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SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF SUNFLOWER SEEDS AND RAPESEEDS OILS

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Pressing as well as extraction with organic solvents are used widely in the production of vegetable fats and oils. The complete removal of organic solvents employed for extracting seed oils is mandatory, if the oil is to be used for human consumption. Liquid and supercritical carbon dioxide offer the advantage of being easily removable from the extracted oil. In contrast to organic solvents and some of their contaminating components, carbon dioxide is non toxic, and it cannot easily lead to environmental pollution. Supercritical Fluid Extraction (SFE) is similar to solvent extraction, in both cases, the material to be extracted is «washed» from the substrate using a solvent. The efficiency of the extraction depends on temperature, pressure, contact time between the extracting fluid and the oil-bearing material and the solubility of the oil in the extracting fluid.

Seeds of several varieties were studied: two varieties of sunflower, one with traditionally high linoleic acid content (Gloriasol) and one with high oleic content (Isoleic), and three varieties of rapeseed, spring type (Florin), winter type (Loreto) and third one with high erucic content (Gaspard). For each species the main biological and agronomic characters were recorded. From the seeds the oil was extracted by the Soxhlet and the SFE methods, to prove the possible influence of the different extraction methods on oils composition. The extracted oil was analysed by gas-chromatography (GC) in order to quantify free fatty acids and sterols.

INTRODUCTION

For mediterranean countries, sunflower and rapeseed represent a very interesting potential considering the agricultural point of view. In Sicilia, experimental works have shown that the genotype choice and sowing date of cultivation have an influence on biological cycle, yield, components and oil quality[1-8].The interest of agriculture and food industry for qualified products, needs new technologies which will brink improvement for extraction and conversion of these products issued from cultures.[9]

Pressing and extraction with organic solvents are employed widely in the production of vegetable fats and oils. The yields obtained by pressing are not so high as those achieved by extracting oil seeds. Therefore, pressing of intact or ground seeds, a most convenient process, is often followed by extracting the resulting press cake with hot organic solvents, such as petroleum hydrocarbons, for nearly quantitative recovery of the seed oils. Solvent extraction alone is used, e.g., in the commercial production of soybean oil.

The present communication describes the results of studies aimed at substituting organic solvents by supercritical carbon dioxide, for the extraction of oils from sunflower seeds and rape seeds at fairly low temperatures.

The complete removal of organic solvents used for extracting seed oils is mandatory, if the oil is to be used for human consumption. Liquid and supercritical carbon dioxide offer the advantage of being easily removable from the extracted oil. In contrast to organic solvents and some of their contaminating components, carbon dioxide is non toxic, and it cannot easily lead to environmental pollution. It is the reason why supercritical carbon dioxide has been used for the extraction of soybean oil [10-19]

As in the extraction with organic solvents, the efficiency of extraction with liquid and supercritical carbon dioxide is dependent upon its amount and the time it is in contact with the ground seeds. The yield of oil is also influenced by the size and physical structure of the seed particles. In working with liquid and supercritical gases, pressure and temperature during extraction and recovery of the oil are parameters that receive special attention. The extraction of sunflower seeds [20-23] and rape seeds [23] oils have been studied in the literature. The solvent should be liquid carbon dioxide [19], supercritical carbon dioxide [20,22] or a co-solvent like ethanol is added to CO_2 [21] in order to modify the properties of supercritical CO_2.

The aim of this paper is to compare the oil being extracted by two ways: supercritical carbon dioxide extraction (SFE) and Soxhlet extraction.

EXPERIMENTAL PART

Biological and agronomic characters.

Seeds of two varieties of sunflower, one traditionally high linoleic (Gloriasol) and the other one with high oleic content (Isoleic), and seeds of three varieties of rapeseed, spring type (Florin), winter type (Loreto) and high erucic content (Gaspard), were adopted. The trial was carried out in a locality of Eastern Sicily (10 m a.s.l.) using a randomised blocks experimental design with three replications and a 4 m^2 single plot for each species. The sowing was carried out the 12th of December for rape seed and the 10th of January for sunflower. For each species the main biological(table 1 and 2) and agronomic characters (table 3 and 4)were recorded.

Variety	Numbers of days after seedling				
	levee	bud	flowering beginning	flowering end	maturation
Gloriasol	31	123	138	148	189
Isoleic	34	123	138	148	184

Table 1: Sunflower biological cycle

Variety	Numbers of days after seedling		
	levee	flowering	maturation
Loreto	15	105	163
Florin	15	129	185
Gaspard	15	143	185

Table 2: Rapeseed biological cycle

Variety	Hight (cm.)	head diameter (cm.)	Head φ* (cm.)	Head weight (g.)	seed production ($t.ha.^{-1}$)	1000 seeds weight (g.)
Gloriasol	173.7	16.4	2.35	152.8	0.88	51.1
Isoleic	109	17.3	0.95	182.9	1.3	65.4

Table 3: Sunflower characteristics production (6 plants/m^2).*sterile area head diameter

Variety	Seeds production (g./plant)	1000 seeds weight (g.)
Loreto	6.60	2.74
Florin	7.11	2.5
Gaspard	6.52	2.58

Table 4: Rapeseed characteristics production (70 plants/m^2)

The seeds were chopped by coffee mill and their particles size measured (Mastersizer "long bed", Malvern Instruments S.A.)

Supercritical carbon dioxide extraction apparatus

The design of the equipment (home-made) used is shown in Figure 1.

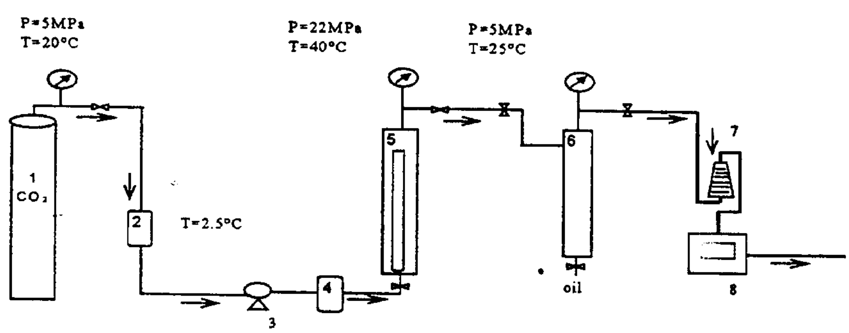

Figure1: SFE-CO_2 Flowsheet
1:CO_2 tank, 2:cold exchanger,3:pump,4:hot exchanger,
5:extraction column,6:separator,7:rotameter,8:mass gas meter

The feed is introduced inside the autoclave, with a stainless steel frit in the inlet and at the outlet column to retain the matrix being extracted.

CO_2 (P=5Mpa, T=20°C) is cooled (T=5°C), pumped (CO_2 flow rate max.=3.2kg./h.) then heated to be a supercritical fluid (P_c=7.23MPa, T_c=31.1°C). It flows through the thermostated autoclave (H=290 mm.,φ_i =19mm., V=92.63 $cm.^3$). Considering the literature data and the operating conditions of the apparatus, the pressure and the temperature extraction were kept constant at 22 MPa. and 313 K. respectively. At the outlet column, the mixture CO2 – solutes is expanded through one valve and are separated in a cyclonic separator [24](P= 5MPa, T= 25°C). At last CO2 is vented through a rotameter and a gas meter. An originality of the process is to withdrawn the solutes at atmospheric conditions every time we need. The solutes (the oil) are weighted and analysed.

Soxhlet apparatus

The solvent extraction is petroleum ether.

Analytical Procedures

Fatty acids analysis:

The fatty acids were recovered from triglycerides by classical procedure (the triglycerides were saponified by NaOH, and methyl esters were formed) and analysed by gas chromatography on a Varian 1400 model equipped with a column 1.5 m. x 1/8"(15% CPSil 84 on Chromosorb WHP 100-120 mesh). The FID temperature was 210°C, the injector at 240°C, the oven temperature was 180°C.

Unsaponifiables:

The unsaponifiable part of the oil is extracted by hexane as recommanded by the French norm AFNOR NF T 60-205-2.

Sterol composition:

The composition of the sterolic fraction is obtained by the norm AFNOR NF ISO 6799 with the class index T 60-232 and determined by gas chromatography.

RESULTS AND DISCUSSION

CO2 Extraction

As we have cyclonic separators, we have the opportunity to withdraw samples at different time and the kinetic of extraction was studied.(Figure2)

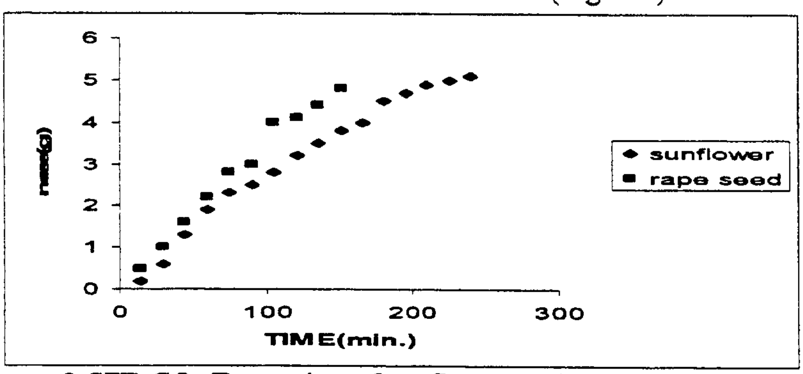

Figure 2:SFE-CO_2 Extraction of sunflower and rape seed oils.

Sunflower (Isoleic): feed mass=10.3g., dp=460.7 µm., moisture = 7%

Rape seed (Florin): feed mass=12g., dp=357.1 µm., moisture = 11%

As the extracted mass oil is 4.6g and CO_2 used during the experiment 2258.63 g., we evaluated the solubility of sunflower oil to be about 2.10^{-3}(kg./kg. CO_2)

Comparison between SFE-CO_2 and Soxhlet results

We have determined the extraction yield, unsaponifiables, sterol fraction (table5,6), fatty acids composition(table 7,8), and sterol composition (table 9,10) and compared the SFE values to the values obtained by Soxhlet method.

Sunflower Variety	Yield *(%)		Unsaponifiables		Sterols	
	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet
Gloriasol H.L.(V1)	41.88	42.5	1.4	1.47	0.42	0.42
Isoleic H.O.(V2)	42.93	43.25	1.6	1.6	0.42	0.43

Table 5: Comparison between SE-CO_2 and Soxhlet results (mass %)

*: (mass of oil / mass of dried product)

Rape seed Variety	Yield *(%)		Unsaponifiables		Sterols	
	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet
Florin(spring type)	39.83	33.40	1.4	1.7	0.49	0.46
Loreto(winter type)	29.66	38.83	1.7	1.4	0.43	0.5
Gaspard	20.12	34.54	1.6	1.67	0.41	0.43

Table 6: Comparison between SE-CO_2 and Soxhlet results (mass %)
*: (mass of oil / mass of dried product)

In both varieties of sunflower the oil yields obtained by SFE and Soxhlet have the same order of magnitude. In rapeseeds the extraction method affected more the seed oil content in Gaspard variety.The unsaponifiables and sterols percentages obtained by the two ways are comparable.

Sunflower Variety	16:0		18:0		18:1		18:2	
	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet
Gloriasol H.L.(V1)	6.86	6.3	4.48	4.5	34.72	28.0	53.55	59.4
Isoleic H.O.(V2)	4.33	3.73	4.29	4.23	83.33	83.2	7.54	8.15

Table 7: Fatty acids composition (mass %). Comparison between SC-CO_2 and Soxhlet results.

Rape seed Variety	16:0		18:0		18:1		18:2		18:3		22:1	
	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet
Florin	4.71	5.0	2.40	1.8	66.15	60.4	19.27	21.9	6.77	7.8		
Loreto	4.99	4.3	1.78	2.2	63.8	64.4	19.35	19.4	8.25	8.6		
Gaspard	4.97	3.96	1.22	1.02	22.95	16.94	16.4	15.37	16.02	5.36	34.97	42.61

Table 8: Fatty acids composition (mass %). Comparison between SC-CO_2 and Soxhlet results.

Sunflower Variety	Campesterol		Stigmasterol		β-Sitosterol		Δ7-Stigma stenol		Δ5-Aveno sterol	
	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet
Gloriasol	7.57	7.74	8.54	8.54	64.78	64.83	12.22	12.63	2.55	2.87
Isoleic	8.04	8.34	9.35	9.35	66.07	66.49	9.88	9.72	2.55	2.5

Table 9: Sterols composition (mass %) Comparison between SC-CO_2 and Soxhlet results.

Rape seed Variety	Brassicasterol		Campesterol		β-Sitosterol		Δ7-Stigma stenol	
	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet	SFE	Soxhlet
Florin	12.99	13.04	33.02	33.03	53.28	53.7		
Loreto	13.17	13.42	32.98	33.56	49.98	49.86	3.68	3.11
Gaspard	15.12	15.34	27.76	27.44	56.74	57.21		

Table 10: Sterols composition (mass %).Comparison between SC-CO_2 and Soxhlet results.

And it can be seen from table 7 and 8 the different extraction method influenced the fatty acids composition as followed:
-the GC analysis of oil showed slight differences only for oleic and linoleic acids in Gloriasol variety (28% of oleic acid by Soxhlet method and 34.7% by SFE method; 59.4 of linoleic by Soxhlet method and 53.5 by SFE method),

-remarkable differences wer observed only for linoleic and erucic acids in Gaspard variety (linoleic acid 5.36 by Soxhlet method and 16.0 by SFE method; erucic acid 42.6 by Soxhlet method and 34.9 by SFE method),

-as it can be seen from table 9 and 10,the extraction method doesn't influence the sterol content

PERSPECTIVES

We are pursuing this study regarding the analytical part with more details(tocopherols, acidity, proteins, phosphorus), the CO_2 flowrate effect, the possibility of modelling the process in order to optimize for industrial applications.

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