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15 minutes of reading

News

Fundamental Research

Engineering sciences | Chemical engineering and process engineering



IFP Group deploys processes on the world market that are as much about recycling plastics, capturing CO_2 and producing bioproducts as they are about refining or petrochemicals. Whether they are emergent or mature, all these sectors demand innovations to reduce their environmental impact, improve their competitiveness and move towards the energy transition.

The philosophy within the Process Design and Modeling Division is one of **risk control when extrapolating to an industrial scale concepts** and ideas initially verified on a small scale. This involves defining individual step sequences, dimensioning rules, operating conditions and methods of conduct enabling us to confidently begin prototyping and industrializing new processes.

To do so, the Division is supported by multidisciplinary fundamental research, ranging from **kinetics to hydrodynamics**, via **matter and energy transfers**, using data obtained using original experimental methods and structured by dedicated mathematical approaches. This research must meet the permanent challenge of industrial relevance.

The articles in this issue illustrate this constant back-and-forth interaction between science and operational reality facing the Division's researchers on a daily basis.

Have a good reading!

Pierre Porot
Process Design and Modeling Division Director

 **See the PDF of the letter**

LES BRÈVES

The industrial production of ethanol from lignocellulosic biomass was demonstrated by the **Futurol™ project**[a]. The extrapolation and optimization of the process, along with its flexibility in terms of raw materials, required work on numerous individual operations - the most critical of which are pretreatment, enzyme production, **hydrolysis and fermentation** (figure) - as well as on various complex liquid/solid separations. For all these individual operations, preliminary tests were carried out in the laboratory and with equipment suppliers.

Studies and technological choices were subsequently validated on the Pomacle- Bazancourt (Marne) pilot, which has a capacity of 1 t/d. Extrapolation of the pretreatment technology to the industrial scale was also confirmed on larger equipment (100 t/d) on the IPX unit located in Bucy-le-Long (Aisne). Similarly, for the extrapolation of enzyme production, industrial-scale tests (180 m^3) were performed on the ARD BioDémo unit.

A multitude of fundamental research activities, in particular PhD research[b], have been carried out at IFPEN with the aim of gaining a clearer understanding of the phenomena at play in these various individual operations. In particular, studies on hydrodynamics and the reaction have been performed on bioreactors, in the context of both enzymatic hydrolysis(1) and enzyme production(2).



Futurol™ pilot - Hydrolysis and fermentation workshop.

The enzymatic hydrolysis study enabled better incorporation of the variability of biomass types and the impact of pretreatment conditions. For the enzyme production study, a scaledown methodology made

it possible to reproduce the constraints and specific characteristics encountered in industrial fermenters on a laboratory scale.

a - https://www.ifpenergiesnouvelles.com/article/advancedbioethanol-futurol-technology-set-market-launch

b - M. Chauve (2011), J-C. Gabelle (2012), E. Jourdier (2012), M. Huron (2014), N. Hardy (2016)

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(1) S. Boivineau, R. Rousset, P. A. Bouillon, F. Battista, M. Gomez Almendros, Bioresource Technology, Vol. 250, February 2018, pp. 191-196.
DOI:10.1016/j.biortech.2017.11.049

(2) C. Plais, D. Marchisio, F. Augier, L. Gemello, V. Capello, Chemical Engineering Research & Design, Vol. 136, August 2018, pp. 846-858.
DOI: 10.1016/j.cherd.2018.06.026

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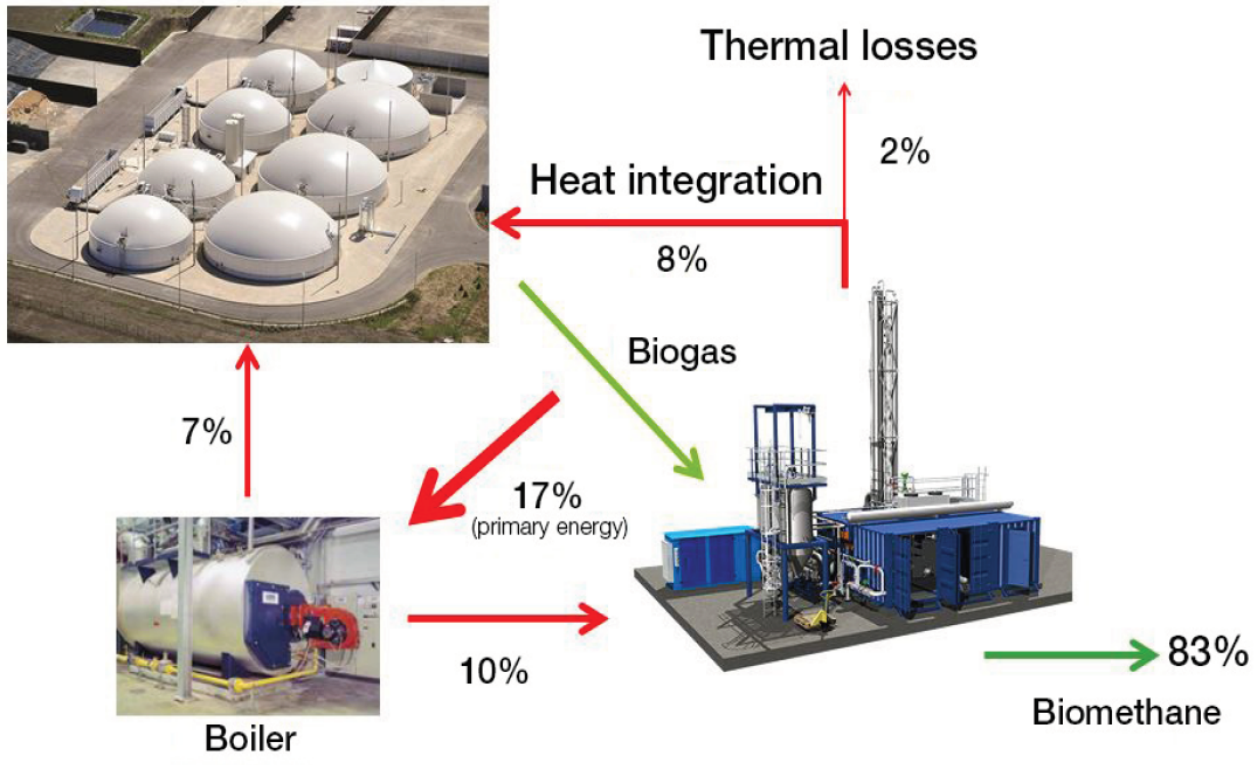
Extrapolating ethanol-from-biomass production technologies

In partnership with Arol Energy, a **new methanization-based biogas purification technology** has been developed to extract methane (CH_4) and inject it into the natural gas network. The process uses an **amine solvent** developed by IFPEN for capturing CO_2 in biogas and demonstrates a superior energy efficiency to conventional membrane solutions.

The development was supported by knowledge acquired in the field of natural gas treatment(1) and CO_2 capture, transposed to biogas[a] and incorporating
its specific characteristics(2). The process thus produces a gas containing 97.5 vol% CH_4, meeting the specifications of distribution networks. To achieve this,
a calculation tool was developed to simulate the absorption column, integrating the equilibrium models, physicochemical properties, mass transfer correlations and reaction mechanisms associated with the new solvent, with all the data having been derived from small-scale experiments.

In addition, to improve the absorber design with these data, an original approach was chosen **to model the reaction transfer**, making it possible to separate the diffusion and reaction phenomena. This consisted in discretizing the equations within the liquid film, close to the interface with the gas, where all the mass transfer phenomena are meant to occur.



Thermal integration and use of the new IFPEN solvent (source: Arol Energy).

On the industrial demonstration unit, an advanced energy integration[b] resulted in the proposal of an innovative and competitive process in terms of converted biogas rates, with the biomethane yield of the unit increasing from 69% to 83%(3).

a - Available at atmospheric pressure; composition 50 vol% CO_2 - 50 vol% CH_4
b - Global approach, on a process or plant scale, with a view to optimized energy use

(1) M. Meyer, L. Hegely, P. Alix, J. Roesler, D. Rouzineau, AIChE Journal, Vol. 63, No 8, 2017, pp. 3246-3275.
DOI: 10.1002/aic.15737

(2) C. Peregrina, E. Flottes, P. Collet, L. Raynal, S. Capela, H. Pierre, A. Favre, Applied Energy, Vol. 192, 15 April, 2017, pp. 282-295.
DOI: 10.1016/J.APENERGY.2016.08.181

(3) J. Grandjean, A. Wender, K. Lettat, M. Dehlinger, J. Roesler, S. Gonnard, V. Carlier, Poster Presentation, 69th LRGCC, 2019.

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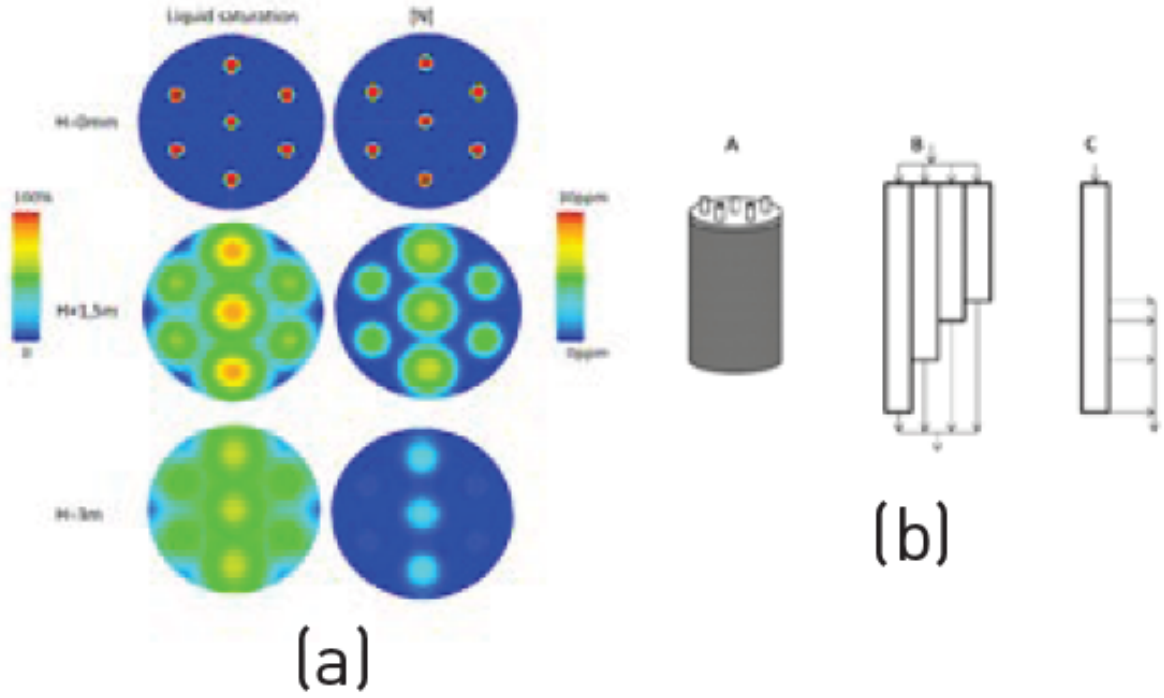
A world first for energy integration: heat and gas at every level

Improvements in chemical processes are regularly achieved as a result of the introduction of new internal geometries within reactors. Conventionally, fixed bed reactor models use an overly simple description of hydrodynamics, based on a “piston”-type reactor configuration. This description demonstrates limitations when seeking to model certain specific technologies and their impact on process performance.

Coupling complex hydrodynamics with kinetic models that are themselves complex makes their incorporation in CFD codes difficult and generates prohibitive calculation times. For reactor simulation requirements, it was therefore necessary to develop a **methodology for obtaining sufficiently representative modeling of hydrodynamics**, and which is compatible with the use of complex kinetic models. To achieve this, a rigorous approach was used to obtain a one-dimensional representation of the impact of hydrodynamics on the basis of 3D CFD simulations. To construct these one-dimensional models taking into account hydrodynamics, the **internal age distribution transport theory**[a] inside the reactor has been used.



(a) Evolution of the liquid fraction and the chemical reactant along a Trickle Bed hydrotreatment reactor. (b) Illustration of the 1D calculation principle.

For example, a Euler-Euler two-phase model was used to model a fixed-bed reactor (figure), subject to poor liquid distribution due to partial blocking of
a distributor tray(1). In order to assess the impact of this problem on reaction performance in the case of hydrotreatment, chemical species transport simulations were performed. Ultimately, the 1D multi-output piston-dispersion model provides excellent performance prediction, equivalent to complex 3D simulations of the reactor.

a - Which consists in calculating the average age of the molecules at every point of the reactor

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(1) M. Fourati, F. Augier, Y. Haroun, Canadian Journal of Chemical Engineering, Vol. 95, No 2, 2017, pp. 222-230.
DOI:10.1002/cjce.22618

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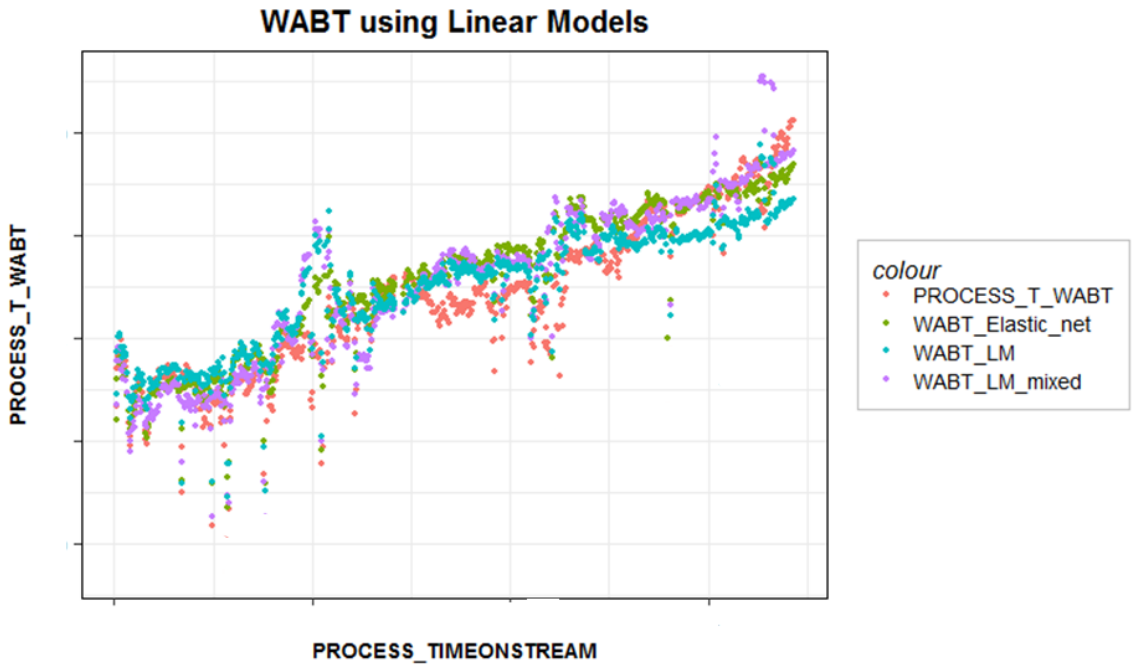
In trickle bed reactor simulators, hydrodynamics count!

Having access to increasingly precise and robust extrapolation models to be able to predict certain properties[a] remains a major challenge for chemical processes industry. For widely used models, be they simple or complex, the objective is to determine pertinent descriptors while reconciling two antagonistic constraints: on the one hand, a need for complexity in order to accept broad variations in feeds entering the process and, on the other, the scarcity of industrial data as well as their inadequacy, since they are generally limited to macroscopic properties.

An original approach consisted in **using machine learning methods to identify key descriptors**(1), adding a priori information on the shape and parameters of the kinetic models in order to guarantee the physical reality of the complete model(2). This approach is proposed both for the design of the reactors and for prediction of catalyst activity evolution during an industrial cycle. In this case, the time on stream (TOS) and catalyst history[b] must be included.

In the model developed, variation of the predictive property is the product of an empirical function of the feed properties (and also, if necessary, of the TOS and past operating conditions) and of the function describing the kinetic model, including any inhibition terms.

The predictive quality obtained is illustrated via the evolution in reactor's temperature as a function of the TOS (figure).



Température moyennée des réacteurs (WABT c) en fonction du temps sous charge (TOS) (Process_T_WABT = température mesurée)

This methodology makes it possible to obtain models that are precise and robust enough to be used industrially, for the design of new units or for the replacement of catalysts. They could be extended to other processes.

a - Nitrogen or sulfur content, conversion degree, reactor temperature, etc.
b - Temperatures, pressures, treated feeds, etc.
c - Weighted Average Bed Temperature

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(1) J. J. Da Costa, F. Chainet, B. Celse, M. Lacoue-Nègre, C. Ruckebusch, N. Caillol, D. Espinat. Energy Fuels 2017,
DOI: 10.1021/acs.energyfuels.7b03266.

(2) P. J. Becker, N. Serrand, B. Celse, D. Guillaume, H. Dulot. Fuel 2016, 165, 306–315,
DOI: 10.1016/j.fuel.2015.09.091.

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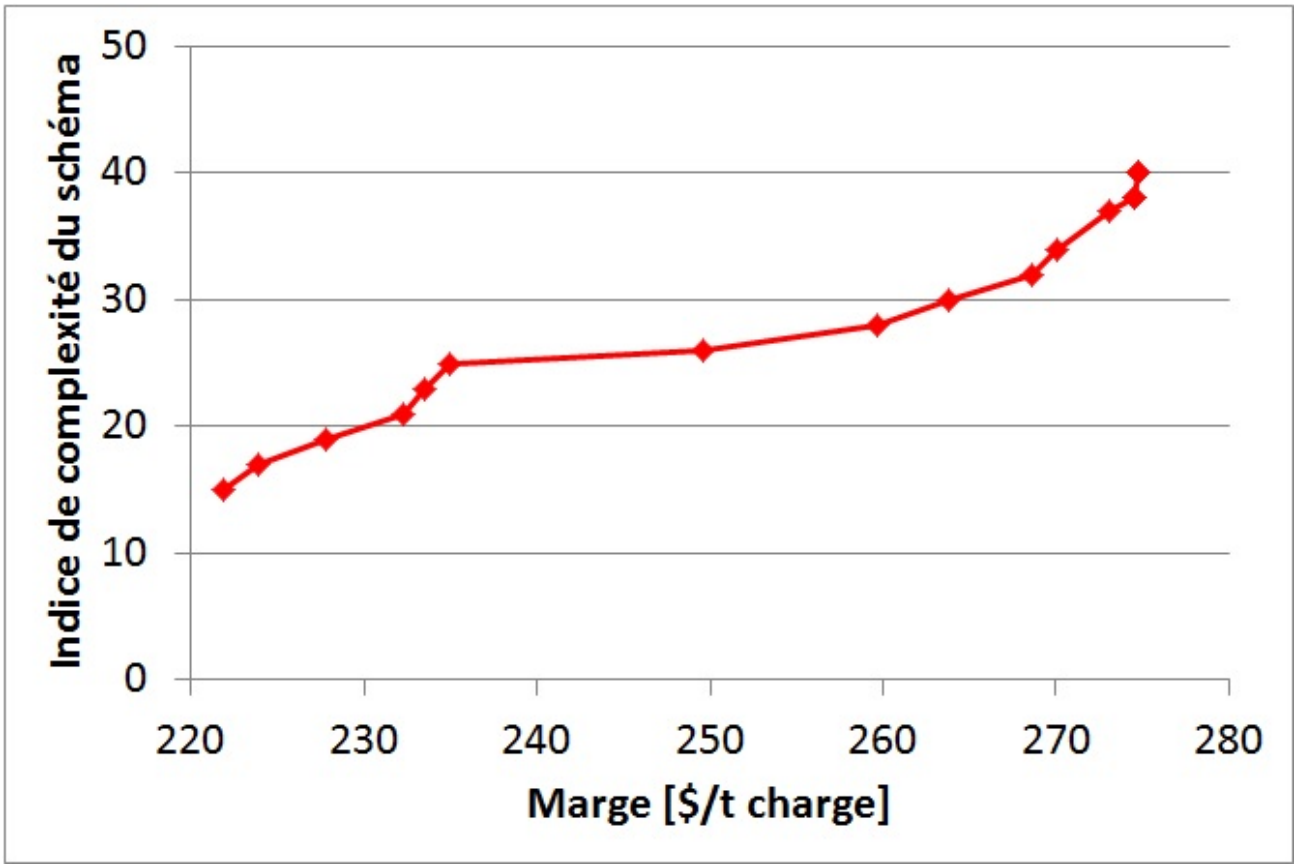
Mix between kinetic and machine learning models

In order to optimize the use of very expensive installations, the development of industrial processes needs to take into account integration between units, both for developments relating to mature subjects and as prerequisites for new subjects (bioproducts, petrochemical complexes).

Automatic synthesis - combining choice of technological building blocks, routing of flows between them and an optimization step - is a scientific approach that addresses these requirements. Having emerged as a concept in the 1970s, it has been difficult to develop due to the complexity of optimizations with decision making variables (binary). Optimization methods based on detailed modeling of the problem are very limited. In addition, reducing the complexity of the system, via the use of a global meta-model[a] only, very partially resolves the limitations induced by optimization methods with mixed variables.

IFPEN has adopted an **approach using the most advanced MINLP**[b] solvers that make it possible **to take into account binary variables**. The approach is based on breaking down the problem into blocks represented by simple meta-models(1). For conversion units, the challenge was to reduce the complexity of models while maintaining their representativeness. Furthermore, the separation of effluents was conceptualized taking into account cutting points[c] only, without considering energy(2).



Evolution of margins for a set of processes dependingon their complexity.

This new approach enables the automatic synthesis and optimization of a set of processes, resulting in economic savings (figure) and opens up avenues
for intensifying process sequencing system studies. However, the treatment of separation in the tool remains cursory and the current focus is on better
incorporation of different types of separation units: liquid/liquid extraction, by solvent or simulated

moving bed.

a - Neural network, kriging
b - Mixed Integer Non Linear Programming
c - Separation threshold of chemical compounds

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(1) L. Mencarelli, A. Pagot, P. Duchene. Computers and Chemical Engineering, Dec. 2019.

(2) L. Mencarelli, A. Pagot. Escape30, Milan 24-27 mai 2020.

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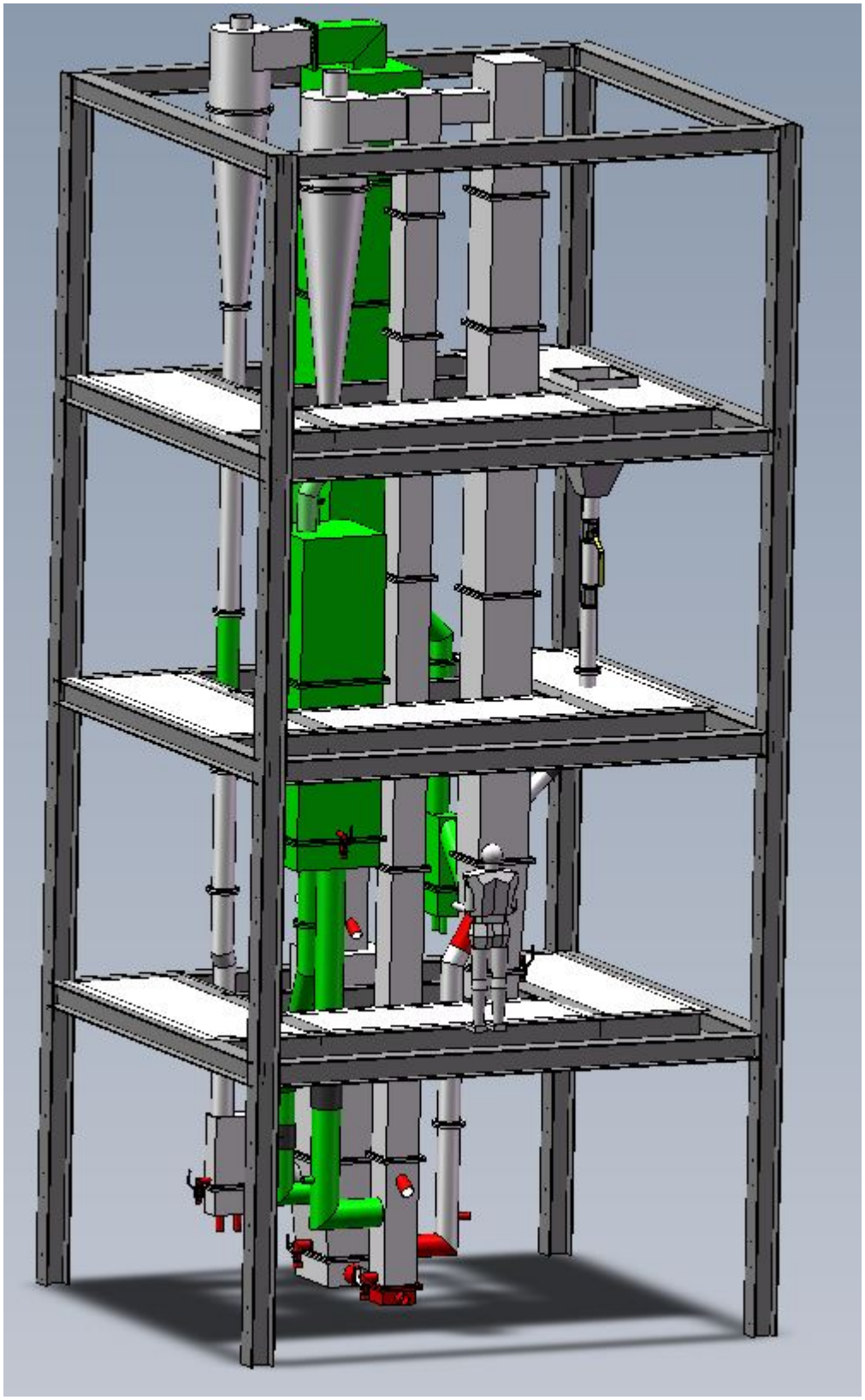
Process efficiency: a matter of integration!

Chemical Looping Combustion (CLC) is an airless combustion technology using oxygen carrier materials (OCM), which circulate between an oxidation and a
reduction reaction zone. Separation into two zones enables nitrogen-free combustion, generating an effluent composed solely of CO_2 and steam, which
are easy to separate.

Most research in the field of CLC has been conducted on small-scale pilots (<150 kW). This was the case for the development of reaction zones at IFPEN, with models on different scales and a 10 $kWth^a$ pilot leading to the characterization of the combustion kinetics on the basis of feed and OCM(1).

However, to prepare for industrial extrapolation(2), demonstration on a larger scale (> MW) is necessary, in representative hydrodynamics and reaction
conditions whereby the main technological challenges can be addressed:
- **extrapolation and optimization** of reaction zones and energy loss minimization;
- **controlled, stable circulation** of OCM between reactors;
- **performance of the various OCM** over a very large number of redox cycles;
- **control of tightness** between the two reaction zones to prevent leaks.



1.5 MWth model of the whole loop operated for different solid and gas flow conditions.

The Sino-European collaborative project CHEERS[b] aims to construct and operate a 3 MW demonstrator, based on an innovative concept[c] **aimed at using oil industry waste as feeds**. Recently, a cold flow model (figure), with a size equivalent to a 1.5 MWth

unit, of the entire reaction section was constructed and operated in China to study:
• the hydrodynamics of each section,
• the efficiency of separation between the unburned components of the solid feed,
• and the OCM, and control of solid circulation.

a - Thermal kW
b - Chinese European Emission Reduction Solutions
c - Developed with Total

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(1) A. Lambert, A. Tilland, W. Pelletant, S. Bertholin, F. Moreau, I. Clémençon, M. Yazdanpanah, Fuel 216 (2018): 71-82.
DOI: 10.1016/j.fuel.2017.11.115

(2) T. Gauthier, M Yazdanpanah, A. Forret, B. Amblard, A. Lambert, S. Bertholin, Powder Technology 316 (2017): 3-17.
DOI: 10.1016/j.powtec.2017.01

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