DSS for winemaker: A dynamic modeling approach

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Abstract. We present a decision support system for the fermentation step in winemaking based on a mathematical model of kinetics of alcoholic fermentation. We used an optimization technique in order to predict the fermentation step. This optimization technique was carried out using the method of factorial analysis. The first interesting application of this system, rather than existing ones, comes from the fact that it can predict the evolution of pH during alcoholic fermentation. Recall that pH is used in oenology as an indicator of censorial properties, efficiency of sulfating and contamination risks. The second interesting application of this software is that it allows users "online" monitoring of the evolution of the constituents of grape musts.

Keywords: dynamic modeling, simulation, optimization, decision support systems, oenology.

1 Introduction

Decision support systems (DSSs) are generally designed for supporting decision makers in their decisional processes. Decision support systems are born in the 70's [1] and [2]. Their background has first of all to be presented.

Difference between Information and Decision must be shown. Decision-makers must take into account a lot of information coming from different entities and have sometimes a large amount of information to aggregate in order to reach the best solution. They need a personal and direct control on systems, which are designed for them. Decision and Information have to be classified referring to the level of management. We could distinguish three levels of management: operational level, control level and strategic management level. According to [3] at the operational level, information is numerous and very detailed. The same phenomenon could be observed for decision: there are a lot of decisions to make at the operational level and information usable for them is also in great proportion. At the control level, information is less numerous than in the previous case and decisions to make are more important. Information at this level is more aggregated. At the strategic management level, information is aggregated and not numerous and decisions to make have a very high impact in the management [4].

Decision-makers have to be supported in their task by systems like Decision Support Systems regardless of the level of management type.

The decisional process handled by "winemakers" is generally not supported by software and it still remains a human process. Nevertheless, some systems have been developed in order to improve the production of wine and more specifically the organization of wine-makers cooperatives. For example [5] has developed a DSS in order to organize the production of wine.

Independently from the organization of the wine-maker cooperatives, the control and understanding of the alcoholic fermentation has been a subject of many investigations in the last few years. Indeed, several models of fermentation kinetics have been proposed and constitute the base of few existing decision support systems. [6] developed software named MEXTAR, which can be used to simulate alcoholic fermentations by combining kinetic and thermal models. [7] obtained good results on the prediction of the crystallization of tartaric salts in hydro-alcoholic solutions by using MEXTAR. However, the MEXTAR software did not take into account the evolution of pH. Recall that the optimization criteria of the quality of wine are generally accessible only by sensory analysis. This technique is very expensive and is not best suited to the control of alcoholic fermentation. Moreover, the pH is considered as an important decision criterion by winemakers and therefore, pH is an interesting indicator for the quality of wine which can at least replace the sensory analysis[1].

In this sense, [8] has developed a model to predict accurately pH evolution during alcoholic fermentation of must. We first extend this model to take into account amino acids and then use in the software that we developed. In this context, our main objective is to develop a modeling tool able to simulate the evolution of pH during fermentation and it is designed to assist winemakers to optimize tank management and to act upstream, if necessary, in the process.

Our approach is based on a mathematical model to predict the evolution of pH over time during fermentation. To develop this mathematical model, we use the data obtained by [8] from the fermentation in synthetic and natural grape. We have introduced into the mathematical model for predicting pH from the initial composition of the medium species of positively charged amino acids, neutral charge and negative charge and the dissociation equilibrium constraints. To establish a dynamic model of the alcoholic fermentation, it must first control the parameters that influence the evolution of pH throughout the fermentation. To do this, we conduct a sensitivity study on the constituents of the must to remove any component that does not have a great influence on the evolution of pH during fermentation. With this sensitivity analysis we have identified six principal constituents namely, the sugar, ethanol, biomass, amino acids, carbon dioxide and nitrogen.

This work is divided into four parts. The first part is introductory, and it contains the construction of the mathematical model and gives a preliminary analysis needed for the rest of this work. In particular, we give and test the validity of the mathematical model for predicting the evolution of pH during the alcoholic fermentation. We also describe the kinetic model and give dynamic characteristics of the process.

The purpose of the second part is to develop a decision support system for fermentation in winemaking by using the mathematical model of kinetics of alcoholic

[1] Sensory analysis consists in using human sensory to define the quality of the product.

fermentation developed in the first part. We first give a complete database that lists all components required for the inputs of the mathematical model developed before. The rest of this section is devoted to the decision support system and its functionalities.

Finally, in the last part, we validate the software by using four different mediums whose composition is well known.

2 Models and simulation

The purpose of this section is to develop a mathematical model for predicting the evolution of pH during the alcoholic fermentation. This model is required to construct the decision support system and is part of the Model Base of the global system.

2.1 pH simulation

[8] proposed a model to predict pH evolution during alcoholic fermentation of specific must by the microorganism QA-23 [9]. To do this, [8] used two kinds of models. The first one is used to calculate pH knowing the composition of the medium and the second model represents the dynamic of fermentation to find the evolution of the composition of the medium.

pH as a mathematical function

As shown in the introduction, the pH value is an important decision criterion for winemaker and it is necessary to give a mathematical model able to predict its evolution. To do this, we first establish the mathematical function modeling the evolution of pH.

pH is a measure of the acidity of a solution and it expresses the activity of hydrogen ions. The mathematical formula of pH, using a logarithmic scale, is given by:

where $\gamma H+$ is the ion activity coefficient and $mH+$ is the molality of hydrogen ions. The activity coefficient $H^{+}(_{H+})$ is calculated using the method of [10].

By writing a mass balance on each species in solution, one can easily formulate the reactor model and then get a model including as many variables as the number of reactions in the medium. Otherwise, we will show in the next section that the number of reactions in the medium is reduced to three reactions.

The initial model developed in [8] takes into account: the temperature, the concentrations in sugar, ethanol, nitrogen compounds, mineral elements and some organic acids. We extend this model by adding mainly amino acids.

The initial difficulty can be overcome by reducing the numerical problem which is easy by writing the mass balance on an invariant of the reactive system. Then, the pH value is determined by solving a non-linear algebraic equations system consisted of mass balances, chemical equilibrium equations and the principle of electro-neutrality. Model implementation and simulations were carried out using fortran90 language. This enabled the application of different numerical methods and the Runge-Kutta fourth was used in all simulations.

Model validation

In order to test the validity of the model, the synthetic medium was used and its constituents composed the inputs of the model. This medium was chosen because its composition is perfectly known. Experimental and simulated pH values are in a well agreement as shown in Figure 1.

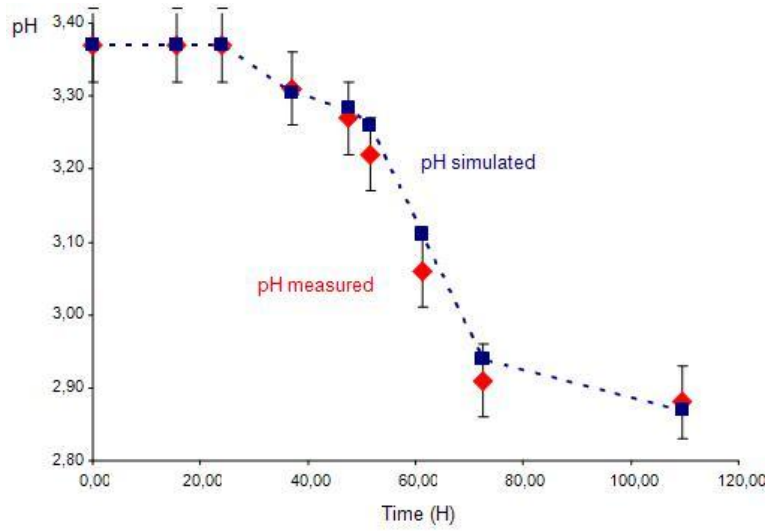

Fig. 1. pH evolution

2.2 Kinetic model

Decision support criterion to be developed here requires modeling the evolution of each component that significantly influences the pH during the alcoholic fermentation. To do this, it is necessary to study the kinetic of the reaction scheme obtained by the study of sensitivity. According to the study of sensitivity, the compounds of the fermentation to be modeled are sugars, ethanol, biomass, amino acids, carbon dioxide and nitrogen. These constituents were specifically determined for alcoholic fermentation in winemaking conditions and based on the initial conditions. Taking into account the results of the study of sensitivity, the reaction scheme we have adopted is:

- Production of ethanol from glucose
- Biomass production from amino acids and sugars.

Therefore, this reaction scheme can be schematically represented as:

(R1): $C_6H_{12}O_6 \rightarrow 2CH_3 - CH_2 - OH + 2CO_2$

(R2): $C_6H_{12}O_6 + aNH_3 \rightarrow bCH_xO_yN_z + cCO_2 + dH_2O$

(R3): $CH_pO_qN_r + iC_6H_{12}O_6 \rightarrow ebCH_xO_yN_z + fCO_2 + gH_2O + hNH_3$

where *a*,*b*,*c*,*d*,*e*,*f*,*g*,*h* and *i* are the stochiometric coefficients to be found by the carbon balance, $CH_xO_yN_z$ and $CH_pO_qN_r$ are respectively the molecular formula of biomass and amino acids.

The constants *x*,*y* and *z* are calculated from elemental analysis of biomass. However, the molecular formula of the amino acids cannot be calculated directly. The experimental data used in this study takes into account 23 types of amino acids. The rate of consumption of each amino acid is almost the same. Therefore, it is very interesting to find a molecular formula $CH_pO_qN_r$ of one group of amino acids. To do this, we will take the CHON (carbon, hydrogen, nitrogen and oxygen) formula equal to the average of each amino acid formulas, weighted by the initial concentration of each amino acid in the reaction. Consequently, the molecular formulas of biomass and amino acids become respectively $CH_{1.79}O_{0.5}N_{0.2}$ and $CH_{2.14}O_{0.47}N_{0.43}$.

By using the above equations and the carbon, oxygen, hydrogen and nitrogen balance, the following four different sets of linear algebraic equations are derived:

(1):

The number of unknowns in the above system exceeds the number of equations and, therefore, it cannot be solved directly. To solve this system we first use a factor analysis for mixed data see [11, 12] and then use the optimizer by setting the stochiometric coefficient of biomass *e*, and respecting the carbon, hydrogen, nitrogen and oxygen balance for the stochiometric coefficients. According to our experiments data, the optimal value of *e* is equal to 10.60.

2.3 Mathematical model

The purpose of this part is to model the evolution of compounds that significantly influence the pH during the alcoholic fermentation. The components included in this study, are the following: sugar, ethanol, nitrogen, CO2, biomass and amino acids. Models representing the dynamics of these compounds in wine are not available in the literature. They should be developed to obtain a final model that could predict the development of lead compounds, to calculate the duration of fermentation and give at any time the pH of must. The various mathematical models most frequently used to represent the kinetics of microbial growth are summarized in Table 1. These models are all based on establishing a mass balance on one or more components.

Table 1. Mathematical models representing the kinetics of microbial growth

Model	Maximum specific cellular growth rate
Moser(1958)	$\mu = \mu_{max}\ S^n / S^n + K_s$
Hanson and Tsao(1972)	$\mu = \mu_{max}\ S^n / S^n - K_s$
Andrews (1968)	$\mu = \mu_{max}\ S / (K_s - S)(1 + SK_l)$
Han and Levenspiel(1988)	$\mu = \mu_{max}\ (1 - SS_n)^n\ S / S + K_s\ (1 - SS_n)^m$
Aiba et coll.(by Han and Levenspiel)	$\mu = \mu_{max}\ \exp(-SK_l)\ S / K_s + S$
Teissier. (by Han and Levenspiel)	$\mu = \mu_{max}\ \{ \exp(-SK_l) - \exp(-SK_s)\}$

Luong(1987)	$\mu = \mu_{max} (1 + SS_c)^n S / S+K_s$
Aiba et coll. (1968)	$\mu = \mu_{max} K_p P S / K_s + S + K_p$
Kishimoto et coll. (1983)	$\mu = \mu_{max} S / (K_p + S)(1 + P^2)$
Han and Levenspiel(1988)	$\mu = \mu_{max} S(1 - PP_c)^n / S + K_s(1 - PP_c)^m$
Luong(1987)	$\mu = \mu_{max} (1 - KP) S / K_s + S$
Aiba et coll. (1968)	$\mu = \mu_{max} \exp(-KP) S / K_s + S$

Dynamic characteristics of the process

It was observed in [13, 14, 15, 16] that the evolution of pH depends only on the kinetic of the considered reactions. Therefore, let r_1, r_2 and r_3 be the speeds of the three previous reactions *R*1, *R*2 and *R*3 respectively. The following equations describe the time course of biomass, ethanol, sugar, amino acids and nitrogen:

(2):

where *X*, *Eth*, NH_3, CO_2, *AA* and *S* correspond respectively to biomass, nitrogen, carbonic anhydride, amino acids and sugar.

We have a system of six differential equations of first order. To solve it we must give explicit expressions of r_1, r_2 and r_3.

According to [17], [18], the production of biomass from sugar is given by the following equation:

(1)

where μ_{max} is the maximal specific growth rate and the saturation parameter to be found.

However, according to our experimental data, the production of biomass depends also on nitrogen concentration. It is therefore necessary to take into account this concentration in the last equation. Therefore, the equation (1) can be formulated as bellow:

(2)

For the first reaction, we use the generalized logistic model, which serves conveniently for mathematical fitting. Consequently, the rate at which the concentrations of ethanol and sugar change is given by the following equation:

$r_1 = k_1 [X] [S]$ (3)

By the experimental data used to develop this model, we remark that the speed of the last reaction is proportional to the concentration of amino acids, namely:

$r_3 = k_3 [AA]$ (4)

With respect to the expression of *r*1, *r*2 and *r*3, the dynamic model is described by the following differential equations:

(3):

Parameters Determination

The purpose of this part is to describe how to find optimal parameters which make agreed simulated results from the equations system and experimental data. To do this, we used the system of differential equations to recalculate the concentrations of each component of the each environment studied.

The following partial criterion

$$Crit = \frac{}{}$$

is chosen for each component and then a global criterion which is equal to the sum of all criteria. For each fermentation medium, we then used an optimizer to find the best values of system parameters.

3 Oenodecision: the Decision Support System

The second part of this work is to develop the decision support software for fermentation in winemaking by using the mathematical model of kinetics of alcoholic fermentation developed in the first part of this paper. As mentioned previously, the proposed system is composed by a data base, a model base and a user friendly interface. The model base is described in the previous section and the data base is developed in the next section. The conceptual model of the data is built on specifications in Entities-Relationship model as shown in Figure 2.

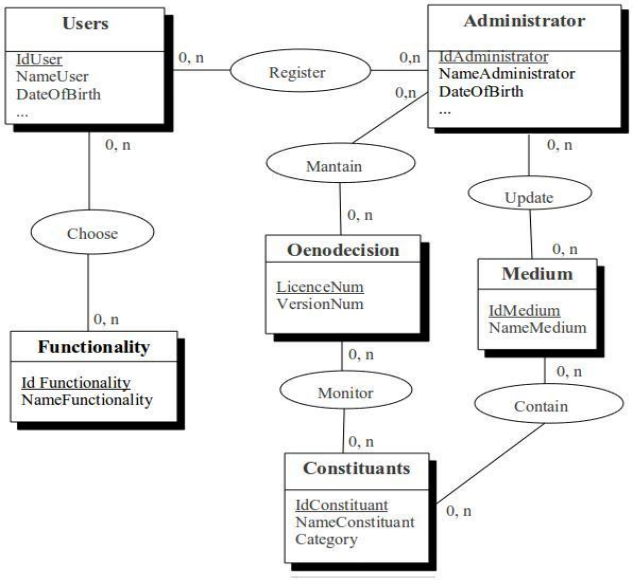

Fig. 2 Conceptual model of data

This software is designed to allow the user to easily set up a system to monitor up to six variables (the concentrations in sugars, biomass, ethanol, amino acids and nitrogen) but it can be easily extended for other inputs.
Our objective was to develop a system available in a Web platform; it is implemented thanks to MySQL for the database and PHP for the interface. FORTRAN90 was used to solve the dynamics models and the model base is usable by the system through a DLL routines.

3.1 The Database

The Database is composed by 12 tables. Some tables are very simple and are not described in this study. We only describe the tables Constituents and the table Users.

Based on the figure 2, the relational schema is the following:
CONSTITUANTS (IdConstituant , NameConstituant , Category)
USERS (IdUser , NameUser , DateOfBirth,…)
ADMINISTRATOR (IdAdministrator , NameAdministratot , DateOfBirth,…)
MEDIUM (IdMedium , NameMedium)
FUNCTIONALITY (Id_Functionality , NameFunctionality)
OENODECISION (LicenceNum , VersionNum)
REGISTER (IdUser* , IdAdministrator*)
MAINTAIN (IdAdministrator* , LicenceNum*)
CHOOSE (IdUser* , Id_Functionality*)
UPDATE (IdAdministrator* , IdMedium*)
CONTAIN (IdMedium* , IdConstituant*)
MONITOR (LicenceNum* , IdConstituant*)

Database table: CONSTITUANTS

Developing software monitoring the evolution of constituents of grape must, according to the evolution of pH, requires a database that lists all chemical components that influence the kinetics of alcoholic fermentation. In this study, we create a database including all inputs of the above model. This database can be upgraded easily by other entries according to the evolution of the mathematical model.

According to experimental data on which this study is based, we restrict ourselves to the following components: mineral elements (magnesium, calcium, potassium and sodium), the concentration of sugars, nitrogen compounds, mineral elements (magnesium, calcium, potassium and sodium), main organic acids and amino acids.

Database table: USERS

This table contains personal data of all registered users by using the Registration form. In order to secure the session, users must choose a username and password.

To upgrade this data base, the data tables do not need to be modified. Only the type of data stored in those tables needed to be modified. The proposed interface automatically allows adding new compounds and hence, it requires a minimal maintenance.

3.2 Interactions among DSS modules

All necessary data for ph calculation and simulation are recorded in the Database.
One principal routine written thanks to the PHP language calls two main programs written in Fortran 90. These two algorithms calculate for one the ph level and for the other the evolution of the ph at delta time. These two main programs constitute the models base of the DSS. The date exchanges between the database and the calculation routines are written directly in the PHP code thanks to call functions the database.
The human/machine interface is coded in PHP language.

3.3 Software interface and functionalities

The functionalities of the software developed here are described through a user-friendly interface and provide support for the design and implementation of application facilities as shown in Figure 3.

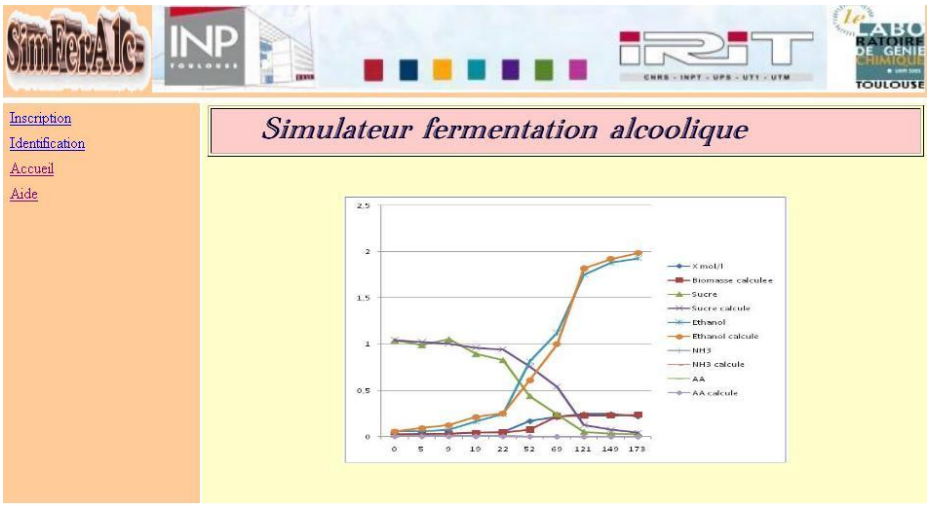

Fig. 3 Software interface

First step: registration and identification

To use this software, a user must first register using the "Registration" form and choose a username and password. The information entered on this form is stored in the local database. The need for a secure session ensures that only the manager of the winery has the privilege to act in the process of fermentation.

Second step: identification and functionalities

Once the new user is registered in the database and has chosen the appropriate login and password, he can now log in and choose between the two essential functionalities of the software described below.

pH simulation:

The first feature of this interface consists on the computation of pH of the fermentation. To predict the final pH value of the fermentation, user completes the initial data from the must of grapes needed for this issue. These data are: temperature, mineral elements (magnesium, calcium, potassium and sodium) and the concentration of sugars, nitrogen compounds, mineral elements (magnesium, calcium, potassium and sodium), main organic acids and amino acids.

The entered data will constitute the inputs of the mathematical model developed in the first part of this paper. Once all required inputs are entered, the user validates by clicking on the button "submit" in the bottom of data form.

After validation, the program written in FORTRAN90 runs automatically in order to integrate the system of differential equations and then returns respectively, the pH value of the end of fermentation and the graphic of the evolution of the pH. The response times are very satisfactory and it is almost instantaneous.

Online kinetic monitoring:

The second feature of this software consists on the online monitoring of fermentation. As shown in the development of the kinetic model and according to the absolute sensitivity analysis that was carried out, the compounds of the fermentation

to be monitored in this software are sugars, ethanol, biomass, amino acids, carbon dioxide and nitrogen.
The user selects the feature that allows monitoring the evolution of each component of the medium; a form appears containing boxes to be filled by respectively, the suitable time interval and the initial concentrations of each component of the chosen medium. When the form is filled out, the data from the form is added automatically to the database associated with this software. The user can then choose between three settings:
• View data table with respect to the given time interval;
• View of the graphical display of the results, namely, the evolution curve of each component from the start time to the end of each fermentation (figure 4);
• View the data table and curves simultaneously.

The user has the possibility here to see how the medium will evolve. The winemakers generally know when the fermentation is critical. Thanks to this expertise the system offers them the possibility to check if the fermentation will be critical or not. In that sense the wine-makers judgment is used in order to control the evolution of the fermentation. By this control the quality of the decision will necessarily be improved and by consequence the wine also will be improved.

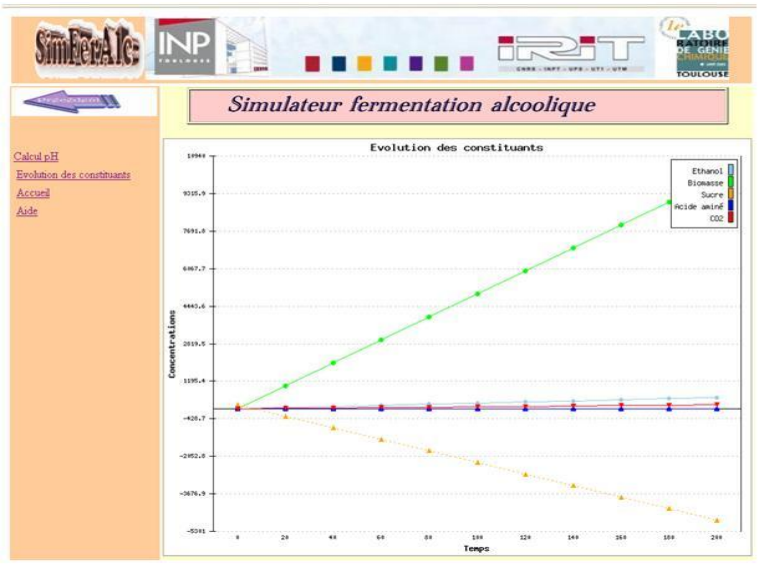

Fig. 4 Curves of simulated compounds

The effect of temperature has been studied by many authors [18, 20, 6], and has a significant effect on the duration of the fermentation and also for the maximum rate of sugar consumption. However, it is important to mention that the temperature is not taken into account in the model and in this software and we assumed that it is kept constant during fermentation. That is not necessarily the case in real life.

4 Models validation

In order to test this software, we worked on four different mediums whose composition is well known. The initial concentrations of sugars, ethanol, biomass, amino acids, carbon dioxide and nitrogen of each medium are injected into the soft and the output results are compared with experimental results.
The experimental data (table 2) used here was those used by Akin, [8] that were obtained during the fermentation of a synthetic grape medium by *S.cerevisae* [20, 21, 22, 23]. The figure 5 below shows the comparison of the evolution of the pH simulated and the pHmeasured during the alcoholic fermentation of the white grape by *Saccharomycescerevisae*.

Table 2: Table of experimental data of synthetic medium

Time (h)	pH	Biomass cel/mL	ethanol (g/L)	amino-acids (mg N/L)	co2 (g/L)
0	3,23	1000000	0,642832	305	0
15,7	3,23	2115340	0,771872	256	1,83
24	3,23	9249600	1,639648	243	2,474
36,937	3,16	46245000	7,435832	163	8,874
42,63	3,13	75845000	14,433968	93	20,09
47,53	3,13	133555000	22,346624	0	26,683
51,58	3,13	171865000	45,51024	0	41,551
61,16	3,15	204050000	59,769808	0	55,251
72,55	3,17	217035000	94,008568	0	85,953
109,54	3,25	22129000	0	0	0

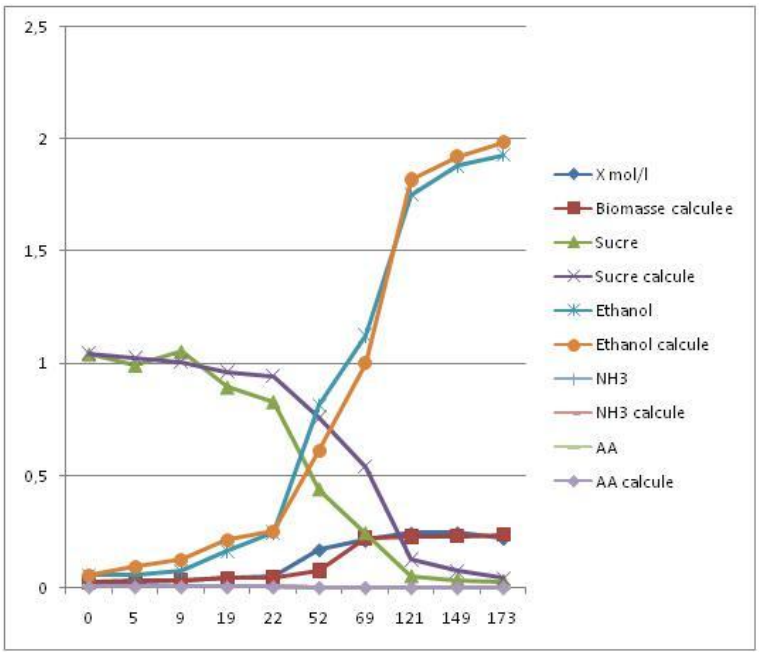

Fig. 5: Evolution of experimental and simulated compounds of grape

In the figure 5, experimental and simulated values of each compound are plotted. As can be seen, the predicted curves and experimental results are in excellent approximation.

5 Conclusion

The presented software is the first software based on the model of prediction of pH. This is contrary to the concept what exists in the literature based on measurements of released during fermentation which is usually difficult **and** very expensive.

We also presented another functionality of the system for fermentation in winemaking based on a mathematical model of kinetics of alcoholic fermentation. The optimization was carried out using the method of factorial analysis. The software developed here can simulate both the evolution of different compounds and predict pH from measurement of the main compounds of the medium.

In order to test different control structures, a parametric sensitivity analysis was carried out. The proposed software has been tested and validated on four different mediums. The system has also been proposed to real winemakers and was really successfully. One way to improve the system usability would be to connect the software to pH sensors.

One limit must be drawn, the model presented here does not take in account variation temperature and we assumed that it is constant equal to 20°c. Therefore, in the long term, the model must be extended to take in account this phenomenon.

Acknowledgments. This work has been conducted in collaboration with the Chemical Engineering Laboratory (LGC: http://lgc.inp-toulouse.fr/) at Toulouse University.

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