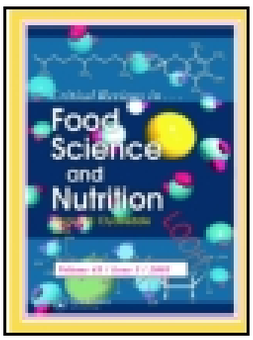

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Running head: Advances in New Hulless Barley Research

Synchrotron-Based and Globar-Sourced Molecular (Micro)spectroscopy Contributions to Advances in New Hulless Barley (with Structure Alteration) Research on Molecular Structure, Molecular Nutrition and Nutrient Delivery

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ABSTRACT:

This article aimed to review synchrotron-based and globar-sourced molecular infrared (micro)spectroscopy contributions to advances in new hulless barley (with structure alteration) research on molecular structure, molecular nutrition and nutrient delivery in ruminants. First it reviewed recent progress in barley varieties, utilization for animal and human, inherent structure

features and chemical make-up, evalution and research methodology, breeding progress, rumen degradation and intestinal digestion. The emphasis of this review was focused on the effect of alteration of carbohydrate traits of newly developed hulless barley on molecular structure changes and nutrient delivery and quantification of the relationship between molecular structure features and changes and truly absorbed nutrient supply to ruminants. This review provides an insight into how inherent structure changes on a molecular basis affect nutrient utilization and availability in ruminants.

Keywords

Hulless barley, Molecular structure, Nutrient delivery, Alteration of carbohydrate traits

1. Barley Utilization in Canada

1.1. Barley Varieties and Inherent Structure Profile

Barley was introduced to western Canada from Europe by the earliest settlers (Juskiw et al., 2011). Early barley production was mainly used by the malting industry. As trade barriers limited the development of the brewering industry, barley production turned to feed (Metcalfe, 1995). Barley now is one of the major cereal grains grown in Canada with 8.1 million tonnes of production in 2012 (MacLeod et al., 2012). Ninety percent of the barley is grown in Western Canada. The vast majority (80%) is used in feed production domestically (Ullrich, 2011).

Barley is superior in growing at the areas with humid climate and variable precipitation than corn (*Zea mays* L.) due to its less water-holding capacity (Thomason et al., 2009). Barley grain mainly consists of a fibrous hull, pericarp, aleurone layer, endosperm and germ (Evers et al., 1999). Pericarp and seed coat both play protective roles by covering the whole seed. Endosperm tissue is the main storage site of starch granules and with the aleurone layer, usually accounts for the major portion of the barley kernal (Black, 2000; Kulp and Ponte, 2000). The aleurone layer is composed of cells which include starch granules. In the aleurone layer, non-starch polysaccharides, ɓ-glucan and arabinoxylan are mainly found in the cell wall (Bacic and Stone, 1981; Newman and Newman, 1992). Thicker cell walls in barley can be found in the varieties that are higher in ɓ-glucan (Oscarsson et al., 1997; Zheng et al., 2000). Overall, there have been 200 barley cultivars registered in Canada, of which over 50 produced in western Canada, including 8 hulless cultivars and 13 malting cultivars (CFIA, 2009; Du et al., 2009; Du and Yu, 2010, 2011; Damiran and Yu, 2012).

1.1.1. Hulled barley (*Hordeum vulgare L.*): Two-Row Barley vs. Six-Row Barley

The early barleys were generally two- and six-rowed types (Juskiw et al., 2011). Wild and cultivated barleys have sessile spikelets. Sterile lateral spikelets can be found in two-row barley, whereas fertile ones are found in six-row barley due to a pair of mutations (von Bothmer and Komatsuda, 2011). Both varieties are important for beer production historically that two-row barley is more widely used in England and German, while six-row barley was predominant in Canada, especially in southern Alberta, until the mid 1990s (Metcalfe, 1995; Juskiw et al., 2011). However, changes began in Saskatchewan when the advent of the two-row malting barley cultivar ôHarringtonô replaced six-rowed barley (Harvey and Rossnagel, 1984). As reported by Campbell et al. (1995), two-row barleys grown in Manitoba had higher starch content on average than did six-row cultivars whereas six-row barley had higher protein and less starch than two-row barley, which resulted in wider utilization as animal feed.

1.1.2. Hulled vs. Hulless Barley

Hulled barley has a hull that covers the caryopsis. Hulless barley is superior in nutritional characteristics such as protein, starch, ß-glucan, total dietary fibre and limiting amino acids compared with hulled cultivars (Bhatty, 1986; Edney et al., 1992; Boros et al., 1996).

In the early 1970s, investigations on the nutritional quality of barley found the hull content of barley affected the digestible energy in monogastric animal feeding (Bhatty et al., 1975), which led to the registration of some hulless barley cultivars in order to further extend the use of hulless barley in food, malt and brewing (Bhatty, 1999). Hulless barley production was found in Canada with more than 800,000t in 1998 (Bhatty, 1999). However, due to the lack of a hull, hulless barley is more likely affected by mechanical damage and invation by insects

compared to hulled barley (Thomason et al., 2009). Thus, there is usually lower grain yield for hulless barley when compared to hulled barley (Choo et al., 2003).

2. Benefits of Hulless Varieties for Animal Nutrition

Barley is widely used as a feed grain for various livestock species such as beef, dairy cattle, goat, swine and poultry (Blake et al., 2011), although feeding barley could result in digestive disorders due to its rapidly degradable carbohydrate content (Yang et al., 1997). Hulless barley has been reported to have higher energy values and better nutrient availability due to its reduced fibre and increased starch content compared to hulled cultivars (Zinn et al., 1996; Bowman et al., 2001; Shon et al., 2007; Pieper et al., 2008; Jha et al., 2010). There is an interest in increasing the use of hulless barley in ruminant rations due to concerns with animal health, nutrient availability and potential profit in dairy and beef production. Yang et al. (2013a,b) showed that hulless barley have higher nutrient value and higher metabolizable protein value than hulled barley.

2.1. Nutritional Effects on Monogastric Animals

Hulless barley was developed primarily for swine and poultry feeding (Bhatty, 1999). Previous studies indicated that hulless barley had higher energy and digestibility than hulled barley in pigs (Lehman et al., 1995; Beames et al., 1996). Hulless barley varied in ɓ-glucan and amylose levels had a strong effect on gut microbial profiles of pigs compared with hulled barley (Pieper et al., 2008). In a study on weaned piglets, a hulless barley based diet was found higher in ileal organic matter, crude protein and total non-starch polysaccharide digestibility as well as short-chain fatty acids (SCFA) and lactic acid (LA) compared to hulled barley or oat (Jha et al., 2010). This indicated hulless barley has a potential to improve nutrient digestibility and also gut

health in weaned piglets. Hulless barley applied in poultry diets is usually combined with ß-glucanase or phytase in order to reduce the viscous condition in the digestive tract due to the high ß-glucan level in barley which is considered as an anti-nutrition factor for broiler chickens (White et al., 1983; Hesselman et al., 1986; Missct 1996). Recent study on dilution of whole hulless barley in broiler chicken diets revealed that inclusion of hulless barley in the diet with a dilution level of 7.5% could be beneficial to chicken growth in the grower period and at 15% in the finisher period (Anderson et al., 2012).

2.2. Nutritional Effects on Ruminants

Barley is the third most readily degradable cereal for ruminants due to its superior starch and energy content (Yang et al., 2013a,b). However, the impact of barley in ruminants includes bloat, acidosis and laminitis when the diet is high in barley starch (Blake et al. 2011). The incidence of digestive disorders could be more severe when ruminants are fed with hulless barley as its lack of a hull coating would expose more adhering area for micro-organisms. This would result in faster starch digestion and accumulation of acidic products (Zinn et al., 1996; Yang et al., 1997). However, in a feedlot steer trial reported by Zinn et al. (1996), cattle fed hulless barley had greater digestibility of postruminal OM, starch and N as well as net energy as compared to hulled barley. This indicates there is potential to use hulless barley to improve cattle performance.

3. Newly Developed Hulless Barley Varieties

3.1. Breeding Targets for Newly Developed Hulless Barley

The early registered hulless barley cultivars included two- and six-row, low and high ß-glucan, and waxy and normal starch (Bhatty, 1999). New hulless barley varieties used in this

project were developed by the University of Saskatchewanôs Crop Development Centre with special targets for amylose and ß-glucan levels. The four hulless barley lines include: zero-amylose but very high ß-glucan levelð CDC Fibar; low-amylose but high ß-glucan levelð CDC Rattan; normal-amylose and normal ß-glucan levelð CDC McGwire, as well as high-amylose but normal ß-glucan levelð HB08302 (Damiran and Yu, 2010, 2011, 2012; Yang et al., 2013a, b).

3.2. Barley Starch

3.2.1. Starch Digestiblity

Starch is the major strogae carbohydrate in plants (Singh et al., 2010). Starch digestion mainly occurs in the small intestine in the non-ruminant but differs in the ruminants due to the action of microorganisms in the rumen (Cerrilla and Martinez, 2003). Digestion of starch requires enzymes produced by salivary glands, rumen microorganisms or the pancreas (Cerrilla and Martinez, 2003; Singh et al., 2010). Starch or starchy products can be classified by the rates of starch digestion (Singh et al., 2010). Diversified morphological characteristics of starches can be found among botanical sources and vary with the genotype (Singh et al., 2010). These morphological characteristics include the size and shape of the starch granules. Several studies confirmed a negative relationship between granule size and starch digestibility (Langworthy and Deuel, 1922; Lindeboom et al., 2004). The reason for this is that the large granule starches are lower in susceptibility to enzymatic hydrolysis due to smaller granule-specific surface area for enzyme binding, resulting in less hydrolysis than with small granules (Tester et al., 2006). Dreher et al. (1984) suggested that the surface characteristics of starch granules affect enzymatic digestion and were responsible for higher digestibilities for cereal starches than for tuber and

legume starches. This may due to pores on the surface which facilitate the entry of the digestive enzymes (Singh et al., 2010). Non-starch substances such as protein and lipid on the granule surface are considered to limit the rate of enzymatic hydrolysis by blocking adsorption sites, impacting enzyme binding and reducing surface accessibility (Oates, 1997; Singh et al., 2010). The molecular structure of the starch granule influences the hydrolysis pattern by the arrangement of the different polymeric forms of the starch, especially A-type and B-type crystallites, which vary in the packing of the amylopectin double helices (Lehmann and Robin, 2007; Singh et al., 2010). For ruminants, barley starch is easily degraded by rumen microorganisms and considered to be associated with metabolic disorders (Cerrilla and Martinez, 2003). McAllister et al. (1993) reported that ruminal starch digestion was not affected by starch granule size but was a function of the protein and structural carbohydrate matrix within the grain. Yu et al. (2004) revealed the impact of protein to starch matix within cellular diamentions in barley on rumen degradation and intestinal digestion in ruminant using advanced synchrotron-based IR microspectroscopy (Yu, 2004). Therefore, studies to improve barley quality have been concentrated on how to increase by-pass starch and reduce starch degradation in the rumen (Juskiw et al., 2011). For examples, reducing starch degradation of barley is done through dry heating, moist heating, microwave irradiation (Yan et al., 2013) and blending (Abeysekara et al., 2011; Damiran et al., 2012; Zhang and Yu, 2012a,b)

3.2.2. Starch Components: Amylose and Amylopectin

The main polymers in barley starch granules are amylose and amylopectin, which normally account for 15-25% and 75-85% of the starch, respectively (Ullrich et al., 1986). Amylose is composed of Ŭ-1,4 glucopyranosidic units, whereas there is branching at the sixth

carbon in amylopectin (Zobel, 1988). Amylopectin has a much larger molecular weight (10^5 to 10^6) than does amylose (10^4) and a much larger surface area per molecule than amylose, which makes it a preferable substrate for amylolytic attack (Singh et al., 2010). Compared to amylopectin, the glucose chains of amylose are more tightly bound to each other by hydrogen bounds, resulting in less availability for enzyme hydrolysis (Singh et al., 2010). In cereal grains, varieties high in amylopectin are termed ówaxyô which originally referred to the translucent property of the endosperm of high amylopectin corn (Dieckmann, 2011). The variation of amylose and amylopectin composition in barley starch will affect functional properties of starch. For example, a higher percentage of amylopectin increase solubility, whereas the higher the amylose content, the lower the starch digestibility due to a positive correlation between amylose content and resistant starch formation (Singh et al., 2010). Variations in starch among different cereal grains, as well as variations within cultivars, are considered to influence starch degradability in the rumen (McAllister and Cheng, 1996; Mills et al., 1999; Offner et al., 2003; Svihus et al., 2005; Hart et al., 2008; Liu and Yu, 2010, 2011). Genetic modification allows variation of starch composition for targeted functionality (Martin, 2012). The alteration of starch in barley was primarily applied in food barley for humans (Izydorczyk and Dexter, 2008). However, these barley varieties may affect nutrient availability in animals (Yang et al., 2013a,b,c). Previous studies found that genetic differences in barley varieties in amylose to amylopectin ratios affected starch degradability in the rumen (Yang et al., 2013a,b,c), which was associated with the Ŭ-amylase activity of rumen microorganisms. Low amylose to amylopectin ratios in barley starch resulted in higher sensitivity to Ŭ-amylase and a higher starch degradation rate (MacGregor and Fincher, 1993; Hristov et al., 2002).

3.3. β-Glucan

3.3.1. Physical Properties and Chemical Structures of β-Glucan

As one of the non-starch polysaccharides, ɓ-glucan can be found in different organic sources including cereal grains, bacteria and algae, but is mainly concentrated in the internal aleurone and endosperm cell walls of cereals (Charalampopoulos et al., 2002; Demirbas 2005; Holtekjølen et al., 2006) such as oat and barley (Havrlentová and Kraic, 2006). In cereals, ɓ-glucan consists of ɓ-d-glucopyranose units linked through (1Ÿ 4) and (1Ÿ 3) glycosidic bonds (Havrlentová et al., 2011). Molecular weights of ɓ-glucan vary between cultivars. Higher molecular weights of ɓ-glucan will result in higher viscosity of viscous slurries (Juskiw et al., 2011). In barley, ɓ-glucan accounts for 2-7% of DM with around 75% in cell wall polysaccharides (Zhang et al., 2000; Ullrich, 2011). The ɓ-glucans found in yeast and fungi are different from those found in cereals as they consist of a 1,3 ɓ-linked glycopyranosyl backbone with 1,6 ɓ-linked side chains. ɓ-glucan in food grains is important for human health, while in feed grains, glucan is indigestible by monogastric animals due to a lack of ɓ-glucanases, but digestible by ruminants due to microorganism activities (Ullrich, 2011; Yang et al., 2013a,b,c).

3.3.2. Nutrient Effects of β-Glucan in Humans

Hulless barley has been successfully used for food by humans with the advantage of the higher ɓ-glucan level (Bhatty, 1986). ɓ-glucan plays an important role in maintaining some blood biochemical parameters such as lowering plasma cholesterol, reducing glycaemic index, reducing the risk of colon cancer, and reducing the risk of coronary heart diseases (Maki et al., 2007; Vasiljevic et al., 2007; Izydorczyk and Dexter, 2008). Some studies reported the potential effect of ɓ-glucan in prevention of colonic diseases (Nilsson et al., 2008; Kim et al., 2006). Its

significance in improving resistance to infections was reported by Cheol-Heui et al. (2003). Bae et al. (2009) reported inclusion of ß-glucan in the diet could significantly reduce the body weight of model mice. In the food industry, ß-glucan was superior in improving sensoric and gustatory properties in beverages or breadmaking due to its high viscosity (Lyly et al., 2003; Gajdoġová et al., 2007; Butt et al., 2008; Lazaridou et al., 2004; Lee et al., 2009).

3.3.3. Nutritional Effects of β-Glucan in Livestock

ß-glucans extracted from the cell wall of bakerôs yeast (*Saccharomyces cerevisiae*) is reported to simulate the immune system (Miura et al., 1996; Cox and Dalloul, 2010). Chae et al. (2006) reported that broilers fed diets with 0.02% and 0.04% of ß-glucan supplementation had improved feed intake and weight gain. In another study, male broilers fed with ß-glucan at 50 and 75 mg/kg inclusion rate showed higher intake and weight gain compared with birds fed a normal diet or diet with a higher ß-glucan inclusion rate (Zhang et al., 2008). On the effect on the immune response, the proliferating ability of macrophages in chickens was enhanced when chickens were fed a ß-glucan supplemented diet (Guo et al., 2003). Moreover, Lowry et al. (2005) reported the enhancement of protection against pathogens when ß-glucan was applied as a feed additive.

In pigs, some studies observed that ß-glucan supplementation could improve average daily gain (ADG). The optimal inclusion rates of ß-glucan in pig diets varied in several reports but all were between 250 and 500 ppm (Dritz et al., 1995; Hiss and Sauerwein, 2003). Being a soluble non-structure polysaccharide (NSP), ß-glucan may increase viscosity. Some studies reported an increase in retention time of digesta in gastro-intestinal tract (GIT), which may influence microbial activity in the upper GIT by affecting bacteria growth (Leterme et al., 2000;

Charalampopoulo et al., 2002). Pieper et al. (2008) reported that the mixed-link ɓ-glucan content of barley and oat influenced significantly the composition of the microbial community in the intestine. As ɓ-glucan in hulless barley varieties increased, it reduced microbial diversity. Bird et al. (2007) also mentioned that the number of *Lactobacilli.* can be increased by ɓ-glucan and resistant starch.

ɓ-glucan is assumed to be completely digested in the rumen of cattle. As reported by Gruve et al. (2006c), ɓ-glucan digestibility varied between cultivars. ɓ-glucan content has been observed to be positively correlated to barley qualities such as viscosity, gelation, particle size and barley starch cell wall (Bleidere and Gaile, 2012). However, this trait may lower the starch degradation rate in the rumen (Oscarsson et al., 1997; Zheng et al., 2000; Izydorczyk and Dexter, 2008). The greater bypass ɓ-glucan will then be useful for stimulating the immune system in ruminants (Gruve et al., 2008; Juskiw et al., 2011).

4. Conventional Feed Evaluation Methods for Ruminants

4.1. Cornell Net Carbohydrate and Protein System for Feed Evaluation

The Cornell Net Carbohydrate and Protein System (CNCPS), was first published by Russell et al. (1992), Sniffen et al. (1992), and Fox et al. (1992). The system was intended to summarize empirical and mechanistic approaches into models and programs in order to estimate feed intake, fermentation, passage and intestinal digestion of feed protein and carbohydrate, nutrient utilization, reserves, and excretion (Chalupa and Boston, 2003; Tylutki et al., 2008).

Carbohydrate and protein fractionation in CNCPS is used to describe feed composition by their variation in digestion rates and passage, and estimate the amount of structural

carbohydrate (SC) and non-structural carbohydrate (NSC), metabolizable energy and available protein animal in feed (Sniffen et al., 1992; Tylutki et al., 2008).

The crude protein content of feed is partitioned into three major fractions, including non-protein nitrogen (NPN) such as ammonia, peptides or amino acids (PA), true protein (PB) and unavailable nitrogen or protein (PC). The true protein fraction is furthered divided into three subfractions based on differences in degradation rate in the rumen and which are: PB1, PB2 and PB3. PB1 is known as the rapidly-degraded protein or soluble true protein fraction with a degradation rate of 120ï 400% /h. Fraction PB2 is true protein with an intermediate degradation rate of 3ï 16% /h. Fraction PB3 is slowly degraded protein referred to as insoluble true protein bound to fibre with a degradation rate of 0.06ï 0.55% /h (Van Soest et al., 1981; Krishnamoorthy et al., 1983; Sniffen et al., 1992).

Carbohydrate fractions are computed based on NSC, SC and indigestible fibre content of feed. Carbohydrates are partitioned into five fractions: fraction CHO A (CA), fraction CHO B1 (CB1), fraction CHO B2 (CB2), fraction CHO C (CC) and fraction CNSC (nonï starch carbohydrate). CA is sugar with a rapid degradation rate of 300% /h. CB1 is starch and pectin with an intermediately degradable with degradation rate of 20ï 50% /h. A slowly degradable fraction CB2 is available cell wall with a slow degradation rate of 2ï 10% /h. An unfermentable fraction CC is the unavailable cell wall (Sniffen et al., 1992). In CNCPS ver.6, CA is further partitioned into four subfractions (CA1 to CA4) in considering the usage of carbohydrate in microbial activities and rumen fermentation in various feedstuffs (Lanzas et al., 2007; Tylutki et al., 2008).

CNCPS shows advantages in predicting feed ME, rumen N and amino acid availability when developing diets for cattle, thanks to its coverage of effects of feed variation (Lanzas et al., 2008). The system is widely used in farm management for balancing feeds and related costs, optimizing herd size, and improving the annual return, although the system is not ideal for planning feeding strategies for whole herds (Tylutki et al., 2004; Fox et al., 2004; Tylutki et al., 2008).

4.2. Energy Value Estimation in Feed Ingredients

The National Research Council (1996) defined energy as ótheô potential to do work and can be measured only in reference to defined, standard conditionsô and regarded the ódefined units are equally absoluteô. Although people are familiar with the energy unit óJouleô, the calory is more welcomed by nutritionists. In animal studies, the megacalorie (1 Mcal=1,000 Kcal) is more widely used in energy values of animal requirement standards (National Research Council, 1996). There are two ways to describe the energy content of feed or food: one is the underlying biochemical pathways of nutrient-ATP based modeling while the other is based on energy partitioning (GE/DE/ME/NE) (National Research Council, 1996). The later one is most commonly used in animal studies.

Energy values are estimated differently due to various feed sources as well as the energy requirement of the animal. Gross Energy (GE) is the energy in organic substrates, such as fat, protein and carbohydrate, when oxidized to carbodioxide and water via a series of reactions producing ATP. In animal feeding, precise estimation of the energy value of feed is essential for cost-effective farm management as well as for nutrient availability (National Research Council, 1996). DE, which stands for digestible energy, is the difference between gross energy and fecal

energy. In the new edition of NRC Dairy (National Research Council, 2001), DE at 1X maintenance is calculated from the estimated digestible nutrient content instead of 0.04409 times total digestible nutrients (TDN) because of the variation in gross energy values among different feedstuffs. Metabolizable energy is considered as useable energy supply and is the energy from feed after energy loss from feces; urine and gas are accounted for. It can be described by heat increment and retained energy (National Research Council, 1996), and also calculated from DE with the equation ME=1.01×DE-0.45 (National Research Council, 2001).

In NRC Dairy 2001, net energy for lactation units (NE_L) is used to describe energy values for feed, diets and the requirements of adult cows, including maintenance, lactation and pregnancy. NE_L of feeds in NRC Dairy 2001 is calculated at 74 percent of a total diet TDN_{1x} with the assumption of intake at 3X and 4X maintenance.

TDN is used to describe feed values and determined via experimental methods. In the previous edition of NRC Dairy (National Research Council, 1989), ME, DE and NE_L were calculated from old TDN at 1X maintenance. However, due to a lack of ME and NE_L values and a direct method to measure TDN of many feeds nowadays, the calculation of TDN is revised by measuring the feed composition in the 7th edition of the Nutrient Requirements of Dairy Cattle (National Research Council, 2001). TDN_{1X} now is calculated from truly digestible non-fibre carbohydrate (NFC), CP, fatty acids (converted from estimates of ether extract) and NDF of each feed (Weiss et al., 1992; National Research Council, 2001).

Tyrrell and Moe (1975) reported the negative relationship between digestibility of diets fed to dairy cattle and feed intake. A discounted TDN value is then introduced using TDN_{1X} of the entire diet instead of an individual feed, along with a discount value in determining TDN_{3X},

further applied in calculation of DE, ME and NE_L at productive levels of intake (National Research Council, 2001).

In the net energy system, NE of feed can be separated based on physiological activities of the animal without considering the influence of the diet. NE_m and NE_g are two net energy values used to estimate the energy requirement of maintenance and growth in the net energy system. They both can be calculated from ME using equations reported by Garrett (1980), in which ME was assumed as DE times 0.82 (National Research Council, 1996).

4.3. In Situ Technique—Estimation of Rumen Degradability and Kinetics of Feed Nutrients

The *in situ* technique, initially called the ófibre bag techniqueô, was first reported by Quin et al. (1938) to estimate feed digestion in cannulated sheep by incubating silk bags together with feed samples in the rumen of sheep. The *in situ* technique was aimed at estimating the degradability of protein (Mehrez and Ørskov, 1977; Ørskov and McDonald, 1979) although this technique is now widely used in studying digestion of feedstuffs within the rumen and considered as a standard tool to obtain the digestion parameters as inputs in models for feed evaluation (Vanzant et al., 1998). A brief procedure is as follows: A feed is milled to pass a 3-mm screen or roller ground depending on feed quality, and then samples are placed into nylon bags with a pore size of 40-60 ε m, which allows few particles to escape but does not inhibit the accessibility of microorganisms to the feed in the bags. The tied-up bags and samples are gradually introduced into the rumen of cannulated cattle at different time intervals with no more than 30 bags in each animal. Bags are then withdrawn at certain time points, washed and dried. Degradation characteristics of DM, CP, starch and NDF can be measured by analyzing the residues in bags against time after incubation, while the soluble materials within samples can be

obtained by reweighing the bag and samples after washing and drying (Ørskov, 2000). Combined with the retention time effects and degradation characteristics in the rumen, Ørskov and McDonald (1979) developed the first order kinetic nonlinear model to dynamically assess the degradability of nutrients in a feed. The model was then modified by Robinson et al. (1986) and Dhanoa (1988) as the equation below:

$$R(t) = U + (100 - S - U) \times e^{-Kd \times (t - T0)},$$

where R(t) = the residue after t h incubation (%), S = soluble fraction determined from the 0 h incubation (%), U = undegradable fraction (%), T_0 = lag time (h), and K_d = degradation rate (%/h).

Based on the parameters above, the effective degradability (ED), or the extent of degradation of nutrients (Yu et al; 2000; Nuez-Ortín and Yu, 2010a,b; 2011) is thus estimated according to Tamminga et al. (1994):

$$ED\ (\%) = S + [(100 - S - U) \times Kd)] / (Kp + Kd),$$

where S = soluble fraction (%) and K_p = estimated passage rate of digesta from the rumen (%/h) and it is assumed to be 2.5%/h for structural carbohydrate and 6%/h for concentrates (Tamminga et al., 1994). These parameters together with incubation time intervals, can further be applied to estimate the hourly effective degradation ratio with the equation reported by Sinclair et al. (1993):

$$\text{Hourly ED (g/kg DM)} = S+[(D\times Kd)/(Kp +Kd)]\times 1 - e^{-t\times(Kd+Kp)},$$

$$\text{Hourly ED ratio N/CHO}_t =$$

$$1000\times(HEDN_t - HEDN_{t-1})/[(HEDNDF_t - HEDNDF_{t-1})+(HEDNFC_t - HEDNFC_{t-1})],$$

where N/CHOt = ratio of N to CHO at time t (g N/kg CHO); $HEDN_t$ = hourly effective degradability of N at time t (g/ kg DM); $HEDN_{t-1}$ = hourly effective degradability of N 1 h before t (g/kg DM); $HEDCHO_t$ = hourly effective degradability of CHO at time t (g/kg DM); $HEDNDF_t$ = hourly effective degradability of neutral detergent fibre at time t (g/kg DM); $HEDNDF_{t-1}$ = hourly effective degradability of neutral detergent fibre at 1 h before t (g/kg DM) $HEDNFC_t$ = hourly effective degradability of non-fibre carbohydrate at time t (g/kg DM); $HEDNFC_{t-1}$ = hourly effective degradability of non-fibre carbohydrate at 1 h before t (g/kg DM).

As reported in previous studies (Tamminga et al., 1990; Sinclair et al., 1993), the ratio of 32 g N/kg CHO truly digested in the rumen is the optimum ratio to balance microbial protein synthesis and energy cost in regards to rumen fermentation.

The advantage of this technique is its cost-effectiveness for less labour or feed required to evaluate feed quality. However, the potential problem with this technique is overestimating the actual digestibility of feed in the diet compared with *in vivo* measurement due to no or a lack of chewing and rumination to break down feed particles (Ørskov et al., 1980). Therefore, it is difficult to estimate the actual feed intake accurately via the *in situ* technique. However, the *in situ* technique is still considered an adequate and cost-effective methodology in assessing degradation characteristics of feed in the rumen environment (Ørskov et al., 1980; Ørskov, 2000).

4.4. In Vitro Technique—Estimation of Intestinal Digestibility of Feed Nutrients

The *in vitro* technique used to estimate intestinal protein digestion is considered to be cost-effective, rapid and reliable in revealing the characteristics of protein digestion in the rumen environment. A three-step *in vitro* technique was described by Calsamiglia and Stern (1995) to

estimate protein digestibility in the small intestine, which aims to further predict the intestinal absorbable dietary protein of each feed. Residues from 12 h or 16 h of pre-ruminal incubation are used in this technique. After exposing the ground residues to HCl solution for 1h and then neutralizing pH with phosphate buffer, the solution is incubated at 38°C for 24 h.Trichloroacetic acid (TCA) solution is then added to precipitate undigested protein. Intestinal digestibility of protein is determined by the percentage of TCA-soluble N in the N of the rumen residue (Calsamiglia and Stern, 1995).

4.5. Prediction of the Truly Digestible Protein Supply in the Small Intestine of Dairy Cattle

There are several models used to evaluate truly absorbed protein values for dairy cattle. Two modern protein evaluation systems, DVE/OEB system (Tamminga et al., 1994), known as the truly absorbed protein in small intestine (DVE) and degraded protein balance (OEB), and the NRC Dairy 2001 model (National Research Council, 2001) have been developed, based on previous models (National Research Council, 2001; Tamminga et al., 1994), to estimate the potential protein supply in feeds or diets for dairy cattle. However, the two models are applied differently in different countries, is that the DVE/OEB system is more welcomed in some European countries, while the NRC Dairy 2001 model is widely used for research in North America. Therefore, various studies have been conducted to compare the two models in evaluating feedstuffs in order to extend their application worldwide (Yu et al., 2003a,b; Yu, 2005a; Nuez-Ortín and Yu, 2011; Damiran and Yu, 2012; Gamage and Yu, 2013).

4.5.1. DVE/OEB System

Prior to estimating the truly digestible protein in the small intestine, studies on metabolic characteristics of nutrients including rumen degradation and intestinal digestion of feed are vital.

In the DVE/OEB system, DVE stands for total truly digested protein in the small intestine. The DVE value of feed is calculated from the sum of digestible rumen bypass true protein (ARUP) and truly absorbed microbial protein synthesized in the small intestine (AMCP) minus a correction of endogenous protein losses in the digestive tract (EDCP). AMCP can be estimated from digestibility correction factors times fermentable organic matter, while ARUP is calculated from the digestibility of rumen undegraded protein in the small intestine, estimated from the *in vitro* technique, in proportion of total rumen undegraded protein. ENDP is estimated as 75 g/kg of undigested dry matter (Tamminga et al., 1994; Yu et al., 2003a,b). All parameters are in g/kg DM.

The synthesis of microbial protein requires energy supplied from carbohydrate digestion in the rumen. Therefore, the balance between efficient energy and N supply from feed is essential to maximize microbial protein synthesis. The OEB value of each feed in the DVE/OEB system is used to describe the degraded protein balance, also known as the difference between microbial protein synthesis from rumen degradable CP and that synthesized from energy available for anaerobic fermentation in the rumen. A positive OEB value indicates potential loss of energy, while a negative value represents a shortage of N supply, resulting in impaired protein synthesis (Tamminga and Jansman, 1993; Tamminga et al., 1994; 2007).

4.5.2. Comparison between DVE/OEB System and NRC Dairy 2001 Model

Both the DVE/OEB and the NRC Dairy 2001 models target two outputs: 1) the truly digested and absorbed protein in the small intestine (DVE) and 2) the degraded protein balance (OEB) (Damiran and Yu, 2012), which are aimed to maximize animal productivity with the minimum amount of dietary CP input and more efficient energy utilization, although in NRC

Dairy 2001, microbial protein synthesis in the rumen of a feed is calculated from total digestible nutrients (TDN). In the NRC Dairy 2001 model, the concept of metabolizable protein is introduced as composed of truly absorbed rumen undegraded feed CP (ARUP), truly absorbed microbial CP (AMCP) and truly absorbed rumen endogenous protein in the small intestine (AECP). Differing from the DVE/OEB system, MP is calculated as the sum of $ARUP^{NRC}$, $AMCP^{NRC}$, and $AECP^{NRC}$, which considers endogenous protein as gain instead of losses, in comparing to the DVE/OEB system (Yu et al., 2003a, b; Nuez-Ortín and Yu, 2011).

5. Mid-IR Spectroscopy Techniques in Feed Science

5.1. Infrared Molecular Spectroscopy

Infrared Molecular spectroscopy is one of the spectroscopic techniques used by chemists. It measures the absorption of different IR frequencies by positioning a sample in the path of an IR beam. Previous studies suggest that the absorption of infrared radiation is proportional to energy changes, which also correspond to the various types of vibration of molecules, such as stretching and bending (Hsu, 1997). Due to the different absorption frequencies of different chemical functional groups, IR spectroscopy can be used to determine the functional groups in the sample based on the frequencies, intensities and patterns of the peaks of functional group bands (Jackson and Mantsch, 2000; Stuart, 2004). IR spectroscopy can be applied to a wide range of sample types such as gases, liquids and solids, which makes IR spectroscopy a popular tool for identifying unknown compounds and elucidating sample structures (Hsu, 1997).

The IR region consists of three smaller areas including near IR, mid IR and far IR. Near IR means the light source region at wave numbers between ca. 13,000-4,000 cm^{-1}, mid IR located in the region of ca. 4,000-200 cm^{-1} while far IR means the region at ca. 200-10 cm^{-1},

among which mid IR is the most commonly used region. Near IR spectroscopy requires minimal or no sample preparation, while far IR requires special optical materials and equipment (Hsu, 1997). The chemical structures of specific compounds are assigned to certain absorption bands within associated infrared radiation regions. However, the regions for certain functional group are not the same among different studies owing to sample types (Yu, 2006a; Griffiths and Haseth, 2007). For example, using synchrotron-based FTIR to detect the protein amide I region of barley varieties, Liu and Yu (2010) detected the protein amide I region of six barley varieties at ca. 1722-1578 cm^{-1}, while Yu (2006a) reported the region of ca. 1710-1576 cm^{-1} as the absorption band for the protein amide I region for Valier and Harrington barley. Most commercial instruments use a dispersive spectrometer or a Fourier transform spectrometers to measure IR radiation.

5.2. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a method of infrared spectroscopy. Compared to a dispersive IR spectrometer, a Fourier transform spectrometer has advantages of speed and sensitivity (Hsu, 1997; McCluskey, 2000). A typical dispersive IR spectrometer generates the electrical signal from the beams that impinge on the detector after passing through the sample and being dispersed by a monochromator. Each result frequency is viewed sequentially in a dispersive IR spectrometer. All frequencies are examined at the same time in Fourier Transform Infrared Spectroscopy (FTIR), which extend the capabilities of infrared spectroscopy in analyzing areas limited by dispersive instruments (Hsu, 1997).

5.2.1. Basic Principles

There are three fundamental spectrometer components in a Fourier transform system the radiation source, the interferometer and the detector. Although the radiation sources used in Fourier transform spectrometers are the same as in dispersive spectrometers, the source is water-cooled in FTIR instruments for better stability (Hsu, 1997). The key component within a FTIR system is the interferometer, and the most commonly used type is the Michelson interferometer. It consists of three components a beamsplitter, a moving mirror and a fixed mirror (Hsu, 1997). The analysis process begins with radiation from the broadband IR source. The radiation is collimated and directed into the interferometer. Then the semitransparent beamsplitter divides the beam into two parts. Half of the IR beam is transmitted to a fixed mirror and the other half is reflected off a moveable mirror. The divided beams then are combined again at the beamsplitter to pass through the sample and then impinge on a detector which will show the proportional intensity of the interfered beam. The plot of intensity versus optical path difference is called the interferogram, which will be shown as a plot of the spectrum in frequency space when the interferogram is Fourier transformed (McCluskey, 2000). Improved sensitivity and higher optical throughput with FTIR is mainly contributed by its more sensitive detectors. The two most commonly used detectors for FTIR are deuterated triglycine sulfate (DTGS) and mercury cadmium telluride (MCT), which helped increase the response times although MCT detectors need to be maintained at liquid nitrogen temperature to be effective.

5.2.2. Application of FTIR in Feed Analysis

FTIR can be applied in all materials in any forms but is separated into various series according to samples characteristics. For example, known as one of the most versatile sampling techniques, FTIR attenuated total reflectance (FTIR-ATR) accessories are applicable in

obtaining IR spectra of difficult samples such as thick or highly absorbing solid and liquid materials in energy-limited situations (Hsu 1997; Gamage et al., 2012; 2014). As a non-destructive method, FTIR provides rapid and precise measurement with good signal-to-noise ratios (Hsu 1997; McCluskey, 2000; Jonker et al., 2012; Peng et al., 2013; Zhang and Yu 2012a,b; Yu, 2012; Gamage et al., 2014). Vibrational spectroscopic techniques like FTIR are now applied commonly in physics, chemistry and biology, as they require little or no sample preparation, and are reagent-free, high-throughput and cost-effective analysis methods. Examples include investigating molecular changes in crops after genetic modification (Jonker et al., 2012; Yu, 2010), or identifying the chemical compositions of microorganisms or unknown compounds in feed or food (Kizil et al., 2002; Zotti et al., 2008; Mauer et al., 2009; Santos et al., 2010). In feed analyses, it is considered that the metabolic characteristics of feed nutrients can be determined by their related molecular structures and biopolymer conformation. However, conventional reagent-based analysis methods are not able to identify the biopolymer conformations of feeds on a molecular basis due to the harsh damage of chemicals to feed samples and related internal structure during chemical reagent-based analysis (Budevska, 2002; Yu, 2004; Liu and Yu, 2011). Recent studies showed that the FTIR-ATR technique can be used as a powerful molecular means of investigating biomolecular spectral characteristics of animal feeds, e.g. changes caused by heat processing and gene transformation, without chemical damage to the feed sample (Yu, 2010; Jonker et al., 2012; Gamage et al., 2012). By combining results of multivariate analysis [agglomerative hierarchical cluster analysis (CLA) and principal component analysis (PCA), univariate analyses and conventional statistical analysis] (Yu, 2005b), the relationship between molecular structure differences in relation to nutrition availability can

be detected (Damiran and Yu, 2011; Liu and Yu, 2011; Jonker et al., 2012; Liu et al., 2012; Gamage et al., 2012; Xin et al., 2013a,b).

5.3. Synchrotron-Based Fourier Transform Infrared Microspectroscopy (SR-FTIRM)

5.3.1. Why Synchrotron Technology?

The synchrotron is known as a particle accelerator turning electrons into light. The major components of a synchrotron include the electron gun, linear accelerator, booster ring, storage ring, beam lines and end experimental stations (Yu, 2010). Synchrotron light, also known as a full spectrum photon beam, is generated by accelerated high-speed and high-energy electrons. Beam light (100ï 1000 million times brighter than sunlight) produces synchron-based data at experimental stations where researchers collect molecular structure information to determine the biomolecular characteristics of a sample (Yu, 2010). Compared to globar-sourced FTIR microspectroscopy, synchrotron beam light has the advantages of higher speed and higher spatial resolution, and a smaller effective source size which could be as fine as 3-10 μm (Miller et al., 1998; Holman et al., 2002; Yu et al., 2003c, 2004a,b). This improves data collection efficiency and accuracy (Yu, 2010).

5.3.2. Application of SR-FTIRM in Plant-Based Food and Feed Research

Similar to FTIR, advanced synchrotron-based Fourier Transform Infrared Microspectroscopy (SR-FTIRM) is a non-destructive bioanalytical technique capable of detecting the biomaterial structure of plant-based foods and feeds at molecular and cellular levels with the advantages of brilliant light brightness, fast data collection, higher accuracy and small effective source size (Yu, 2010). SR-FTIRM is used in physics, biology, environmental science and human health research, as in FTIR. SR-FTIRM has been used to probe the structure of model

boundary lubricant layers in nanotribology to identify the effect of the chemical structure of a lubricant on the friction and wear characteristics of a system (Beattie et al., 2012). In human health research, SR-FTIRM is used to analyze the biochemical composition of neurons to diagnose pathological changes in human body (Zhu et al., 2012). SR-FTIRM is able to image the molecular chemistry of different botanical parts (Wetzel et al., 2003; Yu et al., 2007). Several studies applied advanced SR-FTIRM techniques to evaluate and screen feed quality, detect inherent structure of plant-based feeds, such as protein strucutre (Becker and Yu, 2013), such as dried distillers grains with solubles (DDGS), wheat, triticale, canola and barley, with processing-induced and treatment-induced changes in relation to rumen degradation characteristics and intestinal digestion (Yu et al., 2008; Doiron et al., 2009; Yu, 2010; Liu and Yu, 2010; Liu et al., 2012).

5.3.3. Spectral Analysis Methods—Univariate and Multivariate Analyses

There are two types of statistical analyses used to interpret spectral information of functional group bands into biological meaningsð univariate and multivariate analysis (Yu, 2006b). In univariate analysis, band intensities, integrated intensities, band frequencies and band intensity ratios are available for researchers from spectra images for quantifying spectra intensity information on a mathematical basis in relation to biological significance. Regardless of the mathematical means associated with spectral assignments for each functional group bands, multivariate analysis provides a more convenient means to distinguish differences between samples using entire spectra information with consideration of multiple properties of several objectives (Naumann et al., 2009). Multivariate analyses consist of two methods, hierarchical cluster analysis (CLA) and principal component analysis (PCA). CLA groups samples into

cluster classes based on the similarity with other spectra and displays results in dendrograms with a calculated distance matrix (Yu, 2006b). A cluster is formed by the minimal distance between two spectra at the beginning. After that, the distances between all remaining spectra are recalculated and resorted accordingly to an algorithm to generate a tree diagram (Yu, 2006b). PCA focuses on the effect of independent principal components on the spectra characteristics of samples by transforming the original data with interrelated variables into a new dataset with uncorrelated principal components (PCs) in which the first few PCs may account for 95% variance. Results are usually exhibited by two-dimensional (two PCs) or three dimentional (three PCs) scatter plots depending on how many PCs are needed to distinguish the variability. Both CLA and PCA need no prior knowledge about the spectral assignments (Martin et al., 2004; Yu, 2005b).

6. Recent Research on Molecular Structures of New Hulless Barley in Relation to Nutrient Delevery in Ruminants

Recently, four new hulless lines have been developed by the Crop Development Centre at the University of Saskatchewan. The four hulless barley lines are: zero-amylose but with very high ϐ-glucan level--CDC Fibar; low-amylose but with high ϐ-glucan level--CDC Rattan; normal-amylose and normal ϐ-glucan level--CDC McGwire; and high-amylose, high ϐ-glucan level--HB08302 (Yang et al., 2013a). Concerning the nutrient impact of hulless barley to ruminants, understanding the properties of the newly developed hulless barleys is essential for animal health and for inclusion in rations. This project aims to investigate the influence of these carbohydrate traits of the new hulless barley cultivars on chemical profiles and nutrient availability to ruminants, using chemical analysis, *in situ* rumen incubation technique, and *in*

vitro intestinal nutrient digestion to predict potential protein supply by the models of DVE/OEB system and NRC Dairy 2001. Two non-destructive spectroscopic techniques, Fourier Transformed Infrared Spectroscopy (FTIR) and advanced synchrotron-based FTIR microspectroscopy, also have been used to determine the differences of molecular structure features in the new hulless barley cultivars in relation to metabolic characteristics in dairy cattle.

6.1. Project Objectives and Hypotheses of New Hulless Barley Research Program

The objectives of this program were to: I. Determine the quantitative effect of altered carbohydrate conformation features (1) amylose level, (2) amylopectin level, (3) amylose to amylopectin ratio, and (4) ɓ-glucan level on the nutrient utilization and availability of newly developed hulless barleys in ruminants; II. Quantify the molecular structure spectral features of hulless barley with altered CHO traits in relation to nutrient availability; III. Extend information on newly developed hulless barley lines from the aspects of nutritional values and molecular structure spectral and chemical characterization. The hypotheses of this study were that: I. Newly developed hulless barleys with specific CHO traits contain higher nutrient, digestible energy and metabolizable protein content which improves nutrient utilization and availability for ruminants; II. There are structural effects on nutrient availability of different hulless barley cultivars with altered CHO traits, which could be detected by FTIR and SR-FTIR techniques. The brief results of each project as follow:

6.2. Effect of Altered Carbohydrate Traits in Hulless Barley (*Hordeum vulgare L.*) on Nutrient Profiles and Availability and Nitrogen to Energy Synchronization

In this study (Yang et al., 2013a), four hulless barley varieties with with Multi-Year Samples were studied with differences in carbohydrates traits on the basis of amylose (1 to 20%

DM) and ß-glucan (5 to 10% DM) contentò (Yang et al., 2013). Their results showed that new hulless barley lines with altered carbohydrate traits have the potential to increase rumen and intestinal nutrient availability to ruminants. The altered carbohydrate conformation of hulless barley affected hourly ED ratios, thus affecting rumen nitrogen to energy synchronization in the rumen.

6.3. Effect of Altered Carbohydrate Traits in Hulless Barley (*Hordeum vulgare L.*) on Predicted Truly Absorbed Protein Supply to Dairy Cattle

In this study (Yang et al., 2013b), the autor used various models to predict the effect of altered carbohydrate traits in hulless barley on truly absorbed protein supply to dairy cattle. According to the models, truly absorbed protein supply to dairy cattle from hulless barley consisted of absorbed rumen bypassed protein, absorbed rumen microbial protein and endogious protein loss (Tamminga et al., 1994) or contributions (NRC, 2001). The results showed that ñaltered carbohydrate traits in the hulless barley varieties have the potential to increase intestinal nutrient availability to ruminants and significantly improved the truly absorbed protein supply to dairy cattle compared to hulled barley. Hulless barley with lower amylose and higher ß-glucan level could provide greater truly digested protein in the small intestine, better synchronized available energy and N and increase metabolizable protein supply to ruminantsò (Yang et al., 2003b).

6.4. Effect of Altered Carbohydrate Traits in Hulless Barley (*Hordeum vulgare L.*) on Molecular Structure Features and Relation to Nutrient Utilization and Availability

This study (Yang et al., 2013c) aimed to ñreveal molecular structure features in the four hulless barley cultivars with altered carbohydrate traits using conventional ATR-FT/IR

molecular spectroscopy, and quantify the molecular structural features in relation to rumen degradation kinetics, intestinal nutrient digestion and predicted protein supply to dairy cattleò (Yang et al., 2013c). The results showed weak correlation between identified functional group bands and ruminal degradation kinetics and estimated protein supply from both models. The molecular structure differences of hulless barley cultivars were detected by molecular infrared-vibration spectroscopy technique and potential truly protein supply (MP) was significantly affected by protein molecular structure characteristics.

6.5. Investigating the Molecular Structure Features in Hulless Barley Endosperm Tissue (*Hordeum vulgare L.)* in Relation to Metabolic Characteristics, Using Synchrotron-Based Fourier Transform Infrared Microspectroscopy

In this study (Yang et al., 2013d), the authors used advanced synchrotron-based Fourier transform infrared microspectroscopy (SR-FTIRM) to study the effect of altered carbohydrate traits in hulless barley (Hordeum vulgare L.) on molecular strucutre feature in endosperm tissue and quantify relationship between tissue structure features detected by SR-FTIRM and metabolic characteristics in ruminants. The results showed that moleculars structure feature in terms of amide I, II, protein fine structure, ß-glucan and carbohydrate conformation in the tissue within cellular diamentions affect nutrient utilization and availability (Yang et al., 2013d).

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