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Distillation: The behaviour of volatile compounds during distillation of hydro-alcoholic solutions and during hydro-distillation

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When food ingredients are cooked, many volatile compounds are formed and escape. The goal of this chapter is to give some information on the behaviour of odorant compounds during the distillation of hydro-alcoholic solutions, on one hand, and to make a link with their elimination through steam distillation.

Characterization of volatility

Distillation is a unit operation that makes it possible to separate compounds all together present in one phase by using volatility differences. It is generally performed at pressures close to atmospheric pressure (from 0.2 bar to some bars).

For each pure species separately, it is possible to calculate the saturating vapour pressure P^{sat} as a function of temperature by using Equation 1. The coefficients are generally given in handbooks or databases (Perry *et al.*, 1997; ProSim, 2019).

$$P^{sat} = \exp\left(a + \frac{b}{T} + c \cdot \ln(T) + d \cdot T^e\right) \quad (1)$$

Where T (kelvins) is the absolute temperature, P^{sat} (Pascal) the saturating vapour pressure, and a , b , c , d and e are particular constants for the various compounds. For example, **Table 1** gives the values for water, ethanol and some categories of volatile compounds of the families of alcohols, esters, aldehydes and terpenes.

Separately, at a particular temperature, water and ethanol do not have the same partial pressure; the vapour pressure of ethanol is always higher than the one of water. For example, at 100 °C, the vapour pressure for water is 101.3 kPa, and it is 224.5 kPa for ethanol. Ethanol, having a vapour pressure much higher than that of water (by a factor 2.2), is thus said more volatile than water.

Partial pressures for the liquid-vapour equilibrium

According to Dalton's law, the total pressure for a vapour of n compounds is equal to the sum of the partial pressures for each compound of the mixture. In Equation 2, P_i is the partial pressure of the i -th compound in the vapour phase, and P is that total pressure:

$$\sum_{i=1}^n P_i = P \quad (2)$$

At the pressure traditionally used in distillation or hydro-distillation, the behaviour of the vapour phase can be described using the ideal gas law. As a consequence, the partial pressure P_i of the i -th compound in the vapour phase can be expressed as a function of the molar fraction y_i of this compound in the vapour phase and the total pressure P (Equation 3):

$$P_i = y_i \cdot P \quad (3)$$

Interactions in the liquid phase can be described using activity coefficients. Hence, the partial pressure P_i

of the i -th compound can be expressed using the activity coefficient γ_i of the molar fraction x_i of the i -th compound of the liquid phase and the saturating vapour pressure at the considered temperature (Equation 4):

$$P_i = \gamma_i(T, x_i) \cdot x_i \cdot P_i^{sat}(T) \quad (4)$$

Absolute and relative volatility

In order to know the behaviour of the volatile compounds in a solution, one needs to look for the data for the equilibrium liquid-vapour (how do the compounds distribute between the boiling liquid and the saturated vapour phases). Each compound, i , is characterized by an absolute volatility coefficient, K_i , which is the ratio of molar concentrations y_i of the i -th compound in the saturated vapour and the molar concentration x_i in the boiling liquid (equation 5):

$$K_i = \frac{y_i}{x_i} \quad (5)$$

Generally, the volatile compounds are present in very low concentrations, and the interactions between them can be neglected. In contrast, the influence of the solvent is often very important. For mixtures, one can define relative volatilities $\alpha_{i/j}$, for example for the i -th compound relatively to the j -th one (Equation 6):

$$\alpha_{i/j} = \frac{K_i}{K_j} = \frac{y_i/x_i}{y_j/x_j} \quad (6)$$

All these concepts being defined, we shall now examine (1) the principle of the distillation of a hydro-alcoholic distillation, (2) the behaviour of volatile compounds in a hydro-alcoholic solution during a simple distillation, and (3) the behaviour of volatile compounds in water during hydro-distillation.

Distillation of a hydro-alcoholic solution

The equilibrium data for the binary mixture water-ethanol are well known. They can be represented in a diagram of composition (**Figure 1**) giving, for a particular pressure, the molar concentration of the boiling liquid in equilibrium with the saturated vapour. Such data were calculated using the software *Simulis Thermodynamics* (ProSim, 2019) using the NRTL coefficients given by Puentes *et al.* (2018a). The two phases in equilibrium are at the same temperature. Using the diagram, one can determine, for a pressure of 1.013 bar, the temperature at which the liquid reaches its boiling temperature and the composition of the vapour in equilibrium at this temperature. One can observe that the water-ethanol system is forming an azeotrope for a molar fraction equal to 0.8943: for this composition, the mixture behaves like a pure species, i.e., the vapour has the same composition as the liquid. Hence it is impossible, even in a highly complex distillation system, to produce pure ethanol.

In the European food industry, the official unit for the characterization of the ethanol concentration of a solution is the Alcoholic strength By Volume (ABV in % v/v) (Official Journal of the European Regulation, 2019, article 4, 23th point). This is the ratio in percentage between the volume of pure ethanol at a temperature of 20 °C, in a solution, and the total volume of this solution at the same temperature. Using relationships published by the International Organization of Legal Metrology (1975) between ABV and densities, a polynomial relation were established between ethanol molar fraction and ABV (Equation 7) where x_{Et} is the ethanol molar fraction and c_i the constants of the **Table 2**.

$$ABV = \sum_{i=1}^5 c_i \cdot (x_{Et})^i \quad (7)$$

The one can trace the composition diagram using the ABV unit system, more convenient for culinary uses (**Figure 2**).

Such plots of the composition of a hydro-alcoholic solution at its boiling temperature is useful for a simple batch distillation. Let us consider the example of a hydro-alcoholic solution with an ABV equal to 10 % v/v. At a pressure of 1.013 bar, it reaches its boiling temperature at a temperature of 92.8 °C (at this temperature, the vapour pressure due to the liquid is equal to 1.013 bar). The vapour from this solution is at 54.5 % v/v. The production of this vapour, richer in ethanol than the liquid, generates a drop in the ethanol concentration of the liquid, and by the way an increase of the boiling temperature and a decrease in the ethanol concentration of the vapour produced. This phenomenon goes on until nearly all the ethanol of the liquid is evaporated. It is important to understand that, in a solution with many compounds, the vapour is composed of most volatile compounds, but in different proportions. In the case of a water-ethanol solution with 10 % v/v which is set to boil, with a condensation of the vapour being formed, the evolution of the content in ethanol of the liquid and the vapour can be described as in **Figure 3**.

In some cases, distillations (simple evaporation) are performed at a pressure under the atmospheric pressure (so called “vacuum pressure”). The equilibrium data are modified, with a strong decrease in boiling temperatures when the pressure is low (as shown in **Figure 4** for the water-ethanol system), and a slightly increase of the relative volatilities of ethanol.

Distillation of volatile compounds in a hydro-alcoholic solution

The goal of distilling hydro-alcoholic solutions is to extract from the initial liquid the volatile compounds, and to separate them when possible or when needed. For fermented must (grapes, apples, pears, grain), the main compound (except water) is of course ethanol, but the primary interest is to fractionate volatile compounds that influence the quality of the distillate. The key question is then their volatility in the boiling medium.

For the distillation of hydro-alcoholic solutions, the volatility of most compounds depends on the ethanol content of the solution. Puentes *et al.* (2018a) reviewed the published equilibrium data and they determined the coefficient of the NRTL model (Non-Random Two Liquid) for using such data in simulation software. It is then possible to determine the absolute volatility of these compounds according to the ethanol concentration of the liquid. As an example, **Figure 5** shows the shape of the absolute volatility (K_i ; equation 5) of some compounds, including ethanol. Obviously, some compounds are always more volatile than ethanol (ethyl acetate, acetaldehyde), whereas others have a volatility that varies with the ethanol content in the liquid (3-methylbutan-ol, methanol), or a volatility always lower than that of ethanol (ethyl lactate, acetic acid, 2-phenylethanol).

Puentes *et al.* (2018a) proposed a classification for 44 compounds based on their relative volatility (Equation 6) with respect to ethanol or water ($\alpha_{i/Et}$ or $\alpha_{i/W}$): (i) light compounds, which are always more volatile than ethanol, whatever the ABV of the liquid ($\alpha_{i/Et} > 1$); (ii) intermediate compounds, with a relative volatility higher than that of ethanol at low ABV but a lower volatility at high ABV; and (iii) heavy compounds, always less volatile than water ($\alpha_{i/W} < 1$) (**Table 3**). Depending on the distillation process (simple or with column), the compounds do not have the same distribution in the distillate and the residue.

During simple distillation (evaporation), the compounds are more concentrated in the first vapour fractions when their volatility with respect to ethanol is higher; this is the case, for example, for ethyl

acetate. Because their strong extraction in the vapour phase, the concentration of such compounds decreases rapidly in the liquid. By consequence their concentration decreases also in the vapour. Such compounds belong to “heads” because they are extracted at the beginning of the distillation process. The compounds with a volatility comparable to that of ethanol, such as methanol or 3-methylbutan-1-ol, have a distillation behaviour similar to ethanol, and are particularly difficult to separate from ethanol. Among intermediate compounds, some, such as 2-phenylethanol or ethyl lactate, have volatility that are always lower than ethanol, but their volatility with respect to water increases when the ethanol content decreases. These compounds are evaporated at the end of distillation, when the ethanol content is strongly decreased. Finally, the compounds with a volatility lower than water remain in the liquid. As an example, **Figure 6**, the behaviour of some compounds during a distillation of cognac was shown by Douady *et al.* (2019).

One can consider that, in a column distillation, when the initial solution is separated into a distillate with high ethanol content and a residue with low ethanol concentration, all light compounds are extracted by the distillate and heavy compounds by the residue. In contrast, the distribution of the intermediate compounds depends on the ethanol content of the distillate; the lower this content, the greater the extraction of the compounds in the distillate. This occurs for example during Armagnac production, for which the ABV of the liquid in the column is less than 10 % v/v (Puentes *et al.*, 2018b).

Finally, for the production of ethyl alcohol of agricultural origin with a minimum ABV of 96.0 % v/v and limit concentrations in other volatile compounds (Official Journal of the European Regulation, 2019, article 5), more than seven distillation columns, each with a high number of plates, are coupled in order to eliminate all the volatile compounds except ethanol (Esteban-Decloux *et al.*, 2014).

It is important to remember that the matrix and the method of distillation have an essential role on the behaviour of volatile flavouring compounds during distillation.

Behaviour of volatile compounds in boiling water

Hydro-distillation (or steam distillation) is a particular distillation for which the solvent is water or steam. As we have seen before, the compounds are more volatile when the ethanol content is low. This is due to their relative affinity for organic and aqueous phases, which can be characterized by the partition coefficient k_{ow} (octanol/water). The partition coefficient is a measurement for a compound of its differential solubility in octanol and water but, because of very large values, the logarithm of this partition coefficient is used. The higher the $\log k_{ow}$, the more lipophilic the compounds are (and the less hydrophilic they are).

When the concentration of a compound in a solution is higher than its solubility limit, its partial pressure in the vapour does not depend on its concentration, but only on the temperature. It can then be extracted at a temperature lower than its own boiling temperature when pure. For example, limonene is the main compound of the essential oil of most citrus fruits and extracts (Deterre *et al.*, 2011). Its solubility in water at 25 °C is 13.8 mg.L⁻¹, its boiling temperature at 1.013 bar is 176 °C and its molar mass is 136.23 g.mol⁻¹ (The Good Scents Company, 2019). When a water-limonene system (with a concentration of limonene higher than the solubility limit) is put to the boil, the partial pressure for each compound depends only on temperature (Equation 1 and coefficients in Table 1) and the total pressure is equal to the sum of partial pressures (Equation 2). Because the solution reaches its boiling temperature when the total vapour pressure is equal to the atmospheric pressure, the boiling temperature of water with an excess of limonene is 97.49 °C (**Table 4**). This value is less than the individual boiling temperatures of limonene and water at the same pressure.

The molar fraction of limonene in the vapour phase can be calculated from the pressures of each compound at the boiling temperature and Equation 3, giving Equation 8.

$$y_{lim} = \frac{P_{lim}^{sat}}{P} = \frac{P_{lim}^{sat}}{P_{lim}^{sat} + P_{water}^{sat}} \quad (8)$$

Thus, the molar fraction in the vapour phase at 97.49 °C is $8.66 \cdot 10^{-2}$, corresponding to a mass fraction of $0.4178 \text{ g}\cdot\text{g}^{-1}$. This value is much higher than the solubility limit, and so the condensed vapour separates into two phases: a light organic phase (the “essential oil”) and a heavy aqueous phase, called the floral water.

Conclusion

This chapter intended to show the behaviour of volatile compounds when solutions are put to the boil, during distillation or hydro-distillation. The importance of knowing the properties of these compounds, in particular their saturating pressure vapour with respect to temperature, and their absolute volatility with respect to the nature of the solvent, is stressed. During the simple distillation of hydro-alcoholic solutions, the volatile compounds distribute between some that are concentrated in the first fractions of vapour, some that distribute as ethanol, and some that are more concentrated in the end of the process. With hydro-distillation or steam distillation, one can extract poorly water-soluble compounds at a temperature much lower than their own boiling temperature; indeed, their vapour pressure depends only on temperature. Their concentration in the vapour depends only on the ratio of the saturating vapour pressures and, through the condensation of the vapour, they can be separated by simple decantation as essential oil. Finally, by simple distillation or by steam distillation, one can lower the boiling temperature by reducing the pressure.

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Table 1. Coefficients for the Riedel equation (equation 1) according to ProSim (2019) for water and some compounds of the families of alcohols, esters, aldehydes and terpenes

Compound	T _{min} (°C)	T _{max} (°C)	a	b	c	d	e
Water	0	374	73.64900	-7258.20000	-7.30370	4.1653E-06	2
Ethanol	-114	241	73.30400	-7122.30000	-7.14240	2.8856E-06	2
Methanol	-98	239	82.11780	-6905.50000	-8.86220	7.4664E-06	2
1-propanol	-126	263	84.66416	-8307.24422	-8.57673	7.0509E-18	6
3-methyl-1-butanol	-117	304	117.0740	-10743.2000	-13.1654	1.1670E-17	6
2-phenylethanol	-27	411	65.07600	-8985.10000	-5.70340	4.6087E-18	6
Ethyl acetate	-84	250	66.82400	-6227.60000	-6.41000	1.7914E-17	6
Hexyl acetate	-81	345	74.72700	-8352.60000	-7.29240	7.1794E-18	6
Ethyl caproate	5	189	64.83120	-7853.33462	-5.82651	0.000	0
Ethyl lactate	-26	334	72.66870	-8249.65000	-6.91582	7.5520E-18	6
Acetaldehyde	-124	193	52.91070	-4643.14000	-4.50683	2.7028E-17	6
Linalol	10	198	128.0810	-12163.63200	-14.7440	0.000	1
d-limonene	-74	380	75.57400	-8079.70000	-7.55960	8.3872E-18	6

Table 2. Coefficients for the determination of ABV using Equation 7.

$c_1 = 320.68$	$c_2 = -560.14$	$c_3 = 654.94$	$c_4 = -439.14$	$c_5 = 123.76$
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Table 3. Classification of volatile compounds according to their relative volatilities with respect to ethanol ($\alpha_{i/Et}$) and water ($\alpha_{i/W}$), over a wide ethanol composition range in the liquid phase (Puentes *et al.*, 2018a).

	$\alpha_{i/Et}$		$\alpha_{i/W}$			$\alpha_{i/Et}$		$\alpha_{i/W}$	
	min	max	min	max		min	max	min	max
Light compound					Intermediary compound				
3-methylbutanal	1.3	19.8	1.2	239.6	3-methyl-1-butanol	0.1	2.7	0.1	32.1
propan-2-yl ethanoate	1.7	14.2	1.7	172.0	2-methyl-1-propanol	0.4	2.5	0.3	30.0
2-methylpropanal	1.1	12.8	1.0	154.6	2-methyl-1-butanol	0.1	2.5	0.1	30.2
ethyl acetate	1.8	10.8	1.6	131.2	1-butanol	0.2	1.9	0.2	23.1
butanal	1.7	10.5	1.5	125.9	cis-3-hexen-1-ol	0	1.9	0	23.4
acetaldehyde	5.1	6.3	5.3	61.6	1-propanol	0.6	1.4	0.5	16.9
1,1-diethoxyethane	3.3	6.8	5.6	40.0	methanol	0.6	1.5	1.4	6.8
propanal	1.8	6.5	1.7	51.3	2-phenylethyl ethanoate	0	1.5	0	18.8
2-methylpropyl methanoate	1.7	6.0	1.6	72.8	octanoic acid	0	1.4	0	17.2
prop-2-enal (acrolein)	2.4	4.5	2.4	30.1	allyl alcohol	0.5	0.9	0.5	10.8
Intermediary compound					hexanoic acid	0	0.7	0	8.1
ethyl decanoate	0	82.9	0	1,005.3	furan-2-carbaldehyde	0.1	0.4	0.1	5.3
ethyl 2-methylpropanoate	1.0	33.0	0.9	399.3	ethyl lactate	0.1	0.3	0.1	3.9
ethyl octanoate	0	28.0	0	339.4	3-methylbutanoic acid	0	0.3	0	4.0
3-methylbutyl ethanoate	0.1	18.5	0.1	224.0	2-methylpropanoic acid	0	0.2	0	2.1
ethyl 3-methylbutanoate	0.5	18.1	0.4	219.5	butanoic acid	0	0.2	0	2.0
pentanal	0.9	10.1	0.8	122.9	diethyl butane-1,4-dioate	0.1	0.2	0.1	1.9
linalool	0	8.2	0	99.5	2-methylbutanoic acid	0	0.2	0	2.0
ethyl hexanoate	0.6	6.7	0.5	81.6	2-phenylethanol	0	0.1	0	1.3
Linalool oxide	0	5.2	0.1	63.4	propanoic acid	0.1	0.1	0	1.0
2-methyl-2-propanol	0.7	2.7	0.7	33.2	Heavy compound				
1-hexanol	0.1	2.9	0.1	35.3	acetic acid	0.1	0.1	0.1	0.8
2-propanol	0.9	1.8	0.8	22.0	Formic acid	0	0.1	0.1	0.5

Table 4. Boiling temperatures of limonene and water at various total pressures P.

T (°C)	P_{lim} (Pa)	P_{water} (Pa)	P (Pa)
97.47	8768	92459	101,227
97.48	8771	92493	101,264
97.49	8775	92526	101,300
97.50	8778	92560	101,338
97.51	8782	92593	101,375

Figures

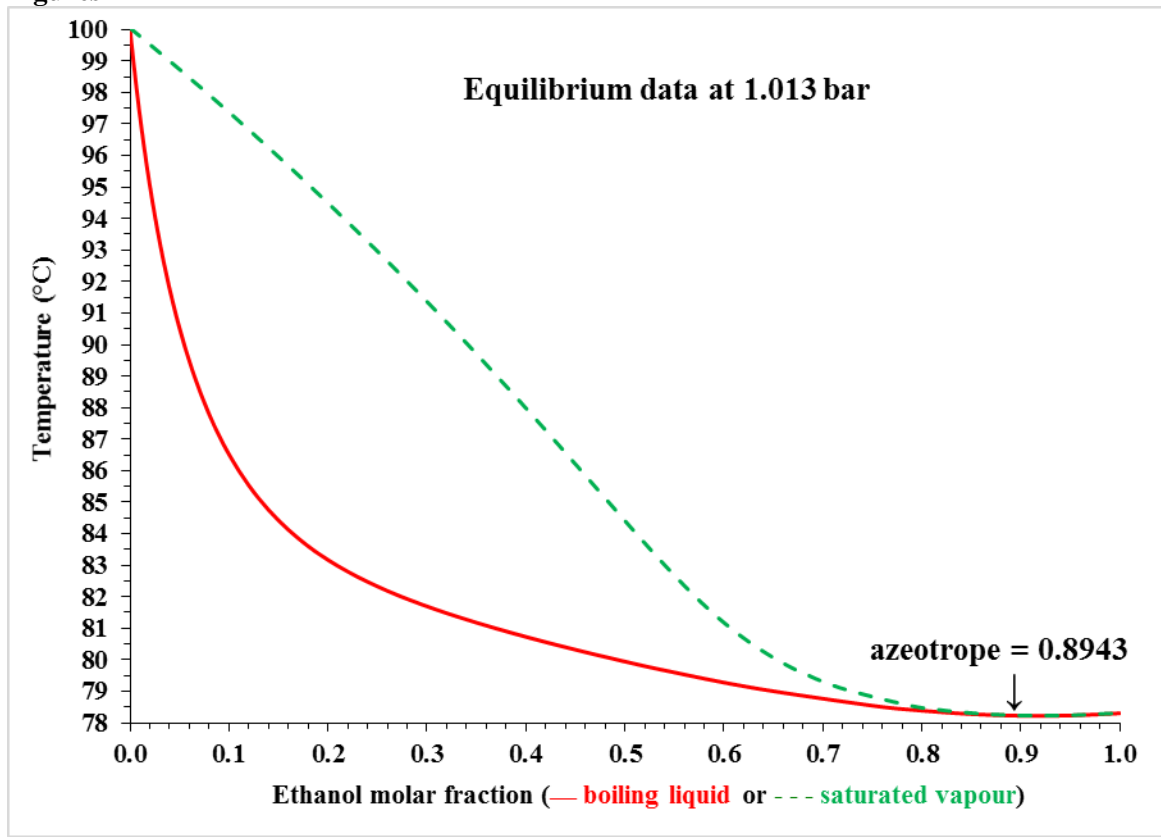


Figure 1. The composition diagram for water-ethanol system at a pressure of 1.013 bar in molar fractions.

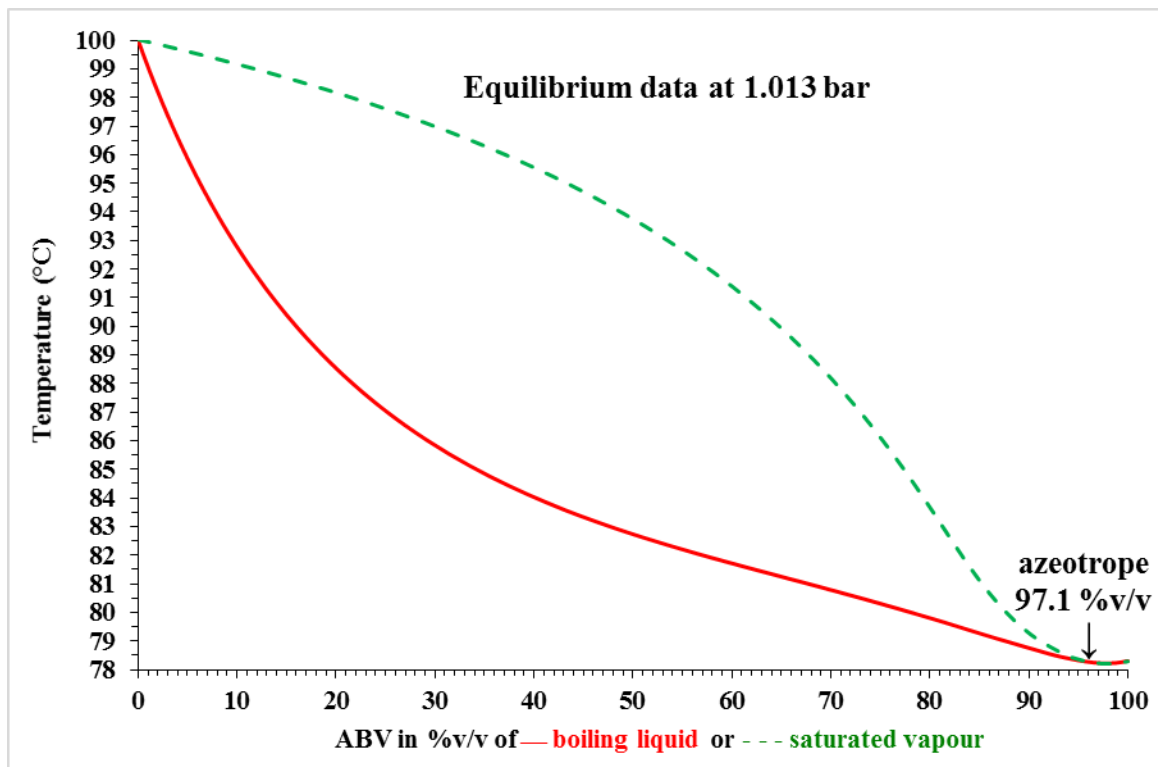


Figure 2. The composition diagram for water-ethanol system at a pressure of 1.013 bar in ABV (% v/v).

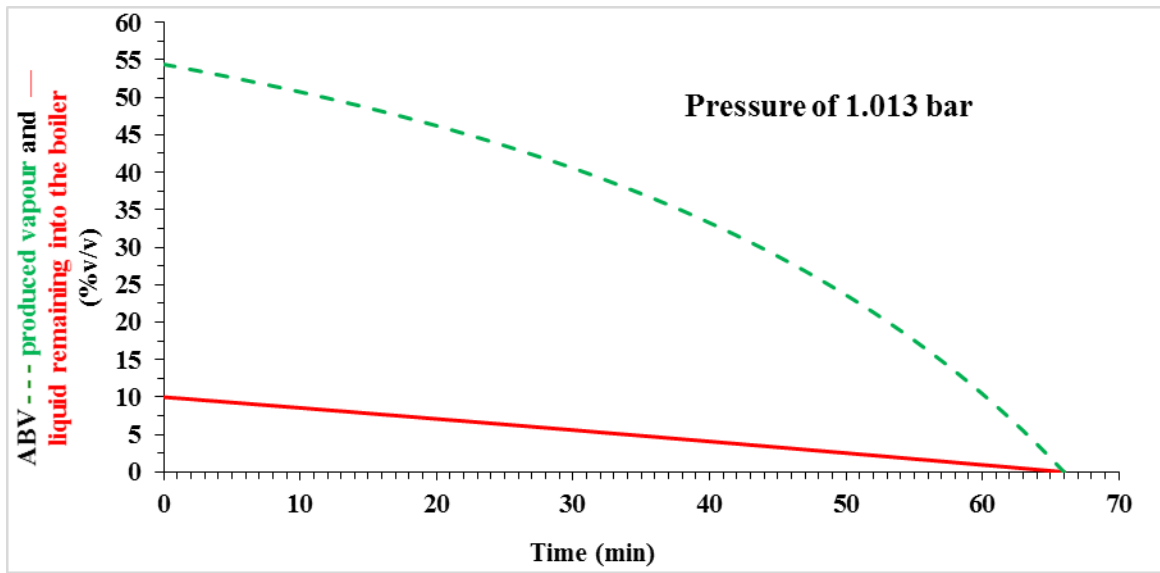


Figure 3. Evolution of the ABV for the produced vapour (---) and the liquid remaining in the boiler (—) in function of time.

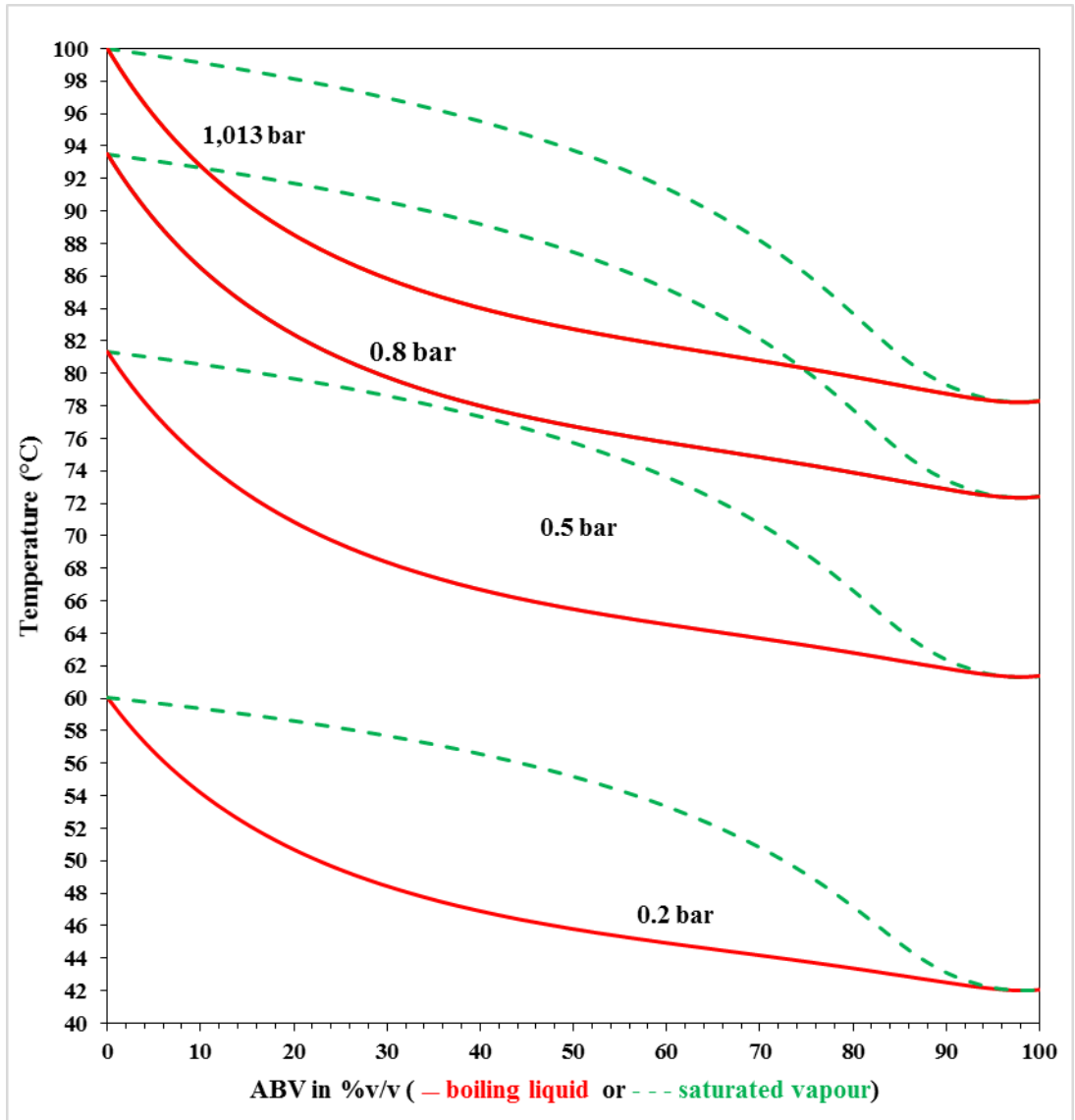


Figure 4. Equilibrium data in ABV (% v/v) for water-ethanol system as affected by pressure.

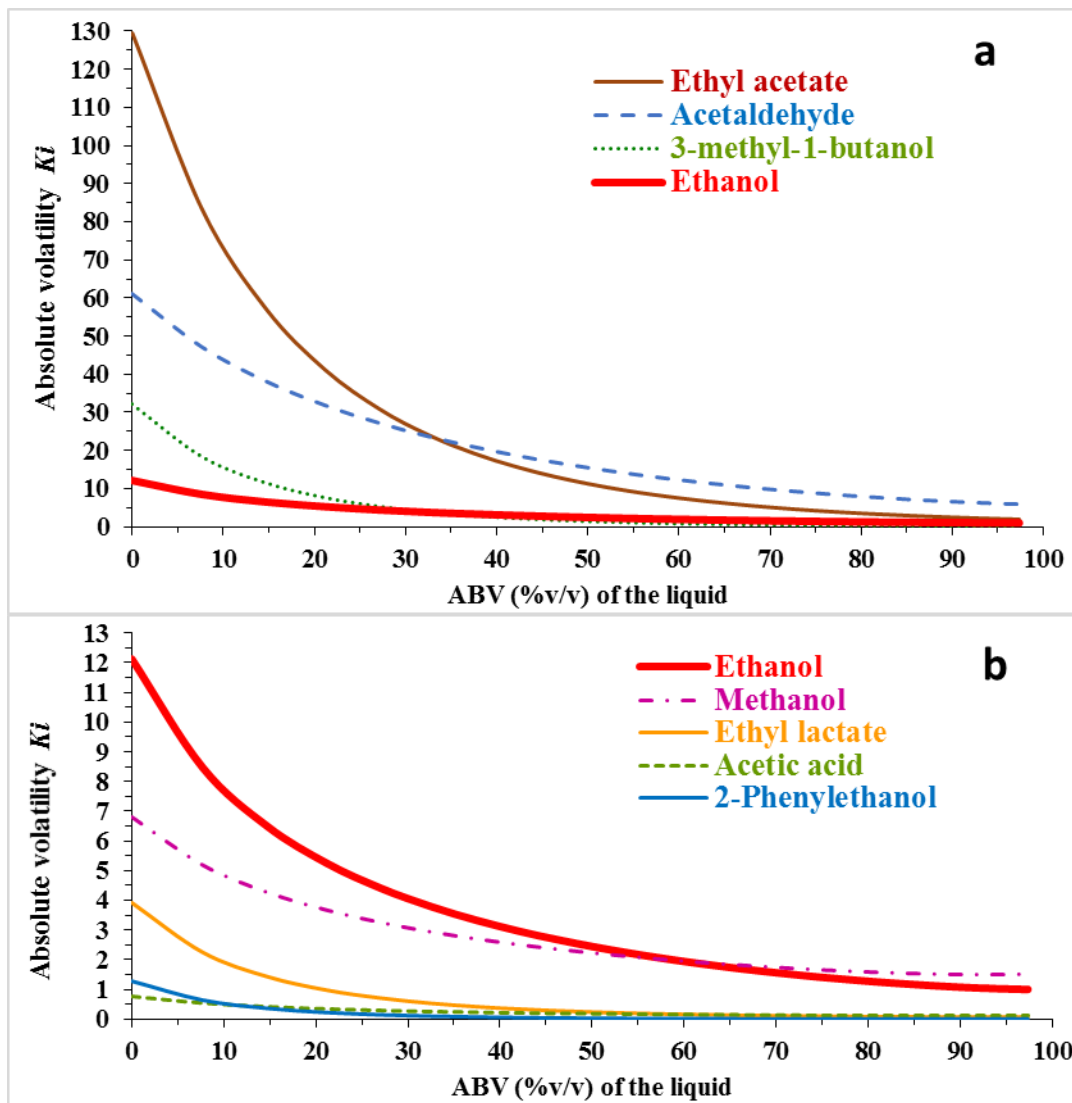


Figure 5. Variation of the absolute volatility (K_i) of some compounds as a function of the ethanol content of the liquid (a) volatilities always higher than ethanol and (b) volatilities lower than ethanol.

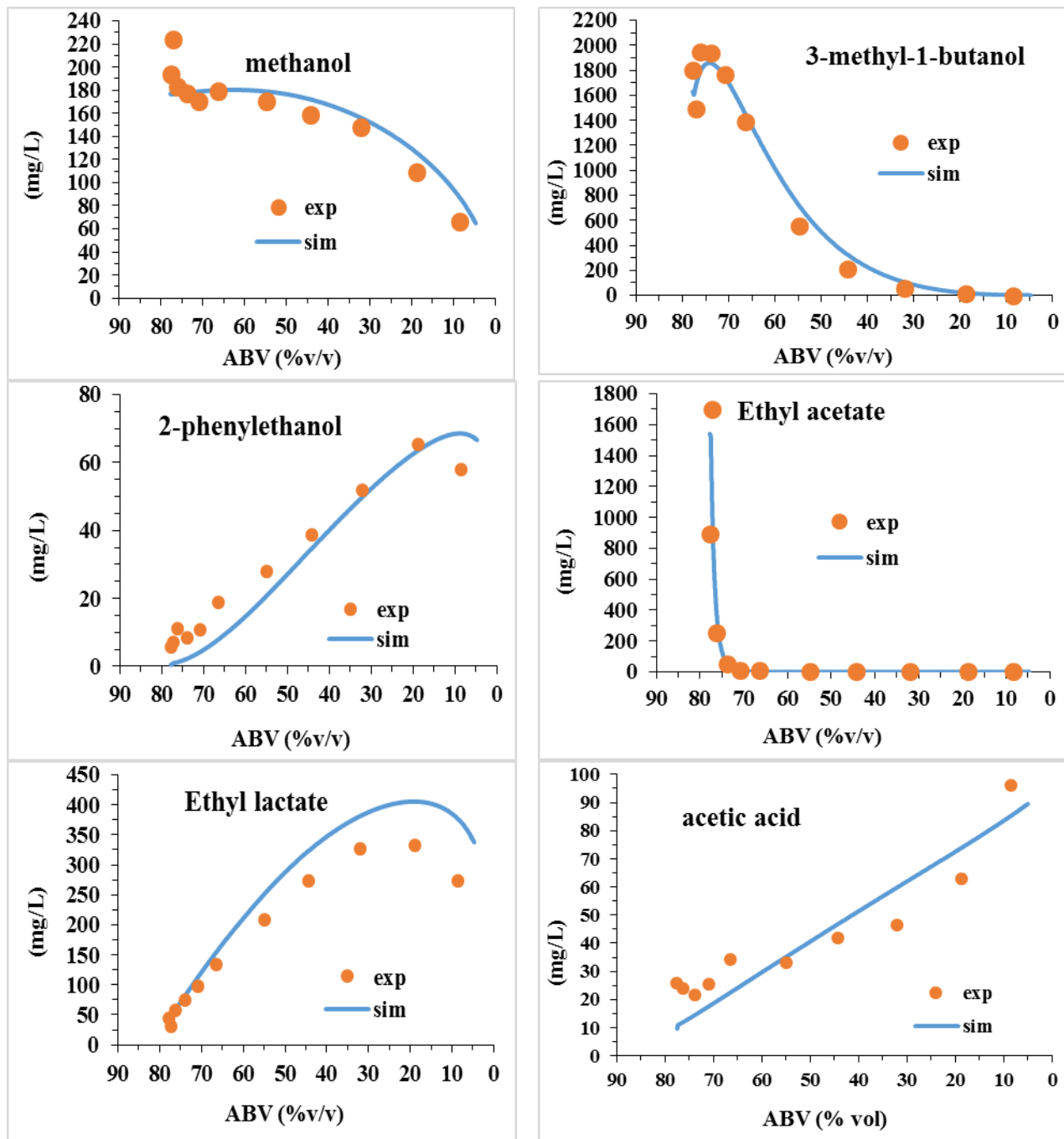


Figure 6. Evolution of some odorant compounds during the distillation of cognac; the experimental values are compared to simulated values with BatchColumn software from ProSim® (Douady *et al.*, 2019).