Sustoil

D2.1: Report about dehulling, the first step of oilseeds bioreffining

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Dehulling

Table of content

Raw material

Rapeseed

The rapeseed seed is has no albumen; the embryo is wrapped in tegument, a thin black coat composed mainly of fiber, of which a strong proportion of lignified material.

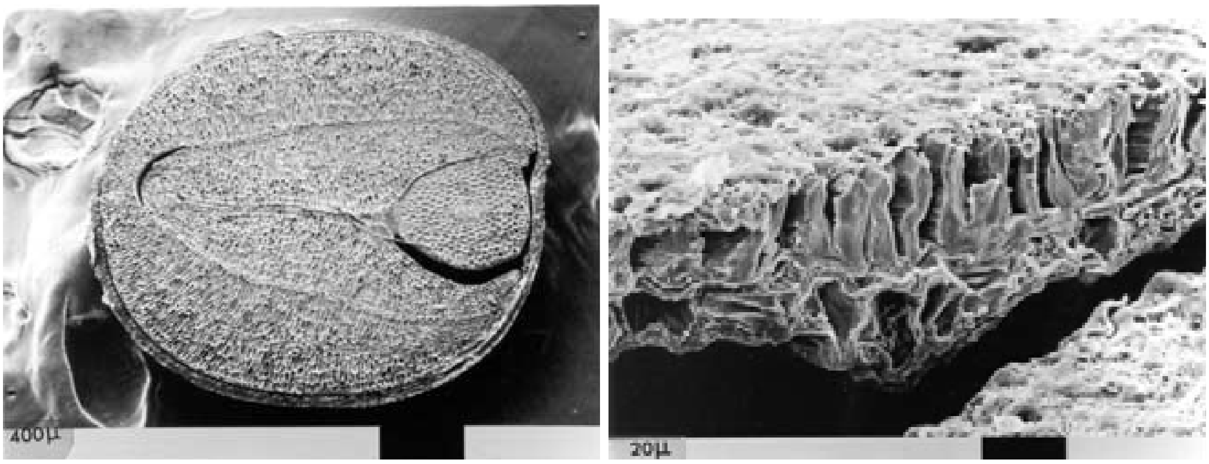

Figure 1: rapessed embryo and hull [1]

Table 1: composition of rapeseed seeds, hulls and kernels

	Seeds	Kernels	Hulls	Meal from seeds	Meal from dehulled seeds
Dry matter (DM) %	91.9	93.4	14.3	93.3	93.5
Oil (%/DM)	47.7	53.3	12.0	1.0	1.0
Proteins kjeldahl (%/DM)	21.8	24.5	15.2	40.7	44.2
Crude fibers (%/DM)	8.1	2.7	32.3	15.2	6.4
Ashes (%/DM)	4.7	4.7	6.6	8.5	9.7
NDF (%/DM)	14.9	5.27	50.7	30	11.2
ADF (%/DM)	11.2	3.3	41.8	22.5	6.7
ADL (%/DM)	5.9	0.3	23.1	11.1	0.9

Source : CETIOM CREOL / N29 (INRA seeds "temoin", Feedbase[2])

The percentage of hulls in rapeseed is 12-13 % according CETIOM. Other sources are situating the hulls percentage in a wider range (12-20%).

According to these results, one can consider that rapeseed hulls contain around 3 % of seeds oil and protein and more than 70 % of its fibers, of which 95 % of the lignin.

[1] M. Rass, Zur rheologie des biogenen Feststoffs unter Kompression Am Beispiel geschälter Rapssaat, PhD thesis, dem Fachbereich 12 - Maschinenwesen - der Universität Gesamthochschule Essen, May 2001.

[2] Feedbase is a data base of the French association for animal production. This database contains 1.5 million analytical data about feed stuff supplied by 19 members who are research organization and feed companies. http://www.feedbase.com/technical.php?Lang=E

The removal of this material could enable the production of an improved meal quality thanks to dramatic reduction of its fibers content (reduction of NDF, ADF and ADL respectively of 63, 70 and 92%).

Provided that it can be desolventized without damaging the protein solubility, this meal could be used after hydro-alcoholic extraction of soluble sugars or protein extraction for human food or non food applications.

The CETIOM studied the composition of the oil stemming from the hulls in industrial conditions. It was noticed that the oil extracted from hulls after 11 days of storage has a very high acid value a dark color and has a very low quality. The oil quality just after dehulling has been investigated. Acidity was 3.3 % versus 1.0 and 1.4 for the press and extraction oils, para-anisidine index 4.4 vs 2.1 and 2.8, tocopherol 850 ppm, vs 916 and 1180 ppm. Although low, this quality was not considered too decreased to authorize a valorization by extraction.

Liu[3] and al. (1996) have studied the composition of the fats of Canadian and Australian rapeseed hulls. According to their results, rapeseed hull contains waxes and polar compounds that can sediment during cold storage. These waxes are not the same than in sunflower, the average chain length is shorter and in consequence, the standard winterization treatment is not convenient. These waxes can cause some trouble in rapeseed oil after refining although dewaxing is not a common practice in Europe concerning the rapeseed oil.

Sunflower

Sunflower seed is an achene, therefore, a dehiscent fruit. The coats of sunflower are produced by the ovule.

The percentage of kernels and hull in sunflower are variable according to the cultivar, the size of the seeds and their oil percentage. Most of the values are comprised between 22 to 28 %. Breeders have done considerable work to increase the oil composition of the seed. Part of this change comes from a reduction of the hull percentage in the seeds. In general, the varieties with high oil content have low hulls percentage. The consequence of this change is a reduction of the seeds ability for dehulling.

[3] Liu H., Przybylski R., Dawson, Eskin N.A.M. and Biliaderis C.G., Comparison of the composition and properties of canola and sunflower oil sediments with canola seed hull lipids. J.A.O.C.S. Vol 73n°4, 493-498

Table 2: composition of sunflower seeds, kernel and hulls.

SUNFLOWER	Seeds	Pure kernels	pure hulls	Meal from seeds	Meal from dehulled seeds
Dry matter (DM) %	92.8	90.5		88.8	90.5
Oil (%/DM)	48	61.25	2.5	2.2	1.2
Proteins kjeldahl (%/DM)	16.7	20.6	6.2	31.9	52.6
Crude fibers (%/DM)	17.3	2.4	57.6	28.1	6.2
Ashes (%/DM)	3.5	3.6	3.2	7.05	9.24
NDF (%/DM)	26.6	5.4	83.9	45.1	13.7
ADF (%/DM)	19.5	2.7	64.9	32	7
ADL (%/DM)	6.3	0.4	22.3	10.5	0.9

Protein content of pure defatted kernels is very high and could be compared with soybean.

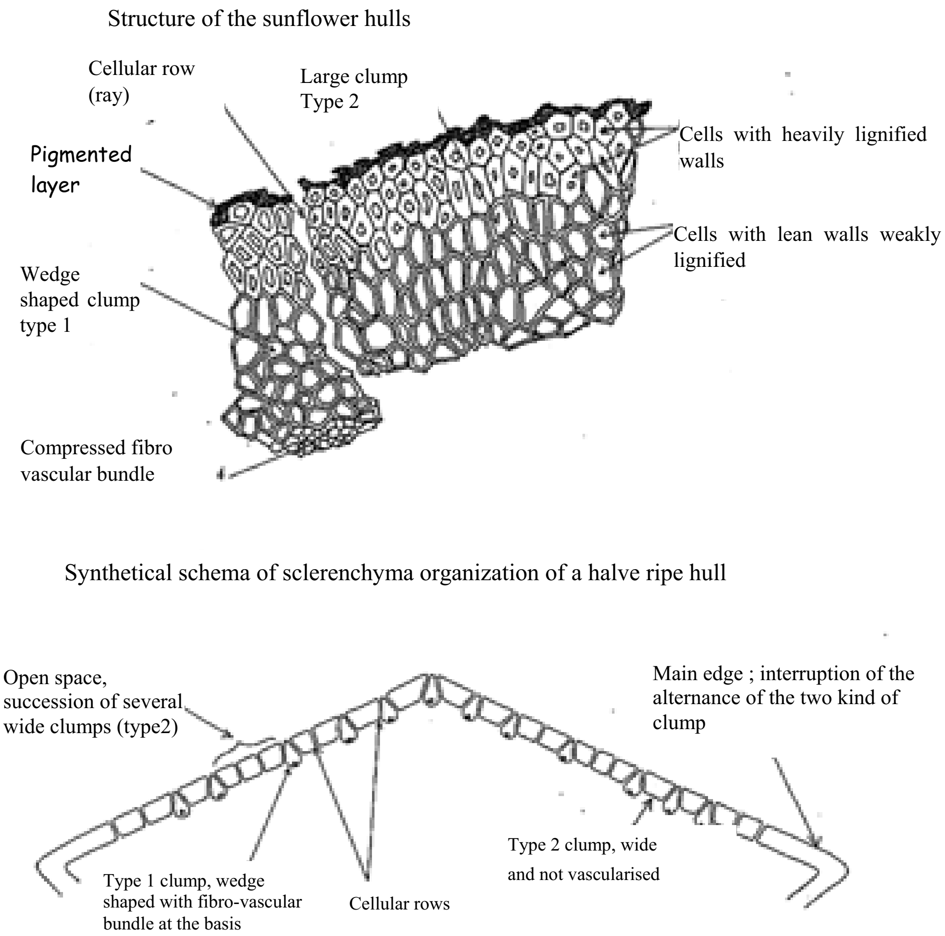

Figure 2: Structure of sunflower hulls[4]

[4] Beauguillaume A., Architecture des coques de tournesol – OLEOSCOPE, Bulletin du CETIOM, 1982, N°8, 20-21

Hulls in sunflower contain 2-3 % of seed oil, 10 % of the seeds protein and 85, 90 and 95 % of the NDF, ADF and lignin of the seeds.

The architecture of the hulls has been studied by Agnès Beauguillaume in a PhD thesis work. She explained the hullability of the seeds by the repartition of two kinds of sclerenchymas (type 1 / type 2, see fig.2). Type 1 clumps are wedge shaped and have fibro-vascular bundle at their base while type2 clumps are not vascularised and wide. In cultivar with favorable ability for dehulling, type 1 clumps are more frequent. Their structure gives more rigidity to the hulls which are more likely to break under the impact of the dehuller. A greater abundance of type structures gives more elasticity to the hull that will deforms under the chock instead of cracking. This character is genetically determined and could be improved by selection.

A particularity of sunflower is the presence of waxes in the oil. Waxes are concentrated at the surface of the hulls where they play a role to protect the seeds against the water, therefore, against the molds that need some water to live and to attack the seeds. The table n°3 gives some information about the composition of oil according to the dehulling.

Table 3: waxes in sunflower oil and dehulling[5]

Product	Waxes in oil (mg/kg)
Oil stemming from hulls	17 250 – 14 955
Whole seeds	1 254 – 1 008
Dehulled seeds	759 – 580
Cold pressed oil	771
Warm pressed oil	947
Hexane extracted oil	1 073
Refined (marketed oils)	366 – 624

Denise[6] in its book about the refining indicates that the dehulling enables the production of crude oils with 40 to 300 ppm of waxes when non dehulled seeds are containing 600 to 900 ppm (up to 1200 ppm for oils coming from the USA). Winterization has to reduce the waxes content of oils up to 50-150 ppm.

Figure 3: Wax bundle on a sunflower hull magnified 2500 times

It is possible to explain the differences between the information from the two authors by the kind of dehulling that they are taking in consideration.

[5] A. Carelli, Frizzera L., Forbito P., Crapiste G. – Wax composition of sunflower seed oil – JAOCS vol 79, n°9 pp763-768 (2002)

[6] J. Denise Le raffinage des corps gras – Westhoeck Editions – Les éditions du Beffrois – pp153 - 1982.

Another characteristic of the sunflower hulls is their content in silicon that makes them a very abrasive product that cause some wear in the presses. The removal of hulls is likely to reduce maintenance costs on the side of the press spare parts but, it will generate a constraint on the dehulling equipments, especially if some pneumatic transportation is used.

Dehulling equipments

Rapeseed

CETIOM dehuller

The French institute for oilseeds has patented in the 70's a centrifugal propeller in which the seeds are projected against a target with controlled speed in order to separate meats and hulls. Seeds are fed in the center of a rotating disk bored of radiating channels. By centrifuge force, the seeds are propelled against the wall of the device and the impact makes the seed shatter. Speed of the disk and flow rates are both adjustable.

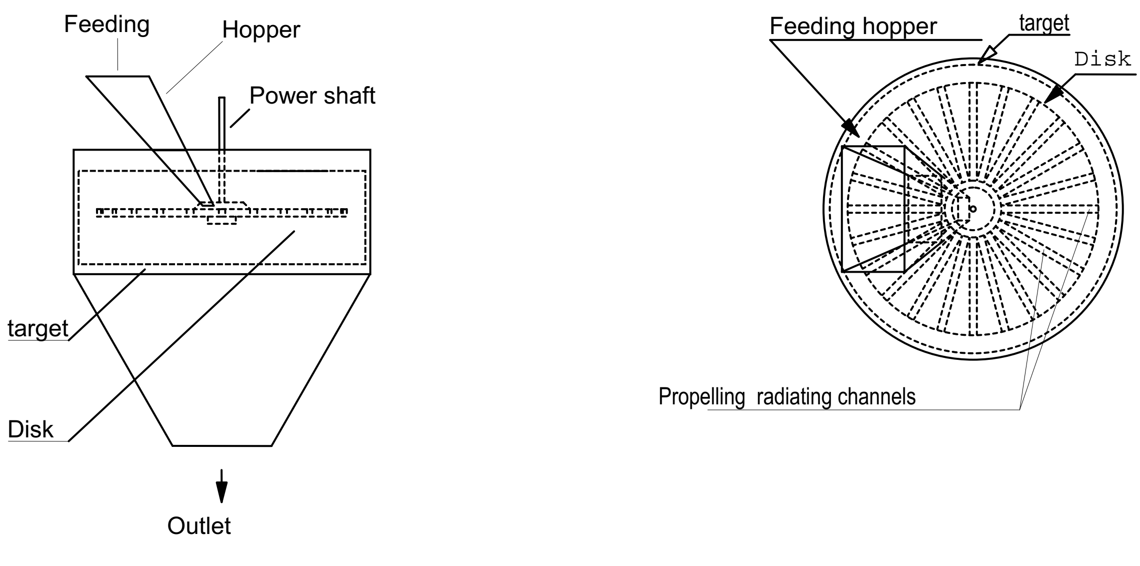

Figure 4: the CETIOM dehuller

Abrasive dehuller[7]

Abrasion is the common mean way o produce white rice. The seeds are introduced in a rotating device whose wall is abrasive. The coats of the seeds are removed by abrasion. By adjusting the rotating speed and the throughput of seeds, it is possible to adjust the percentage of biomass that is removed.

[7] Ikebudu, J. A., Sokhansanj, S., Tyler, R. T., Milne, B. J., Thakor, N. S. « Grain conditioning for dehulling of canola. » - Canadian Agricultural Engineering Vol 42, n°1, 4.1-4.13.

Rolls dehuller[8].

The seeds are briefly passed through co-rotating rolls with a carefully adjusted gap. This method has been described by Schneider in 1979. The seeds have to be sorted before treatment in order to remove the little ones and hydrothermal conditioning is carried out to improve the hullability. A 0.6 mm space between rolls would permit to reach the better efficacy. No data were provided concerning the percentage of fat of the hulls thus obtained.

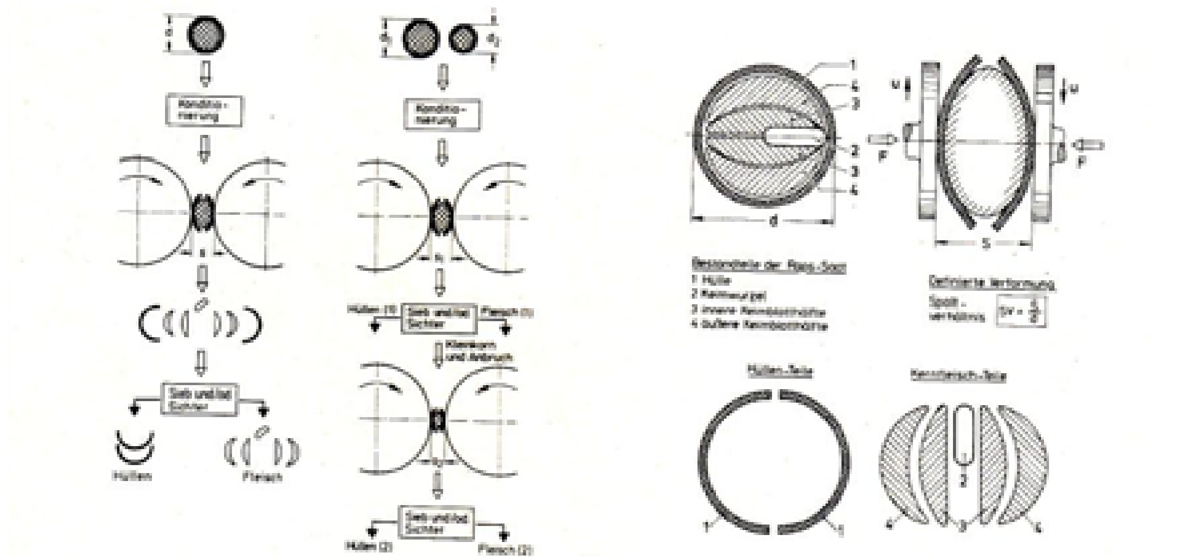

Figure 5: Principe schema of controlled deformation dehulling[9]

Tail-end hull separation[10]

Hulls are separated from meats after oil extraction by air transportation. The separation is based on supposed differences of behavior between meats and hulls. The meals must be milled prior to this treatment. According to the available information, that kind of treatment is not very efficient.

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8 Sneider F.H. – Zur Bewertung der trennergebnisse bei der shälung of rassaat – Fette 1982, n°6 213-220

9 Schenieder F.H. – Schâlung von Rapessast durch definierte Verformung. Teil I : Untersuchungen zur Saatanatomie – Fette, 1979, Vol 81 n°1, 11-16

10 Mustafa A.F./Christensen D.A./Mckinnon J.J. Chemical characterization and nutrient availability of high and low fiber canola meal. 1996 – Canadian Journal Of Animal Science - Vol. 76, n° 4, p. 579-586

Table 4: Performance of tail-end separation according to Mustafa et al.

Tail end hull separation	Low fiber canola meal (%)	Ordinary CM (%)	High fiber CM (%)
Proteins	40.2	37.7	35.2
NDF	24.6	26.7	35.2
ADF	14.4	19.3	23.9

Infrared + microwaves[11]

By use of targeted radiation, it is possible to provoke a quick vaporization of water at the surface of the seeds and the vaporization of this water can loosen the hulls / meat linkage enabling a weak constraint such as a compressed air flux to separate the two fractions. This process has been developed for the removal of fruits like walnuts, chestnuts and almonds.

Sunflower

Impact type.

The most popular decorticator for sunflower is proposed by the Bühler Cie. It consists in a rotating blade that propels the seeds by centrifuge force against a wall. It functions on one impact. It is designed for partial removal of hulls because due to its principle, it is not able to carry out a good dehulling without increasing the force of the impact. The kernel oil content is so high in sunflower that under the violence of he chock, some oil can be transferred to the hulls and is lost. Moreover, increasing the rotating speed of such dehuller drives to increase the production of fines that are difficult to separates from hulls.

Another mono-chock kind of dehuller is air-jet impact where the propelling of the seeds is done by a strong current of air.

Multi-chocks dehullers like the Ripple mill improve the dehulling quality because they carry out several impacts on the achene with milder violence and enable en enhanced separation of hulls without generating an excess of fines.

[11] Jean H. INOVFRUITS, personnal communication

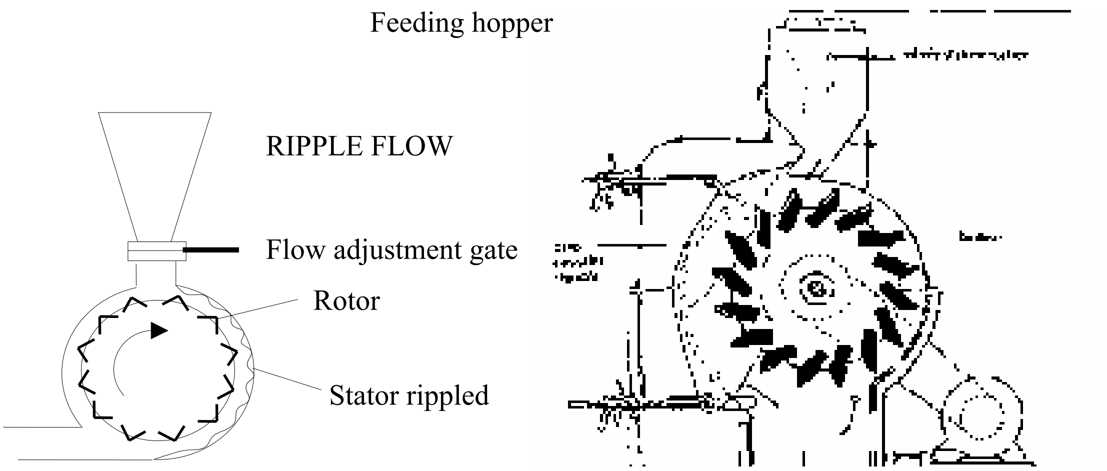

Figure 6: Ripple flow dehuller (left) and "Russian dehuller" (right)

Cutting type[12]

The Impco company proposes a cutting apparatus in which the seeds are open by a scissor effect provided by two co-rotating cylinders fitted with grooves and thanks to a differential rotating speed. The separation of hulls and meats is pursued in a secondary stage where rotating beater are shaking the cut seeds in order to separate them. The sorting of the hulls is done by sieving and air classification.

This apparatus has been designed for the cotton seeds but according its builder, it can be used with sunflower with good results.

Figure 7: The Impco decorticator and its sorting equipment

Compression/decompression

The principle of this apparatus is to place the achenes in a tight chamber in which compressed air is introduced. Once the pressure is stable, a brutal decompression is provoked enabling the air comprised in meats and hulls to expand quickly in order to crack the hulls and remove them. This apparatus was set up for the decortication of striated sunflower for human food. Its advantage is that it does not damage the kernel with percussions.

With oil rich seeds, this process is not efficient and is energy consuming.

[12] Davis B.W. – The Impco decorticating and separating system – Oil Mill Gazetter Oct.83 10-14

Separation.

Hulls have a large difference of density with the seeds and the meats so that, most of the separators remove the hulls in a flow of air that is adjusted in force to carry away the hulls without taking the meats. The drawback of this principle of separation is that one need to remove the fines prior to the aspiration of hulls otherwise; the fines are going in the hull fraction while fines are mainly meats fragments.

The eviction of fines can be done by sieving or by a previous air sorting adjusted to aspirate only the fines. The first solution is adopted for sunflower while the second one functions with rapeseed.

In the case of sunflower, it is possible to purify the hulls by removing the fines after aspiration in rotating sieve with help of brushes.

The best way to obtain hulls without excess of oil is to carry out a dehulling producing the fewer fines possible.

The separation of meats from non dehulled seeds is required if a total dehulling is wanted. To achieve this goal, it is necessary to eliminate the little seeds in order to process them separately. When all the seeds have a minimum size, it is possible to obtain a good separation of the whole seeds and the meats by size separation on a sieve.

In the case of sunflower, specific gravimetric separator can be used for the same function.

Electrostatic separation has been proposed by Sket Cimbria[13] for the separation of hulls. The dehulled particles are charged with electrostatic charge then they are passed in a chute within a electromagnetic field of the opposite sign attracting the seeds particles. Because hulls have a large surface compared to their mass, they can bear more charge per unit of mass and are able to be moved by the electrical field. This technology requires less energy that the regular one involving big ventilators.

Figure 8: Picture of the Sket electrostatic separator

[13] Dehulling of oilseeds. SKET's new electrical dehulling process is employed for large-scale processing of sunflower seed. Oils and Fat Internationan – 1991 – Vol 7 N°2, 44-47

Industrial performances

Rapeseed

In Europe, dehulling is a very marginal practice not developed in the large plants that function with solvent extraction.

The **Teutoburger Ölmühle** in Germany has developed an original technology to dehull rapeseed and valorize the oil obtained by this process.

The manager of this enterprise is Dr. Rass, who devoted its PhD to the expelling of dehulled rapeseed. He has developed the knowledge enabling the cold pressing of rapeseed meats. The seeds are dried before dehulling, and then the meats are cold pressed, cooked and passed on a second expeller. According to the website of the company, the hulls are fermented to produce biogas after oil recovery by expelling. The oil stemming from the hulls is used by cogeneration to produce energy for the process (drying of the seeds and cooking of the cake of the first expelling before the second one).

In France, a small scale oil mill has practiced dehulling of rapeseed during a few years in Châlon sur Saône. The technology used for dehulling was the one developed by the CETIOM. Hulls were not extracted but sell has feed for rabbits. This mill was closed because of a low profitableness due to its small size.

The reasons that have limited the adoption of rapeseed dehulling are:

- Low profitability caused by the loss of oil in hulls
- Low valorization of the hulls
- Difficulties encountered to process the meats.

In the industrial reality, the oil content in oil was rather high due to the presence of meats in the hulls. Around 18 % of oil in hulls was considered has reasonable level to expect.

Table 5: The French experience ; comparison of the composition of dehulled rapeseed meal (RM) with whole seed RM and soybean meal grade "48".

Statistical data	Whole seed RM (%)	Dehulled RM (%)	Soybean meal (48) (%)
Dry matter	88.7	89.0	87.8
Crude protein	33.7	36.5	45.3
Crude fibre	12.4	9.1	6.0
Crude fat	2.3	2.1	1.9
Ash	7.0	7.3	6.4
NDF	28.3	18.1	12.2
ADF	19.6	11.0	7.3
Lignin	9.5	5.5	0.7
Gross energy kcal/kg	4090	4125	4130

Source: feedbase

Effect of the dehulling on the profitability:

In the French experience, the mater balance for 100 kg of seeds was

Table 6: Dehulling and mater balance.

	Dehulled	Non dehulled
Hulls	20.0 kg	
Meal	40.3 kg	56.4 kg
Oil (refined)	37.0 kg	39.4 kg

In 1980, the market prices were the following:

- Oil: 380 €/t
- Regular meal: 137 € /t
- Hulls (based on dehydrated alfalfa) 99 €/t
- Dehulled meal 163 € /t (based on the value of proteins).

In 1980, the value of the dehulled products was 226 € / t of seeds versus 227.0 € /t of seeds for non-dehulled.

The cost of dehulling was assessed at 1.8 €/t of seed in 1980 but this cost was compensated by improvement of the flow rate of the factory. Thanks to the dehulling, it was possible the save 4.5 € / t of crushed seeds. The global balance was positive but the earning was rather low 1.7 € /t.

These data were collected during a campaign of observation and don't take into account the multiple problems encountered during the period where the mill has functioned. The expelling the meats was difficult, it was necessary to increase the hydrothermal treatments before expelling and the quality of the cake was not every time satisfactory for the extraction.

Another problem was the valorization of the hulls. The rabbits market is not very important therefore, the development of the technology to a larger scale was rather uncertain.

Table 7: dehulling profitability.

Dec 2008 prices	Non dehulled	Hulls 20 %	Hulls 10.5 %
Seeds cost (€/t)	320	320	320
Oil price (€/t)	741	741	741
Non-dehulled meal (€/t)	137	137	137
Dehulled meal (€/t)		163	155
Hulls (€/t)		134	105
Ratio of oil (%)	40.55	38.04	39.71
Ratio of meal (%)	57.15	40.3	47.88
Ratio of hulls (%)		20	10.5
Oil value (€/t of seed)	300.5	281.9	294.3
Meal (€/t of seed)	78.3	65.6	74.3
Hulls ((€/t of seed)		26.7	11.0
Sum products (€/t of seed)	378.8	374.4	379.5
Margin	*58.77*	*54.37*	*59.49*

The third hypothesis is based on a more efficient dehulling where the percentage of hulls produced is lower like the oil losses. This performance was measured at industrial scale but for a shorter duration and was not considered as realistic.

The values of dehulled meals are calculated according to their protein content. It is supposed that their value is a linear function of the proteins, the meal from the 20 % dehulling had 41.8 % or protein and the 10.5 % meal, 38.8 % of proteins while the standard meal had 35.1 %. This hypothesis is the one of the 1980 prices assessment.

The value of hulls is based on the value of the seeds has source of oil. The fat content of 20 % dehulled hulls was 18.4 % and the oil content of the 10.5 % dehulled hulls was 14.4 % while the seeds are supposed to contain 42 % of oil.

The gap between non-dehulled and dehulled in today prices is wider that in 1980 prices and is unfavorable to the dehulling (20%). To have a positive result it is necessary to reach a good technical performance that was not feasible in the industrials conditions.

<u>How would it be possible to improve the balance?</u>

- Proposition 1: improve the dehulling in order to get better technical performances in terms of oil losses and hulls purity. If possible, this direction has the advantage of being not based on market values hypothesis.
- Proposition 2: recovery of 60 % of the oil left in the hulls. By expelling the hulls, it is possible to decrease their oil content from 14.4 to 6 %. A 0.9% output of oil is possible. The recovery costs are easily covered by the gains.
- Proposition 3: improvement of the value of oil: According to the OPTIM'OILS study, it is possible to obtain press oil after dehulling with a better quality in regard with micronutrients provided that a soft refining could be carried out.

This proposal could take advantage of research in progress and generate more value than all the other ones.

- Proposition 4: improvement of the value of the meal, the lower fiber content is supposed to improve the digestibility of the meal therefore a better utilization of biomass by the animals. In consequence, the value of the feed should be increased. According to the experience of the past, these amelioration will be difficult since the dehulled meals have to compete with soybean meals that are abundant and widely used while rapeseed meal must deal with antinutritional factors like glucosinolates.
- Proposition 5: define a better valorization for the hulls. This point is the one that seems the most difficult due to the fibrous constitution of the hulls. They have to compete with numerous sources of ligno-cellulosic material and they need to be pelletized to be transported.

SUNFLOWER

Industrial dehulling of sunflower is a common practice but the dehulling is generally limited by two factors:

1. The valorization of the hulls by combustion: the oil mill cannot valorize more energy than it needs to process the sunflower. The order of magnitude of the energy need is 350 kWh/t of seeds for the crushing. The part required for heat consumption is 85% (300 kWh). The theoretical calorific power of sunflower hulls is 5.1 kWh/kg. Therefore, around 60 kg of hulls are necessary for the heat supply of the mill. It means that the removal of 6% of the seeds mass is enough. On this basis, if one supposes that the seeds contain 25 % of hulls, only 25% of these hulls can be valorized.
2. The hulls oil content. As it has been indicated previously, the industrial dehuller and the bad ability for dehulling of the modern sunflower seeds make it impossible to produce a large dehulling percentage without enrichments of the hulls by oil. Therefore, it is necessary to limit the dehulling percentage in order to avoid oil losses.

The marketed meals have 33 % of proteins versus 29 % for the non-dehulled. It is necessary to remove about 34 % of the hulls to obtain that increase in proteins content.

One can note that it is more than the 25 % necessary for the heat production, that can be explained by the energy yield of the burner and the boilers that are not optimal when the combustible is biomass.

Improvement of the performance of dehulling by use of multi-chocks dehuller is possible but 100 % dehulling is not feasible with the existing cultivar. It would be possible to select some varieties easy to dehull if one would to produce such dehulling for the production of pure kernel meal but this unit would have to pay a prime to get the right raw material. At global scale, a reorientation of breeding is necessary to supply cultivar having the necessary ability to be dehulled. Breeding studies[14] have demonstrated that hullability is a heritable character and has a negative however weak correlation with oil content. Inbreds and hybrids producing achenes with quite small hull content, high oil content but a good hullability were found the most promising for improvement of the quality of sunflower seed meal. Such genotypes are rare so that a recurrent selection program was recommended to increase the frequency of favorable genes

In the current state of the market an oil mill that would carry out the best possible dehulled sunflower meal would have to use a diagram with a separation of the seeds according to their size prior to the dehulling. The seeds would be dried before dehulling and the dehulling would be carried out with a multi-chocks dehuller.

The dehulled seeds are to be sorted on a sieve to separate kernels from non-dehulled seeds and both fractions are passed on an air classifier to remove the hulls. In the case of the small size fraction, the hulls have to be sieved to recover the fines.

The small seeds are generally difficult to dehull. The simplest way to treat them is to crush them separately without dehulling. A dehulling is possible but it is not possible to get the same quality than with the bigger seeds.

According to the works done by the CETIOM on the subject, the protein content in the meal from such a dehulling scheme is 40 %. Around 66 % of the hulls have to be removed to obtain that result. That means that 100 kg of seeds having 25 % of hulls are going to give 16.5 kg of hulls.

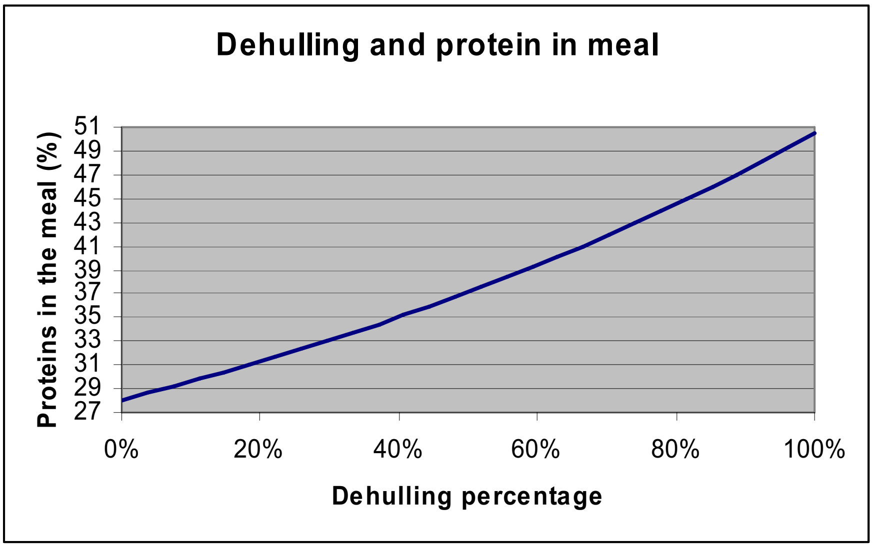

Figure 9: effect of the intensity of dehulling on the protein content of the meal

We have seen previously that the steam production requires around 50% of this biomass, which let 8-9 kg of hulls to valorize per 100 kg of crushed seeds.

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[14] Denis L., Vear F. Variation of hullability and other seed characteristics among sunflower lines and hybrids, Euphytica, 1996, Vol 87, N°3, 177-187.

Increasing the removal of hulls will decrease the amount of raw material entering in the oil mill. In consequence, that could decrease the need of energy necessary for the crushing but we have seen that some drying is necessary to improve the seeds hullability in consequence; the 50 % ratio of valorization for needs of the crushing can be accepted as a rough estimation.

Consideration to take into account for the valorization of the hulls.

An important characteristic of the hulls is their low density. According to the cultivar, the range of the hulls density is 0.15 to 0.20. This low density generates flow problems because in bulk storage, the hulls are bridging. Moreover, low density makes it impossible to ship the hulls in their state to distant customers. If pelletizing presses are to be used, the structure of the fiber will be damaged and could cause the impossibility of certain valorizations as biomaterial.

Another problem already mentioned is their abrasive quality that interferes with air transportation.

A simple possibility to valorize more hulls in the boiler is to use high pressure boiler in order to run turbines activating an electrical generator and use the turbine extraction steam at 10 bars tin the processing areas. The excess of energy will become easy to export by the electric grid. The limit is that to produce 1 kWh of electricity, it is necessary to valorize 2 kWh of heat. The needs of steam of the plant are not sufficient to valorize all the biomass extracted thanks to the potential dehulling.

Combustion of the hulls

Table 8: Characteristics of sunflower hulls as fuel[15]

	Characteristics
Density	0.16
Carbon	40% (mass)
Hydrogen	6% (mass)
Oxygen	41% (mass)
Nitrogen	1% (mass)
Sulfur	1 % (mass)
Moisture	9 % (mass)
Ashes	2% (mass)
Ashes melting temperature	1290°C
Calorific power	14 000 BTU/kg 4.1 kWh/kg

According to a 1982 paper of Posschelle (De Smet) the cost of hulls boiler is 7 times more expensive than an oil boiler. According to information given in that article, the particularity of the hulls combustion is that the gasification of the fuel occurs quickly and the particles size is small. The firing and air distribution system must be adapted to this particular raw material. The fly ashes born by fluegas have a very thin particles size, are very concentrated and are very hydroscopic with a high tendency to bind and form a concrete like material. In consequence, the design of boiler must avoid the presence of features allowing deposits of ashes such as horizontal tubes for heat recovery and manage the self cleaning of these tubes during operation without damages. Some devices like soot blower or mechanical rapping and shaking system are necessary to keep the exchange surfaces clean. The exhaust requires filters that are able to treat small particles size, that means extra costs for the cleaning the fumes.

[15] Posschelle G., Burning Sunflower Hulls For Boiler Fuel, Oil Mill Gazetter, July, 1982 27-32.

Possible utilizations of the hulls

Rapeseed

Animal feed

In the French experience, this is the mode of valorization that was privileged. The hulls were not very pure so that they had the following composition:

Table 9: Rapeseed hulls (RH) composition, comparison with dehydrated alfalfa grade L17 (DAL17) (feedbase)

Statistical data	Rape. Hulls as fed (%)	RH on DM (%)	Dh. Alfaalfa as fed (%)	Dh Alfalfa on DM (%)
Main analysis				
Dry matter	87.18	-	90.01	
Crude protein	14.53	16.66	15.83	17.58
Crude fibre	20.88	23.95	26.79	29.76
Crude fat	13.17	15.11	1.96	2.17
Ash	4.73	5.43	10.75	11.94
Calcium	1.16	1.33	2.15	2.39
Phosphorus	0.21	0.25	0.24	0.26
Potassium	0.77	0.88	2.48	2.76
Sodium	0.010	0.010	0.010	0.020
Magnesium	0.12	0.14	0.16	0.18
NDF	45.12	51.75	41.93	46.58
ADF	34.96	40.10	28.82	33.13
Lignin	19.62	22.50	8.11	9.01
Gross energy kcal/kg	4700	5392	3821	4245

L17 dehydrated alfalfa (DAL17) is a low grade of alfalfa designated to rabbits and horses.

The value of dehydrated alfalfa (DA) is rather high compared to rapeseed meals (Table 9:).

The presence of omega3 fatty acid in the rapeseed hull could bring an advantage to this fodder since this nutrient is taking more importance in cattle feed.

To market a valuable DA substitute, it would be necessary to recover a part of the oil left in the hulls by expelling or by extraction and to improve their protein content by addition of some meal. Of course, this product needs to be pelletized to be used in the same condition than dehydrated alfalfa.

Production of energy

With 4700 kcal/ kg (5.4 kWh/kg) the hulls at 13 % of fat could be used as fuel for the energy supply of the oil mill. In the case of rapeseed, the need of heat for the process is 350 kWh/t, theoretically, 65 kg of hulls would be enough for this supply. We have seen for sunflower that it is necessary to burn 8.25 kg of hulls to supply the equivalent of heat provided by 6.25 kg of sunflower hulls, the yield of hull burner is approximately 75%.

The calorific power of 1 kg of RH is therefore 4.05 kWh/kg. To cover 350 kWh/t, the oil mill must burn 86.5 kg of RH.

By choosing cogeneration, it is possible to use 50 % of fuel more, so that 130 kg of hulls could be valorized for each ton of seed to crush. In France the electricity produced by cogeneration from combustion of biomass is bought 0.06 €/ kWh.

The crushing of 1 t of seed will generate 0.173 MWh of electricity and 0.3 MWh of heat. The price of the substituted heat can be evaluated at the level of coal because like coal, it requires special burners to be properly used. The coal kilowatt hour has an approximate value of 0.01€. The combustion of the hulls in this conditions gives 1.34 MWh of electricity and 2.71 MWh of heat therefore, 107 € of value.

This valorization has the advantage of not requiring either transport nor storage of the hulls. It can make the oil mill more than auto-sufficient in energy and able to deliver better quality meals. However, it requires high capital investment and we are not able to estimate these capital costs. On the second hand, this disadvantage could be compensated by fiscal measures or direct help of the public powers in a context of reduction of the greenhouse gas emission.

The limit of that possible valorization is the nitrogen content of the hulls. Because of its high level, it is impossible to imagine the combustion of that material without a treatment of the smoke. Considerable investment would be required and would decrease the economical feasibility of that valorization.

Methanogenesis

As previously exposed, the hulls can be used in order to produce biogas. This biotransformation occurs in absence of oxygen and is due to the degradation of biomass by micro-organisms. Around 90 % of the energy of the biomass is converted, 10 % are used for the metabolism of the micro-organisms.

This solution requires long residence time in digesters and seems difficult to use with large amount of biomass. The investment for a large oil mill seems to be important and compared to combustion, this solution appears not competitive.

Pyrolysis and gasification.

The transformation of biomass in liquid or gaseous fuel is induced by heating at temperature comprised between 450°C and 550°C. Most of the organic matter is vaporized (see combustion) then condensed to produce a liquid similar to oil. Some incondensable matter is usable as gas.

According to conditions (concentration in O_2, temperature), the proportion of gas/liquid resulting of these transformation are variable.

A lot of processes have been proposed to use lingo-cellulosic biomass as commodity fuel but the industrialization of these processes is still not satisfactory.

Use as substrate for growing fungus

In china, during the Wuhan 12th international rapeseed congress (2007), a new process including dehulling was presented by the Wuhan University. They proposed to use the RH as substitute for DA and as support for the cultivation of fungus[16].

Conclusion about rapeseed hull possible valorization

The most promising possibility to valorize RH is as dehydrated alfalfa substitute. Because of the CAP evolution, the volume of available DA is likely to decrease after 2012 generating a opportunity to sell off RH.

SUNFLOWER

Production of energy by cogeneration

Practical considerations

This point has already been approached previously in the frame of the current industrial practices. We are only treating of economical aspect in this paragraph.

Because the calorific power of sunflower is 4.1 kWh/kg and the possible valorization of heat is limited to 300 kWh/t of crushed seeds, only 11% of the seed mass can be valorized by this process (44% dehulling, 36 % of proteins in the meal).

One ton of hull can supply 1353 kWh of electricity and 2706 kWh of heat. On the same basis than for rapeseed oil, it valorizes the ton of hull at 108 €.

In the case of a 100 % dehulling, it would be interesting to supply steam to another plant in order to valorize all the hulls. In the case of the production of biodiesel, the crushing plant has a semi-refining plant near to it and possibly, an inter-esterification plant that could use this available energy. However, it is unlikely that the needs are going to match the supply. A priori, even if the seed quality becomes very favorable to dehulling, it seems probably more realistic to imagine that the plant will process two meal grades, a first quality one with the seeds having a good hullability that will be used in high added value products and a lower grade meal resulting from the crushing of the seeds of poor hullability. The quantity of hulls extracted would be adjusted according to the energy needs and the quality of the meal to be marketed. In consequence, it seems unavoidable to produce a small percentage of hulls that will be not absorbed by the production of energy. A small percentage in a plant that crushes 1 000 t / day can represent a few tens tons, at least 100 cubic meters, a volume that the plant manager cannot neglect and for which a sure customer is necessary.

The exportation of the sunflower hulls to distant customers is imaginable because it is a source of combustible biomass available in significant quantities with low water

[16] Evrard J. Compte rendu du 12ème congrès international sur le colza, 26-30mars, Wuhan, Chine. *OCL* VOL. 14 N° 6 NOVEMBRE-DECEMBRE 2007 327-331

content with a regular composition. To compress this material is the indispensable treatment enabling storage and transport in acceptable conditions.

The compression of hulls could be done in pelletizing press after a conditioning by steam.

Pollution and combustion of sunflower hulls

Compared to wood, SH contain much more nitrogen and this nitrogen during combustion will produce nitrogen oxides that are likely to be much more important. According to a German study cited in a review[17] of the French Agency for Energy and environment preservation, the emission of pollutants resulting of the combustion of biomass depends on their composition and it seems that wheat straw produces 3.3 fold more NO_x than wood. It is not possible to predict the real emission of SH in NO_x, but it is sure that they will be stronger than the one of the straw because of their higher content in nitrogen.

The regulation for industrial boilers (>300MWh) limits the concentration of NO_x to 200 mg/m^3 (300 mg/m^3 for power comprised between 100 and 300 MWh). The wheat straw produces already 330 mg/m^3, therefore, it is a problem for SH in one consider that SH has almost twice its protein content.

[17] Bodineau L., Pouet JC. Etude bibliographique sur la combustion de produits issus de cultures annuelles(blé, paille, maïs) - http://www.ofme.org/bois-energie/documents/Combustible/Combustion_cereales.pdf

Animal feeding

At the difference of RH, the sunflower hulls (SH) are poor in protein and oil.

Table 10: Comparison of sunflower hull with wheat straw and sawdust

Statistical data	SF as fed (%)	SH on DM (%)	Wheat straw as fed (%)	Sawdust as fed (%)
Dry matter	90.97		91.05	90.40
Crude protein	6.21	6.83	3.87	0.77
Crude fibre	46.47	51.49	37.94	47.28
Crude fat	4.86	5.84	1.25	1.04
Ash	3.35	3.38	5.99	3.66
Calcium	0.40	0.44	0.46	0.62
NDF	68.01	74.76	72.51	83.26
ADF	53.82	59.17	45.88	69.88
Lignin	19.88	21.85	6.68	16.72
Gross energy kcal/kg	4395	4831	3854	3535

Source: Feedbase

If SH have a little more protein than wheat straws, they have thrice their content of lignin. This high lignin content is even superior to one of sawdust.

These figures made of SH a very bad fodder, more a litter material than a fodder.

The wheat straw is sold 50 €/t provided that if can be compressed to a 0.3-04 density. SH have a 0.16 density.

Several kind of treatments have been studied in order to increase the SH digestibility:

- mechanical treatments (milling, pelettizing)
- Physical treatment (Steam, extrusion)
- Treatment by alkalis ($NaOH$, $Ca(OH)_2$, NH_4OH) or oxidants ($NaClO$, SO_2, Cl_2)
- Enzymatic treatments or biologic digestion by unicellular organisms able to digest lignin.

Due to the weak increase in value bring by these treatment, their industrialization was never done[18].

Biomaterial

Thanks to their high lignin content and hydrophobic compounds found at their surface, SH are interesting to build construction materials.

The presence of SH in particleboard panels was decreasing their mechanical resistance and dimensional stability but up to 50 % of incorporation was possible.

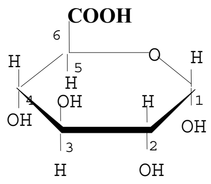
SH have been studied to build bricks or tiles that were very light, solid and insulating. The incorporation of hulls in concretes enables a reduction of the density (15-20 % of

[18] Bazus A. Rigal L., Gaset A. – Valorisation des coques de tournesol : bilan et perspectives (Mise au point). Revue Française des Corps Gras, 1992 -N°39 v11/12, 345-350

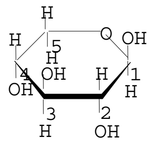
SH decreases the density to 1 vs 2.4) and improves the insulating properties of the material. (λ = 0.1 W/m.°C vs 1.6 to 2.1 W/m.°C for ordinary concrete).

Production of hemicelluloses

A process has been proposed by the "Laboratoire de chimie des Agroressources" in Toulouse to extract hemicelluloses frum sunflower hulls. Diluted soda is used to dissolve the hemicelluloses, then the pH is decreased to 5.4 in presence of ethanol to obtain the precipitation of solute than can be filtered and dried. Yield of 17 % were obtained in laboratory conditions. The carbohydrates thus obtained are glucuronoxylan (polymer of glucuronic acid and xylose)



Glucuronic acid



Xylose

Glucoroxylan have promising possible utilizations in numerous domains (food, cometic, paints, glues, …).

Organic amendment for the soils

In Argentina where large amounts of seeds are processed, the composting of SH was proposed as an environment friendly way of valorization.[19] Because of high C/N ratio (83), SH cannot be composted alone and the addition of nitrogen is necessary to obtain acceptable compost. Inorganic nitrogen addition was not an efficient mean to improve the decomposition of SH. Co-composting of SH with alfalfa or vetch gave better results, even with relatively high C/N ratios (64). The article does not present economical aspects of the treatment which is simply opposed to simple combustion presented as a pollutant activity in urban areas. In the European conditions, composting can be considered as a low added value valorization, more a way to eliminate wastes than a way to produce value.

Conclusion about sunflower hulls valorization

Whatever the pollution problems stemming from the SF combustion, production of energy by combustion seems to be the best way of using these materials in great amounts. For large oil mills, the cost of equipments to reduce the pollutants emission could be affordable in a context of high energy prices and with encouragements of the public powers to reduce the carbon footprint of the biofuel production.

[19] Conghos M.M., Aguirre M.E., Santamaria R.M. – Sunflower hukks degradation by co-compositing with different nitrogen sources – Environmental Technology, 2006 vol 27, 969-978

Problems posed by extraction of oil from pure kernels

Oil extraction problems

The extraction of oil from pure kernel in regular screw presses is difficult and sometimes impossible due to the rheological properties of these materials.

If the principle of continuous expelling is based on the reduction of the volume generated by the rotation of a screw thread which causes the pressurization of the material, it is necessary that the matter can be conveyed by the screw. In single screw apparatus, the matter is pushed by the screw provided that its consistency authorizes the friction of the barrel to prevent its rotation with the screw. In the case of pure kernels, the absence of fiber gives a matter with poor coherence which does not fit screw conveying. The presses are not able to convey the solid which behaves like a paste and cannot push the cake if some cake can be formed (otherwise, it goes out of the expeller without realizing any oil).

In general, it is necessary to let a percentage of hulls in the kernels to authorize an effective deoiling by expelling.

In the perspective of obtaining pure kernels to carryout biorefining it would be necessary to define new processes of oil extraction.

The following section describes the solutions to manage that problem.

Very low rotation pressing of non-flaked meats. When the kernels have not a 100 % purity, it is possible to achieve a certain level of mechanical extraction by reducing the rotation speed of the screw while avoiding to use any mechanical preparation in order to preserve the structure of the meats. The fact of reducing the rotating speed of the press will limit the mechanical shearing of the material and preserve the coherence of the solid. By this way one can obtain some oil expression but the yield is not important and depends of the percentage of hulls left in the kernels.

Thermal preparation (cooking). The thermal preparation will destabilize oil and proteins bodies in the kernel cells. The effect of heating is a coalescence of oil-bodies and the fusion of protein-bodies resulting of the protein tridimensional change caused by cooking. Coalesced oil droplets are supposed to be easier to extract under pressure when the drying and the change in the protein structure could modify the rheological behavior of the non-lipid content of the cells in the sense of an increased rigidity.

The combination of reduction of the rotating speed or the screw and improved cooking are generally necessary to process dehulled rapeseed with ordinary presses. The thermal treatment does not damage the proteins value as stuff for animal feeding but in the perspective of protein extraction, these treatments will reduce the protein solubility and extractions yields. Therefore, other means are required to extract oil and preserve the quality of the proteins.

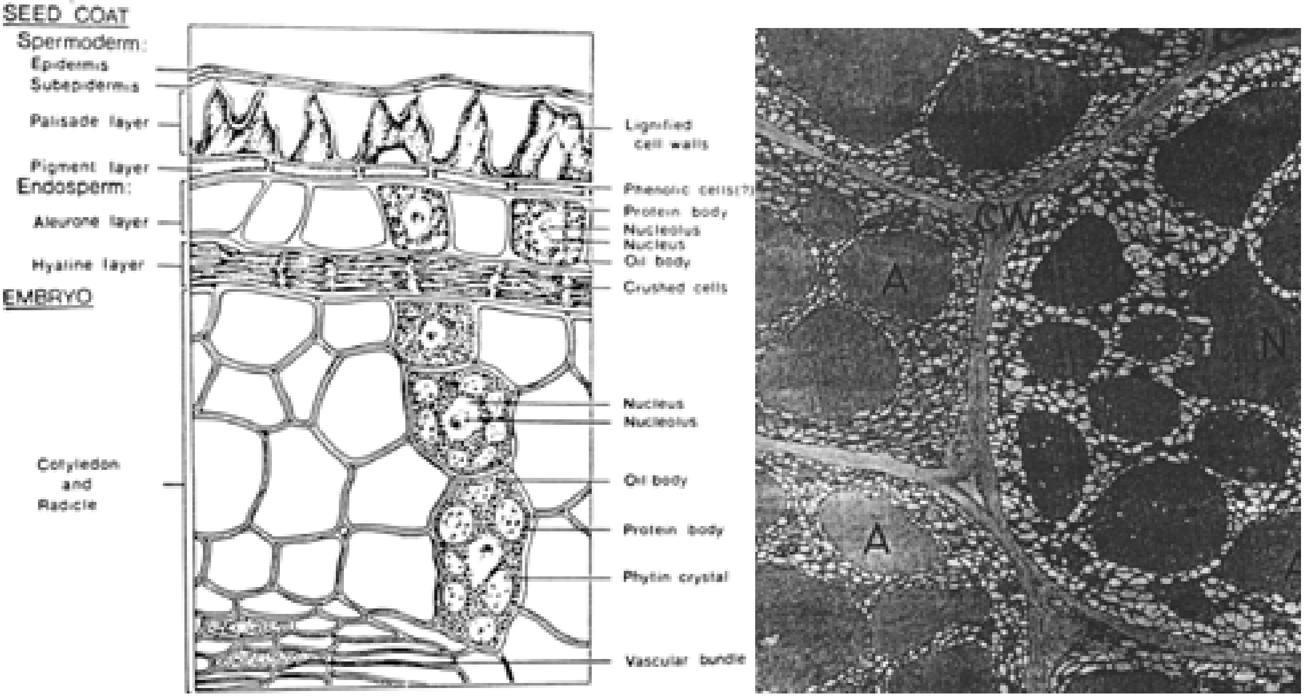


Figure 10: Line drawing of the detailed structural and microchemical organization of rapeseed[20] and electron micrograph (x8000) A: aleurone grains, L: oil-bodies, CW: cell wall, N: nucleus[21]

Direct extraction of the meats. Flaking the kernel and direct solvent extraction can permit to avoid mechanical extraction. Flakes of pure kernels cannot be extracted by counter current extraction like pre-press cake because of poor percolation. Extractors must be adapted to treat that kind or products. Vertical columns with counter flow (continuous extraction), rotating extractors or agitated filter (batch extraction) are possible solutions.

In these processes, the circulation of the liquid around the solid does not depend on the porosity of the solid material and is not submitted to compaction occurring in a layer of flakes receiving a strong flow of solvent. In vertical columns, the quality of extraction depends on the homogeneity of the solid circulation and the residence time.

[20] Yiu S.H., Altosaar I., Fulcher R.G. –b The effects of commercial processing on the structure and microchemical organzation of rapeseed – Food microstructure, vol 2, pp165-173 SEM Inc. AMF O'Hare (Chicago) IL 60666 U.S.A.

[21] Appelquist LA, R Ohlson - RAPESEED 1972 - Elsevier Publ. P46

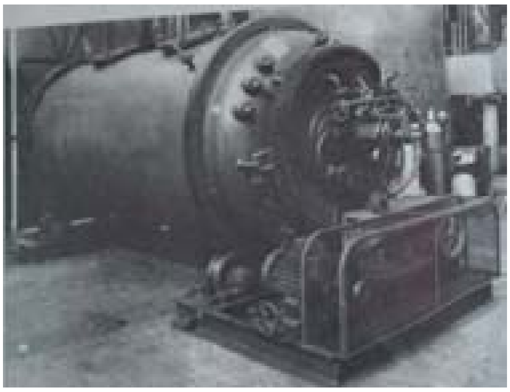


Figure 11: Rotating extractor

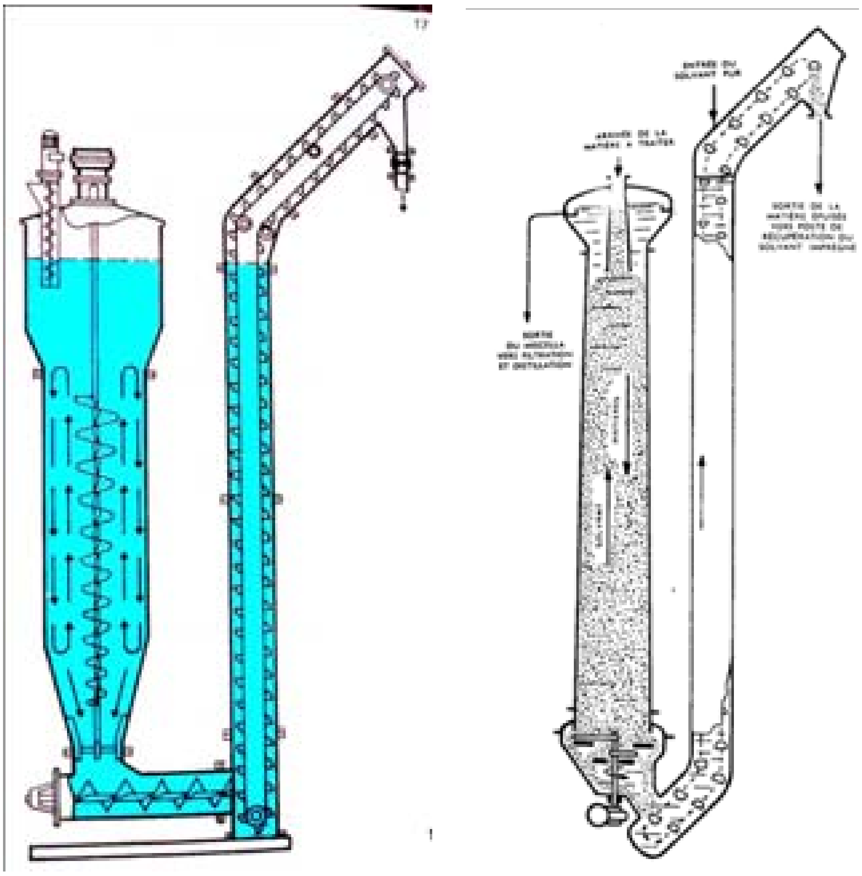


Figure 12: Vertical extractors (respectively Lugi and Speichim)

Whatever the principle of these columns could be theoretically simpler than the current continuous extractor this solution has not been industrialized in the large scale oil mills which use mainly belt or basket extractors.

According To Laisney[22], these vertical extractors were abandoned because of the huge amounts of solvent which were in service. The problem is that to maintain the particles in suspension (fluidization) in the flux of solvent, one must have a sufficient speed of vertical movement otherwise the solid will sediment and the liquid will create privileged channels of circulation. Trials of pulsating columns where the solvent circulation was

[22] Laisney J. – L'huilerie Moderne, « Arts et techniques », Pub. Cie Française pour le Développement des Fibres Textiles, France, 1984

animated by pulses were carried out in order to work with less solvent but were not successful.

<u>Twin-screw presses</u>[23] have been designed to treat such products. In such a press, the pressure is not obtained by increasing the volume of the shaft but only by reduction of the threads pitch. The screws are co-penetrating so that each screw is cleaned by the thread of the opposite one so that the matter cannot turn with the screw.

According to the article of Isobe and al. it has been possible with such a press to expel pure kernels of sunflower to reach 93.6 % of oil recovery when only 19.7 % mere possible in a single screw press.

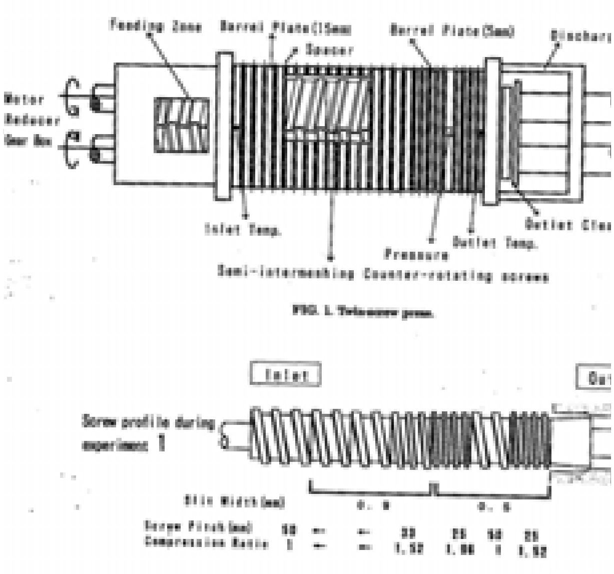
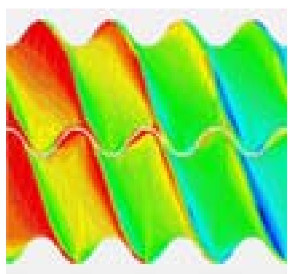


Figure 13: Japanese pilot twin-screw press

Twin-screw extruder[24] (Clextral BC45). Twin-screw extruders have the capacity to process products with a larger range of rheological behavior since both parallel screws fit one into another so that they clean themselves reciprocally and offer the possibility for the material to stick to the screw. 200 bars (20 MPa) and temperatures up to 220°C. This paragraph describes the CREOL's prototype.



The screw elements are movable allowing the composition of screw profiles adapted to the specific goal of the processing. The barrel is composed of 7 modules of 200 mm. Modules 2, 4 and 5 are equipped with heating resistance and have the possibility of being cooled down by water circulation commanded by electro-valves. Module number 3 is fitted with a

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[23] Isobe S., Zuber F., Uemura K., Noguchi A. – A new twin-screw press design for oil extraction of dehulled sunflower seeds – J.A.O.C.S. – 1992 – Vol 9 n°9, 884-889

[24] Quinsac A./De Greyt W./Schonweitz C./Bagger C. - Quality of life management of living resources. Contract n° QLK5 CT 1999 01442. Green chemicals and biopolymers from rapeseed meal with enhanced end-uses performances. ENHANCE. Final report for the period from 01/02/2000 to 31/01/2003. 2003

filter adapted on a regular barrel while modules 6 and 7 are replaced by a special filtering piece of equipment that is entirely perforated and with an internal diameter reduced to 46 mm. In that area, the parallel screws are no more in contact and work like two single-screw press. The compression of the material is obtained by increasing the shaft diameter along the 400 mm of this part of the screw. Each module is fitted with a temperature gauge connected to an automat that secure the thermal control of each module by commanding the resistances or the electro-valves of the cooling water. The motor has a power of 44 kW allowing a maximal rotating speed of the screw of 614 rotations per minute. The feeder is equipped with an anti-bridging device and is fitted with double threaded twin-screws. The barrel is capped with a front die plate containing two removable dies of 8 or 6 mm in diameter. The headspace (space between the point of the screws and the die) is adjustable by moving the die thanks to a threaded support.

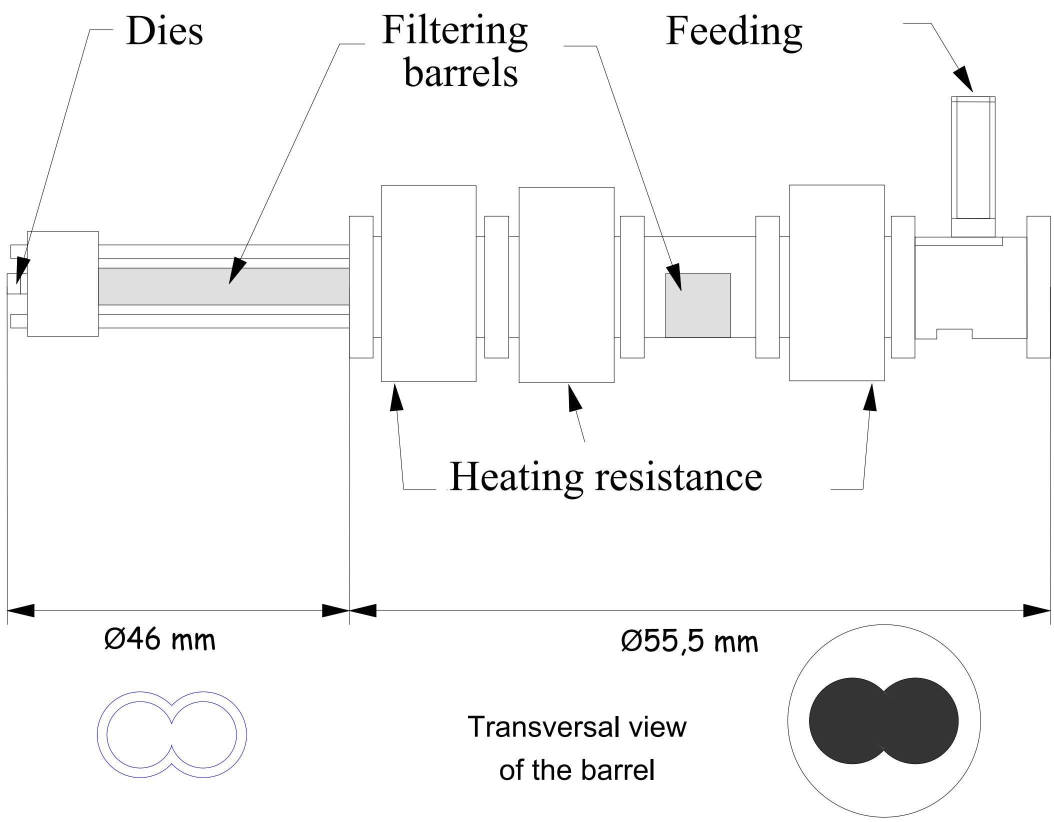


Table 11: Schema of the twin-screw extruder BC45

In the case of rapeseed, the twin-screw extruder was able to expel and deoil purified meats without damaging the proteins that were used in the frame of the European program Enhance aiming at the valorization of rapeseed proteins.

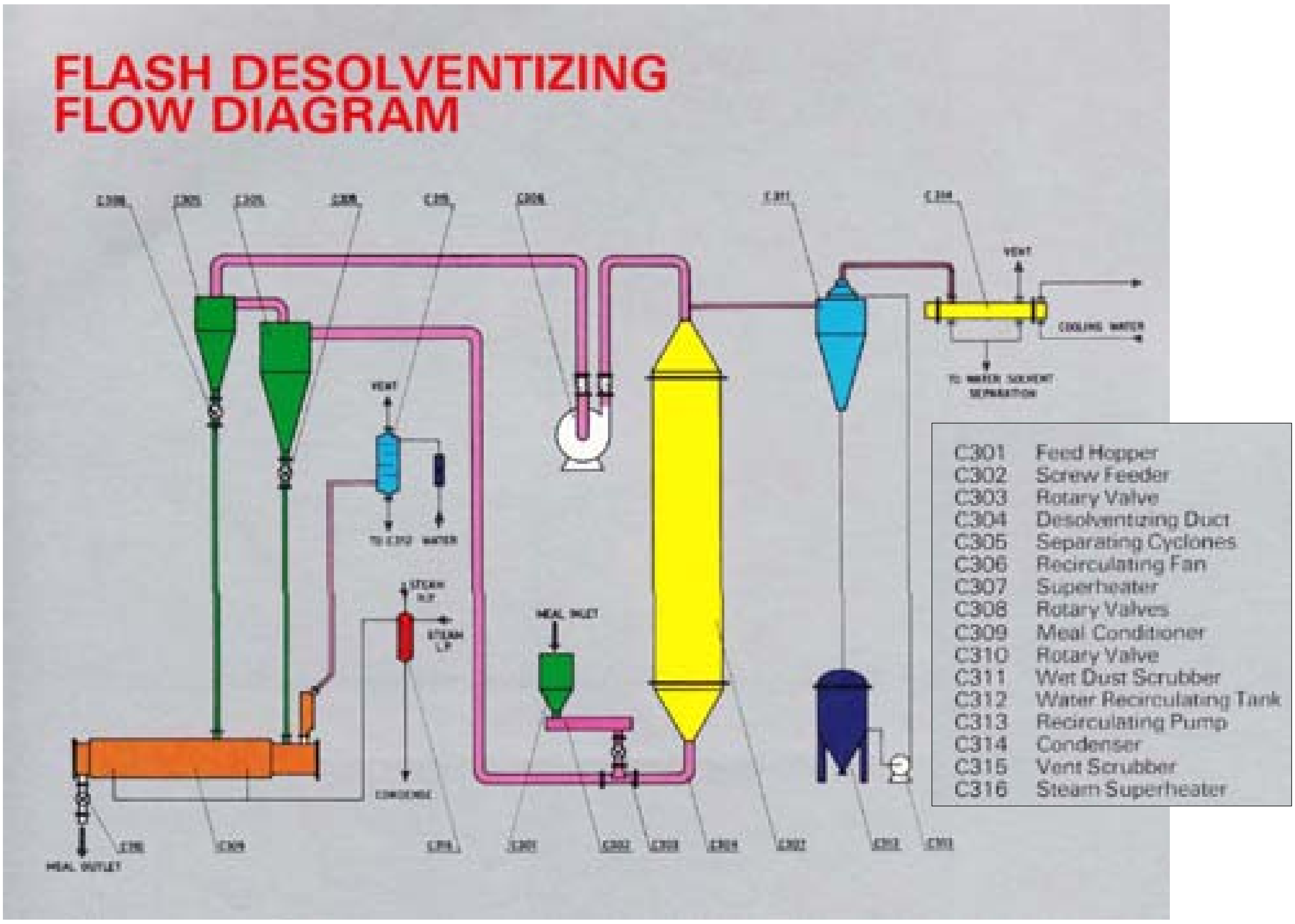
However, it was necessary to heat the material up to 90°C at the dies place to achieve some deoiling. Without this heating, the matter was behaving like a paste allowing no oil expression.

This problem underlines that to achieve mechanical deoiling, the transportation of the matter is a condition but is not sufficient. To get a resistance to allow carrying out some pressure is equally necessary. Cooking by disrupting the oil-bodies was enabling a better solid/liquid separation and the formation of a solid cake plugging the dies on which the screw can exert more pressure. Once that this plug is formed, external heating can be decreased because the mechanical work supplied by the screw is going to maintain the warming of the material.

The cake thus obtained has slightly decreased protein solubility but fitted the requirement of protein production.

Desolventization problems

In the case of soybean, the removal of the solvent following hexane extraction is carried out in a special device called "flash desolventizer" which can eliminate almost all the solvent without damaging the proteins.



The principle of such apparatus is to use superheated solvent to vaporize the solvent in the marc in a very short time so that the protein solubility is not damaged. This process does not perform the same level of desolventization than in regular desolventizer but the following steps of processing are able to remove the residues[25].

In the case of rapeseed meal, the flash desolventization does not achieve sufficient solvent removal to be accepted. This question was investigated during the FP5 European project Enhance by Desmet[26]. The rapeseed kernels were extracted in a pilot scale extractor simulating one stage of a belt-type extractor. The extracted meal was subsequently desolventized with superheated hexane or combined superheated hexane and superheated steam. The effect of the different desolventization processes on the general quality of the meal (residual hexane, NSI, volatile matter,…) was investigated.

Extrusion cooked and cooked-pressed rapeseed kernels were successfully extracted on pilot scale. Desolventization with superheated steam was detrimental for protein solubility since the NSI of rapeseed meal was largely reduced by conventional steam desolventization.

Independently of the variety of rapeseed and the applied pretreatment, desolventization with superheated hexane had only a slight negative effect on the protein solubility, expressed as NSI. Desolventization with superheated hexane could have a negative effect on NSI if the temperature of the meal exceeded 140-150°C for a longer period.

Desolventization with only superheated hexane led to too high residual hexane levels (1500- >5000 ppm). An additional stripping (with superheated steam, air or nitrogen) was required to obtain sufficiently low hexane levels in the desolventized meal samples. These treatments are not acceptable because they are going to increase the solvent losses beyond the limit allowed by the regulation on VOC emissions.

Further works would be necessary to improve the desolventization process in the case of rapeseed kernels.

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[25] Erickson, David R., ed. Practical Handbook of Soybean Processing and Utilization. Champaign, IL, AOCS Press and St. Louis, MO, United Soybean Board. 1995. p. 69 .

26 A. Quinsac, W. De Greyt, C. Schönweitz, C. Bagger - Green chemicals and biopolymers from rapeseed meal with enhanced end-uses performances "ENHANCE" Final Report, 2003. Quality of Life and Management of Living Resources Contract n° QLK5 CT 1999 01442

General conclusion

Dehulling is a step which must be addressed if one wants to achieve a better valorization of the oilseeds in the frame of a bioreffining project. The main reason which explains that dehulling is practically not realized in the case of rapeseed and only to a weak percentage for sunflower consists in the practical impossibility to extract hulls without generating oil losses. Secondary, the crushing of pure kernels meets technical problems, first for expelling soft materials, second to remove the hexane residues of the meal without decreasing the protein solubility.

These three hurdles must be resolved to allow the valorization of the proteins from oilseeds.

Concerning sunflower, it would be necessary to work upstream in order to select varieties with good hullability. Some existing cultivar could be used in order to produce seeds easy to dehull and to get pure kernels and pure hulls without requiring complicated equipments.

In the case of rapeseed, it seems possible to imagine a good valorization of hulls to replace dehydrated alfalfa which production is likely to diminish after 2011. In this case, the presence of oil could be valorized thanks to its content in omega three fatty acids for cattle feed. The presence of that nutrient has an effect on the quality of animal products which is requested by consumer for health concern.

Concerning mechanical oil expression, the technology of presses should be improved to gain efficiency. Twin screw presses are looking a promising way to reach that goal but other mean are possible like the use of expanders with deoiling cage.

About hexane removal after solvent extraction, some works carried out at the CREOL pilot plant let foresee that working on the kernel preparation before extraction could enhance the desolventization. Water and oil content of the cake have strong influence on solvent retention in rapeseed marc.

Over these technique considerations, the main determinant of the bioreffing feasibility is the valorization of the proteins. A factory of the Solae Cie manufacturing soybean protein concentrates for the animal feeding market located in the area of Bordeaux (France) has been compelled to stop its activity[27] at the end of 2008 because of a brusque drop in demand for these stuffs. If the demand of the society for a more sustainable use of renewable source is not supported by market prices or legal obligation to use these products, one must fear that progress will be slow and concretization scarce.

[27] Broustet B. – Solae envisage de fermer son usine – 2009, Sud Ouest, 9 janvier 2009 (press article).