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# Water and waste *recycling and recovery*

## Seeking durable materials and membrane processes

The ***European Membrane Institute*** **(UMR IEM, ENSCM-CNRS-UM2)**, founded in 1998, is an internationally-recognized reference laboratory for membrane materials and processes. Its research objectives are in keeping with a multidisciplinary and multi-scale approach:
- the development and characterization of novel membrane materials;
- their implementation in membrane processes having applications in, for example, sewage treatment, gas separation, and biotechnology as it relates to food and health sciences.

| The main teams |
|---|
| **UMR IEM**<br>**European Membrane Institute**<br>(ENSCM/CNRS/UM2)<br>*50 scientists* |
| **UPR Recycling and Risk**<br>(CIRAD)<br>*13 scientists* |
| **UR LBE**<br>**Laboratory of Environmental Biotechnology**<br>(INRA)<br>*16 scientifiques* |

...continued on page 22

IEM comprises three research departments:
- design of membrane materials and multifunctional systems;
- polymer interfaces and physical chemistry;
- membrane process engineering.

The Institute's green-technology-related activities are based on process intensification and have three main foci, with the general objectives of increasing process efficiency and moving towards sustainability (less consumption of energy and solvents, waste minimization, optimum resource use):
- development of multifunctional reactors combining different functions within the same technology;
- development of new processes, new materials for use in traditional processes, or new operating conditions;
- use of modelling to gain a better understanding of reaction and transfer mechanisms, which can then be used to improve the efficiency of existing processes.

The work the Institute carries out under this approach, through the activities of its "Membrane Process Engineering" department, relates mainly to:
- the use of bio-based products and materials: the development of membranes from bio-polymers; the development of biodegradable membranes; fractionation for by-product recovery;
- water and waste recycling and recovery: effluent concentration and production of pure and ultra-pure water; degradation of pollutants in wastewater using membranes combined with photocatalysed biological or physico-chemical reactions; sorption; a combination of membranes and enzymatic reactions.

Regional collaborations have been put in hand, in particular with the ELSA cluster *(cf. p. 32)*, to integrate LCA and eco-design aspects into research projects dealing with the development of new processes for the "solvent-free" production of membrane materials (ANR POMEWISO project, *cf. p. 13)* or the implementation of intensive processes combining membranes and sorption on functionalized polymers (ANR Copoterm "Copolymers for Water Treatment and Metal Recovery").

# DIVA project
## characterization of digestate and its agricultural upgrade processes

Significant progress in anaerobic digestion of organic waste has propelled the emergence of new industrial processes such as the methanation of agricultural and household waste. Thus, new types of uncharacterized or poorly characterized digestate (the residues generated by anaerobic digestion of organic matter) have made their appearance, and they end up being disposed of in a more or less inappropriate manner, generally on the ground. More knowledge is needed, therefore, to see that such digestate is properly managed and that France can make up its serious technological deficit in this area relative to Scandinavia and Germany.

As for the most part the ultimate beneficiary of the upgrade is agriculture, there is a significant demand for (a) characterization of all types of digestate products currently on offer in France and (b) development of processing methods so that the new product's agricultural value can be better realized. In addition, such emerging environmental issues as energy efficiency, recycling of raw materials and control of gaseous emissions from land-farming raise a number of issues that must be considered today in preparation for tomorrow's management processes. Thus, with the participation of the UMR IEM in the collaborative (IRSTEA, Armines, Géotexia, IEM, INRA, Suez, Solagro) DIVA project, it is expected that membrane-based or other post-processing techniques will be proposed in an effort to achieve and maintain the correct product status. This scientific approach—separate, upgrade, standardize—promises the best possible way of promoting the sustainable development of digestates.

**Contact: Marc Heran, marc.heran@univ-montp2.fr**

◀ *Separation unit: membrane filtration.*

## Controlling the environmental risk of recycling organic waste

The ***UPR "Recycling and Risk"*** **(CIRAD)** conducts activities on the cusp of the analytic and systemic approaches in the field of organic waste recycling. The central hypothesis is that some of these products are sources of energy and/or organic matter that could support sustained and sustainable agricultural production. The objective is to find solutions and agricultural practices involving controlled agro-environmental risks, with optimal use of processing technologies and the purifying power of soil and plants.

The unit addresses this problem by delving into the biophysical processes of organic waste transformation, the transfer of elements in the water/soil/plant/atmosphere system, and taking into account the management of stocks and material flows within a territory. It produces knowledge and tools for the assessment and design of integrated recycling solutions that combine respect for natural resources and the environment with economic efficiency.

The unit's research is along two scientific lines:

- **Under "territorial organic waste transformation and management of organic waste products",** it develops models to simulate composting- and methanation-based organic waste processing technology, as well as ways of evaluating the environmental impact of recycling. Two levels of organization are considered: the smallholding (individual management) and organized farm groups (collective management).
- **Under "dynamic of the interactions of organic waste products with water, soils and crops",** it investigates the dynamic of how organic matter, nitrogen and metallic trace elements interact with the cropping system and soil type. Environmental risk indicators are developed for the region, the plot and the laboratory (at molecule and rhizosphere level).

Both lines of research work are based on analytical and experimental platforms, as well as partnerships with other research units, development agencies and businesses. The unit has two main sites, in Montpellier and on Réunion. Under a strategic partnership with the European Centre for Research and Education in Environmental Geosciences (CEREGE) at Aix-en-Provence, the unit is located on the Centre's premises. Innovative partnerships are maintained with private companies, especially the Frayssinet Group, the leading manufacturer of organic fertilizer in France.

On Réunion the unit works closely with local authorities, and primarily with the Réunion region. In Senegal, one of the unit's researchers is assigned to the Laboratory of Microbial Ecology of Tropical Soils and Agro-systems (LEMSAT). The unit's financial resources come mainly from the public sector (ANR, ministries other than Higher Education and Research, Environment and Energy Management Agency). The resources devoted to activities on Réunion come from the European Community and local authorities. The private sector and expert assessments also contribute to the unit's financial stability. •••

▲ *A bird's-eye view of INRA's Environmental Biotechnology Laboratory in Narbonne, with a lagoon for microalgae production in the foreground.*

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## Ecosystems "for" and "in" processes as part of an environmental biorefinery concept

The ***Laboratory of Environmental Biotechnology* (Research Unit [UR] LBE, INRA)** located in Narbonne, is part of the INRA departments of "Environment and Agronomy" and "Microbiology and the Food Chain". For more than 25 years, LBE research has focused on processing and/or upgrading the waste products of human activity, be they liquid effluents (especially from the agri-food sector), solid waste (agricultural residues, household waste and sewage sludge), or such specific biomass types as micro- or macro-algae. Its pollutant transformation processes depend on microbial communities that are complex by virtue of their composition, diversity and functional dynamics.

These communities' characteristics, together with the fact that they can be established only in an "open" environment, have led the laboratory to seek a type of processing/upgrade wherein the microbial responses are influenced by changes in the operating conditions of the bioprocess. In performing the upgrade, great care is taken to observe health safety constraints (e.g. those related to the presence of pharmaceutical residues, detergents and/or pathogens).

Hence, the pollutant transformation processes are studied:
- at the whole process level, by characterizing kinetics, key physiological systems and dynamics of microbial populations;
- at the level of individual procedures, by developing innovative procedures, optimizing the hydrodynamics or functioning of the bioreactors, and implementing physicochemical co-processing techniques.

Research activities have always been done with due regard for both levels as they relate to sustainable industries, in an effort to develop means of pollution control or effluent and waste recovery that comply with economic and regulatory constraints and to achieve simple, efficient, reliable and scalable bioprocesses.

There are six research areas, covering a broad spectrum of disciplinary skills: microbiology, microbial ecology, bio-engineering, process engineering, modelling, automation, LCA, project engineering, industrial transfer:
❶ research into the generic characterization of organic matter and associated by-products;
❷ knowledge and role of biotic/abiotic parameters with respect to the services rendered;
❸ means of action and control of processes and ecosystems, to take an active stance, no longer a passive one;
❹ assessment and management of the fate of the products of the treatment processes and their environmental and health impacts;
❺ descriptive/explanatory/predictive engineering and ecological models;
❻ process engineering and eco-design.

LBE is among the world's leading laboratories in the field of anaerobic digestion (ranking first among publishing laboratories as referenced in the *Web of Science* with the entry term *"anaerobic digestion"*). Its facilities cover 4,757 m², including an experimental centre of 1,882 m², and it boasts high-performance experimental and scientific equipment including more than 50 digesters (capacity from 1 litre to several cubic metres), in operation 24/3/365. LBE relies on research excellence, a variety of study topics and a multidisciplinary approach, but also possesses know-how in technology transfer and innovation (6 patents, 11 licence agreements, and Pollutec innovation awards in 2007, 2009 and 2010). ■

### Other teams working in this area

**IAM team**
**Engineering and Macromolecular Architectures**
**ICGM - Institut Charles Gerhardt, Montpellier UMR CNRS 5253**
(ENSCM/CNRS/UM2/UM1)
*60 scientists*

**UMR ITAP**
**Information/Technologies/Environmental Analysis/Agricultural Processes**
(Montpellier SupAgro/IRSTEA)
*27 scientists*

**UPR CMGD**
**Materials Research Centre**
(EMA)
*40 scientists*

**UPR LGEI**
**Engineering Laboratory for Industrial Environmental Engineering and Industrial and Natural Risks**
(EMA)
*29 scientists*

**UR Biomass & Energy**
(CIRAD)
*12 scientists*

## PETZECO project
### combined ozone/zeolite treatment of petrochemical effluent

Pollution of water and sediments by polycyclic aromatic hydrocarbons (PAHs) is indisputably happening, and poses real risks to the environment and health; this has led the European Commission to classify PAHs as priority substances. The conventional countermeasures, chemical oxidation or adsorption on activated carbon, have limitations in terms of cost and implementation. Advanced oxidation processes can degrade bioresistant or toxic compounds through the use of hydroxyl radicals. The work proposed in the PETZECO collaborative project (with ICGM, Chemical Engineering Laboratory, National Institute of Applied Sciences in Toulouse, Total) aims to develop an advanced technique for the treatment of resistant industrial wastewater.

The main idea is to use ozone combined with innovative zeolitic materials, the ozone serving to break down the waste into hydroxyl radicals which are then adsorbed onto the solid zeolites. This combination should increase degradation rates synergetically. The use of a solid, porous mineral should ensure good resistance to oxidative attack and maintain long-term catalytic and adsorptive properties. The development phase of this new solid, mesoporous zeolitic adsorbent/catalyst is one of the project's challenges, as very few studies exist in this area. Another of its challenges is to implement this ozone/catalyst combination in an efficient and inexpensive way. Its reactive and mechanical properties will be the subject of careful study so that in synthesizing the zeolites the most valuable functionalities can be targeted. An in-depth study is underway of the sizing parameters of the oxidation process in various configurations (from fluidized beds to membrane separation of the catalyst). The project's ultimate goal is to use monolithic materials containing the new catalyst on real petrochemical effluents.

**Contact: Stephan Brosillon, stephan.brosillon@univ-montp2.fr**

## Seeking a new green channel within a circular economy:
### from phytoextraction to bio-based chemical catalysis and back again

The Opportunité (E)[4] programme (Environmental, Ecological, Ethical and Economic) outlines an innovative process of chemical enhancement of phytoextraction technologies and of waste contaminated with metallic trace elements. The project takes advantage of certain plants' remarkable adaptive ability to hyperaccumulate $Zn^{2+}$, $Ni^{2+}$, $Mn^{2+}$, $Cu^{2+}$ and/or $Al^{3+}$ cations in their aerial parts; its design is based on the direct use of metal species of plant origin as "Lewis acid" catalysts for organic chemical reactions on mining waste (tailings and slag) or combustion by-products.


The programme draws on public and semi-public research laboratories and three private private companies, all of which pool their phytoextraction skills for the environmentally sustainable remediation of mine sites in the department of Gard and in New Caledonia while respecting local biodiversity. Plant waste and bound metals are directly recovered and transformed into green catalysts, then spread and stabilized on comminuted mining waste. These unique polymetallic systems are used as heterogeneous catalysts in synthetic transformations that give access to high-added-value molecules (aromatic building-block molecules, heterocyclic compounds and biologically useful oligomers…). The process design allows for recycling simply through filtration; it is also suited to the new economic constraints and represents a concrete solution to the critical non-renewability of mineral materials.

This scientific programme is carried out with local stakeholders from the communities and State bodies. It engages in sustained recovery actions involving industry groups working in complementary application areas (restoration ecology, mining and chemical industries). It now rests on a solid foundation of scientific results, so that specific objectives are sure to be met; as a result, funding has been approved for an ANR project, a CNRS-IRSTEA project, a project of the European Regional Development Fund, two industrial contracts, ten confidentiality agreements, two thesis funding agreements and a collaboration with a private company specializing in technology transfer. This interdisciplinary research work—applied, industrial research—is intended as an engine of environmental and socio-environmental reconstruction of sites scarred by industrial and mining activities.

**Contact: Claude Grison, claude.grison@cefe.cnrs.fr**

**For further information:** www.agence-nationale-recherche.fr/programmes-de-recherche/environnement-et-ressources-biologiques/ecotechnologies-ecoservices/fiche-projet-ecotech/?tx_lwmsuivibilan_pi2%5BCODE%5D=ANR-11-ECOT-011

▲ *A 40-m³ TRANSPAILLE digester in Senegal.*

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▲ *Composting test on Wallis.*

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# Upgrading of organic waste by anaerobic digestion and composting in hot regions

| Equivalence 1 m³ of methane |
|---|
| ▶ 9.7 kWh of electricity |
| ▶ 1.3 kg of coal |
| ▶ 1.15 l of petrol |
| ▶ 1 l of fuel-oil |
| ▶ 2.1 kg of wood |
| ▶ 0.94 m³ of natural gas |
| ▶ 1.7 l of fuel alcohol |

In hot regions, where average temperatures are high, biological upgrading processes for organic waste are particularly effective. Unlike thermochemical processes, they save part of the organic material, which can then be recycled to preserve soil fertility.

Methanation, or anaerobic digestion, is fermentation in the complete absence of oxygen. Degradation of organic matter leads to the formation of a gas—biogas—which is rich in methane ($CH_4$). Biogas can be used directly as fuel. The final residue of anaerobic digestion, called methanogenic digestate, can be used directly as fertilizer or composted to improve its properties. Since the late 1970s, with its African partners, CIRAD has been developing various biogas technologies suited to local conditions. Thus, the TRANSPAILLE process will methanate solid waste such as manure, dung materials, cassava peelings or coffee pulp. The AGRIFILTRE® process will filter liquid effluents rich in organic matter so they can soak into straw before anaerobic digestion.

Composting is a biodegradation of organic matter in the presence of oxygen, producing carbon dioxide and water vapour. The reaction is exothermic (raising the temperature of the medium). Because composting is often done in the open air in piles or windrows, it is difficult to control. In creating a model of the composting process, we must formalize the relationship between the physicochemical characteristics of organic waste and the gaseous, liquid and solid outputs. This modelling is used to set the parameters of flow models (operation, area) for an environmental assessment.

**Contacts: Jean-Luc Farinet, jean-luc.farinet@cirad.fr**
**& Jean-Marie Paillat, jean-marie.paillat@cirad.fr**

**For further information:** www.cirad.fr/innovation-expertise/produits-et-services/equipements-et-procedes

## Seeking better-quality end-of-life sorting and recycling/upgrading of electrical and electronic waste


▲ *Trial of near-infrared spectroscopy (NIRS) to sort/separate WEEE plastics.*

The recycling of waste electrical and electronic equipment (WEEE) is at the centre of numerous research projects, as its annual volume (about 24 kg per capita) is constantly increasing (3-5%). When WEEE is discarded, the plastics it contains remain as a source of pollution. That is very wasteful, as the industrial plastics in WEEE still have good potential uses after their first life cycle. Although many scientific studies conducted in developed countries involve recycling, use of such recycled plastics is not widespread, in part because of the poor quality, to date, of the material available (which is dependent on sorting quality and the main additives). With improved sorting, identification and separation, high-quality recycled plastics will become available for applications in various industrial sectors.

Deposits of WEEE plastics are highly complex: many plastics are incompatible with one another, and a large percentage are dark in colour, making some sorting and identification techniques ineffective, or incorporate brominated flame retardants, requiring separate sorting.

CMGD has been working on WEEE recycling and upgrading for ten years, and, since 2008, conducting two projects:

- The REDEMPTIR project (ADEME funding) seeks to maximize the recovery rate and the purity of sorted plastics by online near-infrared spectroscopy using actual light-coloured WEEE deposits, to monitor their polymer and flame retardant content.
- The TRIPLE-VALEEE project (Single Interministerial Fund (FUI) is split into two development foci:
  - The TRIPLE project aims to provide a standardized methodology for sampling and analysis of plastics deposits derived from WEEE processing and to implement efficient sorting patterns.
  - The goal of the VALEEE project is to identify the different ways WEEE may be incorporated into industrial products, taking the place of all or some of the virgin materials that would otherwise be used, according to specifications setting out the desired polymer types or performance.

**Contacts: Didier Perrin, didier.perrin@mines-ales.fr**
**& Rodolphe Sonnier, rodolphe.sonnier@mines-ales.fr**

## Adding value by chemical waste recycling: the example of PET



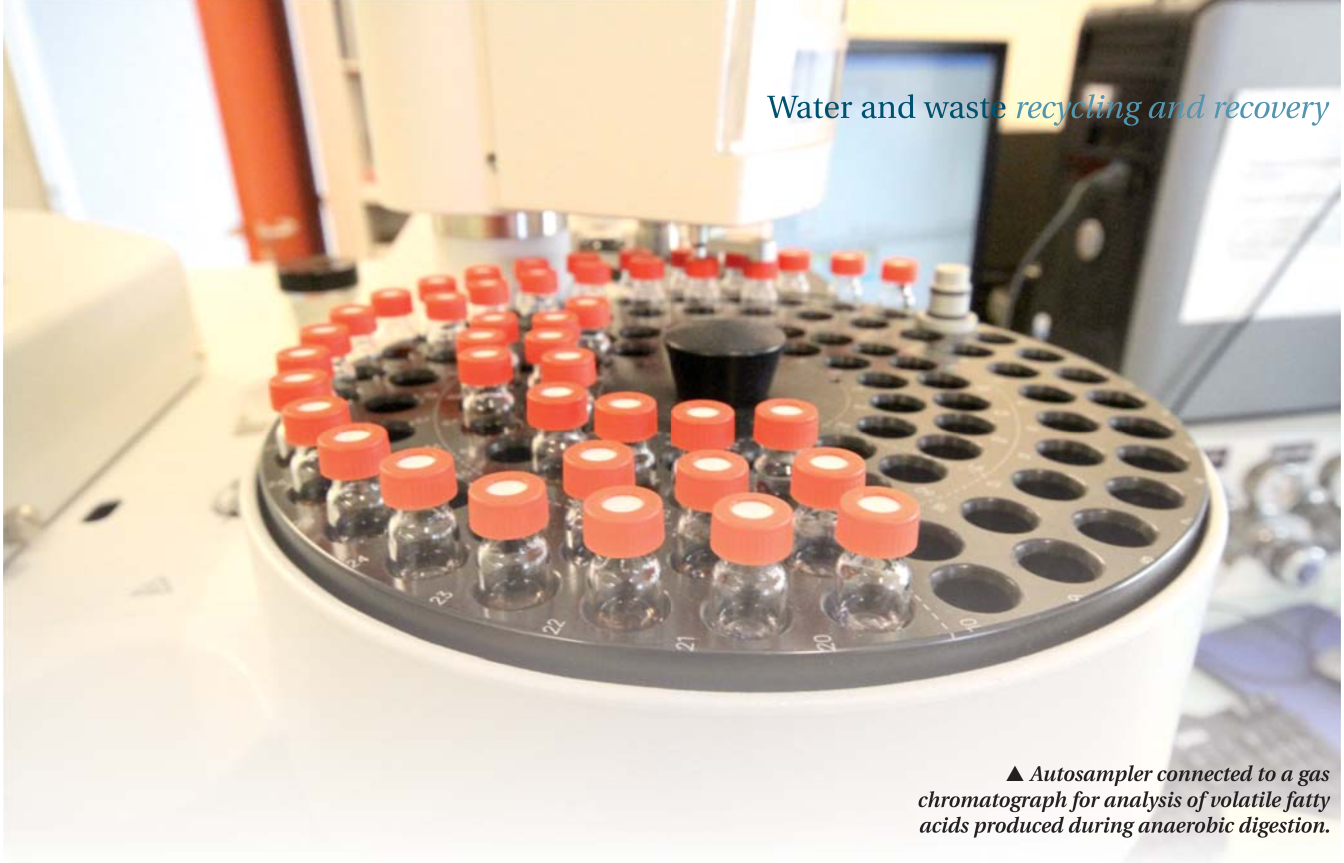


❶ *PET flakes from the recycling industry.*
❷ *PET depolymerized in an extruder.*
❸ *Product after laboratory reaction.*
❹ *Material obtained after photopolymerization (thickness 0.5–0.7 mm).*
❺ *Application in the coatings sector.*

The polyethylene terephthalate (PET) waste used in industry comes primarily from the recovery and sorting of bottles. At present, PET recycling is mainly (75%) in the form of fibre (quilt batting, sweaters…). Other applications arising from research may be targeted. Here is one example:

PET bottles are first ground to the desired size, then washed to remove contaminants as far as possible (paper, glue, PVC, etc.). The PET chips thus obtained *(photo ❶)* are then dried and undergo an initial transformation, called glycolysis. This results in a lower molecular weight product in the form of a green paste *(photo ❷)*. After chemical treatment, an unsaturated polyester is obtained; much more fluid, transparent and slightly yellow in colour *(photo ❸)*. This product then undergoes a photopolymerization reaction with reactive diluents, resulting in a transparent, flexible material. The flexibility of the material can be controlled through the choice of reactive diluent *(photo ❹)*. One possible application for this type of product is wood coatings *(photo ❺)*, as initial testing has shown that it is easily applied and adheres well to wood.

**Contact: Rémi Auvergne, remi.auvergne@enscm.fr**



▲ *Autosampler connected to a gas chromatograph for analysis of volatile fatty acids produced during anaerobic digestion.*

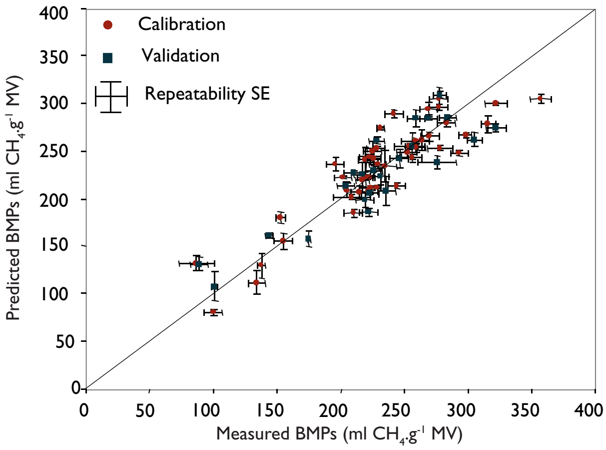


# Evaluating the methane potential of organic waste through near-infrared spectrometry

To optimize methane production through anaerobic digestion of organic waste, it is essential to know in advance the potential methane value, for which purpose the *Biochemical Methane Potential* (BMP) test is performed, consisting of at least one month's fermentation. That is too long a period in an industrial context, as it generates inventory management constraints and risks a loss of bacterial population in the reactors should the waste prove not very biodegradable.

To optimize industrial-scale methane production processes, near-infrared spectroscopy (NIRS) is an innovative way of rapidly determining the waste's BMP: it can analyse the overall organic matter after a quick sample preparation and calculate the methane potential within a few minutes. Hence, there is less risk of methanating waste with little biodegradability, and the co-digestion process will be better controlled.

The EcoTech-LR platform allowed UMR ITAP, LBE and LGEI to jointly develop a methodology whereby freeze-dried, triturated waste is analysed by reflection using NIRS. The predicted BMP results are very accurate, particularly in the light of the complexity of the medium studied: a prediction error of 10% (28 ml $CH_4.g^{-1}$ of volatile matter [MV]) out of 70 representative samples of household waste (values between 89 and 357 ml $CH_4.g^{-1}$ MV), a good repeatability error (about 7 ml $CH_4.g^{-1}$ MV) and no bias between the prediction for the calibration batch and the test batch. Interpretation of the spectra and the prediction model also provides characterization data on the waste, such as the presence of hydrocarbons, lipids and proteins, which improve BMP, and of other compounds that will impair it because they are not degraded during anaerobic digestion (e.g., fibre or plastics).




▲ ***Comparison of measured and predicted values.***

The diagonal represents a 1:1 ratio.
Prediction error: 28 ml $CH_4.g^{-1}$ MV ;
Repeatability error: 7 ml $CH_4.g^{-1}$ MV . $R^2$=0.8.

The next step is to move to industrialization of the method, which promises strong growth and substantial economic benefits, given the significant need for agricultural and household waste treatment. For that purpose, as the spectral response is very sensitive to the type of medium studied, calibration will be required for each type of waste.

**Contacts: Jean-Michel Roger, jean-michel.roger@irstea.fr**
**Éric Latrille, latrille@supagro.inra.fr**
**& Catherine Gonzalez, gonzalez@ema.fr**

This research, as embodied in the thesis of Mr. Lesteur, a PhD student at the ECOTECH-LR Regional Technology Platform, received the ADEME award for innovative technology at the 2009 Pollutec salon. It then led to a technology transfer to Ondalys under the MethaNIR project.

▲ *Slurry impeller for open-air microalgae cultivation.*

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