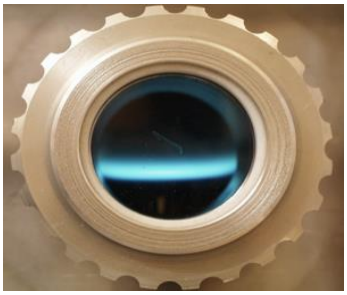
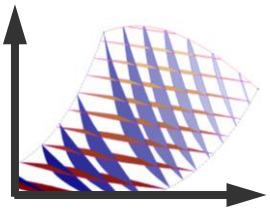
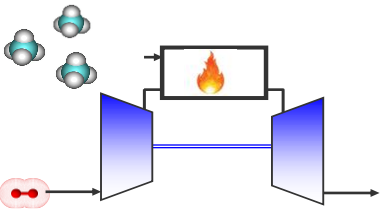
Laboratoire Réactions et Génie des Procédés
LRGP - UMR CNRS - UL 7274

PROCESS ENGINEERING FOR ENERGY







LABORATOIRE
RÉACTIONS
ET GÉNIE
DES PROCÉDÉS

LRGP - Laboratoire Réactions et Génie des Procédés - UMR 7274
1 rue Grandville - BP 20451
54001 Nancy Cedex

Contact: Laurent Falk, Head of the laboratory
laurent.falk@univ-lorraine.fr

Table of contents

INTRODUCTION ____ *5*

PART 1 : Presentation of tools and methodological skills, present in the LRGP, related to the topic "Process Engineering for Energy" ____ *13*

THERMODYNAMIC MODELLING OF FLUID MIXTURES ____ **14**

PROCESS AND PRODUCT DESIGN METHODOLOGIES ____ **16**

TOOLS FOR EXERGY ANALYSIS ____ **18**

TOOLS FOR PINCH ANALYSIS AND PROCESS INTEGRATION ____ **20**

TOOLS FOR PROCESS INTENSIFICATION ____ **22**

TOOLS FOR ENVIRONMENTAL ANALYSIS ____ **24**

KINETIC STUDY OF PYROLYSIS AND COMBUSTION REACTIONS ____ **26**

SOLID FUELS THERMAL CONVERSION ____ **28**

EVALUATION OF PERFORMANCE IN MEMBRANE FUEL CELLS ____ **30**

BIOPROCESS ENGINEERING FOR ENERGETIC BIOMOLECULES ____ **32**

PART 2: Overview of research studies dealing with energy issues at the LRGP ____ *35*

Oil & gas ____ **36**

EXPLORATION & PRODUCTION: THERMODYNAMICS ____ 36

EXPLORATION & PRODUCTION: KINETICS ____ 37

OIL REFINING ____ 38

Biofuel ____ **39**

METHANE THROUGH BIOPROCESSES ____ 39

SYNGAS THROUGH GASIFICATION ____ 40

BIODIESEL THROUGH TRANSESTERIFICATION ____ 41

AROMATICS THROUGH DEOXYGENATION ____ 42

H_2 ____ **43**

H_2 THROUGH REFORMING ____ 43

H_2 THROUGH MICROBIAL PROCESSES ____ 44

H_2 PHOTOPRODUCTION ____ 45

MEMBRANE FUEL CELLS ____ 46

Combustion ____ **47**

JET FUEL THERMAL DECOMPOSITION ____ 47

AUTOMOTIVE FUEL COMBUSTION ____ 48

ALTERNATIVE FUELS IN GAS TURBINES 49

Heat & Power 50

POWER CYCLE 50

INNOVATIVE FLUIDS FOR ENGINES AND CYCLES 51

NUCLEAR FUEL CYCLE 52

ABSORPTION HEAT PUMPS 53

Heat 54

THERMAL INSULATION 54

CO_2 55

CARBON CAPTURE AND STORAGE 55

CARBON CAPTURE AND USE 56

Process 57

ENERGY NETWORK 57

PROCESS INTENSIFICATION 58

PROCESS SYSTEMS ENGINEERING 59

List of technical software and databases used as tools by LRGP researchers for addressing energy issues 61

Databases 62

Software 62

Index 65

INTRODUCTION

▶ The challenges of energy transition in chemical engineering

TTransformation processes of raw materials into basic or specialty products for chemicals, materials, food, energy or services are confronted with the considerable challenges of sustainable development, where energy is at the forefront. Currently, the chemical industry operates largely as an open system, heavily dependent on non-renewable and cheap resources, but environmental and economic constraints will be major challenges for the plant of tomorrow.

These challenges of **limiting the environmental footprint of transformation processes and products** are found in multiple critical issues which strongly interact with each other and which are confronted by fast dynamic evolution including: climate change, scarcity of fossil resources, problems accessing cheap energy, water and food resources, population increase accompanied by increased urbanization, erosion of biodiversity and soils, pollution and waste management, safety, health and well-being.

The **energy transition** and the **mitigation of CO_2 emissions** are then key challenges in chemical engineering. In order to mitigate CO_2 emissions and environmental impacts, industry is seeking to increase **energy and resource efficiency** (i.e. reduce the energy intensity) of its processes. Significant results have been achieved in the chemical industry over the last 20 years, but further improvement is required. Energy consumption has halved for a production that has doubled, resulting in a 55% reduction in greenhouse gas emissions, and today one euro of added value by the chemical industry generates 59 grams of hazardous industrial waste and 1.6 kg of CO_2[1].

The means of reducing energy intensity affect the entire transformation chain, starting with the synthesis process for which the **principles of green chemistry** can be applied (e.g., atom economy, choice of milder operating conditions and more efficient solvents, improvement of catalysts to reduce working temperatures etc.).

The **development of energy-efficient separation systems** is also a major challenge for energy reduction. Traditional operations such as distillation are known to be energy consuming operations. For instance, the U.S. Dept of Energy estimates that the distillations units in North America consume about 40% of the total energy used to operate plants in the refining and bulk chemical industries. The challenges are to replace distillation by less consuming downstream units and / or to drastically reduce energy consumption through **process intensification** such as distillation wall columns. The **development of thermodynamic models**, combined with experimentation, is also essential for a better understanding of the behavior of complex fluids involved in processes and also to propose **new thermodynamic cycles** for energy applications.

While each single operation can be improved independently, it is also necessary to have an overall view of the whole process, in which the reaction and separation steps have to be optimized together. In this global vision, **energy integration**, but more generally **the recovery of fatal heat**,

[1] ref, Economic changes in the chemical industry, PIPAME report, February. 2010

is one of the methods of energy saving. In France, ADEME estimates that waste heat (or fatal heat) from industry represents a pool of more than 100 TWh of which 60% is at over 100 °C.
But energy recovery and energy integration may have a significant capital cost, which can make the proposed solutions unsuitable for application. The challenge therefore lies not only in improving synthesis and separation conditions, but also in **reducing the capital expenditure (CAPEX)**.

The **increasing use of decarbonized renewable energies** (biomass, wind and sun) raises the problem of a possible energy market taking into account the decarbonized rate, with a penalty that may vary, which will be highly volatile depending on time and place. In the case of industrial sectors where the energy cost of the final product is high, it can be expected that **intermittent and flexible processes** will have to be designed that can be quickly shut down or restarted or that operate at certain periods of the year when supply is plentiful, and prices are low. The challenge of process engineering therefore also concerns the **design of intermittent processes** that can respond to variations in operation without reducing product quality (performing catalysts, mechanical strength of materials, thermal insulation, design of adapted architectures etc.).

Another aspect specifically concerns **energy conversion processes and power production, CO_2 capture and its reuse** and the integration of renewable energy sources. These are oriented towards optimizing non-renewable resources (oil and gas) but also towards seeking new sources and transformation of renewable energy sources including **biofuels and bio-products**, technologies for production, **energy management and storage**.

The use of **bio-sourced materials** is an important and promising issue, but it raises challenges, first and foremost that of the land **competition between energy, raw materials and food**. This requires the development of rational **transformation processes in biorefineries** that make full use of all resources with respect to the reduction in greenhouse gas emissions. **Life cycle assessment** (LCA) is then an integral part of both environmental and energy assessment methods which has to be considered for the design and the improvement of new processes. The substitution of materials derived from petroleum with bio-sourced products also requires the **development of alternative and adapted processes and catalysts**. The rational processing of bio-sourced materials remains a difficult task because it is a complex matter, in particular with regard to variability if the collection, sorting and separation systems are not adequately ensured. This variability can also be found in the composition of bio-sourced raw material according to the nature of the soil, fertilizers, seeds, climate etc. Last but not least, variability can also be affected by price volatility in a context of tighter supply and demand markets.

More than 80% of the world's **energy is produced by burning fossil fuels and biofuels**. Even with the development of renewable energies, **combustion processes** will remain essential for a long time to come and are evolving to improve efficiency and limit CO_2 and pollutant emissions. It is important to develop new technologies for internal combustion engines operating at lower temperatures and in partially or totally homogeneous mixtures, thus reducing the formation of

particles and NOx. **Energy issues are therefore closely linked to environmental issues in order to limit emissions of pollutants** such as nitrogen oxides and particulate matter, which are responsible for around several hundred thousand premature deaths in Europe each year. The challenges of **improved theoretical combustion and pyrolysis models** are therefore related to a **better understanding of the combustion chemistry of new types of fuels entering the market** (e.g. biogas from methanization, which also contains traces of sulphur and nitrogen compounds, and fuels from biomass pyrolysis, also known as bio-oils, made up of many oxygenated, sometimes nitrogenous molecules).

Chemists and chemical engineers have the ability to meet energy challenges by developing innovative materials for several applications. Making an exhaustive list of all chemistry's contributions in the field of energy would be utopian, but among the different sectors the following can be cited: **sustainable mobility** (energy for vehicles, lighter materials, bonding rather than welding), **sustainable housing** (building insulation, multifunctional coatings), new materials with the properties required to achieve **energy conversion systems** (batteries, super-capacitors, fuel cells, membrane electrolysers, photovoltaics), and new and improved **energy storage technologies** (batteries and hydrogen).

Regarding electric mobility, in order to get beyond the 500 km range, new battery technologies under development such as lithium-sulphur technology show real potential. Fuel cells achieve electrical conversion efficiencies in the order of 40%, well above those of combustion engines (nearly 25%)[2]. Used in co-generation of heat and electricity, this efficiency easily reaches 90%, and cogeneration systems can now be designed from a few kilowatts (micro-home cogeneration) to several megawatts (collective buildings, commercial, public or industrial buildings). The challenges concern the **development of catalytic electrodes with reduced platinum content** (or without platinum) and high-performance proton conductors, and the **increase in the lifetime** of these systems. As a matter of fact, electric mobility implies enormous needs for metallic raw materials while resources are limited. Despite improvements in electrochemical conversion systems, **the reduction of the consumption of catalytic or mineral elements** will not be sufficient. This indirectly raises the problem of **recycling and recovery of metallic elements**, for which chemical engineering has to invent and develop new hydrometallurgical processes.

The hydrogen carrier is one of the storage solutions for renewable energies. To date, it is produced mainly through reforming from fossil fuels with a high CO_2 emission, but the use of biomethane could become a green substitution solution. The development of **intensified reforming reactors** opens interesting economic prospects for the development of the **hydrogen economy**. Other prospects include hydrogen production by electrolysis with decarbonized electricity or by **biomass thermal conversion**. The challenges are the design of electrochemical hydrogen production

[2] Chimie pour l'énergie, Mathieu Morcrette, Gérald Pourcelly, Vision Chimie 2030, Résultats des ateliers avec les Académiques, 2016

systems (**electrolysis materials, photocatalysis, photoelectrochemistry**) and the development of **hydrogen storage** methods, particularly through solid metal hydrides.

The chemical storage of energy offers much larger capacities thank to "**power to gas**", which is an integral part of future solutions for the seasonal storage of electrical energy. Large capacities are planned by 2050: from 20 to 73 TWh, i.e. more than the energy currently stored in pumped storage power plants (PSP)[3]. "**Power to gas**" consists in transforming hydrogen to produce synthetic gas through the **methanation process**, where CO_2 is covalorized to generate methane. Further development towards the production of **methanol as a platform molecule or synthetic fuels such as dimethyl ether** (DME), in particular as alternative aviation fuel, is envisaged. There is a significant challenge to develop **economic processes**, based on **high-performance catalysts and intensified reactors and separators**, which can respond flexibly according to the carbon-free electricity resource for **on-site and on-demand energy**.

▶ Research activities of the LRGP in the fields of Energy

Energy is both a central topic and a transversal research field at the LRGP. Significant efforts are devoted by LRGP researchers to meet the huge energy challenges our modern societies have to face. As LRGP core activities are centered on chemical-engineering issues, studies dealing with energy are approached from this particular angle and can be classified into four major areas:

- Advanced exploitation of fossil resources including non-conventional deposits or nuclear resources,
- Energy transition involving energy recovery from biomass and refuse-derived fuels,
- Study of pollutants created from combustion processes of fuels, having a serious impact on health and the environment,
- Optimization of energetic systems for energy saving and a better management of pollutant emissions.

As a noticeable feature, the combination of thermodynamic, kinetic and chemical-engineering skills appears as a common denominator for most of the works mentioned in the present report.

In order to get a fair overview of research activities developed at the LRGP addressing energy issues, a graphical illustration is given in Figure A. This figure highlights the multiple links between the various areas and is organized according to energy forms:

- a selection of **primary energies** (i.e., energy forms found in nature that have not been subjected to any human engineered conversion or transformation process) at the basis

[3] "Efficacité énergétique dans l'industrie : verrous et besoins en R&D" Enea (2012) report for Ademe – Total (http://www.enea-consulting.com/efficacite-energetique-dans-lindustrie-besoins-et-verrous-en-rd/)
"Etude portant sur l'hydrogène et la méthanation comme procédé de valorization de l'électricité excédentaire", GRTgaz, GRDF, Ademe Study, September 2014, (http://www.grtgaz.com/fileadmin/engagements/documents/fr/Power-to-Gas-etude-ADEME-GRTgaz-GrDF.pdf)

of research studies developed at the LRGP is first introduced: fossil, renewable, nuclear resources and waste heat as well.

- **Energy carriers** are defined as a substance or phenomenon that can be used to produce mechanical work or heat or to operate chemical or physical processes. E.g.: liquid or gaseous fuels (including methane), cycle fluids, nuclear fuels, H_2, recovered heat or work

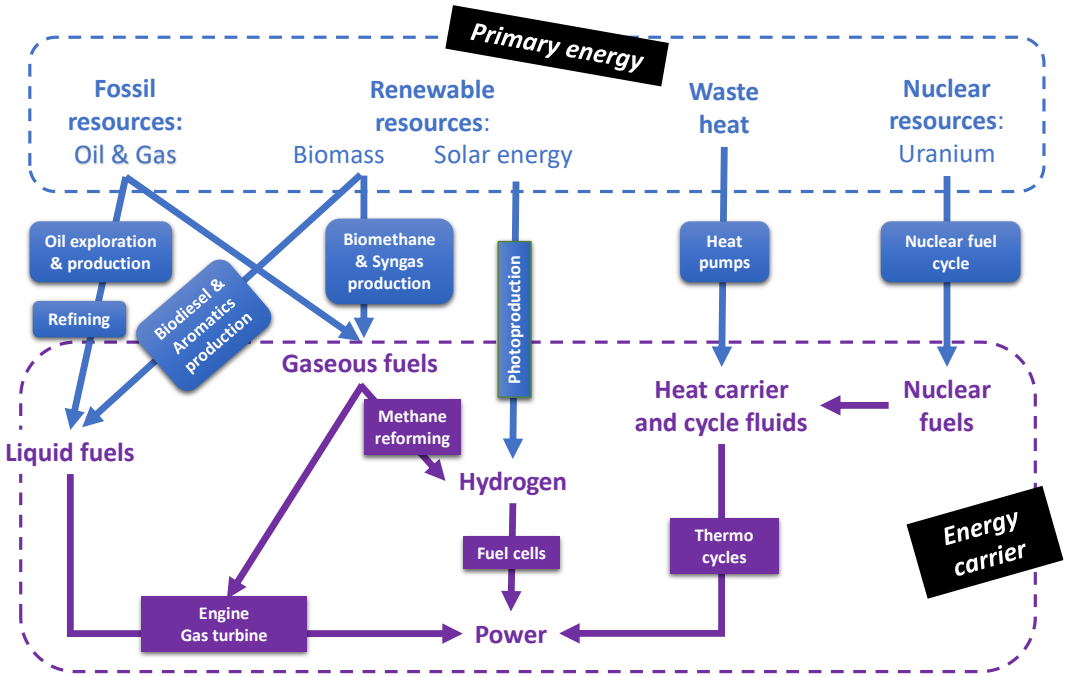


Figure A: overview of energy topics addressed by LRGP researchers. Full (blue and violet) frames indicate energy conversion processes specifically studied by LRGP teams

Research activities described hereafter address all aspects of the **energetic chain**, from the **extraction** of primary energies to their **transportation** and **conversion** to energy carriers.

In addition, and as mentioned in figure B, many studies are devoted to the development of methodological tools for the study of any part of the energetic chain. This includes PSE (Process System Engineering) aspects, CO_2 management (Carbon Capture and Storage / Carbon Capture and Use), analysis tools (exergy, pinch, techno-economic, environmental).

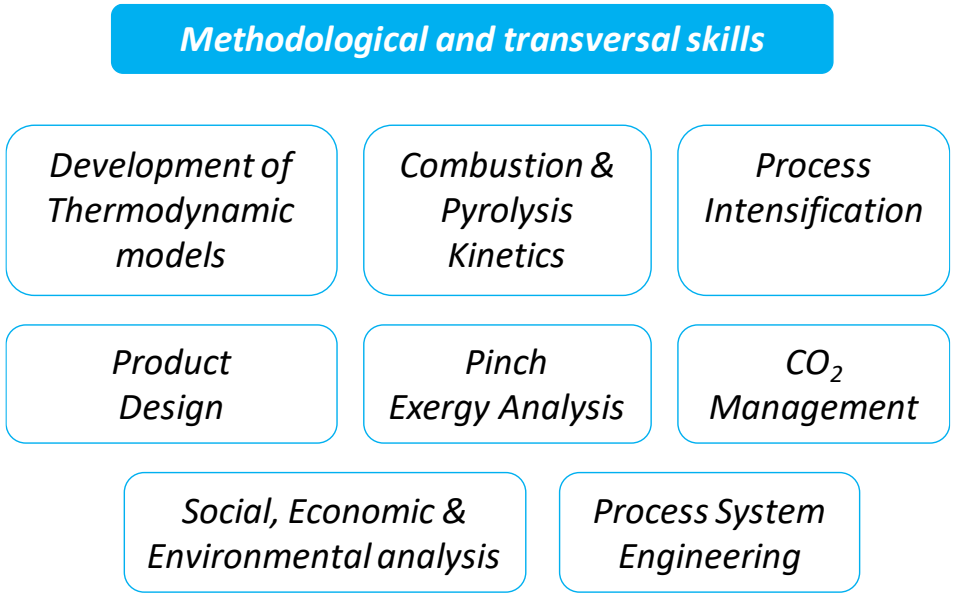


Figure B: (non-comprehensive) overview of methodological and transversal skills developed by LRGP teams for studying the energy topics presented in Figure A

The present report is made up of two parts:

1) The first part deals with a non-comprehensive description of the various methodological skills used by LRGP researchers as starting tools for conducting research related to energy issues.

2) The second part is a selection of 24 pieces of research deemed illustrative of LRGP research activities in the field of energy. These works are described through 1-page summaries aimed at reflecting their spirit and the context where they take place..

PART 1 :
Presentation of tools and methodological skills, present in the LRGP, related to the topic “Process Engineering for Energy”

THERMODYNAMIC MODELLING OF FLUID MIXTURES

What is it?

Thermodynamic models are required for estimating the properties of fluid mixtures flowing in chemical or energy processes.
The target properties are generally:

- Phase-behavior properties (e.g., solubility, critical properties),
- Enthalpy, heat capacity (for performing energy balances, pinch analysis etc.)
- Entropy (for implementing exergy analysis etc.)

Although different model classes could be used for modelling thermodynamic properties of fluid mixtures, **equations of state have the great advantage of having the capacity to predict both sub- and super-critical states**. They can thus be applied from low to high pressures and from low to high temperatures.

Equations of state are expressed as a mathematical relationship between the pressure, temperature, molar volume and composition of a fluid mixture in a uniform 1-phase state.

How difficult is the modelling of a multicomponent mixture?

In complex models for mixtures, the intermolecular interactions are most often assumed to be limited to ***binary interactions***. The thermodynamic phase behavior of real complex mixtures containing N components is thus seen as the summation of the thermodynamic phase behaviors of the $N(N-1)/2$ pairs of molecules that it is possible to form from N molecules.
Consequently, the estimation of all binary-interaction parameters in mixtures containing more than 10 to 20 compounds is difficult if not impossible.
To circumvent this issue, some models integrate appropriate methods for predicting binary-interaction parameters. Such models are called predictive.

For instance, the E-PPR78 model, developed in the LRGP, uses the group-contribution concept to estimate binary parameters.
Molecules are split into elementary groups all interacting together. Binary-interaction parameters can then be estimated by integrating group-interaction parameters.

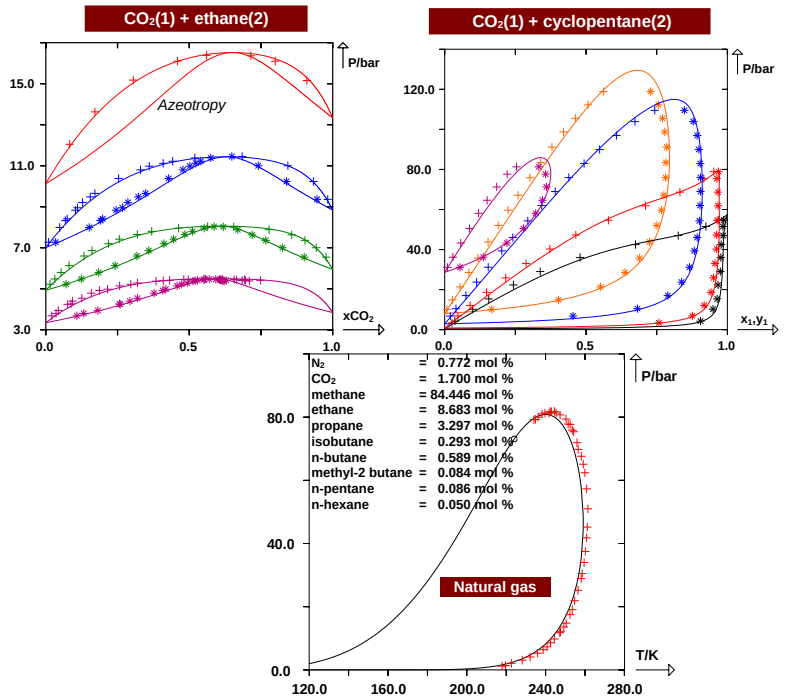
Our area of expertise

- ▶ Development of tailor-made equations of state for specific applications.
- ▶ Estimation of binary interaction parameters.
- ▶ Development of predictive (SAFT-type or cubic-type) equations of state.
- ▶ Use of multiparameter equations of state (e.g., GERG-2008, Span-Wagner etc.) to generate very-accurate thermodynamic properties of specific pure components (CO_2, Ar, some refrigerant etc.) or fluid mixtures (natural gases).

Graphical illustration of fluid-property predictions obtained by using the E-PPR78 model

The E-PPR78 model is one example of the various thermodynamic models developed in the LRGP.

Here are a set of phase behaviors predicted from this model:



Contacts

Jean-Noël Jaubert jean-noel.jaubert@univ-lorraine.fr

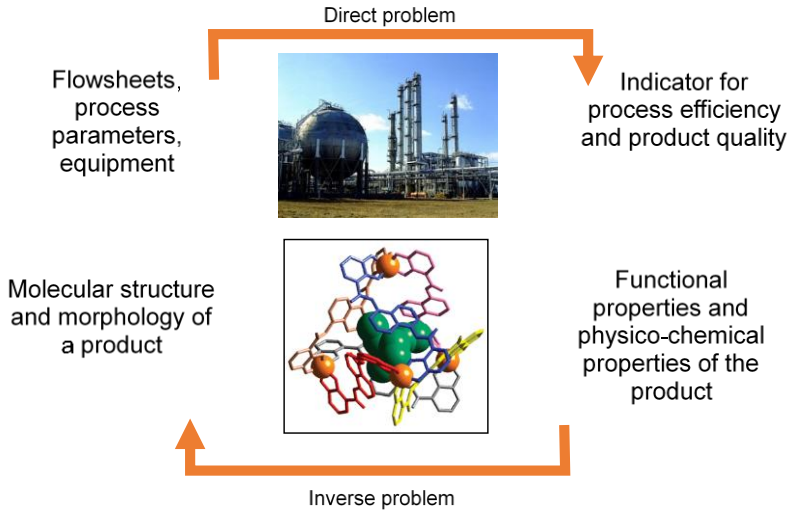
Romain Privat romain.privat@univ-lorraine.fr

PROCESS AND PRODUCT DESIGN METHODOLOGIES

What is it?

A **direct problem** consists in identifying effects from causes. For instance, the simulation of a chemical process is a direct problem as it enables the estimation of performance indicators (efficiency, purity etc.) from the knowledge of process flowsheets and process parameters.

On the contrary, an **inverse problem** is the identification of causes from effect. Inverse problems can be applied to chemical processes:it consists ins determining the flowsheets and process parameters as well by specifying the expected process indicators. Such an approach is named ***process design***.



In the same way, inverse problem can be applied to the formulation of a product. It consists in determining the nature of the chemicals and their relative compositions to reach a series of target functional properties. In this case, the approach is called ***product design***.

Usefulness and implementation

PROCESS-DESIGN:

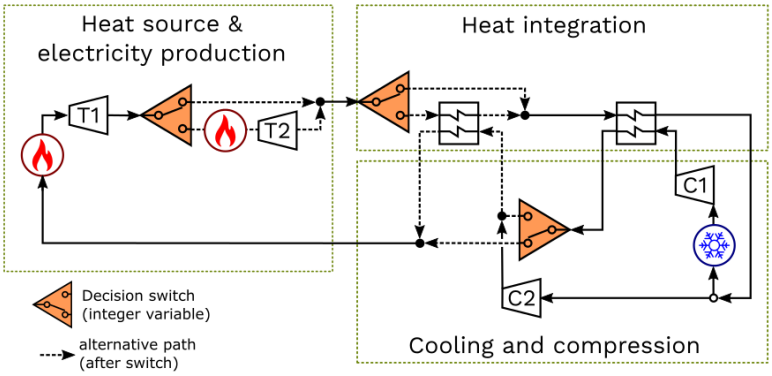
Applying the process-design approach makes it possible to build flowsheets of energy or chemical processes from the mere specification of the expected indicators of the process.

As a basic approach, inverse problems could be solved by generating a very high number of potential flowsheets and by testing them one by one in order to identify the best match with respect to process specifications.

Due to the complexity of such problems and in particular, the high number of alternatives, it is generally necessary to introduce constraints on the generation of potential algorithms to get a chance to reach a solution in a reasonable time.

Superstructures are defined as process flowsheets representing all the alternative structures on the same flowsheet by means of *decision switches*.

As an example, the following (very simple) superstructure was used for identifying an optimal Brayton with the aim of maximizing the cycle efficiency:



In order to avoid testing all the possible alternatives defined by the superstructure, it is also possible to solve inverse problems by using specific optimization methods (called MINLP) accounting both for integer and real variables.

PRODUCT DESIGN:

In the same spirit, a product-design problem consists in identifying the optimal fluid among a very high number of potential pure components and mixtures. To do so, one needs to predict the properties of each tested fluid by means of an appropriate predictive model.

Our area of expertise

- ► Implementation of the product-design approach for identifying an optimal solvent or an optimal working fluid for a given cycle.
- ► Implementation of the process-design approach for designing optimal power cycles.

Contacts

Romain Privat romain.privat@univ-lorraine.fr
Jean-Noël Jaubert jean-noel.jaubert@univ-lorraine.fr

TOOLS FOR EXERGY ANALYSIS

What is it?

Energy is a fundamental concept of thermodynamics and one of the most significant aspects of engineering analysis. As a basic feature, energy cannot be destroyed (as stated by the law of conservation of energy). Energy can be stored and can be converted from one form (shaft work, electricity, heat, flowing stream of matter etc.) to another.

However, energy conservation alone is inadequate for depicting some important aspects of resource utilization and in particular:

- the existence of **irreversible phenomena** (heat transfer, spontaneous chemical reaction, friction, inelastic deformation etc.) occurring in any real-life transformation,
- the fact that **the various forms of energy are not equivalent in terms of potential of use in processes**. As a well-known illustration, although work and heat have the same unit (joule), they are not equivalent or interchangeable quantities if one wants to produce electricity, for instance. Indeed, by assuming steady-state conditions, the maximum quantity of work (W) that can be developed from a net quantity Q of heat extracted from a reservoir at temperature T and released in surroundings at T_0 is:

$$W = Q\,(1 - T_0 / T)$$

Therefore, in the absence of irreversibilities, only a fraction of one joule of heat can be converted into electricity, thus highlighting the non-equivalency of heat and work for use in processes.

Exergy has been introduced as a property **having the dimension of energy** and **reflecting the potential of use of a form of energy**. By definition, this potential is defined as the *maximum theoretical work obtainable from an overall system consisting of a system and the environment as the system comes into equilibrium with the environment*.

Usefulness of the exergy concept

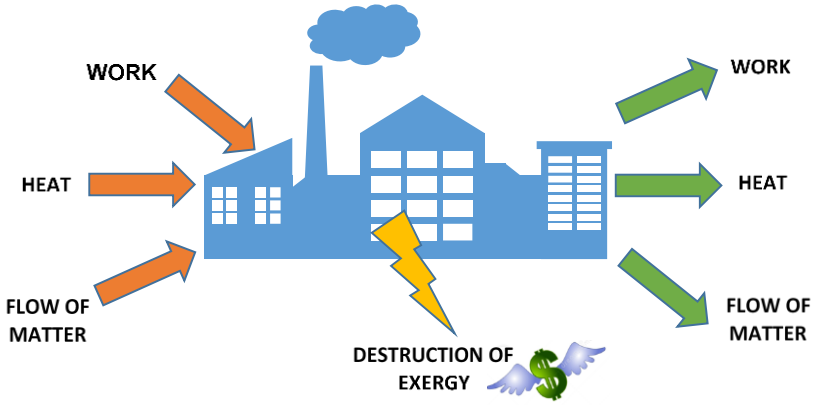
While energy is conserved, **exergy is destroyed through irreversibilities.** Such destructions have a significant impact on the costs of design and operation of chemical and energy processes. ***The reduction of destroyed exergy is a major challenge for process improvement.***

The **exergy analysis** of a given process consists in:

- estimating the destruction of exergy in each elementary unit of the process,
- analyzing how the quantity of destroyed exergy could be minimized.

How does it work?

Exergy balances are deduced from the combination of the 1st and 2nd law of thermodynamics. For a steady-state system, the application of exergy balance makes it possible **to estimate the destroyed exergy** as the difference between the incoming and outgoing quantities of exergy:



The accuracy of an exergy analysis strongly depends on the accuracy of the models describing unitary operations and the properties of fluids and solids as well.

Our area of expertise

- ▶ Performance of exergy analyses of complex processes,
- ▶ Proposal of appropriate thermodynamic models for performing proper exergy analysis of a given process,
- ▶ Proposal of solutions for minimizing exergy destructions in processes,
- ▶ Valorization of unused quantities of energies (e.g., residual hot heat) through processes enabling of their whole exergy potential to be used.

Contacts

Romain Privat romain.privat@univ-lorraine.fr
Jean-Noël Jaubert jean-noel.jaubert@univ-lorraine.fr

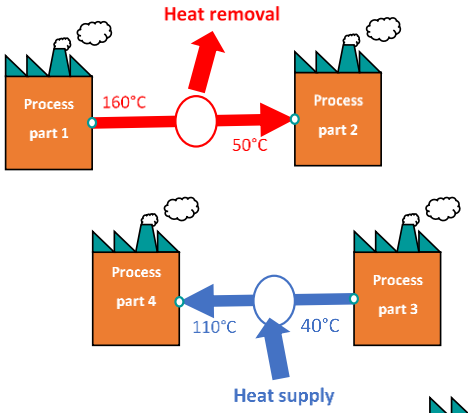
TOOLS FOR PINCH ANALYSIS AND PROCESS INTEGRATION

What is it?

Generally, traditional processes from energy and chemical industries involve numerous heat exchangers which all require hot and cold utilities to reach the temperature objectives for the process fluid.

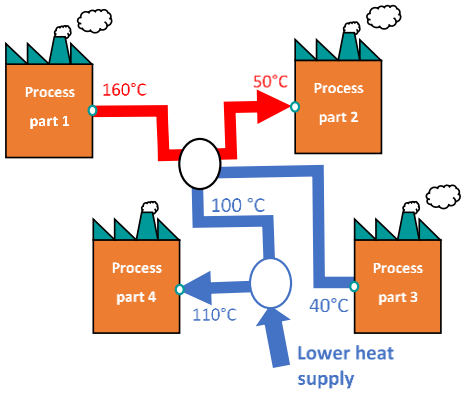
The goal of the pinch-analysis methodology is to decrease the cost of utilities by thermally integrating the process. In other words, where possible, a hot process fluid is used to heat a cold process fluid and reciprocally.

Usefulness of the concept



To illustrate the concept, let us consider a schematic process involving two heat exchangers: a hot stream is cooled from 160 to 50 °C while a cold stream is heated from 40 °C to 110 °C.

Thanks to a thermal integration, the quantity of heat to remove from the hot process fluid can be used – at least partially – to heat the cold process fluid. Doing so, there is no longer need for cold utility and the need for hot utility can be significantly decreased.



By performing a *pinch analysis*, it is thus possible:

- **To estimate the quantity of hot and cold utilities that could be saved by thermally integrating the process,**
- **To design the corresponding nets of heat exchangers.**

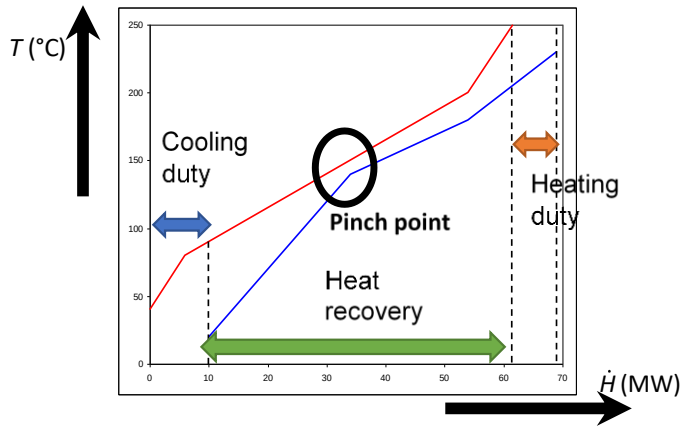
How does it work?

Pinch analysis is very simple to perform when the process of interest involves only a single hot stream to cool and a single cold stream to heat. The complexity of the analysis dramatically increases with the number of hot and cold streams in the process.

To handle the multiplicity of hot and cold streams, the concept of hot and cold "*composite curves*" is introduced as a fundamental tool for pinch analysis.

A composite curve is a continuous curve plotted in a *temperature versus enthalpy diagram*. To construct such curves, heat loads (or heat capacity flowrates) of all streams existing over any given temperature range are added. Hence, a single composite of all hot streams and a single composite of all cold streams can be produced.

The determination of the quantity of heat that can be recovered by thermal integration is obtained from a graphical construction similar to this one:



The user specifies the value of the pinch which is the lower difference between the hot and cold composite curves. These are then shifted horizontally until the specified pinch is reached. **The overlap between the composite curves represents the maximal amount of heat recovery possible within the process**. The corresponding net of heat exchangers can be then deduced by applying complex algorithms.

Our area of expertise

- ▶ Performance of pinch analyses in complex processes,
- ▶ Proposal of appropriate nets of heats exchangers,
- ▶ Determination of optimal nets of heat exchangers by conjugating both pinch and techno-economic analyses

Contacts

Jean-François Portha jean-francois.portha@univ-lorraine.fr
Jean-Noël Jaubert jean-noel.jaubert@univ-lorraine.fr
Romain Privat romain.privat@univ-lorraine.fr

TOOLS FOR PROCESS INTENSIFICATION

What is it?

Process intensification includes the development of methods and devices that enable the design of smaller, safer, cleaner, less energy-demanding and cheaper processes, whose production capacity exceeds that of conventional processes. More specifically, process intensification combines miniaturization of devices with acceleration of physical/chemical phenomena to increase the overall volume rate of transformation/transfer in the equipment [mol/m^3/s].

Process intensification of an existing process, or development of an intensified technology, can be performed by application of strategies that cover a wide spectrum of scales to suppress a variety of process limitations:

Limitations to be suppressed	Potential intensification strategies
Elementary limitations • Heat transfer • Fluid-solid mass transfer • Fluid-fluid mass transfer • Mixing, single-phase mass transfer • Kinetics • Residence Time Distribution • Thermodynamic phenomenon • Dynamics, inertia, transient effect **Complex limitations** • Fluid or equipment volume • Non-uniform properties/conditions • Size distribution • Difficult activation • Saturation effect • Safety • Pressure drop / mechanical energy • Energetic consumption • Utilities consumption	**Molecular scale** • Change of phases / solvents • Fluid phase properties • Inert species addition • Concentration • Temperature • Pressure **Equipment scale** • Geometric structuring • Gravity, centrifugal force • Catalyst structuring • Material properties • Shear rate **Process scale** • Segmentation • Periodic operation • Phase contacting • Parallelism, multi-scale • Coupling with separation • Alternative energy sources

Typical examples of process intensification technologies/methods are: microstructured reactors, spinning disc reactors, rotating packed beds, membrane reactors, batch-to-continuous conversion of syntheses, reactive distillations etc.

Usefulness

Process intensification enables:

- design of miniature devices for decentralized and mobile applications,
- development of processes with fast dynamics for operation with intermittent energy inputs or under transient conditions,
- precise coupling of mass/heat fluxes and reaction needs for an optimal allocation of the energy requirements,
- conversion of batch protocols to continuous operation for improved safety and better control of the local operating conditions,
- operation under radically new operating conditions to explore new chemical pathways.

How does it work?

Literature and handbooks provide a few methodologies based on fundamental concepts, or lists of technologies, or computer-aided decision tools and equipment databases to choose/design intensified technologies. The LRGP has developed a set of quantitative methodologies and dedicated tools:

- to analyze the characteristic times of a given problem/process to establish a short list of impacting strategies and select technologies that implement these strategies or design innovative designs to couple these strategies,
- to apply a computer-aided Taylor-designed DoE campaign to select the optimal technology and operating conditions from among a set of conventional and intensified technologies including fed-batch protocols, CSTR operation, microreactors etc.

Our area of expertise

► Performance of intensification analyses of existing processes to estimate their intensifiability potential and to identify the most appropriate strategies and the corresponding BAT technologies and operating conditions,

► Design of compact heat-exchanger reactors for decentralized applications,

► Characterization of intensified equipment in terms of fluid dynamics, mixing, heat transfer, system dynamics and operation,

► Design, development and operation of pilot-scale set-ups including intensified equipment,

► Conversion batch syntheses to continuous flow operations.

Contacts

Jean-Marc Commenge	jean-marc.commenge@univ-lorraine.fr
Jean-François Portha	jean-francois.portha@univ-lorraine.fr
Laurent Falk	laurent.falk@univ-lorraine.fr

TOOLS FOR ENVIRONMENTAL ANALYSIS

What is it?

Environmental analysis can be performed by **Life Cycle Assessment (LCA) which is a standardized methodology to evaluate environmental impacts** associated with all the stages included in the life cycle of a system (process, product or service) from raw material extraction through materials processing, manufacture, distribution, use, maintenance, and disposal or recycling.

Usefulness of LCA

In particular, the methodology can be applied to **chemical and energy processes**. The environmental impacts associated with each stage of the process can be calculated (e.g., global warming, eutrophication, acidification, ozone depletion, toxicity, eco-toxicity, natural resource depletion etc.). They depend on the **mass and energy balances** applied on the unit operations included in each stage.

The reduction of environmental impacts is a significant challenge for process improvement.

The **LCA** of a given process consists in:

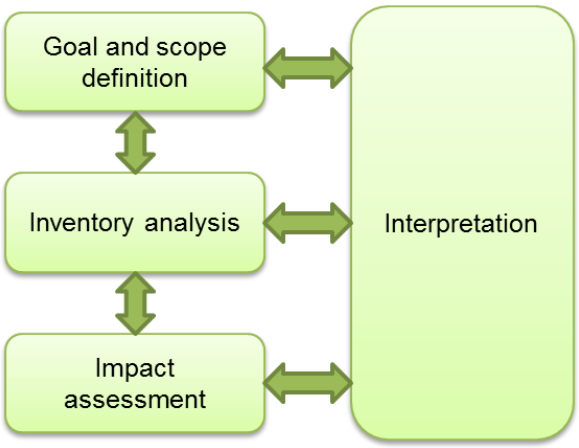
- estimating the environmental impact in each elementary unit of the process,
- analyzing how the environmental impacts could be minimized.

How does it work?

A set of ISO norms (ISO 14 040 to ISO 14043) describes the four steps of a LCA as follows:

- definition of the goal of the study and definition of the system boundaries,
- inventory analysis (data collection, mass and energy balances),
- impact assessment (calculation of environmental impacts; impact classification and characterization; results aggregation),
- improvement analysis (interpretation of the results and enhancement of the considered system).

These four steps interact with each other making this methodology iterative:



As LCA can be applied to chemical and energy processes, a coupling between a piece of computer-aided design software (supplying mass and energy balances) and a piece of LCA software (calculating environmental impact based on the previous balances) can be performed. The pieces of LCA software used in the laboratory are GABI and SIMAPRO.

The accuracy of a LCA strongly depends on the accuracy of the data considered for the analysis.

Our area of expertise

- ▶ Performance of the LCA of a given process using commercial software,
- ▶ Proposal of solutions for minimizing the environmental impacts of the considered process,
- ▶ Coupling LCA with an exergy or an energy analysis in order to valorize unused quantities of energies (e.g., residual hot heat).

Contacts

Jean-François Portha jean-francois.portha@univ-lorraine.fr
Marie-Noëlle Pons marie-noelle.pons@univ-lorraine.fr
Marie-Odile Simonnot marie-odile.simonnot@univ-lorraine.fr

KINETIC STUDY OF PYROLYSIS AND COMBUSTION REACTIONS

What is it?

Pyrolysis and combustion are complex phenomena taking place in energy processes involving the thermal degradation of organic compounds, as in automotive or jet engines, biomass thermal conversion or thermal evolution of petroleum in oil reservoirs. The kinetic study of such reactions involves experimental and theoretical investigations which aim to provide information on their reactivity and to assist in the development and operability of energy systems. Detailed kinetic modelling of these complex reactions requires a description of the chemistry at the molecular level, i.e., by considering elementary processes. The detailed mechanisms involve several "generic" elementary processes leading ultimately to mechanisms containing several hundred species (molecules and radicals) and several thousand reactions. These mechanisms are reliable and can be extrapolated within a wide range of operating conditions (T, P, composition) in contrast to global or empirical mechanisms.

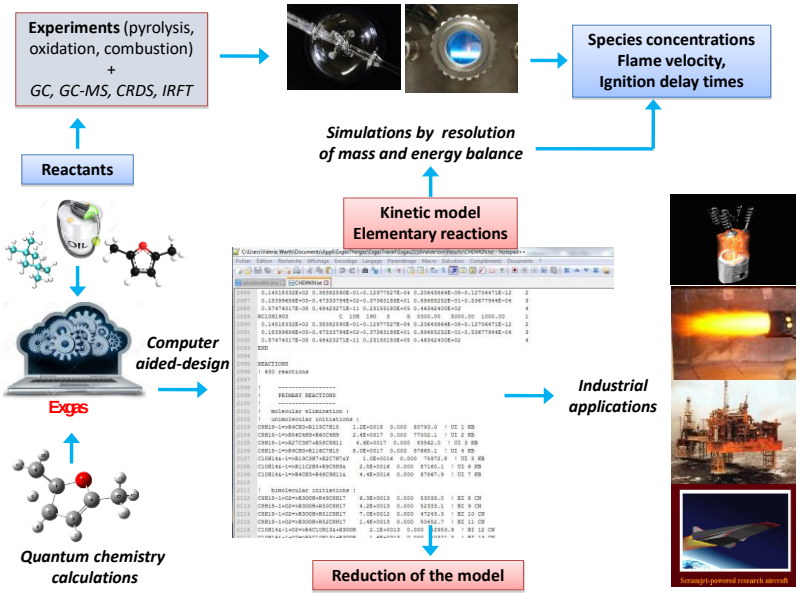
Usefulness of the kinetic study

Experimental and theoretical kinetic studies can provide useful information about energy systems, such as ignition temperatures, ignition delay times, inflammability limits and laminar flame velocities. Moreover, the molecular approach developed makes it possible to gain an accurate and quantitative description of the temporal evolution of species concentrations during the thermal degradation of a fuel. Thermal evolution of petroleum, development of new combustion modes for engines (HCCI, RCCI etc.), (bio)fuel formulations and the effect of additives on the formation of pollutants are some examples where kinetic studies are very helpful.

How does it work?

The kinetic study of pyrolysis and combustion reactions is mainly centered on the development of detailed mechanisms that make it possible to gain a quantitative description of the chemistry involved in most energy systems. To achieve this goal, several studies are being carried out jointly. First, experimental studies are performed in perfect reactors (jet-stirred, plug-flows, batch, laminar premixed flames, shock tube, etc.) and coupled with analytical apparatus for the detection and the quantification of species (GC, GC-MS, CRDS, IRTF etc.). This information is needed to develop mechanisms and validate them. In parallel, the development of the kinetic model requires several thousand reactions to be written. The use of computer-aided kinetic modelling is a powerful tool to automatically generate such huge mechanisms. The software EXGAS has been developed for this purpose and currently enables the

generation of detailed mechanisms for hydrocarbons and some biofuels such as alcohols and esters.



The rate constant of each elementary reaction, as well as the thermodynamic data ($\Delta_fH°_{298K}$, $S°_{298K}$, $C_p(T)$) of each species, can be provided by means of structure-reactivity relationships. These relationships are derived either from experimental data or most often, from quantum chemistry calculations (*ab initio* and DFT methods combined with reaction rate theories). Numerical simulations involving the resolution of mass and energy balance enable the mechanism to be validated through comparison with experimental data. Finally a reduction of the model can be done to include it in computational fluid dynamics codes.

Our area of expertise

► Performance of experimental pyrolysis/combustion studies in perfect reactors (jet-stirred, laminar premixed flame, shock tube, batch and plug flow reactor) coupled with analytical techniques (GC, GC-MS, CRDS, IRTF).

► Generation of (automatically) detailed combustion/pyrolysis mechanisms for hydrocarbons or organic compounds containing heteroatoms (O, N, Cl, S, F, P, As etc.).

► Study of the combustion/pyrolysis pathways for a given molecule by means of quantum calculations and derivation of rate coefficients and thermodynamics data.

► Performance of kinetic simulations associated with reaction path analysis and mechanism reduction.

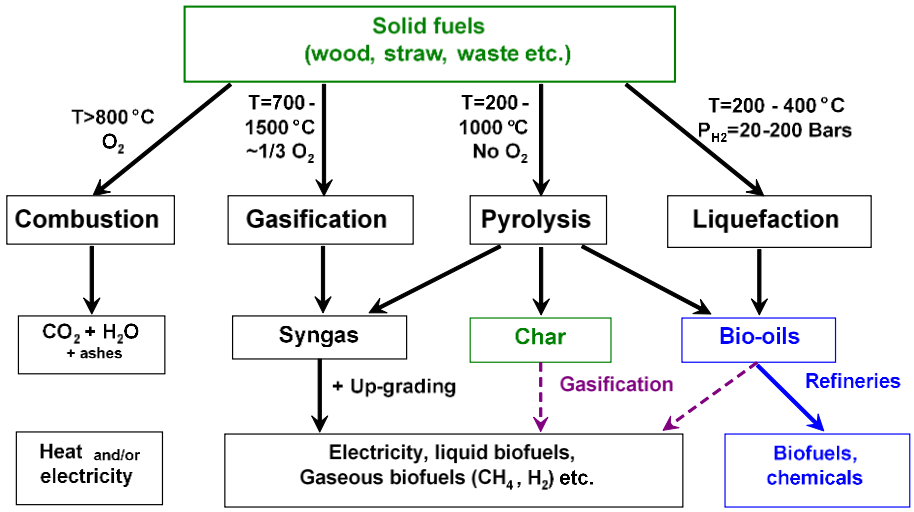
Contacts

René Fournet rene.fournet@univ-lorraine.fr

SOLID FUELS THERMAL CONVERSION

What is it?

Solid fuels are renewable resources (wood, straw etc.) and non-renewables. Among these non-renewables, we should distinguish fossil fuels (coal, lignite etc.) and wastes (urban waste, sewage sludge etc.). All these types of solid fuels can be converted into different forms of energy by thermal conversion: combustion, gasification, pyrolysis or liquefaction.

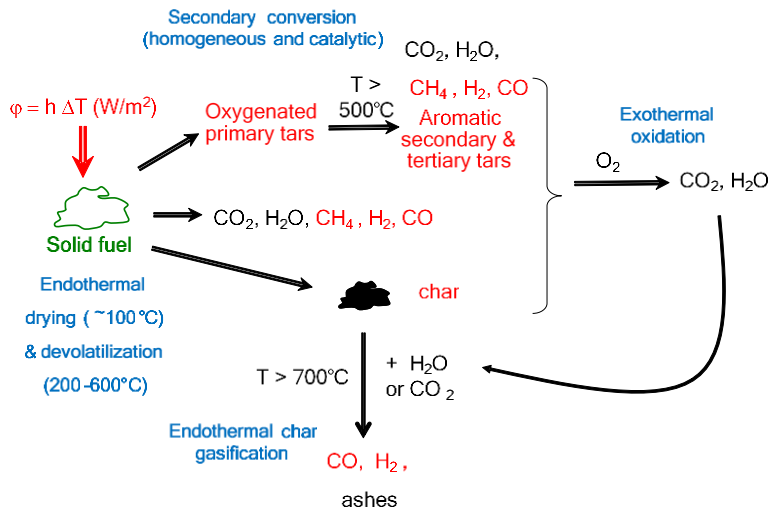


Usefulness

Solid fuel combustion has been developed at commercial scale for a long time (heat generation at domestic and industrial scale, electricity production through steam cycle). The other types of thermal conversion were also discovered a long time ago, but are not yet well developed because of different technical concerns (tar cleaning, bio-oil upgrading etc.). However, these processes may play a significant role for energy transition in the coming years (liquid and gaseous bio-fuels production).

How does it work?

Different phenomena are observed during thermal conversion of solid fuels (drying, devolatilization, homogeneous / catalytic tar conversion, char gasification, oxidation).



Our area of expertise

► Characterization of solid fuels by different analytical technics: elemental analysis, ICP-OES, bomb calorimeter, size distribution etc.

►Experimental determination of the kinetics of the different phenomena and the products yields: TGA, DSC, in-situ H^1 NMR, micro fixed bed, micro fluidized bed, laser heater etc. that are coupled to on-line analysis (SPI-TOF-MS for tar species, -GC for permanent gases). Off-line analysis of tar (GCxGC-FID-MS, HPLC) and char (elemental analysis, ICP-OES, SEM, TEM, solid-state NMR).

► Assessment of the performances of solid fuel conversion in pilot-scale reactors (5 kg/h fluidized bed for fast pyrolysis and gasification, twin screw reactor for pyrolysis and liquefaction, 300 mL and 3 L autoclaves for liquefaction)

► Modelling of the industrial-size thermochemical reactors and implementation of the models in process simulators. This methodology enables the mass & energy balances of the whole processes to be obtained.

Contacts

Guillain Mauviel guillain.mauviel@univ-lorraine.fr
Yann Le Brech yann.le-brech@univ-lorraine.fr
Anthony Dufour anthony.dufour@univ-lorraine.fr

EVALUATION OF PERFORMANCE IN MEMBRANE FUEL CELLS

What is it?

Polymer electrolyte membrane fuel cells are electrochemical energy converters, producing heat and electricity from fuels e.g. hydrogen with (air) oxygen. Fuel cells also have to remain reliable over time and tolerant towards their environment. Performance criteria are therefore expressed in terms of:

- Clean, efficient and reliable power,
- Tolerance towards their environment and extreme operating conditions,
- Durability in their applications.

Usefulness of such evaluation

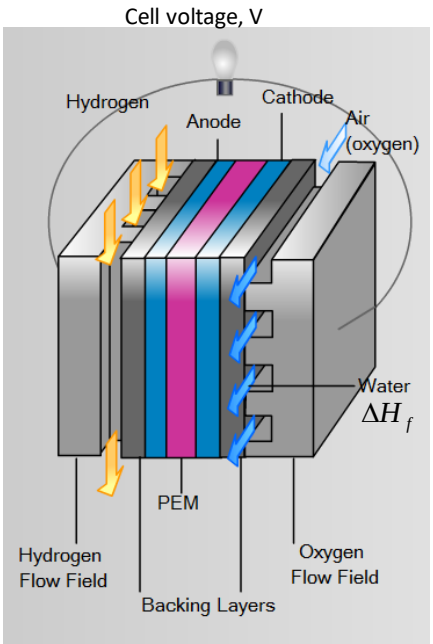
Precise characterization of fuel cell performance enables the identification of its capacities to produce electricity as well as more crucial aspects of its behavior e.g. decaying catalyst, increase in membrane porosity, poor water management caused by degradation of gas diffusion (backing) layers.

Evaluation results make it possible to investigate routes to mitigate the evidenced weak points by:

(i) modifying operating conditions;
(ii) improving component materials and design.

How does it work?

The principle of PEM fuel cells is illustrated below:



Power efficiency η_{el} $\eta_{el} = \frac{V}{\Delta H_f / 2F}$

Criteria, Cell component	Required behavior	Techniques used for evaluation
Cell reliability: Voltage stability	Tolerance to op. conditions, Resistance to aging	Extreme conditions Accelerated Stress Tests In situ vs. Ex situ
PE Membrane	High ionic conductivity Negligible gas permeability	Electrochem. techniques Post mortem: TEM, XPS
Catalyst	Low overpotentials, High electroactive surface area	Electrochem. techniques Post mortem: TEM, SEM, Spectroscopic techniques
Backing layers	Stable water management: no change in hydrophobicity	Electrochem. techniques Post mortem: XPS, EDX Planned: transport phenomena, pressure spectroscopy

Our area of expertise

► Performance of various in-situ and ex-situ accelerated stress tests, with suitable characterization of the cell components,

►Deduction of an accurate evaluation of the cell behavior by interpretation of the above characterization with a view to forming a diagnosis,

► Proposal of more suitable operating conditions or cell use with colleagues of other engineering labs.

► Proposal of improvement routes for cell component design and fabrication, with colleagues from material sciences, and test the improved new components.

Contacts

Francois Lapicque francois.lapicque@univ-lorraine.fr
Caroline Bonnet caroline.bonnet@univ-lorraine.fr

BIOPROCESS ENGINEERING FOR ENERGETIC BIOMOLECULES

What is it?

Biochemical conversion of biomass feedstock is based on enzymatic (hydrolysis) and microbial bioreactions (fermentation or anaerobic digestion).

Main applications

The end products of biochemical conversion processes are typically liquid or gaseous fuels among which it is important to identify:

- The production of 1st, 2nd and 3rd generation **liquid biofuels** (such as alcohols and biodiesel) using respectively food, non-food and algal biomass by alcoholic fermentation of sugars.
- The production of **gaseous biofuels** such as methane in anaerobic digesters using organic waste from agriculture, household wastes or industry as substrate (methanization) or hydrogen synthesis using *Clostridia* bacteria, for instance.

How does it work?

Bioprocess engineering for the production/separation of energetic biomolecules relies on a multi-scale strategy which is jointly based on (bio)chemical engineering (process modelling and optimization) and microbiology/biochemistry (genetic/metabolic engineering, molecular modelling) skills and scientific developments **(see Figure below)**.

Our area of expertise

► Optimization of energy production by:

- Experimental studies of production bioprocess at lab- and pilot scale using dedicated set-ups,
- Proposing innovative technical solutions or bioprocess routes to increase production yields,
- Modelling of microbial kinetics, rheology, hydrodynamics, heat and mass transfer (FLUENT),
- A better characterization of (bio)catalyst and substrates: microbial population dynamics, metabolism modelling, biomass structure and reactivity etc.

► Set up of separation processes specific to the purification of energetic biomolecules (dissolved or gaseous molecules).

► Proposal of integrated flowsheets of bioenergy production processes using bio(energy) refineries concepts and process macro-modelling (ASPEN).

► Application of Life Cycle Analysis or supply-chain modelling.

Contacts

Eric OLMOS	eric.olmos@univ-lorraine.fr
Emmanuel GUEDON	emmanuel.guedon@univ-lorraine.fr
Stéphane DELAUNAY	stephane.delaunay@univ-lorraine.fr

PART 2:
Overview of research studies dealing with energy issues at the LRGP

EXPLORATION & PRODUCTION: THERMODYNAMICS

Context & Objectives

- Thermodynamics plays a key role in the simulation and sizing of **Enhanced Oil Recovery** (EOR) processes.
- **Prediction of phase-behavior diagrams** (and in particular, isopleth P-T projections) of petroleum mixtures is a prerequisite. Phase diagrams can be generated from appropriate models provided enough experimental information is available. Generally, petroleum fluid is characterized by the boiling point, molecular weight and/or density of its associated cuts.
- Estimation of petroleum fluid properties such as saturation pressures or **minimum miscibility pressure** (MMP) must be known to develop strategies for recovering oils from wells.

LRGP Skills

- **Estimation of single-phase properties and phase-equilibrium properties** of petroleum fluid and related mixtures (e.g., mixtures involved in swelling-test experiments).
  - ➔ Predictive methods are developed to make it possible to estimate such properties from the mere knowledge of data obtained from classical characterization experiments.
- **Development of algorithms** for determining miscibility mechanism type and estimating MMP.

Projects

- Development of accurate MMP determination algorithms, TOTAL (industrial funding).
- Prediction of binary interaction parameters from group-contribution methods, collaboration between the LRGP and developers of the commercial simulator PRO/II (Schneider Electrics).
- Development of predictive equations of state (relying on the group-contribution concept), e.g., the PPR78 model (industrial funding from TOTAL, Air Liquide, General Electrics).

Results

- Phase envelopes of petroleum fluids (isopleth P-T projection) can be predicted for heavy oils, gas condensates and natural gases with an uncertainty lower than 5% in terms of saturation pressures or MMP.
- The PPR78 model and related methods for petroleum fluid characterization have been incorporated in several commercial simulators (ProSim software, PRO/II etc.)

Figure 1: Prediction of a P-T phase envelope using our method for guesstimating binary interaction parameters

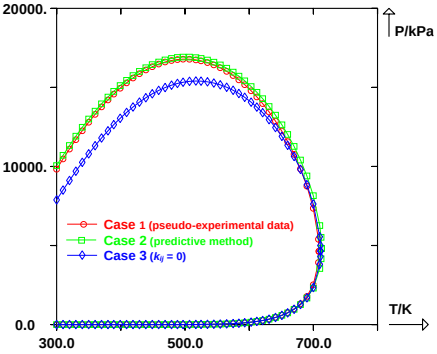
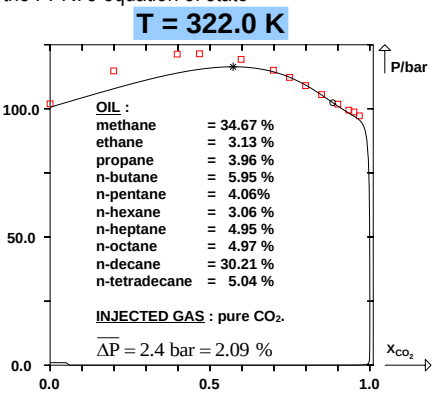


Figure 2: Modelling of a swelling experiment using the PPR78 equation of state



References

J.N. Jaubert et al., *AIChE Journal*, 56(12), 3225-3235, 2010

X. Xu et al., *IECR*, 54, 2816-2824, 2015

A. Pina et al., *Int J. Thermophys*, 37(23), 1-19, 2016

J.N. Jaubert et al., *IECR*, 37, 4854–4859, 1998

J.N. Jaubert et al. *IECR*, 41, 303–310, 2002

✉ jean-noel.jaubert@univ-lorraine.fr ✉ romain.privat@univ-lorraine.fr

Oil & gas

EXPLORATION & PRODUCTION: KINETICS

Context & Objectives

- The composition of petroleum in deeply buried reservoirs (T > 200 °C, P up to 1000 bar and more) is of strategic interest
- Thermal stability of liquid reserves should be predicted under geologic conditions
- Rate laws for the formation and destruction of hydrocarbons are not easily obtained because of the complexity of the chemical composition of oil and the difference between experimental (>400 °C) & geologic temperature (<300 °C)
- Robust kinetic models should be constructed

LRGP Skills

- **Modelling of hydrocarbon fate in geologic oil reservoirs** at high pressure and high temperature, sulphured or not
- **Construction of detailed kinetic models** based essentially on free-radical mechanisms and their intrinsic kinetic parameters
- **Ab initio studies** of the pathways involved in the thermal decomposition
- **Lumping procedure of kinetic models** for size reduction.

Projects

- Sequestration of sulphur in petroleum reservoirs, ICEEL (ANR Carnot), coord. LRGP, partners: GeoResources, LEMTA
- Pyrolysis of cycloalkanes: contribution to the thermal evolution of petroleum, TOTAL (industrial funding), coord. LRGP
- PetroStab: thermal evolution of petroleum by coupling kinetic and transport models, ICEEL (ANR Carnot), coord. GeoResources, partners: LRGP, LEMTA
- Theoretical study of pyrolysis mechanism of cycloalkanes and iso-alkanes, TOTAL (industrial funding), coord. LRGP
- Study of the reactions between alkanes and H_2S in oil reservoirs, ICEEL (ANR Carnot), coord. GeoResources, partner: LRGP.

Results

- Robust kinetic model enables the thermal evolution of oil fractions to be predicted.
- The n-alkanes, iso-alkanes, cycloalkanes (figure 1), and numerous aromatic compounds were studied
- The effect of H_2S mostly produced by the Thermal Sulphate Reduction is also modelled (figure 2), showing the consumption of alkanes and the production of heavy sulphur compounds.

Figure 1: Pyrolysis of butylcyclohexane

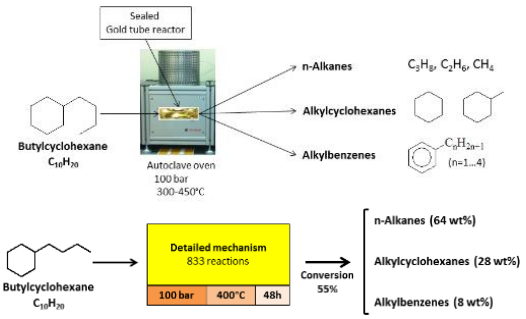
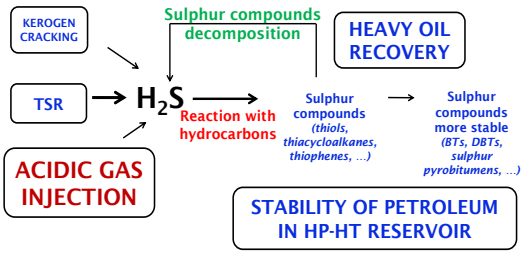


Figure 2: Sulphur cycle in reservoirs



References

V. Burklé-Vitzthum et al. JAAP, 125, 40-19, 2017
R. Bounaceur et al. JAAP, 124, 542-562, 2017
D. Rakatoalimanana JAAP, 123, 204-215, 2017
R. Bounaceur et al. JAAP, 122, 422-451, 2016
D. Rakotoalimanana et al., JAAP, 117, 1-16, 2016
N. Razafinarivo et al., JAAP, 117, 282-289, 2016
V.P. Nguyen et al., JAAP, 113, 46-56, 2015
R. Bounaceur et al., JAAP, 103, 240-254, 2013
V.P. Nguyen et al., JAAP, 103, 307-319, 2013
V. Burklé-Vitzthum et al., Org. Geochem., 42, 439-450,2011
F. Lannuzel et al., JAAP, 87, 236-247, 2010

✉ valerie.vitzthum@univ-lorraine.fr ✉ roda.bounaceur@univ-lorraine.fr

OIL REFINING

Context & Objectives

- The LRGP develops studies focusing on the rational use of energy in refineries.
- Atmospheric oil distillation process requires huge amounts of energy. The application of energy integration methods to the preheating train makes it possible to save up to 20% of the required energy.
- Due to the uncertainty of models used to perform the sizing calculation, refineries equipment is frequently oversized. For many years, we have been developed accurate and nonetheless, predictive thermo-dynamic model for reducing such uncertainties.
- Environmental aspects are also taken into account through our studies, e.g., the removal of sulphur compounds from gasoline using green solvents.

LRGP Skills

- **Thermal integration of refineries'** units leading to process re-designs. Implementation of pinch analysis and pinch technology methods.
- Development of **accurate predictive equations of state** (e.g., PPR78) capable of modelling mixtures flowing in refineries and predicting heat effects.
- Design of **ionic liquids used in extraction process** dedicated to removing sulphur compounds from gasoline.

Projects

- Industrial funding (TOTAL, Air Liquide)

Results

- Patent: "Petroleum distillation method and facility reusing low-thermal-level energy." EP 2419186 A1
- The PR2SRK, PPR78 and E-PPR78 models are predictive equations of state capable of accounting for various series of compounds: paraffins, naphthenes, aromatic compounds, permanent gases (H_2, CO, He), olefins, sulphur compounds.
- Ionic liquids making it possible to reduce the thiophene content in gasoline by 96% were found out. Moreover, such ionic liquids render it possible to eliminate 97.5% of the dibenzothiophene contained in gasolines in a 3-stage process.

Figure 1: Energy integration in refineries: new preheating train process developed by Benali et al.

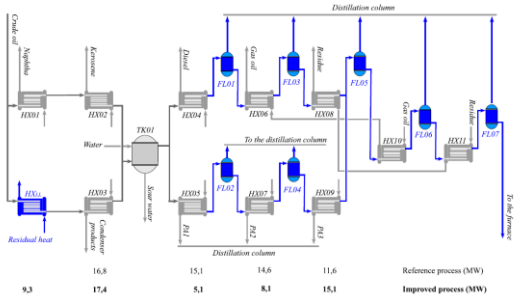


Figure 2: Prediction of enthalpy of mixing by using the PPR78 model.

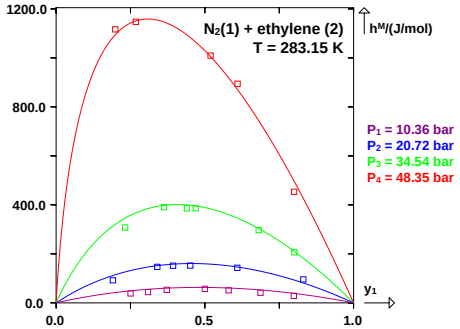
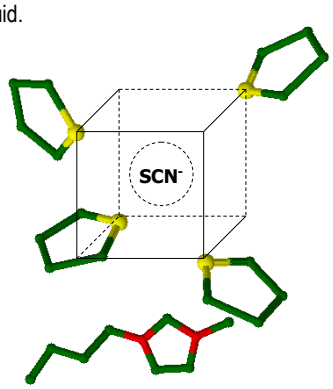


Figure 3: Highlight of the interactions between thiophene and an ionic liquid.



References

T. Benali et al., Appl Therm Eng 32,125–131, 2012.
R. Privat et al., Energy, 55, 594–609, 2013
X. Xu et al., IECR, 54, 9494-9504, 2015
K. Kedra–Krolik et al., Ind. Eng. Chem. Res., 50, 2296–2306, 2011
K. Kedra–Krolik et al., Energy Fuels., 25, 1559–1565, 2011
Y. Chen et al., J. Chem. Eng. Data., 59, 603–612, 2014

✉ jean-noel.jaubert@univ-lorraine.fr ✉ romain.privat@univ-lorraine.fr
✉ fabrice.mutelet@univ-lorraine.fr

Biofuel

METHANE THROUGH BIOPROCESSES

Context & Objectives

- French authorities wish to expand bio-methane production from agricultural wastes of variable availability and composition
- The goal is to inject bio-methane produced by microbial anaerobic digestion (AD) in the gas grid or to produce liquefied gas
- Need for intensification of the biomethane production process
- Need for better prediction of the variable feed effect
- Need for robust gas purification techniques

LRGP Skills

- **Characterization of potential substrates:** bio-methane production potential, composition via chemical and physical (infra-red spectroscopy) techniques
- **Analysis of micro-organism metabolism at micro and macro scales** using offline and online analytical tools (HPLC, ICP-MS, GC, GC-MS, LC-MS, MALDI-TOF, UV-VIS spectroscopy etc.)
- **Construction of detailed dynamic models** based on internationally accepted kinetics and coupled with a detailed energy balance
- **Numerical simulation** of liquid-solid (Euler-Lagrange), gas-liquid flows (Euler-Euler / PBM) and gas-liquid mass transfer in bioreactor.
- **Study of transport phenomena** in anaerobic digesters at the macro-, meso- and micro-scales (flow, turbulence, multiphase flow, mass transfer).
- **Methanization of agricultural wastes** at the lab and pilot scale using fully instrumented bioreactors (2 to 100 L).
- **Gas on-line analysis**.
- **Life cycle assessment and techno-economical analyses**

Projects

- AUTOFERM: Control of anaerobic digestion at the farm level, (ANR), coord. ENSAIA, partners: LRGP, La Salle Beauvais, BioEntech, UTT, UTC
- VALORCO: Valorization and reduction of industrial CO_2 emissions, Task: CO_2 uptake by intensification of anaerobic digestion. coord. Michel Fick / coll. with ENSAIA. ADEME funding.

Results

- Robust dynamic model combining a multi-substrates version of ADM1 (IWA) and a detailed thermal model.
- Development of an instrumented pilot bioreactor (100 L)
- CFD simulations of average velocity and viscosity using various agitators in an anaerobic digester containing cattle manure.
- Design of an anaerobic digester with incorporation of gas (hydrogen).

Figure 1: Farm anaerobic digestion process.

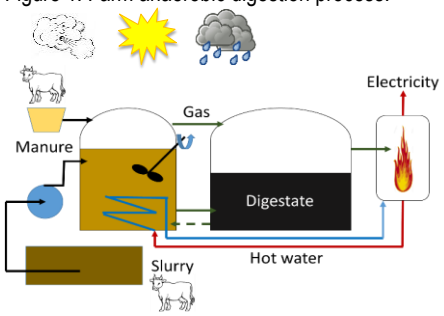


Figure 2: Instrumented 2 L anaerobic digester.

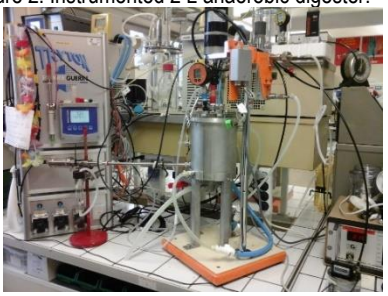
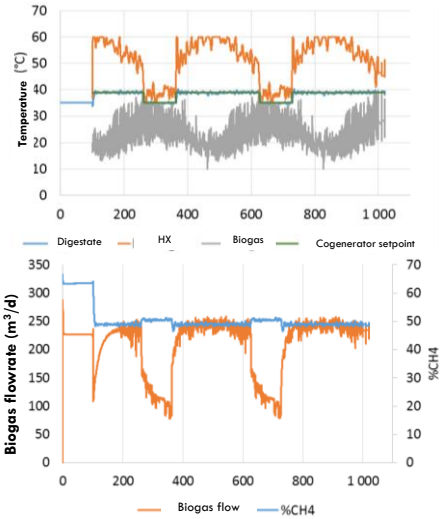


Figure 3: Control of T, %CH4 and flowrate in a farm AD



References

R. Hreiz et al., CHERD, 119, 101-116, 2017
R. Hreiz et al. CHERD, 119, 47-57, 2017
N. Adouani et al., IFAC-PapersOnLine, 49(7), 1169-1174, 2016
A. Lebranchu et al. Bioresource technology, 245,1139 -1147, 2017

✉ nouceiba.adouani@univ-lorraine.fr ✉ marie-noelle.pons@univ-lorraine.fr
✉ eric.olmos@univ-lorraine.fr ✉ stephane.delaunay@univ-lorraine.fr

Biofuel

SYNGAS THROUGH GASIFICATION

Context & Objectives

- The simultaneous production of heat & power enables high energy efficiency to be reached.
- Solid fuel gasification produces syngas (CO + H_2) that could be burned in an Internal Combustion Engine to produce electricity and heat.
- Methane may be reformed to produce H_2 that may be fed into a Fuel Cell to produce electricity and heat.
- In both cases, an assessment of these new technical solutions through experimental and modelling work is needed.

LRGP Skills

- **Gasification in fluidized bed (5 kg/h, 700<T<900°C)** fed with biomass or Solid Refused Fuels. Analysis of the gases (H_2, CO, CO_2, CH_4, H_2S, NH_3, HCN, HCl), tar (BTX, PAH, phenols) and solids (bed material, char, ashes).
- **Absorption of tar with a Venturi scrubber** coupled to the fluidized bed.
- **Thermal cracking of tar (1000<T<1300°C)** coupled to the fluidized bed.
- **Reactor modelling** and implementation in process simulation software. **Determination of mass & energy balances, cold gas efficiency, thermal efficiency etc.**

Projects

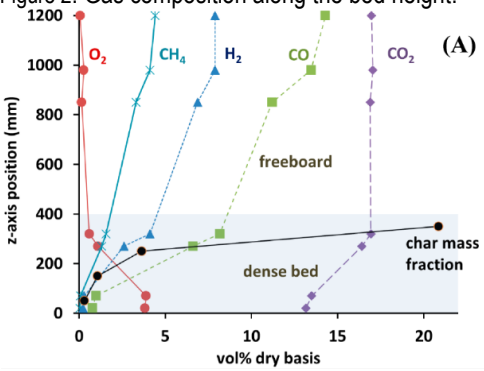
- GAMECO (ANR), coord. EDF, partners: LRGP, LERMAB, CEMHTI
- TERRACOTTA (ADEME), coord. EDF, partners: LRGP, LERMAB, TIRU
- ASTARTE (ANR Labcom), coord. LRGP, partner: LLT
- ADELITHER (ADEME), coord. LLT, partners: LRGP, RAGT
- FAIR (BPI), coord: Air Liquide, partners : AUER, ADISSEO, Polyshape, IJL, PIMM, SPCTS, Cirimat, DynFluid.

Results

- Gas composition profile along the fluidized bed: comparison between experiments and model predictions.
- Fluidized bed segregation: char particles tend to float over olivine particles.
- Characterization of agglomeration between olivine sand and miscanthus ashes in fluidized bed.
- Optimized design of micro-CHP process based on PEMFC or SOFC including microstructured SMR heat exchanger reactor.

Figure 1: Fluidized bed gasifier (5 kg/h).

Figure 2: Gas composition along the bed height.



References

B. Cluet et al. Fuel Proc. Technol, 133, 80, 2015.

G. Lardier et al., Energy & Fuels, 30, 10, 8316-8326, 2016.

R. Weh, Master's thesis dissertation, Lorraine University & Hochschule Mannheim, 2017.

✉ guillain.mauviel@univ-lorraine.fr ✉ jean-marc.commenge@univ-lorraine.fr

Biofuel

BIODIESEL THROUGH TRANSESTERIFICATION

Context & Objectives

- **Heterogeneous catalytic transesterification of vegetable oil by methanol** has been studied to decrease the excess of methanol used at industrial scale.
- The use of methanol in excess implies a high CAPEX/OPEX of the separation processes.
- Simultaneously, **another low-cost and environmentally friendly alternative** integrating the biorefinery concept was investigated for producing a 100% renewable fuel (**ethyl biodiesel of non-edible vegetable oils by homogenous catalysis under mild conditions** followed by **dry-purification with the plant residues**).
- Aimed at **rural areas and developing countries**, this alternative also targets **flexibility** as a supplementary criterion to easily switch production of energy carrier (**ethyl biodiesel**) for high-added value chemicals (**biolubricants**).

LRGP Skills

- **Development, at the laboratory, of a modular pilot unit** working at high pressure (50 bar) and temperature (200 °C) to measure experimental parameters (Fig. 1).
- Determination of glycerides, free glycerol and fatty acid ester concentrations by **gas chromatography**.
- **Modelling of the heterogeneous reactor** by the finite volume method, by taking into account the coupling between different phenomena (kinetic and mass transfer limitation etc.)
- **Development of an optimization model**.
- **Modelling of the whole process** by considering reactors in series, recycling loops and gas/liquid thermodynamic equilibria in flash-separators.
- **Phase equilibria measurement and modelling of systems involved in ethyl biodiesel production**

Projects

- Esterfip Project: LRGP, IFP Energies Nouvelles
- Collaborations with Burkina Faso and Australia

Results

- Development of a **modular pilot unit** at the laboratory.
- Development of **separator and reactor models** accounting for thermodynamic, kinetic and transport phenomena (Fig. 2).
- Identification of **kinetic constants and mass transfer coefficients** by optimization.
- **Improvement** of the overall performance of the industrial unit: minimization of the energy used in the process.
- **Pilot-scale production of ethyl biodiesel** close to standard specifications from Balagnites aegyptiaca, Azadirachta indica, and Jatropha curcas oils (conversion with KOH; 35°C; 1 bar; 4 L reactor; dry-purification with rice husk ash (Fig. 3))

Figure 1: Modular pilot unit developed at the laboratory.

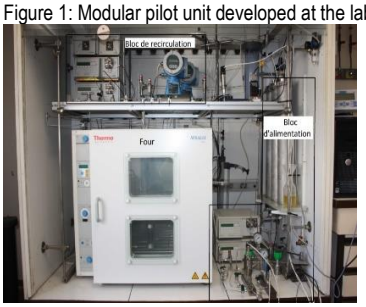


Figure 2: Concentration profile of mono-olein.

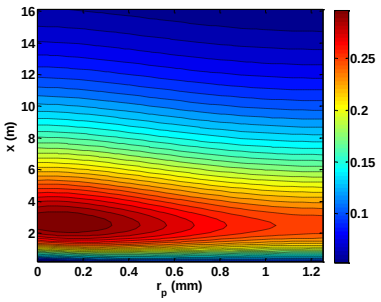
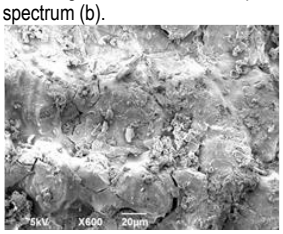
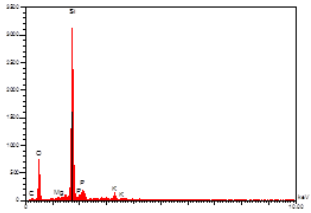


Figure 3: Scanning Electron Microscopy (SEM)/Energy Dispersive X-ray Spectroscopy (EDS) analyses of outer epidermis of a virgin rice husk ash sample. Image (a) and EDS spectrum (b).





References

J.-F. Portha et al., CEJ, 207-208, 285-29 2012
L. Coniglio et al., PECS, 39, 340-382, 2013
L. Coniglio et al., PECS, 43, 1-35, 2014
S. Nitièma-Yefanova et al., Energy Fuels, 29, 150–159, 2015
F. Allain et al., CES, 283, 833-845, 2016
S. Nitièma-Yefanova et al., Renew Energy, 96, 881-890, 2016
S. Nitièma-Yefanova et al., Renew Energy, 109, 634-645, 2017
F. Muhammad et al., Fuel, 203, 633-641, 2017

✉ jean-francois.portha@univ-lorraine.fr ✉ lucie.coniglio@univ-lorraine.fr

Biofuel

AROMATICS THROUGH DEOXYGENATION

Context & Objectives

- Biomass is the most important renewable carbonaceous resource to produce biofuels or green chemicals.
- Biomass presents a too high oxygen content compared to crude oil.
- Oxygen should be removed selectively from biomass in order to produce targeted chemicals or fuels.
- New catalyst systems have to be designed to selectively deoxygenate biomass.

LRGP Skills

- Hydrodeoxygenation (HDO) of lignin. Pyrolysis combined with a catalytic HDO of the vapor phase. Direct hydropyrolysis. Liquefaction of lignin in batch or in continuous reactor. Analysis of bio-oils by GC*GC/MS and high-resolution MS (with LCPA2MC, Metz).
- Catalytic pyrolysis of biomass with zeolites (in collaboration with IC2MP, Poitiers) and natural materials (with IS2M, Mulhouse), in fixed bed and fluidized bed reactors.
- Direct liquefaction of wood. Fundamentals and testing of novel catalytic systems (solvent + catalysts).
- Catalytic hydrotreatment of bio-oils in trickle bed
- Reactor modelling and implementation in process simulation software. Determination of mass & energy balances.

Projects

- Hy-RON (prematuration CNRS), coord. LRGP
- PhenoLiq (ANR), coord. LRGP, partners: IRCELyon, CTP
- CATACLAY (Inter-Carnots), coord. LRGP, partner: IS2M

Results

- Iron-based catalysts have been shown to be very selective and green catalysts for the HDO of lignin (5 articles, cited more than 200 times since 2012)
- A novel process is currently being developed for continuous catalytic processing of lignin and wastes
- Hierarchical zeolite has been shown to be more selective and stable than microporous zeolite (HSZM-5) for the catalytic pyrolysis of biomass to produce aromatics (benzene, toluene, p-xylene).

Figure 1: Targeted selectivity for lignin deoxygenation to produce green aromatics as presented in the Van Krevelen diagram

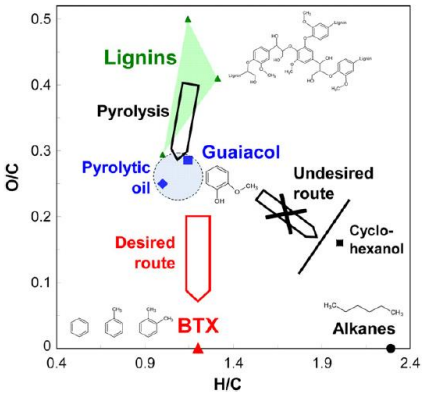
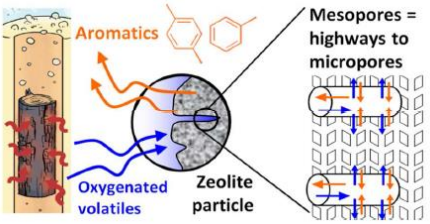


Figure 2: Catalytic pyrolysis of biomass: superior selectivity of hierarchical zeolites to produce aromatic hydrocarbons



References

Olcese et al. Appl. Catalysis B: Env 115, 63-73, 2012.

Olcese et al., Appl. Catalysis B: Env. 129, 528-538, 2013.

Olcese et al., ChemSusChem 6 (8), 1490-1499, 2013.

Olcese et al., Energy & Fuels 27 (2), 975-984, 2013.

Olcese et al., Energy & Fuels 27 (4), 2135-2145, 2013.

Jia et al., Green Chem. 19, 5442-5459, 2017..

✉ anthony.dufour@univ-lorraine.fr ✉ yann.le-brech@univ-lorraine.fr

H_2 THROUGH REFORMING

Context & Objectives

- Hydrogen is considered as a promising energy vector in the future decarbonized energy system
- Its production by thermochemical processes (steam methane reforming, dry reforming, tri-reforming) from fossil or bio-sourced methane has to be adapted to new process specifications: delocalized valorization and production, intermittent process operation etc.
- Miniaturized devices and new process structures must be designed to fulfil these requirements

LRGP Skills

- Process simulation including reforming reactors and hydrogen separations (Figure 3)
- Design of compact heat-exchanger reactors for SMR for mobility and micro-CHP systems (Figure 1, 2)
- Identification of kinetic models for process optimization and design
- Process synthesis including reforming steps and choice of most-appropriate technologies
- Design of processes adapted to intermittent conditions

Projects

- LOKIR (Low Oxidation Kinetics Reactor), FUI, coord. Air Liquide, partners: Fives, IJL, IS, EEIGM
- VITESSE2 (Valorization Industrielle et Energétique du CO_2 par utilisation d'Electricité décarbonée, Stabilisation du Système Electrique et Stockage d'Electricité), ANR, coord: Solvay, partners: Air Liquide, AREVA, EDF, CEA, VEOLIA, RTE, ICPEES.
- VALORCO (Valorization et réduction des émissions de CO_2 en industrie), ADEME, coord: Arcelor-Mittal, partners: Air Liquide, IFPEN, IJL, ICSM, ICCF, IDEEL
- FAIR (Fabrication Additive pour l'Intensification des Réacteurs), BPI, coord: Air Liquide, partners: AUER, ADISSEO, Polyshape, IJL, PIMM, SPCTS, Cirimat, DynFluid.

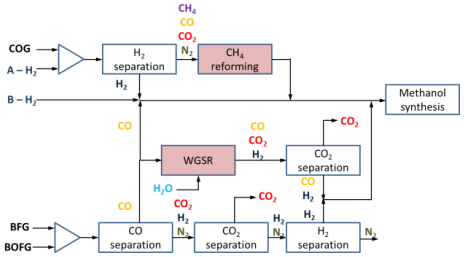
Results

- Kinetics of SMR Rh-based catalyst has been characterized.
- A compact heat-exchanger reactor for SMR has been designed and operated for more than 4000 hours.
- Processes including H2 reforming have been designed for valorization of exhaust gases in the steelworks industry.

Figure 1: Compact heat-exchanger reactor for SMR.

Figure 2: Pilot process with compact HX reactor.

Figure 3: Process synthesis including methane reforming for valorization of steelworks industry gases



References

W. Uribe-Soto et al., *Renewable and Sustainable Energy Reviews*, 74, 809-823, 2017.

J.-F. Portha et al., *Ind. Eng. Chem. Res.*, in press, DOI: 10.1021/acs.iecr.7b01323.

S. Arab et al., *Chem. Eng. Res. Des.*, 92, 2598-2608, 2014.

M. Mbodji et al., *Chem. Eng. Res. Des.*, 92, 9, 1728-1739, 2014.

M. Mbodji et al., *Chem. Eng. J.*, 207-208, 871-884, 2012.

✉ jean-marc.commenge@univ-lorraine.fr

H_2 H_2 THROUGH MICROBIAL PROCESSES

Context & Objectives

- World energy consumption from carbon fossil feedstock is still increasing whereas available resources are decreasing.
- Consequently, global warming (essentially a problem of accumulation of excessive carbon dioxide CO_2 in atmosphere) is resulting in dramatic climate changes.
- Development of processes that produce renewable energies from biomass is one of the solutions.
- Biohydrogen (H_2) associated with volatile fatty acids (VFA) can be used as a primary fuel (H_2) or associated with VFA can stimulate and improve methane production by anaerobic digesters.

LRGP Skills

- **Culture of anaerobic micro-organisms** such as the Clostridium species
- **Implementation of anaerobic bioreactors** from lab to pilot scales
- **Characterization of substrates and products** via chromatographic analyses (HPLC and GC online)
- **Kinetic studies of process fermentations** based on the use of cellulosic biomass after thermal treatments

Projects

- Production of energy and synthons by fermentation of vegetal biomass derivatives. Coord. E. Guedon (Institut Carnot ICEEL and FEDER funding).

Results

- Study of the carbon and energy sources uptake by C. acetobutylicum for the production of hydrogen and VFA.
- Products yield depend on the nature of carbon biomass derivatives after thermal treatments
- Higher product yields (H_2, VFA) were obtained at the highest polymeric degrees of cellulosic derivatives.

Figure 1: Anaerobic Clostridium acetobutylicum culture.

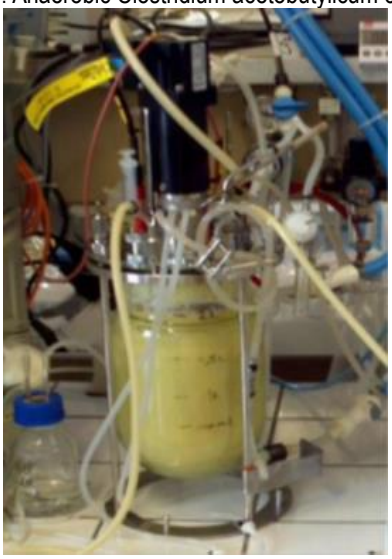
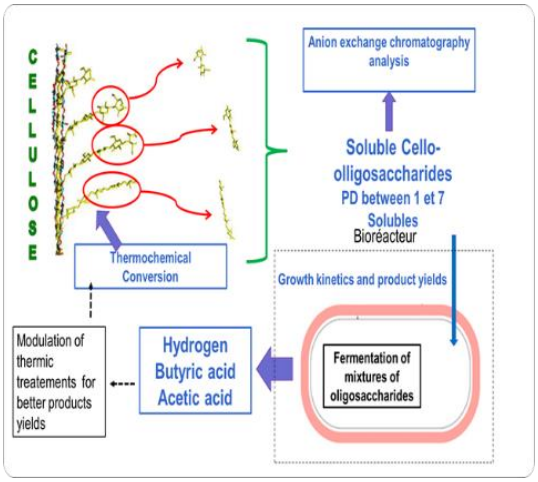


Figure 2: Strategy of anaerobic fermentation of cellulose derivatives.



References

F. Buendia-Kandia et al., Batch fermentation of d-glucose/cellobiose mixtures by Clostridium acetobutylicum ATCC 824: energetic and carbon source regulation in *Green process engineering,* 2016.

F. Buendia-Kandia et al., Diauxic growth of Clostridium acetobutylicum ATCC 824 when grown on mixtures of glucose and cellobiose, representative of cellulose hydrolysis products. *AMB*, 2018.

✉ emmanuel.guedon univ-lorraine.fr ✉ emmanuel.rondags@univ-lorraine.fr

H_2 PHOTOPRODUCTION

Context & Objectives

- H_2 can be generated from hydrocarbons or by steam reforming but emission of CO_2 is associated
- Electrolysis is expensive and this hinders the development of large-scale technological applications
- **Semiconductor-mediated photocatalysis constitutes one of the cheapest and convenient solutions for H_2 production.**
- In this context, efficient and stable photocatalysts are required.

LRGP Skills

- **Preparation and characterization of metal oxide semiconductors** and their association with **graphene-based materials** for the development of **photocatalysts active under solar- or visible-light irradiation**.
- Use of the **heterostructured materials** for H_2 photoproduction
- **Optimization** of the morphology, the structure, the state of the components, the composition and the electronic properties to improve H_2-photoproduction
- Association of the photocatalysts to some specific **cocatalysts** for enhanced H_2 production.

Projects

- Highly efficient photocatalysts made of earth-abundant elements
- Building heterojunctions between semiconductors and graphene-based materials to optimize dynamics and the photogenerated current for water-splitting
- Hydrogen photoproduction using iron oxide-based nanocomposites, ICEEL (Inter Carnot), coord. LRGP, partner: IJL
- Hydrogen production using nanostructured perovskite-type oxide and reduced graphene oxide (ULHyS-LUE PhD thesis), coord. LRGP, partner: IJL.

Results

- Design, synthesis and characterization of new photocatalysts
- Evaluation of the photocatalysts performances for H_2 production. Electric and electronic properties (Fig. 1)
- Multi-scale approach for the investigation of materials' stability
- Development of prototypes for pure H_2 generation via economically and environmentally ways (Fig 2).

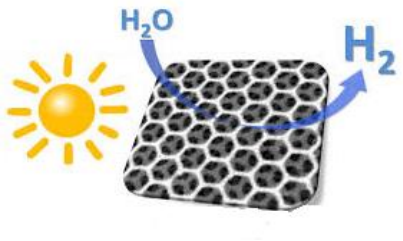


Figure 1: H_2-photoproduction mechanism using perovskite/graphene catalysts.

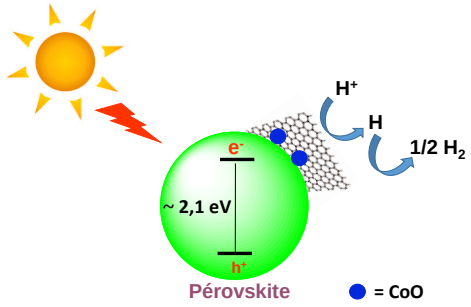
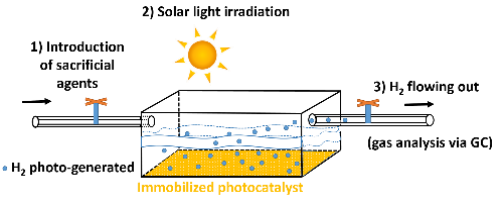


Figure 2: Schematic representation of the prototype device.



References

.S. Teets et al., Chem. Commun., 47, 9268-9274, 2011
Q. Li et al., J. Am. Chem. Soc., 133, 10878-10884, 2011
Q. Xiang et al., J. Am. Chem. Soc., 134, 6575-6578, 2012
Y. Wang et al., J. Mater. Chem. A, 2, 3847-3855, 2014
D. Donat et al., Beilstein J. Nanotechnol., 8, 1080-1093, 2017
H. Moussa et al. Appl. Catal. B, 185, 11-21, 2016
F. Achouri et al. Mater. Des., 101, 309-316, 2016

✉ raphael.schneider@univ-lorraine.fr

H_2 MEMBRANE FUEL CELLS

Context & Objectives

- Too low durability of membrane fuel cells (FC)
- Investigation of degradation phenomena at fuel cell components: membrane, electrode, gas diffusion layer, together with those caused by synergetic effects
- Improvement in FC components design and energy conversion.

LRGP Skills

- **Chemical engineering integrating aspects of transport phenomena, electrochemistry and physical chemistry** (with the help of neighboring disciplines e.g. material sciences and electrical engineering)
- **Electrochemical methods** for operation and evaluation of the **state of health** (SoH) of membrane fuel cells
- Coupling of the above methods to **post-mortem analysis** of cell components by **spectroscopy and microscopy**
- **Operation of fuel cells** (single cells or small stacks) under various modes; **Ex-situ** ageing of cell components
- **Direct hybridization** of fuel cells with energy storage systems for improved hydrogen consumption and cell durability
- Application to other systems for **electrochemical conversion of energy**.

Projects

- PhD M. Belhadj 2014-2017 within the CEATech program with LITEN in Grenoble: optimal design of microporous layer in the diffusion layer with local gradients of properties.
- Hybridization of fuel cells with supercapacity: Post Doc. K. Gérardin 2016, LUE PhD D. Arora 2016-2019 with GREEN lab in Nancy.
- Transport phenomena in porous layers in fuel cells: PhD UL M. Mukherjee from 2017
- N-functionalized graphene as support of catalytic layers: LUE PhD L. Moumaneix (IJL, Nancy) from 2017.

Results

- Pulsed current technique for evaluation of the state of health of each cell forming a fuel cell stack;
- Clear understanding of flow phenomena in fuel cell porous layers, depending on their surface properties and pore size
- Comparison of in-situ and ex-situ ageing protocols
- Proof of concept of fuel cell hybridization with supercapacitors for higher durability and better use of hydrogen fuel.

Figure 1: Pulsed current technique for evaluation of SoH of each cell in a stack (Chatillon et al.).

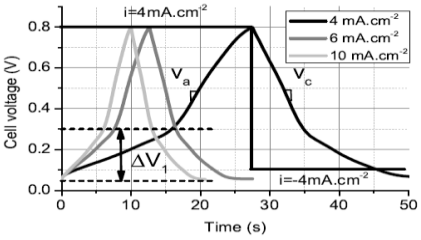


Figure 2: Porous layers in membrane fuel cells.

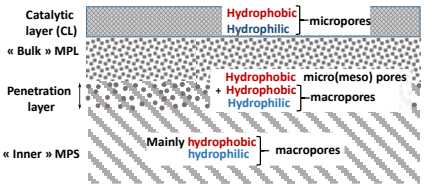


Figure 3: XPS analysis of gas diffusion layers after ex-situ ageing protocols (in percent)

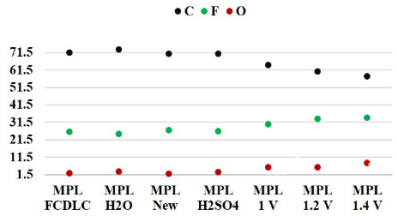
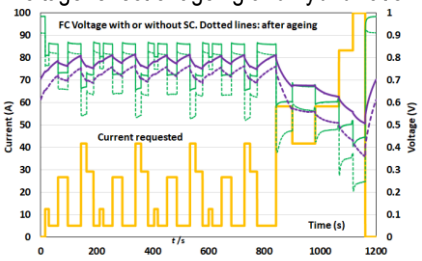


Figure 4: NEDC current profile and response in voltage: effect of ageing and hybridization



References

. Y. Chatilllon et al. J. Appl. Electrochem. 43, 1017-1026, 2013

Y. Chatillon et al., Fuel Cells 14 (4), 581-589, 2014

Y.Z. Xia et al., J. Electroanal. Chem. 767, 1-6, 2016

L. Franck-Lacaze et al., Techniques de l'Ingénieur, AF 6933 1-21, 2016

C. Bonnet et al., Fuel Cells 17 (2) (2017) 157-165, 2016

F. Lapicque et al., J. Power Sources 336, 40-53, 2016

K. Gérardin et al., to be published in Fuel Cells, 2017

✉ francois.lapicque@univ-lorraine.fr ✉ caroline.bonnet@univ-lorraine.fr

Combustion

JET FUEL THERMAL DECOMPOSITION

Context & Objectives

- Development of scramjet, an air breathing engine that could be used for hypersonic flight (Mach 5-10).
- One of the main issues = thermal management of the vehicle and more especially of the engine.
- Development of an active cooling system that consists in using the fuel heat sink capability due to the endothermicity of its thermal decomposition. A consequence of the decomposition of the heavy hydrocarbon fuel is the production of lighter species and poly-aromatic compounds.
- In order to quantify the heat transfer through the walls of the engine and the composition of the fuel entering the combustion chamber, a detailed kinetic model of the thermal decomposition of the fuel is required.
- To respond to this problem, ONERA has developed a plug reactor using a relatively large fuel flow rate, and MBDA-France is collaborating with the LRGP laboratory to study the kinetics of the thermal decomposition of fuels in a small Jet-Stirred Reactor.

LRGP Skills

- Pyrolysis of several hydrocarbons studied in an isothermal continuous perfectly stirred reactor. Residence time is around 1 second, whereas temperature ranges from 500°C to 800°C. The products formed during pyrolysis are identified by GC/MS and quantified by GC.
- Elaboration of the detailed reaction mechanisms, essentially radical ones, instead of global rate laws. Developed mechanisms are formed of elementary processes which represent the behavior of the reactions at the molecular stage including the kinetic intrinsic parameters.

Projects

- Projects with ONERA and MBDA-France

Results

- Study of the thermal decomposition of a complex jet-fuel
- Study of the pyrolysis of model molecules: n-dodecane, iso-dodecane, methyl-cyclohexane, tricyclodecane
- Modelling by a detailed kinetic mechanism based on elementary steps and validated with experimental data.

Figure 1: MBDA ScramJet hypersonic vehicle.

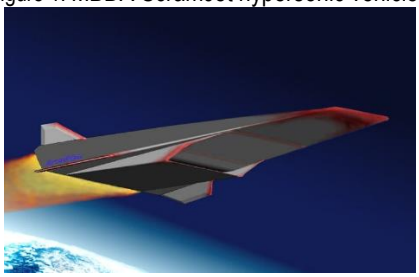


Figure 2: LRGP Jet-Stirred Reactor made in quartz.

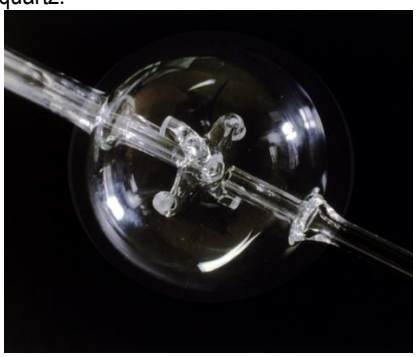
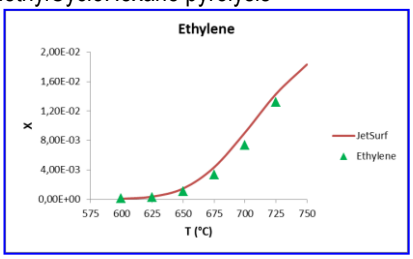


Figure 3: Ethylene production during MethylCycloHexane pyrolysis



References

Edwards, CST, 307-334, 2006
Dahm et al, JAAP, 71, 865-881, 2004
Daniau, et al, AIAA, 3403,2005
Herbinet et al, JPC A, 110, 419-429, 2006
Herbinet et al, JAAP, 78, 11298-11314, 2007
Bouchez et al, AIAA, 2623, 2008
Bounaceur et al, JAAP, 103, 240-254, 2013

✉ yves.simon@univ-lorraine.fr

Combustion

AUTOMOTIVE FUEL COMBUSTION

Context & Objectives

- Efficiency increase and pollutant emission reduction in automotive engine
- Robust detailed kinetic models should be constructed.

LRGP Skills

- **Gas-phase kinetics and radical mechanism development.**
- Experimental investigation **using shock tube, jet-stirred reactors** at pressure from 1 to 10 atm, and **burners for laminar premixed flame** for velocity measurements (1-6 atm) by the heat flux method, and flame structure, including temperature and species profile, determination (6.6 kPa).
- Analysis of a wide range of combustion products using **gas-chromatography, time-of-flight mass spectrometry and cavity ring-down infrared spectroscopy**.
- Theoretical calculations of thermochemical and kinetic data based on **quantum mechanics, statistical thermodynamics and kinetic theories.**
- Software for the **estimation of thermochemical data** and the **automatic generation of detailed kinetic models** (EXGAS).

Projects

- ERC advanced Grant: Clean-ICE: Detailed chemical kinetic models for cleaner internal combustion engines, (2008-2013).
- Contract with Saudi-Aramco: Study of the gas-phase oxidation of a series of alkylbenzenes and alkylcyclohexanes present in diesel fuels, (2010-2013).
- EU Marie Curie contract with SHELL: LOWCAFF-Low Carbon Future Fuels (2011-2014).

Results

- Understanding of the reaction mechanisms associated with the combustion of an increased range of fuels (hydrocarbons: linear, branched and cyclic alkanes, linear and branched alkenes, aromatics; and biofuels: oxygenated compounds such as methyl and ethyl esters, linear and cyclic ethers, aldehydes, alcohols) for a wide range of equivalence ratios (from 0.25 to 4).
- First quantification of some minor species important for improving autoignition and combustion modelling, e.g. H_2O_2, carboxylic acids, alkylhydroperoxides, alkenylhydroperoxides, ketohydroperoxides.
- Automatic generation of detailed kinetic models for the oxidation of saturated methyl esters up to C_{19} and alkyl benzenes up to C_{16}.

Figure 1: Molecular beam probing in a jet-stirred reactor.

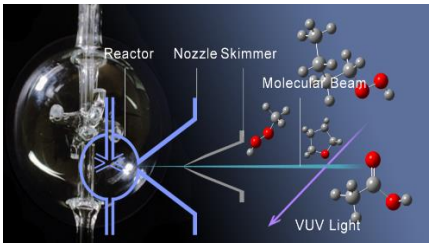
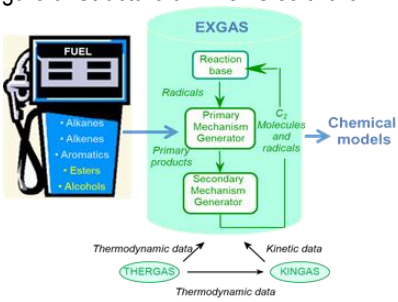


Figure 2: The burner for flame speed measurement at 1 atm.

Figure 3: Structure of EXGAS software.



References

F. Battin-Leclerc et al., Ang. Chem. Int Ed., 49, 3169-3172 7, 2010.

F. Battin-Leclerc et al., Chem. Soc. Rev., 40, 4762-4782, 2011.

F. Battin-Leclerc et al., Proc. Combust. Inst., 35, 349-356, 2015.

P. Dirrenberger et al., Energy&Fuel, 25, 3875-3884, 2011.

H. Hakka et al., Int. J. Chem. Kin., 42, 226-252, 2010.

O. Herbinet and F. Battin-Leclerc, Int. J. Chem. Kin., 46, 619-639, 2014.

O. Herbinet et al., Proc. Combust. Inst., 33, 391-398, 2011

L. Tran et al., Combust. Flame, 162, 1899-1918, 2015.

✉ frederique.battin-leclerc@univ-lorraine.fr

Combustion

ALTERNATIVE FUELS IN GAS TURBINES

Context & Objectives

- Gas Turbine is one of the most flexible power systems.
- Demand for energy valorization of alternative fuels to natural gas (Local resource (ethanol, naphta), Syngas from coal or biomass, Process by-products etc.)
- Assessment of combustion characteristics, pollutant emissions (NOx, CO), safety criteria, risk of deposit formation

LRGP Skills

- Kinetic and thermochemical modelling of the combustion over a wide range of operating conditions
- Validation of models in unusual conditions (high temperature – high pressure, very low temperature for minimum auto-ignition temperature prediction
- Theoretical evaluation of thermochemical and kinetic data using quantum chemistry.

Projects

- Collaborations with GE Energy Products.

Results

- Modelling of gum formation in olefin-containing process gases
- Numerical analysis of combustion properties and emissions of several alternative fuels to natural gas, such as syngas, low PCI gases, oxygenated fuels.
- Unravelling the link between flame temperature of alternative fuels and NOx emission in GT.
- Prediction of Minimum Auto-ignition Temperature and ignition delay times of combustible gas mixtures
- Prediction of flammability limits (LFL and UFL) of gas mixtures with addition of inert gas at high temperature and high pressure.

Figure 1: GE H-class gas turbine.

Figure 2: Adiabatic flame temperatures at 300 K and 1 bar of species contained in fuels.

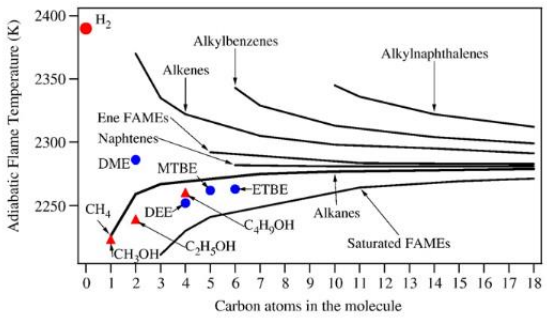
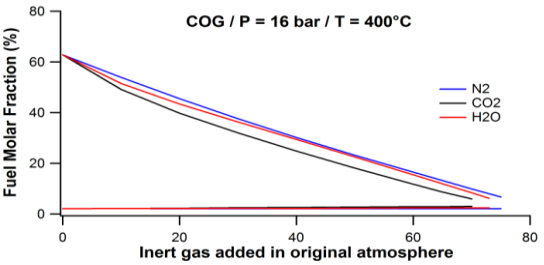


Figure 3: Flammability limits of a Coke Oven Gas at 400 °C under 16 bar with addition of inert.



References

Glaude et al., IECR, 44, 4212-4220, 2005
Glaude et al., FPT, 91, 229-235, 2010
Glaude et al., ASME-TE, GT2010-22338, 2010
Bounaceur et al. ASME-TE, GT2015-42011, 2015
Bounaceur et al., JEGTP, 138, 21505, 2015
Bounaceur et al., JEGTP, GT2017-64172, 2017

✉ pierre-alexandre.glaude@univ-lorraine.fr

POWER CYCLE

Context & Objectives

- Alternative power cycles are receiving increasing attention as solutions to supply future energy demand, which is expected to rise by 70% by 2035.
- Due to the prospect of greenhouse gases reduction, European and worldwide regulations are increasingly moved towards more restrictive rules. Most of the fluids currently in use in thermal machines are affected so that work on alternative solutions is urgently needed.
- The objective of our activities is twofold. On the one hand, our ambition is to develop innovative cycles and on the other hand to optimize a working fluid that meets current environmental standards.

LRGP Skills

- Expertise in the **choice of an equation of state** to estimate the thermodynamic properties (enthalpy, entropy, exergy etc.) of a tested working fluid in order to render possible the comparison of processes through their thermal efficiency.
- Expertise in the estimation of **transport properties** which have a major impact on sizing of the equipment.
- Development of **predictive equations of state** relying on the group contribution concept aimed at making possible a large **screening of working fluids**.

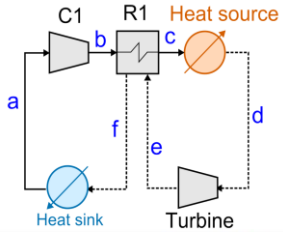
Projects

- Design and optimization of an innovative coal power plant lying on a supercritical CO_2 Brayton cycle (in collaboration with EDF)
- Use of the product-design approach to optimize the working fluids for ORC cycles and heat pumps.
- Development of complex tools to test the pertinence of using reactive working fluids in power cycles (industrial funding from Air Liquide).

Results

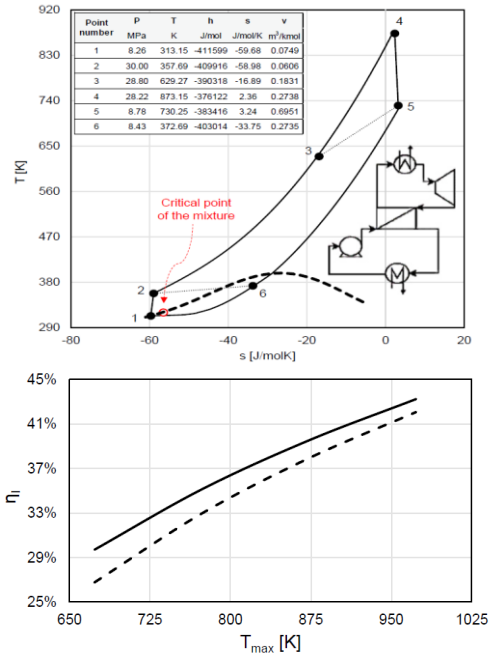
- The properties of working cycle mixtures can be predicted with an accuracy close to the experimental uncertainty.
- The efficiency of the developed supercritical CO_2 Brayton cycle has been increased by 5%.
- The use of reactive fluids makes it possible to greatly increase the efficiency of turbines.

Figure 1: Impact of the selected thermodynamic model on performance indices of a classical Brayton cycle.



	SW (ref EoS)	PR	PR-BM	SRK	LKP	BWRS
		(properties expressed in terms of relative deviations with respect to the SW EoS)				
RC cycle efficiency	0.557	-0.6%	-1.1%	-0.9%	-0.3%	-0.2%
Cycle net power $\dot{W}_{net}$	111 MW	-0.6%	-1.1%	-0.9%	-0.3%	-0.2%
ΔT_{hot}	44.8 K	+8.3%	+12.6%	+8.4%	+4.0%	+1.6%
$\dot{Q}_{IR}$	499 MW	-0.9%	-1.1%	-0.3%	-0.9%	-0.2%
Total mass flowrate $\dot{m}$	603 kg/s	-0.1%	-0.1%	-0.5%	-0.8%	-0.1%
$\dot{Q}_{heat\ sink}$	88.5 MW	+0.7%	+1.4%	+1.1%	+0.4%	+0.2%
Turbine Power $\dot{W}_{turbine}$	164 MW	-0.9%	-1.1%	-0.1%	-0.4%	-0.3%
Compressor work $\dot{W}_{compressor}$	52.8 MW	-1.6%	-1.1%	+1.5%	-0.5%	-0.7%

Figure 2: Replacement of pure CO_2 by CO_2+NOA fluid cycle in an ORC (NOA is an environmentally-friendly Non-Organic Additive currently part of the patenting process). T-s diagram and trend of cycle efficiency (solid line: mixture CO_2+NOA, dashed line: pure CO_2) as a function of the cycle maximum temperature, at maximum pressure of 30 MPa.



References

S. Lasala et al., Energy procedia, 129, 947-954, 2017.
J. Qian et al., *Int. J. Refrigeration*, 73, 65–90, 2017
Q. Zhao et al., *Ind. Eng. Chem. Res.*, 56, 6841−6853, 2017
R. Privat et al., *Energy.*, 55, 594–609, 2013.

✉ romain.privat@univ-lorraine.fr ✉ jean-noel.jaubert@univ-lorraine.fr

INNOVATIVE FLUIDS FOR ENGINES AND CYCLES

Context & Objectives

- The choice of a working fluid for a given energetic application (refrigeration, heat pump, power cycle) has a dramatic influence on the cycle performances (efficiency but also environmental aspects)
- Some dozens of pure fluids are used nearly systematically for such applications. Few mixtures are considered.
- The use of mixtures makes it possible to tune the expected properties of the working fluid by playing both on the component list but also on the composition.
- As a prerequisite, the implementation of the product-design approach requires as many chemicals as possible to be taken into account. To do so, a thermodynamic model capable of guesstimating fluid properties from the mere knowledge of the chemical structures of the compounds must be used.

LRGP Skills

- **Development of thermodynamic models capable of guesstimating fluid properties** from component chemical structures.
- **Implementation of the product-design approach**: resolution of an optimization problem aimed at determining the working fluid composition by maximizing the cycle efficiency and minimizing environmentally negative effects.
- **Use of reactive fluids as working fluids** (this is a very new but promising approach for the design of fluids for cycles).

Projects

- Development of the E-PPR78 for product design applications – industrial funding from companies: Total and Air Liquide.
- ANR SIGARRR.
- Automatic design of fuel – Industrial funding (General Electric)
- ANR Optidemix.

Results

- The E-PPR78 model can deal with mixtures containing permanent gases, water, NH3, hydrocarbons (HC), refrigerants (chloro and fluoro HC).
- Both phase equilibria and energy properties (heat capacity, enthalpy, entropy etc.) are predicted.
- An automatic procedure for fuel conception has been developed for the GE company.
- Theoretical studies have been conducted to highlight the characteristics expected for a binary system flowing in an absorption-demixtion heat pump.

Figure 1: Influence of the biodiesel and aqueous ethanol percentage on liquid-liquid saturation curves in the framework of a biofuel conception.

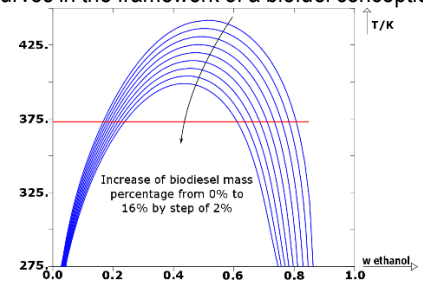
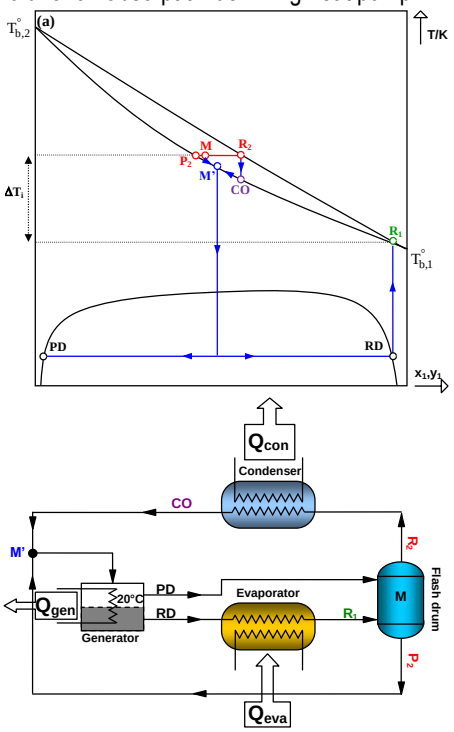


Figure 2: Phase diagram of an 'ideal' working fluid for an absorption demixing heat pump.



References

A. Pina et al., Int J Thermophys 37:23, 2016

R. Privat et al., Energy, 55, 594-609, 2013

N. Juntarachat et al., international journal of refrigeration, 47, 141-152, 2014

J.W. Qian et al., international journal of refrigeration, 73, 65-90, 2017

R. Privat et al., Global journal of physical chemistry, 2, 246-254, 2011.

✉ romain.privat@univ-lorraine.fr ✉ jean-noel.jaubert@univ-lorraine.fr

Context & Objectives

- In the nuclear industry, dissolution and precipitation are used for:
- Dissolution and recovery of spent nuclear fuel,
- Purification and concentration of uranium ore: uranium is recovered by precipitation of uranium peroxide in a fluidized bed reactor,
- Nuclear fuel reprocessing: precipitation of uranium oxalate,
- Radioactive waste management: co-precipitation for radioactive liquid waste decontamination.

LRGP Skills

- Determination of autocatalyzed **dissolution kinetics**,
- **Optimization and modelling of batch and continuous reactors** for the dissolution of uranium dioxide pellets,
- Determination of nucleation, growth and agglomeration mechanisms to provide a **global model of uranium peroxide precipitation in a fluidized bed reactor**,
- **Kinetic study at low supersaturations** for uranium oxalate
- Optimization and modelling of the **continuous process of co-precipitation**.

Projects

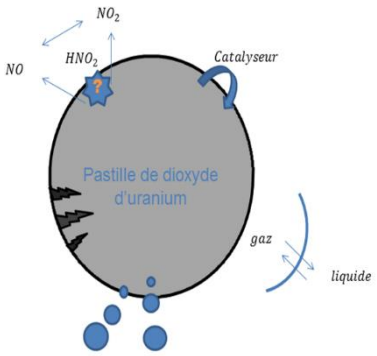
- Study of the dissolution of uranium dioxide in a nitric medium. LRGP, AREVA & CEA (PhD thesis of C. Delwaulle, 2011)
- Study of heterogeneous autocatalytic reactions. LRGP, AREVA & CEA (PhD thesis of P. Marc, 2014)
- Towards the design of industrial reactors for the dissolution of uranium dioxide, LRGP, CEA (PhD thesis of F. Charlier, 2017)
- Uranium peroxide precipitation, LRGP, AREVA & CEA Marcoule (PhD thesis of L.A. Mojica-Rodriguez, 2015)
- Precipitation of uranium oxalate at low supersaturation, LRGP & CEA (PhD thesis of A. Guttierez-Chavida, 2015)
- Treatment of radioactive liquid wastes, LRGP & CEA (PhD thesis of J. Flouret, 2013).

Results

- Understanding, measurement and formalization of the kinetics for the autocatalytic dissolution of uranium dioxide
- Design of new and intensified dissolution reactors
- A new model called Mixed Suspension Separation Product Removal (MSSPR) is proposed and successfully applied to the uranium peroxide precipitation process
- Thermodynamic and kinetic model of oxalate precipitation at low supersaturation
- Design of a new intensified coprecipitation reactor: the reactor/clarifier.

Figure 1: Photograph of the fluidized bed reactor for uranium oxide precipitation.

Figure 2: Heterogenous and autocatalyzed dissolution mechanism of uranium dioxide pellet.



References

Delwaulle et al., *CEJ*, 174, 383-389, 2011
Marc et al., *Nuclear Sciences and Technology*, 3, 2017
Charlier et al., *EPJ Nuclear Sciences and Technology*, 3, 2017.

✉ herve.muhr@univ-lorraine.fr ✉ eric.schaer@univ-lorraine.fr

ABSORPTION HEAT PUMPS

Context & Objectives

- French industrial waste heat production: 51 TWh
- Mid-temperature level waste heat (60-80 °C) hard to use
- Need for heat upgrading processes
- Existing working mixture for absorption heat transformers (H_2O / LiBr) has multiple drawbacks
- New absorption heat-pumps structures and working mixtures should be studied.

LRGP Skills

- **Modelling of heat pumps**
- **Modelling of absorption heat pump working mixtures thermodynamic properties**
- **Heat pump pilot unit design, building and operation**
- **Exergetic analysis**

Projects

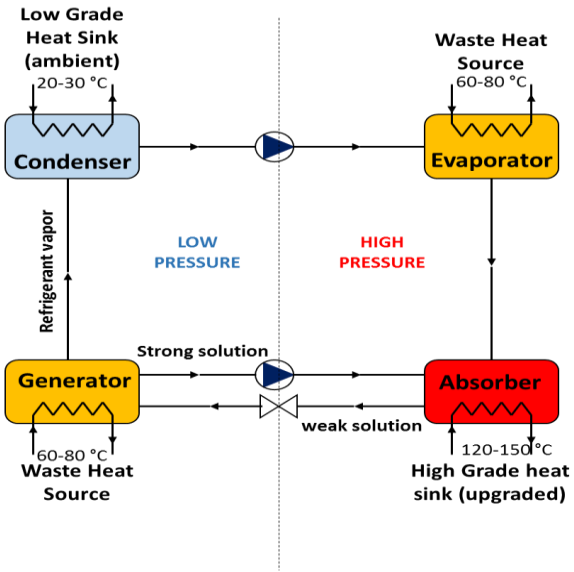
- Development of an absorption heat transformer cycle using partially miscible mixtures (absorption-demixtion cycle)
- Study of the opportunity to use ionic liquids as absorbent in absorption heat transformer
- Development of absorption heat pump cycles based on the use of deep eutectic solvents.

Results

- Technical feasibility of absorption-demixtion heat pump cycles demonstrated (pilot unit successfully operated). Possible working mixtures identified. But also, thermodynamic limitations established.
- Need to study more complex mixtures (ternary, other family of compounds) to obtain satisfactory performances with the absorption-demixtion cycle
- Large number of ionic liquid based heat transformers liquid mixtures studied. Thermodynamic properties measured and modelized. Promising candidate mixtures identified. Performances very close to traditional mixtures (LiBr/H_2O)

Figure 1: Absorption heat pump prototype

Figure 2: Absorption heat pump cycle



References

E. Abumandour et al., Progress and Development in Ionic Liquids, 3-33, 2017
E. Abumandour et al., Appl. Therm. Eng., 94, 579-589, 2016
R. Privat et al., Energy, 55, 594-609, 2013
H. Noubli et al., IJCRE, 8, 2010
D. Alonso et al., IJTS, 42, 631-638, 2003
D. Alonso et al., Appl. En., 72, 583-597, 2002

✉ dominique.alonso@univ-lorraine.fr ✉ fabrice.mutelet@univ-lorraine.fr

THERMAL INSULATION

Context & Objectives

- ***Product-design methodology applied to the conception of thermal insulators:***
  The transport of natural gases in LNG carriers requires high-performance insulation systems to maintain very low temperatures and avoid gas losses due to evaporation.
  Classically used insulators are foams swelled with specially-designed gas mixtures.
  The objective of this study was to design a mixture (i.e., to identify a list of compounds and their related compositions) with optimal insulation properties (high thermal conductivities), enduring temperatures in the range [-160 °C; 40 °C].
- ***Aerogel process: design of a separation process aimed at getting an aerogel from an organogel:***
  Starting from an organogel synthetized by the LCPM laboratory, a separation process is implemented to extract the organic solvent from the gel using supercritical CO_2. The aim of the project was to design an aerogel with higher insulation performance than classical aerogels made from silica.

LRGP Skills

- Implementation of the product-design methodology.
- Relationships between mixture+foam systems and their resulting thermal properties.
- Supercritical carbon dioxide drying.
- Relationships between process operating conditions and aerogel thermal properties.

Projects

- ANR MULOWA (2009-2012)
- ADEME Project AEROSITAN (2017-2020)
- Confidential projects for private companies

Results

- ***Product-design methodology:***
  The project led to the identification of optimal 5-component mixtures making it possible to reduce the amount of LNG evaporated during transportation.
- ***Aerogels:***
  Optimal process operating conditions have been identified, both for aerogel drying and organic solvent recovery. Aerogels exhibit a thermal conductivity near those of inorganic aerogel like silica (measurements by the LEMTA laboratory), a significant hydrophobic character and a very low density.

Figure 1: Temperature change of thermal conductivities of a set of designed mixtures generated from the product-design methodology (points are experimental data of a ref. mixture).

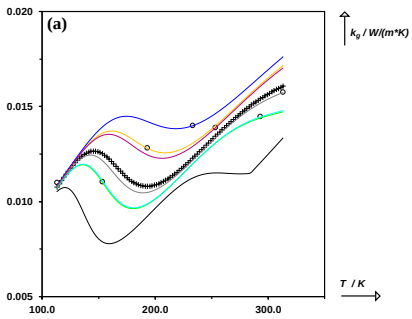
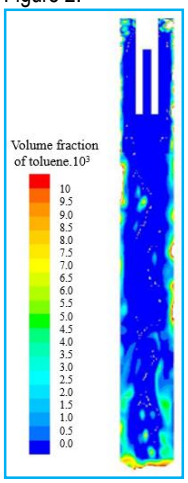
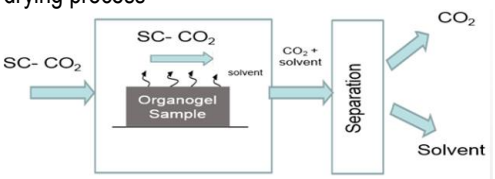


Figure 2:



Hydrodynamic study: cyclonic separator (for the recovery of the organic solvent (toluene) from the CO_2 + organic solvent mixture issued from the aerogel drying process).

Figure 3: Simplified scheme of the supercritical drying process



References

B.Jamart-Gregoire et al. Monolithic organic aerogels derived from single amino-acid based supramolecular gels: physical and thermal properties *RSC Advances* 6, 104, 102198-102205, 2016

M. Lazrag et al. Thermodynamic and hydrodynamic study of a gas-liquid flow in a cyclonic separator downstream supercritical drying, *Journal of Supercritical Fluids* 118, 27-38, 2016.

✉ danielle.barth@univ-lorraine.fr ✉ jean-noel.jaubert@univ-lorraine.fr
✉ romain.privat@univ-lorraine.fr

Context & Objectives

- Carbon capture from large emission points (power plants, steel, cement, refineries) is of major importance in order to mitigate greenhouse gases
- An energy efficient capture process is required for CO_2 recovery and concentration from flue gases
- Numerous carbon capture processes have been proposed, but gas-liquid absorption in chemical solvents (e.g. amines) is the baseline technology.

LRGP Skills

- **Material and liquid selection** for selective carbon capture (solvents, polymers, adsorbents, membranes)
- **Modelling and simulation** of carbon capture processes (membrane contactors, membrane separation)
- **Design and testing of bench-scale units** for proof of concepts studies and model validation
- **Evaluation of energy requirement and size for carbon capture** (PSE simulation with tailor-
- made toolboxes)
- **Scale up and design of demonstration units**
- **Life Cycle Analysis** (LCA) of carbon capture processes.

Projects

- Simulation of CO_2 capture under precombustion conditions IGCC (ADEME EDF PhD grant)
- CICADI Membrane contactor for post combustion CO_2 capture by chemical gas liquid absorption (ANR) Coord LRGP
- CESAR (FP7 project)
- AMELIE Membrane contactor for chilled ammonia process (ANR) Coord LRGP
- Post combustion capture: solvents and processes (EDF PhD grant)
- ENERGYCAPT Membrane contactor for post combustion CO_2 capture by chemical gas liquid absorption (ANR)
- HIPERCAP Chemically reactive membranes for post combustion carbon capture (FP7)
- M4CO2 Metal Organic Framework membranes for CO_2 capture (FP7)

Results

- Experiments, modelling and simulation of membrane contactor and membrane gas permeation units for CO_2 capture
- Process System Engineering toolbox for tailor-made membrane gas separation simulations (e.g. MEMSIC software implemented into ASPEN)
- Design and simulation of membrane contactor demonstration units in real industrial environment

Figure 1: Novel dense skin composite membrane for intensified CO_2 absorption (Cicadi project).

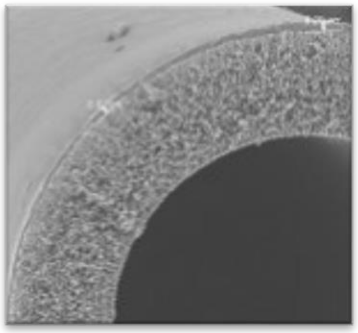
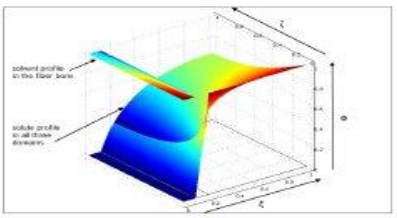


Figure 2: Bench-scale unit for carbon capture experiments by membrane gas separation.

Figure 3: Simulation of gas liquid chemical absorption in a membrane contactor unit (Comsol®)



References

Giordano, L. et al. *Energy*,116, 517-525, 2017

Zhao, S. et al., *Journal of Membrane Science*, 511, 180-206, 2016

Zaidiza, D. et al., *Journal of Membrane Science*, 493, 106-119, 2015

Chabanon, E. et al., *Chemical Engineering*, 91, 7-22, 2015

Makhloufi, C. et al., *Journal of Membrane Science*, 455, 236-246, 2014

Neveux T. et al., *Ind. Eng. Chem. Res.*, 52, 11, 4266-4279, 2013

Belaissaoui, B. et al., *Chemical Engineering J.*, 211, 122-132, 2012

Favre, E. et al., *Journal of Membrane Science*,407-408, 1-7, 2012

✉ denis.roizard@univ-lorraine.fr ✉ christophe.castel@univ-lorraine.fr

CO_2 CARBON CAPTURE AND USE

Context & Objectives

- Carbon capture and use is actively investigated in order to mitigate greenhouse gases emissions
- Numerous solutions have been proposed: catalytic conversion into chemicals, biotechnological and electrochemical transformation
- A rigorous evaluation of energy requirement, greenhouse gases balance and environmental impact is of major importance in order to identify the best process in a sustainable framework.

LRGP Skills

- **Modelling and simulation** of carbon capture and use processes
- **Design and testing of bench-scale units** for proof of concepts studies and model validation
- **Evaluation of energy requirement and size for carbon capture and use** (PSE simulation with tailor-made toolboxes for membrane processes)
- **Scale up and design of demonstration units**
- **Life Cycle Analysis** (LCA) of carbon capture and use processes.

Projects

- Photobioreactors for algae production (Kerosalg)
- Carbon capture from steel production plant (blast furnace) for methanol synthesis (VALORCO project)
- CO_2 use from flue gases for chemical production (ANR C2B project, LRGP coordinator)

Results

- Conceptual design and test of novel carbon capture systems for CCU projects (e.g. intensified gas liquid absorption for chemical conversion)
- Design and test of a pilot-scale photobioreactor for algae production (bio kerosene project)
- Process System Engineering toolbox for tailor-made carbon capture and use simulations (e.g. MEMSIC software implemented into ASPEN)
- Technico-economical analysis of CCU projects

Figure 1: Bench-scale unit for carbon capture & use experiments (intensified gas liquid absorption in reactive solution).

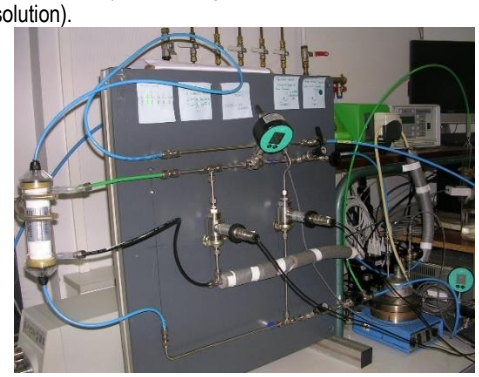


Figure 2: PSE flowsheet of a CCU process for technico-economical analysis (evaluation of energy requirement and capital costs).

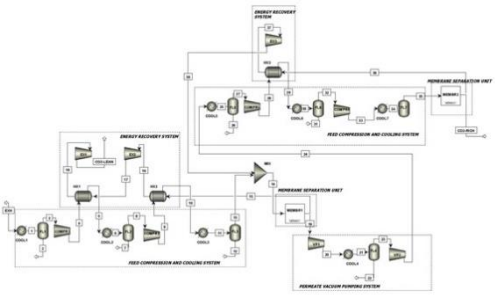


Figure 3: Pilot demonstrator unit for CCU

References

Ramirez A. et al., *Journal of Membrane Science*, 526, 191-204, 2017

Mendez. et al., *Journal of Membrane Science*, 530, 20-32, 2017

Chabanon, E. et al., *Chemical Engineering Science*, 91, 7-22, 2015

Belaissaoui B. et al., *Journal of Membrane Science*, 513, 236-249, 2016

Neveux T. et al., *Ind. Eng. Chem. Res.*, 52, 11, 4266-4279, 2013

Belaissaoui, B. et al., *Chemical Engineering J.*, 211, 122-132, 2012

✉ denis.roizard@univ-lorraine.fr ✉ christophe.castel@univ-lorraine.fr

Process # ENERGY NETWORK

Context & Objectives

The multi-objective optimization of an energy hub with hydrogen as energy vector, including generation and conversion of several energy sources is a challenging problem. Energy and material converters (technological bricks) have to be properly designed and connected to minimize simultaneously energy consumption, total costs and environmental rejections. The methodology is specifically developed for eco-districts' systems but the approach can be applied to industrial eco-parks. Considering the variability of local energy resources and usages, size and performance of equipment may considerably differ and affect the global environomic performance of the district. An important result is to select optimal districts based on proposed appropriate criteria, such as size and geolocalization considering its social and economic activities. The optimization challenge is to consider simultaneously sometimes contradictory design objectives by using a multi-objective algorithm of optimization which has not been done in conventional energy hub approaches.

LRGP Skills

- **Design and modelling of energy and material converters** based on home-made and commercial (Aspen Hysis etc.) simulators
- **Design of intensified chemical reactors** for H_2 transformation (reforming), co-valorization of CO_2 (methane, methanol), bioconvertors (methanization)
- **Techno-economic evaluation** of energy and mass transformers
- **Optimization methods (MNLP, MINLP etc.)** applied to energy hub and complex chemical processes

Projects

The subject is part of the project ULHyS (University of Lorraine - Hydrogen Sciences & technologies) which concerns H_2 production, conversion into other energy carriers, usage in multi-carrier micro-grids and economic, territorial and end users' issues. It is supported though a PhD study "Multi-objective optimization of an eco-district energy hub with Hydrogen as energy vector, including generation and conversion of energy technologies" in close collaboration with ERPI-Nancy, a laboratory specialized in multi-objectives' optimization including technical and social usages. The subject is also supported by PiGaz (collaborative laboratory between the LRGP and Air Liquide company).

Results

- Optimal energy hub structures based on economic costs and environmental footprint
- Pre-design and performances of energy transformers

Figure 1: Energy hub representation.

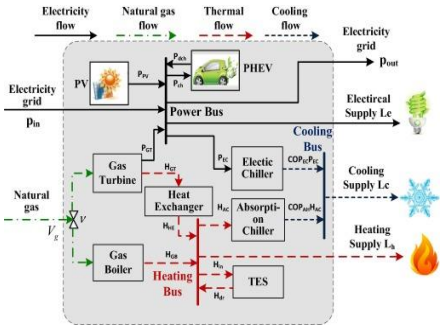
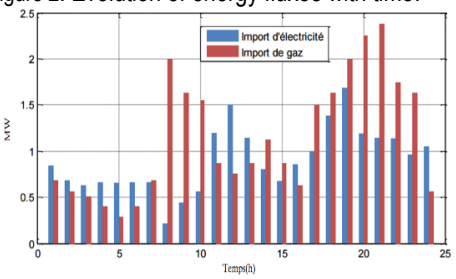


Figure 2: Evolution of energy fluxes with time.



References

Molyneaux, A, Leyland, G , Favrat, D., *Energy* 35(2) 751-758, 2010

Palazzi, F., Maréchal, F., Godat, J. , Favrat, D., *Fuel Cells*, 5, 5-24, 2005

Bautista S., Narvaez P., Camargo M., Chery O., Morel L. *Ecological Indicators*. Volume 60, 84-107, 2016

Bautista S., Enjolras, M., Narvaez P., Camargo M., Morel M. *Ecological Indicators*, 2016

Brissel L., Dupont L, Morel L., Guidat C. *International Journal of Energy, Environment, and Economics*. 23 (2), 1-22, 2016

✉ laurent.falk@univ-lorraine.fr ✉ jean-marc.commenge@univ-lorraine.fr

Process

PROCESS INTENSIFICATION

Context & Objectives

- Energetic transition requires the reduction of the energy consumption of existing processes and the development of processes for delocalized production under unsteady conditions
- Process intensification enables the energy consumption of processes to be reduced by enhancing heat and mass transfer performances and by focusing energy at the right time and place
- Intensification by geometric microstructuring enables miniaturized devices for decentralized applications to be designed.
- Miniature and modular time-responsive equipment is appropriate for the development of new processes submitted to time-varying energy inputs

LRGP Skills

- Design of **compact integrated heat-exchanger reactors**
- Application of **process intensification analysis** for choice of best-available technologies or development of innovative devices
- **Design of responsive devices** for time-dependent operating conditions

Projects

- Development of a micro-structured SMR reactor (LOKIR: Low Oxidation Kinetics Reactor), FUI, coord. Air Liquide, partners: Fives, IJL, IS, EEIGM
- Design of a time-responsive methanol synthesis process submitted to intermittent hydrogen availability (VITESSE2), ANR, coord: Solvay; partners: Air Liquide, AREVA, EDF, CEA, VEOLIA, RTE, ICPEES.
- Development of a compact micro-combined heat and power system (FAIR : Fabrication Additive pour l'Intensification des Réacteurs), BPI, coord: Air Liquide, partners: AUER, ADISSEO, Polyshape, IJL, PIMM, SPCTS, Cirimat, DynFluid.
- Development of an intensified multi-staged catalytic process for transesterification of vegetable oils, partner: IFPEN

Results

- Pilot-scale operation of a microstructured SMR HEX reactor for mobile H_2 production
- Pilot-scale operation of a catalytic transesterification reaction with staged feeds and experimentally fitted kinetics

Figure 1: Process structure for methanol synthesis submitted to unsteady H_2 inlet

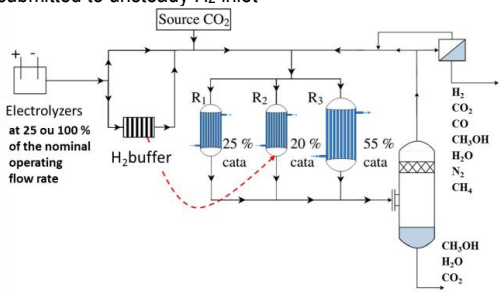


Figure 1: Flow circulations inside a structured heat-exchanger reactor with integrated heat valorization

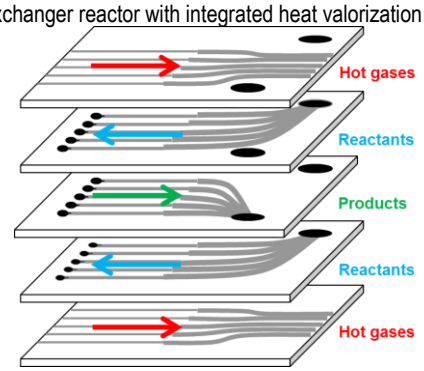


Figure 3: Catalytic pilot set-up for transesterification of vegetable oils.

References

J.-F. Portha et al., *Chemical Engineering and Processing: Process Intensification*, 84, 1-13, 2014.

J.-M. Commenge et al., *Chemical Engineering and Processing: Process Intensification*, 84, 109-127, 2014.

M. Mbodji et al., *Chem. Eng. Res. Des.*, 92, 9, 1728-1739, 2014.

J.-M. Commenge et al., *Chem. Eng. Journal*, 173, 541-551, 2011.

M. Saber et al., *Chem. Eng. Proc.: Process Intensification*, 49, 732-739, 2010.

J.-M. Commenge et al., *Chem. Eng. Technol.*, Vol. 28, Numéro 4, 446-463, 2005.

✉ jean-marc.commenge@univ-lorraine.fr ✉ jean-francois.portha@univ-lorraine.fr

PROCESS SYSTEMS ENGINEERING

Context & Objectives

Process Systems Engineering research activities in the laboratory cover the use, adaptation and development of methods/methodologies in the area of energy-based process synthesis, modelling, simulation (dynamic and CFD), integration and optimization:

- development of in-depth first principle models in close interaction with experiments/pilots,
- simulation of these models using commercial or in-house codes, and eventual development of surrogate models,
- implementation of static, dynamic and real-time (global) optimization methods for the design, optimization and operation of processes,
- application and development of methods for energy-efficient process structures.

LRGP Skills

- **Synthesis, modelling and simulation** of (complex) processes,
- **Estimability analysis and design of optimal experiments** for models' identification and validation,
- **Simultaneous implementation** of optimal experiments and identification of parameters in one run,
- **Steady-state, (real-time) dynamic and mixed optimization**.

Projects

- Dynamic real-time optimization of polymerization processes.
- Reactor shape optimization combined with 3D printing for process integration.
- Modelling, simulation, optimization and control of various processes: plasma-assisted thin films deposition, phosphate ore flotation processes, air purification.
- Design and optimization of innovative coal power plants based on supercritical Brayton cycle.
- Process synthesis for valorization of blast furnace and coke oven gases (VALORCO).
- Process synthesis and optimization of multi-energy eco-districts (ULHyS).

Results

- Synthesis, modelling, simulation, estimability analysis, identification and model validation of various reactors and processes
- Open loop and closed loop dynamic real-time optimization
- Process structure optimization and integration for energy input minimization.

Figure 1: Determination of the optimal low-pressure level maximizing the COP of a power cycle.

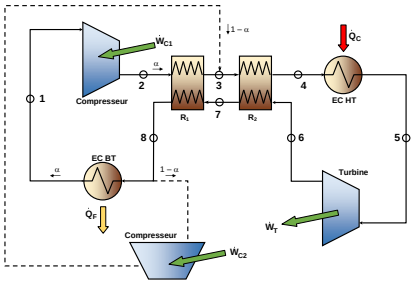
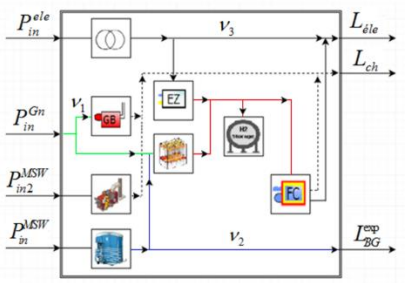


Figure 2: Energy Hub modelling and optimization.



References

R. Bousbia-Salah, F. Lesage, G.-H. Hu, A. Latifi, Comp.-Aided Chem. Eng., 40, 1741 - 1746, 2017.
R. Bousbia-Salah, F. Lesage, G.-H. Hu, A. Latifi, Comp.-Aided Chem. Eng., 40, 2269 – 2274., 2017
S. Bedel, C. Vallieres, A. Latifi, Adsorption, 23, 373–380, 2017.
M. Hamou, V. Meille, D. Schweich, A. Latifi, C. De Bellefon, Chem. Eng. J.l, 304, 209 – 215, 2016.
A. Ramirez-Santos, C. Castel, E. Favre, J. Memb. Sci., 526, 191-204, 2017.
W. Uribe-Soto, J.F. Portha, J.M. Commenge, L. Falk, Ren. Sust. Energy Reviews, 74, 809-823, 2017.
Q. Zhao, M. Mecheri, T. Neveux, R. Privat, J.N. Jaubert, Ind. Eng. Chem. Res., 56, 23, 6841-6853, 2017.

✉ abderrazak.latifi@univ-lorraine.fr ✉ francois.lesage@univ-lorraine.fr

List of technical software and databases used as tools by LRGP researchers for addressing energy issues

Databases

Thermophysical properties:

Pure components:	**DIPPR 801 Database**
Pure components and mixtures:	**DDBST** DORTMUND DATA BANK SOFTWARE & SEPARATION TECHNOLOGY
Pure components and mixtures:	**Refprop:** NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP)

Software

Process simulation:

PRO/II (Schneider Electric company)	PRO/II 9.4 Improve process design & operational analysis SimSci
Aspen suite	aspentech
ProSimPlus	ProSimPlus Steady-state simulation and optimization of processes
Simulis Pinch (ProSim company)	Simulis® Pinch Processes Energy Integration in Microsoft® Excel
Gproms	gPROMS
Memsic (software developed by LRGP to predict membrane module performances)	MEMSIC

Others:

Comsol multiphysics (software to simulate designs, devices, and processes in all fields of engineering, manufacturing, and scientific research)	
CosmoTherm (prediction of thermodynamic properties from quantum chemistry calculation)	
Simulis Thermodynamics	
Fluent (CFD simulation)	
Chemkin (kinetic simulation)	
Exgas (software developed at LRGP for the generation of detailed kinetic mechanisms)	
Matlab (numerical computing)	

Index

biomass, 28, 45, 48, 54
CO_2, 15, 41, 43, 46, 48, 49, 56, 60, 61, 62, 63
combustion, 28, 30, 43, 51, 53, 54
exergy, 14, 18, 56
heat, 14, 18, 19, 20, 21, 24, 27, 30, 32, 40, 43, 46, 51, 53, 56, 57, 59, 64
hydrogen, 32, 34, 41, 46, 48, 50, 63, 64
intensification, 23, 41, 46, 64
kinetics, 28, 31, 39, 41, 46, 54, 58, 64
Life Cycle Analysis, 41, 61, 62
pinch analysis, 14, 20, 40, 68
power, 17, 32, 43, 54, 56, 57, 61, 64
product-design, 16, 17, 56, 57, 60
pyrolysis, 28, 30, 39, 45, 51
techno-economic analysis, 21, 41, 63
thermodynamic models, 14, 38, 40, 57

SITE ENSIC
1, rue Grandville
BP 20451
54001 Nancy Cedex - France
Tel +33 (0)3 72 74 38 00

SITE ENSAIA
2 Avenue de la forêt de Haye
TSA 40602
54518 Vandoeuvre-lès-Nancy - France
Tel +33 (0)3 72 74 40 00

SITE SVS
13 rue du bois de la Champelle
TSA 40602
54500 Vandoeuvre-lès-Nancy - France
Tel +33 (0)3 72 74 39 85

cnrs

UNIVERSITÉ DE LORRAINE