Editorial

Prof. Dr. Martin Aznar

Nesta edição, o Boletim da FEQ cumprimenta as novas professoras do Departamento de Processos Químicos, Melissa Vieira e Roberta Ceriani, cujos perfis aparecem no quadro abaixo. As professoras tomaram posse em agosto e já estão diretamente envolvidas em várias atividades da FEQ.

Um ponto de destaque nas atividades deste trimestre foram as várias palestras ministradas na FEQ, com visitantes internacionais de alto gabarito. Os nossos ex-alunos continuam aproveitando as oportunidades, como no caso do Dr. Alexandre Antunes Ribeiro, que obteve a primeira bolsa de pós-doutorado já concedida pelo INT-RJ. O Jornal da UNICAMP deu destaque às pesquisas desenvolvidas na FEQ, com duas matérias envolvendo a imobilização de rejeitos nucleares e a lógica fuzzy aplicada ao controle de processos.

Por último, a produção científica da FEQ continua de forma bastante expressiva, com 33 artigos em revista nos meses de julho a setembro. Uma boa leitura!

Novas professoras na FEQ

Tomaram posse na primeira semana de agosto as professoras Roberta Ceriani e Melissa Gurgel Adeodato Vieira, ambas lotadas no DPQ. A Profa. Dra. Roberta Ceriani é engenheira de alimentos, com doutorado na FEA/UNICAMP e teve bolsa de pós-doutorado na Universidade Técnica da Dinamarca. Tem experiência na área de engenharia de processos, atuando principalmente na determinação de propriedades físicas, simulação computacional, refino físico e desodorização de óleos vegetais. Recebê-la em 2006 o Prêmio Bunge Juventude na área de Ciência e Tecnologia de Alimentos com sua tese de doutorado. Foi docente na Faculdade de Ciências Aplicadas da UNICAMP. Tem 2 capítulos de livro, 14 trabalhos publicados em revistas indexadas e um fator H de 5.


Sejam bem-vindas!
Artigos Publicados em Revistas Indexadas
Julho - Setembro 2010


Enzymatic hydrolysis of sugarcane bagasse for bioethanol production: determining optimal enzyme loading using neural networks

BACKGROUND: The efficient production of a fermentable hydrolyzate is an immensely important requirement in the utilization of lignocellulosic biomass as a feedstock in bioethanol production processes. The identification of the optimal enzyme loading is of particular importance to maximize the amount of glucose produced from lignocellulosic materials while maintaining low costs. This requirement can only be achieved by incorporating reliable methodologies to properly address the optimization problem.

RESULTS: In this work, a data-driven technique based on artificial neural networks and design of experiments have been integrated in order to identify the optimal enzyme combination. The enzymatic hydrolysis of sugarcane bagasse was used as a case study. This technique was used to build up a model of the combined effects of cellulase (FPU/L) and β-glucosidase (CBU/L) loads on glucose yield (%) after enzymatic hydrolysis. The optimal glucose yield, above 99%, was achieved with cellulase and β-glucosidase concentrations in the ranges of 460.0 to 580.0 FPU L\(^{-1}\) (15.3–19.3 FPU g\(^{-1}\) bagasse) and 750.0 to 1140.0 CBU L\(^{-1}\) (2–38 CBU g\(^{-1}\) bagasse), respectively.

CONCLUSIONS: The dynamic model developed can be used not only to the prediction of glucose concentration profiles for different enzymatic loadings, but also to obtain the optimum enzymes loading that leads to high glucose yield. It can promote both a successful hydrolysis process control and a more effective employment of enzymes.

Porous nanocomposite hydrogel of vinylated montmorillonite-crosslinked maltodextrin-co-dimethylacrylamide as a highly stable polymer carrier for controlled release systems

Nanocomposite hydrogel consisting of dispersed montmorillonite-crosslinked maltodextrin-co-dimethylacrylamide (malt-dex-co-DMAM) as a highly stable device was developed. Carbon-carbon π-bonds issued from glycidyl methacrylate (GMA) were incorporated onto both the MMT (MMT-π) and the malt-dex (malt-dex-π) structures. The nanocomposite copolymer hydrogel was processed via radical crosslinking reaction of malt-dex-π with MMT-π in the presence of DMAAm. The radical reaction of the carbon-carbon π-bonds at the MMT-π was verified by treating the MMT-π with sodium persulfate. There was an excellent dispersion of the MMT-π at the interior of the matrix even after the nanocomposite hydrogel being swollen, demonstrating that the developed methodology can imprint stability of mineral nanoparticles into a porous polymer network preventing diffusion of water-bonded silicate platelets toward the outside matrix. The water absorption profile became more dependent on the polymer relaxation for mineral-loader nanocomposite hydrogels. Higher water absorption had an impact on reduction of elasticity modulus due to softer polymer network in swollen state.

Optimisation of a fermentation process for butanol production by particle swarm optimisation (PSO)

BACKGROUND: The performance of three particle swarm optimisation (PSO) algorithms was assessed in relation to their capability to optimise an alternative fermentation process for the production of biobutanol. The process consists of three interconnected units: fermentor, cell retention system and vacuum flash vessel (responsible for the continuous recovery of butanol from the broth). The dynamic behaviour of the process was described by a non-linear mathematical model. Four constrained
optimisation problems were formulated concerning the operation and design of flash fermentation: (1) maximisation of butanol productivity; (2) maximisation of substrate conversion; (3) and (4) adjustment of operating conditions in the face of problems of fluctuations in the quality of the agricultural raw material and changes in the kinetics of the microorganisms.

RESULTS: The design and operation of the flash fermentation process based on the optimisation of productivity, instead of substrate conversion, resulted in a smaller fermentor and provided satisfactory values of operating conditions able to overcome problems of variations in the glucose concentration in the raw material and changes in kinetics.

CONCLUSIONS: The differences among the PSO algorithms, i.e. the velocity equation and parameters values, had significant effects on the optimisation, the best results being obtained with the original velocity equation with the inertia weight decreasing linearly with each iteration. The PSO algorithms obtained solutions that obeyed constraints, demonstrating that a constraint handling method originally developed for genetic algorithms can be applied successfully to PSO algorithms.

Genetic algorithms (binary and real codes) for the optimisation of a fermentation process for butanol production

In this work, the capability of genetic algorithms (GAs) to optimise an alternative fermentation process for the production of biobutanol was assessed. The process consists of three interconnected units, as follows: fermentor, cell retention system (tangential microfiltration) and vacuum flash vessel (responsible for the continuous recovery of butanol from the broth). The dynamic behaviour of the process is described by a non-linear mathematical model with kinetic parameters determined experimentally, whose non-linearity makes the solution of the optimisation problem difficult through conventional algorithms, thus justifying the use of an evolutionary method based on the GAs. The objective of the optimisation was the search of the process inputs that maximises the productivity of butanol for a desired substrate conversion. The potential of binary and real coded genetic algorithms to solve the optimisation problem was assessed. The GA parameters were evaluated making use of the statistical technique of the factorial design in order to identify the most significant ones to the GAs response and to determine the values of the parameters that improve the GAs performance. With both GA codes similar solutions to the optimisation problem were obtained. However, in relation to computational time, the binary code outperformed the real code. The optimised process ran on concentrated sugar solution (140.7 g/l), reaching a high final butanol concentration (27.1 g/l) and high butanol productivity (9.0 g/l.h). The use of mathematical optimisers in the butanol fermentation is a novel approach and sums up the efforts of recent researches in turning the biobutanol industry commercially viable.

Effect of initiator type and concentration on polymerization rate and molecular weight in the bimolecular nitroxide-mediated radical polymerization of styrene

To increase the polymerization rate in the bimolecular nitroxide-mediated radical polymerization (NMRP) of styrene, without using expensive non-commercial reagents, an experimental study using 2,2,6,6-tetramethyl-1-piperidinoxyl as a controller and tert-butylperoxy 2-ethylhexyl carbonate (TBEC) as the initiator was carried out. The basis for comparison was the bimolecular NMRP of styrene with dibenzoyl peroxide as initiator. It was found that faster polymerization rates and still relatively low polydispersities were possible using TBEC.

Simultaneous momentum, mass, and energy transfer analysis of a distillation sieve tray using CFD techniques: prediction of efficiencies

Conventional models for distillation columns are based on equilibrium and nonequilibrium stage concepts. Although equilibrium and nonequilibrium stage models provide useful results, they neglect the fluid dynamics phenomena by assuming a perfect mixture on the plates in each phase. However, the flow pattern on a distillation tray is of great importance in terms of the mass and energy transfer mechanisms, and this influence can only be analyzed by carrying out a fluid dynamics study. The main objective of this
Evaluation of the effect of ammonium carbamate on the stability of proteins
BACKGROUND: The use of the volatile salt ammonium carbamate in protein downstream processing has recently been proposed. The main advantage of using volatile salts is that they can be removed from precipitates and liquid effluents through pressure reduction or temperature increase. Although previous studies showed that ammonium carbamate is efficient as a precipitant agent, there was evidence of denaturation in some enzymes. In this work, the effect of ammonium carbamate on the stability of five enzymes was evaluated.
RESULTS: Activity assays showed that $\alpha$-amylase (1,4-$\alpha$-D-glucan glucanohydrolase, EC 3.2.1.1), lysozyme (1,4-$\beta$-N-acetylglucosaminidase, EC 3.2.1.17) and lipase (triacylglycerol acyl hydrolase, EC 3.1.1.3) did not undergo activity loss in ammonium carbamate solutions with concentrations from 1.0 to 5.0 mol kg$^{-1}$, whereas cellulase complex (1,4-(1,3;14)-$\beta$-D-glucan 4-glucano-hydrolase, EC 3.2.1.4) and peroxidase (hydrogen peroxide oxidoreductase, EC 1.11.1.7) showed an average activity loss of 55% and 44%, respectively. Precipitation assays did not show enzyme denaturation or phase separation for $\alpha$-amylase and lipase, while cellulase and peroxidase precipitated with some activity reduction. Analysis of similar experiments with ammonium and sodium sulfate did not affect the activity of enzymes.
CONCLUSION: Celullase and peroxidase were denatured by ammonium carbamate. While more systematic studies are not available, care must be taken in designing a protein precipitation with this salt. The results suggest that the generally accepted idea that salts that denature proteins tend to solubilize them does not hold for ammonium carbamate.

Antimycobacterial and cytotoxicity activities of free and liposome-encapsulated 3-(4'-bromo[1,1'-biphenyl-4-yl]-3-(4-bromo-phenyl)-N,N-dimethyl-2-propen-1-amine
The antimycobacterial activity of 3-(4'-bromo[1,1'-biphenyl-4-yl]-3-(4-bromo-phenyl)-N,N-dimethyl-2-propen-1-amine (BBAP), free or incorporated in preformed liposomes, on extracellular M. tuberculosis H37Rv was 8 and 25 $\mu$M (MIC), respectively. Extracellular antimycobacterial activity was not significantly improved by entrapment of BBAP in liposomes, but there was a 6.1-fold reduction of BBAP cytotoxicity on J774 macrophages. Liposomal BBAP or its free form showed IC50 values of 165 and 27 $\mu$M, resulting in a selectivity index (SI=IC50/MIC) of 3.4 and 6.6, respectively. Free BBAP in concentrations from 10 to 80 $\mu$M were quite effective in eliminating intracellular M. tuberculosis while liposomal formulation was less effective at these concentrations.

Morphological and physicochemical characterization of commercial maltodextrins with different degrees of dextrose equivalent
Maltodextrins show increasing industrial applications depending on the extent of the starch hydrolysis. This paper reports a relationship between morphological and physico-chemical characteristics of different maltodextrins (A, B, and C) in order to establish appropriate uses. The moisture content of the
maltodextrins varied from 2.82 to 6.47% and true and bulk density, average particle size, and porosity of the maltodextrins ranged from 1.14-1.44 g/mL, 0.33-0.49 g/mL, 39.44-289.17 µm, and 59.70-67.58%, respectively. Spherical, irregular, and filamentous shapes conduct to low values of wetting times. The increase in the DE level of maltodextrins from the same botanical source caused a decrease in the dissolution time. Results demonstrated that products obtained by supplier B showed the best performance and regularity in the dissolution/dispersion characteristics in water meanwhile maltodextrins manufactured by supplier A would be favored by an agglomeration process.

Agosto

Experimental determination of benzene uptake rate in Tenax TA diffusive samplers
This paper proposes a methodology to predict benzene uptake rate in ambient air, using passive samplers with Tenax TA. Variations in the uptake rate were found to occur as a function of the sampling time; and were greater at the beginning of sampling. An empirical model was obtained and values for uptake rate agree with literature. Concentration prediction errors can be minimized by using sampling times of 4 to 14 days, thus avoiding the influence of excessive uptake rates in the initial days and the influence of back diffusion at the end of the sampling period.

Modeling of high-pressure vapor-liquid equilibrium in ionic liquids + gas systems using the PRSV equation of state
Ionic liquids are environmentally friendly solvents composed of large organic cations and relatively small inorganic anions, whose melting point is below T = 373.15 K. This is an arbitrary limit defined in order to organize the dramatically increasing number of possible applications in chemical processes. These compounds are regarded as potentially environmentally benign solvents due to their almost negligible vapor pressure, which essentially eliminates emission to the atmosphere; besides, they present a wide range of liquid existence. Ionic liquids are applicable in separation processes, such as recovery of valuable products and remotion of polluting agents in effluents and are a new and exciting class of compounds that have the potential to overcome many of the problems associated with current CO2-capture techniques. In this work, high-pressure vapor-liquid equilibrium (VLE) of seventeen binary mixtures ionic liquid + gas have been modeled with the Peng-Robinson/Strylek-Vera (PRSV) equation of state (EoS) applying the Wong-Sandler (WS) mixing rules, including the van Laar (VL) model for the excess Gibbs free energy for the gamma-phi approach and the one-fluid van der Waals (VDW) mixing rules for the phi-phi approach. Critical properties and acentric factor of ionic liquids [pmim][Tf2N] and [hmim][Tf2N] were determined using the extended group contribution method by Lydersen-Joback-Reid, while, for the other ionic liquids, these properties are available in the literature. Experimental data were obtained from literature and the adjustable parameters were fitted by minimizing the errors between predicted and experimental bubble pressure. Van Laar and binary interaction parameters were regarded as temperature-dependent. The results, in terms of main deviations between experimental and calculated pressures for the seventeen binary systems, are reasonably satisfactory (3.62 % and 2.59 % for the gamma-phi and phi-phi approaches, respectively).

A new process of IgG purification by negative chromatography: adsorption aspects of human serum proteins onto ω-aminodecyl-agarose
The adsorbent ω-aminodecyl-agarose was evaluated as to its feasibility for the adsorption of human serum and plasma proteins, aiming at the purification of immunoglobulin G (IgG). The contribution of electrostatic and hydrophobic interactions (mixed-mode) and the effects of buffer system on the adsorption of serum proteins were also studied. The adsorption isotherms of human serum albumin (HSA) and IgG were evaluated, pointing to the existence of cooperative effects in the process. A positive (n = 2.30 ± 0.38) and negative cooperativity (n = 0.63 ± 0.12) were observed for IgG and HSA binding, respectively. High purity IgG was obtained (based on total protein concentration and
nephelometric analysis of HSA, transferrin, and immunoglobulins A, G, and M) with a 75% recovery in Hepes 25 mmol L\(^{-1}\) pH 6.8 feeding human serum. These results indicate that the use of ω-aminodecyl-agarose is a potential technique for purification of IgG from human serum.

**Nanoparticle processes modelling: the role of key parameters for population balances for on-line crystallization processes applications**

The nanoparticle production with well defined properties is of great scientific and technological interest due to the increasing number of applications of such material. Crystallization may be a suitable unit operation for producing nanoparticles, since it may be conceptually designed to be an intensified process. The mean particle size, the particle morphology, the modality and the breadth of the particle size distribution (PSD) are important indications of the quality of a particulate product. By synthesizing nanocrystals with narrow PSD, it is possible to produce advanced nanomaterials with tailored properties. There are possible interaction effects that may be unique to nanoparticles due to the size dependence of properties. These effects must be accounted for in predictive models, which are useful either for exploratory investigations or as a tool for computer operated procedures. For online process control, time calculations should not be greater than a few seconds, and, therefore, a population balance model should be more appropriate than stochastic methods. However, at present there is no consensus and complete knowledge by the scientific community of all needed parameters and which are the computer tools for a workable framework for dealing with nanoparticles reliable process design and on-line applications. This paper proposes to discuss important aspects of nanoparticle crystallization processes in order to bring light to nanoparticle modelling. In order to do so, the key factors influencing nanoparticulate processes and how they can be accounted for, going from a molecular to a process engineering approach, are discussed.

**Supercritical fluid extraction of lycopene from tomato juice and characterization of its antioxidation activity**
Egydio, J.A.; Moraes, A.M.; Rosa, P.T.V. *The Journal of Supercritical Fluids*, 54 (2010), 159-164. ISSN: 0896-8446. doi:10.1016/j.supflu.2010.04.009

A new method to extract lycopene from tomato juice using supercritical CO\(_2\) as solvent and without the need to dry the raw material is presented. To conduct the extraction, the tomato juice was subjected to cycles of centrifugation followed by rinsing with absolute ethanol to partially remove the water present in the solid part of the juice. The influence of the temperature and pressure on the extraction efficiency and on the extract antioxidation activity was studied using a factorial experimental design. The extraction efficiency varied from 7.7 to 76.7 % and only extraction temperature had a statically significant effect on the process. The reversed phase HPLC analysis showed that lycopene is the major compound of the extract. The extract that presented higher antioxidant activity was obtained at 40°C and 350 bar with 12.7 mmol.L\(^{-1}\) Trolox/g of extract using the DPPH radical scavenging method and 61.3 mmol.L\(^{-1}\) Trolox/g of extract using the rubrene singlet oxygen quenching method.

**Simulation and analysis of a sugarcane juice evaporation system**

The production of sugar and alcohol is the main objective of the sugarcane processing industry. The evaporation of sugarcane juice has a high energetic cost and is usually performed in multiple-effect evaporators. The loss of performance during operation due to fouling makes the process more complex. In this study, modeling, simulation, validation, and analysis were performed for a sugarcane juice industrial evaporation system (IES) composed of a falling film evaporator followed by three short vertical-tube evaporators arranged in parallel. The IES model was developed using a commercial process simulator and validated with data from the plant. The IES had marked performance losses in the first 14 days of operation, mainly due to fouling in the first effect, with a 30% decrease in the evaporation rate.
Microbial production of hyaluronic acid from agricultural resource derivatives
Agricultural resource derivatives (ARDs), such as hydrolysate soy protein concentrate (HSPC), whey protein concentrate (WPC), and cashew apple juice (CAJ), were studied with focus on the production of hyaluronic acid (HA) by Streptococcus zooepidemicus. Supplementation of the media with corn steep liquor (CSL) was also evaluated. Synthetic medium containing glucose and yeast extract was used as control. CAJ was a promising medium for the production of HA. It produced the highest amount of HA (0.89 g L\(^{-1}\)), similar to that of the control (0.86 g L\(^{-1}\)). WPC and HSPC media were the most effective for the production of biomass. CSL did not influence the production of HA when HSPC and WPC were used. However, in the synthetic medium it doubled the yield of HA from glucose. The average molecular weight of HA ranged from 103 to 104 Da for the ARDs and 107 Da for the synthetic medium.

Effect of process conditions on particle growth for spouted bed coating of urea
Rosa, G.S.; Rocha, S.C.S. Chemical Engineering and Processing: Process Intensification, 49 (2010), 836-842. ISSN: 0255-2701. doi:10.1016/j.cep.2010.06.005
The aim of this work was to analyze the influences of operational variables on particle growth for urea coating in a conventional spouted bed (CSB). An aqueous polymeric suspension was the coating liquid sprayed on the spouted particles. The effects of inlet air temperature, coating suspension flow rate and atomizing air pressure on particle growth were analyzed by a central composite rotatable design (CCRD) of experiments. The results showed particle growth in the range of 1.1-2.6\%, therefore, some results below the expected for a film coating (2-8\%). A second-order polynomial model was obtained for estimating particle growth as a function of the statistically significant variables: air temperature, suspension flow rate and atomizing air pressure, with percentage of explained variation \(R^2 = 90.72\%\). The urea growth kinetics during coating was analyzed for the optimal operating condition and a linear growth coefficient of \(1.13 \times 10^{-3} \text{ min}^{-1}\) was obtained. The volatilization analyses showed that the polymer film coating provided a decrease of the nitrogen loss in the range of 3 to 57\%. And, SEM analyses demonstrated a total, uniform and homogeneous covering of the urea particles surface.

Liquid-liquid equilibrium in ternary ionic liquid systems by UNIFAC: new volume, surface area and interaction parameters. Part I
Ternary liquid-liquid equilibria (LLE) data in systems involving ionic liquids have been investigated by several years, mainly due to the innovative role of ionic liquids as extraction solvents. The thermodynamic modeling of these systems has been performed almost invariably with the well-known NRTL model. In recent years, the UNIQUAC model have also been used, with structural parameters for ionic liquids determined either by empirical correlations or, more recently, through quantum mechanics calculations. In this work, the structural group volume and area parameters for the group-contribution UNIFAC method have been calculated for six ionic liquids following the quantum mechanics approach. The Density Functional Theory (DFT) was used to optimize the molecular geometry and the Polarizable Continuum Method (PCM) was used to calculate the area and volume. The obtained parameters were used to correlate LLE data for twenty four ternary systems, totaling 169 tie-lines. New interaction parameters were also estimated between the solvent and ionic liquid functional groups. The results are very satisfactory, with root mean square deviations between experimental and calculated compositions about 1.6\%.

Novas tendências em embalagens para alimentos: revisão
O presente estudo teve como objetivo apresentar as mais recentes tendências do setor de embalagens alimentícias no mercado nacional e internacional. Foram abordados os conceitos de embalagens ativas e inteligentes, assim como suas funções, a composição, o formato, as reações químicas envolvidas, a forma
In the enzymatic hydrolysis, such as acid concentration and pretreatment time were evaluated. An experimental design was used to compare the following factors: sulfuric and phosphoric acid concentrations (0.5 %wt to 3.5 %wt) and reaction time (15 to 180 minutes). Pretreatment temperature and the solids concentration were maintained constant at 130°C and 10 %wt of bagasse. The maximum glucose concentration achieved was 404.5 mg glucose/g raw bagasse for the bagasse pretreated with phosphoric acid and 414.9 mg glucose/g raw bagasse for the bagasse pretreated with sulfuric acid.

Pectin-based polymer hydrogel as a carrier for release of agricultural nutrients and removal of heavy metals from wastewater


A pectin-based hydrogel was used as a remover of Cu²⁺ and Pb²⁺ ions from water and wastewater and in the release of phosphate, potassium, and urea. The swelling studies in either aqueous or saline solutions were analyzed at different pressures, and the prediction of profile of water and solute transports was

Rheological characterization of recovery yeast (Saccharomyces cerevisiae) cream from brewing process

Cremasco M.A.; Melo K.P. Chemical Engineering Transactions, 21 (2010), 763-768. ISSN: 1974-9791. doi:10.3303/CET1021128

This study presents models to describe the rheological behavior of recovery Saccharomyces cerevisiae yeast cream after eight fermentations from a brewing process. It was verified that the suspension rheological behavior is influenced by temperature. For temperatures up to 45°C, the suspension behaves as Newtonian fluid. For temperatures between 45°C and 55°C, occurs modification in the yeast consistency, and it depends on the plastic viscosity. For 55°C < T < 75°C, the waste yeast suspension behaves as Bingham plastic. This biomass suspension was centrifuged, and the precipitate follows Ostwald-Waele model, and it is strongly influenced by temperature.

Otimização da produção de álcool de mandioca


Este trabalho objetivou otimizar o processo de hidrólise do amido de mandioca com α-amilase de A. niger e obter o álcool deste xarope. Os ensaios foram realizados a pH 4,8; em que variaram-se a concentração do amido (entre 7-22 g.L⁻¹) e a temperatura (entre 30-59,1 ºC). Durante a fermentação, usaram-se nos mostos 2,2 e 5% de amido de mandioca. Os resultados da hidrólise mostraram que o tempo ficou entre 20-200 minutos; a análise RSM mostrou que o rendimento diminuiu nas concentrações médias; e as condições ótimas foram encontradas entre 55-59,1 ºC e com a concentração entre 7,9-10 ou 20-22 g.L⁻¹, em que se hidrolisou 80% do amido. A melhor condição de fermentação foi obtida para o mosto contendo 5% de amido. Sua composição final foi de 0,668 g.L⁻¹ de ART, 0,572 g.L⁻¹ e de AR, 3,71 ºGL. O rendimento alcoólico foi de 45%, demonstrando que este processo é uma alternativa eficiente à indústria sucroalcooleira.

Pretreatment of sugar cane bagasse with phosphoric and sulfuric diluted acid for fermentable sugars production by enzymatic hydrolysis


In the process of enzymatic conversion of cellulose to ethanol, a pretreatment is required to break the lignocellulosic biomass structure. This work presents the glucose production by enzymatic hydrolysis of sugar cane bagasse pretreated with two diluted acids. The best values of the variables of diluted acid pretreatment that influence glucose production in the enzymatic hydrolysis, such as acid concentration and pretreatment time were evaluated. An experimental design was used to compare the following factors: sulfuric and phosphoric acid concentrations (0.5 %wt to 3.5 %wt) and reaction time (15 to 180 minutes). Pretreatment temperature and the solids concentration were maintained constant at 130°C and 10 %wt of bagasse. The maximum glucose concentration achieved was 404.5 mg glucose/g raw bagasse for the bagasse pretreated with phosphoric acid and 414.9 mg glucose/g raw bagasse for the bagasse pretreated with sulfuric acid.
further analyzed on basis of transport process by diffusion in swellable polymer networks. The hydrogel composed of 0.10 g mL\(^{-1}\) final polymer concentration showed an excellent absorption capacity for removal of Cu\(^{2+}\) and Pb\(^{2+}\) from the solution: 120 mg Cu\(^{2+}\) and 130 mg Pb\(^{2+}\) per g hydrogel, both at pH 5.5. The hydrogel help to conserve water in a pressure range in which a variety of horticultural plants can absorb it. The release process of urea, phosphate, and potassium from the hydrogels is controlled by non-Fickian mechanism with a tendency to macromolecular relaxation. This type of hydrogel is an interesting system for applications in which the efficient use of water is required and release of fertilizers for agriculture.

**Effect of lignosulfonate on the thermal and morphological behavior of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)**


The effect of lignosulfonate on poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV, was studied by scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The PHBV/lignosulfonate samples were prepared by melt mixing in an internal mixer. SEM showed that PHBV/lignosulfonate samples present a cracked surface that is more intense in mixtures with high lignosulfonate proportions. According to DSC, melting and glass transition temperatures of the PHBV matrix decrease with lignosulfonate addition. The same effect was observed for melting enthalpies (\(\Delta H_m\)), which indicates a decrease of crystallinity. TGA showed that thermal stability of PHBV/lignosulfonate samples was shifted to lower temperatures, which indicates the existence of an interaction between the thermal decomposition processes of PHBV and lignosulfonate.

**Analyzing the real advantages of bifunctional initiator over monofunctional initiator in free radical polymerization**


Monofunctional initiators are extensively used in free radical polymerization. To enhance productivity, a higher temperature is usually used; however, this leads to lower molecular weights. Bifunctional initiators can increase the polymerization rate without decreasing the average molecular weight and this can be desirable. A bifunctional initiator is an important issue to be investigated, and it is of great interest to industries. The objective of this work is to study polymerization reactions with mono- and bi-functional initiators through comprehensive mathematical models. Polystyrene is considered as case study. This work collects and presents some experimental data available in literature for polymerization using two different types of bifunctional initiators. Model prediction showed good agreement with experimental data. It was observed that the initial initiator concentration has a huge impact on the efficiency of initiators with functionality bigger than one and high concentrations of bifunctional initiator make the system behave as if it were a system operating with monofunctional initiator.

**Liquid-liquid equilibrium of ternary systems 1-octyl-3-methylimidazolium hexafluorophosphate + aromatic + aliphatic hydrocarbons**


The phase behavior of six ternary systems involving an aromatic hydrocarbon (benzene, toluene or m-xylene), an aliphatic hydrocarbon (nonane or undecane), and a ionic liquid (1-octyl-3-methylimidazolium hexafluorophosphate, [omim][PF_6]) was experimentally studied at 298.15 K and atmospheric pressure, totaling twenty six tie-lines. The main goal is to determine if [omim][PF_6] is a good solvent for the separation of the aromatic and aliphatic compounds, a common operation in the processing of reformed naphtha. All the ternary diagrams are of type 1, with high and wide two-phase regions, which show that [omim][PF_6] is a good solvent for the extraction of aromatic from aliphatic hydrocarbons. The Othmer-Tobias correlation was used for evaluation of the quality of the tie-line data, with good results. The data were correlated with the NRTL model for the activity coefficient, with estimation of new interaction energy parameters by using a modified Simplex method and a composition-based objective function. The results, expressed by root mean square deviations between experimental and calculated compositions, are very satisfactory.
Dynamics of a continuous flash fermentation for butanol production

The ABE (acetone, butanol, ethanol) fermentation is characterized by its low productivity. In this paper, this issue is overcome with an innovative industrial process that employs the flash fermentation technology. The process consists of three interconnected units, as follows: fermentor, cell retention system (tangential microfiltration) and vacuum flash vessel (responsible for the continuous recovery of butanol from the broth). The dynamic behavior of the process is described by a non-linear mathematical model with kinetic parameters determined experimentally. From simulations of the mathematical model the dynamics characteristics of the process were investigated. Analyzes of the open-loop dynamic behavior of the process, after step perturbations in the manipulated variables, determined the best control structures for the process.

Partitioning optimization of lipase from Burkholderia cepacia by PEG 1500/phosphate aqueous two-phase system

This work intended to purify an extracellular lipase from Burkholderia cepacia (ATCC 25416) by aqueous liquid-liquid two-phase using polyethylene glycol 1500 Da and salt phosphate. An experimental planning was done to evaluate the effects of pH (6.0, 7.0 and 8.0) and tie lines lengths (PEG and salt balance concentrations) on the partition coefficient. Lipases were obtained from an environment containing soy oil by fermentation. RSM optimization results show that the enzyme partition coefficient depended on pH and tie line, where the best results were found at pH 6 and tie lines 3, in this case, in relationship the crude extract, the purification factor was amongst 3 times higher. While on the protein partition, the best result was in pH 8.0 and tie line 3. After the ATPS process, the top phase sample of the best system was analyzed by SDS-PAGE. The molecular weight was determined as 33 kDa using a polyacrylamide gel under denaturing conditions.

Syngas production and optimization from glycerol pyrolysis

Glycerol is a by-product from the biodiesel production which represents 10% of product total mass. Due to the present day high demand for biodiesel, the glycerol availability has increased, while its market price decreased substantially. Glycerol pyrolysis is carried out in a fixed bed reactor filled with alumina oxide. The packing material diameter was varied between 0.5-0.85 millimeters. The reaction temperature was varied in the range of 750-850°C, the reaction time from 20 to 40 min, glycerol quantity from 1 to 3 mL and flow rate of carrier gas from 10 to 50 mL/min. The process parameters listed above (factors) were used to evaluate the syngas production yield. The best results, on average, were over 80% v/v of glycerol for gas products and among them the highest amount of gas was of H₂ and CO. Besides these gases, CO₂, CH₄, C₂H₄ and C₃H₈ were also obtained in smaller proportion.

Prediction of liquid-liquid equilibrium for ternary systems containing ionic liquids with the tetrafluoroborate anion using ASOG
Robles, P.A.; Graber, T.A.; Aznar, M. Fluid Phase Equilibria, 296 (2010), 154-158. ISSN: 0378-3812. doi:10.1016/j.fluid.2010.03.018

Liquid-liquid equilibrium (LLE) data for different systems involving ionic liquids are essential for design, optimization and operation of separation processes, such as recovery of valuable products and remotion of polluting agents in effluents. In this work, the ASOG model for the activity coefficient is used to predict LLE data for 32 ternary systems at 101.3 kPa and several temperatures; all the systems are formed by ionic liquids including the tetrafluoroborate anion plus alkanes, alkenes, cycloalkanes, alkanols, ketones, carboxylic acids, esters and aromatics. New group interaction parameters were determined by using a modified Simplex method, minimizing a composition-based objective function. The results, in terms of mean deviation between the experimental and calculated compositions, are satisfactory, with rms deviations of about 4%.
Application of methods of optimization in the calculation of combined chemical and phase equilibria for process with synthesis gas
The development of the internal combustion engines at the beginning of the XX century brought a rupture with the energy source used by steam machines, the mineral coal. The use of modern engines generated a liquid fuel necessity for their functioning. New economical and institutional factors have brought back the interest in processes of synthetic fuel, a new technological trajectory. Availability of natural gas reserves, new requirements in environmental legislation, and the demand for flexibility in the transport of the natural gas have been the main factors for such renewed interest. The synthesis gas is a mixture of carbon monoxide and hydrogen produced from the reaction of water vapor or oxygen with hydrocarbons. The objective of the present work is to identify the most favorable operating conditions for such reactions, using techniques of global optimization in the calculation of combined chemical and phase equilibrium, for processes with synthesis gas. Two sets of processes were considered: the production of synthesis gas from methane, and the use of synthesis gas to produce synthetic fuels.

Bioactive polyelectrolyte multilayers: hyaluronic acid mediated B lymphocyte adhesion
Vasconcellos, F.C.; Swinston, A.J.; Beppu, M.M.; Cohen, R.E.; Rubner, M.F. Biomacromolecules, 11 (2010), 2407-2414. ISSN: 1526-4602. doi:10.1021/bm100570r
A strategy was developed to produce thin, biopolymer-based polyelectrolyte multilayer films, based on hyaluronic acid and chitosan, that are able to effectively bind B lymphocytes. These films explore CD44-hyaluronate interactions and provide a method to make surface-bound B cell arrays without the need for nonselective covalent chemistry. The rational design of these films using solution deposition variables, such as ionic strength and pH, allows one to maximize and fine tune this binding efficiency ex vivo. This work suggests two important conditions for successfully attaching B cells to hyaluronate-containing polyelectrolyte multilayer films: (1) hyaluronic acid is required for the proposed CD44-mediated binding mechanism, and (2) hyaluronic acid deposition conditions that favor loops and tails, such as low pH and with added salt, result in more available CD44 binding ligands and higher cell binding efficiency. Chitosan-terminated films prepared without NaCl in the deposition solutions and hyaluronic acid-terminated films prepared with salt, both under pH 3.0 assembly conditions, presented a similar high lymphocyte binding efficiency. In the former case, however, the binding strength was weaker due to a significant electrostatic contribution to the binding. Bioactive polyelectrolyte multilayers for selective binding of lymphocytes hold great promise in fields ranging from cell-based biosensors to immune system engineering.

Molecular distillation of petroleum residues and physical-chemical characterization of distillate cuts obtained in the process
Molecular distillation is presented as an alternative technique for the separation of petroleum residues. The technique was used to obtain 13 heavy petroleum cuts from three atmospheric residues (ARs) at 673.15 K and above. The cuts present initial and final boiling points between (673.15 and 951.15) K. To evaluate the efficiency of the technique, chemical characterization of residues and distillate cuts, which included SARA fractionation, 13C NMR, elemental composition, and density and viscosity analysis, was performed. In addition, extended true boiling point curves of crude oils by simulated distillation and by molecular distillation were compared. An increase in the viscosity and in the density was observed in all cuts with an increased molecular distillation temperature. Such behavior demonstrates that highly polar components that have a high structural complexity, such as resins and asphaltenes, are concentrated at the higher temperatures of the process. A sensitivity analysis of these two properties, together with the temperature, showed that viscosity and density decreased with increased temperature. On the other hand, the thermal expansion coefficient values obtained were equivalent to those reported in literature for petroleum products. Furthermore, a complete characterization of crude oils was made using the molecular distillation process to extend the true boiling point (TBP) curves.
Mestrado:


Doutorado:


**Notas curtas**

**O betume como imobilizador de rejeitos nucleares**

A engenheira química Márcia Flávia Guzella é responsável, na sua tese de doutorado na FEQ, pelo desenvolvimento de um processo inédito para imobilização de rejeitos radioativos provenientes de usinas nucleares, utilizando uma matriz de betume nacional. A pesquisa foi objeto de matéria no Jornal da UNICAMP (nº 467). Tecnologista do Serviço de Gerência de Rejeitos do Centro de Desenvolvimento de Tecnologia Nuclear (CDTN), um dos centros de pesquisa da Comissão Nacional de Energia Nuclear, Márcia avaliou positivamente dois betumes produzidos no Brasil, evitando dessa maneira a importação do produto de outros países, como aconteceria na Usina Angra 2. A tese foi orientada pela professora Elizabete Jordão e co-orientada pelo Dr. Vanderley de Vasconcelos, do CDTN.

Márcia explicou que a lixiviação, que é um dos métodos de caracterização do rejeito de usina nuclear incorporado em betume, é um experimento bastante demorado, que chega a durar um ano. Em um recipiente, o produto é coberto com água e, de acordo com um período predeterminado, essa água é trocada e analisada. “Essa medição é muito importante porque determina se o rejeito está incorporado ao betume”. Segundo informações da engenheira química, na Usina Angra 1 se utiliza cimento para incorporar os rejeitos gerados, enquanto na Usina Angra 2 se utiliza o betume. Utilizar o betume significa uma incorporação de até 40% em massa de rejeitos, o que gera uma economia muito grande tanto em embalagens para o armazenamento quanto em espaço físico no futuro depósito.

A pesquisa, segundo Márcia, contribuiu não apenas para o desenvolvimento do processo de incorporação de rejeitos em betume, mas também para as melhorias do sistema de betuminização do CDTN e para a implantação dos ensaios e métodos para as caracterizações necessárias. “Não há dúvidas de que os betumes nacionais estudados podem ser usados para a imobilização de rejeitos de usinas nucleares brasileiras, pois foram obtidos produtos com as propriedades requeridas para o armazenamento nos depósitos”, pontuou.

Defensora da energia nuclear como uma das alternativas para produção de energia elétrica, Márcia afirmou que as usinas nucleares de Angra 1 e 2 e, em breve, Angra 3 são importantíssimas para o Estado do Rio de Janeiro. “Não fosse pela operação dessas usinas, certamente o Rio de Janeiro já teria tido outros apagões”, comentou. Para ela, quanto mais usinas construídas, mais barato o custo operacional; atualmente, esse tipo de energia já pode ser comparado em termos de preço com a energia elétrica gerada por outras fontes. Segundo a pesquisadora, existe a previsão do governo federal de implantação de outras usinas nucleares na região Nordeste do Brasil nos próximos dez anos. “Hoje é uma energia complementar, polui menos, diminui a devastação de áreas ambientais, a inundação de cidades e, em termos de preço, estão competitivas. A partir desse ponto de vista é fundamental pensar como tratar os rejeitos”, concluiu Márcia.

**Palestras na FEQ**

No dia 06 de agosto, o Dr. Peter Lednor, cientista aposentado da Royal Dutch Shell e pesquisador visitante da FEQ, ministrou uma palestra sobre sua experiência acadêmica e empresarial. A visita do Dr. Lednor foi organizada pelos professores Gustavo P. Valença e Telma Franco.

No dia 09 de agosto aconteceram duas palestras na FEQ, por ocasião da visita de uma equipe de pesquisadores franceses. Na primeira, a Dra. Hélène Carrere, do Instituto Nacional de Pesquisas Agropecuárias, INRA, apresentou a sua experiência sobre geração de biogás; na segunda, o Prof. Francis Duchiron, da Universidade de Reims, apresentou as suas pesquisas sobre fermentação em estado sólido. O Dr. Abdel Barakat, da Universidade de Montpellier, também fez parte da equipe. A visita foi organizada pelos professores Aline Costa e Rubens Maciel Filho.
No dia 17 de agosto, o Prof. Badie Morsi, do Departamento de Engenharia Química e Petróleo da Universidade de Pittsburgh (USA), ministrou a palestra “Simulation and Optimization of a Commercial-Scale Slurry Bubble Column Reactor for Fischer-Tropsch Synthesis”. A visita do Prof. Morsi foi organizada pelo professor Milton Mori.

No dia 24 de setembro, o Prof. Gerd Maurer, professor emérito do Departamento de Engenharia Mecânica e de Processos da Universidade de Kaiserslautern (Alemanha), ministrou a palestra “The Solubility of Sour Gases in Aqueous Amine Blends”. O Prof. Maurer é um destacado especialista em termodinâmica e equilíbrio de fases, com aproximadamente 280 artigos e livros publicados. A visita do Prof. Maurer foi organizada pelos professores Martín Aznar e Melissa Vieira.

Doutor pela FEQ é o primeiro bolsista de pós-doutorado no Instituto Nacional de Tecnologia - RJ

O Instituto Nacional de Tecnologia (INT) terá, pela primeira vez, um pós-doutorado, através do Programa de Apoio ao Pós-Doutorado no Estado do Rio de Janeiro. A bolsa concedida à Dra. Marize Varella, que atuará como orientadora do Dr. Alexandre Antunes Ribeiro, traz ao INT a oportunidade de aprimorar a formação dos seus quadros no nível de pós-doutorado, o que antes precisava ser feito através das universidades. Alexandre Antunes Ribeiro é engenheiro químico, com mestrado e doutorado pela Faculdade de Engenharia Química da UNICAMP, sob orientação do professor João Sinézio de Carvalho Campos. Financiada pela Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ), a bolsa será destinada ao projeto Desenvolvimento de Tratamentos de Superfície de Titânio com Porosidade Controlada para Aplicações em Bioengenharia. Realizadas pela área de Processamento e Caracterização de Materiais do INT, as pesquisas, voltadas para a área de implantes ortopédicos, tem como objetivo melhorar a fixação dos produtos de titânio no corpo humano. A melhoria se torna possível por meio de tratamentos de superfície em escala nanométrica, que corresponde a dimensões correspondentes a um milionésimo do milímetro. Desenvolvidos pelas áreas de Ensaios em Materiais e Produtos e Processamento e Caracterização de Materiais, os trabalhos envolvendo implantes ortopédicos têm alcançado grandes avanços graças à atuação do INT. Esse desenvolvimento possibilita a transferência de tecnologia, trazendo inovação para o mercado de implantes.

Concurso Projeção M

No mês de outubro aconteceu o concurso “Projeção M”. Realizado pela Mecatron Projetos e Consultoria Jr. e tendo como principais patrocinadores: National Instruments (LabView), Yokogawa Electric Corporation e Toledo do Brasil, é uma competição de propostas de projetos potencialmente inovadores de empresas ou pesquisadores, na área de controle e automação, que resultem em grandes impactos nos processos internos ou externos de empresas, e que promovam o desenvolvimento sustentável. A avaliação dos projetos foi realizada por professores da UNICAMP, representantes da Empresa Mecatron e parceiros/apoiadores institucionais, e os dois primeiros lugares foram conquistados por trabalhos da FEQ:

1º Lugar: “Controle predictivo baseado em redes neurais (aplicação em processo de produção de poliestireno)”
Equipe: Bruno Ferreira dos Santos (mestrando), Manuela Souza Leite (doutoranda), Profa. Ana Maria Frattini Fileti, Prof. Flávio Vasconcelos da Silva e Profa. Liliane Maria Ferrareso Lona.

2º Lugar: “Dessalinizador por processo de congelamento utilizando fonte de energia solar”
Equipe: Marcos Venicius Ramos Estevom (técnico) e Prof. Flávio Vasconcelos da Silva.

Lógica fuzzy pilotando um 747

Conceitos de lógica fuzzy apresentados no artigo “Experimental investigations on fuzzy logic for process control” [Control Engineering Practice, 15 (2007), 1149-1160], de

À primeira vista, pode parecer insólito que conhecimentos obtidos em um laboratório de engenharia química possam ser utilizados no desenvolvimento de controle automático de vôo de aeronaves. A lógica *fuzzy*, porém, tem sido utilizada há vários anos no Laboratório de Controle e Automação de Processos para o estudo de controle automático de processos industriais. A professora Ana Maria Fileti enfatiza que o pesquisador menciona no artigo a parte experimental realizada pelo grupo, mostrando a credibilidade e confiabilidade da lógica *fuzzy* quando implementada em processos químicos e defendendo a possibilidade de aplicá-la no controle automático de um Boeing.

Apesar de disponível desde a década de 1960, a lógica *fuzzy* - um dos ramos da inteligência artificial - ganhou impulso maior a partir de 1980 e não existem ainda muitos trabalhos experimentais que a utilizem. Na maior parte da literatura encontram-se trabalhos envolvendo simulações e poucos se atêm a aplicações práticas. “Nossa publicação descreve várias situações experimentais de sucesso”, destaca o professor Flávio Vasconcelos da Silva.

O professor Flávio explica que a lógica *fuzzy* foge da lógica convencional, que é matemática, cartesiana, que se aplica a uma situação que é ou não é, sem possibilidade de descrever situações intermediárias, abrindo uma série de aplicações nos mais variados processos. Aplicações dessa lógica em vários campos da engenharia química foram apresentadas no artigo que acabou sendo utilizado pelo pesquisador da universidade norte-americana.

A professora Ana Maria afirma que os processos descritos no trabalho publicado são transientes. Ela explica que nos aviões sem dispositivos totalmente automáticos, o piloto precisa levar a aeronave até as condições de cruzeiro para só então acionar o piloto automático. Hoje em dia, as situações transitivas que o piloto conduzia da forma manual também podem ser monitoradas pelas máquinas, através do sistema digital de controle com algoritmos não convencionais como a lógica *fuzzy*.

A editora Nova Science Publishers lançou o livro *Fluid Phase Behavior of Systems Involving High Molecular Weight Compounds and Supercritical Fluids*, de autoria do Dr. Pedro F. Arce e do Prof. Martin Aznar, do Departamento de Processos Químicos da FEQ. Embora os fluidos supercríticos e as suas características únicas como solventes têm sido objeto de interesse científico por longo tempo, o seu potencial para uso em processos químicos ainda não tem sido aproveitado. Nas últimas décadas, solventes supercríticos têm sido foco de intensa pesquisa e desenvolvimento, especialmente na área de processamento de polímeros. O livro traz um estudo aprofundado, resultado de vários anos de pesquisas, sobre o comportamento de fases em sistemas envolvendo fluidos supercríticos e compostos poliméricos a altas pressões.

A editora Wiley lançou a 7ª edição da renomada *Ullmann’s Encyclopedia of Industrial Chemistry*. A obra, que está disponível em formato eletrônico (DVD) e é uma das mais conceituadas fontes de referência em processos químicos e industriais, traz a seção “Oil Shale”, escrita pelo Dr. Hans-Jürgen Weiss, da empresa Lurgi AG (Alemanha) e pelo Prof. Antônio Carlos Luz Lisboa, do Departamento de Termofluidodinâmica da FEQ. O artigo traz informações sobre origem e distribuição das principais reservas de xisto no mundo, bem como sobre os principais processos industriais que o utilizam.