

Abstract

Thermochemical conversion of lignocellulosic biomass offers an attractive route to produce fuels and chemicals. Specifically, catalytic fast pyrolysis (CFP) oils have been shown to contain a high concentration of oxygenated aromatics, which can be isolated as value-added co-products. Purification of oxygenated aromatics can be a viable pathway to more economically competitive biorefineries, yet the isolation of highly pure coproduct streams remains technically challenging due to the high chemical heterogeneity of thermochemical process streams. Here, we demonstrate an industrially scalable process for isolating phenol, a widely used precursor to plastics, from CFP oil. Importantly, we leverage standard industrial processes, such as distillation, liquid-liquid extraction, and crystallization, to achieve phenol with 97% purity. In addition, the primary distillation of the CFP oil yielded several other fractions that contain chemicals with the potential to be isolated (e.g. cyclic ketones, cresols, and guaiacols). This work provides a technically feasible path to high purity oxygenated aromatics that has the potential to offset fuel production costs in a biorefinery.

Introduction

Industrially, phenol is produced using the cumene process (Figure 1B), which uses an oxidation of cumene (isopropylbenzene), followed by a Hock rearrangement to produce phenol and acetone¹. The cumene feed required for this process is produced via a Friedel-Crafts alkylation of benzene with propylene², both of which are derived from petrochemical processes. Here, phenol is separated directly from CFP oil (Figure 1A), using three batch distillations and one liquid-liquid extraction before being recrystallized from hexane. Distillations were performed on a B/R instruments 800 micro fractional distillation system (Figure 1C), which simulates 25 theoretical trays using a spinning Teflon band.

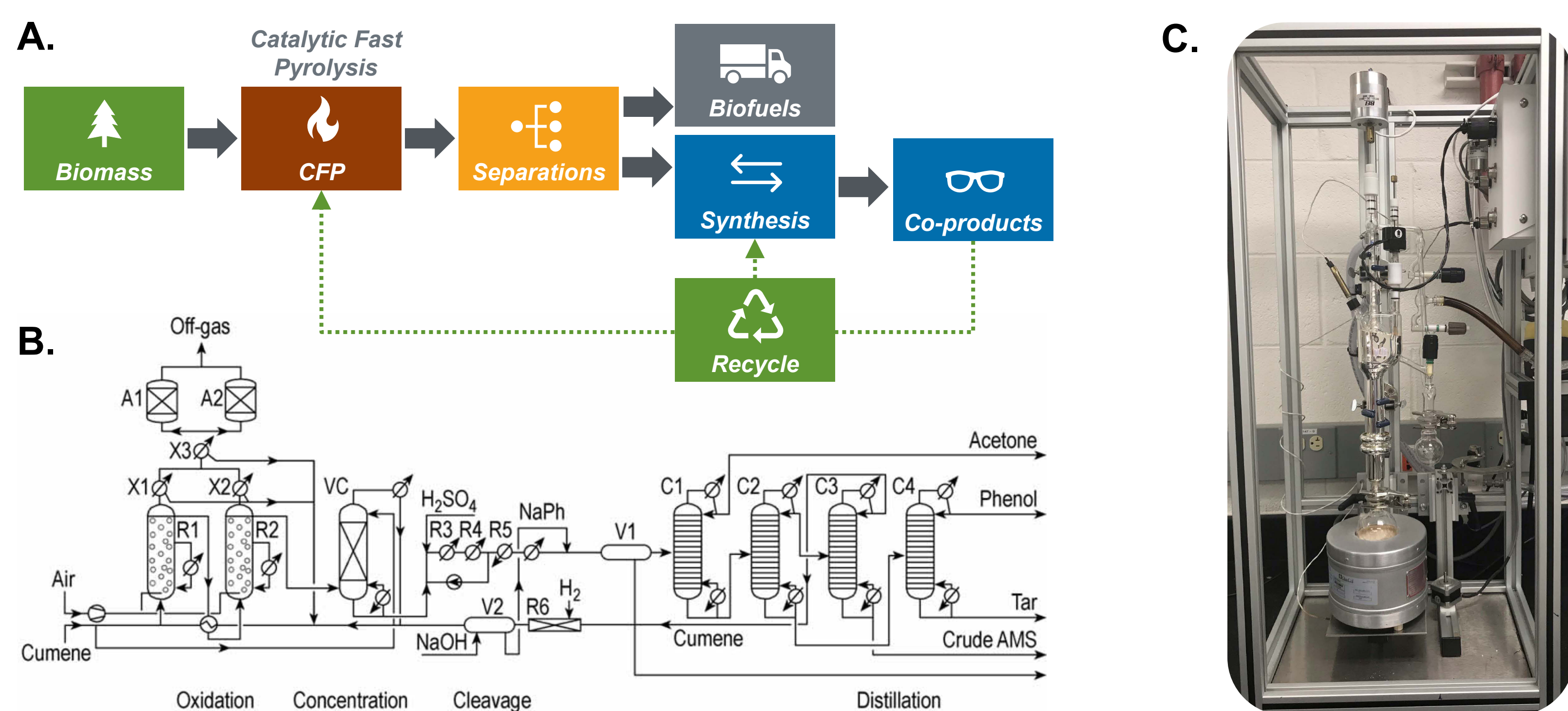


Figure 1: (A) Biomass conversion flow diagram where biofuels can be produced along with polymer products. (B) Cumene process flow diagram¹. (C) B/R instruments 800 micro distillation system.

Experimental

- It was suspected from previous experimental work that phenol and 2-cyclopentene-1-one formed an azeotrope³. A model compound distillation showed that an azeotrope did appear at approximately 179°C at atmospheric pressure (Figure 2A).
- CFP Oil was distilled with fractions collected every 5°C in order to determine the optimal temperature ranges for the first distillation (Figure 2B).
- The azeotrope between phenol and 2-cyclopentene-1-one prevented further purification by distillation beyond the first column, therefore an ethyl acetate liquid-liquid extraction was employed to remove the cyclic ketones. A small-scale study was conducted at various ratios of water to ethyl acetate to determine partition coefficients and yields (Figure 2C).

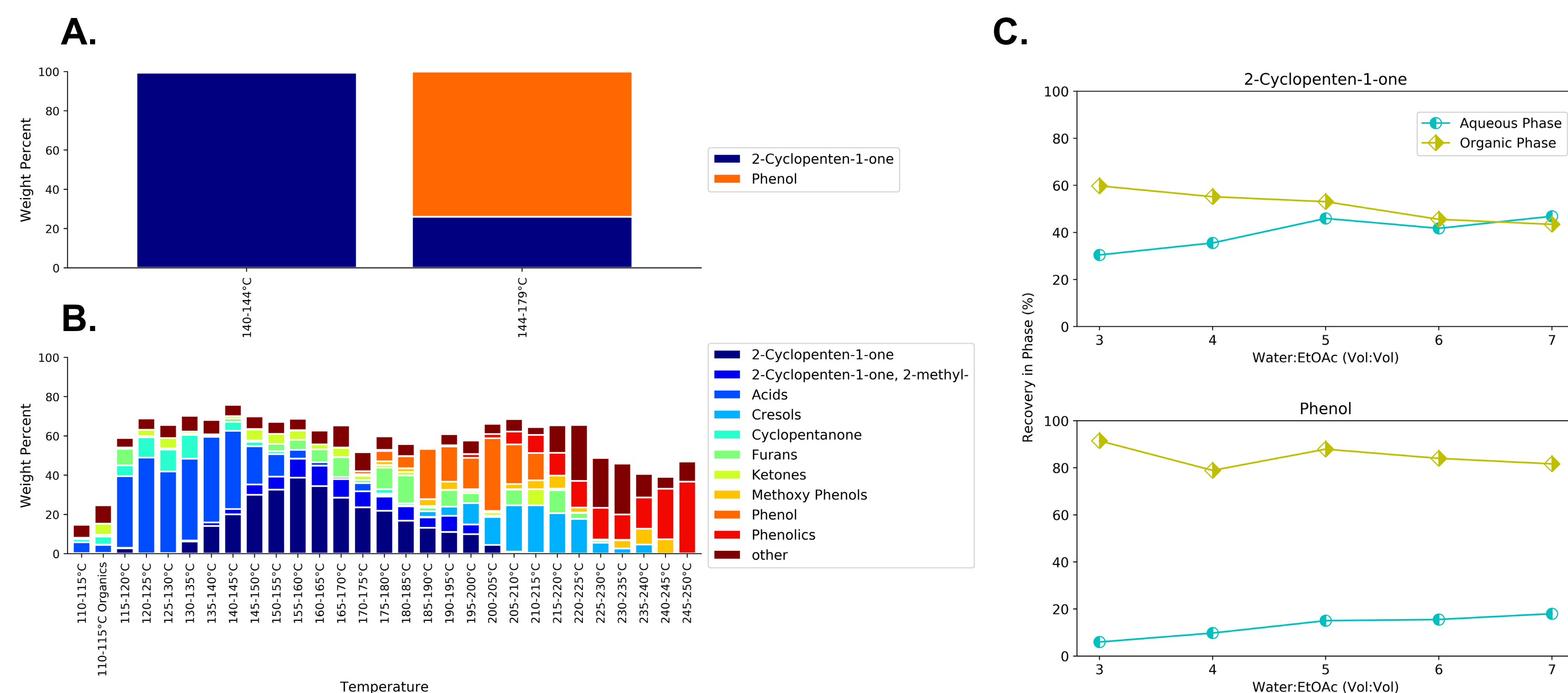


Figure 2: (A) Composition of each distillation fraction from the model compound azeotrope study. (B) Composition of each distillation fraction from the 5°C study. (C) Liquid-liquid extraction product recovery in the aqueous and organic phases as a function of volumetric ratio of water to ethyl acetate.

Results

Raw CFP oil was first distilled into 5 rough fractions: a water fraction, an acids fraction, a cyclic ketone fraction, a phenol fraction, and a phenolic fraction (Figure 3B). An ethyl acetate extraction was employed to break the azeotrope between phenol and 2-cyclopentene-1-one, allowing further purification by two more distillations. Finally, fractions were dissolved in hexanes and cooled to -20°C, resulting in the formation of phenol crystals. The overall phenol yield for the process was approximately 9% (Figure 3A).

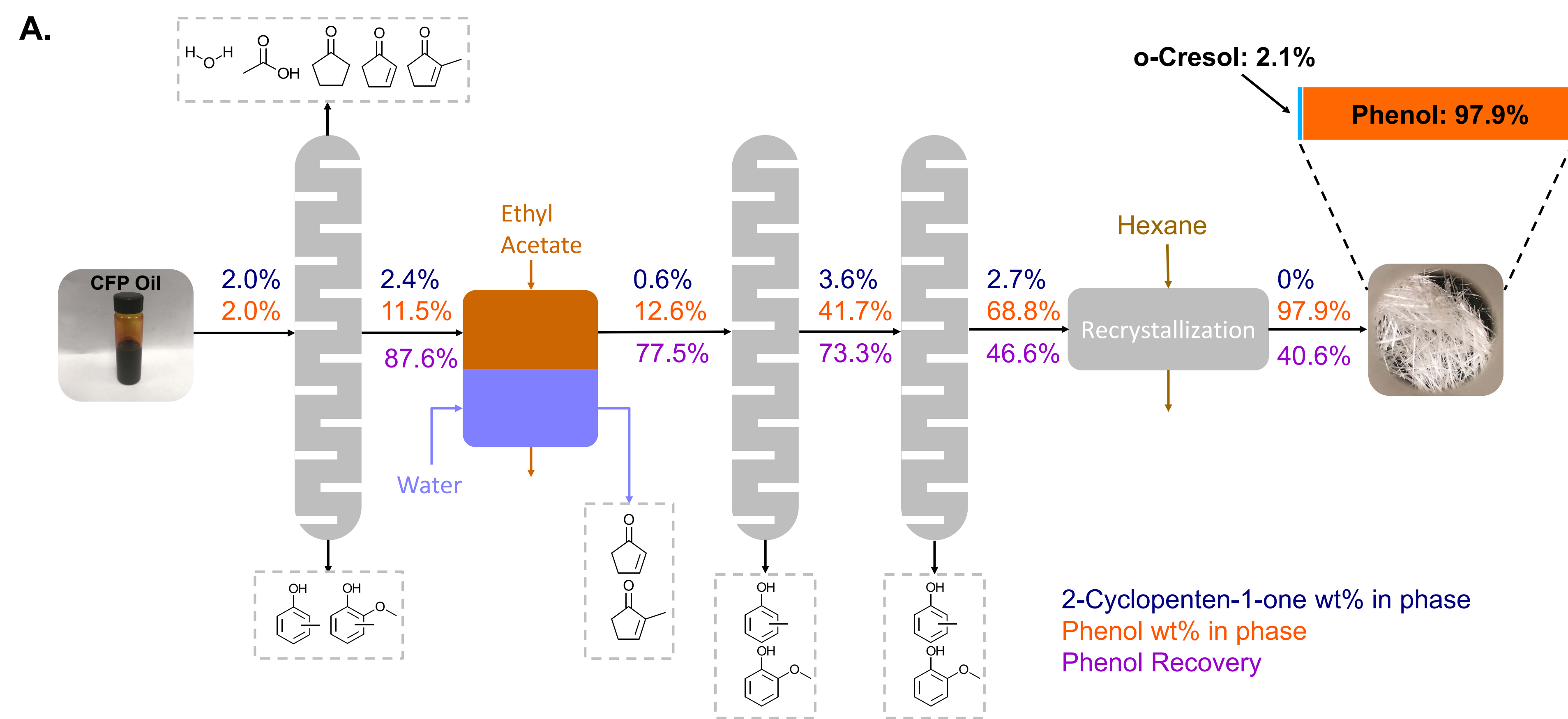


Figure 3: (A) Separation train showing composition by weight of Phenol and 2-Cyclopentene-1-one. (B) Full fractional composition of each distillation, arrows indicate which fractions carried on to the next unit operation

Recrystallized phenol was combined and analyzed using GCMS-FID, ¹H NMR, and differential scanning calorimetry (DSC). Purity calculations using GCMS-FID (Figure 3A) and DSC (Figure 4B) were in good agreement, 97.9% and 97.2%, respectively. The primary impurity is o-cresol (2-methylphenol), as indicated by the appearance of a small peak at approximately 2.3 ppm in the bio-phenol NMR spectrum (Figure 4A).

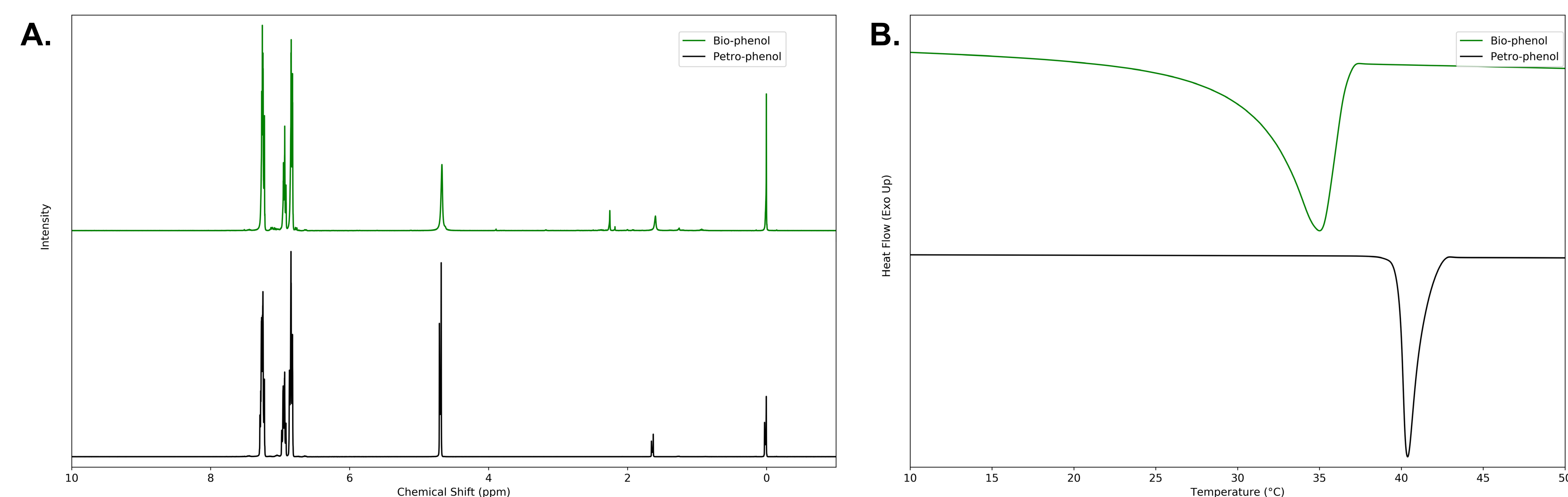


Figure 4: (A) ¹H NMR of the bio-derived phenol, and petroleum-derived phenol purchased from Sigma-Aldrich. (B) Modulated DSC traces of bio-derived phenol and petroleum-derived phenol purchased from Sigma-Aldrich. Traces were taken at 1°C/min under heat-only conditions with a modulation period of 60 seconds.

Conclusions and Future Work

This work shows a scalable route to high purity oxygenated aromatic compounds from CFP oil. These high-value chemicals have the potential to offset the cost of a biorefinery, since they are important precursors in many important industrial products. Namely, phenol, which was separated here to a purity greater than 97%, is widely used in the production of Bisphenol A (BPA), which plays an extremely important role in the production of polycarbonates and epoxy resins. Our future work aims to produce BPA from the phenol separated in this work and acetone that has also been separated from CFP streams, and subsequently, to produce a bio-derived polycarbonate plastic. In addition, product purity and yield is significantly hindered here by the batch operation of the distillation columns. In the future we plan to target these co-products via a continuous distillation apparatus, which will likely have a substantial effect on the yields and purities. Finally, techno-economic analysis will be performed on the process to further assess its industrial viability.

References

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