CHEMICAL ENGINEERING TRANSACTIONS Volume 23, 2010
Editor Renato Del Rosso

DOI: 10.3303/CET1023039

Odour intensity measurement linked to fatty acid mixtures in water

Jean-Michel GUILLOT and Virginie KREIM
Ecole des Mines d'Alès
6 avenue de Clavières, 30319 Ales cedex, FRANCE

Odour emissions from industries can be different depending on odour type linked to the activity. As an example, food and beverage industry such as wineries can also produce odorous compounds. In such activity, the wastewaters (coming from the washing waters of vat, presses and bottles) contain organic residues that are partially transformed in volatile fatty acids by fermentation reactions. These compounds present unpleasant smell and because they are formed in large wastewater storage lagoon, they can have a strong odour impact around these lagoons. In order to have a more precise idea of chemistry responsible of the annoyance, synthetic mixtures with volatile fatty acids were studied. The concentration range for mixtures was based on real measurement and relative proportion of acids was also modified to point out interactions between acids on odour intensity. Several experimental designs were defined. A factorial design, with solutions based on real proportions of acids, had shown than a mixture with high level of propionic acid can be partially inhibited by addition of acetic acid. A mixture design with 35 different mixtures in terms of composition demonstrated the influence of valeric acid by a global increase of the odour intensity when this acid was present in a mixture.

1. Introduction

Due to a size expansion, wine industries produce more wine but also more wastes and especially wastewaters from the washing steps (of vat, presses, bottles) as mentioned by Petruccioli, et al., (2002). If different wastewater treatments are commonly used such as bacterial bed, speeded up muck, opened tank (Racault, et al., 2002), only this last one is considered in the present study. Such opened tanks are built to facilitate natural evaporation of wastewaters but these waters are odorant. The odour is produced by volatile compounds and especially volatile fatty acids that are formed during biological degradations of organic residues. An analysis of winery stored wastewater showed that acetic, propionic, butyric and valeric acids were predominant (Bories, et al., 2007) and for this study, these four acids were selected as models. The interactions between acids are studied with experimental designs.

Please cite this article as: Guillot J.M. and Kreim V., (2010), Odour intensity measurement linked to fatty acid mixtures in water, Chemical Engineering Transactions, 23, 231-236
DOI: 10.3303/CET1023039

2. Materials and methods

The experiments are based on human sensitivity to fatty acid odour exposure. Only intensity is taken into account. All the procedures to carry out the different experiments are explained in this section.

2.1 Smelling protocol for intensity measurement

The protocol for intensity measurement was applied for parts of the present study.

Firstly, five solutions of n-butanol were prepared according to NF X 43-103 French norm. The concentrations in n-butanol in water (v/v) of these solutions were $10^{-2.5}$, 10^{-3}, $10^{-3.5}$, 10^{-4} and $10^{-4.5}$. Based on Erd definition (Erd = -2 log [n-butanol]), Erd intensities of the solutions were respectively 5, 6, 7, 8 and 9.

Secondly, a panel must be selected. The linear aspect of panel member sensitivity is tested by the ability to classify the five n-butanol bottles from low to high intensity (that means low to high concentration).

Thirdly, intensity measurement was carried out by the comparison of a sample with the n-butanol scale used as intensity reference. Because odour quality of fatty acids was really different than n-butanol, the main difficulty for panellists (at least 4 persons) was to just focus on intensity and to neglect odour quality.

2.2 Stevens low and selected acids

Selected acids were acetic, propionic, butyric and valeric acid) and were purchased from Acros. The concentration for each component was based on the highest real concentrations measured in a previous study (Bories, et al., 2007). The real concentration was multiplied by a factor 10^{1}, $10^{0.5}$, 10^{0} and $10^{-0.5}$ to define a concentration range. For butyric acid, the concentration was decreased because the intensity was so hard and the panel members cannot give a note. Concentrations used to determine the slope are given in table 1. Because fatty acid solutions must simulate winery wastewaters, the pH of reconstituted wastewaters was then adjusted to 6.8 to get closer to real conditions. Real acidity conditions must be controlled because volatility depends on the pH and then odour intensity can be easily modified by pH variations. The buffer solution was prepared with protocol defined by Comanici et al.(2006). This buffer is constituted with 6mM Na_2HPO_4, 1mM $Na_2H_2PO_4$, 1mM Na_2EDTA and 185 mM NaCl in Millipore water.

Table 1: Acid concentrations to verify Stevens' Low

Number \ Acids	Propionic (C3)	Butyric (C4)	Valeric (C5)	Acetic (C2)
1	5.11	1.12	3.07	14.40
2	1.62	0.63	0.97	4.55
3	0.51	0.35	0.31	1.44
4	0.16	0.11	0.097	0.45

2.3 Experimental design based on real proportions

An experimental design was built to determine the concentration impact of three acids (propoionic acid, butyric acid and valeric acid) on odour intensity. The addition of a fourth acid (acetic) is also studied. Two levels of concentration (-1 and +1 are selected for a 2^n factorial design) for each acid. The proportions were based on data obtained with concentrations into a storage and the low and high levels presents approximatively the same odour intensity for each acid (table 2). These intensities are globally in the range of 6 to 9 Erd. Because odour intensity decreases with Erd value, results can be expressed in 10-Erd. With all the combination with three acids at -1 or +1 levels, 8 experiments were carried out and with the fourth acid, 24 mixtures were made.

Table 2: Concentrations and odour intensities of pure acid solutions.

Level	Propionic acid (C3)			Butyric acid (C4)			Valeric acid (C5)			Acetic acid (C2)		
	Erd	10-Erd	[C] $g.L^{-1}$	Erd	10-Erd	[C] $g.L^{-1}$	Erd	10-Erd	[C] $g.L^{-1}$	Erd	10-Erd	[C] $g.L^{-1}$
-1	9	1	0.162	9	1	0.112	8	2	0.097	9.2	0.8	0.45
+1	6.3	3.7	1.622	7	3	0.629	6	4	0.971	7.5	2.5	4.55

2.4 Mixture design

A mixture design was carried out based on mass composition with the same variation range for each acid. In that case, proportions observed in real conditions are not considered. For this new design, the global concentration of the four acids was 1 $g.L^{-1}$. Each acid was present at 0, 25, 50, 75 or 100% (mass composition) that gave a total of 35 mixtures with different composition as described in tables 3a and 3b.

Table 3a: Acid concentrations ($g.L^{-1}$) for the design (mixtures without valeric acid)

Number	Acetic (C2)	Propionic (C3)	Butyric (C4)	Valeric (C5)
1	0	0	1	0
2	0.25	0	0.75	0
3	0	0.25	0.75	0
4	0.5	0	0.5	0
5	0.25	0.25	0.5	0
6	0	0.5	0.5	0
7	0.75	0	0.25	0
8	0.5	0.25	0.25	0
9	0.25	0.5	0.25	0
10	0	0.75	0.25	0
11	1	0	0	0
12	0.75	0.25	0	0
13	0.5	0.5	0	0
14	0.25	0.75	0	0
15	0	1	0	0

Table 3b: Acid concentrations (g.L^{-1}) for the design (mixtures with valeric acid)

Number	Acetic (C2)	Propionic (C3)	Butyric (C4)	Valeric (C5)
16	0	0	0.75	0.25
17	0.25	0	0.5	0.25
18	0	0.25	0.5	0.25
19	0.5	0	0.25	0.25
20	0.25	0.25	0.25	0.25
21	0	0.5	0.25	0.25
22	0.75	0	0	0.25
23	0.5	0.25	0	0.25
24	0.25	0.5	0	0.25
25	0	0.75	0	0.25
26	0	0	0.5	0.5
27	0.25	0	0.25	0.5
28	0	0.25	0.25	0.5
29	0.5	0	0	0.5
30	0.25	0.25	0	0.5
31	0	0.5	0	0.5
32	0	0	0.25	0.75
33	0.25	0	0	0.75
34	0	0.25	0	0.75
35	0	0	0	1

3. Results and discussion

3.1 Linearity and Stevens' Low

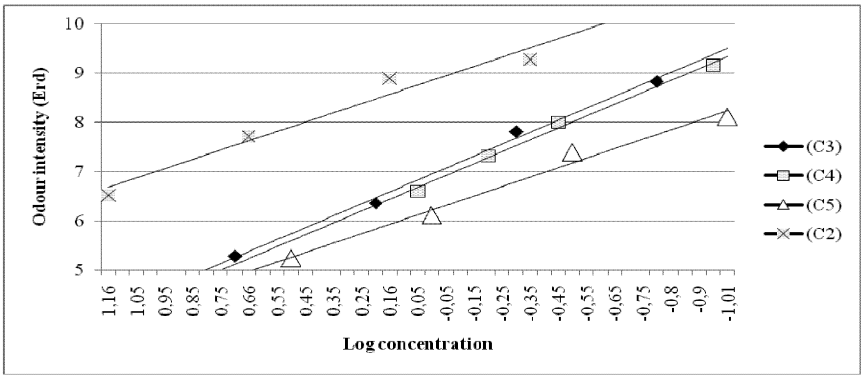


Figure 1: Variation of odour intensity (Stevens slopes) for acids from C2 to C5.

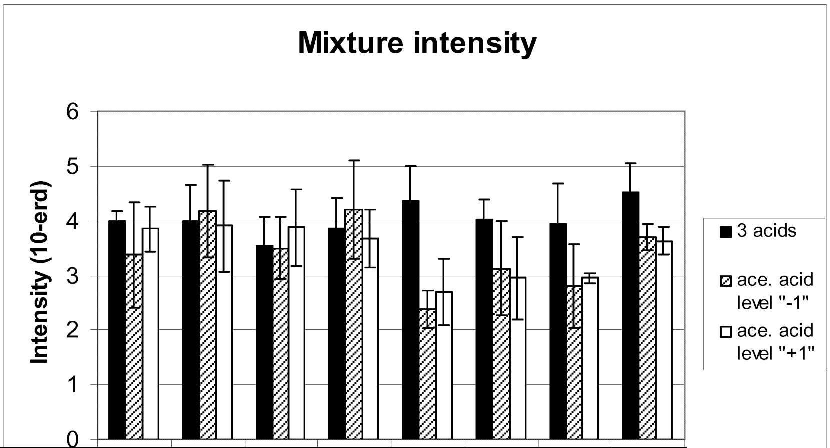
With concentrations from table 1, odour intensities of solutions were measured on the Erd scale. Four plots, shown on figure 1, with odour intensity logarithm measured as a function of concentration logarithm are then obtained. These results show that odour intensities can be considered as linear (in the 5 to 10 Erd range). Considering the slope that defines the persistence, this persistence is increasing with the following classification: Butyric acid = Propionic acid < Valeric acid < Acetic acid. It is easy to see that acetic acid needs higher concentration to give the same odour intensity.

3.2 Experimental design

The intensities of three component mixture (in 10-erd), shown in figure 2, are around 4. In the first four cases, no significant difference is observed even with the addition of acetic acid. However the four next mixtures, when acetic acid is added, the intensity decreases significantly (for both -1 and +1 levels). It means than the amount of acetic acetic in the defined range is not important but the presence of this acid at -1 level at least. The link with the mixtures presenting a decreasing intensity is that propionic acid states at +1 level and that acetic acid is present.

Two phenomena can justify these results:

- An interaction of acetic acid with propionic acid that causes a global inhibition;
- Acetic acid is prickly. This characteristic is transmitted by trigeminal system and trigeminal stimuli can inhibit the signal of the olfactory to the brain. (Brand, 2006 ; Frasnelli and Hummel, 2007).



Propionic acid (C3)	-	-	-	-	+	+	+	+
Butyric acid (C4)	-	-	+	+	-	-	+	+
Valeric acid (C5)	-	+	-	+	-	+	-	+

Figure 2: Mixture intensities (3 component mixtures are shown in black; in grey and white, acetic acid is added respectively at -1 and +1 levels).

3.3 Mixture design

The results are shown in figure 3. Two groups can be distinguished: from the 1st to the 15th bottle (intensity is 3.5 ±0.3) and from the 16th to the 35th bottle (intensity is 4.2 ±0.3). The difference between these two groups is the absence or the presence of valeric acid. With these data, a surface response model can be proposed (calculation with Nemrodw software). Such surfaces responses indicate that without acetic acid, a mixture of acids is always more intense than one acid alone. Valeric acid increases the response especially when it interacts with propionic or acetic acids.

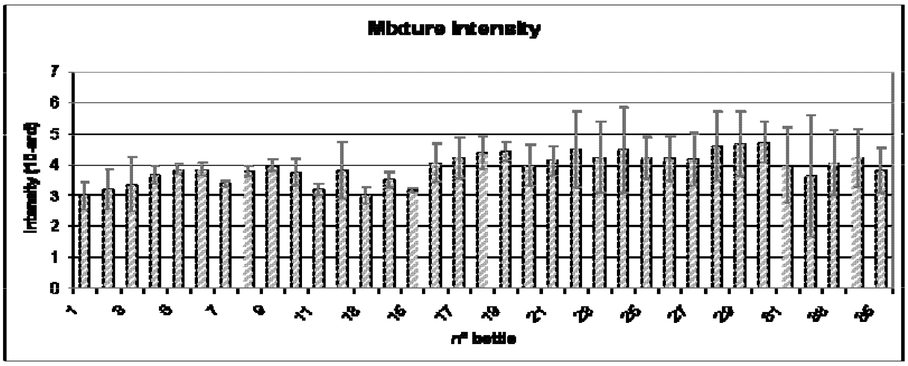


Figure 3: Mixture intensities (Number 1 to 15: without valeric acid).

4. Conclusion

The approach with experimental design to study odour intensity had demonstrated potential inhibition and synergy of acetic acid and valeric acid respectively.

References

Brand G., 2006, Olfactory/trigeminal interactions in nasal chemoreception, Neurosci. Biobehav. Res, 30, 908-917.

Bories A., Guillot J.M., Sire Y., Couderc M., Lemaire S.A., Kreim V. and Roux J.C., 2007, Prevention of volatile fatty acids production and limitation of odours from winery wastewaters by denitrification, Water Res.41, 2987-2995.

Comanici R., Gabel B., Gustavsson T., Markovitsi D., Cornaggia C., Pommeret S., Rusu C. and Kryschi C., 2006, Femtosecond spectroscopic study of carminic acid-DNA interactions, Chemical Phys., 325, 509-518.

Frasnelli J. and Hummel T., 2007, Interactions between the chemical senses: Trigeminal function in patients with olfactory loss, Int. J. Psychophysiol., 65, 177-181.

Petruccioli M., Duarte J., Eusebio A. and Federici F.,2002, Aerobic treatment of winery wasterwater using a jet-loop activated sludge reactor, Process Biochem., 37, 821-829.

Racault Y., Stricker A.-E. and Vedrenne J., 2002, Les effluents vinicoles: problématique du traitement et premier bilan sur la conception et le fonctionnement des procédés biologiques, Ingénieuries, 32, 13-26 (in french).