

Application of Supercritical Fluid Extraction for the Recovery of Aroma Compounds to be Used in Fast Aged Rum Production

I. GRACIA*, M.T. GARCÍA, J.F. RODRÍGUEZ and A. de LUCAS

Departamento de Ingeniería Química. Universidad de Castilla-La Mancha. Facultad de Ciencias Químicas. Avda. Camilo José Cela, 10. 13004 C. Real. España

Received May 13, 2008; Accepted March 14, 2009

Supercritical CO₂ extraction was used for the recovery of valuable aroma components with application in blending steps for fast aged rum processes. Head Alcohol, Crude and Aged Sugar Cane Spirit process streams were used to firstly quantify different concentrated aroma fractions with interest in food applications. Alcohols ratio, esters composition and carboxylic acids concentration criteria were used to determine the quality of extracts. The economical profitability of this technology was especially evident for Head Alcohol and Aged Sugar Cane Spirit extracts, since the most interesting compounds were concentrated more than 300 times compared to commercial aged rum. Additional experiments were performed in the range 8-15 MPa and 313-333 K to obtain empirical correlations to predict solubility data for further scale-up applications.

Keywords: aroma extraction, rum production, supercritical fluid extraction

Introduction

The industrial production of rums involves a complex process that includes fermentation, distillation, additivation, blending and aging steps. This process generates different intermediate and residual streams that contain a large number of valuable compounds that are responsible of the final flavour and aroma characteristics in rums. Even at low concentrations, changes in their content and relative proportion produce important variations in characteristics and quality of aged rums (Moarse, 1991; Canas *et al.* 1999; Boscolo *et al.* 2000).

Considering that the aging step usually varies from 3 to 12 years, this process is the main economical limitation in conventional rum production and in general for aged alcoholic drinks processes. Nowadays there is an increasing interest in developing Fast Aging Processes (FAP) to accelerate the formation of aroma components. As example, Fig. 1 shows the ICIDCA™ FAP (ICIDCA, 2002), which includes an ozone treatment followed by an aging stage in contact with oak chips. This alternative allows reducing up to 50% the global aging time, producing rum with the same qual-

ity and increasing notably the profitability of the process. Other FAP alternatives involve the addition of natural aroma components similar to those produced in the conventional process, although the availability and analytical information about their dosage are generally empirical.

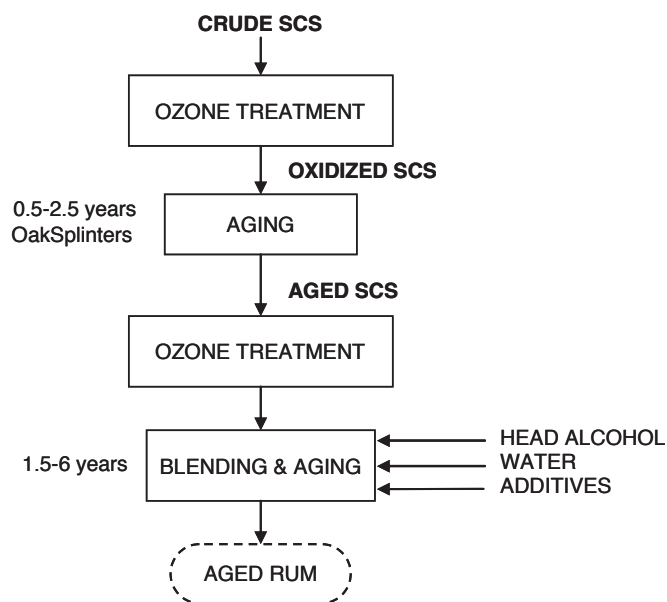


Fig. 1. ICIDCA™ process for fast aging processes of rum.

*To whom correspondence should be addressed.

E-mail: Ignacio.Gracia@uclm.es

In spite of Supercritical Fluid Extraction (SFE) has been used for the recovery of aroma compounds from natural matrixes, SFE applications were focused on dealcoholisation and fractionation procedures without supporting detailed analytical information (Medina and Martinez, 1997; Gamse *et al.* 1999; Señorans *et al.* 2001; Señorans *et al.* 2003). Precise knowledge about quantitative composition of SFE extracted fractions and original rums, in addition to further data requested for scale up procedures, would determine the viability of the use of supercritical technology in FAP.

Therefore, the aim of this work is to quantify the aroma components extracted in different streams to evaluate their potential interest in food applications and rum blending like alternative to FAP. The main advantage of this process consists in incorporate the aroma extracts recovered from low value currents of the same process. The extract quantification leads to perform precise blending formulation, avoiding the classical empirical procedure.

Materials and Methods

Materials Liquid CO₂ (purity 99.5%) was supplied by Carburos Metalicos S.A. (Madrid, Spain).

The rum samples were provided by A. Guiteras Rum Distillery (Havana, Cuba). A complete description of their characteristics is shown in Table 1. The abbreviation SCS has been used to designate Sugar Cane Spirit.

Apparatus and Extraction Procedure A schematic of the extraction system used in this study is presented in Fig. 2. Liquid CO₂ from a stainless-steel cylinder (SC) was cooled (CS), filtered (F), and compressed by a positive-displacement pump (P). The pressure was regulated by a back-pressure regulator (BPR) and checked by a manometer (M). The compressed fluid was passed through a 730 mL stainless-steel cylinder (EX) from the bottom at constant flow rate of 1 SL/min (L/min at standard conditions). The bed was supported with glass balls in order to enhance the mass transfer between the supercritical CO₂ and the liquid phase. To keep the extractor temperature at the desired value, a digital con-

Table 1. Characteristics of rum samples.

STREAM	ALCOHOLIC CONTENT % (V/V)	SOURCE	VALUE	APPLICATIONS
Head Alcohol (HA)	95	Top Distillation #2	Low	Blending , Combustion
Crude SCS	75	Bottom Distillation #1	Low/Medium	Intermediate product in aging process
Aged SCS	75	Aging of Crude SCS	High	Aged rums production (3-5 years old)
Aged rum (Vigía™)	40	Aging & Blending of Aged SCS	Very High	Commercial aged rum (12 years old)

SCS: Sugar cane Spirit

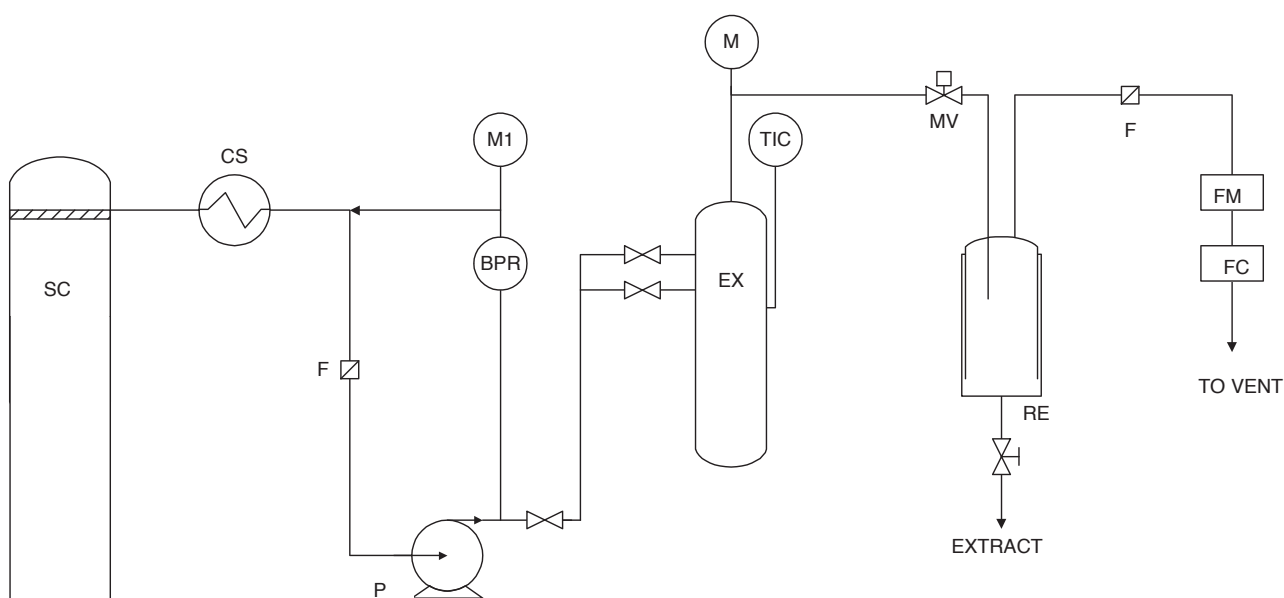


Fig. 2. Schematic diagram of the experimental extraction system.

troller (TIC) was employed to regulate the electric current through the resistor surrounding the extraction cylinder. The extract-laden gas from the extractor was passed through a heated metering valve (MV) where the supercritical CO₂ was depressurized, and the extract was collected in a solid-phase trap (RE) at 253 K and determined gravimetrically. The trap consisted of an ethanol-dry ice cryogenic mixture. The extract was freeze stored until analysis. The gas flow through the extractor was measured by a turbine flow meter (FM) and totalled by a digital flow computer (FC). More detailed information can be obtained in (Rincon *et al.* 2000).

For GC-MS analysis, the extractions were accomplished in 5 h, using the global extract collected in the separator for quantification and sensory evaluation. For solubility data calculations, there were performed kinetic experiments of 5 h global time in which extract samples were collected every 30 min.

Aroma analysis by mass spectrometry gas chromatography The analysis of the aroma compounds in extracts was performed by mass spectrometry gas chromatography (GC-MS). A MD 800 high resolution gas chromatograph (Fisons Instruments) equipped with a J&W Scientific DB-624 column (30 m × 0.25 mm i.d. × length, 1.24 μm film) was used. The initial oven temperature was programmed at 323 K for 10 minutes, with a heating velocity of 5 K/min, raising to 498 K and then kept for 15 min. The injection temperature was 498 K and the splitless injection mode was used. The mass spectrometric analysis was developed with electronic impact emission at 70eV and the scan mode at mass range between 13 and 300 uma's. The solvent delay was 5 minutes and the power supply temperature was 498 K.

The sample was prepared as follows: 20 mL of each fraction were added with 20 microlitres of the internal standard solution, diluted (1:1) with standard ammonium sulphate solution and extracted with 5 mL of diethyl ether/hexane mixture (2:1 v/v). The organic layer was separated, concentrated under a nitrogen flow and one microfilter of the resulting extract was injected into the GC/MS system for analysis.

Compounds were identified by comparison of their mass spectra and retention time with the Wiley 6.0 library (Wiley, New York) and NIST98 (National Institute of Standards and Technology, Gaithersburg) mass spectral database. Determination of the percentage composition was based on peak area normalization without the use of correction factors. Compounds were quantified as area percentages of total volatiles.

Results and Discussion

The first part of this work gives information about quantification of aroma compounds present in the supercritical extracts from the different process streams at extraction con-

ditions leading to higher aroma concentration, 10 MPA and 313 K, determined in a previous work (Gracia *et al.* 2007). Comparison of these results with composition of commercial rum, according to different quality criteria will determine the viability of using SFE in speed aging procedures. Once determined the viability of the process, an additional set of experiment was performed in order to obtain solubility data in a range close to the previous operation conditions. Mathematical treatment of solubility data according to a density-based model led us to obtain empirical correlations requested for further economical analysis and scale up steps.

Aroma quantification of supercritical extracts Table 2 resumes the GC-MS analysis and the global sensory evaluation of the extracts corresponding to the samples tested. In general, the aroma components were detected in very different concentrations and combinations. In spite of the lack of information available in the literature for beverage supercritical extract composition, these results agree with those obtained for the flavor compounds in non extracted wine and distilled alcoholic beverages (Nykänen, 1986).

In order to compare the different fractions isolated, Table 2 components were divided into three groups based on their increasing volatility (Fig. 3). The first group, separated up to 15 minutes on the GC, was formed by the light hydrocarbon aroma fraction. The second (medium hydrocarbons) and third group (heavy hydrocarbons) were separated between 15-30 min and over 30 minutes, respectively.

From Fig. 3 the proportion of light compounds in the Head Alcohol and Aged SCS extracts were similar and much higher than Crude SCS extract, while as the Crude SCS extract has broader distributions of compounds. The variations in the chemical composition of the extracts can be explained considering the different origin of the streams used in the supercritical extraction. The Head Alcohol and Crude SCS represent top and bottom streams of the distillation column, respectively, and therefore, the light hydrocarbon proportion is dominant in the first sample. On the other hand, during the aging steps the large number of chemical changes performed in extraction/reactions with wood (Jimenez and Ancin, 2007) and by microorganisms (Reazin, 1981) produces a notable increase of the volatile compounds concentration for Crude SCS stream increasing again the recovery of light compounds.

In order to select the best extract to perform the alternative blending step in FAP, we used three quality criteria according to the alcohols ratio, esters composition and carboxylic acids concentration. Higher alcohols have desirable aromatic characteristics, representing the most important quality restriction. This quality can be evaluated by the relations between the components 1-butanol, 2-methyl/2-

Table 2. Aroma components in the extracts (soluble fraction in CO₂ at 10 MPa and 313 K^a).

SAMPLE	CASRN	RT (min)	HEAD	CRUDE	AGED
			ALCOHOL	SCS	SCS
Compound			% peak area		
1-propanol	71-23-8	5.767	22.880	17.391	17.519
Methyl butenol	60766-00-9	6.651	-	0.112	-
1-propanol, 2-methyl	78-83-1	7.217	28.490	3.478	26.278
Acetic acid	64-19-7	7.734	-	1.913	-
1-butanol, 3-methyl	123-51-3	12.152	29.183	6.086	33.054
1-butanol, 2-methyl-	1565-80-6	12.219	16.054	1.709	19.998
1,6-heptadien-4 ol	556-82-1	13.586	0.098	-	0.041
3(2H)-furanone, dihydro-2-methyl	3188-00-9	14.619	0.182	1.010	0.107
Pentane	109-66-0	14.919	0.091	-	-
Propanoic acid, 2-methyl	79-31-2	15.520	-	-	0.036
Formic acid, methyl ethyl ester	625-55-8	15.586	0.057	1.348	0.672
1-butanol-3 methyl acetate	123-92-2	17.653	-	0.919	0.030
Propane, 1-methoxy-2-methyl	625-44-5	19.338	0.038	-	0.032
2-butanol, 3 methyl	598-75-4	19.671	0.036	-	-
Ethanone, 1-(2-furanyl)	1192-62-7	20.571	0.027	-	-
Pentanoic acid, 2-methyl	97-61-0	22.371	0.029	-	0.030
Butanoic acid, 3-methyl ethyl ester	108-64-5	22.771	0.030	-	0.029
Pentanoic acid	109-52-4	24.422	0.034	-	0.038
Butanoic acid, 2-ethyl-3-oxo, methyl ester	51756-08-2	24.939	-	-	0.038
3-hexanol, 2,4-dimethyl	13432-25-2	25.039	0.058	-	-
Butanoic acid, 2-ethyl	88-09-5	25.072			0.089
Propane, 1,1-diethoxy	4744-08-5	25.405			0.029
2-methyl-2-vinyloxirane	1838-94-4	26.673	0.909	-	-
1-pentyn-3-ol, 4-methyl	565-68-4	26.689	0.031	-	0.031
Mequinol	150-76-5	27.307	0.034	0,899	0.029
Phenylethyl alcohol	60-12-8	28.507	0.087	-	0.081
Hydroperoxide, -heptyl	764-81-8	29.457	0.046	-	
Octanoic acid, ethyl ester	106-32-1	29.475			0.134
Ethanedial dioxine	557-30-2	29.474	-	1.004	-
Hexanoic acid	142-62-1	30.491	0.111	0.943	0.155
Decanoic acid, ethyl ester	110-38-3	34.975	-	0.950	0.081
Butanoic acid 2-ethyl	88-09-5	35.125	0.149	-	-
Nonanoic acid	112-05-0	35.858	0.124	-	0.128
Nonanoic acid ethyl ester	123-29-5	40.126	0.096	1.175	0.296
Cyclopentaneundecanoic acid	6053-49-2	40.643	0.032	0.950	-
Tridecane, 3-methylene	19780-34-8	41.360	-	-	0.026
Tryciclo 5.1.0.002, 4 Octane-5-	74810-39-2	43.497	0.033	-	-
Butanoic acid, 3-methyl, 2-phenylethyl ester	3188-00-9	46.528	1.065	-	0.026
Nonadecanoic acid, ethyl	18281-04-4	49.713	-	1.223	0.036
Other compounds		>60	-	60.599	0.993

Global Sensory evaluation*

^a Experimental conditions^b Normative PR NF V09-500

CASRN: Chemical Abstracts Service Registry Number

RT: Retention Time

Fruity

Sweat

Whiskey

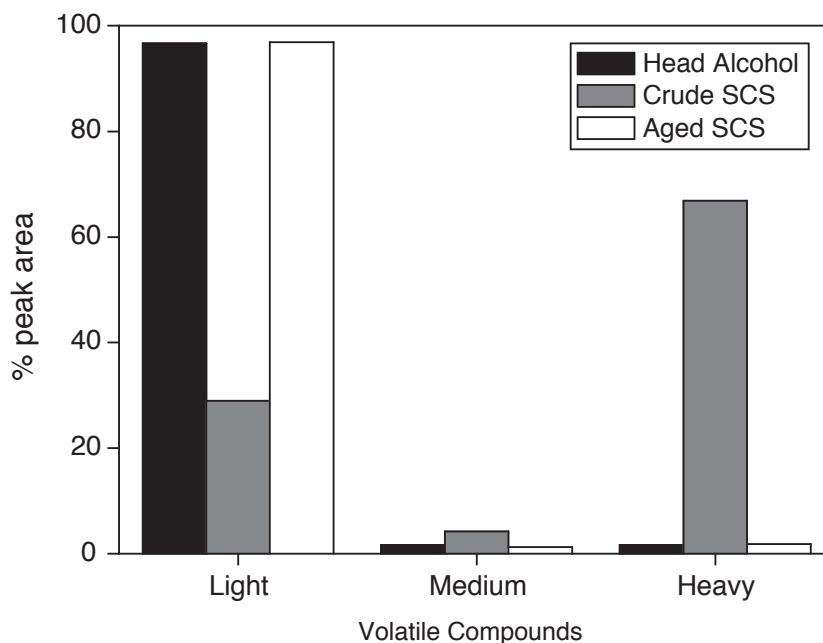


Fig. 3. Volatile compounds distribution in Head Alcohol, Crude SCS and Aged SCS extracts.

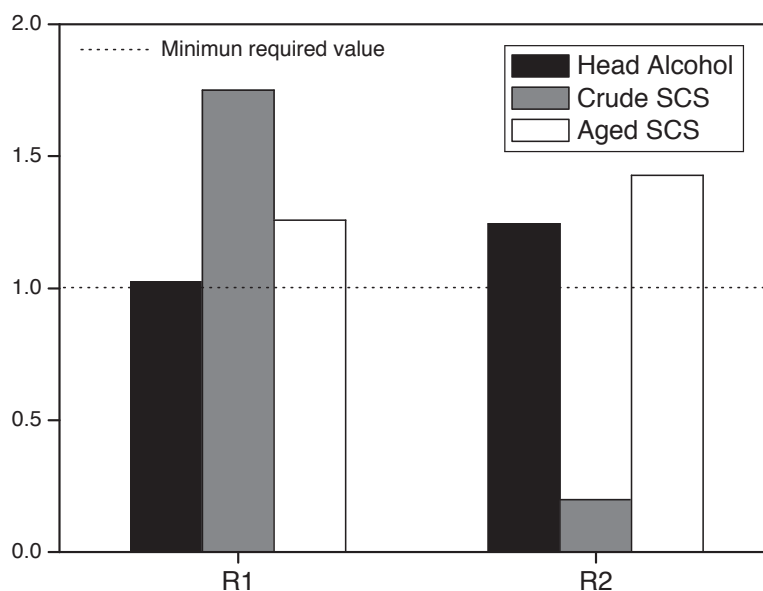


Fig. 4. Quality ratios for alcoholic drink. R1=1-butanol, 2-methyl/2-methyl-propanol; R2=2-methyl-propanol/1-propanol (R2).

methyl-propanol (R1) and 2-methyl-propanol/1-propanol (R2), which have to be higher than unity (Cortés *et al.*, 2005; Hernandez-Gomez, 2005). The esters concentration is related to the fruity note in organoleptic test (Cortés *et al.*, 2005; Hernandez-Gomez, 2005). Carboxylic acids (C_4 - C_{12}) produce unpleasant odor, representing a low quality indicator (Hernandez-Gomez, 2005).

In all supercritical extracts higher alcohols were the most abundant volatile compounds. However, the concentration

of 1-propanol, 2-methyl, 1-butanol, 3-methyl and 1-butanol, 2-methyl is significantly different in the extracts due to the different composition of the original streams as described above. Fig. 4 shows the R1 and R2 ratios for the supercritical extracts, showing that both ratios are only higher than unity for Head Alcohol and Aged SCS. Fig. 5 shows the ester and the carboxylic acids concentration for the samples tested. According to ester concentration, the Head Alcohol extract presented the higher value. This fact is the responsible to

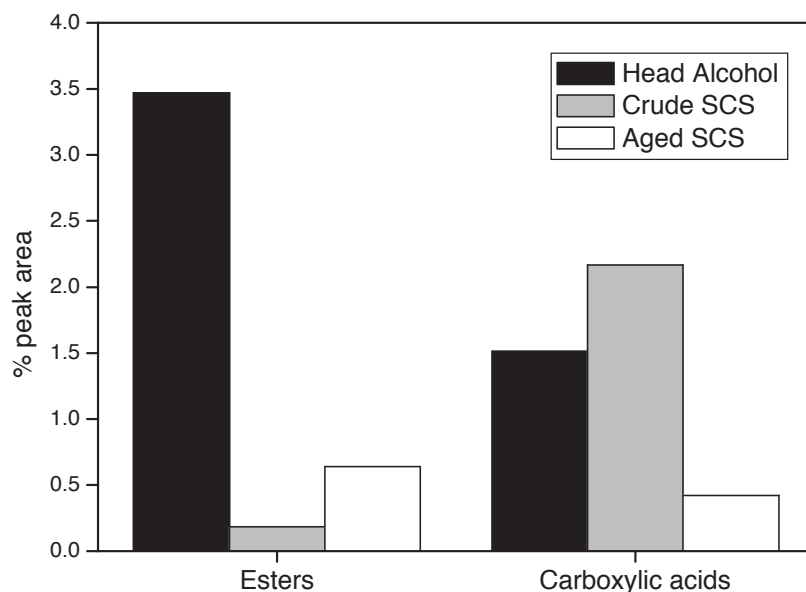


Fig. 5. Esters and carboxylic acids concentration in Head Alcohol, Crude SCS and Aged SCS extracts.

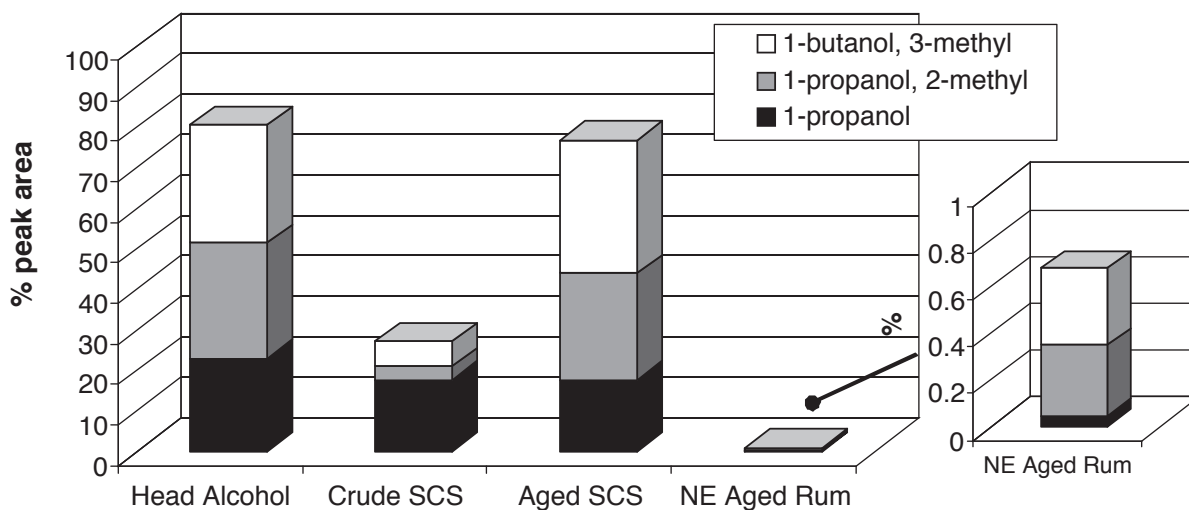


Fig. 6. Esters and carboxylic acids concentration in Head Alcohol, Crude SCS and Aged SCS extracts.

the fruity global note in Table 2 results. Considering carboxylic acids composition, the lower quality extract was Crude SCS. From Head Alcohol to Crude SCS this composition increased due to the previous distillation process. The decrease of carboxylic acids for Aged SCS is due to the esterification of fatty acids in presence of ethanol during the aging process (Orriols, 1992).

To determine the economical interest of the isolated fractions, Fig. 6 compares the composition of extracts in the most interesting aroma components with respect those corresponding to the final commercial rum product. Compared to commercial aged rum composition before extraction (NE), it

can be observed that all fractions were highly concentrated. This effect was especially evident in Head Alcohol and Aged SCS, where the quality compounds were concentrated more than 300 times.

Solubility calculations Solubility data is required information for scale up processes. For this purpose a set of experiments was performed in a range close to the previous operation conditions, in the temperature and pressure intervals from 313 to 333 K and 8 to 15 MPa, respectively. The apparent solubility of aromatic fractions in SC-CO₂ was obtained from the slope of straight line plot of cumulative yield (g oil/g oil-free substrate) according to dynamic flow criteria

Table 3. Solubility data and their correlation.

P (MPa)/T(K)	8/ 313	8/ 333	10/ 313	10/ 333	15/ 313	15/ 333	Solubility correlations
Head Alcohol	47.31	40.22	67.81	51.32	74.50	67.23	$\ln S = 4.7556 - \frac{105.5901}{T} + 0.4378 \ln \rho$ ($s = 0.89$)
Crude SCS	35.32	29.21	58.63	40.82	69.63	65.51	$\ln S = 6.4150 - \frac{629.1891}{T} + 0.6812 \ln \rho$ ($s = 0.74$)
Aged SCS	24.32	18.81	51.12	29.63	62.12	54.13	$\ln S = 6.0547 - \frac{532.7842}{T} + 0.9049 \ln \rho$ ($s = 0.56$)

S: solubility (mg/g); T: Temperature (K); ρ : Density (g/cm³); s: (standard deviation)

(Lucas *et al.*, 2007). The CO₂ flow rate was set at 1 SL/min. This value was previously optimized by taking into account that high yields were produced and assuring CO₂ saturation during solubility measurements. The apparent solubility was correlated using Chrastil empirical model which related directly the solubility with the density of pure gas (Chrastil, 1982). Table 3 shows the results obtained for each sample tested and their Chrastil correlations, where all constants were calculated by minimizing the sum of the square of the differences between experimental and calculated solubility data.

It can be seen that solubility increases with increasing pressure at constant temperature. Because the variation of solvent density with pressure also follows this trend, it is quite obvious that results obtained are related to the value of this parameter. Another factor affecting solutes solubility in supercritical carbon dioxide is temperature. The temperature produces two opposite effects: as the temperature increases, the solute vapor pressure increases and therefore increases the solubility. On the other hand, as the temperature increases the solvent density decreases and therefore the solute solubility decreases. In Table 3 the density effect is dominant in the experimental range, because at a given pressure increasing temperature always decreases the oil solubility. The reported correlations can be used, in the experimental range analyzed, for the predictions of equilibrium parameters. These values will be required in further design and scale-up processes, representing the maximum amount of extract that can be recovered from the aqueous matrix at a given condition.

Conclusion

Considering all previous results, the supercritical extraction seems to be a technically viable alternative to isolate and

concentrate aroma fractions from rum intermediates for pharmacy and food applications, with special interest in developing alternative blending in FAP, using low value streams generated in the same process. Head Alcohol and Aged SCS extracts are the most interesting fractions to perform the process attending to different quality criteria.

References

- Boscolo, M., Bezerra, C.W., Cardoso, D.R., Neto, B.S., Franco, D.W. (2000). A rapid and sensitive method for DMS analysis in Brazilian sugar cane spirits and other distilled beverages. *J. of the Brazilian Chem. Society.*, **11** (1), 86.
- Canas, S., Leandro, M.C., Spranger, M.J., Belchior, A.P. (1999). Low molecular weight organic compounds of chestnut wood and corresponding aged brandies *J. Agric. Food Chem.*, **47**, 5023.
- Chrastil, J. (1982). Solubility of solid and liquids in supercritical gases. *J. Phys. Chem.*, 3016.
- Cortés, S., Gil, M. L., Fernández, E. (2005). Volatile composition of traditional and industrial Orujo spirits. *Food Control.*, **16** (4), 383.
- Gamse, T., Rogler, I., Marr, R. (1999). Supercritical CO₂ extraction for utilization of excess wine of poor quality. *J. Supercrit. Fluids.*, **14**, 123.
- Gracia, I., Rodríguez, J.F., García, M.T., Alvarez, A., García, A. (2007). Isolation of aroma compounds from sugar cane spirits by supercritical CO₂. *J. Supercrit. Fluids.*, **43**, 37.
- Hernández-Gómez, L. F., Úbeda-Iranzo, J., García-Romero, E., Briones-Pérez, A. (2005). Comparative production of different melon distillates: Chemical and sensory analyses. *Food Chem.*, **90** (1-2), 115.
- ICIDCA. (2002). Compendio de los derivados de la caña de azúcar. Editors: ICIDCA, La Habana, Cuba.
- Jiménez, N., Ancín, C. (2007). Binding of oak volatile compounds

- by wine lees during simulation of wine ageing. *Food Sci. and Technol.*, **40** (4), 619.
- Lucas, A., Rincon, J., Gracia, I., García, M.T. (2007). Solubility determination and model prediction of olive husk oil in supercritical carbon dioxide and cosolvents. *Ind. Eng. Chem. Res.*, **46**, 5061.
- Medina, A., Martinez, J.L. (1997). Dealcoholisation of cider by supercritical extraction with carbon dioxide. *J. Chem. Technol. Biotechnol.*, **68**, 14.
- Moarse, H. (1991) Volatile compounds in Food and Beverages. Editors: Marcel Dekker, New York.
- Orrriols, I. (1992) Importancia del control de las diferentes etapas de la destilación para la obtención de un aguardiente de calidad. In Proceedings I Jornada Técnica sobre el Aguardiente Ourense, Galicia, Spain, 85.
- Reazin, G.H. (1981). Chemical mechanisms of whisky maturation. *Am. J. Enol. Vitic.*, **32**, 283.
- Rincón, J., Lucas, A. de, Gracia, I. (2000). Isolation of rock rose essential oil using supercritical CO₂ extraction. *Sep. Sci. Technol.*, **35**, 2745.
- Señorans, F.J., Rodríguez, A.R., Ibáñez, E., Tabera, J., Reglero, G. (2001). Optimization of countercurrent supercritical fluid extraction conditions for spirit fractionation. *J. Supercrit. Fluids.*, **21**, 41.
- Señorans, F.J., Rodríguez, A.R., Ibáñez, E., Tabera, J., Reglero, G. (2001) Countercurrent supercritical fluid extraction and fractionation of alcoholic beverages. *J. Agric. Food Chem.*, **49**, 1895.
- Señorans, F.J., Rodríguez, A.R., Ibáñez, E., Tabera, J., Reglero, G. (2003). Isolation of brandy aroma by counter current supercritical fluid extraction. *J. Supercrit. Fluids.*, **26**, 129.
- Nykänen, L. (1986) Formation and occurrence of flavor compounds in wine and distilled alcoholic beverages. *Am. J. Enol. Vitic.*, **37**, 84.