CIEPQPF
Centro de Investigação

DEQ FCTUC

· U C ·

UNIVERSIDADE DE COIMBRA

PRODEQ

PRODEQ10 – 10 anos ao serviço da Engenharia Química

Dia Aberto – CIEPQPF

Centro de Investigação em Engenharia dos Processos
Químicos e dos Produtos da Floresta

11/11/2011

Departamento de Engenharia Química
Faculdade de Ciências e Tecnologia
Universidade de Coimbra

NOTA INTRODUTÓRIA

A PRODEQ – Associação para o Desenvolvimento da Engenharia Química, completa 10 anos de actividade em 2011.

As actividades desenvolvidas por esta associação durante a sua primeira década de existência, embora bastante diversificadas, têm tido como foco principal o estabelecimento e o reforço de ligações entre o Departamento de Engenharia Química da Faculdade de Ciências e Tecnologia da Universidade de Coimbra (DEQ) e a sociedade exterior, nomeadamente com Empresas, Associações e outros organismos da matriz técnico-científica envolvente. Este papel de instituição de interface tem sido possível através da manutenção de uma estreita colaboração com o Centro de Investigação em Engenharia dos Processos Químicos e dos Produtos da Floresta (CIEPQPF) e com a Direcção do DEQ/FCTUC.

Os esforços desenvolvidos ao longo deste espaço de tempo têm assumido formas bastante diferentes. Com a organização do evento PRODEQ10 procurou-se revisitar algumas das iniciativas concretizadas anteriormente, fazendo um balanço deste percurso de uma década. Em simultâneo, através da divulgação da Investigação actualmente realizada no DEQ e da reflexão sobre as oportunidades e os desafios actuais na concretização de projectos conjuntos, envolvendo aplicação e transferência de conhecimento, e iniciativas de empreendedorismo de base tecnológica, tentamos perspectivar o presente e o (possível) futuro da Engenharia Química, no contexto Português.

Em nome da vasta equipa envolvida na organização do evento PRODEQ10 os nossos agradecimentos por todas as contribuições recebidas, motivadoras da nossa inspiração e acção.

A Comissão Organizadora do evento PRODEQ10

A Direcção da PRODEQ

A Direcção do CIEPQPF

A Direcção do DEQ/FCTUC

PRODEQ: CONCEITO E ESTRUTURA

A **PRODEQ** - Associação para o Desenvolvimento da Engenharia Química, surge no seguimento do Plano Estratégico desenvolvido para o Departamento de Engenharia Química da Faculdade de Ciências e Tecnologia da Universidade de Coimbra. É uma associação sem fins lucrativos que visa promover o estabelecimento de relações, parcerias e projectos do DEQ com o exterior, contribuindo para uma aproximação recíproca. Pretende-se igualmente que possa vir a estabelecer-se enquanto núcleo de reflexão sobre as realidades e políticas de desenvolvimento económico com afinidades relativamente à Engenharia Química.

I. Acções desenvolvidas

As acções desenvolvidas nop momento pela PRODEQ englobam actividades no sentido de estabelecer mais ligações e fortalecer as já existentes entre o DEQ da FCTUC e o exterior, particularmente no que respeita a ex-alunos e empresas (Figura 1). Esta associação pretende também ter uma função relevante em actividades relacionadas com Escolas do Ensino Secundário, Captação ou Selecção de Candidatos aos cursos leccionados no DEQ (Figura 1).

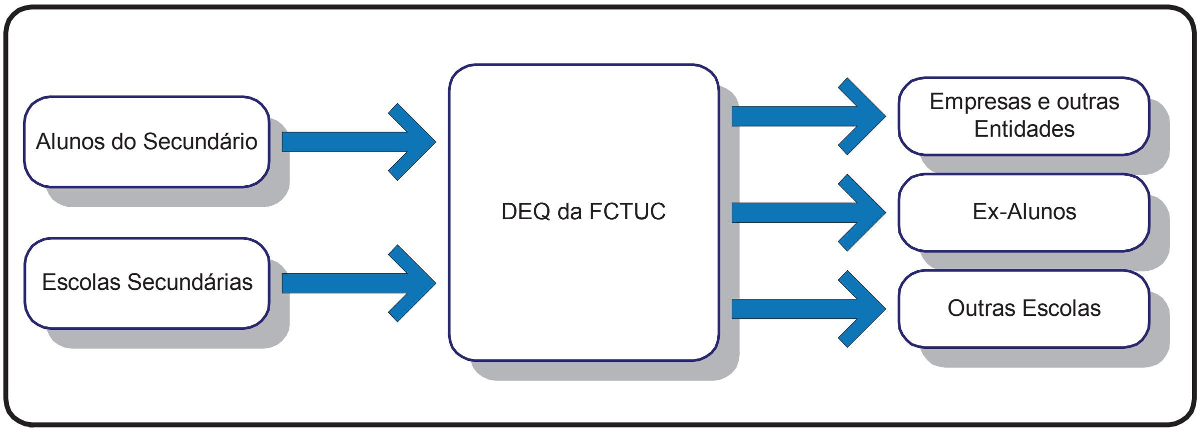


Figura 1 – Acções dsenvolvidas pela PRODEQ.

Assim sendo, as actividades desenvolvidas pela PRODEQ incluem, entre outras, as seguintes:

Infraestrutura

- Conclusão da construção e manutenção actualizada de uma base de dados de ex-alunos do DEQ;
- Criação e manutenção de uma base de dados dos actuais alunos do DEQ;
- Criação e manutenção de portal na Internet.

Comunicação (explorando novas tecnologias da informação)

- Com periodicidade anual, publicação para todos os associados e ex-alunos de uma *newsletter* com novidades sobre o DEQ (Notícias do DEQ);
- Com periodicidade anual,envio para todos os associados um pacote de informação, contendo, entre outros elementos:
    - relatório de actividades e contas da PRODEQ;
    - lista de publicações relevantes de docentes do DEQ;
    - lista de teses de mestrado e doutoramento relacionadas com o DEQ;
    - projectos de investigação em curso e respectivo ponto da situação;
    - desenvolvimentos relevantes do DEQ no domínio do ensino, investigação e extensão universitária;
    - lista de trabalhos de seminário realizados;
    - lista de publicações (periódicas e não periódicas) disponíveis no DEQ.

Promoção

- Realização anual do Dia Aberto do DEQ, onde todos os associados podem participar, preenchido com apresentações das actividades em curso no DEQ, visita às instalações e realização da Assembleia Geral da Associação;
- Elaboração de materiais promocionais do DEQ (CD-ROM, brochura de apresentação ao exterior, stand para feiras; espaço na Internet);
- Implementação de um plano de publicidade (em meios de comunicação social) e de presença em feiras ou exposições relevantes.

Apoio ao Recrutamento

- Criação e Gestão de Bolsas de Estágios e apoio à colocação profissional dos alunos, em colaboração com outras entidades (como a Ordem dos Engenheiros e a UNIVA da FCTUC).

Formação

- Concepção e implementação de um plano anual de formação contínua.

Reflexão, Discussão e Análise

- Realização de sondagem junto dos associados sobre actividades que entendam ser relevante que a PRODEQ venha a desenvolver;
- Criação de espaços de discussão sobre temas relevantes.

II. Estrutura

Na PRODEQ, existem os seguintes tipos de associados:

- Associados individuais (ex-alunos, actuais alunos e qualquer pessoa que pretenda sê-lo, sendo a inscrição aprovada pela Direcção da Associação e possuindo as quotas em dia);
- Associados colectivos (empresas ou outro tipo de entidades);
- Associados Colectivos Patrocinadores.

Para além dos usuais órgãos de gestão da associação (Assembleia Geral, Mesa da Assembleia Geral e Conselho Fiscal), a PRODEQ funciona liderada por uma Direcção, contando com o apoio contabilístico e jurídico que for necessário (por via de avença no primeiro caso), e sobretudo com a responsabilidade de execução de todas as tarefas e actividades por intermédio de um Coordenador Executivo (Figura 2).

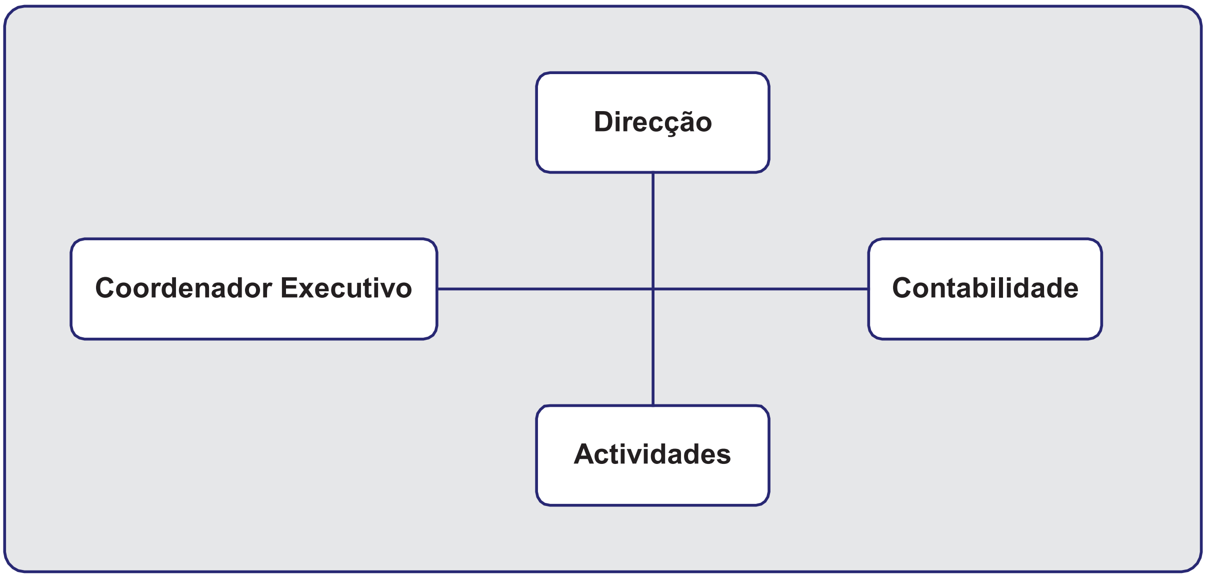


Figura 2 – Estrutura de funcionamento da PRODEQ.

A Direcção da PRODEQ é composta por 3 elementos. O respectivo presidente é um docente indicado pela Comissão Científica do DEQ. Compete a este presidente da direcção constituir uma lista de nomes a integrar a direcção (podendo os restantes 2 elementos ser associados de qualquer tipo), a ser submetida a aprovação pela Assembleia Geral da Associação.

III. Benefícios dos Associados

Todos os associados em geral, para além da manutenção de um cordão umbilical e formas de contacto facilitado com o DEQ (no caso de associados colectivos, estes devem designar um interlocutor para as relações com a PRODEQ, que por sua vez terá um gestor de cliente responsável pelo acompanhamento integral de cada um dos associados colectivos) irão usufruir de:

- Recebimento de informação relevante relacionada com o DEQ e a Engenharia Química (ver pacote de informação referido nas Acções a Desenvolver);
- Possibilidade de participação no Dia Aberto do DEQ;
- Participação na vida da Associação;
- Acesso, mediante apresentação de cartão de associado, a todos os serviços que se encontram disponíveis no DEQ (biblioteca, centro de cálculo, etc.);

- Possibilidade de solicitar serviços de consulta de informação (artigos de revistas, pesquisas de materiais, etc., a preço de custo);
- Desconto de 10% em acções de formação promovidas pela PRODEQ.

Em particular, para os Associados Estudantes:

- Apoio na realização de estágios e saídas profissionais, incluindo envio dos respectivos currículos para algumas empresas.

Em particular, no que diz respeito a associados colectivos:

- Apoio no recrutamento de licenciados em Engenharia Química;
- Tratamento preferencial no que diz respeito ao desenvolvimento de projectos com o DEQ, canalização de estagiários, etc.;
- Desconto de 10% em todas as prestações de serviços fornecidos pelo DEQ (incluindo análises, informação, formação, etc.), directamente ou através de serviços da responsabilidade de docentes do DEQ prestados por intermédio de outras entidades de interface (como o Instituto Pedro Nunes);
- Visita anual do Coordenador Executivo a cada uma das empresas, para identificar formas de a PRODEQ e o DEQ as poderem servir e com elas colaborar.

Em particular, no que diz respeito a associados colectivos patrocinadores:

- Visibilidade em todo o departamento e actividades da PRODEQ, onde os respectivos logotipos serão abundantemente divulgados (o mesmo sucede com todo o tipo de materiais promocionais);
- Atribuição dos nomes das empresas a salas do DEQ;
- Possibilidade de fazer acções de recrutamento e prospecção no DEQ;
- Tratamento duplamente preferencial no que diz respeito ao desenvolvimento de projectos com o DEQ, canalização de estagiários, actividades de ensino, investigação e desenvolvimento, etc.;
- Desconto de 20% em todas as prestações de serviços fornecidos pelo DEQ (incluindo análises, informação, formação, etc.), directamente ou através de serviços da responsabilidade de docentes do DEQ prestados por intermédio de outras entidades de interface (como o Instituto Pedro Nunes);

- Visita trimestral do Coordenador Executivo a cada uma das empresas, para identificar formas de a PRODEQ e o DEQ as poderem servir e com elas colaborar.

Sempre que através da PRODEQ venham a ser prestados serviços a entidades não associadas, esta retém um valor de 20% de overheads sobre os valores recebidos.

Nos projectos desenvolvidos em parceria com a PRODEQ, aos associados será cobrado um overhead de apenas 10% sobre despesas correntes, para os demais será cobrado um overhead de 20% sobre despesas correntes.

Em termos de peso relativo de votos em Assembleia Geral, estabelece-se a seguinte ponderação:

- Associados individuais estudantes: sem direito de voto, não sendo elegíveis para cargos directivos;
- Associados individuais: 1 voto;
- Associados colectivos: 10 votos;
- Associados colectivos patrocinadores: 20 votos.

Qualquer alteração aos Estatutos, para além de carecer de aprovação em Assembleia Geral, tem de merecer igualmente aprovação da Comissão Científica do DEQ da FCTUC.

PRODEQ10 – 10 anos ao serviço da Engenharia Química

Dia Aberto – CIEPQPF

Mestrado Integrado

Biodiesel obtained from supercritical carbon dioxide oil extracts of Cynara cardunculus L.

Agostinho M.R.C. Alexandre[1*], Ana M.A. Dias[1], Inês J. Seabra[1,2], Aantónio A.T.G. Portugal[1], Hermínio C. de Sousa[1], Mara E. M. Braga[1]

[1]*CIEPQPF, Departamento de Engeharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030-790 Coimbra, Portugal*
[2]*ESAC – Politechnic Institute of Coimbra, Bencanta, 3040-316 Coimbra, Portugal*
[*]*agostinho@itqb.unl.pt*

Suitable and alternative crops are recently being explored as efficient and sustainable sources for fuel and energy production. The present work evaluates the use of cardoon (*Cynara cardunculus*, L.) seed oil as a renewable raw material for biodiesel production and aiming to find an alternative to petroleum-based fuels at a regional scale, as cardoon is an endogenous plant of the Mediterranean Flora. Cardoon seed oil was extracted using a supercritical carbon dioxide ($scCO_2$) extraction method and varying $scCO_2$ density from 0.65 up to 0.93 g/cm^3. Hexane Soxhlet extractions were also performed for comparison purposes. Depending on the employed extraction conditions and/or methods, different oil yields and compositions were obtained. In general terms, higher $scCO_2$ densities led to higher cardoon oil yields (around 22%), which were similar to soxhlet oil yields (around 25%)[1]. Two biodiesel synthesis approaches were then used: *i*) direct cardoon oil transesterification in methanol, using an alkali-based process (to convert oil esters into fatty acid methyl esters, FAME) [3]; and *ii*) cardoon oil acid pre-esterification in methanol (to reduce the cardoon oil free fatty acids contents) followed by a methanolic transesterification reaction using an alkali-based process. Employed alkaline catalyst was sodium methoxide while acid catalyst was sulphuric acid [4]. All the obtained biodiesel samples were chemically and physically characterized according to the European Standard EN14214 methods [2]. Results showed that the second approach (acid-catalyzed esterification followed by alkaline transesterification) led to higher biodiesel yields as well as to higher FAME contents (for all employed oils obtained by different methods and conditions). In addition, other obtained properties fulfilled, with a few exceptions, the specified EN14214 values.

References:
[1] Olivier Boutin, Elizabeth Badens, Extraction from oleaginous seeds using supercritical CO_2: Experimental design and products quality, *J. Food Eng.*, 92, 396-402 (2009).
[2] European Committee for Standardization, EN 14214.
[3] Gerhard Knothe, Jon V. Gerpen, Jurgen Krahl. The Biodiesel Handbook. AOCS Press, (2005).
[4] Prafulla D. Patil, Shuguang Deng, Optimization of biodiesel production from edible and non-edible vegetable oils. *Fuel*, 88, 1302-1306 (2009).

A high-pressure/supercritical method to dry silica-based materials prepared by biomimetic aqueous sol-gel methods

Mariline C. Alves[1*], Rita B. Chim[1], Mara E.M. Braga[1], Chris R. Ziegler[2], Jim J. Watkins[2], Hermínio C. de Sousa[1]

[1]*CIEPQPF, Departamento de Engeharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030-790 Coimbra, Portugal*
[2]*Department of Polymer Science and Engineering, University of Massachusetts, 120 Governors Drive, Amherst, MA 01003, USA*
** marilinecastroalves@gmail.com*

Recently, we employed two new small bi-functional bioinspired catalysts for the hydrolysis and condensation of silica precursors in aqueous media and at ambient temperature and pressure: L-glutathione-reduced (GSH) and DL-methionine (Met) [1]. These biomimetic catalysts are non-toxic well-known biomolecules which are widely available at reasonable prices. Because of their different pH character in water solutions, GSH (acidic) and Met (near neutral) together with cysteamine (Cys, strongly basic) can be employed alone or titrated against one another for the facile and non-harsh aqueous formation of amorphous/mesoporous silica-based materials over broad and tunable ranges of pH, including neutral and near-neutral pH. These methodologies present evident advantages in terms of the obtained silica structure/stability, on the absence of potentially toxic substances and when the immobilization of thermo- and pH-labile biopolymers and bioactive molecules is intended [2,3]. However, and after silica formation, water and catalyst residuals should be removed from these silica-based materials. Water may be removed by conventional freeze-drying and evaporation methods but this will not remove catalysts from the prepared materials. In addition, evaporation methods are known to exert a strong capillary pressure on the inorganic/organic pore walls that will promote the collapse of most part of the materials pore volume [2]. Finally, calcination is not a valid option when silica-organic composite biomaterials are foreseen.

In this work, silica was prepared from TEOS [2], in aqueous solutions of different pH, and using the above referred biomimetic catalysts and strategies. Then, a "green" and combined/sequential high-pressure/SCF extraction/drying method (using water, ethanol and supercritical carbon dioxide) was employed in order to recover, purify and dry the obtained biomaterials, in a single unit operation and at moderate temperatures. Conventional freeze-drying and evaporation methods were also employed for comparison purposes. A supercritical solvent impregnation/deposition (SSI) method was also employed to load a bioactive molecule (dexamethasone) into the previously prepared/processed materials [4,5]. Obtained silica samples were chemically and physically characterized using several analytical techniques. The effects of pH and of the employed catalysts and extraction/drying methods were evaluated and compared in terms of silica production yields and of some important silica physical and morphological properties. Preliminary results indicated that these green and biomimetic methodologies may have a great potential for the development and preparation of amorphous microporous/mesoporous silica and silica-based composite biomaterials, which can be used for several biomedical and hard tissue engineering applications.

References:

[1] J.C. Lewin, Silicon Metabolism in Diatom, *J. Gen. Physiol*., 37, 589-599 (1954).
[2] C.J. Brinker, G.W. Scherer, Sol-gel science, Academic Press, (1990).
[3] R. Gupta., N. K. Chaudhury, Entrapment of biomolecules in sol-gel matrix for applications in biosensors: Problems and future prospects, *Biosensors & Bioelectronics*, 22, 2387-2399 (2007).
[4] M.E.M.Braga, M.T.V. Pato, H.S.R. Costa Silva, E.I. Ferreira, M.H. Gil, C.M.M. Duarte, H.C. de Sousa, Supercritical solvent impregnation of ophthalmic drugs on chitosan derivatives, *J. Supercrit. Fluids*, 44, 245-257 (2008).
[5] V.P. Costa, M.E.M. Braga, C.M.M. Duarte, C. Alvarez-Lorenzo, A.Concheiro, M.H. Gil, H.C. de Sousa, Anti-glaucoma drug-loaded contact lenses prepared using supercritical solvent impregnation, *J. Supercrit. Fluids*, 53, 165-173 (2010).

Treatment of liquid effluents by catalytic ozonation and photo-Fenton's processes

Ana S. Fajardo[a], Rui C. Martins[a] and Rosa M. Quinta-Ferreira[a,*]

[a]*CIEPQPF - Centro de Investigação em Engenharia dos Processos Químicos e Produtos da Floresta,*
Departamento de Engenharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra,
3030-790 Coimbra, Portugal
[*]*rosaqf@eq.uc.pt*

Water pollution and its scarcity are the main problems that humankind is facing nowadays. In this regards, great attention is being given to the removal of these pollutants from groundwater and wastewater by advanced oxidation processes (AOPs) that are based on generation of highly reactive species, especially hydroxyl radicals. Among them, ozonation and photo-Fenton's processes, operating at room conditions of pressure and temperature, are of special interest involving lower operational costs. Therefore, aiming to give a contribution in the development of these two processes, a synthetic effluent involving major phenolic compounds typically found in olive oil mill wastewaters, namely gallic, protocatechuic, *trans*-cinnamic, *3,4,5*-trimethoxybenzoic, veratric, and *4*-hydroxybenzoic acids, was used and analysed.

In both single and catalytic ozonation over Pt/Al_2O_3, the medium pH affected the rate of ozone decomposition and the formation of hydroxyl radicals. The optimum values were achieved for the catalytic system - pH 7 with 93.0 % and 47.7 % of TPh and COD removal, after 120 minutes. For pH 3, the catalytic ozonation was strongly affected by the presence of radical scavengers meaning that the reaction pathway developed mainly through hydroxyl radicals produced by the decomposition of ozone over the catalyst surface. No significant morphological or structural differences were observed between the fresh and used solid by SEM and XRD analysis. After 120 minutes of reaction, the recovered catalyst showed negligible aluminium leaching behaviour. Moreover, a sequence of feed-batch trials involving the catalyst reutilization exhibited almost constant activity during the operation time. According to eco-toxicological tests, ecological impact was reduced after the treatment of the initial effluent. Pt/Al_2O_3 seems to be a promising catalyst at industrial scale, which possible leads to lower operational costs, although a depth economic analysis is needed.

In what concerns the photo-Fenton's process our study only involved preliminary experiments carried out with UV light and different H_2O_2 and Fe concentrations, which indicated the need to proceed with other ranges of operating conditions in order to highlight the effective potential of such oxidative treatment.

Studies on the improvement of treatment of urban landfill leachates by fenton-like using ZVI process

Lopes D.V.[1], Martins R.C.[2], Quina M. J.[2a], Góis J.C.[1], Quinta-Ferreira R.M.[2]

[1] Department of Mechanical Engineering, Faculty of Sciences and Technology, University of Coimbra, Rua Luís Reis Santos, 3030-790 Coimbra, Portugal
[2] Centro de Investigação em Engenharia dos Processos Químicos e Produtos da Floresta (CIEPQPF), Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, Rua Sílvio Lima, 3030-790 Coimbra, Portugal - [a]guida@eq.uc.pt

Landfilling has been the broadest method for municipal solid waste (MSW) management [1], and one of the major environmental problems associated with this technology is related to the production of leachate. In practice these liquid effluents are high-strength wastewaters and their depuration is not an easy task for the conventional treatment systems.

Advanced oxidation processes (AOPs) are, generally, recognized by their ability to improve biodegradability being a suitable solution as a pre-treatment before a costless activated sludge reactor. In the last years, Fenton's process ($Fe^{2+} + H_2O_2$) has arisen as an industrially interesting technology. Some researchers [2] pointed out that it would be interesting to use zero valent iron (ZVI - Fe^0) as catalyst to promote H_2O_2 decomposition on the oxidation of organic pollutants which is more cost-saving than the direct application of iron salts.

In this scope, the aim of the present research is to study the applicability of the Fenton-like process using ZVI on the biodegradability improvement of landfill leachate.

The experiments were carried out in batch mode, by using 100 mL sealed flasks. Iron powder and industrial H_2O_2 (50%, w/w) were applied. Chemical oxygen demand (COD) and biochemical oxygen demand (BOD_5) were obtained according to the Standard Methods [3]. Atomic absorption was used to determine the amount of iron dissolved in the liquid effluents whereas silver nitrate titration was applied to appraise chloride. Two samples of leachate were collected from an urban sanitary landfill located in the centre region of Portugal, before (Raw) and after (Treated) the aerobic bio-reactor existent in the plant, and their characteristics were determined.

ZVI Fenton-like process was applied to the bio-treated stream and COD removal was compared with the one achieved when applying only H_2O_2 or ZVI separately. ZVI, by itself, slightly degraded organic matter leading to 5% of COD abatement in 2 h whereas the combination ZVI + H_2O_2 was able to reach 19% which was very similar to the 14% attained when only H_2O_2 was applied. In fact, the high amount of dissolved iron present in solution (85 mg/L) is already able to catalyse H_2O_2 decomposition into hydroxyl radicals not being, thus, necessary to add extra catalyst. Contrarily, in what concerned the raw effluent, comprising a lower concentration of Fe in solution (28 mg/L), the addition of H_2O_2 without ZVI was unable to remove COD whereas the system ZVI + H_2O_2 removed 5% of COD in 120 min of oxidation.

pH is a key parameter in what regards Fenton's peroxidation. In fact, for ZVI + H_2O_2 a decrease on COD removal efficiency was detected when pH rose from 2 (38%) to 9.4 (17%) in the bio-treated effluent. A similar behaviour was found out for the raw stream with 8% of degradation for pH = 2 when compared with barely 3% for pH = 9.4. The effect of the other operating conditions, governing Fenton's process, was investigated. Attention was given to the effluent biodegradability enhancement since the aim will be its discharge throughout the sewage to be refined in the municipal wastewater treatment plant operating with classical activated sludge bio-reactors.

References

[1] Vilar V.J., Capelo, S.M., Silva, T.F., Boaventura, R.A., *Catal. Today*, 161, 228-234 (2011).
[2] Namkung K.C., Burgess A.E., Bremner D.H., *Environ. Technol.,* 26, 341-352 (2005).
[3] Greenberg A., Clesceri L., Eaton A., Standard methods for the examination of water and wastewater, American Public Health Association: Washington DC. (1985).

Performance evaluation of Al, Mg, Ti or Zr and oxygen energetic systems using THOR code with Gordon & McBride polynomials

T. Matias[a], L. Durães[a], A. Andrade-Campos[b], J. Campos[c,d], A. Portugal[a*]

[a] *Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, Pólo II, Rua Sílvio Lima, 3030-790 Coimbra, Portugal*
[b] *Department of Mechanical Engineering, University of Aveiro, Campo Universitário de Santiago, 3810-193 Aveiro, Portugal*
[c] *Department of Mechanical Engineering, Faculty of Sciences and Technology, University of Coimbra, Pólo II, Rua Luís Reis Santos, 3030-788 Coimbra, Portugal*
[d] *LEDAP – Laboratory of Energetics and Detonics, Av. Univ. de Coimbra, 3150-277 Condeixa, Portugal*
**Corresponding author. Tel.:+351 239798741; Fax:+351 239798703. E-mail: atp@eq.uc.pt.*

THOR is a program for the prediction of combustion and detonation processes of energetic mixtures. It requires a large database (THOR DB) that contains the termochemical characteristics of the reactants and possible products of the reaction.

In this work we developed a numerical approach for the calculation of the Gordon and McBride (G & McB) polynomial coefficients. These polynomials are used in THOR to evaluate the energetic state of the detonation/combustion products.

In the present study, the coefficients for common combustion/detonation gaseous products and for compounds that involve Al, Mg, Ti and Zr with oxygen were selected. In this way, we predicted the formation of ceramic produts from detonation or combustion of emulsions that involve the referred metals.

The polynomials coefficients were estimated by least squares by using Matlab version 7.7.0 (R2008b). The obtained coefficients were later used in a number of simulations of various reactive systems, namely, simple gaseous systems and more complex emulsion systems that involve Al, Mg, Ti and Zr together with oxygen. The results for all the systems tested were good, showing the potential of the applied method to obtain data for less studied ceramic compounds.

Produção de Nanopartículas por Via de Detonação

Pedro M.S. Santos[a], Belmiro P.M. Duarte[b,a], Nuno M.C. Oliveira[a,*], José L. Andrade Campos[c], João M. Calado[d]

[a]*GEPSI – PSE Group, CIEPQPF, Department of Chemical Engineering, University of Coimbra, Pólo II, R. Sílvio Lima, 3030-790 Coimbra, Portugal*
[b]*Department of Chemical and Biological Engineering, ISEC, Polytechnic Institute of Coimbra, R. Pedro Nunes, 3030-199 Coimbra, Portugal*
[c]*Department of Mechanical Engineering, University of Coimbra, Pólo II, R. Sílvio Lima, 3030-790 Coimbra, Portugal*
[d]*Inovnano, Materiais Avançados, S.A*

Este trabalho aborda a produção de nanopartículas de óxidos metálicos via detonação. Numa primeira fase, foi estudada a produção de nanopartículas de Alumina pela detonação de emulsões de ANFO enriquecido com Alumínio. Para a obtenção de um maior conhecimento acerca do processo, foi desenvolvido e simulado um modelo fenomenológico, o qual inclui uma descrição matemática da etapa de detonação interligada ao modelo que descreve os fenómenos que ocorrem ao nível das partículas líquidas de Alumina.

O processo de detonação é simulado usando uma combinação do código termoquímico THOR, o qual permite obter as condições do processo de detonação no instante Chapman-Jouguet (CJ), conjuntamente com um modelo espacial homogéneo aproximado que descreve a expansão radial da matriz de detonação. As condições no ponto de CJ são utilizadas como condições iniciais do modelo dinâmico da detonação. É ainda utilizada a Equação de Estado (EoS) Mie-Gruneisen, sendo a "curva fria" de referência representada pela EoS JWL.

Os fenómenos particulares que representam a formação das nanopartículas de Alumina a partir de gotículas de líquido são descritos por uma Equação de Balanço Populacional (EBP), na qual foram contabilizados os mecanismos de coalescência e coagulação. As variáveis associadas à dinâmica da detonação interagem com os kernels característicos de movimentos brownianos de ambos os fenómenos, bem como com a concentração de partículas devido ao aumento do volume do sistema. A abordagem numérica utilizada na resolução da EBP assenta numa discretização espacial com base no esquema de pivôs fixos. A solução dinâmica dos modelos que representam ambos os processos evolui ao longo do tempo. Para tal, recorreu-se a um *solver* de Equações Diferenciais Algébricas (EDA) implícito presente na plataforma *Wolfram Mathematica*.

Dos resultados da simulação foi possível observar que a principal fase de crescimento das partículas ocorre nos primeiros instantes da expansão. Este facto pode ser associado não só à elevada frequência de colisão neste período, como também às condições iniciais do sistema, nomeadamente no que diz respeito à concentração das partículas líquidas de Alumina. Para o sistema em estudo, obteve-se um diâmetro médio final as partículas da ordem dos 156 nm, o qual foi obtido após um período de crescimento de 46 μs.

Os resultados obtidos quer para a expansão radial da matriz de detonação quer para o crescimento das partículas, apresentam uma boa concordância com os que estão disponíveis na literatura e em testes laboratoriais. Este facto mostra o potencial desta ferramenta para alcançar um maior conhecimento relativamente a esta técnica de produção de nanopartículas.

References:

[1] P.M.S. Santos, Produção de Nanopartículas por Via de Detonação, Tese de Mestrado, Universidade de Coimbra (2009).

PRODEQ10 – 10 anos ao serviço da Engenharia Química

Dia Aberto – CIEPQPF

Projectos de Investigação

Development of new polymer-liposome complexes

P. Alves[a,*], Joana Mendes[a], J.F. Coelho [a], M.H. Gil [a], and P.N. Simões[a]

[a]*CIEPQPF, Departamento de Engeharia Química, Faculdade de Ciências e Tecnologia,*
Universidade de Coimbra, 3030-790 Coimbra, Portugal
[*]*palves@eq.uc.pt*

Liposomes are self-assembled vesicles that consist of an aqueous core domain entrapped by a lipid bilayer. They are attractive materials for drug delivery systems (DDS) due to their biocompatibility, non-immunogenicity, non-toxicity and ability to entrap both hydrophilic and hydrophobic compounds [1,2]. Despite the promising capabilities as DDS, liposomes have shown low transfection efficiency and low stability in the systemic circulation. To overcome these drawbacks, functional polymers are being proposed, aiming at the development of polymer-caged liposomes (PCL). This strategy also allows the preparation of PCL that can respond to environmental stimuli (pH and temperature), enhancing their usefulness as DDS. Here resides the motivation of this project, in which the overall goal is: 1 - to engineer new macromolecules capable of promoting both stability and site-specific targeting ability of standard liposomes; 2 - to ensure a tight control over the molecular weight of the polymers, their biodegradability and biocompatibility; 3 - to strive for solutions that can avoid the PCL cross-linking step.

The main objective within the polymer synthesis/characterization framework is to synthesize tailored stimuli responsive polymer structures that stabilize the liposome and release the drug in defined conditions (temperature, pH and targeting). For this proposes, the synthesis of these macromolecules is based on a Living Radical Polymerization (LRP) method, more specifically a metal catalyzed method, known as Atom Transfer Radical Polymerization (ATRP). This strategy presents several advantages over other methods, such as mild work conditions, fast kinetics and very high tolerance to different functionalities, as well as a strict control of the molecular weight and polydispersity of the polymers.
The new block copolymer is composed of: (i) poly(N-isopropylacrylamide) (PNIPAM), chosen in virtyue of its thermoresponsive attribute that exhibits a coil/globule transition in aqueous solution at *ca*. 32 ºC, known as lower critical solution temperature (LCST); (ii) poly(acrylic acid) (PAA), to provide a pH-sensitive character; (iii) poly(ethylene glycol) (PEG), to promote the biodegradability of the system and to diminish the cell and plasma protein adhesion; (iv) cholesterol end-group, which acts like an anchor, thus allowing an easy incorporation in the liposome system; and (v) folic acid for targeting. The strategy defined consists in the synthesis of three different architectures: (a) linear polymer made of cholesterol terminated-PNIPAM-b-PAA-b-PEG-folate; (b) brush-shaped polymer made PEG-b-PAA-b-PNIPAM-b-PAA-b-PEG-b-folate-g-cholesterol; (c) star-shaped block copolymer with one arm of cholesterol and two (to four) arms of PNIPAM-b-PAA-b-PEG-b-folate.

References:

[1] L. Paasonen, B. Romberg, G. Storm, M. Yliperttula, A. Urtti and W.E. Hennink, Temperature-Sensitive Poly(N-(2-hydroxypropyl)methacrylamide mono/ dilactate)-Coated Liposomes for Triggered Contents Release , *Bioconjugate Chem.,* 18, 2131–2136 (2007).
[2] S.-M. Lee, H. Chen, C.M. Dettmer, T.V. O'Halloran and S.T. Nguyen, Polymer-Caged Lipsomes: A pH-Responsive Delivery System with High Stability, *J. Am. Chem. Soc.*, 129, 15096–15097 (2007).

Multivariate linear regression models for heterogeneous liquid-liquid reactions in microstructured reactors

C.M.S.G. Baptista[1], T. Mendes[1], C. Dias[1], M. S. Reis[1], P. Löb[2]
[1]*Chemical Engineering Department, Faculty of Sciences and Technology-University of Coimbra, 3030-790 Coimbra, Portugal*
[2]*Institut für Mikrotechnik Mainz GmbH (IMM), Carl-Zeiss-Strasse 18-20, 55129, Mainz,Germany*

Many bulk chemical processes are multiphase, often liquid-liquid, and in these heterogeneous systems several complex mechanisms for mixing, mass and heat transfer and chemical reaction take place simultaneously, affecting the reaction selectivity and yield. Mass transfer through the interfacial area and temperature control are known to influence the formation of by-products and microstructured reactors are being developed to improve mixing efficiency, while enhancing heat and mass transfer processes. Scale-up of these microreactors will certainly benefit from data collected in experiments and the modelling of these results, enabling to obtain valuable kinetic information.

A broad range of experimental conditions were explored at labscale while processing an exothermic liquid-liquid reaction. After a preliminary analysis for screening the most influent operating conditions and colinearity, these experimental data were used to develop Multivariate Linear Regression (MLR) models capable of describing the formation of products as well as the two main by-products. Apart from reactor temperature, the independent explanatory variables were found to be inlet conditions or their nonlinear relationships. These include flow rates, concentration of main reactants or residence time, which can be set during operation in order to reach the target productivity and selectivity. To minimize the information required and facilitate its use, even during operation of an industrial plant, the models are based on the minimum number of variables still allowing for good prediction ability.

Acknowledgement
The authors acknowledge the funding support from the 7th European Framework Program within the PILLS Project.

Anti-inflammatory activity of Jucá (*Caesalpinia ferrea*) extracts obtained by SFE and by ESE

Mara E.M. Braga[1], Inês J. Seabra[1,2], Ana M.A. Dias[1], Paula Ferreira[1,3], Joana Gaspar[4], Maria H. Gil[1], Franscisco Ambrósio[4], Raul C. Júnior[5], Hermínio C. de Sousa[1]

[1]CIEPQPF - Chemical Engineering Department, FCTUC, University of Coimbra, Rua Sílvio Lima, Pólo II – Pinhal de Marrocos, 3030-790 Coimbra, Portugal.
[2]ESAC - Politechnic Institute of Coimbra, Bencanta, 3040-316 Coimbra, Portugal.
[3]UCP - Departamento de Ciências da Saúde, Universidade Católica Portuguesa, Estrada da Circunvalação, 3504-505, Viseu, Portugal.
[4]IBILI – Instituto Biomédico de Investigação da Luz e da Imagem, Celas, 3000-548 Coimbra.
[5]UFPA - Faculdade de Engenharia de Minas e Meio Ambiente. Campus II da UFPA, Folha 17, Quadra 04, Lote Especial, Nova Marabá, 68505-080 Pará, Brasil.
**hsousa@eq.uc.pt*

Wound repair processes, in which skin repairs itself after some kind of injury, are generally formed by several sequential and overlapping phases, such as haemostasis/inflammatory, proliferative and remodelling. Several substances, obtained from different natural sources, are known to act on the skin to treat the first injury phase, thus helping and accelerating the overall wound healing process [1]. *Caesalpinia ferrea*, commonly known as Pau Ferro or Jucá, is a native tree from north eastern regions of Brazil, and its stems, fruits, leaves and bark extracts are traditionally used in folk medicine as natural analgesic, wound healing and anti-inflammatory agents [2,3]. Amongst other phenolic compounds, eucalyptol, β-sistosterol, gallic acid and the specific phenolic compound present in Jucá fruit extracts, pauferrol A, are generally associated to the observed biological activities [4,5]. The main objective of this work was to characterize and to evaluate the anti-inflammatory activities of Jucá fruits phenolic extracts which were obtained by supercritical fluid extraction (SFE) and by enhanced solvent extraction (ESE). Carbon dioxide (CO_2) and/or CO_2/EtOH/H_2O mixtures were employed as extraction solvents at fixed (250 bar and 50 ºC) operational conditions. Conventional techniques like hydrodistillation and Soxhlet extraction were also employed. Extracts composition was explored by TLC and HPLC; total phenolic compounds were quantified by the Folin-Ciocalteau´s method. Extracts anti-inflammatory activities were determined by the Griess Reaction method. Despite the obtained lower extraction yields of hydrodistillation and of SFE (CO_2), these extracts led to the highest anti-inflammatory activities (around 68 % for SFE and 51 % for HD, at 300 μg of extract). Phenolic and alkaloid compounds were observed qualitatively by TLC and HPLC. There was not a direct relation between the extracts phenolic compounds amounts and their anti-inflammatory activities and obtained results were most probably related to the presence of some specific phenolic compounds and not to their overall quantity. Although cell oxidation and inflammation processes may be associated, not all antioxidant substances have anti-inflammatory activity on cells. Results indicate that extracted compounds from Jucá fruits present a relevant anti-inflammatory activity, which may be a strong indication that they can be employed to help wound healing processes.

References:

[1] J.C.T. Carvalho, J. R.N. Teixeira, P.J.C. Souza, J.K. Bastos, D. Santos Filho, S.J. Sarti, Preliminary studies of analgesic and antiinflammatory properties of *Caesalpinia ferrea* crude extract, *Journal of Etnopharmacology*, 53, 175-178 (1996).
[2] E.M. Bacchi, J.A.A. Sertie, N. Villa, H. Katz. Anti-ulcaration and toxicity of *Styrax camporum* and *Caesalpinia ferrea*. *Planta Medica*, 61, 204-207 (1995).
[3] U.P. Albuquerque, P.M. Medeiros, A.L.S. Almeida, J.M. Monteiro, E.M.F. Lins Neto, J.G. De Melo, J.P. Santos. Medicinal plants of the caatinga (semi-arid) vegetation of NE Brazil: a quantitative approach. *Journal of Ethnopharmacology*, 114, 325-354 (2007).
[4] Frasson, A.P.Z.; Bittencourt, C.F.; Heinzmann, B.M. Caracterização físico-química e biológica do caule de *Caesalpinia ferrea* Mart. *Revista Brasileira de Farmacognosia*, 13, 35-39 (2003).
[5] Nosaki et al 2007. Pauferrol A, a novel chalcone trimer with a cyclobutane ring from *Caesalpinia ferrea* Mart exhibiting. *Tetrahedron Letters*, 48, 8290-8292 (2007).

Molecularly imprinted therapeutic contact lenses by SCF processes: improved drug loading/release capacity

Mara E.M. Braga[1], Fernando Yañez[2], Carmen Alvarez-Lorenzo[2], Angel Concheiro[2], Catarina M.M. Duarte[3], Maria H. Gil[1], Hermínio C. de Sousa[1,*]

[1]CIEPQPF, Chemical Engineering Department, FCTUC, University of Coimbra, Rua Sílvio Lima, Pólo II – Pinhal de Marrocos, 3030-790 Coimbra, Portugal
[2]Departamento de Farmacia y Tecnología Farmacéutica, Facultad de Farmacia, Universidad de Santiago de Compostela, Spain
[3]Nutraceuticals and Delivery Laboratory, ITQB/IBET, Aptd. 12 – 2780 Oeiras, Portugal
[*]hsousa@eq.uc.pt

Conventional topical ophthalmic formulations generally present low bioavailability which is mainly due to several ocular protective mechanisms such as tear drainage and blinking. To overcome these problems, several types of ophthalmic polymer-based drug delivery systems (DDSs) have been developed, including therapeutic contact lenses. Drug-loading of contact lenses by soaking in concentrated drug aqueous solutions is usually poor and limited to water-soluble drugs. On the other hand, molecular imprinting methods are known to originate polymeric systems which incorporate specific template molecules, such as drugs, with high yields, selectivity and affinity, leading to more efficient DDSs [1,2]. Nevertheless, these methods are very time consuming and also present limitations associated to the employed drug incorporation/leaching processes. The present work deals with the impregnation and extraction of contact lenses with hydrophobic drugs using supercritical carbon dioxide (scCO_2). The main objective of this work is to improve the flurbiprofen loading capacity of Hilafilcon B commercial contact lenses, using an innovative SCF-assisted molecular imprinting method, namely by the use of sequential SCF drug impregnation and extraction procedures, in order to develop more efficient therapeutic contact lenses. Conventional drug soaking and drug leaching methods were also employed for comparison purposes. scCO_2 impregnation assays were performed at 12.0 MPa and at 313 K, while scCO_2 extractions were performed at 20.0 MPa and at 313 K. Impregnated/extracted drug amounts were quantified for all experiments. Processed samples were characterized by SEM and by helium picnometry method. Monthly imprinted contact lenses were recharged over night (12 hours) and released for 8 hours, in order to simulate typical contact lenses patient wearing. In vitro drug release profiles were obtained and compared. Results were discussed in terms of impregnation and release contact lenses capacities. Obtained results demonstrated the feasibility of preparing improved and more efficient flurbiprofen-loaded Hilafilcon B monthly contact lenses using this innovative SCF-assisted molecular imprinting method. These methods are "tunable", i.e., the amount of impregnated/extracted drug can be controlled by simple manipulation of operational conditions, and they do not employ any organic/toxic solvent. Moreover, they enable the preparation of hydrophobic drug-based therapeutic contact lenses in much shorter process times than those using conventional molecular imprinting methods.

References:

[1] B. Sellergren, C.J. Allender, *Adv. Drug Deliv. Rev.* 57, 1733-1741(2005).
[2] C. Alvarez-Lorenzo, F. Yanez, R. Barreiro-Iglesias, A. Concheiro. *J. Control. Release* 113, 236-244(2006).

Modeling the effect of mixing in biodiesel production

Ana S. R. Brásio[a], Andrey Romanenko[b], Lino O. Santos[a], and Natércia C. P. Fernandes[a]

[a]*CIEPQPF, Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, 3030-790 Coimbra, Portugal, lino@eq.uc.pt*
[b]*Ciengis, SA, 3030-199 Coimbra, Portugal, Andrey.Romanenko@ciengis.com*

The transesterification reaction models available in the literature are valid only for one particular mixing condition. In this work, a modeling strategy is presented in order to predict the effect of mixing conditions in the transesterification process. The proposed methodology was applied to independent sets of experimental data available in the literature that show the dependency of the transesterification reaction on the frequency of rotation of the stirrer. The accuracy of the developed models corroborates the validity of the proposed modeling approach.

References:

M. Bambase, N. Nakamura, J. Tanaka and M. Matsumura, Kinetics of hydroxide-catalyzed methanolysis of crude sunflower oil for the production of fuel-grade methyl esters. Journal of Chemical Technology and Biotechnology, 82 (2007), pp. 273–280.

H.J. Berchmans, K. Morishita and T. Takarada, Kinetic study of methanolysis of Jatropha curcas-waste food oil mixture. Journal of Chemical Engineering of Japan, 43 (2010), pp. 661–670

D. Frascari, M. Zuccaro, D. Pinelli and A. Paglianti, A pilot-scale study of alkali-catalyzedsunflower oil transesterification with static mixing and with mechanical agitation. Energy and Fuels, 22 (2008), pp. 1493–1501.

D. Frascari, M. Zuccaro, A. Paglianti and D. Pinelli, Optimization of mechanical agitation and evaluation of the mass-transfer resistance in the oil transesterification reaction for biodiesel production. Industrial and Engineering Chemistry Research, 48 (2009), pp. 7540–7549.

R. Hemrajani and G.B. Tatterson, Mechanically Stirred Vessels, John Wiley & Sons (2004), (Chapter 6), pp. 345–390.

F. Ma, L.D. Clements and M.A. Hanna, The effect of mixing on transesterification of beef tallow. Bioresource Technology, 69 (1999), pp. 289–293.

H. Noureddini and D. Zhu, Kinetics of transesterification of soybean oil. Journal of the American Oil Chemists' Society, 74 (1997), pp. 1457–1463.

O. Stamenković, M. Lazić, Z. Todorović and V. Veljković, The effect of agitation intensityon alkali-catalyzed methanolysis of sunflower oil. Bioresource Technology, 98 (2007), pp. 2688–2699.

J.C. Thompson and B.B. He, Biodiesel production using static mixers. Transactions of the ASABE, 50 (2007), pp. 161–165

G. Vicente, M. Martínez, J. Aracil and A. Esteban, Kinetics of sunflower oil methanolysis, . Industrial and Engineering Chemistry Research, 44 (2005), pp. 5447–5454

Liquid-Liquid Equilibria, Surface and Interfacial Tension for Water+N-Butyl Acetate+1-Propanol at 323.15 K

H. F. Costa[1], I. Johnson[2], F. M. Gonçalves[1], Abel G. M. Ferreira[1], Isabel M. A. Fonseca[1]
[1]Departamento de Engenharia Química, Universidade de Coimbra, Pólo II, Rua Sílvio Lima 3030-790 Coimbra, Portugal; [2]Department of Physics, St. Joseph´s College, Trichy-620 002, India

The importance of liquid-liquid extraction in separation technology has increased over the last 30 years. It is now usually used in pharmaceutical and food industries for recovering valuable organic materials for example the alcohols from aqueous solutions. The problems associated with the development and construction of industrial extraction units are the complexity of the materials to be extracted, the heterogeneity of the liquid medium and the necessary low separation time required. The published studies on liquid-liquid equilibrium and on the thermophysical properties data of ternary systems of practical interest are scarce when compared with the wide variety of binary systems which have been investigated. The surface and interfacial tensions of solutions has a great effect on the efficiency of the extraction. In the last years we have made measurements of this properties and we have correlated the data for systems of the type water+alcohol+ester.[1-3] The aqueous solutions of alkanols can be efficiently extracted with esters.

The purpose of this study is to determine the liquid-liquid equilibria for the water+1-propanol+N- butyl acetate at 323.25 K. For this system the surface tension was measured in the homogeneous region and the interfacial tension was determined in the immiscible range at the same temperature. The binodal curve was found by the clound-point method, using a solubility cell assembled for this. The tie-lines were determined by sampling the liquid phases from a cell carefully designed for LLE and the composition was determined in a TRE METRICS 9001 gas chromatograph with a J & W Scientific DB-1 column. N-buthanol was used as internal standard for the calibration of the detector (FID). The LLE data for the system water+ N- butyl acetate+1-propanol at 323.25 K is shown in Figure 1. In Figure 2 we present the function used for correlation of the surface tension of the ternary system comparing the experimental results with the fitted data. The interfacial tension γ´ data was correlated with the Li and Fu model [4].

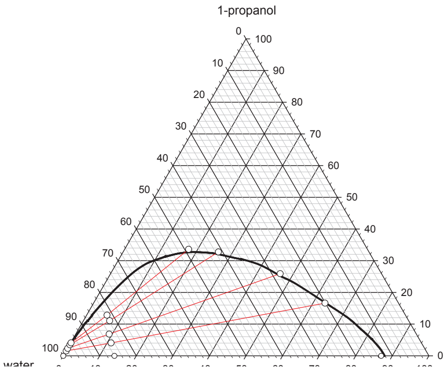


Figure 1. Binodal curve (—)and tie-lines(–○–) for LLE o
water + 1-propanol+N- butyl acetate at 323.25 K.

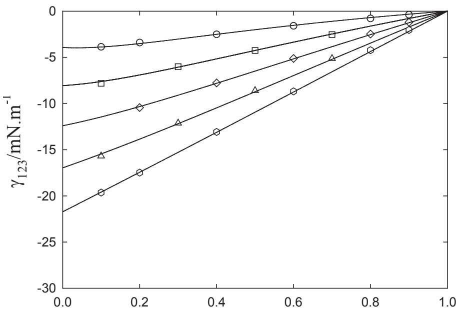


Figure 2. Function, γ_{123} for the ternary system water(1)+N-butyl acetate(2)+1-propanol(3), at 323.15 K and atmospheric pressure, along the curves of constant ratio z = x_1/x_3 as a function of the ester composition,x_2:(○), z = 0.111; (□), z = 0.250; (◊), z = 0.429; (Δ), z = 0.667 and (○), z = 1.000. (—) Correlation with eq (4).

References

[1] Santos, B. M. S., Ferreira A. G. M., Isabel M. A. Fonseca, "Surface and interfacial tensions of the systems water + n-butyl acetate + methanol at 303.15 K", *Fluid Phase Equilibria* 208 (2003) 1-21.

[2] Mirjana Lj. Kijevcanin, Inês S. A. Ribeiro, Abel G. M. Ferreira, Isabel M. A. Fonseca, "Densities, Viscosities and surface and interfacial tensions of the ternary mixture water + ethyl butyrate + methanol at 303.15 K", *J. Chem. Eng. Data*. 48 (2003) 1266-1270.

[3] Mirjana Lj. Kijevcanin, Inês S. A. Ribeiro, Abel. G. M. Ferreira, Isabel M. A. Fonseca "Water+esters+methanol: experimental data, correlation and prediction of surface and interfacial tensions at 303.15 K and atmospheric pressure", *Fluid Phase Equilibria* 218 (2004) 141-148.

[4] B. Li and J. Fu, Interfacial Tensions of Two-Liquid-Phase Ternary Systems. *J. Chem. Eng. Data* 37 (1992) 172-174.

Natural-based biopolymers loaded with natural drugs for biomedical applications

Ana M. A. Dias, Mara E. M. Braga, Paula Ferreira, M. Helena Gil, Hermínio C. de Sousa*

CIEPQPF, Departamento de Engeharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030-790 Coimbra, Portugal
**hsousa@eq.uc.pt*

Systems capable of deliver bioactive agents into cutaneous/subcutaneous levels are of great interest as therapeutic or cosmetic approaches for effective treatment and prevention of skin disorders [1]. Such bioactive dressings could be used to inhibit infection and/or inflammation, to provide real-time diagnostic information about the state of the wound and to stimulate healthy healing responses [2].

N-carboxybutyl chitosan (CBC) is a biodegradable and biocompatible natural-based polymer which can form highly hydrophilic networks that may swell and increase its volume by absorbing large amounts of water or of aqueous solutions. This characteristic is essential to allow an efficient drug release kinetic, as it is responsible for prolonging the residence time of drugs at the absorption site, maintaining drug release and improving drug bioavailability for convenient periods. Moreover, chitosan-based materials are already known to be applied as interesting and valuable materials for several biomedical applications, mainly because of their good film-forming properties, wound-healing benefits, bacteriostatic effects and bioadhesive properties [3]. Flavonoids, such as quercetin, are naturally occurring substances known for their anti-allergic, anti-inflammatory, anti-microbial and anti-cancer activities. Moreover, they normally present significant antioxidant capacity which can provide novel possibilities for the treatment and prevention of several oxidative stress-mediated skin diseases by scavenging oxygen radicals and by protecting against lipid peroxidation [4]. Thymol is a monoterpene phenol which presents a pleasant aromatic odor and strong antiseptic properties. It is recognized as a safe food additive and it is frequently used in several products as a flavoring and/or as an antimicrobial agent, showing a broad-spectrum of activities against bacteria, yeasts and fungi [5].

In this work quercetin and thymol were impregnated/deposited into CBC membranes using a Supercritical Solvent Impregnation (SSI) method and employing supercritical carbon dioxide ($scCO_2$) as the carrier solvent and the polymer swelling/plasticizing agent. Besides its greener characteristics, the SSI method also permits to tune drug loading and drug depth penetration by controlling the depressurization step, impregnation period or by changing the mobile phase solvent density by simple pressure and temperature manipulation. The long term goal of this work is to develop process-tailored materials which may be able to originate different biological and chemical environments to enhance wound healing processes and to permit extended wearing periods between dressing changes.

References:

[1] H. Wagner, K. H. Kostka, C. M. Lehr, U. F. Schaefer, Interrelation of permeation and penetration parameters obtained from in vitro experiments with human skin and skin equivalents, J. Control. Rel., 75, 283-295 (2001).

[2] M. Cabodi, V. L. Cross, Z. Qu, K. L. Havenstrite, S. SchwartZ, A. D. Stroock, An active wound dressing for controlled convective mass transfer with the wound bed, J. Biom. Mat. Res. Part B, 82B, 210-222 (2007).

[3] C. A. Haller, P. Jacob, N. L. Benowitz, Short-term metabolic and hemodynamic effects of ephedra and guarana combinations, Clin. Pharmacol. Ter., 77, 560-571(2005).

[3] T. N. Yudanova, I. V. Reshetov, Modern wound dressings: Manufacturing and properties, Pharmaceutical Chem. J., 40, 85-92 (2006).

[4] T. P. T. Cushnie, A. J. Lamb, Antimicrobial activity of flavonoids, Int. J. of Antimicrobial Agents, 26, 343-356 (2005).

[5] A. Sivropoulou, E. Papanikolaou, C. Nikolaou, S. Kokkini, T. Lanaras, M. Arsenakis, Antimicrobial and cytotoxic activities of Origanum essential oils, J. of Agr. and Food Chem., 44, 1202-1205 (1996).

Optimal strategies for quality improvement programs - a discrete time Mathematical Programming formulation

Belmiro P. M. Duarte[a,b], Nuno M. C. Oliveira[b], and Lino O. Santos[b]

[a] *Department of Chemical and Biological Engineering, Polytechnic Institute of Coimbra, R. Pedro Nunes, 3030-190 Coimbra, Portugal. bduarte@isec.pt*
[b] *Gepsi Group, CIEPQPF, Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, 3030-790 Coimbra, Portugal, {nuno,lino}@eq.uc.pt*

Organizations that improve the performance of processes, goods and services through Quality Management Systems (QMS) feature major benefits in various areas, ranging from a clear and functional chain of responsibility to market position. Very often the adopted improvement strategy requires a continuous set of active projects to achieve gains in the quality level of the delivered goods/services. Because of the resources limitations, the Quality improvement programs should be traded off with the quality gains within the specified time horizon of the improvement programs. Toaddress this problem it is of great interest to develop an optimal policy for the quality improvement programs that takes simultaneously into account the most relevant costs and the target quality level. We propose a mathematical programming strategy to find an a priori optimal quality improvement policy, able to determine the best sequence of investments over a given time horizon. The model representing the quality level depends on the improvement investment, and on the costs of quality accounting for prevention-appraisal and failure.

References:

Allen, E., 2007. Modeling with Itô Stochastic Differential Equations, 1st Edition. Springer, Dordrecht.

Burgess, T., 1996. Modelling quality-cost dynamics. International Journal of Quality & Reliability Management 13, 8–26.

Campanella, J., 1999. Principles of Quality Costs: Principles, Implementation, and Use, 3rd Edition. ASQC Quality Press, New York.

Dixit, A. K., Pindyck, R. S., 1994. Investment under Uncertainty, 1st Edition. Princeton University Press, New Jersey.

Kim, S., Nakhai, B., 2008. The dynamics of quality cost in continuous improvement. International Journal of Quality& Reliability Management 25, 842–857.

Li, G., Rajagopalan, S., 1998. Process improvement, quality, and learning effects. Management Science 44, 1517–1532.

Little, J. D. C., 1970. Models and managers: the concept of decision calculus. Management Science 16, 466–485.

Sandoval-Chávez, D., Beruvides, M., 1998. Using opportunity costs to determine the cost of quality: a case study ina continuous-process industry. The Engineering Economist 43, 107–124.

Schiffauerova, A., Thomson, V., 2006. A review of research on cost of quality models and best practices. International Journal of Quality & Reliability Management 23, 647–669.

Taguchi, G., Elsayed, E. A., Hsiang, T. C., 1988. Quality Engineering in Production Systems, 1st Edition. McGraw-Hill, New York.

Synthesis of flexible silica based xerogels and aerogels

Luísa Durães[1], Sofia Nogueira[1], Ana Santos[1], Jessica Hernandez[2],
António Portugal[1]

[1] CIEPQPF–CEM group, Department of Chemical Engineering, University of Coimbra,
Pólo II, Rua Sílvio Lima, 3030–790 Coimbra, Portugal
[2] Active Space Technologies, Rua Pedro Nunes, 3030–199 Coimbra, Portugal

Keywords*:* sol-gel synthesis, silica based aerogel/xerogel, flexible nanomaterial.

Silica aerogels synthesized with $Si(OR)_4$ precursors have a nanostructured three-dimensional network and exhibit low density (~ 40 Kg/m^3), high surface area (~ 1000 m^2g), low thermal conductivity (0,02 W/mK) and high transparency (~ 90 %); these unique properties allow their use in several applications, namely as thermal or acoustic insulators, dielectric or optical materials, filters and catalysts (Pierre and Pajonk, 2002, Rao et al., 2006). However, these aerogels are very brittle, absorb moisture and deteriorate with time. Flexible and hydrophobic aerogels would allow achieving improved performance of these materials in particular applications. Using methyltrimethoxysilane (MTMS) as precursor, the obtained silica based aerogels can fulfill this need. In MTMS, one OR group of $Si(OR)_4$ is replaced by R, with $R=CH_3$. This group is not attacked during the hydrolysis step of the synthesis and remains in the aerogel structure, providing the hydrophobicity and flexibility required (Rao et al., 2006, Baghat et al. 2007). The density and the surface area are also controlled by the drying technique, being the ambient pressure dried gels – xerogels – more dense and less porous than the gels dried in supercritical conditions – aerogels.

References

Bhagat, S.D., Oh, C.-S., Kim, Y.-H., Ahn, Y.-S., Yeo, J.-G. (2007). Methytrimethoxysilane based monolith silica aerogels via ambient pressure drying. Microporous and Mesoporous Materials, 100, 350-355.

Pierre, A.C., Pajonk, G.M. (2002). Chemistry of Aerogels and Their Applications. Chemical Rev., 102, 4243-4265.

Rao, A.V., Bhagat, S.D., Hirashim, H., Pajonk, G.M. (2006). Synthesis of flexible silica aerogels using methyltrimethoxysilane (MTMS) precursor. Journal of Colloid and Interface Science, 300, 279-285.

High performance computing in chemical engineering: multiscale molecular modeling of polymer-liposome complexes targeted for drug delivery systems

André F.S. Ferreira[a,*] and P.N. Simões[a]

[a]*CIEPQPF, Departamento de Engenharia Química,*
Faculdade de Ciências e Tecnologia,
Universidade de Coimbra, 3030-790 Coimbra, Portugal
[*]*aff@eq.uc.pt*

Chemical product/process engineering is entering into a new paradigm. Thanks to the dramatic evolution of high-performance scientific techniques and computational resources thereof, the multiscale modeling and simulation approach has been advocated as a cost-effective and crucial strategy in modern R&D programs [1]. Broader length ranges and time scales are starting to be addressed in a unified fashion, making the development of new products/processes not only more efficient but also an invaluable source of scientific knowledge.

Chemical computer modeling and simulation are exceptional tools that have been adopted in several fields. Quantum mechanics (QM) is one possible approach, which can provide highly reliable chemically relevant data. Nevertheless, the mathematical load of QM calculations demands huge computational power, even when applied to relatively small molecular systems (few tens of atoms). Molecular dynamics (MD) is a complementary alternative computational tool, which, in its basic framework (Newton's classical mechanics based MD), allows to model and simulate large molecular systems and timescales. The simulation of self-assembly and other macromolecular phenomena [2, 3] involving systems formed by large molecules like polymers [4] are noticeable examples.

This work reports a molecular modeling and simulation study in which different scales were accounted. The studied system includes: i) poly(acrylic acid) (PAA), a polymer that is under analysis to be used in polymer-liposome complexes targeted for drug delivery systems; and ii) a lipid bilayer to mimic the liposomal element of the complex. The first approach of the study (atomic-molecular scale) was accomplished by atomistic calculations performed within the QM framework, and was focused on small PAA oligomers (up to pentamer). The outcomes of these computations provided the lower energetic conformations, which were crucial to model the PAA molecule force-field for the MD simulations. The second step was directed to the nanoscale, and various MD runs were performed aiming at the prediction of some thermal characteristics of the PAA, by submitting a bulk simulation to a heating ramp. A simulation of a PAA oligomer in the presence of water molecules was also performed to understand its tridimensional arrangement in the light of its hydrogel characteristics. Finally, the mesoscale was addressed by simulating a biomembrane in the presence of PAA oligomers. This study has provided relevant understanding on how the oligomer interacts with a biomembrane.

References:

[1]W. a. de Jong, E. Bylaska, N. Govind, C. L. Janssen, K. Kowalski, T. Muller, I. M. B. Nielsen, H. J. J. van Dam, V. Veryazov, and R. Lindh, "Utilizing high performance computing for chemistry: parallel computational chemistry.", *Phys. Chem. Chem. Phys.*, vol. 12, pp. 6896–920, July 2010.
[2] D. G. Truhlar, "Molecular modeling of complex chemical systems.", *J. Am. Chem. Soc.*, vol. 130, pp. 16824–7, Dec. 2008.
[3] D. Lu, A. Aksimentiev, A. Y. Shih, E. Cruz-Chu, P. L. Freddolino, A. Arkhipov, and K. Schulten, "The role of molecular modeling in bionanotechnology.", *Phys. Biol.*, vol. 3, pp. S40–53, Mar. 2006.
[4] Q. Wang, D. J. Keffer, S. Petrovan, and J. B. Thomas, "Molecular dynamics simulation of poly(ethylene terephthalate) oligomers.", *J. Phys. Chem. B*, vol. 114, pp. 786–95, Jan. 2010.
[5] Filippov, A., Munavirov, B., Sparrman, T., Ishmuhametova, V., Rudakova, M., Shriram, P., and Tavelin, S, "Interaction of a poly(acrylic acid) oligomer with dimyristoylphosphatidylcholine bilayers.", *Langmuir*□, vol. 27, pp. 3754-61, Mar. 2011.

Java: an important tool to learning thermodynamics

A.G. M. Ferreira
Departamento de Engenharia Química, Faculdade de Ciências e Tecnologia da Universidade de Coimbra, Pólo II, Rua Sílvio Lima 3030-790 Coimbra, Portugal

Keywords: Java, Liquid-Gas, Maxwell construction, Vapor pressure

Abstract

In teaching thermodynamics to engineering students the use of simulation programs using Java applets in HTML environment offer advantages because the process allows fast interactive actions and learning theoretical issues at same time. Links to selected www is possible. Simulation programs can help to visualize the values of abstract properties for the thermodynamic processes, they allow for a more "experimental" approach complementing theoretical derivations in a lecture, and they provide examples, which show the relation between the thermodynamic state variables and their use in a given context. To prove these claims two example programs are discussed in detail using JAVA: (i) the study of liquid-gas phase equilibria of pure substances, using the Maxwell equal-area criteria for van der Waals (VDW) type equations of state (EOS), and (ii) the prediction of the vapor pressure from the corresponding states principle.

1. Introduction

At principle Thermodynamics should be a nice subject to learn because its topics are well defined and a lot of good books exist (e.g. [1]), the needed level of mathematical sophistication is not too high and well defined procedures for calculations are provided (e.g. perfect gas equation of state, Clapeyron equation). But for several engineering (including chemical) students it is one of the most hated subjects translated in generally poor results of the final examinations. This is due to the abstract concepts that form the heart of thermodynamics, and some difficulties in understanding the procedures for calculations as is the case of the variables describing phase equilibrium. One device to promote understanding is the use of simulation programs for performing “virtual experiments”. Their general usefulness is well established [2] and they can provide insights into abstract concepts leading to better mental models and help to engage the students in active learning. There exist large collections of simulation programs for many engineering subjects, based mainly on Java and JavaScript [3]. Software modeling proposals in educational activities covering phase equilibria exist [4, 5]. This interest, both in the number of publications and in the number of sites with simulations, for pedagogic proposals, is due to the countless advantages offered by the use of these tools in teaching, with the use of virtual laboratories (VLabs). Such activities are possible due to the advancement of computer science technologies, especially in the use of the Java programming language (JPL). With the growth of the www, java became an important tool for teaching. In the area of the sciences, (JPL) is behind the (VLabs) environments that simulate some physical phenomenon and uses small programs – applets - running in Internet browsers. The Java programming language was presented to the public by Sun Microsystems [6], in 1994. One of the main features of the (JPL) that makes it attractive and functional for the network, is the independency of platform - programs written in this language run on any machine / system. Thus, computers using Windows, Linux or any other platform running the same application developed in Java. Furthermore, it has other characteristics that give it advantages over other languages, such as simplicity (presents a cleaner structure, making programming easier) and orientation to objects - allows the reuse of code thereby increasing productivity. The java language is praised even by well-documented set of libraries. Because these features, java has fans and is one of the programming languages taught in university courses. Active learning in the classroom, using java applets, is known to benefit students in a variety of ways and come in the form of group projects, in-class exercises, case studies, and many other. In typical chemical thermodynamics courses the concepts behind some subjects can be understood and manipulated by students through the use of java applets designed for learning. As special topics we can took: (i) the calculation of liquid-gas phase equilibria of pure substances, using the Maxwell construction for the VDW type equations of state, and (ii) the prediction of the vapor pressure from the corresponding states principle. In the first case the mathematics needed is difficult for the average chemistry student (what is needed are the roots of cubic polynomials). This makes it difficult to show how the liquid–gas phase diagram is obtained from the equation of state. In the second case the student will be faced with the problem of selection and use of some fundamental properties to predict the vapor pressure of pure substances, and at the same time to learn how vapor pressure can be analitically represented. The java apletts used to teach the before mentioned topics were developed for the thermodinamic classes of the Chemical Engineering Course and are used here.

3. Simulations

In teaching thermodynamics has, among others, the purpose of illustrating and questioning the student about concepts and models. Thus, the computational modeling is a teaching resource in the teaching of thermodynamics to update and enrich the activities of teaching.
Some of the advantages that the modeling activities performed on a computer can offer in the process of teaching and learning are: (i) allows graphical visualization of subtle elements of the theoretical model; (ii) enables the active involvement of students - interactive systems require responses and decision allowing to the students construct their own knowledge; (iii) interpretation of physical models - using virtual laboratories and testing hypotheses, getting estimates on these systems, the student will be able to reflect on different theoretical models.
It is important to make the distinction between simulation and experimental methods. The sciences are human constructions based on observation and conjecture. Thus, experience is crucial in the theoretical development. The modelling and simulation are theoretical models of the reality based on the observations of the real world. Thus, it is understood that simulations can not replace the experimental activity, and the use of laboratories in education is absolutly needed for students understand the scientific activity. It is the objective of this work to stress the importance of developing and use of Java near the students and the the teachers. In our department Java applets are used as important tools at the classes to teach thermodymamics and on thermophysical properties calculation. In the learning process the students – in groups of three - are asked to choice an (property(ies)+substance(s)) set to be predicted/modelized with an appropriate HTML / Java applet combination using computer calculation center facilities or conducting the work from home.

3.1 Equations of state and Maxwell equal-area rule

In this first example the values of vapor pressure and molar volumes of liquid and gaseous phases in equilibrium for pure substances using the Maxwell equal-area rule were determined. The equations of the family of VDW can be expressed by the general equation,

$$P = \frac{RT}{V-b} - \frac{\theta}{V^2 + \delta V + c} \tag{1}$$

where R= gas constant; P= pressure; T=temperature; V= molar volume and θ, δ and c are parameters. The java applet developed here uses the following equations of state: van der Waals (VDW, 1873, θ=a, δ=0, c=0); Redlich- Kwong (RK, 1949, $\theta=a/T^{0.5}$, δ=b, c=0); Soave-Redlich-Kwong (SRK, 1972, $\theta=a_{srk}(T)$, δ=b, c=0); Peng and Robinson (PR, 1976, $\theta=a_{PR}(T)$, δ=2b, $c=-b^2$). Eq (1) is of third degree in the molar volume. In Figure 1 a subcritical isotherm of a pure substance is depicted for the Redlich-Kwong EOS. There is the vertical asymptotes (Vm =-b 0, b) and only the section I of the isotherm has physical significance (values of $V_m > b$). For a fixed pressure (the vapor pressure) in this section three roots for the molar volume exist: V_A, V_C and V_E. V_A is the molar volume of the liquid phase in equilibrium with the gas (with molar volume V_E). Root V_C has no physical meaning since it is located on the curve where the molar volume increases with pressure which is contrary to what is observed experimentally.
The (PVT) properties of the liquid and vapor at equilibrium (the vapor pressure and molar volume of liquid and gaseous phases) are calculated using the Maxwell equal-area rule, illustrated in Figure 2.

According to this rule for a given equation of state the equilibrium values of the properties above mentioned are those that make the areas [ABCA] and [CDEC] the same. For a demonstration see the reference [1], pg 347. Calculations can be made following the scheme given in Figure 1(b).

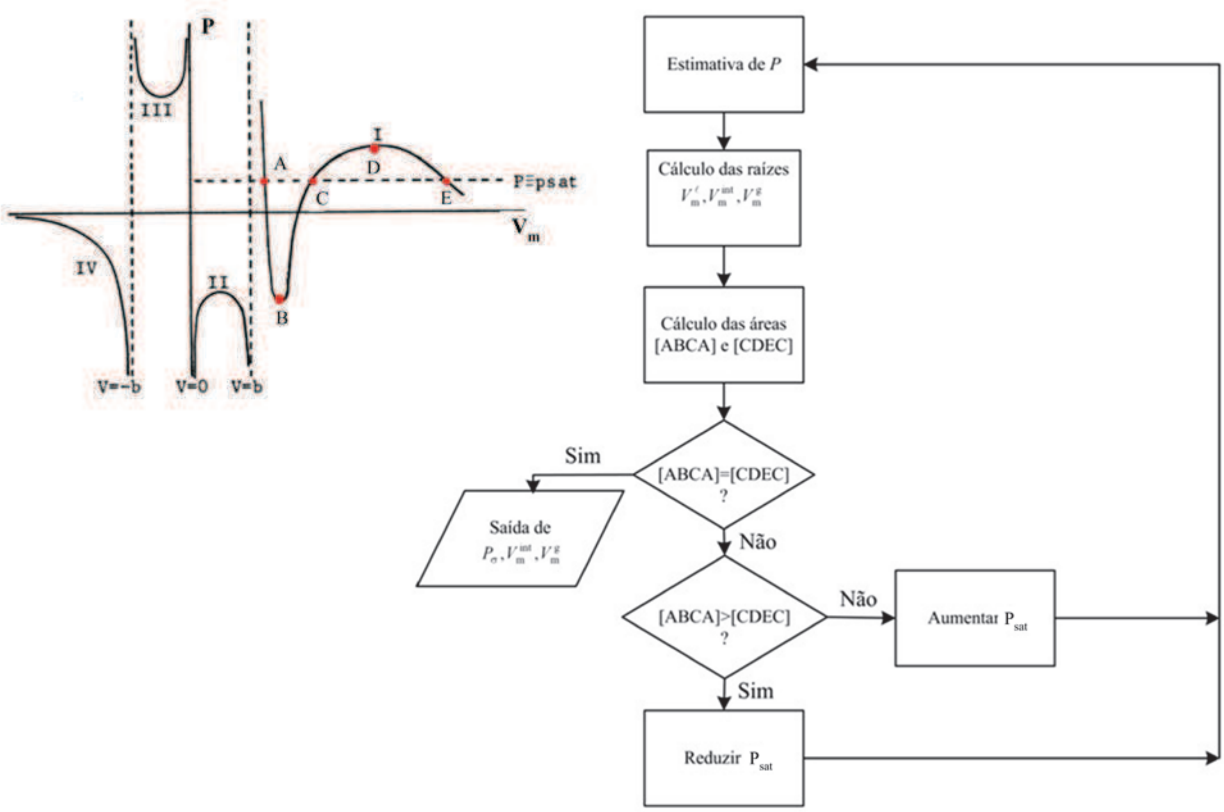
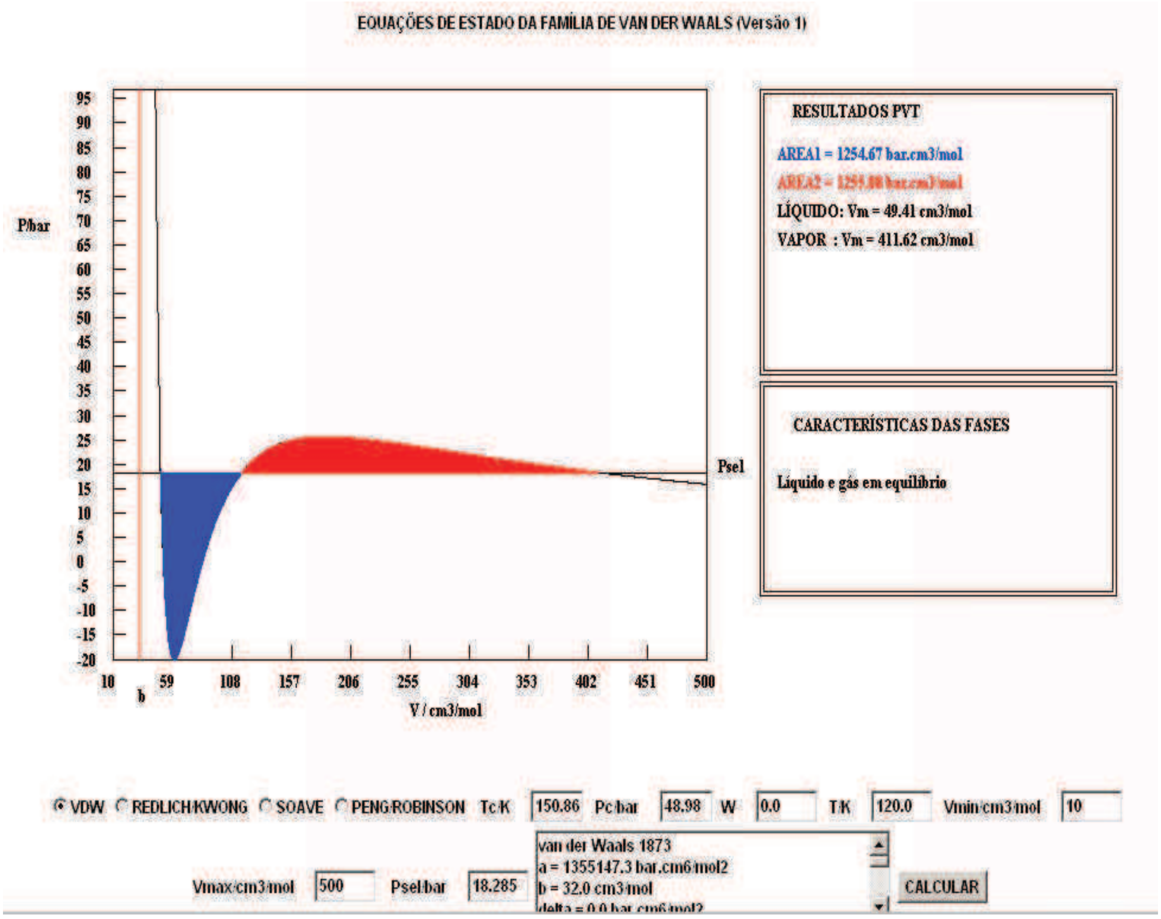


Figura 1. (a) (P, V) plot for an RK subcritical isotherm; (b) calculation procedure for the Maxwell equal-area rule.

The applet depicted in Figure 2 shows the calculation of liquid+gas PVT equilibrium properties for argon at 120 K as a case study. At the bottom the (radio) buttons allow to select the EOS while the necessary properties (critical temperature, T_c, critical pressure, P_c , acentric Pitzer factor w and working temperature,T) are placed in the text boxes. The process uses a trial and error strategy by selecting appropriate values of the pressure in the text box (Psel/bar). Selecting a value for the pressure and pressing the CALCULAR button the values for the blue and red areas are shown on the panel RESULTADOS PVT. Bellow in CARACTERÍSTICAS DAS FASES the state of the phases is shown. In the text area we can found the PVT values and calculated parameters for the selected EOS.



EQUAÇÕES DE ESTADO DA FAMÍLIA DE VAN DER WAALS (Versão 1)

RESULTADOS PVT

AREA1 = 1254.67 bar.cm3/mol
AREA2 = 1255.88 bar.cm3/mol
LÍQUIDO: Vm = 49.41 cm3/mol
VAPOR : Vm = 411.62 cm3/mol

CARACTERÍSTICAS DAS FASES

Líquido e gás em equilíbrio

● VDW ○ REDLICH/KWONG ○ SOAVE ○ PENG/ROBINSON

Tc/K 150.86
Pc/bar 48.98
W 0.0
T/K 120.0
Vmin/cm3/mol 10
Vmax/cm3/mol 500
Psel/bar 18.285

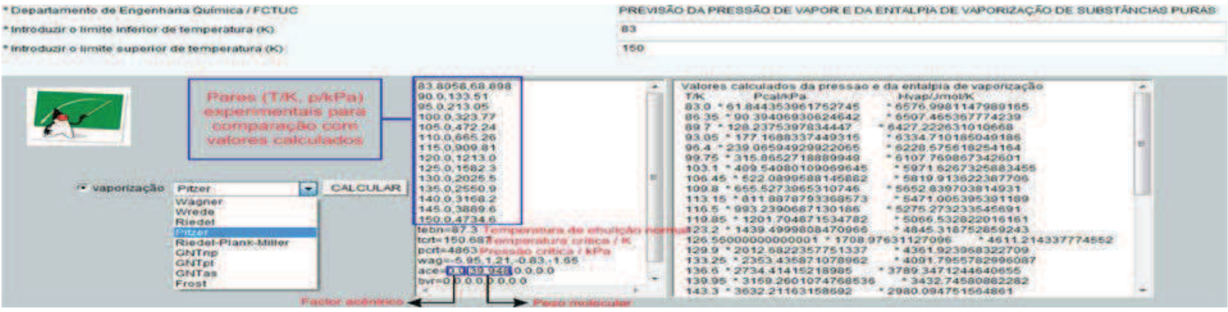
```
van der Waals 1873
a = 1355147.3 bar.cm6/mol2
b = 32.0 cm3/mol
delta = 0.0 bar.cm6/mol2
```

Figure 2. Simulation using the Maxwell equal-area rule.

The results can be used for further processing in excel for example.

3.2 Prediction of the vapor pressure from the corresponding states principle

The reduced vapor pressure P_r (= P / P_c) is a function of reduced temperature T_r (= T / T_c). In terms of the corresponding states principle (CSP) we may state that if many pure substances are evaluated at the same value of reduced temperature then the reduced vapor pressure will be the same. Since the famous equation of Wrede proposed more than one hundred years ago up today several different methods of CSP based methods for calculation of vapor pressure have emerged: those of Pitzer, Riedel, Gomez-Nieto-Thodos are among the most used. The applet box depicted in Figure 3 shows the calculation of the vapor pressure of argon as case study using the most popular methods: Wrede, Riedel, Pitzer, Riedel-Plank-Miller, Gomez-Nieto-Thodos and Frost-Kalkwarf-Thodos. The selection box allows the choice of the method. The placement of the necessary entering parameters are presented. Once the applet started the user will immediately have at its disposal the following frames (Figure 3): (i) the plot of the predicted values of the vapor pressure as a function of temperature and that for the percentual deviation of calculated values from those taken from the literature, (ii) the diagram showing the dependence of the calculated enthalpy of vaporization on the temperature, (iii) the calculated pressure and enthalpy of vaporization as a function of temperature (21 points) and the details of the selected model.



*Departamento de Engenharia Química / FCTUC

PREVISÃO DA PRESSÃO DE VAPOR E DA ENTALPIA DE VAPORIZAÇÃO DE SUBSTÂNCIAS PURAS

*Introduzir o limite inferior de temperatura (K) 83
*Introduzir o limite superior de temperatura (K) 150

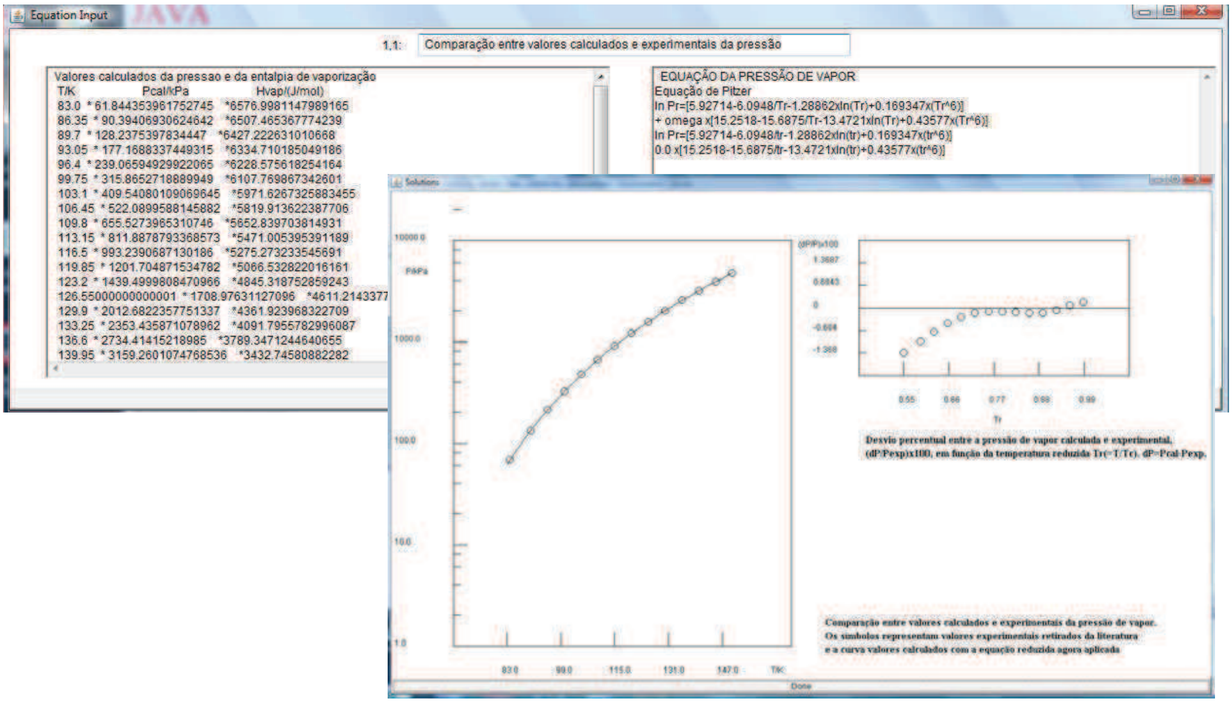
● vaporização Pitzer

Pares (T/K, p/kPa) experimentais para comparação com valores calculados

```
83.8058,68.898
90.0,133.51
95.0,213.05
100.0,323.77
105.0,472.24
110.0,665.26
115.0,909.81
120.0,1213.0
125.0,1582.3
130.0,2025.5
135.0,2550.9
140.0,3168.2
145.0,3889.6
150.0,4734.6
tebn=87.3
tcrt=150.687
pcrt=4863
wag=-5.95,1.21,-0.83,-1.65
ace=0.0,39.948,0.0,0.0
bvr=0.0,0.0,0.0,0.0,0
```

tebn: Temperatura de ebulição normal
tcrt: Temperatura crítica / K
pcrt: Pressão crítica / kPa
Factor acêntrico
Peso molecular

```
Valores calculados da pressao e da entalpia de vaporização
 T/K        Pcal/kPa                Hvap/J/mol/K
 83.0  * 61.84435396175274 5       * 6576.9981147989165
 86.35  * 90.39406930624642        * 6507.465367774239
 89.7  * 128.2375397834447        * 6427.222631010668
 93.05  * 177.1688337449315        * 6334.710185049186
 96.4  * 239.0659492992206 5       * 6228.575618254164
 99.75  * 315.8652718889949        * 6107.769867342601
 103.1  * 409.5408010906964 5       * 5971.6267325883455
 106.45  * 522.0899588145882        * 5819.913622387706
 109.8  * 655.527396531074 6       * 5652.839703814931
 113.15  * 811.8878793368573        * 5471.005395391189
 116.5  * 993.2390687130186        * 5275.27323354569 1
 119.85  * 1201.7048715347 82       * 5066.532822016161
 123.2  * 1439.4999808470966        * 4845.318752859243
 126.55000000000001  * 1708.97631127096        * 4611.214337774552
 129.9  * 2012.5822357751337        * 4361.923968322709
 133.25  * 2353.435871078962        * 4091.7955782996087
 136.6  * 2734.41415218985        * 3789.3471244640655
 139.95  * 3159.2601074768536        * 3432.74580882282
 143.3  * 3632.21163158692        * 2980.094751564861
```



```
Valores calculados da pressao e da entalpia de vaporização
 T/K              Pcal/kPa               Hvap/(J/mol)
 83.0  * 61.844353961752745   *6576.9981147989165
 86.35  * 90.39406930624642   *6507.465367774239
 89.7  * 128.2375397834447   *6427.222631010668
 93.05  * 177.1688337449315   *6334.710185049186
 96.4  * 239.06594929922065   *6228.575618254164
 99.75  * 315.8652718889949   *6107.769867342601
 103.1  * 409.54080109069645   *5971.6267325883455
 106.45  * 522.0899588145882   *5819.913622387706
 109.8  * 655.5273965310746   *5652.839703814931
 113.15  * 811.8878793368573   *5471.005395391189
 116.5  * 993.2390687130186   *5275.273233545691
 119.85  * 1201.704871534782   *5066.532822016161
 123.2  * 1439.4999808470966   *4845.318752859243
 126.55000000000001  * 1708.97631127096   *4611.2143377
 129.9  * 2012.6822357751337   *4361.923968322709
 133.25  * 2353.435871078962   *4091.7955782996087
 136.6  * 2734.41415218985   *3789.3471244640655
 139.95  * 3159.2601074768536   *3432.74580882282
```

```
 EQUAÇÃO DA PRESSÃO DE VAPOR
Equação de Pitzer
ln Pr=[5.92714-6.0948/Tr-1.28862xln(Tr)+0.169347x(Tr^6)]
+ omega x[15.2518-15.6875/Tr-13.4721xln(Tr)+0.43577x(Tr^6)]
ln Pr=[5.92714-6.0948/tr-1.28862xln(tr)+0.169347x(tr^6)]
0.0 x[15.2518-15.6875/tr-13.4721xln(tr)+0.43577x(tr^6)]
```

Desvio percentual entre a pressão de vapor calculada e experimental, (dP/Pexp)x100, em função da temperatura reduzida Tr(=T/Tc). dP=Pcal-Pexp.

Comparação entre valores calculados e experimentais da pressão de vapor.
Os simbolos representam valores experimentais retirados da literatura
e a curva valores calculados com a equação reduzida agora aplicada

Figure 3. Simulation of vapor pressure (argon) using Pitzer method.

In Figure 5 the results from the several methods applied to benzene are presented.

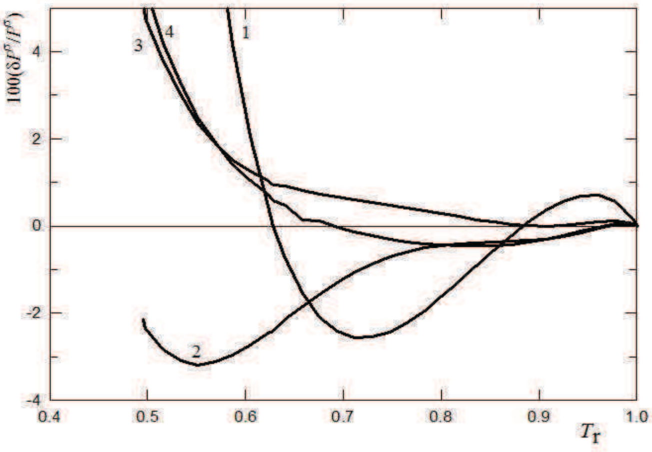


Figure 5. Relative deviations between the experimental and calculated vapor pressure of benzene using the principle of corresponding states equations. Tr is the reduced temperature. Legend: 1 - eq of Wrede, 2 - eq of Pitzer, 3 - eq of Gomez-Nieto-THodos; 4 - eq of Frost-Kalkwarf-Thodos.

4. Conclusions

In this paper educational software using java applets, has been used to understand and to visualise: (i) the (PVT) phase equilibrium data of pure substances resulting from the application of Maxwell equal-area rule to equations of state; and (ii) vapor pressure calculation using the corresponding states methods.

More educational applets covering other topics of thermodynamic property data calculation and vieweing (density, heat capacity and fundamental properties using group contribution methods) can be found at www.eq.uc.pt/~abel/ . For the future it is planned to construct new applets covering other areas including phase equilibria in multicomponent systems and methods for non equilibrium properties (viscosity, thermal conductibility and diffusion).

References

[1] H. C. Van Ness, M. M. Abbott Classical thermodynamics of non-electrolyte solutions, McGrawHill (1982)
[2] N. D. Finkelstein, W. K. Adams, C. J. Keller, P. B. Kohl, K. K. Perkins, N. S. Podolefsky, S. Reid, When learning about the real world is better done virtually: A study of substituting computer simulations for laboratory equipment, Phys. Rev. ST Phys. Educ. Res. 1, (2005) 010103,
[3] W. Christian, M. Belloni, M., Physlets - Teaching Physics with Interactive Curricular Material. Upper Saddle River: Prentice Hall (2001).
http://webphysics.davidson.edu/physletprob,
[4] http://labvirtual.eq.uc.pt/
[5] http://www.et.byu.edu/~rowley/VLEfinal/simulator.htm
[6] http://java.sun.com/.

Quaternary phosphonium-based ionic liquids: thermal stability and heat capacity of the liquid phase

A. F. Ferreira [a], P. N. Simões [a], A. G. M. Ferreira [a,]*

[a] *Departamento de Engenharia Química, Faculdade de Ciências e Tecnologia,Universidade de Coimbra, Pólo II, Rua Sílvio Lima, 3030-790 Coimbra, Portugal,*abel@eq.uc.pt*

Great attention has been dedicated over the past years to the physicochemical properties of imidazolium, ammonium and piridinium based ILs. On the contrary, very few investigations involving phosphonium-based ILs have been reported in the literature. This appears to be surprising considering its increased wider application, such as in chemical reaction in polymer synthesis, or as greener plasticizers for biomedical applications in supercritical processes. Several other examples can be found in liquid phase extraction, gas solubility, electrochemical research, and tribology.

Heat capacity (C_p) is one of the basic thermodynamic properties whose knowledge is critical for many engineering calculations. Typical examples are the design of processes that include ILs as thermal storage media, such as solar thermal electric power systems, or the case of absorption heat pumps or chillers, which are important units of air conditioning and refrigeration. Only two references can be found regarding C_p measurements of phosphonium ILs. Gardas *et al.* [1] focused on the study of amino acid based tetrabutylphosphonium ILs, while Gee *et al.* [2] reported measurements on $[(C_6)_3PC_{14}][NTf_2]$.

This work reports a thermoanalytical study on the linear alkyl quaternary phosphonium-based RTILs tretrabutylmethylphosphonium methylsulfate, $[(C_4)_3PC_1)][MeSO_4]$, and trihexyltetradecyl-phosphonium bis(trifluoromethylsulfonyl)imide, $[[(C_6)_3PC_{14}][NTf_2]$. The thermal stability of the ILs was evaluated by thermogravimetric analysis (TGA) up to 873 K, while the C_p measurements were performed by Modulated Differential Scanning Calorimetry (MDSC) within the temperature range from ca. 310 K to 515 K. The C_p of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[EMIM][NTf_2]$ was used as reference in virtue of the wealth of data based on different techniques, provided by several authors since 2004.

The $[(C_4)_3PC_1)][MeSO_4]$, and $[(C_6)_3PC_{14}][NTf_2]$ samples were obrained from CYTEC. The $[EMIM][NTf_2]$ was supplied by IoLiTec with a stated purity > 99%. The ILs samples from CYTEC were firstly washed several times using suitable solvents to ensure the removal of any remaining impurities. Furthermore, in order to reduce the water content and volatile species to negligible values, a vacuum of about 1 Pa and moderate temperature (70 ºC) were applied to the IL samples for several days prior to the thermoanalytical measuremetnts.

The TGA measurements were performed in a TA Instruments Q500 thermogravimetric analyzer (thermobalance sensitivity: 0.1μg). The temperature calibration was performed in the range 25-1000 ºC by measuring the Curie point of nickel standard, and using open platinum crucibles and a dry nitrogen purge flow of 100 mL min^{-1}. This procedure was performed the heating rate used throughout the experimental work (2 ºC min^{-1}).

The C_p measurements were carried out using MDSC equipment from TA Instruments (model Q100). The heat flow and heat capacity were calibrated at 2 ºC min^{-1} using, respectively, indium and sapphire standards. A modulation period of 120~s, and a temperature amplitude of ± 0.53 ºC were employed. A dry nitrogen purge flow of 50 mL min^{-1} was applied in the calibration and measurements. It should be mentioned that great care was taken to avoid the contact of the sample with moisture during transportation. The relative humidity in the room where the experiments were performed was kept under tight control. The samples were placed in aluminum pans with an ordinary pressed aluminum lid with a small hole (ca. < 0.5mm), and submitted to program in the TGA apparatus to ensure the elimination of possible traces of moisture. The procedure consisted in heating the set pan/lid/sample up to 120 ºC, an isothermal for 5 min, and an equilibration at 25 ºC. The sample mass observed at this stage was then used as input in the subsequent MDSC run for measuring C_p. Three or more series of measurements were made for each IL.

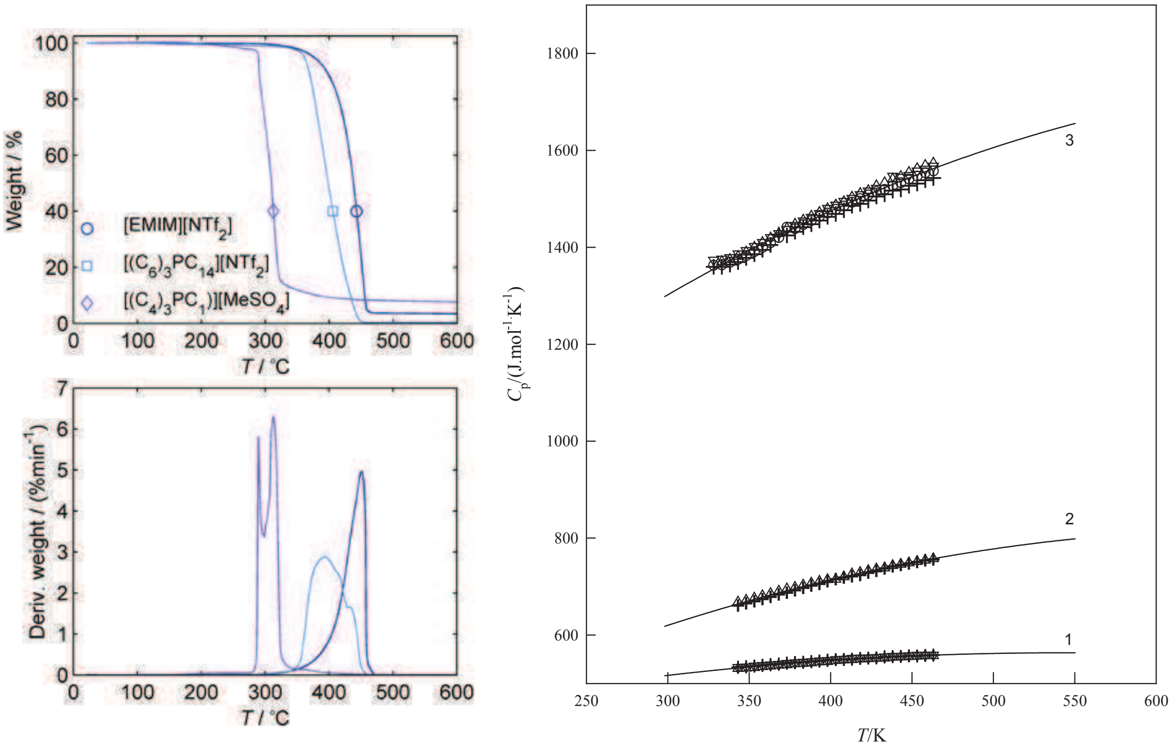
Figure 1-(a) compares the thermal stability of the ILs considered in this work. The TG and DTG profiles are quite distinct among the ILs, the clearly less thermally stable being $[(C_4)_3PC_1)][MeSO_4]$,

which exhibits a decomposition temperature (extrapolated onset temperature, T_{on}) of *ca*. 561 K. The T_{on} values for $[(C_6)_3PC_{14}][NTf_2]$ and $[EMIM][NTf_2]$ are *ca*. 637 K and *ca*. 690 K, respectively.

In what concerns to the measurements of C_p, it was found that the experimental results are well correlated using polynomial expressions. The Joback group contribution method for predicting ideal gas heat capacities which has been extended to ILs by Gee *et al*. [2] was applied in this work to the estimation of the liquid heat capacity in the range $T = (256 \text{ to } 470)$ K. The methods due to Valderrama *et al*. [3-5] were also used with the same purpose.

Figure 1-(b) presents the experimental and correlated data for C_p *versus* T of the studied ILs. Significant changes in C_p as a function of the anion are observed. The values of C_p increase at any temperature in the order $[C_2mim][NTf_2] < [(C_4)_3PC_1)][MeSO_4] < [(C_6)_3PC_{14}][NTf_2]$. The C_p of $[(C_6)_3PC_{14}][NTf_2]$ with a value of 1381 $J.mol^{-1}.K^{-1}$ is much higher than the value of 531 $J.mol^{-1}.K^{-1}$ for $[C_2mim][NTf_2]$, which demonstrates the cumulative effect of increasing the length of hydrocarbon chains on the cation.

It was found that the predictive methods work very well for the low temperature data of $[C_2mim][NTf_2]$ and $[(C_6)_3PC_{14}][NTf_2]$, wich is explained by to the use of heat capacity data sets in this temperature range of the two ILs in the development of the predictive models. For the other ILs the results are of variable quality, suggesting that the existing methods must be revised to include phosphonium-based ionic liquids.



(a) (b)

Figure 1 – (a) TG-DTG curves of ILs samples obtained at 2 °C min^{-1}. **(b)** Heat capacity of the ionic liquids. The symbols refer to experimental data and the lines to the correlation with polynomial equations. 1- $[EMIM][NTf_2]$; 2- $[(C_4)_3PC_1)][MeSO_4]$; 3- $[[(C_6)_3PC_{14}][NTf_2]$.

[1] R. L. Gardas, R. Ge, P. Goodrich, C. Hardacre, A. Hussain, D. W. Rooney, J.Chem. Eng. Data **55** (2010):1505-1515.

[2] R. Ge, C. Hardacre, J. Jacquemin, P. Nancarrow, D. W. Rooney, J.Chem. Eng. Data **53** (2008):2148-2153.

[3] J. O. Valderrama, R. E. Rojas, Fluid Phase Equil. 297 (2010):107-112.

[4] J. O. Valderrama, G. Martinez, R. E. Rojas, Termochim. Acta 513 (2011):83-97.

[5] J. O. Valderrama, A. Toro, R. E. Rojas, J. Chem. Thermodyn. 43(7) (2011):1068-1073.

Application of the exactly integrated Clapeyron equation to the sublimation curve of the rare gases

Abel G. M. Ferreira, Lélio Q. Lobo

Departamento de Engenharia Química, Universidade de Coimbra, Pólo II, Rua Sílvio Lima, 3030-790 Coimbra, Portugal

In this work the exactly integrated form of Clapeyron equation found by Mosselman *et al.*[1] has been applied to the calculation of the sublimation pressure and sublimation enthalpy of the rare gases. The integration of Clapeyron equation for sublimation leads to

$$T^{-1}\int_{p_0}^{p} \Delta_{\mathrm{s}}^{\mathrm{g}} V_{\mathrm{m}}(p,T)\,\mathrm{d}p + \int_{T_0^{-1}}^{T^{-1}} \left\{\int_{\mathrm{T}_0}^{\mathrm{T}} \Delta_{\mathrm{s}}^{\mathrm{g}} C_{p,\mathrm{m}}(p_0,T)\,\mathrm{d}T\right\} \mathrm{d}T^{-1} = \Delta_{\mathrm{s}}^{\mathrm{g}} H_{\mathrm{m}}(p_0,T_0)(T_0^{-1}-T^{-1}) .$$

(1)

where $\Delta_{\mathrm{s}}^{\mathrm{g}}\mathrm{C}_{p,\mathrm{m}}(p_0,T)$ is the difference in the molar heat capacity at constant pressure p_0, of the solid and gas phases at equilibrium and the symbol $\Delta_{\mathrm{s}}^{\mathrm{g}}X$ indicates the difference between the values of the thermodynamic property X of the two phases at equilibrium (*e.g.*, $\Delta_{\mathrm{s}}^{\mathrm{g}} H_{\mathrm{m}} = H_{\mathrm{m}}^{\mathrm{g}} - H_{\mathrm{m}}^{\mathrm{s}}$ is the molar enthalpy of sublimation). The application requires the knowledge of only one (reference) point on the solid+gas equilibrium line. The triple point was chosen as reference. The corresponding molar enthalpy of sublimation, and some other ancillary data (molar volumes and heat capacities of the solid and the gas at equilibrium) are also needed. The equation developed from the exactly integrated form of Clapeyron equation can be regarded as a source for calculating *a priori* the phase equilibrium curves in the sence that no fittings to (*p*, *T*) experimental data is needed. For the sublimation curve one obtains (2)

$$\ln p = A_{\mathrm{s}} - B_{\mathrm{s}}/T + C_{\mathrm{s}}\ln T + \sum_{i=2}^{4} D_{s,i}T^{i-1} + E_{\mathrm{s}}(T)p/T ,$$

(2)

where the parameters are calculated from the above mentioned thermodinamic properties.
The results have been compared with experimental (*p*, *T*) sublimation data in Figure 1a. In Figure 1b the calculated values of $\Delta_{\mathrm{s}}^{\mathrm{g}} H_{\mathrm{m}}$ are plotted as function of the temperature.

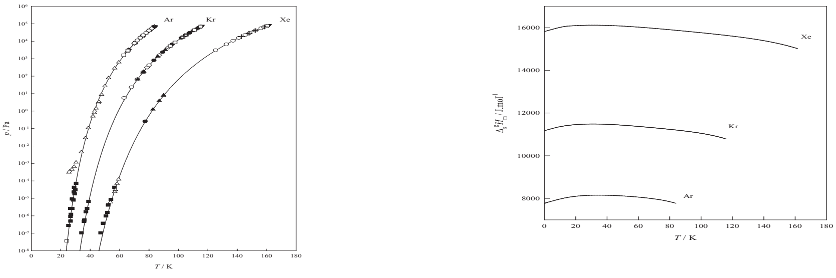


Figure 1. (a) (*P, T*) sublimation curves of the rare gases. The symbols refer to the experimental data and the curves are calculated with equation (2). **(b)**Molar enthalpy of sublimation, $\Delta_{\mathrm{s}}^{\mathrm{g}} H_{\mathrm{m}}$, of the rare gases as function of the temperature *T*. The curves are calculated from Clausius-Clapeyron equation using equation (2).

References

(1) C. Mosselman, W. H. van Vugt, H. J. Vos *J. Chem. Eng. Data* 27 (1982) 246-251.
(2) L. Q. Lobo, A. G. M. Ferreira, J. Chem. Thermodyn. 33 (2001) 1597-1617.

A Robust Multi-Model Predictive Controller for Distributed Parameter Systems

Míriam R. García[a], Carlos Vilas[b], Lino O. Santos[c], and Antonio A. Alonso[b*]

[a]*Hamilton Institute -- National University of Ireland, Maynooth, Ireland, Miriam.Garcia@nuim.ie*
[b]*Process Engineering Group, IIM-CSIC, Eduardo Cabello 6, 36208 Vigo, Spain,*
*carlosvf@iim.csic.es, *antonio@iim.csic.es*
[c]*CIEPQPF, Departamento de Engenharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030-790 Coimbra, Portugal, lino@eq.uc.pt*

In this work a robust nonlinear model predictive controller for nonlinear convection-diffusion-reaction systems is presented. The controller makes use of a collection of reduced order approximations of the plant (models) reconstructed on-line by projection methods on POD (Proper Orthogonal Decomposition) basis functions. The model selection and model update step is based on a sufficient condition that determines the maximum allowable process-model mismatch to guarantee stable control performance despite process uncertainty and disturbances. Proofs on the existence of a sequence of feasible approximations and control stability are given.

Since plant approximations are built on-line based on actual measurements the proposed controller can be interpreted as a multi-model nonlinear predictive control (MMPC). The performance of the MMPC strategy is illustrated by simulation experiments on a problem that involves reactant concentration control of a tubular reactor with recycle.

References:

L. Sirovich, Turbulence and the dynamics of coherent structures. Part I: Coherent structures, Quaterly of Applied Mathematics 45 (1987) 561-571.

G. Berkooz, P. Holmes, L. Lumley, The Proper Orthogonal Decomposition in the analysis of turbulent ows, Annual Review of Fluid Mechanics 25 (1993) 539-575.

P. J. Holmes, J. L. Lumley, G. Berkooz, J. C. Mattingly, R. W. Wittenberg, Low-dimensional models of coherent structures in turbulence, Physics Reports-review Section of Physics Letters. 287 (1997) 337-384.

R. Padhi, S. F. Ali, An account of chronological developments in control of distributed parameter systems, Annual Reviews in Control 33 (2009) 59-68.

E. Balsa-Canto, A. A. Alonso, J. R. Banga, Reduced-Order Models for Nonlinear Distributed Process Systems and Their Application in Dynamic Optimization, Industrial & Engineering Chemistry Research 43 (2004) 3353-3363.

L. O. Santos, L. T. Biegler, A tool to analyze robust stability for model predictive controllers, Journal of Process Control 9 (1999) 233-246.

M. R. García, Identication and Real Time Optimization in the Food Processing and Biotechnology Industries, Ph.D. thesis, University of Vigo, 2008.

A. A. Alonso, C. E. Frouzakis, I. G. Kevrekidis, Optimal sensor placement for state reconstruction of distributed process systems, AIChE Journal 50 (2004) 1438-1452.

Towards a systematization of profile analysis methods as a basis for the development of flexible and generalized data analysis framework

Véronique M. Gomes[a], Ana C. Pereira[a], Pedro M. Saraiva[a] and Marco S. Reis[a,*]

[a]*CIEPQPF, Department of Chemical Engineering, University of Coimbra Pólo II-Pinhal de Marrocos, 3030-290 Coimbra, Portugal*
[*]*marco@eq.uc.pt*

Data generated by current processes or collected in activities of product characterization, tend to present increasingly complex structures. The traditional arrangement of data in two-way arrays of variables vs time, variables vs production units, or similar, is no longer enough to accommodate the structures found in process and product quality data, nor are the classical methods able to analyze them, in an effective and efficient way. For instance, batch processes typically generate 3-way data arrays (or even higher-order arrays, if spectral measurements or hyperspectral images, for instance, are collected over time), and products can be characterized by 1-way profiles (chromatograms, spectra, particle size distribution curves, etc.), 2-way profiles (GC-MS, HPLC-DAD, grey images), 3-way profiles (hyperspectral images, 3-way hyphenated instruments), etc. In this context, there is a current need to evolve to more general environments for data analysis frameworks, which are able to handle data with such different data structures while pursuing the analysis goals. A profile can be abstractly defined as a data array, indexed by time and/or space, that characterizes a given entity (product or process):

$$\textbf{Profile}:\left\{\mathrm{Y}\left(ix,iy,iz,it\right)\right\}\in\Re^{m},\ \text{with}\left(ix,iy,iz,it\right)\in\Omega_x\times\Omega_y\times\Omega_z\times\Omega_t \qquad (1)$$

where Y represents the profile with dimensionality *m*, whose spatial or temporal features (if existent) are indexed by the set of indices $\left(ix,iy,iz,it\right)\in\Omega_x\times\Omega_y\times\Omega_z\times\Omega_t$ (*x*,*y* and *z* stand for the spatial indices and *t* for the time index).

In this context, we purpose in this paper: i) to interpret all these different data structures as different manifestations of what we call, in an abstract sense, "profiles" (in the sense of the above definition); ii) a systematization of the profiles found in practice regarding the methods required to analyze them and the task in question, in order to find cross-dimensional patterns about how to analyze data more effectively, irrespectively of their intrinsic dimensionality, and, possibly, to develop a coherent ontology that facilitates the development of new integrated approaches for profiles analysis; iii) a comparison study of multiway methods for handling similar tasks (namely, calibration and process monitoring).

Acknowledgements

The authors acknowledges financial support through project PTDC/EQU-ESI/108597/2008 co-financed by the Portuguese FCT and European Union's FEDER through "Eixo I do Programa Operacional Factores de Competitividade (POFC)" of QREN (with ref. FCOMP-01-0124-FEDER-010398).

References

[1] A. Checa, R. Oliver, J. Saurina, S. Hernández-Cassou, Anal. Chim. Acta 572 (2006) 155.
[2] Honglu Yu and John F. MacGregor, Ind. Eng. Chem. Res., 42 (2003), 3036-3044.
[3] P. Valderrama, R.J. Poppi, Anal. Chim. Acta 623 (2008) 38.
[4] G.Parisotto, M.Marques, A.L.Hermes, E.M.M.Flores, M.F.Ferrão. Orbital 1 (2009) 38-48.
[5] R. C. Lyon, D. S. Lester, E. N. Lewis, E. Lee, L. X. Yu, E. H. Jefferson and A. S. Hussain AAPS PharmSciTech,17 (2002).
[6] Xujun Ye , Kenshi Sakai, Akira Sasao, Shin-ichi Asada, Chemometrics and Intelligent Laboratory Systems 90 (2008) 132–144.
[7] R.Bro, (1998) Ph.D. Thesis, University of Amsterdam (NL) & Royal Veterinary and Agricultural University (DK).

PVT and surface tension measurements of ethanol

F. M. Gonçalves, A. R. Trindade, Abel G. M. Ferreira*, I. M. A. Fonseca, P. N. L. Simões

Centro de Investigação em Engenharia dos Processos Químicos e dos Produtos da Floresta, Faculdade de Ciências e Tecnologia da Universidade de Coimbra, Departamento de Engenharia Química, Pólo II, Rua Sílvio Lima 3240 Coimbra, Portugal

Keywords: Ethanol, PVT, Surface tension, Tait equation of state

New PVT measurements of the liquid phase within the temperature range of (278 to 353 K) and up to 35 MPa are presented for ethanol. Measurements were made by means of a vibrating-tube densimeter, model DMA 512P from Anton Parr. The calibration of the densimeter was performed with water and n-heptane as reference fluids. The experimental data have been correlated by a Tait equation with an average absolute deviation of 0.1 %. Isothermal compressibilities, isobaric expansivities, thermal pressure coefficients, and changes in the isobaric heat capacity have been calculated from the volumetric data.

Also new experimental data on the surface tension of ethanol are reported in the range (275 to 319) K. The data was obtained using a PC controlled KSV Sigma 70 tension balance which employs the Du Noüy ring-detachment method. At each temperature, several individual measurements have been carried out. The estimated overall standard uncertainty in the surface tension at particular temperatures is ±0.01 $mN \cdot m^{-1}$. Using the data of the present work and critically assessed data of other authors compiled from the literature, a form of the IAPWS equation was used to correlate the surface tension with the temperature from 225 K to the critical point (513.9 K). Some results are illustrated bellow.

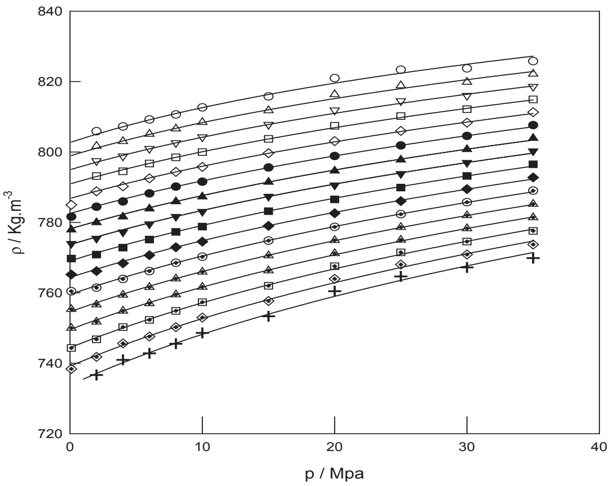


Figura 1. Isotherms of density, ρ, of ethanol from 278K (○) to 353 K(+) with increments of 5 K. The symbols refer to the experimental data and the lines to calculation with Tait equation.

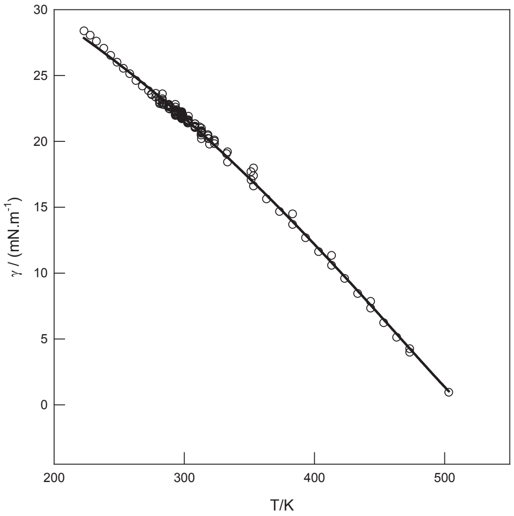


Figura 2. Surface tension, γ, of ethanol as function of temperature. Symbols refer to experimental data and the curve corresponds to the IAPWS equation of this work.

---

[*] Corresponding author. Tel + 351 239 798 729. E-mail: abel@eq.uc.pt

Norfloxacin-loaded intraocular lenses loaded by supercritical carbon dioxide impregnation

Clara González-Chomón[1], Mara E.M. Braga[2], Angel Concheiro[1], Carmen Alvarez-Lorenzo[1], Hermínio C. de Sousa[2*]

[1]*Departamento de Farmacia y Tecnología Farmacéutica, Facultad de Farmacia, Universidad de Santiago de Compostela, 15782-Santiago de Compostela, Spain.*
[2]*CIEPQPF, Chemical Engineering Department, FCTUC, University of Coimbra, Rua Sílvio Lima, Pólo II–Pinhal de Marrocos, 3030-790 Coimbra, Portugal*
**hsousa@eq.uc.pt*

Cataracts treatment usually involves the extraction of the opaque crystalline lens and its replacement by implanted intraocular lenses (IOLs) [1]. A serious problem associated to this procedure is the appearance of a post-surgery infection called endophthalmitis, which is mainly caused by *Staphylococcus epidermidis*, *S. aureus* and *Pseudomonas aeruginosa* [2,3]. To overcome these issues, acrylate-based IOLs were synthesized in order to load and to release norfloxacin in a controlled way and at efficient therapeutic levels. Different acrylate-based copolymers were prepared using 2-hydroxyethyl methacrylate (HEMA) and 2-butoxyethyl methacrylate (BEM) as comonomers in different proportions (from 100:0 up to 0:100). Ethyleneglycol dimethacrylate (EGDMA) was added as the cross-linker. Norfloxacin was loaded into the prepared polymers using a supercritical solvent impregnation/deposition (SSI) method [4], at 313 K and at pressures from 15.0 up to 30.0 MPa. Processing/loading time was 14 h, while venting rate was 0.1 MPa min^{-1}. Norfloxacin aqueous immersion loading experiments were also performed for comparison reasons. All prepared and processed samples were characterized by several different techniques. Loading capacities and drug release profiles were obtained, compared and discussed in terms of the copolymer composition and of the employed drug-loading method and operational conditions. Samples BEM composition and SSI operational pressure strongly affected norfloxacin loaded amounts. Additional research work is currently being carried out to clarify these results. Finally, the obtained thermomechanical, water-sorption, wettability and optical properties of prepared and processed samples seemed to be adequate for their potential application as IOL materials.

References:

[1] A.W. Lloyd, R.G.A. Faragher, S.P. Denyer. *Biomaterials*, 22, 769-785 (2001).
[2] E.M. Anderson, M.L. Noble, S. Garty, H. Ma, J.D. Bryers, T.T. Shen, B.D. Ratner. *Biomaterials*, 30, 5675-5681(2009).
[3] C. Parsons, C.P. McCoy, S.P. Gorman, D.S. Jones, S.E.J. Bell, C. Brady, S.M. McGlinchey. *Biomaterials*, 30, 597-602 (2009).
[4] F.Yañez, L. Martikainen, M.E.M. Braga, C. Alvarez-Lorenzo, A. Concheiro, C.M.M. Duarte, M.H. Gil, H.C. de Sousa. *Acta Biomater.*, 7, 1019-1030 (2011).

Numerical simulation of a fluidized bed reactor and validation of Eulerian-based model for the ozonation of high-strength phenolic wastewaters

R J G Lopes*, R Quinta-Ferreira

CIEPQPF, Department of Chemical Engineering, University of Coimbra
Pólo II – Rua Sílvio Lima, 3030-790 Coimbra, Portugal.

**rodrigo@eq.uc.pt, rosaqf@eq.uc.pt*

In the realm of multiphase reaction engineering, fluidized bed reactors are widely used in a variety of industrial processes that goes from the large-scale production of base chemicals and synthetic fuels to advanced environmental technologies to detoxify highly-contaminated wastewaters. In these processes, gas-liquid mass transfer is coupled with chemical reactions between the gas oxidant and the liquid pollutants.

Regardless of the widespread application of fluidized bed reactors and substantial experimental and theoretical research efforts devoted to understand their behaviour, the methodical knowledge on the multiphase flow hydrodynamics, mass transfer and chemical reactions as well as their interactions are still lacking [1]. As long as the ozonation rate depends on the local availability of the species which is determined by the interphase mass transfer process and the mixing induced by the oxidant phase, these complex interactions embrace the overall prediction of performance and the scale-up of fluidized bed reactors is often envisaged as a cumbersome task [2].

In this work, a 3D Eulerian-based model is developed to investigate the complex behaviour involving hydrodynamics, mass transfer and chemical reactions in a fluidized bed reactor for the ozonation of high-strength wastewaters. In this model a continuum description is adopted for the liquid phase and additionally each individual bubble is tracked in a Lagrangian framework. The mass transfer rate of ozone into the wastewater is calculated using a surface renewal model which accounts for the instantaneous and local properties of the liquid phase in its vicinity [3]. The computational spatial mappings of chemical species residing in the liquid phase are computed from the coupled species balances considering the mass transfer from the oxidant carrier and reactions between the species.

First, we will focus on the hydrodynamics of the column and compare our results with experimental data. Subsequently, the mixing characteristics of the fluidized bed will be studied with the use of hydrodynamics and species tracking models. Afterwards, the chemical oxidation of biological-refractory pollutants promoted by ozone will be addressed to finally investigate the reactive flow behaviour of the fluidized bed reactor. From the comparison between the computed results and experimental data the model is able to predict the ozone distribution as well as temporal and spatial distributions of each chemical species involved.

References:

[1] J. Sanyal, D.L. Marchisio, R.O. Fox, K. Dhanasekharan, On the comparison between population balance models for CFD simulation of bubble columns, *Industrial and Engineering Chemistry Research* 44, 5063-5072 (2005)

[2] M. Higuchi, T. Saito, Quantitative characterizations of long-period fluctuations in a large-diameter bubble column based on point-wise void fraction measurements, *Chemical Engineering Journal* 160 284-292, (2010)

[3] A. Behkish, R. Lemoine, L. Sehabiague, R. Oukaci, B.I. Morsi, Gas holdup and bubble size behavior in a large-scale slurry bubble column reactor operating with an organic liquid under elevated pressures and temperatures, *Chemical Engineering Journal* 128, 69-84 (2007)

Experimental and CFD studies of reactive pulsing flow in the catalytic wet oxidation in trickle-bed reactors

R J G Lopes*, V S L Sousa, R Quinta-Ferreira

CIEPQPF, Department of Chemical Engineering, University of Coimbra
Pólo II – Rua Sílvio Lima, 3030-790 Coimbra, Portugal.

rodrigo@eq.uc.pt, rosaqf@eq.uc.pt

A comprehensive CFD model is proposed to bring new insights of pulsing flow from the perspective of catalytic reactor engineering of wet oxidation [1]. The reactive flow behaviour of environmentally-based trickle-bed reactors (TBRs) is addressed by a multiphase model and validated accordingly with experimental data on the detoxification of phenolic wastewaters. In this work, attention is focused on the CFD simulation of TBRs when the trickling flow regime changes into the pulsing flow regime at an elevated pressure, along with the parameters that characterize this latter regime. These parameters include the velocity at which the pulse front travels along the bed, the frequency of pulsations, and the structure of pulses being formed. Several parameters that characterize the pulsing flow, namely, the velocity of pulses traveling along the bed, the frequency of pulsations and their structure, the length of the pulses, and the length of the liquid-rich zone, are examined at high pressure by means of an Eulerian CFD model.

For the purpose of TBR industrial applications, liquid-induced periodic operations are preferable because reactor operation with natural pulsing is difficult for large reactors. Therefore, it is worthwhile to apply state-of-the-art CFD modelling to simulate the periodic operation of a TBR [2]. In the natural pulsing flow regime, liquid-enriched pulses form after some distance from the inlet, and they accelerate while moving downward. Formation of the pulses is associated with complex interactions among capillary forces, wall adhesion, and convective forces [3].

First, our case study encompassed the development of a CFD framework which accounts for the chemical kinetics and interphase coupling hydrodynamics in the constitutive equations. On the optimization of mesh density and time step, the CFD model correctly handled the effect of these numerical solution parameters on the computations of TOC conversion and temperature. Second, particular attention was paid to the axial profiles of temperature and TOC depletion rates. The enlargement of the pulsing flow regime in liquid-induced operation and the necessary gas flow rate and available column length for pulse formation were investigated under high-pressure operation. Finally, the interstitial flow was analysed by 3D computational mappings of gas-liquid distribution as well as TOC and thermal representations highlighting the inhomogeneous reactive pulsing flow environment within the trickle-bed reactor.

References:

[1] S. K. Bhargava, J. Tardio, J. Prasad, K. Foger, D.B. Akolekar, S.C. Grocott, Wet Oxidation and Catalytic Wet Oxidation. *Industrial and Engineering Chemistry Research* 45 (4), 1221-1258 (2006)

[2] P.R. Gunjal, M.N. Kashid, V.V. Ranade, R.V. Chaudhari, Hydrodynamics of Trickle-Bed Reactors: Experiments and CFD Modeling. *Industrial and Engineering Chemistry Research* 44, 6278-6294 (2005)

[3] R.J.G. Lopes, R.M. Quinta-Ferreira, CFD modelling of multiphase flow distribution in trickle beds. *Chemical Engineering Journal* 147 (2-3), 342-355 (2009)

A comprehensive study on the final bleaching of eucalyptus kraft pulps with hydrogen peroxide

Pedro E.G. Loureiro[a,b*], Dmitry V. Evtuguin[b] and M. Graça V.S. Carvalho[a]

[a]*CIEPQPF, Departamento de Engeharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030-790 Coimbra, Portugal*
[a]*CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal*
[*]*ploureiro@eq.uc.pt*

A sustainable production of highly bleached cellulosic pulps for the production of high grade paper products demands elemental chlorine free (ECF) and totally chlorine free (TCF) multi-stage bleaching. These sustainable process developments through the use of 'green chemistry' enabled dramatic reductions in effluent loads and toxicity, including dioxins in the effluents as well as in the pulps.

Final bleaching chemistry and technology is crucial for the quality of the market end product, namely with respect to strength, brightness and brightness stability at acceptable production costs. The most common approach is the arbitrary use of chlorine dioxide bleaching (D stage). In spite of the extraordinary performance of this chemical in terms of bleaching selectivity, it is not, in many cases, a rational or justified final bleaching option. In this study the use of hydrogen peroxide final bleaching (P stage) under optimized operating conditions of chemical charges, temperature, reaction time and hydrogen peroxide stabilizers (magnesium and/or chelants) proved to be more beneficial with regard to the brightness gain, brightness stability, pulp beatability and strength properties of the fully bleached pulp. After the established recognition of the advantages of a final hydrogen peroxide stage in the ECF bleaching of *Eucalyptus globulus* kraft pulps, a comprehensive study was undertaken to fully scrutinize the bleaching chemistry of hydrogen peroxide. Moreover, the fundamental reasons for the better performance of a final hydrogen peroxide stage instead of conventional chlorine dioxide were investigated towards the use of advanced final bleaching strategies.

The final stage in a DEDP bleaching sequence was carried out in 230 bleaching trials devoted to the study of hydrogen peroxide stabilization systems, pulp brightening and degradation kinetics, hydrogen peroxide decomposition and finally a detailed bleached pulp characterization and chromophore assessment. A different pulp was also used to study the influence of pulp bleaching history (OQ(PO)DP) on the performance of a final hydrogen peroxide stage.

There is no universal stabilizing system towards optimal bleachability and selectivity results in alkaline peroxide bleaching because of pulp bleaching history dependence. *In-situ* pulp degradation during peroxide bleaching was evidenced and related to iron and copper bound to pulp.

For the first time using 325 nm laser excitation UV-RR spectra were acquired in bleached eucalypt kraft pulps, which revealed to be appropriate for selective analysis of polyconjugated chromophore structures in polysaccharides. Moreover, spectroscopic data were coupled to wet chemistry and mass spectrometry analyses of products arisen upon thermal ageing of bleached pulps.

The analysis of UV-RR spectra revealed isolated xylan from bleached pulps as an important source of chromophores in eucalypt kraft pulp. Chlorine dioxide final beaching increased the amount of conjugated structures whereas hydrogen peroxide (DEDP) decreased them. The comprehensive results gathered have evidenced the role of carbohydrate hydrothermal degradation on inducing ageing reactions and of the remaining xylan-lignin component dictating their extent.

References:

- Pedro E. G. Loureiro, Studies on the final bleaching of *Eucalyptus globulus* kraft pulps with hydrogen peroxide, *Doctoral Thesis*, Universidade de Coimbra (2010).

Two-layer coated Papers Using Precipitated Calcium Carbonate

Ana F. Lourenço[a], José A.F. Gamelas[a,*], Paulo J. Ferreira[a,*]

[a] *Departamento de Engenharia Química, Universidade de Coimbra, Centro de investigação CIEPQPF, Pólo II – R. Sílvio Lima, 3030-790 Coimbra, Portugal*

* *jafgas@eq.uc.pt; paulo@eq.uc.pt;*

The need of a quality paper for the day-to-day use is becoming increasingly important. This work aims at developing a premium quality printing and writing paper using new simple and not expensive processes for the modification of the paper surface. For that, high values for the physical, optical and printing quality properties should be achieved.

Precipitated calcium carbonate (PCC) is used since, when compared with other pigments, it is not expensive; it has an excellent rheological behavior, high brightness, a small loss of gloss and less binder demand. Starch, used as a binder in the coating process, promotes the runnability and readability of the paper and polyvinyl alcohol (PVOH) is also used for surface treatments due to its good properties such as the solubility in water, film-forming properties and good adhesion.

In this work, a reference paper without surface sizing was coated with formulations containing PCC as pigment, PVOH or starch as binders, and ammonium polycarbonate as dispersant. A single and a double coating were performed by combining different formulations, with pick-ups of about 3 and 8 g/m^2, respectively. The coated papers were characterized by the measurement of the surface energy and of the mechanical and optical properties. After inkjet printing, gamut area, optical densities and print-through were measured.

For the two-layer coated papers gamut areas higher than 10000 and black optical density around 1.6 could be achieved.

This work was included in the research project QREN-PADIS 5348, promoted by gPS-Grupo Portucel-Soporcel with RAIZ-Instituto de Investigação da Floresta e Papel. It was firstly presented at the PaperCon 2011 in Cincinnati, USA.

Keywords: paper coating, PCC, printing quality, optical properties.

Papers coated with a modified pigment obtained by *in situ* synthesis of silica film on PCC

Ana F. Lourenço[a], José A.F. Gamelas[a,*], Paulo J. Ferreira[a,*]

[a] *Departamento de Engenharia Química, Universidade de Coimbra, Centro de investigação CIEPQPF, Pólo II – R. Sílvio Lima, 3030-790 Coimbra, Portugal*

* *jafgas@eq.uc.pt; paulo@eq.uc.pt;*

Different silica grades and precipitated calcium carbonate (PCC) particles are commonly used as pigments for the coating of printing and writing papers aiming to improve the inkjet printability. These pigments present high reflectance in all the visible wavelength range, superior brightness and refractive index, and also good compatibility with the other components commonly used for the coating process (such as binders, co-binders, dispersants, etc.), which are important characteristics to consider in order to immobilize them at the paper surface and to obtain better printing quality properties. In particular, for the silica, its high porosity may help on a better retention of the dyes molecules at the paper surface.

Papers coated with porous silica particles are considered to have better performance regarding inkjet printing quality. On the other hand, PCC, a much cheaper material, is not so effective in the printing process. In this context, a new material which combines the best of the properties of silica and PCC could be of great interest. Therefore, the purpose of this project is a) to effectively change the surface of PCC particles with small amounts of silica, and b) to use the modified PCC's for paper coating in order to improve printability and paper optical properties.

Silica was produced *in situ* at the surface of PCC by sol-gel method *via* hydrolysis of tetraethyl orthosilicate (silica precursor) in ethanol/water solutions. The presence of silica in the modified PCC particles was clearly detected by infrared absorption spectroscopy, *i.e.*, by the bands due to the stretching and bending vibrations of the Si-O bonds. On the other hand, by scanning electron microscopy it was possible to identify the deposition of a nanometric film of silica sol at the surface of the PCC particles. The amount of silica retained on the surface of the modified PCC particles was determined by thermogravimetry. Their value was found to vary between 5% and 30%, depending on the experimental conditions used, namely the ammonium concentration of the reaction medium. By granulometric analysis it was possible to say that the medium sizes of the particles have not been considerably changed by the incorporation of silica at the PCC surface.

The new PCC's modified with silica were used in distinct formulations with selected binders, co-binders and dispersants, and these were then applied at the paper surface. The results of inkjet printing quality for the new coated papers are presented and compared with those of commercial papers.

This work was included in the research project QREN-PADIS 5348, promoted by gPS-Grupo Portucel-Soporcel with RAIZ-Instituto de Investigação da Floresta e Papel. It was firstly presented at the TAPPI International Conference on Nanotechnology for the Forest Product Industry in Espoo, Finland, 2010.

Keywords: coating, inkjet printing, silica, sol-gel, PCC.

Systematic selection of extraction solvents in the aromatics production

Dina M.J. Machado[a], Filipe J.M. Neves[b], Fernando P. Mendes[b], Paulo P. Araújo[b], Belmiro P.M. Duarte[c], Nuno M.C. Oliveira[a]

[a]*University of Coimbra, GEPSI-PSE Group, CIEPQPF, Dep. Chemical Engineering, R. Sílvio Lima – Pólo II, 3030-790 Coimbra, Portugal*
[b]*CUF – Químicos Industriais, S.A., Process Development Dep., Quinta da Indústria, 3860-680 Estarreja*
[c]*Polytechnic Institute of Coimbra, Chemical and Biological Engineering, R. Pedro Nunes, 3030-190 Coimbra*

The choice of appropriate extraction solvents for liquid-liquid (L/L) extraction operations is a common problem in the chemical process industry, and can benefit from a systematic approach based on a mathematical formulation as an inverse problem. Original approaches [1-2] relied on physical insights for an effective exploration of the combinatorial solution space, using physical property representations based on the combination of group contribution (GC) approaches, such as the UNIFAC methods, and empirical relations, together with structural feasibility constraints. These approaches were later formulated more rigorously as MINLP (optimization) problems. Common characteristics of these problems are the nonlinear non-convex formulations used, with a significant number of discrete variables, and the presence of multiple local optima, thus requiring robust and reliable solution algorithms.

Here we consider the application of this methodology to the problem of solvent selection for L/L extraction of aniline (ANL), produced by liquid phase hydrogenation of mono-nitrobenzenze (MNB). Water (W) is a by-product of the main reaction, which needs to be separated in the output streams of the reactors. Due to the existence of an ANL/W azeotrope, and because of the considerable solubility of ANL in water, an extraction agent is used to promote the separation of ANL and the light by-products, such as cyclohexylamine (CHA) and cyclohexanol (CHOL). Often, this solvent is chosen as a substance already present in the process, such as MNB or benzene (BZ). However, various problems are usually associated to these simple choices (e.g., operational, or environmental factors).

We consider a sequential approach, structured similarly to [3], to significantly reduce the total solution effort required. The methodology includes two major solution levels:
1. The generation of *feasible molecular structures* that satisfy the *property constraints* posed as bounds (problem P1).
2. The *solution of the optimization problems* over the feasible points generated during the solution of P1, or implicitly represented by a set of constraints originating from P1 (problem P2).

A set of objective indices Φ is considered to assess the quality of alternative solutions. These are partitioned into class subsets, e.g., $\Phi = \Phi_p \cup \Phi_s$, where Φ_p denotes the subset of objectives related to the performance of the product, and Φ_s represents the subset of objectives related to its safety characteristics. Combined objective indices are then generated for each class of objectives (PIO and SIO, respectively), allowing the evaluation of alternative solutions in a multiattribute decision framework. This methodology was used to evaluate the relative performance of simple (linear and cyclic) hydrocarbons, considering the possibility of single and double substitutions in the families of amines, aldehydes, and alcohols.

References:
[1] R. Gani, E.A. Brignole, *Fluid Phase Equilibria*, **13**, 331-340 (1983).
[2] E.J. Pretel, P.A. López, S.B. Bottini, E.A. Brignole, *AIChE J.*, **40**, 1349–1360 (1994).
[3] A.T. Kurananithi, L.E.K. Achenie, R. Gani, *Ind. Eng. Chem. Res.*, **44**, 4785-4797 (2005).

Influence of chemical structure on the equilibrium solubility of naphthoquinone derivatives in supercritical carbon dioxide: experimental determination and correlation

Sofia Marceneiro[1*], Patrícia Coimbra[1], Mara E.M. Braga[1], Ana M.A. Dias[1], Hermínio C. de Sousa[1]

1 CIEPQPF, Chemical Engineering Department, FCTUC, University of Coimbra, Rua Sílvio Lima,
Pólo II – Pinhal de Marrocos, 3030-790 Coimbra, Portugal
**smarceneiro@eq.uc.pt*

Naphthoquinones are natural phenolic compounds and plant secondary metabolic groups which can be found in their roots, leaves, bark and wood [1]. The main interest in these compounds arises from their well-known and broad-range biological activities which include phytotoxic, insecticidal, antibacterial, fungicidal and antiviral activities [2]. The extraction of naphthoquinones from vegetal matrices under mild temperature conditions and avoiding the use of non-friendly solvents, as well as their potential impregnation/deposition into polymeric materials (in order to prepare natural-based sustained drug delivery systems) can be efficiently achieved by using supercritical fluid (SCF) processes. This work reports the experimental measurement and the correlation of the equilibrium solubility of three naphthoquinone derivatives, namely naphthoquinone (1,4-Naphthoquinone), juglone (5-hydroxy-1,4-naphthoquinone) and plumbagin (5-hydroxy-2-methyl-1,4-naphthoquinone) in supercritical carbon dioxide ($scCO_2$) [3,4]. Results were obtained using a static analytical method, at 308, 318 and 328K, and in a pressure range from 9.0 up to 24.0MPa, and compared with values already reported in the literature using different methodologies and for compounds with similar chemical structure. Experimental data were correlated with three density-based models (Chrastil, Bartle and Méndez-Santiago-Teja) and with two cubic equation-of-state (EOS) models (Peng-Robinson (PR-EOS) and Soave-Redlich-Kwong (SRK-EOS)), together with the conventional van der Waals mixing and combining rules. Several different sets of solid properties, estimated by different methods available in literature, were used in EOS correlations. The importance of the estimation methods used for the determination of solid properties (namely sublimation pressure) was discussed in terms of the cubic EOS correlation results quality. A comparison between the three naphthoquinones shows that: i) when the hydroxyl group is "added" to the 1,4-naphthoquinone molecule (forming juglone), the solubility in $scCO_2$ decreases - due to the unfavorable hydroxyl/CO_2 interactions; and ii) when the methyl group is "added" to the juglone molecule (forming plumbagin), the solubility greatly increases and plumbagin becomes even more soluble in $scCO_2$ than 1,4-naphthoquinone - due to the favorable methyl/CO2 interactions. This means that the low polarity methyl group contribution for the solubility overcomes the high polarity hydroxyl group unfavorable contribution.

References:

[1] Anita Solar, Mateja Colarič, Valentina Usenik and Franci Stampar, Seasonal variations of selected flavonoids, phenolic acids and quinones in annual shoots of common walnut (*Juglans regia* L.), *Plant Science*, 170, 453-461 (2006).

[2] Petr Babula, Vojtěch Adam, René Kizek, Zdeněk Sladký and Ladislav Havel, Naphthoquinones as allelochemical triggers of programmed cell death, *Environ. Exp. Bot.*, 65, 330-337 (2009).

[3] Sofia Marceneiro, Patrícia Coimbra, Mara E. Braga, Ana M. Dias and Hermínio C. de Sousa, Measurement and correlation of the solubility of juglone in supercritical carbon dioxide, *Fluid Phase Equilib.*, 311, 1-8 (2011).

[4] Sofia Marceneiro, Mara E. Braga, Ana M. Dias and Hermínio C. de Sousa, Measurement and Correlation of 1,4-Naphthoquinone and of Plumbagin Solubilities in Supercritical Carbon Dioxide, *J. Chem. Eng. Data*, Accepted manuscript (2011), DOI: 10.1021/je200675g.

Characterization of Biomedical Grade Poly(vinyl chloride) Films Plasticized Ionic Liquids

Sofia Marceneiro[1*], Ana M.A. Dias[1], Mara E.M. Braga[1], Jorge F.J. Coelho[1], Abel G.M. Ferreira[1], Pedro N. Simões[1], Ana Matias[2], Catarina M.M. Duarte[2], Liliana C. Tomé[3], Isabel M. Marrucho[3], José M.S.S. Esperança[3], Luís P.N. Rebelo[3], Hermínio C. de Sousa[1]

[1]CIEPQPF, Chemical Engineering Department, University of Coimbra, Coimbra, Portugal
[2]Nutraceuticals and Delivery Laboratory, Instituto de Biologia Experimental e Tecnológica (IBET), Oeiras, Portugal
[3]ITQB, Institute for Chemical and Biological Technology, New University of Lisbon, Oeiras, Portugal
** smarceneiro@eq.uc.pt*

Poly(vinyl chloride) (PVC) finds extensive application in the medical field being intensively used to produce a large number of medical devices [1,2]. The development of new materials, using “greener” and friendlier solvents and plasticizers with lower toxicity, but still able to improve the chemical, physical and mechanical properties of the polymer is an actual concern of the scientific community [3,4]. Phthalates are the most commonly used plasticizers for PVC. Nevertheless, many reports alerted to the toxicity caused by the leaching of these plasticizers to the human body (with retention in the vital organs). Ionic liquids (ILs) may represent interesting alternatives to replace harmful plasticizers due to their well known physical-chemical-toxicological properties which can be tailored by a selective conjugation of different cations and anions [5]. In this work, medical grade non-plasticized suspension PVC resin was dissolved in THF and different amounts of phosphonium-based ILs were added (from 0 to 20% w/w) to the solution in order to prepare films with different plasticization characteristics. A conventional organic plasticizer (di-isononyl phthalate, DINP) was also used for comparison purposes. Samples were characterized by TGA, DMTA, SEM-EDX, permeability to gases (oxygen and carbon dioxide), contact angle measurement, water sorption capacity, plasticizer leaching, cytotoxicity against caco-2 and HepG2 human cell lines and blood compatibility. Results show that it is possible to “tune” PVC properties, mainly hydrophobicity, thermal resistance and elasticity, by changing the incorporated IL type and amount. Amongst all the employed ILs, trihexyltetradecylphosphoniumbis(trifluoromethylsulfonyl)imide, presented the most interesting and promising thermo-mechanical and biocompatibility results.

References:
[1] Joseph R. Davis, Handbook of Materials for Medical Devices, ASM International, 2003.
[2] Paul H. Daniels, A Brief Overview of Theories of PVC Plasticization and Methods Used to Evaluate PVC-Plasticizer Interaction , *J. Vynil Addit. Technol.,* 15, 219-223 (2009).
[3] Mustafizur Rahman and Cristopher S. Brazel, Ionic liquids: New generation stable plasticizers for poly(vinyl chloride), *Polym. Degrad. Stab.,* 91, 3371-3382 (2006).
[4] George Wypych, Handbook of Plasticizers, ChemTec Publishing, Toronto - New York, 2004.
[5] Thomas Welton, Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis., *Chem. Rev.,* 99, 2071 (1999).

Effect of the R and R' groups (methyl and ethyl) on the microstructure of xerogels/aerogels synthesized from $RSi(OR')_3$ precursors

Telma Matias[a], Marta Ochoa[a], Nuno Rocha[b], António Portugal[a], and Luisa Durães[a*]

[a] *CIEPQPF, Department of Chemical Engineering, Faculty of Sciences and Technology,*
University of Coimbra, Pólo II, Rua Sílvio Lima, 3030-790 Coimbra, Portugal
[b]*AST-Active Space Technologies, IPN – Instituto Pedro Nunes, 3030-199 Coimbra, Portugal*
[*]*luisa@eq.uc.pt*

The influence of the R and R' groups (methyl and ethyl) of $RSi(OR')_3$ precursors on the sol-gel synthesis and microstructure of silica based xerogels/aerogels is studied. The published works with several precursors, namely methyltrimethoxysilane (MTMS), ethyltrimethoxysilane (ETMS), methyltriethoxisylane (MTES) and ethyltriethoxysilane (ETES) are reviewed, comparing the synthesis conditions and the products properties. Special emphasis will be given to key properties required for insulation applications, such as the bulk density, surface area, porosity and hydrophobicity.

A two-step chemistry of hydrolysis-condensation reactions is used to prepare the gels, which can be dried at ambient pressure or at supercritical conditions to produce xerogels and aerogels, respectively. The R and R' groups have a significant influence on the hydrolysis and condensation rates and, consequently, on the growth of the inorganic solid network and thus on the microstructure and properties of the final materials. Furthermore, other reactions can occur in the sol-gel process such as reesterification, depolymerisation and transesterification due to the presence of all the components in solution, for example catalysts and solvents [1].

The orthosilicates (TMOS and TEOS) are the most studied silane precursors but the obtained materials are brittle and hydrophilic. The R group of the trialkoxysilanes remains in the 3D-solid network of the materials conferring them hydrophobicity and flexibility. On the other hand, it causes the decrease of the cross linking degree and, consequently, an increase of porosity and specific surface area [2].

Organic-inorganic silica based xerogels/aerogels can be obtained using MTMS and MTES or combining these with TEOS or TMOS. MTMS precursor leads to products with high contact angle, porosity and surface area and very low density [3-9]. With MTES precursor, the interlinked units are larger than with MTMS precursor due the steric effect of the alkoxide group (Figure 1)[8]. ETMS and ETES precursors only produce gels when combined with TMOS and TEOS because the size of the R group (ethyl) makes the growth of the solid network difficult [10]. Table 1 shows some properties of materials synthesized with the considered precursors. It can be concluded that only with MTMS and MTES precursors the products density can be lower than 0.050 g/cm^3, achieving a porosity of 98%. All the precursors lead to highly hydrophobic materials.

Table 1 – Properties of the materials obtained with $RSi(OR')_3$ precursors (R, R' = methyl, ethyl).

Precursor	Gelation time (h)	Bulk density (g/cm^3)	Porosity (%)	Surface area (m^2/g)	Contact angle (°)	Reference
MTMS	0.833	0.220	-	-	173	[3]
	16	0.040	-	-	164	[4]
	13.5	0.062	-	520	152	[5]
	9	0.037	98	-	149	[6]
	10	0.042	98	-	-	[7]
	5	0.088	93	409	148	[8]
	-	0.053	95	512	147	[9]
TMOS/MTMS	0	0.050	-	1120	-	[11]
MTES	4.88	0.037	98	-	160	[12]
	5	0.101	92	362	145	[8]
TMOS/ETMS	-	0.064	96	-	153	[13]
TEOS/ETES	-	0.148	93	-	151	[14]

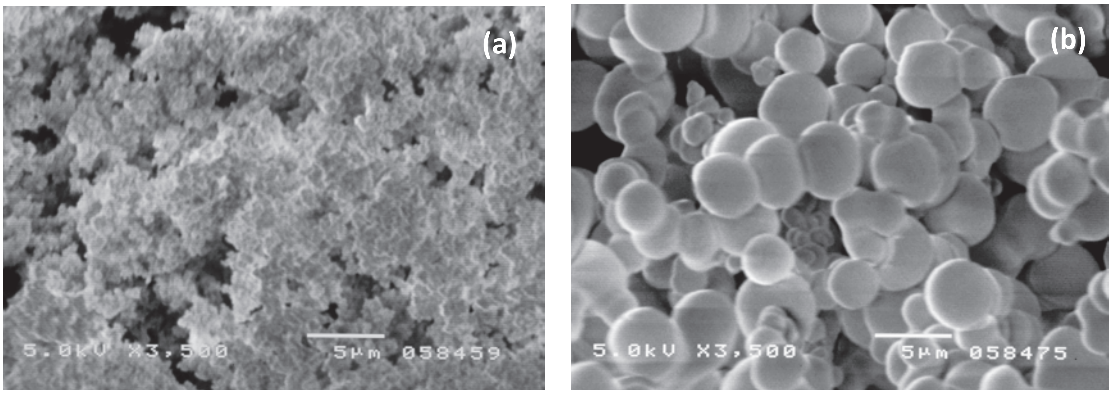


Figure 1 – SEM images of aerogels obtained with a) MTMS precursor and b) MTES precursor.

This work is funded by FEDER funds through the Operational Programme for Competitiveness Factors - COMPETE and National Funds, through FCT - Foundation for Science and Technology under the project PTDC/EQU-EPR/099998/2008 – GelSpace-Silica Based Aerogels for Insulation of Spatial Devices.

References:

[1] A. Jitianu, A. Britchi, C. Deleanu, V. Badescu, M. Zaharescu, Comparative study of the sol-gel processes starting with different substituted Si-alkoxides, J. Non-Cryst. Solids, 319 (2003) 263-269.
[2] L. Durães, S. Nogueira, A. Santos, C. Preciso, J. Hernandez and A. Portugal, Flexible silica based xerogels and aerogels for spatial applications, in: Proc. 10th Int. Chem. Biol. Eng. Conf. – CHEMPOR 2008, edited by E. Ferreira and M. Mota, Department of Biological Engineering of University of Minho, Braga, (2008), p.563 and CD-ROM.
[3] A. Rao, M. Kulkarni, D. Amalnerkar, T. Seth, Superhydrophobic silica aerogels based on methyltrimethoxysilane precursor, J. Non-Cryst. Solids, 330 (2003) 187-195.
[4] A. Rao, S. Bhagat, H. Hirashima, G. Pajonk, Synthesis of flexible silica aerogels using methyltrimethoxysilane (MTMS) precursor, J. Colloid Interface Sci. 300 (2006) 279-285.
[5] S. Bhagat, C. Oh, Y. Kim, Y. Ahn, J. Yeo, Methyltrimethoxysilane based monolithic silica aerogels via ambient pressure drying, Microporous Mesoporous Mater. 100 (2007) 350-355.
[6] N. Hedge, A. Rao, Physical properties of methyltrimethoxysilane based elastic silica aerogels prepared by the two-stage sol-gel process, J. Mater. Sci. 42 (2007) 6965-6971.
[7] D. Nadargi, S. Latthe, A. Rao, Effect of post-treatment (gel aging) on the properties of methyltrimethoxysilane based silica aerogels prepared by two-step sol-gel process, J. Sol-Gel Sci. Technol., 49 (2009) 53-59.
[8] L. Durães, M. Ochoa, A. Portugal, N. Duarte, J. Dias, N. Rocha, J. Hernandez, Tailored silica based xerogels and aerogels for insulation in space environments, Adv. Sci. Technol., 63 (2010) 41-46.
[9] L. Durães, M. Ochoa, N. Rocha, R. Patrício, N. Duarte, V. Redondo, A. Portugal, Effect of the drying conditions on the microstructure of silica based xerogels and aerogels, J. Nanosci. Nanotechnol. (2011) (In press).
[10] D. Loy, B. Baugher, C. Baugher, D. Schneider, K. Rahimian, Substituent effect on the sol-gel chemistry of organotrialkoxysilanes, 12 (2000), 3624-3632.
[11] P. Wagh, S. Ingale, S. Gupta, New technology for rapid processing and moulding of silica aerogel materials in prescribed shapes and sizes and their characterization, J. Sol-Gel Sci. Technol, 2011
[12] D. Nadargi, A. Rao, Methyltriethoxysilane: New precursor for synthesizing silica aerogels, J. Alloys Compd. 467 (2009) 397-404.
[13] A. Anderson, M. Carroll, E. Green, J.Melville, M. Bono, Hydrophobic silica aerogels prepared via rapid supercritical extraction, J. Sol-Gel Sci. Technol. 53 (2010) 199-207.
[14] A. Rao, N. Hedge, P. Shewale, Imperviousness of the hydrophobic silica aerogels against various solvents and acids, Appl. Surf. Sci. 253 (2007) 4137-4141.

Prediction of reaction pollutants and products properties of pyrolysis and combustion processes using THOR code

T. Matias[a], L. Durães[a], J. Campos[b], A. Andrade-Campos[c] and A. Portugal[a]

[a]*CIEPQPF, Chem. Eng. Dep., Fac. Sci. Technol., University of Coimbra, Polo II, Rua Sílvio Lima, 3030-790 Coimbra, PORTUGAL (tmatias@eq.uc.pt, luisa@eq.uc.pt, atp@eq.uc.pt)*
[b]*LEDAP/ADAI, Mech. Eng. Dep., Fac. Sci. Technol., University of Coimbra, Polo II, Rua Luís Reis Santos, 3030-788 Coimbra, PORTUGAL (andrade.campos@dem.uc.pt)*
[c]*Mech. Eng. Dep., University of Aveiro, 3800-193 Aveiro, PORTUGAL (gilac@ua.pt)*

The existing reactions in pyrolysis and combustion processes generate intermediary chemical species and compounds and are very hard to follow by experiments, since these processes are very fast and exhibit a sharp increase in pressure and/or temperature. Consequently a prediction method of reaction path and final composition of reaction products is very useful. The here presented method uses a thermochemical computer code, named THOR, with four calculating clusters. The first is related to the thermal equation of state (EoS) that allows the calculation of the PVT state of the products. The second calculating cluster is related to the energetic equation of state, corresponding to the internal energy calculation using thermochemical data and polynomial expressions of Gordon and McBride applied to intermediate and final products. The third cluster is related to the conservation equations - mass, atomic species, momentum and energy, being the thermodynamic equilibrium achieved for G=Gmin(P,T,xi). The last cluster corresponds to the reaction regime, which may be adiabatic isobaric or isochoric combustion or detonation.

A thermodynamic property database – THORDB – of more than 18 000 species and compounds was installed, to allow the interaction of data with the calculating clusters. The reaction path is estimated theoretically assuming thermodynamic equilibrium for all possible reaction products, including intermediary molecules, as a function of temperature and pressure conditions. Several case studies are presented, from simple gaseous to more complex condensed reactant mixtures. Their combustion/pyrolysis products (and pollutants) formation are discussed.

Keywords: Combustion prediction, thermochemical computer code, equations of state, combustion products, products formation, decomposition path, pollutants prediction.

Lignocellulosic biomass valorisation in a pulp and paper mill

Cátia V. T. Mendes[a,*], M. Graça V. S. Carvalho[a] and Jorge M. S. Rocha[a]

[a]*CIEPQPF, Departamento de Engenharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030-790 Coimbra, Portugal*
[*]*catvan@eq.uc.pt*

The forest biorefinery is well represented by pulp and paper mills that use renewable raw-materials (lignocellulosic biomass) to produce different commodities like pulp, paper and energy, through a combination of different technologies and equipments. Other biomass conversion processes can be integrated to optimize the available lignocellulosic biomass and produce value-added products, like chemicals or biofuels, in addition to their mainstay products. By these means pulp and paper mills can increase their incomes and competitive advantages and decrease environmental impacts. Figure 1 shows two different strategies to optimize lignocellulosic biomass conversion in bioethanol, integrated in a Portuguese pulp and paper mill, which is the main goal of this study.

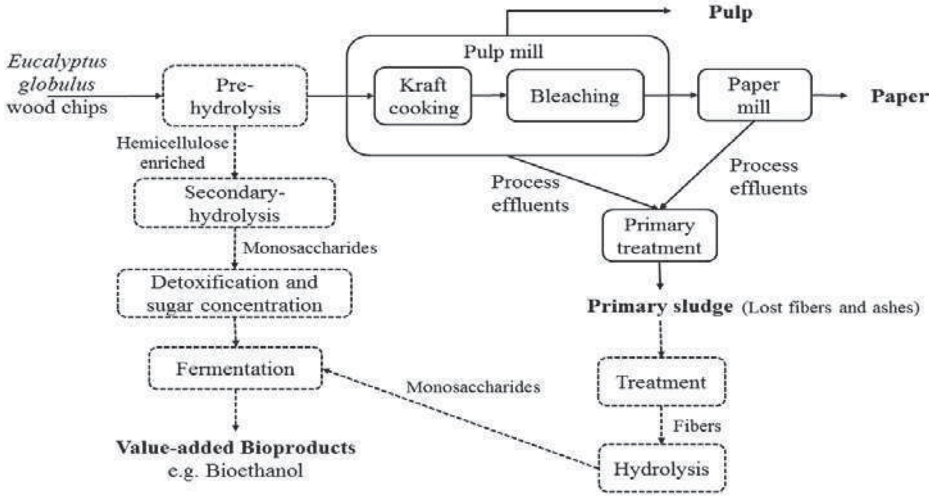


Figure 1 – Pathways to extend the biorefinery concept in a pulp and paper mill (dashed lines).

The first one consists in the pre-extraction of nearly 50% wood hemicelluloses prior to kraft cooking stage, preventing their dissolution in the black liquor by introducing a pre-treatment to wood chips. The final pulp quality must not be compromised by the pre-treatment selected and the extracted hemicelluloses must be further processed to produce fermentable monosaccharides. Pre-extraction was carried out by acid and auto-hydrolysis processes. Pulp quality was less affected by auto-hydrolysis pre-extraction. Second hydrolysis (acid or enzymatic) and detoxification and sugar concentration methods (overliming and vacuum evaporation) were applied to the extracts from the auto-hydrolysis before the ethanolic fermentation [1] The other strategy consists in the valorisation of the cellulosic fraction present in the pulp and paper mill primary sludge, an inexpensive, abundant and readily available raw-material. However, primary sludge also contains a high inorganic fraction (mostly carbonates) that has negative effects upon the hydrolysis process to convert the cellulosic fraction into fermentable sugars. The use of an acid hydrolysis releases CO_2 and the application of an enzymatic hydrolysis is uneffective unless the inorganic content is decreased (as carbonates provide a high pH to primary sludge). Therefore, the primary sludge must be previous submitted to an efficient treatment to remove the inorganic fraction in order to enhance the hydrolysis and fermentation steps [1].

References:

[1] M. Graça V. S. Carvalho, Cátia V. T. Mendes, Belinda I. G. Soares, Gabriel D. A. Sousa and Jorge M. S. Rocha, Valorisation of lignocellulosic biomass for an integrated biorefinery in he pulp and paper industry, 5th International Colloquim on Eucalyptus Pulp, Porto Seguro, Bahia, Brasil, 9-12 May 2011.

Multivariate SPC / EPC Integration in MIMO Chemical Processes

Raquel D. Moita[a*], Tiago J. Rato[a], Pedro M. Saraiva[a], Lino O. Santos[a] and Marco S. Reis[a*]

[a]*CIEPQPF, Department of Chemical Engineering, University of Coimbra, Pólo II – Rua Sílvio Lima, 3030-790 Coimbra, Portugal.*
[*]*raqueldurana@gmail.com; marco@eq.uc.pt*

Several works have appeared in the literature regarding the integration of Engineering Process Control (EPC) and Statistical Process Control (SPC). These contributions can be conceived as belonging to two fundamentally distinct classes of integrative approaches: one in which the SPC mechanism supervises, without interfering, with an EPC controller, which is active all the time, and another in which the SPC mechanism acts as a trigger of the EPC control scheme.

Regarding the first class of approaches, where both techniques act simultaneously, there are at least three possibilities to monitor the EPC controlled process: a) Monitoring the quality characteristic, using control charts to signal large deviations from the target; b) Monitoring the adjustable variables: large deviations in the quality characteristics will result in large adjustments made and thus these variables should also have information that can be used for process monitoring; c) Monitoring both the process inputs and outputs.

In this work, we consider the first class of approaches, in which the EPC control is active all the time, exemplified with two study cases, with characteristics that have not been addressed before in the literature. In the first case, a multivariate monitoring scheme is implemented in a chemical process together with existent PI feedback controllers. It consists of a continuous stirred tank reactor (CSTR), where a first-order endothermic and irreversible reaction takes place, which is also fitted with a heating jacket for thermal control. The second case considered refers to the multivariate monitoring of a lab-scale fed-batch Escherichia coli biomass production process, subject to a nonlinear model predictive controller (NMPC).

Results show that the SPC/EPC integration improves the system performance, allowing simultaneously detecting special events and compensating for disturbances.

Keywords: SPC/EPC, integration, Multivariate monitoring, model predictive control, PI controller

Transesterification of crude cotton seed oil and ethanol by zirconia doped with cerium IV sulphate

Walter G. Morales[a], Julio Fernández[b], Ester Chamorro[a], Mara E.M. Braga[d], Abilio Sobral[c], Hermínio C. de Sousa[d,*], Eduardo R. Herrero[b]

[a]*Research Group on Biological Organic Chemistry (QUIMOBI), National Technological University. Regional Faculty Resistencia, French 414, C.P. H3500CHJ, Resistencia, Argentina,*
[b]*Research Center and Chemical Technology (CITeQ), National Technological University, Regional Faculty Córdoba. Cruz Roja Argentina esq. Maestro López, University City, C.P. X5016ZAA, Córdoba, Argentina.*
[c]*FCTUC,University of Coimbra, Chemical Department, Rua Larga, 3000 Coimbra, Portugal.*
[d] *CIEPQPF, Chemical Engineering Department, FCTUC, University of Coimbra, Rua Sílvio Lima, Pólo II – Pinhal de Marrocos, 3030-790 Coimbra, Portugal.*
**hsousa@eq.uc.pt*

Many of the solid catalysts were already reported in the literature such as additivated $AlCl_3$, zeolites, heteropoly acids and bi-functional catalysts. The strong acidity of zirconia-supported sulphate has attracted much attention because of its ability to catalyse a large number of chemical reactions such as isomerisation, alkylation, dehydration, esterification and transesterification [1-3]. In this work, we report the preparation and characterization of a solid superacid catalyst by doping zirconium oxide (ZrO_2) with cerium (IV) sulphate. This catalyst was employed in the transesterification of cotton seed oil with ethanol (EtOH) in order to obtain biodiesel. Zirconium oxide was obtained by precipitation of zirconium oxychloride with an ammonium solution, aged for 2 hours at pH 10±0.2, dried and doped with a cerium (IV) sulphate solution (5 %, w/w). Catalyst was then calcined at 600 ºC for 2 hours in an air atmosphere. In order to determine catalyst chemical structure, X-ray diffraction (XRD) analyses were performed. Fourier-Transform Infrared spectroscopy (FTIR) was also employed for functional groups analysis. Specific surface area was determined (BET method) for the catalyst. Samples acidity was measured by the adsorption/desorption of pyridine at 150, 250 and 350 °C, followed by FTIR analysis. The prepared/characterized solid catalyst (zirconium oxide doped with 5 % (w/w) of cerium sulphate) was tested for the transesterification of crude cotton seed oil in ethanol. Different cotton seed oil:EtOH mixtures (molar ratios of 1:10, 1:20 and 1:30) were tested in the presence of a pre-determined amount of catalyst (10.0, 2.5, 1.0 and 0.5 %, w/w of vegetable oil). Reactants were stirred at 700 rpm which was adequate to maintain a suspension reaction. Reaction temperature was raised and maintained at the desired reaction temperature (100, 150 and 200 ºC), by a heater with a programmable PID temperature controller for the desired and pre-determined reaction time (1, 2 and 4 hours), at a self-generated pressure. The biodiesel product was analyzed by thin layer chromatography (TLC) and by gas chromatography (GC-FID, Tremetrics 9001).

Amongst all the tested experimental reaction conditions, best reaction yield (73% conversion) was obtained for a 2 hour reaction period, with 10 wt% catalyst concentration, at 200 ºC and employing a 1:30 oil:EtOH ratio. Produced biodiesel TLC analyses revealed the presence of ethyl esters and also of triglycerides when the reaction was incomplete. Biodiesel composition presented, as its main compounds, ethyl linolenate, ethyl oleate and ethyl palmitate with approximately 50, 20 and 20 % respectively. In this work, the production of biodiesel from cotton seed oil catalysed by zirconium oxide doped with cerium IV sulphate in ethanol was evaluated. Results showed that the reaction carried out for 2 hours, at 200 ºC, using an oil:EtOH molar ratio of 1:30 and 10 % (w/w) of catalyst was the best condition, leading to the highest conversion yield (73%). Therefore and in conclusion, these results indicate that zirconium oxide doped with cerium IV sulphate may present a great potential to be used as catalyst in the biodiesel production from crude cotton seed oil.

References:

[1] G.D. Yadav and J.J. Nair, *Microporous and Mesoporous Material* 33, 1-48 (1999).
[2] D.E. López, J.G. Goodwin Jr., D.A. Bruce and S. Furuta, *Applied Catalysis A* 339, 76-83 (2008).
[3] J. R. Sohn, S.H. Lee and J.S. Lim, *Catalysis Today* 116, 143-150 (2006).

Influence of additives on the properties of silica based xerogels

Marta Ochoa[a], Luísa Durães[a], Nuno Rocha[b] and António Portugal[a*]

[a] *CIEPQPF, Department of Chemical Engineering, Faculty of Sciences and Technology,*
University of Coimbra, Pólo II, Rua Sílvio Lima, 3030-790 Coimbra, Portugal
[b]*AST-Active Space Technologies, IPN – Instituto Pedro Nunes, 3030-199 Coimbra, Portugal*
[*]*atp@eq.uc.pt*

The influence of the additives N,N-dimethylformamide (DMF), glycerol (GLY) and polyethylene glycol (PEG) on the synthesis of silica based xerogels using MTMS precursor is investigated in this paper.

The preparation of these materials follows a three step procedure: synthesis, aging and drying [1]. The synthesis is a two-step acid-basic catalysed reaction. At this step a wet gel is obtained after which is aged for an increase of the solid network connectivity/cohesion. The aging period is important for the next drying step since it minimizes the collapse of the pores [2]. Ambient pressure drying (evaporative – xerogels) and supercritical fluid drying (SFD – aerogels) are both used to carry out the final step. In the evaporative method, the effect of capillary forces causes the cracking and shrinkage of the three-dimensional network. The highest product porosity is obtained with SFD. However this technique is expensive and hazardous due to the high temperature and pressure required [3].

During evaporative drying, the solvent is removed from the pores and the capillary pressure damages the physical structure of the gel network. As the capillary pressure is inversely proportional to the pore size larger pores allow faster drying and less shrinkage [4]. The drying stress depends on the vapour pressure of the liquid in the pores. Therefore, in this work various drying control chemical additives (DCCAs) were investigated to evaluate their effect in the pore/particle structure of silica based xerogels. DMF, GLY and PEG were used to improve the properties of the xerogels prepared from MTMS precursor and methanol as solvent. The boiling point and vapour pressure of the additives used in this study are presented in the Table 1.

Table 1 – Boiling point and vapour pressure of DCCAs and solvent used in this work [5].

DCCA/Solvent	Boiling point (ºC)	Vapour pressure at 20 ºC (bar)
Methanol	65	0.13
DMF	153	2.38×10^{-4}
GLY	182	2.13×10^{-6}
PEG	200	1.33×10^{-5}

In the literature, the influence of these additives have been studied for gels based in different chemical precursors, namely, tetramethylortosilicate (TMOS) and tetraethylortosilicate (TEOS) [5-9]. Haranath *et al.* [5] investigated various DCCAs, such as DMF, GLY, formamide and oxalic acid. They concluded that GLY leads to an increase in the specific surface area of silica aerogels. Rao and Kulkarni [6] selected GLY as DCCA due to the low vapour pressure it possesses (than methanol). As a result they obtained gels with a uniform pore size and managed in this way to reduce the drying stress. The best properties were attained for a GLY/TMOS = 0.025 molar ratio. Vollet *et al.* [7] and Rao *et al.* [8] studied the effect of DMF, observing a decrease of porosity and pore mean size without modification of the specific surface area of the produced gels. Martin *et al.* studied the effect of the PEG additive [9] obtaining aerogels with low density when compared to aerogels obtained from the analogous chemical system without additive.

In a previous study we obtained density data for a chemical system based on MTMS precursor without additives. This values were 78.4 ± 10.5 kg/m^3 for xerogels and 53.6 ± 6.1 kg/m^3 for aerogels [10]. In this study we present in Table 2 the results obtained for the analogous chemical system with DCCAs

COMPETE
QUADRO DE REFERÊNCIA ESTRATÉGICO NACIONAL
UNIÃO EUROPEIA
Fundo Europeu de Desenvolvimento Regional

(and MTMS precursor). Several molar ratios of the DCCA/MTMS were tested. The drying conditions were the same used in a previous paper [10]. For all the additives used in this work the bulk density increases with the additive/MTMS ratio. This behaviour is different from what was reported in the literature of gels from TMOS and TEOS precursors. Therefore, we can conclude that the tested additives decrease density for dense gels – case of TMOS and TEOS systems, but have an adverse effect when we are dealing with more porous structures originated from MTMS precursor.

Table 2 – Bulk density obtained with DCCAs used in this work.

DMF/MTMS	Bulk density (kg/m^3)	GLY/MTMS	Bulk density (kg/m^3)	PEG/MTMS	Bulk density (kg/m^3)
0.2	82.86± 9.2	0.025	76.97±8.5	0.025	87.56±7.5
0.4	80.56± 3.3	0.05	80.74±2.3	0.05	88.01±7.6
0.6	88.59± 8.3	0.075	90.64±15.9	0.075	91.87±9.7
0.8	89.79± 8.9	0.1	90.43±12.1		
1	90.89±8.9				

This work was developed under the project "AerTPS - Aerogel Thermal Protection Systems" by the Consortium "AST/FCTUC/IPN", funded by QREN, under the Operational Programme for Competitiveness Factors granted by the European Regional Development Fund.

References:

[1] A. Dorched and M.H. Abbassi, Silica aerogels; synthesis, properties and characterization, J. Mater. Process. Technol. 199 (2008) 10-26.
[2] D. Nadargi, S. Latthe and A. Rao, Effect of post-treatment (gel aging) on the properties of methyltrimethoxysilane based silica aerogels prepared by two-step sol-gel process, J. Sol-Gel Sci. Technol. 49 (2009) 53-59.
[3] S. Bhagat, C. Oh, Y. Kim, Y. Ahn and J. Yeo, Methyltrimethoxysilane based monolithic silica aerogels via ambient pressure drying, Microporous Mesoporous Mater. 100 (2007) 350-355.
[4] C. Brinker and G. Scherer, Sol-gel Science, Academic Press, Boston (1990).
[5] D. Haranath, A. Rao and P. Wagh, Influence os DCCAs on optical transmittance and porosity properties of TMOS silica aerogels, J. Porous Mater. 6 (1999), 55-62.
[6] A. Rao and M. Kulkarni, Effect of glycerol additive on physical properties of hydrophobic silica aerogels, Mater. Chem. Phys. 77 (2002) 819-825.
[7] D. Vollet, W. Sousa, D. Donatti and A. Ruiz, Mass fractal characteristics of sonogels prepared from sonohydrolysis of tetraethoxysilane with additions of dimethylformamide, J. Non-Cryst. Solids 353 (2007) 143-150.
[8] A. Rao, H. Sakhare, A. Tamhankar, M. Shinde, D. Gadave and P.Wagh, Influence od N,N-dimethylformamide additive on the physical properties of citric acid catalyzed TEOS silica aerogels, Mater. Chem. Phys. 60 (1999) 268-273.
[9] J. Martin, B. Hosticka, C. Lattimer and P. Norris, Mechanical and acoustical properties as a function of PEG concentration in macroporous silica gels, J. Non-Cryst. Solids 285 (2001) 222-229.
[10] L. Durães, M. Ochoa, N. Rocha, R. Patrício, N. Duarte, V. Redondo, A. Portugal, Effect of the drying conditions on the microstructure of silica based xerogels and aerogels, J. Nanosci. Nanotechnol. (2011) (in press).

Production and characterization of biodegradable scaffolds for dental pulp regeneration

P J Palma[a], P Ferreira*[b], P Coimbra[b], P. Alves[b], I Correia[c], J C Ramos[a], M H Figueiredo[d], J M Santos[a]

[a] Faculdade de Medicina da Universidade de Coimbra
[b]*CIEPQPF, Department of Chemical Engineering, University of Coimbra, Pólo II – Rua Sílvio Lima, 3030-790 Coimbra, Portugal.*
[c]*Centro de Investigação em Ciências da Saúde, Faculdade de Ciências da Saúde, Universidade da Beira Interior, Covilhã*
[d]*Faculdade de Medicina da Universidade de Coimbra, Coimbra, Portugal*

**pferreira@eq.uc.pt*

The tooth is a living structure and its health is dependent on the integrity of all its constituents (both hard and soft tissues). The pulp is a soft tissue composed by several types of cells and endues a number of functions that include dentin production and providing its nutrition. It has been stated that pulp regeneration is not essential for the longevity of a tooth. However, the maintenance of the dental pulp vitality provides many benefits since endodontically-treated teeth become devitalized, brittle and susceptible to postoperative fracture or other complications, including re-infections. Therefore new strategies are needed to regenerate the tissue, hence restoring dental pulp properties. The aim of this work was to develop a porous biodegradable matrix and to evaluate its potential to be applied as a scaffold for dental pulp regeneration. For that purpose, a 3-D matrix was prepared using a mixture of chitosan (CS) and sodium hyaluronate (HA).

Aim: To evaluate the biocompatibility of two biodegradable scaffolds, based on pectin/chitosan (PEC/CH) and hyaluronan/chitosan (HA/CH), designed for pulp regeneration.
Methodology: One percent (w/v) solutions of pectin and chitosan were prepared by dissolving each polysaccharide in a 0.01 M acetate buffer (pH=4.5). Hyaluronan solution was prepared in a 2% (w/v) concentration using the same buffer solution. The polyelectrolyte complexes (PECs) between the polymers were formed by mixing the solution of the two chosen polymers at room temperature (PEC/CH and HA/CH) under homogeniser agitation. After PECs formation and precipitation, they were isolated by centrifugation, frozen under liquid nitrogen and finally freeze-dried for 8 hours. The samples were prepared in a cylindrical mould (4 mm high and 2 mm diameter) in order to fit the tooth cavity. The obtained materials were characterized by a set of techniques including ATR-FTIR, swelling determination and weight loss studies. The morphology of the scaffolds was observed by SEM. Thermal characterization of the scaffolds was also performed by DMTA and TGA. Finally, the cytotoxic profile of the prepared scaffolds was evaluated in vitro, using mesenchymal stem cells (MSCs). Optical microscopy and a non-radioactive assay (3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium) – MTS) were used to characterize cell viability.
Results: The weight loss studies showed that the scaffolds are resistance to dissolution, maintaining about 60% of their weight after 5 weeks of submersion in PBS at 37ºC. SEM analyses allowed the visualization of the highly porous and irregular morphology of the scaffolds. Thermal characterization showed that decomposition of PEC sponges appeared at nearly 200ºC and that the sponges were not a perfect blend between the two polymers since two distinct peaks were obtained either in the DMTA as in TGA analysis. MTS assay results showed a significant difference between cells exposed to the two scaffolds (PEC/CH and HA/CH) and the positive control (dead cells) ($p<0.05$), and between cells exposed to the scaffolds and the negative control (live cells) ($p<0.05$), after 24, 48 and 72 hours of incubation. The results obtained for both scaffolds were not statistically different.
Conclusions: The results obtained so far suggest that the prepared scaffolds are appropriate to be applied as matrices for dental pulp regeneration. *In vivo* studies are currently being conducted in order to fully characterize the applicability of this scaffold for dental pulp regeneration.

Projecto APCFAME

Equipa: Andrey Romanenko[b], João R. Leal[b], Ana S. R. Brásio[a,b],Lino O. Santos[a], Natércia C. P. Fernandes[a]

[a]CIEPQPF, Departmento de Engenharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030-790 Coimbra, Portugal
[b]Ciengis, SA, 3030-199 Coimbra, Portugal,
Email: andrey.romanenko@ciengis.com

O projecto visa desenvolver uma aplicação de técnicas de controlo avançado ("Model Predictive Control - MPC") para a produção de biodiesel a partir de óleos usados. A empresa promotora, Ciengis, em estreita cooperação com a FCTUC pretende, com este projecto, manter a sua posição pioneira nesta área a nível internacional.

O Consórcio é constituído pela Ciengis, uma empresa tecnológica que actua na área de controlo avançado e optimização de processos industriais, pela Faculdade de Ciências e Tecnologia da Universidade de Coimbra, uma entidade do SCT com renome internacional, e, na qualidade de parceiro, pela Space Ecocombustíveis, Lda uma empresa de gestao de resíduos e produção de biodiesel. Assim os membros providenciam a necessária complementariedade das capacidades ao Consórcio, nomeadamente, as capacidades de I&D industrial e aplicado, transferência e valorização de tecnologia, ligação entre o mundo industrial e académico e experiência prática na área do projecto.

Efectuar-se-á um estudo preliminar conducente ao levantamento dos modos de operação e de controlo actuais, com uma avaliação do desempenho do sistema de controlo convencional, e identificação dos melhoramentos necessários ao nível de aquisição de dados e supervisão da instalação, definição da estratégia, da arquitectura e dos objectivos do sistema de controlo avançado da unidade. Na posse desta informação, proceder-se-á ao desenvolvimento/adaptação de um modelo matemático que permita prever em tempo real o comportamento dinâmico da unidade. Seguir-se-á a imprescindível adaptação dos parâmetros do modelo à especificidades deste tipo de unidade industrial e da matéria-prima usada. O modelo desenvolvido será utilizado para optimizar as condições operatórias do processo maximizando o seu desempenho económico. A aplicação protótipo de controlo avançado desenvolvida com base no programa PLANTEGRITY da Ciengis será sintonizada e testada por simulação e no processo real.

Nonlinear model predictive control of fed-batch cultures of micro-organisms exhibiting overflow metabolism: assessment and robustness

Lino O. Santos[a], Laurent Dewasme[b], Daniel Coutinho[c], and Alain Vande Wouwer[b]

[a]*CIEPQPF, Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, 3030-790 Coimbra, Portugal, lino@eq.uc.pt*
[b]*Service d'Automatique, Université de Mons, Boulevard Dolez 31, B-7000 Mons, Belgium, {Laurent.Dewasme,Alain.VandeWouwer}@umons.ac.be*
[c]*Department of Automation and Systems, Federal University of Santa Catarina, 476 Florianopolis, 88040-900, Brazil, Coutinho@das.ufsc.br*

Overflow metabolism characterizes cells strains that are likely to produce metabolites as, for instance, ethanol for yeasts or acetate for bacteria, resulting from an excess of substrate feeding and inhibiting the cell respiratory capacity. The critical substrate level separating the two different metabolic pathways is generally not well defined. This occurs for instance in *Escherichia coli* cultures with aerobic acetate formation. This work addresses the control of a lab-scale fed-batch culture of *Escherichia coli* with a nonlinear model predictive controller (NMPC) to determine the optimal feed flow rateof substrate. The objective function is formulated in terms of the kinetics of the main metabolic pathways, and aims at maximizing glucose oxidation, while minimizing glucose fermentation. As bioprocess models are usually uncertain, a robust formulation of the NMPC scheme is proposed using a min-max optimization problem. The potentials of this approach are demonstrated in simulation using a Monte-Carlo analysis.

References:

L. Chen, G. Bastin, V. van Breusegem, A case study of adaptive nonlinear regulation of fed-batch biological reactors, Automatica 31 (1) (1995) 55–65.

L. Dewasme, A. Richelle, P. Dehottay, P. Georges, M. Remy, P. Bogaerts, A. Vande Wouwer, Linear robust control of *S. cerevisiae* fed-batch cultures at different scales, Biochemical Engineering Journal 53 (1) (2010) 26–37.

Z. Nagy, R. D. Braatz, Robust Nonlinear Model Predictive Control of Batch Processes, AIChE Journal 249 (7) (2003) 1776 – 1786.

L. O. Santos, L. Dewasme, A.-L. Hantson, A. Vande Wouwer, Nonlinear model predictive control of fed-batch cultures of micro-organisms exhibiting overflow metabolism, in: IEEE Multi-Conference on Systems and Control (MSC), Yokohama, Japan, 1608 – 1613, 2010.

I. Rocha, Model-based strategies for computer-aided operation of a recombinant *E. coli* fermentation, Ph.D. thesis, University of Minho, Portugal, 2003.

B. Sonnleitner, O. Kappeli, Growth of Saccharomyces cerevisiae is controlled by its limited respiratory capacity : Formulation and verification of a hypothesis, Biotechnology & Bioengineering 28 (6) (1986) 927–937.

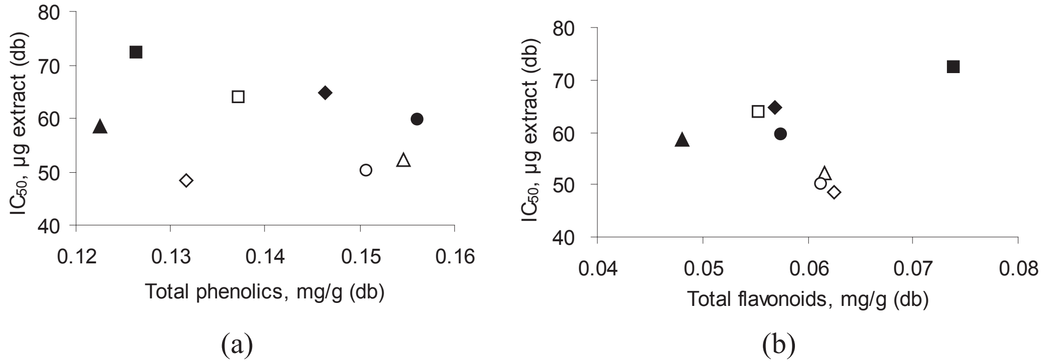
L. Dewasme, B. Srinivasan, M. Perrier, A. Vande Wouwer, Extremumseeking algorithm design for fed-batch cultures of microorganisms with overflow metabolism, Journal of Process Control 21 (7) (2011) 1092–1104.

Fractioned HPE from Elderberry pomace

Inês J. Seabra[a,b], Mara E.M. Braga[a], Maria T.P. Batista[c], Hermínio C. de Sousa[a,*]

[a]CIEPQPF, Chemical Engineering Department, FCTUC, University of Coimbra, Rua Sílvio Lima,
Pólo II – Pinhal de Marrocos, 3030-790 Coimbra, Portugal.
[b]ESAC, Politechnic Institute of Coimbra, Bencanta, 3040-316 Coimbra, Portugal.
[c]CEF, Pharmacognosy Laboratory, Faculty of Pharmacy, University of Coimbra, 3000-295 Coimbra, Portugal.
** hsousa@eq.uc.pt*

Commercially, elderberries (*Sambucus nigra* L.) are mainly used to produce cordials, beverages, soft spreads, wine, tea and nutraceutical beverages. These berries are a well known rich source of phenolic compounds, namely anthocyanins [1, 2, 3], and have insulin-stimulating and anti-angiogenic properties and also anti-carcinogenic potential. Its pomace, which is constituted by fruit seeds and skins, accounts for around 15 % of total fruit weight and contains higher amounts of polyphenolic compounds than those present in the edible fleshy parts of the fruits [4]. Fractioned High Pressure Extraction (FHPE) was carried out, at 313 K and 20 MPa, in two steps: i) elderberry byproduct was extracted with CO_2 to recover less polar compounds, like volatile oils; ii) a second step was performed using CO_2 + ethanol/water (8:2, v/v) to recover more polar compounds, like phenolics. Different percentages of ethanol/water (10-100 %, v/v) were employed and their effects on global yields, total extract phenolics, total flavonoids and total anthocyanins (quantified by spectrophotometric assays) and on extracts antioxidant activities (measured by the DPPH assay), are discussed. Higher ethanol/water percentages in the 2nd extraction step tended to result in extracts possessing higher antioxidant activities (lower IC_{50} values), though there was not a direct relationship to the amount of anthocyanins and total phenolics present in extracts (Figure 1.a). Total flavonoids and antioxidant activities were also not directly related, though the extracts with higher antioxidant activities were among the ones with higher total flavonoid contents (Figure 1.b). Total phenolic contents in the obtained extracts were high, showing that this residue is an excellent source of these substances.



(a) (b)

Figure 1 - Antioxidant activities (IC_{50} values) versus total phenolics (gallic acid equivalents) (a) and total flavonoids (epicatechin equivalents) (b) for 2nd step elderberry pomace extracts, using CO_2 + ethanol/water in the following percentages: ■ 20 %, ♦ 40 %, ▲ 50 %, • 60 %, □ 70 %, ◊ 80 %, Δ 90 %, o 100 %.

References:
[1] U. Mulleder, M. Murkovic, W. Pfannhauser, Urinary excretion of cyanidin glycosides, *J. Biochem. Biophys. Methods*., 53, 61-66 (2002).
[2] M.J. Bermúdez-Soto, F.A. Tomás-Barberán, Evaluation of commercial red fruit juice concentrates as ingredients for antioxidant functional juices, *European Food Res. Technol*., 219, 133-141 (2004).
[3] X. Wu, L. Gu, R.L. Prior, S. Mckay, Characterization of anthocyanins and proanthocyanidins in some cultivars of *Ribes*, *Aronia* and *Sambucus* and their antioxidant capacity, *J. Agric. Food Chem.*, 52, 7846-7856 (2004).
[4] N. Balasundram, K. Sundram, S. Samman, Phenolic compounds in plants and agri-industrial by-products: anti-oxidant activity, occurrence, and potential uses, *Food Chem.*, 99, 191-203 (2006).

Separation Of Volatile Fractions From Elder Flowers By Supercritical CO_2 Extraction

Inês J. Seabra[a,b], Mara E.M. Braga[a], Hermínio C. de Sousa[a,*]

[a]*CIEPQPF, Chemical Engineering Department, FCTUC, University of Coimbra, Rua Sílvio Lima,*
Pólo II – Pinhal de Marrocos, 3030-790 Coimbra, Portugal.
[b]*ESAC, Politechnic Institute of Coimbra, Bencanta, 3040-316 Coimbra, Portugal.*
**hsousa@eq.uc.pt*

Elder (*Sambucus nigra* L.), a plant native to most of Europe, northwest Africa and southwest Asia, is used either as an ornamental plant or a medicinal plant. Fresh, frozen or dried elder flowers have been used to produce distillates and extracts to be applied as natural ingredients in diverse alcoholic and non-alcoholic beverages, yoghurts, ice creams, cakes and candies. In recent years, elder cultivation is significantly increasing in Portugal. Besides the pleasant flavour that elder flower extracts impart to the food to which they are added to, their high phenolic acids and flavonoids contents [1] may contribute to reduce the risk for some virus induced and infectious diseases [2, 3]. Isoquercitrin, hiperoside, rutin and ferulic, caffeic and chlorogenic acids are among the phenolic compounds identified in these flowers [4], and terpenoid alcohols and oxides constitute the major part of the volatile compounds emitted from their extracts [5]. In this work, extraction of aromatic flavour compounds from dried elder flowers was done using supercritical carbon dioxide, following an experimental design where temperature (308-328 K) and solvent density (300-900 kg/m^3) were varied in a 3^2 factorial experiment. Composition of the extracts was explored using TLC and GC, and their potential to act as antioxidants was inferred by the coupled reaction of linolenic acid and β-carotene. Extraction temperature and solvent density greatly influenced extracts yield and composition. Antioxidant activity results confirmed that these extracts are highly active and may be used as natural aromatic flavour additives in pharmaceutical, cosmetic or food products, which suggests new high-value applications for elder flowers.

References:

[1] K. Jensen, L.P. Christensen, M. Hansen, U. Jørgensen, K. Kaack, Olfactory and quantitative analysis of volatiles in elderberry (*Sambucus nigra* L.) juice processed from seven cultivars. *J. Sci. Food Agric.*, 81, 237-244 (2000).
[2] Z. Zakay-Rones, E. Thom, T. Wollan, J. Wadstein, Randomized study of the efficacy and safety of oral elderberry extract in the treatment of influenza A and B virus infections. *J. Int. Med. Res.*, 32, 132-140 (2004).
[3] N.E. Hernandez, M.L. Tereschuk, L.R. Abdala, Antimicrobial activity of flavonoids in medicinal plants from Tafí del Valle (Tucumán, Argentina). *J. Ethnopharmacol.*, 73, 317-322 (2000).
[4] Z. Males, M. Madic-Saric, Investigation of the flavonoids and phenolic acids of Sambuci flos by thin-layer chromatography. *J. Planar Chromatogr.*, 12, 345-349 (1999).
[5] K. Kaack, L.P. Christensen, M. Hughes, R. Eder, Relationship between sensory quality and volatile compounds of elderflower (*Sambucus nigra* L.) extracts. *Eur. Food Res. Technol.*, 223, 57-70 (2006).

Extraction Kinetics Of Maritime Pine Bark Using (CO_2+EtOH) High Pressure Mixtures

Inês J. Seabra[a,b], O. Gomes[a], Mara E.M. Braga[a], Hermínio C. de Sousa[a,*]

[a]*CIEPQPF, Chemical Engineering Department, FCTUC, University of Coimbra, Rua Sílvio Lima,*
Pólo II – Pinhal de Marrocos, 3030-790 Coimbra, Portugal.
[b]*ESAC, Politechnic Institute of Coimbra, Bencanta, 3040-316 Coimbra, Portugal.*
* *hsousa@eq.uc.pt*

Maritime pine (*Pinus pinaster*) is one of the most important forest species consumed in Portugal by the furniture, wood and pulp and paper industries. Typical phenolic compounds present in pine bark are catechin, epicatechin, dihydroquercetin, phenolic acids, and most of them being procyanidin dimers, trimers, oligomers and polymers, i.e. condensed tannins. Although chrome leather tanning is faster than vegetable tanning, condensed tannins from pine bark have been used for specific tanning applications as an alternative to conventional chemical tanning agents, following recent regulations, market demands and avoiding environmental and health problems. Conventional solid-liquid extraction with alcohols and/or acidified alcohols is usually employed for the extraction of condensed tannins. However, additional steps are then usually required in order to concentrate desired compounds and to remove the other undesired substances. Thus, high pressure extraction (HPE) may represent an attractive option to conventional solid-liquid extraction processes. In some cases, supercritical fluid extraction (SFE) can also be applied, offering advantages concerning selectivity, separation and usage of environmental friendly technology and solvents. The main goal of this work is to recover phenolic compounds from pine bark using fractioned supercritical extraction (FSFE), supercritical extraction (SFE) and high pressure extraction (HPE). Operational conditions were selected based on the literature [1] and CO_2 was the chosen solvent to separate pine bark volatile fraction. EtOH was then added to recuperate rich phenolic fractions, in a fractionated procedure. For SFE, a solvent mixture CO_2+EtOH (10%) was used. For both methodologies, different solvent flow rates (6, 12 and 18×10^{-5} kg/s) were employed. The best SFE solvent flow rate found (in terms of yield) was 6×10^{-5} kg/s, and was then also chosen to perform the subsequent HPE assays with different EtOH percentages (30, 50, 70, 90 %, v/v). Kinetic parameters (M_{CER}, Y_{CER}, and t_{CER}) were obtained using a Matlab R2006a computer routine [2]. Volatile oil was qualitatively characterized by thin TLC and identified by GC-MS. Phenolics and condensed tannins present in ethanolic extracts were characterized by several spectrophotometry methods. For FSFE, first step yield was around 0.5-0.7 % (db) and second step represented ~80% of total global yield, at 30 ºC and 25 MPa. For the first FSFE step (CO_2), the highest flow rate originated the lowest M_{CER} (constant extraction rate mass) while, for the second step FSFE and SFE (CO_2 + 10 % EtOH), it conduced to the highest one. For first step, extract solubility in the CER period (Y_{CER}) was inversely proportional to the flow rate while, in the second step, the extract solubility from a co-extracted raw material was independent of solvent flow rate. This showed solvent selectivity in the process. Total phenolic compounds and condensed tannins in ethanolic extracts are also reported in this work and the amount of ethanol used in HPE had a positive effect on the amount of phenolics and condensed tannins present in extracts.

References:

[1] I.J. Seabra, M.E.M. Braga, M.T.P. Batista, H.C. de Sousa. Extracção fraccionada de taninos condensados de subprodutos de *Pinus pinaster* e *Sambucus nigra* L. Aplicaciones Industriales de los Taninos Vegetales. Eds. Cassel, E.; Vargas, M.F. E-book - CYTED and CNPq, Porto Alegre, Brazil (2007).

[2] V.M. Rodrigues, E.M.B.D. Sousa, A.R. Monteiro, O. Chiavone-Filho, M.O.M. Marques, M.A.A. Meireles, Determination of the solubility of extracts from vegetable raw material in pressurized CO_2: a pseudo-ternary mixture formed by cellulosic structure + solute + solvent. *J. Supercrit. Fluids*, 22, 21-36 (2002).

Application of a Statistical Mixture Design in the Pressurized Solvent Extraction From Tara Seed Coat

Inês J. Seabra[a,b], Mara E.M. Braga[a], Hermínio C. de Sousa[a,*]

[a]*CIEPQPF, Chemical Engineering Department, FCTUC, University of Coimbra, Rua Sílvio Lima,*
Pólo II – Pinhal de Marrocos, 3030-790 Coimbra, Portugal.
[b]*ESAC, Politechnic Institute of Coimbra, Bencanta, 3040-316 Coimbra, Portugal.*
* *hsousa@eq.uc.pt*

Carbon dioxide solubility capacity is greatly diminished if the target compounds to be extracted have hydroxyl, amino and nitro groups. The solubilities of such molecules may be greatly enhanced by the addition of a polar cosolvent. In this case, for practical reasons, it is desirable to avoid regions of multiple phases involving vapor, liquid and solid phases. Accordingly, a designer needs to select the conditions of pressure and temperature, as well as the mixture composition at which extraction of natural components is technically attractive. Considering this, and using a well known ternary solvent system, this work proposes the study of statistical mixture design in pressurized solvent extraction of tara (*Caesalpinia spinosa*) pods seed coat as a case study. Tara seed coat does not have a commercial application, thus representing an agro-residue of tara processing industries that could be explored as a raw material for the production of valuable phenolic- and antioxidant-rich extracts. In this work, a statistical mixture design was applied to optimize solvent mixtures for selective extraction of phenols from tara seed coat. Pressurized solvent extractions were performed at 313 K and 20 MPa, using homogeneous CO_2, ethanol and H_2O solvent mixtures. Total phenols contents and antioxidant activities of extracts were evaluated. A linear mixture model predicted total yields and it was verified that H_2O was the most effective solvent to obtain high extraction yields. A quadratic model predicted total phenols extracts´ contents and it was verified that H_2O and CO_2 had an antagonistic effect and that maximum phenolic contents can be expected for EtOH-rich mixtures. For the antioxidant activity, no model revealed to be significant (at a 95% confidence level). Nevertheless, high antioxidant activities were observed (above 80% of oxidation inhibition for most extracts). The obtained results strongly suggest that tara seed coat is a residue that has a great potential to be valorized for the production of phenolic-rich extracts presenting high antioxidant activities.

References:

[1] T.S. Chamblee, R.R. Weikel, S.A. Nolen, C.L. Liotta, C.A. Eckert, Reversible *in situ* acid formation for β-pinene hydrolysis using CO_2 expanded liquid and hot H_2O, *Green Chem.*, 6, 382-386 (2004)
[2] V.J. Barwick, Strategies for solvent selection - a literature review, *Trends Anal. Chem.*, 16, 293-309 (1997).
[3] P.C. Lapa, Aprovechamento integral y racional de la tara. *Caesalpinia spinosa* - *Caesalpinia tinctoria*, *Rev. Inst. Invest. FIGMMG*, 7, 64-73 (2004).
[4] E. Haslam, R.D. Haworth, P.C. Keen, Gallotannins. Part VII. Tara gallotannins, *J. Chem. Soc.*, 3814-3818 (1962).
[5] M.E.M. Braga, R.M.S. Santos, I.J. Seabra, R. Facanali, M.O.M. Marques, H.C. de Sousa, Fractioned SFE of antioxidants from maritime pine bark, *J. Supercrit. Fluids*, 47, 37-48 (2008).
[6] V.L. Singleton, J.A.jr. Rossi, Colorimetry of total phenolics with phosphomolybdic - phosphotungstic acid reagents, *Am. J. Enol. Viticult.*, 16, 144-158 (1965).
[7] P.A. Hammerschmidt, D.E. Pratt, Phenolic antioxidants of dried soybeans, *J.Food Sci.*, 43, 556-559 (1978).
[8] N.E. Durling, O.J. Catchpole, S.J. Tallon, J.B. Grey, Measurement and modelling of the ternary phase equilibria for high pressure carbon dioxide-ethanol-water mixtures, *Fluid Phase Equilib.*, 252, 103-113 (2007).
[9] R. Canals, M.C. Llaudy, J. Valls, J.M. Canals, F. Zamora, Influence of ethanol concentration on the extraction of color and phenolic compounds from the skin and seeds of Tempranillo grapes at different stages of ripening, *J. Agric. Food Chem.*, 53, 4019-4025 (2005).

Vapour + liquid equilibria of binary mixtures of H_2S with C_2H_6, C_3H_8, and n-C_4H_{10}, at 182.33 K

Ana M. P. Senra, Isabel M. A. Fonseca, Abel G. M. Ferreira, Lélio Q. Lobo,

Departamento de Engenharia Química, Universidade de Coimbra, 3030-210 Coimbra, Portugal

Hydrogen sulphide is always found as a component of natural mixtures with hydrocarbons, from light refinery gases to heavy petroleum systems. Since it is a corrosive, toxic, and noxious substance, H_2S should be removed from the reservoir raw material. The separation of hydrogen sulphide from hydrocarbons by chemical separations using amines as long been substituted by fractionation operations. In the process design of these operations it is essential to have knowledge of the vapour+liquid equilibria of these systems. Reamer, Sage, ans Lacey (1951) [1] studied the binary system of H_2S+CH_4 which is perhaps the more important of such mixtures. Their experiments were carried out at pressures up to about 70 MPa and at temperatures between 280K and 445K. These limits are far up those within which our apparatus can be used. For this reason methane has been excluded from our study. On the other hand, binary mixtures of H_2S with C_2H_6, C_3H_8, and n-C_4H_{10} are well in the experimental VLE range of (P, T) conditions used in our laboratory. This paper deals with such systems. The results are compared with previous studies [2-6] in spite of these had been carried out at much higher temperatures and pressures.

The vapour pressure measurements on H_2S+ C_2H_6, +C_3H_8, and + n-C_4H_{10} were carried out at T=182.33 K (the triple-point temperature of N_2O), using the technique introduced by L. Staveley. The results are shown in Figure 1. In this Figure the VLE lines have been calculated using the γ-φ approach, the vapour fugacities being determined by using the virial equation of state, and the G_m^E (*i e*, the activity coefficients γ_i in the liquid) being obtained from the raw experimental data by using Barker's method in conjunction with the so called Redlich-Kister model for the molar excess Gibbs energy.

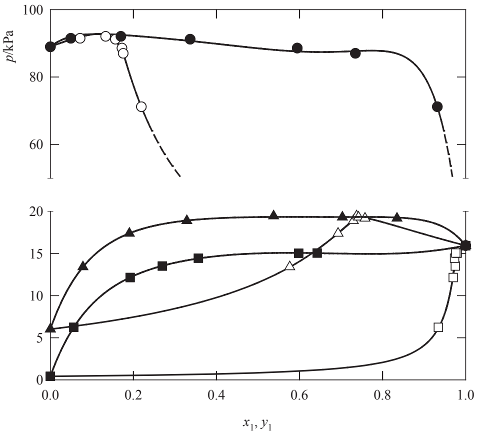


Figure 1. Vapour pressure p of the systems {x_1 H_2S+x_2 alkane} at the temperature T=182.33 K. x_1 and y_1 are, respectively, the mole fraction of H2S in the liquid and in the vapour phase. The open symbols are for the vapour and the full symbols refer to the liquid phase. Legend: (●,○),{x_1 H_2S+x_2 C_2H_6};(▲,Δ), {x_1 H_2S+x_2 C_3H_8};(■,□),{x_1 H_2S+x_2 n-C_4H_{10}}. Lines are calculated from the vapour-liquid equilibria equations with the Redlich-Kister model for G_m^E.

As pointed out in previous experimental studies H_2S+C_2H_6 exhibits an azeotrope in the ethane-rich end, at x_1=0.115; and the azeotrope for H_2S+C_3H_8 appears on the opposite end of the diagram (for x_1=0.742). The binary mixture of H_2S+n-C_4H_{10} shows no azeotrope, in accordance with the measurements of Robinson *et al.* (1964) [6] at higher temperatures and pressures (8 MPa and 311 K to 408 K).

References

[1] H. H. Reamer, B. H. Sage, W. N. Lacey, *Ind. & Eng. Chem.* 43 (1951) 976-981
[2] W. B. Kay, D. B. Brice, *Ind. & Eng. Chem.* 45 (1953) 615-618
[3] E. R. Gilliland, H. W. Scheeline, *Ind. & Eng. Chem.* 32 (1940) 48-54
[4] W. B. Kay, G. M. Rambosek, *Ind. & Eng. Chem.* 45 (1953) 221-226
[5] J. Brewer, N. Rodewald, F. Kurata, *AIChE Journal* 7 (1961) 13-16
[6] D. B. Robinson, R. E. Hughes, J. A. W. Sandercock, *Can. J. Chem. Eng.* 42 (1964) 143-146

Describing complex solid/liquid flows using CFD and Electrical Impedance Tomography
(Project SLTOMOFLOW)

R. Silva[a*], M. G. Rasteiro[a], F. A. P. Garcia[a], P. M. Faia[b], A. R. Ferreira[b], M. J. Santos[b], J. B. Santos[b], A. P. Coimbra[b]
[a] Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, 3030-790 Coimbra, Portugal
[b]Department of Electric and Computers Engineering, Faculty of Sciences and Technology, University of Coimbra, 3030-790 Coimbra, Portugal
[*] *e-mail address: rsilva@eq.uc.pt*

Multiphase flows are very complex and of concern in engineering. Despite the extensive work and data produced in the past much has still to be investigated for a better understanding and optimisation of the phenomena involved. This was the leitmotif for the present work.

An Electrical Impedance Tomography (EIT) hardware and software were developed to non-invasively generate data and new Computational Fluid Dynamics (CFD) models, more general and accurate, were developed to describe suspension flow characteristics such as spatial distribution of phases, flow regimes, velocity profiles, and relative velocity between phases.

CFD models of multiphase flows can follow either a Eulerian-Eulerian or a Lagrangian-Eulerian approach, both using most often the k-ε equations to model the turbulence.

The Lagrangian approach is too complex for practical applications while the Eulerian-Eulerian approach is still scarcely studied for the highly concentrated slurries of our concern and suffers from a lot of uncertainties associated with the parameters in the constitutive equations.

The work on CFD modelling has been focused on evaluating the influence of inlet conditions and closure coefficients in the k-ε turbulence model for homogeneous and heterogeneous flows, and in characterizing the turbulence damping phenomena that occur in multiphase pipe flows. A custom k-ε turbulence model is being constructed to better describe heterogeneous flow phenomena, but with openness for other turbulence models to be used in the future.

A new Electrical Impedance Tomography (EIT) hardware, based on the assumption of unique electrical properties for each material, was designed and constructed and the software was developed [1] to map the phases distribution in a horizontal pipe flow of aqueous glass beads suspensions. The application of this EIT system was successfully demonstrated [1], through differential reconstructed tomographic images, in the case of low glass beads concentrations. The system was capable of identifying the particles concentration distribution under different test situations. It performed at a high frame rate and produced images with a superior resolution when compared with images found in literature of similar systems, therefore opening good opportunities for industrial applications. The system is under current development for application to highly concentrated suspensions and for the measurement of velocity profiles through cross-correlation between adjacent rings.

Figure 1 – Average glass beads concentration profiles for flow rates of 12 (left) and 52 m^3/h (right).

References: [1] P.M. Faia, R.Silva, M.G. Rasteiro, F.A.P. Garcia, A.R. Ferreira, M.J. Santos, J.B. Santos, A.P. Coimbra, "Imaging particulate two-phase flow with Electric Impedance Tomography", *Particulate Science and Technology*, 2011. (In press)

PRODEQ10 – 10 anos ao serviço da Engenharia Química

Dia Aberto – CIEPQPF

DOUTORAMENTO

Integration of traditional systems and AOP´s technologies on the industrial treatment of Olive Mill Wastewaters

Nuno Amaral-Silva[1], Rui C. Martins[1], Sérgio Castro-Silva[2] and Rosa M. Quinta-Ferreira[1*]

[1]CIEPQPF – Centro de Investigação em Engenharia dos Processos Químicos e Produtos da Floresta; GERSE – Group on Environment. Reaction and Separation Engineering, Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, 3030-790 Coimbra, Portugal.

[2]ADVENTECH – Advanced Environmental Technologies, Centro Empresarial e Tecnológico, Rua dos Fundões, 151, 3700-121 – São João da Madeira, Portugal.

*Corresponding author: rosaqf@eq.uc.pt (R. M. Quinta-Ferreira)

Olive Mill Wastewaters (OMW) are characterized by high organic content due to the existence of pollutants, such as polyphenols, that may exhibit high toxic properties [1] and strong resistance towards the degradation by activated sludge microorganisms. Nowadays, one of the most common applied methods is the OMW storage in lagoons. However this procedure reveals serious drawbacks such as low efficiency and sludge-disposal problems since it can only concentrate OMW to the extent of 70–75%. Besides, it favors the separation/dehydration and not as much organic matter degradation. Biological treatments, though ineffective in practice when used solely, when combined with chemical or physical systems, can seriously contribute to the reduction of the OMW pollutants [2].

The advanced oxidation processes are arising as suitable technologies able to degrade bio-refractory pollutants. In these systems hydroxyl radicals are the main oxidants involved. This radical is a very powerful oxidant which leads to a very efficient oxidation as is the case of the Fenton reagent, a cost effective method, easy to apply, involving a homogeneous catalytic reaction through a mixture of hydrogen peroxide and iron (II) salts. Hydrogen peroxide catalytic decomposition generates hydroxyl radicals that have a high oxidation potential able to oxidize a large family of pollutant compounds [3],. Fentons‘ peroxidation also possesses the advantage of combining both oxidation and coagulation processes. A complete industrial treatment system involving the integration of coagulation/flocculation and Fenton Process to treat wastewaters from the olive oil production has been studied.

The experimental results indicated that COD is reduced up to 90% and the total polyphenols concentration is decreased upon to 92%. The treated stream biodegradability (BOD_5/COD) reached 0.65 and the TSS and TDS decreased 95 and 69% respectively. Throughout Fenton’s experiments the suppression of the pH adjustment step and diferentes procedures for hydrogen peroxide addition (either initially or gradually along the treatment) were analysed. Our results demonstrated that the initial pH correction can be eliminated, besides, progressive hydrogen peroxides additions seems to be advisible. Moreover, the use of coagulants instead raising pH to promote final iron sludge settling imparted low impact to the final step of iron precipitation revealing, therefore, to be essential the NaOH addition stage to a better sludge formation.

References:

[1] Andreozzi R., Canterino M., Somma, I., Giudice, R., Marotta, R., Pinto, G. and Pollio, A., Effect of combined physico-chemical processes on the phytotoxicity of olive mill wastewaters, WATER RESEARCH, 42, (2008), 1684–1692

[2] Kestioglu, K., Yonar, T., Azbar, N.,: Feasibility of physico-chemical treatment and Advanced Oxidation Processes (AOPs) as a means of pretreatment of olive mill effluent (OME), Process Biochemistry 40 (2005) 2409–2416

[3] Lucas, M. S., Peres, J. A., Removal of COD from olive mill wastewater by Fenton’s reagent: Kinetic study, Journal of Hazardous Materials 168 (2009) 1253–1259

Poly(ester amide)s based on (*L*)-lactic acid oligomers and α-amino acids: the role of the α-amino acid side chain

Ana C. Fonseca[a,*], Maria H. Gil[a] and Pedro N. Simões[a]

[a]*CIEPQPF, Departamento de Engeharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030-790 Coimbra, Portugal*
[*]*anafs@eq.uc.pt*

Poly(ester amide)s (PEAs) are a class of synthetic polymers whose importance in the biomedical field has increased in the last years. PEAs gather in the same entity the best properties of polyamides (good mechanical and thermal properties) and polyesters (biodegradability).[1] PEAs containing α-amino acids and α-hydroxy acids (e.g., L-lactic acid) in their structure also demonstrated their potential in biomedical applications.[2] Such PEAs release normal metabolites in the human body upon degradation, and for this reason the toxicity induced by these materials is very low. Because both acid and basic natures of the degradation products, a neutralization effect occurs, thus avoiding an accentuated decrease in the pH, which can cause undesirable host reactions.[3] Besides, the presence of the α-amino acid opens the possibility of these materials being degraded also enzymatically, increasing their biodegradability.

This work reports the synthesis of PEAs (Figure 1) by interfacial polycondensation between diamines derived from glycine or L-phenylalanine,[3] and diacyl chlorides derived from L-lactic acid oligomers.[4] The obtained PEAs were characterized in terms of chemical structure (FTIR and ^{1}H NMR spectroscopies), thermophysical (TGA, mDSC) and thermomechanical (DMTA) properties. The biodegradation behaviour in PBS (pH=7.4) at 37ºC was also evaluated. The influence of the α-amino acid lateral group in the properties (thermal, mechanical, biodegradation) of the PEAs was studied.

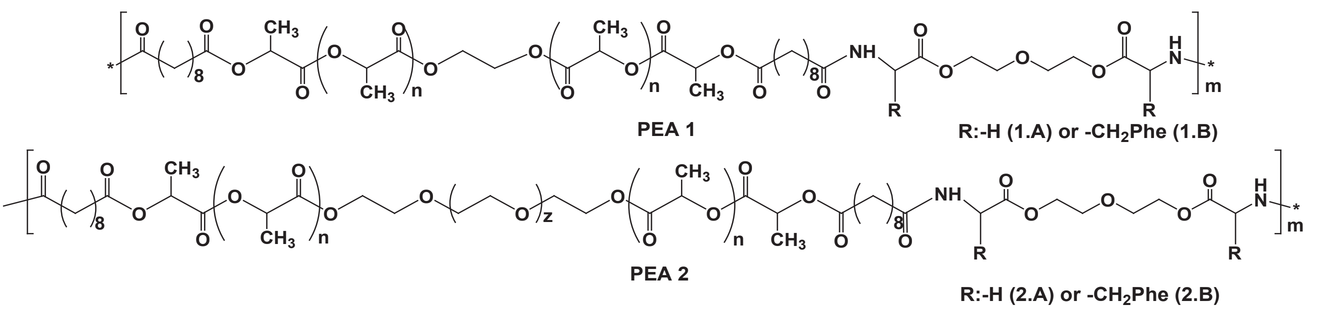


Figure 1-Representation of PEAs structures.

Both FTIR and ^{1}H NMR analysis demonstrate that PEAs were successfully obtained by interfacial polycondensation. The pendant group of the α-amino acid showed to have important influence in the thermal properties as well as in the hydrolytic degradation behaviour.

References:
[1] Nair, L. S.; Laurencin, C. T. *Prog. Polym. Sci.* 2007, *32*, 762.
[2] Feng, Y.; Lu, J.; Behl, M.; Lendlein, A. *Macromol. Biosci.* 2010, *10*, 1008.
[3] Karimi, P.; Rizkalla, A.S.; Mequanint, K. Materials. 2010, *3*, 2346.
[4] D'Angelo, S.; Galletti, P.; Maglio, G.; Malinconico, M.; Morelli, P.; Palumbo, R.; Vignola, M. C. *Polym.* 2001, *42*, 3383.

An extractive fermentation process to recover and purify bioethanol using phosphonium-based ionic liquids

José F.O. Granjo[a,*], Catarina M.S.S. Neves[b], Mara G. Freire[b], Al Robertson[c], Nuno M.C. Oliveira[a] and João A.P. Coutinho[b]
[a]*CIEPQPF, Departamento de Engenharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030-790 Coimbra, Portugal*
[b]*Departamento de Química, CICECO, Universidade de Aveiro, 3810-193 Aveiro, Portugal*
[c]*Cytec Canada Inc., 9061 Garner Road, Niagara Falls, Ontario, Canada L2E 6S5*
[*]*josegranjo@eq.uc.pt*

Nowadays bioethanol is being actively studied as an alternative for transportation fuels, used either as an additive to gasoline or as a standalone fuel. One of the main problems associated with ethanol production is its separation from fermentation broths. Distillation is commonly used; however, due to the presence of the ethanol-water azeotrope, the production of anhydrous ethanol is economically and energetically expensive compromising the competitiveness of the process [1]. A less energy intensive approach is studied here using liquid-liquid extraction for the separation of ethanol-water mixtures coupled with the use of extractive fermentations.

Phosphonium-based based ionic liquids are proposed as extraction solvents instead of imidazolium-based counterparts used elsewhere [2], because are less expensive, thermally more stable, available on a multi-ton scale and already been used in industrial processes. Therefore are particularly interesting candidates for liquid-liquid extraction purposes. Previously [3], a study on ternary phase diagrams comprising water, ethanol, and ionic liquid, was performed using tetradecyltrihexylphosphonium-based ionic liquids combined with several anions, namely bis(trifluoromethylsulfonyl)imide, dicyanamide, bromide, chloride, bis(2,4,4-trimethylpentyl) phosphinate, decanoate, and methanesulfonate. The experimental ternary phase diagrams were correlated with the NRTL model and compared with predictions from the COSMO-RS model. The gathered data indicated that phosphonium-based ILs are the best ionic solvents yet reported to perform ethanol-water separations.

In this work, a preliminary design for an alternative to classical distillation was carried out. A liquid-liquid extraction stage coupled to an extractive fermentation was proposed, where the IL is continuously recycled to the fermentator and the ethanol concentration to an anhydrous product is done by pervaporation, aiming at reducing the overall energy costs involved in the purification of ethanol (figure 1). At the end, energy costs were also estimated and compared with the common distillation-based process using data from [1].

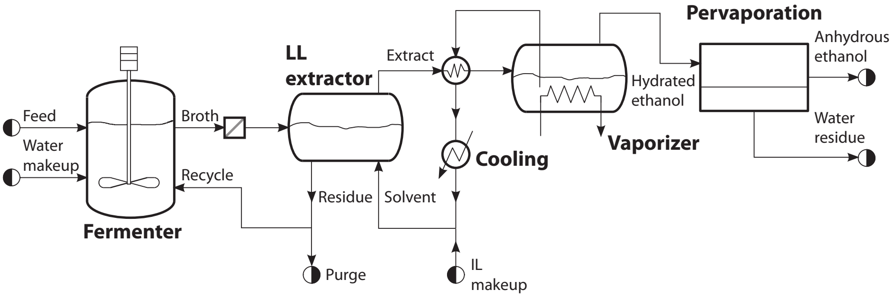


Figure 1 Block diagram for ethanol purification based on LL extraction and pervaporation.

References:

[1] Leland M. Vane, Separation technologies for the recovery and dehydration of alcohols from fermentation broths, *Biofuels, Bioprod. Biorefin.*, 2, 553–588 (2008).

[2] Matthias Seiler, Carsten Jork, Asimina Kavarnou, Wolfgang Arlt, and Rolf Hirsch, Separation of azeotropic mixtures using hyperbranched polymers or ionic liquids, *AIChE J.*, 50, 2439–2454 (2004).

[3] Catarina M.S.S. Neves, José F.O. Granjo, Maria G. Freire, Al Robertson, Nuno M.C. Oliveira, and João A.P. Coutinho, Separation of ethanol-water mixtures by liquid-liquid extraction using phosphonium-based ionic liquids, *Green Chem.* 13, 1517–1526 (2011).

Integrated biofuel production processes based on systematic optimization methodologies

José F.O. Granjo*, Nuno M.C. Oliveira
[a]*CIEPQPF, Departamento de Engenharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030-790 Coimbra, Portugal*
**josegranjo@eq.uc.pt*

The growing interest in biofuels has motivated governments and companies from various countries to invest heavily in its research and marketing, as complements or substitutes for fossil fuels. Despite the considerable R&D effort that has been taking place, the application of systematic methodologies of process systems engineering (PSE) in these studies has been rather limited so far. However, preliminary initiatives in this direction demonstrate the potential gains of using these tools to support decision-making in a variety of activities from conceptual design, to optimal process design and supervision tasks of these units [1].

The present work involves the conception of both industrial plant structures and efficient supervision schemes for the integrated production of biofuels and food products from oleaginous biomass, of various origins. In order to achieve this goal, a significant vertical integration between adjacent products/processes is sought, including the extraction of oil from seeds, the production of biodiesel, the production of alkali catalyst for biodiesel manufacture, the purification of glycerol, the extraction and valorisation of proteins from the oleaginous seeds, the extraction of sugars and their fermentation to produce ethanol, and the extraction of additional special compounds from the fermentation products.

To accomplish these goals, are builded detailed models for the various process units (eg, reactors, fermenters, distillation and extraction columns, pervaporators) based on mass balances, conditions of equilibria, and heat and mass transfer. Are constructed and/or use of existing kinetic models whenever possible on a mechanistic basis of acid hydrolysis, enzyme and fermentation in the case of bioethanol, and the different types catalysis for biodiesel. In the case of biodiesel, were already performed regression studies of the kinetic parameters using experimental data in the literature [2]. These equations, expressing precisely the influence of several variables operative in reactional behavior of multiphase systems, are then incorporated into models of the units.

It is also considered the integration of separation units with other non-traditional separation operations (pervaporators, pressure-swing adsorption, reactive distillation, eg), with a view to obtaining more economical separation sequences. In this phase flexibility studies are made on the physical robustness of the solutions obtained, to ensure the implementability of the optimal solutions obtained. In this context, a detailed study of the manufacturing process of the currently most widely used catalyst in the process of biodiesel (sodium methylate) was performed. An alternative design based on reactive distillation was proposed with preliminary results showing a value of 2.33 M€·year^{-1} compared with the traditional process (1.26 M€·year^{-1}) for the economical potential, for a 3000 ton·year^{-1} base production of sodium methylate.

In a latter phase are applied and extended methods for the synthesis of optimal reaction and separation networks based on the concepts of superstructures and sequential modules in the design of reactors/fermentators and separation systems for the processes production of biodiesel and bioethanol. Here the aim is also to study the application of techniques to reformulate discrete problems (MINLP) to contiuous problems like NLP and introduce the concept of flexibility of the reaction network, using techniques of multi-criteria optimization. In the latter case, the solutions can be simultaneously optimized to maximize/minimize the production of a given chemical species (due to difficulties of separation, or economic value) and to improve the adaptability of production (producing more or less certain products depending on market).

References:

[1] http://www.cit.cmu.edu/media/press/2007/pr_07_jan27.html, visited on 17-10-2011.

[2] José F.O. Granjo, Belmiro P.D. Duarte, and Nuno M.C. Oliveira, Kinetic models for the homogeneous alkaline and acid catalysis in biodiesel production, *in 10th International Symposium on Process Systems Engineering* (2009).

Modelling industrial nitration reactors

Anabela G. Nogueira[a,b*], Dulce C. M. Silva[b], Cristina M. S. G. Baptista[a]

[a]*Department of Chemical Engineering, University of Coimbra, Pólo II, Rua Sílvio Lima, 3030-790 Coimbra, Portugal*
[b]*CUF - Químicos Industriais, Quinta da Indústria, Beduído, 3860-680 Estarreja, Portugal*
* *anabela.nogueira@cuf-qi.pt*

Chemical processes modelling plays an important role in chemical industry especially because it has the ability to enable diagnosing abnormal behaviour of process equipment. This is particularly valid when information from the process and operating data are used to build the mathematical models. When these models are available they are good instruments for setting the operating conditions that may lead to maximum production, increased selectivity and a decrease in the environmental impact of the process. Furthermore, optimization may target other objectives like minimization of energy consumption or reduction of operation costs. Mathematical models can be constructed for every unit in a chemical plant, but chemical reactors are often the first addressed, as they are considered the heart of a chemical process. A well-designed and optimized reactor allows a proper operation of the whole plant.

Heterogeneous reactions have been playing a leading role in chemical industries and due to their complexity they are considered a great challenge to modelling purposes. Liquid-liquid reactions are among these and the nitration of aromatic compounds is in this category. Despite being one of the oldest processes in the chemical industry, over the past and even recently, benzene nitration has received considerable attention by researchers in order to understand the chemical reaction [1-4] and mass transfer phenomena [5,6] that occur simultaneously in these two-phase liquid-liquid reactions. The importance of this reaction arises not only from the complexity of the phenomena at stake, but also because mononitrobenzene, the main product, is an important commodity chemical. Mononitrobenzene is an intermediate for a wide range of other products such as explosives, dyes and pigments, pesticides, pharmaceuticals and solvents. However, the main use is as raw material for aniline's production, which is an important compound with a huge variety of applications, especially in the manufacture of MDI for automotive industries [7]. The industrial production, of mononitrobenzene is achieved, with high yield, by adiabatic benzene nitration with mixed acid (nitric, sulphuric and water) in continuously stirred tank or tubular reactors. Despite the high yield reached, phenolic by-products formation is still a challenge for nitration process optimization and they contribute to the costs and environmental footprint of the plant [8].

The benzene nitration reaction is a well-described process in terms of mass transfer phenomena and chemical reaction. Quadros [9] performed a set of benzene nitration experiments in a pilot scale reactor and his data fitted both Film and Danckwerts penetration models from the literature, which are two well known theories to describe mass transfer between two phases. On the other hand, understanding the chemical reaction mechanism in benzene nitration is extremely important for modelling this reaction. A great contribution in this area was given by Deno and Stein [10] and Marziano *et al.* [11] that have estimated the observed kinetic constant at mild operating conditions. However, the lack of information on by-products formation, the reaction mechanism and their physical properties, has limited the development and use of mechanistic models. In fact, the oxidizing agent that leads to the formation of phenol – nitrophenols precursor – is not yet consensual. In addition, solubility data, mass transfer coefficients and kinetic constants for the reactions producing phenolic species are not available. To overcome these limitations, Quadros [12] developed empirical models based on regression methods, where the influence of different independent variables is analysed with respect to a dependent variable.

Modelling industrial nitration reactors is still a great challenge but a predominantly mechanistic model based on the knowledge that has been acquired over the past years has been built. The mathematical model for the reactors, which consists in a set of mass and energy balances, has been validated and refined based on industrial data. The results obtained so far confirm a good fitting of model predictions and industrial operating parameters, namely temperature, and mononitrobenzene's production. However, nitrophenols are under estimated by this model and this may be a consequence of using the nitrophenols regression models beyond their validity range. To overcome this, industrial data are now being used to develop new empirical models that aim at better explaining the industrial by-products formation in this nitration process.

The development and improvement of mathematical models for the industrial reactors confirms to be an important contribution to increase the understanding of benzene nitration and is a great opportunity for optimizing the mononitrobenzene production process, leading to a continuously improved process with respect to productivity, selectivity and safety aspects.

References

[1] – E.D. Hughes, C.K. Ingold and R.I. Reed, Kinetics and mechanisms of aromatic nitration. Part II. Nitration by nitronium ion, NO_2^+ derived from nitric acid, J. Chem. Soc. (1950) 2400-2473.
[2] – G.A. Olah, Preparative and mechanistic aspects of electrophilic nitration, in: Industrial and laboratorial nitrations, Albright & Hanson, Washinghton (1989) 1-47.
[3] – J.M. Zaldivar, E. Molga, M.A. Alós, H. Hernández and K.R. Westerterp, Aromatic nitrations by mixed acid. Slow liquid-liquid reaction regime, Chem. Eng. Process. 34 (1995) 543-559.
[4] – J.M. Zaldivar, E. Molga, M.A. Alós, H. Hernández and K.R. Westerterp, Aromatic nitrations by mixed acid. Fast liquid-liquid reaction regime, Chem. Eng. Process. 35 (1996) 91-105.
[5] – J. Giles, C. Hanson and H.A.M. Ismail, A model for rate of nitration of toluene under heterogeneous conditions, in: industrial and laboratorial nitrations, Albright & Hanson, Washinghton (1976) 190-209.
[6] – C. Hanson, J.G. Marsland and G. Wilson, The macrokinetics of aromatic nitration, Chem. Ind-London (1966) 675-683.
[7] – Nexant, PERP Report – Nitrobenzene/Aniline, in: Nexant Chem Systems, New York (2003).
[8] – C. Hanson, T. Kaghazchi and M. W. T. Pratt, Side reactions during aromatic nitration, in: Industrial and laboratory nitrations, Albright & Hanson, Iran (1976).
[9] – P.A. Quadros, N.M.C. Oliveira, C.M.S.G. Baptista, Benzene nitration: validation of heterogeneous reaction models, Chem. Eng. Sci. 59 (2004) 5449-5454.
[10] – N. C. Deno and R. Stein, Carbonium Ions. III. Aromatic nitration and the C_0 acidity function, J. Am. Chem. Soc. 78 (1956) 578-581.
[11] – N.C. Marziano, A. Tomasin, C. Tortato and J.C. Zaldivar, Thermodynamic nitration rates of aromatic compounds. Part 4. Temperature dependence in sulphuric acid of $HNO_3 \rightarrow NO_2^+$ equilibrium, nitration rates and acidic properties of the solvent, J. Chem. Soc. Perkins Trans. 2 (1998) 1973-1982.
[12] – P.A. Quadros, M.S. Reis, C.M.S.G. Baptista, Different modelling approaches for a heterogeneous liquid-liquid reaction process, Ind. & Eng. Chem. Res. 44 (2005) 9414-9421.

Bio-based polymers: Synthesis of high molecular weight Poly(Lactic Acid)

Dina A.S. Marques[a,*], M. H. Gil[a], Cristina M. S. G. Baptista[a]

[a]*CIEPQPF, Departamento de Engenharia Química, Faculdade de Ciências e Tecnologia,*
Universidade de Coimbra, 3030-790 Coimbra, Portugal
[*]*dinam@eq.uc.pt*

Recently, with the effort in reducing the environmental impact and developing sustainable alternatives to petrochemical origin feedstocks, a new class of biodegradable materials has emerged. Among them, poly(lactic acid) (PLA) is one of the most promising materials showing a high potential market. It is a synthetic biodegradable thermoplastic obtained from a 100 % renewable raw material the lactic acid. The properties of the PLA allow a wide range of applications from biomedical and pharmaceutical to the conventional large scale polymer uses such as fibres, films and packaging [1] .

At industrial scale high molecular weight PLA is synthesized by a multi step process called ring opening polymerization of lactide, ROP, an intermediate compound. This is an effective but quite complex process that requires several purification steps of the lactide increasing the price of PLA comparing to other petrol based thermoplastics and preventing it large usages [1]. This justifies the effort to work on the development of a different synthesis route that may enable reducing production costs and the environmental footprint of the process and leading to an increase in PLA competitiveness comparing to other petrol based polymer competitors such as polyethylene terephthalate (PET) [1].

To achieve this goal we have been studying the direct lactic acid polycondensation [2] and molecular weights higher than 100 000 g/mol have already been synthesised. These are encouraging results aiming at producing high molecular weight PLA for different applications. Figure 1 shows the simplified reaction mechanism and a PLA film, obtained in the frame of this project. The experiments were carried out in a 500 mL pilot scale reactor with mechanical stirring, temperature and vacuum system, in the presence of a metal-based catalyst. At large scale polyesters production, the viscosity plays an important role, therefore torque measurement was recorded for polymerization control.

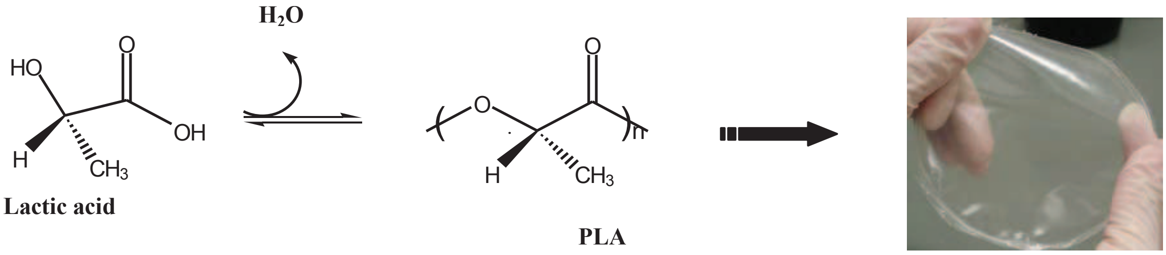


Figure 1: Lactic acid polycondensation and a PLA film obtained with this reaction.

Acknowledgements
The financial support from FCT for Ph.D. Grant SFRH/BD/42245/2007 is gratefully acknowledged.

References:

[1] A. P. Gupta, V. Kumar, New emerging trends in synthetic biodegradable polymers-Polylactide: A critique, European Polymer Journal 43 (2007) 4053-4074.
[2] Dina A.S. Marques, Susana Jarmelo, Cristina M.S. G. Baptista, M.H. Gil, Poly(lactic acid) Synthesis in Solution Polymerization, Macromol. Symp. 296 (2010) 63-71.

Development of Biocompatible Polyesters based Formulations for Microstereo-thermal-lithography

Filipa Gonçalves[a,*], Wei Sun[c], Paulo Bártolo[b] and Jorge Coelho[a]

[a]*CIEPQPF, Departamento de Engeharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030-790 Coimbra, Portugal*
[b]*Centro para o Desenvolvimento Rápido e Sustentado do Produto, Instituto Politécnico de Leiria*
[c]*Department of Mechanical Engineering and Mechanics College of Engineering, Drexel University*
**filipad@eq.uc.pt*

The study and development of new biocompatible materials for advanced processing methods such as microstereo-thermo-lithography (μSTL) is extremely important to allow the preparation of 3D scaffolds with controlled properties – size, shape, porosity – that can be used in Tissue Engineering [1]. The use of μSTL technology allows the fabrication of new biocompatible resins with a high polymerization rate that can be applied in several fields, namely biomedical areas [2]. The curing reactions used in this type of technologies revealed to be very powerful processes to prepare, in few seconds, high crosslinked networks. The reactions are promoted by just applying an UV light or thermal energy to materials with unsaturated moistures (e.g. unsaturated polyesters, vinyl and acrylic monomers). This photopolymerization process has been applied in many industrial fields such as the surface treatment of several types of materials, the manufacturing of optical discs, the inline coatings of optical fibers or even in electrical fields and dentistry. Also, the capability of printing complex 3D patterns turned polyesters resins to be very promising, not only in terms of cost and time, but also in terms of accuracy and potential applicability.

Unsaturated polyesters (UP) present some interesting characteristics to be used in this application since its internal doubles can easily be photo polymerized forming crosslinked networks. This process involves the preparation of a formulation that typically is composed of: UP, unsaturated monomers (UM), crosslinkers, photo and thermal initiator and an accelerator. This PhD project aims the development of new biocompatible formulations based on suitable UP to be used in the μSTL equipment. The first step of this project will be focused on understanding the curing behavior of a commercial UP formulation named Crystic 272, previously used by Prof. Paulo Bártolo's research group [3]. This commercial resin presents the suitable characteristics for this processing method; however it is not biocompatible, and therefore cannot be used in the biomedical field. In order to understand its curing behavior, several tests will be carried out involving: synthesis of UP with different compositions; and curing tests using different UM.

The next step of this project will deal with the design and synthesis of new classes of UP and the preparation of different formulations using only biocompatible compounds. Kinetic studies of the curing process of the formulations will be carried out using a kinetic model in order to understand the relative importance of the different reactions involved in the curing, as a function of the formulation. The UP formulations developed in this project will be processed by μSTL to prepare 3D scaffolds with different sizes, shapes and porosities.

The properties of the prepared 3D scaffolds will be optimized considering the thermal and mechanical properties required for different potential applications. The biodegradability and cytotoxicity of the 3D scaffolds will be studied using standard methods in view to understand the relationship between these two very important parameters and the formulation used [4].

References:

[1] [1] P. J. Bártolo, *Stereolithography: Materials, Processes and Applications*, Springer, **2011**.
[2] F. P. W. Melchels, J. Feijen, D. W. Grijpma, *Biomaterials* **2010**, *31*, 6121-6130.
[3] P. J. D. Bartolo, *Int. J. Adv. Manuf. Technol.* **2007**, *32*, 480-491.
[4] P. Ferreira, J. F. J. Coelho, M. H. Gil, *Int. J. Pharm.* **2008**, *352*, 172-181.

Neurotensin and chitosan-based dressings: a new approach for diabetic wound healing treatment

Liane Moura[1,2*], Ana M. A. Dias[2], Ermelindo Leal[1], Hermínio C. de Sousa[2], Eugénia Carvalho[1]

[1]Center of Neuroscience and Cell Biology, University of Coimbra
[2]CIEPQPF, Chemical Engineering Department, University of Coimbra, Coimbra, Portugal
**moura.liane@gmail.com*

Diabetes mellitus is one of the most widespread diseases in the world. It may cause chronic and non-healing diabetic foot ulcers (DFU) [1]. Some neuropeptides may act as inflammatory modulators and may improve the wound healing process [2]. Natural biopolymers like chitosan and their derivatives, are presently receiving attention as wound dressing materials for wound healing applications due to several favorable properties such as biocompatibility, biodegradability and non-toxicity. Some chitosan derivatives such as *N*-carboxymethyl chitosan (CMC), *N*-carboxybutyl chitosan (CBC) and *N*-succinyl chitosan (SC) are known to be potential materials for wound healing applications [3]. Employing these chitosan derivatives simultaneously as dressings and as platforms for the delivery of neuropeptides, such as, neurotensin (NT) has not yet been evaluated. In this work chitosan was reacted with glyoxylic acid, levulinic acid or succinic anhydride, for the synthesis of CMC, CBC and SC, respectively. After, known amounts of a glutathione (GSH) solution (5mM) were loaded into previously weighted samples of each polymer. GSH was used as o model drug to study its release profile from the different polymeric matrices. After drying, samples were immersed in PBS at different pHs at 37ºC for 8h. The quantification of released GSH was based on the Ellman's Test [4]. In *in vivo* models, diabetes was induced by an intraperitoneal injection of 200mg/kg streptozotocin (STZ) dissolved in 200ml citrate buffer (pH 4.2) or buffer alone (non-diabetic mice). Control or STZ-treated mice were anesthetized and two 6 mm excision wounds were created dorsally using a punch biopsy tool. CBC alone, NT alone (50ug/wound/per day), CBC loaded with NT (50ug/wound/per day) or PBS were placed daily on wounds and the progress of wound closure was monitored by acetate tracing up to 10 days. Results showed that GSH release was not strongly affected by the release media pH (over a range between 6 and 8). However, SC presented a faster GSH release when compared with CMC and CBC at pHs of 6 and 7. In *in vivo* studies, CBC treated wounds showed a significant reduction in the wound area as compared to PBS treated wounds (29.5%: $p<0.001$), wounds treated with NT alone also showed a reduction of (7.4%: $p<0.02$), while it is with the combination of the two treatments that we observed the greatest reduction in wound area (32.8%, $p<0.001$), already at 3 days post-wounding, in normal mice while in diabetic animals the observed differences are even more pronounced with the combined treatments showing a reduction of 39.8%, $p<0.001$. In addition, wounds treated with CBC and CBC plus NT, at day 10 in the same experiments, showed a smaller difference in wound reduction as compared to the PBS treated wounds at day 10. Results demonstrated that CBC films incorporated with NT could be potentially advantageous as NT-releasing wound dressings for the treatment of diabetic foot ulcers.

References:

[1] V. Falanga, Wound healing and its impairment in the diabetic foot, *Lancet*, 366, 1736-1743 (2005).

[2] L.Silva, M. T. Rosete, E. Carvalho, Role of neuropeptides in skin inflammation and its involvement in diabetic wound healing, *Expert Opin. Biol. Ther*, 10, 1427-39 (2010).

[3] R. Muzzarelli, R. Tarsi, O. Filippini, E. Giovanetti, G. Biagini, P. E. Varaldo, Antimicrobial Properties of N-Carboxybutyl Chitosan, *Antimicrobian Agents and Chemotherapy*, 2019-2023 (1990).

[4] S. C. Garcia, K. Schott, M. Charão, R. Bulcão, D. Grotto, J. Valentini, D. Bohrer, S. Cardoso, V. Pomblum, Quantification of reduced glutathione by HPLC in erythrocytes of hemodialysis patients, *Biomedical Chromatography*, 22, 460-468 (2008).

A comparison of two-way and three-way methodologies for the prediction of wine age

Ana C. Pereira[a], Véronique M. Gomes[a], Pedro M. Saraiva[a] and Marco S. Reis[a,*]

[a]*CIEPQPF, Departamento de Engeharia Química, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3030-790 Coimbra, Portugal*
[*] *marco@eq.uc.pt*

Data generated by modern hyphenated instruments, i.e. instruments that combine two or more measurement principles (such as, GC-MS, HPLC-DAD, Excitation-Emission spectroscopy, among others), have been raising relevant challenges to analysts, given the large amount of information conveyed and the structure in which it is organized, usually consisting of three-mode data arrays or cubes of data. Usually, two of these modes regard the two analytical measurement principles considered in the technique, while the third one is relative to the various samples under analysis. The analysis of such type of data can be implemented either by unfolding the cube of data in a two-way matrix, followed by the application of a classical technique (such as PLS or PCR) or it can be analyzed directly using three-way chemometric methods, already proposed and developed.

The goal of this work is to compare these two approaches for empirical modeling, namely the two-way unfolded methodology, for which the PLS methods is adopted, and the three-way approach, where the PARAFAC, N-PLS and Tucker3 methods, were contemplated. The real world application scenario involves the analysis of data regarding the use of the HPLC-DAD technique, applied to Madeira wine samples with different ageing periods (1 year up to 19 years). The two and three-way chemometric methods applied to such datasets, allowed for the development of useful predictive models for the wine age, and we assess their individual merits in this case study. The root mean square error for wine age prediction varies from 1 up to 2 years, being the best results achieved for PLS approach. We verify that PARAFAC, N-PLS and Tucker3 have poorer performances when all samples are considered for modeling. However, when the first 10 years aged samples were taken into account, the model's performance improves, namely the same obtained using PLS approach. For aged wines, the three-way models present lower prediction ability, suggesting an additional and adequate data pretreatment or even non-linear three-way methodologies.

Acknowledgements
A. C. Pereira acknowledges the Portuguese Foundation for Science and Technology for the financial support through PhD grant SFRH / BD / 28660 / 2006.
The authors also acknowledge Madeira Wine Company for kindly supplying all the wine samples used in this work.
The authors also acknowledge financial support through project PTDC/EQU-ESI/108597/2008 co-financed by the Portuguese FCT and European Union's FEDER through "Eixo I do Programa Operacional Factores de Competitividade (POFC)" of QREN (with ref. FCOMP-01-0124-FEDER-010398).

References:

[1] Ana C. Pereira, Marco S. Reis, Pedro M. Saraiva, José C. Marques, Chemom. Intell. Lab. Syst 105 (2011) 43.
[2] A. Smilde, R. Bro, P. Geladi, Wiley: Chichester, 2004.
[3] K.Danzer, L.A. Currie, Pure Appl. Chem. 70 (1998) 993.
[4] K.S. Booksh, B.R. Kowalski, Anal. Chem. 66 (1994) A782.
[5] S. Gurden, J. Westerhuis, R. Bro, A. Smilde, Chemom. Intell. Lab. Syst. 59 (2001) 121.
[6] A. Rinnan, J. Riu, R. Bro, J. Chemom. 21 (2007) 76.

Wine Characterization through Multivariate Statistics

Ana C. Pereira[1,2], Marco S. Reis[1], Pedro M. Saraiva[1], José C. Marques[2]

[1]Department of Chemical Engineering, University of Coimbra
Pólo II - Pinhal de Marrocos, 3030-290 Coimbra
[2]Madeira Chemistry Research Centre, Department of Chemistry, University of Madeira,
Complexo da Penteada, 9000-390 Funchal

Several studies have been carried out recently in order to differentiate and authenticate wines, encompassing numerous analytical methodologies that generate large amounts of experimental data presenting strong correlations among them. In this regard, Multivariate statistical techniques have become a powerful tool to address such modern measurement systems, as they allow one to explore and to take the most out of the large amounts of data available, in order to deepen the understanding about relevant phenomena going on during wine production and to improve wine quality assessment.

This work is focused in the production of Madeira wine, a Portuguese fortified wine, famous for its exceptional longevity and peculiar bouquet. Our main research goal is centered in the characterization of Madeira Wine at different ageing stages, for different types of Wine, following a wine flavour chromatography data collection step.

An exploratory data analysis was conducted using two different tools: biplots and contributions plots. The latter was found to be suitable for making comparisons between the importance of the variables under study in explaining a given trend identified in the Principal Components Analysis subspace. In order to take advantage of the maximum amount of information provided by the chromatography data sets, a new approach was developed and tested to complete the exploratory data analysis study, which consists of estimating variable contributions, by considering their intrinsic variability. In this way, it was possible to analyze which volatile compounds have statistically significant and/or similar contributions regarding the observed separation of wine samples from different groups, in the principal components space.

The results reached so far indicate that the combined use of GC/MS results, together with appropriate advanced multivariate statistical techniques, does allow us to come up with adequate procedures to identify different types of Madeira wines in terms of their aromatic characteristics and ageing time, as well as to interpret the differences observed.

Fault detection in the Tennessee Eastman process using integrated dynamic principal components analysis and missing data methods

Tiago J. Rato[a] and Marco S. Reis[a,*]

[a]*CIEPQPF, Department of Chemical Engineering, University of Coimbra, Rua Sílvio Lima, 3030-790, Coimbra, Portugal*
[*]*marco@eq.uc.pt*

The objective of statistical process control (SPC) is to monitor the performance of a process over time to verify that it is remaining in a state of statistical control [1]. In order to do that, traditional SPC charts are used to monitor key product quality variables in an univariate way [1, 2]. It should be noted that many of these variables are correlated, and an abnormal event may affect more than one variable at the same time, which difficults the isolation and determination of the problem's source [2]. To address this issue, multivariate monitoring methods, such as those based upon the use of the Hotelling's T^2 statistic have been developed. This statistic is typically calculated based on a model from principal component analysis (PCA) and is complemented with the Q statistic (also known as square predicted error, SPE) leading to a superior performance over univariate charts [3].

However, these methods assume that the variables are uncorrelated in time, a hypothesis that is often not met in practice, especially with the high sampling rates currently achieved with modern instrumentation. To address this issue, Ku *et al.* [3] proposed an SPC procedure based on dynamic principal component analysis (DPCA), which is an extended version of PCA that includes time-lagged variables, in order to accommodate and tacitly model the dynamic behaviour of variables within the same PCA model. Unfortunately, one can easily verify that the direct implementation of such methods still leads to autocorrelated statistics, which raises problems in their implementation.

To handle these issues we propose a combination of DPCA and Missing Data methods that allow for the reduction of the autocorrelation effect present in the monitoring statistics. These methods also led to an improvement of the monitoring performance on the studied systems.

In this work we assess the monitoring performance when applied to the Tennessee Eastman process model developed by Downs and Vogel [4], which has been widely used by the process monitoring community for comparison purposes.

To assess the performance of the proposed method (DPCA-MD), we used a paired t-test between all the statistics adopted in the study. From this analysis, we can conclude that, with a 5% significance level, the DPCA-MD statistics are significantly better than the ones from PCA and DPCA, being able to detect 19 of the 21 faults. Furthermore, DPCA-MD statistics also presented lower autocorrelation and are able to maintain the out of control signals, while PCA and DPCA statistics returned to their in control range, creating the conditions for a false sense of safety. Therefore, we believe that the new statistics based on MD estimation, are eligible for future applications in alternative to the current ones based strictly on PCA and DPCA.

References:

[1] Theodora Kourti and John F. MacGregor, Process analysis, monitoring and diagnosis, using multivariate projection methods, *Chemometrics and Intelligent Laboratory Systems*, 28, 3-21, (1995).

[2] Theodora Kourti, Application of latent variable methods to process control and multivariate statistical process control in industry, *International Journal of Adaptive Control and Signal Processing*, 19, 213-245, (2005).

[3] Wenfu Ku, Robert H. Storer, and Christos Georgakis, Disturbance detection and isolation by dynamic principal component analysis, *Chemometrics and Intelligent Laboratory Systems*, 30, 179-196, (1995).

[4] J. J. Downs and E. F. Vogel, A plant-wide industrial process control problem, *Computers and Chemical Engineering*, 17, 245-255, (1993).

Statistical monitoring of control loops performance

Tiago J. Rato[a] and Marco S. Reis[a,*]

[a]*CIEPQPF, Department of Chemical Engineering, University of Coimbra, Rua Sílvio Lima, 3030-790, Coimbra, Portugal*
[*]*marco@eq.uc.pt*

In this work we address the problem of monitoring the performance of automatic control loops (APC) using data collected from the process. This topic has been gaining importance in recent times not only because the performance of the controller is significant to the quality and efficiency of the process but also because it can be traced back to malfunctions located at the level of controllers actions. The proposed index (I_M) is a generalization of an historical data benchmark index (I_v) [1] and presents less variation and fewer false alarms while maintaining its ability to detect the controller's performance deterioration. This can be seen in Table 1, where the percentages of errors detected for different perturbations are presented. This statistic is also useful to identify the affected cycles and load variables involved through control chart procedures. The results were compared to the ones obtained using some of the methods presented in the literature, supporting such claims. As an example, in the 2x2 system presented in [2],the correct fault was detected 87 to 98% of the times.

Table 1 Percentage of errors for each load variables variance and perturbation.

Perturbation	I_v			I_M		
	Load variables variance			**Load variables variance**		
	A*	**B**	**C**	**A***	**B**	**C**
No perturbation	1,0 ± 0,2	91,6 ± 0,6	100 ± 0	1,2 ± 0,3	0,9 ± 0,2	0,9 ± 0,2
I	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0	100 ± 0
II	4,9 ± 0,4	97,6 ± 0,5	100 ± 0	6,1 ± 0,2	6,2 ± 0,9	6,3 ± 1,7
III	16,7 ± 0,8	40,5 ± 1,3	99,8 ± 0,2	20,4 ± 0,8	17,8 ± 0,9	20,2 ± 2,4
IV	25,3 ± 0,5	100 ± 0,1	100 ± 0	28,4 ± 1,4	28,9 ± 1,1	30,1 ± 2,3

* Reference variance

The proposed index was also tested in a more realistic system, consisting of a reactor equipped with a heating jacket. The results show that the proposed index maintained its ability to detect changes in the controller's performance about 100% of the times when they are due to perturbations occurred in the discharge coefficient. When the changes happened in the heat transfer coefficient, the index detected the disturbance 40% to 100% of the times depending on the disturbance magnitude.

Our index is easy to calculate and only requires the measurement of the controlled variables over time. It can also be considered a good alternative compared to other indexes found in the literature. The results obtained illustrate the potential of the approach and highlight its simple and effective structure, two important requirements for being implemented in real world scenarios.

References:

[1] Jie Yu and S. Joe Qin, Statistical MIMO controller performance monitoring. Part II: Performance diagnosis, *Journal of Process Control*, 18, 297–319, (2008).

[2] Qiaolin Yuan, Barry Lennox, and Matthew McEwan, Analysis of multivariable control performance assessment techniques, *Journal of Process Control*, 19, 751–760, (2009).

Reuse of homogeneous Fenton's sludge from detergent industry as new Fenton's catalyst

André F. Rossi*; Rui C. Martins; Rosa Quinta-Ferreira

*GERSE, Group on Environment, Reaction and Separation Engineering. Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, Pólo II – Rua Sílvio Lima, 3030-790 Coimbra, Portugal. * rossiaf@eq.uc.pt*

Fenton's reaction is an advanced oxidation process. Classically, hydrogen peroxide is the oxidizing agent and an iron catalyst promotes the formation of hydroxyl radicals (•OH). Many studies evaluated different metals as Fenton's catalysts. Our group of investigation has recently used cerium-based solids as heterogeneous catalysts for slurry reaction and, in this work, iron sludge coming from an industrial Fenton's reactor used for detergent production wastewater is being appraised while treating a synthetic effluent containing 0.1 mg.L^{-1} of seven phenolic acids commonly found in olive mill wastewaters – one of our group's major focus. The treatment facility uses homogeneous Fenton's process and the created sludge contains approximately 20 % (w/w) iron content. As it comes directly from the plant and it is a pretty raw mud, it is expected to find high amounts of organic matter in the catalyst, because there are no further steps besides baking to enhance its efficiency, which could undesirably dissolve and increase the organic charge. In other words, the mud was only dried, baked and milled to become the catalyst. A baking temperature of 300 °C was employed and a comparison with the non-baked catalyst was performed. Chemical oxygen demand (COD) and total phenolic content (TPh) removals reached good levels (40 % and 80 %, respectively), which were better than the ones achieved by the non-baked catalyst. Biological oxygen demand in five days (BOD_5) was also increased, which can enable the application of a subsequent biological treatment step. Adsorption tests are being carried out in order not to erroneously associate the abatements to oxidation and have proved that COD and TPh are removed by chemical reaction rather than single adsorption.

Studies on the recycling of calcium rich waste for producing high quality fertilizers

Micaela R. Soares[a], Crechula C. Matsinhe[b], Margarida Quina[b], Rosa Quinta-Ferreira[b]

[a]*Cernas – Natural Resources, Environment and Society Research Centre, Coimbra College of Agriculture,*
Polytechnic Institute of Coimbra, Bencanta, 3040-316 Coimbra, Portugal
[b]*CIEPQPF-, Chemical Engineering Department, Faculty of Sciences and Technology, University of Coimbra,*
Rua Sílvio Lima - Pólo II, 3030-790 Coimbra, Portugal

The industry of pasteurised liquid and boiled eggs produces large amounts of eggshell (ES), which is classified as an animal by-product not intended to human consumption. In an annual basis, it is estimated that about 30 million kg of eggshell are industrially produced in Europe [1]. Adequate management strategies are not yet well established for this industrial waste, most of which has been traditionally landfilled [2,3]. Current EU policies recommend mostly recycling and waste recovery.

Due to the high nutrition contents of eggshell, namely in calcium, its application to acid soils with calcium deficiency may constitute an option to promote eggshell transformation in a value-added product and consequently recover a natural resource contained in ES.

According to the European Regulation (EC) Nº 1774/2002 the controlled application of eggshell in soils is only possible after pre-treatment, being the composting process one of the technologies recommended. Nevertheless to our knowledge, eggshells composting is scarcely addressed in literature [4].

Composting process may be defined as the biological decomposition and stabilization of organic subtracts, under aerobic conditions that allow development of thermophilic temperatures as a result of biologically released heat, to produce a final product that is stable, free of pathogens and plant seeds, and can be beneficially applied to land [5]. Since temperature determines the relative advantage of some microorganisms over others, during composting pathogen reduction can be attained by thermal inactivation [6, 7] as a result of the high temperatures achieved (>55ºC) due to biological degradation of the organic matter present in the composting mixture.

Once eggshells have an high inorganic content (about 94% (w/w) is $CaCO_3$ [3]), its composting will only be successful in terms of hygienization if it is mixed with easily biodegradable materials, so that the energy available is enough to expose the composting mixture to thermophilic temperatures during a certain period of time.

This work aims to define the maximum amount of ES that can be recycled by composting to ensure adequate level of hygienization. This assessment was performed by developing a dynamic model for aerobic composting process which was compared with several experimentally measured dynamic state variables. Experimentally, potato-peel, grass clippings, sawdust were mixed in four different ratios and composted in self heating reactors with 120 L of internal volume. Then for each blend, increasing amounts of inorganic material were simulated with the developed model.

The dynamic mathematical model developed for aerobic composting process described well the experimental results obtained without ES incorporation. Incorporating up to 60% appears to meet the criterion for hygienization. However, in this preliminary study, temperature gradients inside the reactor were not taken into account. Nevertheless, composting seems to be suitable method for the ES by-product treatment as long as the mixing and operate conditions are adequate for guarantee the maintenance of thermophilic temperature for several days to assure the maximum degradation and the hygienization of the compost.

References

[1] A. C. Consulting, Study on the socio-economic implications of the various systems to keep laying hens- Final Report for The European Commission, 2004.

[2] D. Jones and J. Gittins, Utilisation of Egg Shell Waste from UK Egg Processing and Hatchery Establishments. London: ADAS Consulting Ltd, 2002.

[3] W.-T. Tsai, *et al.*, Bioresource Technology. 99 (2008) 1623-1629.

[4] N. P. Kemper and H. L. Goodwin, Jr., J. Appl Poult Res. 18 (2009) 172-184.

[5] R.T. Haug, The practical handbook of compost engineering. Boca Raton, FL, USA: Lewis Publishers (1993).

[6] B. Vinnerås, A. Björklund and H. Jönsson, , Bioresource Technology. 88 (2003) 47-54..

[7] K.M. Wichuk and D. McCartney, J. Environ. Eng. Sci. 6 (2007) 573-586.

PRODEQ

PRODEQ 10 – 10 anos ao serviço da Engenharia Química

Dia Aberto – CIEPQPF

Centro de Investigação em Engenharia dos Processos
Químicos e dos Produtos da Floresta

· U C ·

UNIVERSIDADE DE COIMBRA

PROGRAMA

11/11/2011

09.00h – 09.15h	Recepção dos participantes
09.15h – 09.30h	Sessão de Boas Vindas

SESSÃO 1 – INOVAÇÃO E EMPREENDEDORISMO

09.30h – 10.00h	"Capital de Risco: Capital de Oportunidade" **Dr. Agostinho Matos, *InovCapital***
10.00h – 10.30h	"Do Projecto Industrial à Empresa Inovadora" **Prof. Doutor Sérgio Simões, *Bluepharma***
10.30h – 10.50h	Espaço para debate
10.50h – 11.10h	*COFFEE BREAK*

SESSÃO 2 – PERCURSOS DE INOVAÇÃO

11.10h – 11.30h	PRODEQ – Um percurso de 10 anos **Prof. Doutor Jorge Rocha – *DEQ/FCTUC***
11.30h – 11.50h	"Projecto Innovinil" **Prof. Doutor Jorge Coelho – *DEQ/FCTUC*** **Engenheiro Pedro Gonçalves – *CIRES***
11.50h – 12.10h	"Ciengis: uma spin-off no mercado global" **Doutor Andrey Romanenko**
12.10h – 12.30h	Espaço para debate *ALMOÇO*

SESSÃO DA TARDE – INVESTIGAÇÃO NO CIEPQPF

14.00h – 15.00h	**Comunicações Orais:** "Treatment of liquid effluents by catalytic ozonation and photo-Fenton's processes" - Ana Sofia Fajardo "Bio-based polymers: synthesis of high molecular weight poly(lactic acid)" - Dina Marques "Lignocellulosic biomass valorisation in a pulp and paper mill" - Cátia Mendes
15.00h – 15.45h	Sessão de posters/*COFFEE BREAK*
15.45h – 17.10h	Mesa redonda – "**Interface Universidade/Empresas: Desafios e Oportunidades**"
17.10h – 17.30h	Entrega de prémios – comunicações / posters
17.30h – 18.00h	**Sessão de encerramento com participação de:** Grupo de saxofones do Conservatório de Música de Coimbra

DEQ FCTUC

CIEPQPF
Centro de Investigação

Departamento de Engenharia Química
Faculdade de Ciências e Tecnologia
Universidade de Coimbra