

Improving Bio-oil quality by fractional condensation of partially upgraded Fast Pyrolysis vapors

Stefano Dell'Orco^{1,2}, Nolan Wilson³, Braden Peterson³, Chaiwat Engtrakul³, Kellene Orton³, David Chiaramonti^{1,2} and Kimberly A. Magrini³

¹ DIEF/University of Florence, Department of Industrial Engineering, Florence, Italy - ² RE-CORD Consortium, Scarperia, Florence, Italy

³ National Renewable Energy Laboratory (NREL), Golden, Colorado, United States

Introduction

Fast pyrolysis of lignocellulosic biomass produces an organic mixture containing hundreds of compounds with a wide range of molecular weights that are condensed into a bio-oil or aqueous phase. The utilization of condensates from fast pyrolysis is challenging due to several unwanted properties, and in order to be used in specific applications or further upgrading, a separation step is necessary. Isolating different organic fractions can have several objectives: knocking-out of heavy-sugary compounds to improve oil quality, increasing the stability of the bio-oil for transportation by separating acids, separating aqueous and oil phases for further processing, or targeting compounds for co-products and fuel precursor extraction. In this work, an approach has been investigated for the initial separation of the pyrolytic vapors with minimal energy requirements through controlled condensation of the vapor stream in a fractional condensation train (FCT). The FCT is downstream of a catalytic hot gas filter (CHGF) that partially tunes the vapors composition to further improve oil quality.

Materials and Methods

Pyrolysis and CHGF

- Biomass Feedstock: Pine
- Catalysts for vapors upgrading: modified TiO₂.
- Micro-scale pulsed-flow screening tests (Figure 1):
 - WHSV of ~2 h⁻¹ in He or H₂/He mixtures (30 mg of biomass used per pulse in 4 slm carrier gas).
- Continuous pilot-scale tests (Figure 3):
 - WHSV of 2 - 10 h⁻¹ in N₂ or H₂/N₂ mixtures (1.8 kg/h of biomass in 24 slm carrier gas).
- Pyrolysis conducted at 500 °C.
- Catalytic filtration at 400°C.
- Molecular beam mass spectrometry (MBMS) for real-time analysis of products.

Fractional Condensation of Pyrolysis vapors

- Condensation units (Figure 3) comprised of:
 - Passive-cool condenser (HX-02)
 - Electrostatic precipitator (ESP)
 - Cold trap condenser (HX-01)
- Liquid products analyzed in GC-MS
 - organic samples were diluted 20:1 in acetone
 - aqueous samples were diluted 1:1 in methanol

Results and Discussions

Vapors composition tuned by CHGF: from micro-scale pulsed-flow to continuous pilot scale

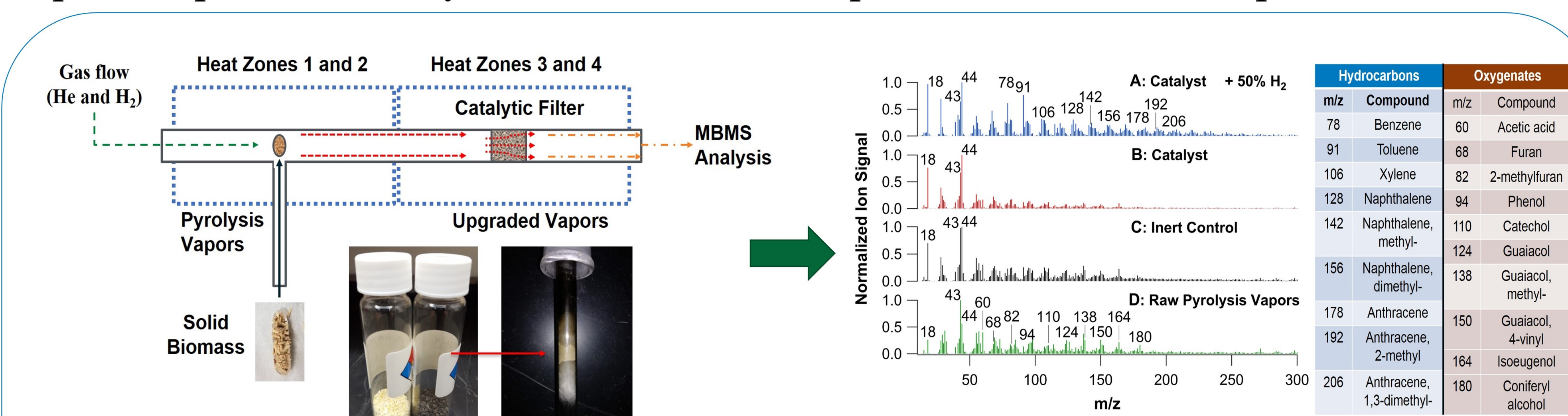


Figure 1. Lab scale pulsed-flow experimental setup showing the horizontal quartz reactor system (upper left) coupled to a molecular beam mass spectrometer (MBMS, right) for real-time analysis of products. Catalyst is shown pre- and post-reaction (coked).

Figure 2. A) Molecular beam mass spectrometer (MBMS) spectra for modified TiO₂ catalyst under 50 vol.% hydrogen (H₂). B) MBMS spectra for catalyst without H₂. C) MBMS spectra for inert control without H₂. D) MBMS spectra for raw pyrolysis vapors without H₂.

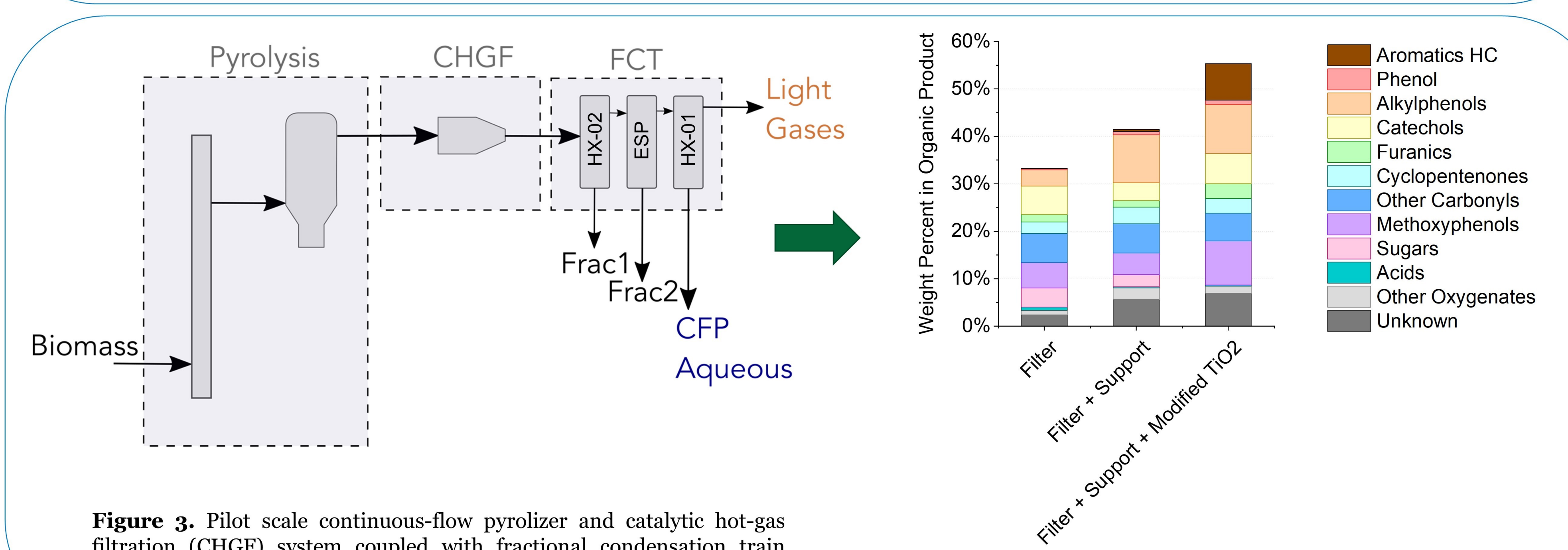


Figure 3. Pilot scale continuous-flow pyrolyzer and catalytic hot-gas filtration (CHGF) system coupled with fractional condensation train (FCT).

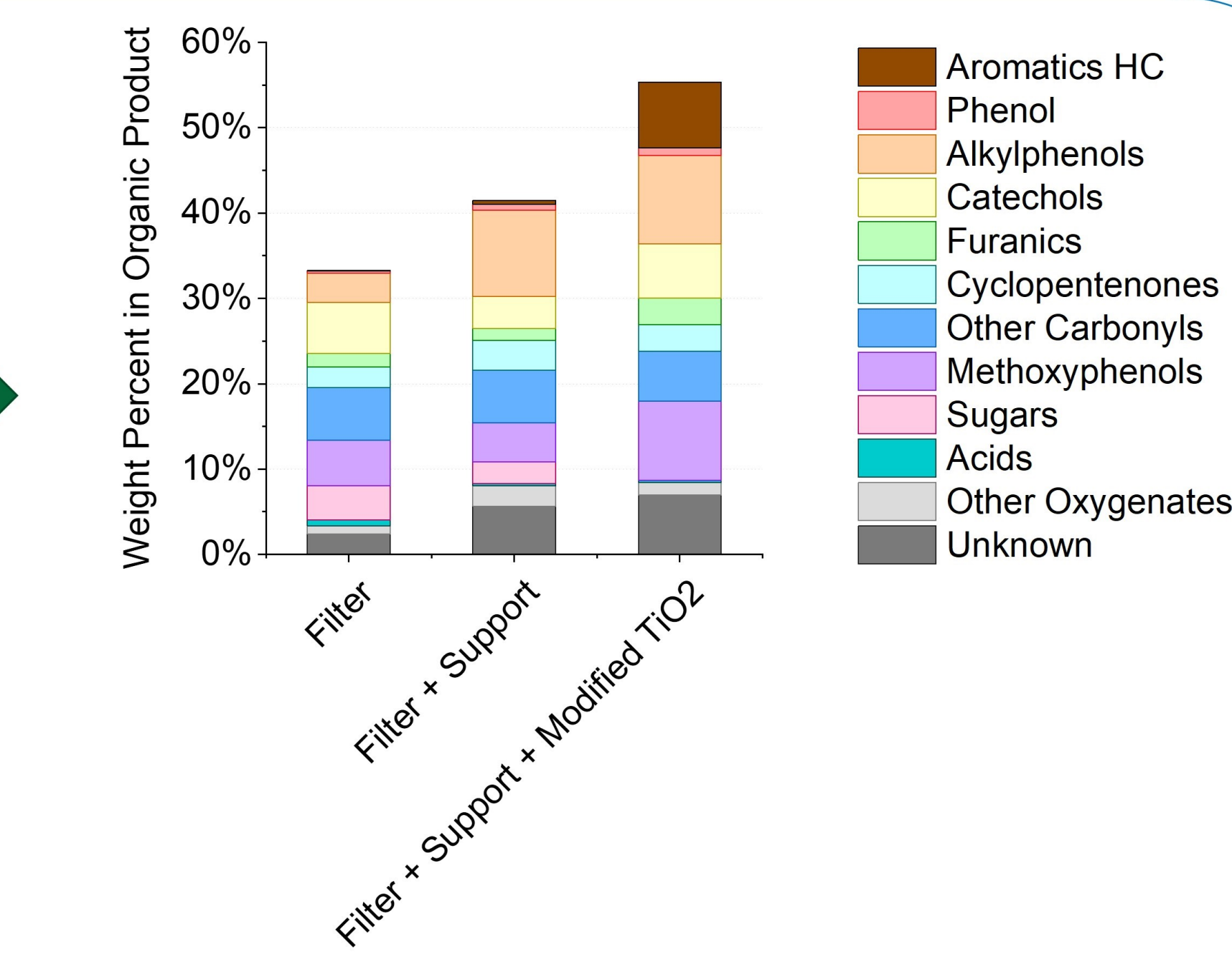


Figure 4. GC-MS data for condensed organic fraction (Frac 1 + Frac 2) with and without partial upgrading with modified TiO₂ and H₂.

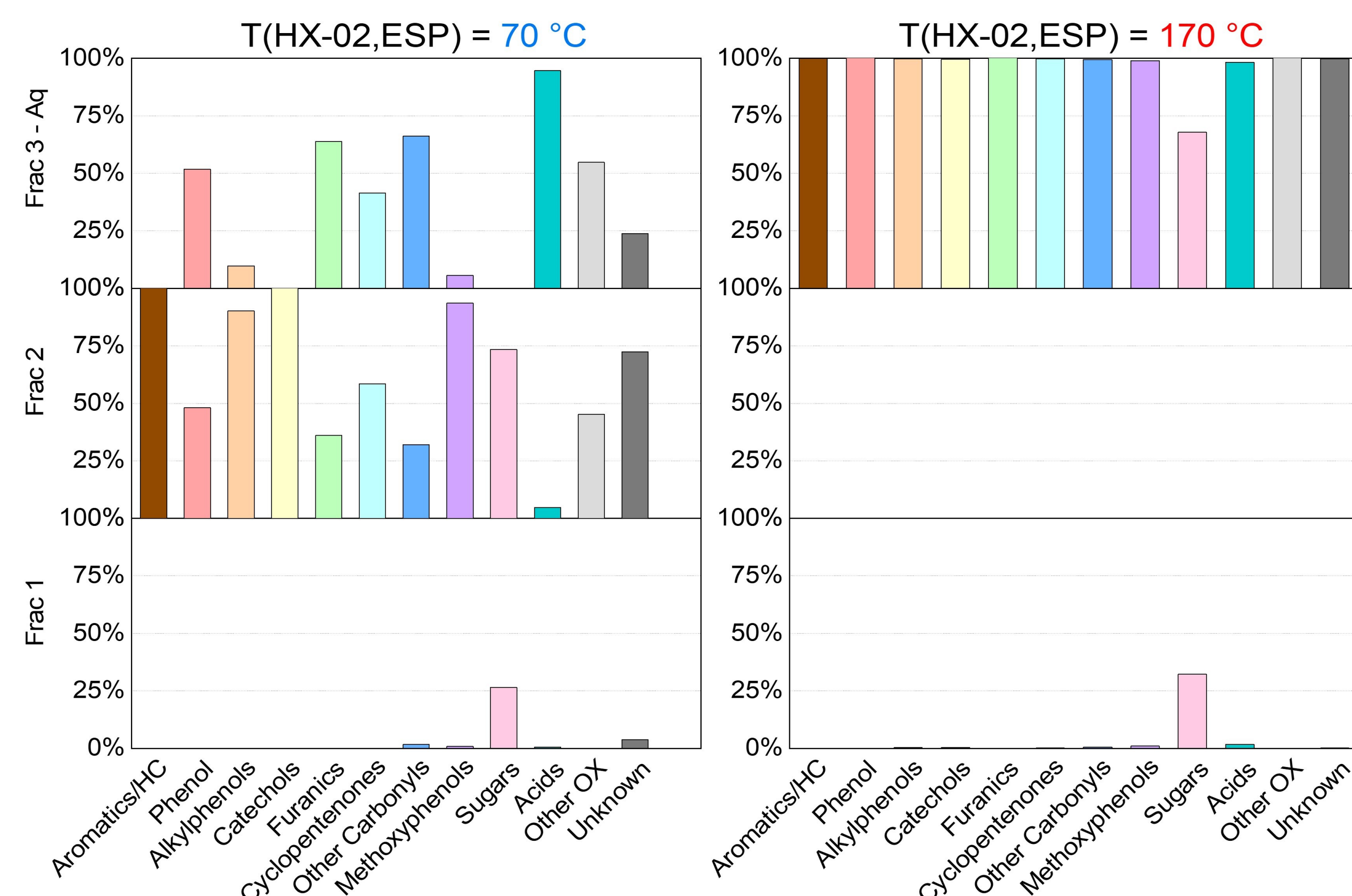


Figure 5. Distribution Plot of Fractions obtained by condensing partially upgraded vapors at different temperatures. HX-02 and ESP set at 70°C (left) and 170°C (right), HX-01 set at -15°C.

Class-selective separation

- Separation mechanism based on compounds dew points
- When HX-02 and ESP were set at 70°C:
 - Acids collected in Frac 3 (aqueous phase)
 - Phenolics remains in Frac 2 (oil fraction)
 - Cyclopentenones and other carbonyls partially separated from oil
 - Aromatics HCs (heavy 2-3 rings) remains in Frac 3
- When HX-02 and ESP were set at 170°C:
 - Heavy sugars (mostly levoglucosan) remain in Frac 1

Conclusions and Future Works

CHGF was successfully implemented using a continuous-flow pilot-scale pyrolyzer unit. This CHGF process produced clean and partially upgraded fast pyrolysis vapors, enhancing aromatic, alkylated hydrocarbons production. Coupling CHGF to a FCT demonstrated an additional means for enhancing oil stability. Class-selective condensation at 70°C was achieved for most of the phenolics compounds and carboxylic acids. Aldehydes and ketones were partially separated from oil. High molecular weight (mostly sugars) were removed at high and low condensation temperature. Future works will investigate more detailed fractionation to separate narrowed cuts for co-products and fuel precursors extraction.

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