Catering wastes conversion to bio-crude oil via hydrothermal liquefaction

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The ever-increasing energy and transportation fuels demand, as well as the new European regulations, have intensified the need to explore new sustainable fuel production pathways. Second generation biofuels will demonstrate an important role in coverage of these needs, as they are originated from residues and wastes, thus appear as very promising candidates for green fuels production[1]. There are two main thermochemical processes that can be applied in residual biomass conversion into transportation biofuels, pyrolysis, and hydrothermal liquefaction (HTL)[1]. HTL prevails over pyrolysis in numerous ways such as the absence of the costly drying step of the feedstock before the reactions, the catalytic behaviour of HTL solvents, and the enhanced oil yield and fuel properties. Also, HTL is suitable for the conversion of a wide variety of materials, including municipal wastes, algae, forest, and agricultural residues, which are available in large quantities[1]. As coffee is a largely traded and consumed good (the annual consumption of coffee is estimated at 10 million tonnes in the last five years according to the international coffee organization[2]), and due to its lignocellulosic nature, coffee-derived wastes appear as a sustainable residual feedstock. So, the investigation of spent coffee grounds via HTL appear as a very promising pathway in the biofuel production chain.

In this study, residues form coffee shops (spent coffee grounds, in raw and pre-treated form, lignin and proteins from spent coffee and orange peels) are converted to bio-crude oil via HTL. The pre-treatment step of spent coffee grounds included the removal of lipids, antioxidants, and some proteins from the raw feedstock. Coffee is a lignocellulosic material, meaning its structure is consisted of cellulose, hemicellulose, and lignin. The elemental analysis of the raw and pre-treated biomass is presented in Table 1. The aim of the study was to assess the potential production of bio-crude oil via HTL and find the optimal conditions to achieve maximum oil yield. The solvent used in the process was deionized water, while the conditions under investigation include temperature (280° - 350°C) and residence time (10 and 60 min). No catalyst was used during the study, the initial pressure of the reactor was constant at 30 bar with nitrogen and the solid-to-liquid ratio was 1/10 in all sets of conditions. Each set of conditions was applied twice to ensure higher accuracy of the results.

Table 1: Results of pretreated spent coffee grounds structural analysis

	Raw spent coffee grounds	*Pre-treated spent coffee grounds*
Carbon (wt%)	47.43	45.74
Hydrogen (wt%)	7.11	6.53
Nitrogen (wt%)	1.96	2.41
Sulfur (wt%)	0	0
Oxygen (wt%)	43.5	45.32

The experiments were conducted in a bench top, high-pressure stirred batch reactor with internal vessel volume of 250 mL (Parr 4576A). The reactor is coupled with a J type thermowell for heating and a U-type cooling coil for rapid temperature drop. During a typical experiment, the vessel was loaded with 10g of feedstock (raw or pre-treated) and 100 mL of deionized water (to set the solid to liquid ratio to 1/10). Then, the reactor was sealed and purged 3 times with nitrogen to remove air (absence of oxygen during the reactions). Finally, the reactor inlets were compressed to 30 bars with nitrogen as compression gas (to keep the water in liquid state during heat up), then heated and kept to the desired temperature according to the set of conditions, before finally cooling to room temperature.

The products of HTL process include solid, liquid and gas streams. Upon decompression of the reactor, a gas product sample was collected in a sample bag and analyzed via GC-FID. The collection of the products after the reactor cooldown is initiated with vacuum filtration of the slurry mix in a Buchner funnel with filter paper. The collected liquid from the flask was the aqueous phase product, and it contained the aquatic solvent and some dissolved organic compounds. Then, the remaining cake in the filter paper was washed with 250 – 300 mL of acetone to separate bio-crude oil from solids (hydro-char) and collected it in the flask. The solids were dried in an oven at 105°C overnight and weighted, while the acetone was completely removed in a rotary evaporator at 40°C under reduced pressure to collect the final bio-crude oil product.

While the study is still in progress, there are some premature results regarding the HTL of pretreated coffee. According to literature, temperature directly affects the liquefaction of biomass as lignin chains start to decompose at 280°C, while on the other hand cellulose and hemicellulose start decomposition in less severe conditions (lower temperature)[3]. Yang et al. studied the effect of temperature and residence time in HTL of raw spent coffee grounds. In the range of 200° – 300°C they noticed an increment in oil yield as the temperature rose to 275°C. At higher temperatures (300°C) they found a lower yield with higher proportions of aqueous and gas products[4].

In this study though, the bio-crude oil yield increased along with the reaction temperature even at 320°C as presented in Figure 1. As the main parameter affecting the optimal temperature is the feedstock structure, raw and pretreated coffee differ in lipid and extractives content. These components are easier to liquefy at mild conditions and therefore lead to higher oil yield at lower temperature. Nevertheless, pretreated coffee grounds consist only of the structural materials such as cellulose, hemicellulose, lignin, and some proteins. Cellulose and hemicellulose require mild conditions to liquefy but most of the products are mitigated at the aqueous phase. So, in this case, the liquid yield is strongly depended on the lignin liquefaction which require severe conditions (over 280°C). With approximately 30 %wt. of structural lignin in pre-treated coffee, high temperature is essential to get most of lignin chains in oil product (22.3%wt. at 320°C). These findings are also confirmed by the reduction of the solids at higher temperatures. So, by the end of the study it is expected to fully understand the process and optimize the parameters for each residual feedstock.

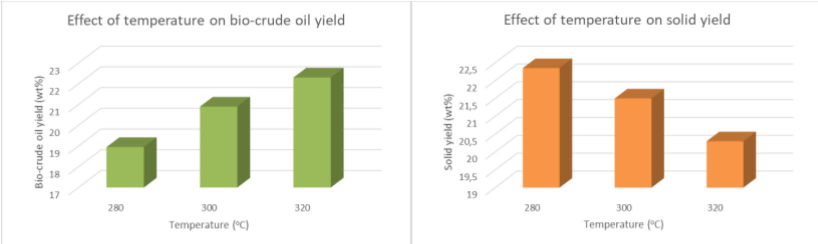

Figure 1: Effect of reaction temperature on bio-crude oil yield

Apart from the liquid and solid products analysis, this study also focused on distribution of molecules in gas products which is innovative as in most studies the gas is accounted as 100% CO_2. According to Table 2, CO_2 is indeed the main gas product based on decarbonylation and Boudouard reactions, but there are also some other light hydrocarbons present. The secondary decomposition reactions produce ethane (~0.1 v/v%), $C6^+$ (~0.2 v/v%) and more importantly methane at significant proportions (~7 v/v%), which confirms that secondary decomposition of biomass is causing loss of useful hydrocarbons in gas.

Table 2: Composition of gas product in HTL of pre-treated spent coffee grounds

Gas molecule	**Concentration (v/v%)**
Carbon dioxide (CO_2)	91.0 – 93.0
Hydrocarbons with 6 or more carbon atoms	0.1 – 0.3
Ethane (C_2H_6)	0 – 0.12
Methane (CH_4)	6.5 – 7.3
Hydrogen (H)	0 – 0.5

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