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Micropyrolysis study to evaluation the potential for add-value to residual biomass from coffee beans after supercritical fluid extraction process

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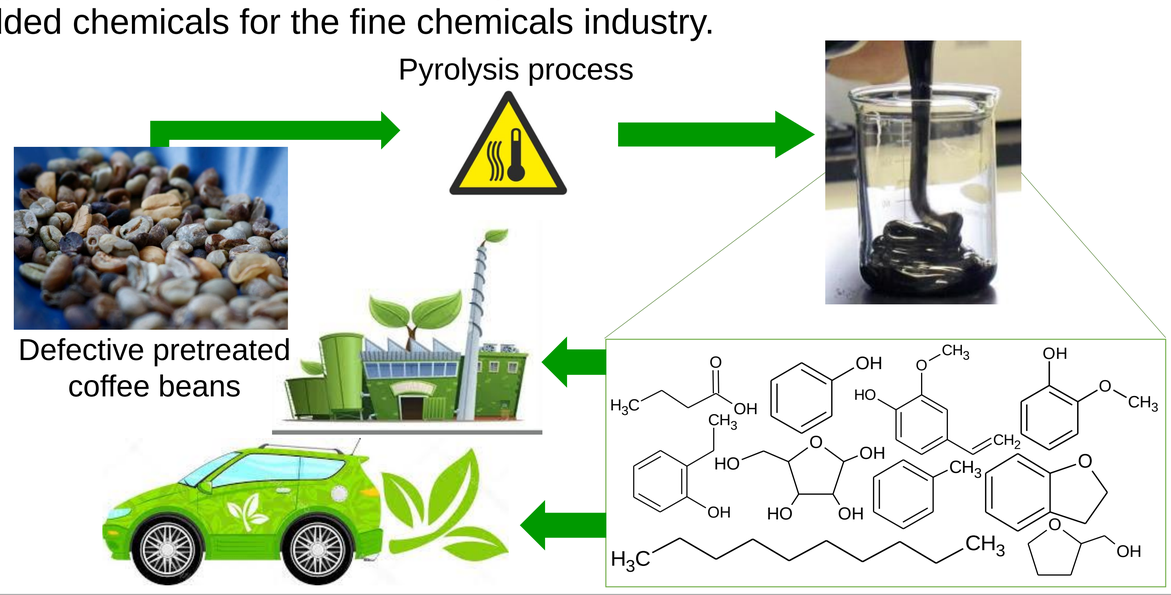
INTRODUCTION

Brazil is one of the largest coffee producers in the world and about 20% of total productions are defective coffee beans, inadequate for exportation [1]. One proposed process to add-value to this product is the coffee oil recovery (COR) through pressurized fluid extraction (PFE), however, to close the sustainable circle and full biomass harnessing, the pyrolysis process can be used [2].

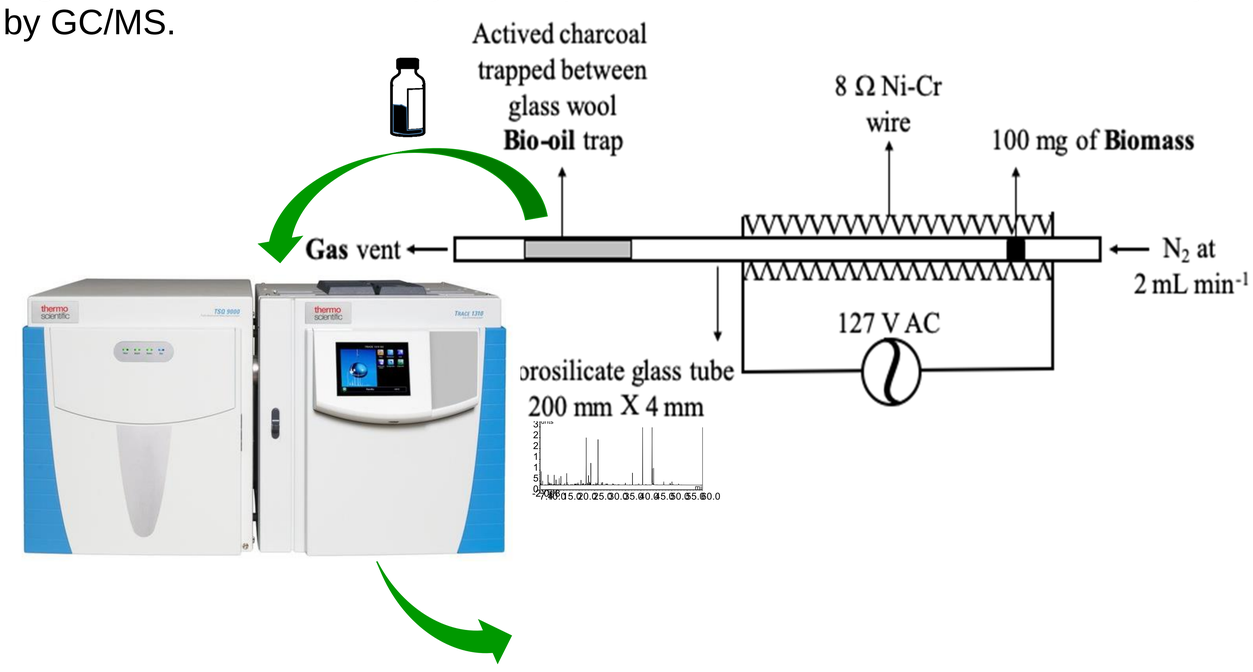
In this work, microscale pyrolysis experiments were applied to the biomass of defective residual coffee beans pretreated with pressurized fluid, in order to evaluate pyrolysis as a secondary process in the conversion of this biomass into products of economic value, such as bio-oil, a product with potential application as a renewable transport fuel and an alternative source of value-added chemicals for the fine chemicals industry.



METHODOLOGY

The micropyrolysis assays were performed in a homemade system [3], **Figure 1**. 100 mg of DCB was placed inside the reactor, purged with N_2 and the heating process was started in a range of 500 °C min^{-1} and maintained at the final temperature (500 ºC) for 0.5 min. N_2 at 2 mL min^{-1} was maintained throughout the process. The trapped bio-oil was eluted with THF for subsequent chemical characterization analysis by GC/MS and HESI-FT Orbitrap MS. The pyrolysis results of the biomasses from the PFE were compared with the biomass before PFE, Raw.

Figure 1. Scheme of the pyrolysis process of the biomass and bio-oil analysis by GC/MS.



RESULTS AND DISCUSSIONS

13 subcritical fluid extraction tests were performed under different conditions using propane as solvent. The residual biomass (DCB) submitted to different extraction conditions were elected based on the extracted coffee oil yields, to evaluate the effects of extraction process on the pyrolysis products. The products yields are shown in **Table 1**.

Table 1. Yields of coffee oil extraction and pyrolysis products process.

Extraction assays		Pyrolysis assays		
Biomass	**Coffee oil yields (wt. %)**	**Biochar (wt. %)**	**Total liquid fraction (wt. %)**	**Biogas (wt. %)**
Raw	-	23,6 ± 0,5	59,4 ± 1,0	17,0 ± 0,5
Assay 3	10.65	27,9 ± 0,5	53,1 ± 0,8	19,0 ± 0,3
Assay 6	6.38	27,5 ± 1,0	53,5 ± 1,5	18,9 ± 0,5
Assay 7	9.97	29,0 ± 0,4	52,5 ± 0,8	18,5 ± 1,2
Assay 9	6.68	28,6 ± 0,8	53,3 ± 0,9	18,1 ± 0,2

The coffee oil extraction resulted in the yield reduction of the total pyrolysis net fraction of the DCB residual biomass from the PFE process, while the yields of the biochar and biogas increased when compared with the raw biomass pyrolysis products. Was not significant difference between the yields of pyrolysis products of the residual DCB biomasses.

The total ion current chromatograms (TICC) of the bio-oils from the raw and SFE pre-processed residual biomass are shown in **Figure 2**. The results of bio-oil characterization by GC/MS and HESI-Orbitrap MS are presented in **Figure 3**.

Figure 2 – Total ion current chromatograms of bio-oils analyzed by GC/MS and main identified compounds.

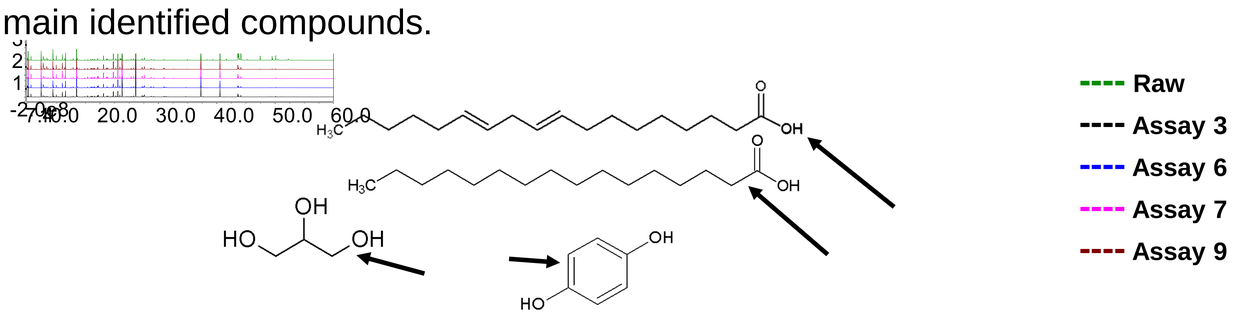
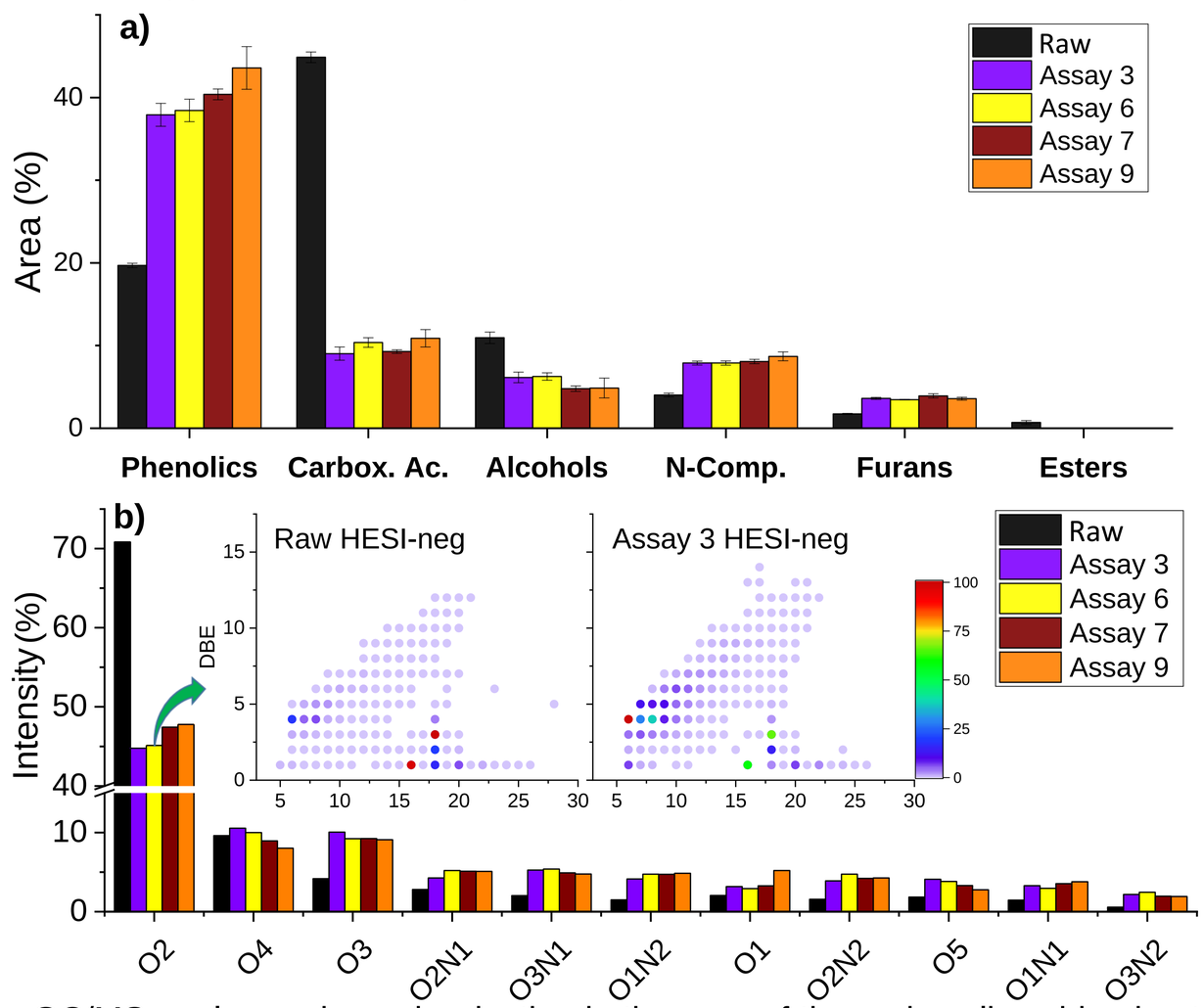


Figure 3 – chemical classes distribution of organic fraction compounds from (a) GC/MS and (b) HESI-FT Orbitrap MS analysis.



The GC/MS analyses showed reduction in the area of the carboxylic acids, due to the extraction of the triglycerides from the biomasses, and relative increases in the area of the other classes, mainly that of the phenolic compounds. In the negative mode of the HESI-FT MS analyses, it was observed the reduction in the relative intensity of the O2 class, the graphs of C vs DBE for this class showed no difference in the distribution of ions, only the reduction of the carboxylic acids intensity due to the reduction of concentration in the bio-oils. No variations in the positive mode classes were observed.

CONCLUSION

The yields of pyrolysis products were significantly affected by PFE process, as well affected the chemical composition of the organic fraction, elevating the phenolic load in bio-oils. Thus, the pyrolysis process can be applied as a secondary process in the treatment and value generation for a coffee industry waste.

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