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# GREEN HYDROGEN FROM BIOMASS TOWARDS INTEGRATED BIOREFINERY

**The forecast through 2050 underlines a 50% increase in world energy consumption [1]. In parallel, the energy sector is the main source of greenhouse gas emissions. This raises interest in a complete transformation of the current energy system. The Net Zero by 2050 roadmap aims to reduce global $CO_2$ emissions through the deployment of the available clean and efficient energy technologies [2]. This meets A.SPIRE's (the association of European Process Industries) Strategic Research and Innovation Agenda for hydrogen integration, namely 4.2 on Hydrogen integration [3].**

In such a scenario, hydrogen is projected as a fascinating energy carrier among the environmentally friendly solutions by using sustainable resources for its production. The hydrogen demand is expected to increase almost sixfold to reach 530 megatons of hydrogen by 2050, with half of this demand by industry and transport [4]. Tremendous efforts have been made in hydrogen production pathways, transport, storage, endpoint applications, and safety over the last decade. Renewables and green/biohydrogen were already expanding, but the global energy crisis called for an acceleration of steps for hydrogen uptake.

The unavoidable intermittence of solar and wind has hampered their expansion. A solution to overcome this obstacle is to associate these resources with a non-intermittent and widely available renewable resource, namely lignocellulosic biomass. Produced by photosynthesis, lignocellulosic biomass is a non-related-food biomass family and is the most abundant and well-spread on earth. It consists of three biopolymers: cellulose, hemicellulose, and lignin. Biomass can be converted into bioenergy and fuels using several routes such as thermochemical and biological processes.

Alike the concept developed for crude oil refining, lignocellulosic biomass resources can be converted into added-value products and renewable electricity. This concept of biorefinery is a strategic pillar to develop the circular economy. Furthermore, biomass valorisation coupled to intermittent renewable energies may contribute to the development of rural areas, thus delocalising energy production and reducing distribution costs.

The chemical fractionation of biomass is a key step to develop high-efficient integrated biorefineries. This step consists of the separation of cellulose by isolating lignin and hemicelluloses. The separation can be achieved through chemical pulping processes mainly used in the paper industry. These processes are based on dissolving solvents to break lignin intramolecular bonds, as well as lignin-cellulose intermolecular linkages, by preserving cellulose fibres. Kraft and sulphite are common methods since they dominate the paper and pulp industries. However, these processes use a sulphur-containing solvent which engenders atmospheric and effluent emissions. Along with the pollution, the presence of sulphur in the products limits their sustainable utilisation.

The use of organosolv processes offers the possibility for more efficient utilisation of lignocellulosic biomass. In organosolv processes, lignocellulosic feedstock is treated with a broad range of low-boiling organic solvents. These sulphur-free treatments fit well with the valorisation of biomass as they enable the separation of biomass components with minor degradation and without forming inhibitor products.

Despite their attractive advantages such as solvent recovery and mild environmental conditions, the high energy consumption and the high cost of solvent are the main challenges hurdling the commercialisation of organosolv treatment.

In this context, BioEB has patented an innovative process, for refining lignocellulosic material. The process is branded as **LEEBIO**™ referring to **L**ow **E**nergy **E**xtraction of **BIO**mass. A wide range of lignocellulosic residues can be treated including softwood, hardwood, cereal straws, and energy crops. The process consists of a non-degrading separation of lignocellulosic residues to cellulose, hemicelluloses, and lignin. This process uses only formic acid under mild conditions (<95°C and atmospheric pressure).

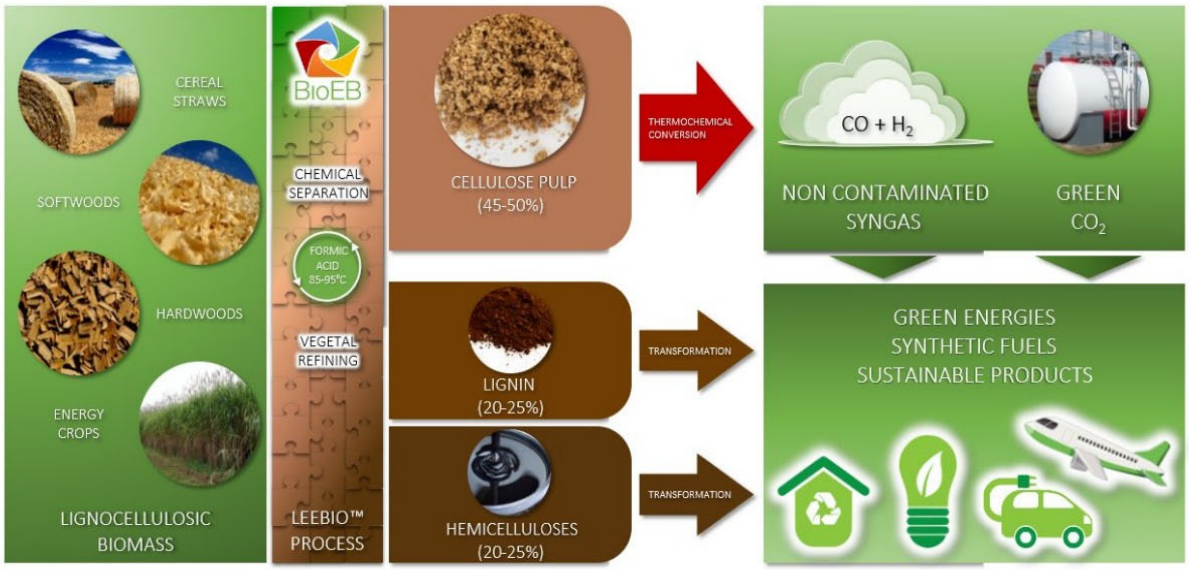


*Figure 1: LEEBIO™ technology – Cellulose pulp, green energies, fuels and products from biomass*

The profitability of this process is advocated by the fact that the extracted lignin and hemicelluloses can be used in industrial sectors without changing the existing technologies or infrastructures. Lignin is the most valuable component in terms of price. It is an industrial prospect to substitute phenol and polyols derivatives, or low-cost carbon fibre precursors. In addition to its conventional use, cellulose pulp can be converted into syngas through thermochemical conversion. Along with pyrolysis, steam gasification is one of the main thermochemical conversion routes of lignocellulosic feedstocks to produce high-quality syngas (containing a very low amount of pollutants). Syngas is a mixture of carbon monoxide and hydrogen, which can be used as a building block for the production of numerous biofuels and biochemicals including **$H_2$** (Figure 1). Steam gasification of cellulose is a highly-endothermic process which takes place at high temperatures. This endothermicity offers the possibility to store intermittent energy, such as those from solar and wind, in $H_2$ as the final universal energy carrier.

In this framework, the production of $H_2$-rich syngas from an organosolv cellulose pulp was investigated. The results presented in the following were the findings obtained in the doctoral thesis [5]. The work is in the process of being patented [6].

## Biomass fractionation

Softwood sawdust was selected for **LEEBIO™** treatment as it is a main biomass residue in Occitanie region (France). Firstly, the treatment was carried out at laboratory scale to optimise the process in terms of pulping time to reduce energy consumption. The inorganic composition of the obtained cellulose pulp was impacted by the activity of formic acid used in **LEEBIO™** treatment. Silicon (Si) was the main inherent mineral element while alkali metals were dissolved. Secondly, the process was validated at a pilot scale with RoLab filter dryer. 40 kg of softwood sawdust and 200 Kg of formic acid were employed. 27 kg of **LEEBIO™** dried pulp were produced, containing up to 60% wt.% of cellulose.

To produce $H_2$-rich syngas, the obtained cellulose pulp was subject to steam gasification at laboratory scale at the RAPSODEE research centre (Albi, France). Gasification tests of biochar were performed in a semi-continuous fixed bed reactor under different experimental conditions. The process was divided into two stages: pyrolysis and gasification. Volatile matter and biochar are produced within pyrolysis stage. Volatiles were removed from the reactor and were not taken into consideration in the gasification stage. The obtained biochar is then gasified under a steam atmosphere.

The hydrogen yield and carbon conversion at temperatures below 950°C were strongly affected by the severe inhibitory effect of silicon (Si) and carbon-gas reactions.

At 950 °C, **LEEBIO™** cellulose pulp shows great potential for high-quality $H_2$-rich syngas production. A Potential hydrogen yield and $H_2$ : CO ratio of 52.9 g/Kg (cellulose) and 1.8 were obtained, respectively.

Despite its inhibiting effect, the high silicon content (Si) in **LEEBIO™** cellulose pulp permits to retain of alkali species and prevents their loading in the syngas. Compared to the raw lignocellulosic biomass, the gasification of **LEEBIO™** cellulose shows lower tendencies to slagging/fouling and agglomeration, as a result of formic acid pulping.

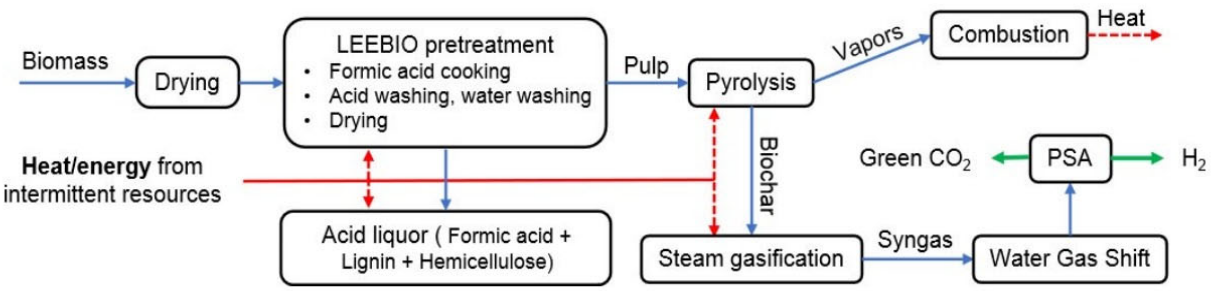


*Figure 2: Hydrogen production scheme*

## Process optimisation

For real scale application, the process is evaluated in terms of $H_2$ production efficiency and energy requirement. For this end, the process integrated **LEEBIO**™ treatment and steam gasification was simulated using Aspen Plus software. The process involves three additional parts: syngas upgrade, hydrogen separation and combustion of volatiles from pyrolysis (Figure 2).

The simulation results demonstrated that biomass pre-treatment was the highest energy demand stage in the process. When integrating organosolv treatment to steam gasification, hydrogen production efficiency dropped from 41.5 to 26.2 % while the energy requirement raised from 77 to 111 kWh/kg ($H_2$).

Further assessment in terms of solvent and by-product recovery are necessary to improve the process efficiency. Thus, hydrogen from integrated biorefineries could potentially complement electrolysis (51%, 50-65 kWh/$_{kgH2}$).

## Prospects

Unprecedented efforts are being deployed on the full hydrogen value chain. Current challenges are associated with the improvement of technologies (development of robust and affordable catalysts, development of local scale technological solutions among others), shortage in the value chain, with the lack of large-scale production infrastructure, high cost and low efficiency of current solutions. In addition, cross-sectorial innovation could offer the advantage of faster deployment and impact at scale. SPIRE, for example, has shown the effectiveness of the unique cross-sectorial innovation approach under Horizon 2020. In P4Planet the synergies in cross-sectorial innovation approach will be developed further. This is an echo of our research on Circular Bio-based innovation for Energy and Environmental Transitions.

### Literature references

(1) U.S. Energy Information Administration's (EIA). *International Energy Outlook 2021*; 2021. www.eia.gov/outlooks/ieo/.
(2) International Energy Agency (IEA). *Net Zero by 2050 – Analysis*; 2021. www.iea.org/reports/net-zero-by-2050.
(3) A.SPIRE. Strategic Research and Innovation Agenda. **2021**, 293.
(4) International Energy Agency. *Global Hydrogen Review 2021*; OECD, 2021. www.doi.org.
(5) Elsaddik, M. Gazéification de La Cellulose Pour La Production d'un Syngas Riche En Hydrogène Une Approche Bioraffinerie. These en préparation, Ecole nationale des Mines d'Albi-Carmaux, 2019. www.theses.fr (accessed 2023-02-02).
(6) Elsaddik, M.; Nzihou, A.; Delmas, G.-H.; Delmas, M. Gaz de Synthèse Obtenu à Partir de Cellulose. FR2206388.