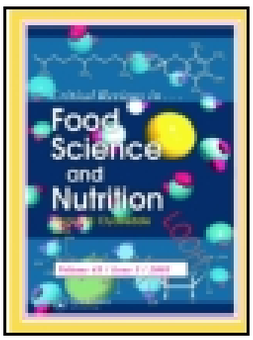

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Connection of inherent structure with nutrient profiles and bioavailability of different co-products and by-products after processing using advanced grading and vibrational molecular spectroscopy

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Running head: Connection of inherent structure with nutrient profiles and bioavailability

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ABSTRACT:

This study aims to reveal connection and implication of molecular structure with nutrient profiles, utilization and bioavailability of both conventional and new co-products from bio-energy and bio-oil processing using grading and vibrational molecular spectroscopy with chemometics including univariate and multivariate techniques. The study focused on strategies to improve the utilization of the conventional and new co-products through chemical and heat processing treatments as well as the relationship of the molecular structural changes to nutrient bioavailability. The updated methods advanced molecular spectroscopy techniques with grading NIR, Globar FTIR, ATR-FTIR and Synchrotron SRFTIRM to study feed molecular structures were reviewed. This study provides an insight and a new approach on how to use grading and vibrational molecular spectroscopy to study molecular chemistry and molecular structure and molecular nutrition interaction.

Keywords: Molecular chemistry, Molecular nutrition, Molecular structure, Grading and vibrational spectroscopy, Processing impact, Technological treatments, Co-products and by-products

I. INTRODUCTION

Manufacturing oils from oil seeds is one of the most important industries in the world. This is due to the high demand of oils and increasing demand for fuel for the industry. Co-products from processing the seeds, which can be used for animals feed, such as conventional co-product (canola meal) from bio-oil processing of canola seeds, become available (Canola Council of Canada, 2015), new co-product (carinata meal, not registered as animal feed by Canadian Food Inspection Agency) from bio-fuel processing of Brassica carinata seeds (Edwards et al., 2011), and co-products of pea screening from the pulse processing industry (Xin and Yu, 2013a; Ban, 2016; Ban et al., 2017).

Canada is the first country to produce canola oil (15 million tonnes of canola seeds per year; Canola Council of Canada, 2015). Saskatchewan has the largest production of canola oil in Canada (Thiyam-Hollaender et al., 2013). Canola meal is a great palatable protein source (about 36-39% crude protein (CP); furthermore, canola meal has a great source of amino acid (Canola Council of Canada, 2015). Also, the new co-product (carinata meal) is an excellent protein source (approximately 48% CP; Xin and Yu, 2013) and amino acid (Guevara, 2017). Canada is the second country to produce peas. Peas are a source of protein (approximately 24%) and energy (high level of starch 46% dry matter; Hickling et al., 2003).

Due to the relatively high level of the degradability (rate and extent) of canola meal (Canola Council of Canada, 2015), carinata (Ban, 2016; Ban et al., 2017), and peas (Yu et al., 2002; Kudlinskiene et al., 2016), it is important to slow down their degradation in the rumen to protect protein and amino acids (AA). Heat treatment and chemical treatment are the most common methods to maximize the utilization of protein and protected the AA. It is important to use the heat treatments to improve the nutritional,

chemical, hygienic, physical, and other animal feed characteristics (Lević et al., 2010). Heat treatment could modify the amino acid residues of proteins by reacting with other compounds to decrease ruminal protein degradation. There are different types of heat treatments, such as dry roasting, steam flaking, pelleting, extrusion etc. (Jansen, 1991; Riaz, 2007). The chemical treatments, such as formaldehyde (Crooker et al., 1983), tannins (Chung et al., 2013), lignosulfonate (LSO_3) and xylose (McAllister et al., 1993), could also decrease rumen degradable protein in different rations.

During the pelleting process, it is essential to know the impacts of time and temperature applied during feed processing on feeding value and bioavailability of co-products. But using the wet chemistry analysis could not evaluate the inherent structure of the feed because of the strict effect of chemical reagents that could destroy them (Dixon and Coates, 2009). Wet chemistry analysis procedures could not clarify the variations between different feeds in terms of their bioavailability in ruminants (Yu, 2004; Dixon and Coates, 2009). Therefore, evaluating the inherent molecular structure of feed ingredients and detecting their changes during feed processing could be an assistance to researchers to explore the effects of feed processing on feed ingredients on a molecular basis (Yu, 2004; Dixon and Coates, 2009). The near infrared red spectroscopy (NIRS) and Fourier transform infrared spectroscopy (FTIR) have been used in feed analysis as a rapid, non-destructive, and relatively accurate tool to distinguish the inherent feed structures (Xin and Yu, 2013b; Xin et al., 2014).

This article aims to systematically review the production, processing, and utilization of biofuel, bio-oil processing, and pulse co-products (carinata meal, canola meal, and pea screenings) and discuss the most important strategies involved in

enhancing the utilization of protein in dairy cows. Studying of structural changes of feed on a molecular basis using molecular spectroscopy will be also discussed in this article.

II. DEVELOPMENT AND PRODUCTION OF CANOLA AND CARINATA CO-PRODUCTS

Canola is Canada's main crop, currently ranked amongst the top three oilseeds worldwide (Thiyam-Hollaender et al., 2013). Canada has the highest production of canola oil worldwide; Canada produces about 15 million tonnes of canola seeds per year (Canola Council of Canada, 2015). Saskatchewan is the first Canadian provincial for production of canola oil (Thiyam-Hollaender et al., 2013).

Canola is an offspring of rapeseed, bred through traditional plant breeding between *Brassica napus* and *Brassica campestris*/*rape* (Newkirk, 2009). This crossbreeding resulted in decreasing two-negative components from the rapeseed plant (Newkirk, 2009). The most common species of canola in western Canada are *Brassica juncea* and *rapa* (yellow-seeded) and *Brassica napus* (brown-seeded) (Newkirk, 2009).

Brassica carinata is a species of Brassica family, created from a hybridization between *Brassica nigra* and *Brassica oleracea* (Warwick et al., 2006). It is common called Ethiopian mustard (Rakow, 2004). Agriculture and Agri-Food Canada (AAFC) have successfully grown *Brassica carinata* in the mid-1990s in the dry prairies of Western Canada (Alberta, Saskatchewan, Manitoba; Rakow and Getinet, 1998; Taylor et al., 2010; Ban and Yu, 2016). This crop has been found to produce high yield with great oil content in these areas, regardless of heat and drought; in addition, this crop shows good salinity tolerance and blackleg resistance (Rakow and Getinet, 1998; Taylor et al.,

2010; Ban and Yu, 2016). Canada has two species of carinata bred by AAFC. The AAC A100 was released in 2012, and small quantities of AAC A110 were available in 2015 (Practices, 2015).

2.1. Features of canola and carinata meal from bio-energy and bio-oil processing

Canola meal is divided into the yellow-seeded and the brown-seeded species. The protein content in the yellow-seeded species is higher than the protein content in the brown-seeded species (Theodoridou and Yu, 2013b). Canola meal is a great palatable protein source for ruminant animals. By comparing a mash diet feed to the heifers, canola meal vs soybean meal, consumption of the canola meal in the first three minutes (221 g) is more than the consumption of the soybean meal (96 g; Newkirk, 2009). Canola meal contains about 36-39% CP (N×6.25, %; Canola Council of Canada, 2015).

The first negative component of canola meal was the glucosinolates, which decreased to a lower level (< 30 μmol/g). The second negative component is the erucic acid in the oil part, believed to be toxic in high doses (Canola Council of Canada, 2015).

AAFC carinata seed comprises approximately 44% oil and 28% CP (Resonance Carinata, 2012), and it has high level of erucic acid (>30% of total fatty acids; Warwick et al., 2006). The high level of erucic acid in carinata seeds is utilized in bio-fuel processing (Cardone et al., 2003); however, the high level of erucic acid in carinata seeds is harmful for humans, who must consume no erucic acid (Getinet et al., 1994). The yellow seeds of carinata have a higher protein content than the brown seeds of carinata (Simbaya et al., 1995). Carinata meal is a great source of crude protein, which could reach about 48 %CP (Xin and Yu, 2013b).

2.2. Conventional canola meal and new carinate meal processing

The co-product from the bio-oil processing of canola seed is canola meal. Processing of canola seeds is called pre-press solvent extraction (Canola Council of Canada, 2015; Newkirk, 2009), which includes the following steps: (1) cleaning the seeds from the dockage materials and crush those seeds; (2) drying the seeds at approximately 35 to 45ºC for 35 to 45 min before flaking; (3) flaking the seeds by roller mills to rupture the seed coat without damaging the quality of the oil; (4) cooking the flakes at 80-105 ºC for 15-20 min; (5) pressing the cooked seeds flakes to remove as much oil as possible from the cooked canola (removing about 50-60% of the seed oil content) to produce the presscake. Because the pressing process cannot remove all oil from the seed (the remain oil 18-20%), solvent extraction is performed to remove the remaining canola presscake; (6) solvent extraction includes the following steps: first, the cake is placed in the extractor, then the cake is flooded with solvent or miscella, then a sequence of pumps sprays the miscella over the presscake with each stage using a successively "leaner" miscella to increase the ratio of solvent to oil. Afterwards, the solvent infiltrates by gravity through the cake bed, diffusing into and soaking the cake fragments. Finally, the marc (hexane-saturated meal) that leaves the solvent extractor, after a fresh solvent wash, contains less than 1% oil (Canola Council of Canada, 2015; Newkirk, 2009).

The co-product from bio-fuel processing of Brassica carinata seed is carinata meal (Edwards et al., 2011). During the bio-fuel processing of carinata, the oil in the seeds is

extracted by crushing and filtrating the seeds by conventional crush infrastructure (Edwards et al., 2011).

2.3. Utilization of canola and carinata meal in ruminant livestock system

The nutrient composition of canola meal includes: dry matter (DM) 88 %; CP 36.7 % DM; neutral detergent fiber (NDF) 25.4 %DM; acid detergent fiber (ADF) 16.2 %DM; lignin 5.8 %DM; ether extract 3.3 %DM; starch 5.1 %DM; ash 6.7 %DM. Canola meal has a great source of the amino acids such as lysine 5.92%CP, histidine 3.39 %CP, methionine1.945%CP, cystine2.31%CP, and threonine 4.27%CP (Canola Council of Canada, 2015).

It is important to provide the dairy cows with an adequate level of rumen degradable protein (RDP) and rumen undegradable protein (RUP) in the diet (NRC, 2001). The RDP level is important to maximize the microbial protein synthesis (NRC, 2001). It has been reported that any decrease in the RDP content of the ration below the recommended 10% of DM (NRC, 2001) could reduce microbial protein synthesis due to a lower ruminal NH3-N and total free amino acids (Brito, Broderick et al., 2007). The RDP of canola meal had been reported to range from 47.5% to 70% (Mustafa et al., 1996; Piepenbrink and Schingoethe, 1998).

There is no limit regarding the inclusion level for canola meal in dairy cow ration (Canola Council of Canada, 2015). For instance, it has been found that milk production of dairy cows was maintained for over 44kg, with diets that contained 20% canola meal (Swanepoel et al., 2014). Brito, et al. (2007), replacing 12% soybean meal and 4.5% corn

meal with 16.5% canola meal in diets for high-producing cows. Dry matter intake increased by 0.3 kg, while milk yield increased by 1.1 kg.

Brito and Broderick, (2007) showed adding 16.5% of canola meal instead of soybean (12%) and corn meal (4.5%) into diets led to increasing the milk yield of dairy cows by 1.1kg milk/d.

The nutrient composition of carinata meal includes : DM 88.5 %; CP 44.3 %DM; NDF 23.7 %DM; ADF 16.3 %DM; lignin (ADL) 5.9 %DM; ether extract 2.1 %DM; starch 2.3 %DM; non-fibrous carbohydrate 24.5 %DM; ash 7.6 %DM; glucosinolates 11.5 µmol/g (Ban, 2016). Although there is a high level of glucosinolates in carinata seeds, increasing heat or time under heating during the bio-fuel processing of carinata seeds could decrease the glucosinolates content (Guevara, 2017). It has been found that the canola meal pellet has relatively higher levels of total glucosinolates than the carinata meal pellet (4.76 vs. 4.28 µmol/g; Guevara, 2017). Carinata meal has a rich source of amino acids, containing arginine 10.8 %CP, glutamic acid 20.7 %CP and proline 6.5 %CP, but lower in isoleucine 4.1 %CP, leucine 6.8 %CP, valine 4.9 %CP, tyrosine 2.5% CP, lysine 4%CP, and methionine 1.8 % CP compared with canola meal (Ban, 2016).

The carinata meal has been reported to have a higher RDP level compared with canola meal (75 vs. 60 %CP; Ban, 2016). The rumen degradation rate of potential degradable fraction of CP is much higher in carinata meal (ranged from 33 to 22 %/h) than canola meal (ranged from 11 to 17 %/h; Ban, 2016; Xin and Yu, 2014).

III. DEVELOPMENT AND PRODUCTION OF PULSE PROCESSING CO-PRODUCT

Pea (*Pisum sativum L.*) is a member of the Leguminosae family (Khorasani et al., 2001). Canada has increased its production of peas and become the second country for production of peas (Hickling et al., 2003). Alberta has the highest production of peas in Canada. Canada uses peas for human consumption and animal feeding (Hickling et al., 2003). Saskatchewan grew about 64% of the dry pea crop and 90% of chickpea crop of the total production in Canada in 2014 (Saskatchewan Pulse Growers, 2015).

3.1. Pulse peas processing and their by-products

The co-product from the pulse processing industry is pea screening that resulted after cleaning foreign materials (Yu et al., 2002). The material obtained is dockage (the material removed after cleaning includes chaff, other grain, weed, or inseparable seeds, and/or pieces of a stem). After cleaning dockage, it will produce three products, including No. 1, No. 2, and No. 3. Refuse screenings are No. 3 product. No. 1 and No. 2 products are relatively high in value (McKinnon, 2015). Peas are a source of protein and energy (a high starch level).

3.2. Utilization of pulse peas and by-products in ruminant livestock system

The CP in field peas is approximately 24% (Fonnesbeck et al. 1984). The nutrient composition of peas includes: DM 90 %; CP 23 %DM; crude fiber (CF) 5.5 %DM; starch 46 %DM; ash 3.3 %DM (Hickling et al., 2003). It contains a high level of starch, about 47.8 % (Valentine and Bartsh, 1987). Peas have high levels of essential amino acids, such as histidine 2.52 %CP, methionine1.03 %CP, cystine1.55%CP, and threonine 3.59%CP; also, by comparing the pea protein with the cereal grains and most oilseed meals, pea

protein is the highest in lysine (6.84% CP). Also, peas have appropriate amino acid balance (Hickling et al., 2003).

The RDP of peas is high, roughly estimated to be about 78% RDP as a % of CP. It could meet microbial N requirements (Kudlinskiene et al., 2016). The remaining moderate amount of RUP with a good AA (Lys and Met) balance is good for milk production in high-producing dairy cows (Kudlinskiene et al., 2016). Previous study showed replacing soybeans with peas in dairy cows diets resulted in increasing milk fat and protein content, but it had a negative effect on milk yield (Kudlinskiene et al., 2016).

IV. STRATEGIES TO IMPROVE THE UTILIZATION OF CO-PRODUCTS OR BY-PRODUCTS THROUGH TECHNOLOGICAL TREAMENTS

It is important to slow down the degradation (extent and rate) of ruminal degradation of feed proteins for many reasons (Schwab, 1995). For example, there are many feeding situations where the ration does not provide acceptable amounts of absorbed AA supply comparative to the absorbed energy supply (Schwab, 1995). This could take place due to the following reason; first, several feed components in the ration contain an inadequate amount of RUP compared to RDP; second, diet shortage in fermentable carbohydrates or RDP are required for microbial protein synthesis; third, providing dairy cows with fat supplement rich in metabolizable energy but not for microbial cell growth (Schwab, 1995). In addition, if feeding high quality forages occurs that contain a high level of RDP, it is important to provide the diet with adequate amount

of RUP to balanced RDP and RUP (Schwab, 1995). The utilization of rich undegradable protein sources would enhance the efficiency of NPN supplements and have less dependence on more degradable protein sources of true protein for microbial protein synthesis in the rumen (Schwab, 1995).

There are many approaches to raising the proportion of RUP in the diet. One approach is to provide dairy cows with high-protein co-product feeds, such as corn gluten, meat, hydrolyzed feather, fish, and blood meals (Chalupa, 1975; Waldo, 1977; Kaufmann and Liipping, 1982; Broderick et al., 1991). The issues of using these co-products is their higher cost and lower commercial availability, uniformity, AA balance, and intestinal digestibility and palatability of product dictate their use. Another approach is artificially decreasing the rate of ruminal degradation of high protein sources with a good AA profile and better intestinal availability, but which are rapidly degraded (Chalupa, 1975; Waldo, 1977; Beever and Thomson, 1981; Kaufmann and Liipping, 1982; Broderick et al., 1991). This approach would have the advantage to protect the AA from rumen degradation and maximize their utilization in dairy cows (Chalupa, 1975; Waldo, 1977; Beever and Thomson, 1981; Kaufmann and Liipping, 1982; Broderick et al., 1991). The following section will highlight the most common methods successfully used to maximize protein utilization and protect the AA.

4.1. Heat-related treatments to improve nutrient utilization

It is important to use heat treatments to improve the nutritional, hygienic, chemical, physical, and other animal feed characteristics (Lević et al., 2010). Heat treatment can modify the amino acid residues of proteins by reacting with other

compounds or through cross-linking, and this reaction decreases ruminal protein degradation, protecting the proteins from hydrolytic activities of rumen microbiota (Petit et al., 1999). Therefore, heating could provide a more gradual release of feed in the rumen, enhancing the digestibility of nutrients and the milk production of dairy cows (Petit et al., 1999).

There are different types of heat treatment, and each type is different in its heat source, structure of the system, and its efficiency. The temperature and the heating time are the two main mutual factors among all heat treatments (Yu et al., 1998). Most procedures that are used are hydrothermal treatments. The main types of heat treatments in animal feed processing include dry roasting, steam flaking, pelleting, extrusion etc. (Jansen, 1991; Riaz, 2007).

4.1.1. Dry roasting

Roasting is a dense dry heating of raw material under temperature 110 - 170°C (Kumar et al., 2015). Its temperature depends on the device used and the anticipated product quality. If the temperature of roasting is too high, it could lead to reducing the availability of nutrients in the surface layers of grain (Kumar et al., 2015). One of the main objectives of dry roasting is to improve the energy availability. It deactivates enzymes and inhibiting factors, enhancing the feeding value of the feedstuff (Kumar et al., 2015).

The effect of roasting on feed utilization is more pronounced in ruminant studies compared to non-ruminants, where it has been reported the roasting had decreased the RDP of barley, corn, oats, and wheat in ruminant's diets (McNiven et al., 1994). The

roasting of soybean meal increased the RUP and decreased protein degradation (rate and extent) in the rumen (McNiven et al., 1994). The reduction of protein degradation in the rumen is attributed to the Maillard reaction between free amino groups and sugar aldehyde group (Dhiman et al., 1997). The roasting process had been found also to increase the starch gelatinization in corn and decrease the nitrogen solubilization in the ruminant, resulting in improved microbial synthesis, increasing body weight gain and feed efficiency of utilization in calves (Sinclair et al., 1993; Abdelgadir et al., 1996). Dry roasting of faba beans was effective in shifting the CP degradation from the rumen to the intestine, hence, decreasing nitrogen losses in the rumen (Yu et al., 1998).

Numerous protein sources that were subjected to roasting processing has been found to reduce or to deactivate anti-nutritional factors. Roasting processing can modify the structure of protein (denaturation), causing the deactivation of protein sources' anti-nutritional factors (i.e., trypsin inhibitors, lectins, etc.), because these proteins require their structure integrity to employ the effects (Van der Poel et al., 1990).

Although the roasting is a typically inexpensive method as a heat treatment, uneven heating has often resulted in inconsistent results. Some studies (Scott et al, 1991) detected no effect of increased milk production when cows were fed roasted soybeans (meal or raw soybeans). But other researchers (Faldet et al., 1991) observed improved milk production when feeding roasted soybeans (meal or raw soybeans).

4.1.2. Steam flaking

Steam-flaking is a widespread processing system. Grain is steamed for 30 to 60 min in a steam chamber to increase grain moisture to 20% and then flaked between large

rollers preheated to obtain a specific desired flake density (usually 309 to 386 g/L; Smoje et al., 1996). The rollers become hotter as the steamed grain goes through, which is important in the flaking process. The extent of processing (flaking pressure) increases as flake density decreases. The quality of steam-flaking grain is routinely measured by flake density and laboratory methods (enzymatic starch hydrolysis or percent starch gelatinization (Smoje et al., 1996; Sredanović et al., 2007).

The main mode of action of steam flaking on feed digestibility is a consequence of disruptions of the protein matrix surrounding the starch granules in the grain endosperm and disorganization of the starch granules (Palić, 2008). Steam-flaked cereals grains are more extensively used in finishing cattle diets and have consistently improved feed efficiency by increasing starch utilization (Heimann, 1999). Steam-flaking of corn could enhance the milk protein yield of lactating dairy cows with maintaining the milk fat yield, compared with dry-rolling of sorghum or steam-rolling of corn (Theurer et al., 1999). The higher milk yield with feeding steam-flaking grain is attributed to a high digestion of starch in rumen, increasing the absorption of AA and other nutrients by the mammary gland (Theurer et al., 1999).

4.1.3. Pelleting

Pelleting is a feed processing technology, where the smaller particles of feedstuff are agglomerated into larger particles by using moisture, heat, and pressure (Falk,1985). The pelleting process includes the following steps, first, crashing the larger feed portion into smaller feed portion and passing the mixed ground mash through the conditioner. The mash is exposed to some pre-treatments before granulation, such as mixing with

molasses or fats, conditioning with steam to enhance the binding ability, softening the feed, denaturing protein, and gelatinizing starch. Then, the feed is passed to the pelleting chamber and pressed through a die to make pellets. The temperature of pellets after leaving the die is generally higher (60 to 95ºC). Finally, pellets are cooled with ambient air (Thomas and van der Poel, 1996).

The good physical quality of a pellet is characterized by the ability of the pellet to tolerate the fragmentation and abrasion during the mechanical and the pneumatic handling without breaking up the feed or without generating a high proportion of fine (Cramer et al., 2003). The pellet durability index (PDI) and pellet hardness are the most two parameters in use to estimate the physical quality of pellets (Thomas and van der Poel, 1996). The PDI can be measured by the "Ptost" procedure (Thomas and van der Poel, 1996) or by using the Holmen pellet durability tester. In the Holmen pellet durability tester, the air is used to create abrasion of the pellets opposite the tumbling action (ANAC, 2013). Pellet hardness is another measurement of pellet quality and can be defined as the necessary force to crush a pellet. The "Kahl" device is used to measure pellet hardness (Abdollahi et al., 2013).

Using pellets in the feed industry and animal nutrition has many benefits; by increasing the bulk density and transfer efficiency of feed more than mash feeds (Thomas and van der Poel, 1996), the pelleting process could reduce microbial bioactivity, and it could improve the health status of animal feed (Abdollahi et al., 2013), increasing feed palatability (Abdollahi et al., 2013), inhabiting the adverse effect of anti-nutritional factors (i.e. glucosinolates) by making them inactive (Abdollahi et al., 2013), improving rumen crude protein degradation in dairy cows (Goelema et al., 1999), and increasing

resistant of starch degradation in the rumen (Tamminga and Goelema, 1995; Huang, 2015).

4.1.4. Extrusion

The processing of extrusion includes pushing the feedstuff through the barrel by using means of screws of several formations and then pressing them through the die at the end of the barrel (Lević et al., 2010). The requisite of extrusion processing exposes the feedstuff to high temperature in a short time, where extrusion processing includes heating the feed in 155°C for 43 seconds by using a Multi-purpose twin-screw extrusion system (Lević et al., 2010). Due to the different pressure between the inside of the extruder and the external environment, it will lead to partial evaporation of water at the exit point and the development of the product (Lević et al., 2010). However, extrusion processing is a complex technology, but it is very flexible in the same time it provides the processing of a variety of several raw material such as soybean, sunflower, rapeseed, wheat, corn, barley, oats, beans, peas etc. (Smoje et al., 1996).

Extrusion could protect dietary protein from microbial degradation in the rumen. For example, extrusion of oilseeds, such as canola seed, leads to increases in the production of milk in dairy cows (Ingalls and Grumpelt, 1987). In addition, extrusion of lupin seeds could reduce the degradability of crude protein in the rumen, enhancing the value of nutrition seed, such as the source of undegraded protein (Cros et al., 1992). Studies on Extrusion processing reported ineffective in improving the post-ruminal supply of amino acids from flaxseed-based diets (Mustafa et al., 2003)because of increasing the ruminal CP digestibility and reducing the quantity of CP supply for post-

ruminal digestion for cows fed diets of extruded flaxseeds (Mustafa et al., 2003). Nevertheless, the impact of extrusion processing on CP digestion in the rumen could vary if the processing procedure modified, particularly the temperature used for the processing procedure and resident time during the processing, which may alter the effect of extrusion on CP digestion for different flaxseed (Mustafa et al., 2003).

4.2. Chemical treatments to improve nutrient utilization

Many chemical factors lead to decreased RDP of protein in the different ration. Many studies have been attempted to increase the proportion of RUP reaching the small intestine of ruminants by treatments with formaldehyde (Crooker et al., 1983), tannins (Chung et al., 2013), lignosulfonate (LSO_3), and xylose (McAllister et al., 1993).

4.2.1. Lignosulfonate chemical compound

The lignosulfonate (LSO_3) is a feed additive that can be used as a pellet binder in animal feed to improve pellet quality (Corey et al., 2014). Lignosulfonate (Calcium Lignosulfonate) has been used industrially in several applications. Windschitl and Stern (1988) displayed that adding lignosulfonate to soybean meal, followed by heating at 90-95 C for 45 min, decreased CP digestion in the rumen. Canola meal treated with 7% LSO_3 heated to 100°C increased rumen escape protein content (McAllister et al., 1993; Stanford et al., 1995). In addition, the treatment of canola meal with 5% LSO_3 heated to 100°C for 60 min and 25% moisture (moist heat) resulted a higher reduction in effective rumen degradability of CP than heat treatment without LSO_3 (McAllister et al., 1993). Other studies (Mansfield and Stern, 1994; Stanford et al., 1995) reported the OM

digestibility of soybean meal or canola meal were not affected by LSO_3 supplementation. Güçlü (1999) reported that LSO_3 supplementation decreased DM digestibility of cottonseed meal. Supplementation of LSO_3 would have a beneficial effect in inhibiting the adverse effect of antinutritional factors in feed (Guevara, 2017) has found adding lignosulfonate to blend pelleted products of canola meal or carinata meal could reduce the total level of glucosinolates in blend pelleted products.

4.2.2. Tannin chemical compounds

Tannins were primarily considered anti-nutritional biochemicals due to their adverse effects on feed intake and nutrient utilisation (Kumar, 1990). But in recent years, they have been recognised as useful phytochemicals for modulating rumen microbial fermentation (Kumar, 1990). Many researches have reviewed the effects of tannins on ruminants, which focused mostly on adverse effects of tannins on animal systems with some discussion on the beneficial effects on prevention of bloat and protein degradation (Mueller-Harvey, 2006; Waghorn, 2008). Recent reviews by Mueller-Harvey (2006) and Waghorn (2008) discussed little on methane inhibition by tannin- containing forages. Since the latest reviews, a great number of studies have been published on the effects of tannins on inhibition of methanogenesis and decreasing the protein degradability in the rumen, which justify a fresh appraisal of the present scenario on the influences of tannins on rumen metabolism and animal performance.

The tannins are divided into condensed tannins and hydrolyzed tannins (Khanbabaee and Ree, 2001). Though, as a rule, hydrolysable tannins have a more capability to bond with feed protein, they may be degraded in the rumen enzymatic

hydrolysis into several structural units (mainly phenolic acids), with a lower capacity of attachment to feed protein (Khanbabaee and Ree, 2001). Instead, condensed tannins have a higher stability in the rumen compared to hydrolyzed tannins, where they have higher resistance to ruminal enzymes. The stability of condensed tannins are attributed to their high molecular weight; meanwhile, this could decrease their capacity to bond with feed proteins when compared to hydrolysable tannins (Frutos et al., 2004). Frutos et al., (2004) found the condensed tannins of quebracho decreased the degradability of soybean meal significantly when compared to commercial tannic acid. Other studies by Frutos et al., (2000); Hervas et al., (2000) treated soybean meal with different doses of tannic acid or commercial quebracho condensed tannins extract, and they found both treatment doses reduced the extent of crude protein degradation in the rumen.

V. ADVANCED GRADING AND VIBRATIONAL MOLECULAR SPECTROSCOPY TECHNIQUES

The electromagnetic spectrum comprises the following rays based on wavelengths from short to long, the gamma rays, soft X-rays, hard X-rays, ultraviolet, visible light, near infrared, mid-infrared, far infrared, radio waves, and microwaves. Gamma rays have the strongest diffusion capability and greatest frequency. Soft X-rays are utilized to analyze the classification of several layers of plant tissues; on the other hand, X-rays are commonly utilized in science and medical areas (Karunakaran, 2009; Yu, 2012a). Near infrared (NIR) and mid-infrared could evaluate the quality of feed. There are many molecules in the mid-IR spectral region (ca. 4000–400 cm^{-1}) with strong characteristic

vibrational transitions, particularly in the wave length ranged between ca. 1800 and 800 cm^{-1}, which is called the "fingerprint region" (Yu, 2004; Liu, 2009).

The internal molecular structure energy of plants is made up the electronic, vibrational energies, translational, and rotational (Ying and Yu, 2016). Normally, the functional groups (protein, CHO, and lipids) in the organic molecules are vibrated separately, and they are weakly interacted with each other. But with interfering electromagnetic radiation from the outside, it could activate the non-equilibrium phase and generate energy changeovers between the vibrational energies and rotational energies, which could cause the absorption of the IR (Ying and Yu, 2016). As the ratio of transmission IR to absorption IR varies between molecules, IR spectrometry could be successfully used to categorize molecular functional groups (protein, CHO, and lipids; Yu, 2004).

5.1. Study molecular structure of feed using near infrared spectroscopy

The near infrared spectrometer (NIRS) with grading capacity includes different components: 1) tools for selecting wavelengths, 2) source of light, 3) part for placing the sample, 4) computer for processing the collected signals and data, and 4) detector for collecting the reflected radiation. When the sample is irradiated, the incoming radiation is reflected and absorbed, and part of the diffuse reflected radiation that goes back to the detector is evaluated (Jancewicz, 2016).

The grading near infrared spectroscopy could be used to predict the chemical composition of unknown samples by utilizing statistical measures and grade the quality of various biological samples. Multivariate linear regression is usually used as statistical

measures for the sample measured using NIRS (Jancewicz, 2016). A multivariate statistical model has been established to explain the association between the most important chemical components (i.e. protein, CHO and lipids) and NIR spectral absorbance that correlated to the chemical components by using Beer's Law (Shenk and Westerhous, 1993). Afterwards, the statistical model could be used to predict the chemical composition of any unknown samples that belong to the same population (Shenk and Westerhous, 1993).

In the animal feed production industry, NIRS analysis is expanded, and the calibrations are constantly being updated for feed components, such as DM, protein, starch, fat, and fiber content (available neutral detergent fiber and indigestible neutral detergent fiber contents) of all feed grain types, grain screenings, many other co-products, and distiller's grains (Jancewicz, 2016). The technology could lessen the costs of feed by developing the formulation of ration and enhanced the capability of the industry to predict the value of co-product feeds. Collaboration between technicians, NIRS researchers, and feed mill operators has enabled calibration equations to be continuously improved and updated and has been expanding to consider more sample populations (Jancewicz, 2016).

Even though the NIR spectroscopy (750–2500 nm) is commonly used in many feed industries, especially for monitoring the grain quality (Wang and Paliwal, 2007; Shi and Yu, 2017), the NIR technique generally produces weak and broad peaks when measuring the blend bands and overtones of fundamental vibrations (Shi and Yu, 2017). Most peaks in the mid infrared (MIR) region are sharp and narrow because of the molecular vibrations of matrix composites (Yang and Irudayaraj, 2001). The degree of

resolve of MIR spectra is much greater than the degree of resolve NIR spectra (Shi and Yu, 2017).

5.2. Study molecular structure of feed using vibrational FTIR spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy are based on the basics of the mathematical Fourier-transformation method and interferometry (Stuart, 2004). Every FTIR machine is based on an interferometer (Smith, 2011). The most common interferometer is Michelson interferometers, which consists of four arms. The top arm composed a collimating mirror and the infrared source. The bottom arm includes a fixed mirror. The left arm contains a moving mirror. The right arms, where the samples and the detector are located, while a beam splitter is placed in the middle of the interferometer (Smith, 2011). The IR beam from the infrared source emits to the collimating mirror and then produces parallel rays across the beam splitter (Smith, 2011). After that, the beam is split by the beam splitter to two beams (one beam (50%) moves to the fixed mirror and the other one (50%) moves towards the moving mirror; Smith, 2011). The reflected beams by the steady and moving mirrors will encounter at the beam splitter and recombine to form a final beam. The combined beam will pass through samples after leaving the interferometer and receiving a combined beam by the detector to produce an interferogram (Smith, 2011).

The Fourier transformation method could process the interferogram and could analyze the frequencies (Stuart, 2005; Smith, 2011). By comparing the FTIR with the other types of infrared instruments, FTIR can provide fast, easy, and exact gauges with

good signal-to-noise ratios (SNRs). FTIR needs little sample preparation, saving labor. FTIR lets high throughout and multiplex scans (Stuart, 2005; Smith, 2011).

Recently, in feed science, it has become important to utilize FTIR to reveal structural changes of molecules and conformation of biopolymers between several types of feed stuff in relation to the nutrient values and nutrient utilization (Theodoridou and Yu, 2013; Xin and Yu, 2013c). For instance, FTIR with attenuated total reflection (ATR) could reveal the variances between the components of feed, feed-based crop varieties, impact of gene modification and processing of feed on spectral characteristics, and impact of protein and CHO degradation in rumen related structure (Theodoridou and Yu, 2013; Xin and Yu, 2013c).

5.3. Study molecular structure of feed using ATR-FTIR spectroscopy

The feeding value and fermentation features of animal feedstuff have been reported to be influenced by inherent molecular structure (Yu, 2012b). The infrared spectroscopy can detect and identify molecular information of feed (Yu, 2012b). Molecular spectroscopic methods, such as Fourier transform infrared spectroscopy with attenuated total reflectance (ATR-FTIR), is a rapid, direct, non-destructive, and non-invasive bioanalytical technique used to detect infrared spectrum of absorptions or emissions of liquid, gas, or solids (Smith, 2011). The ATR-FTIR comprises three essentials spectrometer elements: (1) the radiation source; (2) the interferometer; (3) the detector (Hsu, 1997).

In recent years, studies in animal feed science reported the success of ATR-FTIR to reveal structural changes of molecules for different types of feed in nutrient values,

nutrient utilization, and availability (Abeysekara et al., 2013; Peng et al., 2014; Xin and Yu, 2013a, 2013b). For instance, the ATR-FTIR has been used to identify the molecular structural for different crop varieties, feed ingredients, and to study the impacts of feed processing on protein- and carbohydrate-related structures (Abeysekara et al., 2013; Peng et al., 2014; Xin and Yu, 2013a, 2013b).

There are two common methods for spectral analysis, the univariate and the multivariate analyses (Yu, 2005, 2012b). The univariate analysis uses a mathematical parameter related to spectra, such as band height and area intensities, band frequencies, and the band intensity ratios (Yu, 2012b). The univariate analysis can be used to correlate with the chemical and biological features of feeds (Yu, 2012b). The drawback of the univariate analysis is its limited ability to analyze and compare massive spectral data. The multivariate analysis is favored (Yu, 2005). The multivariate analysis includes the hierarchical cluster analysis (CLA) and principal component analysis (PCA; Yu, 2005c).

The protein metabolism in dairy cows could be affected by type of proteins and hydrolytic enzyme activities in the gastrointestinal tract and protein molecular structure (Yu and Nuez-Ortín, 2010; Huang et al., 2017). The protein secondary structures comprise α-helix and β-sheet (Marinkovic and Chance, 2002). The primary molecular structure of protein (amide I and amide II and their ratio) and secondary structure of amide I (α-helix and β-sheet) may affect protein utilization, protein bioavailability, and digestive behavior in ruminants (Yu and Nuez-Ortín, 2010; Huang et al., 2017), mostly because molecular structure of protein influences accessibility of rumen bacteria and gastrointestinal tract enzymes, which affect protein values and protein availability (Yu and Nuez-Ortín, 2010).

5.4. Studying molecular structure of feed with synchrotron radiation-based Fourier transform infrared microspectroscopy

Due to the wavelength range of radiation light and the gap size of equipment, some shortages of the globar light source could be observed, particularly when implementing examinations at the cellular level (Raab and Martin, 2001; Yu, 2004; Ying and Yu, 2016). Some globar light sources, such as unsatisfied signal-to- noise ratio and diffraction, could be reduced by using the application of synchrotron light. The synchrotron of infrared photons is 100-1000 times brighter than globar source. Besides, it is the only white source in which it could transfer the total range of IR wave length from near-IR to far-IR region (Raab and Martin, 2001; Yu, 2004; Ying and Yu, 2016). The researchers use a microscope to focus the radiation light onto small portions of the samples and separate the histological structures in the sample (Doiron and Yu, 2015).

The synchrotron radiation-based Fourier transform infrared microspectroscopy (SFTIRM) is created from gathering FTIR spectroscopy, microscopy, and a synchrotron light source (Yu, 2004). The SFTIRM could provide great information on the structure, composition, chemistry, and environment of specific tissue in the same time (Yu, 2004). The SFTIRM is utilized for studying molecular chemistry at a cellular or subcellular level, without breaking down the inherent structure of biological tissues (Yu, 2004). But there are limited studies about the relationship between the chemical composition and bio-availability and essential structural characteristics of the samples of feed.

The SFTIRM could be applied extensively in the research area as a greater spectroscopy technique (Shi and Yu, 2017). To date, the chemical composition of several

ingredients has been centralized and recognized at cellular and subcellular levels by many interdisciplinary studies. For example, SFTIRM is used to discover the ultrastructure alterations and the combination of single cells (Whelan and Bell, 2015). In agricultural research, the SFTIRM technique has been applied to discover the composition and structural characteristics of feeds (Whelan and Bell, 2015). The SFTIRM could discover the structural changes in which these changes occur due to feed processing. Hence, the SFTIRM technique could estimate the relationship between protein structure and its degradative parameters. In addition, the SFTIRM technique could meaure ruminal and intestinal digestive kinetics in dairy cow (Huang et al., 2017).

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