Valorization of rendering industry wastes and co-products for industrial chemicals, materials and energy: review

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Abstract
Over the past decades, strong global demand for industrial chemicals, raw materials and energy has been driven by rapid industrialization and population growth across the world. In this context, long-term environmental sustainability demands the development of sustainable strategies of resource utilization. The agricultural sector is a major source of underutilized or low-value streams that accompany the production of food and other biomass commodities. Animal agriculture in particular constitutes a substantial portion of the overall agricultural sector, with wastes being generated along the supply chain of slaughtering, handling, catering and rendering. The recent emergence of bovine spongiform encephalopathy (BSE) resulted in the elimination of most of the traditional uses of rendered animal meals such as blood meal, meat and bone meal (MBM) as animal feed with significant economic losses for the entire sector. The focus of this review is on the valorization progress achieved on converting protein feedstock into bio-based plastics, flocculants, surfactants and adhesives. The utilization of other rendering streams such as fat and ash rich biomass for the production of renewable fuels, solvents, drop-in chemicals, minerals and fertilizers is also critically reviewed.

Keywords
Biomass, chemicals and materials, rendering, slaughterhouse, valorization

Introduction
The modern industrial system is built on large-scale utilization of non-renewable hydrocarbon feedstock. In order to address pressing economic and environmental concerns, significant research efforts are underway to develop technology platforms that enable chemical building blocks compatible with the present hydrocarbon infrastructure using feedstock from renewable and low-value or waste streams. The conversion and utilization of non-edible agricultural feedstock, agricultural by-product and waste streams is a centerpiece in this strategy owing to its abundance and relatively widespread geographical accessibility (Ruiz et al., 2013). Animal agriculture constitutes a substantial portion of the overall agricultural sector, with a significant quantity of non-utilized and underutilized by-products that has direct impact on the profitability of the sector not only in the form of loss of revenue but also due to added cost of disposal.

Animal livestock operators report that 40–60% of the weight of livestock (including poultry) is not consumed by humans (Meeker & Hamilton, 2006). These non-edible portions of slaughtered animals are collected and processed by the rendering industry to recover hide and skin, fats and oils and protein rich meals. In 2013, the North American rendering industry recycled approximately 27.8 million tonnes of perishable material generated by the beef, swine and poultry processing facilities, food processing, supermarkets and restaurants (National Renderers Association, 2013). While a significant portion of the fat fraction is absorbed by the oleochemical industry for the production of cosmetics, feed additives, industrial commodity chemicals, pharmaceuticals and more recently for biofuel production (Mekonnen et al., 0000; National Renderers Association, 2013), the protein stream finds only limited and low-value market applications. Rendered protein meals such as blood meal, meat meal, meat and bone meal (MBM) and feather meal are used as ingredients for pet food, aquaculture, poultry and the livestock feed industry (Figure 1).

The rendering industry is crucial as it is closely intertwined with the livestock sector, the environment and public health. It is important to emphasize that without rendering processes, a serious disposal crisis from slaughterhouse, farms, food processors, and restaurants – would occur that could challenge environmental and public health (Meeker & Hamilton, 2006; Nutsch & Kastner, 2010). Currently, dry rendering is the most common rendering process that uses physical, thermal and chemical systems to convert waste animal products, by-products and mortalities into usable proteins and fats (Figure 1). While the current rendering process has shown to destroy food-borne pathogenic micro-organism laden raw materials, including Clostridium perfringens, Listeria monocytogenes, Campylobacter jejuni and
Salmonella species (Troutt et al., 2001), it does not inactivate prion proteins that are known to cause transmissible spongiform encephalopathies (Meeker & Hamilton, 2006).

The emergence of bovine spongiform encephalopathy (BSE) in the 1980s in England and later in the European Union (EU), Japan, North America and other countries changed the whole paradigm of rendering for product utilization. While the use of animal meal (such as blood meal and meat and bone meal) has since been limited to only non-ruminant animals in Canada and the US, the EU has banned it from all animals including fish apart from pets and fur animals (EU, 2013). Certain cattle tissues, known as Specified Risk Materials (SRM), are completely banned from use as animal feed, pet food or fertilizer applications in many countries that employ SRM control. These tissues are also effectively categorized as hazardous waste because they are the highest-risk tissues to contain BSE causing misfolded proteins, known as prions. As a result of the implementation of these provisions, significant quantities of slaughterhouse wastes and the rendering industry lost their economic value. This review addresses current research progress achieved with regard to valorization of these animal co-products for bio-based industrial applications.

BSE emergence and its economic impact

The case of Canada and the US

In 1997, Canada adopted a feed ban that prohibited proteins derived from most mammals from being fed to ruminant animals (such as cattle, sheep, goats, deer, elk bison, etc.) acting on the recommendations of the World Health Organization. Following the discovery of the first BSE positive cow in 2003, Canada defined high-risk tissues known as SRM, and excluded them from the human food chain, and from being fed to ruminants but not to other species (CFIA, 2013). In 2007, the Canadian Food Inspection Agency (CFIA) implemented an enhanced feed ban that eliminates SRMs not only from ruminant and human food chain, but also from all animal feed, pet foods and fertilizer applications (CFIA, 2012). SRM tissues are believed to be the highest risk material to contain the misfolded, disease causing proteins known as prions (PrPSc) in animals. These tissues include the skull, brain, trigeminal ganglia, eyes, spinal cord, and dorsal root ganglia from cattle over 30 months of age and the distal ileum and tonsils from cattle of all ages. Cellular prions (PrPC) are present in all cells of the body, with a high concentration in the brain. Consequently, the BSE causing misfolded prions (PrPSc) predominantly concentrate in tissues associated with the nervous system.

After the 2003 BSE outbreak in Canada, the US government banned imports of Canadian beef to minimize the risks to the US beef industry. Moreover, the US placed Canada under its BSE restriction guidelines and stopped accepting any ruminants or ruminant products from Canada (Jin et al., 2012). Prior to 2003, more than 18% of all live cattle export, and 32% of all beef slaughtered within Canada, was exported to the United States (Sumner et al., 2006). For example, Canada exported more than 47% of its beef production to the world market in 2002, however that entire export opportunity was closed in 2003 (Mathews et al., 2013). The disruption of these exports caused severe repercussions to the country’s livestock sector. Prior to 2003, prices for cattle in Canada and the US were closely aligned. The crisis however resulted in price collapse in Canada and a price rise to a record high in the US (Jin et al., 2012; Mathews, 2013; Sumner et al., 2006). Canadian beef producers gained some relief as the US partially lifted its ban in August 2003, by allowing imports of boneless beef from Canadian cattle slaughtered less than 30 months of age.

In response to the discovery of BSE in 2003, Canadian renderers restructured their facilities to be species specific by segregating handling of ruminant and non-ruminant in separate plants (Koch, 2013). In order to comply with the enhanced feed ban of the 2007, a second restructuring involving the construction of entirely separate infrastructures, including dedicated SRM lines, was implemented. Furthermore, the dedicated line processed SRM has to be separately stored, and trucked to a government-permitted landfill (CFIA, 2012).

The most common method of handling SRM in Canada remains rendering in order to recover lipids while the remaining fractions are land filled. Currently, over three hundred thousand tonnes of such rendered SRM, previously sold as meat and bone meal, are disposed of to the landfill annually or incinerated, posing economic challenges to the rendering industry with repercussions to the whole livestock industry. These challenges include costs attributed to segregation of SRM from non-SRM animal tissues, segregation of processing lines to handle SRM and non-SRM tissues, and costs associated with SRM storage, transporting and disposal fees. The cost of producing tallow for feed has also increased as a result of the regulatory requirement that bans the feeding of ruminant fats containing more than 0.15 percent of insoluble impurities, since most tallow now has to be polished.
to achieve the standard set by the regulation (CFIA, 2012). The non-SRM meat and bone meal, and blood meal are still allowed to be fed to non-ruminant animals such as hogs, poultry, etc. (Table 1). However, only Philippines and Indonesia are the existing export market destinations for Canadian meat and bone meal beside domestic consumption.

Similar to Canada, the US also banned feeding mammalian tissue to ruminants in 1997. In response to the discovery of the first BSE infected cow in Washington state of the US, beef importers, notably Japan, Korea and Mexico began importing from alternative supplies that curtailed beef and cattle exports from the US that resulted in drop-off of economic prices for cattle and beef (Mathews et al., 2013). These resulted in new regulations to enhance protection against the spread of BSE and to reassure consumers that beef was safe to consume (Dewell et al., 2008). These regulations include the listing of SRM tissues and banning these tissues from human and animal consumption. Canada (CFIA, 2012) and the US (DHHS-FDA, 2008) enlisted similar high-risk tissues (SRM).

The current status of the utilization of animal meals as feed, food and fertilizer in Canada and the US is shown in Table 1. While by-products such as meat and bone meal and blood meal are still an important segment of income for the meatpackers, renderers, and the overall livestock industry, significant value was lost by the disposal of SRM that used to be sold as meat and bone meal. Furthermore, the reduced export demand for the rendered products, price decline as a result of its restriction and cost incurred for SRM disposal were an added burden to the industry.

The case of European countries

The recognized association between BSE and feeding of ruminant derived meat and bone meal (MBM) to cattle led to the introduction of the 1988 UK ban on feeding ruminant-derived proteins to ruminants (Wilesmith et al., 1988). The UK also introduced a complete ban of other high-risk bovine tissues, such as the brain and spinal cord from human food, and from entering rendering facilities that still produce MBM for consumption by non-ruminants (Taylor & Woodgate, 2003). The 1992 downturn of BSE incidence in the UK (World organization for animal health, 2013) is an implication of the effect of the feed ban in 1988. The reason for the delay could be because of the possibility of BSE exposure at calf hood and the average age at which cattle display clinical signs of BSE that is around five years (Taylor & Woodgate, 2003).

Additionally, the UK in 1995, and the European Union in 2001, banned the use of all processed mammalian protein in fertilizers and feeds for farmed animals (Wells, 2011). The European Union’s ban includes the prohibition of feeding these mammalian proteins to non-ruminants such as chicken and hogs. Similar hazardous SRM tissues that are completely removed from the food chain of animals and fertilizer applications in North America are also completely removed across the European Union. Moreover, the use of mechanically recovered meat from all ruminant bones was also banned in 2001 (Food Safety Agency, 2013). From 1996 to 2005, the UK implemented a ban that eliminated the use of cattle older than thirty months for human consumption (Food Safety Agency, 2013). This regulation turned European rendering industry into not much more than a waste disposal industry.

Though the BSE outbreak involved relatively small numbers of livestock outside the European landmass, policy and regulatory implementation has still resulted in large changes in protein feedstuff markets. The changes on the use of rendering products and by-products occurred even in countries with no confirmed cases of BSE, as every country imposed regulations to prevent the spread of the disease (Mathews, 2013). This caused a far-reaching impact to consumers, rising environmental costs associated with disposal of hazardous materials, loss of value for the rendering industry, including a decline in value of meat and bone meal; and costs of supply disruptions and substitutions within the feed market sector (Mathews, 2013). These created a strong demand for technological solutions to valorize the animal co-product biomass into non-food/feed value added applications.

### Valorization of animal processing co-products and wastes

Animal co-products are composed of three principal ingredients: proteins, lipids and ashes in varying quantities. The perishability and inherent variability of the ingredients in each stream represents a major challenge for direct processing of such materials into valuable products. Rendering industries produce low moisture content products (less perishable) that are protein and ash rich co-products and waste biomass (such as blood meal, meat and bone meal, feather meal and SRM) and lipid rich biomass including fat and grease. With regard to rendered SRM waste there are four government approved methods of disposal in Canada (CFIA, 2012) and the US (DHHS-FDA, 2008): alkaline hydrolysis, thermal hydrolysis, incineration and landfilling at designated sites. However, rendering of SRM to recover fats and landfilling the remaining fractions is by far the most common SRM disposal method in North America (Mekonnen et al., 2013b) and combustion and incineration in EU countries (Deydier et al., 2005). Valorization of these animal co-products and wastes into high-value products using a biorefinery approach, and the conversion of each main ingredient into products is reviewed in the following sub-sections.

### Protein rich biomass valorization

**Conversion of protein biomass into bio-based plastics**

Plastics are amorphous and semi-crystalline organic polymers covering a wide range of polymerization products suitable for the manufacture of diversified products. Worldwide annual

| Rendered meal       | Ruminants | Non-ruminants | Pets | Fertilizer |
|---------------------|-----------|---------------|------|------------|
| Blood meal (ruminants) | NA        | A             | A    | A          |
| MBM (ruminants)     | NA        | A             | A    | A          |
| Blood meal          | NA        | A             | A    | A          |
| MBM (non-ruminants) | NA        | A             | A    | A          |
| Fish meal           | NA        | A             | A    | A          |
| SRM                 | NA        | NA            | NA   | NA         |

A – Allowed; NA – Not allowed.
plastics production is expected to surpass 300 million tons by 2015 (Halden, 2010) representing trillions of dollars in terms of global economic returns (Reddy et al., 2013). Plastics are highly valued materials that constitute the second largest petroleum application next only to utilization in production of energy-related commodities (Gervet, 2013). The material science community has been striving for decades to generate bio-based plastics to displace or complement synthetic plastics.

The first generation of bio-based polymers developed from renewable feedstock is represented by poly (lactic acid) (PLA), polyhydroxyalkanoates (PHAs), starch plastics, cellulosic esters and protein-based plastics. Other bio-based plastics, such as bio-enriched polyurethane manufactured using modified vegetable oils, polyethylene monomers derived from the dehydration of bio-ethanol that have at least have partial renewable source constitute a set of emerging technologies that are expected to make a significant market impact in the near future (Mekonnen et al., 2013c). The focus of the second generation of bio-based polymers is on developing materials from the efficient utilization of inedible or waste streams or low-value by-products from rendering and slaughterhouses, food processing and agricultural industries (Bier et al., 2012).

In general, the utilization of proteins as a bio-based material feedstock hinges on the rational exploitation of the functional groups associated with the end group of protein chains and the amino acid residues for chemical modification. Moreover, their capability to form a continuous and cohesive matrix received attention for the production of biodegradable plastics films and sheets (Gennadios et al., 1996; Mekonnen et al., 2013c). It is important to mention here that while thermoplastic processing of proteins involves processing above their softening and well below their degradation temperatures with the addition of denaturants and plasticizers, thermoset processing on the other hand involves cross-linking their active functional groups with an external agent, known as cross-linking agent.

A notable example of successful utilization of low-value animal protein is represented by blood meal. Blood meal is non-hazardous with regard to BSE contamination, in addition to its high protein concentration (Verbeek & van den Berg, 2011). The high protein concentration in blood meal helps to avoid the necessity of a costly protein concentrating and isolating efforts, and allowing its direct modification into thermoplastic and thermosetting materials. Blood meal and chicken feathers meals have been successfully converted into thermoplastic and thermosetting materials. Some studies reported direct processing of animal meals (Bier et al., 2013) into protein plastics, others researchers reported (El-Thaher et al., 2013; El-Thaher et al., 2013a,b; Mekonnen et al., 2013b) the use of extracted proteins for the development of protein-based plastics. As shown in Table 2, direct processing of blood meal with 20% plasticizers resulted in a plastic with high-ductility. On the other hand, direct processing of meat and bone meal into plastics with 30% plasticizer exhibited lower elongation. The reason for this observation can be attributed to the physical and chemical characteristics, including the amino acid composition, of the feedstock. Blood meal is composed of about 90% protein (Verbeek & van den Berg, 2011), whereas meat and bone meal is composed of about 50% protein and 35% ash (Lukubira & Ogale, 2013). Ash in meat and bone meal acts as inorganic reinforcing filler making the meat and bone-meal-based plastic a composite with high modulus and low-ductility behavior.

The marked elongation difference observed between 30% propylene glycol and 30% ethylene glycol plasticized chicken feather protein extracts (Table 2), was attributed to the

| Resource                                      | TS (MPa) | Modulus (MPa) | ε (%) | Comment                                      |
|-----------------------------------------------|----------|---------------|-------|----------------------------------------------|
| Blood meal (Bier et al., 2013)                | 5.7      | 251           | 53    | Plasticized with 20% Tri (ethylene glycol)   |
| Meat and bone meal (Lukubira & Ogale, 2013)   | 3.96     | 341           | 2.1   | Plasticized with 30% glycerol                |
| Chicken feathers protein extract (Ullah & Wu, 2013) | 22.3     | 811.2         | 7.6   | Plasticized with 30% propylene glycol        |
| Chicken feathers protein extract (Ullah & Wu, 2013) | 17.8     | 354           | 43.8  | Plasticized with 30% ethylene glycol         |
| Feather quill protein extract (Ullah et al., 2011) | 20.5     | 529.5         | 11.2  | Plasticized with 30% propylene glycol        |
| SRM hydrolyzate protein extract (Mekonnen et al., 2013b) | 58.56    | 1463          | 4.34  | Used as epoxy crosslinker (30%)              |
| Native chicken feather (Jin et al., 2011b)     | 55.7     | 4400          | 14.2  | Grafted with methyl acrylate, no plasticizer |
| Native chicken feather (Jin et al., 2011b)     | 206.3    | 28,800        | 1.1   | Grafted with methyl acrylate, no plasticizer |

TS – Tensile strength at break; ε – elongation at break.
plasticization efficiency (Ullah & Wu, 2013). Dynamic mechanical analysis (DMA) and Fourier transform infrared spectroscopy (FTIR) studies (Ullah et al., 2011) exhibited that ethylene glycol, being a smaller molecule, has higher ability to reduce polymer-polymer associations and interact with the protein polypeptide chains through hydrogen bonds compared to propylene glycol.

Thermosetting protein-based plastics developed from crosslinking of hydrolyzed SRM protein extracts with epoxy resin exhibited a different set of mechanical performance compared to the thermoplastic proteins. Such materials are characterized by high tensile moduli, intermediate tensile strengths and relatively low elongations at break (Table 2) (Mekonnen et al., 2013b) similarly to synthetic thermosetting plastics (Hanoosh & Abdelrazaq, 2009). Potential applications of these SRM-based plastic materials include adhesives, matrix of composites and biocomposites, concrete and flooring (El-Thaher et al., 2013b; Mekonnen et al., 2013b; Mekonnen et al., 2013a).

A major limitation to the industrial deployment of protein-based plastics, with the notable exception of keratin, is their sensitivity towards humidity (Zheng et al., 2003). For example, Zheng et al. (Zheng et al., 2003) reported that soy protein sheets submerged in water for 20 h absorbed moisture up to 180% of their initial weight. The presence of hydrophilic protein functional groups, including –NH₂, –NH, –OH, –SH is the molecular driver for this phenomenon. A possible solution to this problem could be the formation of covalent bond bridges between proteins hydrophilic moieties to form a thermoset using a crosslinking agent. For example, the crosslinking of hydrolyzed SRM protein extract with glutaraldehyde resulted in only 5–10% weight loss of the resulting bio-based plastic under 24 h water soaking (El-Thaher et al., 2013a).

SRM protein hydrolysate extracts are very soluble in water (Mekonnen et al., 2013d). However, SRM hydrolysates crosslinked with epoxy resins, compounds with epoxide functional groups capable of forming covalent bridge between amine (primary and secondary), hydroxyl, carboxyl, and sulphydryl groups (El-Thaher et al., 2013b; Mekonnen et al., 2013b) are virtually insoluble in water. Figure 2 shows the moisture resistance of SRM-based plastics. This is on the same order of magnitude to other commercial epoxy polymers cured with diamines (Bellenger et al., 1989). The observed variations in water resistance of these plastics were due to variation in crosslinking efficiency as influenced by the molecular dynamics of the hydrolyzed protein in epoxy resin.

Another strategy pursued to develop thermoplastic materials using animal proteins is the graft polymerization of proteins with synthetic polymers. This approach keeps the advantage of proteins and the grafted synthetic polymers to generate hybrid materials.

Conversion of protein biomass into industrial flocculants

Another emerging industrial application of animal waste proteins is as feedstock for the production of coagulants and flocculants for waste-water treatment. Flocculation is the process of addition of chemicals to promote the separation of colloidal solid-liquid suspensions through-particle aggregation (Singh et al., 2003). Coagulants destabilize colloidal suspensions that were formed as a result of electrostatic repulsion between negative charge carrying particles. Flocculation processes are among the most widely used techniques for water and industrial wastewater treatment, sludge dewatering, oil recovery and de-emulsification. The use of flocculants could also be further extended to applications in soil erosion control and soil conditioning in agriculture and construction (Sojka et al., 2007), oil recovery and de-emulsification (Feng et al., 2010), water and waste-water treatment (Deng et al., 2006), paper manufacture (Xiong et al., 2010), concentration during chemical operations such as flotation (Feng et al., 2010; Xiong et al., 2010), dewatering and thickening in mineral processing (Svarovsky, 2000) etc. Common synthetic polymers used as flocculants include polyacrylamide, polyacrylic acid, poly (styrene sulfonic acid), poly (diallyl dimethyl ammonium chloride) (Brostow et al., 2009; Deng et al., 2006; Sharma et al., 2006).

While synthetic flocculant polymers can be effective at very low dosage, the resulting flocs are typically unstable under shear, limiting their range of applications. Additional challenges are posed by unsatisfactory chemical stability of some of these synthetic polymers and by the demonstrated toxicity of their monomers to aquatic life forms. These factors...
have driven the development of non-toxic biomass-based flocculant systems such as starch, guar gum, chitosan, cellulose, alginate, glycogen, dextran etc. (Brostow et al., 2009; Ghori et al., 2012; Ghori et al., 2013).

A key driver in the utilization of proteins as feedstock for flocculants is their high-solubility in aqueous medium and their polyampholite nature combined with the functional groups of the composing amino acids and. The flocculating activity of proteins, similar to synthetic polymer flocculation, could take place through a variety of mechanisms, including electrostatic patch flocculation and bridging (Hjorth & Jorgensen, 2012). The potential of proteins as renewable flocculants through various modification techniques is a rapidly growing area of research. Bioflocculants from soy protein (Liu et al., 2012), egg albumin (Maruyama et al., 2009) and milk casein (Seki et al., 2004) modified by methylation has been reported as efficient flocculant for wastewater treatment. While these systems have been demonstrated in the laboratory, concerns over the utilization of high-value edible proteins in industrial applications are likely to persist and discourage the implementation of these systems on a large scale.

The flocculation potential of meat and bone meal extract and gelatin (Piazza & Garcia, 2010a), chicken blood extract (Piazza et al., 2011), bovine blood extract (Piazza et al., 2012), hydrolyzed meat and bone meal extract (Piazza & Garcia, 2010b; Piazza & Garcia, 2013) has been investigated and reported in the literature. Similar to other renewable feedstocks, modification of protein is essential to enhance its flocculation capability. Most of the reported modification techniques involve charge modification either by varying the pH of the aqueous solution or by capping some functional groups of the protein. The other protein modification technique is grafting of the protein with other synthetic polymers.

The protein charge modification by either varying the pH of the solution or capping the functional groups is to provide the protein net positive charges that would result in binding of the mostly negative charged colloidal particles (such as clay, diatomite, etc.) through electrostatic interactions (Laird, 1997). Since protein molecules achieve a net positive charge below their isoelectric point, acidification of the solution below their isoelectric point provides the desired flocculation activity. The use of divalent cations that could serve as a bridge between the protein and colloidal particles are also reported to improve the flocculation efficacy of animal proteins (Piazza et al., 2011; Piazza & Garcia, 2010b).

Methylation of proteins, usually with alcohols, aims to cap the carboxyl functional group (main negative charge contributor) that would give rise to a cationic protein (Fraenkelkonrat & Olcott, 1945) (Scheme 1). As such, methylation could be considered as an alternative to acidification of protein.

For instance, the successful development of methylated soy protein-based flocculant and its performance was investigated with suspensions of kaolin clay and loam from deposits of volcanic ash by Liu et al. (Liu et al., 2012). The results were compared with another well studied bio-based flocculant chitosan in terms of clarification efficiency and settling rate at various pH ranges in the same study. Results of the study showed that methylated soy protein showed much higher flocculation performance than chitosan at pH 3–7, in terms of both the clarification efficiency and the settling rate. The clarification efficiency of methylated soy was almost the same as that of chitosan at pH 7–10, however the settling rate of floc formed by chitosan increased sharply at pH 7–8 and surpassed that formed by methylated soy protein (Liu et al., 2012). While the major limitation of developing methylated protein-based flocculant is the abatement of solubility, it is however possible to balance the level of methylation and keep the solubility at the desired level.

Grafting of proteins with synthetic polymers is an emerging research area with important application in diverse field of applications including drug delivery, biotechnology and nanotechnology (Broyer et al., 2011; Bhattacharjee & Bong, 2011; Shu et al., 2013). However, studies on grafting proteins for flocculant applications are nearly absent in the literature. Sinha et al. (Sinha et al., 2013) have recently investigated and reported grafting of casein with PAM for flocculant application. According to the group’s investigation, the grafted co-polymer of casein and PAM exhibited a higher hydrodynamic volume/higher radius of gyration of the macromolecule (Sinha et al., 2013) that led to higher flocculation efficacy (Brostow et al., 2007). Higher grafting was indicated to be positively correlated to higher flocculation efficacy due to the more cationization achieved by the –NH2 of the PAM (Sinha et al., 2013). This innovative approach could be tailored to graft hydrolyzed animal proteins as such or onto other polymers.

**Conversion of protein biomass into wood adhesives**

The remarkable progress in engineering wood products over the past three decades allowed the development of low-value plant wood species as well as forest and mill residues. Engineered wood products such as particle board, medium density fiberboard (MDF), parallel and laminated strand lumber, oriented strand board (OSB), plywood, are high-tech products with good performance, and dimensional stability, that are totally integrated with other construction materials (Council, 2013) for various applications. An important element in all modern industrial production technologies of engineered wood composites including oriented strand board, particle board, glued laminated timber (glulam) and plywood is the use of petrochemical adhesives such as urea-formaldehyde (UF), methyl urea formaldehyde (MUF), phenol-formaldehyde (PF), and isocyanates (MDI). These adhesives are however, derived from non-renewable sources and some of their constituent components have deleterious effects on

![Scheme 1. Methylation of proteins with alcohols catalyzed by mineral acids.](image-url)
human health and the environment. For example, isocyanates can react rapidly with many compounds present in the human body, posing safety issues during manufacturing and handling (Bello et al., 2007; Frihart, 2013). They are also known as asthma inducers and sensitizers (Bello et al., 2007). Formaldehyde, a major component in the manufacture of UF, PF or MUF, on the other hand has been classified as a human carcinogen by the International Agency for Research on Cancer (International Agency for Research on Cancer (IARC), 2004). Substantial research efforts have been placed into substituting these ingredients with safe and renewable materials derived from biomass feedstock.

Proteins have been used for centuries to prepare adhesives until petroleum-based adhesives started to dominate the market in the early twentieth century (Liu & Li, 2007). Bone glues have been traditionally used in carpentry and blood used as an additive in plywood glue-mixes (Pizzi, 2006). Modern chemical modifications have built on this early knowledge and allowed the development of engineered wood adhesives based on bovine and porcine blood meal (Yang et al., 2006), blood protein extract (Lambuth, 2003), whey protein (Wang et al., 2011), casein (Lambuth, 2003), spent hen (a by-product of the poultry industry) protein extract (Wang & Wu, 2012), meat and bone meal protein extract (Park et al., 2000), hydrolyzed SRM extract (Mekonnen et al., 2014). Historically, animal protein-based glues were the adhesives of choice for paper manufacture and converting, bookbinding, text sizing, abrasives, gummed tape matches, and a variety of other applications (Pearson, 2013).

Amino acids such as cysteine, lysine, and tryptophan, present in animal proteins, contain polar functional groups that interact with components of wood such as cellulose, hemicellulose and lignin. However, these functional groups need to be exposed from an otherwise prohibitive internal hydrogen bonding among themselves (Park et al., 2000). Controlled breakage of these protein internal bonds through the use of denaturants and chemical modifications are necessary to produce an effective adhesive with suitable bond strength and moisture resistance. Another common modification of proteins for adhesive application is chemical crosslinking (Park et al., 2000; Park et al., 2000). The crosslinking gives rise to a rigid protein-based adhesive with higher bond strength and water resistance. Some of the common protein crosslinking agents that can be applicable for adhesive development in the literature include aldehydes (glutaraldehyde, glyoxal) (El-Thaher et al., 2013a; Wang et al., 2007), epoxy resins (El-Thaher et al., 2013b), maleic anhydride (Jang et al., 2011) etc. Scheme 2 below shows the reaction of secondary amino group of protein with the dialdehyde functional group of glyoxal forming a networked and more rigid structure.

Unfolding of native globular proteins and as a result exposing hidden polar functional groups also enhance the interaction of proteins with the constituents of the wood. For instance, sodium dodecyl sulphate (SDS), an amphiphatic molecule containing a polar group with a long hydrophobic carbon tail, is one known chemical that can cause protein unfolding. The denaturation and unfolding takes place by the binding of hydrocarbon tail of SDS with protein exposing normally buried regions (Bhuyan, 2010). Such unfolding could be brought about by one or a combination of the following: (i) electrostatic repulsion between the charges of SDS bound proteins (ii) penetration of the hydrocarbon tail of SDS into the polar regions of the protein; (iii) binding induced changes in the protein–hydrogen ion equilibrium, resulting in an increase in electrostatic repulsion between charged species (Bhuyan, 2010; Huang & Sun, 2000; Reynolds et al., 1967). Unfolding and treatment of proteins by urea (Jang et al. 2011; Li et al., 2010; Wang & Wu, 2012), cationic detergents such as hexadecyltrimethyl ammonium bromide, and dodecyltrimethyl ammonium bromide (Wang et al., 2005), alkali and protease enzymes (Hettiarachchy et al., 1995; Kumar et al., 2004) were also shown to improve adhesive performance of several animal and plant proteins.

Conversion into surfactants and firefighting foams

Surfactants are important industrial chemicals widely used in the manufacture of household cleaning, industrial process, personal care and cosmetics, agricultural and food products and other industrial applications (Nnanna & Xia, 2001). The application of surfactants in microbiology and biotechnology and several other industries including petroleum oil recovery, bioremediation, emulsification and de-emulsification applications, pharmaceuticals and therapeutics, downstream processing etc. has been excellently reviewed by Singh et al. (Singh et al., 2007). Surfactants are characterized by a universal molecular structure consisting of hydrophilic and hydrophobic moieties with the main property to adsorb at interfaces, reducing surface or interfacial tension, foaming properties, and emulsification. Proteins are amphipathic molecules that exhibit surface activity. Given their biodegradability and low toxicity, the use of agricultural protein, including modified amino acids and hydrolyzed proteins as surfactants is well documented in the literature. Applications include foaming agents in food products (Raymundo et al., 1998), personal care products (Wu & Hettiarachchy, 1998) and firefighting foams (Alsaati et al., 2003; Clapes & Infante, 2002; Ji, 2009).

While native and denatured proteins can be used unmodified for these applications, several modification strategies have been pursued with the goal to improve their surfactant properties. For example, chemical modifications such as phosphorylation through dry heating in the presence of pyrophosphate (Hayashi et al., 2009), acylation (Rondel et al., 2011), acetylation and succinylation (Lin & Chen, 2006; Lin & Chen, 2000) have been shown to improve the foaming capacity and stability. Acetylation and succinylation

Scheme 2. Crosslinking reactions between protein and glyoxal.
modification of proteins for surfactant preparation is shown in Scheme 3 (a and b). Lin & Chen, (Lin & Chen, 2006; Lin & Chen, 0000) investigated the covalent attachment of hydrophobic functional groups in improving the surface activity of soy protein and gelatin hydrolyzates. Results of the investigation showed that increasing the hydrophobic character of the proteins and hydrolyzates resulted in a greater reduction in surface tension and an improvement in surface activity (Lin & Chen, 2006; Lin & Chen, 0000).

A study on the use of bovine blood and rendered blood meal protein for the development of firefighting foams exhibited that mild hydrolysis improved foaming ability (Ji, 2009). The reason for the foam ability improvement as a result of the hydrolysis is due to the change in the relative amounts of hydrophilic and hydrophobic moieties. The same study showed that attaching hydrophobic groups such as fatty acids (C2–C18) to mildly hydrolyzed blood proteins greatly improved the foam stability of protein-based surfactants. The variation in amino acid profile with the feedstock protein and the processing conditions cause variation in functional group and the balance of hydrophobic and hydrophilic functional groups. Thus, modifications in hydrophobicity or hydrophilicity of proteins depending on the protein feedstock could balance the functional groups to achieve the best surface-active properties.

Hydrolysis of proteins and chemical acylation of the resulting polypeptides with acid chlorides in order to produce anionic lipopeptide surfactants has also been reported (Rondel et al., 2011). Similar acylation modifications using amino acid feedstocks was also reported (Rondel et al., 2009). The resulting lipopetide surfactants have comparable foaming capacity and foam stability to commercial surfactants (Rondel et al., 2011, Rondel et al., 2009). The surface active properties of the formulations, such as critical micelle concentration, surface tension, foaming capacity and stability were shown to be dependent on the alkyl chain length (Rondel et al., 2011). For instance with the peptide-based surfactant, the shorter the lipophilic chain, the higher the foaming capacity (Rondel et al., 2011). For the amino acid-based surfactants on the other hand, the most desirable surface properties were observed for the longer chains (Rondel et al., 2009).

The use of protein hydrolyzates in other functional utilization has been extensively reported. For example, peptones produced through enzymatic and alkaline hydrolysis of rendered animal protein including blood meal, meat and bone meal and feather meal to support the growth of microorganisms has been evaluated by Garcia et al. (Garcia et al., 2010). Small peptides and amino acids have also been used as foliar fertilizers (Quartieri et al., 2002). Espinoza et al. (Espinoza et al., 2012) reported potential of protein hydrolyzates that have high amino acid content in enhancing plant growth, climate tolerance, chlorophyll concentration, and chelation transport of micronutrients (Espinoza et al., 2012). Waste protein biomass may also be integrated in the generation of biogas through anaerobic digestion for the production of electricity and thermal energy (Gilroyed et al., 2010).

An example of an industrial scale venture that converts animal waste protein to energy is represented by BioRefinex Inc., a company based in Lacombe, Alberta, Canada. BioRefinex’s technology (Schmidt, 0000) is based on a thermal hydrolysis reaction protocol to process animal byproducts, mainly SRM, other organic residue and waste materials. This process destroys BSE causing prions and other pathogens (Somerville et al., 2009) and yields dry pelletized organic fertilizer, liquid organic fertilizer, inedible tallow, biogas etc. (Figure 3). The novelty of the company’s process is the possibility of integrating all processes together and the flexibility where a number of various products can be processed.

Valorization of animal fat and ash

Animal fat valorization

Around 0.6, 2.8 and 4.5 million tons per annum of rendered animal fat and grease, mainly obtained from animal byproducts, are being produced in Australia, EU and the US, respectively as of 2011 (Alm, 2013; Coelenbier, 2013). This fat and grease are composed of inedible tallow, grease, edible tallow, poultry fat and lard in a decreasing order of quantity (Alm, 2013). Based on the data collected from European Fat Processors and Renderers Association, the 2011 utilization of fat and grease and lipids was for energy (33%), animal feed (29%), soap and cosmetics (22%), pet food (11%), food (4%) and the remaining 2% for other applications (Alm, 2013). Though the traditional uses for these tallow and lard included fuel, cosmetic precursors and components of feed and food supplements, the emergence of BSE and the regulation changes as an increase in biofuel production from these fats in the EU, US and Canada (Lin et al., 2013).

Triglycerides, the basic constituent of animal fats and vegetable oils, have the potential to be a suitable source of
fuel and other hydrocarbons. However, the direct use of triglycerides as fuels in modern combustion engines is hindered by high-viscosity, low-volatility, high-flash point, low volumetric heating values, reactivity of polyunsaturated hydrocarbons, and low heating value. Derivatization and modifications are therefore essential to circumvent these limitations. Several techniques have been developed to convert animal and plant triglycerides into usable biodiesel: pyrolysis, microemulsification, dilution and transesterification (Levine et al., 2010; Maher et al., 2008). These valorization techniques are summarized (see supplemental information).

**Ash biomass valorization**

Ash is the third major ingredient of rendering product stream obtained from the rendering operations. Additional volumes of ash are also generated during the valorization of meat and bone meal and SRM by a thermal degradation process such as incineration and pyrolysis as fuel in cement kilns (Chaala & Roy, 2003). Ash residues are rich in calcium and phosphorus (Deydier et al., 2005; Mekonnen et al., 2013d), two major constituents of bones and as such it can be used a low-cost source of phosphorus and other minerals, or as an organic fertilizer.

Minerals such as dicalcium phosphate, commonly produced from animal bones as a by-product of gelatin manufacturing (Grobben et al., 2004), find use as an animal feed ingredient to supply calcium and phosphorus required for animal bone growth and to improve milk yield of dairy cattle (Grobben et al., 2006). Valorization approaches could be adopted to process ash residues from SRM or other rendering industry products into dicalcium phosphate. However, consumer acceptance remains uncertain owing to concerns over incomplete destruction of prion material in SRM.

The utilization of animal-derived ash for the production of hydroxyapatite is another emerging technology. Natural forms of hydroxyapatite, found in bones, have application as an absorbent, a catalyst, and other various biomedical applications (Saeid et al., 2009). Sobczak et al. (Saeid et al., 2009) demonstrated that using two stages of bone sludge waste calcination at temperatures of 650 and 950°C, high quality hydroxyapatite could be obtained.

A study by Deydier et al. (Deydier et al., 2005) showed that the combustion residue (between 550 and 1000°C) of meat and bone meal were chiefly composed of calcium (30.7%) and phosphate (56.3%) rich compounds, that are a mixture of Ca_{10}(PO_{4})_{6}(OH)_{2} and Ca_{3}(PO_{4})_{2}. The work further showed that the residues do not contain any of the investigated heavy metals (Ni, Cr or Cd). This shows that such ash residue can be utilized as organic soil enrichment fertilizer and source of minerals for the industry. The potential use of bone ashes collected from thermal and alkaline hydrolysis of SRM residue as organic fertilizer is the other potential area of application (Mekonnen et al., 2013d). Other biotechnological approaches of bone degradation for the production of phosphorus fertilizers and low-molecular organic acids that is useful for plant fertilizer was also investigated and reported in the literature (Saeid et al., 2012; Saeid et al., 2012; Saeid et al., 2013).

**Conclusion and outlook**

The rapid industrialization of modern society results in increasing demand of chemical building blocks. In order to address growing environmental concerns related to resource depletion and sustainability, low-value or waste streams must be efficiently upgraded to high-value useful product. This is a particularly pressing issue for the slaughterhouse and rendering industry animal waste protein in advanced economies. The emergence of the bovine spongiform encephalopathy changed most of the traditional uses of the wastes generated from these industries. While the values of some rendering products (for example, blood meal, meat and bone meal etc.) became extremely limited, SRM tissues were completely banned from use as either feed/food or fertilizer application and effectively handled as hazardous waste posing economic challenges to the rendering industry with repercussions to the whole livestock industry.

This review presents the technological state-of-the-art and emerging trends in the conversion of rendering and slaughterhouse wastes with a specific focus on the production of
new renewable materials, energy and chemicals. A modern biorefinery approach aiming to valorizing all ingredients and co-products of the animal processing industry waste including protein, fat, and ash underpins the discussion presented here. The protein fraction can be valorized into components that are useful for applications including bio-based plastics, adhesives, flocculants, surfactants, nitrogen-rich fertilizers and microbial feedstock. The fat fraction can be valorized into products and co-products that are utilisable in the biodiesel and oilochemical industries. The ash fraction can also be valorized into minerals and fertilizers. While there are still challenges of heterogeneity of the compositions of these materials, there is huge potential of transforming these and other organic waste materials into safe, environmentally positive, and valuable products at competitive costs.

Declaration of interest

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