

Novel Process to Convert Wet and Dry Organic Feedstocks into 2nd Generation Biofuels: A Scientific Review of the Heat-to-Fuel Project [†]

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Abstract: Heat-to-Fuel is a 48-month research and innovation project, funded under the European Union's Horizon 2020 (EU H2020) Framework Program, which the main objective is to deliver the next generation of biofuel production technologies supporting the decarbonization of the transportation sector by integrating its novel technologies together with innovative activities on design, modeling, development of hardware and processes, testing and life cycle analysis of a fully integrated system. The Heat-to-Fuel concept consists of a biorefinery that combines hydrothermal liquefaction, aqueous phase reforming and Fischer–Tropsch processes to convert wet and solid organic wastes into 2nd generation biofuels with the highest efficiency. Having reached almost 75% of the Heat-to-Fuel project's execution, a review on the main research outcomes and publications derived from the Heat-to-Fuel project activities are presented within this paper.

Keywords: biofuel; decarbonization; transportation sector; biorefinery; Fischer–Tropsch; aqueous phase reforming; hydrothermal liquefaction; gasification; organic feedstocks

1. Introduction

Heat-to-Fuel [1] is a H2020 EU-funded project carried out by 14 partners from across Europe that aims to deliver the next generation of biofuel production technologies supporting the decarbonization of the transportation sector. Heat-to-Fuel will achieve competitive prices for biofuel technologies while delivering higher fuel qualities and significantly reduced green-house gases emissions. The project will also result in increased energy production savings and enhanced EU's energy security by the use of local feedstocks, which in turn ensured local jobs are increased.

The Heat-to-Fuel project [2] will investigate and validate an advanced concept integrating dry and wet biomass residues processing, thus exploiting the huge potential of carbon conversion efficiency improvement arising from this configuration. Dry biomass and organic waste conversion through gasification routes is characterized by large heat excess, which can be exploited by wet biomass and waste conversion routes. On the other hand, wet organic wastes, from hydrothermal liquefaction (HTL) can be conveniently treated with aqueous phase reforming (APR) to produce renewable hydrogen (H₂). The Heat-to-Fuel combines APR with a Fischer–Tropsch (FT) reactor, both promising technologies for the efficient production of 2nd generation biofuels.

Using the synergies between these technologies maximizes the total process efficiency. Thus, Heat-to-Fuel aims will be met due to the diversification of feedstocks available for the production of biofuels, reducing the supply costs and upgrading the conversion efficiencies. At the end of the Heat-

to-Fuel project, the know-how acquired will allow scalability at a demonstration level before commercialization, representative of the next generations of sustainable biofuel technologies.

2. Scientific Review

Reaching the 38th month of project execution, several scientific publications have been released confirming the applicability of the proposed Heat-to-Fuel concept. Those research activities will set the groundwork to demonstrate the approach and to overpass the current state-of-art in the field. As a continuation of the proceedings published in 2019 [3], this paper shows a collection of the key scientific publications derived from the main results achieved so far during the execution of the Horizon 2020 Heat-to-Fuel project.

2.1. Towards the Sustainable H₂ Production by Catalytic Conversion of C-Laden Biorefinery Aqueous Streams

An extensive screening of representative molecules of a post-hydrothermal process side stream has been performed with the aim of producing a gas mixture rich in hydrogen by catalytic APR [4]. The paper enlightens possible routes of valorization of these byproducts, scarcely investigated with other processes so far. The influence of reaction temperature was studied in the 230–270 °C range, looking at both the composition of the gas phase and the characterization of the liquid products. Binary and ternary mixtures of four selected compounds were tested to investigate synergistic and inhibiting effects, going towards the direction of a real biorefinery stream. The alumina-supported catalyst was characterized, outlining possible deactivation mechanisms of the catalytic system, and reused in two successive tests. Due to this work, the Heat-to-Fuel project is contributing to fill a gap in the field of the hydrothermal processes, where there is a lack of information in the study of the C-laden aqueous phases and their valorization.

2.2. Lignocellulosic Ethanol Biorefinery: Valorization of Lignin-Rich Stream through HTL

Hydrothermal liquefaction (HTL) of lignin-rich stream from lignocellulosic ethanol production at an industrial scale was carried out in a custom-made batch test bench [5]. Light and heavy fractions of the HTL biocrude were collected following an ad-hoc developed two-steps solvent extraction method. A full factorial design of experiment was performed, investigating the influence of temperature, time and biomass-to-water mass ratio (B/W) on product yields, biocrude elemental composition, molecular weight and carbon balance. Total biocrude yields ranged from 39.8% to 65.7% w/w. The temperature was the main influencing parameter as regards the distribution between the light and heavy fractions of the produced biocrude: the highest amount of heavy biocrude was recovered at 300 °C, while at 350 and 370 °C the yield of the light fraction increased, reaching 41.7% w/w at 370 °C. Instead, the B/W ratio did not have a significant effect on light and heavy biocrude yields. As proposed in the Heat-to-Fuel project, this research points out the suitability of HTL for the valorization of lignin-rich streams coming from the bioethanol industry.

2.3. CO₂ Gasification in a Dual Fluidized Bed Reactor System: Impact on the Product Gas Composition

The use of CO₂ as gasification agent in the 100 kWth dual fluidized bed (DFB) gasification pilot plant was investigated at TU Wien [6]. For this purpose, steam as a gasification agent was replaced stepwise by CO₂. Softwood was used as fuel and olivine as bed material. Starting from 100 vol.-% steam as gasification agent, substituting it by 32, 45 and finally 68 vol.-% CO₂. Additionally, a CO₂ gasification test campaign was investigated. For this case, the gasification agent was composed of 65 vol.-% CO₂ and 35 vol.-% steam. The use of CO₂ as a gasification agent led to changes of the product gas. Instead of an H₂-enriched product gas, which was produced during steam gasification, CO and CO₂ occupied the major share of the product gas. Consequently, the H₂/CO ratios and the lower heating values decreased when substituting steam by CO₂. Tar contents were lower for CO₂/steam gasification compared to pure steam gasification. In the frame of the Heat-to-Fuel project, encouraging results have been found regarding recycling CO₂ for biomass gasification. This approach

presents a promising concept to produce biofuels in the future, however, further research is required in order to enhance the CO₂ conversion.

2.4. CO₂ Gasification of Biogenic Fuels in a Dual Fluidized Bed Reactor System

In this paper [7], the conversion of different biogenic fuels in combination with the utilization of CO₂ as an alternative gasification agent was investigated in the DFB gasification pilot plant mentioned in the previous paper. Five experimental campaigns were carried out aiming at the investigation of softwood as reference fuel, and rapeseed cake, bark and lignin as alternative fuels. Pure olivine and a mixture (90/10 wt %) of olivine and limestone were used as bed materials. The product gas compositions of the different biogenic fuels changed depending on the elemental composition of the biogenic fuels. Thus, a high amount of carbon in the fuel enhanced CO formation, whereas an increased content of oxygen led to higher CO₂ contents. Additionally, the presence of alkali metals in the biomass ash favored the production of CO. The addition of limestone enhanced the H₂ and CO contents via the water gas shift reaction and steam and dry reforming reactions, but had no significant effect on tar contents. Overall, in line with Heat-to-Fuel research outcomes, this paper presents the feasibility of the DFB gasification process of different biogenic fuels with CO₂.

2.5. Dual Fluidized Bed Steam Gasification: Change of Product Gas Quality along the Reactor Height

In relation to the abovementioned 100 kWth DFB steam gasification pilot plant, this paper investigates the impact of the counter-current column of the gasification reactor on the product gas quality [8]. Through the advanced design of the gasification reactor by operating the lower part as bubbling bed and the upper part as countercurrent column, the gas–solid interactions between downward flowing hot bed material particles with upwards flowing product gas could be enhanced. Thus, the conversion efficiency of the fuel including the tar was improved. For the investigations, three different experimental campaigns converting softwood pellets using different bed materials were conducted. Higher H₂ contents and lower contents of higher hydrocarbons could be detected along the height of the counter-current column. These two effects are explained by enhanced water gas shift and steam reforming reactions. In case of catalytically inactive quartz, only thermal effects are available and therefore lower effects on tar reduction could be obtained. Another important effect was figured out during the investigations: the height of the column. Further research could be carried out in a DFB gasification system with reduced height.

2.6. Dual Fluidized Bed Biomass Gasification: Temperature Variation Using Pure CO₂ as a Gasification Agent

The climate-damaging gas CO₂ is produced as an undesired byproduct in many industrial processes. The DFB biomass gasification technology offers the opportunity to solve this problem by using the produced CO₂ within the process as the gasification agent. Therefore, the 100 kW pilot plant at TU Wien was used to investigate the use of CO₂ as a gasification agent [9]. A temperature variation from 740 to 840 °C was conducted to investigate the change of the main product gas components over the gasification temperature. With increasing temperature, CO and H₂ increased and CO₂ decreased. Additionally, another parameter variation was conducted, where the typically used gasification agent steam was substituted stepwise by CO₂. Thereby, the amount of CO and CO₂ increased and the content of H₂ decreased. These trends resulted in a declining H₂/CO ratio and a decreasing lower heating value when CO₂ was increased as the gasification agent. In conclusion, an advantageous effect of using CO₂ as a gasification or fluidization agent is the possibility to recycle produced CO₂ within the process and therefore reducing CO₂ emissions of the Heat-to-Fuel process.

2.7. Influence of Pressure and CO₂ in Fluidized Bed Gasification of Waste Biomasses

An autothermal fluidized bed reactor was used to carry out research on the influence of pressure on the gasification process of different types of biomasses [10]. The gasified feedstocks were bark, lignin and softwood pellets. The gasification was done with a mixture of O₂/CO₂/H₂O. The impact of

the application of CO₂ on the yield of H₂ in syngas was determined. Resulting high content of CO makes use of the syngas in chemical synthesis applications very difficult without pretreatment. On the other hand, the CO₂ proved to improve carbon conversion efficiency of the gasification and to be an option for its chemical sequestration (negative carbon footprint). Increasing system pressure led to syngas changes, which were seen primarily by higher yields of CH₄ and lower overall production of syngas. For each pressure level and a standard 850 °C gasification temperature, a set of stable gasification parameters were achieved. The conducted experiments show that the concept of chemical sequestration of CO₂ is a technically feasible option in biomass gasification reactors, as proposed in the Heat-to-Fuel project. However, due to the fact that addition of CO₂ into a gasification system changes the usefulness of commonly applied process efficiency indicators it is important to adapt them in a way that would not influence highly their original meaning.

2.8. Aqueous Phase Reforming of the Residual Waters Derived from Lignin-Rich Hydrothermal Liquefaction: Investigation of Representative Organic Compounds and Actual Biorefinery Streams

Secondary streams in biorefineries, such as Heat-to-Fuel, need to be valorized to improve the economic and environmental sustainability of the plants. Representative model compounds of the water fraction from the HTL of biomass were subjected to APR to produce H₂ [11]. The molecules prone to reforming were identified, while the study of a synthetic mixture highlighted competitiveness issues on the active sites. This outcome is crucial for the valorization of secondary streams as they are complex mixtures constituted by several different classes of compounds. Finally, residual water resulting from the HTL of a lignin-rich stream originating from an industrial-scale lignocellulosic ethanol process was tested for the first time. The stability of the catalyst was found to be correlated to the presence of aromatics in the aqueous feedstock. For this reason, the influence of an extraction procedure for the selective removal of these compounds was explored, leading to an improvement in the APR performance. Despite the coupling of HTL and APR needs further investigation, it gives promising results in the direction of decreasing the need of hydrogen for a biorefinery, helping to reduce both the economic and environmental impact of the Heat-to-Fuel process.

2.9. Aqueous Phase Reforming of Sugar-Based Biorefinery Streams: From the Simplicity of Model Compounds to the Complexity of Real Feeds

Glucose, xylose and corresponding sugar alcohols were subjected to APR for the production of H₂ as representative compounds of a stream coming from the hydrolysis treatment of a bioethanol plant [12]. The aim was to explore new valorization pathways for pentoses sugars, currently still not effectively exploited. The influence of the reaction temperature and carbon concentration were investigated in the 230–270 °C and 0.3–1.8 wt % range, respectively, to evaluate their impact on the APR performance. Wheat straw hydrolysate was subjected to the same reaction conditions, and a net hydrogen production was obtained. Deactivation phenomena were investigated during the APR of sugars reusing the catalyst after the reaction. The characterization of the catalysts allowed one to confirm the presence of superficial organic deposits responsible for the lack of the catalyst stability. Further studies on the optimization of the reaction configuration hydrogenation-APR, or on the reaction conditions may allow to make a step forward in the exploitation of the pentoses, helping to satisfy the need of renewable H₂ of a biorefinery.

2.10. Hydrothermal Depolymerization of Biorefinery Lignin-Rich Streams: Influence of Reaction Conditions and Catalytic Additives on the Organic Monomers Yields in Biocrude and the Aqueous Phase

Hydrothermal depolymerization of lignin-rich streams (LRS) from lignocellulosic ethanol was successfully carried out in a lab-scale batch reactors unit, varying parameters such as temperature, time and introducing KOH and supercritical carbon dioxide (sCO₂) as catalysts for process optimization [13]. A partial depolymerization was achieved using subcritical water as a reaction medium. The influence of temperature and time was investigated to identify the optimal condition

on the monomers yields in the lighter biocrude (BC1) and aqueous phase (AP) fractions, focusing on specific phenolic classes and carboxylic acids and alcohols. The effect of base catalyzed reactions was compared to the control tests and to acid-catalyzed reactions obtained with a biphasic medium of $s\text{CO}_2$ and subcritical water. KOH addition resulted in enhanced overall depolymerization without showing a strong influence on the phenolic generation, whereas $s\text{CO}_2$ demonstrated higher phenolic selectivity even though no effect was observed on the overall products mass yields. In conclusion, a comparison between two different biocrude collection procedures was carried out in order to understand how the selected chemical extraction mode in the Heat-to-Fuel process influences the distribution of compounds between BC1 and AP.

2.11. Aqueous Phase Reforming of Pilot-Scale FT Water Effluent for Sustainable H_2 Production

The water fraction produced by Fischer–Tropsch (FT) synthesis, containing light oxygenates, has been investigated for its valorization via APR [14]. The low carbon concentration of the organics makes its thermal recovery unprofitable. In this work, the APR of the wastewater obtained from a 15 kWth FT plant was explored as a promising process to produce H_2 at mild temperatures. The FT product water was subjected to the reforming at different reaction temperatures and time, using a reference platinum-based catalyst. The increase of temperature affected both the activity and the selectivity of the catalyst, increasing the hydrogen production. In order to get more insights into the reaction mechanism and product distribution derived from the APR of FT product water, several tests were performed with single compounds. Representative model compounds have been tested in similar conditions to understand the phenomena involved in the APR of the real mixture. The difference in the product distribution for primary and secondary alcohols reforming pointed out the importance of the position of the hydroxyl group in the molecule and helped to propose a general reaction mechanism for the studied substrates. Moreover, no interference among the substrates was reported despite the mixture being constituted by several molecules: in fact, the results obtained with the real FT product water were analogous to the linear combination of the single compound tests. Finally, the reuse of the catalyst showed no appreciable deactivation phenomena.

2.12. Aqueous Phase Reforming of Lignin-Rich HTL by-Products: A Study on Catalyst Deactivation

The water fraction derived from the HTL of a lignin-rich feedstock was subjected to APR reforming to produce H_2 [15]. Deactivation of the catalyst was observed, and it was ascribed to fouling phenomena caused by phenolic oligomers. Simple aromatics and inorganics were proved not to be the cause of the deactivation. The influence of using activated carbon as a pretreatment was studied, leading to a strong improvement of the performance when it was carried out at high temperature. The extent of deactivation was assessed using APR of glycolic acid as a model reaction test. The results were found to be correlated with the surface area of the catalyst. Thermal regeneration in inert conditions was evaluated as a mode of catalyst regeneration. While the textural properties were partially recovered, the performance of the catalyst only slightly improved. A spectroscopic analysis of the solids in the aqueous solution was carried out, highlighting the structural similarities between their nature and the lignin residue. The results obtained in this research helped to enlarge the knowledge on APR of real complex mixtures, looking at indicators of paramount importance for a possible industrial application such as the stability of the catalyst.

2.13. Design, Commissioning and Start-Up of a New Hydrothermal Liquefaction Continuous Pilot Unit

HTL has been demonstrated to be an effective technology for converting various biomass slurries into valuable biofuels and bioproducts precursors. Many studies have been carried out to understand the conversion process applied on several wet materials. Some examples of continuous systems have been implemented and tested worldwide as the first step for the industrial scale-up of the technology. This work [16] focuses on the development from the design to the start-up and commissioning of a new continuous HTL unit, established in the laboratories of Heat-to-Fuel partner RE-CORD. The plant is capable of converting 1–2 kg/h of slurry at about 10 wt % of biomass to water

ratio. The HTL unit comprises a high-pressure slurry feeder, an indirectly heated plug flow reactor, a cooling system, a pressure let-down system and liquid–gas separator. The reactor can reach and keep the converting material at 350 °C at a pressure of 220 bar for a residence time of 5–24 min. The solid content can be filtered in-line or separated at the end of the process depending on the physical characteristics of the suspended solid residues. Two different depressurizing systems have been designed and implemented in parallel for the continuous discharge of the liquid products, widening the operability of the system to a larger selection of feedstock. The plant commissioning allowed the process analysis in terms of heating, pressurizing and reaction control.

3. Conclusions

The Heat-to-Fuel project has been very active carrying out an intense research activity. This research effort is not only validating the Heat-to-Fuel concept, but also surpassing the current state of the art, while pointing out the pathway to successfully produce a new generation of biofuels. The researching activities are ongoing and new scientific publications will be released before the end of the project in August 2021.

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