

# **Workshop sobre “Instrumentação e Automação Agrícola e Agroindustrial”**

**Projeto Programa de Pesquisa em Políticas Públicas**

**Painel 2:**

**“Etanol de 2ª Geração – Desafios para a  
Instrumentação e Automação”**

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## **Etanol de 2ª geração - desafios para a instrumentação e automação**

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### **Introduction – Production of 2<sup>nd</sup> generation bioethanol**

The great potential for increase in sugarcane production in Brazil and in the forecasted international demand for the bioethanol, as a substitute or complement of gasoline for the reduction of greenhouse gas emissions, motivate the investigation and development of more efficient process configurations for bioethanol production, including processes using lignocellulosic materials as raw materials. Ethanol from lignocellulosic materials (ligbioethanol) has been investigated during the past few years with great interest, but its production in industrial scale has not yet become viable. Studies taking into account process integration, increase of fermentation yields and integration of unit operations are still needed in order to make hydrolysis a competitive technology (Zaldivar et al., 2001; Cardona and Sánchez, 2007).

Bagasse, the by-product of the bioethanol manufacture from sugarcane fermentation, is a very promising raw material for bioethanol production. It is already available on the ethanol plant site, since it is produced in the mills where sugar is extracted from sugarcane, and better technologies of cogeneration allow for increasing surplus of bagasse at plant site. Bioethanol from sugarcane bagasse may share the infrastructure where conventional bioethanol is produced, such as fermentation and distillation units, what diminishes equipment costs. The product obtained after hydrolysis (hydrolyzed liquor) may be diluted in the sugarcane juice, thus decreasing the impacts of potential fermentation inhibitors, such as furfural and its derivatives formed during cellulose hydrolysis.

Typically, in the sugarcane processing, large amounts of sugarcane bagasse are produced (approximately 280 kg of bagasse with 50 % humidity per ton of sugarcane) which are nowadays burnt in boilers for steam and electricity generation. Better technologies for cogeneration and optimization of bioethanol production process allow it to have a bagasse surplus, which may be used as raw material for producing bioethanol and other biobased products. In order to be used as raw material for bioethanol production, sugarcane bagasse must be processed to yield fermentable sugars (e.g., glucose), since its structure is comprised by carbohydrate polymers (cellulose and hemicellulose) and lignin. There are many process configurations that may be used to achieve this goal. The DHR process, which is being tested under semi-industrial scale in Brazil (Rossell et al., 2005), is based on an Organosolv process with dilute acid hydrolysis, in which simultaneous

delignification and cellulose hydrolysis take place in a continuous reactor. Alternative process configurations based on the Organosolv process with dilute acid hydrolysis may consider pre-hydrolysis of the hemicellulosic fraction, allowing its removal prior to cellulose hydrolysis, which takes place at more extreme conditions (temperature, pressure, and pH), consequently increasing sugars decomposition and production of fermentation inhibitors. Since the hemicellulose fraction is easily hydrolyzed, its pre-hydrolysis and the separation of the pentoses produced would allow a more efficient use of the 5-carbon sugars and better fermentation conditions, since *Saccharomyces cerevisiae* can not convert pentoses into ethanol and there is no commercial technology available for pentose fermentation into ethanol. Besides that, the removal of the hemicellulosic fraction would allow the production of a more concentrated hexoses liquor on the cellulose hydrolysis step, which would decrease energy consumption on the following steps of liquor concentration and product purification. Pre-hydrolysis of hemicellulose may be carried out under relatively mild conditions of temperature (around 120 °C) and low sulphuric acid concentration (2 wt%) for short reaction times. Aguilar et al. (2002) obtained a conversion of pentose equal to 81 %, after 24 minutes of reaction.

Delignification is achieved through the use of an Organosolv solvent (ethanol 75 - 50 % + water 25-50 % - w/w), which promotes lignin dissolution. Removal of the dissolved lignin prior to cellulose hydrolysis may be considered in order to avoid formation of phenols derived from lignin, which are fermentation inhibitors, as well as to avoid lignin contamination with sulphates, in the case of cellulose hydrolysis catalyzed by sulphuric acid.

Cellulose hydrolysis can be achieved through dilute acid hydrolysis or enzymatic hydrolysis. In either process the Organosolv process with hemicellulose pre-hydrolysis may be used as the pre-treatment method for the lignocellulosic material. Dias (2008) performed simulations of the integrated production of bioethanol using sugarcane juice and bagasse through the Organosolv process with dilute acid hydrolysis on three separate steps: pre-hydrolysis of the hemicellulose, Organosolv delignification and cellulose hydrolysis (catalyzed by H<sub>2</sub>SO<sub>4</sub>). Cellulose hydrolysis using dilute sulphuric acid takes place at extreme conditions of temperature (around 200 °C) and pressure (20 – 30 bar), so there is a considerable decomposition of sugars into furfural and HMF. On the other hand, high yields (conversion of 80 - 90 % of cellulose) can be achieved under residence times in the reactor of seconds or minutes (Lee et al., 2000; Xiang et al., 2003).

Enzymatic hydrolysis takes place under milder process conditions than that of dilute acid hydrolysis, thus leading to a decreased formation of by-products. On the other hand, reaction times are very long (1 – 2 days) and the process requires large concentrations of enzymes in order to achieve high conversions of cellulose (Rabelo, 2007), which increases process costs dramatically. Development of enzyme

technology and consequent decrease of enzymes cost may increase enzymatic hydrolysis feasibility in the years to come.

### **Instrumentation and automation**

In general, monitoring of ethanol profiles in industrial fermentation is carried out as off-line analysis, often with a significant time delay between sampling and availability of the analysis results. For instance, in an industrial site located in São Paulo state, where a feed-batch fermentation process is used, the following analyses are carried out in the laboratory: ethanol content of the wine at the end of every fermentation cycle; sugar (Brix) content of the substrate every 2 hours; etc. These laboratory analyses are often available with a considerable time delay, which may bring problems to the process.

Considering the current limitation of more advanced analytical instruments (including near infrared spectrophotometers), the following challenges must be solved: insufficient accuracy, long dead-time, slow dynamics, large noise, low reproducibility and aged deterioration, among others (Kano and Nakawa, 2008). In alcoholic fermentation processes analytical instruments are difficult to calibrate, mainly due to the characteristics of industrial culture media, such as turbidity of the culture, presence of dissolved CO<sub>2</sub>, among others (Macedo, 2003). Nowadays the software sensor is the preferred alternative for monitoring state variables in biotechnological processes (Soons et al, 2008).

The so-called software sensors are algorithms for on-line estimation of state variables and model parameters that are not measurable in real-time (Bastin and Dochain, 1990). This approach is a promising research area with significant impact on industrial operation (Arauzo-Bravo et al., 2004, Gonzaga et al., 2008, Kano and Nakagawa, 2008). Software sensor is a software where several measurements are processed together. The interaction of the signals from online instruments can be used for calculating or to estimate new quantities that cannot be measured. Software sensors can also be understood as an association of a sensor (a hardware), which allows on-line measurements of some process variables, with an estimation algorithm (a software) in order to provide on-line estimates of immeasurable variables, model parameters or to overcome measurement delays (Gonzaga et al., 2008).

More recent works on software sensor for solving biotechnological complex problems are presented by Osorio et al., (2008), Arranz et al, (2008), Yu et al, (2008), Soons et al, (2008), Lee (2008) among others. The major purpose of using software sensor in bioprocesses is to assess quality of the final product through its online estimation and validate on-line analyzers providing redundant measurements

when compared with the software sensors predictions. Artificial Neural Networks (ANN) has been predominant in literature in the field of software sensor design.

Artificial Intelligence techniques such as ANNs have been widely applied for bioprocess modeling, monitoring and control. This technique is sought to efficiently combine all available knowledge and to direct the development towards an improved process operation strategy (Rivera et al., 2006). Besides, ANNs can be used to offer adaptive solutions, since the reestimation of their parameters is a straightforward procedure (Rivera et al., 2007). These characteristics are suitable for analyzing data from more complex processes, such as bioethanol production, which has a great number of variables.

One of the most important aspects of the strategies of optimization and control of biotechnological processes is the capacity of monitoring all important state variables. Sensor for measuring these variables in real-time is today available. However, a review of latest research has shown that analytical instruments are not robust in the industrial environment.

Taking into consideration bioethanol production, changes in raw material composition, dominant yeast lineage and deviations in temperature, which cause inherent process variability, are some of the problems that often must be dealt with in industrial fermentation.

### ***Perguntas sugeridas***

#### **1- Em termos de caracterização da matéria-prima lignocelulósica e qualidade dos produtos gerados, quais as necessidades de instrumentação para avaliação/ monitoramento/controlado das variáveis relevantes do processo de conversão?**

Taking into consideration the quality of the products generated during the production of 2<sup>nd</sup> generation bioethanol, the variables that impact sugar decomposition and consequent production of fermentation inhibitors (e.g. temperature, pressure, pH) must be determined. These variables may change for each type of pretreatment and hydrolysis processes, and must be monitored and controlled in order to decrease production of inhibitors.

Concerning quality of the lignocellulosic raw material, chemical characterization is important in order to define pretreatment and hydrolysis processes conditions. Variations on feed composition will eventually influence some of the processes monitored/controlled variables (for instance, temperature and pH).

## 2- Quais os desafios do processo de conversão em termos de instrumentação/automação?

Identification of variables and definition of the most adequate sensors are necessary. An example is verified by examining the pre-hydrolysis of sugarcane bagasse, simulated by Dias (2008) and represented on Figure 1.

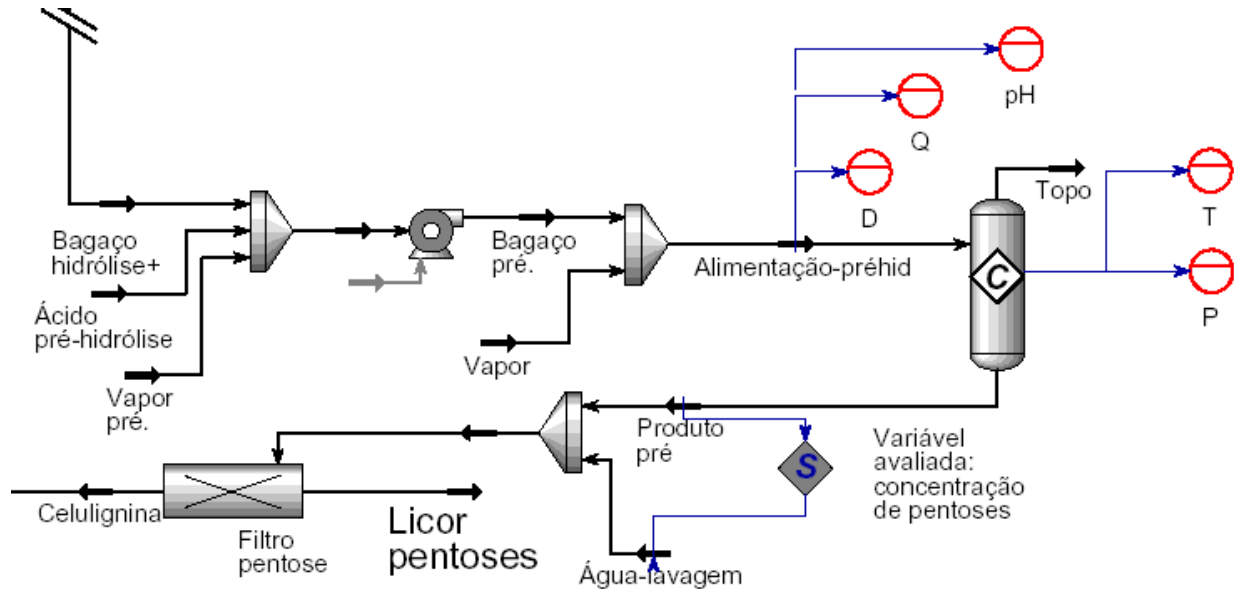


Figura 1. Fluxograma da simulação da etapa de pré-hidrólise do bagaço da cana-de-açúcar.

During pre-hydrolysis, sugarcane bagasse receives sulphuric acid and steam, in order to achieve acid concentration of 2 wt% and to rise mixture temperature to about 122 °C. This mixture is pressurized and fed to the pre-hydrolysis reactor, in which hemicellulose is converted to pentoses, pentose is decomposed into furfural, acetic acid and glucose are produced.

Some examples of the variables that must be monitored in this process are: pH of the reactor feed (pH), feed flow (Q), dilution (amount of solids) in the feed mixture (D), temperature (T) and pressure (P) of the pre-hydrolysis reactor. The variable that must be evaluated in this case would be concentration of pentoses in the reactor product stream.

In order to identify equipments and instrumentation and automation equipments in the production of 2<sup>nd</sup> generation bioethanol, it is necessary to define all unit operations of the processes and to verify the variables that influence process behavior. Software sensor can be employed if a large number of experimental trials are carried out, which can provide the results necessary (hundreds of thousands of parameters, due to the large number of variables that are present in bioethanol production) to determine the models; in this case the software sensor could be used to estimate pentose concentration in the product stream as a function of the variables pH, Q, D, T e P.

### **3- É possível fazer uma adaptação da instrumentação e automação dos processos de 1ª geração para os de 2ª geração?**

Depending on the types of pretreatment and hydrolysis processes used, pressure and temperature conditions may be more extreme than those observed during the production of 1<sup>st</sup> generation bioethanol, so it would be necessary to employ different types of instruments suitable to each process.

Taking into consideration the fermentation step, when hydrolyzed liquor and sugarcane juice are mixed and fermented simultaneously, there would not be significant changes on process conditions, so it would not be necessary to adapt instrumentation and automation equipments, as long as the concentration of sugars do not differ much. Nevertheless, concentration of fermentation inhibitors eventually produced during pretreatment and hydrolysis processes must be monitored.

### **4- Quais os desafios para a implantação de sistemas integrados para a simulação/monitoramento e controle do processo de conversão?**

The main challenge of integrated system is to improve the productivity of existing ethanol generation (sugar cane molasse fermentation), the so-called First Generation Bioethanol, as well as proposing the study of manners of improving the Second Generation Bioethanol (from biomasses). Even now it is possible to talk about testing the viability of a Third Generation of Bioethanol, which is produced from catalytical or biological fermentation of synthesis gas. The Third Generation Bioethanol has a major appeal of consuming carbon dioxide produced in the First and Second Generation processes, causing the great impact of almost zero CO<sub>2</sub> emission within the whole integrated process.

By considering bioethanol produced on 2nd and 3rd generation processes, it is expected that many problems will be detected when optimal operation is a target. Among them, it is expected to find the lack of processes robustness in the presence of fluctuations in operational conditions, which leads to changes in the kinetic behavior, with impact on conversion. These changes are very common in plants of 1st generation bioethanol production, where they occur not only due to the variations in the quality of the raw material but also due to variations of dominant microorganism in the process.

In an integrated system the performance will be significantly influenced by the relationships between process variables in the units operation, and that means that a simple, though realistic, mathematical models is required to promote the development of the process. This model would allow the monitoring the process state which is an important aspect of the decision making in the ethanol production.

In general, monitoring of ethanol profiles is carried out as off-line analysis, often with a significant time delay between sampling and availability of the analysis results.

Nowadays the software sensor is the preferred alternative for monitoring state variables in biotechnological processes (Soons et al, 2008). This is a promising research area with significant impact on biotechnological industry, which requires an efficient monitoring with reliable sensors to control setting of the process. Thus, for a reliable performance prediction through modeling, the software sensor should be implemented on a platform able to provide a powerful toolset for process identification and control with interface directly to instruments, sensor and actuators.

The proposal of an on-line monitoring system based on software sensor should comprises basically of three essential elements: (i) An array of sensors of multisensor system, which consists of a bioreactor where on-line sensors (for instance pH, CO<sub>2</sub> flow rate, temperature, turbidity among others) are situated. Such features as relatively simple instrumentation, short measuring time and low prices make the primary on-line sensors are a right choice for the approach proposed in a integrated system. (ii) A communication module that transfers the measurement data from bioreactor to a monitoring and data acquisition system. That consists of devices to convert the protocol of the output of the primary sensors. (iii) A monitoring and data acquisition system, which monitor the bioprocess based on programme to fully automate the implementation of software sensors in a PC with a data acquisition card, it is a general-purpose graphical programming environment (for instance Aspen, Yokogawa, LabView, among others). The monitoring system represents thus a robust model-based approach which is expected to contribute for improving the implementation of suitable operating strategies of optimization as well as advanced control to achieve high operational performance.

## References

- Aguilar, R. et al. (2002), *J. Food Eng.*, 55, 4, 309-318.
- Aráuzo-Bravo, M.J., Cano-Izquierdo, J.M., Gómez-Sánchez, E., López-Nieto, M.J., Dimitriadis, Y.A. and López-Coronado, J. (2004), *Control Eng. Pract.* 12, 1073-1090.
- Arranz, A., Bordel, S., Villaverde, S., Zamarreño, J.M., Guieysse, B., Muñoz, R. (2008), *J. Hazard. Mater.* 155, 51-57.
- Cardona, C.A. and Sánchez, Ó.J. (2007), *Biores. Technol.*, 98:2415-2457.
- Dias, M.O.S. *Simulação do processo de produção de etanol a partir do açúcar e do bagaço, visando a integração do processo e a maximização da produção de energia e excedentes de bagaço*, Dissertação (Mestrado em Engenharia Química). Faculdade de Engenharia Química, Universidade Estadual de Campinas, 2008.

- Gonzaga, J.C.B., Meleiro, L.A.C., Kiang, C., Maciel Filho, R. (2008), *Comput. Chem. Eng.* doi:10.1016/j.compchemeng.2008.05.019, 2008.
- Kano, M., Nakagawa, Y. (2008), *Comput. Chem. Eng.* 32, 12-24.
- Lee, M.W., Hong, S.H., Choi, H., Kim, J.H., Lee, D.S., Park, J.M. (2008), *Process Biochem.* 43, 1107-1113.
- Lee, Y.Y., Wu, Z., Torget, R.W. (2000), *Biores. Technol.*, 71:29-39.
- Macedo, I. (2003), *Estado da arte e tendências das tecnologias para energia. Brasília: Ministério da Ciência e da Tecnologia.* CTEnrg Secretaria Técnica do Fundo Setorial de Energia. CGEE Centro de gestão e Estudos estratégicos.
- Osorio, D., Pérez-Correa, J.R., Agosin, E., Cabrera, M. (2008), *J. Food Eng.* 87, 571-577.
- Rivera, E.C., Costa, A.C., Wolf-Maciel, M.R. and Maciel Filho, R. (2006), *Appl. Biochem. Biotechnol.* 129-132, 969-984.
- Rivera, E.C., Costa, A.C., Andrade, R.R., Atala, D.I.P., Maugeri, F. and Maciel Filho, R. (2007), *Biochem. Eng. J.* 36, 157-166.
- Rossell, C.E.V. et al. (2005),. *Intern. Sugar J.*, 107, 192-195.
- Soons, Z.I.T.A., Streefland, M., van Straten G., van Boxtel, A.J.B. (2008), *Chemom. Intell. Lab. Sys.* doi:10.1016/j.chemolab.2008.07.009, 2008.
- Xiang, Q., Kim, J.S., Lee, Y.Y. (2003), *Appl. Biochem. Biotechnol*, 105-108:337-352.
- Yu, R.F., Chen, H.W., Cheng, W.P., Shen, Y.C. (2008), *Resour. Conserv. Recycl.*, 52, 1015-1021.
- Zaldivar, J. Nielsen, J. Olsson, L. (2001), *Appl. Microbiol. Biotechnol.*, 56, 17-34.