HYDROTHERMAL LIQUEFACTION PROCESS OF FOOD WASTE IN BATCH AND CONTINUOUS LAB SCALE REACTORS

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Key Words: Hydrothermal liquefaction, food waste, continuous reactor, key parameters

Due to the energy burden that represents the drying step, wet biomass is often underexploited for energy purpose. Indeed, this step represents one of the most energy consuming step in a thermochemical process and is often economically prohibitive. During hydrothermal liquefaction, conversion of biomass takes place at temperatures between 250 and 374 °C and at pressures above the saturation pressure to ensure that water remains in the liquid phase, typically above 100 bars, avoiding enthalpy energy penalties [1]. To avoid competitive use of land for food supply and excessive cost of entrance biomass, blackcurrant pomace and brewery's spent grains have been selected and tested on liquefaction as food residues. Experiments have been carried out in a 600 mL batch reactor (PARR), allowing maximum temperature of 320°C and maximum pressure of 130 bars. Effects of operating parameters such as temperature and holding time, biomass pretreatment and reactor configuration are investigated on mass yields, aqueous phase composition and energy balance. Results obtained in the batch reactor constitute the reference of this study, in the comprehension of the mechanism of the liquefaction of food residues. Also, these results form the basis for a model to scale up the process, and are confronted to the results on a continuous lab scale plant.

Yield of hydrothermal liquefaction of raw blackcurrant pomace was reported by Déniel et al.[2]. In comparison, experimental results show that grinding improves the bio oil yield, compared to liquefaction of raw biomass. Temperature strongly influences mass yields, especially above 15 minutes holding time. This underlines the combined effect of temperature and holding time (Figure 1).

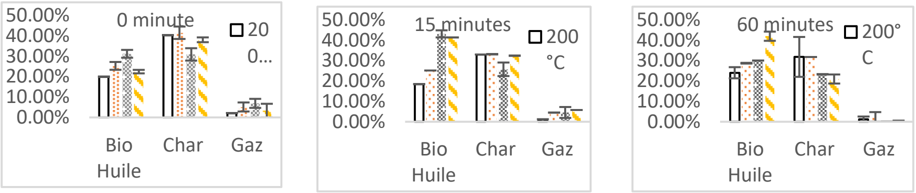

Figure 1 : Evolution of the products yields from the liquefaction of blackcurrant pomace with temperature and holding time

Further experiments were carried out in a continuous lab scale plant with a capacity of 2 kg/h, to understand the role of the reactor configuration in the liquefaction mechanism. The injection system and heating rate are main parameters likely to explain the much of the differences observed. Results on the first experiment in the continuous pilot plant will be presented here on ground black currant pomace.

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AGRICULTURE WASTE, A GREAT OPPORTUNITY TO PRODUCE ENERGY AND HIGH VALUE PRODUCTS: EXPERIENCE IN COLOMBIA

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Key Words: Fast pyrolysis, bio-products, characterization, process yield.

Colombia has high potential from various sources such as fast growing plantations, municipal waste, and sludge from wastewater treatment plants, forest residues and agricultural harvesting. Those sources are considered biofuels of the second generation, which can contribute significantly to the replacement of the currently used fossil energy carriers for transportation fuel production and they can be precursors of new products with high-added value. In this work we show different experiences carrying out in Colombia related to thermochemical process to produce Bio-oil, Bio-char and Syngas. We show the results of our experience in slow and fast pyrolysis consisting of thermal decomposition of the lignocellulosic material in an inert atmosphere or with oxygen shortage (less than stoichiometric), at temperatures between 500 °C - 600 °C, with particle sizes between 0.5mm - 2mm, with the aim of producing a liquid fuel with a high oxygen content, called bio-oil, a solid residue ''bio-carbon'' or char and non-condensable gases with low calorific value (rich in CO, CO_2 CH_4, H_2) which they can be re-circulated in the reactor to supply heating power. Depending on the operating conditions of the reactor, pyrolysis can be classified as: slow pyrolysis and fast pyrolysis (see Figure 1).

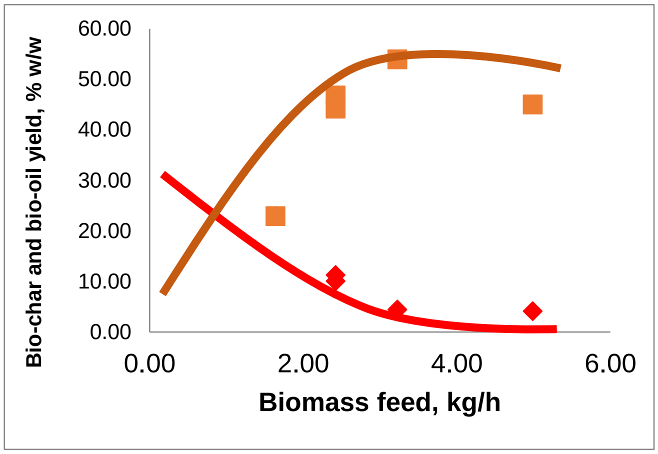

Figure 2 – Bio-oil (diamond) decrease as biomass feed increase; contrary, Bio-char (square) increase as biomass increase.

The development of biofuels derived from thermochemical processes from biomass has grown in recent years as a promising alternative in mild and long term to supply partially rising energy consumption. Thermochemical conversion processes use mostly agro-industrial wastes as main source of raw materials, so they do not threaten food security, not required complex pre-treatments and reaction times are short; which are striking advantages over biological transformation processes for the same proposes.

TWO STEPS UPGRADING OF BEECH WOOD FAST PYROLYSIS BIO-OIL WITH NICKEL-BASED CATALYSTS

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Key Words: hydrotreatment, pyrolysis oil, hydrodeoxygenation, nickel catalyst

Upgrading of fast pyrolysis bio-oil through catalyst hydrotreatment has been suggested as a complementary step to produce oil with improved properties. The upgrading reduces the oxygen and water concentration at the same time that allows the carbon recovery in the bio-oil. Reactive compounds are stabilized and organic acids are mostly concentrated in the aqueous phase formed after the reaction. Due to the high activity and low cost, nickel-based catalysts are promising for production of upgraded oils. Although almost half of the oxygen is removed with a single step upgrading, deeper hydrodeoxygenation is required in order to obtain organic liquids miscible with petroleum-derived products. It can be achieved by sequential hydrotreatment with specific catalysts in each of the steps. Hence, in the present work a beech wood fast pyrolysis bio-oil was upgraded in two steps applying two nickel-based catalysts. A catalyst with higher hydrodeoxygenation activity (Ni/SiO_2, 7.9 wt.%) was used in the first step, whereas a catalyst with higher hydrogenation activity ($Ni-Cr/SiO_2$, 30 wt.% metallic nickel, 26 wt.% NiO, 15 wt.% of Cr_2O_3 and 1.5 wt.% of graphite in diatomaceous earth support 27 wt.%) was employed in the second step. The reactions were conducted in a batch autoclave at 325 ºC and 80 bar of H_2. The bio-oil initially hydrotreated with a Ni/SiO_2 catalyst prepared by wet impregnation showed a reduction of 44.85 % of the oxygen content and 77.8 % less water in comparison to the initial bio-oil. Carbon, on the other hand increased from 59.9 wt.%, dry basis to 72.9 wt.%, dry basis, respectively. After the second upgrading reaction with $Ni-Cr/SiO_2$, the oxygen concentration was further reduced to 11.6 wt.%, reducing 64.8 % of the original oxygen concentration, and reducing around 90 % of the water content. Additionally, most of the organic compounds were concentrated in the upgraded oil, as the aqueous phase after the second upgrading step was composed by 97 % of water. Such improvement was reflected in the high carbon concentration in the upgraded oil ([C] = 78.6 wt.%), in the HHV (36.9 MJ/Kg), 90.1 % higher in comparison to the original beech wood fast-pyrolysis bio-oil and in the hydrocarbons identified in the two-steps upgraded oil. Hence, the two steps hydrotreatment with adequate catalyst seems to be a promising upgrading process in order to obtain fast pyrolysis oil with improved properties.

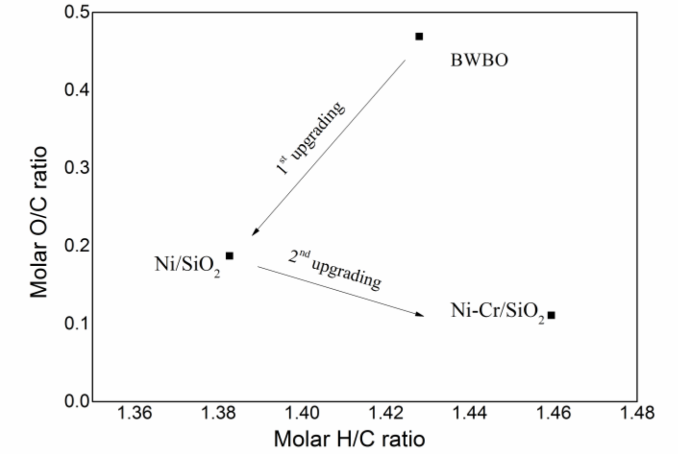

Figure 3 – Van Krevelen Plot in dry basis of beech wood fast pyrolysis bio-oil and upgraded oils after the first and second hydrotreatment reaction

BIOFUELS FROM WASTE TO ROAD TRANSPORT

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Key Words: biofuels, biogenic waste, pyrolysis, liquefaction, co-refining

Biofuels from Waste to Road (WASTE2ROAD) is an EU funded project under the Grant Agreement No. 818120 within the LC-SC3-RES-21-2018 call, “Development of next generation biofuels and alternative renewable fuel technologies for road transport”, as a Research and Innovation Action of the European Union's Horizon 2020 Programme. The project started in the fall 2018 and will run for 4 years.

In 2014, total waste production in the EU amounted to 2.5 billion tons. From this total only a limited (albeit increasing) share (36%) was recycled, while the rest was landfilled or burned, of which some 600 million tons could have been recycled or reused. Conversion of all sustainably available biogenic wastes and residues to biofuels could provide 27% of total transport fuel by 2050, achieving around 2.1 gigatons of CO_2 emission reductions per year. The increasing demand for biofuels[1] implies the need for the transformation of diverse bio-resources into liquid fuels, and includes transformation of the biogenic part of municipal and industrial wastes into such biofuels. This clearly is a stepping stone to achieve the European goals[2] but it also poses challenges, such as 1) diversity and inhomogeneity of wastes throughout Europe (variable composition depending on the type of waste and geographical location), 2) the complexity of the conversion of wastes compared to fossil oils, 3) the technological aspects of co-refining and 4) high overall costs with moderate process performance.

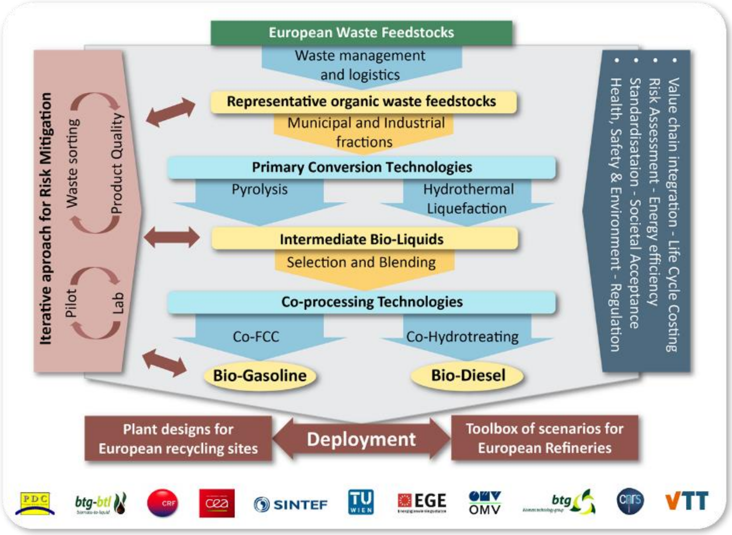

Figure 4 – The WASTE2ROAD concept.

While addressing these challenges, WASTE2ROAD aims to develop a new generation of cost-effective biofuels from a selected range of low cost and abundant biogenic residues and waste fractions, aiming to achieve high overall carbon yields > 45% while reducing greenhouse gases emissions (GHG) by > 80% compared to fossil fuels. The Consortium (involving 11 partners from 6 European countries) covers the full value chain from waste collection and recycling, to bio-conversion (liquefaction) and co-refining, through to validation of the biofuels for the use of road transport. The project will deploy risk-mitigation pathways to realise industrial implementation, with primary processing at European waste recycling sites and co-processing within European refineries, achieving pilot testing at TRL 5.

The WASTE2ROAD project is highly relevant to the themes of the Pyroliq 2019 Conference. The poster session will give an opportunity to the participants of the conference to learn about the project, its objectives and the main targets.

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SYNTHESIS OF TAILORED HIERARCHICAL ZSM-5 ZEOLITES AND AGGREGATES FOR THE CATALYTIC PYROLYSIS OF BIOMASS

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Key Words: Catalytic fast pyrolysis, ZSM-5, Hierarchical zeolites

Catalytic fast pyrolysis (CFP) is a one-step process for the conversion of lignocellulosic biomass into valuable chemicals and a deoxygenated liquid energy carrier (bio-oil) with improved properties compared to bio-oil from conventional fast pyrolysis. In the process, the vapors produced from the thermal decomposition of biomass react on the surface of a heterogeneous catalyst and are deoxygenated, cracked and converted into more desirable products. Many materials have been investigated as candidate catalysts for CFP, with the most commonly studied one being the ZSM-5 zeolite. ZSM-5 has been found to be a very effective catalyst due to its high acidity and unique micropore structure that is very shape selective for the production of monoaromatic hydrocarbons and the minimization of unwanted coke[1].
However, bulky oxygenates and oligomers that are formed form the thermal decomposition of biomass cannot diffuse into the micropores of the ZSM-5 and can only react on the limited external surface area of the catalyst. For this reason, the purely micropore structure of the ZSM-5 may not be optimal for the CFP of biomass and recently, there is increasing interest for hierarchical mesoporous zeolites as candidate catalysts for the process. These materials combine the high acidity and shape selectivity of the zeolite microporous structure with the enhanced accessibility that is provided by a secondary mesoporous network. The desilication of conventional zeolites is reportedly one of the most effective, versatile and easily scalable methods available to synthesize hierarchical zeolites[2]. Hierarchical zeolites synthesized via desilication have been tested for the CFP of biomass in small-scale reactors by several groups[3-6]. Provided that desilication was carried out at mild conditions, these materials performed better in terms of activity and desirable product formation. At more severe desilication conditions, the performance of the materials deteriorated, most likely due to a collapse of the zeolite structure, macropore formation and severe loss of microporosity and shape-selectivity.

In this work, the mild desilication (0.2M NaOH aqueous solution) of a microporous ZSM-5 catalyst (Si/Al = 40) was carried out at variable temperatures (50, 65 and 80 ºC) and contact times (15, 30 and 45 min). The aim was the controlled formation of mesopores in the ZSM-5 catalyst with minimal loss of the micropore structure in order to increase accessibility and preserve shape selectivity, properties that are desirable for the CFP of biomass. Desilication at 50 ºC was found to be effective for the increase of the total and external surface area of the zeolite to levels comparable or higher to those achieved at the higher and more commonly used temperatures of 65 ºC and 80 ºC, provided enough contact time was allowed (≥ 30 min). Moreover, desilication at the lower temperature of 50 ºC resulted in a zeolite with a markedly narrower mesopore size distribution, between 2-20 nm, compared to desilication at 65 ºC or 80 ºC where wider mesopore size distributions were observed (2-40 nm), as well as some macropore formation (> 50 nm). The smaller mesopore sizes achieved with desilication at 50 ºC may prove to be beneficial for biomass CFP, in which shape-selectivity plays a crucial role to inhibit the formation undesirable byproducts, such as coke. A simple laboratory procedure was developed to prepare the most interesting hierarchical zeolite samples into aggregates with a binder (bentonite) in order to carry out catalyst screening studies in medium-scale fluidized bed reactors with wood biomass. The prepared aggregates were also characterized in depth to identify any interactions between the zeolite and the binder phases.

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KINETIC STUDY OF TIRE CARBON BLACK AND BIOMASS SOOT STEAM ACTIVATION USED FOR THE REMOVAL OF PHENOL AND CHLORINE FROM DRINKING WATER

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Keywords: wastewater filters; biomass soot; carbon black from tires; H2O activation; kinetic model.

This study aims to demonstrate a novel method for removing toxic chemicals using soot produced from wood and herbaceous biomass pyrolyzed in a drop tube reactor and tire pyrolytic carbon black. In order to improve the economic performance and reliability of entrained flow gasification, biomass soot has the potential to be captured, activated and further used as a sorbent to remove a broad range of pollutants from wastewater. In recent years, the disposal of waste tires has become an important issue. The liquid hydrocarbons and solid char residue from thermal conversion of waste tires have potential to be used as environmentally benign fuel and activated carbon. In the present work, the influence of ash content, nanostructure, particle size, and porosity on the filter efficiency of steam activated carbon materials was studied. It has been shown for the first time that steam activated soot and carbon black can remove phenol and chloride with the filter efficiencies as high as 95 %. The correlation of the filter efficiency to material properties showed that the presence of alkali and steam activation time were the key parameters affecting filter efficiencies. Kinetic parameters for the steam activation of tire pyrolytic carbon black and biomass soot have been determined by thermogravimetric analysis using steam as an activation agent. The feedstock for the soot production, activation temperatures and residence time were varied. The results showed that the rate of steam activation is 10 times faster than the activation at lower temperature. This study demonstrated that the steam activation process is suitable to prepare activated soot with the high surface area at the short residence time and at temperatures below 800°C. Reaction evolution has successfully been modelled, including the maximum reaction rate obtained in experimental results. Moreover, intrinsic kinetic parameters of the activation reaction order, activation energy and pre-exponential factor – were calculated.

PRELIMINARY ACTIVITY ON THE PYROLYSIS OF A PLASTIC BASED SOLID RECOVERED FUEL

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Key Words: plastic waste, wax, batch catalyzed pyrolysis, alumina, SRF.

Plastic is a versatile, lightweight, resistant, and inexpensive material, and an increase of its global demand has been observed in the last years (from 299 milion tonnes in 2013 to 348 in 2017) [1], with the dominant role played by the packaging sector, which absorbs almost 40% of the overall production. Management of post–consumer plastic packaging waste poses a serious environmental problem, and a number of strategies have been devised to reuse/recover these materials, mainly with the aim of recovering useful materials and avoiding landfilling. Among these strategies, pyrolysis can play a significant role for recovering useful products and energy from the post–selection mixed packaging waste, that is not amenable to other uses [1]. A large amount of studies has been developed to assess the possibility to convert waste plastic to oil by pyrolysis processes [1] either catalytic or non catalytic. Nevertheless, only a limited numbers of papers refer to the use of real plastic waste rather than simulated mixtures [2] even if the performances obtained are strongly influenced by the feedstock characteristics.

Figure 5 – Batch of SRF

In this work, a real SRF (Solid Recovered Fuel), mainly made by plastic resulting from the process of the plastics recycling has been used to perform pyrolysis experiments. The effect of temperature on the yield of gas, condensable and solid has been evaluated in addition to the use of high surface g-alumina as catalyst to upgrade the pyrolysis products. The SRF used for this work has been gently supplied by P.R.T. srl. The feedstock has been characterized by means of proximate and ultimate analysis carried out by LECO TGA 701, LECO CHN 628, LECO SC 144 DR, Metrohm 883 Basic IC plus ionic chromatograph, and by PARR 6200 calorimetric bomb for the determination of HHV. Pyrolysis experiments were carried out at different temperatures in the range 500-800 °C under nitrogen flow (60Nl/h), using a fixed bed quartz micro-reactor having an ID of 26mm. For each test, a mass of about 3 g of sample has been loaded in the reactor and heated up to the required temperature with a heating rate of 30°C/min and maintaining the chosen final temperature until no further gas production was detected. For the catalytic tests, a weight ratio of about 6 has been adopted between the g-alumina and the SRF batch. The produced gas was vented from the end of the reactor into a set of condenser cooled at -12°C were the condensed compounds (oil and wax) were collected and weighted in order to evaluate their yield. The oil and wax have been characterized by means of GC-MS Agilent 7890A, a TGA-DSC Perkin Helmer STA 6000 and LECO CHN 628. The permanent gas leaving the condensation block was sent to a set of on line analyzers to measure in continuous the concentration of CH_4, CO, CO_2 and H_2. Further analysis of gas has been performed collecting a batch of gas, at the exit of condenser, in a Tedlar bags, at different reaction time, and analyzed by means of a micro-GC Agilent 3000, for the determination of light hydrocarbon (up to c5). At the end of the test, the reactor was cooled at room temperature under nitrogen flow and the solid residue was weighted to calculate the solid yield and subsequently analysed by a LECO CHN 628. The results show that, as expected, the gas yield is strongly enhanced by both the increases of temperature and the presence of catalyst; the quality of the condensed compounds is affected by the presence of the catalysts. In particular, a higher fraction of gasoline (C_5-C_{11}) and diesel fraction (C_{11}-C_{20}) and the formation of cyclic and aromatic hydrocarbons is obtained in presence of alumina. Finally, a coke deposition is also observed.

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BIOMASS PYROLYSIS IN A BUBBLING FLUIDIZED BED: EFFECT OF BIOMASS COMPOSITION AND REACTOR TEMPERATURE

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Key Words: Bubbling fluidized bed, Pyrolysis, Tar characterization.

Flash pyrolysis of two types of woody biomass (Pine Wood, PW, and Green Wastes, GW) was carried out in a Bubbling Fluidized Bed of olivine particles between 700°C and 850°C. Experiments were conducted in a laboratory scale reactor (height of 2.5 m and internal diameter of 0.214 m) with continuous fuel feeding. Products distribution was determined through a global approach: incondensable gases yield were measured with an online microGC, condensable products yield, obtained by tar protocol, were quantified using GC-MS and Karl-Fischer titration and char yield was determined through high temperature combustion of the accumulated char at the end of each experiment. The results (*Figure 6 a)*) showed that the pyrolysis of green waste leads to higher amounts of condensable species (tars and water) and char compared to those obtained by the pyrolysis of pine wood. These results can be attributed to the high values of ash content as well as H/C and O/C molar ratios for green waste compared to pine (*Table 1*). In addition, GC-MS analysis of pyrolysis tars (*Figure 6 b)*) showed that BTEX compounds account for more than 70% in mass of the produced tars for both types of biomass. Furthermore, a drastic increase in incondensable gas yield (from 626 g/kg,daf to 726 g/kg,daf) as well as an important reduction in tar yield (from 129 g/kg,daf to 67 g/kg,daf) were observed when the pyrolysis temperature was increased from 700°C to 850°C.

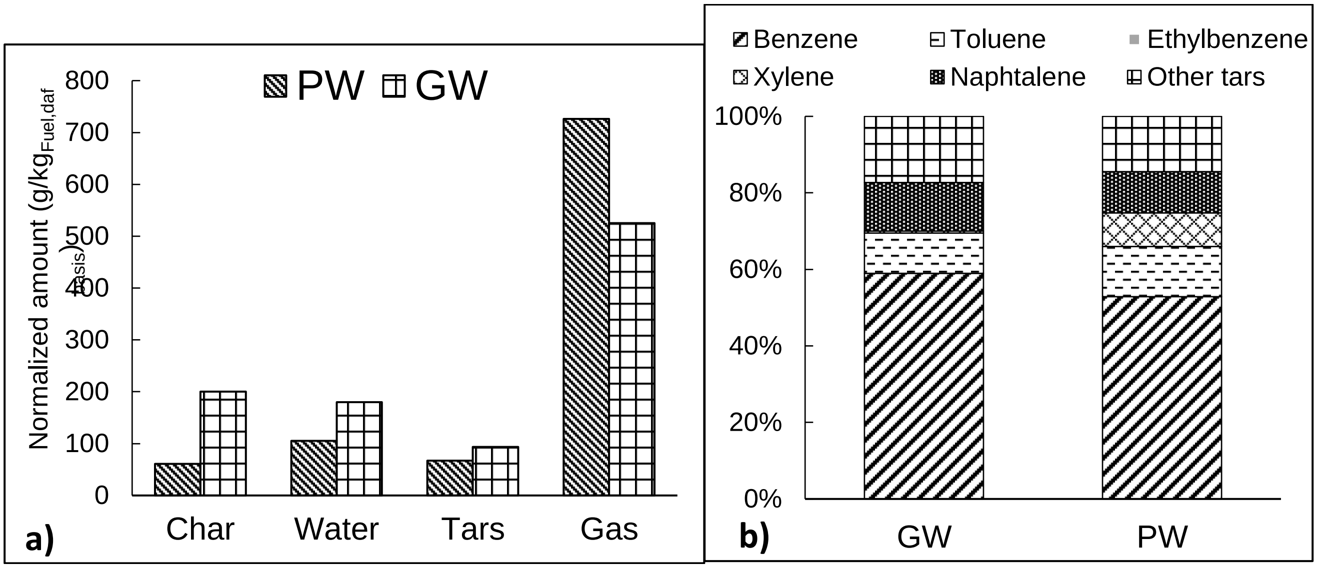

Figure 6 - Products distribution for pyrolysis at 850°C : a) Global products distribution b) Tars distribution

Table 1 - Woody biomass compositions

Fuel	**Chemical composition (%m, daf basis)**					**Molar ratios**		**Moisture (%m)**	**Ash (%m)**
	C	H	O	N	S	H/C	O/C		
PW	50.50	5.86	43.40	0.24	0.00	1.39	0.64	5.00	<1.00
GW	45.20	5.80	48.55	0.44	0.00	1.54	0.80	9.50	2.01