Hydrothermal liquefaction of spent coffee grounds targeting liquid biofuel intermediates

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The ever-increasing demand in energy and transportation fuels, as well as the new European regulations, have led to the need to exploit new feedstocks for fuel production. Second generation biofuels will play a major role in coverage of these needs as they are produced from residues and wastes, and thus appear as the most qualified candidates for greener energy generation[1]. The conversion of residual biomass into liquid biofuel intermediates can be achieved through two main thermochemical processes, pyrolysis, and hydrothermal liquefaction (HTL)[1]. HTL has numerous advantages over pyrolysis such as the absence of the costly drying step of the feedstock before the reactions (in pyrolysis it is necessary), the optional use of catalysts (in HTL the solvent also acts as catalyst), and the enhanced oil yield and properties. Also, HTL can convert a wide variety of feedstocks, including municipal wastes, algae, forest, and agricultural residues which are available in relatively large quantities[1]. Coffee is one of the most traded and consumed goods. In the last five years the annual consumption of coffee is estimated at 10 million tonnes according to the international coffee organization[2]. Coffee is a lignocellulosic biomass and so, coffee wastes appear as a sustainable residual feedstock. Thus, exploiting spent coffee grounds via HTL appears as a very promising pathway in the biofuel production chain.

In the present study, raw and pre-treated spent coffee grounds (de-oiled coffee) were converted to bio-crude oil via HTL. The pre-treatment of spent coffee grounds included the removal of lipids, antioxidants, and some proteins from the raw feedstock, so they can be used in a different scientific object. Coffee is a lignocellulosic biomass, meaning its structure is comprised mainly of cellulose, hemicellulose, and lignin. The structural analysis of the pre-treated biomass is presented in Table 1. The solvent used in the process was deionized water and the experiments were conducted in the absence of a catalyst. The aim of the study was to examine the potential production of bio-crude oil and find the optimal conditions for maximum oil yield. So, the conditions investigated were temperature (three different sets of temperature 280°- 300°- 320°C) and residence time (15 and 30 min). The initial pressure of the reactor was constant at 30 bar and the solid-to-liquid ratio was 1/10 in all sets of conditions. Each set of conditions was conducted twice to ensure higher accuracy of the results.

Table 1: Results of pretreated spent coffee grounds structural analysis

	Pre-treated spent coffee grounds
Ash (wt%)	1.94
Proteins (wt%)	15.24
Cellulose (wt%)	12.10
Hemicellulose (wt%)	33.53
Lignin (wt%)	31.81

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 dropping. In a typical run, the reactor was loaded with 10g of feedstock (raw or pre-treated) and 100 mL of deionized water (solid to liquid ratio of 1/10). Then, the reactor was sealed and purged 3 times with nitrogen to remove air. Finally, the reactor inlets were compressed to 30bars by using nitrogen (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 cooling to room temperature.

HTL of biomass produces solid, liquid and gas products. Upon decompression of the reactor a gas sample was collected in a sample bag and analyzed via GC-FID. The collection of the products after the reactor cooldown begins with vacuum filtration of the mix in a Buchner funnel with filter paper No.5. The collected liquid from the flask is the aqueous phase product, and it contains the water solvent and some dissolved organic compounds. Then, the remaining products in the filter paper are washed with 250 – 300 mL acetone to separate bio-crude oil from solids (hydro-char) and collect it in the flask. The solids are dried in an oven at 105°C overnight and weighted, while the acetone is evaporated in a rotary evaporator at 40°C under reduced pressure to collect the final bio-crude oil product.

While the study is still ongoing, some main results have been generated from the HTL of pretreated coffee. The reaction temperature directly affects the liquefaction of biomass as lignin starts to decompose at 280°C while cellulose and hemicellulose start decomposing in milder conditions[3]. Yang et al. studied the effect of temperature and residence time in HTL of raw spent coffee grounds. In the range of 200º – 300ºC they noticed an increment in oil yield as the temperature rose to 275ºC. At higher temperatures (300ºC) they found a lower yield with higher proportions of aqueous and gas products[4]. They justified these results based on the secondary decomposition reactions in more severe conditions which lead to gas and solids formation from liquified organic compounds[4].

In this study, the bio-crude oil yield rose along with the reaction temperature even at 320ºC 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 easily liquefied at mild conditions and therefore lead to greater liquid yields at lower temperature. On the other side, pretreated coffee grounds consist only of cellulose, hemicellulose, lignin, and some proteins. Cellulose and hemicellulose require mild conditions to liquefy but mot of the products mitigate to the aqueous phase. So, in this case, the liquid yield is strongly depended on the lignin liquefaction which require severe conditions (over 280ºC). With approximately 30 %wt. of structural lignin, high temperature is essential to get most of lignin molecules in oil product (22.3%wt. at 320ºC).

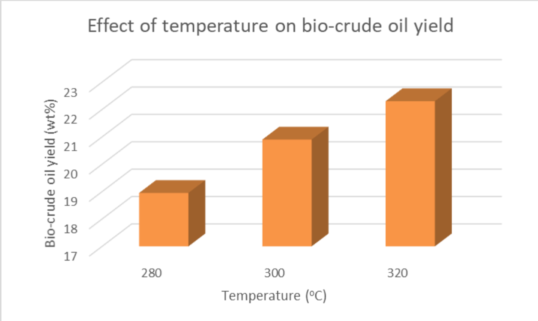

Figure 1: Effect of reaction temperature on bio-crude oil yield

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