






Clean Forest—Project Concept and Early Results

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Abstract: The Clean Forest project aims to valorize forest biomass wastes (and then prevent their occurrence as a fuel source in forests), converting it to bioenergy, such as the production of 2nd generation synthetic biofuels, like bio-methanol, bio-DME, and biogas, depending on the process operating conditions. Valorization of potential forest waste biomass thus enhances the reduction of the probability of occurrence of forest fires and, therefore, presents a major value for local rural communities. The proposed process is easy to implement, and energetically, it shows significantly reduced costs than the conventional process of gasification. Additionally, the input of energy necessary to promote electrolysis can be achieved with solar energy, using photovoltaic panels. This paper refers to the actual progress of the project, as well as the further steps which consist of a set of measures aimed at the minimization of the occurrence of forest fires by the valorization of forest wastes into energy sources.

Keywords: forest waste valorization; generation of synthesis gas; biofuels; biorefinery



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1. Introduction and Background

Over the past years, Portugal, as well as the majority of Mediterranean countries, has been greatly affected by wildfires resulting in the degradation of natural resources and loss of human life [1,2]. The increased agriculture and forest lands that are unmanaged are one of the main contributors to wildfires. Bearing this in mind, a research project, called Clean Forest, was devised to contribute to the solution of this problem.

This project aims to valorize forest biomass wastes (and then prevent their occurrence as a fuel source in forests) by achieving the production of 2nd generation synthetic biofuels, such as bio-methanol, bio-dimethyl ether (bio-DME), and biogas.

Therefore, the present project intends to contribute to the reduction of wildfires by collection and valorisation of the forest biomass growing in lands of higher wildfire susceptibility. The project was partially supported by the Portuguese Fundação da Ciência e Tecnologia, under grant PCIF/GVB/0167/2018. It is coordinated by ISEL, Lisbon Polytechnic, and comprises, as partners, CERENA—Center for Environment and Natural Resources, from the University of Lisbon and the School of Agriculture; also from the University of Lisbon. Being a multidisciplinary approach, the project requires competencies and know-how mainly from the management of forestry resources and chemical and energetic engineering, which justifies the composition of this research partnership. The valorization of potential forest waste biomass results in the reduction of the probability of occurrence of forest fires and presents a major value for local rural communities. This way, forest wastes are collected from the forests, the biomass is dried and then grounded to reduce its granulometry, and, finally, liquified at temperatures between 100–200 °C. Afterwards, using the electrocracking technology, the liquified biomass is now mixed with an alkaline aqueous electrolyte and

fed to an electrolyzer (which is an electrochemical reactor where the electrolysis process takes place) using a specific catalyst, in order to produce syngas (mainly composed of CO, CO₂, and H₂). Further on, the syngas produced can be used for the production of synthetic biofuels in a tubular catalytic reactor. This process is quite easy to implement and shows lower costs than the more conventional process of gasification. Besides that, the energy needed to perform electrolysis can be solar energy, by using a photovoltaic panel. Apart from that, during the production of biogas in the catalytic reactor, another major value of this process is the co-production of water. Additionally, it is expected to produce a new bio-oil from this kind of biomass, with properties similar to a fossil fuel than wood bio-oils, which can be used as fuel or as a source of several hydrocarbons. This can be used in wood treatment or as a phenol source, for several industrial applications. Therefore, this makes that a new and valorised application can be found for forest biomass wastes, which are to be incorporated into the biorefinery concept.

2. Project Clean Forest Scope and Formulation

The first step for biomass valorisation passes through a detailed characterization (anatomical, chemical, physical and thermal properties) 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 recent years, there was an increase in the number of published works related to this technology [3], in particular, using forest biomasses (e.g., eucalyptus; cork residues) [4]. This process proceeds through the following steps: depolymerization, decomposition, and recombination of biomass compounds at high temperatures. Then, biomass is decomposed into bio-oil, solid, and small gas components. The critical process parameters, such as temperature, residence time, re-polymerization process, condensation, and compound decomposition of the different phases can change [5].

The biomass liquefaction was applied first by Mateus et al. [4], using cork dust from the cork stoppers rectification process. The dust was dried at 120 °C, and mixed in 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 is needed to supply energy, or from an electric source, also producing oxygen and half the quantity of hydrogen [6]. It uses an electric current through two electrodes: the anode (oxygen production) and the cathode (hydrogen production) [7].

Natural gas, coal, and biomass can be converted into biofuels and chemical products: biodiesel (by the Fischer-Tropsch process); methanol/dimethyl ether, hydrogen, and ammonia (all of them used as raw-materials); and 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 [6]. Besides that, it is possible to produce syngas (CO/CO₂/H₂), 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 chemical synthesis, and also in the production of clean fuels, such as methanol, dimethyl ether and biogas [8,9]. The main production processes result from the reforming process, especially used in the crude oil and petrochemical industries. The methanation reaction proceeds by the Sabatier process. Recently, the methanation of carbon dioxide gained interest due to its application in Power-to-Gas technology, as a form of biogas upgrading, producing natural gas. Hydrogen reacts with carbon monoxide and carbon dioxide, and they are transformed into methane and, water as a co-product. The methanation of carbon monoxide/dioxide is an overall exothermic chemical process [10].

The GreenSynFuel technology is patented by GSYF, a small Portuguese company that has been working with ISEL and IST-ID partners, to produce 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 differentiating point since the produced gas is not separated, as there is no physical separation of the hydrogen and oxygen gases. This electrolyzer presents a significant reduction in costs from the conventional electrolyzer technology. This process can be used to produce renewable synthetic biofuels as an alternative to fossil fuels. Biofuels obtained from forest biomass are considered environmentally friendly and sustainable if the electric source is a renewable one, like solar or wind energy [7,11–13]. GSYF technology belongs in this category. The production and utilization of these biofuels can play a very important role in the decarbonization of the energy supply, maximizing the utilization of renewable sources (such as forest biomass), meeting the Energy Roadmap 2050 objectives of the EU, also defined in the National Scenarios of Low Carbon. A preliminary step, already performed at ISEL, was the build-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 later production of biomethane and bio-methanol through water electrolysis using steel electrodes and liquified biomass as a renewable source of carbon. The valorisation of the produced biogas can also be used in the production of heat and electricity off-grid with a particular emphasis on rural electrification. After technology validation has been done, it is intended to proceed with the scale-up for modules with more power (in megawatt range), where potential clients are storage of renewable electric energy, the network management of low voltage, and also the production of synthetic fuels. In this project, the main purpose is to produce biogas with this renewable process, valorising the liquified biomass from the forest wastes, to prevent the probability of occurrence of wildfires. Nevertheless, the last tasks of the project comprise a life-cycle analysis (LCA) of the new proposed process, as well as a techno-economic evaluation to be able to assess the economic competitiveness of the proposed approach.

3. Materials and Methods

Up to now, the main executed tasks of the project have been focused on selecting forestry species that are suitable for valorisation for energy production (Section 3.1) as well as its chemical analysis in what is relevant for this process (Section 3.2). Further on, the project progressed through the study and technical definition of the process for the production of bio-oils, comprising its characterization (Section 3.3), and also the optimization of operating parameters for the electrolysis process (Section 3.4). It should be noted that, to our knowledge, this type of multidisciplinary approach has never been tried out to contribute to the reduction of the occurrence of forest fires and/or the management of forest resources.

The project is now progressing to the technical definition of the process for the obtention of synthesis gas, and finally, it will be concerned with the LCA and techno-economic final evaluation.

3.1. Sampling and Fractionation

Residues from *Acacia melanoxylon* were collected with the cooperation of Parques de Sintra/Monte da Lua, located in Sintra, Portugal, as this is an invasive species more abundant in Portuguese forests. 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), which are, in fact, the types of forest wastes more likely to appear in Portuguese forests [1]. The samples were dried in the laboratory for 1 month, then milled in a Retsch SM 2000 mill and finally, sieved in a Retsch ISO 9001 vibratory screen. Only the 40–60 mesh fraction was used for further chemical analysis.

3.2. Chemical Analysis

Forest residues from *Acacia melanoxylon* (chips—wood and bark; crown residues—leaves and branches; and a mixture of both) were collected and characterized by pyrolysis

analysis (PY-GC/MS). The extractive-free samples were milled into a fine powder and pyrolyzed at 550 °C for 1 min according to the literature [14]. The content of carbohydrates ranged from 42.6% (crown) to 52.4% (mixture), while lignin ranged from 19.6% (mixture) to 24.0% (chips). The monomeric lignin composition was similar between the samples, with a predominance of syringyl (S) units (15.2%, 11.1%, and 12.6%), followed by guaiacyl (G) units (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 [3] since the *Acacia* species belongs to hardwoods, and in this group, the S and G-units prevail.

3.3. Bio-Oil 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 in order to increase the contact surface area between the feedstock and the solvent, and no further treatments were applied to the feedstocks. The standard chemical used as a solvent in the process was 2-ethyl hexanol, but studies were done utilizing pork lard (PL) and glycerol carbonate (GC). Regarding the catalyst, it primarily used *p*-toluenesulfonic acid (PTSA), although some tests were done using sulfuric acid (SFA). Additionally, a liquefaction procedure was tried using an acid-catalysed liquefaction process. Liquefaction of lignocellulosic material occurred through a solvolytic reaction in an acid catalyst medium to form smaller fragments, where there is still the further possibility that these fragments continue reacting between themselves or with the solvent in order to originate 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 their elemental composition as well.

3.4. Optimization of Electrolysis Parameters

Electrolysis operating parameters have also been optimised in what concerns maximizing the flow rate of synthesis gas, maintaining at the same time an acceptable composition of the synthesis gas, bearing in mind the subsequent reforming on the tubular catalytic reactor.

4. Preliminary Results

The chemical composition of the residues of *Acacia melanoxylon* is presented in Table 1. The studies performed on the solvent showcased the problem of using either PL (pork lard) or GC (glycerol carbonate) 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 conducted about the catalyst and temperature, the best results using PTSA (*p*-toluenesulfonic acid) were produced when it was fed in higher amounts to the reactor, whilst the SFA (sulfuric acid) 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 behaviour. 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. 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 High Heating Value (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. Additionally, bio-oil production was performed

by the thermochemical liquefaction method. For different species of woody biomass such as burnt pine heartwood and *Acacia Melanoxylon* bark wood, p-toluenesulfonic acid was used as a catalyst, and 2-ethyl hexanol was used as a solvent. This procedure is a moderate acid-catalysed liquefaction process, and it was applied under different conditions with the MODDE 12.1 Pro[®] software program to obtain the model. After numerous trials, the optimised conditions resulted in achieving a bio-oil yield of 86.03% at 160 °C for 180 min 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 min 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 exhibited an ideal correlation with the experimental data as $R^2 = 0.988$. The model accurately predicts responses having 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. Liquefied products were then characterized by Thermogravimetric Analysis (TGA), and by Fourier Transformed Infrared (FTIR). Scanning electron microscopy (SEM) was also performed to confirm the existence of morphological changes on the surface area of the solid samples.

Table 1. Chemical Composition of chips (wood and bark), crown residues (branches and leaves), and a mixture of chips and crown residues of *Acacia melanoxylon* trees. (Average of 3 repetitions per sample).

Component (% of the Initial Mass Fraction)	<i>Acacia melanoxylon</i>		
	Chips	Crown Residues	Mixture
Ash	1.4	3.9	2.4
Extractives	7.3	13.3	10.0
Dichloromethane	0.6	1.8	1.0
Ethanol	4.0	5.8	4.3
Water	2.7	5.7	4.7
Total lignin	25.6	34.1	27.7
Klason lignin	23.2	31.3	24.4
Acid-soluble lignin	2.4	2.8	3.3
Total Polysaccharides	65.1	47.5	58.4
Arabinose	1.2	1.5	1.3
Galactose	1.3	1.1	1.1
Glucose	39.0	28.3	35.9
Mannose	1.0	0.6	0.8
Rhamnose	0.5	0.6	0.6
Xylose	17.3	12.1	14.4
Galacturonic acid	1.1	0.2	0.5
Glucuronic acid	-	-	-
Acetic acid	3.7	3.1	3.8

The higher HHV of the liquefaction products, compared with the original biomass, indicates that the process was useful in producing a lower volume and higher density combustible that can be used in some industrial operations, such as kilns found in cement factories.

Table 2 shows the optimised electrolyser operation parameters, obtained for the 1 kW pilot electrolyser, which resulted in the obtention of a flow rate of 43.6 L/h of synthesis gas with a volumetric composition of: CO: 0.92%; CO₂: 33.3%; H₂: 36.27%; CH₄: 25.51%; and O₂: 4.0%, measured after the catalytic tubular reactor using a HY zeolite as a catalyst as described elsewhere [13]. In this reactor, the conversion was estimated as 44.2% for CO₂ conversion and the selectivity on CH₄ was estimated as 96.5%.

Table 2. Optimised electrolysis operation parameters.

Temperature: 60–80 °C
Electrolyte: NaOH: 0.4–0.5 M
Voltage: 12–15 V
Current: 1.2–1.5 A
Reaction time: >20 min

The Clean Forest project is now progressing to the technical definition of the process for the obtention of synthesis gas, and finally, it will be concerned with the LCA and techno-economic final evaluation. Techno-economic evaluation will be performed by the calculation of the following indicators: (a) Levelized Cost of Energy (LCOE); (b) Levelized Cost of Hydrogen (LCOH); and (c) Energy Return On Investment (EROI), whereas biomass valorization potential will be assessed by estimating the amount of potential use by this technology versus other traditional uses.

5. Conclusions and Further Prospects

Up to now, the tests conducted show 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 products, such as bio-oils, that have a higher HHV and can be used in several industrial processes as fuels.

This is the progress, so far, of the Clean Forest project. Further on, it will continue, after the optimization processes of syngas and biogas production (in terms of composition, flow rate and HHV) executed in previous tasks by an energetic integration for all the processes, using specific software tools such as HYSYS to modulate the process. Additionally, in this task, another purpose is to perform an economic analysis of the cost–benefit of the overall process and compare it with the conventional thermochemical processes, which are very expensive ones, and to perform a life cycle assessment (LCA) analysis, using specific software. Another purpose of this task is to perform an environmental analysis of impacts, identifying the major environmental impacts, both negative and positive, and compare them with the conventional thermochemical processes of reforming, pyrolysis, and gasification, thus highlighting the major importance of using a renewable energy source such as solar energy and lignocellulosic biomass collected from the recovery and cleaning of the forest solid wastes from the forest territory to prevent and avoid the probability of occurrence of major fires and the potentialities of local economies for this strategy.

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