Food Chemistry 185 (2015) 219–225

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Calorimetry, chemical composition and *in vitro* digestibility of oilseeds

Luís Carlos Vinhas Ítavo [a,*], Cláudia Muniz Soares [a], Camila Celeste Brandão Ferreira Ítavo [a], Alexandre Menezes Dias [a], Hélène Veronique Petit [c], Eduardo Souza Leal [b], Anderson Dias Vieira de Souza [b]

[a] Universidade Federal de Mato Grosso do Sul, Faculdade de Medicina Veterinária e Zootecnia – FAMEZ, Av. Senador Filinto Müller, 2443, Cidade Universitária, 79070-900 Campo Grande, MS, Brazil
[b] Universidade Católica Dom Bosco, Av. Tamandaré, 6000, Jardim Seminário, 79117-900 Campo Grande, MS, Brazil
[c] Agriculture and Agri-Food Canada, Dairy and Swine Research and Development Centre, Sherbrooke, QC J1M 0C8, Canada

ARTICLE INFO

Article history:
Received 8 August 2013
Received in revised form 2 March 2015
Accepted 3 March 2015
Available online 21 March 2015

Keywords:
Nutritional properties
Ruminants
Thermal analysis

ABSTRACT

The objective of the study was to determine the quality of sunflower, soybean, crambe, radish forage and physic nut, by measuring chemical composition, *in vitro* digestibility and kinetics of thermal decomposition processes of mass loss and heat flow. Lipid was inversely correlated with protein of whole seed ($R = -0.67$), meal ($R = -0.95$), and press cake ($R = -0.78$), and positively correlated with the enthalpy (ΔH) of whole seed. Soybean seed and meal presented a high *in vitro* digestibility but poor energy sources with ΔH averaging 5907.5 J/g and 2570.1 J/g for whole seed and meal, respectively. As suggested by the release of heat, measured by ΔH, whole seeds of crambe (6295.1 J/g), radish forage (6182.7 J/g), and physic nut (6420.0 J/g) may be potential energy sources for ruminant animals. The thermal analysis provided additional information besides that obtained from the usual wet chemistry and *in vitro* measurements.

1. Introduction

Thermal analysis generates important information on thermal stability and reaction mechanisms (Santos et al., 2011) for the prediction of properties associated with quality of ruminant feed (Marvin et al., 1996; Sharma, Mellon, Johnston, & Fletcher, 2008). The principles underlying this technique are based on the variation of mass over time or temperature in thermogravimetric (TG) analysis and measurement of heat flow within samples at a set temperature in differential scanning calorimetry (DSC) analysis (Santos et al., 2011). Heating rate is the change in temperature as time passes (dynamic measurement) or the time at a constant temperature (static measurement) (Kok, 2011). The simultaneous measurements of TG and DSC out perform wet chemistry of samples to predict chemical components, such as carbohydrates, ash and energy (Marvin et al., 1996), and identify changes in proportions of non-structural and structural carbohydrates and inorganic compounds (Sharma et al., 2008).

Thermal analysis could predict the nutritional value of ruminant feeds. A preliminary study on the use of TG for assessing digestibility of perennial ryegrass has been reported (Sharma et al., 2008). As *in vitro* bioassays using rumen fluid can accurately predict *in vivo* degradability of fodders (Marvin et al., 1996), and *in vitro* techniques may be more attractive than *in vivo* trials as they require less time and money than animal trials. Moreover, *in vitro* digestibility could indicate the presence of toxic compounds in feed ingredients such as condensed tannins, saponins, gossypol, and trypsin inhibitors. Indeed, these components may limit feed quality and animal productivity, and decrease rumen microbial activity, thereby, lowering microbial protein flow from the rumen (Wanapat et al., 2012).

Biodiesel, one of the biofuels, is attractive for its biodegradable, nontoxic and clean renewable characteristics as well as for its properties similar to those of conventional diesel fuels (Saengea, Cheirsil, Suksarogea, & Bourtoomc, 2011). The biodiesel industry has the potential to utilize a vast amount of oilseeds if production methods can be cost effective (Barrows, Gaylord, Sealey, Haas, & Stroup, 2008). Many oilseeds have been evaluated for biodiesel production (Saengea et al., 2011) and their chemical composition and some effects on rumen fermentation have been reported (Wanapat et al., 2012).

In Brazil, the potential of oil sources such as radish forage (*Raphanus sativus*) (Santos et al., 2010), crambe (*Crambe abyssinica*) (Souza, Favaro, Ítavo, & Roscoe, 2009), sunflower (*Helianthus annuus*), soybean (*Glycine max*) (Soares et al., 2010) and physic nut (*Jatropha curcas*) for feeding animals has been examined to find

* Corresponding author. Tel.: +55 67 3345 3649; fax: +55 67 3345 3600.
E-mail addresses: luis.itavo@ufms.br (L.C.V. Ítavo), claudiabiotec@gmail.com (C.M. Soares), camila.itavo@ufms.br (Camila Celeste Brandão Ferreira Ítavo), alexandre.menezes@ufms.br (A.M. Dias), helene.petit@agr.gc.ca (H.V. Petit), eduardoleal.zoo@gmail.com (E.S. Leal), anderson.dias.vieira@hotmail.com (A.D.V. de Souza).

http://dx.doi.org/10.1016/j.foodchem.2015.03.007
0308-8146/

a way of valorizing biofuel by-products such as press cake and meal (Santos et al., 2010). Press cake is the solids obtained by cold pressing the whole seed and meal is the solids remaining after extraction with solvents. Press cake and meal are classified as protein and energy ingredients with high nutritional value for animal feed (Oliveira, Mota, Barbosa, Stein, & Borgonovi, 2007). However, chemical composition of seeds varies along with water (Colombo, Ribotta, & León, 2010) and mineral concentrations (Ingale & Shrivastava, 2011), which affects the quality of resulting by-products. For example, water content affects conformation of proteins present in food or by-products (Colombo et al., 2010). However, individual chemical components and structural features that are known to affect microbial degradation can be assessed with the use of DSC and TG thermograms as shown for cell walls (Marvin et al., 1996). Therefore, it was hypothesized that thermal analysis has the potential to predict, in association with *in vitro* digestibility, the nutritional value of by-products from the biodiesel industry for ruminants.

The aim of this study was to assess the quality of whole seeds (sunflower, soybean, crambe, radish forage and physic nut), press cakes (crambe, radish forage and physic nut), meals (soybean, crambe, radish forage and physic nut) and hulls (sunflower, crambe and physic nut) by measuring chemical composition, *in vitro* digestibility and kinetics of thermal decomposition processes of mass loss and heat flow.

2. Materials and methods

The experiment was carried out at the Biotechnology Applied Animal Nutrition Laboratory of the Dom Bosco Catholic University, and Applied Animal Nutrition Laboratory of Federal University of Mato Grosso do Sul located in Campo Grande, Mato Grosso do Sul, Brazil. This work was approved by the Local Ethical Committee for use of animals in experiments of Federal University of Mato Grosso do Sul (protocol n. 633/2014).

2.1. Samples and design

Seeds of radish forage (cultivar IPR 116 from the Agronomic Institute of Paraná, Brazil), crambe (FMS-Brilhante variety from Foundation-MS, Maracaju, MS, Brazil), physic nut (from Paradise Farm, Dourados, MS, Brazil), sunflower and soybean (from commercial lots in Campo Grande, MS, Brazil) were analyzed. Press cakes were obtained after double mechanical extraction of oil through expeller pressing at a rate of 150 kg h^{-1} and an output temperature of 90–110 °C. Meals were obtained after mechanical extraction of oil through expeller pressing and washing with an organic solvent. Oil extraction from the soybean and radish forage seeds was performed with the hulls and oil extraction from sunflower, crambe and physic nut was done after removal hulls manually. The meals were heated to a temperature of 110 °C for 40 min, and the roasting process lasted for 20 min. Seeds, press cakes and meals were homogenized with an analytical mill (IKA A11 basic model, Quimis, Diadema, SP, Brazil) and stored at 25 °C for 24 h until analysis. There were five seeds (sunflower, soybean, crambe, radish forage and physic nut), three press cakes (crambe, radish forage and physic nut), four meals (soybean, crambe, radish forage and physic nut) and three hulls (sunflower, crambe and physic nut).

2.2. Chemical analysis

The samples were dried in a forced-air oven at 55 °C for 72 h and ground through a 1 mm mesh for chemical analysis. Concentrations of dry matter (DM), organic matter (OM), crude protein (CP), and ether extract (EE) were determined, respectively, according to methods 930.15, 942.05, 976.05 and 920.39 of AOAC (2000). Ash was calculated as 100-OM. Determinations of neutral detergent fiber (aNDF) and acid detergent fiber (ADF) were performed according to Mertens (2002) using a heat-stable α-amylase (Termamyl 120 L® Novozymes A/S, Bagsvaerd, Denmark) and without sodium sulphite, and expressed with residual ashes. The content of hemicelluloses (Hemi) was calculated by the difference between aNDF and ADF concentrations after sequential analysis. Chemical analyses were performed in triplicate.

2.3. In vitro digestibility

The *in vitro* digestibility was performed in triplicate using the modified technique of Tilley and Terry (1963) adapted to the Ankom Daisy^{II} system (Ankom Technology Corp., Macedon, NY, USA) as described by Holden (1999). Fifteen 0.5 g samples (whole seeds, press cakes, meals and hulls) were weighed in triplicate into polypropylene synthetic tissue filter bags that were 5 × 5 cm in size with a pore size of 50 μm. The bags were placed in two glass jars. One jar contained 22 sample bags plus 2 blanks (empty, sealed bags) and the other jar contained 23 bags plus 2 blanks. The blanks were used to calculate a correction factor that adjusted for weight loss or gain from the sample bags. The jars were kept for 72 h in the same incubator with the temperature maintained at 39 °C. Rumen fluid was obtained before feeding from three non-lactating ruminally fistulated Holstein cows fed 9 kg of bahiagrass hay supplemented with 0.4 kg of soybean meal daily. Upon completion of the incubation, the filter bags were gently rinsed with cold tap water until the water ran clear and then placed in a 50 °C forced-air oven to dry for 24 h. Once dried, the bags were weighed and corrected for bacterial contamination using blank bags (Holden, 1999). *In vitro* digestibility of DM (IVDMD), aNDF (IVaNDFD), ADF (IVADFD) and Hemi (IVHEMID) was calculated from differences between the amount of nutrients in feed and that in the residue after incubation according to methods previously described (Velásquez et al., 2010).

2.4. Kinetics of thermal decomposition processes of mass loss and heat flow

The kinetics of thermal decomposition of mass loss and heat flow were analyzed according to Faria, Leles, Ionashiro, Zuppa, and Antoniosi Filho (2002) and Soares et al. (2010) using the simultaneous application of TG and DSC. The module included a thermogravimetric analyzer with a differential scanning calorimetry detector, a differential thermal analysis (DTA) and a differential scanning calorimetric analyzer (DSC-TGA – SDTQ600; Mettler-Toledo, Im Langacher, Switzerland). Duplicate samples of meal (10 mg) were weighed into aluminum containers (6 mm in diameter and 2.5 mm in height) and measurements of thermogravimetric analysis were performed in air flowing at 100 ml/min. Initial temperature of 25 °C was increased at 10 °C/min to 600 °C.

2.5. Statistical analysis

The data were analyzed by a one-way ANOVA using the General Linear Models procedure of SAS (1998). Significance was declared at $p < 0.05$. When a significant *F*-test was detected, multiples comparisons were done using a Tukey's adjustment for the probability. Pearson's correlation was used to determine strength of the relationships among variables analyzed with the CORR procedure of SAS (SAS Institute, 1988).