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EVALUATION OF THE QUALITIES OF *Camelina sativa* OIL AS RAW MATERIAL FOR BIOKEROSENE

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ABSTRACT

The advanced biofuels are an important target within EU considering the 2030 Energy View. There is a rising demand in finding alternative second generation bio-fuels. With the aim of describing the characteristics of the oil obtained from crops grown in Transylvania and to compare them with values reported from other countries, the following chemical analyses were performed: free fatty acids, fatty acid composition, water content, nitrogen, sulfur, aluminum, calcium, iron, phosphorus, magnesium, sodium, potassium and unsaponifiable residue. The obtained results were compared with the results found in the literature and a comparison was made between the *Camelina sativa* oil and *Brassica napus* L. oil regarding fatty acid content. No significant difference were found between the results from the literature and results obtained by us, regarding fatty acid content. The most abundant fatty acid found was α-linolenic acid in concentration of 32.79% mg and 36.96% mg. The sulfur content was between 22-33 ppm (m/m). Calcium was found in the highest concentration of 1630-1670 ppm (m/m).

Keywords: *Camelina sativa*, vegetable oil, fatty acids, water content, sulfur, unsaponifiable residue, biokerosene.

INTRODUCTION

In the last decades there has been an extension of the surface cultivated with oleaginous crops dedicated to biofuels production all over the world and mainly in Europe. *Camelina sativa* is an "old new plant" that was used thousands of years ago for oil lamps and now for bio kerosene production (Megaloudi, 2006; Dalby, 2003).

Directive 98/70/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 April 2009 on the promotion of the use of energy from renewable sources, declares the sustainability criteria in promoting the security of energy supply, promoting technological development and innovation and providing opportunities for employment and regional development, especially in rural areas (DIRECTIVE 2009/28/EC, biofuelstp).

Due to the rising demand of high quality oils for biofuels production and sustainability criteria, great efforts have been made to reduce, or even eliminate, the quantities of fertilizers and pesticides used for these types of crops. This can be achieved by developing new varieties and hybrids or by cultivating indigenous crops. For the temperate climate one such crop is *Camelina sativa*, which has minimum requirements and is well adapted for light or medium soils (Naghiu, 2012; FAO Food Outlook).

Camelina sativa is a flowering plant in the family *Brassicaceae* (Hunter, 2010; Ehrensing, 2008) and a member of the mustard family and a distant relative to canola. The optimum *Camelina sativa* crop imposes the practice of precise agriculture and it can be integrated very easy in the crop rotation (Ehrensing, 2008; Gugel, 2006).

For this reason we chose to evaluate the quality of the oil of *Camelina sativa* to be used as an advanced biofuel.

Camelina oils, that were obtained using different technological conditions, were analyzed to determine their main

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characteristics. The analyses performed were: free fatty acids, fatty acid composition, water content, nitrogen, sulfur, aluminum, calcium, iron, phosphorus, magnesium, sodium, potassium and unsaponifiable residue.

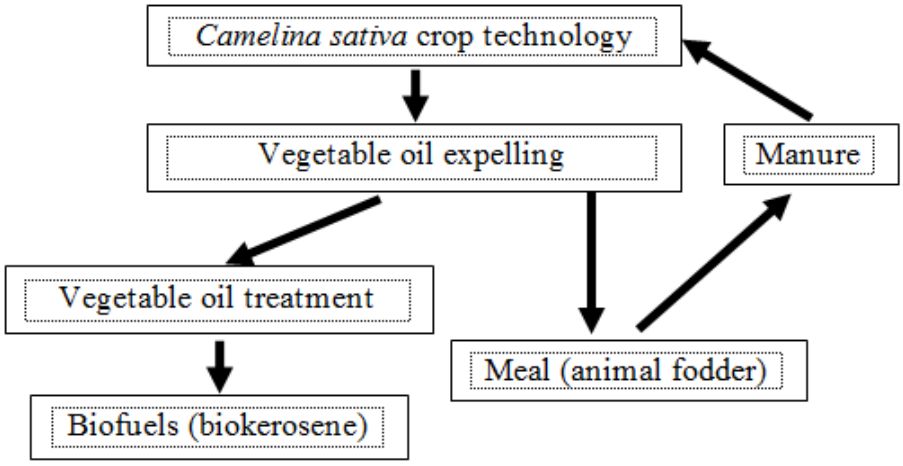

Figure 1. Use of *Camelina sativa* oil

MATERIAL AND METHODS

Sampling

The *Camelina sativa* (Celine cultivar) was cropped in the conditions of the Transylvanian Plain together with the best capitalization of the seeds out in the fields of the Cultivar Testing Center (CIOS) Luduș.

The oil expelling was done in the cold conditions by using a screw press. The two different oil samples were obtained using the same sort of seeds by applying different pressures during processing. Changing the pressure during the expelling process had as result the difference of the final product temperature (10ºC temperature difference between the two samples). The two oils where then analyses in order to evaluate their quality and to see in what way the temperature influences the oils characteristics.

Determination of free fatty acids content

Free fatty acid content value was determined according to AOAC Official Methods 940.28. The analysis was done in triplicate and the average of the values was the final result.

Determination of fatty acid composition

Sample extraction was done according to SR EN ISO 5509. The fatty acid content was determined by GC-FID (Agilent technologies, 6890N GC) equipped with a DB-WAX capillary column (30 m x 0.25 mm x 0.25 µm) and a flame ionization detector. The carrier gas was helium with a constant flow rate of 1 mL min^{-1}. The temperature program was the following: initial oven temperature set at 50ºC, held for 1 min., followed by an increasing of temperature with a rate of 25ºC min^{-1} to 200ºC, temperature increase of 3ºC min^{-1} to 230ºC, and finally maintained for 18 min. The injector and detector temperature was set to 250 and 280ºC, respectively. The internal standard was heptadecanoate methyl ester. The analysis was done in triplicate and the average of the values was the final result.

Determination of water content

Method from SR EN ISO 12937/2003 was used to determine the water content. No sample preparation was needed. 1 ml of sample was injected in the 831 Karl Fischer Coulometer form Metrohm using a disposable syringe that was weighed using an analytical balance before and after the injection. The analysis was done in triplicate and the average of the values was the final result.

Determination of nitrogen

Method from STAS 7184/2 85 and SR ISO 7150-1:2011 was used to determine the nitrogen content.

Determination of sulfur content

Method from SR EN ISO 20846:2012 was used to determine the sulfur content**.** No sample preparation was needed. 10 µl of Camelina oil was injected in the ANTEK 9000 Low level of Sulfur Analyzer. The analysis was done in triplicate and the average of the values was the final result.

Determination of aluminum, calcium, iron, phosphorus, magnesium, sodium and potassium

Reagents and standards: all reagents used for this research work were of p.a. grade and purchased from Merck, Darmstadt. For all dilutions ultrapure water (18.2 MΩ/cm) obtained from a Millipore Direct-Q3 UV system (Millipore, France) was used.

Sample preparation: 100 mg sample was accurately weighted in a microwave vessel, then 5 mL of HNO_3 65% and 2 mL of HF 40% were added to each sample and the samples were left 4 h to react. The samples were digested using a first digestion program: 140ºC, 10 min.; 160ºC, 3 min.; 190ºC, 3 min. The vessels were opened and 20 ml H_3BO_3 saturated solution were added and a second digestion program was applied: 140ºC, 5 min.; 100ºC, 1 min. After mineralization, the samples were filtered and diluted up 50 mL with deionized water. Blank, consisting of deionized water and reagents, was prepared in the same way as the sample. For each sample, three replicates were prepared.

Instruments: for the microwave digestion of samples, a closed-vessel microwave system Berghof MWS-3+ with temperature control mode (Eningen, Germany) was used. The contents of studied elements were determined by Perkin Elmer ICP-OES OPTIMA 5300 DV.

Determination of unsaponifiable Residue value

Unsaponifiable Residue value was determined according to AOAC Official Methods 933.08 [16]. The analysis was done in triplicate and the average of the values was the final result.

RESULTS AND DISCUSSION

A comparison of the results obtained for the two oils is presented in Table 1. Significant differences can be noticed in the free fatty acids content, water content and phosphorus, sodium potassium contents (Figure 2). The pressured applied during the fabrication process influenced the quantity of water in the final product. A higher concentration of water results in a higher concentration of several compounds like phosphorus and sodium. The higher value of water content explains the higher concentration of fatty acids in the first oil sample.

Table 1. Results obtained for the two oils

Crt. no.	Name of characteristic determined	Units of measurement	Values obtained for the lower temperature oil	Values obtained for the higher temperature oil
1	free fatty acids	mg KOH/g	8.66	1.7
2	water content	ppm (m/m)	485.5	602
3	nitrogen content	ppm (m/m)	58.4	59.7
4	sulfur content	ppm (m/m)	33.6	22.5
5	aluminum	ppm (m/m)	25	19
6	calcium	ppm (m/m)	1630	1670
7	iron	ppm (m/m)	32	24
8	phosphorus	ppm (m/m)	33.3	260
9	magnesium	ppm (m/m)	55.6	34
10	sodium	ppm (m/m)	96.7	320
11	potassium	ppm (m/m)	<5	60
12	unsaponifiable residue	%	0.1	4.45

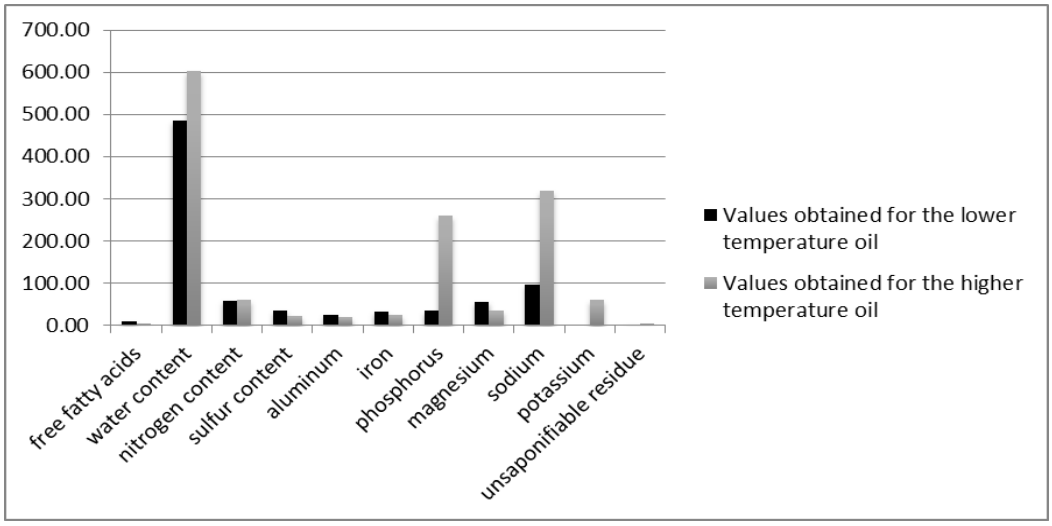

Figure 2. Comparison of values obtained after analysis the two oils

The fatty acid composition is presented in Table 2 for the lower temperature oil and, in Table 3, for the higher temperature oil. There is no significant difference between the oils regarding the fatty acid composition. The results were also compared to those of Ambrovic (2005) and Rodrigues-Rodrigues (2013). The oleic and linoleic acids where found in a higher concentration compared to those found by the other authors. The difference in the composition is due to the different pedoclimatic conditions in which *Camelina sativa* was cultivated. The content of erucic acid was below the permitted value of 5% under the EU legislations that establishes the maximum values allowed for the edible oils (EC, Council Directive 80/891/EEC). The most abounded fatty acid found was α-linolenic acid in concentration of 32.79% mg and 36.96% mg.

Table 2. Fatty acid composition of the lower temperature oil

Crt. no.	Name of characteristic determined	Units of measurement	Values obtained	Ambrovic (2015)	Rodrigues-Rodrigues (2013)
1	palmitic acid (C16:0)	% mg	6.09	6.43	7.0
2	stearic acid (C18:0)	% mg	2.72	2.57	2.5
3	oleic acid (C18:1n9)	% mg	23.80	17.4	6.9
4	linoleic acid (C18:2n6)	% mg	27.40	16.9	14.5
5	α-linolenic acid (C18:3n3)	% mg	32.79	35.2	41.0
6	arachidic acid (C20:0)	% mg	1.99	1.24	13.4
7	behenic acid (C22:0)	% mg	0.43	-	-
8	erucic acid (C22:1n9)	% mg	4.34	1.62	4.9
9	nervonic acid (C24:1n9)	% mg	0.20	-	-

Table 3. Fatty acid composition of the higher temperature oil

Crt. no.	Name of characteristic determined	Units of measurement	Values obtained	Ambrovic (2015)	Rodrigues-Rodrigues (2013)
1	palmitic acid (C16:0)	% mg	6.43	6.43	7.0
2	stearic acid (C18:0)	% mg	2.82	2.57	2.5
3	oleic acid (C18:1n9)	% mg	19.36	17.4	6.9
4	linoleic acid (C18:2n6)	% mg	28.81	16.9	14.5
5	α-linolenic acid (C18:3n3)	% mg	36.96	35.2	41.0
6	arachidic acid (C20:0)	% mg	1.63	1.24	13.4
7	behenic acid (C22:0)	% mg	0.33	-	-
8	erucic acid (C22:1n9)	% mg	3.02	1.62	4.9
9	nervonic acid (C24:1n9)	% mg	0.16	-	-

No significant difference was observed between the two oils, so the pressure had no effect on the fractions of fatty acids.

Table 4 presents a comparison between *Camelina sativa* oil and *Brassica napus* L. oil regarding the fatty acid composition. Oleic acid was found in higher concentration in *Brassica napus* L. oil with values of around 47% mg compared with 19-24% mg found in Camelina oil; meanwhile α-linolenic acid was found in higher concentration in Camelina oil, around 33-37% mg, compared to 8.7% mg found in Reaped seed oil.

Table 4. Comparison of fatty acid composition in the *Camelina sativa* oil and *Brassica napus* L. oil

Crt. no.	Name of characteristic determined	Units of measurement	Values obtained for the lower temperature oil	Values obtained for the higher temperature oil	Values found in *Brassica napus* L. oil (Koprna, 2006; Velasco, 1998)
1	palmitic acid (C16:0)	% mg	6.09	6.43	4
2	stearic acid (C18:0)	% mg	2.72	2.82	1.4
3	oleic acid (C18:1n9)	% mg	23.80	19.36	46.8
4	linoleic acid (C18:2n6)	% mg	27.40	28.81	19.5
5	α-linolenic acid (C18:3n3)	% mg	32.79	36.96	8.7
6	arachidic acid (C20:0)	% mg	1.99	1.63	-
7	behenic acid (C22:0)	% mg	0.43	0.33	-
8	erucic acid (C22:1n9)	% mg	4.34	3.02	11.4
9	nervonic acid (C24:1n9)	% mg	0.20	0.16	-

CONCLUSIONS

Pressure level during expelling is a particularly important element that influences the quality of *Camelina* oil, because it has a direct influence on the water content, which is a key factor in evaluating biofuels quality. The water content of the oil influences the compounds mix like phosphorus, sodium and the free fatty acids concentration. The values obtained in Transylvanian *Camelina* seed oils are comparable to values found elsewhere. The comparison with rapeseed oil showed that the two oils have different content of fatty acids.

The *Camelina* oil is a very promising raw material for obtaining the advanced biofuel, due to its qualities and to the fact that *Camelina sativa* is a crop that is very well adapted to the Transylvania's pedoclimatic conditions.

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