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The Influence of Extrusion on Total Glucosinolates and Total Phenols in Rapeseed

Marijana B. Sakac, S. S. Filipovic
University of Novi Sad, Faculty of Technology, Novi Sad, Serbia

C. M. Borojevic
MMB-Inexcoop, Samac, Serbia

M. D. Ristic, S. M. Kormanjos
University of Novi Sad, Faculty of Technology, Novi Sad, Serbia

Abstract: The influence of extrusion as one of the most frequent thermal treatment in our country on total rapeseed glucosinolates and total phenols in rapeseed and mixtures of rapeseeds and agricultural products (corn, wheat, barley, triticale, alfalfa) was investigated in this work.

Rapeseed and mixtures of rapeseed with agricultural products (rapeseed : agricultural product – 30:70 and 50:50, corn : rapeseed : alfalfa – 60:30:10 i 40:50:10, respectively) were extruded in an "Oprema-zootehnička oprema", type M2, model 1000 extruder at 125±1 °C.

Based on the chemico-physical characteristics of obtained feeds, as well as the reduction of the content of total glucosinolates in range 10-15% and not evidented reduction of total phenols content in comparison with untreated products, it can be concluded that dry extrusion can be a good choice for thermal treatment of rapeseed in combination with analysed agricultural products.

Key words: rapeseed, extruding, total glucosinolates, total phenols, agricultural products.

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Introduction

Rapeseed (*Brassica* sp.) is an oilseed crop serving as an important source of dietary proteins, energy and anti-nutrients, mainly glucosinolates. This oilseed plant is primarily used for production of oils, an essential raw material in the production of a wide range of industrial products– plasticizers, surface active agents, detergents, coatings and polyesters (Bhardwaj and Hamama, 2003), and rapeseed meal is produced as a side product of oil processing of rape seed.

Rapeseed meal, as the most frequent rapeseed-based feed is used in many feed formulations, as a good source of proteins, particularly sulphur containing amino acids, i.e. methionine and cystine, as well as lysine (Mansour et al., 1993; Newkirk et al., 2003), but its use is limited due to relatively high level of of crude fiber (30%) (Jensen et al., 1995), phytic acid (2-4%) (Park et al., 2000), polyphenols (Naczk et al., 1998) and glucosinolates.

Potential use of rapeseed in animal feeding is oriented toward the use of its whole seed for the purpose of obtaining high dietary protein rations (Sakac et al., 2004; Filipovic at al., 2004; 2005), which, apart from containing highly valuable components, contain above mentioned antinutritional factors, but, in a lesser extent, and additionally, all rapeseed-based feeds are rather susceptible to lipid oxidation, further affecting their stability, i.e. shelf life (Hamilton et al., 1997).

Glucosinolates, composed of more than hundred forms of organic anions containing sulphur with β-D-tioglucose unit, are the dominant anti-nutrient in rapeseed, present both in rapeseed meal after extraction of oil (Brown et al., 1991), and in full-fat feeds obtained from seeds of rapeseed (Sakac et al., 2004).

Glucosinolates enzyme degradation products adversely affect sensory properties of rapeseed (bitter taste, unpalatability), and may have harmful effects on animal health, particularly in non-ruminants (Fenwick et al., 1982). Microorganisms invading animal hind gut, enable glucosinolates decomposition and formation of various glucosinolates hydrolysis products– namely, isothiocyanates, nitrile and thiocyanates (Rabot et al, 1995), which, depending on their type (Pustai, 1989), have strong goitrogenic effects (Hill, 1979), and have been frequently reported to be implicated in the anti thyroidal activity. For example, when pigs are fed diets with low iodine content in which rapeseed cake with high glucosinolates levels is included, reductions in iodine content in pigs thyroide and serum samples have been manifested, thus confirming the findings that glucosinolates act as iodine-antagonists in animal diets (Schöne et al., 2006). To the top of that, low dietary inclusion of glucosinolates from rapeseed meal have been shown to exert positive effects on weight gain and feed conversion in pigs (Lee and Hill, 1983), that is, to have lower anti-thyroid activity and the higher utilisation of its protein in rats (Eyre and Smithard, 1984).

Comprehensive research efforts have been aimed for years at examining anti-nutritive properties of glucosinolates in rapeseed and reducing glucosinolates content in rapeseed and hence rapeseed meal through breeding (00-rapeseed varieties containing less than 30 μmoles of glucosinolates in unprocessed seed). These rapeseed varieties may be used in animal feed production provided glucosinolates content is not exceeding 20 μmol/g (Downey, 1990), especially in the diets for non-

ruminants (Dakowski et al., 1996), even up to 20%, without adversely affecting animal health.

Alternative possibility involves use of rapeseed with higher glucosinolates contents previously subjected to "detoxification" processing, that is, chemical (alkaline hydrolysis – Goh et al., 1982), microbiological (e.g. fermentation wih *Rhizopus oligosporus* – Vig and Walia, 2001) or thermal treatments, applied either singularly or in combination (Maheshwari et al., 1981; Keith and Bell, 1983), leading to reduction of glucosinolates and glucosinolates hydrolysis products (Mansour et al., 1993), and enabling use of processed rapeseed in diet formulations for less sensitive animal species and categories.

Polyphenolics of rapeseed are represented by phenolic acids and condensated tannins (Naczk et al., 1998), with somewhat higher total phenolic acids contents in rapeseed meal and flour than in other oilseed plants (soya, flax seed, peanut) ranging from 0,64-1,84% (Kozlowska et al., 1991; Naczk et al., 1996). High phenolic acids content, mainly sinapine, the phenolic choline ester of sinapic acid (Krygier et al., 1982), is of particular importance for the purpose of investigating quality of rapeseed-based high protein products, due to the fact that polyphenolics as anti-nutrients cause serious sensory implications (dark colour, bitter taste) and astringency (Shahidi and Naczk, 1992). Additionally, phenolic compound and their oxidation products form complexes with iron, essential amino acid and low-molecular proteins, hence decreasing their nutritive value, that is, making these nutrients less available and digestible for animals and humans (Naczk et al., 1998).

Although polyphenolics are relatively thermally stable compounds, there are some indications in literature that technological processes applied in the production of rapeseed-based feeds may affect content of phenol, in particular, sinapine. Larsen et al. (1983) reported reduction in sinapine content by 17% after toasting of dehulled and defatted rapeseed meal for 30 minutes.

Numerous reports from literature demonstrating partial thermal lability of glucosinolates, namely, the possibility of myrosinase inactivation during dry extrusion processing (Smithard and Eyre, 1986; Fenwick et al., 1986), the enzyme responsible for hydrolysis of glucosinolates and the formation of a series of toxic compounds, and the findings about degradation of phenolic compounds with the application of thermal treatments, have been determining for choosing the objective of this study. Therefore, the objective of this study was to investigate the effects of dry extrusion processing on partial reduction in total glucosinolates and phenols content of rapeseed and mixtures of rapeseed with other plants in order to obtain feeds of enhanced nutritive value.

Material and Methods

Rapeseed and mixtures of rapeseeds and agricultural products - corn, wheat, barley, triticale, alfalfa were used for extrusion.

Rapeseed and mixtures of rapeseed with agricultural products (rapeseed : agricultural product – 30:70 and 50:50, i.e. corn : rapeseed : alfalfa – 60:30:10 and 40:50:10, respectively) were extruded in an "Oprema-zootehnička oprema", type M2, model 1000 extruder (Ludberg, Croatia). Capacity of this extruder is

850-1000 kg/h extruded feed. Nominal power of electric motor is 75 kW, and of screw feeder with engine 1,5 kW.

Working temperature measured in the head of extruder during extrusion of above material was 125±1 °C, extruder capacity was 90%, current strength 85-90 A, and jet diameter 8 mm.

Basic chemical composition (moisture, crude proteins, crude fat, crude fibre and mineral substance contents) of rapeseed and agricultural products - corn, wheat, barley, triticale, alfalfa corn and extruded corn was determined according to A.O.A.C. method(1984).

Content of total glucosinolates was determined according to the Hungarian standard MSZ-08-1908-1989, involving absorbency measurement of Pd-complex glucosinolates at 425 nm.

Determination of total phenols expressed as an equivalent of galic acid in analyzed samples was carried out by spectrophotometric method by means of Folin-Ciocalteu reagent (Singleton et al., 1999).

Results and Discussion

Dry extrussion processing of rapeseed with agricultural products have been used for a long time, as one of the most common heat treatment for rapeseed processing, providing feed of high protein-energy content (Sakac et al., 2004; Filipovic et al., 2004; 2005; Font et al., 2005). This processing approach has been adopted due to the fact that when rapeseed is extruded alone adequate heating of material is not possible because of high crude oil content, responsible for the production of oily extrudate susceptible to lipid oxidation (Smithard and Eyre, 1986), whereas, during dry extrusion of mixtures of rapeseed with agricultural products, a product of longer shelf life is obtained suitable for storage and formulations with other feeds (Eyre and Smithard, 1984).

Dry extrusion processing of rapeseed and mixtures of rapeseed with agricultural products in "Oprema-zootehnička oprema", type M2, model 1000 extruder enabled production of a number of extrudate of satisfying chemical-nutritive profile (Table 1).

Analyses of total glucosinolate content have shown that tested rapeseed grown under local climatic conditions belongs to the rape variety with low glucosinolate content (varieties "00" with glucosinolate content up to 30 μmol/g in unprocessed seed) (Smithard and Eyre, 1986), thus making it suitable for use in feed formulations without pre-heat treatment providing for partial reduction in glucosinolate content.

As heat treatment is used to improve nutritive, hygienic, physico-chemical and other properties of treated material, to inactivate heat-unstable anti-nutrients, enhance nutritional value of ingredients and meet microbiological requirements of the product (Verheul, 1997), extrusion processing is, therefore, considered feasible solution in the production of rapeseed based feeds. This finding is in agreement with literature data on complete inactivation of myrosinase during dry extruding (Smithard and Eyre, 1986; Fenwick et al., 1986), an enzyme responsible for glucosinolates hydrolysis during which harmful and toxic products are generated (Bell et al., 1971).

Dry extrusion processing resulted in total glucosinolate reduction in range from 10-15%, with the highest total glucosinolate reduction level achieved upon extruding mixture of corn, rapeseed and alfalfa in ratio 60:30:10 (15,29%), and the lowest upon extruding mixture of rapeseed and wheat in ratio 50:50 (9,73%) (Table 1). Smithard i Eyre (1986) recorded somewhat higher total glucosinolate reduction levels (19-23%) with dry extrusion processing (135 °C) applied on mixtures of rapeseed with barley, rapeseed meal and sunflower meal, and of rapeseed alone of 19% (Aumaitre et al., 1989).

Table 1. Quality parameters of rapeseed, agricultural products and obtained mixtures before and after extrusion

Sample	*Moisture* (%)	*Crude protein* (%)	*Crude fiber* (%)	*Crude fat* (%)	*Mineral matters* (%)	*Total glucosinolates* (μmol/g)	*Total phenols* (mg/g)
Corn	11,94	7,88	1,97	4,49	1,14	-	0,48
Barley	10,10	10,68	4,21	1,89	2,22	-	0,88
Triticale	9,95	14,58	2,55	1,36	1,90	-	0,60
Wheat	11,62	12,47	2,00	1,29	1,51	-	0,53
Alfalfa	10,10	20,08	22,52	2,64	8,22	-	9,06
Rapeseed	5,63	21,17	9,03	40,56	3,68	21,35	7,36
Rapeseed E	4,78	19,53	9,45	39,26	3,72	18,40	7,35
Mixture 1	9,90	11,67	3,79	14,89	1,94	6,32	2,44
Mixture 1 E	6,82	10,39	2,93	15,35	2,10	5,61	2,46
Mixture 2	8,56	14,12	4,93	22,68	2,37	10,07	3,86
Mixture 2 E	5,80	13,16	4,27	23,44	2,55	9,17	3,92
Mixture 3	8,36	13,65	5,33	13,52	2,80	6,20	2,75
Mixture 3 E	5,66	12,94	5,01	14,62	3,12	6,28	2,74
Mixture 4	7,33	15,78	6,56	21,42	2,90	10,56	4,15
Mixture 4 E	4,79	14,37	6,70	22,16	3,05	9,53	4,19
Mixture 5	8,55	16,45	4,36	13,25	2,42	6,53	2,65
Mixture 5 E	5,90	15,22	4,57	13,60	2,52	5,77	2,63
Mixture 6	7,82	17,96	5,82	21,01	2,79	10,90	3,92
Mixture 6 E	4,77	16,86	5,91	21,49	2,74	9,71	3,97
Mixture 7	9,62	15,22	4,23	13,15	2,22	5 ,98	2,49
Mixture 7E	5,83	14,88	4,90	13,85	2,25	5,37	2,47
Mixture 8	8,52	16,33	5,15	20,80	2,66	10,25	3,96
Mixture 8 E	4,90	16,10	5,25	22,00	2,71	9,61	4,00
Mixture 9	9,79	12,72	5,96	15,01	2,49	6 ,13	3,34
Mixture 9 E	5,76	12,21	6,03	16,02	2,51	5,43	3,32
Mixture 10	7,73	15,35	7,76	22,46	3,10	10,35	4,86
Mixture 10E	4,60	15,07	7,78	22,84	3,14	9,46	4,87

Mixture 1: Rapeseed + corn 30:70
Mixture 2: Rapeseed + corn 50:50
Mixture 3: Rapeseed + barley 30:70
Mixture 4: Rapeseed + barley 50:50
Mixture 5: Rapeseed + triticale 30:70
Mixture 6: Rapeseed + triticale 50:50
Mixture 7: Rapeseed + wheat 30:50
Mixture 8: Rapeseed + wheat 50:50
Mixture 9: Rapeseed + corn + alfalfa 30:60:10
Mixture 10: Rapeseed + corn + alfalfa 50:40:10
E – *extrudate*

In paralell with above mentioned changes recorded in total glucosinolate contents after dry extrusion of examined material, total phenol contents remained unchanged in relation to untreated samples (Table 1), being in agreement with available literature data (Kozlowska et al., 1991; Naczk et al., 1996), and with observations regarding their heat stability (Sakac, 2000; Sakac et al., 2003) .

Previous finding concerning sinapine reduction recorded during toasting of dehulled and defatted rapeseed meal (Larsen et al., 1983) could be due to the duration of exposure time to heat treatment (30 minutes), while in dry extrusion process HT/ST principle of extrusion cooking (125 ± 1 °C for only 10 s) is duly respected, that is, examined samples are exposed to high pressure and temperature for a very short period of time, so that total phenol contents is not compromised (Sakac, 2000).

Preservation of total phenols during dry extrusion processing, although not desirable due to their anti nutritive properties, contributes, in overall, to the stability of resulting feeds with relatively high crude oil contents, regardless of documented antioxidative nature of phenol compounds in rapeseed. In other words, antioxidative effect of rapeseed meal extracts was monitored by examining inhibition of formation of conjugated diene and hexane in the systems containing rapeseed oil (Thiyam et al., 2004), and this effect is primarily due to the effects of esters and glycosides of sinapic acid as the most common phenolic acid in rapeseed, and a powerful scavenger of free radicals and antioxidants (Pekkarinen et al., 1999).

Conclusion

Based on the results of conducted studies relating to application of dry extrusion process on heat treatment of rapeseed in combination with the examined agri-cultures (corn, wheat, barley, triticale, alfalfa) it can be concluded that applied heat treating results in feeds of satisfying nutritional-chemical profile, with the reduction of total glucosinolates in range 10-15% and preservation of total phenols.

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UTICAJ EKSTRUDIRANJA NA SADRŽAJ UKUPNIH GLUKOZINOLATA I UKUPNIH FENOLA ULJANE REPICE

- originalni naučni rad -

Marijana B. Sakač, S. S. Filipović
Tehnološki fakultet, Novi Sad

Č. M. Borojević
MMB-Inexcoop, Šamac

M. D. Ristić, Š. M. Kormanjoš
Tehnološki fakultet, Novi Sad

Rezime

U radu je ispitan uticaj jednog od najfrekventnije korišćenih termičkih tremana u našoj zemlji, procesa ekstruzije, na sadržaj ukupnih glukozinolata i ukupnih fenola uljane repice i kombinacija uljane repice sa poljoprivrednim proizvodima (kukuruz, pšenica, ječam, tritikale, lucerka).

Ekstrudiranje uljane repice i kombinacija uljane repice sa poljoprivrednim proizvodima (uljana repica: poljoprivredni proizvod – 30:70 i 50:50, odnosno kukuruz: uljana repica: lucerka – 60:30:10 i 40:50:10) vršeno je na uređaju "Oprema-zootehnička oprema", tip M2, model 1000, pri radnoj temperaturi 125 ± 1 °C.

Na osnovu sprovedenih ispitivanja može se zaključiti da primenjeni termički tretman rezultira dobijanjem hraniva zadovoljavajućeg nutritivno-hemijskog profila, uz redukciju sadržaja ukupnih glukozinolata u rasponu od 10-15%, dok sadržaj ukupnih fenola ostaje nepromenjen u odnosu na netretirani materijal.