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Analytical Methods

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

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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

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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).

3. Results and discussion

Concentration of seed DM was similar for sunflower, soybean, crambe and radish forage and that of physic nut was higher compared to other seeds (Table 1). The DM contents of whole seeds were higher than the values reported by Silva, Naves, Oliveira, and Leite (2006, 944 g/kg). Discrepancies between these experiments may result of differences in moisture absorption between species due to genetic variations, topographic and climatic factors, drying and storage of seeds. For example, Souza et al. (2009) observed that water absorption was different between press cakes of physic nut and crambe. DM content of crambe and sunflower hulls was similar, and greater than physic nut hull.

The ash contents of press cake, meal and hull from crambe were greater than those of other seeds (Table 1). This agrees with the values for ash concentration reported previously by Souza et al. (2009), for press cake of crambe, radish forage, and physic nut (63.0, 52.5, and 59.4 g/kg, respectively). Physic nut had the highest EE concentration among whole seeds. The EE concentration of physic nut press cake was similar to that of crambe but higher than that of radish forage press cake (Table 1). Similarly, Adebowale and Adedire (2006) reported that seeds of physic nuts have about 660 g of oil per kg DM, which is higher than amount found in most oilseeds. The EE content in crambe meal was similar to that of physic nut meal. The highest concentrations of aNDF and ADF were found in press cake, meal and hull of physic nut.

The lowest IVDMD was observed for whole seed, press cake, meal and hull of physic nut (Table 2), which could be due to the general higher fiber content of the physic nut. Anti-nutritional compounds, such as phenolic, are present in sunflower seeds (Canibe, Pedrosa, Robredo, & Knudsen, 1999) and physic nut (Souza et al., 2009), which could contribute to the decrease IVDMD and protein synthesis by rumen microorganisms. Such compounds are classified as thermosetting, meaning that they do

Table 2
In vitro digestibility (g/kg of DM) of whole seed, press cake, meal and hull of sunflower, soybean, crambe, radish forage and physic nut.

	n	IVDMD	IVaNDFD	IVADFD	IVHEMID
Whole seed					
Sunflower	36	617.7b	454.6b	455.9c	450.8b
Soybean	36	876.0a	845.9a	872.9a	803.0a
Crambe	36	604.0b	782.2a	637.9b	864.7a
Radish forage	36	651.9b	817.4a	653.7b	924.7a
Physic nut	36	453.5c	190.8c	159.7c	346.2b
SE		4.58	8.57	7.97	7.84
p-Value		<0.001	<0.001	<0.001	<0.001
Press cake					
Crambe	36	585.5b	339.8a	207.6	617.0a
Radish forage	36	658.7a	251.3b	129.6	469.1b
Physic nut	36	482.0c	243.4b	167.1	401.6c
SE		3.27	2.05	1.61	4.05
p-Value		0.002	0.027	0.103	0.001
Meal					
Soybean	36	865.0a	865.2a	747.3a	916.2a
Crambe	36	673.9b	275.7c	183.8bc	525.0b
Radish forage	36	784.3ab	573.0b	291.2b	813.4a
Physic nut	36	457.4c	138.8c	104.7c	535.8b
SE		5.86	10.67	9.46	6.53
p-Value		0.001	<0.001	<0.001	<0.001
Hull					
Sunflower	36	379.9a	256.6	185.4	426.0
Crambe	36	461.0a	299.6	229.5	577.3
Physic nut	36	85.8b	42.9	50.6	516.7
SE		7.33	5.58	4.70	3.40
p-Value		0.006	0.082	0.330	0.190

SE, standard error; IVADFD, *in vitro* digestibility of acid detergent fiber; IVaNDFD, *in vitro* digestibility of neutral detergent fiber; IVDMD, *in vitro* digestibility of dry matter; IVHEMID, *in vitro* digestibility of hemicellulose; *n*, number of samples.
Values followed by different letters within a column are significantly different ($p < 0.05$).

Table 1
Chemical composition (g/kg of DM) of whole seed, press cake, meal and hull of sunflower, soybean, crambe, radish forage and physic nut.

	n	DM	Ash	OM	EE	CP	aNDF	ADF	Hemi
Whole seed									
Sunflower	36	980.8b	32.9	967.0	249.0d	208.0c	300.8bc	221.0	79.8
Soybean	36	981.2b	52.9	947.1	222.0e	381.0a	263.0c	161.6	101.4
Crambe	36	980.9b	52.9	947.1	405.0b	178.0c	371.6ab	154.3	217.3
Radish forage	36	981.0b	42.3	957.7	365.0c	276.0b	432.7a	171.4	261.3
Physic nut	36	989.7a	97.3	902.7	449.0a	205.0c	433.3a	361.0	72.2
SE		0.12	0.84	0.84	2.52	2.46	2.34	3.26	3.26
p-Value		0.014	0.081	0.081	<0.001	<0.001	<0.001	0.224	0.214
Press cake									
Crambe	36	981.1b	61.6a	938.4c	139.0a	309.0b	312.7b	211.7b	100.9a
Radish forage	36	981.2ab	52.8c	947.1a	114.0b	414.0a	154.4c	99.0c	55.3b
Physic nut	36	981.3a	57.7b	942.2b	155.0a	280.0b	485.1a	393.9a	91.2a
SE		0.00	0.16	0.16	0.78	2.59	6.05	5.44	0.88
p-Value		0.009	<0.001	<0.001	0.008	0.002	<0.001	<0.001	0.003
Meal									
Soybean	36	985.5a	52.0b	947.9a	26.0b	489.0a	212.8b	64.2d	140.9
Crambe	36	981.7b	70.7a	929.3b	45.0ab	376.0b	334.7b	244.5b	90.0
Radish forage	36	981.5d	58.1b	941.8a	32.0b	477.0a	246.1b	113.3c	130.3
Physic nut	36	981.6c	58.2b	941.8a	63.0a	311.0a	502.0a	411.1a	90.1
SE		0.06	0.26	0.26	0.55	2.81	4.31	5.08	1.19
p-Value		<0.001	0.003	0.003	0.006	0.001	0.002	<0.001	0.191
Hull									
Sunflower	36	981.4a	36.3b	963.6b	52.0c	129.0b	547.4b	385.5b	161.9
Crambe	36	981.3a	82.7a	917.3c	83.0b	181.0a	454.0c	362.5b	91.5
Physic nut	36	967.3b	24.2c	975.7a	113.0a	87.0b	749.7a	626.1a	123.5
SE		0.30	1.13	1.13	1.13	1.76	5.53	5.35	1.45
p-Value		<0.001	<0.001	<0.001	0.003	0.010	<0.001	<0.001	0.098

ADF, acid detergent fiber; aNDF, neutral detergent fiber; CP, crude protein; EE, ether extract; SE, standard error; DM, dry matter; Hemi, hemicellulose; ND, not determined; NS, not significant; OM, organic matter.
Values followed by different letters within a column are significantly different ($p < 0.05$).

not change in the presence of heat (Francis, Makkar, & Becker, 2001). Although similar anti-nutritional compounds were also present in crambe and radish forage (Souza et al., 2009), their concentrations were not high enough to suppress IVDMD to the same extent (Table 2).

The highest IVDMD of whole seed was observed for soybean and IVDMD of meal was similar for soybean and radish forage. According to Souza et al. (2009), among press cakes, radish forage has the highest IVDMD, which probably results from the pressing of seeds without hulls. As lignification of wild radish hulls forage acts like an outer barrier against microbial attack, dehulling enhances digestion and access for rumen microbes. Among the hulls examined, IVDMD of crambe (461.0 g/kg of DM) and sunflower (379.9 g/kg of DM) were greater than that of physic nut (85.8 g/kg of DM) (Table 2), which may be because crambe and sunflower hulls are thinner (Canibe et al., 1999). However, higher temperatures were required for combustion of crambe hull (571.2 °C) and physic nut hull (558.5 °C) than sunflower hull (416.6 °C; Table 3 and Fig. 1).

The IVaNDFD and IVHEMID of whole seed of radish forage were similar to those of soybean and crambe (Table 2), which may explain that microbial fermentation in the rumen is similar for radish forage, an oilseed with a high content in the unsaturated oleic acid (Ávila and Sodré, 2012; Domingos, Saad, Wilhelm, & Ramos, 2008; Valle, Velez, Hegel, Mabe, & Brignole, 2010), and soybean, which is rich in the unsaturated linoleic acid (Silva et al., 2007). The values of IVaNDF (865.2 g/kg of DM) and IVADFD (747.3 g/kg of DM) of soybean meal were higher than those of other meals. However, soybean meal is likely a poor source of energy as suggested by its value of ΔH (2570.0 J/g) that was lower compared to crambe meal (3435.5 J/g) and physic nut meal (3937.0 J/g; Table 3).

The IVHEMID of whole seed from crambe (864.7 g/kg of DM) and radish forage (924.7 g/kg of DM) was higher than that from physic nut (346.2 g/kg of DM; Table 2). Although differences were not significant, ash and ADF concentrations were almost twice (p = 0.081 and 0.224) as high in physic nuts than crambe and radish forage, which may affect digestion negatively.

Thermal properties of whole seeds and by-products showed two distinct regions of reaction in the combustion with TG and DSC. In the first region, oxidation occurred around 100 °C which, according to Kok (2011), is due to the evaporation of light components such as water and light hydrocarbons. The second region, which contributed to most of the exothermic reaction and loss of organic compounds, indicated a peak temperature that ranged from a minimum of 349 °C for soybean meal to a maximum of 571 °C for crambe hull (Table 3 and Fig. 1). There was no difference in ΔW within whole seeds and press cakes. However, processes leading to products with a low fat proportion (i.e., meal and hull) resulted in differences of ΔW within product (Table 3). The ΔW of crambe meal and radish forage meal were similar (Table 3). Physic nut hull had the highest ΔW and crambe hull had the lowest with sunflower producing an intermediate value. The ΔW was positively correlated with IVDMD (R = 0.6963 and 0.7405 for meal and hull, respectively) and IVADFD (R = 0.6660 for meal; Table 5).

The DM content of whole seeds was inversely correlated with IVDMD (R = −0.6542), IVaNDFD (R = −0.7715), IVADFD (R = −0.7684) and enthalpy (ΔH; R = −0.7918; Table 4). This may suggest that DM of whole seeds can influence negatively digestibility by delaying microbial attack in the rumen, degradation and

Table 3
Thermal profile of whole seed, press cakes, meal and hulls of sunflower, soybean, crambe, radish forage and physic nut.

	Sunflower	Soybean	Crambe	Radish forage	Physic-nut	SE	*p*-Value
Whole seed							
Thermogravimetric analysis (TG)							
ΔW (mg/kg)	845.3	907.2	763.3	932.1	887.3	2.53	0.245
TT (min)	29.1	29.0	29.0	29.1	29.1	0.18	NS
$\Delta W/TT$ (mg/kg/min)	2.9	3.1	2.6	3.2	3.0	0.09	0.243
Differential Scanning Calorimetry analysis (DSC)							
Tp (°C)	526.7	494.0	557.0	509.5	491.4	8.99	0.052
ΔH (J/g)	6100.0ab	5907.5b	6295.1a	6182.7ab	6420.0a	61.72	0.015
Press cake							
Thermogravimetric analysis (TG)							
ΔW (mg/kg)	ND	ND	831.2	857.0	888.2	2.00	NS
TT (min)	ND	ND	29.0	29.0	29.3	0.09	0.231
$\Delta W/TT$ (mg/kg/min)	ND	ND	2.9	3.1	2.9	0.07	NS
Differential Scanning Calorimetry analysis (DSC)							
Tp (°C)	ND	ND	516.6	439.4	507.1	19.51	0.234
ΔH (J/g)	ND	ND	5187.8ab	4194.7b	5645.0a	284.42	0.029
Meal							
Thermogravimetric analysis (TG)							
ΔW (mg/kg)	ND	699.7b	903.7a	939.8a	768.3b	3.75	0.001
TT (min)	ND	29.0	29.1	29.0	29.1	0.02	NS
$\Delta W/TT$ (mg/kg/min)	ND	2.4b	3.1a	3.2a	2.6b	0.13	0.001
Differential Scanning Calorimetry analysis (DSC)							
Tp (°C)	ND	349.1b	488.7ab	485.9ab	556.0a	30.82	0.040
ΔH (J/g)	ND	2570.1c	3435.5ab	3062.7bc	3937.0a	195.08	0.006
Hull							
Thermogravimetric analysis (TG)							
ΔW (mg/kg)	744.1b	ND	680.4c	ND	806.5a	2.34	0.005
TT (min)	29.0	ND	29.0	ND	28.5	0.18	NS
$\Delta W/TT$ (mg/kg/min)	2.6ab	ND	2.3b	ND	2.8a	0.09	0.011
Differential Scanning Calorimetry analysis (DSC)							
Tp (°C)	416.6c	ND	571.2a	ND	558.5b	31.33	<0.001
ΔH (J/g)	524.1b	ND	898.8b	ND	1738.5a	231.65	0.008

SE, standard error; ΔW, weight loss; ND, not determined; NS, not significant; TG, thermogravimetry; Tp, peak temperature; TT, total time; ΔH, enthalpy.
Values followed by different letters within a line are significantly different (p < 0.05).

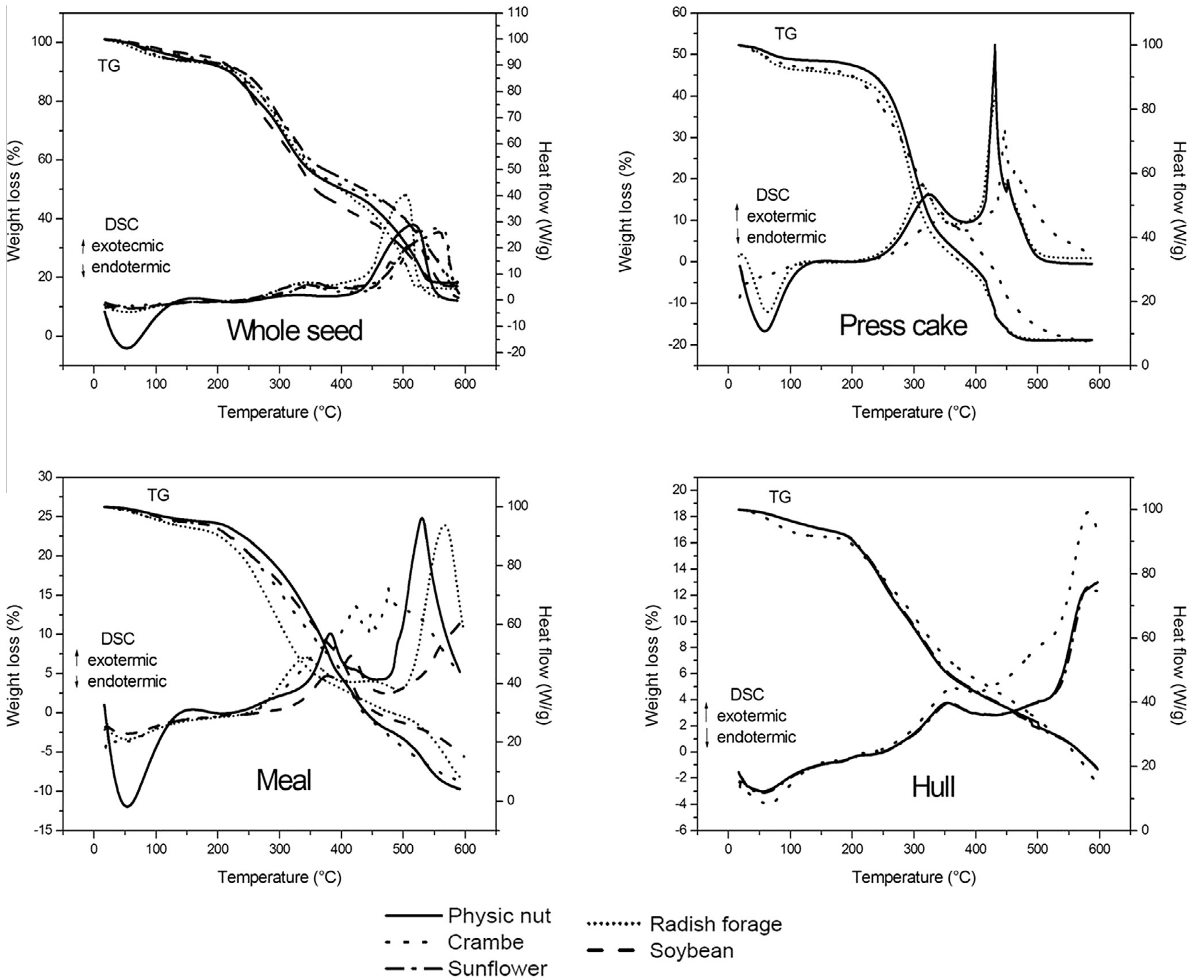

Fig. 1. Behavior of thermal profile of whole seed, press cakes, meal and hulls of sunflower, soybean, crambe, radish forage and physic nut.

energy release from the by-product. DM content of press cake was negatively correlated with IVaNDFD ($R = -0.8876$) and ΔH ($R = -0.9563$; Table 4). Meal DM content showed positive correlations with IVDMD ($R = 0.6214$), IVaNDFD ($R = 0.8064$), IVADFD ($R = 0.9511$), ΔW ($R = 0.6702$) and ΔH ($R = 0.7757$). Meal is expected to be more homogeneous than other by-products due to dehulling of seeds, which may contribute to improve digestibility.

Proportion of EE in whole seeds was inversely correlated (Table 4) with protein content ($R = -0.6747$) and IVDMD ($R = -0.6869$) and positively correlated with ΔH ($R = 0.6670$) with no significant correlation with IVaNDFD and IVADFD. Conversely, correlations of EE content in press cake with IVaNDFD ($R = 0.7494$) and IVADFD ($R = 0.9310$) were positive (Table 4), which may result of better adhesion, growth and biohydrogenation of fatty acids by rumen microbes (Silva et al., 2007) due to mechanical extrusion of seeds. The EE fraction of hull was correlated significantly only with DM ($R = -0.0048$) and OM ($R = -0.7420$) contents. Protein content of whole seed (Table 4) and meal (Table 5) was inversely correlated with EE content ($R = -0.6747$ and -0.9538, respectively). Within whole seeds, energy release was positively correlated with EE contents.

Concentrations of aNDF and ADF of physic nut meal were negatively correlated with ΔW ($R = -0.6886$ for aNDF and $R = -0.6371$ for ADF) and ΔH ($R = -0.7444$ for aNDF and ADF $R = -0.7560$; Table 5). The high fiber content of hull then may be a limiting factor for its use in ruminant diets as high lignification hinders access to nutrients by rumen microbes (Sharma et al., 2008; Silva et al., 2006). Within hulls, aNDF and ADF concentrations were high and positively correlated ($R = 0.9650$) as expected (Wan et al., 1979) due to the cellulose and lignin contents.

The values of IVDMD, IVaNDFD, IVADFD and IVHEMID were highly correlated within whole seeds (Table 4) and meals (Table 5). The IVDMD of hulls was inversely correlated with concentrations of aNDF ($R = -0.9758$) and ADF ($R = -0.9693$) and positively correlated with IVaNDFD ($R = 0.9541$) and IVADFD ($R = 0.8256$) as previously reported by Anderson, Obadiah, Boman, and Walters (1984). Hull DM content was positively correlated with IVDMD ($R = 0.9659$).

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. Moreover, meal of crambe (3435.5 J/g), radish forage (3062.0 J/g) and physic nut (3937.0 J/g) also may be interesting

Table 4
Pearson's correlations (*R*) between chemical composition, *in vitro* digestibility and thermal properties of whole seed and press cake.

	DM	OM	EE	CP	aNDF	ADF	IVDMD	IVaNDFD	IVADFD	ΔW	ΔH
Whole seed											
DM	–	−0.9465	0.3531	−0.2533	0.4920	0.7095**	−0.6542*	−0.7715**	−0.7684**	0.2426	−0.7918**
OM	−0.9465***	–	−0.3999	0.1391	−0.4325	−0.5628*	0.5079	0.5538*	0.5596*	−0.0988	0.8185**
EE	0.3531	−0.3999	–	−0.6747*	0.7942**	0.1487	−0.6869*	−0.1485	−0.4038	0.3363	0.6670*
CP	−0.2533	0.1391	−0.6747*	–	−0.4862	−0.2976	0.8541***	0.5202	0.6831*	−0.7051*	0.2219
aNDF	0.4923	−0.4325	0.7942**	−0.4862	–	0.3564	−0.7227**	−0.3171	−0.5583*	0.2599	−0.8281**
ADF	0.7095*	−0.5628*	0.1487	−0.2976	0.3564	–	−0.5896	−0.7517**	−0.7235**	−0.0536	−0.5268
IVDMD	−0.6542*	0.5079	−0.6869*	0.8541***	−0.7227**	−0.5896*	–	0.7568**	0.9096***	−0.6365*	0.5897*
IVaNDFD	−0.7715**	0.5538*	−0.1485	0.5202	−0.3171	−0.7517	0.7568*	–	0.9537***	−0.5324	0.3796
IVADFD	−0.7684**	0.5596*	−0.4038	0.6831*	−0.5583*	−0.7235**	0.9096***	0.9537***	–	−0.6138*	0.5198
ΔW	0.2429	−0.0988	0.3363	−0.7051*	0.2598	−0.0536	−0.6365*	−0.5323	−0.6138*	–	−0.0037
Press cake											
DM	–	0.4147	−0.3844	−0.2311	0.5230	0.6099	−0.5980	−0.8876**	−0.5145	−0.2741	−0.9563**
OM	0.4147	–	−0.9664***	0.7859*	−0.5365	−0.4400	0.4736	−0.7367*	−0.8700*	−0.581	−0.2262
EE	−0.3844	−0.9664**	–	−0.7845*	0.5780	0.4911	−0.4976	0.7494*	0.9310**	0.4346	0.2262
CP	−0.2311	0.7859*	−0.7845*	–	−0.9396**	−0.8961	0.9164**	−0.1906	−0.5926	−0.3943	0.2081
aNDF	0.5230	−0.5365	0.5780	−0.9396**	–	0.9937***	−0.9927***	−0.1059	0.3834	0.2471	0.4134
ADF	0.6099	−0.4400	0.4911	−0.8961**	0.9937***	–	−0.9936***	−0.2050	0.3020	0.1817	−0.6678
IVDMD	−0.5980	0.4736	−0.4976	0.9164**	−0.9927***	−0.9936***	–	0.1987	−0.2905	−0.2102	−0.7355*
IVaNDFD	−0.8876**	−0.7367*	0.7494*	−0.1906	−0.1059	−0.2050	0.1987	–	0.8368*	0.2914	0.7308*
IVADFD	−0.5145	−0.8700*	0.9310**	−0.5926	0.3834	0.3020	−0.2905	0.8368*	–	0.1867	0.8002*
ΔW	−0.2741	−0.5081	0.4346	−0.3943	0.2471	0.1817	−0.2101	0.2914	0.1867	–	0.4206

ADF, acid detergent fiber; aNDF, neutral detergent fiber; CP, crude protein; EE, ether extract; DM, dry matter; IVADFD, *in vitro* digestibility of acid detergent fiber; IVaNDFD, *in vitro* digestibility of neutral detergent fiber; IVDMD, *in vitro* digestibility of dry matter; IVHEMID, *in vitro* digestibility of hemicellulose; ΔW, weight loss; OM, organic matter.
* $p < 0.05$.
** $p < 0.01$.
*** $p < 0.001$.

Table 5
Pearson's correlations (*R*) between chemical composition, *in vitro* digestibility and thermal properties of meal and hull.

	DM	OM	EE	CP	aNDF	ADF	IVDMD	IVaNDFD	IVADFD	ΔW	ΔH
Meal											
DM	–	0.6192	−0.6011	0.5706	−0.5502	−0.6035	0.6214*	0.8064**	0.9511***	0.6702*	0.7757*
OM	0.6192	–	−0.3111	0.4424	−0.2633	−0.3550	0.2824	0.5996	0.6360*	−0.0952	0.1650
EE	−0.6011	−0.3111	–	−0.9538***	0.9597***	0.9779***	−0.9758***	−0.9031**	−0.7681*	−0.6507*	−0.7134*
CP	0.5706	0.4424	−0.9538***	–	−0.9216***	−0.9768***	0.9493***	0.9298***	0.7744*	0.4922	0.6758*
aNDF	−0.5502	−0.2633	0.9597***	−0.9216***	–	0.9810***	−0.9715***	−0.8731**	−0.7391*	−0.6886*	−0.7444*
ADF	−0.6035	−0.3550	0.9779***	−0.9768***	0.9810***	–	−0.9857***	−0.9287***	−0.7946**	−0.6371*	−0.7560*
IVDMD	0.6214*	0.2824	−0.9758***	0.9493***	−0.9715***	−0.9857***	–	0.9248***	0.8054**	0.6963*	0.7763*
IVaNDFD	0.8064**	0.5996	−0.9031***	0.9298***	−0.8731**	−0.9287***	0.9248***	–	0.9429***	0.5838*	0.7492*
IVADFD	0.9511***	0.6360*	−0.7681*	0.7744*	−0.7391*	−0.7946**	0.8054**	0.9429***	–	0.6660*	0.8188**
ΔW	0.6702*	−0.0952	−0.6507*	0.4922	−0.6886*	−0.6371*	0.6963*	0.5838	0.6660*	–	0.9032**
Hull											
DM	–	−0.6574	−0.0048	0.8145*	−0.9485***	−0.9929***	0.9659***	0.8980**	0.7180	0.8584*	0.7294
OM	0.6574	–	−0.7420*	−0.9425**	0.8586*	0.7152	−0.7885*	−0.6955	−0.5971	−0.1988	0.0187*
EE	−0.0048*	−0.7420*	–	0.5169	−0.2968	−0.0831	0.2084	0.1424	0.1718	−0.4613	−0.6442
CP	0.8145*	−0.9425**	0.5169	–	−0.9404**	−0.8579	0.8844**	0.7585*	0.6215	0.4108	0.2189
aNDF	−0.9485**	0.8586*	−0.2968	−0.9404**	–	0.9650***	−0.9758***	−0.8961**	−0.7316*	−0.6574	−0.4818
ADF	−0.9929**	0.7152	−0.0831	−0.8579*	0.9650***	–	−0.9693***	−0.8744*	−0.6801	−0.8169*	−0.6618
IVDMD	0.9659**	−0.7885*	0.2084	0.8844**	−0.9758***	−0.9693***	–	0.9541**	0.8256*	0.7405*	0.5976
IVaNDFD	0.8980**	−0.6955	0.1424	0.7585*	−0.8961**	−0.8744*	0.9541**	–	0.9440**	0.7183	0.6292
IVADFD	0.7180	−0.5971	0.1718	0.6215	−0.7316*	−0.6801	0.8256*	0.9440**	–	0.5474	0.5226
ΔW	0.8584*	−0.1988	−0.4613	0.4108	−0.6574	−0.8169*	0.7405*	0.7183	0.5474	–	0.9601**

ADF, acid detergent fiber; aNDF, neutral detergent fiber; CP, crude protein; EE, ether extract; DM, dry matter; IVADFD, *in vitro* digestibility of acid detergent fiber; IVaNDFD, *in vitro* digestibility of neutral detergent fiber; IVDMD, *in vitro* digestibility of dry matter; IVHEMID, *in vitro* digestibility of hemicellulose; ΔW, weight loss; OM, organic matter.
* $p < 0.05$.
** $p < 0.01$.
*** $p < 0.001$.

sources and used as an alternative to soybean, which could be devoted to human nutrition. Radish forage press cake presented attractive characteristics as a potential protein source (414 g/kg DM) for ruminant diets.

In conclusion, the correlations indicated that concentration of fiber in oilseeds negatively influenced *in vitro* digestibility of cellulose, hemicellulose and lignin, resulting in lower weight loss of DM and lower potential as an energy source for ruminants. The higher ether extract concentration in seed led to higher energy content but also to lower crude protein proportion and *in vitro* digestibility of dry matter. The thermal analysis provided additional information to that obtained from the common wet chemistry and *in vitro* measurements. These results suggest that correlating chemical components, such as protein content to the release of energy determined by thermal analysis, contributes to more precise determination of nutritional content of bioproducts from the biodiesel industry.

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