wood pellets are not generally stored outside or for a long time because their hydrophilic nature promotes moisture uptake, which lowers their calorific values and leads to decomposition of the biomass. To overcome these challenges, the wood pellet industry is investigating transitioning towards torrefied wood pellets.

Torrefaction is a thermal pretreatment of woody biomass in a temperature range of 200-300 °C without air or oxygen, and has been shown to improve the heating value, hydrophobicity, and grindability of the resulting woody biomass[12, 13]. However, torrefied wood still suffers from a low bulk density, and thus pelletization is required, which requires more energy input. Furthermore, since lignin, the natural binding component of traditional wood pellets, undergoes structural changes during torrefaction[14] or is blocked from coming to the surface, the torrefied material does not pelletize very well and often requires the use of an external binder[15].

Currently, there is no commercial binder available for the pelletization of torrefied wood, but the torrefied wood pellet industry has great interest in producing a cheap and renewable binder. A few materials such as lignin[16, 17], sawdust[17], starch[16, 17], calcium hydroxide[16], and linear low-density polyethylene[18] (LLDP) have been tested for pelletization of torrefied material using a single pellet press. However, these materials resulted in pellets with lower heating values and higher equilibrium moisture than pellets without binders. In addition, calcium hydroxide significantly increased the ash content[16], and to melt LLDP, a

higher die temperature of 150 °C is needed compared to the die temperature typically used for pelletization (70-110 °C). The effects of die temperature, compaction, moisture content, and binders on the quality of torrefied wood pellets have been studied by pelletization using a single pellet press[13, 16-18]. However, there are few studies that have scaled-up pelletization using parameters obtained from the single pellet press. In addition, the durability of pellets when they reach their equilibrium moisture content is highly relevant from an industrial perspective, but has not yet been reported.

Protein is a natural binder and has been shown to improve the inter-particle bonding during pelletization and briquetting[19]. Specified risk materials (SRM) are protein-rich by-products from cattle tissues where prions, the causative agent of mad cow disease, are most likely to concentrate[1]. Because of their connection with mad cow disease, these tissues are currently banned from animal feed, food, and fertilizer applications by the Canadian Food Inspection Agency (CFIA). As a result, it is estimated about 300,000 tonnes of SRM are landfilled/buried or incinerated annually in North America[1]. This results in a great economic loss to the rendering industry. Thermal hydrolysis has been shown to be an effective method of prion inactivation, and results in the production of a peptide-rich by-product stream. Thus, the objective of this research is to utilize peptides recovered from thermally hydrolyzed SRM to develop a proteinaceous binder for pelletization of torrefied wood.

In order to improve bonding strength and water resistance of the resulting binder, peptides were subjected to chemical crosslinking and/or modification. In a previous study from our lab, peptides recovered from thermally hydrolyzed SRM were chemically crosslinked using polyamidoamine epichlorohydrin (PAE) and used as an effective plywood adhesive. Plywood specimens bonded with the peptides-PAE adhesive had good dry and soaked lap shear strength

that far surpassed industrial requirements[2]. Here, the potential of peptides-PAE to function as a binder for the pelletization of torrefied wood was studied.

In addition, the research in this thesis examined alternative processing mechanisms that are anticipated to positively impact commercial adoption and process economics. For example, peptides recovered from thermally hydrolyzed SRM were historically freeze-dried to generate a dry powder. Here, we examined spray drying as a more industrially relevant process for the drying of peptides. Furthermore, chlorine levels are tightly regulated in the torrefied wood pellet space and thus we explored different mechanisms for reducing chlorine in the resulting torrefied wood pellets.

Based on the above background description, it is hypothesized that if a crosslinking agent can promote formation of large crosslinked peptides structures through modification of hydrophilic functional groups, then this binder will improve the durability of the resulting torrefied wood pellets.

1.2 Objectives

The overall objective of this project is to develop a peptides-based binder to improve interparticle binding and water resistance of torrefied wood pellets.

1.2.1 Long-term objectives

1) To develop a technology to valorize SRM

2) To develop a renewable binder for the torrefied wood pellet industry

1.2.2 Short-term objectives

1) To replace freeze drying with spray drying for processing of SRM hydrolysates

2) To remove chlorine from peptides by washing SRM before thermal hydrolysis

3) To improve binding strength of peptides by chemical crosslinking with PAE resin

4) To investigate effects of moisture content, binder types, and binder level on the durability of torrefied wood pellets

2 Literature review

2.1 Wood composition

Woody biomass is one of the most abundant biomass sources on the planet and is receiving much interest as a renewable resource for the production of fuels, chemicals, and other products. It is mainly composed of cellulose, hemicellulose, and lignin. The structure of lignocellulosic biomass is shown in Figure 2.1..

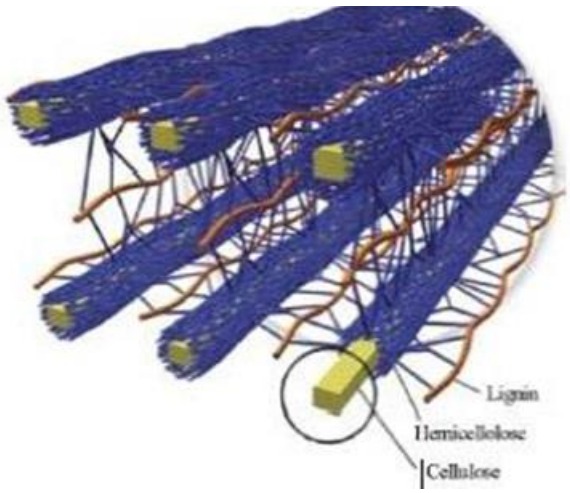

Figure 2.1. The structure of lignocellulosic biomass[20] (Reuse from the open access journal: International the Journal of Natural Resource Ecology and Management)

2.1.1 Cellulose

Cellulose is made up of D-glucose units, which are linked together by β(1→4) glycosidic bonds[7]. The general formula of cellulose is $(C_6H_{10}O_5)n$, and the polymerization degree (n) could be up to 8,000 -10,000 glucose molecules[21]. Through forming intramolecular and intermolecular hydrogen bonds between hydroxyl groups within the same cellulose chain and the surrounding cellulose chains, the chains tend to arrange in parallel and form a crystalline structure which gives strength to cellulose[22]. Cellulose accounts for 40-60 % dry weight of wood[23], and typically has a heating value of 17-18 MJ/Kg[24].

2.1.2 Hemicellulose

Hemicellulose is a branched mixture of various polymerized monosaccharides including glucose, xylose, galactose, mannose, arabinose, and glucuronic acid[7]. The general formula of hemicellulose is $(C_5H_8O_4)n$, where the polymerization degree (n) could be up to 50-200 glucose/saccharide molecules[21]. The monosaccharide composition of hemicellulose often differentiates the various biomass types. For example, xylan is the most dominating constituent of hemicellulose in hardwood, while glucomannan is predominant in softwood[24]. Hemicellulose makes up 20-40 % dry weight of wood[23], and has a heating value of 17-18 MJ/Kg[24].

2.1.3 Lignin

Lignin is a complex, highly branched, crosslinked, and amorphous polymer. It is made up of basic phenyl propane units, including p-coumaryl, coniferyl, and sinapyl alcohol[24]. Coniferyl alcohol and a small amount of p-coumaryl is found in softwood, while coniferyl, sinapyl alcohol and a small amount of p-coumaryl are found in hardwood[22]. Lignin contributes to the mechanical strength of wood by gluing the fibers together between the cell walls[22]. The

lignin makes up 10-25 % dry weight of wood[23], and has a heating value of 23.3-26.6 MJ/Kg[24].

2.2 Pretreatment of woody biomass for energy production

The use of woody biomass as an energy fuel suffers from its low heating value and hygroscopic nature (affinity for water)[7, 10]. There are several technologies available that are used to upgrade woody biomass, such as torrefaction, oxidative torrefaction, and hydrothermal carbonization.

2.2.1 Torrefaction

Torrefaction is also called mild pyrolysis. It is a thermal pretreatment of woody biomass in a temperature range of 200-300 °C without air or oxygen and low particle heating rates (< 50 K min^{-1}) with a long residence time[21]. The main purpose for torrefaction of woody biomass is to improve the heating value and hydrophobicity of the resulting biomass[12, 13, 25]. Torrefaction products include a solid residue (torrefied wood), condensable gases like water and acetic acid, as well as non-condensable gases like CO_2, CO, and CH_4[26]. It is reported that 70 % of the mass of woody biomass is typically retained in the solid residue, which contains 90 % of the initial energy. Conversely, the other 30 % of mass is converted into gas, which contains only 10 % of the initial energy content of the woody biomass[12, 25].

2.2.2 Oxidative torrefaction

In contrast to torrefaction, oxidative torrefaction is carried out in presence of 3-6 % oxygen instead of an inert atmosphere (i.e. nitrogen)[27, 28].It is reported that the oxidative torrefaction process produced torrefied sawdust and pellets similar to non-oxidative torrefied sawdust and corresponding pellets in regards to characteristics such as density, energy consumption for pelletization, heating value and energy yield[27, 28]. Moisture absorption and

hardness of the pellets from oxidative torrefaction were not significantly different from those of pellets from non-oxidative torrefaction[27]. Conversely, a key advantage of oxidative torrefaction is the possibility of incorporating oxygen-laden combustion flue gases as the carrier gas for torrefaction of biomass, which would help reduce operating costs.

2.2.3 Hydrothermal carbonization

Hydrothermal carbonization is also called wet torrefaction. It is carried out at a temperature range of 180-260 °C in the presence of hot compressed subcritical water under pressure (2 to 6 MPa) for 5 to 240 min[24, 29]. The advantage of hydrothermal carbonization is the elimination of the pre-drying requirement for the feedstock since this process is carried out in the presence of water. Three different products: solid (hydrochar), liquid (aqueous soluble) and gas (mainly CO_2) are produced from hydrothermal carbonization[24]. It has been reported that 55-90 % of the mass is retained in the solid product (hydrochar), which has 80-95 % of the energy content of the original feedstock[29].

2.2.4 Steam explosion

Steam explosion is widely used to pretreat biomass for the production of lignocellulosic bioethanol[7]. It is usually performed at a temperatures range of 200-260 °C for 5-10 min followed by rapid decompression[30]. The calorific value and carbon content of biomass are increased after steam explosion, while the bulk density and equilibrium moisture content are decreased[31]. Similar to torrefaction, an increase of steam temperature or explosion time could increase the degree of steam explosion[7]. The recovered solid residue, mainly cellulose and lignin, accounts for 70 % of original feedstock, while hemicellulose is washed out during a solid-liquid separation.

2.3 Physical and chemical changes of woody biomass during torrefaction

The torrefaction process can be divided into the following stages[26, 32]: 1) a non-reactive drying stage (50-150 °C); 2) a reactive drying stage (150-200 °C); 3) a destructive drying stage (200-300 °C). In the non-reactive drying stage, the biomass loses moisture and shrinks, while most of the constituents of biomass remain intact. At the higher temperature range of this stage (120-150 °C), lignin softens and acts as a binder for densification. During the reactive drying stage, breakage of hydrogen and carbon bonds is initiated and results in the emission of lipophilic extractives as well as the depolymerization of hemicellulose. Finally, the destructive drying stages results in devolatilization (the first step in all thermal processes and produces various volatile species and char[33]) and carbonization. Temperatures over 300 °C are not recommended as this could initiate the pyrolysis process, which results in extensive devolatilization of biomass[26]. During torrefaction, the heating value, hydrophobicity, and grindability of woody biomass are improved[12, 13, 25]. However, bulk density and interparticle bonding of torrefied wood are decreased.

2.3.1 Heating value

The heating value is also called calorific value or heat of combustion[34], which refers to the total energy released as heat when a material is completely combusted with oxygen under standard conditions. The heating value is generally reported as higher heating value/gross calorific value or lower heating value/net calorific value[34]. The higher heating value of a fuel refers to the amount of heat released by a specified quantity (initially at 25 °C) once it is combusted and the products have returned to the initial temperature of 25 °C and the latent heat of vaporization of water is recovered by condensation of water vapor in the combustion products[35]. The lower heating value of a fuel refers to the amount of heat released by

combusting a specified quantity (initially at 25 °C) in oxygen with all of the products being gaseous and in which the latent heat of vaporization of water in the reaction products is not recovered[35].

One of the objectives of torrefaction of biomass is to increase its heating value, which is achieved by the removal of moisture and some low heating value organic compounds from the original biomass[36]. A typical mass and energy balance for torrefaction of wood is that 70 % of remaining mass (torrefied wood) contains 90 % of the initial energy content of wood, resulting in increased energy density[25]. The heating value of torrefied biomass depends on the original biomass, torrefaction temperature, and torrefaction residence time. It has been reported that the higher heating value of softwood species such as spruce, pine, and fir is improved from 19.4 to 21.5 MJ/kg, 20.4 to 22.1 MJ/kg, and 19.5 to 22.3 MJ/kg, respectively, when they are torrefied at 280 °C for 52 min[37]. When the torrefaction temperature is increased from 270 to 300 °C and the torrefaction residence time is kept at 16.5 min, the higher heating value of the resulting torrefied spruce is increased from 21.1 to 22.5 MJ/kg[38]. For hardwoods like willow, when the torrefaction temperature was increased from 230 to 290 °C and the torrefaction residence time was kept at 30 min, the higher heating value increased from 20.2 to 21.9 MJ/kg[39]. For grass-like reed canary, when the torrefaction temperature was increased from 250 to 290 °C and the torrefaction residence time was maintained at 30 min, the higher heating value increased from 20.0 to 21.8 MJ/kg[39]. Thus, torrefaction is an effective way to increase the heating value of biomass.

2.3.2 Hydrophobicity

Another advantage of torrefaction is the improved hydrophobicity (water resistance/reduced moisture affinity). There are two possible explanations that account for the

improved hydrophobicity of torrefied biomass. The first one is the destruction of hydroxyl groups after torrefaction, which limits the ability of the torrefied biomass to form hydrogen bonds with water[7, 12]. Alternatively, the formation of non-polar unsaturated structures may prevent the passage of moist air through the torrefied biomass[7].

There are two methods to determine hydrophobicity of torrefied biomass, namely direct water immersion and equilibrium moisture content. As the name indicates, direct water immersion is carried out by immersing the torrefied biomass or torrefied biomass pellets into water for a specific time, and then determining the increase in mass after immersion. It was reported that torrefied wood pellets did not disintegrate and showed little water uptake even after 15 hours immersion in water[12]. The equilibrium moisture content is done by placing torrefied biomass or their pellets into a humidity chamber until they reach constant weight. It is reported that the equilibrium moisture content of non-torrefied sawdust pellets is 20.73 % when they are exposed to 90 % humidified air at 30 °C. In contrast, the equilibrium moisture content of torrefied sawdust pellets drops to 13.6 %; an increase of torrefaction temperature does not further improve the equilibrium moisture content[40]. A similar result was also reported by Peng *et al.*[13].

2.3.3 Grindability

When biomass is used for co-firing in coal-fired power plants, it needs to be pulverized as the coal to facilitate injection and fast combustion[7]. Thus, for this application, an additional benefit of torrefaction is the improved grindability of the torrefied material. This is mainly due to the breakdown of the hemicellulose matrix and depolymerization of the cellulose during torrefaction[26, 36]. The improved grindability could lead to increased production of fine particles under the same grinding conditions and 70-90 % less specific energy consumption[7,

12]. According to Ghiasi *et al.*[41], to grind 1 kg of torrefied wood chips, the total energy requirement is 39 kJ/kg, which is substantially less than the 292 kJ/kg required when non-torrefied wood chips are used.

2.3.4 Inter particle bonding

In general, an increase in torrefaction temperature or torrefaction residence time results in the establishment of fewer interparticle bonds, which are of great importance for production of high-quality pellets. This is due to the removal of hydrogen bonding sites, as well as depolymerization and destruction of fibrous structures (i.e. less entanglement)[42]. Consequently, more energy input or an additional binder is needed for effective pelletization of torrefied wood. According to Li *et al*., the total energy consumption required to pelletize torrefied sawdust is significantly higher than that of sawdust, and the total energy consumption increases with the degree of torrefaction[40]. A similar result was also reported by Peng *et al*.[37], who reported that while a die temperature of 170-230 °C is needed to densify unconditioned torrefied softwood[37], a die temperature of 230 °C or above is needed to make strong torrefied pellets of high density and low moisture uptake from 30 wt % weight loss torrefied samples[13].

2.3.5 Hemicellulose decomposition during torrefaction

Hemicellulose is the most reactive biomass component during torrefaction, followed by cellulose, and then lignin[26, 32, 43]. Depolymerization of hemicellulose starts at 150 °C, while most thermal decomposition take places at 200-300 °C[26]. A “reacting” intermediate hemicellulose could result from partial depolymerization of native hemicellulose[26]. This “reacting” intermediate is further decomposed and recombined to form torrefied hemicellulose. Water and acids from these reactions are released into the reaction environment and may be used

to further depolymerize hemicellulose or to release acids from the hemicellulose[26]. The products of hemicellulose during thermal decomposition include water, acetic acid, carbon dioxide/monoxide, chars, and tars[26, 43].

2.3.6 Cellulose decomposition during torrefaction

The degree of polymerization of cellulose decreases in the temperature range of 150-190 °C[43], while most thermal degradation occurs at 240-350 °C[26]. The crystalline structure of cellulose helps resist thermal decomposition better than unstructured hemicellulose[26]. In the temperature range of 250-300 °C, cellulose undergoes dehydration via bond scission, elimination of carbonyl and carboxyl groups resulting in the formation of CO and CO_2, respectively, and limited devolatilization and carbonization with formation of tars and chars[21]. Extensive devolatilization resulting from free radical cleavage of the glucosidic bonds takes place when the temperature is above 300 °C[21].

2.3.7 Lignin decomposition during torrefaction

Softening of lignin without any significant weight loss could be observed when temperatures are below 200 °C[43]. Thermal decomposition of lignin occurs in a wide temperature range of 280-500 °C, and results in phenols by cleavage of ether bonds and scissioning of carbon-carbon bonds[14, 26]. Lignin is difficult to dehydrate and thus more chars could be generated from lignin than from hemicellulose and cellulose[26].

2.4 Main applications for torrefied wood

Torrefaction results in biomass with higher calorific value, improved hydrophobicity, and better grindability[12, 13, 25], which makes them suitable for co-firing with coal in existing coal-fired power plants or gasification[6, 7, 25, 26, 32, 36, 44].

2.4.1 Co-firing with coal

Co-firing is generally defined as the combustion of two different types of material at the same time or use of a supplemental fuel in a boiler besides the primary fuel that the boiler is originally designed to burn[6]. Co-firing of biomass has been shown at large scale (Figure 2.2.) and can reduce the net carbon emissions from coal-fired power plants[6, 44]. However, raw woody biomass can only be used at a relatively low co-firing rate (1-20 %, based on mass)[6] with the existing infrastructure. Higher co-firing rates could lead to loss in boiler efficiency[6] and require modification of existing infrastructure[36]. Torrefaction makes resulting woody biomass more similar to coal, and thus a higher co-firing rate could be achieved with the existing infrastructure when torrefied wood is used as a replacement for coal[6, 12, 32].

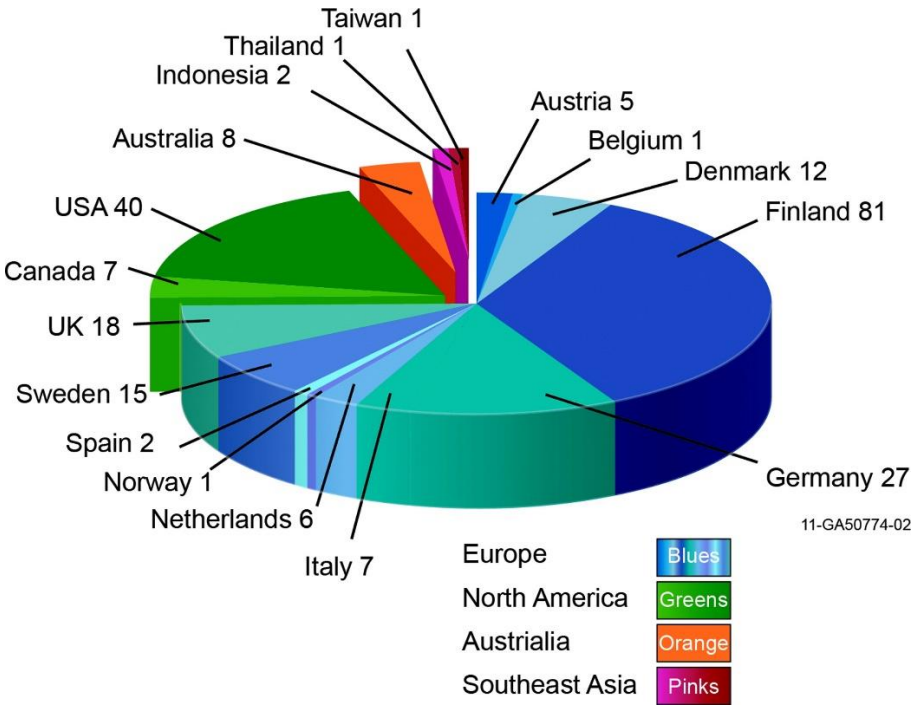

Figure 2.2. Number of power plants demonstrating co-firing capabilities in International Energy Agency member countries[6] (Reuse from the open access journal: Industrial Biotechnology)

In the coal to electricity process, the coal is usually pulverized before entering boilers to facilitate efficient burning. In the co-firing torrefied wood with coal in pulverized coal boilers experiments, more elongated co-fired flames as well as torrefied biomass flames were observed compared to coal flames[42, 45]. In addition, replacement of coal with torrefied biomass results in lower emissions of NO_x and SO_2[42, 45]. Slower combustion reactivity of torrefied biomass[44] and reduction of NO_x and SO_2 emissions in co-firing experiments were also reported in another two studies[44, 46].

2.4.2 Gasification

Gasification refers to the partial oxidation of carbonaceous feedstock above 800 °C to produce a syngas, a mixture of CO and H_2, which can be used for applications like gas turbines, engines, fuel cells, methanol and hydrocarbons production[25]. As a pretreatment of biomass, torrefaction results in biomass with improved hydrophobicity, better grindability, and appropriate C/H and C/O ratios[12, 13, 25]. As a result, gasification using torrefied biomass could possibly benefit from better flow properties of feedstocks, higher levels of H_2 and CO in the syngas, and improved overall process efficiencies[36]. In a study of Sarkar *et al.*, it is reported that combined torrefaction and densification of switchgrass results in the best gasification efficiency, followed by that of densified, raw and torrefied switchgrass[47]. Gasification of combined torrefied and densified switchgrass led to the highest yields of H_2 and CO, highest syngas lower heating value at 900 °C[47]. The quantity of syngas produced is increased with severity of torrefaction[48].

2.5 Densification

Densification of biomass is achieved by forcing particles together using mechanical force to create interparticle bonding, leading to defined shapes like pellets and briquettes etc.[9, 19]. The end-product typically has a bulk density of 600-800 kg/m^3. A pelletizer consists of a

perforated hard steel die with one to three rollers (Figure 2.3.). The feed material is forced through the perforations (die channels) by rotating the die or rollers. The friction between the feed particles and the wall of the die resists the free flow of feed particles and thus particles are compressed against each other inside the die to form pellets[8, 9].

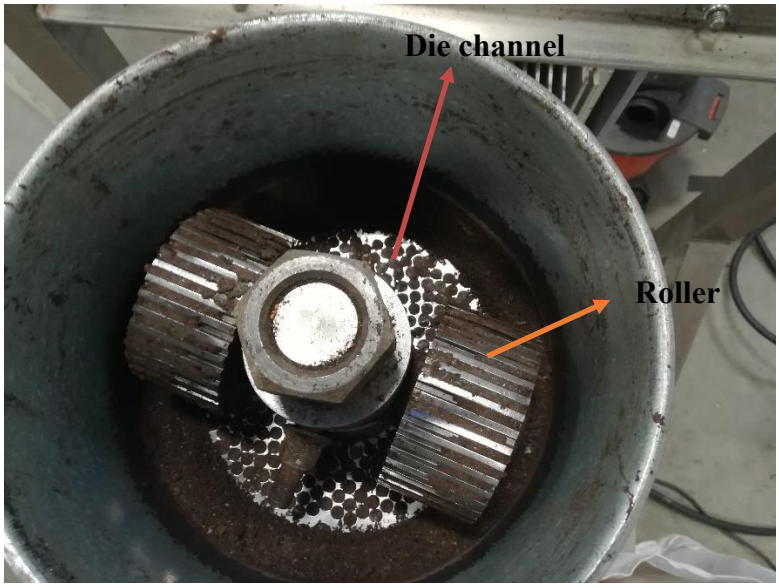

Figure 2.3. A flat die pelletizer used in this research

Three postulated stages may be involved during densification of biomass according to Mani *et al.*[49]: In stage one, feed particles form closely packed mass by rearranging themselves. Most particles still retain their own properties and identities, and the energy is dissipated due to interparticle and particle-to-wall friction; In stage two, the particles are forced against each other by the applied pressure, and undergo plastic and elastic deformation. The interparticle contact is significantly increased because of solid bridging, Van der Waals, or electrostatic forces, as well as mechanical interlocking; In stage three, the volume is further reduced by the applied pressure until the maximum density of the feed materials is reached. The bonding will be compromised if more pressure is applied after the maximum density of the feed materials is reached.

2.5.1 Mechanism of particle bonding during densification

The strength and durability of densified products depend on the physical forces that bond the particles together[9]. The binding forces between particles of densified products could be classified into the following categories: solid bridges, mechanical interlocking, adhesion and cohesion, attraction forces between solid particles, interfacial forces and capillary pressure[50]. One or more of these mechanisms contribute to the overall strength of densified products.

Solid bridges are predominately responsible for the strength in the final densified product[51], and typically result from the hardening of the binder, diffusion of molecules from one particle to another at points of contact, chemical reactions, crystallization of some constituents, or solidification of melted components[9, 19]. Mechanical interlocking is prominent when fibrous or needle shaped particles are mechanically agglomerated together[23]. These bonds result from interlocking or folding of fibers, flat-shaped particles, and bulky particles during compression[9]. Attraction forces between particles include Van der Waals' forces, electrostatic force, and magnetic force[9], which are inversely related to the distance between

particles. Adhesion and cohesion are forces introduced by addition of highly viscous binders or thin adsorption layers[9, 23]. Binders like molasses and tar could stick to surfaces of solid particles to generate strong solid bridges like bonds[9, 23]. Strong bonds could also be formed between particles from immobile thin adsorption layers, which smoothen surfaces thereby increasing the interparticle contact area or by decreasing the interparticle distance and allowing intermolecular attractive forces to participate in the bonding mechanism[9, 51]. Interfacial forces and capillary pressures arise from surface tension between liquids (i.e. moisture) and air systems, and attraction between moisture and the surface of the solid substance, respectively[23].

2.5.2 Measurement of strength of torrefied wood pellets

The strength of torrefied wood pellets depends on the forces that bind torrefied wood particles together. Hardness, durability, impact resistance, and water resistance are often used to evaluate strength of torrefied wood pellets.

2.5.2.1 Hardness

Hardness is also called compressive resistance, and represents the maximum force needed to break up or fracture the pellets[9, 52]. It is carried out by placing a single pellet between two flat, parallel platens, followed by application of an increasing load at a constant rate until cracking or breaking up of the single pellet is observed[9, 52]. The hardness test simulates compressive stress due to weight of the top pellets on the lower pellets during storage in bins or silos, as well as the crushing of pellets in a screw conveyor[9]. However, this test will not predict how much dust will be produced from pellets during handling, transportation, and storage[9]. The effect of moisture content, die temperature, binder level, compression force, and particle size on the strength of the resulting pellets are mostly studied using a single pellet press[52] as this is a more cost-effective approach considering the time and materials required. The strength of

resulting single pellet is evaluated by the hardness test. Meyer hardness (H_M) is often used to represent durability of pellets[13]. It is calculated by the following equation[13]:

$$Meyer\ hardness = \frac{F}{\pi(Dh - h * h)}$$

where F is maximum force to break a pellet, D is the probe diameter, and h is the indentation depth.

However, it is worth noting that the hardness assessed using single pellets may show great variations[40, 52].

2.5.2.2 Durability

The durability test is an industrially adopted standardized method that is different from the hardness test, and there is no direct relationship between them[52]. Durability is also called abrasive resistance, and is a quality parameter defined as the ability of densified materials to remain intact when handled during storage and transportation. Thus, pellet durability represents a pellet's physical strength and resistance to being broken up[26]. Fine particles could be produced by abrasion, impact, and shearing of pellets over each other and over the wall of the tumbling can[9]. The durability of pellets is tested in the following way: 500 g of dust free pellets are put into a tumbling can, followed by tumbling at 50 rpm for 10 min. The fine particles are removed by a standard sieve (0.8 times the pellet diameter), and mass of pellets remaining on the sieve is weighed[9]. Durability is calculated as the following equation[9, 52]:

$$Durability = \frac{mass\ of\ pellets\ after\ tumbling}{mass\ of\ pellets\ before\ tumbling} * 100\ \%$$

The minimum requirement for the durability of torrefied wood pellets is 95 %. Only a few studies have reported durability of torrefied wood pellet up to or above 95 % and in these studies, however, the standard deviation was not reported[41, 42, 53].

Durability of single pellet can also be analyzed using a wrist action shaker, a method that is similar to the tumbling can method. Nevertheless, the durability of single pellets from a wrist action shaker is distinct from that of the tumbling can method, and there is no established direct relationship between them. A key advantage of the wrist action shaker is that much less materials (a single pellet) is needed compared to the tumbling can method (500 g pellets).

2.5.2.3 Impact resistance

Impact resistance is also known as drop resistance or shattering resistance[9]. This test mimics the forces encountered during emptying of densified products from trucks onto the ground, or from chutes into bins, and possibly indicates the safe height for pellet production[9]. It is carried out by dropping the densified product onto a concrete surface several times from a certain height until it fractures[9, 54]. The impact resistance index is calculated as the following equation[6, 52]:

$$Impact\ resistance\ index = \frac{N}{M} * 100\ \%$$

Where *N* is the number of drops of the densified product, *M* is the number of pieces the densified product is broken into.

2.5.2.4 Water resistance

Water resistance is a desirable characteristic for commercial torrefied wood pellets. Torrefied wood pellets that exhibit high levels of water resistance may be stored outside as is the case for coal. Although there is no standard method to analyze the water resistance of torrefied wood pellets, two methods are often used, namely the immersion test and equilibrium moisture content[10, 14, 26, 52, 53]. Equilibrium moisture content refers to the moisture of a sample in thermodynamic equilibrium with its surrounding atmosphere, at a certain relative humidity, temperature, and pressure[55]. The immersion test, as its name implies, is done by immersing

torrefied wood pellets in water for a certain amount of time; the weight change of torrefied wood pellets before and after immersion is expressed as a percentage of moisture adsorption[55, 56]. However, one drawback of the immersion test is the potential disintegration of the torrefied wood pellets. As a result, the percentage of moisture adsorption may not be accurate. The hardness or durability of torrefied wood pellets after the immersion or equilibrium moisture content tests is rarely reported.

2.6 Factors affect strength of torrefied wood pellets

Hardness, durability, and water resistance of torrefied wood pellets typically depend on the processing parameters used for manufacturing the pellets. Such parameters include particle size, die temperature, compression force, moisture, severity of torrefaction, die speed, and the binder used[14, 16-18, 29, 37, 38, 41, 55, 57, 58] (Figure 2.4.).

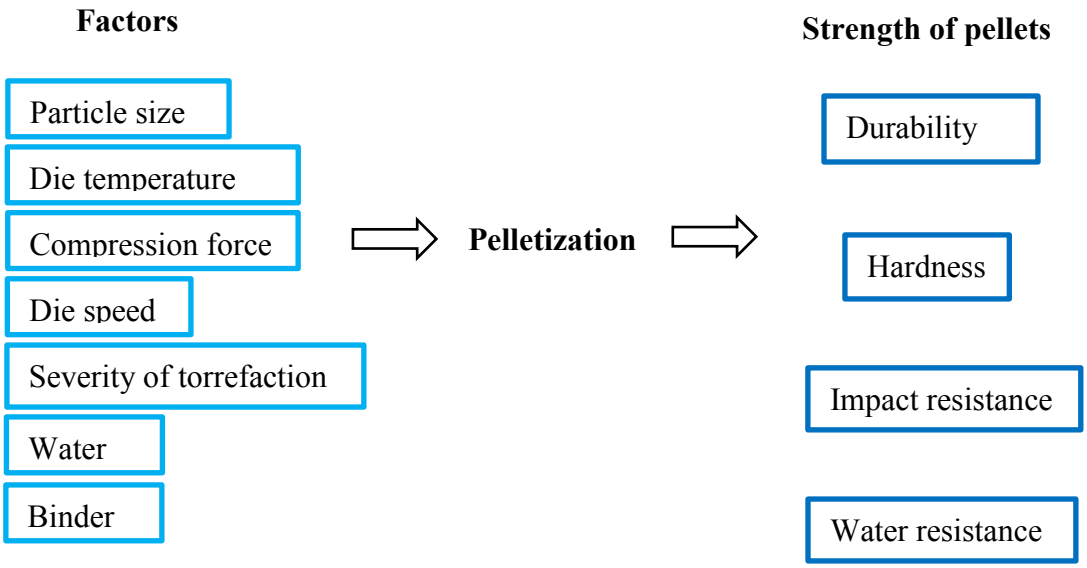

Figure 2.4. Factors affect strength of torrefied wood pellets

2.6.1 Particle size

Particle size plays an important role in determining pellet hardness/durability. In general, the finer the particles, the better the resulting pellet durability[9]. Because fine particles generally accept more moisture than large particles, and thus undergo a higher degree of conditioning[9], and larger particles are fissure points that could lead to fractures and cracks in pellets[9].

In a study by Rudolfsson *et al.*, two particle size distributions (less than 500 μm, and between 500 μm and 2000 μm) were used, and they concluded that more fine particles could lower compression work but increased pellet strength and static friction to some extent[58]. In briquetting/densification of kernel shell biochar by Bazargan *et al.*, five particle size distributions were used: as-received, less than 300 μm, between 300 and 700 μm, between 700 and 3000 μm, and more than 3000 μm[54]. Their research showed that a particle size above 300 μm resulted in a decrease in tensile crushing strength whereas as received feedstock, which was a mixture of various particle sizes, exhibits acceptable tensile strength. Their explanation was that smaller particles have greater surface area per unit volume and thus have a higher number of contact points during compression compared to the as received feedstock. In the latter case, the larger particles could aid in mechanical interlocking and finer particles could increase the number of contact points[54].

The different particle sizes used in above studies may depend on the capacity of the pelletizers, severity of torrefaction, and the compaction forces. However, it is also worth noting that grinding of feedstock is an energy consuming process[9] and production of extremely fine particles may result in jamming within the pelletizer and adversely affect the product line[54].

2.6.2 Die temperature

The typical die temperature employed for pelletization of non-torrefied woody biomass ranges from 70 to 110 ℃. Heat is important for pelletization as it activates the inherent binders of woody biomass, softening lignin and denaturing proteins that are of great importance for bond formation[9, 19]. Peng *et al.* demonstrated that torrefied sawdust samples could not be densified into strong pellets when subjected to the same conditions used for non-torrefied sawdust[37]. The die temperature had to be increased to over 170 ℃, and further increasing of the die temperature resulted in only slight improvements in Meyer hardness and a small decrease in equilibrium moisture content[37]. Peng *et al.* also showed that a die temperature of 110-170 ℃ was needed for pelletization of torrefied wood pellets when pine sawdust was used as a binder[17]. The pelletization temperature of torrefied Norway spruce ranged from 125-180 ℃, and increasing pelletization temperature resulted in improved pellet strength and a reduction in energy consumption for the pelletization process[58]. To pelletize torrefied pine with hydrothermal carbonized pine as a binder, a die temperature of 140 ℃ was needed[29]. Similarly, to pelletize torrefied wheat and barley straw with linear low-density polyethylene, a die temperature of 150 ℃ was needed[18].

Using a single pellet press, the die temperature can be well controlled, but the die temperature used in most studies are well above commercial scale pelletization die temperatures. In commercial scale pelletization processes, however, the die temperature could not be controlled, which typically ranges from 70-110 ℃.

2.6.3 Compression pressure/force

In a pellet mill, compression pressures of 100-150 MPa and higher can be expected[9, 59]. Higher compression pressures cause better connection at points of contact leading to denser

and more durable products and decreased sample porosity[54]. In addition, high compression pressures can also squeeze natural binders like starch, protein, and lignin out of biomass particles, which promotes interparticle bonding[9].

In briquetting of palm kernel biochars, the crushing strength of resulting briquettes increased with increasing compression pressure and approached a plateau above 60 MPa in the presence of 30 % moisture content[54]. To engineer torrefied pine into pellets with hydrothermal carbonized pine as a binder, a compression force of 250 MPa was applied[29]. A compression force ranging from 4000 to 6000 N was used to pelletize torrefied sawdust in the study of Li *et al.*[40]. Stelte *et al.* used a compression pressure of 200 MPa to pelletize torrefied spruce[14]. To optimize the combination of torrefaction and pelletization, a compression force of 200 kN was used in the study Rudolfsson *et al.*[58]. To pelletize torrefied pine with sawdust as a binder and torrefied softwood residues, a compression pressure ranging from 125 to 156 MPa was used by Peng *et al.*[17, 37]. The difference in compression force/pressure required for pelletization likely resulted from the configuration of the pelletizer, the feedstock, the presence of moisture and binder, as well as the severity of torrefaction.

2.6.4 Die speed

Die speed determines the residence time of biomass particles within the die[60]. In general, slower die speed results in pellets with better durability. This is because biomass particles reside in the die longer, which promotes bond formation. In most studies available, a single pellet press is often used for pelletization of torrefied biomass. However, the die of a single pellet press is static, and thus residence time of torrefied biomass in the die is not available other than the compression holding time, which ranges from 5 to 180 seconds[11, 13-15, 26, 28, 38, 53, 55-

[57]. At pilot or commercial scale pelletization of torrefied biomass, the die and rollers move, but the die speeds that were used in such studies[36, 39, 40, 51, 60]are not available.

2.6.5 Severity of torrefaction

In general, an increase in the severity of torrefaction improves the heating value, hydrophobicity, and grindability of the material, but leads to increased difficulties relating to densification of resulting biomass and decreased strength of densified products. As mentioned earlier, this is because the natural binder lignin undergoes debilitating structural changes and the bond promoting hydroxyl sites are removed from the surface of the material.

Loblolly pine was torrefied at 250, 275, 300, and 350 ℃ by Reza *et al,* and it was shown that pellet density and durability decreased with increasing torrefaction temperature[29]. Li *et al.* showed that when sawdust was torrefied in the range of 260-300 ℃ with a residence time of 10-90 min, the energy consumption necessary to pelletize torrefied sawdust increased and the equilibrium moisture content, pellet density, and Meyer hardness all decreased with increased severity of torrefaction[40]. Spruce was torrefied at 250, 275 and 300 ℃ then the resulting material was used to produce pellets, the pelletization pressure in the die channel increased directly with the torrefaction temperature[14]. This was likely due to the removal of moisture and the low hemicellulose content in the resulting torrefied spruce. In this study, both pellet compression strength and pellet density decreased with increasing torrefaction temperature, probably due to the removal of hydrogen bonding sites and poor adhesion between adjacent particles[14]. Miscanthus was hydrothermally carbonized at 190, 225, 260 ℃ for 5 mins by Kambo and Dutta and then used to make pellets, both impact resistance durability and compression strength of resulting pellets decreased with an increase of hydrothermal carbonization temperature[55]. The decreased impact resistance durability was attributed to fine

particles (< 100 μm) were produced with increased hydrothermal carbonization temperature, and the decreased compression strength of pellets resulted from the fact the high percentages of remaining lignin acts as a natural binder during pelletization but could also make pellets highly brittle[55].

2.6.6 Water

Water is of great importance for the pelletization of torrefied biomass. Water behaves both as a lubricant to reduce friction between torrefied biomass particles with the die channels, and as a plasticizer, lowering the glass transition temperatures of inherent binders such as lignin, protein, starch[8, 9, 61]. Water can also form a thin film between particles, which promotes binding via Van der Waals forces, due to increased interparticle contact areas[5, 57]. There is an optimum moisture content for production of durable pellets. Above this optimum moisture level, it is difficult to form durable pellets likely because of the incompressibility of water; moisture trapped in particles may prevent complete flattening and the release of natural binders from the particles[5, 57].

0 to 50 % moisture was used to compact palm kernel shell biochars into briquettes by Bazargan *et al.*[54]. When no water is used, the densified product was not durable and completely crumbled during extrusion. An increase in moisture content from 0 to 30 % resulted in better briquette strength, and a further increase in moisture content to 40 and 50 % content led to weaker briquette strength[54]. During pelletization of biochar obtained using different pyrolysis temperatures, Hu *et al.* found that at 15 % moisture content, pellets could not be formed or were so weak that they could not be measured[57]. When moisture was increased from 20 to 35 %, the compression strength of pellets increased, but decreased again at higher moisture levels. Furthermore, the volume density of pellets increased with an increase in moisture content,

though energy consumption for pelletization decreased[57]. During a pilot scale pelletization, 11 % and 15 % moisture could cause handling problems as it was extremely difficult to get torrefied Norway spruce to flow through the conveyor system and feed into the pelletizer due to the materials' bridging tendencies[38]. Rudolfsson *et al.* found that increasing moisture content from 0 to 10 % decreased the energy consumption required for compression[58]. The moisture used in above studies may result from the capacity of pelletizers, the severity of torrefaction, the compaction force, and particle sizes.

2.6.7 Binder

A binder (or additive) can be a liquid or solid material that forms a bridge, film, matrix, or causes a chemical reaction to promote strong interparticle bonding[9]. A binder can also act as a lubricant, thus reducing the wear on production equipment and increasing the abrasion resistance of the fuel[8]. Currently, there is no commercial binder available for the torrefied wood pellet industry. However, there is great interest in developing a cheap and sustainable binder. Some materials, such as lignin, sawdust, starch, calcium hydroxide, linear low-density polyethylene, and hydrothermally carbonized biochar, have been tested as a binder for pelletization of different torrefied biomass using a single pellet press or bench scale or pilot scale pelletizer.

2.6.7.1 Lignin

The lignin molecules in woody biomass function in many different ways, including adhering cellulose fibers[8]. Lignin helps to create solid bridges at elevated temperatures and plays a very important role in biomass densification, allowing adhesion in the wood and acting as a rigidifying and bulking agent[5, 61]. It is reported that lignin exhibits thermosetting properties at temperatures above 140 °C and acts as an intrinsic resin, forming more durable pellets[62].

In a study from Hu *et al.*[16], 5-20 % lignin was used to densify rice husk biochar, and it was found that the compressive strength of the resulting pellets increased with an increasing amount of lignin (up to 10 %). However, a further increase of lignin to 20 % did not result in improved strength. The bonding forces involved in densification of the biochar pellets with lignin were mainly attributed to attraction and cohesion forces, including hydrogen bonds, Van Der Waals forces, and mechanical interlocking[13, 16]. The softening of the lignin during pelletization binds particles like a bridge[19, 61]. The energy consumption for pelletization of rice husk char decreased with increasing amounts of lignin[16]. This was because lignin contributed to the cementation of biochar particles, which resulted in decreased energy consumption for deformation and plasticization[63]. However, the equilibrium moisture content of resulting rice husk char pellets increased with increasing lignin, and the presence of lignin also led to decreased maximum heating values and energy densities, compared to pellets formed without any lignin[16]. Peng *et al.* used 5 and 10 % lignin to pelletize torrefied pine[17]. They found that the density of single biochar pellets produced using lignin as a binder was comparable to that of biochar pellets without any binder, but the Meyer hardness of the pellets made using lignin was much higher[17]. However, the heating value of biochar pellets decreased with increasing lignin because the heating value of lignin is lower than that of biochar. Additionally, the equilibrium moisture content of the pellets made with lignin was slightly higher than that of pellets without any binder[17], most likely because the lignin cannot fill pores of torrefied materials at a die temperature below its melting temperature.

Sawdust was also proposed as a binder for pelletization of torrefied sawdust based on the assumption that the large amount of natural lignin present in the raw biomass could be used as a natural binder[17]. Using 10, 20, and 30 % sawdust, Peng *et al.*[17] showed that increasing

sawdust content decreased the energy consumption required for pelletization and increased Meyer hardness. Conversely, the equilibrium moisture content increased and the higher heating value decreased when compared to those obtained from torrefied sawdust pellets produced without any binder.

Reza *et al.* used hydrothermally carbonized pine as a binder for pelletization of torrefied pine[29]. This was because the hydrothermally carbonized pine had enough available natural binder lignin and the lignin from the hydrothermally carbonized pine has a similar glass transition behavior to that of the raw biomass[29]. In their studies, 10, 25, and 50 % hydrothermally carbonized pine were used for pelletization of pine torrefied in the temperature range of 250-350 °C[29]. They observed that an increase of hydrothermally carbonized pine resulted in improved durability, likely by filling void spaces and making solid bridges between torrefied biochar particles during pelletization[29].

2.6.7.2 Starch

Starch consists of linear amylose and branched amylopectin, linked together by α-D-glucose, and has an ordered, densely packed, and semi-crystalline structure[54]. Starch can act as a binder by gelatinization, in which ordered starch is transitioned into a disordered state and dispersed starch molecules in the aqueous medium re-associate and form three-dimensional gel network structures[8, 9, 54, 64]. Furthermore, starch can also act as a lubricant to ease the flow of biomass particles through the die[8].

When palm kernel shell biochars were compacted into briquettes, 10 % starch (wet basis of mass) was used by Bazargan *et al.*[54]. They showed that the tensile crushing strength of briquettes made with starch as a binder was much better than that of briquettes made without starch. In addition, briquettes made with starch could retain their strength even after storage[54].

Similarly, 5-20 % starch was used for pelletization of rice husk char in a study of Hu *et al.*[16]. However, their research showed that the compressive strength of pellets did not improve substantially, and pellets made with starch had higher equilibrium moisture content, and slightly lower higher heating values and energy densities, compared to those of pellets made without any starch[16]. Similar results were reported by Peng *et al.*[17]. In a pilot scale production of torrefied *Eucalyptus globulus* pellets, 1 % starch was used both as a lubricant to avoid overheating and as a binder to improve durability of resulting pellets[53].

Wheat flour is mainly comprised of starch and protein. Protein undergoes denaturation in the presence of heat, moisture, and pressure during densification, resulting in the formation of new bonds and structures with other biomass components, helping to improve the binding capacity[8]. In a bench scale pelletization of torrefied Douglas fir, 7 % wheat flour was used as a binder by Ghiasi *et al.* and they found that using wheat flour greatly eased pelletization and lowered the energy consumption during pelletization[41].

2.6.7.3 Calcium hydroxide

Calcium hydroxide can enhance compressive strength/hardness of resulting pellets, probably because of the formation and subsequent hardening of calcium carbonate. 5-20 % calcium hydroxide was used by Hu *et al.* to pelletize rice husk biochar, and it is was shown that the compressive strength of pellets increased with increasing calcium hydroxide until 10 % is used; above 10 %, the compressive strength did not show further improvements[16]. The equilibrium moisture content of pellets made with calcium hydroxide was higher than that of pellets without calcium hydroxide. Conversely, the higher heating value and energy density decreased with increasing calcium hydroxide, compared to that of control pellets[16].

2.6.7.4 Linear low-density polyethylene

Linear low-density polyethylenes (LLDPEs) are common extractable plastics obtained from municipal solid wastes, and can be used as a binder because of its ability to promote strong mechanical interlocking[18]. Emadi *et al.*[18] showed that fracture load, tensile strength, and higher heating value of pellets made from torrefied wheat and barley increased compared to that of control pellets. Conversely, the ash content generally decreased for pellets made with increasing LLDPE. However, a die temperature of 150 ℃ was needed to melt linear LLDPE[18].

2.7 Specified risk materials

Specified risk materials (SRM) are protein-rich by-products from cattle tissues where prions, which are believed to cause a neurodegenerative disease known as Bovine Spongiform Encephalopathy(BSE) or Mad Cow Disease in cattle, are most likely to concentrate[17, 18]. SRM include skull, brain, trigeminal ganglia, eyes, palatine tonsils, spinal cord and dorsal root ganglia of cattle aged 30 months or older, as well as the distal ileum of cattle of all ages[65](Figure 2.5.). SRM have been banned from food, fertilizer, and animal feed applications through implementation of an enhanced feed ban[66]. In Canada, SRM are rendered to recover lipids while the remaining parts are landfilled[1]. As a result, about 300,000 tonnes of such rendered SRM is either landfilled or incinerated each year[1]. This results in great economic challenges for related industries and the wasting of biomass resources. These economics challenges included costs resulting from segregation of SRM from non-SRM tissues and segregation of processing lines to handle SRM and non-SRM tissues, and costs associated with SRM storage, transportation, and disposal fees[1]. Disposal tipping fees range from $75 to $200 per tonne and costs of transportation are $ 250 per tonne on average[1]. However, most research efforts and

funds in this area have been spent on the prevention and treatment of BSE (and similar prion-related diseases), with only a very few efforts focused on valorization of the resulting SRM[67, 68].

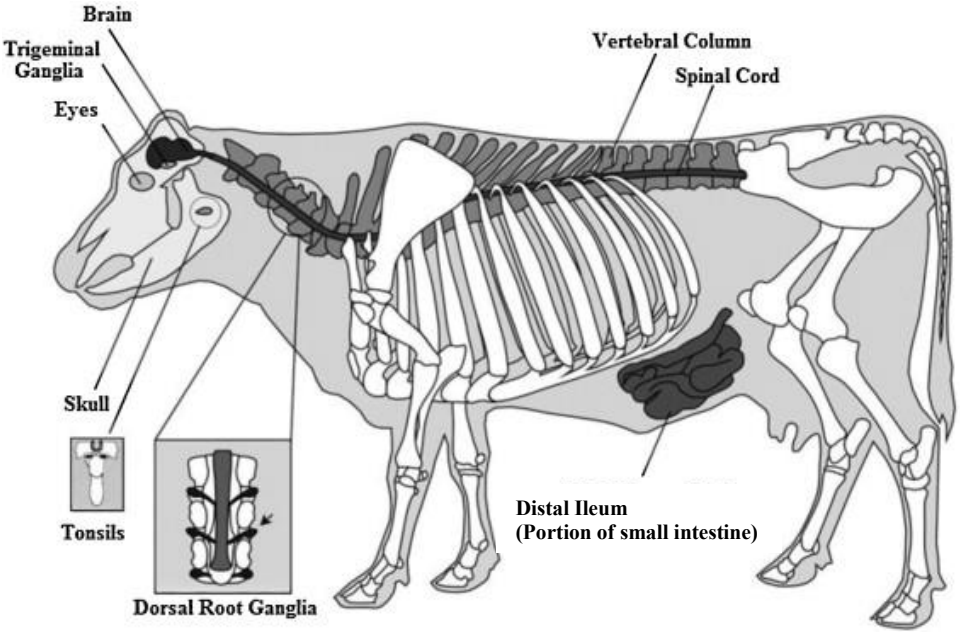

Figure 2.5. SRM in cattle[1]. Reuse with the permission of Process Chemistry, Elsevier ©

There are currently four disposal methods for SRM that have been approved by the CFIA: landfilling, incineration, alkaline hydrolysis, and thermal hydrolysis[1, 2]. Landfilling is a containment method, and prions are not destroyed. Incineration, alkaline hydrolysis, and thermal hydrolysis are three destruction methods for prions[67]. Incineration is an effective option, but it is an energy-intensive process and the product generated has limited value-add oportunties[67]. Alkaline hydrolysis and thermal hydrolysis also require substantial energy input, but a key advantage is that these treatments are more amenable to the recovery of products from thermal hydrolysates, although the former is much more harsh and generates smaller molecules[17, 18].

2.7.1 Recovery and characterization of peptides from SRM hydrolysates

The thermal hydrolysis protocol used for treatment of SRM was developed in the Bressler lab at the University of Alberta[1, 2]. In this process, 1 kg of SRM and 1 kg of water are placed in a thermal hydrolysis reactor, and hydrolyzed under the following conditions: 180 °C for 40 min, ≥ 174 psi. The resulting hydrolysates are then diluted, centrifuged (to remove bones and insoluble matter), filtered (to remove insoluble particulates), washed with hexane (to remove any lipids), and dried[1, 2]. The dried SRM hydrolysates are referred to as peptides hereafter.

Freeze drying, also called lyophilization, is a drying process in which the solvent (usually water) and/or suspension medium is frozen, then placed under vacuum to allow for sublimation of the frozen water[68]. Freeze drying is widely used for thermal sensitive samples including proteins, enzymes, peptides, vaccines, and antibodies[68]. However, spray drying, a more industrially relevant drying process, has never been used to dry SRM hydrolysates. In spray drying, the solution/suspension/emulsion is atomized into fine particles by a nozzle, and then the moisture present in the fine particles is quickly evaporated through contact with hot air[69].

The molecular weight distribution and functional group assessment of peptides are characterized by different techniques. Sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) and size exclusion high performance liquid chromatography (SEC-HPLC) are two tools used to analyze molecular weight distribution of peptides. Using these techniques, it was shown that main molecular weight distribution of peptides from thermal hydrolysis is in the range of 5-15 kDa. Conversely, the molecular weight of peptides from alkaline hydrolysis is less than 1 kDa[1]. This is because alkaline hydrolysis is more severe and thus a higher degree of cleavage is possible[1]. The functional groups of peptides were also analyzed using Fourier-Transformed Infrared (FTIR) Spectroscopy[70]. The carboxylic group and primary amine groups were also estimated by pH titration and using an *o*-phthalaldehyde (OPA) method, respectively. Using these techniques, the carboxylic and primary amine groups were estimated to be 1.66 mmoles/g peptides and 0.60 mmoles/g peptides, respectively[2]. The difference in the amount of carboxylic groups and primary amine groups may result from a combination of deamination and thermolysis of peptides under subcritical conditions[2].

2.7.2 Products from thermally hydrolyzed SRM

Peptides from thermal hydrolysis of SRM could be used as a starting material for several products mainly due to the availability of functional groups. For example, biocomposites[71], thermoset plastics[72], and adhesives[2, 70, 73-75]have been developed using proper chemical modification and/or crosslinking.

2.7.2.1 Biocomposites

A biocomposite is comprised of a matrix (resin) and a reinforcement of natural fibers. In a study by Mekonnen *et al.*, the fibres used included woven rovings, chopped strand mat fiber glass, and hemp fiber mats, and the matrix used was diglycidyl ether of bisphenol A epoxy resin

cured with peptides (hydrolyzed SRM)[71]. The functional groups found in peptides, such as primary and secondary amines, hydroxyls, and carboxyl groups, could react with the epoxide groups of the diglycidyl ether of bisphenol A epoxy resin through a ring opening reaction[71]. It was found that the biocomposites developed exhibited good flexural strength, tensile strength and tensile modulus, but relatively poor moisture resistance[71]. This is likely due to the unreacted functional groups of peptides and as well as the presence of incomplete network chains[71].

2.7.2.2 Thermoset plastics

Peptides from SRM were chemically crosslinked with diglycidyl ether of bisphenol A epoxy resin to prepare thermoset plastics by Mekonnen *et al.*[72]. A range of peptides (20-50 %) were used in different formulations and the plastics developed had good tensile strength and solvent resistance, with the plastics manufactured using a 20 % peptides formulation exhibiting the highest tensile strength, lowest temperature curing, and better solvent resistance[72].

2.7.2.3 Adhesives

An adhesive is defined as a non-metallic, polymeric material, which could bind two surfaces together by adhesion and cohesion forces. Peptides have been chemically modified and/or crosslinked to prepare adhesives for different applications. Mekonnen *et al.* demonstrated that peptides chemically crosslinked with 4,4-diphenylmethane diisocyanate could function as an adhesive for oriented strand board manufacturing[70]. In this mechanism, isocyanate groups reacted with active hydrogen atoms in the peptides (i.e. hydroxyls, primary amines, secondary amines, and carboxyls)[70, 76], creating a crosslinked structure after curing[76]. The peptides in the adhesive formulation ranged from 40 % to 85 %. The static bending of panels produced using adhesive formulations with 40, 50 and 60 % peptides, and the internal bond strength of panels

produced with 40 and 50 % peptides met the CSA 0437 requirement, but bond durability of panels did not[70]. This probably resulted from association of hydrophilic functional groups of peptides with water, which could lead to leaching out and consequently decreased adhesion and bond durability[70].

In another study by Mekonnen *et al.*, peptides were co-polymerized with resorcinol and glutaraldehyde for the development of a plywood adhesive[75]. The effects of peptides concentration (20, 30, and 40 %), glutaraldehyde and resorcinol concentration (10, 25, and 40 %), glutaraldehyde to resorcinol ratio (1:2, 1:1, and 2:1), and hydrolysis temperature of SRM (180, 200, and 220 ℃) on lap shear strength under dry and wet conditions of plywood were optimized using the Taguchi method. In this manner, it was shown that eight of the nine adhesive formulations met the minimum dry shear strength requirement for urea formaldehyde type adhesives, and three of the formulations also met the soak shear strength requirement[75]. Among the adhesive formulations meeting the soak shear strength requirement, the combinations included: 1) 30 wt% protein concentration, 40 wt% glutaraldehyde-resorcinol, mole ratio (glutaraldehyde : resorcinol) 1:2, and 200 ℃ SRM hydrolysis; 2) 20 wt% protein concentration, 40 wt% glutaraldehyde-resorcinol, mole ratio (glutaraldehyde : resorcinol) 1:0.5, and 220 ℃ SRM hydrolysis; and 3) 20 wt% protein concentration, 25 wt% glutaraldehyde-resorcinol, mole ratio (glutaraldehyde : resorcinol) 1:1, and 200 ℃ SRM hydrolysis.

Kislitsin examined the esterification of peptides using alcohols like methanol, ethanol, and propanol, then crosslinking the modified peptides with glutaraldehyde[73]. Esterification was proposed to cap the carboxyl groups within peptides thereby improving water resistance, while crosslinking of the esterified peptides with glutaraldehyde, which reacts with amine groups by a Schiff base reaction, was proposed to improve the adhesive strength. Different ratios of

peptides to methanol, ranging from 1:10 to 1:100 w/v, were studied and demonstrated that an increased peptides to methanol ratio led to an increased degree of esterification[73]. When the ratio of methylated peptides to glutaraldehyde was varied from 1:1 to 9:1, no improvements in dry and soaked lap shear strength were observed in the resulting adhesive formulations[73]. However, when the hot pressing temperature was increased from 120 to 160 ℃, the soaked lap shear strength improved, but the dry lap shear strength did not[73]. When peptides modified with ethanol or propanol were further crosslinked with glutaraldehyde, the dry shear strength of adhesives did not improve, but the soaked lap shear strength improved for the latter[73]. Similar to what was observed with methylated peptides, when the hot pressing temperature was increased from 140 to 180 ℃ using ethylated or propylated peptides, the soaked lap shear strength of adhesive passed the ASTM D4690-12 minimum requirement of 1.93 MPa[73] .

In recent studies by Adhikari *et al.*, peptides were chemically crosslinked with polyamidoamine epichlorohydrin (PAE) for production of a plywood adhesive[2]. The azetidinium groups within the PAE resin could react with carboxyl, amine, and hydroxyl groups of peptides through a ring opening reaction, and thus a crosslinked structure could be formed, resulting in improved adhesive strength and water resistance[2] (Figure 2.6.). The PAE used in the adhesive formulations ranged from 11.4 to 57.1 %, and a minimum of 23 % PAE was shown to be needed to pass the soaked lap shear strength test. It should be noted that the dry and wet soaked lap shear strength did not improve much after 34 % PAE addition[2]. The hot pressing temperature for the peptides-PAE adhesive ranged from 110 to 140 ℃; the dry lap shear strength of the peptides-PAE adhesive did not improve substantially with increasing hot pressing temperature, however the soaked lap shear strength showed enhanced binding qualities[2]. Furthermore, the dry and soaked lap shear strength of the peptides-PAE adhesive when hot

pressed at 140 ℃ were comparable to those of phenol formaldehyde resins hot pressed at 120 ℃[2].

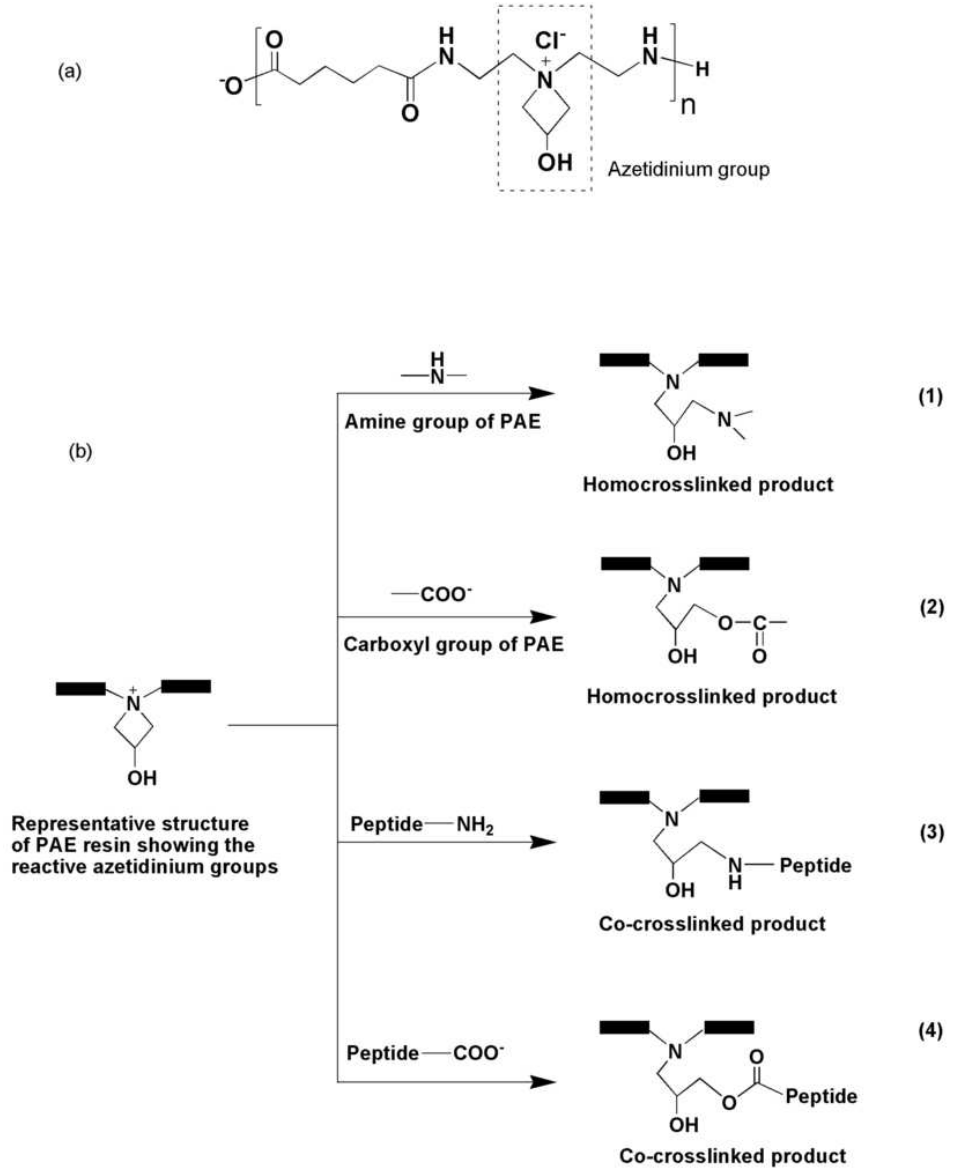

Figure 2.6. Chemical structure of PAE resin (a); and plausible chemical reactions occurring during chemical crosslinking of PAE resin with peptides (b)[2]. (Reuse from the open access journal: Polymers)

2.8 Chlorine corrosion mechanism

Chlorine that is present in biomass, including SRM, can be easily released into the gas phase as HCl and KCl during combustion[77]. HCl can be condensed in the presence of moisture in the flue gas and lead to corrosion of expansion joints, air heater seals, precipitators or baghouses[78]. Furthermore, KCl could deposit on the pendant tubes and other heat transfer surfaces, resulting in corrosion[19, 78]. This corrosion mechanism by KCl is explained by Nielsen *et al.*[79] as follows:

$$2\ KCl\ (s) + SO_2\ (g) + \tfrac{1}{2}\ O_2\ (g) + H_2O\ (g) \leftrightarrow K_2SO_4\ (s) + 2\ HCl\ (g) \quad (1)$$

$$2\ KCl\ (s) + SO_2\ (g) + O_2\ (g) \leftrightarrow K_2SO_4\ (s) + Cl_2\ (g) \quad (2)$$

The HCl gas formed through Eq. (1) can be further oxidized into chlorine gas[80]. HCl gas could also diffuse through deposits and reach the metal surface where it can form volatile $FeCl_2$ or $CrCl_2$. Volatile $FeCl_2$ or $CrCl_2$ could diffuse through cracks and pores of the oxide scale toward areas with high partial pressures of oxygen, forming metal oxides and releasing chlorine or HCl gas. The process can then be repeated, and metallic surface beneath the non-protective oxide scale is sustainably oxidized.

$$Fe + Cl_2 \leftrightarrow FeCl_2\ (s) \quad (3)$$

$$FeCl_2\ (s) \leftrightarrow FeCl_2\ (g) \quad (4)$$

$$3\ FeCl_2 + 2\ O_2 \leftrightarrow Fe_3O_4 + 3\ Cl_2 \quad (5)$$

$$2\ FeCl_2 + 3/2\ O_2 \leftrightarrow Fe_2O_3 + 2\ Cl_2 \quad (6)$$

2.9 International standards for densified solid fuels

The standards for densified biomass application as a solid fuel in America are governed by the Pellet Fuel institute (PFI) and in European countries, by International Standard

Organization (ISO). Some requirements specified by PFI and ISO are cited here in Table 2.1. and Table 2.2..

Table 2.1. Standard specifications for residential/commercial densified fuel by PFI

Fuel property	PFI Premium	PFI Standard	PFI Utility
Pellet durability index (%)	≥ 96.5	≥ 95.0	≥ 95.0
Chloride (ppm)	≤ 300	≤ 300	≤ 300
Heating value	N/A	N/A	N/A
Inorganic ash (%)	≤ 1.0	≤ 2.0	≤ 6.0
Moisture (%)	≤ 8.0	≤ 10.0	10.0

(PFI premium, PFI standard, and PFI utility are three grades of densified fuel specified by PFI, and they could be used/burned in different appliances)

Table 2.2. Standard specifications for thermally treated and densified biomass fuels by ISO/DIS 17225-8

Property class	TW1a	TW1b	TW2a	TW2b	TW3a	TW3b
Mechanical durability (%)	≥ 97.5	≥ 97.5	≥ 96.0	≥ 96.0	≥ 95.0	≥ 95.0
Nitrogen (%)	≤ 0.5	≤ 0.5	≤ 0.5	≤ 0.5	≤ 1.0	≤ 0.5
Sulfur (%)	≤ 0.04	≤ 0.04	≤ 0.05	≤ 0.05	≤ 0.1	≤ 0.1
Chlorine (%)	≤ 0.03	≤ 0.03	≤ 0.05	≤ 0.05	≤ 0.1	≤ 0.1
Net calorific value, MJ/kg (%)	≥ 21.0	≥ 16.9	≥ 20.2	≥ 16.9	≥ 18.7	≥ 16.0
Ash (%)	≤ 1.2	≤ 1.2	≤ 3.0	≤ 3.0	≤ 5.0	≤ 5.0

(TW1a, TW1b, TW2a, TW2b, TW3a, and TW3b are different grades of pellets from thermally treated virgin wood and chemically untreated wood residues specified by ISO. TW1a and TW1b represents fuels which are low in ash and nitrogen content, while class TW2a and TW2b has slightly higher ash, and TW3a and TW3b higher ash and nitrogen content.)

3 Materials and methods

3.1 Materials

Specified risk materials (SRM) were provided by West Coast Ltd. (Calgary, Canada), and torrefied wood used was kindly supplied by Airex Energy (Bécancour, Canada).

3.2 Chemicals

Environ® LpH® (Steris Corporation, St. Louis, MO, USA) was used to decontaminate any surfaces in contact with SRM. The crosslinker PAE resin (Kymene™ 557H resin) was purchased from Solenis (Wilmington, DE, USA). 0.1N standardized sodium hydroxide (Acros, Organics, New Jersey, USA) and 0.1N standardized hydrochloric acid (Ricca Chemical Company, Arlington, TX, USA) were used for pH adjustment of peptides solution and estimation of carboxylic and primary amine groups of peptides. L-leucine (Sigma-Aldrich, St. Louis, MO, USA) was used as a standard for estimation of primary amine groups of peptides. 2,4,6-Trinitrobenzenesulfonic acid solution (TNBSA) (Sigma-Aldrich, St. Louis, MO, USA) was used to react with primary amine groups of peptides. Sodium bicarbonate (Fisher Chemical, Fair Lawn, NJ) was a buffer solution for peptides. Sodium dodecyl sulphate (MP Biomedicals, LLC, IIIkirch, France) and hydrochloric acid (Sigma-Aldrich, St. Louis, MO, USA) were used to terminate reaction between TNBSA with primary amine groups of peptides. Sodium hydroxide (Fisher Chemical, Fair Lawn, NJ) was used to adjust the pH value of sodium bicarbonate buffer solution (for peptides).

3.3 Methods

3.3.1 Recovery of peptides from thermally hydrolyzed SRM

A CFIA approved protocol that was developed in the Bressler lab was used to thermally hydrolyze SRM. The thermal hydrolysis conditions were: 180 ℃ for 40 min, at a pressure of ≥

174 psi[17, 18]. Specifically, 1 kg of SRM and 1 kg of Milli-Q water were placed into a 5.5 L thermal hydrolysis reactor (Parr 4582, Parr Instrument Company, Moline, IL, USA), which was connected to an external cooling system (Cat. No.: 89202-986, VWR, Radnor, PA, USA). All the surfaces that came into contact with the SRM were disinfected with 5 % Environ LpH for 30 min followed by a wipe down using 70 % ethanol. During the reaction, the mixture of SRM and Milli-Q water was constantly agitated at 200 rpm. The moment that the temperature of the reactor reached 180 ℃ was regarded as the starting point of the thermal hydrolysis reaction, and the reaction was kept around 180 ℃ for 40 min. After 40 min, the heater of the reactor was turned off, and the cooling system was kept on to cool the reactor down to room temperature. After thermal hydrolysis, the SRM hydrolysates were collected and diluted with 9 L Milli-Q water. The diluted SRM hydrolysates were mixed well, followed by centrifugation (Avanti J-26 XP, Beckman Coulter Canada LP, Mississauga, ON, Canada) at 7000 × *g* for 40 min to remove insoluble matter. The supernatants from centrifugation were then vacuum filtered (Whatman No.4 filter paper (Cambridge, UK), pore size: 20-25 μm) to remove any remaining insoluble matter that was not removed during centrifugation. The filtrate was washed with hexane to remove lipids, followed by freeze drying (50 L Virtual EL-85, SP Scientific, Stone Ridge, NY, USA) or spray drying (Buchi mini spray drier B-290, New Castle, DE, USA). For spray drying, the inlet temperature of the spray drier was kept at 165 ℃, with outlet temperatures of 85-90 ℃ achieved by adjusting pump rates.

3.3.2 Prewashing of SRM before thermal hydrolysis

For initial experiments focused on integration of a prewashing step into the SRM processing strategy, smaller reactions were used to minimize the amount of waste material that needed to be treated. Washing was performed as follows: 200 g of SRM were thoroughly mixed

with 400 g of Milli-Q water, and the mixture was then centrifuged for 10 min at 7000 × *g* (Avanti J-26 XP, Beckman Coulter Canada LP, Mississauga, ON, Canada), after which the supernatant was removed. The washing process was repeated a total of three times. The prewashed SRM was collected for hydrolysis; the resulting water was also treated through thermal hydrolysis for decontamination purposes. After hydrolysis, the SRM hydrolysates were collected, diluted, centrifuged, filtered, hexane washed, and spray dried or freeze-dried sequentially as described in the section 3.3.1 above.

For subsequent experiments using pre-washed SRM, 1 kg of SRM was evenly distributed among five 1 L centrifuge bottles, then 400 g of Milli-Q water were added into each bottle, followed by mixing and centrifugation at 7000 × *g* for 10 min. The SRM in each bottle was washed using Milli-Q water a total of three times. After washing, the SRM with residual water was weighed, and collected. The total mass was brought up to 2 kg to maintain the ratio of SRM to Milli-Q water of roughly 1:1. This mixture was then subjected to thermal hydrolysis as described in the section 3.3.1 above. The decanted water from SRM washing was collected and thermally hydrolyzed prior to disposal.

3.3.3 Characterization of peptides from thermally hydrolyzed SRM

3.3.3.1 Estimation of carboxylic and primary amine groups

A titration method was used for the estimation of the carboxylic group present in peptides[2, 81]. Briefly, 0.33 g of peptides was put into a 125 mL flask containing 50 mL Milli-Q water. Under constant stirring with a magnetic bar, the pH of the solution was adjusted to pH 7 using 0.1 N sodium hydroxide. At this pH, all the carboxylic groups within the peptides were deprotonated. Then the pH of the solution was adjusted from pH 7 to pH 3 using 0.1 N hydrochloric acid; at pH 3 all the carboxylic groups of peptides were protonated. Estimation of

the carboxylic groups was done based on the assumption that the amount of hydrochloric acid consumed when adjusting the pH of the solution from pH 6 to 3 corresponds to the number of carboxylic groups present.

The method of Hermanson[82], with minor modifications, was used for estimation of primary amine groups of peptides: Briefly, ~0.5 g of peptides was solubilized in a 100 mL volumetric flask with 0.1 M sodium bicarbonate (pH 8.5). A purchased 5 % solution of 2,4,6-trinitrobenzene sulfonic acid (TNBSA) was diluted 100 times with 0.1 M sodium bicarbonate (pH 8.5) in a 100 mL volumetric flask. 20 µL of the peptides solution, 480 µL of 0.1 M sodium bicarbonate (pH 8.5), and 250 µL of the diluted TNBSA solution were added into a 2 mL tube, followed by mixing with a vortex, and a 2 h incubation in a 37 ℃ water bath (Isotemp 228, Fisher Scientific). After 2 h, the reaction was terminated by adding 250 µL of 10 % SDS and 125 µL of 1 N hydrochloric acid. The absorbance of the solution was measured using a UV-spectrometer (Ultrospec 4300 pro, Biochrom Ltd, Cambridge, England) set at 335 nm. The control used for this experiment was 500 µL of 0.1 M sodium bicarbonate (pH 8.5) mixed with 250 µL of the diluted TNBSA solution. To estimate the primary amine groups of peptides, L-leucine was used to draw a standard curve following the above-mentioned procedure.

To minimize the potential interference of colored compounds from peptides, another experiment was run: 20 µL of the peptides solution was mixed with 730 µL of 0.1 M sodium bicarbonate (pH 8.5) in a 2 mL tube (i.e. no TNBSA added), followed by mixing with a vortex, and incubation at 37 ℃ in a water bath. The reaction was then terminated through addition of 250 µL of 10 % SDS and 125 µL of 1 N hydrochloric acid. The absorbance was measured by a UV-spectrometer at 335 nm, with the corresponding control mixture obtained through mixing of 500 µL of 0.1M sodium bicarbonate (pH 8.5) and 250 µL of 0.1 M sodium bicarbonate (pH 8.5).

When calculating the amount of primary amine groups, the absorbance from the second experiment was deducted from the first run experiment.

3.3.3.2 Metals and chlorine content of peptides

To determine the metal content of the peptides, 4 g of peptides were dissolved and brought to 100 mL in a volumetric flask using Milli-Q water. The resulting solution was filtered through a 0.45 μm nylon membrane (Millipore, Millex-HN). The metals were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS; Elan 6000, Perkin-Elmer Sciex, Toronto, ON, CA) in the Department of Earth and Atmospheric Sciences, University of Alberta. Chlorine content was assessed using colorimetry following the method of EPA 325.2 in the Natural Resources Analytical Laboratory, University of Alberta.

3.3.3.3 Elemental analysis of peptides

The elements CHNS of peptides were analyzed by a Thermo Flash 2000 CHNS-O analyzer (Thermo Scientific, Rodano, Italy) at the Department of Chemistry, University of Alberta. The dried peptides power was used for analysis. The peptides contained within a tin cup were sampled by an autosampler into a combustion reactor, where the peptides were completely combusted in the presence of oxygen. The elements carbon, hydrogen, nitrogen, and sulfur present in the peptides were converted into CO_2, H_2O, NOx, and SO_2, respectively. Excess oxygen was removed in the copper reduction portion of the combustion chamber and NOx was reduced to N_2. The combustion products were detected by a thermal-conductivity detector.

3.3.3.4 Insoluble material in prewashed and spray dried peptides

When the SRM was washed by Milli-Q water to remove chlorine and salts before thermal hydrolysis, it was found that the resulting peptides cannot be completely dissolved in the Milli-Q water for binder preparation. In order to improve the solubility of prewashed and spray dried

peptides, a simple pH adjustment method was proposed. Specifically, 4 g peptides were mixed with 100 mL with Milli-Q water in a 250 mL centrifuge bottle. The pH of the solution was recorded, followed by centrifugation at 5000 × *g* for 10 min. After this, the supernatant was decanted and the solid residues in the centrifuge tube were dried to constant weight in an oven set at 105 ℃. To reduce the amount of insoluble material, prior to centrifugation, the pH of the mixture was adjusted to pH 7.0 with 2 M sodium hydroxide.

3.3.4 Peptides-PAE binder preparation

A procedure established by Adhikari *et al*.[2] was followed to prepare the peptides-PAE binder. The solid content of the binder was set at 20 % to ensure proper viscosity of the formulation. The peptides and PAE resin were mixed well using a magnetic stir bar, and an appropriate amount of Milli-Q water was added. The pH of the peptides-PAE binder, if not specified, was without any adjustment. Otherwise, the pH of the binder was adjusted with 2 M sodium hydroxide to desired pH values. The mixture was mixed well at room temperature for 2 h before use.

3.3.5 Conditioning of torrefied wood

Torrefied wood (4 % moisture) from Airex Energy (Laval, QC, Canada) was mixed well with the required amount of Milli-Q water using a blender (SM300, Doyon Inc. Liniere, QC, Canada). After blending, the torrefied wood was collected in a bucket and sealed with a lid, and stored at room temperature overnight.

3.3.6 Mixing the peptides-PAE binder with conditioned torrefied wood

The conditioned torrefied wood (Section 3.3.5) was mixed with the prepared peptides-PAE binder (Section 3.3.4) in the blender for 10 min. When necessary, additional Milli-Q water was added during blending to adjust the moisture content to the desired level.

3.3.7 Pelletization with a semi-pilot scale pelletizer

3.3.7.1 Pelletization

The pilot scale pelletizer (PM810, Buskirk Engineering, Ossian, In, USA) was warmed up by running regular wood pellets. After the die surface temperature was about 70-80 ℃ (analyzed using a portable IR thermometer), the torrefied wood with or without binder was fed manually into the pelletizer. In a typical experiment, 3 kg of torrefied wood (moisture content 4 %) was well mixed with the peptides-PAE binder in the presence of 27-28 % moisture. The torrefied wood pellets produced during the first few minutes were discarded to ensure the homogeneity of the pellets to be further analyzed. The temperature of the die was not controlled, and it ranged from 80-100 ℃. The flow chart of pilot scale pelletization and durability test is as follows (Figure 3.1):

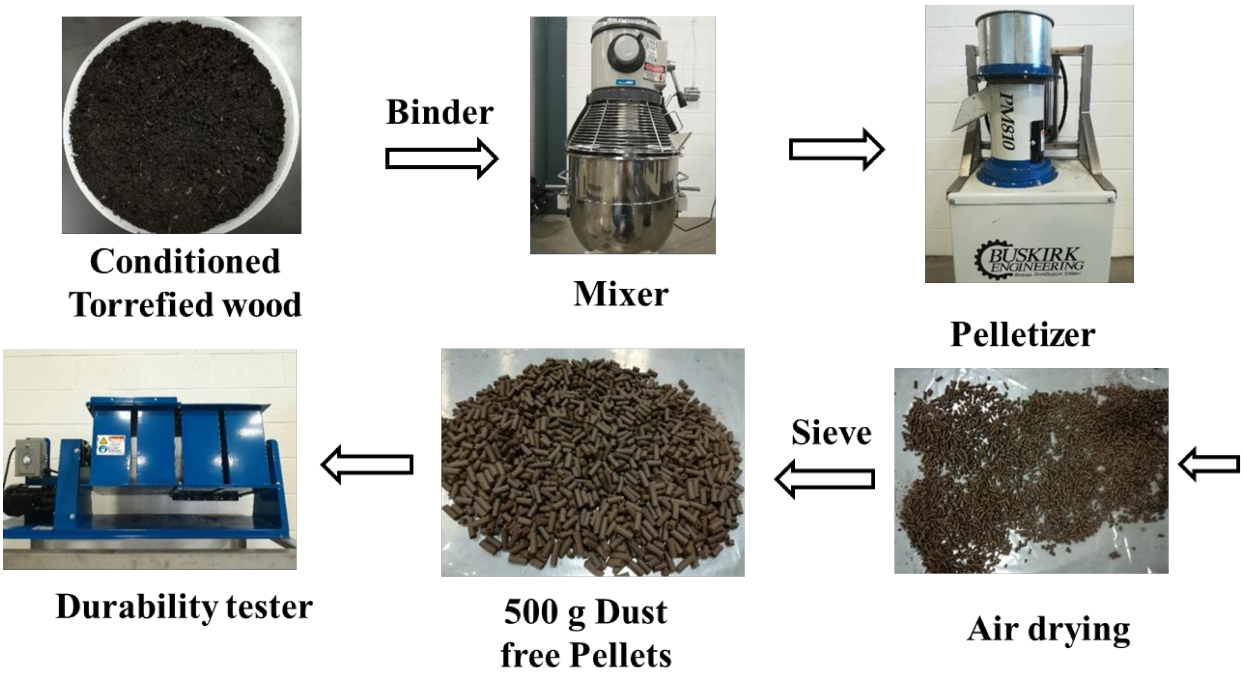

Figure 3.1. Flow chart of pilot scale pelletization and durability test

3.3.7.2 The effect of altering parameters on the durability of torrefied wood pellets

3.3.7.2.1 Percentage of unmodified peptides

Untreated peptides (i.e. without any chemical crosslinking or chemical modifications) were used as a binder for the pelletization of torrefied wood. The percentages of peptides used were set at 0.5 %, 1.0 %, 1.5 %, and 2.0 %, based on the dry mass of torrefied wood. For these experiments, the moisture content of the material to be pelletized was kept at 28 %.

3.3.7.2.2 Moisture content

The effect of moisture on the durability of resulting torrefied wood pellets under different conditions was studied. For experiments using 1 % of the peptides-PAE binder, moisture contents of 28 % and 34 % (dry weight basis) were used for pelletization. Conversely, for experiments where 2 % of the peptides-PAE binder was used, 27 % and 28 % moisture (dry weight basis) were used. Furthermore, pelletization using a 2 % peptides-PAE binder was also attempted at 20 % moisture (dry weight basis), but in the presence of 0.5 % vegetable oil. For all experiments described in this section, the peptides/PAE binder was comprised of 25 % PAE.

3.3.7.2.3 The pH value of peptides-PAE binder

In experiments to assess the influence of pH on pelletization, a 1 % peptides-PAE binder (25 % PAE) was used. The peptides-PAE binder was used as is (pH of ~5.5) or adjusted to pH 8.0 using 2 M sodium hydroxide. The moisture content used for these experiments was 28 %.

3.3.7.2.4 The percentage of PAE

The ratio of peptides: PAE influences the degree of crosslinking and thus can impact the strength of the resulting binder. To determine how the peptides: PAE ratio impacts pelletization, the various binders were used at 2 %, with a moisture content of 27 %. The percentage of PAE used in the binder was either 23 % or 25 %.

3.3.7.3 Durability testing

After the torrefied wood pellets were air dried for 48 h, their moisture content was ~4 %. The fine particles produced were removed using a 3.18 mm sieve. 500 g of dust-free torrefied wood pellets were put into a tumbling can (PDT 110, Gamet Manufacturing Inc., St. Paul., MN, USA), followed by tumbling at 50 ± 2 rpm for 10 min. After tumbling, the fine particles produced were removed using the 3.18 mm sieve, and the mass of pellets remaining on the sieve was measured. The durability was calculated by the following equation:

$$Durability\ (\%) = \frac{mass\ of\ pellets\ after\ tumbling}{mass\ of\ pellets\ before\ tumbling} * 100\ \%$$

3.3.8 Pelletization with a single pellet press

In order to lower moisture content and further improve durability of resulting pellets, a single pellet press (MTI 50 K, Measurements Technology, Marietta, GA, USA) was used for pelletization of torrefied wood. This work was done in collaboration with Dr. Sokhansanj at the University of British Columbia.

3.3.8.1 Preparation of peptides-based binder for the single pellet press

Different binder formulations were prepared for pelletization of torrefied wood, including raw peptides and peptides-PAE. For all of the experiments using the single pellet press, peptides used were prewashed and spray dried and the solid content of all binders was set at 20 %.

For the peptides-PAE binder, peptides and Milli-Q water were added to a 250 mL flat bottom flask. Sodium hydroxide (2 M) was used to adjust the solution to pH to 7 to help improve solubility of the peptides. Next, PAE was added into the flask drop by drop, and the mixture was mixed with a magnetic stir bar on a hot plate (70 °C) for ~10 h. After the reaction, the mixture was collected and freeze-dried, then subjected to grinding to produce a fine powder.

3.3.8.2 Pelletization

20 g of torrefied wood (moisture content of 2.6 %; particle size ≤ 710 μm) was thoroughly mixed with the different binders and deionized water to a final moisture content of 10 %. The diameter of the die channel was 6.35 mm, and the length was 70 mm. 0.4-0.5 g samples were placed into the hole of the die. The sample was compressed by a piston that was 6.30 mm in diameter. The die temperature was 120 ℃.The protocol developed by Peng *et al.[17]* with some modification was used for pelletization. The compression force increased gradually until 7300 N was reached, and then the compression force was kept for 2 min. When the compression process was completed, the pellet was extruded. Torrefied wood with 10 % moisture content (no binder) was used as a control.

3.3.8.3 Durability of single pellets

The single pellet was air dried for about 24 h. The mass was then measured, and the single pellet was put into a steel container, which was connected to a wrist action shaker (Model 75, Burrell Corporation, Pittsburgh, PA, USA) and shaken for 10 min at 416 rpm. After shaking, the fine particles produced were removed using a 3.18 mm sieve, and the mass of the single pellet remaining on the sieve was measured. The durability of the single pellet was calculated as follow:

$$Single\ pellet\ durability\ (\%) = \frac{mass\ of\ single\ pellet\ after\ shaking}{mass\ of\ single\ pellet\ before\ shaking} * 100\ \%$$

3.9 Statistical analysis

All the experiments were performed in triplicate. One-way analysis of variance (ANOVA) was conducted by Tukey test (95 % confidence level) on Minitab17 statistical software.

4 Results and discussion

4.1 Characterization of peptides

In the protocol developed by the Bressler lab, SRM is thermally hydrolyzed, followed by dilution, centrifugation, filtration, hexane washing, and freeze drying[17, 18]. This standardized and commonly used lab protocol has been demonstrated to be an effective method for recovering peptides that can be valorized through various bioconversion strategies[2, 70-75]. The freeze-dried peptides obtained through this protocol were characterized using elemental and metal analyses to assess feasibility of incorporating this material into torrefied wood pellets.

The results of elemental analysis are shown in Table 4.1.. According to the ISO/DIS 17225-8 standard, the minimum and maximum allowable nitrogen in torrefied wood pellets is 0.5 % and 1.0 %, respectively. Consequently, peptides could account for 3.3 % to 6.5 % of torrefied wood pellets if other sources of nitrogen were not considered. The minimum and maximum allowable sulphur is 0.04 % and 0.1 %, respectively, which means that 6.9 % to 17.3 % peptides could be added into torrefied wood, if other sources were not considered.

Table 4.1. Elemental Analysis of Freeze-dried Peptides

Peptides	**C (%)**	**H (%)**	**N (%)**	**S (%)**
Freeze-dried	49.5 ± 0.2	6.66 ± 0.09	15.3 ± 0.1	0.579 ± 0.052

Metals and chlorine were also present in the freeze-dried peptides (Table 4.2.). The presence of large amounts of inorganic material in peptides is not desirable when used for torrefied wood pellet binder applications as this will result in high ash production or corrosion and fouling when torrefied wood pellets are burned[77]. While the metal content of the freeze-dried peptides was shown to be relatively low, the chlorine levels observed were of concern as the chlorine content of torrefied wood pellets is tightly regulated.

Table 4.2. Main inorganic elements found in peptides isolated through various strategies

Peptides	Na (%)	Mg (%)	K (%)	Ca (%)	Cl (%)
Freeze-dried	1.19 ± 0.11	0.033 ± 0.004	1.08 ± 0.09	0.052 ± 0.031	1.77 ± 0.09
Prewashed & Freeze-dried*	0.537 ± 0.097	0.046 ± 0.005	0.439 ± 0.091	0.031 ± 0.001	0.513 ± 0.059
Prewashed & Spray-dried*	0.462 ± 0.041	0.039 ± 0.007	0.357 ± 0.048	0.038 ± 0.002	0.395 ± 0.042

* For prewashing, 200 g of SRM were washed with Milli-Q water, and then brought up to 400 g with Milli-Q water prior to thermal hydrolysis. The averages and standard deviations of triplicate experiments are shown.

4.2 Prewashing SRM before hydrolysis for removal of chlorine

As mentioned in the last section, the high chlorine content observed in peptides could limit the amount of peptides/peptides-based binder applied in torrefied wood pellet applications. Based on the Pellet Fuels Institute (PFI) standard, the maximum allowable chlorine in densified fuels is 0.03 %, while according to the ISO/DIS 17225-8 standard, the minimum and maximum allowable chlorine in torrefied wood pellets is 0.03 % and 0.1 %, respectively. In order to reduce the amount of chlorine in peptides and thus increase the amount of peptides that could be incorporated into torrefied wood pellets, a prewashing step was introduced to the SRM processing strategy.

To minimize the amount of wastewater produced in the prewashing experiments, initial experiments employed only 200 g SRM, which was washed three times with Milli-Q water, brought up to 400 g with Milli-Q water, then subjected to thermal hydrolysis. After this, SRM hydrolysates were collected, diluted, centrifuged, filtered, hexane washed, and freeze-dried as routinely performed in the Bressler lab. As shown in Table 4.2., prewashing of the SRM resulted in a substantial decrease in the amount of sodium, potassium, and chlorine in the resulting peptides, which suggested that these elements were present as salts that could be easily removed through the prewashing step. Thus, these data suggest that a prewashing step could be used to reduce the amount of salt present in the peptides, which would enable higher loading of this material in torrefied wood pellets.

The water used for SRM washing was thermally hydrolyzed prior to disposal to address safety concerns. While increased water use and disposal may negatively impact process economics for SRM processing, it should be noted that the solution remaining after thermal hydrolysis is no longer considered hazardous and could be handled safely. Another possibility is

to incorporate this solution into a lipid pyrolysis technology as a water replacement during lipid hydrolysis[83, 84].

4.3 Adaptation of a spray drying process into SRM hydrolysates drying

One of the key issues of the SRM processing strategy that was developed in the Bressler lab is the use of freeze drying to remove water from the hydrolysates. This is because at an industrial scale, freeze drying is not cost-efficient and thus spray drying is the preferred method of drying. To address this issue, initial studies focused on the determining whether spray drying could be integrated into the protocol for the processing of SRM hydrolysates. For these studies, during spray drying, the inlet temperature was kept at 165 °C and two outlet temperatures, 85 and 90 °C, were tested. The two outlet temperatures were chosen because when the outlet temperature was below 83 °C, peptides cannot be dried; to maintain a 90 °C outlet temperature, the pump speed had to be slowed down and a higher outlet temperature could possibly result in further degradation of peptides. After spray drying, the recovered peptides were characterized and compared to those obtained from freeze drying. It should be noted that for these preliminary experiments involving spray drying and carboxylic and amine group determination (described in the section below), the SRM used was not washed prior to thermal hydrolysis.

4.4 Carboxylic and amine groups determination

The quantification of carboxylic and primary amine groups was first performed as these are the two main functional groups of peptides, and thus the two most promising sites for chemical modification or crosslinking. When the outlet temperature was 85 °C, the carboxylic and primary amine groups were quantified at 1.58 ± 0.0 mmol/g and 0.510 ± 0.062 mmol/g, respectively (Table 4.3.). Similarly, when the outlet temperature was raised to 90 °C, the carboxylic groups were observed at 1.61 ± 0.03 mmol/g, and the primary amine groups were

measured at 0.525 ± 0.07 mmol/g (Table 4.3.). Thus, changing the outlet temperature from 85 ℃ to 90 ℃ did not result in any significant differences with regards to the amount of carboxylic and amine groups present. Furthermore, the amounts of these functional groups were statistically similar to those quantified for freeze-dried peptides, which were measured at 1.60 ± 0.05 mmol/g and 0.496 ± 0.019 mmol/g for the carboxylic and primary amine groups, respectively. Thus, these results indicated that spray drying under the conditions described (inlet temperature of 165 ℃ and outlet temperature of 85-90 ℃) did not change the chemical properties of the resulting peptides, indicating that spray drying could be adapted for the processing of SRM hydrolysates. Considering the energy consumed and the pump rate, an outlet temperature of 85 ℃ was chosen for SRM hydrolysates drying in all future experiments.

Table 4.3**.** Carboxylic (-COOH) and primary amine ($-NH_2$) groups of peptides

Peptides	**-COOH (mmol/g)**	**$-NH_2$ (mmol/g)**
Freeze-dried	1.60 ± 0.05^a	0.496 ± 0.019^b
Spray-dried (85 °C)	1.58 ± 0.00^a	0.510 ± 0.062^b
Spray-dried (90 °C)	1.61 ± 0.03^a	0.525 ± 0.070^b

Note: Within a given column, averages of triplicate experiments annotated with the same letter are statistically similar at a 95 % confidence level (Tukey test). For all averages, the standard deviations are also shown.

It should be noted that although the amount of carboxylic groups observed (1.60 ± 0.05 mmol/g) were consistent with research from of Adhikari *et al.*[18], the quantity of primary amine groups (0.496 ± 0.019 mmol/g) was lower that the value 0.60 mmol/g peptides previously obtained[2]. This difference can be likely attributed to the methods used as a TNBSA method was used in this study while the *o*-phthaldehyde (OPA) method was used by Adhikari *et al*[18]. In the TNBSA method, SDS and hydrochloric acid were used to terminate reactions, while in the OPA method the reaction was not terminated, which could result in an artificially higher amount of primary amine groups.

4.5 Characterization of spray-dried peptides derived from prewashed SRM

After demonstrating that spray drying of peptides obtained from standard thermal hydrolysis of SRM did not impact the carboxylic and primary amine groups of the peptides, further analyses were performed using spray-dried peptides derived from prewashed SRM. As described in section 3.3.2 above, 200 g of SRM were used for these experiments to minimize the amount of wastewater generated. The spray-dried peptides obtained from prewashed SRM displayed 1.84 ± 0.04 mmol/g and 0.476 ± 0.032 mmol/g of carboxylic and primary amine groups, respectively. While the value of primary amine groups was statistically similar to those obtained for freeze-dried and spray-dried peptides obtained from unwashed SRM (Table 4.3.), there was a significant increase in the amount of carboxylic acid groups present. The metal and chlorine content of the spray-dried peptides were also assessed (Table 4.2.). Similar amounts of metals were found in the freeze-dried and spray-dried peptides. Conversely, a small decrease in chlorine was observed in the spray dried peptides. The reason for the different chlorine levels in the two peptide preparations is unknown. It should be noted that the yield of peptides obtained

from freeze-dried and spray-dried hydrolysates of prewashed SRM were statistically similar: 29.2 ± 1.4 % and 27.1 ± 0.3 %, respectively.

4.5.1 Scale-up of Thermal Hydrolysis using Prewashed SRM

To determine whether the prewashing and spray drying steps could be incorporated into the thermal hydrolysis process at a similar scale commonly used in the lab, the process was scaled up to allow for thermal hydrolysis of 1 kg of SRM, rather than 200 g. The chlorine content of the resulting peptides was determined to be 0.436 ± 0.050 %, which was similar to the value obtained in previous small scale (200 g) experiments using prewashed SRM (Table 4.2.). Based on this number, the amount of spray-dried peptides that could be applied as a binder in torrefied wood pellets without surpassing the regulatory requirements for chlorine (0.03 %) is roughly 7.5 %. In our previous proof of concept experiments, use of 3 % peptides-based binder (cross-linked with 23 % PAE) resulted in torrefied wood pellets with 97 % durability, surpassing industrial requirements. However, in this case, the chlorine content in pellets was 0.12 %, which was substantially higher than regulatory standards. Thus, washing of SRM before hydrolysis was hypothesized to enable to use the binder level of 3 % peptides-PAE (23 % PAE) while meeting the ISO regulatory standards for chlorine content in torrefied wood pellets.

4.5.2 Insoluble material in spray-dried peptides

When the spray-dried peptides recovered from hydrolysates of prewashed SRM were dissolved in water, a substantial amount (11.9 ± 2.9 wt%) of insoluble material was observed. For comparison, when the amount of insoluble materials was quantified in aqueous solutions generated using freeze-dried peptides obtained from prewashed SRM, only 0.339 ± 0.156 wt% was recovered. This extremely large increase in insoluble material observed when using spray-dried peptides could have a dramatic impact on their adhesive properties as the effectiveness of

protein-based adhesives depends on the ability of protein to disperse in the solution and to wet the surfaces that are to be bonded.

A key factor relating to the solubility of peptides is the pH of the solution. When 4 g of the spray-dried peptides were dissolved in 100 mL of Milli-Q water, the pH of the resulting mixture was 4.91 ± 0.09. Since this pH is very close to the estimated isoelectric point of SRM-derived peptides, which is pH 4.5[1], it is possible that pH was responsible for the increased amount of insoluble material observed. Indeed, when the pH of the mixture was increased to 7, the insoluble material decreased from 11.9 ± 2.9 wt% to 0.549 ± 0.102 wt%, which resembled values obtained from solutions of freeze-dried peptides (0.339 ± 0.156 wt%). These data clearly showed that the solubility of spray-dried peptides obtained from thermal hydrolysates of prewashed SRM could be increased through pH adjustment.

4.6 Pelletization of torrefied wood on a pilot scale pelletizer

The effects of parameters like moisture content, compression force, die temperature, and binder on the hardness of resulting torrefied wood pellets have been investigated using a single pellet press. However, there are few reports concerning scaled up pelletization of torrefied wood using parameters obtained from single pellet press. Pellets made by a single pellet press are not produced continuously and the flow of biomass into the openings of die channels cannot be simulated exactly as it is in a pilot scale or commercial scale pelletizer[83]. In this study, we first examined parameters like peptides percentage, moisture content, and the peptides-PAE binder level during pilot scale pelletization. It should be noted that for all of the experiments performed using the pilot scale pelletizer, freeze-dried peptides derived from unwashed SRM were used. This was because at the time of experimentation, the prewashing and spray drying studies had not yet been performed.

4.6.1 The effect of peptides percentage

The possibility to utilize peptides without any chemical modification or crosslinking as a binder was first investigated at pilot scale. It was found that when using peptides as-is, increasing the peptides percentage from 0.5 to 2.0 % did not improve durability of resulting torrefied wood pellets (Figure 4.1.), which ranged from 68.6 ± 7.4 to 80.3 ± 3.5 %. A similar result was reported by Adhikari *et al.* [18] who reported that when SRM-derived peptides without any chemical modification or crosslinking were used as an adhesive for plywood, the dry and soaked shear strength of plywood did not meet the minimum requirements. The likely explanation for the poor adhesive quality of SRM-based peptides is their low molecular weight. Thus, similar to the research conducted by Adhikari *et al.*[18], application of SRM-derived peptides as a binder for torrefied wood pellets will likely necessitate an increase in the molecular weights of peptides through chemical modification and/or crosslinking. Nevertheless, these experiments helped to establish a baseline for all future experiments using the pilot scale pelletizer.

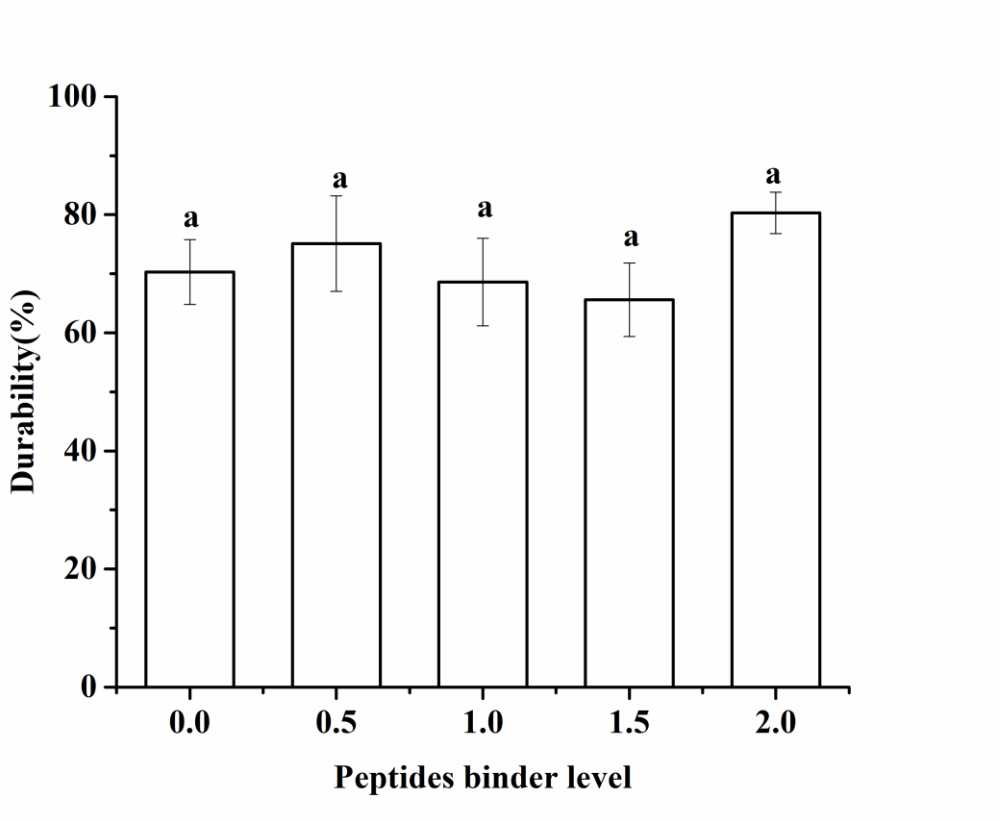

Figure 4.1**.** The effect of the peptides concentration on the durability of resulting torrefied wood pellets. Averages of triplicate experiments annotated with the same letter are statistically similar at a 95 % confidence level (Tukey test). For all averages, the standard deviations are also shown.

4.6.2 The effect of moisture

Moisture content also plays a substantial role during the pelletization of biomass. Water can function as a plasticizer, lowering the glass transition temperatures of inherent binders like protein, starch, lignin, and it could also behave as a lubricant, reducing friction between biomass particles and the die channel, resulting in reduced energy consumption during pelletization[8, 9, 61]. Conversely, too much moisture could result in weaker pellets due to the incompressibility of moisture[8, 61]. The effect of moisture on the durability of resulting torrefied wood pellets was studied in two different situations as described below.

In the first set of experiments, a 1 % peptides-PAE (25 % PAE) binder level was chosen. In terms of chlorine content, a 1 % binder level represents the maximum amount of unwashed peptides that could be incorporated while satisfying the requirements of the TW1a property class of torrefied wood pellets, which is the highest quality of torrefied wood pellet according to the specifications outlined by ISO/DIS 17225-8. For these experiments, moisture contents ranging from 20 to 25 % were examined, but unfortunately, pellets could not be obtained as the material could not be properly loaded into the die due to flow issues. Based on these results, a moisture content of 28 % was then examined, which facilitated production of pellets with low durability of 81.7 ± 2.0 % (Figure 4.2.). The palm kernel shell biochars was compacted into briquettes by Bazargan *et al.*, in which strength of briquettes was increased when moisture was increased from 0 to 30%, and decreased when moisture was further increased to 40 % and 50 %[54]. When biochar from different pyrolysis temperatures was pelletized, at 15 % moisture content pellets could not be formed or were so weak that their strength could not be measured[57]. Moisture was then enhanced from 20 to 35 % and the compression strength of pellets increased consequently, but decreased again at higher moisture levels[57]. To determine whether an

increase of moisture content could result in better durability of the torrefied wood pellets, a moisture content of 34 % was then used. Unfortunately, the durability of pellets produced in our experiments at 34 % moisture level was dramatically reduced (49.5 ± 2.6 %). This can likely be attributed to the incompressibility of water, or because of cracks or pores created when the water was evaporated during the drying of pellets.

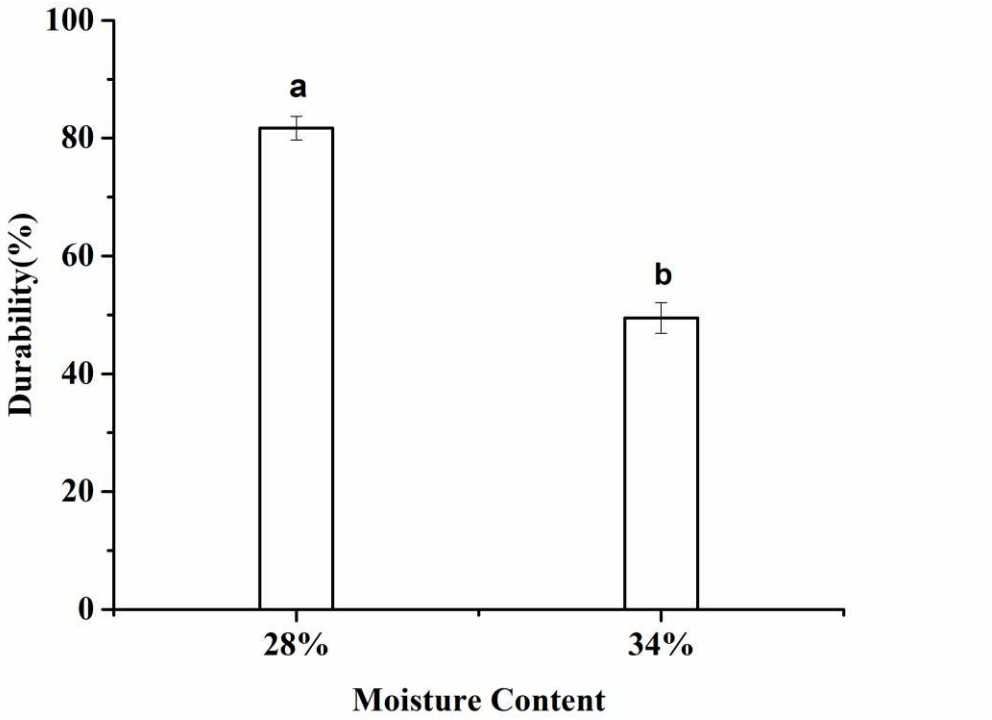

Figure 4.2. The effect of moisture on the durability of torrefied wood pellets made using 1 % peptides-PAE (25 % PAE) as a binder. The averages and standard deviations obtained from triplicate experiments are shown. Values annotated with different letters are significantly different (Tukey Test, 95 % confidence level).

In the second set of experiments, a 2 % peptides-PAE (25 % PAE) binder level was employed as this would satisfy the chlorine requirements for TW2a pellets, the next highest quality of torrefied wood pellet. As was the case in the experiments described above, a 28 % moisture level was first employed, which resulted in torrefied wood pellets with a durability of 88.6 ± 1.0 % (Figure 4.3.). It is worth noting that this durability was significantly higher than that obtained using a 1 % peptides-PAE (25 % PAE) binder level (Figure 4.2.), which confirms that increasing the binder level results in better durability. However, neither binder level was able to produce torrefied wood pellets that met the minimum durability requirements.

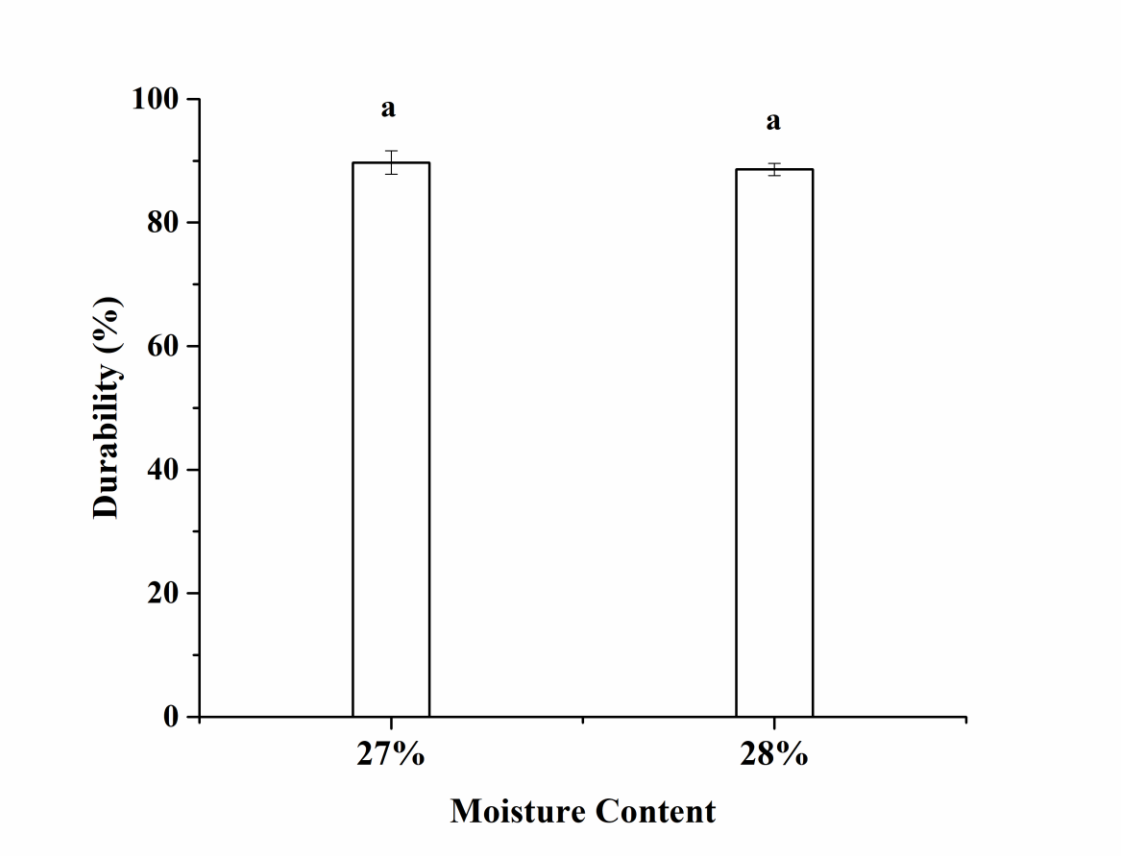

Figure 4.3. The effect of moisture content on the durability of torrefied wood pellets produced using 2 % peptides-PAE (25 % PAE). The averages and standard deviations obtained from triplicate experiments are shown. Values annotated with the same letters are significantly similar (Tukey Test, 95 % confidence level).

Since increasing the moisture content to 34 % dramatically decreased the durability of pellets made using a 1 % binder level (Figure 4.2.), for experiments using a 2 % peptides-PAE (25 % PAE) binder, a slightly lower moisture content of 27 % was chosen. As shown in Figure 4.3, decreasing the moisture content to 27 % did not further change the durability of the resulting torrefied wood pellets. Additional experiments using a 20 % moisture content, but supplementing with 0.5 % vegetable oil to act as a lubricant, were also performed using 2 % peptides-PAE (23 % PAE), but the pelletizer was jammed and the pellets could not be extruded. Thus, future experiments looked at adjusting parameters other than binder and moisture levels.

4.6.3 The effect of pH of peptides-PAE binder

In another approach to improve the binding capabilities of the peptides-PAE binder, the pH under which the peptides-PAE crosslinking reaction was performed was adjusted from pH 5.5 to 8.0. At pH 5.5, the PAE is expected to react with the carboxylic group, but at a pH above 7.0, the PAE could also react with the amine groups. By adjusting pH, the crosslinking reaction between peptides and PAE may be improved; as a result, the binding strength of peptides-PAE binder could be improved. However, adjustment of the pH used during the peptides-PAE (25 % PAE) crosslinking reaction from 5.5 to 8.0 did not improve the durability of pellets generated using a binder level of 1 % peptides-PAE (Figure 4.4.). It is possible that the overall crosslinking density of peptides-PAE binder did not improve as this was never assessed. Another possibility was that the 1 % peptides-PAE binder level did not provide enough binding sites for the torrefied wood particulates. In support of this possibility, other studies using wheat flour, starch, or lignin as a binder for torrefied wood pellets used much higher binder levels (5-10%)[17, 41]. Ghiasi *et al.*, used 7 % wheat flour for pelletization of torrefied wood using a bench scale pelletizer and the durability of resulting pellets was 98.6 %[41]. Peng *et al.*, showed that when 5 % and 10 %

starch or lignin were used, and the hardness of the resulting pellets was comparable to that of the control pellets (regular wood pellets)[17] .

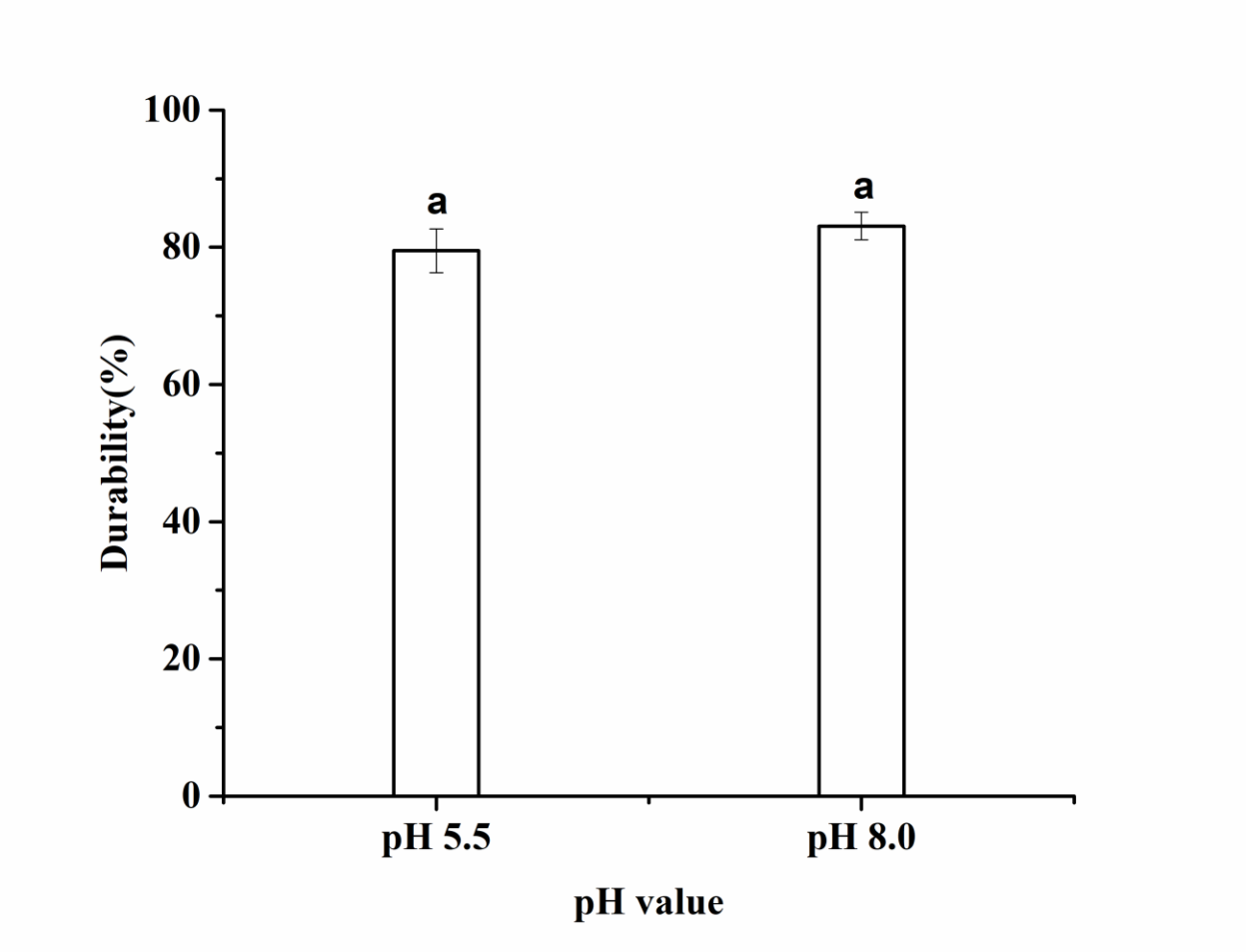

Figure 4.4. The effect of changing the pH of the peptides-PAE (25 % PAE) crosslinking reaction on the durability of pellets. For these experiments, a 1 % peptides-PAE (25 % PAE) binder level was employed. The averages and standard deviations obtained from triplicate experiments are shown. Values annotated with the same letters are significantly similar (Tukey Test, 95 % confidence level).

4.6.4 The effect of PAE percentage

In proof of concept experiments performed using an industrial scale pelletizer at Alberta Innovates, when 2 % peptides-PAE (23 % PAE) was used, the average durability of pellets met the minimum requirement of PFI and ISO/DIS 17225-8 (≥ 95 %). However, due to concerns surrounding cost and the amount of materials necessary to test various binder formulations at industrial scale, the pelletization experiments described in previous sections were performed using a bench scale pelletizer that had been used routinely to produce white wood pellets. In addition, while 23 % PAE was used in crosslinking reactions with peptides to generate binder for the industrial scale experiments, we had used a PAE concentration of 25 %. Previous work from Adhikari *et al.*[2] demonstrated that peptides-PAE plywood adhesives prepared using 23 % or 34 % PAE during the crosslinking reaction resulted in significantly similar adhesive strength. However, given that we were not able to produce pellets with ≥ 95% durability in any of the conditions examined, including experiments using a 2 % peptides-PAE (25 % PAE) binder level, we wanted to confirm whether production of torrefied wood pellets using the bench scale pelletizer and conditions similar to those used during industrial scale trials would produce pellets with ≥ 95% durability. In our experiments, the moisture content used was about 27 %, and the durability of resulting pellets with 2 % peptides-PAE (23 % PAE) was 92.2 ± 1.0 %. In our proof of concept experiments from Alberta Innovates, the durability of pellets with 2 % peptides-PAE (23 % PAE) was 95.6 ± 1.4 % in the presence of about 19 % moisture content. As discussed in the earlier section, we cannot get any pellets when moisture content was below 27 %. The difference in durability of pellets between of our experiments with proof of concept experiments may come from the moisture difference, as higher moisture content could result in lower durability pellets due to incompressibility of high moisture[8, 61].

As shown in Figure 4.5., the durability of torrefied wood pellets generated using a bench scale pelletizer did not change when 25 % PAE was used in the crosslinking reaction with peptides rather than 23 % PAE. Significantly, neither of the peptides-PAE binders resulted in torrefied wood pellets with ≥ 95% durability. One possible explanation is that the bench scale pelletizer used in these experiments does not pelletize torrefied wood as well as the industrial pelletizer used in previous proof of concept studies. Thus, it is possible that some of the formulations used in experiments above are capable of producing torrefied wood pellets that meet the minimum durability requirements when employed in an industrial pelletizer, even though the durability obtained using a bench scale pelletizer did not.

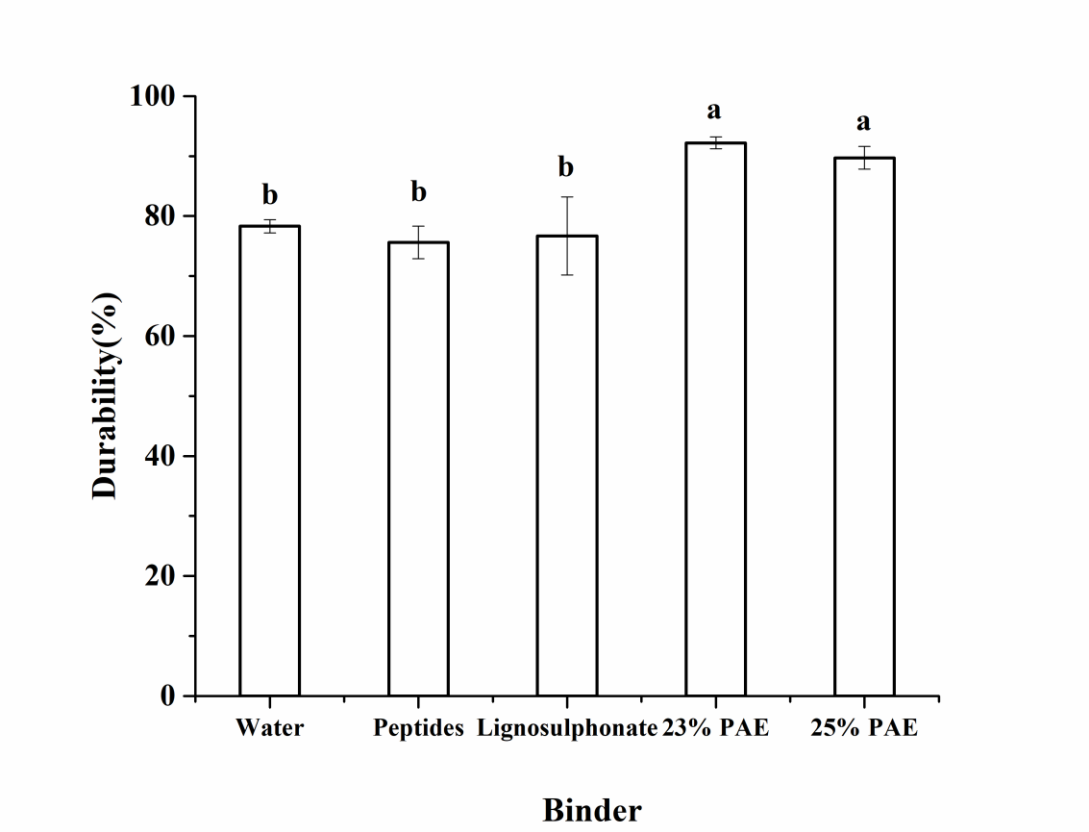

Figure 4.5. The effect of binders on the durability of pellets. Several different binders were assessed as binders for torrefied wood pellets: water, unmodified peptides (Peptides), sodium lignosulphonate (Lignosulphonate), peptides crosslinked with 23 % PAE (23 % PAE), and peptides crosslinked with 25 % PAE (25 % PAE). In all cases, the binder level used was 2 % and the moisture content was 27 %. The averages and standard deviations obtained from triplicate experiments are shown. Values annotated with the same letters are significantly similar (Tukey Test, 95% confidence level).

Because sodium lignosulphonate is often used in pelletization of regular wood, it was also employed for torrefied wood pellets in these experiments for comparison purposes. Using a 2 % sodium lignosulphonate binder level, the durability of pellets was 76.7 ± 6.5 %, which was lower than that of pellets made with either of the two peptides-PAE binders. Furthermore, use of sodium lignosulphonate resulted in pellets that had similar durability as those produced using water or unmodified peptides. Based on these data, sodium lignosulphonate is not a suitable binder for the pelletization of torrefied wood pellets.

4.7 Pelletization of torrefied wood on single pellet press

The fabrication of torrefied wood pellets using a bench scale pelletizer was originally performed to provide information on scaled-up production using a variety of formulations. Unfortunately, once it became apparent that the bench scale pelletizer was not capable of producing torrefied wood pellets with the necessary durability, other alternatives for pelletization were explored. Consequently, testing of various binder formulations was performed using a single pellet press and in collaboration with Dr. Shahabaddine Sokhansanj at the University of British Columbia. This allowed us to minimize material consumption, while examining the effects of various parameters, such as die temperature, compression force, moisture content, biomass species, and additives, on the quality of resulting pellets prior to bench scale and industrial scale up[83]. It should be noted that for these experiments, prewashed and spray dried peptides were used to reduce the amount of chlorine present and maximum the theoretical binder levels.

For experiments using a single pellet press, unmodified peptides or peptides crosslinked with PAE (33 %) were used as a binder at 3 % loading. Use of a single pellet press enabled use of a much lower moisture content of 10 %. As shown by Adhikari *et al.*[18] , although the dry shear

strength of plywood with peptides-PAE adhesive did not improve after 23 % PAE was used, the soaked shear strength of plywood with peptides-PAE adhesive improved significantly when PAE was increased from 23 to 34 %, but after 34 %, the soaked strength of plywood did not improve much. A loading of 33 % PAE instead of 34 % was chosen for ease of sample preparation, as the ratio of peptides to PAE was 2:1. Also the durability of pellets was not improved when PAE percentage was increased from 23 to 25 % on a pilot scale pelletizer.

As shown in Figure 4.6., only the peptides-PAE formulation displayed durability greater than the no binder (water) control. However, there were no differences between the durability achieved using any of the three peptides-based binders, including the unmodified peptides. It should be noted that for any of the binders, there was great variation in the durability of single pellets, as evidenced by the large standard deviations (Figure 4.6.). This variation likely stems from the heterogeneous nature of torrefied wood, which leads to inconsistency of pellets with regards to their mechanical properties. In industrial settings, the torrefied materials used to make pellets display a wide distribution of sizes and densities[40], but these materials are ground during processing to produce much smaller particles that are then incorporated into pellets. Thus, future work using the single pellet press will employ ground torrefied materials that have a smaller particle size and are more homogenous.

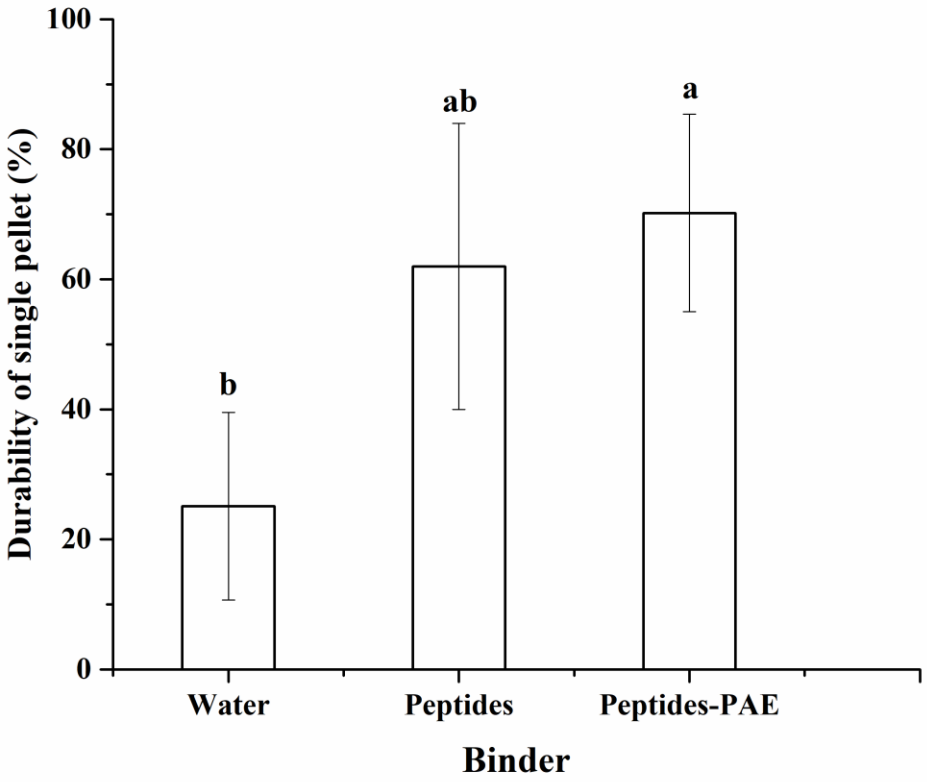

Figure 4.6. The effect of different binders on the durability of single pellets. Three different binders were tested in these experiments: 1) unmodified peptides (Peptides); 2) peptides crosslinked with 33 % PAE (Peptides-PAE); pelletization without the use of a binder (Water) was also performed. For these experiments, the binder level was 3 % and moisture content was 10 %. Averages and standard deviations of triplicate experiments are shown. Averages annotated with the same letters are statistically similar (Tukey Test; 95 % confidence level).

Li *et al.*[40] also reported great variation in terms of energy consumption and Meyer hardness when assessing single torrefied wood pellets. The researchers also ascribed this to the heterogenous nature of the torrefied sample. It should also be noted that although the durability of single pellets was different from that of pellets obtained from pilot scale pelletizers, there is no direct relationship between the two numbers and thus they are not at all comparable.

General discussion, conclusion, and recommendation

There is a great effort around the world to reduce greenhouse gas emissions and to utilize energy from renewable resources, including wind energy, solar energy, tidal energy, and energy from woody biomass. Among them, energy from woody biomass has gained popularity in the past decade. Woody biomass used as energy is usually densified as wood pellets to increase bulk density, to ease handling and transportation, and to reduce associated costs. Wood pellets are mainly used in coal-fired power plants and for residential heating. However, wood pellets are not perfect, suffering from lower heating value and hygroscopicity. As a pretreatment of woody biomass in a temperature range of 200-300 °C, torrefaction could upgrade woody biomass in term of heating value, hydrophobicity, and grindability. However, it is much more difficult to pelletize torrefied woody biomass, as the natural binder lignin would undergo structural changes during torrefaction. An external binder is thus needed for pelletization of torrefied wood. Currently, there exist no binders available for the torrefied wood industry. This research aimed to develop a cheap and renewable binder from hydrolyzed specified risk materials (SRM), a protein-rich by-product from cattle tissues where the prions are most likely to concentrate.

The challenges of this research included: 1) how to improve binding strength of peptides, as thermal hydrolysis breaks down SRM into smaller peptides and amino acids; 2) whether spray drying could replace freeze drying for SRM hydrolysates processing; 3) how to control chlorine level in the resulting pellets; 4) how to optimize parameters associated with durability of pellets on a pilot scale pelletizer, as there were few pilot scale pelletization methods available from references.

The peptides alone did not improve durability of resulting pellets at 0-2 % binder level. This result indicated the necessity to improve binding strength of peptides by proper chemical

crosslinking and/or chemical modification. For enhancement of binding strength of peptides, the crosslinker PAE was used. This was because peptides-PAE has been developed successfully as a plywood adhesive in a previous study in our lab. The possibility of peptides-PAE as a binder for pelletization of torrefied wood pellets in this research was explored. The drawback of PAE was the presence of chlorine, which could limit the amount of peptides-PAE that could be added into the pellets. Thus, the PAE percentage and peptides-PAE binder level were studied. However, pellets made from these studies did not meet the minimum durability requirement. For use of peptides-PAE binder, it is worth mentioning that their percentage should not exceed 3.5 % in the resultant pellets due to limitation of nitrogen requirement. Peptides-PAE binder level could be up to 10 % if only sulphur content was considered. However, for sodium lignosulphate which is commonly used in pelletization of regular wood pellets, and only 1-2 % binder level could be used due to limitation of sulphur. One advantage of peptides-PAE binder over sodium lignosulphonate is the durability of pellets with peptides-PAE binder is much better than that of sodium lignosulphonate at the same pelletization conditions.

Another way to reduce chlorine was to pre-wash SRM before thermal hydrolysis. We hypothesized that the chlorine would be in its salt form. By prewashing SRM, the chlorine of resulting peptides was significantly reduced. As a result, the peptides-PAE (23 % PAE) binder level chosen in this case could be used. Prewashing of SRM gave us more flexibility to use peptides-PAE binder. For safety concerns, it is also required to thermally hydrolyze water from prewashing SRM. This may be a disadvantage of prewashing SRM due to the energy cost of thermal hydrolysis and the loss of some water-soluble proteins. The resultant hydrolysates may be used as a liquid fertilizer due to the presence of salts and ammonium, to offset some of the related costs. The water from prewashing SRM may also be incorporated into lipid pyrolysis

technology. Obviously, more researches have to be done to test these ideas. Using other crosslinkers like glutaraldehyde and condensed tannins may be other feasible ways to control chlorine level in the final pellets.

The carboxylic and primary amine groups of spray dried peptides and freeze-dried peptides were estimated. It was found that carboxylic and primary amine groups of spray dried peptides were not significantly different from those of freeze-dried peptides. The yield of spray dried peptides was not significantly different from that of freeze-dried peptides. It was interesting that the chlorine of spray dried peptides was much lower than that of freeze-dried peptides. More research is needed to determine the causality of this phenomenon. These results clearly showed that spray drying could replace freeze drying for SRM hydrolysates drying. The binding strength of spray dried peptides-PAE and freeze-dried peptides-PAE could be compared in the future to further confirm the above conclusion, to be on the safe side.

The parameters for pelletization of torrefied wood on a pilot scale are scarcely available. In this research, the moisture and peptides-PAE binder level were studied on a pilot scale pelletizer. These could provide valuable information for future experimental design. In general, increasing peptides-PAE binder level could result in better durability of pellets, as increasing binder level could provide more binding sites. Water could reduce friction between torrefied wood particles and die channels, and also behave as plasticizer, lowering glass transition temperature of inherent binders like protein, lignin. But too much water would lead to pellets with low durability. In this research, the lowest moisture content was around 27-28 %, which was much too high from the perspective of the industry, could result in pellets with low durability as water evaporation could leave cracks and pores in pellets. One option to overcome this problem is to choose a proper high duty pelletizer on a pilot or commercial scale.

To study the effect of parameters on hardness/compressive strength of single pellet on a single press unit is relatively cost effective and time saving. However, parameters optimized from a single press unit may not be used for a pilot or commercial scale pelletizer as their infrastructures are quite different and the hardness of single pellet is different from durability of pellets from a pilot or commercial scale pelletizer.

In summary:

The objectives of this thesis include: 1) to enhance binding strength of peptides by chemical crosslinking with PAE resin; 2) to study the effects of moisture content, binder types, and binder level on durability of pellets; 3) to use spray drying instead of freeze drying for SRM hydrolysates processing; 4) to remove chlorine from peptides by washing SRM before thermal hydrolysis. This research showed that: 1) an increase of unmodified peptides to 2 % binder level did not improve durability of torrefied wood pellets, which justified the necessity to improve binding strength of unmodified peptides by chemical crosslinking with PAE resin; 2) at 1 % peptides-PAE (25 % PAE), an increase of moisture from 28 % 34 % resulted in durability of pellets decreased from 81.7 ± 2.0 % to 49.5 ±2.6 %, and an increase of pH of peptides-PAE from 5.5 to 8.0 did not improve durability of pellets; 3) at 28 % moisture content, an increase of peptides-PAE (25 % PAE) from 1 to 2 % led to pellets with 88.6 ± 1.0 % durability; 4) durability of pellets with peptides-PAE binder was better than that of pellets with sodium lignosulphonate; 5) the lowest moisture achieved with the pilot scale pelletizer used in this study was 27 %; 6) carboxylic groups, primary amine groups, and yield of peptides by spray drying were not significantly different from those of peptides by freeze drying; 7) by washing SRM before hydrolysis, the chlorine of peptides was dropped from 1.29 ± 0.06 % to 0.436 ± 0.050 %; 8) the moisture could be lowered to 10 % using a single pellet press, and addition of 3 % peptides-PAE

could significantly improve durability of single pellet, compared to single pellet without any binder.

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Appendices

For the first two years of my program, I was working on a project entitled, “Incorporation of biosolids into lipid pyrolysis technology for biofuels production”. Specifically, the goal of this project was to extract metals from thermally hydrolyzed biosolids. Based on my contributions, I was included as an author on two papers (see below), with two more planned publications.

For the first paper “Value-added products from urea glycerolysis using a heterogeneous biosolids-based catalyst” (Appendices A)[84], I worked on the thermal hydrolysis of biosolids, preparation of the solid phase from thermally hydrolyzed biosolids (i.e. the biosolids-based catalyst), and metal analysis of biosolids-based catalyst.

For the paper “Accelerating Settling Rates of Biosolids Lagoons through Thermal Hydrolysis” (Appendices B)[85], I helped with thermal hydrolysis of biosolids.

Appendices A

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Value-added products from urea glycerolysis using a heterogeneous biosolids-based catalyst

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Abstract: Although thermal hydrolysis of digested biosolids is an extremely promising strategy for wastewater management, the process economics are prohibitive. Here, a biosolids-based material generated through thermal hydrolysis was used as a catalyst for urea glycerolysis performed under several conditions. The catalytic system showed remarkable activity, reaching conversion values of up to 70.8 ± 0.9 % after 6 h at 140 °C using a catalyst/glycerol weight ratio of 9 % and an air stream to remove NH_3 formed during the process. Temperature played the most substantial role among reaction parameters; increasing temperature from 100 °C to 140 °C improved conversion by 35 % and glycidol selectivity by 22 %. Furthermore, the catalyst retained good activity even after the fourth catalytic run (conversion rate of 56.4 ± 1.3 %) with only a slight decrease in glycidol selectivity. Thus, the use of a biosolids-based catalyst may facilitate conversion of various glycerol sources (i.e. byproduct streams from biodiesel

production) into value-added products such as glycidol, and may also improve the economic feasibility of using thermal hydrolysis for treatment of biosolids.

Keywords: Biosolids, urea glycerolysis, glycidol, glycerol carbonate

1. Introduction

Over the last twenty years, the increased accountability of companies with regards to environmental issues has represented a formidable driving force for the development of sustainable industrial processes[86, 87]. As a consequence, the production of fuels and chemicals has started to use recycled or renewable feedstocks in place of oil-based raw materials[88, 89] in an attempt to improve process sustainability while maintaining performance of traditional commodities. Nowadays, biodiesel is one of the most well-established technologies based on renewable resources[90] and its production has been increasing every year, partly because of government environmental policies[91]. The increase in biodiesel production has made available abundant amounts of glycerol, a byproduct stream that can be used as feedstock for several chemical syntheses[92]. Among them, the production of glycerol carbonate is of key interest as it could be used for the synthesis of high-performance hyperbranched polymers[93, 94].

Glycerol carbonate is typically produced in a two-step process from the carboxylation of ethane or propene oxide and a subsequent reaction with glycerol[95]. A one-step synthesis of glycerol carbonate has also been reported by several authors through reaction of glycerol with supercritical CO_2[96], or using urea[97, 98] or other reagents[99]. Urea glycerolysis is an economically attractive procedure because of the low cost of the reagents and higher yields compared with other routes[100]. In addition, during urea glycerolysis, glycerol carbonate can

undergo decarboxylation with the formation of glycidol, a highly reactive compound that could potentially replace glycerol carbonate in the production of polymers, leading to higher quality materials[94]. Despite the better performance of glycidol in polymer applications, its synthesis is particularly hazardous and environmentally unfriendly as it involves hydrolysis and dehydrochlorination of epichlorohydrin[101].

To improve classical synthetic pathways, several authors have reported new catalytic systems for the selective conversion of glycerol to glycerol carbonate[102, 103]. However, the synthesis of glycidol has remained challenging and catalytic systems generally lead to the formation of both glycerol carbonate and glycidol[97, 102, 104, 105]. Radical decarboxylation of glycerol carbonate is an interesting alternative procedure that could be combined with the urea glycerolysis process because urea undergoes radical heterolytic cleavage at temperatures higher than 130 °C[106] forming highly reactive species that lead to the degradation of cyclic carbonates[107]. Several catalytic systems were proposed to enhance the urea reactivity during alcoholysis[108], but metal oxides are typically employed because of their low cost, high recyclability and good catalytic performances[109, 110].

Recently, our group reported that thermal hydrolysis of biosolids, a byproduct generated during the treatment of municipal wastewater, dramatically increased natural settling rates[85]. Although thermal hydrolysis offers an intriguing solution for treatment and disposal of biosolids, the capital and operating costs may be prohibitive to mainstream adoption. Here, we report that the solid residue remaining after thermal hydrolysis of biosolids, which contains a high concentration of metals, particularly metal oxides (i.e. Fe_2O_3, Al_2O_3, ZnO, TiO_4 and silica), acts as a catalyst for conversion of glycerol to value-added products. Finding value for this solid residue may improve the process economics for the thermal hydrolysis of biosolids, making it a

more attractive solution for wastewater treatment facilities. In this work, the metal-rich solid residue recovered after thermal hydrolysis of biosolids was successfully used as a heterogeneous catalyst for urea glycerolysis. For these experiments, several parameters were investigated: temperature, time, catalyst loading, urea/glycerol molar ratio, and residual atmosphere. Based on our findings, the solid residue obtained after thermal hydrolysis of biosolids has great potential for enhancing urea glycerolysis.

2. Results and Discussion

2.1. Assessment of the biosolids-based catalyst

Urea glycerolysis can proceed through two different mechanisms, a radical or a non-radical pathway (Figure 1.). The first step of both pathways involves the formation of a urethane intermediate. This compound evolves through an intermolecular esterification into glycerol carbonate. Subsequently, glycerol carbonate could undergo decarboxylation, which results in the formation of glycidol.

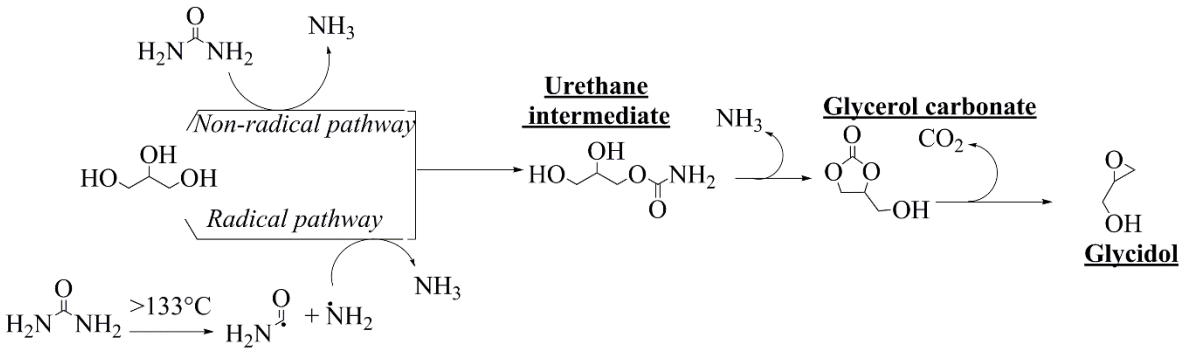

Figure 1. Radical and non-radical reaction pathways for formation of glycerol carbonate and glycidol during urea glycerolysis.

It has been shown that urea glycerolysis could be performed under catalytic conditions using several metal-based materials containing Zn, Al, Fe, Ti and other metals[111]. The biosolids-based material used as catalyst in these experiments contains an inorganic fraction (30.3 ± 0.6 wt%) that comprises several metal species (Table 1.), mainly as oxides, and silica[85]. As reported by Climent *et al*.[97], the direct interactions between urea, glycerol, and the surface of metal oxides can promote the alcoholysis process. Thus, a heterogeneous catalyst containing a mix of aluminum and zinc oxides, such as the biosolids-based material used in these experiments, has great potential in the production of glycerol carbonate and glycidol. In addition, the biosolids-based catalysts showed a remarkable concentration of surface acidic sites (5.32 ± 0.03 mmol/g) that could enhance the decarboxylation of carbonates[112, 113]. Finally, as shown by the FT-IR spectrum (Figure 2.), carboxylic bands ($\nu_{\text{-OH}}$ = 3400-3300 cm^{-1}, $\nu_{\text{-C=O}}$ = 1800-1700 cm^{-1}) are weaker compared with $\nu_{\text{-CH}}$ (2900-2800 cm^{-1}) and $\nu_{\text{-C=C}}$ (1680-1600 cm^{-1}), supporting the hypothesis that acid sites are mainly inorganic rather than carboxylic functionalities.

Table 1. Concentration of the main metal species in biosolids-based catalysts as determined by ICP-OES.

	Concentration of main metal species [mg/g]								
	Cr	Fe	Mn	Sr	Al	Cu	Zn	Pb	Ti
Biosolids-based catalyst[1]	0.39 ± 0.02	26 ± 1	0.58 ± 0.03	0.37 ± 0.02	26 ± 1	0.71 ± 0.04	1.06 ± 0.05	0.10 ± 0.01	3.2 ± 0.2
Recycled biosolids-based catalyst[2]	0.28 ± 0.01	18 ± 1	0.39 ± 0.5	0.28 ± 0.01	20 ± 1	0.74 ± 0.03	0.72 ± 0.05	0.08 ± 0.01	0.16 ± 0.02

[1] The native biosolids-based catalyst obtained through thermal hydrolysis of biosolids

[2] A recycled biosolids-based catalyst that had been used for four urea glycerolysis reactions.

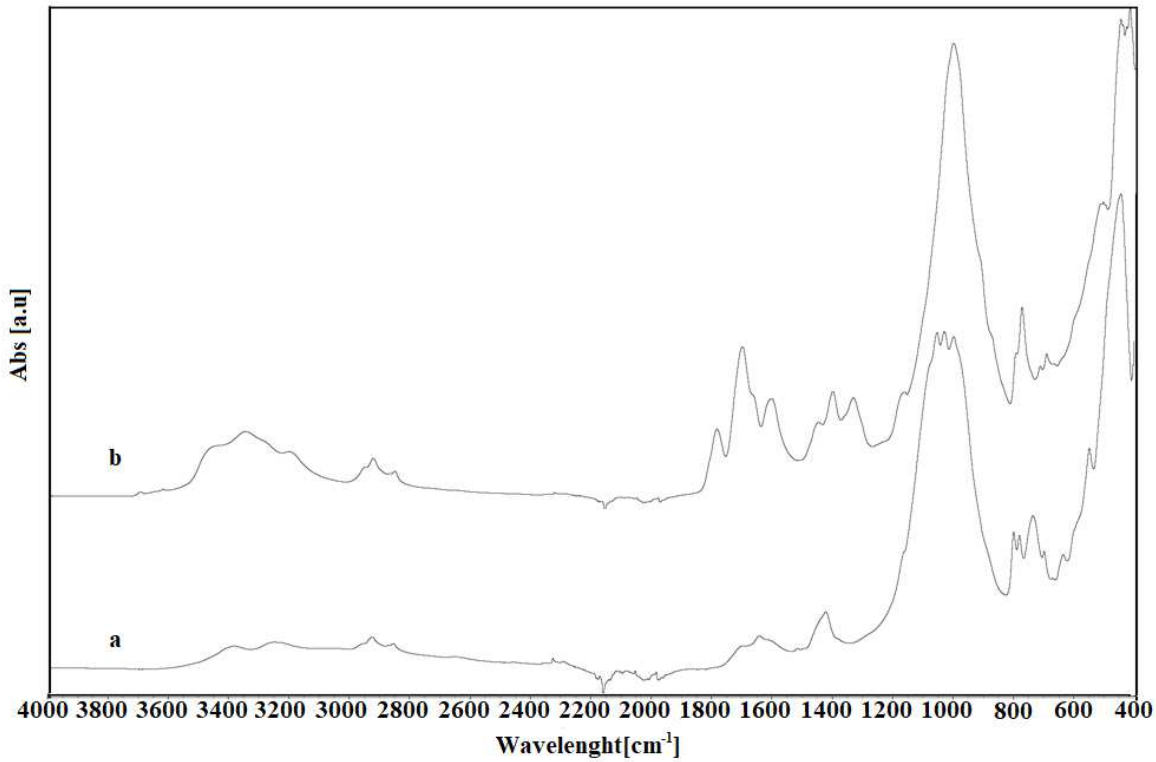

Figure 2. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). The spectrum generated in the range of 4000 to 400 cm^{-1} is shown for the native biosolids-based catalyst (a) and a recycled catalyst that had been used in four catalytic reactions (b).

2.2. Influence of catalyst loading

The influence of catalyst loading on conversion and selectivity of urea glycerolysis was studied at 140 °C with a 2:1 molar ratio of urea:glycerol and an air stream to remove NH_3 formed during the reaction (Figure 3.). The conversion rates achieved with the non-catalytic system were lower than those obtained using any combination of reaction time and catalyst loading, with a maximum conversion value of 46.8 ± 0.6 reached after 6 h. Increasing the catalyst loading from 0 to 3 wt% improved the conversion and after 6 h, a value of 64.1 ± 0.4 % was achieved. Further improvements in conversion were observed for catalyst loading of 6 wt% (66.5 ± 0.4 % after 6 h) and for 9 wt% (69.4 ± 0.9 % after 6 h), but with a catalyst loading of 12 wt% the conversion values were not significantly different ($p < 0.05$) from those achieved using 9 wt%. The glycidol selectivity for the non-catalytic system was quite high (up to 83.4 ± 0.6 % after 6 h), meanwhile the highest value achieved using the catalytic system was 70.8 ± 0.4 after 6 h using 12 wt% of catalyst loading.

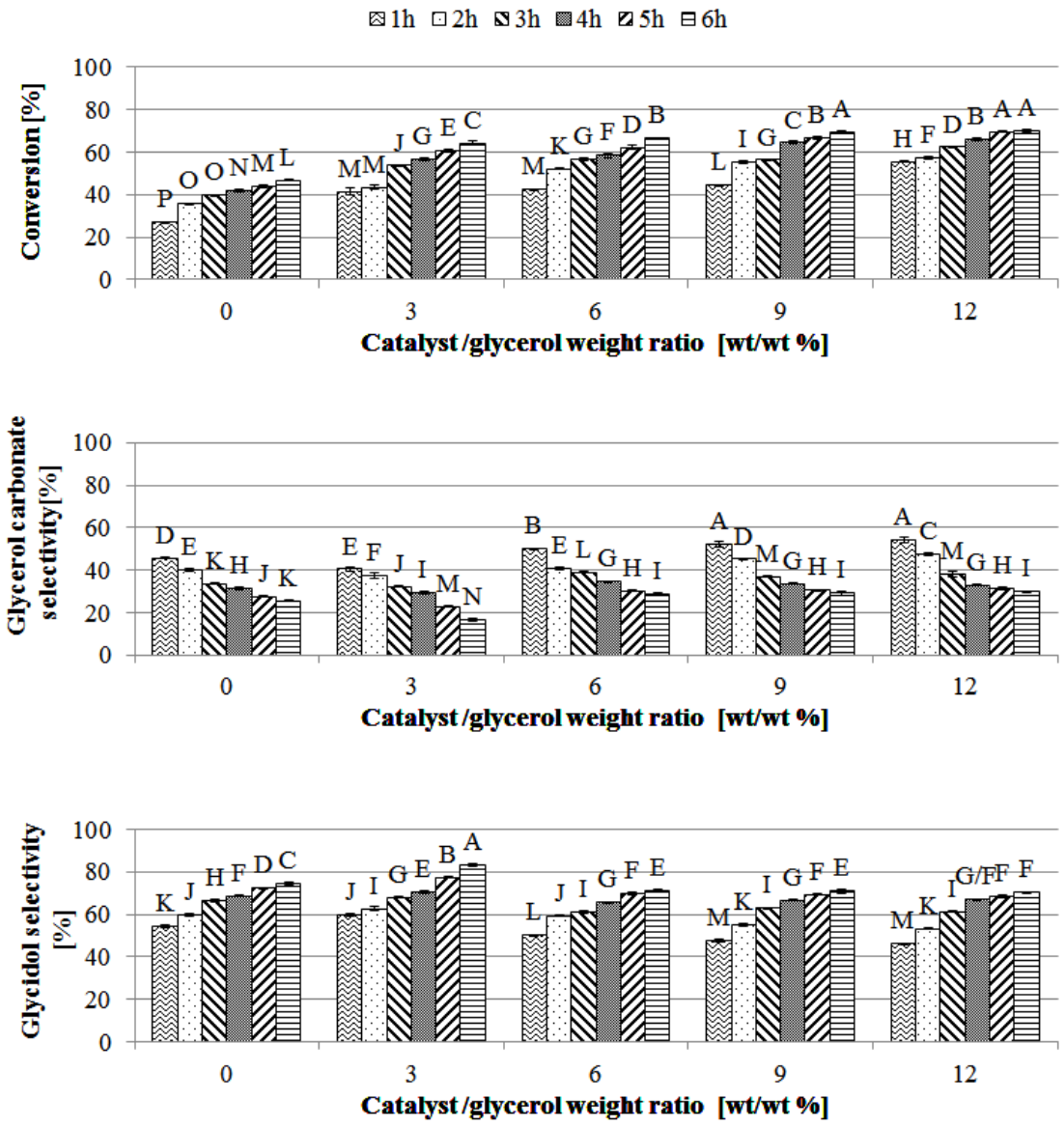

Figure 3. The influence of catalyst loading on the catalytic performance of a biosolids-based catalyst. Reactions were performed at 140 °C, with a 2:1 molar ratio of urea:glycerol, and use of an air stream to promote the forward reaction. For these experiments, different catalyst:glycerol loading ratios (0 wt%, 3 wt%, 6 wt%, 9 wt%, 12 wt%) were examined. The means of triplicate experiments are reported, with the error bars representing standard deviations. Data annotated with different letters are significantly different (confidence level of 95 %).

As reported by Aresta *et al.*[96], the formation of glycerol carbonate is slower than the decarboxylation process, so in the non-catalytic system at 140 °C, carbonates were degraded to glycidol due to the radical-rich environment granted by the heterolytic splitting of urea. Conversely, the catalytic system increased the reaction rate between reactive species formed by radical degradation of urea and glycerol leading to an increase in conversion and an increase in decarboxylation. Thus, considering the glycidol yields (calculated as the conversion multiplied by selectivity), the catalytic system outperformed the non-catalytic one with maximum glycidol yields of 49.7 ± 0.9 % (after 6 h using 9 wt% of catalyst) and 39.0 ± 1.0 % (after 6 h without catalyst), respectively.

2.3. Influence of temperature

Temperature is a key parameter for every catalytic conversion and was shown to have a dramatic effect on urea glycerolysis (Figure 4.). At 100 °C, the maximum conversion achieved after 6 h was 44.2 ± 0.2 %, with a drastic decrease to 13.6 ± 0.9 % for the 1 h reaction. Increasing the temperature to 120 °C improved the conversion rate after 1 h and 2 h, but the conversion values for the remaining reactions (3 h to 6 h) were not significantly different ($p < 0.05$) from those achieved at 100 °C at a given reaction time. A further increase of temperature up to 140 °C drastically improved the conversion of the reaction. After only 1 h at 140 °C, the conversion achieved (44.3 ± 0.2 %) equaled those obtained at 100 °C and 120 °C after 6 h.

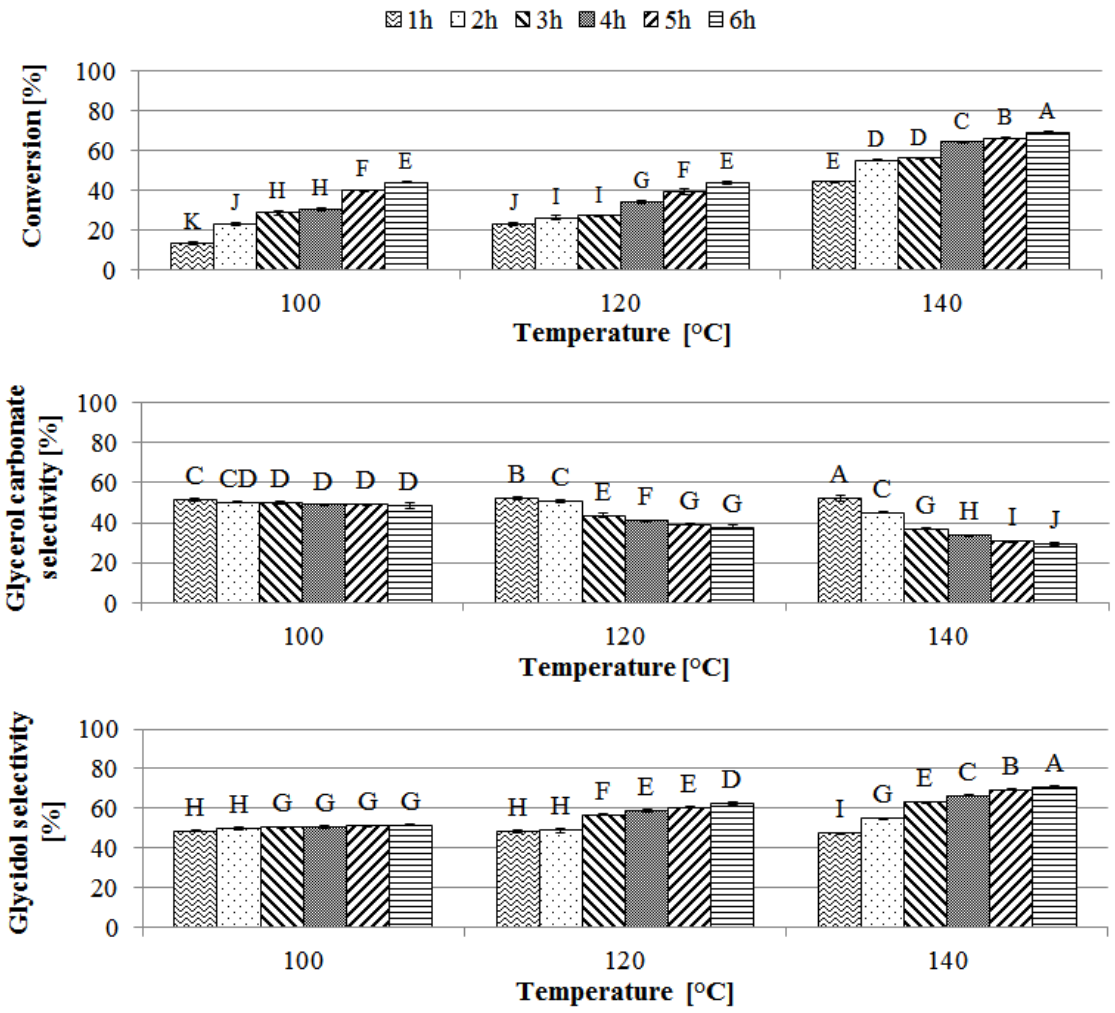

Figure 4. The influence of temperature on the catalytic performance of a biosolids-based catalyst. Reactions were carried out using a catalyst:glycerol ratio of 9 % (wt/wt), a 2:1 molar ratio of urea:glycerol, and an air stream. The conversion and selectivity at three different temperatures were examined: 100 °C, 120 °C, and 140 °C. The errors represent the standard deviations calculated according to the values of three experiments. The means of triplicate experiments are reported, with the error bars representing standard deviation. Data annotated with different letters are significantly different (confidence level of 95 %).

The catalytic system at 100 °C was not selective at any reaction time tested, leading to the formation of an equal amount of glycerol carbonate and glycidol. At 120 °C, moving from 1 h to 6 h increased the selectivity for glycidol from 48.2 ± 0.4 % to 62.7 ± 0.9 %. This trend was clearer at 140 °C with an increase in selectivity from 46.2 ± 0.2 after 1 h to 70.2 ± 0.4 % after 6 h. Decarboxylation of glycerol carbonate to glycidol is due to the synergistic effect of acidic-basic functionalities on the surface of the catalysts and the radical-rich reaction environment promoted by urea splitting[96]. The contribution of urea splitting was magnified with as the temperature was increased to 140 °C, becoming the predominant driving force of the process.

2.4. Influence of the molar ratio of urea/glycerol

The effect of urea/glycerol ratio was also investigated at 140 °C using a catalyst loading of 9 wt% and an air stream to facilitate the removal of NH_3 formed during the reaction (Figure 5). Decreasing the molar ratio of urea/glycerol from 2:1 to 1:1 led to a significant ($p < 0.05$) decrease in conversion values for each time tested, with a maximum conversion of 59.9 ± 1.2 % achieved after 6 h. In addition, a urea/glycerol molar ratio of 1:1 led to a decrease in the maximum glycidol production (down to 65.7 ± 0.9 % after 6 h), caused by the decreased amount of radical species in the reaction environment. These results support the hypothesis that the radical heterolytic splitting of urea played a major role in the process at reaction temperatures greater that 140 °C, promoting the radical reaction pathway instead the non-radical one.

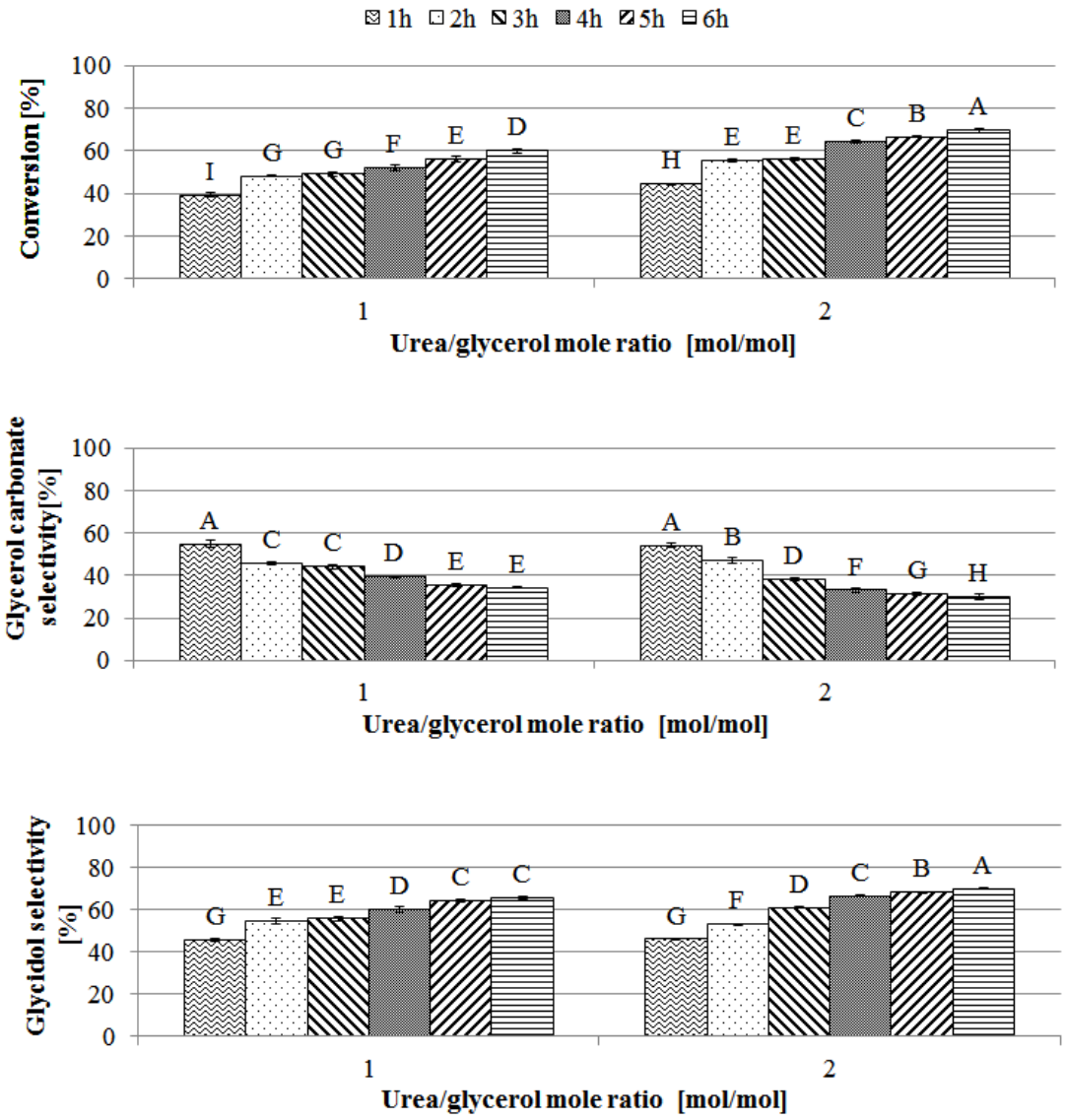

Figure 5. The influence of molar ratio on the catalytic performance of a biosolids-based catalyst. For the reactions shown below, the catalyst:glycerol ratio was maintained at 9 wt% at a reaction temperature of 140 °C and using an air stream. To determine the effect of using different urea:glycerol ratios, two molar ratios were employed: 2:1 and 1:1 (mol/mol). The means of triplicate experiments are reported, with the error bars representing standard deviation. Data annotated with different letters are significantly different (confidence level of 95 %).

2.5. Influence of residual atmosphere

Formation of NH_3 as a byproduct during urea alcoholysis is a considerable issue in terms of both the reaction kinetics and the sustainability of the process. In order to remove NH_3 from the reaction environment, urea glycerolysis could be carried out using reactive distillation procedures[114], reduced pressure[111], or using a stream of air. In order to remove NH_3, three different gas streams (air, N_2, CO_2) were evaluated at 140 °C using a catalyst loading of 9 wt% and a 2:1 molar ratio of urea:glycerol (Figure 6.).

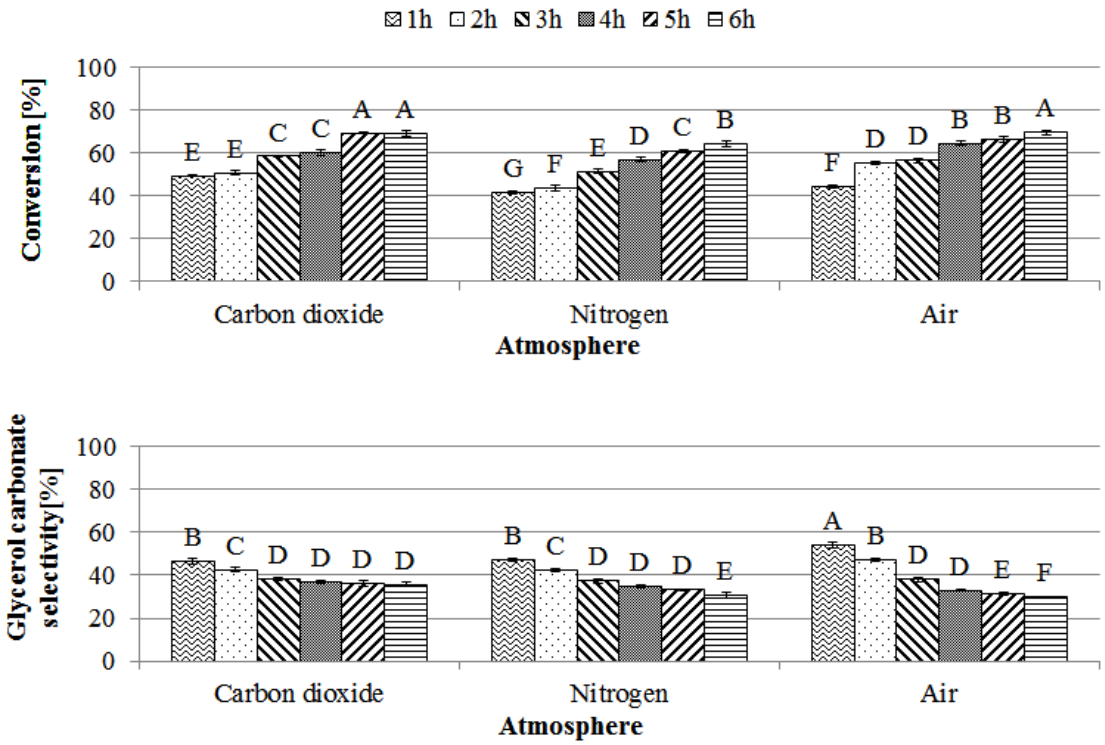

Figure 6. The influence of atmosphere on the catalytic performance of a biosolids-based catalyst. The following reaction conditions were used: a catalyst:glycerol ratio of 9 wt%, a temperature of 140 °C, a 2:1 molar ratio of urea:glycerol, and three different gas streams to remove NH_3 formed during the reaction (air, N_2, CO_2). The errors represent the standard deviations calculated according to the values of three experiments. The means of triplicate experiments are reported, with the error bars representing standard deviation. Data annotated with different letters are significantly different (confidence level of 95 %).

Adopting a N_2 stream in place of the air stream that was used in the experiments describe above did not result in a significant difference in the maximum conversion after 6 h. For the N_2 stream, a significant ($p < 0.05$) increase in conversion values was observed as the reaction time was lengthened from 1 h to 5 h, but no further increase was observed when the reaction time was increased to 6 h. Using CO_2, the conversions were generally lower with a maximum conversion of 64.0 ± 1.2 % achieved after 6 h, which was significantly lower than the values achieved using air or N_2 for an equivalent reaction time. Furthermore, the selectivity of glycidol was lower (35.8 ± 1.2 %) when CO_2 was used as the atmospheric gas, likely because the increase in CO_2 partial pressure decreased the rate of decarboxylation of glycerol carbonate. Based on the results shown, the use of an air stream for the removal of NH_3 is likely preferred given that it had the highest conversion rate and glycidol selectivity, and is the cheapest option as well.

2.6. Influence of recycling on urea glycerolysis on the conversion rate

Next, we examined whether or not the biosolids-based catalyst could be recycled. The activity of the catalyst was monitored after each of four runs, with each reaction conducted at 140 °C for 6 h using a catalyst loading of 9 wt%, a 2:1 molar ratio of urea:glycerol, and a stream of air to remove NH_3 formed during the reaction (Figure 7.). The activity of the biosolids-based catalyst decreased from 69.4 ± 0.9 % for the first run to 56.4 ± 1.3 % for the fourth run. Similarly, the glycidol selectivity dropped from 71.1 ± 0.7 % to 65.6 ± 0.9 %. The decreased catalyst activity was likely attributable to the leaching of metals (Table 1.), caused by the formation of soluble metal species as a consequence of reactions between urea-derived radicals and metal surface sites. In addition, chemical modification of the organic fraction of the biosolids-based material was observed through ATR-FTIR analysis of the recycled catalyst recovered after the fourth catalytic run (Figure 2.). The chemical modifications could be ascribed

to the formation of amino and amido groups (IR bands of $\nu_{\text{-NH}}$ in the range of 3500-3400 cm^{-1} and amido $\nu_{\text{-C=O}}$ in the range of 1800-1700 cm^{-1}) caused by the reaction between the urea-derived radicals species and the aromatic organic matrix.

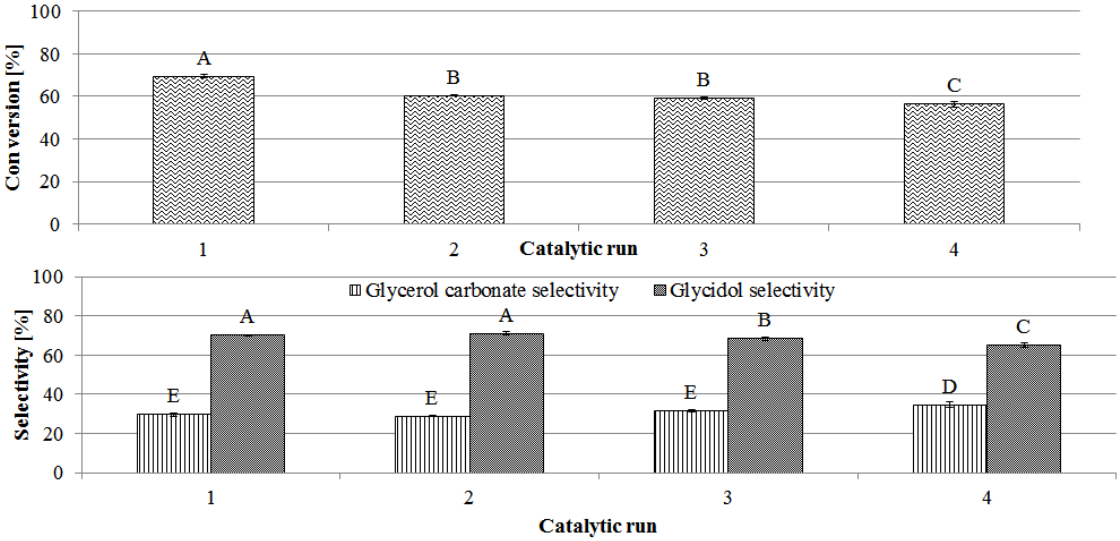

Figure 7. Recyclability of the biosolids-based catalyst during four catalytic runs (catalyst/glycerol 9 wt%, 140 °C, urea/glycerol 2 mol/mol, air stream, 6 h).The errors represent the standard deviations calculated according to the values of three experiments. The means of triplicate experiments are reported, with the error bars representing standard deviation. Data annotated with different letters are significantly different (confidence level of 95 %).

3. Materials and Methods

3.1. Materials

Tetrahydrofuran (HPLC grade, > 99.9 % without stabilizers), methanol (HPLC grade, > 99.9 %), urea (98 %), NaOH (> 99 %), HCl (37 %) and methyl nonadecanoate (used as internal standard for gas chromatography) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Glycerol (98 %) and heptane (> 99 %) were purchased from Fisher Chemical (Fair Lawn, NJ, USA). Gases (Air, CO_2, N_2, H_2, He) were purchased from Praxair Inc. (Edmonton, AB).

3.2. Methods

3.2.1. Catalytic acetylation of glycerol

10 g of glycerol were put into a single-neck round-bottom flask with urea (urea/glycerol molar ratio (mol/mol) of 2 or 1), the biosolids based catalyst (catalyst/glycerol weight ratio (wt/wt) of 12 %, 9 %, 6 %, 3 %, 0 %), which was then connected to a condenser. The reaction mixtures were stirred and heated at different temperatures (100° C, 120 °C, 140 °C) for 6 h with sampling every hour. During the reaction, a stream of air, N_2, or CO_2 was employed to remove NH_3 formed during the process. After 6 h, the reaction mixtures were cooled at room temperature and the catalyst was recovered through centrifugation (7155 × *g* for 10 min), washed with acetone three times (5 mL for each wash), dried overnight at 105 °C, and then analyzed. Each test was replicated three times.

3.2.2. Gas chromatography and mass spectrometry

100 μL of the crude reaction mixture were diluted with 0.5 mL of tetrahydrofuran and 0.5 mL of methanol, with 10 mg of methyl nonadecanoate added as internal standard. The solution

was analyzed using a gas chromatograph (6890N; Agilent Technologies, Fort Worth, TX) equipped with an autosampler (Agilent 7683 series; Agilent Technologies, Fort Worth, TX), a flame ionization detector, and a mass spectrometer (Agilent 5975B inert XL EI/CI MSD; Agilent Technologies, Fort Worth, TX). Analyses were carried out by injecting 1 μL of the samples onto a DB-5 column (100 m x 250 μm x 0.25 μm; Agilent Technologies, Fort Worth, TX) using the gas chromatographic method described above[115]. The concentration of unreacted glycerol was evaluated using a five-point calibration curve ($m = 0.185 \pm 0.02$, $R^2 = 0.994$) obtained using methyl nonadecanoate as the internal standard.

3.2.3. Characterization of inorganic content in the biosolids-based catalyst

The amount of inorganic residue contained in the solid material recovered after thermal hydrolysis of biosolids at 280 °C for 1 h was determined through incineration of 5 g of the sample at 450 °C for 6 h using a 48000 Furnace (Barnstead Thermolyne, Dubuque, Iowa, USA) in accordance with the method developed by Benitez et al.[116]. This test was repeated three times. Compositional analysis of the inorganic content was performed using a Thermo iCAP 6000 series Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES; Thermo Fisher Scientific, Madison, WI, USA) at the Natural Resources Analytical Laboratory (Department of Renewable Resources, University of Alberta).

3.2.4. Quantification of total surface acidic groups

The total surface acidic groups present in the biosolids-based catalyst were determined through titration based on the procedure proposed by Boehm[117]. Briefly, 150 mg of catalyst were put in a plastic tube with 50 mL of 0.05 N NaOH and stirred at room temperature for 24 h.

Afterwards, the mixture was centrifuged at 7155 × *g* for 10 min and the solid was removed. 25 mL of centrifuged solution were then neutralized with a standard solution of 0.05 N HCl. The total surface acidic groups were determine as the difference between the mmol of NaOH 0.05 N before and after the titration, which is equivalent to the mmol of 0.05 N HCl added.

3.2.5. Attenuated total reflection Fourier transform infrared spectroscopy

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) analyses were carried out using a Nicolet iS50 (Thermo Fisher Scientific, Madison, WI, USA) in the range of 4000-600 cm^{-1} with a band of resolution of 2 cm^{-1}. These analyses were performed at the nanoFAB Centre at the University of Alberta.

3.2.6. Statistical Analysis

One-way and Two-way ANOVA tests with a significance level of 0.05 ($p < 0.05$) were carried out using Excel™ software (Microsoft Corp.) and the "Data analysis" plug-in.

4. Conclusions

The solid recovered after hydrolysis of biosolids at 280 °C for 1 h has been successfully employed as a catalyst for urea glycerolysis. It showed a remarkably activity reaching a maximal conversion value of 70.1 ± 0.5 % and a glycidol selectivity of up to 70.8 ± 0.9 %. Temperature had the greatest impact on the conversion and selectivity, and was likely caused by the elevated heterolytic radical splitting of urea that drastically enhanced the reaction efficiency as the temperature was increased. For the same reason, increasing the molar ratio of urea:glycerol to 2:1 showed better performance compared with values obtained using a ratio of 1:1. Increasing

catalyst loading slightly improved the conversion, but did not strongly affect the selectivity. Also, the use of an air or N_2 stream to remove NH_3 formed during the process was shown to more effective than the use of CO_2. The catalyst could be recycled, but a decreased catalytic activity was observed after the fourth catalytic run, though conversion rates were still reasonably high. In future studies, a continuous process (distillation of products and supplemental addition of reagents) will be studied to improve the life of the catalyst. In conclusion, we have proven that the biosolid-based material functions as a reliable catalyst for production of glycidol through urea glycerolysis reaction, providing potential benefits to both the biodiesel industry and wastewater management facilities.

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Appendices B

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Accelerating settling rates of biosolids lagoons through thermal hydrolysis

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Abstract

Although the improved dewaterability and digestibility of primary biosolids subjected to thermal hydrolysis has been studied for decades, there are a surprisingly small number of studies exploring the use of this thermal treatment for digested biosolids that are typically left to settle in large settling lagoons. This is likely because of the high capital and operating costs associated with thermal hydrolysis, coupled with the limited applications and value of the resulting products. However, due to the anticipated increases in the amount of generated biosolids combined with issues surrounding potential environmental release and the limited availability of land for additional lagoons, other biosolids management strategies are being explored. Here, we show that thermal hydrolysis at 280 °C for 1 hour resulted in 78.2 ± 0.8 % settling after 2 hours.

Furthermore, addition of phosphoric acid to lower the pH of the hydrolysate to pH 3 resulted in increased settling rates, but the final volume of unsettled material after 2 hours was statistically similar to the thermally hydrolyzed material without pH adjustment (75.7 ± 2.3 %). Remarkably, when the pH of the digested biosolids was adjusted to 3 prior to thermal hydrolysis, a settling rate of 87.3 ± 1.1 % was observed after just 15 minutes. Significantly, the dewaterability of thermally hydrolyzed biosolids was measured in our experiments through natural settling, without the use of external mechanics. Taken together, the data presented in this paper demonstrate that high temperature thermal hydrolysis is a promising method for accelerating the settling rates of digested biosolids and may represent a viable alternative to building and maintaining biosolids lagoons.

Keywords: Biosolids; sewage sludge; dewaterability; settling; thermal hydrolysis

1. Introduction

Wastewater treatment facilities typically employ an aerobic or anaerobic digestion to breakdown the organic contents within sewage sludge and reduce odor emissions[118, 119]. The digested biosolids can then be transferred to biosolids lagoons to facilitate cheap and low-maintenance dewatering through natural settling of solid materials. As the global population continues to increase towards an estimated 9-10 billion by 2050[120], associated increases in the volume of wastewater produced will place pressure on treatment facilities, particularly those that operate in urban areas where space is limiting. In addition, digested biosolids contain heavy metals, organic molecules, and pathogens that can cause adverse effects if released or spilled into the environment in substantial quantities[121, 122]. Thus, there is an increasing interest to

incorporate novel strategies for biosolids management and disposal that will help mitigate these concerns.

Many pretreatments strategies have been explored that can breakdown complex molecules in the primary sewage sludge into simpler molecules that are more easily metabolized by microorganisms during aerobic or anaerobic digestion. This includes alkaline[123], ultrasonic[124], mechanical[125], and thermal[126, 127] pretreatments. While all of these pretreatment strategies have been shown to improve digestibility of sewage sludge, thermal hydrolysis has already been incorporated into over 30 wastewater treatment facilities around the world, including the Davyhulme plant in Manchester, England, which can process 121,000 tonnes of dry biosolids per year[128].

The operating temperature for thermal hydrolysis that is applied for pretreatment of sewage sludge varies, but is typically in the range of 165-180 °C[128, 129]. The main reason for this is likely that[130] demonstrated that thermally hydrolyzed sludge displayed toxic effects during subsequent digestion when the temperature used for hydrolysis was above 175 °C. Strong *et al.*[131] reported that thermal hydrolysis at 165 °C for 2 hours resulted in a 22 % reduction in volatile suspended solids and a 13 % increase in methane production through subsequent anaerobic digestion, relative to the untreated control sample. Furthermore, Pérez-Elvira *et al.*[132] demonstrated that anaerobic digestion of thermally hydrolyzed sewage sludge (170 °C, 30 minutes) led to a 40 % increase in biogas generation in only 60 % of the time. An advanced thermal hydrolysis (ATH) has also been proposed for pretreatment of sewage sludge that combines thermal hydrolysis and oxidation with hydrogen peroxide[133]. This strategy generally improved dewaterability and solubility of organic matter.

Although there are numerous studies exploring the use of thermal hydrolysis to improve digestibility and dewaterability of primary or activated sludge, few have examined the use of this thermal treatment on digested biosolids that are normally left to settle naturally in biosolids lagoons. Neyens *et al.*[134] examined the use of thermal hydrolysis for treatment of digested biosolids (5-6 % dry solids) and found that at temperatures ranging from 80-155 °C, there were significant improvements in dewaterability. To establish dewaterability, they used two different methods of filtration to assess the amount of dry solid remaining after their hot acid hydrolysis procedure. In this manner, they determined that the amount of solids in hot acid hydrolyzed thickened sludge was about 70 % lower than the untreated control.

As an extension of the work of Neyens *et al.*[134], we examined the thermal hydrolysis of digested biosolids at a temperature regime (280 °C) that was much higher than previous studies, which may promote even faster settling as a result of enhanced hydrolysis of organic material. Furthermore, we chose to assess natural settling rates in order to provide insight into how the biosolids hydrolyzed at high temperatures would settle without additional mechanical intervention that is currently employed, which may help improve the overall process economics. Our results provide proof-of-concept that thermal hydrolysis at 280 °C leads to significant improvements in the natural settling rates of digested biosolids. Thus, thermal hydrolysis of digested biosolids may be a promising treatment strategy for dewatering digested biosolids, particularly if it can be incorporated into high temperature process such as hydrothermal treatments or lipid hydrolysis [135, 136].

2. Materials and Methods

2.1. Biosolids

Digested biosolids (~3.5 % dry solids; pH ≈ 9) were obtained from a biosolids lagoon at a wastewater treatment in Edmonton, Alberta, Canada. Samples were stored at 4 °C prior to their use in experiments. Biosolids were subjected to thermal treatments as is, or after adjustment to pH 3 using phosphoric acid (Fisher Scientific, Fairlawn, NJ). For some experiments, pH adjustment (to pH 3) was performed after thermal treatments.

2.2. Thermal treatments

In the experiments described below, biosolids were treated in an autoclave (Beta Star Life Science Equipment, Honey Brook, PA) at 121 °C and a minimum of 15 psi for 1 hour, or by thermal hydrolysis in a 5.5 L batch reactor (Model 4580, Parr Instrument Company, Moline, Il, USA) at 280 °C for 1 hour at an initial pressure of 100 psi. After autoclaving, the pH of the system remained at ≈ 9. For thermal hydrolysis, the reaction start point was considered to be when the reaction reached the desired temperature. At this point, the pressure stabilized at 1200-1300 psi. Following thermal hydrolysis, the reactor was cooled using a refrigerated circulating bath (Model 89202-986) from VWR (Edmonton, Canada) set to -20 °C, which was shut off once the sample reached room temperature (~22 °C). At this point, the pH of the hydrolysate was in the range of 7 to 8.

2.3. Settling Experiments

Following autoclaving or thermal hydrolysis (and pH adjustments when necessary), the sample was homogenized and then 1 L was transferred to a 1 L glass graduated cylinder. The settling of solid material in biosolids was observed over a 2-hour period, with measurements of

the volume of unsettled material being taken every minute for the first hour, and every 3 minutes for the following hour. All experiments were performed in triplicate.

2.4. Statistical Analysis

Data were subjected to statistical analysis to establish whether or not any differences were statistically significant. Specifically, one or two way-ANOVA with mean comparison by Tukey test (GraphPad Prism 6 software, La Jolla, CA) was performed at a 95 % confidence level.

3. Results and Discussion

3.1. Biosolids

At waste treatment facilities around the world, storage lagoons contain digested biosolids that are concentrated through settling and evaporation over a period of 1-3 years [137]. The poor settling rate of biosolids, their rising volumes worldwide, the increasingly limited options for lagoon locations, and the safety concerns surrounding potential release of pathogens and metals into the environment, have collectively led to an increased interest in the development of biosolids management strategies.

The large settling lagoons found at many wastewater treatment facilities around the world contain digested material that is relatively viscous (Figure 1A). Digested biosolids displayed poor settling after storage at room temperature for 4 months (Figure 1B). It should be noted that for the experiment shown in Figure 1. and others described below, autoclaving was used as a necessary precaution to eliminate all pathogens in biosolids thereby removing safety concerns surrounding the handling of biosolids in the laboratory. This mild thermal treatment is commonly

employed in the laboratory and is not believed to have a substantial impact in the qualities and characteristic of the material.

A) **B)**

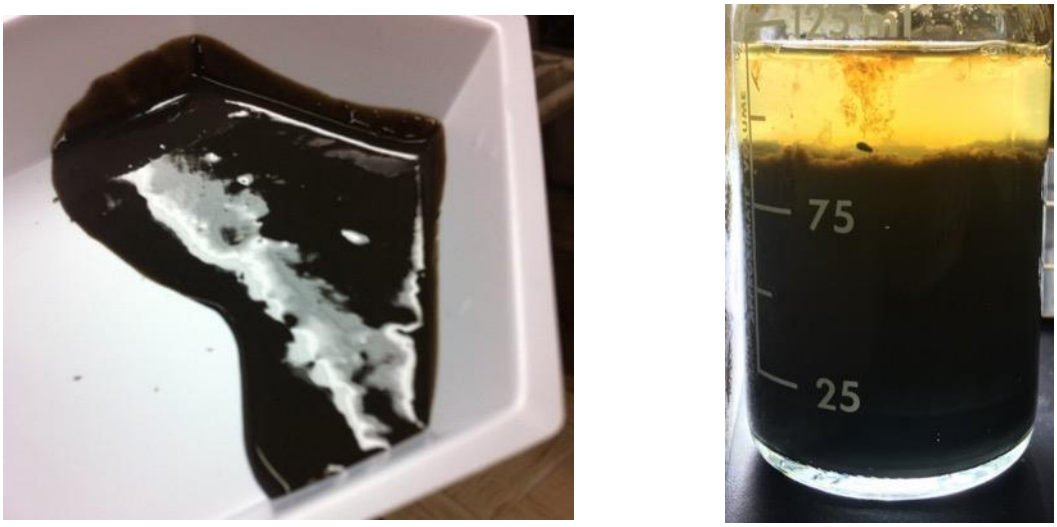


Figure 1. Images of digested biosolids acquired from a wastewater treatment facility in Edmonton, Alberta, Canada. To facilitate safe handling of the material, biosolids were subjected to autoclaving at 121 °C and a minimum of 15 psi for 1 hour. The resulting material is shown in A. The poor settling rate of digested biosolids is demonstrated in B, which shows the amount of settling observed after the autoclaved material was placed in a sealed bottle and left undisturbed for 4-months.

3.2. Thermal Hydrolysis of Biosolids

To explore whether or not a thermal hydrolysis treatment at 280 °C would improve settling rates of biosolids, we monitored natural settling in 1 L graduated cylinders over a period of 2 hours. A temperature of 280 °C was chosen for these experiments as this temperature was used in previous studies involving hydrothermal treatment of algal material or lipid hydrolysis, two processes into which biosolids could potentially be applied[135, 136]. Compared to the autoclaved sample where no settling was observed during the 2-hour period, the hydrolyzed sample displayed remarkably better settling, with 48.0 ± 6.2 % and 78.2 ± 0.8 % settling after 0.5 and 2 hours, respectively (Table 1.; Figures 2. and 3.). From these data, it is clear that thermal hydrolysis at 280 °C is an effective treatment to promote settling of digested biosolids. The impact of pH adjustment (Systems 2, 4, and 5) will be discussed in Section 3.3.

System	Settling (%)					
	0 min	**15 min**	**30 min**	**60 min**	**90 min**	**120 min**
1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
2	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0
3	0.0 ± 0.0	27.0 ± 4.4	48.0 ± 6.2	70.0 ± 3.5	76.2 ± 0.8	78.2 ± 0.8
4	0.0 ± 0.0	40.7 ± 7.1	62.8 ± 4.4	71.0 ± 1.0	74.5 ± 1.8	75.7 ± 2.3
5	0.0 ± 0.0	87.3 ± 1.1	88.5 ± 0.3	88.7 ± 0.3	88.7 ± 0.3	88.7 ± 0.3

Table 1. Settling rates of the 5 different biosolids systems at various time points. Systems: 1) Autoclaved; 2) Autoclaved with pH adjustment after; 3) Hydrolyzed; 4) Hydrolyzed with pH adjustment after; 5) Hydrolyzed with pH adjustment before.

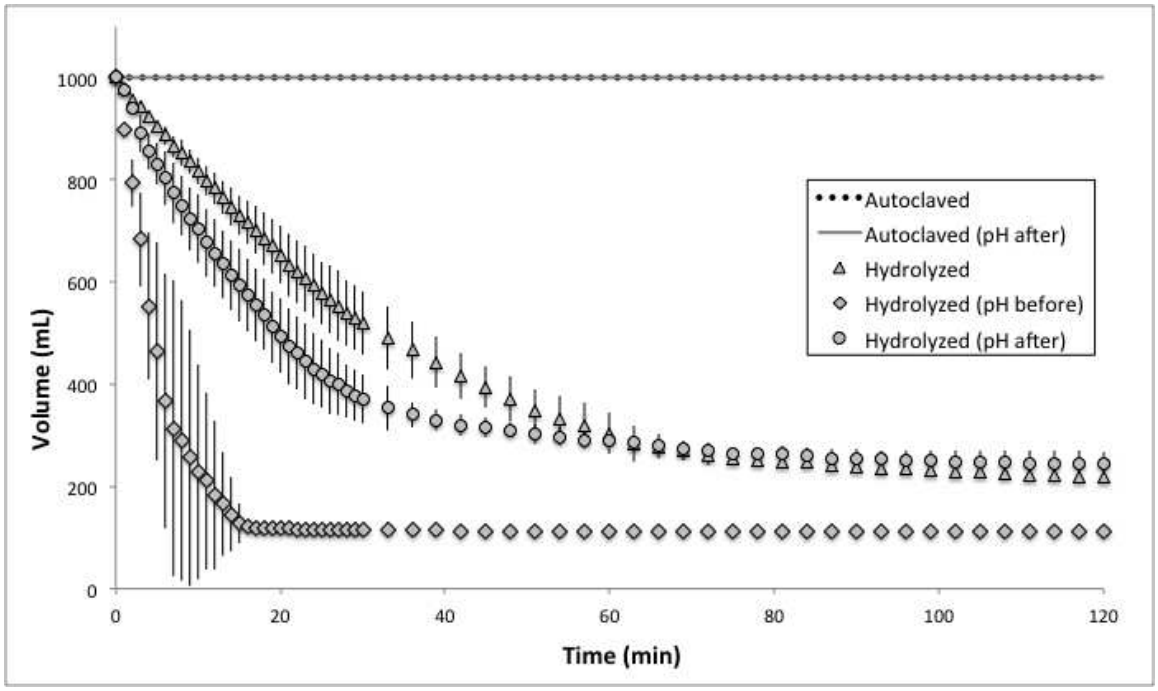
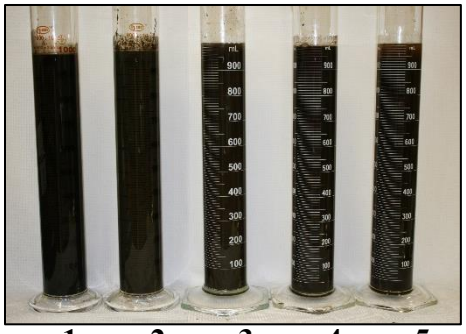


Figure 2. Settling of biosolids over time. Biosolids subjected to 5 different treatment strategies were homogenized and then placed in 1 L graduated cylinders. The indicated volumes represent the amount of unsettled material. Autoclaved samples were treated at 121 °C and a minimum of 15 psi for 1 hour. Hydrolyzed samples were treated at 280 °C for 1 hour and an initial pressure of 100 psi. When indicated, the pH of biosolids was adjusted to pH 3 using phosphoric acid, either before or after thermal treatment.

A)

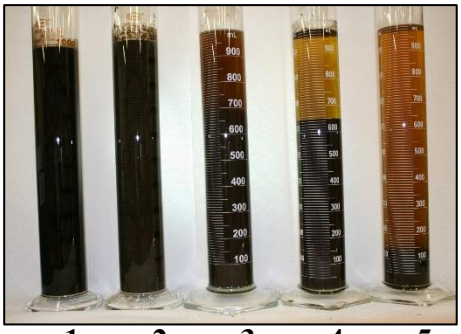
0 min



1 2 3 4 5

B)

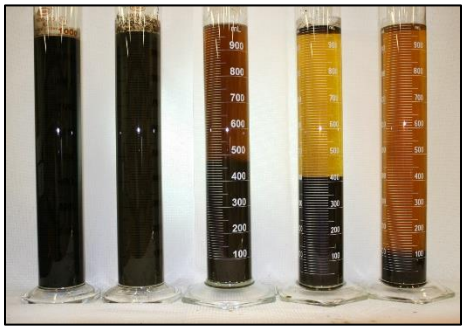
15 min



1 2 3 4 5

C)

30 min



1 2 3 4 5

D)

60 min

1 2 3 4 5

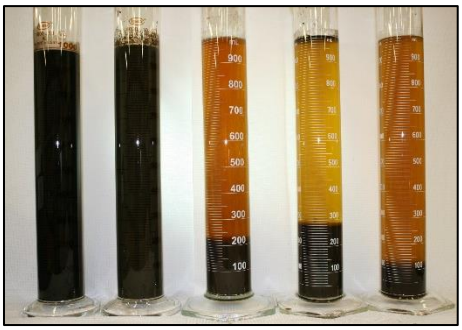
E)

90 min

1 2 3 4 5

F)

120 min



1 2 3 4 5

Figure 3. Settling experiments. Photos were taken at 0 (A), 15 (B), 30 (C), 60 (D), 90 (E), and 120 min (F) to illustrate settling rates. The 5 treatment systems were: 1) Autoclaved; 2) Autoclaved with pH adjustment after; 3) Hydrolyzed; 4) Hydrolyzed with pH adjustment after; 5) Hydrolyzed with pH adjustment before. Although the experiment was performed in triplicate, only one set of photos is being displayed.

Feng *et al.*[138] studied the rheological behavior of raw municipal sludge and observed that after thermal treatment, the mixture displayed properties more consistent with a Newtonian fluid than the untreated sample. They reasoned that after the 1-hour thermal treatment at 170 °C, organic materials contained in the biosolids were denatured, causing them to precipitate. Furthermore, the enhanced degradability of thermally hydrolyzed sludge has been attributed to breakdown of large molecules[129]. It is likely that both of these factors contributed to the increased settling rates observed when digested biosolids were subjected to thermal hydrolysis.

It should be noted that while our studies focused on the settling rate of solid particles in biosolids with or without thermal hydrolysis, there are other indicators that could be used to further define optimal biosolid treatment conditions. For instance, when examining the efficacy of different materials in chemically assisted primary sedimentation (CAPS) of raw wastewater, De Feo *et al.*[139] examined chemical oxygen demand and turbidity along with sedimentation ability. Although outside of the scope of this study, it would be interesting to monitor the chemical oxygen demand and turbidity of the solution released following thermal hydrolysis at varying conditions (i.e. temperature and/or time).

While thermal hydrolysis at 280 °C may be associated with elevated operating costs, it may be possible to incorporate the digested biosolids into other processing platforms that employ high temperature treatments, such as hydrothermal liquefaction and lipid hydrolysis. In this way, it may be possible to valorize this waste stream and eliminate the need for biosolids lagoons or other dewatering strategies, particularly since many wastewater treatment facilities already possess infrastructure and expertise relating to thermal hydrolysis[128]. Furthermore, some jurisdictions may require biosolids management strategies that can handle the increasing volumes of biosolids anticipated in the future and thus may be forced to incur high capital and

operating costs. The data presented here may advocate for the incorporation of thermal hydrolysis for management of digested biosolids.

3.3. Effect of pH on Biosolids Settling

One characteristic that has been shown to improve dewatering of activated sludge is pH. Chen *et al.*[140] demonstrated that addition of sulfuric acid to activated sludge resulted in improved centrifugal dewatering as the pH was dropped from 7 to 1.5. To examine whether lowering the pH could improve settling rates of digested biosolids before or after thermal treatment, phosphoric acid was added to bring the pH of biosolids to 3. When the pH of autoclaved biosolids was adjusted to pH 3, no settling was observed during the 2-hour period, which was identical to what was observed for the autoclaved samples without pH adjustment (Figures 2. and 3.). Conversely, when the pH of hydrolyzed biosolids was adjusted to pH 3 after the thermal treatment, the initial rate of settling improved significantly compared to the untreated hydrolyzed sample. Interestingly, although the hydrolysates subjected to pH adjustment after thermal treatment reached its minimum settling volume in a shorter timeframe than the untreated hydrolysates, after 48 minutes, there was no significant difference in settling rates between the two systems at a given time point for the remainder of the 2-hour experiment. Taken together, this implies that lowering the pH of digested biosolids to 3 after thermal hydrolysis increases the rate of settling, but does not improve the final settling volume.

Lowering the pH prior to thermal hydrolysis resulted in the highest settling rates, with the lowest volume of unsettled material observed (Figures 2. and 3.; Table 1.). Strikingly, while the maximum settling of biosolids adjusted to pH 3 after thermal treatment occurred at roughly 30 minutes, biosolids subjected to pH adjustment prior to thermal hydrolysis displayed 87.3 ± 1.1 %

settling in only 15 minutes, reaching a maximum settling of 88.7 ± 0.3 % at 60 minutes (Table 1). To further illustrate the differences in settling rates, photos of the five systems at various time points (0, 15, 30, 60, 90, 120 min) are shown in Figure 3..

One possible explanation for the effect of lowering pH on settling rates of biosolids is that the acid removes molecules from the surface of particles, enabling them to aggregate more efficiently[140, 141]. As evidence, Chen *et al.*[140]. showed that by treating activated sludge with sulphuric acid, the concentrations of polysaccharides and protein in the liquid fraction recovered after filtering were significantly higher. Acids have long been known to function as a catalyst for hydrolysis of a wide variety of organic molecules, and in a temperature dependent manner[142]. The addition of acid is also believed to result in lysis of microbes in the biosolids, allowing better accessibility of cell contents[134]. All of these factors likely contributed to the improved settling of digested biosolids when acid was added either before, or after thermal hydrolysis. When acid is added before thermal hydrolysis, the high temperature promotes higher reaction rates, resulting in enhanced degradation and hydrolysis of organic materials. In the future, one interesting possibility would be to explore using other acids, including organic acids, to adjust the pH of biosolids prior to thermal hydrolysis as this may generate solid and liquid streams more amenable to downstream valorization processes.

4. Conclusion

The data presented above demonstrate that thermal hydrolysis of digested biosolids at high temperature (280 °C) serves as an extremely effective method to improve settling rates. While higher temperatures for hydrolysis of biosolids has typically been avoided due to high operating costs as well as the formation of toxic compounds that inhibit subsequent digestion, the research presented demonstrates the effectiveness of using high temperature thermal hydrolysis

to dramatically improve settling rates. Through acidification and subsequent thermal hydrolysis of digested biosolids, a settling rate of approximately 88 % was observed after only 15 minutes of natural settling. Thus, thermal hydrolysis of digested biosolids may serve as an invaluable biosolids management protocol that could eliminate the need for biosolids lagoons. Future work will focus on the valorization of the liquid and solid streams generated through thermal hydrolysis of digested biosolids, as well as the incorporation of digested biosolids into existing high temperature processing platforms.

Conflict of interest

The authors confirm that there are no conflicts of interest to declare.

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