FAST PYROLYSIS OF COCOA BEAN SHELL

VICHO, Maria Milagros[1]; TELLEZ, Jhoan Francisco[2]; MOYANO, Elizabeth Laura[3]

[1,2,3] National University of Córdoba, Organic Chemistry Department, Faculty of Chemical Sciences. Córdoba, Argentina.

INTRODUCTION

The depletion of crude oil reserves and the impact of greenhouse gases on global warming highlight the need to replace petrochemical processes with biomass-based alternatives. Biomass, being a renewable resource, is the only raw material capable of supporting the sustainable production of chemicals. The use of waste biomass has become increasingly important due to its significantly lower cost compared to virgin biomass. In the case of cocoa production, large amounts of by-products, such as pod husks and bean shells, are generated and often considered waste, creating an opportunity to utilize these materials in biomass-based processes. Pyrolysis of these cocoa waste materials can produce bio-oil and other valuable products, contributing to sustainable chemical production and efficient waste management.

METHODOLOGY

Fast pyrolysis experiments were conducted in a quartz reactor under nitrogen to prevent oxygen interference. Biomass was heated to target temperatures (300, 400, or 500 °C) for 20 minutes, and products were collected as solids and liquids. Bio-oil was extracted with acetone and analyzed using GC-MS.

Bio-oils characterization. Bio-oil was dissolved in acetone, homogenized, filtered, and analyzed by GC-MS using a Shimadzu QP-2020 ULTRA spectrometer. Compound identification was based on peak area percentages and databases like Wiley and NIST (> 85% match).

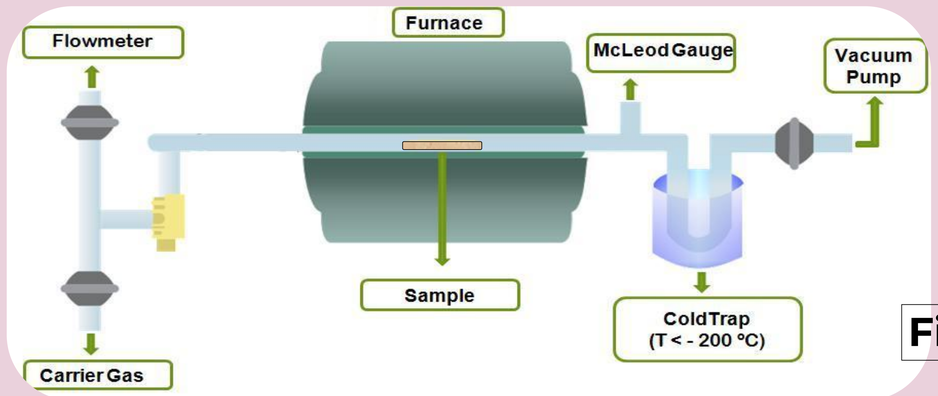

Fig. 1

RESULTS AND DISCUSSION

The variations in the fractions obtained (liquid bio-oil, solid biochar, and gaseous syn-gas) are shown in **Figure 2.**

- Results for untreated cocoa shells (CS) are labeled as 300-CS, 400-CS, and 500-CS, while those for acid-pretreated cocoa shells (CS-A) are labeled as 300CS-A, 400CS-A, and 500CS-A.
- Biochar formation was notably significant, especially at lower temperatures.
- The gaseous fraction was the predominant product, accounting for 47% to 68% w/w, regardless of the biomass used.
- Bio-oil yields ranged from 8% to 20% w/w, aligning with values reported in other pyrolysis studies.
- A slight increase in bio-oil yield was observed when using acid-washed cocoa shells, with maximum pyrolytic oil production achieved at 500 °C for both types of biomass.

Fig. 2

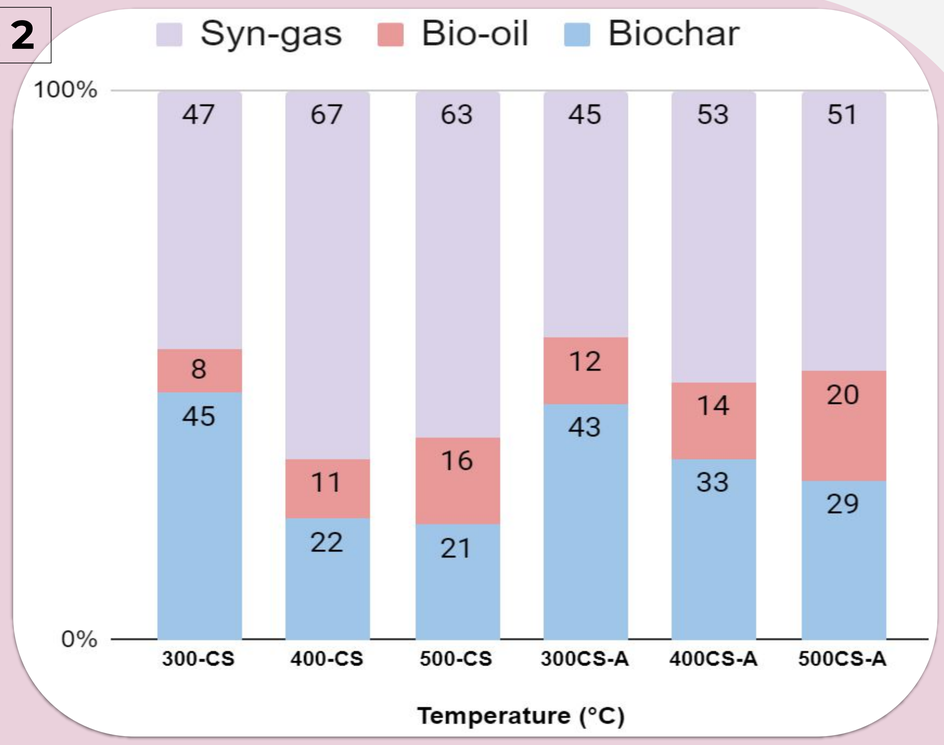

Fig. 3.

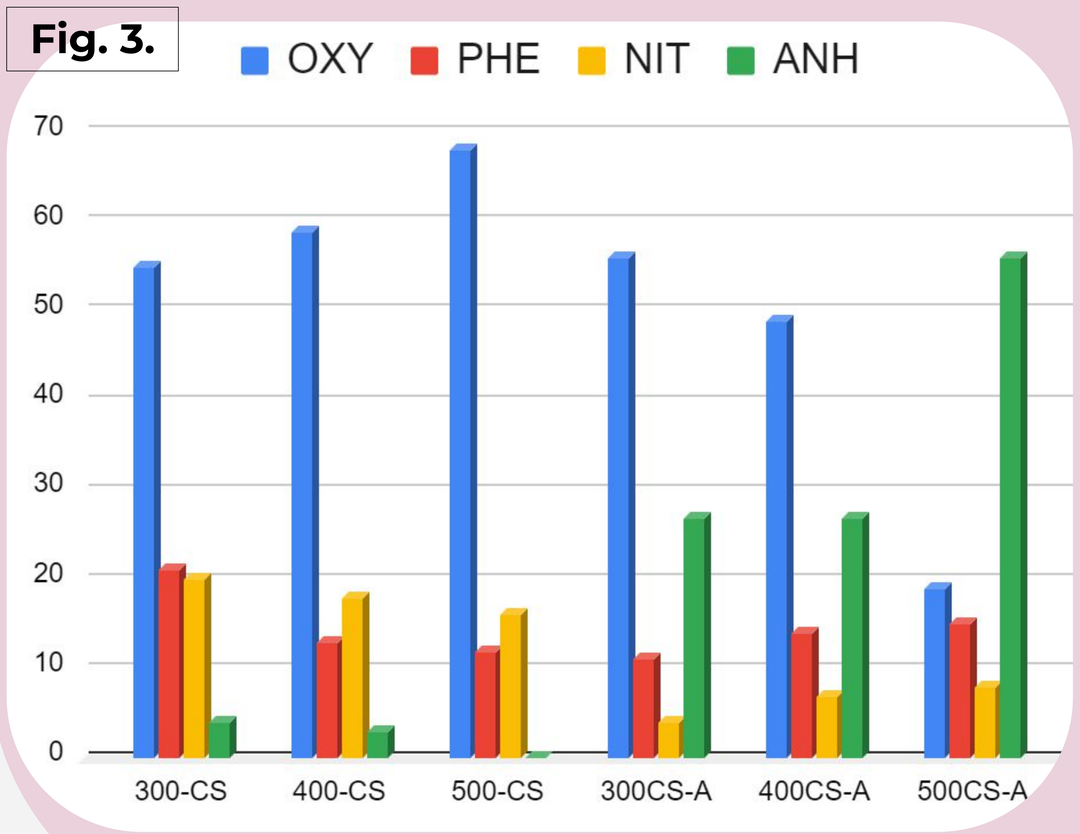

Fig. 3. Composition of bio-oils CS and CS-A. The following groups could be distinguished: OXY: oxygenated, PHE: phenolic compounds, NIT: nitrogenated compounds and ANH: anhydrosugars.

Phenolic compounds were found in small amounts, consistent with previous studies on similar lignocellulosic biomass like cocoa pods. Main derivatives included phenol, cresols, and catechols, derived from lignin fractionation.

Nitrogen-containing compounds, such as caffeine and theobromine, were prominent in raw cocoa shells, confirming the presence of methylxanthines. These valuable compounds can be efficiently extracted using thermal processes.

Oxygenated compounds were detected in all pyrolysis reactions, especially in non-acid-washed bio-oil at 500 °C. Key compounds included fatty acids like palmitic acid, cis-vaccenic acid, stearic acid, and glycidyl palmitate. Palmitic acid was the most abundant, accounting for 20-25% of the oxygenated compounds.

The sugar fraction was prominent in oils from CS-A, with anhydrosugars dominating at 500 °C, where pyrolysis achieved the highest yield, comprising about 55% of the total area. Acid treatment significantly influenced sugar production, aligning with findings in other lignocellulosic biomasses. Levoglucosan was the main sugar, representing ~20% of the total area in 300CS-A and 400CS-A, increasing to 50% in 500CS-A.

CONCLUSIONS. The study explored the fast pyrolysis of cocoa shell (CS) and acid-treated cocoa shell (CS-A) at temperatures between 300 and 500 °C, revealing that acid treatment enhanced bio-oil yields by up to 20% at 500 °C. While untreated CS primarily produced fatty acids at higher temperatures, pyrolysis of CS-A generated bio-oils rich in sugars, with levoglucosan (LG) emerging as the main component at 500 °C. These findings demonstrate that the same biomass can be tailored to produce different high-value compounds depending on the treatment applied, highlighting the potential of cocoa shell, a common waste product, to be transformed into valuable resources. Future research should aim to optimize extraction methods to improve the isolation and recovery of these compounds for broader applications.