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PRELIMINARY STUDY OF THE INFLUENCE OF CO_2 EXTRACTION CONDITIONS ON THE ESTER, ALDEHYDE, KETONE AND HYDROCARBON CONTENT OF GRAPE BAGASSES FROM JAM PRODUCTION

J. Santos[1], R. Dariva[1], A. Mossi[1], G. Stuart[2] and I. Nascimento[3*]

[1]Department of Food Engineering, URI, Campus de Erechim-RS, Brazil.
[2]PETROBRÁS - CENPES / GEHP. Rio de Janeiro - RJ, Brazil.
[3]Physics and Chemistry Department, Institute of Environmental Sanitation, Caxias do Sul University, Rua Francisco Getúlio Vargas 1130, CEP: 95070-560, Caxias do Sul - RS, Brazil.

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Abstract - The main objective of this work was to assess the influence of temperature and pressure on the chemical characteristics of the essential oil obtained from CO_2 extraction of grape bagasses in the production of jam. The experiments were performed in a laboratory-scale unit, where the effect of temperature (290 and 303 K) and pressure (15 and 25 Mpa) was investigated in terms of liquid yield and chemical composition of the extracts. The CO_2 mass flow rate was kept within a range of 2.5 to 3.0 g/min. The instrumental analysis was performed by gas chromatography with a mass spectrometer detector (GC-MS). The extraction conditions investigated in this work had no significant influence on the mass of essencial oil extracted. The main compounds identified in the extracts by the GC-MS spectra library (match quality higher tan 90%) were octadecane, dihydroxy ergostene-dione and phenylethyl n-decanoate when the temperature was increased from 290 to 303 K. Heptanal, ethyl ester of decosonoic acid and hexatriacontane were the individual compounds with the greatest increase in the chromatographic peak area when the pressure was increased from 15 to 25 Mpa. The most important class of compounds were hydrocarbons at 303 K and 15 MPa and were ketones and aldehydes at 25 Mpa and 290 K.
Keywords: Grape bagasse; GC-MS; Chemical composition; High pressure; CO_2 extracts.

INTRODUCTION

The Isabella grape is one of the most important varieties of *Vitis labrusca*, and today it is the most widely diffused variety in the Serra Gaúcha viticultural region in southern Brazil, where it represents near 45% of the total production. The Isabella grape is used to make red table wine and jam and it is also commercialized as table grapes (Rizzon et al., 2000). Grape seed matrix is very complex, containing approximately 40% fiber, 16% oil, 11% proteins and 7% complex phenols, tannins, sugars, mineral salts and other components (Murga et al., 2000*)*. Some research has been published on supercritical extraction of oil from grape seeds (Murga et al., 2000; Sovová et al. 1994; Molero et al., 1996) but, according to Reverchon (1997) papers describing the extraction with supercritical fluids of vegetable matter are focused mainly on the analytical aspects. Therefore, knowledge about the chemical

*To whom correspondence should be addressed

composition of many matrices, including Isabella grape bagasses, is very scarce. Currently grape bagasses are used only in the production of animal feeds.

Essential oils are commonly obtained by distillation at atmospheric pressure and an elevated temperature (Fischer et al., 1988). Carbon dioxide has been widely employed in the extraction of essential oils (Reverchon, 1992) because it is a nontoxic solvent and does not leave residues at the end of the extraction. Another advantage of SCFE is that no refining process is needed (Molero et al., 1996).

Gas chromatography with mass spectrometry detection (GC-MS) is currently an important tool for the analysis of several kinds of complex samples (Möder et al., 1998; Nascimento et al., 2004; Nascimento and Caramão, 2004; Nascimento et al., 2003). This technique is also widely employed in the chemical characterization of natural products (Melecchi et al., 2002; Zeng and Khan, 1995; Mossi et al., 2004).

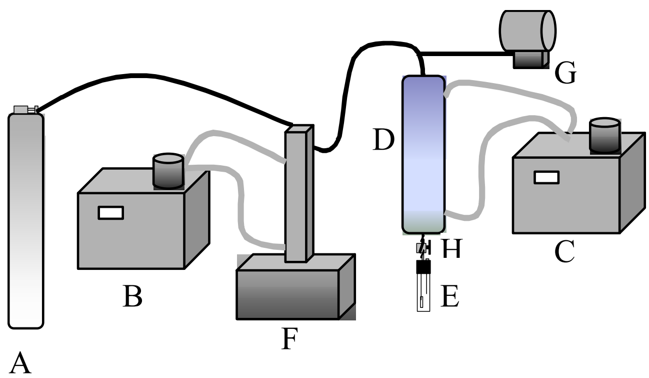
Aldehydes, esters, hydrocarbons and ketones are important classes of compounds, which are widely used in the chemical, food, pharmaceutical and perfumery industries. Due to the large amount of grape bagasse produced in the southern viticultural region of Brazil, this work is aimed at investigating the influence of temperature and pressure on the yield of these important substances obtained from carbon dioxide extraction of Isabella grape bagasses in the production of jam.

For this purpose, a semi-batch laboratory unit operated at 290 and 303 K and at 15 and 25 MPa with a CO_2 flow ranging from 2.5 to 3.0 g/min was employed. The instrumental analysis was performed by GC-MS and the main compounds of each extract were identified by the GC-MS spectra library (Wiley).

MATERIALS AND METHODS

Isabella grape bagasse samples from jam production, kindly provided by artisan producers, were collected, dried, crushed and stored under refrigeration. The carbon dioxide (99.9% purity) was purchased from White Martins (Rio Grande do Sul – Brazil).

The experiments were performed in a laboratory-scale unit used in previous work (Mossi et al., 2004), which consists basically of a CO_2 reservoir, two thermostated baths (one for the pump and the other for the extractor temperature control), a syringe pump (ISCO 260D), a 0.2 dm^3 jacketed extraction vessel, an absolute pressure transducer (Smar, LD301) equipped with a portable programmer (Smar, HT 201) with a precision of ± 0.012 Mpa and a collector vessel with a glass tube and a cold trap (Figure 1).



A - CO_2 reservoir;
B, C - thermostatic baths;
D - extraction vessel;
E - collector vessel with a glass tube;
F - high pressure pump;
G - absolute pressure transducer;
H - electrical heater).

Figure 1: Schematic diagram of the high-pressure extraction apparatus

Around 40 g of dried grape bagasse were charged into the extraction vessel. The CO_2 was pumped into the bed, which is supported by 300 mesh wire disks at both ends, and was kept in contact with the raw material for one hour to allow for system stabilization. Then the essential oil was collected by opening the micrometering valve. The CO_2 mass flow was monitored by the pump recordings (within a range of 2.5 to 3.0 g/min for all experiments). The mass of the extracted oil was weighed and the glass tube was connected to the equipment. The extraction time was 60 minutes for each extraction. The experiments were initially performed at 290 and 303 K with constant pressure (15 Mpa). Later, the operating conditions were changed to 15 and 25 MPa with constant temperature (290 K). These working conditions were selected on the basis of lower operational costs. Duplicate runs were made for all conditions and the variations were about 2% of the average values. A set of extractions with the mass of CO_2 varing from 50 to 450 g were performed to determine the mass of CO_2 that allows the maximum extraction yield in accordance with the extraction conditions described in this work.

The extracts were analyzed using a GC-MS system, Shimadzu GC-17A, GC-MS – QP 5050 A, in the SCAN mode, using a capillary DB-5 (30m x 0.25mm x 0.25μm) column. The injection was done in the split mode (1:50 ratio) with an electronic impact of 70 eV. Column temperature was programmed from 60 °C to 300 °C at 3 °C/min and then held for 5 min. Helium was the carrier gas, the injection port temperature was 280 °C and the detector temperature was 300 °C. The injection volume was 0.2 μL (in 10% CH_2Cl_2 (v/v)). The sample components were identified by matching their mass spectra with those of the Wiley library database and by comparison of retention times. The semiquantitative approach used was the peak area summation of the TICs (total ion chromatograms) (percentages of the compounds in the samples).

RESULTS AND DISCUSSION

The liquid yield (weight percentage of the oil extracted with respect to the initial amount of raw material in the extractor) was around 1.04% (maximun standard deviation of 0.04%). The higher liquid yield was obtained with 250 g of CO_2. The extraction conditions investigated in this work had no significant influence on the extraction yields.

Figures 2 and 3 show the influence of temperature and pressure, respectively, on the chromatographic profiles of extracts of grape bagasses from jam production. Table 1 contains the identification (GC-MS library) of the numbered peaks in Figures 2 and 3. Only compounds with a match quality of at least 90% were tentatively identified.

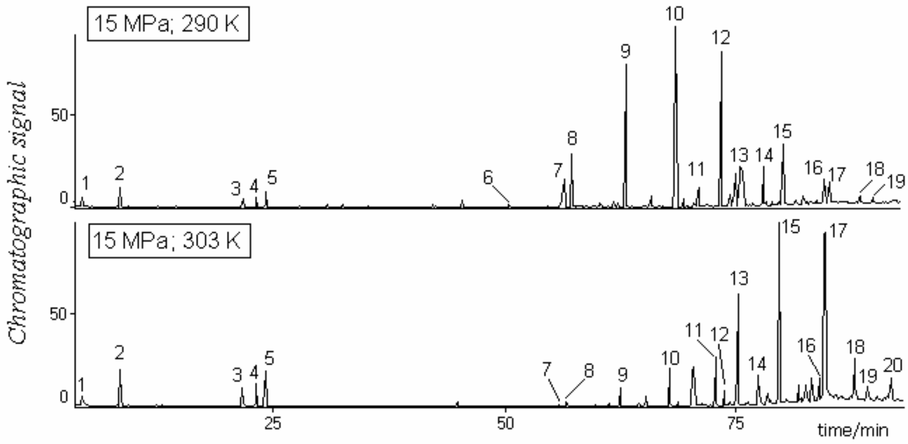


Figure 2: Effect of extraction temperature on the chromatographic profiles of extracts of grape bagasses from jam production.

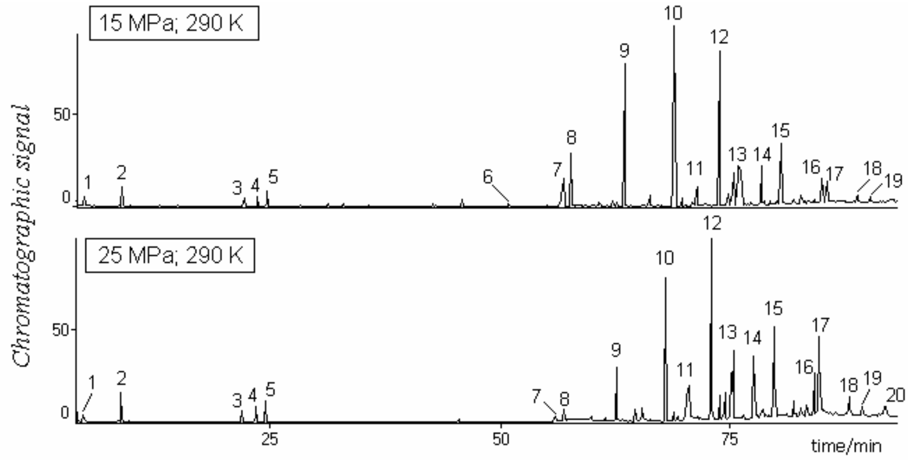


Figure 3: Effect of extraction pressure on the chromatographic profiles of extracts of grape bagasses from jam production.

Table 1: Identification (GC-MS Wiley library) of the numbered peaks in Figures 1 and 2. Effect of changes in temperature and pressure on their percent areas.

Compound	# Peak	Peak area (%)		
		290 K 15 MPa	290 K 25 MPa	303 K 25 MPa
n-Hexanal	1	trace[b]	trace	trace
Heptanal	2	1.5	2.5	1.4
Decanal	3	0.6	0.8	1.4
Decadienal	4	0.7	1.0	1.7
Decadienal, trans-trans	5	1.1	1.5	2.6
Ethyl ester of dodecanoic acid	6	trace	trace	trace
Methyl ester of octadecadienoic acid	7	2.2	trace	trace
Ethyl ester of nonanoic acid	8	4.3	0.7	trace
Ethyl ester of tetradecanoic acid	9	15.5	4.3	1.3
Ethyl ester of hexadecanoic-acid	10	25.2	12.0	2.9
Octadecane	11	1.5	2.5	3.0
Ethyl ester of docosonoic acid	12	trace	16.5	4.1
Hexatriacontane	13	3.9	6.6	13.5
Ethyl ester of decosonoic acid	14	3.5	5.0	2.7
Octasane	15	8.8	3.5	15.9
Phenylethyl n-decanoate	16	1.9	9.4	24.0
Dihydroxy cholestan-one	17	trace	trace	0.8
Dihydroxy ergostene-dione	18	trace	2.1	5.5
Phenylethyl isovalerate	19	trace	trace	1.1
Ursenal	20	trace	trace	2,8

trace < 0.03%

Although compound identification using only the GC-MS apparatus database is a tentative identification, the high match quality is a good approach for determining the matrix chemical profile for all the class compounds (Melecchi et al., 2002). Figure 4 shows the effects of temperature and pressure on the distribution of total aldehydes, esters, hydrocarbons and ketones in the jam bagasses. The percent content was obtained by summation of the relative areas of the chromatographic peaks of the individual compounds.

Figure 4 shows that changes in temperature from 290 to 303 K at constant pressure increase the total area of aldehydes, hydrocarbons and ketones. On the other hand, the total area of esters was reduced. The highest increase in percentual area observed for the hydrocarbons (Figure 4A) can be explained by the increase in the solvent intermolecular atractive forces (like London forces). When the solvent density is reduced (by the increase in temperature), the possibility of London forces occurrig decreases, the solvent polarity is reduced and hydrocarbons (lowest density class) are the most soluble compounds.

On the other hand, when the pressure is increased from 15 to 25 MPa at constant temperature, the proximity of the solvent molecules is increased. Thus, inducted dipole forces can occur among the solvent molecules and ketones and aldehydes (highest polarity class) are the most soluble compounds (Figure 4B).

Table 2 shows that, of the class compounds investigated in this work, octadecane, dihydroxy ergostene-dione and phenylethyl n-decanoate were the individual compounds with the greatest increase in the total area as a function of the increase in temperature. Heptanal, ethyl ester of decosonoic acid and hexatriacontane were the individual compounds with the greatest increase increase in total area as a function of the increase in pressure.

In general, the best extraction conditions were 25 MPa and 303 K (for hydrocarbons) and 25 MPa and 290 K (for aldehydes and ketones).

At this point it is clear that at least one more temperature and pressure condition must be investigated to assess selectivity and solvent capacity. However, these preliminary results might be very important if one considers the possibility of obtaining a variety of essential oils from jam bagasses with higher or lower contents of different class compounds, in accordance with industrial interests, by simply varying the extraction conditions.

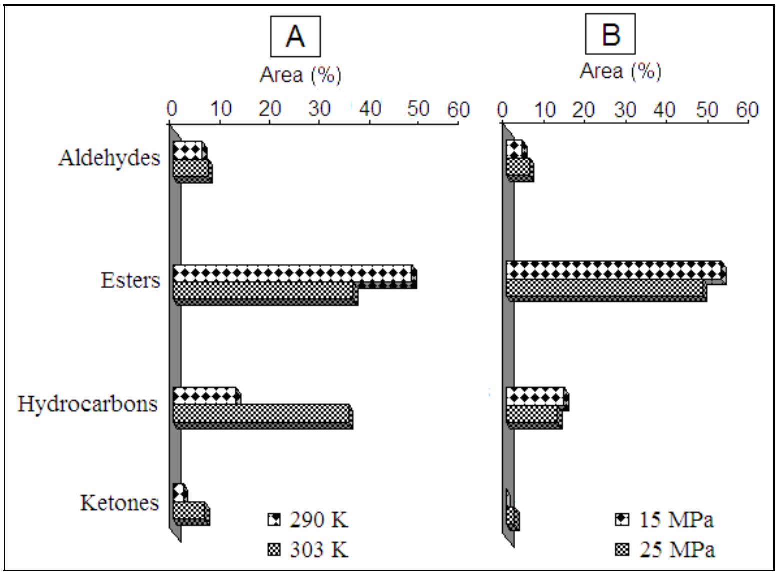


Figure 4: Effects of temperature (A) and pressure (B) on the yield of aldehydes, esters, hydrocarbons and ketones in the CO_2 extracts of grape bagasses from jam production. Pressure in (A) = 15 MPa; temperature in (B) = 290 K.

Table 2: Effect of the increase in temperature and pressure on the percentages of the main compound contents in each class

Effect of temperature on the peak area (%)					Effect of pressure on the peak area (%)				
Compound	**Chemical class**	**290 K 25 MPa**	**303 K 25 MPa**	**Increase (%)**	**Compound**	**Chemical class**	**15 MPa 290 K**	**25 MPa 290 K**	**Increase (%)**
Decadienal, trans, trans	Aldehyde	1.5*	2.6	1.1	Heptanal	Aldehyde	1.5	2.5	1.0
Phenylethyl n-decanoate	Esther	9.4	24.0	14.6	Ethyl ester of decosonoic acid	Esther	3.5	5.0	1.5
Octadecane	Hydrocarbon	3.5	15.9	12.4	Hexatriacontane	Hydrocarbon	3.9	6.6	2.7
Dihydroxy ergostene-dione	Ketone	2.1	5.5	3.4	-	-	-	-	-

*Individual chromatographic peak area (%)

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