

# **ADVANCES IN FOREST FIRE RESEARCH**

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## Clean Forest – Project concept and preliminary results

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### Abstract

The aim of this project is to valorize forest biomass wastes (and then prevent their occurrence as a fuel source in forests) into bioenergy, more precisely, production of 2nd generation synthetic biofuels, such as biogas, biomethanol, bio-DME, etc., depending on the process operating conditions, such as pressure, temperature, and type of solid catalyst used. The valorization of potential forest waste biomass enhances the reduction of the probability of occurrence of forest fires and presents a major value for local communities, especially, in rural populations. Biogas produced can be burned as biofuel to produce heat and/or electricity, for instance, in cogeneration engines applied for domestic/industrial purposes. After the removal of forest wastes from the forest territory, this biomass is dried, grounded to reduce its granulometry, and liquified at temperatures between 100-200 °C. Then, using the electrocracking technology, this liquified biomass is mixed with an alkaline aqueous electrolyte located in an electrolyzer (electrochemical reactor which performs an electrolysis process), using a potential catalyst, in order to produce syngas (fuel gas, mainly composed of CO, H<sub>2</sub>, and CO<sub>2</sub>). In a second reaction step, the syngas produced can be valorized in the production of synthetic biofuels, in a tubular catalytic reactor. The whole process is easy to implement and energetically, shows significative fewer costs than the conventional process of syngas gasification, as the energy input in the conventional pyrolysis/gasification process is higher than 500 °C, with higher pressures, while, in the electrochemical process, applied in this project, the temperatures are not higher than 70 °C, with 4 bars of pressure, at maximum. Besides that, the input of energy necessary to promote the electrolysis process can be achieved with solar energy, using a photovoltaic panel. In the production of biogas in the catalytic reactor, there is another major value from this process, which is the co-production of water, as Sabatier reaction converts CO<sub>2</sub> and H<sub>2</sub> into biomethane (CH<sub>4</sub>) and steam water, at atmospheric pressure, with 300 °C of temperature, maximum, with a high selective solid catalyst. Finally, it is expected to produce a new bio-oil from this kind of biomass, with properties closer to a fossil fuel than wood bio-oils, which can be used as a fuel or as a diolefins/olefins source and, also, to produce, from forest biomass wastes, pyrolytic bio-oils with complementary properties and valorized characteristics. This can be used in the wood treatment or as a phenol source, for several industrial applications. A new and valorized application can be found for forest biomass wastes, which can be incorporated into the biorefinery concept.

### 1. Project background

Over the past years, Portugal has been affected by wildfires resulting in the degradation of natural resources and human life. The increased agriculture and forest lands that are unmanaged are one of the main contributions to wildfires. The present project intends to contribute to the reduction of wildfires by collection and valorization of the forest biomass growing in lands of higher wildfire susceptibility. The first step for biomass valorization passes through a detailed characterization (anatomical, chemical, physical and thermal properties) in order to establish the best platform for their transformation into energy or chemicals. Liquefaction and syngas production are two processes where the biomasses can be transformed into added-value products. Biomass liquefaction is a recent method that converts biomass into bio-oil. In the last years, there was an increase in the number of published works related to this technology (Huang, 2017), in particular, using forest biomasses (e.g. eucalypt, cork residues) (Mateus, 2016). Generally, this process has three main steps: depolymerization, decomposition, and recombination of biomass compounds at higher temperatures. The biomass is decomposed into bio-oil,

solid, and small gas components. The critical process parameters, such as temperature, residence time, repolymerization process, condensation, and compound decomposition of the different phases can change (Gollakota, 2018). The biomass liquefaction was applied first by Mateus et. al. (2016), using cork dust from the cork stoppers rectification process. The dust was dried at 120 °C, and mixed under a glass reactor, with a mixture of organic solvents, and an acid catalyst at 160 °C (90 min). The bio-oil was recovered after a purification process and, the solid waste obtained was dried. Hydrogen can be produced by water electrolysis, an electrochemical process, where it's needed to supply energy, from an electric source, producing also, oxygen, half the quantity of hydrogen (Carmo et al., 2013). It uses electric current through two electrodes: the anode (oxygen production) and the cathode (hydrogen production) (Guerra, 2015).

The natural gas, coal, and biomass can be converted into biofuels and chemical products, like biodiesel by the Fischer-Tropsch process, methanol/DME, hydrogen, and ammonia, all of them used as raw-material, syngas, depending on their quality, operating conditions, etc., through thermochemical processes, like, reforming, pyrolysis, partial oxidation, and gasification. Due to the higher energetic input costs, these processes are only economically feasible at large scales (Venvik, 2017). Besides that, it's possible to produce syngas (CO/CO<sub>2</sub>/H<sub>2</sub>), by water co-electrolysis with a carbon source. Today, syngas is indispensable in the chemical industry, crude oil, and energy industries. It is considered an attractive raw material in the chemical synthesis, as well, as in the production of clean fuels, like biofuels (biogas, methanol, DME) (Nguyen, 2015) (Khodakov, 2007). The main production processes result from the reforming process, especially used in the crude oil and petrochemical industries. The methanation reaction is called the Sabatier process. Recently, the methanation of carbon dioxide gained interest due to its application in the Power-to-Gas technology, as well, as the biogas upgrading, into natural gas. Hydrogen reacts with carbon monoxide and carbon dioxide and they are transformed into methane and, water as co-product. The methanation of carbon monoxide/dioxide is an overall exothermic chemical process (Stangeland et al., 2017).

The GreenSynFuel technology, patented by GSYF, a small Portuguese company that has been working with ISEL and IST-ID partners, with the purpose of producing syngas in only one reaction step, through an innovative electrochemical process of water alkaline electrolysis, using graphite as electrodes and, with electricity supply. The design of the electrolyzer used in this project is a quite differentiating point since the produced gas isn't separated, as there is not a physical separation of the hydrogen and oxygen gases. This electrolyzer presents a significant reduction in costs, from the conventional electrolyzer technology (alkaline, PEM, and SOEC). This process can be used to produce renewable synthetic biofuels, as alternatively to fossil fuels. Biofuels obtained from forest biomass, are considered environmentally friendly and sustainable ones, if the electric source is a renewable one, like solar or wind energy (Guerra et. al, 2015) (Guerra et. al., 2018a) (Guerra et. al., 2018b). GSYF technology belongs to this category. The production and utilization of these biofuels will play an important role in the decarbonization of the energy mix, maximizing the utilization of renewable sources, like the forest biomass, going to meet the Energy Roadmap 2050 objectives of the EU, also defined in the National Script of Low Carbon.

A preliminary step, already performed at ISEL, was the built-up of a lab prototype, to test/validate this technology. Then, it was possible to build a pilot plant of this electrolyzer (with modules of 1 kW power) applied to produce syngas, with posterior production of biomethane and biomethanol, through water electrolysis with steel electrodes and liquified biomass, as the renewable carbon source. The valorization of biogas produced can be used, also, to produce heat/electricity, for the off-grid market, with special emphasis on the rural electrification. After technology validation, it's our purpose to perform the scale-up for modules with more power (megawatts), where the potential clients are the network management of low voltage, storage of renewable electric energy, and production of synthetic fuels. In this project, the main purpose is to produce biogas with this renewable process, valorizing the liquified biomass from the forest wastes, to prevent the probability of occurrence of wildfires.

## **2. Project preliminary results**

### **2.1. Sampling and fractionation**

Residues from *Acacia melanoxylon* were collected with the cooperation of Parques de Sintra - Monte da Lua, in Sintra, Portugal. Three types of residues were collected: i) chips (composed of wood and bark); ii) Crown

residues (composed of branches and leaves); and iii) a Mixture of the first two types of residues (chips and crown residues). The samples were air-dried in the laboratory for 1 month and then milled in a Retsch SM 2000 knife mill, sieved in a Retsch ISO 9001 vibratory screen, and the 40-60 mesh fraction was used for chemical analysis.

## **2.2. Chemical analysis**

Forest residues from *Acacia melanoxylon* (chips – wood and bark; crown residues – leaves and branches; a mixture of both) were collected and characterized by pyrolysis analysis (PY-GC/MS). The extractive-free samples were milled to a fine powder and around 0.10mg pyrolyzed at 550°C for 1 min. The content in carbohydrates ranged from 42.6% (crown) to 52.4% (mixture), while lignin ranged from 19.6% (mixture) and 24.0% (chips). The monomeric lignin composition was similar between the samples, with a predominance of syringyl units (S, 15.2%, 11.1%, and 12.6%), followed by guaiacyl units (G, 7.8%, 7.1%, and 5.5%), and a minor percentage of *p*-hydroxyphenyl units (H, 0.3%, 0.7%, and 0.3%). This agrees with the literature since the *Acacia* species belongs to hardwoods, and in this group, the S and G-units prevail.

## **2.3. Bio-oils production and characterization**

Several materials were used as feedstock for the process, such as heartwood, sapwood, bark, and branches from the burnt remains of a tree caught in the fires in Leiria national park, and pinewood sawdust was used as the standard feedstock material. Besides the shredding of some of the samples, such as the heartwood, sapwood, and bark samples, to increase the contact surface area between the solvent and the feedstock, no further treatments were done to the feedstocks. The standard chemical used as a solvent in the process was 2-Ethylhexanol, but studies were done utilizing pork lard (PL) and glycerol carbonate (GC). Regarding the catalyst, it was used *p*-Toluenesulfonic acid (PTSA) primarily, although some tests were done using sulfuric acid (SA). Also, a liquefaction procedure was tried which consisted of a moderate acid-catalyzed liquefaction process. The liquefaction of lignocellulosic material occurs through a solvolytic reaction under acid catalysts to form smaller fragments, with the further possibility that these fragments continue reacting with either themselves or with the solvent to form higher molecular fragments or solvent-derived compounds. The types of biomass used in the liquefaction processes were tested to find out their water and ash content, and the elemental analysis as well.

The studies performed on the solvent showcased the problem of using either PL or GC as a solvent, with the first producing low conversion rates and the second-highest viscosity products that are difficult to work with at an industrial scale. As for studies done about the catalyst and temperature, the best results using PTSA were produced when it was fed in higher amounts to the reactor, and whilst the SFA showed better conversion yields for reaction temperatures below 170 °C, as the temperature increased the conversion gap between the two catalysts tested decreased. Some of the lignocellulosic samples, heartwood, and sapwood, produced consistently higher conversion yields for the type of feedstock used, showcasing similar behavior. At the same time, the reaction times increased, with the standard pine trailing behind them. As for the bark and branches samples, their conversion rates were mostly lower than those of other samples, similar to the increasing liquefaction time. Some bio-oil samples, produced from heartwood, sapwood, and bark, had their excessive solvent removed and their TAN and OHN calculated through titration, with both of those values following opposite trends to the ones expected by the literary research. The OHN of the samples was also mostly lower than the lowest limit necessary for rigid and semi-rigid polyurethane production. As a whole, the tests conducted showed that the samples from burned wood, especially samples of heartwood and sapwood, can be used in liquefaction processes and produce high conversion yields that originate in final products, such as bio-oils, that have a higher HHV and can be used in several industrial processes as fuels. This indicates that liquefaction is a possible way to somewhat reduce the economic impact felt by landowners who suffered due to the fires that raged through the country last summer and autumn, by using the valueless waste resulting from the burnt wood and creating a value-added product that can be used as fuel.

Also, bio-oil production was performed by the thermochemical liquefaction method. Different species of woody biomass such as burnt pine heartwood, *Acacia Melanoxylon* bark wood; 2-Ethylhexanol was used as a solvent and *p*-Toluenesulfonic acid was used as a catalyst. The procedure consisted of a moderately acid-catalyzed liquefaction process., and it was applied under different conditions in accordance with MODDE 12.1 Pro® software program to obtain the model. After numerous trials, optimal results showed a bio-oil yield of 86.03% at 160 °C for 180 mins of reaction time and by using 5.5% *p*-TSA catalyst concentration overall mass and an HHV of 36.41 MJ/kg, energy densification ratio of 1.96 times greater than the HHV of burnt pine heartwood.

In addition, the liquefaction conversion of the bio-oil from acacia bark wood was 83.29% at 170 °C for 30 mins of reaction time and by using 10% p-TSA catalyst concentration overall mass. A reaction surface methodology (Box-Behnken design) was applied for liquefaction reaction optimization. The obtained model for the liquefaction of Burnt Pine heartwood offers an ideal correlation with the experimental data as  $R^2=0.988$ . The model predicts accurate responses with a probability of 98.8%. Furthermore, the software offers relatively more accurate responses with a probability of 99.8% ( $R^2=0.998$ ). In the proposed model for Burnt pine heartwood, the most effective coefficient was temperature, while the most effective was the catalyst concentration for acacia bark wood. The liquefied products were characterized by Fourier Transformed Infrared (FTIR) and thermogravimetric analysis (TGA); Scanning electron microscopy (SEM) was also performed to confirm the effect of the morphological changes on the surface area of the solid samples.

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### **4. References**

- Carmo, C. (2013). A comprehensive review on PEM water electrolysis. *Journal of Hydrogen Energy*, 8 (12), 4901-4934.
- Gollakota, A.; Kishore, N.; Gu, S. (2018). A review on hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*, 81 (Part 1), 1378-1392.
- Guerra, L.; Gomes, J.; Puna, J.; Rodrigues, J. (2015) Preliminary study of synthesis gas production from water electrolysis, using the ELECTROFUEL concept. *Energy*, 89, 1050-56.
- Guerra, L.; Rossi, S.; Rodrigues, J.; Gomes, J.; Puna, J.; Santos, M. (2018) Methane production by a combined Sabatier reaction/water electrolysis process. *Journal of Environmental Chemical Engineering*, 6, 671-76.
- Guerra, L.; Moura, K.; Rodrigues, J., Gomes, J.; Puna, J.; Santos, T. (2018) Synthesis gas production from water electrolysis using the Electrocracking concept. *Journal of Environmental Chemical Engineering*, 6, 604-09.
- Huang, H.; Yuan, X. (2015). Recent progress in the direct liquefaction of typical biomass. *Progress in Energy and Combustion Science*, 49, 59-80.
- Khodakov, A.; Shu, W.; Fongarland, P. (2017). Advances in the development of novel cobalt Fischer-Tropsch catalysts for synthesis of Long-Chain hydrocarbons and Clean Fuels, *Chemical Reviews*, 7, 1692-1744.
- Mateus, M.; Bordado, J. C.; Santos, R. G. (2016). Potential biofuel from liquefied cork – Higher heating value comparison. *Fuel*, 174, 114-117.
- Stangeland, K.; Kalai, D.; Li, H.; Yu, A. (2017). CO<sub>2</sub> Methanation: The Effect of Catalysts and Reaction Conditions. *Energy Procedia*, 105, 2022-2027.
- Venvik, H.; Yang, J. (2017). Catalysis in microstructured reactors: short review on small-scale syngas production and further conversion into methanol, DME and Fischer-Tropsch products. *Catalysis Today*, 285, 135-146.