BIO-BASED PRODUCTS FROM WOODY BIOMASS PYROLYSIS FOR A SUSTAINABLE BIOECONOMY

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ABSTRACT: This paper presents a pyrolysis biorefinery concept in which energy and bio-based products are generated from the pyrolysis of forest residues. Pyrolysis experiments were carried out with woody biomass using an auger reactor to better understand the impact of the pyrolysis operational parameters on the properties of the co-products. The response surface methodology (RSM) approach was used to set an experimental design, aiming at optimizing pyrolysis parameters (temperature, solid residence time and nitrogen flow rate) to produce high yield of bio-oil with the lowest water content possible. Further pyrolysis tests were carried out to study the fractional condensation of bio-oil into two phases: a heavy phase with a high-energy content (bio-crude oil) and a light phase containing phenol compounds and acetic acid, called wood vinegar. The fungicide potential of the wood vinegar was evaluated in laboratory. Based on the experimental results, a biorefinery scenario was established towards a future endeavor of modelling the role of pyrolysis within the French bioeconomy. The starting point is 1000 kg dry matter (DM) of soft wood forest residues, which are harvested, chipped, stored, grinded, dried and pyrolysed. In this scenario, the bio-crude oil and non-condensed syngas are used to substitute heat, wood vinegar is used as a bio-fungicide, and biochar is used as a soil amendment. This work will allow studying the environmental consequences of this concept through a life cycle assessment.

Keywords: Pyrolysis, Forest residues, Biorefinery, Bioenergy, Bio-based products, Pesticides

1 INTRODUCTION

Pyrolysis biorefineries for the conversion of residual biomass into a variety of high quality bio-based products can be a solution towards a sustainable bioeconomy [1]. However, the environmental performance of pyrolysis is variable as product yields and properties are influenced by the characteristics of both biomass feedstock and pyrolysis operational parameters. Pyrolysis, which is the thermochemical conversion of biomass at elevated temperature (350-700°C) in limited-oxygen environment, produces a solid biochar, a liquid bio-oil and uncondensed gases. Biochars with high porosity and high nutrients content can be used for soil amendment and serve as a so-called carbon dioxide (CO_2) removal (CDR) technique [2]. Studies reported that biochars with ratios $O/C_{org} < 0.2$ [3] and $H/C_{org} < 0.6$ [4] have high potential for C sequestration. Moreover, biochars with a low N content, and consequently high C/N ratio (> 30), can reduce soil N_2O emissions under specific conditions [5]. Bio-oil contains a multitude of compounds, such as sugars, terpenoids, phenols and acids, conferring interesting properties for different applications [1]. For example, it can be used directly as a low-grade fuel to substitute fossil oil in furnaces. It can also be fractioned into a high-energy and low water contents heavy phase containing the heavy organics that can be called bio-crude oil, and a light phase having a high water content (WC), also referred to as wood vinegar. The first phase can be used to substitute fossil fuels and the latter can be valorized into a variety of bio-based products. Finally, non-condensable syngas can be used in a gas burner to produce heat.

There are 3 075 kt DM of soft wood primary forest residues available per year in France. At least, 1 113 kt DM of these residues could be harvested without causing soil depletion, which is called the technical and economical availability [6]. Currently, most of forest residues are left on forest soils, which can facilitate the passage of machinery. Sometimes, forest residues have to be burned to reduce fire hazard [7]. Many studies concluded that the valorisation of forest-based biomass for bioenergy production has a lower GHG impact than fossil energy systems [7]. However, environmental benefits in other impact categories (e.g. ecotoxicity and human health) can be compromised.

This study focuses on the valorization of primary forest residues by pyrolysis. Products yield and properties are influenced by both the characteristics of biomass feedstock and the pyrolysis operational parameters. Therefore, the objectives are: (i) to better understand the impact of the pyrolysis operational parameters on the properties of the pyrolysis products and (ii) to establish the mass and energy balance for a realistic scenario in which all bio-based products from pyrolysis are valorized in the relevant markets. This work will later feed a life cycle assessment (LCA) to evaluate the role of this technology within the future French bioeconomy.

2 IMPACT OF PYROLYSIS OPERATIONAL PARAMETERS ON CO-PRODUCTS YIELDS AND PROPERTIES

2.1 Methodology
2.1.1 Overview

Pyrolysis experiments with specific objectives were recently carried out at the Research and Development Institute for the Agri-Environment (Quebec City, Canada). A pilot-scale auger reactor (Patent US 9,486,774 B2; Figure 1) was used for the pyrolysis experiments. Woody biomasses grinded and sieved to keep particle size between 1 to 3.8 mm were selected as feedstock. The first experiment (section 2.1.2) was carried out to optimize the production of bio-oil with the lowest water content possible. In the second experiment (section 2.2.2), the fractional condensation was studied to produce a bio-crude oil and a wood vinegar for evaluation of the antifungal effect of the latter. Further pyrolysis experiments are underway to produce a bio-crude oil with reduced water content. All experiments are independent, as the biomasses used and the pyrolysis operational parameters are not exactly the same. These experiments allowed a better understanding of the impact of pyrolysis operational parameters on yields and properties of co-products. Moreover, results were used as indicative for the establishment of a realistic pyrolysis scenario.

2.1.2 Optimization of bio-oil production without fractional condensation

A mixture of Black Spruce (*Picea mariana*) and Jack Pine (*Pinus banksiana*) was used for this experiment. Bio-oil was obtained by the condensation of pyrolysis gas using a double shell condenser in which tap water at room temperature circulated counter flow. Fifteen pyrolysis experiments were carried out based on the Box-Behnken design [8]. The evaluated independent variables were temperature (500, 575 and 650 °C), biomass residence time in the reactor (60, 90 and 120 s) and nitrogen (N_2) flow rate (1, 3 and 5 L min^{-1}). Products yields were calculated after each run and the water content (Karl-Fisher method) and pH of bio-oil were analysed in laboratory. Response surface methodology (RSM) was used to determine the optimal pyrolysis parameters to produce bio-oil with the lowest water content possible, as well as biochar and syngas as co-products. Syngas was sampled using Tedlar® bags and characterized by gas chromatography for CO, CO_2, CH_4, C_2H_4 and C_2H_6 contents. The volumetric concentration (%vol.) of these components in the syngas was estimated as accounting for 100%, despite the H_2 %vol. was not measured in these experiments [9].

2.1.3 Fractional condensation for bio-crude oil and wood vinegar production and evaluation

This pyrolysis experiment was carried out with grinded wood bark. Thermogravimetric analysis allowed the selection of the pyrolysis temperature of 600 °C for this biomass. The biomass residence time and N_2 flow rate were set at 90 s and 3 L min^{-1}, respectively. The temperatures of the first and second condensers were set at 90 °C and 4 °C, respectively, in order to produce bio-crude oil and wood vinegar (Figure 2).

The water content of both bio-oil fractions was analyzed in laboratory using the Karl-Fisher method. The wood vinegar was analyzed for its acetic acid content by

gas chromatography – mass spectrometry (GC-MS), its polyphenol content was analyzed using the Folin-Ciocalteu method [10] and the carbohydrates were quantified using a colorimetric method.

The fungicidal effect of the wood vinegar was evaluated in laboratory using the simplified AOAC 955.17 method – Fungicidal activity of disinfectants. Accordingly, solutions of wood vinegar diluted in water (acetic acid concentration in the range of 0.4 – 1 %) with suspension of fungi were evaluated. The fungicidal effect on fungi causing disease, particularly in potato crops, was observed by the color of the solution after 10 min.
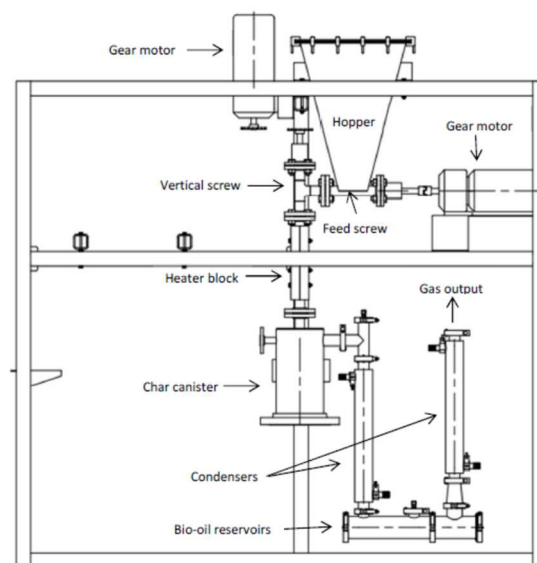

Figure 1: Schematic view of the vertical auger pyrolysis reactor [8].

2.2 Results
2.2.1 Optimization of bio-oil production without fractional condensation

Water content was selected as the indicator of bio-oil quality. Results from the 15 experimental runs demonstrated that water content of bio-oil ranged from 32.0 to 43.0 wt% and was generally lower at lower temperatures and residence times. The total yield of bio-oil varied from 48.6 to 63.6 wt% and was lower as the temperature and residence time decreased. Biochar yield decreased with an increase of temperature and residence time and consequently, syngas yield increased. Based on the statistical analysis, the optimal pyrolysis parameters were as follows: temperature of 559 °C, biomass residence time of 61 s and N_2 flow rate of 3 L min^{-1}.

The quadratic response surface regression model was validated with the pyrolysis operational parameters expected to produce the bio-oil with the best potential to be used as a fuel. Two validation runs were carried out and the water and energy contains of the obtained bio-oil were analyzed (Table 1). On average, bio-oil yield was 58.3%. The water content and higher heating value (HHV) of this bio-oil were 31.9% and 13.8 MJ/kg. These values are still slightly below the standard specifications for pyrolysis liquid biofuel ASTM D7544 [11] in which maximum water content of 30% and minimum HHV of 15 MJ/kg are specified. This highlights the need to continue research for

reducing water content of bio-crude oil by fractional condensation.

Figure 2: Wood vinegar (left) and bio-crude oil (right)

2.2.2 Fractional condensation for bio-crude oil and wood vinegar production and evaluation

The yields of wood vinegar and bio-crude oil obtained from the pyrolysis experiment were 13.0 and 23.0 wt%, respectively (Table 1). The wood vinegar had a water content of 76.2 wt%, a phenolic compounds content of 3.7%, an acetic acid content of 17.6 wt% and a pH of 2.6. The bio-crude oil had a water content of 33.0 wt% and an acetic acid content of 5.9 wt%.

For the evaluation of fungicidal activity, a growth inhibition of fungi was observed, as the color of the inoculated solution containing wood vinegar was transparent (after 10 min) as compared to the control treatments, free of wood vinegar. An example of the experiment for visual evaluation of fungicidal effect is showed on Figure 3.
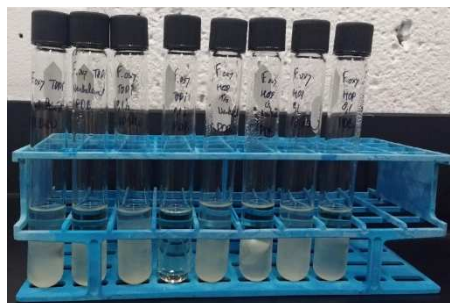

Figure 3: Visual evaluation of fungicidal effect of wood vinegar. The fourth treatment has a fungicidal effect.

2.3 Discussion and ongoing work

The summary of pyrolysis experimental parameters as well as the yields and properties of co-products are presented in Table 1. Predictive RSM models showed that high yields of bio-oil (58.3%) can be obtained if proper pyrolysis parameters are selected, but with a relatively high water content (31.9%).

Fractional condensation with higher pyrolysis temperature and longer biomass residence time allowed producing a wood vinegar with water content as high as 76.2 wt% and a bio-crude oil with water content of 33.0 % (section 2.2.2). The total bio-oil yield was 36.0 wt%, which is slightly above half of the yield obtained when the bio-oil is not separated into two phases (section 2.2.1). This lower yield is probably due to higher temperature and residence time, resulting in higher syngas yield. It may also be due to the higher ash content of the feedstock.

As the water content of the obtained bio-crude oil was still high, further pyrolysis experiments of Black Spruce studying fractional condensation are underway (still unpublished). This work allowed to produce bio-crude oil with water and energy contents of 18.8 wt% and 18.3 MJ kg^{-1}, respectively, as well as a wood vinegar.

Table 1: Summary of experimental data – Main results

	2.2.1 [1]	2.2.2 [2]
	Spruce / Pine	Wood bark
Optimal pyrolysis parameters		
Temperature (°C)	559	600
Residence Time (s)	61	90
N$_2$ flow rate (L min^{-1})	3	3
1st condenser Temperature (°C)	21	90
Resulting products yields		
Bio-oil (wt%)	58.3	36.0
Wood vinegar (wt%)	-	13.0
Bio-crude oil (wt%)	-	23.0
Biochar (wt%)	26.6	25.0
Syngas (wt%)	15.2	39.0
Water content of the resulting bio-oil		
Total (wt%)	31.9	-
Wood vinegar (wt%)	-	76.2
Bio-crude oil (wt%)	-	33.0

[1]Optimisation of bio-oil production (average of two validation runs); [2]Wood vinegar and bio-crude oil production (single experiment).

3 ESTABLISHMENT OF THE PYROLYSIS BIOREFINERY SCENARIO

3.1 Biomass supply chain

A pyrolysis biorefinery scenario for the valorisation of primary forest residues was established (Figure 3). The selected feedstock can be defined as the by-products of wood harvesting, which generally include treetops and small branches of less than 7 cm (stumps are excluded). The feedstock supply chain includes passive drying in forest, piling by the roadside, chipping, transport to a biomass depot for mixing, grinding (< 4 mm) and drying at 10 wt% water content.

It is assumed, based on the study by Routa et al. [12], that logging residues are left on soil for passive drying during at least a six-weeks period. Thereafter, residues are harvested with a forwarder and transported to the roadside where they are properly piled to prevent re-moistening. Based on data compilation from a literature review, the water content of the harvested biomass that was passively dried in dry weather conditions is set at 29.9 wt.%. In these drying conditions, dry matter losses are expected to be negligible [12]. Chipping is performed directly in the forest using a mobile chipper, which is a typical operation of wood harvesting activities [7]. This allows an increase of the bulk density of feedstock, which facilitate the transport to the biomass depot where it is stored for about six weeks. The maximum moisture content for storage stability of woodchips is, according to literature, between 15 and 30 % [13]. Drying in forest to fewer than 30 % water content prior to chipping and storage therefore allows stable storage conditions with few loss of dry matter. As reported by Eriksson [14], the accumulated dry

matter losses after six weeks of storage of waste wood chips was 2.0 wt%, which was selected in the present study.

Biomass with 29.9 % water content is then grinded to particle size of less than 4 mm using a hammer mill. This is in accordance with the experiments that were done with wood particle size between 1 and 3.8 mm. Moreover, most of the published data recommend a range of particle size of 1-2 mm for pyrolysis [15]. Finally, biomass is dried with a large rotary dryer to 10 % water content, which is needed in order to minimise the water in the pyrolysis bio-oil [14; 15].

A mass balance was established considering the pyrolysis of 1082 kg of biomass entering the process, which corresponds to the harvest of 1000 kg DM of primary forest residues (Table 2).

Table 2: Mass balance (in kg) of forest residues harvesting and conditioning prior to pyrolysis

	Harvested biomass	Stored biomass	Grinded biomass	Dried biomass
Total mass	1427	1411	1397	1082
Water content	427.0	427.4	423.1	108.2
Dry matter	1000	984.0	974.2	974.2
Volatile matter	800.3	784.3	776.5	776.5
Fixed carbon	186.9	186.9	185.0	185.0
Carbon (C)	513.7	507.1	502.1	502.1
Oxygen (O)	406.6	398.4	394.4	394.4
Hydrogen (H)	59.5	58.3	57.8	57.8
Nitrogen (N)	4.4	4.3	4.3	4.3
Sulfur (S)	24.1	23.6	23.4	23.4
Ashes	14.6	14.6	14.5	14.5

The number of digits in this table is not an expression of the uncertainty, but is only included as the values are the foundation for further calculations.

3.2 Pyrolysis

A pyrolysis scenario in which all co-products are valorized was established (Table 3). The pyrolysis operating parameters are the same than those used in the experiment for optimization of bio-oil production (section 2.2.1), except the temperature of the first condenser, which is set according to the fractional condensation experiments (section 2.2.2).

The main hypothesis for the estimation of pyrolysis products yields and properties is that total bio-oil, biochar and syngas yields are those from the bio-oil yield optimization experiment (section 2.2.1). The bio-oil is then fractioned efficiently into a heavy phase (bio-crude oil with water content of 18.8 % and HHV of 18.3 MJ kg^{-1}, and a light phase (wood vinegar), as reported in section 2.2.3. With these parameters selected for the pyrolysis scenario, the yield of the bio-crude oil and the yield and water content of the wood vinegar were calculated consequently by iteration (Table 3). This resulted to a bio-crude oil yield of 36.1 wt% (18.8 % water content) and a wood vinegar yield of 22.2 wt% (53.1 % water content), which is slightly differing from what was obtained in the experiments; Table 1).

The concentrations of acetic acid, phenolic compounds and total sugars in wood vinegar were calculated based on the characterization of both phases of bio-oil in the fractional condensation experiment (section 2.2.2). Based on these results, it is assumed that the concentration of acetic acid and total sugars is proportional to the water content of the wood vinegar. Therefore, the calculated concentration of acetic acid and total sugars in the wood vinegar is 11.4 and 5.7 wt%, respectively. On the other hand, results showed that the concentration of phenolic compounds is generally higher as the water content decreases. Consequently, the calculated phenolic compounds content of the wood vinegar in the scenario was 8.2 wt%. The addition of all measured components of wood vinegar results to 78.4 wt%, as the quantitative analysis did not include all chemical compounds (e.g. furan derivatives and ketones).

The biochar characterization comes from the bio-oil optimisation experiment [8], but was adjusted for ash content based on the mass balance of the studied scenario. The lower heating value of syngas was calculated as reported by [18] based on the molar concentration of CO, CO_2, CH_4, C_2H_4 and C_2H_6 in the syngas of two experiments.

Table 3: Pyrolysis scenario – Products yields and properties

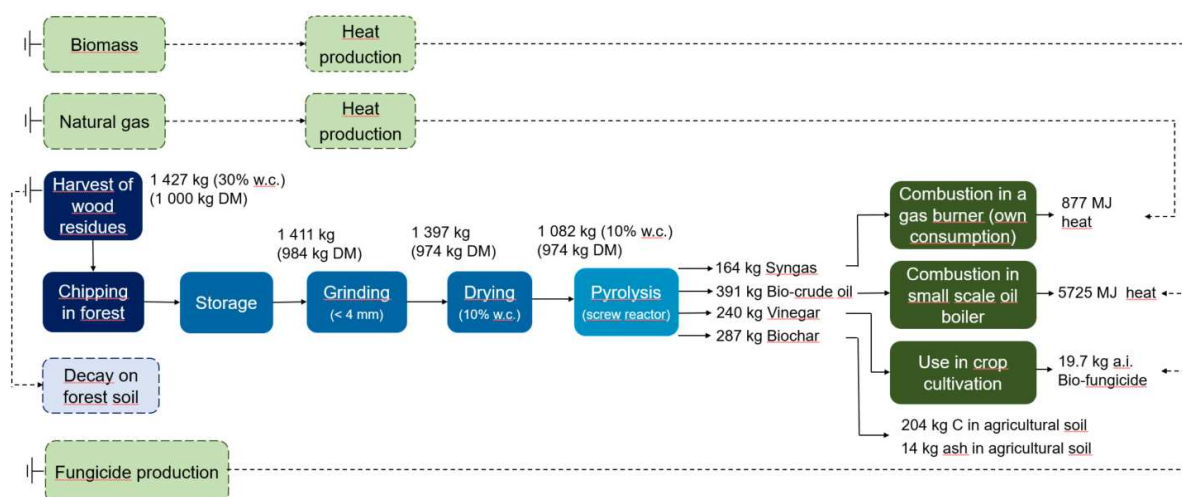| Pyrolysis parameters	Unit	Value
Temperature	°C	559
Biomass residence time	s	61
N_2 flow rate	L min^{-1}	3
Condensation temp. (T1)	°C	120
Condensation temp. (T2)	°C	4
Products yields		
Bio-oil	wt%	58.3
Wood vinegar	wt%	22.2
Bio-crude oil	wt%	36.1
Syngas	wt%	15.1
Biochar	wt%	26.6
Products properties		
Wood vinegar		
Water content	wt%	53.1
Phenolic compounds	wt%	8.2
Acetic acid	wt%	11.4
Total sugars	wt%	5.7
pH		2.59
Bio-crude oil		
Water content	wt%	18.8
Higher heating value	MJ kg^{-1}	18.3
Syngas		
CO	%vol.	45.6
CO_2	%vol.	45.2
CH_4	%vol.	7.74
C_2H_4	%vol.	0.62
C_2H_6	%vol.	0.78
Lower heating value	MJ kg^{-1}	6.59
Biochar		
Carbon	% (d.b.)	71.1
Nitrogen	% (d.b.)	0.143
Hydrogen	% (d.b.)	4.29
Oxygen	% (d.b.)	19.53
Ashes	% (d.b.)	5.02

All wt% are on wet basis.

Figure 4: Process flow diagram

3.3 Valorization of pyrolysis co-products: building the scenario for an ongoing consequential LCA

The quantity of each pyrolysis co-products in the pyrolysis biorefinery scenario illustrated on the process flow diagram (Figure 4) was calculated based on their yields for the pyrolysis of 1082 kg biomass at 10 % water content, as reported in Table 2. In this scenario, 391 kg of bio-crude oil (18.3 MJ kg^{-1}) is produced. The vision is to use this high-energy content bio-oil in small-scale oil boilers in areas without access to the gas grid. In the short-term, bio-crude oil would likely substitute fossil fuel oil, while in the longer-term, it may rather prevent the deployment of biomass boilers or even electric boilers and heat pumps [19]. As the results of the LCA to be performed are intended for strategic investment decisions, it is the longer-term that is considered herein, where the heat produced by bio-oil burning (5725 MJ, which considers 80% conversion efficiency for the oil burner) would replace the equivalent quantity of heat provided by biomass combustion.

Similarly, syngas is envisioned to be used in a gas burner for own consumption of the pyrolysis plant. A total of 877 MJ of heat is produced considering 75% conversion efficiency from syngas to heat [20], and this would replace the heat that would have been used by the plant otherwise (taken as stemming from a <100 kW natural gas boiler).

Some studies reported that phenolic compounds in the wood vinegar have an antifungal potential [19, 20, 21, 22, 23]. These phenolic compounds are produced from the pyrolytic decomposition of lignin [26]. Therefore, the hypothesis of this scenario is that the production of 240 kg of wood vinegar is used as bio-fungicide for agricultural crops. Considering the concentration of phenolic compounds as the active ingredient, 19.7 kg of chemical active ingredients would be substituted. Based on a typical application rate of 0.29 kg a.i. ha^{-1} for a potatoes crop, 67 ha of agricultural soil would be covered for one application.

Finally, the production of 287 kg of biochar is left for use as a soil amendment, adding 204.4 kg of C and 14.4 kg of ashes in agricultural soils, among others. Considering an application rate of 24 Mg ha^{-1} [27], the produced biochar would be applied on a surface area of 119.6 m^2. Biochar produced from wood pyrolysis showed a high potential for C sequestration when pyrolysis operating parameters are properly selected [28]. Therefore, most of this C could be sequestered in soil for more than 100 years. Moreover, as biochar C/N ratio is higher than 30, it could contribute to the reduction of soil GHG emissions [5], but not necessarily under all soil and climate conditions. Alternatives uses of biochar include activation to increase its surface area for use as an adsorbent in waste water treatment plant.

4 CONCLUSION

Results of the experiments presented in this paper show that pyrolysis is a flexible technology for the valorisation of woody biomass, allowing to produce bio-crude oil, wood vinegar, biochar and syngas by selecting the appropriate pyrolysis and condensation operational parameters. A biorefinery scenario in which all the co-products are used in the relevant market was established. The scenario involves the harvest of 1000 kg (DM) of forest residues, which are thereafter conditioned and pyrolysed. In this scenario, 391 kg of bio-crude oil is produced to substitute 5725 MJ of heat from biomass combustion in remote areas without access to the gas grid and 164 kg of syngas is produced to substitute 877 MJ of heat from natural gas. The production of 240 kg of wood vinegar can substitute 19.7 kg of fungicide active ingredient, and 287 kg of biochar can be added to soil, corresponding to 204 kg of C and 14 kg of ashes.

The results of this study, which will be supplemented by a literature review, will be used to feed a first iteration of a LCA model, allowing to quantify the environmental performance of the studied valorisation pathways. The fate the woody biomass would have had, if not used as an input for pyrolysis (so-called counterfactual), will also be considered. This will be spatially investigated for France, the geographical scope of interest for the LCA to be performed [6].

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5   ACKNOWLEDGMENTS

5   LOGOS

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