2009 Report of CRERG Research Activities

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CRERG | Catalysis and Reaction Engineering Research Group

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Annual Report
Contents

4 Executive Summary
5 Catalysis and Reaction Engineering Research Group
6 Research Highlights
28 Publications
29 Proceedings
31 Master and PhD theses completed
33 Patents
33 Industry Contract Research
34 Internationalization
34 Outreach/Science and Society
34 Facilities
37 CRERG Members
The Catalysis and Reaction Engineering Research Group (CRERG), integrates the Centre for Biological and Chemical Engineering (CEBO) of IST. CEBQ is now part of the associated Laboratory Institute for Biotechnology and Bioengineering (IBB). CRERG has started as a group working mostly on catalysis by zeolites and has evolved into a multi-disciplinary group with interests and activities in several areas, ranging from environmental catalysis, bio-catalysis and hydrocarbon transformations, to multiple-scale analysis and modelling of complex dynamic systems.

CRERG is now an internationally recognized research group, with a large number of national and international collaborations and with activities in various fields.

The transformation of hydrocarbons over zeolites is still being pursued and, significant advances are still being made in the fundamental understanding of acid catalysis in the transformation of hydrocarbons with the development of models that are able to predict the activity and selectivity of zeolitic catalysts, both in cracking and oligomerization reactions, which are of particular interest for the industry. On the experimental level the analysis of the possibility of inclusion of biomass in an FCC unit and of the conversion of polyolefin waste into valuable liquid fuels is also being pursued.

The group also develops research in the field of environmental catalysis, namely on the reduction of emission of different pollutants. The reduction of nitrogen oxides (NOx) and volatile organic compounds is an active area of research which involves both the analysis of different methodologies and the development of new catalysts.

These areas are supported by well-equipped and functional synthesis and characterization laboratories.

The development of knowledge and scientific basis for the design and synthesis of new reactive polymers, with the emphasis on the use of renewable resources is also an active research line with visible results on the successful development of new reactive binders for high performance aggregated cork stoppers.

The group has always dealt with very complex reaction systems and this has lead, in a natural way, to the development of expertise in dynamic systems analysis and modelling, at different levels, from process to kinetic and molecular. This has been applied in such diverse fields as the analysis of industrial reactors and the development of kinetic models for the expansion/differentiation of stem cells, a collaboration with BERG. Another important field is process dynamics and control where collaborations have been made with both industrial and other academic partners.

Within the Centre for Biological and Chemical Engineering CRERG has developed synergic partnerships with BERG resulting in the development of new applications for zeolitic materials, namely pioneering the use of enzyme/zeolite catalytic systems.

It is our objective to develop high-quality research in the field of catalysis and reaction engineering, particularly using our expertise to participate in multi-disciplinary projects with partners, both from IBB and from other research units, while keeping a strong focus on catalysts for energy and the environmental applications.

Fernando Ramôa Ribeiro
CRERG Head
CRERG has developed its interests in several research areas, covering environmental catalysis, bio-catalysis and hydrocarbon transformations (resorting to zeolitic type catalysts), as well as multi-scale analysis and modelling of complex dynamic systems, namely chemical reaction ones.

- Development of efficient catalysts for environmental catalysis – In this research programme catalysts for the removal of NOx and VOC from fuel exhausts are studied and developed.
- Novel acidic and bi-functional zeolites for hydrocarbons transformation – This line of research covers a wide range of reactions, starting with the conventional application to catalytic cracking and going up to the use of zeolites as catalysts for the production of fuels from biomass or from recyclable plastics.
- Novel applications of microporous materials – The use of zeolites for applications outside their conventional range is being developed. Applications include the use of zeolites in combination with biocatalysts, in collaboration with BERG, and the use of microporous electrodes, containing microporous materials like zeolites, for sensors, synthetic and analytical applications.
- Design and synthesis of new polymers. These new polymers include reactive polymer and the development of new polyester and polymeric films with controlled permeability.
- Dynamic systems analysis and control – This is also a wide field of research covering conventional system dynamics and process control but also including the multi-scale analysis and modelling of complex reaction systems, from industrial reactors to the microscopic level, including hydrogenation reactions, catalytic cracking, polyolefin production reactions and the expansion and differentiation of hematopoietic stem cells (in collaboration with BERG). Methodologies used include process, kinetic and molecular modelling.
Introduction

Among the solid acid catalysts, zeolites and zeotypes are of a great importance in industry and have found a wide application in oil refining, petrochemicals and chemicals.

Silicoaluminophosphate (SAPO) materials also possess interesting properties, i.e. the presence of ordered porous systems with well defined size and shape, a good thermal stability and finally the possibility to finely tune strength and number of acid sites by controlling the incorporation of Si and/or transition metal ions M⁺.

Medium Bronsted acidity generated makes these materials good candidates for specific acid-catalyzed reactions that require weak to moderate acidity and specific pore sizes, as for example methanol to olefins (MTO) conversion (SAPO-34), hydroisomerization (SAPO-11, -31, -41), etc...

The CRERG group recently developed an original synthesis strategy which consists in using a small amine (methylamine, MA) as co-template during materials synthesis.

Although rarely employed in microporous synthesis, MA has been shown to demonstrate interesting features as mineralizing/complexing agent and even as sole template (IST-1 material). When used as co-template in SAPO-11 synthesis, MA was shown to strongly influence Si incorporation and hence the acidity properties.

Consequently, different SAPO-11 materials with AEL structure have been synthesized in presence of methylamine and used as acid and bifunctional catalysts in hydroisomerization of n-decane and dehydration of xylose, a monosaccharide.
Catalytic applications

Hydroisomerization of n-decane

This study aims at investigating MA effect during SAPO-11 synthesis on the catalytic properties of the final materials in n-decane hydroisomerization (collaboration with Â. Martins, ISEL). Different Si and MA amounts were used in the initial gels. Niobium was also introduced, in some cases, as promoter agent.

First results demonstrated a strong effect of methylamine on textural and acidity properties: MA favours larger SAPO particles formation and minimizes the formation of large Si islands, increasing the overall number of Brønsted acid sites. Consequently, MA based catalysts essentially show higher n-decane conversion but also higher cracking product formation, due to higher diffusion pathways.

UV-Vis DRS measurements show that niobium preferentially incorporates the SAPO framework. As a result, the final materials crystallinity significantly decreases, as well as acidity. However, final Nb based materials demonstrate a better platinum dispersion together with enhanced hydrogenating properties.

Dehydration of carbohydrates

Acid-catalysed hydrolysis and dehydration of saccharides, which constitute the bulk of carbohydrates, into furfural (FUR) and 5-hydroxymethyl-2-furfuraldehyde (HMF) are important processes, since these are platform chemicals for generating a variety of nonpetroleum derived products.

The previous SAPO-11 materials have been also tested in D-xylose dehydration reaction and their catalytic behaviour compared with those of other SAPO materials presenting different structures and acidity properties (collaboration with A. Valente, CICECO). SAPO-5 (AFI) and SAPO-40 (AFR) materials were also prepared using conventional recipes.

SAPO materials have demonstrated good catalytic behavior for xylose dehydration into furfural under aqueous-organic biphasic conditions. From the different structures studied, SAPO-11 materials seem to be the most promising (FUR yields of about 34-38%, comparable with HMOR zeolite with Si/Al ~ 6). Furthermore, SAPO-11 synthesized with MA proved to be more selective into FUR, when compared with the free MA catalyst. Indeed, the higher selectivity observed can be related to the decrease of Lewis acid sites as a consequence of MA use during the crystallization phase.
This work is conducted at CRERG and at the Laboratoire de Catalyse et Spectroscopie (LCS), ENSICAEN - Université de Caen, Basse Normandie (Frédéric Thibault-Starzyk).

Introduction

Fossil fuels will remain, in a next future, the main source of fuel supplying, mainly in the field of transportation. Two main aspects seem to stress the necessity of, in the short-term, to develop the exploration of deposits of heavy fractions: (i) the fast exhaustion of the lightest reserves of crude oil and (ii) the foreseen increase of liquid fuel consumption, as a result of the economic growth in countries as China and India.

The exploitation of such heavy fractions demands its transformation in products able to be transformed in liquid fuels (gasoline, jet-fuel and diesel) through catalytic processes of hydrocracking.

Overview

Between 3 and 10 trillions of barrels of hydrocarbons are estimated to exist in heavy oil deposits, bituminous sands and oil shales. In the case of the oil shales, the initial separation of the organic composite mixture (kerogen), of the ores in which is impregnated, is traditionally performed through a pyrolysis, that originates a gaseous fraction, a liquid fraction and a solid residue (coke).

Different technologies have been proposed for the transformation of kerogen in the interior of the deposits (in situ), including the injection of superheated water vapour (EGL) or previously heated gases (Chevron, PetroProbe), or through the heating of delimited zones of the deposits, using electric resistances at great depth (Shell).

The use of heating systems based on microwaves fields was equally proposed, using the dielectric properties of the bituminous shales (PhoenixWY, Raytheon/Schlumberger): the use of generators that work between 100 KHz and 100Mhz, it was possible to reach speeds of ing of the deposits up to 50 superior times to those reached with electric heating, despite the heating efficiency decays very fast with the distance from the microwaves antenna.
The second step in the exploitation of these non-conventional sources consists on the transformation of the products previously obtained. Little information exists in literature on the composition of the products formed for pyrolysis of kerogen: the non-condensed fraction is constituted by C1-C4 compounds, the liquid fraction mainly is constituted by linear paraffins and olefins, naphthenes, substituted aromatics; heteroatoms are also present, mainly sulphur and nitrogen.

The transformation of this liquid fraction is clearly included in the set of reactions known as hydroconversion, where reactions of hydrocracking and hydroisomerization are promoted, under hydrogen pressure, by bifunctional catalysts that associate a hydrogenating-dehydrogenating function (Pt, Pd) to an acidic function (zeolite).

Objectives

The main objectives of this work are:

1) the exploitation of Oil Shales for production of Liquid Fuels;

2) the development of a system of heating, based on the generation of a field of microwaves (of adequate frequency), adapted to the decomposition/transformation of the organic compounds (kerogen) constituting the oil shales;

3) the study of the decomposition of kerogen: comparing traditional heating with microwaves, both in the presence of the ore (argyles, silico-aluminas), as well as in the presence of water;

4) the study of the catalytic transformation of the liquid fraction, obtained by kerogen decomposition, through a stage of hydrocracking: (i) cracking of linear molecules of bigger molecular weight, (ii) the isomerization of the alkanes (iii) the hydrogenation of unsaturated C-C bonds. Acidic zeolites exchanged with metals that fulfill the hydrogenating/dehydrogenating function will be catalytically evaluated;

5) the modification of the used catalysts, (i) in order to create a mesoporosity system, that makes possible the access of more voluminous molecules in the framework of zeolites (desilication) and (ii) acidity tuning (dealumination);

6) the study of the regeneration of the deactivated catalysts, through processes that will try to minimize any negative effect on the structure of the catalysts (occurrence of hot spots, among others). Methods of controlled combustion will be tested as well as new methods of regeneration as coke hydrocracking. The use of the system of heating for microwaves, previously referred, equally will be tested in the regeneration of the catalysts.
This study is included in a project aiming to adapt post-synthesis methods of dealumination and desilication to intermediate pore size zeolites, presenting remarkable catalytic properties: TON, able to the selective isomerisation of long chain n-alkanes; MCM-22, very stable and selective for the commercial synthesis of ethylbenzene and cumene.

Controlled desilication of zeolite TON, presenting a silicon rich framework (Si/Al $\geq 30$) and a one dimensional linear pore system of $\sim 6$ Å (Fig. 1), was achieved by treatment with sodium hydroxide solutions.

This new post-synthesis method is particularly interesting to induce some mesoporosity generation in silicon rich zeolites, without a relevant acidity change. The detailed characterization of the desilication induced changes in textural properties is under study from adsorption studies of Nitrogen and hydrocarbon molecules with different dimensions. Acidity has been evaluated from FT-IR of OH and pyridine adsorption.

Possible consequences of the desilication in the transport limitations inside the monodimensional porosity of TON should be reflected in the final catalytic properties of the samples, which are being investigated through their test in different model transformations related to industrially relevant processes: alkane cracking, butene isomerization, xylene isomerisation.

Testing of metal-loaded samples in bifunctional alkane hydroisomerization transformations is also envisaged.

Some interesting results have already been obtained concerning the porosity modification, with positive consequences in the catalytic properties evaluated on the 1-butene isomerization and $h$-heptane cracking (Fig. 2).
Lignocellulosic biomass seems to be a promising renewable energy source that can be easily converted into bio-oils by pyrolysis. Nevertheless, the presence of O-Compounds (50 wt.%) is unacceptable for its use as commercial liquid fuels. A possible and advantageous alternative concerning the investment costs for the near future is co-feeding the bio-oils with the conventional Fluid Catalytic Cracking (FCC) feedstocks.

The aim of this study has been to evaluate the influence of O-compounds on the catalytic properties of the active phases of FCC catalysts (HY and HZSM-5 zeolites), and of the equilibrated industrial catalyst.

Several model O-compounds are used, such as phenols, guaiacol. Different model transformations are also being tested: cracking of methylcyclohexane (MCH), n-Heptane (n-Hp). The detailed characterization of the fresh and deactivated catalyst samples, for different degrees of deactivation, is also under study, in order to better understand the induced modifications in the acidity and porosity and its relation to the influence on the activity, selectivity and deactivation.

The addition of phenol and guaiacol increase the deactivation of the Y zeolite along time-on-stream, due to the O-Compound adsorption on both Brønsted and Lewis acid sites, but the initial activity is not significantly affected in the case of MCH (Fig.3). For n-Hp, a transformation only achieved over the fraction of strongest acid sites, there is already an induced initial deactivating effect. The increase of the reaction temperature (from 350 °C to 450°C) limits the influence on the zeolite activity and stability.

In opposition to HY zeolite, and independently of the reaction temperature, the activity of ZSM-5 is greatly affected since the lowest time-on-stream values, for both MCH (Fig.3) and n-Hp reactions.

The results being obtained in the industrial catalytic transformation of gasoil under the influence of the same O-compounds, from the collaboration with Petrobras, may be partially understood considering the model reactions performed over the pure zeolites. Namely, the observed reduction of the additive effect of ZSM-5 in the industrial catalyst, is in line with its fast and extensive deactivation induced by the presence of the O-compounds in the model transformations. No important induced changes have been detected in the conversion of gasoil over the industrial catalyst.

Some development of this study is still envisaged, namely concerning the test of mixtures of zeolites HY and ZSM-5 over the model transformations.
Plastics have gained a very significant place in our daily life and are the origin of a large portion of the wastes that are generated both by urban and industrial activities.

In particular polyethylene and polypropylene are present in a very significant number of materials that are used on a daily basis by everyone. Polyethylene and polypropylene that are used in such simple products as plastics bags and food wrappers are produced from oil-based materials and are mainly constitute by very large hydrocarbon molecules with a paraffinic structure.

Acid zeolites have been used for a very long time as catalytic cracking catalysts, which are able to convert large hydrocarbon molecules into smaller ones, and this has been a major process in the production of liquid fuels, namely gasoline.

In this project we have used acid zeolites to degrade polyethylene so as to produce hydrocarbons in the range of the ones that are used in the composition of liquid fuels.

This process can be used with a two-fold advantage: on one hand it can help solve the problems arising from the growing use of polyethylene in urban and industrial waste and, on the other hand, it can increase the range of sources that are used to obtain liquid fuels.

It is true that this kind of process does not correspond to an alternative to the use of oil-based fuels, since, in fact, polyethylene and polypropylene themselves are produced from oil, but it contributes to the efficient use of oil, which is becoming a scarcer commodity, and contribute to the useful recycling of plastic materials.

These reactions differ significantly from conventional catalytic cracking since the initial reactant is a solid composed of very large molecules with a wide range of molecular weights. In order to produce hydrocarbons in a range that is suitable for, for instances, the gasoline pool, many bonds have to be broken in each molecule.
Since we are dealing with very high molecular weight hydrocarbons, the first bonds that are broken still produce molecules that are very heavy.

This characteristics imply a certain difficulty in following the reaction progress since the intermediate products are very heavy and difficult to detect and we will only observe gas-phase products when the reaction has proceeded extensively already.

However, even before the products become sufficiently light to evaporate, we can follow the reaction rate if we look at the amount of energy that is used to break the bonds in the polymer molecules. The cracking reaction is endothermic and, the heat flow that is required to keep the reaction going can be used as a way to measure the reaction rate.

In order to study these reactions a methodology was developed using a simultaneous TG/DSC apparatus.

By performing a detailed heat balance to the pan where the reaction is taking place we can separate the various heat components in the heat flow, which are: the heat capacity of the sample, the heat required for the reaction to proceed and the heat that is spent in evaporating the volatile components.

In this way we can have a clear picture of the reaction that is taking place and estimate kinetic rate constants for the reaction under study.

Since this is a dynamic experiment, using non-isothermal conditions, we can estimate the activation energies for the reaction with a single run and data interpretation relies heavily on the development of suitable computational models.
Overview

Acid catalysis using zeolites have been around for many years and catalytic cracking is one of the most important processes in the production of the gasoline pool.

The fears that have been raised in recent years in relation to a near-future oil shortage has been leading the refineries to consider diversifying the feedstock to be used in the cracking process. This diversification implies not only the use of increasingly heavier oil fractions but also feedstock's coming from other sources, like plastic wastes, biomass or Fischer-Tropsch synthesis.

Also, the changing fuel market is forcing the refineries to develop more flexible strategies to convert feeds that are ranged for a particular type of fuel so that they can be used to in another type of fuel. This is particularly relevant for instances, in the need to adapt to the market that is changing from a predominant gasoline consumption towards an increase in diesel consumption.

Olefin Oligomerization

Olefin reactivity over acid sites in zeolites is relevant for all kinds of purposes. CRERG has been studying the conversion of olefins over acid zeolites in the context of understanding the mechanism of catalytic cracking. In fact, olefins are much more reactive molecules than paraffins or aromatics and, thus, play a major role in the mechanism of catalytic cracking.

However, the transformation of olefins by themselves is also a relevant process since they can provide a way to convert surplus lighter olefins into heavier hydrocarbons and thus contribute to the flexibility of the overall process.
The main achievement that have been obtained in the last year is the possibility of describing the transformation of a range of light olefins, on an extended range of operating conditions and over catalysts with different acidities using a single kinetic mechanism and a single set of kinetic parameters. The model developed is now capable of describing both the overall activity and the selectivity in relation to the various products.

This model can not only open the way to the prediction of a catalyst behaviour based solely on its characterization but also allow the optimization of an oligomerization reactor based on the knowledge of catalyst being used and on the composition of the feed that is to be processed.

**Fischer-Tropsch Feedstock**

Fischer-Tropsch synthesis has been a source for fuels for quite some time and it has been used by various countries in situations where access to oil was limited, namely during the Second World War.

The declining of the petroleum resources and the new environmental legislation are contributing to change the strategies of the oil companies: more sustainable and cleaner feedstocks are preferred. The Fisher-Tropsch Synthesis (FTS) represents an alternative route to obtain high-quality fuels and chemicals, from natural gas, coal or biomass, via conversion of synthesis-gas (CO + H2). The contents of sulphur, nitrogen and aromatic compounds are exceptionally low and the expensive purification operations become redundant [1]. The products resulting from FTS process are, fundamentally, straight chain paraffins, in the range C1 – C50 that can be separated and processed independently. Naphtha fraction (C5 – C16) can be fed in fluid catalytic cracking (FCC) units to produce essentially light olefins (C2 – C4), notably propylene, which is a valuable material for petrochemical production.

The work carried out at CRERG, in collaboration with Petrobras and the University of Poitiers, aims at the study of the transformation of these heavy linear hydrocarbon feedstock into a more diversified hydrocarbon pool using catalytic cracking catalysts.

Once again the expertise gained from the work on the degradation of polyethylene can be put to use so that a better understanding of the transformation of these heavy hydrocarbons can be achieved.
Overview

Processing of heavy petroleum cuts is of paramount importance in the current context of possible oil shortage. This oil shortage requires that the oil is used to the fullest extent possible and, thus, hydrotreating operations, which are used to rid the oil cut of substances which may be harmful for further processing, namely heavy metals, sulphur and nitrogen.

In this work, that was carried-out in cooperation with the Institut Français du Pétrole (IFP) the objective was to develop a complete kinetic model that would be able to provide an accurate description of the hydrotreating reactor for any charge and for any catalyst.

Model Development

The model that was developed had different levels of complexity that had to be dealt with:

- The charge that is fed to the reactor is very complex, consisting of a mixture of molecules of different chemical nature and with varying contents in the species to be removed, nickel vanadium, sulphur and nitrogen;
- The molecules present in the charge also cover a wide range of sizes and the description of the diffusion processes cannot easily be described by the simple Fick’s Laws;
- Since the molecules are very large the catalysts are usually macroporous but, in view of the very large size of the molecules, even these macropores are of dimensions comparable to the molecules themselves;
- The conversion proceeds through an intricate network of reactions that involve both changes in the size of the molecules and in the chemical nature of the species involved.
In order to achieve an adequate description of the charge it was fractioned according to a Saturated, Aromatics, Resins and Asphaltens (SARA) analysis.

Two methodologies were developed in parallel:

° On one hand a complete diffusion model using the Stefan-Maxwell approach was developed. For this model a simple lumping scheme was used to describe the kinetics and the diffusion model was written using a Fornasiero formalism;
° On the other hand a kinetic model with a complex lumping scheme, where various subdivisions inside each of the main groups from the SARA analysis were considered and both conversions inside each group and from group to group were accounted for.

The development of these models allowed us to have some insight into the parameters that are relevant for the description that is intended.

Using the data provided from these two models a full model combining both the detailed diffusion description and the more complex lumping scheme and kinetic network was also developed for a setup consisting of two reactors in series (HDM + HDS sections).

Main Achievements

Although the model that was developed still requires improvements, this methodology has shown that it is possible to develop a model that is capable of being applied to a variety of charges, over the same catalysts, using a single set of kinetic parameters which are mainly independent of the charge being processed.

The goal is, now, to provide the refiner with a methodology that will allow him predict the behaviour of a reactor based on the knowledge of the catalyst and on a simple characterization of the charge.
Nowadays, a great deal of attention is being put in the search of alternative fuels, as biofuels, in order to decrease the CO2 emissions (Kyoto agreement) and the petroleum dependency. Biodiesel production from vegetable oils has been the subject of much interest and the mixtures of biodiesel with fossil based diesel have been implemented to car engines. Despite the beneficial impacts on engine emissions (PM, COx, HC), biodiesel has a major drawback of increasing NOx in exhaust gases. On the other hand, current and upcoming air quality regulations are requiring drastic reductions in NOx emissions from diesel engines, which claim for catalytic after treatments. Currently, two distinguishable NOx removal treatments are being developed: NOx-trapping and selective catalytic reduction with ammonia (SCR-NH3) or with hydrocarbons (SCR-HC). SCR-NH3 has already been implemented for engine exhaust of heavy duty vehicles, but it has several drawbacks. SCR-HC is a promising solution because it can use the HC present in the fuel or in the exhaust gases, although until now it was not possible to find active and stable catalysts to reduce NOx with high enough efficiency, in presence of oxygen excess (DeNOx process) and suitable for commercial uses.

The scope of the project is the SCR-HC of NOx in presence of oxygen excess (DeNOx) using model molecules from biodiesel (methyl laurate) and fossil diesel (hexadecane) as reductants. The innovative approach of the project is the design of novel DeNOx catalysts based on metal zeolites, which shall involve the preparation of single or multifunctional catalysts that after washcoating onto corderite monoliths or foams will result in structured catalysts to be tested under real close conditions.

The presence of water in exhaust gases is the main responsible for metal zeolites deactivation. Our previous studies with metal zeolites on NO SCR, with methane and propene, have shown that catalytic improvements are possible, and encourage us to seek for catalysts whose structural features favour the formation and stabilisation of metal active species for SCR of NO in presence of H2O. We have managed to identify the main steps involved in SCR-HC mechanism and we know that depending upon the zeolite structure, Si/Al ratio and acidity, some types of metal species can become catalytically active. The role of NO2 on SCR-HC is also well proved and the metal active species for NO oxidation to NO2 have been identified.

Now, our main challenge will be to stabilise active metal species in zeolites and achieve NO SCR activity and stability in a large temperature range, with biodiesel typical hydrocarbon molecules. Taking into account the promising results of Ag based catalysts for SCR-HC, and the effect of H2 co-feeding, Ag/zeolite catalysts will be investigated as potential DeNOx catalysts.
Two different types of catalysts will be prepared: a catalyst based on small pore zeolites with active metal species (noble metal or oxide transition metal) and a catalyst based on Ag supported on modified large pore zeolites with mesoporosity created by Si leaching from zeolite network through a basic treatment (desilication).

Evaluation of both catalytic performances of metal/small pore zeolites for NO oxidation to NO₂ and of Ag/modified zeolites for NOx reduction with methyl laurate and hexadecane in presence of oxygen excess.

Comparative study of the influence of single molecules of biodiesel or conventional diesel, or their mixtures; influence of hydrogen co-feeding and presence of water on DeNOx activity.

After the selection of the most active and stable catalytic formulation for both NO oxidation and DeNOx reactions, a combination of these catalysts will be proposed to prepare multifunctional/dual pore system catalysts that will be tested using similar feed and operating conditions.

The most promising catalyst formulation for NOx SCR with methyl laurate or hexadecane, in presence of water, will be selected for wash-coating cordierite monoliths and foams and testing under real close conditions. Washcoated cordierite monoliths and foams will be manufactured and characterized in collaboration with F. Oliveira from INETI.
Conceptual modelling and simulation of chemical and environmental systems

Filipe Gama Freire, Francisco Lemos, Susete Martins Dias (EnvERG) and Fernando Ramôa Ribeiro

Objectives

Nowadays the chemical industry is making a giant effort for economical and environmental improvements, using process intensification and optimization among other methodologies that require a high level of understanding. Modelling and simulation can be the best tools to help in this effort.

Conceptual modelling, as it is based on a simple interpretation of reality, can give a comprehensive and easy working image of complex systems such as chemical reactors.

Main achievements

In the last years, successful conceptual models were developed for a gas-liquid-solid catalytic CSTR (GLS-CSTR) reactor for nitrobenzene hydrogenation and for constructed wetlands with pulsed vertical flow (VFCW) in azo-dyes treatment.

This knowledge granted funds from QREN / AdI and FCT projects wich total sum for all partners will achieve some million euros in the next three years.

Nitrobenzene hydrogenation

VFCW for azo-dye treatment conceptual modelling.

In collaboration with ENVERG, VFCW are being studied.

With a new approach, data in non pseudo-stationary state can now be used leading to a great economy of time and efforts. Also, some natural phenomena, such as precipitation and evapotranspiration patterns, can now be regarded as changes in inlet flow. Dye absorption and the intrinsic problems of variable saturation media flow are the major improvements that are being introduced (Figure - 6).
Soya bean oil hydrogenation

Agitated Hydrogenation reactors have some solid dispersed phase separation problems. One of our industrial partners, which has a strong knowledge of these problems and wants to reduce process failures due to agitation (moving parts), challenged us to produce a new design for such reactors. Modelling and simulation suggested a kind of jet loop reactor, which is under construction in order to validate the simulations.

Facilities

A great effort, in terms of work and money, is being done to validate developed models by constructing and/or modifying reactor systems, fast analytics and catalyst characterization. Our group is collaborating with ENVERG, which is also doing a great effort on the role of plants in VFCW by genomic and proteomic plant characterization.
Objectives

Process modelling and intelligent control aims to use advanced process system engineering tools for the analysis and control of nonlinear complex processes. The use of advanced process system engineering tools is often based on a model of the process. Research is focused on: i) development and validation of dynamic models for chemical and biological processes; ii) development of model-based control systems; and iii) development of fault tolerant control algorithms.

Research Topics and Main Achievements

- **Dynamic Modelling, Control and Real Time Optimization of Industrial Fluid Catalytic Cracking (FCC) Processes**

  The optimal performance in FCC units is usually achieved near physical and operating constraints of this process, which makes FCC process a challenging example for the implementation of advanced control and optimization strategies. Current research is focused on nonlinear dynamic modelling, model-based control and optimization of oil refinery nonlinear complex processes such as FCC process. The main goal is to study the possible use of more sophisticated model-based control strategies in order to establish an efficient approach for integrating Model Predictive Control (MPC) and Real-time optimization for FCC industrial units.

  In 2009, the previously developed dynamic model of an industrial UOP FCC operating unit with a high-efficiency regenerator derived from fundamental principles, was upgraded from FORTRAN code into GAMS programming code. The model previous numerical implementation was done in FORTRAN in a sequential modular approach, in order to preserve the modular nature of the blocks, and to facilitate testing different modelling approaches in each block without incurring in the difficulties associated to the global convergence of large sets of differential and algebraic equations (DAE). The model implementation in GAMS code uses an orthogonal collocation method on finite elements to solve the global system of differential equations. The method considers the roots of an interpolation second order Lagrange polynomial function as the collocation points. A particularity is the fact that the length of a fixed number of finite elements changes in an adaptive way to produce the minor possible error by evaluation of one non-collocation point on each element. For example, the riser model was solved in GAMS with 30 finite elements and 3 thousand points in Euler initialization.

  Figure 1 shows the comparison of the results obtained for the predicted flowrate of Vacuum Gas Oil (VGO) along the riser by the same model implemented in FORTRAN and in GAMS with the maximum predicted error of 0.002.

  Figure 1 – Predicted flowrate of VGO and gasoline (GLN) along the riser.
Nonlinear Modelling and Fault-Tolerant Control of a Pilot Scale Distillation Column

In order to overcome the limitations of conventional control, new controllers are being developed which are capable of tolerating component and process faults for the case study of a pilot-scale continuous distillation column at the Chemical Engineering Department of ISEL for the separation of a non-ideal binary liquid mixture of ethanol/water. Figure 2 shows the user interface of the programming task developed in LabView® for the column data acquisition and control system.

In 2009 two main classes of nonlinear black box models were derived: Fuzzy Models, and Composite Local Linear Models, which were estimated directly from experimental data and from simulated data provided by a previously developed First Principles Model implemented in Matlab®/Simulink. These models were used in model based control strategies: Internal Model Control and Nonlinear Model Based Predictive Control. The optimization problem in the nonlinear controller case is addressed using either Branch and Bound and a composition of multiple local linear optimal solutions.

A Fault Tolerant Controller is proposed to cope with an actuator failure. An abrupt failure in the feed flow valve was considered in this work which was simulated as a stuck valve. These methodology detects that one of the inputs does not respond as expected, so use the other inputs as corrective actions. New controller configurations are adopted, which modify the MPC controller in order to safely continue operation.

Expedite Supervision and Control of Decentralized Wastewater Treatment Plants

The objective of this work is the development of an expedite supervision and control system for a decentralized wastewater treatment plant. This framework makes use of on-line data acquisition, partly processed through "software sensors", integrated in a dynamic model structure, which will be used for the design of a multivariable based predictive control strategy for fault tolerant control of the case-study plant. In 2009 a mechanistic nonlinear dynamic model has been developed in MATLAB® to simulate the dynamic behaviour of a real small size WWTP used as case-study (Fig. 3). "Software sensors" providing estimates on output variables and disturbances acting on the WWTP process have also been developed based on routine operational data.

Modelling of SolidLooping Cycle for Carbon Capture and Storage

The process studied in the present work is a post-combustion process which consists in the removal of CO₂ from flue gas with a solid sorbent, limestone. A collaboration was established with the CPSE at Imperial College of London, for the development of a multiscale model in gPROMS software to simulate the post-combustion CO₂ capture based on CaO solid looping cycle. The developed model is based in first principles and takes into account heat and material transfer inside the reactor, particle, main pores and side pores. The structural changes inside the particle were also taken into account in the model by changing the structural parameters at side pores. It was assumed that reaction occurs only inside side pores and the global rate reaction is calculated with base on the local conditions. The model results were compared with experimental data and the results are similar.
General Objectives

One of the main goals is to develop scientific basis, technological knowledge and intellectual property ground in order to design and synthesize new reactive polymers, primarily by using renewable resources, as well as, the design and manufacture of new polymers using developed reactor systems. The knowhow acquired is aimed to provide qualified and useful collaboration with the industry.

Mission and Scope of Activities

To contribute to the well recognized scientific prestige of IBB and IST in the Chemical and Biological Engineering field.

To stimulate young scientists and engineers for the field of industrially applied research, contributing to the success of their research activities, and latter on for their successful integration in the Industry.

Main Research Areas:

a) Catalysis and Mechanisms of Polymerization Reactions; b) New Functional Polymers. c) New polymer films with controlled permeability for energy production (Salinity power process).

Progress

A start review of the progress in each of the working lines is presented together with the forecast actions. The projects were mainly funded by FCT and QREN/Adi.

Surgical suturing and stapling have been so far the most common clinically procedures to fasten soft body tissues together; however numerous disadvantages have been reported. Generally, biodegradable urethane-based prepolymers containing free isocyanate groups have excellent physical properties in addition with blood and tissue compatibility which sustained their use as biomaterials.

The aim of this work was to develop urethane-based polymers containing free isocyanate groups capable of reacting with the amino groups present in living tissues and several new polymers were obtained and characterized.

The in vitro cell culture experiments performed in some formulated polymers shown that 3T3 mouse fibroblast cells could adhere to the surface of the polymer and proliferate over time with low toxic response.

The cell adhesion to the polymer surface was also observed by SEM micrographs. Despite this good results, the intense used of catalysts proved to be essential due to undesired polymer curing times. Catalysts with low water affinity will be tested, with further improvement of the prepolymer structure.
The development of new polyester structures with biodegradable segments and biocompatibility has started and samples with new structures were already supplied to the industrial partner for mechanical testing.

In the scope of a QREN project in cooperation with the company Multirecolha (Multirecolha-Recolha de Resíduos Industriais para Reciclagem, Lda) the study of the used vegetable oil is being performed. The separation of this components, which have a deep influence on viscosity, limiting their used as fuel raw material, as well the separation of other non-desirable components, will be implemented at Multirecolha, after a carefully scale-up.

Isocyanate terminated prepolymers are replacing all the other polymers that in the past were used for the production of cork agglomerates and specially in the field of technical stoppers, class in which the stoppers for champagne are included. The qualification and certification for food contact have been performed for many years by laboratories in France, Germany and more recently in United States of America.

In cooperation with company Fabrines-Produtos Quimicos, S.A. and with National Institute for Health (INS), within the scope of a QREN project, new polymers are being developed utilizing renewable raw materials and the aggregated samples will be interactively extracted and qualified by INS.

New surface active agents based on renewable raw material were successful synthesized and samples delivered to Protec & Gamble (Germany) and CIBA (UK). Comparative tests were performed against other surface active agents and the performance was considered outstanding (“better than Ariel”). New surfactants with higher HLB are being synthesized in order to cover a larger range of technical requirements.

New methodologies for the synthesis of C-glycosylflavonoids employing rare-earth metals based catalysts have been investigated under the main theme of catalysis. These compounds are widespread in nature and are embodied of a great biological significance. Bioactivities such as anxiolytic, anti-diabetic, Anti-hypercholesterolemic, anti-oxidant among others are presented by those polyphenolic derivatives. The studies conducted over the last year involved the optimization of the one pot synthesis promoted by lanthanides triflates as an alternative to the classical methodologies. A coupling reaction followed-up by a in situ rearrangement, commonly known as Fries-type rearrangement, leaded exclusively to the aimed molecules. Different reaction conditions such as solvent mixtures, temperatures, and reaction time were tested. The desired compounds were synthesized and characterized by NMR experiments.

Ultrasounds were also applied in order to shorten the reaction time and to enhance the catalyst performance. The results encourage us to continue to develop this methodology in order to access those compounds in a very simple and easy way.
General Objectives
The main goal of this research is to develop scientific basis, technological knowledge and intellectual property ground for solving industrial problems related with environment and energy utilization, contributing to the optimization of new cleaner processes and fuels for industrial and motor use, with the development of newer and improved unit operations and techniques. The acquired knowhow is aimed to provide qualified and useful collaboration with the industry.

Mission and Scope of Activities
To contribute to the well recognized scientific prestige of IBB and IST in the Chemical and Biological Engineering field. Also, to stimulate young scientists and engineers for the field of industrially applied research, contributing to the success of their research activities, and latter on for their successful integration in the Industry.

Main Research Areas:
a) Development of heterogeneous catalysts for biodiesel production; b) Development of new absorbant substances and techniques for CO2 capture; c) Use of new membranes for wastewater and energy production (Salinity Power process).

Progress
A review of the progress in each of the working lines is presented together with the forecast actions. The projects are mainly funded by FCT and QREN/Adi.

♦ Biodiesel, as a renewable fuel, can be used in conventional diesel engines, pure or mixed with conventional diesel, without significant modifications of the engine. This fuel has higher O2 content than petroleum diesel and its use in diesel engines have shown great reduction in the emission of particulate matter, CO, SO2, polyaromatics and other hydrocarbons. In addition, burning of vegetable-oil based fuel does not contribute to net atmospheric CO2. Biodiesel (FAME) is mostly produced through a transesterification reaction between a lipid source and an alcohol yielding a mixture of long chain esters and a valuable co-product, glycerol. An important drawback related with the use of homogeneous catalysts in biodiesel production is that they have to be neutralized after the end of the reaction, thus producing salt streams. Therefore, there is currently a drive towards the development of industrial processes for biodiesel production using solid catalysts. The key benefit of using these heterogeneous catalysts is that no polluting by-products are formed and the catalysts do not mix with biodiesel and can be covered and reused. In addition to lower separation costs, less maintenance is needed as these catalysts are not corrosive. Several experiments were performed in a glass batch reactor, in order to promote the conditions for transesterification reaction with solid alkaline catalysts.

Figure 1. FAME content and density (by NIR) for the diesel phases obtained using the prepared catalysts (T=67°C, Wcatalyst/Woil=5%, methanol/oil=12:1 molar ratio, reaction time=4h)

From the presented results it can be inferred that CaO and CaO modified with Li are promising catalysts. In fact, these catalysts showed high catalytic activity and stability with biodiesel yields higher than 93% for both reaction batches. So they will be further studied in detail.
The capture of CO₂ from flue gases can be done by chemical absorption with aqueous amine solutions like MEA (monoethanolamine): Although this is a proven process, there are still some operational problems to be overcome, namely those resulting from solvent degradation, precipitation, corrosion and foaming. Apart from that, the absorption capacity of the most current amines should be improved in order to obtain a more profitable operation. It has been shown previously that relationships exist between the amine structure and the activity and capacity for CO₂ absorption. Apparently, the introduction of amine substituents at the α-carbon creates a carbamate instability, which causes the hydrolysis to go faster, thus increasing the amount of bicarbonate, allowing for higher CO₂ loadings. To obtain a better understanding of the structure-activity relationship it is necessary to perform solvent screening experiments, in order to investigate the effect of variables such as chain length, increase in number of functional groups, side chain at α-carbon position, alkyl group position in cyclic amine and side effect of cyclic amine with different functional groups. The description of these effects, in a quantitative way, on the initial rate of absorption for CO₂, as well as the capacity of various solvents for CO₂ absorption is also supported by simulation and will greatly benefit on designing more efficient absorption systems for CO₂ capture from flue gases.

Pickling of stainless steels is a very important process because of the increasing surface quality standards and increasing consumption of stainless steel products in the chemical, petrochemical, construction and food industry accounting for 25x10⁶ ton of processed steel. The most important stainless steel pickling acid in use is the mixture of nitric and hydrofluoric acid. The combination of nitric and hydrofluoric acid is also used for pickling of titanium. Nitrogenous compounds in the arising pickling process water, like nitrate, have to be eliminated before the disposal of wastewater. Previously it was shown that most pickling process waters contain no organic carbon, and therefore it is necessary to dose a low cost and easy biological degradable carbon source. Investigations with different industrial carbon sources like methanol, lactose or sugar concentrate from food industry, desulfurification water from steel industry or organic acids regenerated by the disposal industry were performed. Main results regarding these investigations is, that for optimal and most cost effective biological nitrate reduction different carbon sources have to be mixed to give the all necessary nutrients, and the treatment costs were also estimated. Regarding the costs for biomass retention an adaptation of the filtration membrane is important. Investigated polymer membranes showed a low filtration performance because of membrane fouling. These effects can be avoided by the development of a polymer membrane with special regard to the demand of the biological treated pickling process water. An operational concept has been developed and successfully proved in bypass tests. A nitrate elimination of 100% was achieved in laboratory and operational bypass tests. The implementation of the developed process in operational scale by this pilot and demonstration project is an logical and important step to the zero emission strategy for pickling with nitric and hydrofluoric acid. For this purpose, the research included the development of newer specific membranes. The performed chemical and biological resistance test points out to a membrane structure with a polyamide selective layer over a polyamide support layer. This type of asymmetric membrane structure was prepared by a thin film coating process over a pre-casted porous layer of polyamide. This support layer acts most as mechanical support, since the selective layer is very often prepared with a thickness below 100Å, and carefully controlled microporosity to avoid excessive salt loss. For the special application to TFC (Thin Film Composite) membranes, the interfacial polymerization was conducted in unstirred system. The first results indicate that none of the three composite membranes types present high rejection to NaCl, but the EAP-TMC thin film shows higher percentages of rejection, around 25-30%. Comparative selectivity tests for composite membranes with chemically different thin films were also performed.

Pickling of stainless steels is a very important process because of the increasing surface quality standards and increasing consumption of stainless steel products in the chemical, petrochemical, construction and food industry accounting for 25x10⁶ ton of processed steel. The most important stainless steel pickling acid in use is the mixture of nitric and hydrofluoric acid. The combination of nitric and hydrofluoric acid is also used for pickling of titanium. Nitrogenous compounds in the arising pickling process water, like nitrate, have to be eliminated before the disposal of wastewater. Previously it was shown that most pickling process waters contain no organic carbon, and therefore it is necessary to dose a low cost and easy biological degradable carbon source. Investigations with different industrial carbon sources like methanol, lactose or sugar concentrate from food industry, desulfurification water from steel industry or organic acids regenerated by the disposal industry were performed. Main results regarding these investigations is, that for optimal and most cost effective biological nitrate reduction different carbon sources have to be mixed to give the all necessary nutrients, and the treatment costs were also estimated. Regarding the costs for biomass retention an adaptation of the filtration membrane is important. Investigated polymer membranes showed a low filtration performance because of membrane fouling. These effects can be avoided by the development of a polymer membrane with special regard to the demand of the biological treated pickling process water. An operational concept has been developed and successfully proved in bypass tests. A nitrate elimination of 100% was achieved in laboratory and operational bypass tests. The implementation of the developed process in operational scale by this pilot and demonstration project is an logical and important step to the zero emission strategy for pickling with nitric and hydrofluoric acid. For this purpose, the research included the development of newer specific membranes. The performed chemical and biological resistance test points out to a membrane structure with a polyamide selective layer over a polyamide support layer. This type of asymmetric membrane structure was prepared by a thin film coating process over a pre-casted porous layer of polyamide. This support layer acts most as mecha-
Publications

Journals and Conferences

Books/Book Chapters


Articles in International Peer-Reviewed Journals


Proceedings (Oral Presentations)


Bordado, J.C., Fernandes, S., Fernandes, T.F., Downes, S., “Development of a polyurethane-based pre-polymer to be applied as a bioadhesive”, X Congreso Adhesión y Adhesivos, Alicante, Spain, September


Fonseca, N., Santos, L.R.M., Lam, Y.L., Lemos, F., Ramôa Ribeiro, F., “Catalytic Cracking of Fisher-Tropsch Naphtha Fraction with ZSM-5 Zeolite”, EuropaCat IX–Catalysis for a Sustainable World, Salamanca, Spain, August-September


dos Santos, R.G., Fonseca, T., Bordado, J., Rauter, A.P., “Sugar as Scaffolds in Eco-Friendly Reactions Promoted by Lanthanides Triflates”, ICHAC 9, Oviedo, Spain, June-July


Proceedings (Poster Presentations)

Ferreira, C., Tayakout, M., Guibard, I., Lemos, F., Touilhoat, H., Ramôa Ribeiro, F., “Model for a catalyst sequence in residue hydrotreatment reactors”, EuropaCat IX–Catalysis for a Sustainable World, Salamanca, Spain, August-September


Matias, P., Lopes, J.M., Magnoux, P., Guisnet, M., Ramôa Ribeiro, F., “Effect of desilication of a TON zeolite on its physical and catalytic properties”, EuropaCat IX–Catalysis for a Sustainable World, Salamanca, Spain, August-September


dos Santos, R.G., Neng, N., Nogueira, J., Bordado, J., Rauter, A.P., “C-Glycosylphenolic derivatives – Studies Towards the use of Lanthanide-based Catalysts as a Reliable Alternative for their Synthesis”, EuropaCat IX, Salamanca, Spain, August-September
Vázquez, N.A.R., Valdês, B.S.G., Fernandes, S., Moura, J.C., Bello, A., “Resonancia Magnetica Nuclear de H y 13 C de Pre-polímeros”, XXII Congreso Nacional de la Sociedad Polimérica de México, Colima, Mexico, October

Master and PhD theses completed
Master (Post-Bologne)
Alberto Silva Servia “Enhancement of a hydrocracking pretreatment kinetic model”, IST (Supervisors: Fernando Ramoa Ribeiro, Helena Gonzales-Peñas)
Alexandre Jorge Salgueiro Chambel “Modelling of solid looping cycle for carbon capture and storage”, IST (Supervisors: Carla Pinheiro, Costa Pantelides)
Ana Filipa Ferreira da Silva Dionísio “AltaFoam Monitor Optimization”, IST (Supervisors: João Bordado, Aster de Schrijver)
Ana Luísa Aires Duarte “Analysis of the various parameters influencing the fixation of EPS panels to walls using various One Component PU foams in aerosol cans and pressure vessels”(Supervisors: João Bordado, Aster de Schrijver)
Ana Luísa do Val Moreira Serra, “Aditivos para estabilização de cor e estrutura de monofilamentos poliméricos”, IST (Supervisors: João Bordado, Humberto Ferreira)
Anabela Gonçalves Nogueira “Synthesis of inorganic fullerene-like sulfide catalysts: Application in hydrotreatment catalysis”, IST (Supervisors: Fernando Ramoa Ribeiro, Denis Uzio)
Andrea Joana Paiva Carvalho Mota “Development of an one component PU foam system in aerosol cans, with a free MDI monomer content of less than 1% of the total chemical weight”, IST (Supervisors: João Bordado, Aster de Schrijver)
Bruno Santos Custódio “Controlo estatístico e análise multi-variada de um processo industrial de produção de Cremes para barrar”, IST (Supervisors: Carla Pinheiro, Ana Paula Guedelha)
Carina Domingues, “Avaliação dos níveis de concentração de poeiras suspensas em atmosferas interiores”, ISEL (Supervisors: João Gomes, Paula Albuquerque)
Catarina Ministro, “Implementação e validação do método de determinação de metais e fósforo por ICP em biodiesel”, ISEL (Supervisors: João Gomes, Maria Lobato)
Cátia Folgado Saturnino Gordicho Costa “Cumene oxidation to cumene hydroperoxide”, IST (Supervisors: Filipa Ribeiro, Jesus Lazaro Munoz)
Célia Lourenço, “Cromatografia Preparativa: Caracterização e Purificação de Produtos e Impurezas com Aplicação na Indústria de APIs”, ISEL (Supervisor: João Gomes, António Ramos)
Clara Sofia Rodrigues Sá Couto “New Bifunctional Catalysts for the deep conversion of vacuum residues”, IST (Supervisors: Fernando Ramoa Ribeiro, Denis Uzio)
Cláudia Silva, “Desenvolvimento de uma Ferramenta de Cálculo para Determinação da Pegada de Água”, ISEL (Supervisors: João Gomes, Cátia Carías)
Daniel Vergueiro, “Produção de Biodiesel a partir de Matérias-Primas Ácidas e de Gorduras Animais”, ISEL (Supervisors: João Gomes, Joana Correia)
Duarte Miranda Neiva “Development of accelerated
test-method to study the influence of the stem composition on the valve stability for polyurethane foam cans" IST (Supervisors: João Bordado, Aster de Schrijver)

Fábio Emanuel Mendes Fernandes "Pré-Polímeros de MDI: Ensaios de síntese de novos ligantes reac- tivos e desenvolvimento de adesivos monocompone ntes" IST (Supervisors: João Bordado, Ricardo Spencer)

Filipe Manuel Marques Mota "Selective Hydrogena tion Catalysts: Poisoning with Silicon" IST (Supervisors: Fernando Ramôa Ribeiro, Anne-Claire Dubreuil)

Helena Domingos, "Development of membranes for purification of liquid effluents from stainless steel pickling" ISEL (Supervisors: João Bordado, João Gomes)

Inês da Mata Cecílio "Study of Simulated Moving Bed Reactor (SMBR) for para-xylene produc tion" IST (Supervisors: Fernando Ramôa Ribeiro, D. Leinekugel-le-Coq)

Inês Isabel Viana Pacheco dos Santos "Avaliação do desempenho do sistema de determinação das características do gás natural em pontos de amostragem (in loco) e da funcionalidade gas quality tracking" do simulador dinâmico de fluidos" IST (Supervisors: Henrique Leite, Carlos Hen riques)

Joana Bernardo, "Catalisadores heterogêneos básicos para a produção de biodiesel", ISEL (Supervisors: João Gomes, Joana Correia)

Joana F. L. Pereira, "Modified metal-zeolite catalysts for Selective Catalytic Reduction of NOx with meth ane" Supervisors: C. Henriques e S. Capela (Gaz de France-Suez)

João Dionísio Teixeira de Sousa "Characterization of the acid-base properties of (gamma)-alumina by model reaction: Sodium and sulphate ion effects" IST (Supervisors: Fernando Ramôa Ribeiro, Patrick Magnoux)

Joaquim Guilherme Gandara Marques "Estudo Sis temático dos Aspectos de Perigosidade no Ar mazenamento de Produtos Químicos" IST (Supervisors: João Bordado, Lúelia Penedo)

José Oliveira, "Contribuição para o estudo da in corporação de materiais poliméricos em membranas betuminosas" ISEL (Supervisors: João Bordado, João Gomes)

Karina Silvestre Veloso "Optimization of the waste water treatment in the refinery of Grandpuits: Re duction of the pollutant charges in the source; opti mization of the physical-chemical treatment and the final discharge" IST (Supervisors: Filipa Ribeiro, Elisabeth Doyelle)

Luis Carvalho Pereira de Oliveira "Stochastic kinetic and complex network: Application to oligomeriza tion process" IST (Supervisors: Fernando Ramôa Ribeiro, Denis Guillaume)

Luís Pereira, "Catalisadores heterogêneos básicos para a produção de biodiesel" ISEL (Supervisors: João Gomes, Joana Correia)

Luis Pedro Hernandez Martins "Ethanol from wheat straw: Experimental design and economical evaluation for optimization of the operating conditions of dilute acid pretreat ment" IST (Supervisors: Fernando Ramôa Ribeiro, Dominique Casanave)

Maria Leonor Rodrigues Alves "Liquid phase Sulfa tiation of NiMoP gas oil catalysts: Influence of sulfi dation additives on gas oil HDS and HDA" IST (Supervisors: Fernando Ramôa Ribeiro, Antoine Hugon)

Marta Sofia Paulo da Silva "Improvement study of the Grandpuits? refinery crude oil distillation pre heat train" IST (Supervisors: Filipa Ribeiro, Marie Andrée Senegas)

Miguel António Alves Fiuça "Estudo da eficiência de revestimentos fotocatalíticos na decomposição dos NOx e suas propriedades auto-limnantes" IST (Supervisors: Carlos Henriques, Maria de Fátima Piteira)

Pedro Manuel Mendes Rivotti "Modeling of vacuum residue hydrotreatment: Impact of the feedstock description on model output" IST (Supervisors:
Fernando Ramoa Ribeiro, Victor Costa

Raquel Alexandra Coelho Bértolo, “Preparação e avaliação das propriedades catalíticas de materiais do tipo SAPO-11 na hidroisomerização de n-deceno”, ISEL (Supervisors: Ângela Nunes, Auguste Fernandes, Filipa Ribeiro)

Rebeca Maria Ferreira Lourenço “Hydrogenation of alpha-Methylstyrene”, IST (Supervisors: Filipa Ribeiro, Rosario Rodríguez Pardo)

Ricardo Franco, “Optimização da lixiviação de um concentrado de sulfureto de zinco”, ISEL (Supervisors: João Gomes, Joana Correia)

Rui Manuel Ferreira Monteiro “Optimização de Processo de Tratamento de Efluentes: Estudo comparativo de cinéticas de floculação e avaliação do potencial fertilizante das lamas espessadas”, IST (Supervisors: João Bordado, Henrique Gama)

Sandra Gabriela Bagagem da Silva “Development of Low Density Polyurethane Foam Systems ( Megafoam) Dispensed out of an Aerosol Can and Applied by a Dispensing Gun or Straw Adapter at Different Ambient Conditions”, IST (Supervisors: João Bordado, Aster de Schrijver)

Sandro Matos, “Study of the production of polyurethanes from polyesters at pilot plant scale”, ISEL (Supervisors: João Bordado, João Gomes)

Susana Lopes Silva “Study of Hydrocracking catalysts based on modified USY zeolites”, IST (Supervisors: Fernando Ramóa Ribeiro, Laurent Simon)

Tiago Filipe Francisco Lopes “Synthesis and Evaluation of Bifunctional Catalysts for Biofuels Production”, IST (Supervisors: Fernando Ramóa Ribeiro, Cuong Pham-Hua)

Tiago Fonseca, “Production of Polymer-Surfactants from Bio-Materials”, IST (Supervisors: João Bordado, João Gomes)

Tomy Alves, “Extracção líquido-líquido do ferro de soluções produzidas na lixiviação de um concentrado de sulfureto de zinco”, ISEL (Supervisors: João Gomes, Joana Correia)

PhD

Cristina Loureiro da Silva Ferreira, “Modelização do processo de hidrotanamento de resíduos em leito fixo
- Estudo da reactividade da carga”, IST (Supervisors: Fernando Ramóa Ribeiro, Hervé Touihoc; Co-Supervisor: Francisco Lemos)


Sandra Cristina de Oliveira Capela, “Estudo Meccanístico do Processo de NOx: Activação do Metano com NO2 sobre Pd Co Ferrierite, IST (Supervisors: Carlos Henriques, Filipa Ribeiro)

Patents


Industry contract research

CRERG has actively developed collaborations with
industrial partners in Portugal. Researchers from CRERG have cooperated in the production increase activities undertaken by CUF in their reactor for the production of aniline. This work has involved the analysis of the reactors that were operating, building of a model that allowed the analysis of the way the reactor was functioning and proposing new operating conditions that have been implemented in the reactor. This work has continued throughout 2008 and will be pursued in the future with the development of more detailed models that can account for the production of secondary products so that the operating conditions can be further improved, not only to ensure an increased production but also to reduce unwanted products and reduce separation costs. A journal publication was produced in association with this project (J. Relvas, R. Andrade, F.G. Freire, F. Lemos, P. Araújo, F. Ramôa Ribeiro, “Liquid Phase Hydrogenation of Nitrobenzene over an Industrial Ni/SiO2 Supported Catalyst”, Catal. Today, 133-135 (2008) 828-835.). An additional goal is to allow the operation to be carried-out at higher temperatures so that the reactor, where the highly exothermic reaction is taking place, can be used to produce high-quality steam. Funding for this project has been requested under QREN.

CRERG is also participating in a Science for Peace project that involve various academic partners in NATO and industrial and academic partners in Russia. The goal of this project is to produce reliable analytical methods for the detection of chemical warfare agents and CRERG participation is related to the analysis and modelling of the adsorption/desorption processes on porous materials.

Internationalization

There are several PhD thesis that are being undertaken as double degrees between IST-UTL and the Univ. of Poitiers, IFP (Institut Français du Pétrole) and Univ. Pierre et Marie Curie (Paris); there is also a collaboration with the Univ. of Caen, Univ. Haute Alsace (Mulhouse). CRERG collaborates with Univ. Granada (Spain) and Petrobrás (Brazil). Participation in the Science for Peace project “Chemical threat detectors based on multisensor arrays and selective porous concentrators” involves various academic and industrial partners in NATO countries and Russia.

Outreach/Science and Society

CRERG members actively produce contents in the areas of Chemistry for the e-learning scientific website “e-escola” (in Portuguese) (http://www.e-escola.pt). The scientific contents (at basic, medium and advanced levels) focus on Chemical Equilibrium, Kinetics and General Chemistry. This e-learning resource is being used by high-school students, by university students attending various courses and by the common citizen, depending on the thematic and the approach level. E-escola is being assessed (around 50,000 visits/month) from Brazil (40,000 visits/month), Portugal (15,000/month) and from Angola, Mozambique and the USA (300, 250 and 200 visits/month respectively).

CRERG members also participate in science divulging activities, like the Open Laboratories at IST, with interactive experiments on catalysis.

Facilities

CRERG is currently a well equipped laboratory for the study of heterogeneous catalysis, with a wide range of equipment to support the research made within the group and to support the community. Laboratories include:

- **Synthesis / modifications and Characterization**
  - The preparation laboratory also allows various basic/common techniques to fully characterize the freshly prepared catalyst. This includes:
    - X-Ray diffraction – this technique allows to check both purity and crystallinity of the synthesized materials and the presence of amorphous phase/imurities.
    - Thermogravimetry and differential scanning calorimetry analyses –templates decomposition, dehydration, phase changes, etc…
    - Nitrogen adsorption –evaluation of solids specific surface area, as well as micro/ mesopores volume (zeolites, aluminophosphates, mesoporous).
    - TPR/TPO/TPD measurements - temperature-
programmed experiments including reduction, oxidation, desorption, pulse chemisorption (H2/CO) and temperature programmed reaction.

- Mass spectrometry.

UV-Vis/IR Spectroscopy Laboratory

UV-Vis/IR Spectroscopy Laboratory is part of the Zeolites Laboratory and is specially devoted to UV-Vis/DRS (diffuse reflectance spectroscopy) and infrared spectroscopies for heterogeneous catalysts characterization. The laboratory is equipped for basic spectroscopies techniques, which include:

- IR with KBr pellets for powders.
- IR / ATR (Attenuated total reflectance) for liquids and films.
- UV-Vis spectroscopy for liquid solutions.
- UV-Visible/DRS for films and powders.

There is also equipment for in-situ and Operando techniques that allow the observation of the catalysts during in-situ thermal treatments and/or in contact with different probe molecules for specific purposes:

- with basic molecules (pyridine, CO, etc…) to evaluate qualitatively and quantitatively the acidity of the support.
- with NO, CO, to evaluate the characteristics of the metallic species adsorbed at the surface of the catalysts (oxidation state, coordination, metal dispersion).
- with molecules of similar nature when compared with reagents used for catalytic processes – simulate and characterize the interaction reagent-support.

Dynamics and Catalysis

CRERG is also equipped for the testing of heterogeneous catalysts under dynamic conditions, using custom in-house built apparatus. There are various apparatus to test catalysts at ambient pressure using in-line gas-chromatographic analysis, and also apparatus for high pressure reactions, namely to perform hydrogenation reactions.

It is also equipped with a simultaneous TG/DSC apparatus which, apart from the work done on projects developed by the group is also used in collaboration with the Analysis Laboratory of IST to perform analysis for various entities.

There is also equipment to perform dynamic electrochemical experiments, notably cyclic voltammetry and controlled potential electrolysis.

In order to support some of the projects, there are also facilities to perform molecular modelling calculations at various levels, from semi-empirical to ab initio and dft quantum models.

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In order to support some of the projects, there are also facilities to perform molecular modelling calculations at various levels, from semi-empirical to ab initio and dft quantum models.
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