Heat treatment of rapeseed as an alternative to formaldehyde use for protecting proteins in rumen

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Abstract

Formaldehyde treatment is currently used as a procedure to protect the proteins of feedstuffs in rumen and decrease, in this way, their degradability. 60% of rapeseed meal actually used in France by dairy cows are treated by formaldehyde. Nevertheless, questions about risks of formaldehyde for consumers have been recently raised. If this chemical compound ought to be forbidden by European regulations, alternative treatments of meals must be used and prove a technical and economical equivalence with the actual practice. The objective of this study was to evaluate alternative ways to the traditional crushing process : 1) for protecting rapeseed proteins through heating treatments, 2) with preserving a good quality for crude oil. Five experimental crushing processes were tested in the oil-mill pilot plant of CREOL (Pessac-F) in comparison with the traditional crushing process (flaking-cooking-pressing-classical solvent extraction [C]). The five treatments were : cooking before flaking (135°C during 60 min and 135°C during 80 min, cooking before pressing (105°C), pressing and classical solvent extraction [CBF60 and CBF80], cold pressing, extrusion (two values for the die-wormshaft spacing) and classical solvent extraction [PE1 and PE2], flaking-cooking-pressing-long term solvent extraction [LTD]. The treatments CBF60, CBF80, PE1 and PE2 highly decreased protein solubility of deoiled meal (respectively 24%, 22%, 33% and 28%, as measured by the solubility in NaOH), the solubility of the control being 45%. The ruminal degradability of meals obtained by treatments CBF80 and PE2 were 55% vs 63% for the control and 30% in the case of a formaldehyde treatment. Nevertheless, the quality of crude oil, as measured by peroxide and para-anisidine index, was altered, probably due to heat treatments. The LTD treatment (heat treatment on deoiled meal) is probably the best way to protect the meal proteins (solubility in NaOH of 20%) while preserving the quality of the crude oil. Further studies are actually done in the pilot plant of CREOL for optimizing the parameters of desolventation.

Introduction

High producing animals (dairy cows) need essential amino-acids (lysine, methionine) at the small intestine. These amino-acids are not synthesised in sufficient amounts by the rumen micro-organisms (Vérité et Peyraud, 1988) and must be supplemented under the form of protected protein able to be transferred through the rumen without degradation (by-pass effect). Rapeseed meal is appreciated in animal feeding because of its high content of protein and the well balanced amino-acid composition. Associated in a diet, with grass silage containing highly degradable proteins, the rapeseed meal proteins will be optimally utilized if they are able to by-pass the rumen. Several processes were studied to lower the degradability of the protein and currently, the more efficient consists in a chemical reaction with formaldehyde. This treatment, called tanning, has been carried out industrially, for more than twenty years, on the oil cakes of rapeseed and soybean. The tanning by formaldehyde currently used in France (INRA, 1992) is effective since the degradability is lowered from 69 % to 30 % (for rapeseed meal proteins) and the increase of the quality allows its payback. The major part (60%) of rapeseed meal actually used in France by dairy cows is treated by formaldehyde. However, questions about risks of formaldehyde for consumers have been recently raised and this treatment, even accepted by the French agency for food safety (AFSSA, 2004), remains potentially suspect because of its chemical nature and the hazardous handling during the process. On the assumption of a future limitation of formaldehyde by the European rules, alternative ways avoiding chemicals could be then proposed. A few years ago, such processes based on thermal treatment have been experimented on seeds (Expro process), flakes or meal (Herlam, 1996). Heating before the extraction steps may have significant effects on the quality of the oil. The phospholipase-D enzymes could be inhibited and the phospholipids content of the oil, modified. In addition, an oxidation of the oil may occur. These effects have to be precisely evaluated to determine the nutritional and economical interest of the thermal tanning processes compared to the current practice.

In the present work, five crushing processes have been studied in comparison with the traditional crushing process, in the oil-mill pilot plant of CREOL (Pessac-F). These processes involved a heating treatment (cooking or extrusion) before, between or after the pressing and solvent extraction steps. Two technical criteria were evaluated: degradability of rapeseed proteins measured *in sacco* on fistulated cows, quality of the crude oil (peroxide and para-anisidine indexes, phosphorus content).

Experimental

Material **:** the different batches of rapeseed seeds used for the experiments were produced in France in 2003 in the Charentes-Poitou area. The cultivars were not identified, but the quality of the seeds was in agreement with the national trade rules (moisture, impurities and glucosinolates).

Technological treatments : the classical process used in industry and the five processes studied are described in the figure 1. The classical process C consisted in flaking at 300 kg/h (Flaker Damman-Croes with distance between rolls : 0,1 mm), cooking (vertical cooker heated by jacket steam, 95 °C, 60 min), pressing at 300 kg/h (Press Mécanique Moderne model MBU 75), continuous solvent extraction (Belt extractor De Smet, 50-55 °C; flow rates cakes and solvent : 130 kg/h and 220 l/h) and desolventisation (Desolventiser-toaster De Smet, Schumacher type, steam injection : 20 kg/h, temperature lower plate : 110 °C, duration 90 min). The miscella was distilled in a continuous three stages stainless-steel distiller (De Smet, at 90°C and vacuum in the stages at 400 hPa, 200 hPa and 45 hPa).

Two processes, CBF60 and CBF80 (cooking before flaking), used the heating treatment before the oil extraction. The heating was carried out by cooking the seeds at high temperature (135 °C) during 60 min and 80 min before flaking. The flow-rate was 300 kg/h. The flakes were then kept at 105 °C during 10 min, then pressed, extracted by solvent and desolventised following the classical way.

Two other processes, PE1 and PE2 (pressing-extrusion), used the heating treatment after the cold pressing and before the solvent extraction of the oil. The seeds were pressed at 300 kg/h and the cake was then extruded at 200 kg/h. The die-wormshaft spacing of the extruder (France-Extrusion) was adjusted to give different temperatures (135 °C for PE1 and 162 °C for PE2). The extruded cakes were then extracted by solvent and desolventised following the classical way.

The process LTD (long-term desolventisation) followed the classical way, except for the desolventisation step. The temperature in the desolventised-toaster (DT) was like in industry (110 °C) but the duration of the treatment was increased until 4 h by stopping the flow of matter in the DT.

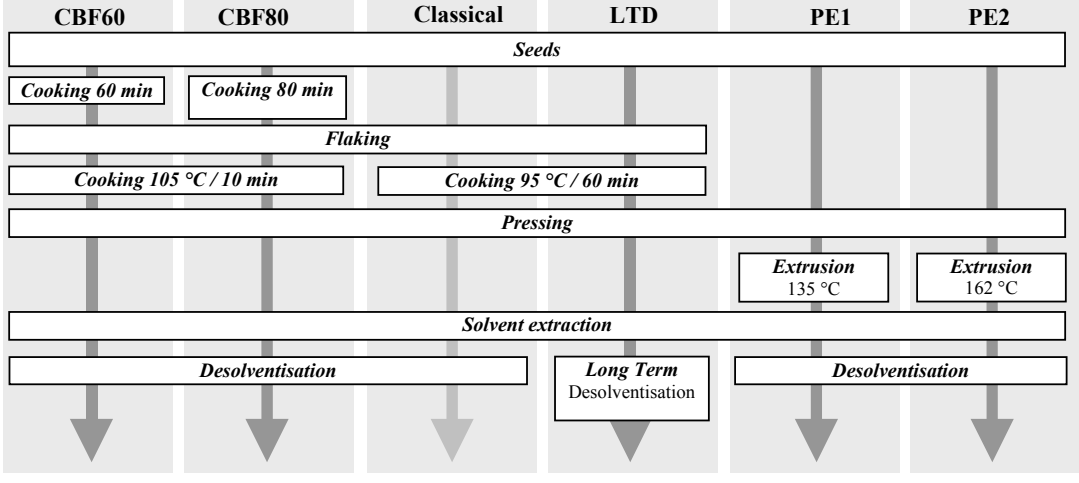

Figure 1: the different processes studied in the CREOL pilot plant, for tanning rapeseed proteins.

Analysis of meal and seed : standardized methods were used to determine the content of oil (ISO 659 and ISO 10565), moisture (V03-909), protein (NF V18-120 and ISO 5983), glucosinolates (ISO 9167-1). In-house validated methods were used for protein solubility in NaOH, enzymatic digestibility 1 h (DE1). The theoretical degradability (Dth) was determined *in sacco* (Nylon bag method) on non-lactating cows (Holstein) equipped with a rumen canula.

Analysis of oil : as the heating treatment of CBF60, classical and processes occurred before pressing, the oil quality was determined on the press oils. On opposite, for PE2 process, the impact of the heating treatment was determined after the extrusion step, on the oil obtained by pressing the extruded cake. Oil quality was not measured with LTD, CBF80 and PE1 processes.

Standardized methods were used to determine the oleic acidity (ISO 660), peroxide index (ISO 3960) and p-anisidine index (ISO 6885). Phosphorus was determined according to IUPAC 2.423 before and after degumming with 3 % water at 75 °C during 30 min and centrifugal separation.

Results and discussion

Cooking Before Flaking (CBF) and Pressing Extrusion (PE) Processes

The materials processed by CBF and PE (seeds or expeller meal) have an important content of oil. As the processes used a heat treatment (cooking or extrusion) for tanning the proteins, which may have a detrimental effect on the oil quality, the determination of the quality of both meal and oil was then necessary (table 1).

Quality of the de-oiled meals : processes CBF60, CBF80, PE1 and PE2 decreased protein solubility (in NaOH), from 85 % for the seeds to respectively to 24, 22, 33 and 28 % for the de-oiled meals. For the Classical process, the decreasing is lower: from 85 % to 45 %. The contribution of the tanning step in each process can be observed in figure 2, by comparing the effect of the treatment before the solvent extraction. Results show logically, that CBF80 is more efficient than CBF60, and PE2 than PE1. In addition, lower is the solubility of the proteins of the meal before the solvent extraction, weaker is the effect of the classical desolventisation treatment.

The theoretical degradability (Dth) was only measured on BCF80, PE1 and the Classical meal. Compared to the

Classical meal, the PDIA value (content of protein which by-passes the rumen) of CBF80 and PE1 meals were increased by respectively 27 % (from 122 to 155 g/kg DM) and 17 % (from 122 to 143 g/kg DM). These results must to be compared to the tanning effect obtained by the action of formaldehyde. The Dth of a rapeseed meal tanned with formaldehyde is around 30 % and the PDIA value is 212 g/kg DM (INRA-AFZ, 2002). The efficiency of the heat tanning is then lower than the chemical one. The levels of hexane residue in the meals BCF60, BCF80, PE1 and PE2 are significantly lower than in the "Classical" meal. In addition, compared to the classical process, only PE1 and PE2 allowed a better extraction of the oil (1,6 % versus 2,3 %). These results could be explained by the beneficial effects of the cooking and extrusion treatment on the extractability (rate of extraction under specific conditions) and the inextractible oil content and by the low moisture content of the cakes before extraction by solvent.

Table 1: Quality of the oils and meals obtained par the processes CBF60, CBF 80, Classical, PE1 and PE2.

Process		CBF60	CBF80	Classical	PE1	PE2
Quality of seeds						
Oil content (% DM)		48,9	48,9	48,9	48,9	
Protein solubility in NaOH (%)		85	85	85	85	
Quality of expeller cakes						
Cooking before pressing		130 °C/ 60 min	130 °C/ 80 min	95 °C/ 60 min	no	
Moisture content (%)		4,4	4,0	7,0	8,3	
Oil content (% DM)		17,2	16,6	15,0	18,4	
Protein solubility in NaOH (%)		35	29	75	86	
Quality of the press oil						
Oleic acidity (%)		0,39	nd	0,46	0,19	
Peroxide index ($meqO_2$/kg) (IP)		2,2	nd	2,8	1,9	
p-anisidine index (Ian)		4,8	nd	1,4	1,8	
Tot-Ox Index (Ian + 2 IP)		9,2	nd	7,0	5,6	
Phosphorus (mg/kg)	Before degumming	177	nd	351	15	
	After degumming	6	nd	302	5	
Quality of the extruded flakes						
Extrusion conditions		no	no	no	135 °C	162 °C
Moisture content (%)		nd	nd	nd	4,2	3,3
Oil content (% DM)		nd	nd	nd	18,0	19,2
Protein solubility in NaOH (%)		nd	nd	nd	48	42
Quality of the residual oil *						
Oleic acidity (%)		nd	nd	nd	nd	3,3
Peroxide index ($meqO_2$/kg) (IP)		nd	nd	nd	nd	1,7
p-anisidine index (Ian)		nd	nd	nd	nd	18,1
Tot-Ox Index (Ian + 2 IP)		nd	nd	nd	nd	21,5
Phosphorus (mg/kg)	Before degumming	nd	nd	nd	nd	3110
	After degumming	nd	nd	nd	nd	50
Quality of the de-oiled meal						
Moisture content (%)		7,9	8,0	8,5	9,6	8,2
Oil content (% DM)		2,0	2,3	2,3	1,6	1,6
Hexane residue (mg/kg)		105	108	494	176	182
Protein solubility in NaOH (%)		24	22	45	33	28
Enzymatic digestibility (%)		nd	14,0	31,0	14,8	nd
Theoretical degradability in sacco (%)		nd	55,3	63,2	55,5	nd
PDIA (g/kg DM)		nd	155	122	143	nd

nd : no determined PDIA : proteins digestible in intestine * obtained by pressing

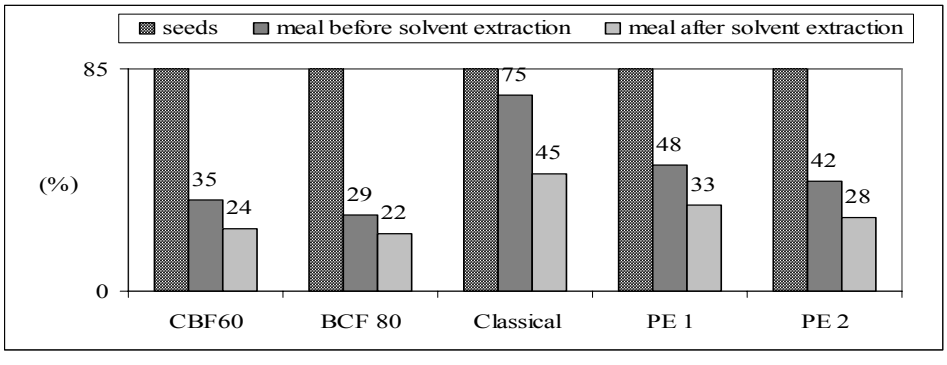

Figure 2: Solubility of proteins (in soda) measured at different steps of the five processes.

Quality of the oil : The effects of the thermal treatments can be checked (table 1) on the Tot-Ox index of the press oil which increases from 5,6 for the PE1 oil (cold pressing) to 7,0 for the "classical" oil (cooking at 95 °C and pressing) and 9,2 for the CBF60 oil (cooking at 130 °C and pressing). The level of non-hydratable phospholipids is low in the CBF60 press oil (6 mg/kg) because of the inactivation of the phospholipases-D during the cooking. With the classical process, the phosphorus content is high (350 mg/kg) and the main part (86 %) is in the non-hydratable form. For the PE process, the press oil obtained before extrusion has a lox Tot-Ox value (< 6) and a low total phosphorus content (15 mg/kg) as it is usual with cold pressing oils. In contrast, the quality of the oil obtained (by pressing) after the cooking-extrusion treatment has dramatically decreased since Tot-Ox value is more than 20 and the content of total phosphorus is very high (> 3000 mg/kg).

Long-Term Desolventisation Process (LTD)

Previous experiments to optimise the tanning during the desolventisation showed that the high temperature (> 125 °C) necessary to obtain a significant effect, was difficult to apply in the DT because of the high pressure of steam necessary (1 MPa). In addition, the control of the duration of the treatment in a continuous flow was found difficult because of the geometry of the DT (important dead volumes). To apply a heat treatment, the alternative way to high temperature, was to maintain the usual temperature (110 °C), to stop the steam injection, and to increase the duration of the presence of the meal in the DT. The supposed beneficial is the saving of energy and a better control of the treatment duration.

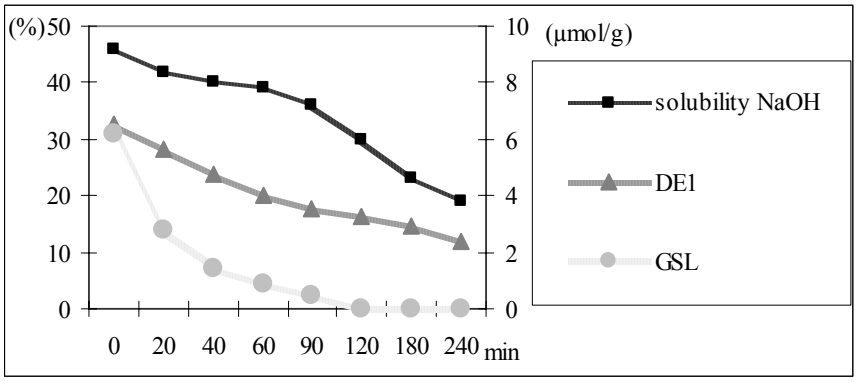

Figure 3: Decrease of the solubility (in NaOH) of the proteins, of the enzymatic digestibility 1 hour (DE1) and the glucosinolates (GSL) content of rapeseed meal in the DT at 110 °C without steam injection.

Figure 3 shows preliminary results on the" response" of the meal when treated during a long time in the DT. The solubility of the proteins, the DE1 value and the glucosinolates (GSL) content was decreasing during four hours. These results were obtained by stopping the flow of the matter and their reproducibility indicates that the optimisation of the process to reach the control of the tanning effect, the breakdown of the GSL and the hexane residue will be more efficient on equipment working in batch than on a continuous flow. Then, our future experiments on this process will be carried out on a small sized reactor simulating the desolventisation.

Conclusion

This study showed that heating rapeseed for tanning the proteins is accompanied by an oxidation of the oil. Such processes applied on seeds or expeller meals in a way to reduce significantly the theoretical degradability of the proteins, produce press or solvent extraction oil with an alteration which may not be reduced by refining. On opposite, the heating treatment may have a beneficial effect on the phosphorus content and the nature, hydratable or not, of the phospholipids.

These results direct our research on the way of the long-term desolventisation (LTD) because this process does not involve the heating of the non extracted oil. This process may also save energy since, the heat absorbed by the meal does not need to be increased but only maintained for a longer period. Moreover, the equipment involved is less expensive than an extruder or a cooker and could be easily applied in industrial plants.

The optimisation of the LTD process will be possible only if the experimental conditions are well controlled. Our experience with a pilot-scale DT shows that a laboratory scale equipment is necessary to better control the conditions, to get numerous samples of meal (especially when non desolventised), to monitor kinetics and to establish a model for simulation. The pilot-scale experiment will confirm and allow the extrapolation of the results.

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