Groupement de recherche
THERMOBIO Conversion thermochimique de la biomasse et des déchets

6ème Séminaire du GDR Thermobio

« Conversion Thermochimique de la Biomasse et des Déchets »

Nancy, 11& 12 juillet 2023 – hôtel Mercure centre gare

11 rue Raymond Poincaré - 54000 NANCY

Programme

11 Juillet 2023

12h00-14h00: Accueil et Déjeuner au restaurant de l'hôtel Mercure centre gare

14h-14h45 : **Audrey Villot (IMT Atlantique GEPEA) : Le cercle vertueux du biochar : comment un déchet est devenu un matériau d'intérêt.**

14h50-15h10 : **Ksenia Parkhomenko** (ICPEES Strasbourg) : Biochars mixtes comme matériaux versatiles pour diverses applications

15h10-15h30: **Hary Demey** (CEA Grenoble): Supercritical water gasification of biomasses and wastes

15h30-15h50: **Leonela Martes Hernandes** (INSA Rouen): Catalytic cracking of tar model compounds using flax shives biochar and effect of metallic precursors

15h50-16h30: Pause Café

16h30-17h20 : Présentations flash :

- **Saad Nader** (LRGP): Effects of heating rates during barks hydrothermal treatment
- **Muriel Marchand** (CEA Liten) : Procédé de torréfaction et propriétés du biocoal pour les applications de métallurgie
- **Valentina Sierra** (Washington St. Univ., LRGP) : Methodology to interpret characterization data and construct biochar molecular models
- **Enrico Antonuccio** (CP2M): Improvement of methanol synthesis from syngas conversion with Sorption-Enhanced Reactor Process (SERP) approach
- **Nolwenn Daridon** (IRCELYON) : Fonctionnalisation de biomasse lignocellulosique pour la fabrication de bio-liants

17h20-17h40: **Isaline Bonnin (CP2M):** Kinetic study of lignocellulosic biomass transformation into glycols

17h40-18h00: **Nabil Hassibi** (LRGP) : Pyrolysis recycling of polystyrene: Importance of the reflux to maximise the styrene and BTEX components

18h00-18h40 : Présentations Flash :

- **Richard Lainé** (LRGP): Pyrolysis of plastics: highliGHTing the potential interest of a reflux to control liquid products

- **Sary Awad** (IMT GEPEA Nantes): Présentation du projet COCPIT (Horizon Europe, cluster 5)
- **Matteo Pietraccini** (LRGP) : In-operando image analysis of the fluidization behaviour during biomass pyrolysis
- **Andrea Facchin** (BOLOGNA Italy): Coupling HTC and pyrolysis, energy and mass balances

19h30 : Apéritif et Diner au restaurant de l'Hôtel Mercure

12 Juillet 2023

9h-9h45 : Denilson Da Silva, CEA (DRT/LITEN/DTNM/STDC) : Différentes biomasses, différents procédés : quels biochars, quelles applications ? La contribution du projet Européen MOBILE FLIP

9h50-10h10: **Yann Le Brech** (LRGP, Nancy) : Qualités physico-chimiques et potentiels de valorisation des biochars

10h10-10h30: **Lucia Jimenez** (Leroux&Lotz): Gazéification hydrothermale : positionnement de LLT dans la filière

10h30-11h00: Pause Café

11h-11h20: **Christophe Geantet (IRCELYON)** HYCON a européen project on the valorization of HTL crudes

11h20-12h00: Présentations flash :

- **Eya Ghomri** (LRGP): Biochar characterization by Raman spectroscopy
- **Hugo Lilti** (IRCELYON): Tandem depolymerization and hydroxyl content increase of lignin via a catalytic reaction
- **Jean-Michel Commandré** (CIRAD, Montpellier) : Conception et performances d'une chaudière adaptée aux industries agro-alimentaires tropicales par combustion de coques d'anacarde)
- **Peter Opoku Badu** (LERMAB Epinal) Optimisation de la Production d'Hydrogène par Gazéification en lit fluidisé dense de la Biomasse
- **Marcello Tavares Lima** (LRGP): Gasification of Brazilian Biomass to Obtain Integrative Biorefineries

12h00-12h30 : Conclusions et informations (PEPR, Ecole VALOTHERBIO…)

12h30-14h00: *Déjeuner au restaurant de l'Hôtel Mercure et départs*

Le cercle vertueux du biochar : comment un déchet est devenu un matériau d'intérêt.

A. VILLOT, A. ABDELAAL, C. RABBAT, S. AWAD, C. GERENTE & Y. ANDRES / *IMT Atlantique, GEPEA UMR CNRS 6144*

La pyro-gazéification est un procédé flexible qui présente l'intérêt de pouvoir répondre à plusieurs problématiques au travers le monde : i) production de vecteur énergétique, ii) contribuer à la gestion de déchets, et iii) réduction des gaz à effet de serre. Les chars issus de ces procédés étaient considérés comme étant des « déchets », ce qui impliquait de mettre en place une gestion appropriée, qui présentait un coût financier négatif pour les installations industrielles (100-150€/tonne sur le marché européen). Les contributions de la communauté scientifiques ces 15 dernières années dans le domaine ont montré que ce matériau pouvait dans certaines conditions présenter un intérêt pour être valorisé dans différentes applications (support catalytique, charbon actif, amendement pour sol, etc.). Les résultats de ces nombreuses contributions ont conduit le GIEC à citer le char et plus particulièrement le BIOCHAR comme pouvant être une solution de remédiation au réchauffement climatique au travers une utilisation en tant qu'amendement pour les sols et/ou puit carbone (AR5 & AR6). Depuis, l'intérêt pour ce matériau est grandissant ce qui a eu des répercussions directes sur sa valeur marchande : une tonne de biochar se vend en moyenne 300€ sans certification carbone et peut aller jusque 1500 € (voir 2000€ dans certains cas) la tonne vendue avec son certificat carbone. L'évolution du contexte aussi bien économique que politique font qu'il est d'autant plus important de développer une vision systémique concernant la valorisation des chars afin d'orienter ce dernier vers les usages les plus pertinents en fonction de ses caractéristiques intrinsèques.

Le char est largement considéré comme un exemple de bouclage de la boucle dans le domaine de l'énergie durable, mais son développement a grande voir très grande échelle est-il soutenable et présenterait-il le même intérêt sans l'existence du marché du carbone. Une tonne de chars permet d'immobiliser 2,5 à 3 tonnes de carbone Il est actuellement considéré comme un moyen de séquestrer du carbone sur le long terme et donc est assimilé sur le marché du carbone à un crédit carbone.

Biochars mixtes comme matériaux versatiles pour diverses applications

Aliénor Beuchat,[1] Ksenia Parkhomenko,[1] Dominique Begin,[1] Claire Courson,[1] Nicolas Tevenin,[2] Lionel Ruidavets,[2] Marine Guilmont,[3] Benedicte Rety,[3] Roger Gadiou[3]

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[2]*RITTMO Agroenvironnement®, Colmar, France*

[3]*Institut de Science des Matériaux de Mulhouse (IS2M), CNRS, Université Haute-Alsace, Mulhouse, France*

Dans ce projet la préparation et l'activation de biochars à partir de biomasses de natures différentes – lignocellulose (marc de raisin, bois) et boue d'épuration, ont été visées. La biomasse provenant d'une station d'épuration contient une grande quantité de composés inorganiques (cendres) et notamment 1,6 mass% de Fe provenant essentiellement du floculant largement utilisé dans le traitement des eaux usées.

Les biochars mixtes ont été préparés par la copyrolyse par la voie « lente » et la voie « rapide » : bois mélangé avec boue d'épuration et marc de raisin mélangé avec boue d'épuration, dans différentes proportions. Les conditions de la synthèse sont les suivantes – séchage à 110°C pendant 12h, puis la pyrolyse « lente » à 800°C (vitesse de chauffage 10°C/min, un four vertical, diamètre de 30 mm) ou la pyrolyse « rapide » à 800°C dans le four-cuillère sous atmosphère inerte. L'activation des biochars à la vapeur d'eau (800°C, 10 °C/min, 2h) était effectuée post-synthèse. Les propriétés des biochars mixtes avant et après l'activation ont été comparées.

Le but de cette étude est la préparation de familles des matériaux biosourcés chargés naturellement de métaux, avec des propriétés physico-chimiques et morphologiques améliorées par rapport à la surface des oxydes seuls. Les biochars activés ont été testés dans plusieurs applications : en traitement d'air comme adsorbants de CO_2; en électrocatalyse comme matériaux super-capaciteurs prometteurs et en catalyse hétérogène comme catalyseurs de reformage du méthane et d'autres molécules pour la production d'hydrogène.

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Hydrogen and Methane Production by Catalytic Supercritical Water Gasification of HTL liquid effluents

Hary Demey *, Gilles Ratel, Bruno Lacaze, Olivier Delattre, Geert Haarlemmer and Anne Roubaud

In this work, the wastewater obtained from the hydrothermal liquefaction of black liquor was treated and valorized for hydrogen production by supercritical water gasification (SCWG). The influence of the main process parameters on the conversion yield was studied. The experiments were conducted at three different temperatures (below and above the critical point of water): 350 °C, 450 °C and 600 °C. The results showed that by increasing the temperature from 350 °C to 600 °C, the total gas yield was highly improved (from 1.9 mol gas/kg of dried feedstock to 13.1 mol gas/kg of dried feedstock). The H2 composition was higher than that of CH4 and CO2 at 600 °C, and the HHV of the obtained gas was 61.2 MJ/kg. The total organic carbon (TOC) removal efficiency was also improved by increasing the temperature, indicating that the SCWG process could be used for both applications: (i) for wastewater treatment; (ii) for producing a high calorific gas. The experiments with the Raney-nickel catalyst were performed in order to study the catalyst's influence on the conversion yield. The results indicated that the catalyst enhances carbon con-version and gas production from mild to higher temperatures. The maximum total gas yield obtained with this catalyst was 32.4 mol gas/kg of dried feedstock at 600 °C, which is 2.5 times higher than that obtained at the same operating conditions without a catalyst. The H2 yield and the HHV of the obtained gas with the catalyst were 20.98 mol gas/kg dried feedstock and 80.2 MJ/kg, respectively. However, the major contribution of the catalytic SCWG process was the improvement of the total gas yield at mild operating temperatures (450 °C), and the obtained performance was even higher than that obtained at 600 °C without catalyst (17.81 mol gas/kg dried feedstock and 13.1 mol gas/kg dried feedstock, respectively). This is a sustainable approach for treating wastewater at mild temperatures by catalytic SCWG.

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Catalytic cracking of tar model compounds using flax shives biochar and effect of metallic precursors

Leonela Martes Hernández, Lokmane Abdelouahed, Bechara Taouk

Laboratoire de Sécurité des Procédés Chimiques (LSPC), INSA Rouen, Normandie.

This work aims to improve the hydrogen yield in the Syngas resulting from the biomass gasification through the catalytic reforming of tars.
The flax shives biochar was selected as a catalyst for tar cracking due to its economic advantage in comparison with other catalysts as it is a byproduct of the biomass gasification. A parametric study of the reforming reaction was carried out and data about the kinetic characteristics and the internal and external mass transfer limitations were obtained using the toluene as model compound. Similar experiments were made with Benzene and n-Xylene using the same biochar as catalyst.
The results obtained on the toluene catalytic cracking showed that it was possible to reach conversion values near the 99%. The toluene was decomposed into Benzene (C_6H_6), soot, and light gases (H_2, CH_4) with a good selectivity towards the hydrogen in the gaseous phase. On the other hand, the concentration values of benzene were high regarding the final amount of tar desired. To increase the hydrogen yield and reduce the amount of benzene, we modified the biochar with metals (Nickel and Iron), deposited by impregnation. A significant improvement has been obtained and a comparison of the effect of both precursors has been performed.

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Kinetic study of lignocellulosic biomass transformation into glycols

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Glycols as ethylene glycol (EG) and propylene glycol (PG) cover a wide range of applications, in particular for the polymer industry or as synthesis precursors. To date, these compounds are produced from fossil resources. The possibility to obtain polyols on a large scale from renewable biomass, in particular from lignocellulosic biomass, is therefore of particular importance in the context of the development of biorefineries. However, the production of low carbon number polyols starting from complex molecules with a high molecular weight is challenging in view of the complexity of the reaction pathway involving cascading reactions that require various catalytic sites.
As example, the formation of EG or PG from cellulose implies three consecutive reactions: (1) hydrolysis of polysaccharides to sugars by Brønsted acidity, (2) retro-aldol condensation of sugars by Lewis acidity and (3) hydrogenation of low carbon number polyols. An innovative catalysts designed by our group [1] containing nickel tungsten carbides supported on carbon (5%Ni-30%W_2C/AC) is able to conduct the proper reactions successively due to the catalytic synergy between both sites W_2C and the $Ni_{17}W_3$ alloy. The reactions are typically carried out in water at 160-250°C, under 60-100 bar of H_2, giving yields between 40 to 80 mol% of glycols accompanied by various intermediates (as hydroxyacetone) or side products (as mannitol) coming from parallel reactions that compete with the main pathway (Fig. 1) [2]. The comprehension of the reaction pathways involved in the transformation of cellulose to glycols is then required to enhance the glycols productivity. For that, the catalytic conversion of glucose in the presence of 5%Ni-30%W_2C/AC was done with regular sampling over time and the main intermediates compounds were identified and quantified by HPLC-RID-UV in order to study the kinetic of reaction. A design of experiments with the variation of parameters (stirring, temperature, pressure, concentration) has been performed to acquire sufficient experimental data in order to build a consistent kinetic model by computational method. This model will integrate reaction and diffusion for different stages of the reaction allowing the understanding of the mechanisms involved in the transformation of lignocellulosic biomass to polyols.

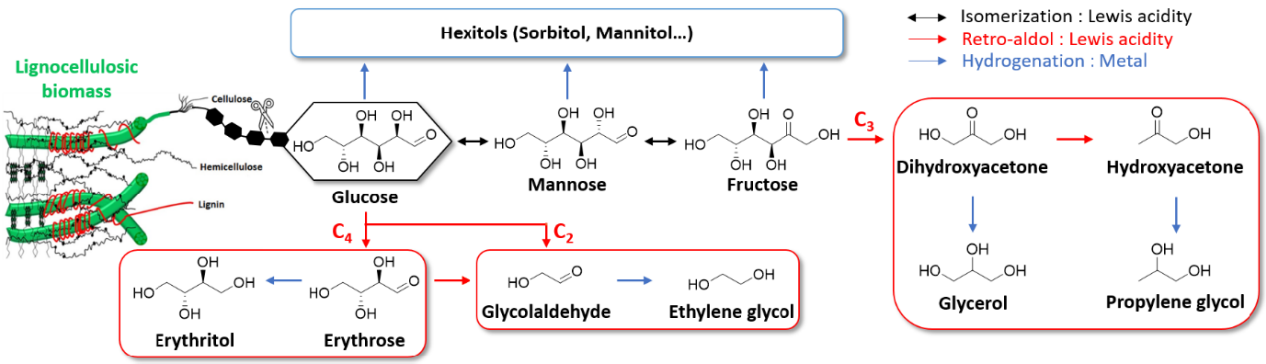

Figure 1: Reaction pathways from glucose to polyols.

[1] F. Goc, T. Epicier, N. Perret, F. Rataboul, Preparation of Carbon-Supported Tungsten Carbides: Comparative Determination of Surface Composition and Influence on Cellulose Transformation into Glycols, ChemCatChem. 15 (2023) e202201496.
[2] N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang, J.G. Chen, Direct Catalytic Conversion of Cellulose into Ethylene Glycol Using Nickel-Promoted Tungsten Carbide Catalysts, Angew. Chem. Int. Ed. 47 (2008) 8510–8513 ; R. Ooms, M. Dusselier, J.A. Geboers, B. Op de Beeck, R. Verhaeven, E. Gobechiya, J.A. Martens, A. Redl, B.F. Sels, Conversion of sugars to ethylene glycol with nickel tungsten carbide in a fed-batch reactor: high productivity and reaction network elucidation, Green Chem. 16 (2014) 695–707.

Qualités physico-chimiques et potentiels de valorisation des biochars

Yann Le Brech[a], Eya Ghomri[a], Marine Guilmont[b], Sébastien Leclerc[c], Sabine Bonnet[d], Younes Bouizi[d], Nicolas Thevenin[e], Fiona Ehrhardt[e], Anthony Dufour[a], Roger Gadiou[b]

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Le développement de la filière biomasse-énergie et la volonté de vouloir préserver la fertilité à long terme des sols (initiative 4/1000), entraine un engouement des gestionnaires de biomasses (agriculteurs et industriels de la fertilisation et de l'énergie) pour les technologies de production de biochars. Ainsi, pour fournir les informations aux futurs porteurs de projet, le projet QUALICHAR (Qualités physico-chimiques et potentiels de valorisation des biochars) financé par l'ADEME (2021-2024), vise à dresser une base de données techniques et méthodologiques de la qualité agroenvironnementale des biochars produits par pyrolyse lente et rapide pour différents gisements de biomasses (Bois, herbacés, Digestats, Fumiers,…). Cette présentation aura pour objectif de donner un bilan de l'avancement du projet concernant : 1) la production et la caractérisation des biochars produits (RMN, Raman, Infrarouge, CHNS, ATG, BET, TPD-MS, XRF, MEB-EDX). 2) l'impact de ces biochars sur les sols : cinétiques de libération de l'azote, assimilation du phosphore, impact sur la capacité de rétention en eau du sol, évolution du pH, biodégradabilité et émission de N2O.

Gazéification hydrothermale : positionnement de LLT dans la filière

Lucia JIMENEZ (Leroux et Lotz Technologies), Sofiane ZALOUK (Leroux et Lotz Technologies).

La gazéification hydrothermale suscite aujourd'hui un intérêt croissant car elle constitue, pour un certain nombre de déchets ultimes, une alternative aux voies existantes d'incinération et/ou enfouissement permettant de produire un vecteur énergétique : le gaz de synthèse composé principalement de CH_4 et H_2.
Elle utilise l'eau supercritique (P > 221 bar et T > 374°C) comme milieu réactionnel permettant de convertir totalement et avec une bonne efficacité énergétique (75 à 90%) des déchets humides en gaz de synthèse.
Leroux et Lotz Technologies, spécialisé dans la valorisation des intrants solides (combustion/gazéification) et humides (développement d'une technologie propriétaire d'oxydation hydrothermale) se positionne comme fournisseur de la technologie GH haute température (non catalytique) en partenariat avec le KIT (Karlsruhe Institut of Technology). Son premier pas dans la filière sera la construction du premier démonstrateur de gazéification hydrothermale en France dans le cadre du projet GHAMa* (**G**azéification **H**ydrothermale **A** **M**ontoir-de-Bretagne **a***) dont l'objectif est de construire et mettre en service un démonstrateur de 2 t/h pour la valorisation des boues d'épuration avec une siccité de ≈ 13% (voir macro-planning ci-dessous). Ce démonstrateur permettra la validation des hypothèses de fonctionnement (caractéristiques/performances/disponibilité) pour définir un business model pour la commercialisation de la technologie.

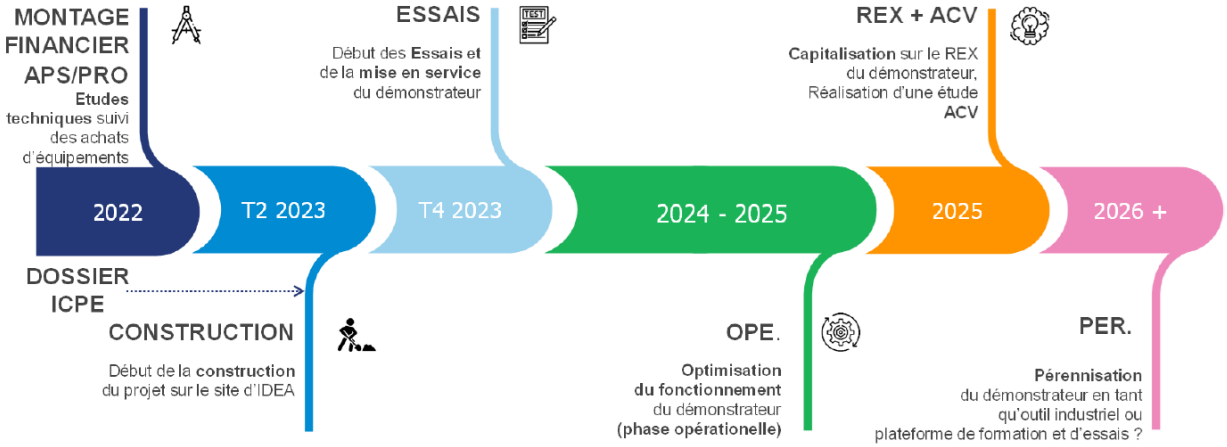

*Figure 1. Macro-planning projet GHAMa**

a*: premier projet

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Pyrolysis recycling of polystyrene: Importance of the reflux to maximise the styrene and BTEX components

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Plastics are one of the most widely used materials due to their various advantages and numerous applications in our daily life. Its consumption and production have increased worldwide every year and the waste generated by their production, transport and disposal creates a variety of environmental problems. Pyrolysis is considered as one of the most promising technologies for plastic waste which are complicated to be recycled mechanically and are also difficult to depolymerize. Despite the usefulness and simplicity of the pyrolysis process, the products are characterized by a very wide distribution of hydrocarbons that leads to a lot of post-pyrolysis treatment to increase the value of the liquids obtained.

In this work the influence of the reflux was studied in order to enhance styrene monomer and BTEX recovery. To this end, a semi- batch glass reactor apparatus equipped with a reflux condenser was developed and investigated for the pyrolysis of polystyrene at 480°C with nitrogen as the carrier gas and operating at atmospheric pressure. The temperature at the top of the reflux zone was ranged from 200°C to 400°C depending on the heating power.

A comprehensive gas chromatography (GC-MS/FID) coupled with a µ-GC-TCD were used to characterize the liquid and gaseous products exhaustively. The use of reflux influenced the yields of styrene, benzene, ethylbenzene and toluene in the liquid output and the C1–C4 content of the gaseous output. As presented in Fig.1, the mass fraction of styrene and toluene monomers related to the analysed oil from GC-MS/FID reached a maximum of 81.2 wt% and 13.5 wt% respectively with an optimal reflux temperature of 200 °C, whereas they only represented 59.3 wt% and 3.7 wt% respectively when the reflux was not used.

The present study illustrates the significant impact of the reflux on the liquid and gas yields. As a consequence, the molecules of interest are maximised, especially those corresponding to styrene, benzene, ethylbenzene and toluene components.

HYCON: a european project on the valorization of HTL crudes

Nuno Batalha [a], Ruben Checa [a], Chantal Lorentz [a], Pavel *Afanasiev [a], Krzysztof Stańczyk[b], Krzysztof Kapusta[b], Dorothée Laurenti [a], Christophe Geantet [a]*

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The **HyCon** project aims to evaluate the potential of biomass and low-grade and high-moisture lignites for the production of synthetic liquid fuels and value-added chemicals through a hydrothermal liquefaction process (HTL). The hydrothermal treatment is well suited for the processing of high-moisture feedstocks because water is used as a main reaction medium. Ircelyon contributes to this European program by performing the upgrading of HTL oils. A fossil resource lignin and 3 types of biomass (2 sewage sludges, oak sawdust and brewer's spent grains) were converted by hydrothermal liquefaction at Katowice (Poland). HTL oils were converted in a batch reactor by hydroconversion with a NiMoS on alumina catalyst. The resulting products of the HTL liquids were characterized in depth and compared. The differences observed in the HDT liquid composition clearly show that the HTL crude oil composition, which depends on the feedstock, dictates the potential for producing hydrocarbon fuels. Indeed, HTL crude oils with a higher concentration of aromatic compounds, like Lignite and Oak Sawdust, will yield preferentially naphthenes and aromatic hydrocarbons. In opposition, crude oils with a higher concentration of aliphatic carbon, like Sewage sludge and Spent Grain, will be more selective towards paraffins. In opposition, Oak Sawdust and Lignite were particularly selective into aromatic hydrocarbon and naphthenes, which are a product of the hydrotreatment of phenol and other aromatic compounds highly abundant in these crude oils Additionally, the type, i.e., N, S, and O, and concentration/nature of heteroatom components must also be considered since these compounds must be imperatively eliminated during HDT.

Présentations Flash:

Effects of heating rates during barks hydrothermal treatment

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With the growth of environmental concerns, researchers are focusing on the replacement of fossil oil-based products by bio-based ones to reduce the climate change impacts. Lignocellulosic biomass is the most abundant source of renewable polymers on earth. Valorisation of biomass presents an environmentally friendly promising source of renewable carbon. Hydrothermal treatment is considered as an environmentally-friendly method to convert biomass into rich carbon material, called Hydrochar. Nowadays, barks, wood sub-products, are not sufficiently valorised. This biomass is mainly used for mulching. The chemical composition of barks, similar to wood, allows the valorisation by hydrothermal treatment to produce chemicals, fertilizers, chars, etc.

For this purpose, barks were treated in water at 300°C during 1 hour in autoclave.

The originality of our work is: (1) the comparison of the chemical transformations of spruce bark by studying the effects of particles size during hydrothermal treatment for 1h, (2) studying the effects of fast (induction) and slow heating rates on the chemical conversions, (3) using original analytical techniques to identify and quantify produced chemicals.

Sampling was done each 20 minutes to follow-up the chemical conversion of lignin and carbohydrates during the process.

Different analytical techniques are used during this study: µ-GC, GC-MS, TOC, elementary analysis, ^{1}HNMR, etc.

Based on ^{1}H NMR area ratios, composition of aqueous phase is quite similar for fast and slow heating at different sampling times (for all particles size). Carboxylic acids, aldehydes and acetates are faster converted for slow than for faster heating (between t0 and t20min) due to longer residence time during the heating for slow heating.

UV fluorescence results showed that there is no important effect of heating rate. Lower depolymerization rates were found for particles > 400µm.

Improvement of methanol synthesis from syngas conversion with Sorption-Enhanced Reactor Process (SERP) approach

Enrico Antonuccio, David Edouard, Pascal Fongarland
(CP2M - Université Claude-Bernard Lyon 1)

Le méthanol reste à l'heure actuelle une molécule d'intérêt soit en tant que vecteur énergétique, soit comme molécule plateforme. Si la conversion du gaz de synthèse en méthanol a fait l'objet d'un grand nombre d'études et est actuellement un procédé industriel, l'utilisation de ressources de type biomasse, d'un CO_2 issu de séquestration ou encore d'H_2 « vert » entraine un besoin d'optimisation du procédé limité entre-autres par les limitations thermodynamiques.
Afin de dépasser ces limites thermodynamiques, la technologie SERP (« Sorption Enhanced Reaction Process »), propose de coupler les réactions avec la séparation in-situ de manière sélective d'un produit. Dans notre étude, il s'agit de l'eau produite durant la synthèse du méthanol à parti d'un gaz de synthèse CO_2/H_2 qui est adsorbée sur des matériaux ayant une capacité d'adsorption entre 200 et 250 °C (zéolites ou des MOFs). Dans le cadre du projet ANR SIMPA en collaboration avec l'ICPEES, l'IMN et l'ICG, notre objectif est d'étudier le couplage entre réaction catalytique et sorption et de trouver une stratégie de cyclage optimale entre la réaction-adsorption et la désorption de l'eau afin d'optimiser le rendement en méthanol (variation de température et/ou pression et/ou composition).
Dans un premier temps, nous avons modélisé à partir de données de la littérature les deux étapes pour un lit fixe unique sous Matlab afin d'évaluer l'impact de la composition, la température et de la pression du mélange réactif, du temps de séjour ainsi que le rapport massique entre catalyseur et adsorbant. Enfin, leur répartition spatiale au sein du lit fixe a été étudiée, ainsi que la durée optimale de chaque phase opératoire. Il a été démontré la grande complexité des interactions entre paramètres et de la possibilité de dépasser les limitations thermodynamiques. Par la suite, ce travail sera comparé à des expériences sur des matériaux obtenus par les partenaires du projet.

PYROLYSIS OF PLASTICS: HIGHLIGHTING THE POTENTIAL INTEREST OF A REFLUX TO CONTROL LIQUID PRODUCTS

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The pyrolysis of plastics is envisioned as a potential technology to produce fuels or depolymerized building blocks (as monomers). Various pyrolysis reactors were tested on a large range of conditions (pressure, temperature, catalyst, etc.): fluidized bed, fixed bed, extruder, melting vessel, etc.[1,2]. One of the main issue of plastic pyrolysis is to control the composition of the liquid products (often presenting a broad distribution of molecular weight) and to reduce waxes. Despite numerous studies and reviews on this topic, the interest to use a reflux combined with the pyrolysis reactor has not been well highlighted. However it has been demonstrated at lab, pilot and industrial scales that a reflux could promote the formation of lighter products by reducing waxes (or oligomers) [3–5]. Indeed, the composition of pyrolysis liquids is controlled by the kinetics of bonds cleavage, their stabilization (notably by H-transfers) and the devolatilisation of the intermediate liquid. The liquid can be evaporated (at the temperature of the pyrolysis reactor) or transported in the form of aerosols. Then it can undergo gas-phase or catalytic conversion. Finally, the products are condensed. A high temperature (400-600°C) is required in the pyrolysis reactor (to promote depolymerization kinetics) which lead to the evaporation of heavy species. A reflux set at a lower temperature than the pyrolysis reactor can condensate the vapours of heavy molecular species which will fall back into the pyrolysis reactor and undergo further depolymerisation reactions. Therefore, the temperature of the reflux may control the molecular weight distribution of the liquids [6].

During this short talk, we will present a novel small pilot reactor (at 1-2kg/h) developed at LRGP Nancy combining: an extruder melt feeder, a stirred reactor, a (catalytic) reflux and a condensation train. We will show how the temperature of the reflux can impact the molecular weight distribution of liquid products for PP pyrolysis. The gases were analyzed on-line. The liquids were analyzed by GC/MS-FID and a bench-top NMR. The potential implementation of pyrolysis-reflux reactors will be discussed.

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THERMOBIO Conversion thermochimique de la biomasse et des déchets

Tandem depolymerization and hydroxyl content increase of lignin via a catalytic reaction.

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Reducing our dependency towards oil is one of the biggest challenges of the next decades. Lignin being the most abundant source of renewable aromatics molecules it is already used in polymer formulation, as a partial replacement for petroleum-based molecules. However, its low reactivity, high polydispersity and versatility makes lignin hard to use at a commercial scale. Increasing the hydroxyl content and partially depolymerizing lignin could reduce the troubles without having to depolymerize completely which is very energy consuming. One way of increasing the hydroxyl content of lignin could consist of demethylate the methoxy groups which are very abundant. In the meantime, lignin can be efficiently depolymerized by breaking only the ether (mainly βO4', a-O-4) inter-unit bond which can represent up to 60% of all inter-units' bond. More, this ether bond can be cleaved to leave a hydroxyl group. Both those reactions are based on the same mechanisms which is the break of an ether bond, finding a one pot one step process to demethylate and depolymerize lignin is therefore at high stake. We investigate the effect of different catalysts and reaction conditions on the hydroxyls content and oligomers distribution of the modified lignin.

Procédé de torréfaction et propriétés du biocoal pour les applications de métallurgie

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L'emploi du biochar issu de la pyrolyse lente de bois et de déchets autour de 500°C est maintenant bien connu pour la décarbonation du secteur de la métallurgie [1], gros émetteur de CO_2 avec près de 20% des émissions industrielles mondiales [2]. Les taux de carbone fixe élevés pouvant être obtenus en pyrolyse font de ce biochar un substitutif efficace au charbon et coke fossiles pour la réduction des oxydes de minerai en haut fourneau ou en Four à Arc Electrique. L'utilisation de biocoal obtenu à des températures plus proches de la torrefaction (~350°C) est une alternative intéressante au biochar, car moins couteuse énergétiquement [3], mais qui mérite des études dédiées du fait des propriétés « dégradées » de ce solide par rapport à l'intrant de référence d'un procédé métallurgique. Dans les projet Européens CIRMET (2018-2022) et DIGISER++ (2019-2021), le CEA a étudié à l'échelle laboratoire puis pilote la production de biocoal par torréfaction sévère de biomasses bois et agricoles [4]. Dans CIRMET, les propriétés physico-chimiques, non seulement du solide mais aussi du gaz issu du procédé, ont été caractérisées dans le double but de substituer le charbon fossile et le gaz de torche à plasma d'un procédé de recyclage d'oxydes non ferreux (Cu, Zn). L'étude à l'échelle laboratoire sur 6 intrants a permis de déterminer les conditions opératoires optimales pour minimiser les rapports atomiques H/C et O/C, tout en maximisant le taux de carbone fixe, ainsi que de sélectionner le meilleur candidat pour l'étude à l'échelle pilote. L'étude à l'échelle pilote dans le four CENTORRE incluant des données de bilan matière et énergie s'est terminée par la production d'une tonne de biocoal. Celui-ci a ensuite été testé avec succès dans un procédé métallurgique de récupération de cuivre en four à Arc Electrique. Enfin, une étude détaillée des mécanismes d'exothermicité et de reprise de feu a permis d'avancer dans la compréhension, et donc la prévention, de ce type d'évènements accidentels fréquents lors de la production et la manutention et le stockage de biocoals, ainsi que de définir des recommandations de sécurité.

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Présentation du projet COCPIT (Horizon Europe, cluster 5) retenu pour financement

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Title: sCalable solutions Optimisation and decision tool Creation for low impact SAF Production chain from a lIpidrich microalgae sTrain

Funding: 5 M€, 11 Partners, 6EU countries, Coordinator: IMT Atlantique/DSEE/GEPEA

Starting date: October 2023, duration 48 Months

COCPIT´s ambition is to enhance the SAF production chain by bringing ground-breaking innovations at each thread of it. It aims also to provide investors with a human centred decision tool in a "test before invest" spirit with a high confidence level to de-risk investments.
A lipid rich microalgae strain is cultivated in an intensified reactor coupled to semi-transparent photovoltaic panels transforming harmful light spectrum into electrical power. The transformation of algal biomass into SAF is studied using two alternative pathways: The most mature one, HEFA, and a very promising one HTL. The project focuses on the circularity, productivity, sustainability and economic viability of the chain. For HEFA pathway, efficient, low impact and regenerable ionic liquids are used to extract lipids and to catalyse hydrotreatment. For HTL pathway, a continuous reactor, tailored to SAF production from the chosen strain is designed and constructed to reduce clogging issues and to size with higher precision the heat exchangers. Furthermore, the mechanistic models that are developed and used in the design increase the scalability of the HTL. Biocrude upgrading is led to give a high flexibility between SAF and shipping fuel production. The system is designed in a circular way to reduce by-products, feed system with endogenous hydrogen, recirculate nutrients and reduce its water intensiveness.
The whole integrated system is simulated with Unism software and all technical, economical, environmental and life cycle indicators are calculated under the COCPIT decision tool and typical scenarios are compiled. The decision tool is delivered within a marketplace that puts at investor's service a range of required technological solutions, equipment and skills. It helps them also to choose the best technology that fits their project specificities. The ambition of this tool is to continue growing up after the end of the project to include all certified and promising SAF production pathways

Coupling HTC and pyrolysis, energy and mass balances

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In this study fir sawdust was selected as a representative lignocellulosic biomass for producing sugar like compounds potentially fermentable trough the combination of HTC and intermediate pyrolysis. Hydrothermal-Carbonization (HTC) was used as pre-treatment and original biomass as well as hydrochars obtained were further pyrolyzed. HTC was performed at two different temperatures (150°C and 200°C) while pyrolysis was performed at 550°C for 15 min in a bench-scale pyrolyze. Aqueous-Phase Liquid (APL) of the obtained bio-oils as well as HTC liquid (HTC-L) were characterized by GC-MS and HPLC-SEC. Energy balance among the entire process was evaluated trough Chemical Oxygen Demand (COD). Moreover, mass balance was performed. HTC of fir sawdust yielded light brown hydrochar and a yellowish liquid (HTC-L). Analysis of HTC-L shows that this process mainly involves hemicellulose fraction with generation of solubilized sugars (mannose, xylose, glucose, etc.), dissolved hemicellulose and organic acids which differ due to the treatment severity. Overall results revealed that combination of HTC-pyrolysis increases mass and COD yield of sugars-like compounds (sugars, and anhydrosugars) and decrease the concentration of high molecular weight compounds in APL fraction.

In-operando image analysis of the fluidization behaviour during biomass pyrolysis

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Biomass auto-thermal pyrolysis is a promising method to overcome heat transfer limitations in pyrolysis reactors, particularly in fluidised beds. However, introducing oxygen into the reactor can cause changes in product composition and alter the fluidisation behaviour. This study examines the influence of oxygen on the oxidative pyrolysis of cellulose and oak wood in a micro-fluidised bed, with a specific focus on the tendency for sand bed agglomeration. To characterise the fluidisation behaviour and agglomeration tendency of the sand bed, in-situ and in-operando image analysis techniques were employed. A high-speed camera behind a quartz window recorded the fluidisation behaviour during pyrolysis. Through analysis of the recordings, key parameters such as bed height, bubble characteristics and surface wave frequency were measured throughout biomass feeding. The results obtained at temperatures of 400 and 500°C under a nitrogen atmosphere revealed that cellulose caused critical compaction of the sand bed, leading to a change in the fluidisation regime. This behaviour was attributed to the agglomeration of the bed with sticky liquid intermediate. However, stable fluidisation was observed when cellulose was subjected to an oxygen atmosphere. The presence of oxygen mitigated the agglomeration by reducing the formation of intermediate liquid.

In the case of oak wood, under a nitrogen atmosphere at 400 and 500°C, the surface wave frequency of the splash zone decreased due to some agglomeration. However, introducing oxygen to the system resulted in a relatively minor improvement in fluidisation stability compared to cellulose. In summary, in-situ and in-operando image analysis using a high-speed camera provided valuable insights into the fluidisation behaviour of a micro-fluidised bed reactor during biomass auto-thermal pyrolysis. The advantage of this approach lies in its ability to capture real-time changes in the bed height and surface bubbling, enabling a better understanding of the effects of oxygen on the fluidisation regime and agglomeration tendencies.

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Biochar characterization by Raman spectroscopy

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Key Words: Biomass, Pyrolysis, Biochar, Soil-amendment.

The contribution of biochars is an opportunity to sequestrate carbon [1] and improve soil fertility [2], without major changes in cultivation practices. The project entitled QUALICHAR funded by ADEME (French Agency of Environment and Energy Management) focuses on the valorisation of selected conventional lignocellulosic biomasses (LBs) (Oak, Douglas, Pectin fir, Beech, Spruce), Crop residue (Corn raids) and unconventional biomasses (UB) (Digestate, Poultry Droppings and Cattle manure) into biochars by pyrolysis in order to assess their agro-environmental as function of their physical and chemical properties. In this study, characterizations of biochar, produced in a tubular furnace under flushing inert gas at two different temperatures (500 and 800°C) for slow (10°C/min) and fast (~1°C/s) pyrolysis are done. Indeed, the fate of organic material (mainly carbon structure) and inorganic material are studied by various characterization techniques (FTIR, Raman, BET surface area, Ultimate and Proximate analysis, Scanning Electron Microscopy - EDX, 13C solid-state NMR, Calorimetry). As an example, Raman spectroscopy results show that temperature influences the nature of carbon structure in biochars. For all the biochars monitored, the D band (Disordered carbon) is more marked when the pyrolysis temperature increases from 500°C to 800°C. The values of the D and G (Graphitic carbon) band intensities have been compared with the paleothermometer [3] which allows to determine the carbonization HTT with a precision of ±20 °C from the heights HD and HG of the D and G bands.

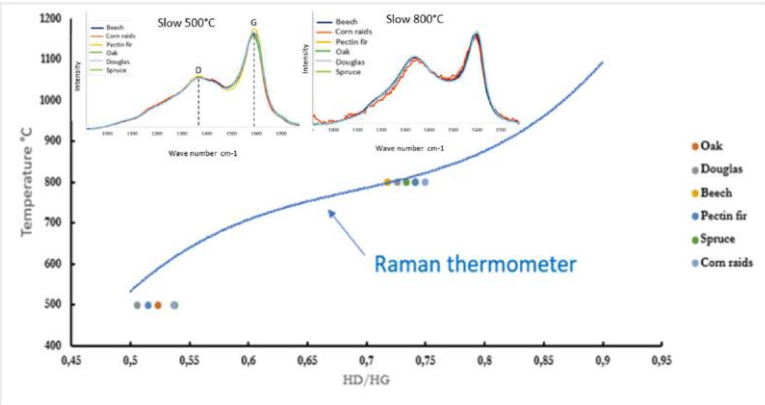

Figure 1. Comparison HD/HG values of different biochars produced by slow pyrolysis with the "Raman thermometer [3] "

Figure 1 shows that intensity ratios of biochars produced by slow and fast pyrolysis are in agreement with the Raman thermometer (H_D/H_G ~0.75 and H_D/H_G~0.5). These intensity ratios seem to not depend on the nature and composition of biochars.

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Methodology to interpret characterization data and construct biochar molecular models

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Establishing a methodology that avoids researcher bias and provides accurate molecular structures of biochar is crucial for interpreting characterization data and the comprehensive study of biochar properties. Such knowledge can aid in enhancing the reactivity and conversion efficiency of biochar in subsequent processes. This work addresses the existing challenges in interpreting biochar characterization data and proposes a novel approach to overcome these limitations. Currently, molecular models rely on subjective and trial-and-error processes, hindering reliable representation of the data. To address these issues, this work presents a high-level modeling approach that employs advanced techniques and computational tools. The proposed methodology offers a robust framework that goes beyond average characterization data and enables the interpretation of biochar structures based on empirical data, capturing their diverse structures, functionalities, and complex behaviors.
Benefits include an improved understanding of biochar molecular structure, enhanced comparability of data, depiction of the inherent nature of biochar, and reduced reliance on distorted interpretations.
This work contributes to biochar research by uncovering intricate details that are vital for further analysis and interpretation.

Gasification of Brazilian Biomass to Obtain Integrative Biorefineries

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Gasification has been a promising strategy for the valorisation of waste biomasses, which produces syngas, an H2-rich mixture that can be used as fuel and chemical platform. Besides that, the produced H2 can play an essential role in the decarbonisation of chemical industries as well as compete with more expensive H2 obtained from electrolysis. In this work, the gasification of agricultural residues, synthesis gas composition, and application in methanol production was evaluated in terms of economic feasibility and uncertainties. To overcome significant supply gaps from harvest seasonality and take advantage of the economy of scale of larger plants, 30 t/h of a mixture of three different wastes is consumed: corn straw, sugarcane bagasse, and soybean straw - the three major agricultural wastes in Brazil. This processing capacity is plausible for construction in any of the top 5 states in agricultural production in the country, where available waste is far beyond than required. The analysis was supported by process simulation in Aspen HYSYS V.12, and the biomass composition model was validated by comparison with experimental HHV, which showed a maximum deviation of 5.97%. The simulated scenarios assumed the use of biomass combinations in different proportions: 100/0/0, 50/50/0, or 33/33/33. The effect of variations in the methanol market price and feedstock cost on process economic performance was evaluated. For the methanol selling price, the scenarios considered 350, 425, or 500 USD/ton. Regarding the feedstock, scenarios with 25%, 50%, and 100% reductions in biomass cost were also studied. The results indicate that with methanol at 350 USD/ton, the proposed renewable methanol plant is not economically feasible. For the scenario with methanol at 425 USD/ton, the soybean bean straw is viable without subsidies. Suppose the methanol price is 500 USD/ton. In that case, all scenarios are feasible without any incentives at feedstock base prices, except if a significant amount of corn straw is availed due to its relatively high price. The results indicate that to create a renewable economy; other players must interfere in the market to make the competition fairer for the renewable source.

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Fonctionnalisation de biomasse lignocellulosique pour la fabrication de bio-liants.

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Plus de 100 000 millions de tonnes par an de bitume sont utilisés dans le monde pour construire des routes. Le remplacement du bitume d'origine pétrolière, représente donc un enjeu considérable. En effet celui-ci, outre les effets néfastes de sa production et de son utilisation sur l'environnement, va venir à manquer en raison de la diminution mondiale de pétrole brut. Il est donc primordial de trouver une alternative au bitume pétrolier. Actuellement, des substituts biosourcés sont utilisés pour remplacer partiellement les bitumes. La lignine par exemple, présente des caractéristiques chimiques qui peuvent se rapprocher des molécules d'asphaltène présentes dans le bitume avec ses cycles aromatiques liés par des chaînes alkyles. Environ 10 à 12 % en masse de lignine peuvent être introduit dans le liant sans modification des propriétés rhéologiques de celui-ci, mais si on augmente le pourcentage de lignine des effets indésirables apparaissent. D'autres alternatives comme les huiles vierges ou usagées sont en cours d'étude mais elles ne permettent pas d'obtenir les mêmes propriétés rhéologiques que le bitume. L'objectif du projet de recherche Post-Oil Pavement (POP) est d'améliorer les propriétés rhéologiques d'huiles alimentaires usagées en les transformant chimiquement et en leur ajoutant de la lignine ou de la cellulose fonctionnalisée. Dans notre équipe, nous réalisons la modification de lignine et de cellulose par estérification ou éthérification en tachant d'utiliser des méthodes catalytiques. La fonctionnalisation de ces biomasses permettrait, en mélange avec des huiles usagées modifiées, d'obtenir des matériaux ayant des propriétés rhéologiques proche de celles du bitume utilisé dans l'industrie.

Optimisation de la Production d'Hydrogène par Gazéification en lit fluidisé dense de la Biomasse

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As part of innovative technology for green hydrogen production from biomass, a multistage approach combining biomass gasification with heat and power cogeneration, and water electrolysis has been proposed. The multistage hydrogen production process will be modelled under the Aspen Plus ® simulator and validated using experimental results. Initially, an oxy-steam gasification of biomass (wood chips; inlet power = 3.8 MW) will be modelled followed by a hydrogen separation step. The retentate gas (CH_4, CO, C2+, and unrecovered H_2 mixtures) will power a gas engine (Jenbacher JMS 320 D47) for heat and power generation. Based on the electrical power generated two scenarios involving the use of 1) a small-size (0.75 MW) and 2) medium-size (2.5MW) proton exchange membranes for extra hydrogen and O_2 production (needed for the process) via the electrolysis of water will be studied. The maximum theoretical yield of hydrogen in the first case scenario is estimated at 40 $gH_2/Kg_{biomass}$ however an additional O_2 stream (240 Kg/h) will be required to complete the oxy-steam gasification process. The second case scenario on the other hand is estimated to produce sufficient O_2 avoiding the use of a vacuum swing adsorption technique. It has an improved H_2 production rate with the maximum theoretical yield reaching 78 $gH_2/Kg_{biomass}$ but an external power source close to 1.7 MW will be needed to meet the electrical requirements. These two scenarios will be compared in terms of economic viability and hydrogen production efficiency. Steam production using heat collected along the process (during the hydrogen-rich gas conditioning) will be evaluated for increased process efficiency. A global overview of the process is illustrated in the graphical abstract below.