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Introducing organoleptic components into wine fermentation modelling: preliminary results

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Abstract: This paper deals with the introduction of the dynamics of some organoleptic compounds in the modelling of wine fermentation. The modelling proceeds in two steps: first the selection of the basic dynamical model (without organoleptic compounds) and the identification of its parameters, and the consideration of the five measured markers and their relation of the process variables. It is shown that those compounds that have been considered exhibits a strong relation with the CO_2 production.

Keywords: Biological systems, modelling, wine fermentation, organoleptic components.

1. INTRODUCTION

Wine making is among the oldest fermentation processes. Wine is basically produced by the fermentation of glucose of the grapefruit into ethanol by yeasts (*Saccharomyces cerevisiae*). If the quality and taste of wine has undergone major changes over the centuries, and if many factors intervene in the taste of a wine, the taste of wine is closely linked to the combination of organoleptic compounds, typically higher alcohols, fatty acids, esters and sulfur compounds, produced during the fermentation, and this although they represent less than 1 % of the consumed sugar and 4% of the produced yeast cells. Identifying the link with the organoleptic compounds and the taste of wine can indeed be very important from the winemaker point of view, e.g. in order to maintain the same taste of one specific wine and therefore to allow to build customer loyalty to one specific wine, an essential issue for many winemakers. And formalizing this link into reliable dynamical models opens the floor for developing appropriate control strategies in order to guarantee the production of the key organoleptic compounds for one specific wine.

Modelling and control of ethanol fermentation is an active research area for many decades. For instance Sevely et al. (1981) combines modelling, identification and control of a cascade reactor. Numerous publications have been concentrating on the ethanol fermentation (see Boulton (1980); Salmon et al. (1993); Slaughter et al. (1991); Caro et al. (1991); Marin (1999)). In 2001, Cramer et al. (2002) proposes a dynamical model that accounts for the nitrogen as limiting substrate for the yeasts. In line with this work, David et al. (2010); David et al (2014) proposed, in the context of the EC project CAFE, to introduce the notion of transporters to further improve the modelling of the ethanolic fermentation. In this context, a controller has been designed and implemented on a multi-stage reactor to control the glucose concentration in each reactor by incorporating a specific anti-windup mechanism (see Casenave et al. (2014, 2019)). Indeed the use of four reactors in cascade refers to the notion of space-time well known in (bio)reactor design to emphasize the analogy between batch reactors and plug flow reactors. The four reactors in the cascade simulate a plug flow reactor and in terms of the space-time analogy, the steady state in each reactor corresponds a specific time in the ethanolic fermentation.

In terms of modelling, a different type of model for the ethanolic fermentation has been developed and experimentally validated that includes a maintenace term (see Rapaport et al. (2022)). However the incorporation of the organoleptic compounds into the ethanolic fermentation has not been considered, largely due to the lack of on-line data of these markers, that are intrinsically difficult to measure due to their very low concentrations.

The main result of this paper is to present a model of the ethanolic fermentation based on that of David et al (2014) that incorporates five aromatic molecules (isobutanol, isoamyl alcohol, isoamyl acetate, ethyl hexanoate, ethyl octanoate). For instance, the isoamyl acetate, the ethyl hexanoate, and the ethyl octanoate are responsible for the aroma of banana, blackberry and pear, respectively. The link of these three markers with the CO_2 production will be emphasized. The obtained results are illustrated on some of the experimental data. An exhaustive presentation of the results can be found in Philippe (2022).

The paper is organized as follows. We first introduce the basic dynamical model that considers the growth of yeast on nitrogen and the synthesis of ethanol from glucose. Section 3 is dedicated to the identification of the

parameters of the basic model. And Section 4 concentrates on the introduction of the organoleptic compounds into the fermentation model.

2. BASIC DYNAMICAL MODEL

The basic dynamical model, i.e. the one considering yeast growth and ethanol synthesis, is a slightly modified version of the model derived in David et al (2014). The modifications have been largely justified by the set of data that have used in the present study that considers a different yeast strain than that in David et al (2014). In particular, the data are exhibiting a delay between the yeast growth and the nitrogen consumption, which has led to the introduction of two nitrogen concentrations (in the reactor and in the cells), and a delayed yeast concentration. Besides preliminary identification has emphasized a very low influence of the transporters on the fermentation dynamics, this has led to remove them from the model. The model equations in a batch reactor read as follows:

$$\dot{X} = \mu_{max} \frac{N_x}{K_x X + N_x} X \tag{1}$$

$$\dot{N}_x = -k_1 \mu_{max} \frac{N_x}{K_x X + N_x} X \tag{2}$$

$$\dot{X}_d = \delta (X - X_d) \tag{3}$$

$$\dot{N}_{x,d} = -k_1 \dot{X}_d \tag{4}$$

$$\begin{aligned} \dot{E} &= C\dot{O}_2 \\ &= \left(\beta_{max,1}(T) \frac{N_{x,d}}{K_x X_d + N_{x,d}} \right. \\ &\quad \left. + \beta_{max,2} \frac{K_E}{K_E + E} \right) \frac{S}{K_S + S} X_d \end{aligned} \tag{5}$$

$$\dot{S} = -k_2 \dot{E} = -k_2 C\dot{O}_2 \tag{6}$$

$$\tag{7}$$

In the above equations, X, N_x, X_d, $N_{x,d}$, E, S and CO_2 represent the yeast concentration, the nitrogen concentration in the reactor, the delayed yeast concentration, the intracellular nitrogen concentration, the ethanol concentration, the glucose concentration and the CO_2 concentration, respectively. Note that a Contois model has been considered for the yeast growth where μ_{max} and K_x are the maximum specific growth rate and the Contois constant, respectively. Note also that another Contois model has been considered in the ethanol equation for the delayed yeast (with another maximum specific growth rate, $\beta_{max,1}$, while there is an inhibition term with respect to the ethanol (with $\beta_{max,2}$ and K_E as maximum reaction rate and inhibition constant, respectively), and also a Monod kinetic expression (with K_S as the saturation constant) for the transformation of glucose into ethanol. k_1 and k_2 are yield coefficients, while δ is the delay parameter between nitrogen consumption and yeast growth.

On the whole, there are 9 parameters to be identified for the basic model. Yet only 8 parameters will be identified since the yield coefficient k_2 is known to be equal to 2.17 (Bely et al. (1990)). Since the experiments had been performed at different temperatures, we might expect to have several kinetic parameters to be dependent on the temperature.

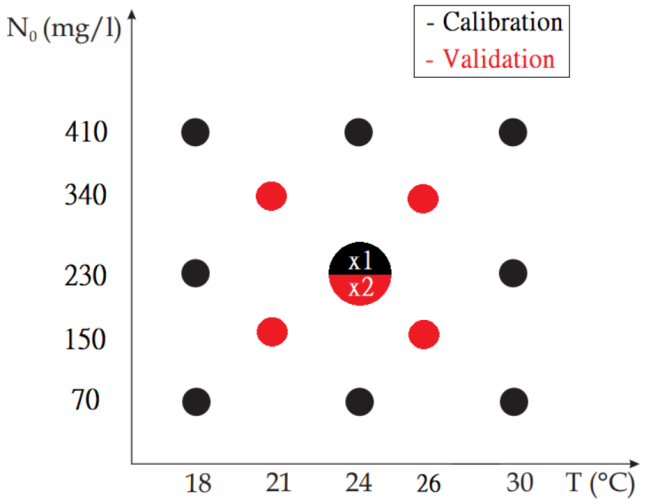

Fig. 1. Spectrum of experiments as a function of temperature and initial nitrogen concentration

3. PARAMETER IDENTIFICATION

A set of data for 15 experiments performed at the oenology lab of the INRAE in Montpellier and that includes data for 5 organoleptic compound concentrations (isobutanol, isoamyl alcohol, isoamyl acetate, ethyl hexanoate, ethyl octanoate) have been considered for the parameter identification, first of the basic model, then to include the organoleptic compounds. 9 experiments have been used for calibration, and 5 for validation (see Figure 1).

The parameter calibration has been performed in two steps: first the calibration of the parameters μ_{max}, K_x, δ and k_1 from the data of yeast and nitrogen concentrations, then the calibration of the other 5 parameters by using the data of glucose and CO_2.The parameter values are summarized in Table 1. It happens that it was not possible to give constant constant values, and correlations have been identified for the dependence μ_{max}, δ, $\beta_{max,1}$, $\beta_{max,2}$, $K_S(T)$ and $K_E(T)$ (see Table 2)(with an extra dependence to N_0 for $\beta_{max,2}$: $\beta_{max,2}(T, N_0) = -0.0015 \times T^2 + 0.0855 \times T - 1.423 \times 10^{-6} \times N_0^2 + 1.556 \times 10^{-3} \times N_0 - 0.8632$).

It is worth noting that an important objective in the parameter identification was to avoid dependence of the parameters with respect to the initial nitrogen concentration N_0. Yet, as mentioned in the above paragraph, we had not been able to get a satisfactory identification without a dependence of $\beta_{max,2}$ with respect to N_0. A possible explanation is that this might be due to the fact that we had been neglecting the transporters' dynamics in the model.

A example of model prediction for calibration data is shown in Figure 2. Model validation has been performed on data sets that did not have measurements of yeast and nitrogen, as illustrated on Figure 3.

4. INTRODUCTION OF ORGANOLEPTIC COMPOUNDS IN THE MODEL

Now that the basic dynamical model (1)-(6) has been identified, let us concentrate on the introduction of five markers (isobutanol, isoamyl alcohol, isoamyl acetate, ethyl

Table 1. identified values of the model parameters

Parameters	Distribution of values	Units
T	18 - 30	°C
$\mu_{max}(T)$	0.085 - 0.214	h^{-1}
K_x	0.0135	-
k_1	0.0566	-
δ	0.046 - 2.7167	h^{-1}
$\beta_{max,1}(T)$	0.1848 - 0.4827	h^{-1}
$\beta_{max,2}(T, N_0)$	0.3007 - 0.7759	h^{-1}
$K_S(T)$	5.8936 - 4.0472	g/l
$K_E(T)$	29.1905 - 86.5721	g/l

Table 2. temperature dependences

Model : $aT^2 + bT + c$			
Parameters	a	b	c
$\mu_{max}(T)$	-0.003	0.0247	-0.266
$\beta_{max,1}(T)$	0.0011	-0.0258	0.3072
$K_E(T)$	0.2334	-7.2538	94.1436
$K_S(T)$	0.0086	-0.5685	13.3282

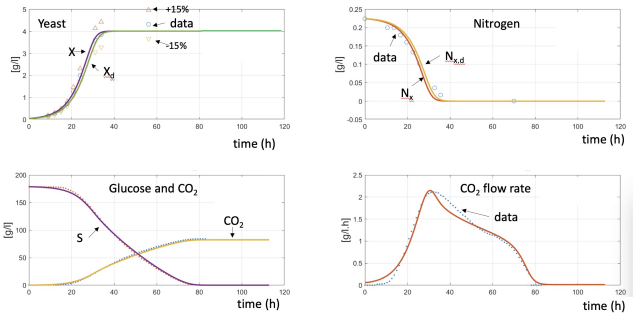

Fig. 2. Model prediction for the dataset at T = 24°C and N_0 = 410 mg/l

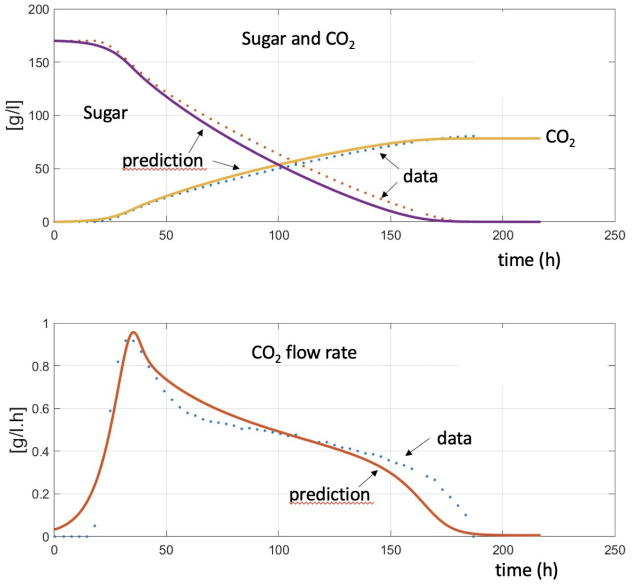

Fig. 3. Model validation for the dataset at T = 21°C and N_0 = 150 mg/l

hexanoate, and ethyl octanoate) for which experimental data used for the parameter identification are available.

Figures 5 shows the experimental data for isobutanol. The other four markers are not presented here due to size

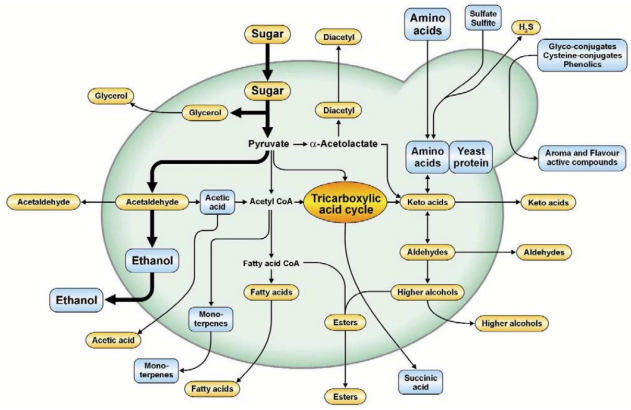

Fig. 4. Schematic view of the synthesis of the aromatic compounds coming from the metabolism of sugar, amino-acids and sulfur compounds

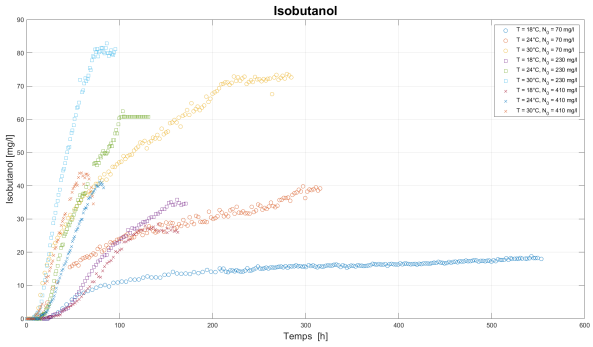

Fig. 5. Isobutanol data for the 9 calibration batchs

limitation of the final version to be submitted to the World Congress, and we shall mainly concentrate on the study of isobutanol in the present paper. First note that the organoleptic compounds exhibit different kinetic profiles as a function of the initial nitrogen concentration N_O. In particular, at N_O = 70 mg/l, the production is lower and with a slower rate. It should be noted that there are differences among the different markers with respect to the dependence to the temperature. In particular isoamyl acetate and ethyl hexanoate (not shown here) appear to be less sensitive to the temperature.

Let us now proceed with the study of the relations between the five markers and the process variables. This has been performed with the 9 calibration data sets. Figures 6 illustrates it with the dataset of isobutanol at T = 24°C and N_0 = 230 mg/l, with 4 graphs in each figure, comparing the normalized value of the organoleptic compound with those of X and N_x (figure a), of S and CO_2 (figure c), and of the CO_2 flow rate (figure d)(the last one, figure b, being the unnormalized data of the organoleptic compound) [1] . The first observation is that the isobutanol has a behaviour quite similar to that of the CO_2 production (the same observation can be done for the other four markers). The start of of the production of the markers is almost

[1] Here again, the results for the other four markers are not presented here due to size limitation of the final version to be submitted to the World Congress, and we shall mainly concentrate on the study of isobutanol

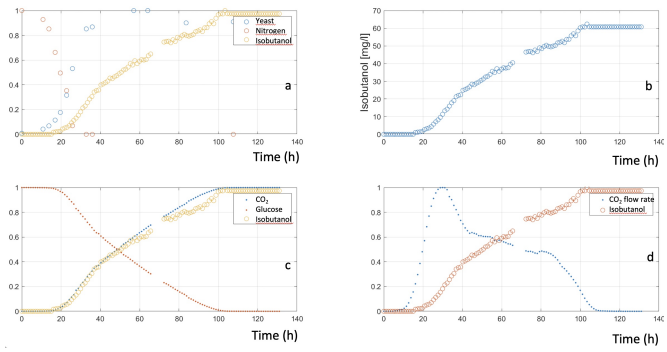

Fig. 6. Comparison of isobutanol data with X, N_x, S, CO_2 and CO_2 flow rate

simultaneous to that of the CO_2 as well as that of the yeast growth. The same conclusion can indeed be drawn for each dataset.

From the above observations, two ideas have been explored. First, due to the good adequacy between the production of the five organoleptic compounds and that of the CO_2, it might be of interest to consider kinetics expressions similar to that of the CO_2, common to all the compounds, yet with specific features, e.g. to account for the initial conditions. A second idea is to explore the link with yeast since it is a central component of the fermentation, and since its growth starts along with the start of the production of the organoleptic compounds. With these in mind, two modelling expressions have been tested:

$$\dot{x}_i = \lambda_i C\dot{O}_2 \tag{8}$$

$$\dot{x}_i = \gamma_i \dot{X} \tag{9}$$

with $i = 1$ to 5, corresponding to each of the five organoleptic compounds. Figures 7 and 8 present the identification results comparing the data of two organoleptic compounds (isobutanol and ethyl octanoate) with the prediction with the identified λ_i and γ_i (Figure a corresponds to the comparison for the CO_2 dependence while Figure b corresponds to that for the dependence on X) for the same dataset as before ($T = 24°C$ and $N_0 = 230$ mg/l). The first conclusion that has been expected is that the correlation between the dynamics of the organoleptic compounds and the yeast is not good. Looking at each Figure a, we note that, on the whole, adequacy is rather satisfactory.

The result for isobutanol (Figure 15a) is quite good except that the plateau is reached a little too early. The result for $T = 18°C$ and $N_0 = 70$ mg/l is not very good (see Figure 20), which might be an effect of the low initial nitrogen concentration.

For the two isoamyls (not shown here), the results present the same type of trend with a faster increase and a lower plateau in the simulated values. Note that the isoamyl acetate is produced from the isoamyl alcohol, and a better understanding of the metabolic pathway between these two compounds might help to get better modelling expressions.

The adequacy (not shown here) between the ethyl hexanoate data and its prediction with the dependence with CO_2 is very good, as in the case of the isobutanol. For

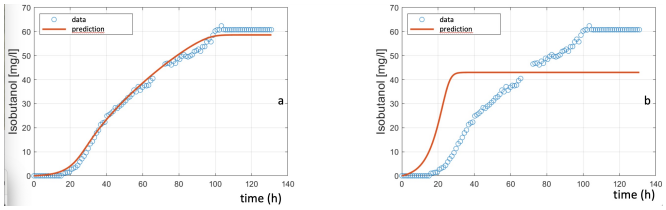

Fig. 7. Comparison of isobutanol data with the dependence on CO_2 and X for the identified λ_1 and γ_1

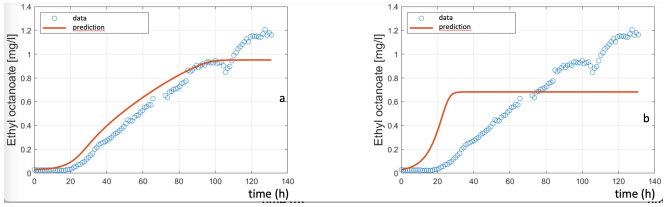

Fig. 8. Comparison of ethyl octanoate data with the dependence on CO_2 and X for the identified λ_5 and γ_5

the ethyl octanoate, the adequacy is quite good until $t = 100$ when the prediction is reaching a plateau. Here again a better understanding of the metabolic pathway of the synthesis of ethyl octanoate should be helpful to improve its dynamical model.

5. CONCLUSION

This paper has been concentrating on the introduction of 5 organoleptic compounds (isobutanol, isoamyl alcohol, isoamyl acetate, ethyl hexanoate, and ethyl octanoate) in the modelling of the ethanolic fermentation for the wine production. The modelling has proceeded in two steps: first the identification of a basic dynamical model that concentrates on the yeast growth and the ethanol synthesis, then the characterization of some dynamical between the 5 organoleptic compounds and the process state variables. The first important conclusion is the relation between the production of CO_2 and that of the five markers. Yet this is a very preliminary step, and many improvements should be done by considering the specificities of each compound, in particular in their respective metabolic pathways.

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