Second-generation biofuels and bio-products: an overview of recent projects at IFPEN

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Biomass Conversion: Green Chemistry & Innovative Processes
10 & 11 Mars 2016, Paris
R&I – Renewable energies

- To limit the transport and petrochemicals sectors’ reliance on oil and gas
- To combat climate change and cut greenhouse gas emissions

3 R&I avenues
- The conversion of biomass into fuels
- The conversion of biomass into biobased chemical intermediates
- Offshore wind power and ocean energies
Lignocellulosic biomass

- Wood, straw, specific production (eucalyptus, poplar, …)
- Wastes from forestry, agriculture, paper industry, …
Outline

- Routes of lignocellulosic biomass conversion: some examples
  - Biochemical route
  - Indirect chemical route
  - Direct chemical route

- Focus on analytical characterization
  - Molecular analysis
  - Separation by molecular size
  - Separation by polarity
Transformation routes of lignocellulosic biomass

- **Biochemical route**
  - Energy crops, short rotation coppice

- **Direct thermochemical route**
  - Agricultural wastes, forest residues

- **Indirect thermochemical route**

Transformation routes of lignocellulosic biomass

agricultural wastes
forest residues

Ligno-cellulosic biomass

energy crops, short rotation coppice

T (°C)

1400
700
500
300
< 100

Biofuels
Energy
Bioproducts

THE FUTUROL PROJECT
CELLULOSIC ETHANOL
INDUSTRIAL PROJECT

THE TARGETS

The process and its biocatalysts (yeasts, enzymes) are to be licensed worldwide.

The FUTUROL PROJECT is an **R&D project** with **commercial targets** in a tough context.
THE PARTNERS

- 1 company: PROCETHOL 2G
- 11 shareholders → Leaders in their activity

R&D PARTNERS

- ard
- IFP Energies nouvelles
- INRA Science & Impact
- LÈSAFFRE

INDUSTRIAL PARTNERS

- VIVESCIA
- Office National des Forêts
- TOTAL
- Tereos

FINANCIAL PARTNERS

- UNIGRAINS
- NORD EST
- CGB
THE R&D PARTNERS

- Specialized in plant fractionation, green chemistry and fermentation, with 70 researchers, leader on biosuccinate
- World’s leader on baker’s yeasts production and alcohol yeasts, with 100 researchers
- Developing innovative technologies on fuel and chemical processes, with 1,170 researchers and 180 patents/y
- 8,600 researchers working on plants, animals and microorganisms, leader of scientific publications in Europe
AIMS:
1. Build crop systems adapted to energy use
2. Preparation of cellulose / hemicellulose / lignin
3. Adaptation / improvement of existing enzymes to raw materials and industrial conditions
4. Optimization of the conversion efficiency of hexoses and valorization of pentoses
5. Limitation of overall consumption of water, energy and emissions
6. Achieve thermal and process integration and upscaling

THE R&D WORK PACKAGES
FUTUROL PILOT PLANT

- 5,000 m²
- +2,200 data outputs
- 10 dedicated technicians
FUTUROL PROCESS

- A simple and integrated 4-step process

1. PRETREATMENT
   - FOREST & AGRICULTURE RESIDUES, STRAWS AND BYPRODUCTS
   - DEDICATED BIOMASS
   → PRETREATED BIOMASS

2. BIOCATALYSTS PRODUCTION
   - ENZYMES
   - YEASTS

3. HYDROLYSIS & FERMENTATION

4. PRODUCTS RECOVERY
   - ETHANOL
   - BIOBASED FUELS AND MONOMERS
   - LIGNIN / STILLAGE
   - ENERGY AND PROCESS INTEGRATION
TECHNOLOGICAL ACHIEVEMENTS

- **BIOMASS**

Aiming *worldwide technology deployment* and *reduced biomass storage*, numerous feedstocks have been studied at crop, lab and pilot scale (switchgrass, miscanthus, poplar, straw, bran, pulp, ...)

→ *Consolidated results are available for wheat straw, miscanthus and poplar with high ethanol yields*

- **PRETREATMENT**

Futuro’s *selected and optimized* pretreatment technology is a result of meticulous research studies.

Our *robust, simple and energy-efficient single-train technology* continuously processes different biomass feedstocks to a standardized pretreated substrate with:

- Low moisture content
- High hemicellulose hydrolysis yield
- High digestibility
**ENZYMES**

Tailor-made enzymes for cellulolysis and hemicellulolysis are:

- Designed and continuously adapted to the process
- Developed using lignocellulosic substrates allowing on-site production with low production cost
- Highly efficient → benchmark compared to the competitors

**YEASTS**

Yeasts have been developed and selected to:

- Ferment both C6 and C5 sugars into ethanol
- Use lignocellulosic substrates for on-site propagation
- Present high resistance to main inhibitors, especially acetic acid
Impact of delignification on the morphology and the reactivity of steam exploded wheat straw

Maïté Huron\textsuperscript{a}, Damien Hudebine\textsuperscript{a,\*}, Nicolas Lopes Ferreira\textsuperscript{b}, Dominique Lachenal\textsuperscript{c}

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This study was part of Projet Futuro, a project supported by BPIFrance
Biomass pretreatment

- Impact of delignification on the morphology and the reactivity in enzymatic hydrolysis of steam exploded wheat straw
  - Delignification of pretreated wheat straw by chlorite method to different grades
  - No significant impact of delignification on morphology of the pretreated substrates, neither on their enzymatic digestibility

SEM pictures of the pretreated wheat straws without delignification (PTT) and after delignification (1h30 or 4h)

Hydrolysis of delignified wheat straws
pH 4.7, 48 °C, cellulose mass concentration: 10 g L⁻¹, K619 mass concentration: 40 mg L⁻¹.
Biomass pretreatment

- Impact of delignification on the morphology and the reactivity in enzymatic hydrolysis of steam exploded wheat straw
  - Addition of commercial lignins to delignified steam exploded wheat straw

Addition of wheat straw lignin
(Green Value SA Protobind 1000)

Addition of softwood kraft lignin
(Mead-Westvaco Kraft)

Hydrolysis of delignified steam exploded wheat straw (4h) without and with addition of lignin
pH 4.7, 48 °C, cellulose mass concentration: 10 g L⁻¹, K619 mass concentration: 40 mg L⁻¹

Transformation routes of lignocellulosic biomass

- Lignocellulosic biomass
  - Agricultural wastes
  - Forest residues
  - Energy crops, short rotation coppice

- Biofuels
- Energy
- Bioproducts

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The BioTfueL project

- **B-XTL route (B = Biomass, X = Fossil FueL)**
  - Biomass availability fluctuates (quality, quantity)
  - Biomass collect in huge quantities (Mt/yr) is a challenge
  - High plants Stream Factors $\Rightarrow$ final product cost reduction
  - King size plants $\Rightarrow$ final product cost reduction

  $\Rightarrow$ **Co-processing is a good opportunity**
  
  Green carbon is introduced upstream the chain,
  
  GHG reduction > 90% for the green part of the product
The BioTfueL project

Objectives

- Develop, demonstrate and commercialize a full B-XTL chain
  - flexible to the widest range of feedstock (solid & liquid, bio & fossil)
  - reliable (SF = 8000 h/yr for industrial application)
  - economically and environmentally competitive

- Realize the complete integration of the various processes and utilities of the B-XTL process chain
  - Process Book elaboration for industrial plant (200 kt/yr of liquid products)

- Validation of the sustainability criteria
  - Life Cycle and multi-criteria Analyses
The BioTfueL project

The partners

R&D
Technologies licensors
Fuels producers

From R&D to market
From field to wheel
The BioTfueL project
2nd generation biodiesel and biojet fuel production chain
The BioTfueL project
Biomass feedstock preparation

- **Torrefaction**
  - Improvement of feedstock properties for
    - fluidization
    - pneumatic transport
    - grindability with lower energy consumption
    - storage & transport (up to 800 kg/m$^3$) + enhanced energy content
  - Moderate process conditions
    - [250 – 300°C]
    - ≈ atmospheric pressure
BioTfueL Technologies

**PRENFLO with Direct Quench**

1.200 MW$_{th}$, 42 bar

**PRENFLO PDQ Features**

- dry coal/petcoke powder feed
- 4 horizontal co-annular burners
- membrane wall
- direct water quench
- operation pressure flexible to requirements (25 - 42 bar)
- raw gas temperature outlet of quench (200 - 250 °C)
- compact gasification system with low plant investment
BioTfueL Technologies

- FT Synthesis & upgrading: 
  *Gasel™ Technology Suite*
  - Axens catalysts manufacturing
  - Axens process design, process integration and licensing know-how
  - Validated with representative feedstock from FT pilot plan

Syngas \( H_2/CO \sim 2 \) \( \xrightarrow{\text{Fischer-Tropsch}} \) Hydrocracking \( \xrightarrow{\text{high cetane diesel + jet fuel}} \)
The BioTfueL project
BioTfueL demo plants

- Multiple scale demo plants
  - to get scale-up data
  - to validate various scheme/configurations

- 2 pilot units in preparation
- Commercialization in 2020

Transformation routes of lignocellulosic biomass

- **Lignocellulosic biomass**
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- **Biofuels**
- **Energy**
- **Bioproducts**

- **Bio-TCat™**

- **FUTUROL**
  - Procethol 2G

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Bio-TCat™ process

The partners

- Anellotech
  - US Start-up founded in 2008
  - Develops the BioTCat process based on Prof Huber laboratory work (Univ Mass) at lab & pilot plant level on Pearl River Site

- IFPEN
  - Main contribution in continuous pilot plant, design, pilot start-up, hydrodynamic studies, and process scale-up to Demo plant/industrial unit

- Axens
  - Industrial development, White Process Book, Marketing & licensing, Basic engineering, start-up services

Direct BTX production process from lignocellulosic biomass through Thermal & Catalytic way
Bio-TCat™ process

- Biomass Suppliers
- Process Design
- Anellotech CFP Process
- BTX Purification
- Traditional Aromatics Processing
- Downstream Processing
- Commercial Plant Site
- Toluene
- Benzene
- Xylene
- PET resins and films
- Bio-MEG
- Px-PTA-PET conversion
- Partnering potentials

Bio-TCat™ process

Bio-TCat Process
Biomass to BTX in One Reactor

Compressor

CO₂ to processing or combustor

Separation Train

BTX

Water

Biomass

Drying & Grinding

Catalytic Fluidized Bed Reactor

Catalyst Separator

Catalyst Regenerator

Steam for electricity

Gas Recycle Loop

Catalyst Recycle Loop

Other ways of biobased chemical intermediates production

- Substitute petrochemical intermediates (ethylene, propylene, etc.)
- Generate new intermediates (lactic, succinic acids, etc.)
- Assess the feasibility of conversion processes

**ATOL™ process**: IFPEN, Axens and Total have developed a process to produce bioethylene via the dehydration of ethanol obtained by fermentation.

**Biobutterfly project**: IFPEN, Axens and Michelin have collaborated since 2013 to develop a biobased butadiene production process and create a French industrial sector of biobased rubber.

**Biobased aromatic hydrocarbons**: IFPEN, Axens and Anellotech partnered in 2015 to develop a chemical intermediate (benzene, toluene and paraxylene) production technology based on non-food biomass.

*marketed by Axens, a subsidiary of IFPEN
Transformation routes of lignocellulosic biomass

For development of innovative Catalysts, Biocatalysts and Processes, analytical characterization of biomass derived-liquids is essential.
Outline

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  - Biochemical route
  - Indirect chemical route
  - Direct chemical route

- Focus on analytical characterization
  - Molecular analysis
  - Separation by molecular size
  - Separation by polarity
Analytical characterisation

- Biomass derived liquids are complex chemical mixtures
  - Sugars, carboxylic acids, alcohols, phenols,…

- Suitable analytical methodology
  - Molecular analysis
  - Fractionation by molecular size
  - Fractionation by polarity

- 2 examples from thermochemical route
  - Organic matrices (Hydrocarbons + Oxygenates) ⇒ Liquids from lignin hydroliquefaction
  - Organic matrices (Oxygenates) ⇒ Biomass fast pyrolysis oils

Analytical characterisation

- Biomass derived liquids are complex chemical mixtures
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2 examples from thermochemical route

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Bidimensionnal gas chromatography (GCxGC)

Injector
Modulator
Détecor
Primary column
Secondary column

PONA x BPX-50
Normal configuration
Solgelwax x RTX-200
Reversed configuration

Liquids from lignin hydroliquefaction
GCxGC analysis

B. Joffres et al.
*Applied Catalysis B: Environmental*
184 (2016) 153–162

Transformation of Protobind 1000 lignin in presence of tetraline at 350°C, 80 bar
NiMo/Al₂O₃ catalyst
Liquids from lignin hydroliquefaction
GCxGC analysis

B. Joffres et al.
Applied Catalysis B: Environmental
184 (2016) 153–162

First Column (min)

Second Column (s)
Liquids from lignin hydroliquefaction
GCxGC analysis

B. Joffres et al.
*Applied Catalysis B: Environmental*
184 (2016) 153–162
Biomass fast pyrolysis oils

- Acidic samples with high water content
- High density (1.1-1.3 g.cm⁻³)
- Heating value ~ 13-18 MJ/kg
- High oxygen content (44-60 wt%)
- Thermal instability
- Non miscible in hydrocarbons

⇒ Complex chemical mixtures
  - Wide range of volatility, polarity, molecular weights
  - Thermo-sensitive compounds
  - Compounds having several chemical functions
Biomass fast pyrolysis oils
Supercritical Fluid Chromatography (SFC)

- Low diffusivity and viscosity
- High density and dissolution strength

⇒ Interesting technique for the analysis of polar and/or thermosensible compounds

T. Dutriez, Gas chromatography and 2D-GC for petroleum industry, Editions Technip 2013
Biomass fast pyrolysis oils
SFC-UV/MS analysis

J. Crepier et al.,
HTC – 14, 27-29/01/16, Ghent

SFC-UV (211 nm) chromatogramm of a wood fast pyrolysis oil


Biomass fast pyrolysis oils
SFC-UV/MS analysis

SFC-UV/MS chromatograms of a wood bio-oil

Analytical characterisation

- Biomass derived liquids are complex chemical mixtures
  - Sugars, carboxylic acids, alcohols, phenols,…
- Suitable analytical methodology

- 2 examples from thermochemical route
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Biomass fast pyrolysis oils
Size exclusion chromatography (SEC)

- Sample elution in columns packed with gels having different porosities
- Separation of compounds according to their size or their hydrodynamic volume in a specific solvent
- Elution inversely proportional to molecular weights

SEC-RI chromatogramm of a wood fast pyrolysis oil

Calibration to convert retention times in molecular weights using polystyrene standards (PS)

* Molecular weights expressed as eq PS
Biomass fast pyrolysis oils
SEC-UV/RI analysis

- At analytical scale
  - Optimized conditions (columns, temperature, mobile phase flow)
  - Resolution and reproducibility

Refractive index

UV 210 nm

UV 254 nm (ex aromatics)

UV 280 nm (ex furans)

SEC chromatograms at analytical scale of a wood fast pyrolysis oil


* Molecular weights expressed as eq PS
Biomass fast pyrolysis oils
SEC-UV/RI analysis

- At a semi-preparative scale
  - Scale up, 100 mg sample injection
  - Recovery of 3 fractions:
    - Fraction 200-3000 g/mol eq PS
    - Fraction 140-200 g/mol eq PS
    - Fraction <140 g/mol eq PS

* Molecular weights expressed as eq PS
Biomass fast pyrolysis oils
SEC-UV/RI analysis

A. Le Masle et al., SEP 2015 – 02/04/15, Paris

* Molecular weights expressed as eq PS

Fractions partially evaporated

Fractions fully evaporated

Whole pyrolysis oil
Sum of the 3 fractions

SEC-UV chromatograms (254 nm) at analytical scale

Biomass fast pyrolysis oils
SEC-UV/RI analysis

A. Le Masle et al., SEP 2015 – 02/04/15, Paris

* Molecular weights expressed as eq PS

SEC-UV Chromatogramms
(254 nm) at analytical scale

Whole bio-oil
Fraction <140 g/mol*
Fraction 140-200 g/mol*
Fraction 200-3000 g/mol*

SFC-UV chromatogram of
the fraction 140-200 g/mol

Analytical characterisation

- Biomass derived liquids are complex chemical mixtures
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- Suitable analytical methodology
  - Molecular analysis
  - Fractionation by molecular size
  - Fractionation by polarity

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High performance thin layer chromatography (HPTLC)

- **Step 1: automated sample deposition**
  - Sample homogeneous deposit, maximum sample amount
- **Step 2: migration automatique multi-étapes**
  - Homogeneous elution, decreasing elution strength
- **Step 3: UV-fluorescence detection**
  - Recovery of several fractions, matter balance
Biomass fast pyrolysis oils
HPTLC-UV analysis

Migration direction

HPTLC-UV chromatogram of a wood fast pyrolysis oil (254 nm)

Fraction Polarity +++
Fraction Polarity ++
Fraction Polarity +

Polarity of mobile phase

A. Le Masle et al., SEP 2015 – 02/04/15, Paris
Summary

- **Large diversity of chemical groups in biomass derived liquids**
  - Wide range of volatility, polarity, molecular weights
  - Polyfunctionnal, thermo-sensitive compounds

- **Sample fractionation prior to analysis**
  - Fractionation by molecular size (ex: SEC)
  - Fractionation by polarity (ex: HPTLC)
  - Optimisation of key parameters at analytical scale
  - Scale up at semi-preparative scale
  - Recovery of fractions

- **Molecular analysis**
  - High resolution chromatography techniques (ex: GCxGC)
  - Multi-detection systems (ex: SFC-UV/MS)

⇒ Analytical multi-techniques approach for development of innovative Catalysts, Biocatalysts and Processes
Thank you for your attention
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