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Sugar and Phenolic Oligomer Recovery from the Heavy-Ends of Fractionated Bio-Oil

Introduction

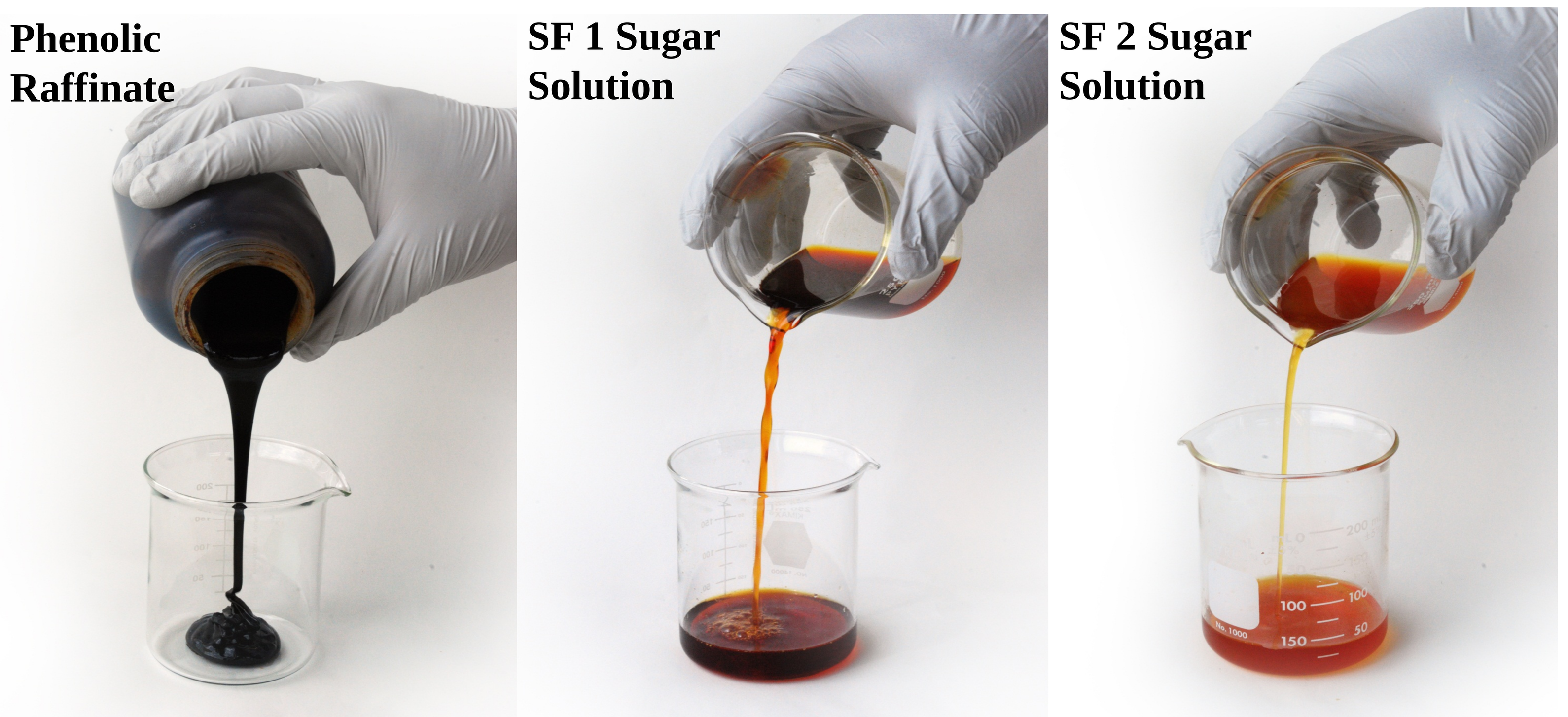
This study explores separate recovery of sugars and phenolic oligomers produced during fast pyrolysis. Bio-oil fractionation is accomplished with a five-stage system, recovering bio-oil according to condensation temperatures of chemical constituents. The first two stages capture "heavy ends"; mostly water soluble sugars and water insoluble phenolic oligomers. Exploiting differences in water solubility allows for recovery of a sugar-rich aqueous phase and a phenolic-rich raffinate. Over 93 wt% of the sugars in stage fractions (SF) 1 and 2 are removed in two water washes. Pyrolytic sugars from SF1 and SF2 are suitable for upgrading to biofuels catalytically or by fermentation. The phenolic raffinate, representing 44-47 wt% dry basis (db) of both SF1 and SF2, is less sticky and viscous than the unwashed SFs. It shows potential for production of fuels, aromatic chemicals, polymers, resins, asphalt, etc.

Materials and Methods

1. Bio-oil was produced in a fast pyrolysis unit consisting of a fluidized bed operated at 450-500°C and a bio-oil recovery system that recovers bio-oil in distinct multiple stage fractions (SF) [1]. A sugar-rich aqueous phase and a phenolic-rich raffinate were separated from SF 1 and SF 2 [2].
2. Bio-oil constituents were evaluated and quantified using GC with a flame ionization detector (GC/FID), acid content was determined by ion-exchange chromatography, sugar content was determined using ultraviolet-visible range spectroscopy [3], and gel permeation chromatography (GPC) was used to determine the molecular weight distributions [2]. Water-insolubles were determined by an in-house method and moisture was determined by Karl Fischer [1]. Ultimate analyses were performed with oxygen determined by difference [2].
3. The minimum amount of water required for the phase separation of bio-oil water-soluble constituents from the water-insoluble constituents was determined by the addition of deionized water drop-wise into SFs 1 and 2 while stirring thoroughly by hand after each addition. The phenolic oligomer-rich raffinate was separated from the water-soluble components using a known amount of oil mixed at different ratios by weight with deionized water.

Results

Sugars and Phenols Recovery from the Heavy Ends of Fractionated Bio-Oil

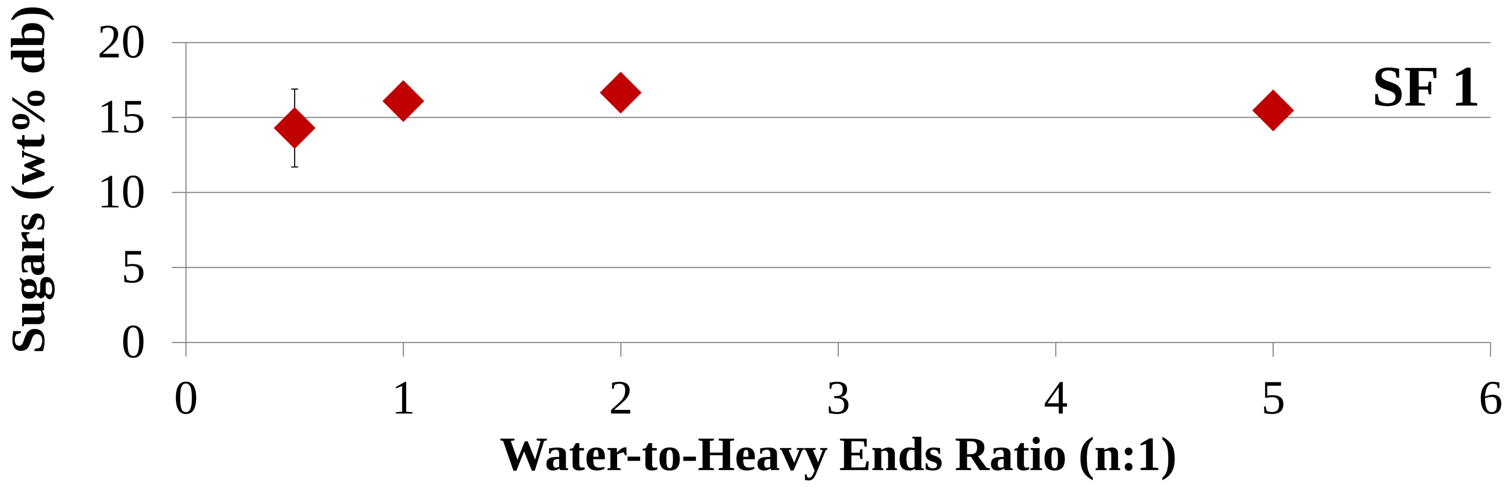


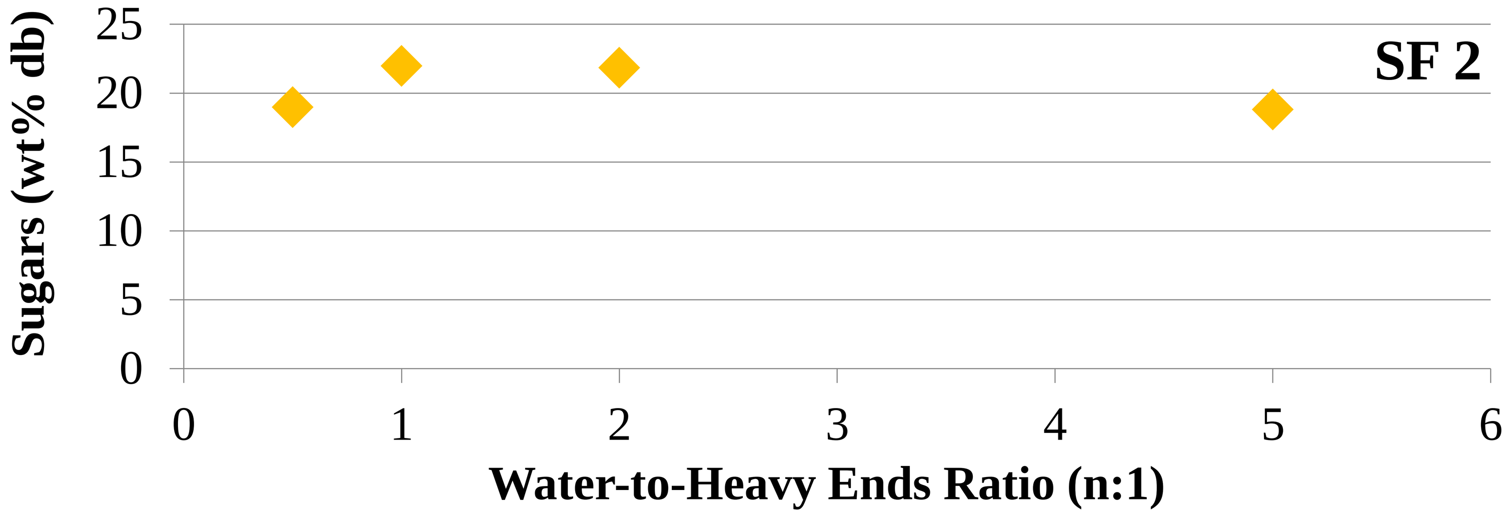
Viscosity Difference


Original Bio-Oil Heated to 80°C


Clean Phenolic Oligomer Raffinate at 21°C After Washing

Extraction of Sugars as a Function of Water-to-Heavy Ends Ratio

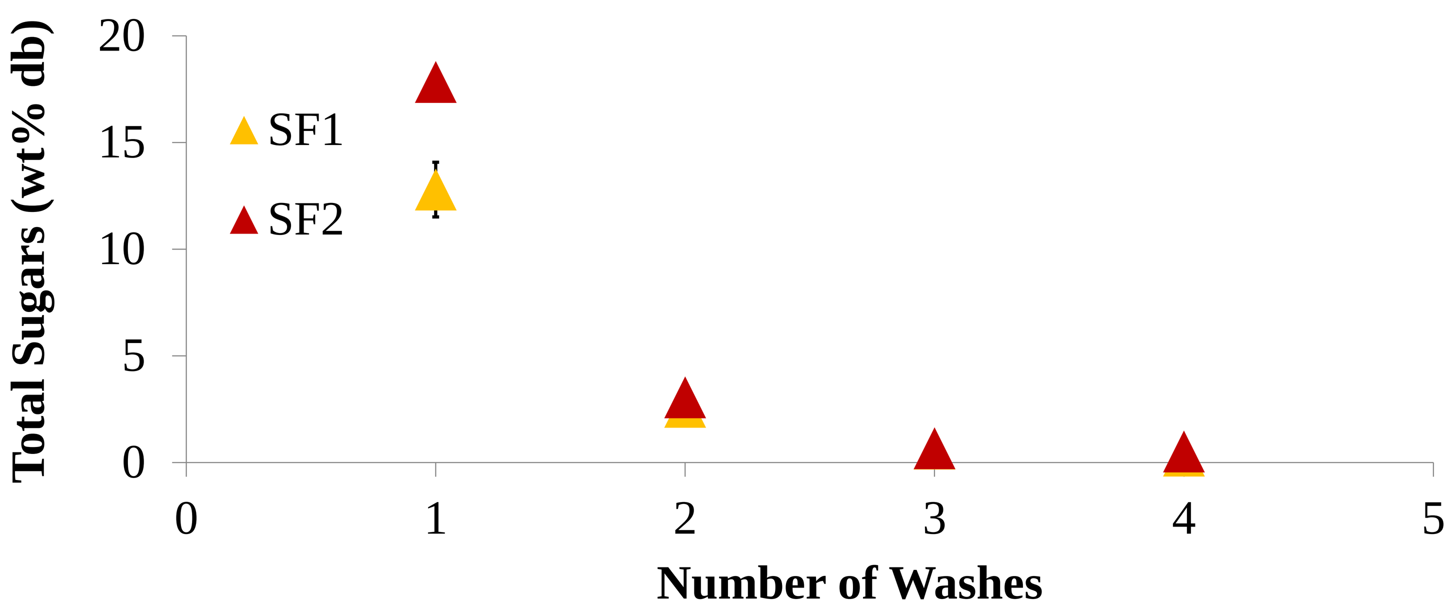


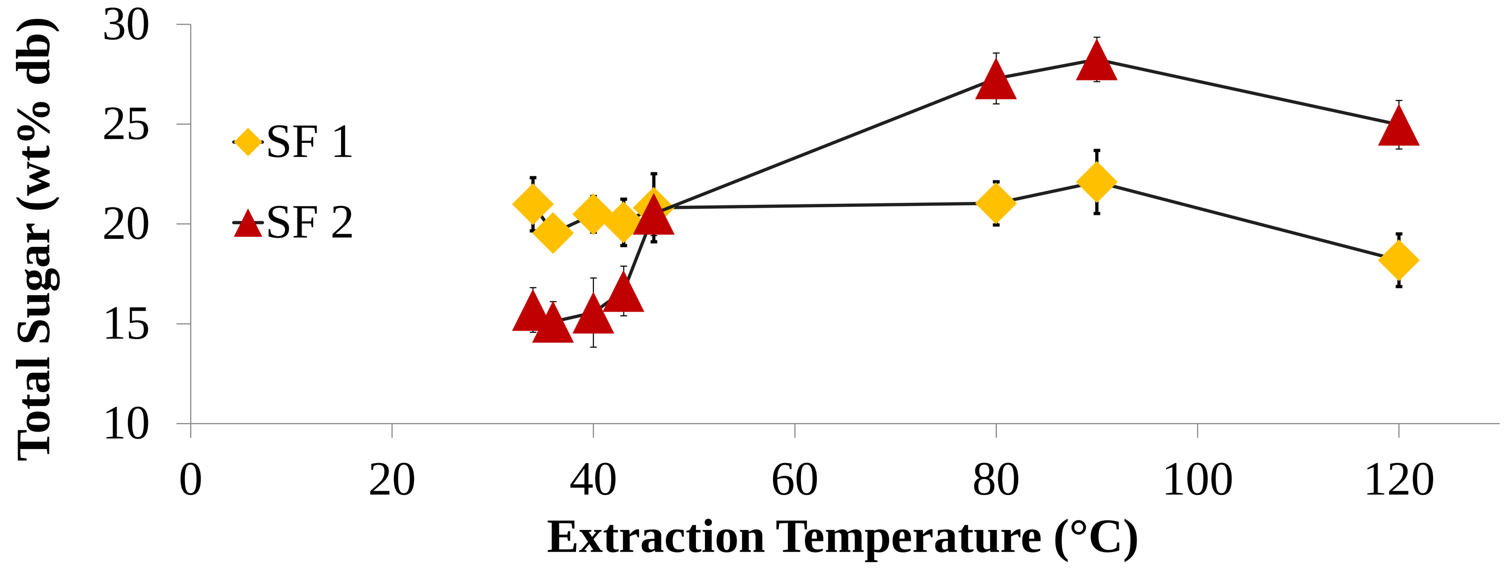


Moisture in Phenolic Raffinate After Removal of Sugars

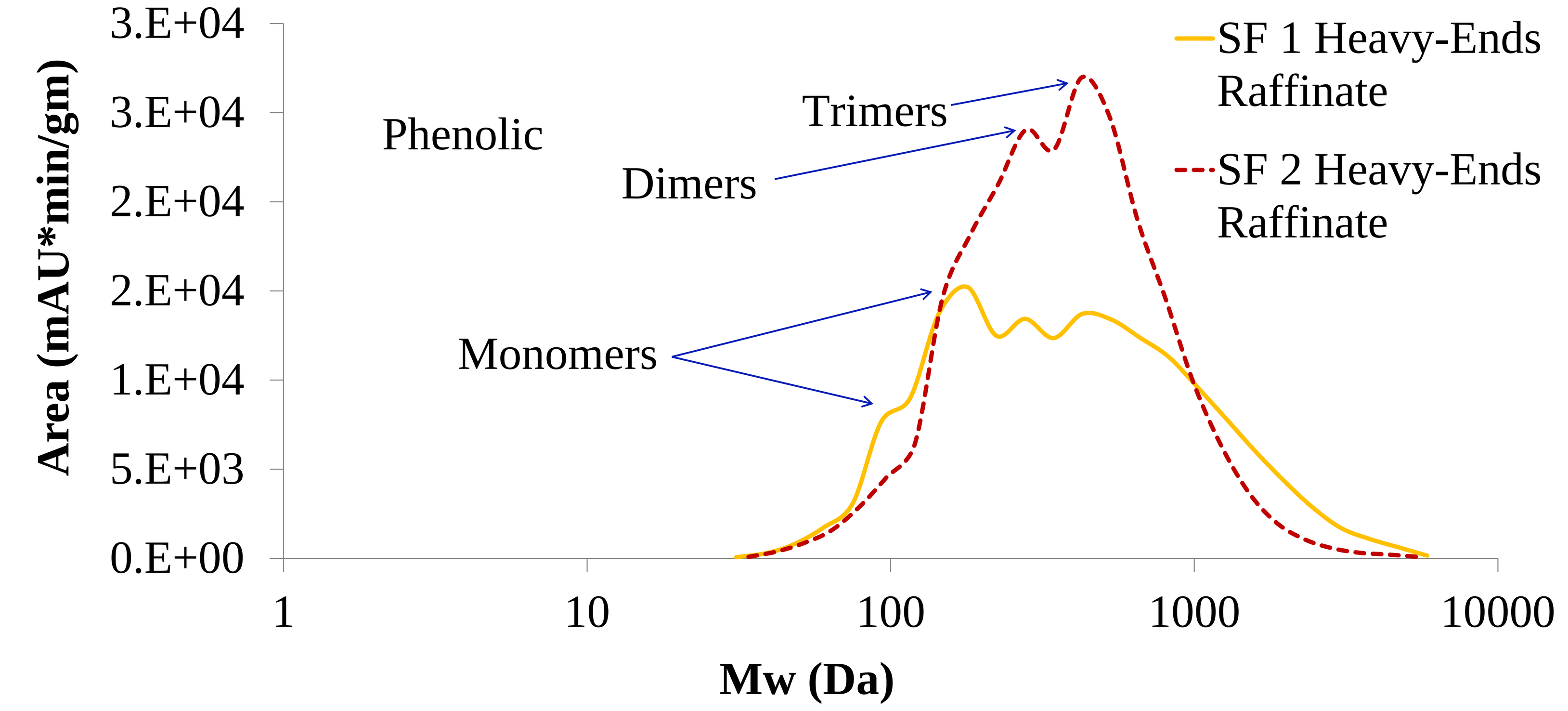
Water-to-Heavy Ends Ratio	Phenolic Oligomer-Rich Raffinate SF1 Moisture (%)	Phenolic Oligomer-Rich Raffinate SF2 Moisture (%)
0.5:1	27.02±1.74	22.57±0.70
1:1	18.30±0.17	17.94±0.49
2:1	22.57±0.42	22.02±0.59
5:1	21.89±0.62	19.70±0.26

One Wash at 80-100°C is Sufficient





Raffinate Relative Molecular Weight Distribution



Conclusions

1. We successfully demonstrated the ability to separate sugars and lignin-derived phenolic oligomers from the heavy fractions of biomass.
2. The sugars were extracted effectively at over 93 wt% with two water washes.
3. Approximately 3-7 wt% of other water-soluble or partially soluble constituents were removed with the water-soluble sugars.
4. This research has shown that sugars and phenolic oligomers can be separated, providing two separate streams for fermentation, catalytic upgrading, or other kinds of conversions to value-added products.

References

1. A.S. Pollard, M.R. Rover and R.C. Brown, *Journal of Analytical and Applied Pyrolysis*, (2012).
2. M.R. Rover, P.A. Johnston, R.G. Smith, R.C. Brown, under review, *Bioresource Technology*, (2013).
3. M.R. Rover, P.A. Johnston, B.P. Lamsal, R.C. Brown, accepted *Journal of Analytical and Applied Pyrolysis*, (2013).

https://www.cset.iastate.edu/tcbiomass2013/

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