

# Interest of hydro-alcoholic treatment of rapeseed for oil extraction and protein enrichment

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#### Interest of hydro-alcoholic treatment of rapeseed seeds for oil extraction and protein enrichment

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Global rapeseed production has steadily grown over the past 20 years. It has been followed by an increase of the rapeseed meal production and sale. The rapeseed meal is rich in proteins characterized by an excellent nutritional value. However, its valorisation is affected by a low digestibility linked to the presence of anti-nutritional factors (fibres, glucosinolates, phenolic compounds...) and to a loss of solubility of the proteins during the current crushing process. Furthermore, the use of hexane as extraction solvent faces to the threat of its utilization restriction even or prohibition. Various solvents, mainly from renewable resources have been tested as a substitute for hexane. Alcohols such as ethanol and isopropanol, seem promising alternative solvent. Being more polar than hexane, alcohols have a greater affinity with non-lipid components such as sugar, phenolic compounds, glucosinolates..., allowing the detoxification of the meal and the protein concentration. However, some constraints have hitherto limited their industrialisation. Indeed, they are characterized by a low selectivity for oil, a low capacity to solubilize the oil at conventional extraction temperatures and a high regeneration cost in comparison to hexane. The aim of this work was to investigate the influence of the alcohol degree and of the processing conditions on the oil extraction and meal quality. Extraction was carried out on rapeseed using hexane, ethanol (92 wt% or 96 wt%) or isopropanol (8 wt% or 88 wt%). Results indicated that hydro-alcoholic extraction increased the protein content of the meal of 12% compared to hexane extraction meal, but without significant influence of the alcohol type and degree. On the contrary, decrease of alcohol degree improved the glucosinolates extractability. In particular, isopropanol 84 wt% eliminated the most of glucosinolates of the seeds, decreasing of the concentration from 56 to 70% compared to meals extracted by the other alcohols.

## **OLEAD Presentation**

- → Center of research and experimentation in oilseeds and protein crops processing created in 1980
- → OLEAD expertise: oil extraction and refining, extraction and valorisation of minor compounds, effects of the technology on oil and meal quality, equipment design and process scaling-up
- → Different equipment reproducing unitary operations of the oilseed extraction and refining process:
  - lab-scale (0,001-15 kg)
  - pilot-scale in batch mode (15-100 kg) and continuous mode (200 kg/h)















#### Conventional process for rapeseed oil extraction



#### Major obstacles limiting rapeseed meal valorisation as protein source:

- Its low digestibility linked to the presence of anti-nutritional factors (fibers, glucosinolates, phenolic compounds...),
- The extensive denaturation of proteins during the oil-extracting process,
- Its low protein concentration (38%),
- The use of hexane as extraction solvent, face to the threat of its utilization restriction or prohibition.

## **Alternative solvents: ethanol and isopropanol**



#### Benefits

- + Less toxic
- + Less flammable
- + From renewable resources
- + Extraction of some non-lipid matters soluble in alcohol
- = Protein concentration and meal detoxification

#### Risks

- Higher distillation temperature
- More polar solvent

= Limited miscibility with oil and limited selectivity of extraction

 $\rightarrow$  Low efficiency if traditional extraction with solvent distillation is applied

To turn minuses into pluses  $\rightarrow$  Alternative scheme with oil separation by chilling

## Solubility of crude rapeseed oil in alcohols



Solubility in ethanol (EtOH) and isopropanol (i-PrOH) / water mixtures (data of OLEAD)



→ Oil solubility decreases with: - increase of water content in the solvent,
- temperature decrease

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ightarrow New scheme adapted to the oil extraction by alcohol

ightarrow Reduction of the energy consumption required to distillate solvent

# New solvent → new process, new conditions and final product quality









#### Rapeseed:

Moisture content	Total oil content	Average proteins content	Glucosinolates content
(%)	(% of dry matter)	(% of dry matter)	(µmol/g of dry matter)
4.8	49.5	19.2	17.2

### Solvents:

Hexane

Isopropanol/water mixture (84 and 87.8 wt. % EtOH)

Ethanol/water mixture (92 and 95.6 wt. % i-PrOH)

## **Tested process and used equipment**







### Oil extraction yield



→ As the solubility of the rapeseed oil decreases with the alcohol content, a larger quantity of solvent will be required and so a larger number of washing steps will be needed to extract the same oil amount.



#### Non-lipid dry matter extraction yield



→ Alcohols are less selective for oil than hexane: they extract some non-lipids compounds.
→ The extracted non-lipids represents 11 – 15 % of the initial defatted matter.



#### Rapeseed meal characterization

Meal	Proteins conte (% of deoiled c matter)		ænt G dry (μm	Glucosinolates (µmol/g deoiled dry matter)		Protein solubility (%)		
Rapeseeds	38			34		-		
Meal_Hexane	38			25		87		
Meal_EtOH 95.6 wt %		42		19			77	
Meal_EtOH 92 wt %		43		14			74	
Meal_i-PrOH 87.8 wt %		43		14			68	
Meal_i-PrOH 84.2 wt %		44		7			60	

→ Extraction of non-lipids (11 – 15 wt. %) increases the protein concentration in the meal on 4 - 6 %.

 $\rightarrow$  Alcohols eliminates glucosinolates from the meal (in particular, 84 % isopropanol)

## **Comparison of oil recovery procedures**





# **Results: Oil recovery**



Quantity of oil recovered by chilling in comparison to the extracted oil



→ Recovered oil proportion increased with decrease in temperature and alcohol content in the solvent.

# **Results: Oil quality**

## Oil composition

	Distillated oil composition					
	Lipid (%)	Non-lipid dry Phosphorous matter (%) (mg/kg on DM				
EtOH 95.6%	87	13	1035			
EtOH 92.0%	75	25	1817			
i-PrOH87.8%	84	16	888			
i-PrOH 84.2%	85	15	1502			
Hexane	100	0	28			

→ After cooling the miscella, non-lipid matters and phosphorous are retained in the solvent, resulting in better oil quality in comparison to the oil recovered by distillation.

→ Residual solvent content in decanted oil: 7-10% depending on the solvent, so, 0.05-0.2% of the initial amount of solvent,

Stripping cost: 11-18% of the energy used in hexane distillation.





✓ New process adapted to the rapeseed extraction by alcohol is analyzed:

	Oil	Oil quality	Rapeseed meal quality			
Solvent	extraction	Phospholipids	Protein	Protein	Gluco-	
	yield	content	content	solubility	sinolates	
Ethanol 95.6 wt %	+	+	+	+	-	
Ethanol 92 wt %	-	+	+	+	++	
Isopropanol 87.8 wt %	+	+	+	-	++	
Isopropanol 84.2 wt %	-	+	+		+ + +	
Hexane	+ +	-		+ +		

- ✓ 12% increase of the protein content of the meal compared to hexane extraction
- ✓ Low concertation of residual glucosinolates in the meal, when alcohols are used for extraction
- ✓ Oil recovery by miscella cooling  $\rightarrow$  high quality crude oil simpler to refine



Oil : lipid and non-lipid content (Folsch )

Rapeseed meal

- extractable and non-extractable oil content (NF v03-908)
- proteins content (NF EN ISO 5983-2)
- glucosinolates content (NF ISO 10633-1)