

Thermal Conversion of Sugarcane Bagasse Coupled with Vapor Phase Hydrotreatment Over Nickel-Based Catalysts: A Comprehensive Characterization of Upgraded Products

Tarcísio Martins Santos ¹, Wenes Ramos da Silva ¹, Jhonattas de Carvalho Carregosa ¹, Caroline Carriel Schmitt ², Renata Moreira ³, Klaus Raffelt ², Nicolaus Dahmen ² and Alberto Wisniewski Jr. ^{1,*}

¹ Petroleum and Energy from Biomass Research Group (PEB), Department of Chemistry, Universidade Federal de Sergipe, São Cristóvão, Sergipe, 49100-000, Brazil.

² Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, 76344, Karlsruhe, Germany.

³ Institute for Technological Research, IPT, São Paulo 05508-901, Brazil

Supplementary materials

1. Feedstock characterization

The proximate analysis of SCB, to determine the moisture content, organic material, and ash content, was measured from the thermogravimetric analysis of biomass using a thermogravimetric analyzer TGA-50 (Shimadzu, TA, America) under an atmosphere of N₂ under a flow of 40 mL min⁻¹. To this end, approximately 5 mg of SCB were placed in a platinum crucible, and from the heating leaving an initial temperature of 30 °C to 1,000 °C under the heating rate of 10 °C min⁻¹, had its mass loss analyzed. Elemental analysis of the bagasse samples was performed on a LECO CHN628 elemental analyzer, and the results were processed in the Software CHN628 ver. 1.30. The equipment was operated with Helium (99.995%) and Oxygen (99.99%) with kiln temperature at 950 °C and post-firing temperature at 850 °C. Other parameters were adjusted for better sensitivity. The equipment was calibrated with a standard of EDTA (41.0% C, 5.5% H, and 9.5% N) using a mass range between 10-200 mg. The analysis was performed using 30.0 mg of bagasse, arranged on tin foil. These results are available in **Table S1**.

Table S1. Biomass properties

Property	Sugarcane bagasse
<i>Proximate analysis (wt%)</i>	
Moisture	6.13
Ash	2.10
Organic matter ^a	91.77
<i>Elemental analysis (wt%)</i>	
C	42.51
H	5.22
N	0.84
O ^b	49.33
H/C molar ratio	0.74
N/C molar ratio	0.02
O/C molar ratio	0.87
HHV (MJ kg ⁻¹)	16.64

^a Determined by the difference

^b Determined by the difference considering the ash content

Since this is a reactor consisting of two furnaces connected, operating at different temperatures, the first at 500 °C where the biomass pyrolysis process takes place, and the second at 350 °C where the pyrolytic vapors catalytic reforming process occurs, the interface zone refers to the place where there is a separation between furnace 1 and furnace 2. As the reactor was arranged horizontally, a fraction of the vapors produced from the cracking of biomass condensed in this interface zone, and this fraction was not affected by the catalytic reforming process, since it did not interact with the catalyst bed, as it remained static near the interface region between the two furnaces. This fraction was defined as Heavy Liquid Fraction (HLF), since it consists of condensable organic compounds at a temperature of 350 °C. The light liquid fraction (LLF) is the fraction that condenses after the second furnace, at the exit of the reactor.

The washing process for recovery of LLF and HLF is schematized in **Figure S1**, and it occurred at different moments. Initially, to recover the LLF, with the help of a suction pear, the solvent tetrahydrofuran (THF) was sucked into the tube, up to the margin where the LLF was contained, and then the solution formed was poured into a 5 mL volumetric flask. This process was repeated until the LLF was completely removed, and after that, the solution contained in the flask was diluted until the volume of the volumetric flask (5 mL) was reached. After the LLF was recovered, the process to recover the HLF was started, where with the help of a Pasteur pipette the solvent THF was placed inside the tube from the top, and by gravity, the whole tube was washed, so that the HLF fraction was recovered. The resulting solution was collected in 2 mL vials with a previously known mass, where after evaporation of the THF the HLF content was calculated.

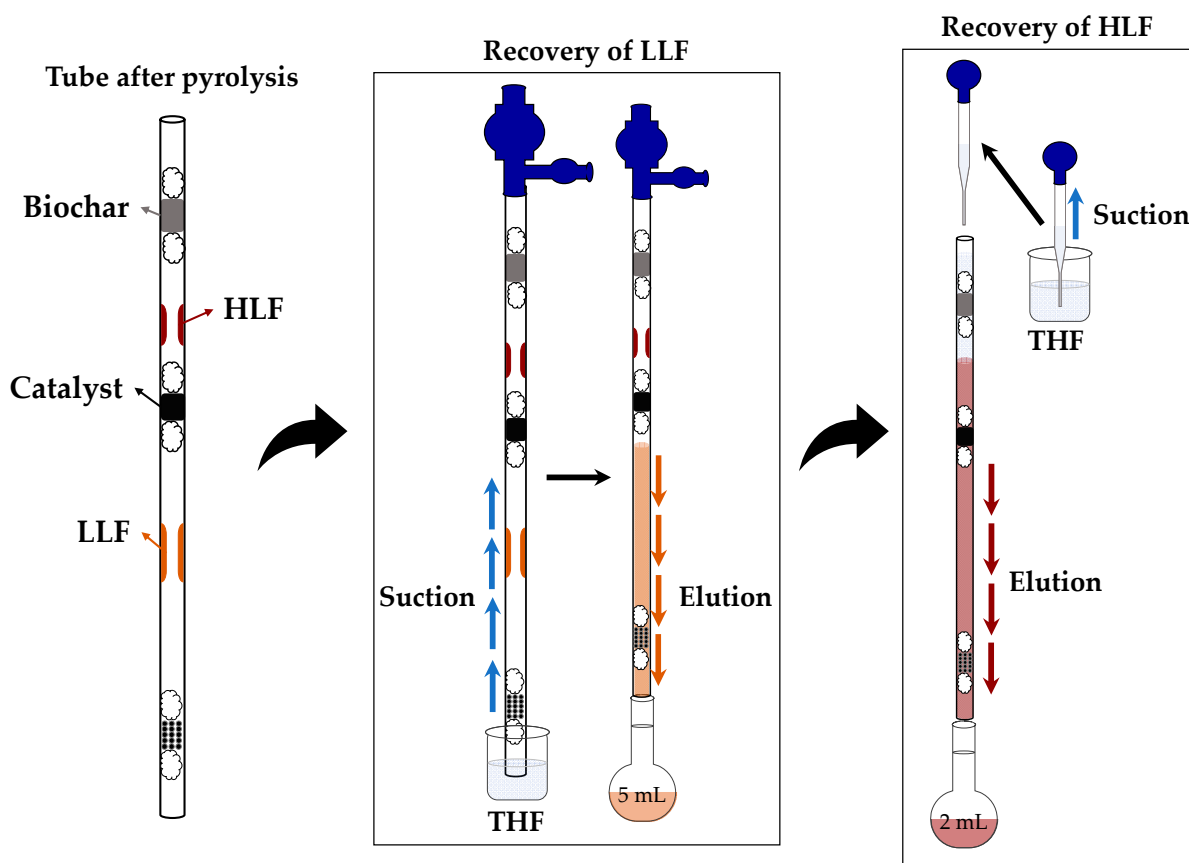


Figure S1. LLF and HLF recovery process.

3.1. Influence of the processes on product distribution and elemental composition of biochar

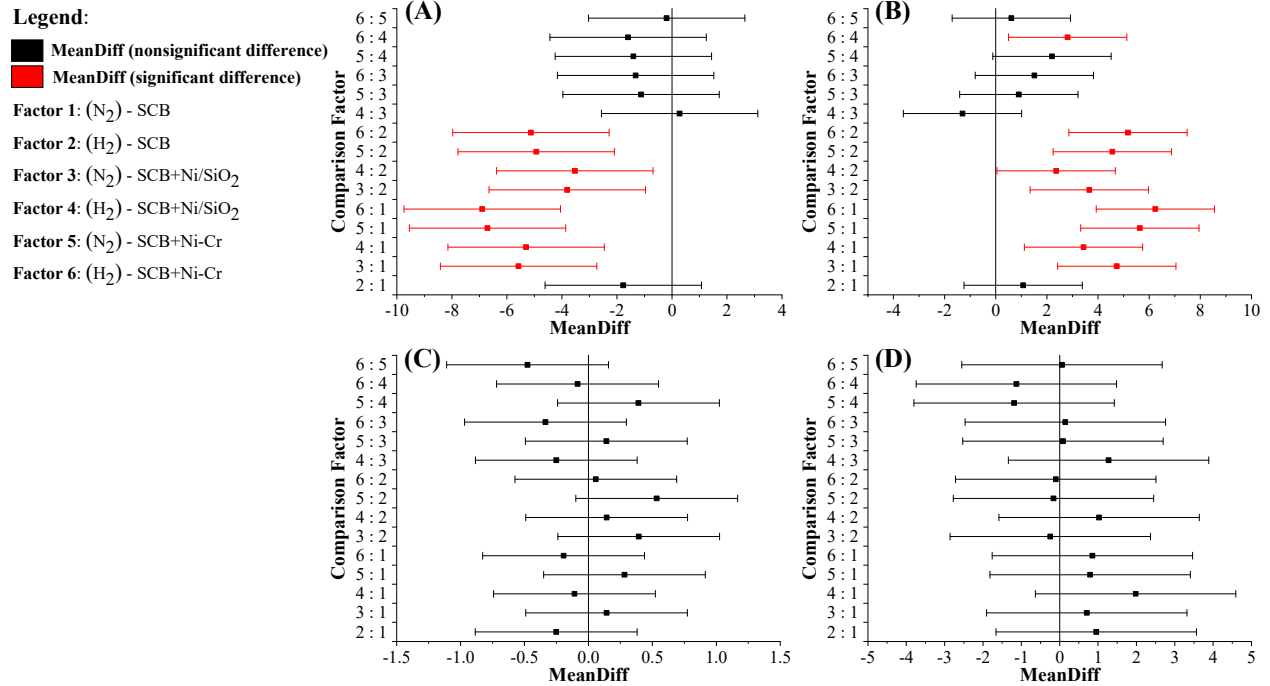


Figure S2. Tukey Post-hoc statistical test from the analysis of variance (ANOVA) for each of the products: (A) LLF, (B) Gases, (C) HLF, and (D) Biochar.

3.2. Effect of the processes upon the composition of the gaseous products

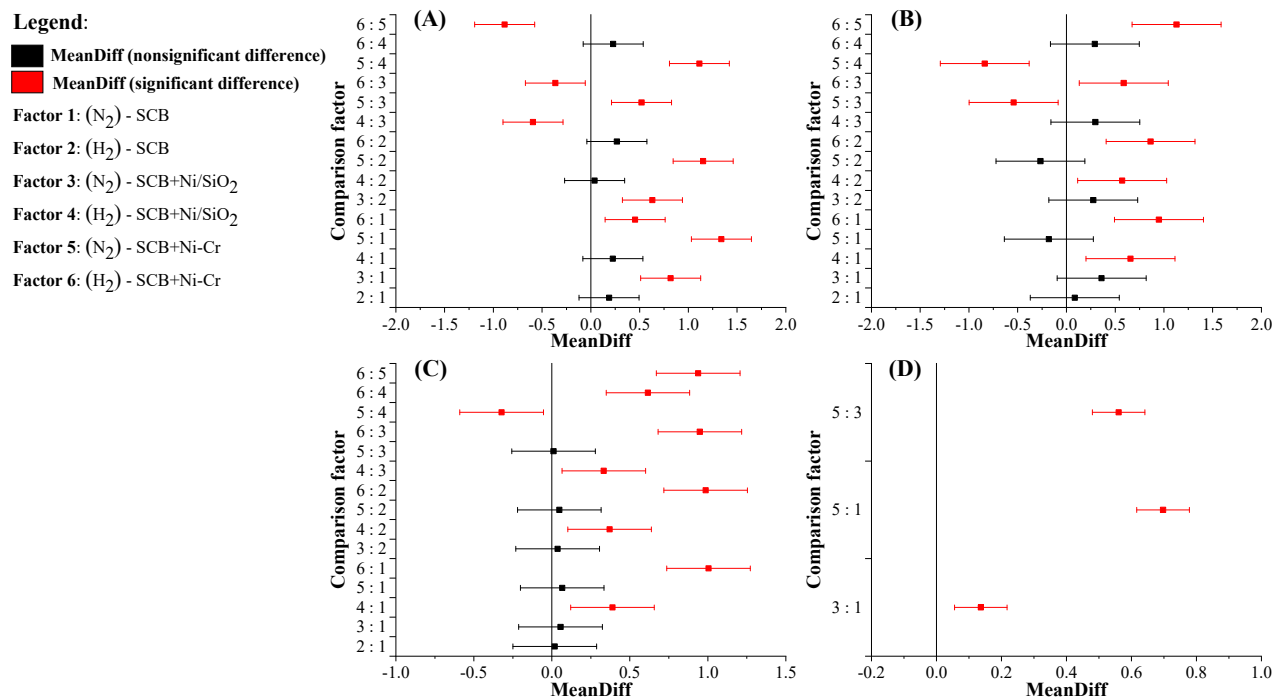


Figure S3. Tukey Post-hoc statistical test from analysis of variance (ANOVA) for each of the species present in the gases: (A) CO₂, (B) CO, (C) CH₄, and (D) H₂

3.3. Influence of the processes on the volatilizable composition of the liquid products

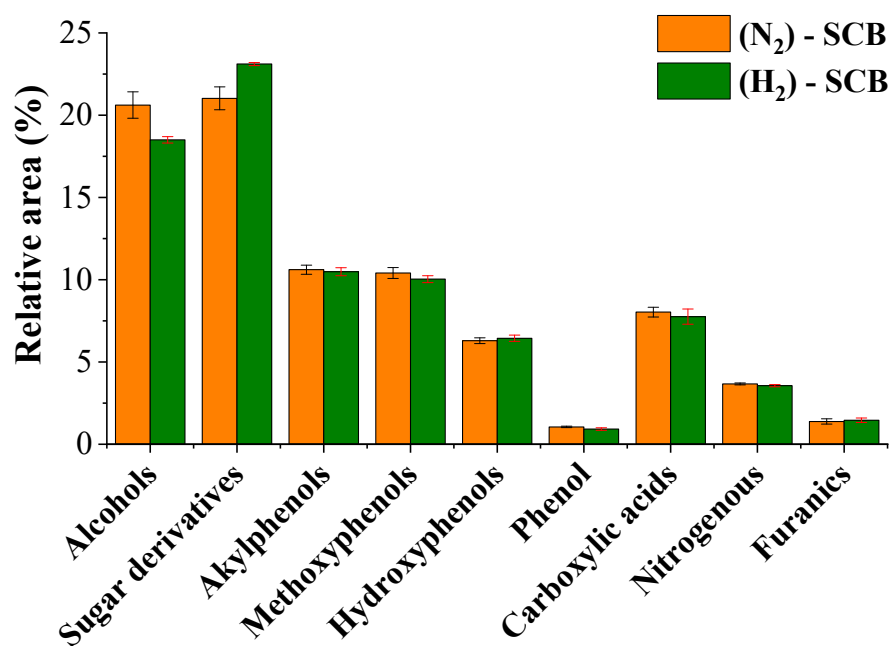


Figure S4. Comparison of the volatilizable composition of LLFs produced in the non-catalytic processes.

3.4. Influence of processes upon the non-volatile composition of liquid products

3.4.1. Negative-ion mode

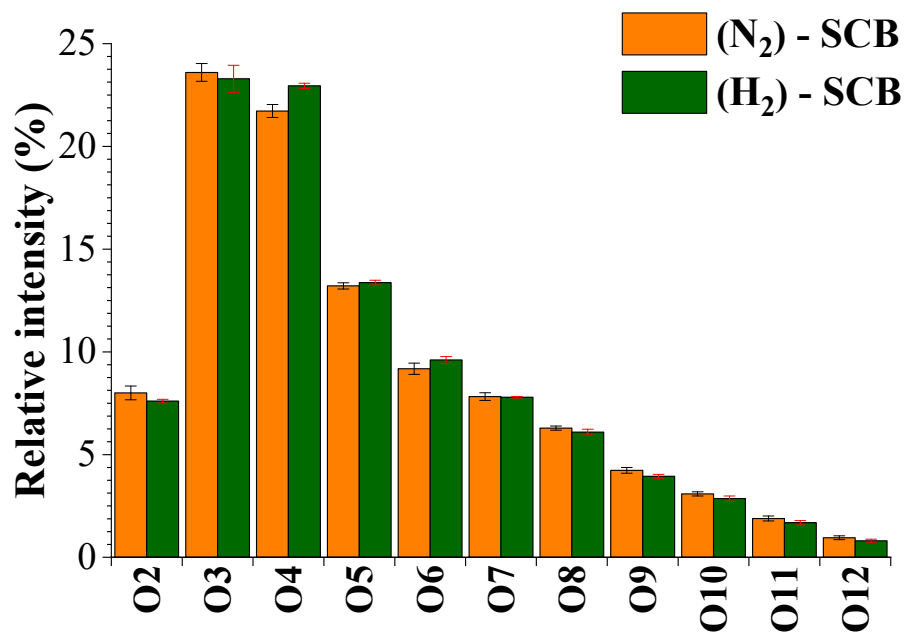


Figure S5. Comparison of the polar composition of LLFs produced in the non-catalytic processes, analyzed by HESI(-)-FT-Orbitrap MS.

3.4.2. Positive-ion mode

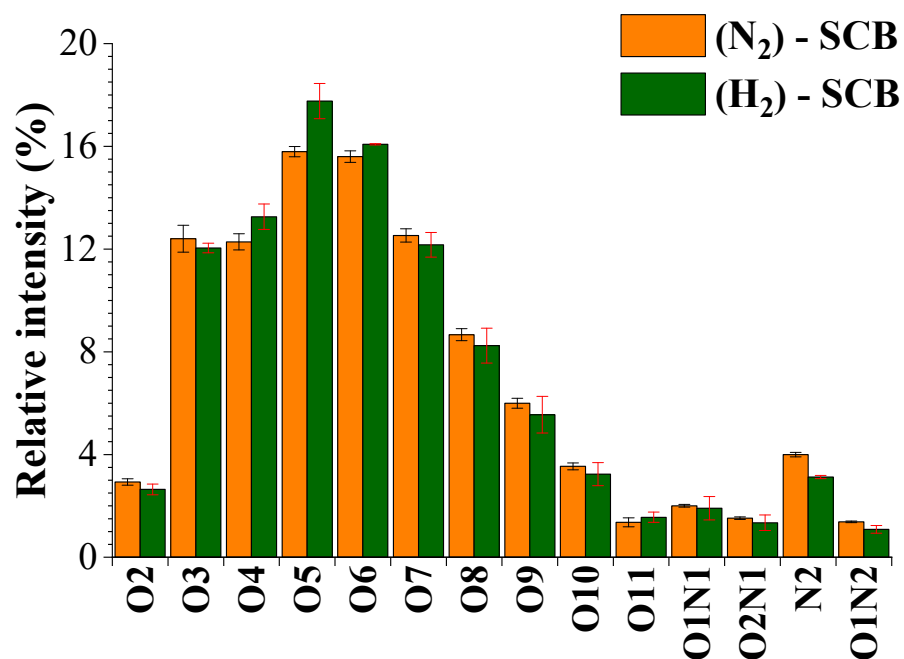


Figure S6. Comparison of the polar composition of LLFs produced in the non-catalytic processes, analyzed by HESI(+)-FT-Orbitrap MS.