



Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Simulation and flavor compound analysis of dealcoholized beer via one-step vacuum distillation

Cristina Andrés-Iglesias^a, Juan García-Serna^b, Olimpio Montero^c, Carlos A. Blanco^{a,*}

^a Departamento de Ingeniería Agrícola y Forestal (Área de Tecnología de los Alimentos), ETS Ingenierías Agrarias (Universidad de Valladolid), Avda. de Madrid 44, 34004 Palencia, Spain

^b High Pressure Processes Group, Department of Chemical Engineering and Environmental Tech., University of Valladolid, 47011 Valladolid, Spain

^c Centre for Biotechnology Development (CDB), CSIC. Boecillo Technological Park, Av. Francisco Vallés 8, 47151 Boecillo, Valladolid, Spain

ARTICLE INFO

Article history:

Received 27 May 2015

Received in revised form 9 July 2015

Accepted 12 July 2015

Available online xxxxx

Keywords:

Alcohol-free beer

Aspen HYSYS simulation

Dealcoholization

Volatile compounds

Flavor perception

HS-SPME

ABSTRACT

The coupled operation of vacuum distillation process to produce alcohol free beer at laboratory scale and Aspen HYSYS simulation software was studied to define the chemical changes during the dealcoholization process in the aroma profiles of 2 different *lager* beers.

At the lab-scale process, 2 different parameters were chosen to dealcoholize beer samples, 102 mbar at 50 °C and 200 mbar at 67 °C. Samples taken at different steps of the process were analyzed by HS-SPME–GC–MS focusing on the concentration of 7 flavor compounds, 5 alcohols and 2 esters. For simulation process, the EoS parameters of the Wilson-2 property package were adjusted to the experimental data and one more pressure was tested (60 mbar).

Simulation methods represent a viable alternative to predict results of the volatile compound composition of a final dealcoholized beer.

© 2015 Published by Elsevier Ltd.

1. Introduction

The market of non-alcoholic brews has experienced a significant improvement during the past years that becomes motivated mainly by highly competitive markets, driving/drinking rules, health conditions incompatible with alcohol consumption and/or religious reasons (Andrés-Iglesias, Montero, Sancho, & Blanco, 2014; Blanco, Andrés-Iglesias, & Montero, 2014; Catarino & Mendes, 2011). Similarly, it is well-known that beer has positive effects and a whole range of properties, such as no fat or cholesterol content, free sugar content, high antioxidant, magnesium and soluble fiber content (Brányik et al., 2012), plus it provides essential vitamins and minerals contributing to a healthy balanced diet (Andrés-Iglesias, Blanco, Blanco, & Montero, 2014; Bamforth, 2001).

Beer aroma profile is made by many volatile organic compounds at very low concentration (ppm level), which are responsible for its unique flavor (Catarino, Mendes, Madeira, & Ferreira, 2007). Levels of different chemical compounds, such as alcohols, esters, aldehydes, ketones, organic acids and phenols, can be found on beer composition, giving a specific flavor that contributes to the overall organoleptic properties of the final beer (Karlsson & Trägårdh, 1997). Among them, esters and alcohols are the main groups of aroma compounds. Esters are

responsible for the sweet and fruity flavors of beer, while alcohols confer it an alcoholic, fruity and immature flavor (Andrés-Iglesias, Blanco et al., 2014; Andrés-Iglesias, Montero et al., 2014; Catarino, Ferreira, & Mendes, 2009).

In low-alcohol and/or alcohol-free beer production, the different techniques used have to be able to reach the maximum alcohol by volume (ABV) established by the different countries legal regulations. In the majority of EU countries beers with low alcohol content are divided into alcohol-free beers ($\leq 0.5\%$ ABV) and low-alcohol beers ($\leq 1.2\%$ ABV). In Spain, alcohol free beers are divided in non-alcohol beers ($\leq 1.0\%$ ABV) and '0.0%' beers ($\leq 0.1\%$ ABV). However, in the United States there should not be alcohol present in alcohol-free beers, while 0.5% ABV corresponds to the upper limit of non-alcoholic beers or 'near-beers' (Olmo, Blanco, Palacio, Prádanos, & Hernández, 2014).

At present, there are several methods for low alcohol beer production (Blanco et al., 2014). The strategies can be divided into two main groups: biological and physical methods (Brányik et al., 2012; Montanari, Marconi, Mayer, & Fantozzi, 2009; Olmo et al., 2014). While physical methods withdraw the ethanol from a fermented beer, biological methods aim at controlling the alcohol production during the fermentation process (Zürcher, Jakob, & Back, 2005).

Biological methods can be achieved by either restricting ethanol formation or shortening the fermentation process. Obtaining low alcohol content via interrupted fermentation is accompanied by low contents of aroma and flavor compounds, and their products are often

* Corresponding author.

E-mail address: cblanco@iaf.uva.es (C.A. Blanco).

characterized by warty off-flavors. They are usually performed using traditional brewery equipment and hence do not require additional investments (Brányik et al., 2012; Catarino & Mendes, 2011).

Other processes to avoid these limitations include the use of special or immobilized yeasts as well as the use of low sugar raw materials (Catarino & Mendes, 2011; Pickering, 2000). The use of special yeasts for a low alcohol beer production process increases the costs with the need of yeast selection, or genetic modification of the production organisms. However, suitable selected yeasts can contribute significantly to the product sensorial quality improvement. Alcohol free beer production processes by continuous fermentation with immobilized yeast, whose objective is limited alcohol formation, and which requires special equipment and material. In this latter case, high investment costs are required but are justified by a higher productivity of the continuous processes. In general, producing alcohol-free beer by biological methods makes impossible the production of alcohol-free beers with alcohol content close to zero (Brányik et al., 2012).

Physical methods require considerable investments into the special equipment for alcohol removal (Brányik et al., 2012). The most common separation processes used for beer dealcoholization are membrane-based processes and heat treatment (Catarino et al., 2007). Membrane-based processes include reverse osmosis, nanofiltration, dialysis and pervaporation (Labanda, Vichi, Llorens, & López-Tamames, 2009). Heat treatment processes comprise evaporation and distillation; they are both under vacuum conditions to preserve the organoleptic properties by avoiding undesired secondary reactions (Belisario-Sánchez, Taboada-Rodríguez, Marin-Iniesta, & López-Gómez, 2009). Furthermore, thermal processes to remove alcohol from regular beers can cause the loss of the original aroma (Blanco et al., 2014; Catarino et al., 2009) but their advantage is that they can remove ethanol from beers to levels close to zero (Brányik et al., 2012).

Among these physical methods, for large scale dealcoholization, the vacuum evaporation is the most economic process (Zürcher et al., 2005). Distillation is a separation operation based on differences in volatility. If a mixture containing substances that differ in their volatility is brought to ebullition, the composition of the vapors released will be different from that of the boiling liquid. After condensation, the vapors constitute the “distillate”. The remaining liquid is called “residue” (Berk, 2013). The application of vacuum to distillation process enables to reduce the evaporation temperature and thus the thermal stress to beer (Zürcher et al., 2005). If the pressure is reduced, alcohol can be drawn off at much lower temperature (Brányik et al., 2012). Thermal processes to produce alcohol free beers are performed at temperatures between 30 and 60 °C at pressures of 60 to 200 mbar (Sohrabvandi, Mousavi, Razavi, Mortazavian, & Rezaei, 2010; Zürcher et al., 2005). The deterioration of beer quality by thermal dealcoholization depends mainly on the evaporation temperature and the period of exposure (Brányik et al., 2012).

It is well known that most of the aroma compounds are lost in alcohol free beers during production by thermal processes. The aroma profile is clearly damaged and other, less pleasant flavors, like bread, warty or caramel notes can appear (Blanco et al., 2014; Catarino et al., 2009; Lehnert et al., 2009; Sohrabvandi et al., 2010). To compensate these disadvantages many breweries use a modified brewing technology for the production of a more aromatic original beer. Another attempt to compensate sensory disadvantages is by blending dealcoholized beer with a small quantity of original beer or a beer aroma extract that can be recovered in evaporation plants with rectification columns. Since these attempts are not yet satisfactory further possibilities to improve the quality of these beers have been investigated (Zürcher et al., 2005).

Owing to beer chemical compound characterization has improved notably nowadays, analysis of beer flavor compounds has been constantly optimized to obtain better results in relation to sensitivity and specificity (Andrés-Iglesias, Blanco et al., 2014; Andrés-Iglesias, Montero et al., 2014). Gas chromatography–mass spectrometry (GC–MS) is currently used to measure volatile compound concentrations

in beer. Ethers, esters, acids, aldehydes, ketones, alcohols, sulfur compounds, hydrocarbon compounds, alicyclic compounds, heterocyclic compounds and aromatic compounds can be measured simultaneously by using GC–MS methods (Andrés-Iglesias, Blanco et al., 2014; Andrés-Iglesias, Montero et al., 2014). The combination of solid phase microextraction (SPME) with gas chromatography (GC) or gas chromatography–mass spectrometry (GC–MS) has proven to be a sensitive and precise method for the analysis of different classes of volatile compounds (Dong et al., 2013).

Beer dealcoholization via vacuum distillation in a batch system can be assumed to resemble differential distillation at reduced pressure. The principles of differential distillation are well established since the beginning of chemical engineering knowledge. Thus, this type of distillation is often known as “Rayleigh distillation”. Lord Rayleigh's law is based on a dynamic material balance to the volatile compound of a two component mixture coupled to the global mass balance (Berk, 2013). Extending the balance to a multicomponent mixture was studied in deep by several authors such as Lang et al. (1994) and, Yatim et al. (1993) who modified the process for the addition of an extractive agent, or including sieves. An interesting comparative study was conducted by Zürcher et al. (2005) using lab scale batch and continuous distillation as well as an industrial scale plant. They investigated the beer dealcoholization at 60 and 150 mbar by following changes in a number of compounds, e.g., ethanol, 1-propanol, ethyl acetate, 2-methylpropanol, 3-methylpropanol and several esters. However, they did not simulate the process.

In addition, several authors have investigated the simulation of spirits production by this process. Claus and Berglund studied fruit brandy distillation using a batch column distillation. They simulated the process using CHEMCAD with good results using NRTL (Non-Random Two Liquids) equation of state (EoS) together with UNIFAC parameters (Claus & Berglund, 2005, 2009). On the other hand, Gaiser et al. simulated the whisky still distillation process using Aspen Plus software and selecting the NRTL-2 property package of that software; they claimed that this EoS provides a good approximation for ethanol–water azeotrope (Gaiser et al., 2002).

Low alcohol and alcohol free beer consumption is increasing year by year, and often, these types of beverages are known to have a poor flavor profile in comparison to the original beer. In this sense, it becomes important to adjust the flavor of non-alcoholic beers to that of regular ones, which needs understanding of how the dealcoholization process modifies it, an issue of which the scientific info is scarce.

In this work, we have combined lab scale differential vacuum distillation, aroma compound analysis and simulation of the dealcoholization process to shed light on this process. The main objective is to test a simulation environment that can explain the lab results, so that, it can be extrapolated to a similar process at industrial scale. For this, we have selected two model beers, one from Spain and one from Germany, and adjusted the interaction parameters of a thermodynamic model. To our knowledge, this is the first time that it is done for beers.

2. Material and methods

2.1. Samples and vacuum distillation dealcoholization experiments

Two different big-scale lager beer brands were chosen for the study, one from Spain (S) and another one from Germany (G). Both of them were lager alcoholic beers containing 5.5 and 4.8% alcohol by volume (ABV) respectively, and were obtained as fresh as possible from the local market. Beer bottles were stored at 4 °C until dealcoholization process. 400 mL of beer were weighted and placed in 1 L flask of the vacuum distillation system for each experiment; the flask was covered with a black plastic material to avoid the light oxidation of the sample components. Subsequently, 10 µL of antifoam emulsion (E-900, AFCA) were added to reduce the foam and CO₂ content.

The experiments of beer dealcoholization by laboratory scale vacuum distillation were done at two different vacuum pressures and water bath temperatures. The temperature needed in the water bath is directly related to the total pressure by the phase equilibrium of the system, but has to be set to a slightly higher value to assure enough heat transfer. Thus, the first set of experiments was conducted at 102 mbar and 50 °C (corresponding to a saturation temperature of pure water, 46.2 °C) and the second set at 200 mbar and 67 °C (corresponding to a saturation temperature of pure water, 60.1 °C). A Rotavapor R-215 with vacuum pump V-700, vacuum controller V-850 and diagonal condenser (BÜCHI Labortechnik AG, Switzerland) was used. The flask rotation was fixed at 20 rpm and remained constant in all experiments. Each dealcoholization process was stopped at 15, 30, 45 and 60 min after the onset for sampling in order to analyze the different volatile compounds evaporated along with the ethanol. At the end of the distillation process, the residual beer was cooled in glass bottles and weighted for the material balance calculation.

For all experiments the same steps were done. At the beginning of each experiment the water batch was refilled until the same volume if necessary, once the batch reached the temperature, the experiment started at the rpm indicated above, the pressure was reached immediately and remained constant (± 1) over the whole experiment and controlled by the vacuum controller.

For the GC–MS analysis 15 mL dark vials sealed with PTFE–silicone septa (Supelco, USA) were used for sample preparation. Vials contained 2 g of NaCl (Scharlau, Scharlab S.L., Spain) and 5 mL of beer were added and stirred to solve the NaCl and homogenize the sample. A total of 60 samples were taken and analyzed from the original beers, and from residual beers at each time and dealcoholization process experiments.

2.2. Gas chromatography–mass spectrometry (GC–MS) equipment

Volatile compounds were separated and detected by gas chromatography using an Agilent GC 6890N (Agilent Technologies, USA) equipped with an Agilent 5973 single quadrupole mass spectrometer (Agilent Technologies, USA) as detector. A headspace solid phase microextraction (HS–SPME) manual equipment (Supelco, USA) was used for the extraction and concentration of the volatile compounds, which was carried out with 100 μ m polydimethylsiloxane (PDMS) fiber (Supelco, USA). Prior to use, the SPME fiber was conditioned at 250 °C for 30 min in the GC injector, according to the manufacturer's instructions. Blank runs of the fiber were completed, before sampling, each day to ensure no carry-over of analytes. The chromatographic separations were accomplished using a BP-1 30 m \times 0.32 mm \times 1 μ m capillary column (SGE Analytical Science, Australia).

2.3. Analysis of volatile compounds

The volatile composition of beer samples was measured by triplicate. Solid phase microextraction of compounds was performed at 30 °C for 45 min. The desorption was achieved in the injector of the GC chromatograph in splitless mode for 15 min, and the temperature was set at 250 °C as indicated by the manufacturer for PDMS fiber. Carrier gas was helium at a constant flow of 1.2 mL/min.

The oven temperature was programmed as follows: initial temperature was set at 35 °C and kept for 7 min, this was followed by 2 ramps in which temperature was risen at 8 °C/min to 200 °C and kept this temperature for 5 min, and then temperature was risen at 10 °C/min to 250 °C, this temperature being kept for 10 min.

The ionization energy was 70 eV, and detection and data acquisition were performed in scan mode from 37 to 350 Da. For identification data obtained in the GC–MS analysis were compared with *m/z* values compiled in the spectrum library WILEY. Validation of compound identification was carried out by comparison of MS spectra and retention times with those of commercial standards. Quantification was carried out by using standard calibration curves of 2-methylbutanol

($\geq 99.0\%$), 3-methylbutanol ($\geq 99.0\%$), 2-phenylethanol ($\geq 99.0\%$), ethyl acetate ($\geq 99.5\%$), isobutanol ($\geq 99.0\%$) (these from Sigma, USA), 1-Propanol $\geq 99.5\%$ (Fluka, Sigma-Aldrich, USA) and isoamyl acetate $\geq 99.0\%$ (Fisher, UK). Because 1-propanol co-eluted with ethanol, the extracted ion chromatogram (EIC) for the ion with *m/z* 60.05 and retention time of 3.10 min was used for quantification of this compound.

2.4. HYSYS simulation and parameters

In order to simulate the system under study for the batch distillation of beer the following assumptions were considered:

- 1) The vacuum is done almost instantly and at $t = 0$ the system is at the constant desired vacuum pressure.
- 2) Liquid composition is homogeneous and heat is uniformly distributed.
- 3) The flask has been simulated by a cylinder to simplify level calculation.
- 4) The heat flux for each data point is determined to match the time required for a certain vaporization volume. This is because the Rotavapor system can provide different heat flux depending on a number of variables (water level, flask location, ambient temperature, rotation speed, etc.).
- 5) No reaction occurs in the bulk liquid.

The simulations have been carried out using HYSYS simulation software (Aspen inc. product) as it has a powerful non-steady state simulation tool.

Wilson-2 property package was chosen in order to simulate the non-ideal behavior of the liquid phase, while ideal gas is considered for the gas phase (as it was under reduced pressure conditions).

The main simulation process flow diagram is depicted in Fig. 1. The main distillation vessel (V-100) has one feed stream-5 (virtual for simulation purposes set at almost zero flow), one heat source (Q-100), one liquid outlet stream-2 (virtual for simulation purposes set at almost zero flow) and one vapor outlet stream-3 (main distillation outlet).

The main calculations were carried out using an Excel spreadsheet to determine the conversion between ppm and molar fraction values from experimental conditions to the simulation and vice versa.

The main components simulated were: sucrose, ethanol, ethyl acetate, 1-propanol, isobutanol, isoamyl acetate, 2-methylbutanol, 3-methylbutanol, 2-phenylethanol, water and nitrogen.

Sucrose was used as a simulation trick to increment the density of water targeting the real value of 1010 kg/m³, for that purpose a concentration of 3% wt. was used in all simulation experiments. Nitrogen was used for simulation purposes mimicking the atmosphere of the Rotavapor.

Initial values for compositions of the liquid were inserted in the “hold-up” values of the distillation vessel. The total pressure of stream-2 was fixed to the experimental absolute pressure, coinciding with the vessel initial pressure (i.e., 102 and 200 mbar).

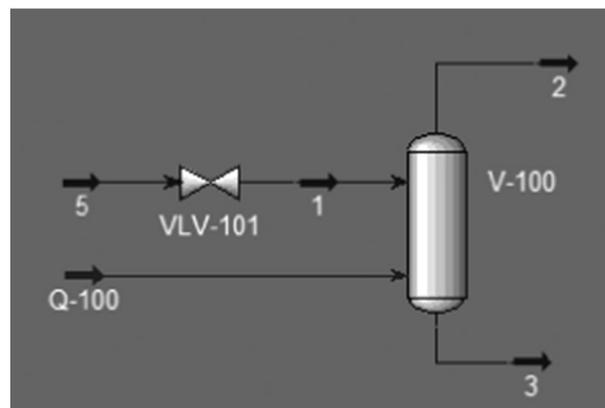


Fig. 1. HYSYS simulation model for a differential vacuum distillation.

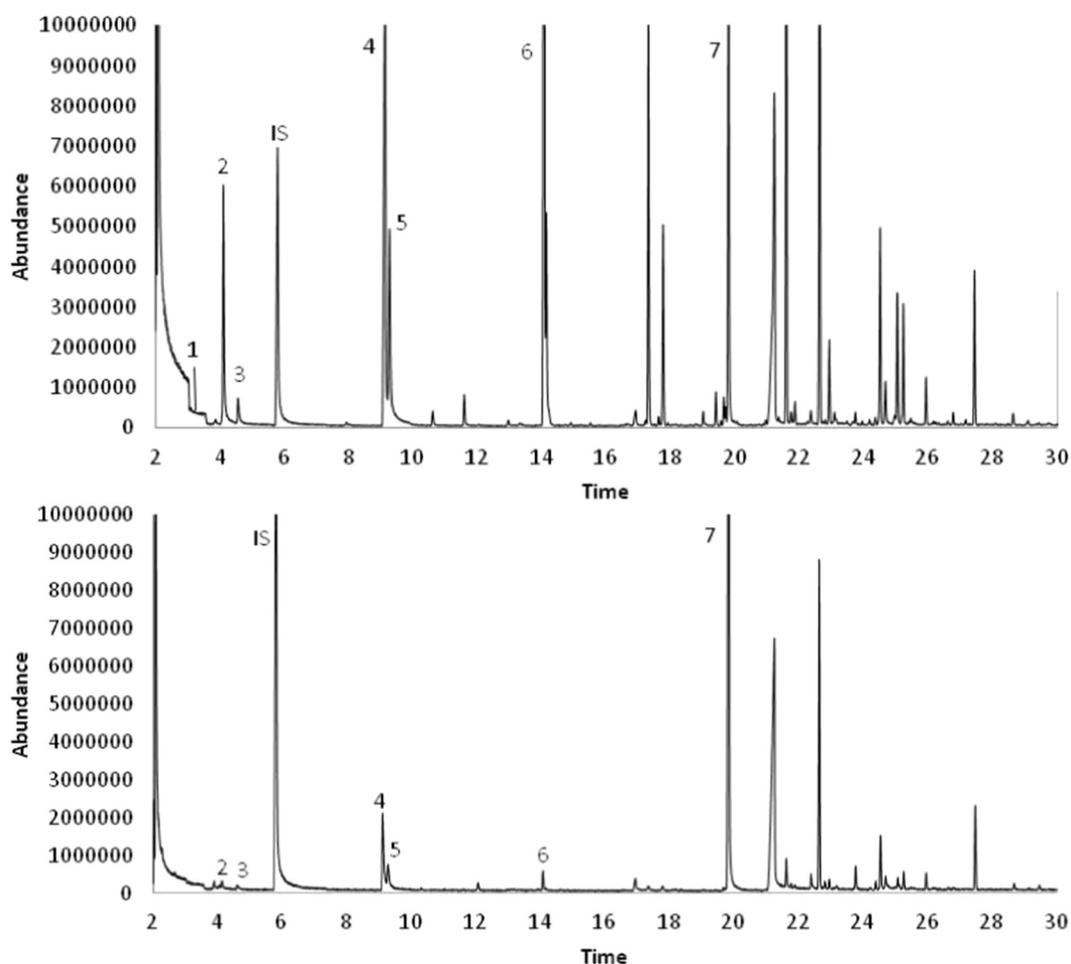


Fig. 2. Sample of TIC chromatogram for S beer sample, alcohol beer on the top and beer dealcoholized by laboratory vacuum distillation on the bottom. (1) 1-propanol, (2) ethyl acetate, (3) isobutanol, (4) 3-methylbutanol, (5) 2-methylbutanol, (6) isopentyl acetate, (7) 2-phenylethanol.

As indicated in the assumptions, the heat flux was estimated to match the mass evaporated at each time sample point. This way, the simulation time is not as important as the evaporated mass, that is used as the x-axis variable as percentage of mass evaporated (%vapor). Thus, all experiments were carried out until 15, 30, 45 and 60 min, time when the dealcoholization process was stopped and the samples were collected. The % of vapor fraction (%Vf) was calculated as the percentage of initial mass of the beer minus the mass at the different points of the simulation until the last mass (at 60 min of simulation) divided by the initial mass. Although the traditional ASTM D-86 curves for petroleum distillation are carried out in volume, in this case, mass was preferred to overcome density variations (ASTM-International, 2012). Furthermore, the heat flux could have varied along with the

experiment. For this reason, we have considered this variable more accurate than experimental time itself. In addition to this, results could be transferred to a real vacuum distillation process with better scale-up chances.

The developed software is available free in the web page of the research group of High Pressure Processes of the University of Valladolid (<http://hpp.uva.es/software/>) in the section for 'Beer Distillation'.

3. Results and discussion

Two *lager* beers were investigated in this study, one sample from Spain (S) and the other sample from Germany (G). Both samples were dealcoholized by vacuum distillation at laboratory scale at 2 different

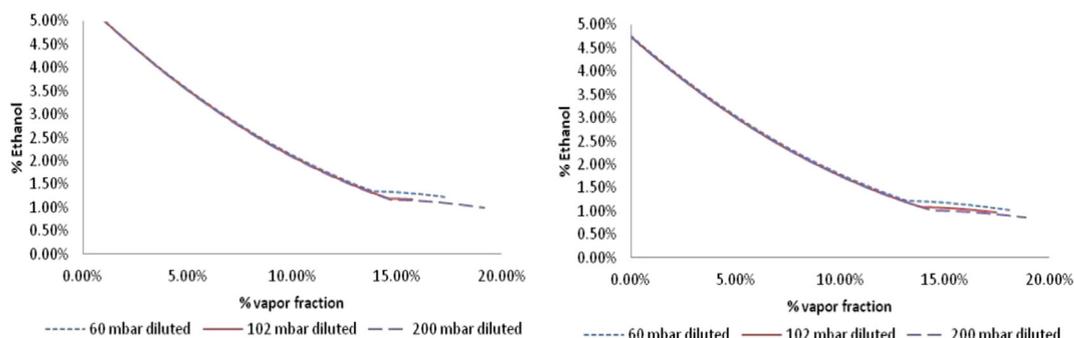


Fig. 3. Ethanol behavior against the %vapor fraction on the left for S sample and for G sample on the right.

Table 1

Percentage of the vapor fractions (% Vf) of S and G samples and its correspondent times, for both lab-scale vacuum distillation processes and the averages (%).

Time, min	0	15	30	45	60
S 102 mbar	0	7.46	9.55	13.40	15.76
S 200 mbar	0	6.17	10.14	15.12	19.22
G 102 mbar	0	5.70	9.00	14.40	17.60
G 200 mbar	0	10.80	13.40	14.80	18.90
Average (% Vf)	0	7.53	10.52	14.43	17.87

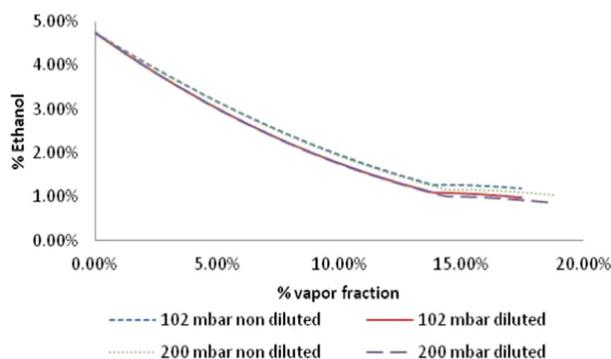


Fig. 4. Ethanol concentration if the final volume is diluted or non-diluted at the two experimental pressures.

Table 2

Retention time (Rt), concentration of volatile compounds (mg/L) dealcoholized at 102 mbar, 50 °C and 200 mbar, 67 °C in the experiment (EXP), in simulations (SIM) and the standard deviation of the experimental value (St Dev).

		SIM	EXP	St Dev	SIM	EXP	St Dev	SIM	EXP	St Dev	SIM	EXP	St Dev	SIM	EXP	St Dev	
102 mbar, 50 °C	Rt	S, 0 min			S, 15 min			S, 30 min			S, 45 min			S, 60 min			
	1-Propanol	3.10	5.56	5.56	2.47	1.22	2.09	0.36	0.50	0.25	0.12	0.05	0.24	0.00	0.01	0.00	0.00
	Ethyl acetate	4.13	17.82	17.82	1.11	1.52	1.07	0.10	0.67	1.23	0.41	0.15	0.86	0.30	0.07	0.54	0.09
	Isobutanol	4.60	9.41	9.41	2.52	5.67	4.97	2.03	4.38	4.68	2.73	2.35	3.67	2.56	1.63	3.26	2.10
	3-Methylbutanol	9.11	40.99	40.99	2.73	25.01	17.44	1.45	19.37	17.15	7.14	10.43	11.51	1.54	7.24	7.33	1.05
	2-Methylbutanol	9.27	13.37	13.37	0.94	7.78	5.26	0.54	5.83	5.29	2.14	2.91	3.55	0.63	1.91	1.93	0.27
	Isopentyl acetate	14.09	1.92	1.92	0.33	0.36	0.11	0.08	0.15	0.10	0.09	0.02	0.09	0.08	0.00	0.09	0.08
2-Phenyl ethanol	19.82	34.01	34.01	1.39	37.07	40.46	6.26	37.95	48.76	17.74	39.51	62.04	9.92	40.16	85.28	3.90	
102 mbar, 50 °C	Rt	G, 0 min			G, 15 min			G, 30 min			G, 45 min			G, 60 min			
	1-Propanol	3.10	8.93	8.93	3.48	2.36	6.99	2.20	0.52	0.28	0.01	0.02	0.17	0.03	0.00	0.00	0.00
	Ethyl acetate	4.13	26.54	26.54	0.74	3.85	3.65	1.08	1.08	2.93	0.47	0.20	1.06	0.17	0.07	0.45	0.06
	Isobutanol	4.60	10.47	10.47	2.66	6.89	6.88	2.08	4.48	4.32	2.21	2.07	2.88	1.93	1.12	2.87	1.93
	3-Methylbutanol	9.11	43.77	43.77	2.12	28.46	27.85	2.79	18.58	13.69	2.02	8.58	4.92	0.82	4.65	5.13	0.88
	2-Methylbutanol	9.27	11.54	11.54	0.42	7.27	7.48	1.18	4.50	3.49	0.70	1.86	1.12	0.43	0.90	1.22	0.25
	Isopentyl acetate	14.09	2.58	2.58	0.25	0.67	0.27	0.15	0.15	0.16	0.10	0.01	0.13	0.09	0.00	0.11	0.08
2-Phenyl ethanol	19.82	37.69	37.69	4.68	40.00	53.95	5.40	41.46	56.92	5.71	43.17	69.57	6.81	43.71	75.17	4.58	
200 mbar, 67 °C	Rt	S, 0 min			S, 15 min			S, 30 min			S, 45 min			S, 60 min			
	1-Propanol	3.10	5.56	5.56	0.69	3.63	3.58	0.90	1.51	2.51	0.94	0.30	0.00	0.00	0.02	0.00	0.00
	Ethyl acetate	4.13	17.82	17.82	1.79	2.99	4.09	1.00	0.79	1.19	0.07	0.22	0.86	0.14	0.07	0.46	0.11
	Isobutanol	4.60	9.41	9.41	2.87	5.60	4.88	1.83	3.06	4.25	1.65	1.40	3.67	1.71	0.53	3.03	1.47
	3-Methylbutanol	9.11	40.99	40.99	4.05	26.58	20.44	4.01	15.70	16.90	0.83	7.88	11.51	2.29	3.34	7.35	0.70
	2-Methylbutanol	9.27	13.37	13.37	1.57	8.40	6.44	1.18	4.70	5.18	0.67	2.17	3.55	0.75	0.80	2.20	0.29
	Isopentyl acetate	14.09	1.92	1.92	0.10	0.63	0.20	0.07	0.17	0.12	0.04	0.02	0.09	0.05	0.00	0.07	0.04
2-Phenyl ethanol	19.82	34.01	34.01	2.59	36.63	43.36	7.14	38.28	53.41	3.85	39.66	62.04	6.35	40.17	70.65	3.61	
200 mbar, 67 °C	Rt	G, 0 min			G, 15 min			G, 30 min			G, 45 min			G, 60 min			
	1-Propanol	3.10	8.93	8.93	3.32	1.11	0.40	0.11	0.26	0.30	0.02	0.22	0.14	0.02	0.01	0.00	0.00
	Ethyl acetate	4.13	26.54	26.54	3.91	0.90	5.18	0.48	0.35	1.24	0.28	0.34	2.91	0.53	0.10	2.73	0.25
	Isobutanol	4.60	10.47	10.47	3.29	2.43	5.07	1.76	1.22	3.46	1.56	1.24	1.93	1.53	0.36	1.82	1.34
	3-Methylbutanol	9.11	43.77	43.77	6.60	12.11	19.95	0.57	6.50	9.48	1.31	6.64	5.04	0.88	2.18	2.94	0.76
	2-Methylbutanol	9.27	11.54	11.54	1.17	2.85	4.85	0.50	1.43	2.29	0.28	1.45	1.17	0.34	0.40	0.64	0.22
	Isopentyl acetate	14.09	2.58	2.58	0.37	0.11	0.49	0.05	0.02	0.16	0.06	0.02	0.09	0.05	0.00	0.08	0.07
2-Phenyl ethanol	19.82	37.69	37.69	5.40	42.27	54.97	2.93	43.47	62.58	10.36	43.27	59.41	8.68	43.98	59.97	1.01	

pressures and temperatures, 102 mbar, 50 °C and 200 mbar, 67 °C. A total of 45 compounds were identified, and 7 of them quantified by peak area. The profile of quantified volatiles consisted of 5 alcohols (1-propanol, 2-methylpropanol, 2-methylbutanol, 3-methylbutanol and 2-phenylethanol) and 2 esters (ethyl acetate and isoamyl acetate). These compounds are considered as ones of the main alcohols and esters in beer (Blanco et al., 2014; Lehnert et al., 2009; Rodrigues, Caldeira, & Câmara, 2008; Willaert & Nedovic, 2006), the most abundant being ethyl acetate, isoamyl acetate, the amyl alcohols and isobutanol (Pidocke, Kreis, Heldt-Hansen, Fog Nielsen, & Olsson, 2009). Also, these compounds are those currently analyzed by other authors because they are relevant flavor compounds in beer (Charry-Parra, Dejesús-Echevarria, & Perez, 2011; Kobayashi, Shimizu, & Shioya, 2008) and chosen as reference compounds when studying industrial processes for production of non-alcoholic beers (Catarino & Mendes, 2011; Mota et al., 2011).

A typical total ion chromatogram (TIC) of a regular beer sample and its dealcoholized beer by laboratory scale vacuum distillation process is shown in Fig. 2.

3.1. Final ethanol content calculated by ASPEN HYSYS simulation

During the differential distillation process, the most volatile fraction (ethanolic fraction) abandons the system in first place together with an increasing amount of water. In this work, we have focused on the analysis of the beer, rather than the evaporated volatile fraction (ethanolic fraction).

Table 3
Losses of total esters and alcohols in percentage (%) by different alcohol free beer production processes: lab-scale vacuum distillation (this work, present as the average of both samples losses), osmotic distillation (Liguori et al., 2015), vacuum rectification (Montanari et al., 2009), falling film evaporation, dialysis (Liguori et al., 2015) and reverse osmosis (Stein, 1993).

	Lab-scale vacuum distillation	Osmotic distillation	Vacuum rectification	Falling film evaporation	Dialysis	Reverse osmosis
Total esters	97 (102 mbar) 83 (200 mbar)	99	100	95–100	99	78
Total alcohols	90 (102 mbar) 95 (200 mbar)	77	78	95–98	96	69

Nevertheless, the concentration of ethanol in the ethanolic fraction in alcohol by volume percentage (% ABV) was estimated by simulation at the two experimental pressures, 102 mbar and 200 mbar and an additional reduced pressure of 60 mbar.

The initial point (IP) was the labeled alcohol content of each beer 4.7% for G and 5.5% for S. The concentration of ethanol in the beer phase exhibited an exponential-like decay against the vapor fraction (Fig. 3). The % of vapor fractions at their correspondent times in the experiment is shown in Table 1.

In general, 1.0% ABV was obtained at about 15% of liquid vaporization. In this study we have analyzed and simulated the compositions considering the instant volume during the process. So, we have not corrected the values considering a possible final dilution with water to the initial volume. This means that if the final residue (dealcoholized beer) would be diluted to the initial volume (e.g., adding water), the % ABV achieved would be lower than 1% of ethanol (that was obtained at 200 mbar for instance). This fact is illustrated in Fig. 4, where we compare the % ABV for diluted distillate and for not diluted distillate.

3.2. Differences of the volatile compound profile during the laboratory scale vacuum distillation process

The volatile compound fraction in beer, apart from ethanol, is mainly comprised of higher alcohols formed during primary beer fermentation (Blanco et al., 2014). Higher alcohols contribute to the aroma of beer and produce a warm mouthfeel (Willaert & Nedovic, 2006). The most significant contribution is owed to propanol, isobutanol and isoamyl alcohols (2 and 3-methylbutanol) (Blanco et al., 2014; Brányik,

Vicente, Dostálek, & Teixeira, 2008). Higher alcohols are the immediate precursors of most flavor active esters; hence, formation of higher alcohols needs to be controlled to ensure optimal ester production (Gonçalves et al., 2014) because of esters have very low flavor thresholds and a major impact on the overall flavor (Willaert & Nedovic, 2006). However, low content of aroma compounds in alcohol free beers could be attributed to the dealcoholization process (Riu-Aumatell, Miró, Serra-Cayuela, Buxaderas, & López-Tamames, 2014).

When we analyzed both regular beers, results showed (Table 2) that for all volatile compounds the concentrations were higher for the G sample than for the S sample with the exception of 2-methylbutanol, which was higher for the S sample (13.37 mg/L). Calculating the percentage of volatiles (different than ethanol) lost in the dealcoholization process at 102 mbar and 200 mbar at the end of the experiment, it was found that almost all volatile compounds studied were evaporated along with ethanol with the exception of 2-phenylethanol. For the S sample, losses of 97% of esters and 88% of alcohols were observed at 102 mbar and 76% of esters and 95% of alcohols at 200 mbar. For the G sample losses of 96% of esters and 92% of alcohols were achieved at 102 mbar, and 90% of esters and 95% of alcohols for 200 mbar. These volatile compound losses can be compared with those reported in previous studies by other authors using different dealcoholization processes (Table 3).

From our results, we can conclude that pressure does not have a substantial impact on the relative volatility between the ethanol and other aroma components; therefore, we suggest that the final volatile profile after dealcoholization cannot be significantly improved by only modifying the pressure. Thus, the main alcohols and esters could be affected by the higher temperature applied at 200 mbar. From data in Table 2 it can be seen that at 200 mbar and 67 °C the volatile compounds losses were higher for all compounds except for the amyl alcohols in S sample and ethyl acetate in G sample. Looking at the seven volatile compounds quantified in this study (Table 2), for the ethyl acetate, the evaporation was almost completed at the first 7.53% vapor fraction (Vf), correspondent with the average of % Vf at 15 min of the process (Table 1), in both samples and pressures (from initial values of 17.82 and 26.54 mg/L to 1.07 and 3.65 at 102 mbar; and to 4.09 and 5.18 mg/L at 200 mbar, for the samples S and G respectively), although for the 200 mbar pressure the evaporation seems more gradually.

Table 4
Boiling points (°C) of the volatile compounds at the different experiment pressures.

Compounds	Boiling points (°C)		
	Atmospheric pressure	102 mbar	200 mbar
Ethyl acetate	77.1	13.7	32.3
1-Propanol	97	33.6	52.2
Isobutanol	107.9	44.5	63.1
Isopentyl acetate	142	78.6	97.2
2-Methylbutanol	127.5	64.1	82.7
3-Methylbutanol	131.1	67.7	86.3
2-Phenyl ethanol	220	156.6	175.2

Table 5
Estimated parameters for Element-1 of Wilson-2 equation in HYSYS.

	Sucrose	Ethanol	Ethyl acetate	1-Propanol	Isobutanol	Isopentyl acetate	2-Methylbutanol	3-Methylbutanol	2-Phenylethanol	Water	Nitrogen
Sucrose	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ethanol	0.0000	0.0000	0.0000	-12.6000	-1.8000	9.5000	2.5000	2.5000	0.0000	-0.0503	0.0000
Ethyl acetate	0.0000	0.3000	0.0000	2.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-1.8000	0.0000
1-Propanol	0.0000	12.6000	-0.8296	0.0000	0.9130	0.0000	3.0350	3.0350	0.0000	1.1919	0.0000
Isobutanol	0.0000	1.8000	0.0000	-0.7573	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Isopentyl acetate	0.0000	-9.5000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	2.0000	0.0000
2-Methylbutanol	0.0000	-0.3000	0.0000	-2.0368	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
3-Methylbutanol	0.0000	-0.7256	0.0000	-2.0368	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
2-Phenylethanol	0.0000	0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Water	0.0000	-2.5035	-1.8000	-7.0000	0.0000	-2.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Nitrogen	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

1-Propanol was almost completely gone within the first of 10.52% Vf in both experiments and beers apart from the S sample at 200 mbar, in which its lost extended to a 14.43% Vf.

Isobutanol was evaporated gradually over the process time course under both experimental conditions but, at the first 10.52% Vf more than a half of the concentration was removed (from 9.41 and 10.47 mg/L to 4.68 and 4.32 at 102 mbar; and to 4.25 and 3.46 mg/L at 200 mbar, for the samples S and G, respectively). A similar trend was observed for isopentyl acetate, but in this case more than a half was removed during the first 7.53% Vf.

For both experiments and samples during the first 7.53% Vf the amount of amyl alcohols (2-methylbutanol and 3-methylbutanol) was reduced by approximately 50%, except for the G sample at 102 mbar. At the end of the laboratory dealcoholization process the amyl alcohols were in higher concentration for the S sample in both experiments (102 mbar, 50 °C and 200 mbar, 67 °C).

At the end of both dealcoholization processes (17.87% Vf) the concentrations of the majority of the volatile compounds analyzed were higher for the S sample.

The aromatic alcohol 2-phenylethanol causes 'sweet' or 'rose' flavors in beer (Šmogrovičová & Dömény, 1999). Surprisingly, in this laboratory scale dealcoholization process 2-phenylethanol was apparently produced during the experimental process. This compound has a high boiling point (Table 4), and it was expected to slightly increase its concentration due to the vaporization process (that reduces the volume of the remaining liquid). This feature was simulated using Aspen HYSYS, obtaining that 2-phenylethanol should have increased its concentration by 3 to 5% maximum, as reported previously by Zürcher et al. (2005). However, its concentration increased after the distillation process by about 30 to 50%, that is from 37.69 ppm up to 59.97 ppm (G at 200 mbar, 67 °C) and 75.17 ppm (G at 102 ppm, 50 °C), and from an initial of 34.01 ppm up to 70.65 ppm (S at 200 mbar) and 85.28 ppm (S at 102 mbar).

It is well known that, during fermentation, 2-phenylethanol is formed by phenylalanine catabolism (Kobayashi et al., 2008). Higher alcohols achieve maximum concentrations during batch fermentation at a time roughly coincident with cell growth arrest and minimum free amino nitrogen (FAN) concentration. Their formation takes place by the so-called anabolic and catabolic routes. In the anabolic route the 2-oxo acids, arising from carbohydrate metabolism, are decarboxylated to form aldehydes, which are reduced to the corresponding alcohols. Simultaneously, 2-oxo acids also derived from amino acid utilization, which is termed the catabolic (Ehrlich) route to higher alcohol formation. The final concentration of higher alcohols is therefore determined by the uptake efficiency of the corresponding amino acid and the sugar utilization rate. The contribution of each biosynthetic pathway is influenced by the amino acid composition of the wort, fermentation stage and yeast strain. In addition, some higher alcohols may originate from the reduction of aldehydes and ketones that are present in the wort (Brányik et al., 2008). However, in the present study, the beers used were commercial beers, so they were filtered and no fermentation option is possible. Therefore, we explain this effect by the potential degradation and/or transformation of other beer components due to a combined effect of temperature and residence time. It has been shown that, at industrial scale, beer stays only for a few seconds in the dealcoholization processes as it happens in thin film evaporators or spinning cone columns (Brányik et al., 2012). Conversely, in the experimental setup used in this study, the interfacial area of evaporation was considerable lower than that in thin film evaporators, and, hence, the time required for reaching the final ethanol content ($\leq 1\%$) was calculated to be nearly 45 min, a residence time long enough to give rise to transformation of other potentially related compounds. In this sense, one of the possible formation routes is from the degradation of the amino acid 2-phenylalanine, but any other component from the same metabolic route, e.g., phenyl pyruvate, phenyl acetaldehyde or phenyl acetic acid can additionally lead to 2-phenylethanol in an acidic

Table 6
Estimated parameters for Element-2 of Wilson-2 equation in HYSYS.

	Sucrose	Ethanol	Ethyl acetate	1-Propanol	Isobutanol	Isopentyl acetate	2-Methylbutanol	3-Methylbutanol	2-Phenylethanol	Water	Nitrogen
Sucrose	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ethanol	0.0000	0.0000	-1000.0000	2066.8071	1159.7832	-3062.4265	-500.0000	-500.0000	0.0000	-69.6372	0.0000
Ethyl acetate	0.0000	-300.0000	0.0000	-500.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1-Propanol	0.0000	51.4504	-500.0000	276.3888	-85.8744	0.0000	0.0000	0.0000	0.0000	-132.9251	0.0000
Isobutanol	0.0000	-1675.7465	0.0000	-29.2113	0.0000	0.0000	-442.0000	-442.0855	0.0000	-247.3062	0.0000
Isopentyl acetate	0.0000	3724.3137	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-1319.7350	0.0000
2-Methylbutanol	0.0000	314.0000	0.0000	843.0000	243.0000	0.0000	0.0000	0.0000	0.0000	-462.0000	0.0000
3-Methylbutanol	0.0000	314.4464	0.0000	843.8578	243.3993	0.0000	0.0000	0.0000	0.0000	-462.4493	0.0000
2-Phenylethanol	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Water	0.0000	346.1512	0.0000	625.5155	-1633.2924	-1716.3821	-2102.0000	-2102.8264	0.0000	0.0000	0.0000
Nitrogen	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

hydrogen donor bulk liquid (i.e., water/ethanol) such as beer. When a prolonged heating of beer is made, probably the remained content of this amino acid or other similar compound forms the compound by reaction. Accordingly, 2-phenylethanol might be used as a marker of overheating or overtiming in beer dealcoholization processes.

3.3. Simulation results and thermodynamic parameters

In order to demonstrate the feasibility of a dynamic Aspen HYSYS simulation for the dealcoholization process, several thermodynamic packages were considered. In the present study, it was necessary to consider an EoS with interaction in liquid phase, such as NRTL or Wilson. For our simulation the best results were found using Wilson-2 thermodynamic package from HYSYS database.

However, the deviations of the simulation results against the experimental results were unacceptable using the default parameters of the software. Thus, we have performed a fit of the selected binary interaction coefficients for the main measured compounds at 15 min, and then the simulation was tested to check whether the system was able to predict or not the other experimental data points.

The best fit parameters for Wilson-2 Element-1 and Element-2 (i.e., interaction parameters according to Aspen HYSYS nomenclature) are listed in Tables 5 and 6 (see also Figs. 5 and 6 for component concentration graphs).

The predictions for the seven compounds analyzed were very acceptable. Average absolute deviations (determined as the absolute value of the simulated instant concentration minus the experimental instant concentration, divided by the initial value of the concentration) were between 6.9 and 15.1% for both S and G beers (excluding the

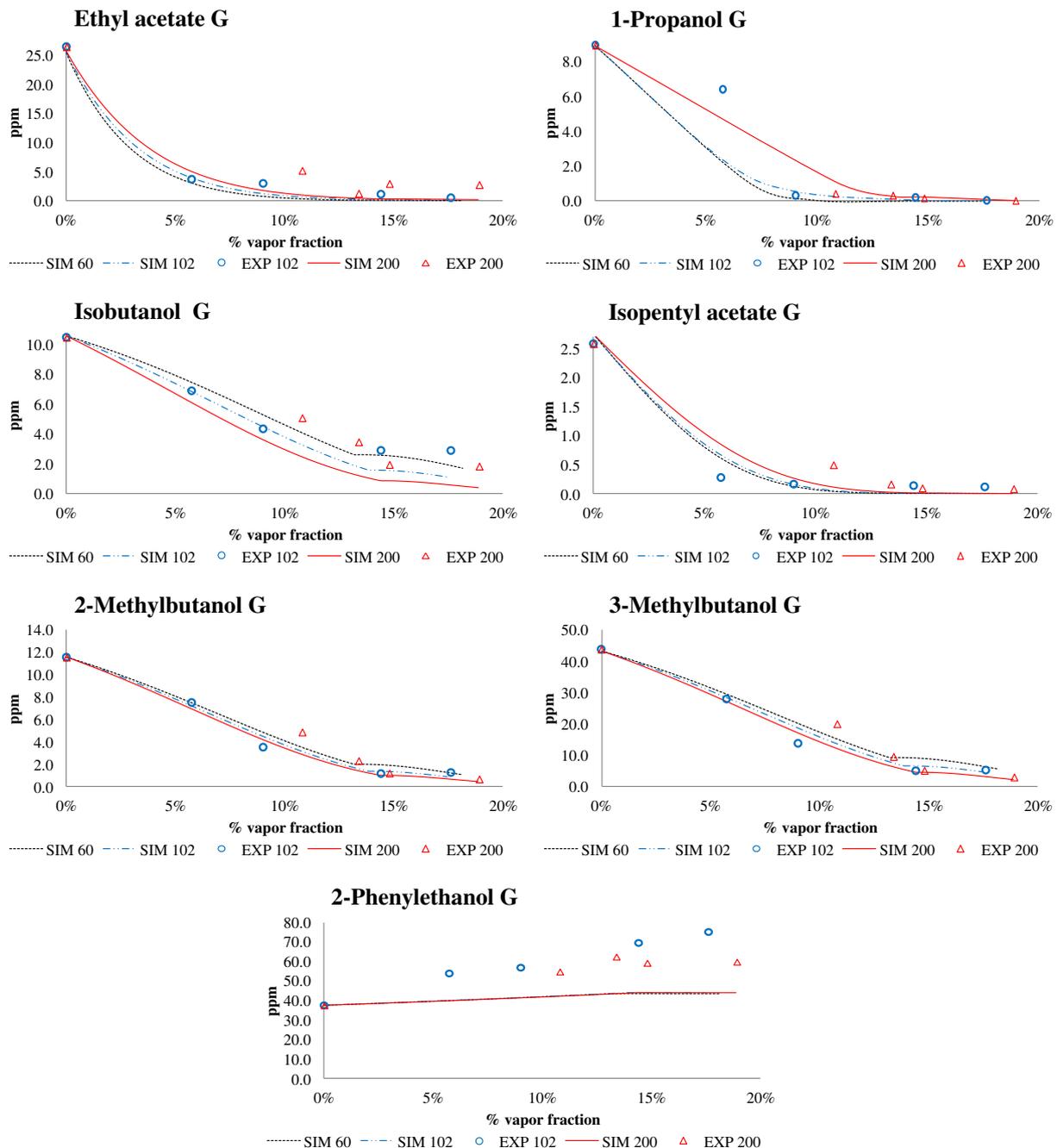


Fig. 5. Concentration profiles of the main aroma compounds analyzed in the German beer (G) after the dealcoholization process.

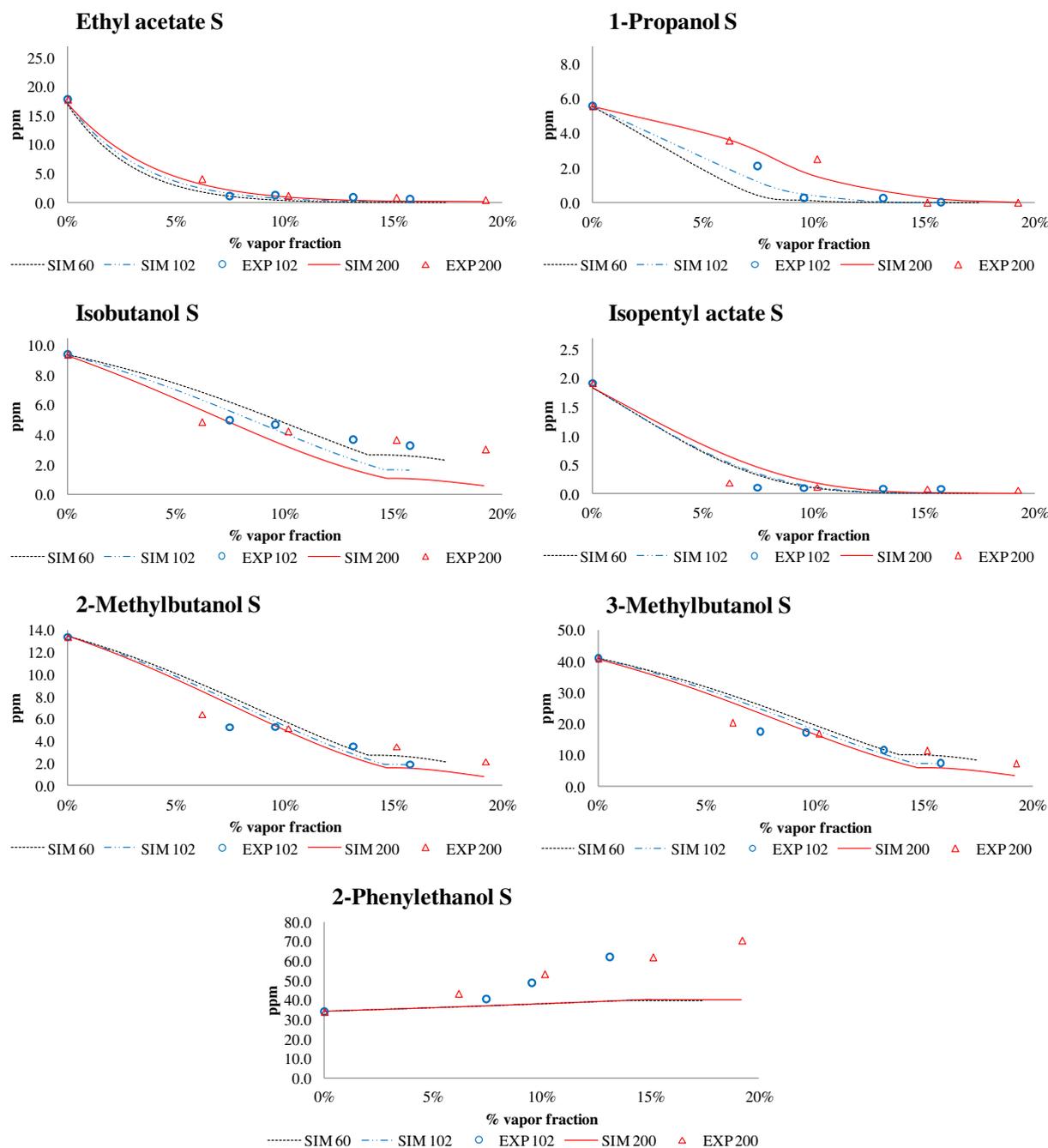


Fig. 6. Concentration profiles of the main aroma compounds analyzed in the Spanish beer (S) after the dealcoholization process.

values of 2-phenylethanol that behaves oddly). The values obtained by simulation (SIM) and experimentation (EXP) are listed in Table 2 (see also Figs. 5 and 6).

For the case of 2-phenylethanol it is clear that the component is generated by reaction, so the simulation cannot predict it as the assumption 5 (see Section 2.4) is not fulfilled.

Considering the difficulty of the analysis and the system itself we consider the simulation values for prediction acceptable. This is the first time, to our knowledge, that beer is dealcoholized and the experimental values are fit to a simulation and thermodynamic model aimed at creating a prediction tool.

From our point of view, the prediction could be improved by studying the kinetics of formation of 2-phenylethanol and by studying a pilot scale plant using a short-residence time equipment (such as falling fill evaporator), but this is out of the scope of this paper. Nevertheless, 2-

phenylethanol appeared from 15 min on, so this means that the thermodynamic approach is valid for times below that time that indicates that it could be used for simulation of short residence time pieces of equipment.

4. Conclusions

Low alcohol and free alcohol beers from thermal dealcoholization (e.g., vacuum distillation) lack of the flavor and aroma compounds that the original beers possesses. Literature data on this is scarce and, so far, no simulation tools to predict the compositions during the dealcoholization process have been published.

In this study, we have observed how flavor compounds analyzed vanished to very low concentration levels in the lab-scale vacuum

distillation process during 60 min at vaporization level of around 20% in mass.

Two pressures were checked (102 and 200 mbar) at two corresponding temperatures (50 and 67 °C respectively). In general, results were similar under both experimental conditions, but slightly more flavor disappearing was measured at 200 mbar.

An unexpectedly high concentration of 2-phenylethanol was found at the end of the process, its concentration increasing by about 30 to 50% with regard to the initial one. The reasons for this result are not yet entirely understood, however it might indicate that one or several reactions of other phenolics arising in the 2-phenylethanol metabolic route were involved and produced it during the distillation process, due to a combined effect of temperature and residence time.

For the first time we have tested a simulation tool for beer dealcoholization against the laboratory results, fitting the thermodynamic binary interaction coefficients of a Wilson Equation of State. Although, more research is needed in this sense, we succeed in the simulation of the behavior of six components, i.e., 2-methylbutanol, 3-methylbutanol, ethyl acetate, 2-phenylethanol, isobutanol and 1-propanol together with the ABV % using Aspen HYSYS with Wilson-2 EoS and a set of binary interaction parameters. Although the residence time is very high in differential bath vacuum distillation compared to the industrial thin film evaporators, the simulation tool is considered to be acceptable because the thermodynamic behavior does not depend on the residence time.

To sum up, the adjusted parameters of the simulation process are the key to overview the behavior of any beer sample and their volatile compound profiles at different temperatures, times and pressures, for real processes such as vacuum distillation or thin film evaporators.

Acknowledgments

The authors acknowledge the Spanish Economy and Competitive-ness Ministry, Project Reference: ENE2012-33613 and the regional government (Junta de Castilla y León), Project Reference: VA330U13 and VA332A12-2 for funding.

References

- Andrés-Iglesias, C., Blanco, C.A., Blanco, J., & Montero, O. (2014). Mass spectrometry-based metabolomics approach to determine differential metabolites between regular and non-alcohol beers. *Food Chemistry*, *157*, 205–212.
- Andrés-Iglesias, C., Montero, O., Sancho, D., & Blanco, C.A. (2014). New trends in beer flavour compound analysis. *Journal of the Science of Food and Agriculture*, *95*, 1571–1576.
- ASTM-International (2012). ASTM D86-12. In W. Conshohocken (Ed.), *Standard test method for distillation of petroleum products at atmospheric pressure*.
- Bamforth, C.W. (2001). Nutritional aspects of beer—A review. *Nutrition Research*, *22*(1), 227–237.
- Belisario-Sánchez, Y.Y., Taboada-Rodríguez, A., Marin-Iniesta, F., & López-Gómez, A. (2009). Dealcoholized wines by spinning cone column distillation: phenolic compounds and antioxidant activity measured by the 1,1-diphenyl-2-picrylhydrazyl method. *Journal of Agricultural and Food Chemistry*, *57*(15), 6770–6778.
- Berk, Z. (2013). Chapter 13—Distillation. In Z. Berk (Ed.), *Food process engineering and technology* (pp. 329–352) (Second ed.). San Diego: Academic Press.
- Blanco, C.A., Andrés-Iglesias, C., & Montero, O. (2014). Low-alcohol beers: Flavour compounds, defects and improvement strategies. *Critical Reviews in Food Science and Nutrition*. <http://dx.doi.org/10.1080/10408398.2012.733979>.
- Brányik, T., Silva, D.P., Baszczyński, M., Lehnert, R., & Almeida e Silva, J.B. (2012). A review of methods of low alcohol and alcohol-free beer production. *Journal of Food Engineering*, *108*(4), 493–506.
- Brányik, T., Vicente, A.A., Dostálek, P., & Teixeira, J.A. (2008). A review of flavour formation in continuous beer fermentations. *Journal of the Institute of Brewing*, *114*(1), 3–13.
- Catarino, M., Ferreira, A., & Mendes, A. (2009). Study and optimization of aroma recovery from beer by pervaporation. *Journal of Membrane Science*, *341*(1–2), 51–59.
- Catarino, M., & Mendes, A. (2011). Non-alcoholic beer—A new industrial process. *Separation and Purification Technology*, *79*(3), 342–351.
- Catarino, M., Mendes, A., Madeira, L.M., & Ferreira, A. (2007). Alcohol removal from beer by reverse osmosis. *Separation Science and Technology*, *42*(13), 3011–3027.
- Charry-Parra, G., Dejesús-Echevarria, M., & Perez, F.J. (2011). Beer volatile analysis: Optimization of HS-SPME coupled to GC/MS/FID. *Journal of Food Science*, *76*, 205–211.
- Claus, M.J., & Berglund, K.A. (2005). Fruit brandy production by batch column distillation with reflux. *Journal of Food Process Engineering*, *28*(1), 53–67.
- Claus, M.J., & Berglund, K.A. (2009). Defining still parameters using CHEMCAD batch distillation model for modeling fruit spirits distillations. *Journal of Food Process Engineering*, *32*(6), 881–892.
- Dong, L., Piao, Y., Zhang, X., Zhao, C., Hou, Y., & Shi, Z. (2013). Analysis of volatile compounds from a malting process using headspace solid-phase micro-extraction and GC-MS. *Food Research International*, *51*(2), 783–789.
- Gaiser, M., Bell, G.M., Lim, A.W., Roberts, N.A., Faraday, D.B.F., Schulz, R.A., et al. (2002). Computer simulation of a continuous whisky still. *Journal of Food Engineering*, *51*(1), 27–31.
- Gonçalves, J.L., Figueira, J.A., Rodrigues, F.P., Ornelas, L.P., Branco, R.N., Silva, C.L., et al. (2014). A powerful methodological approach combining headspace solid phase microextraction, mass spectrometry and multivariate analysis for profiling the volatile metabolomic pattern of beer starting raw materials. *Food Chemistry*, *160*, 266–280.
- Karlsson, H.O.E., & Trägårdh, G. (1997). Aroma recovery during beverage processing. *Journal of Food Engineering*, *34*(2), 159–178.
- Kobayashi, M., Shimizu, H., & Shioya, S. (2008). Beer volatile compounds and their application to low-malt beer fermentation. *Journal of Bioscience and Bioengineering*, *106*(4), 317–323.
- Labanda, J., Vichi, S., Llorens, J., & López-Tamames, E. (2009). Membrane separation technology for the reduction of alcoholic degree of a white model wine. *LWT—Food Science and Technology*, *42*(8), 1390–1395.
- Lang, P., Yatim, H., Moszkowicz, P., & Otterbein, M. (1994). Batch extractive distillation under constant reflux ratio. *Computers and Chemical Engineering*, *18*, 1057–1069.
- Lehnert, R., Novak, P., Macieira, F., Kurec, M., Teixeira, J.A., & Brányik, T. (2009). Optimisation of lab-scale continuous alcohol-free beer production. *Czech Journal of Food Sciences*, *27*(4), 267–275.
- Liguori, L., De Francesco, G., Russo, P., Perretti, G., Albanese, D., & Di Matteo, M. (2015). Production and characterization of alcohol-free beer by membrane process. *Food and Bioproducts Processing*, *94*, 158–168.
- Montanari, L., Marconi, O., Mayer, H., & Fantozzi, P. (2009). Chapter 6—Production of alcohol-free beer. In V.R. Preedy (Ed.), *Beer in health and disease prevention* (pp. 61–75). San Diego: Academic Press.
- Mota, A., Novák, P., Macieira, F., Vicente, A.A., Teixeira, J.A., Šmugrovičová, D., et al. (2011). Formation of flavor-active compounds during continuous alcohol-free beer production: The influence of yeast, strain, reactor configuration, and carrier type. *Journal of the American Society of Brewing Chemists*, *69*, 1–7.
- Olmo, Á. d., Blanco, C.A., Palacio, L., Prádanos, P., & Hernández, A. (2014). Pervaporation methodology for improving alcohol-free beer quality through aroma recovery. *Journal of Food Engineering*, *133*(0), 1–8.
- Pickering, G.J. (2000). Low- and reduced-alcohol wine: A review. *Journal of Wine Research*, *11*(2), 129–144.
- Piddocke, M.P., Kreis, S., Heldt-Hansen, H.P., Fog Nielsen, K., & Olsson, L. (2009). Physiological characterization of brewer's yeast in high-gravity beer fermentations with glucose or maltose syrups as adjuncts. *Applied Microbiology and Technology*, *84*, 453–464.
- Riu-Aumatell, M., Miró, P., Serra-Cayuela, A., Buxaderas, S., & López-Tamames, E. (2014). Assessment of the aroma profiles of low-alcohol beers using HS-SPME-GC-MS. *Food Research International*, *57*, 196–202.
- Rodrigues, F., Caldeira, M., & Câmara, J.S. (2008). Development of a dynamic headspace solid-phase microextraction procedure coupled to GC-qMSD for evaluation the chemical profile in alcoholic beverages. *Analytical Chimica Acta*, *609*, 82–104.
- Šmugrovičová, D., & Dömény, Z. (1999). Beer volatile by-product formation at different fermentation temperature using immobilised yeasts. *Process Biochemistry*, *34*(8), 785–794.
- Sohrabvandi, S., Mousavi, S.M., Razavi, S.H., Mortazavian, A.M., & Rezaei, K. (2010). Alcohol-free beer: Methods of production, sensorial defects, and healthful effects. *Food Reviews International*, *26*(4), 335–352.
- Stein, W. (1993). Dealcoholization of beer. *Technical Quarterly Master Brewers Association of Americas*, *30*, 54–57.
- Willaert, R., & Nedovic, V.A. (2006). Primary beer fermentation by immobilised yeast—A review on flavour formation and control strategies. *Journal of Chemical Technology & Biotechnology*, *81*(8), 1353–1367.
- Yatim, H., Moszkowicz, P., Otterbein, M., & Lang, P. (1993). Dynamic simulation of a batch extractive distillation process. *Computers and Chemical Engineering*, *17*, 57–62.
- Zürcher, A., Jakob, M., & Back, W. (2005). Improvements in flavor and colloidal stability of alcohol free beers. *Paper presented at the Proceedings of the European Brewing Convention Congress, Prague, Czech Republic*.