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Comprehensive Thermal Degradation Study of Bio-Oil Phenolic Oligomers

Introduction

Bio-oil from fast pyrolysis is a promising economical approach to advanced biofuels production and is considered a potential candidate to replace or reduce the use of petroleum fuels. Bio-oil is unstable under long-term storage or upon heating. Understanding the thermal stability of bio-oil is important to upgrading it to transportation fuels, especially if it is to be integrated into petroleum refining operations. The release of vapors from bio-oil samples and their correlation to molecular structure will provide insight for both emissions, as well as sample degradation characteristics that occur during heating processes for specific upgrading technologies. This study explores the thermal behavior of bio-oil phenolic oligomers for its potential to be successfully upgraded to liquid fuels. Bio-oil fractionation was accomplished utilizing Iowa State University's five-stage system that recovers bio-oil as stage fractions (SF) according to the constituents condensation points. The first two SFs collect "heavy ends" comprised of both water-soluble sugars derived from polysaccharides and water-insoluble phenolic oligomers derived from lignin. The phenolic oligomers were heated by a thermogravimetric analyzer (TGA) to determine weight loss characteristics from 30-350°C. Vapors were also collected during the experiments and gel permeation chromatography (GPC) analyses were utilized to determine relative molecular mass. The phenolic oligomer volatiles from SF 1 showed molecular weight (Mw) ranges consistent with monomers-pentamers while SF 2 showed molecular weight ranges consistent with monomers-hexamers. The GPC studies indicated SF 2 phenolic oligomers were more stable versus SF 1.

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 SFs [1]. SF 1 and SF 2 were included in this study.

2. The weight loss analyses were done using TGA. The bio-oil sample size was approximately 45 mg. Approximate temperature ramps included 30-50°C, 50-105°C, 105-150°C, 150-200°C, 250-300°C, 300-350°C, 350-400°C at a rate of 5°C min^{-1}. Each endpoint in the individual ramp was held 30 minutes prior to proceeding to the next ramp. Nitrogen purged the system at 100 mL min^{-1} for the entire experiment.

3. GPC was used to determine the molecular weight distributions [2] of the residue remaining after each temperature ramp and hold time. The polystyrene standards used had a molecular weight range of 162 – 38,640 g mol^{-1}. Each initial sample size was approximately 60 mg. After each temperature ramp the residue remaining in the cup was put into tetrahydrofuran (THF) to dissolve the THF solubles. A new sample cup was placed on the TGA and the temperature ramp was followed until reaching the next highest hold temperature of the preceding sample until reaching 300°C.

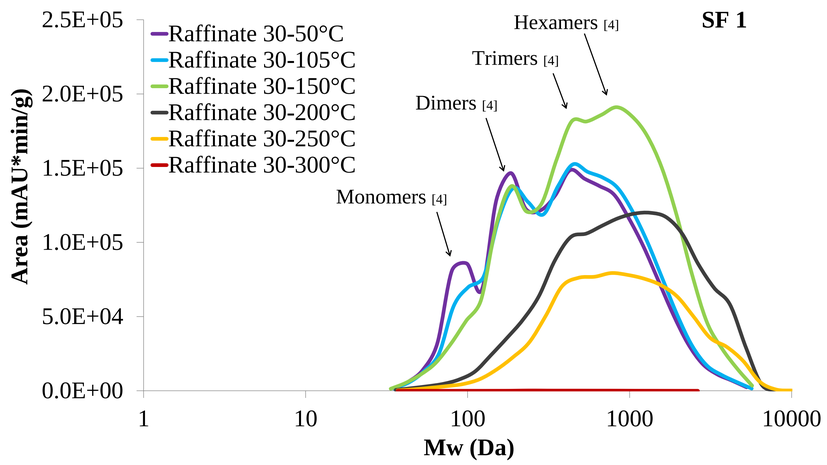
4. The relative molecular weight distribution of the volatiles was also performed using the same described methodology. Each approximate initial sample size was 180 mg. The first sample was not acquired until after the 150°C hold time. The next sample was acquired after the 200°C hold time and so forth until after the 350°C hold time. The volatiles were captured in a 25 mL impinger utilizing ice as the coolant and THF as the solvent. These samples were analyzed by GPC, as previously described.

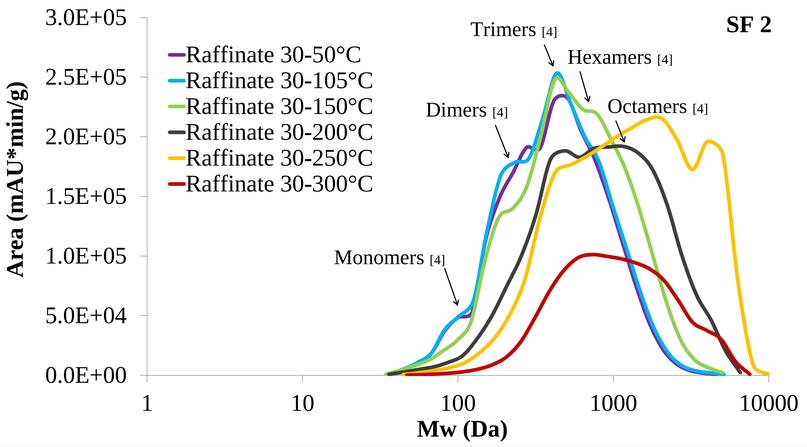
Results

SF 1 and SF 2 Phenol Oligomeric Raffinate Weight Loss (30- 400°C)

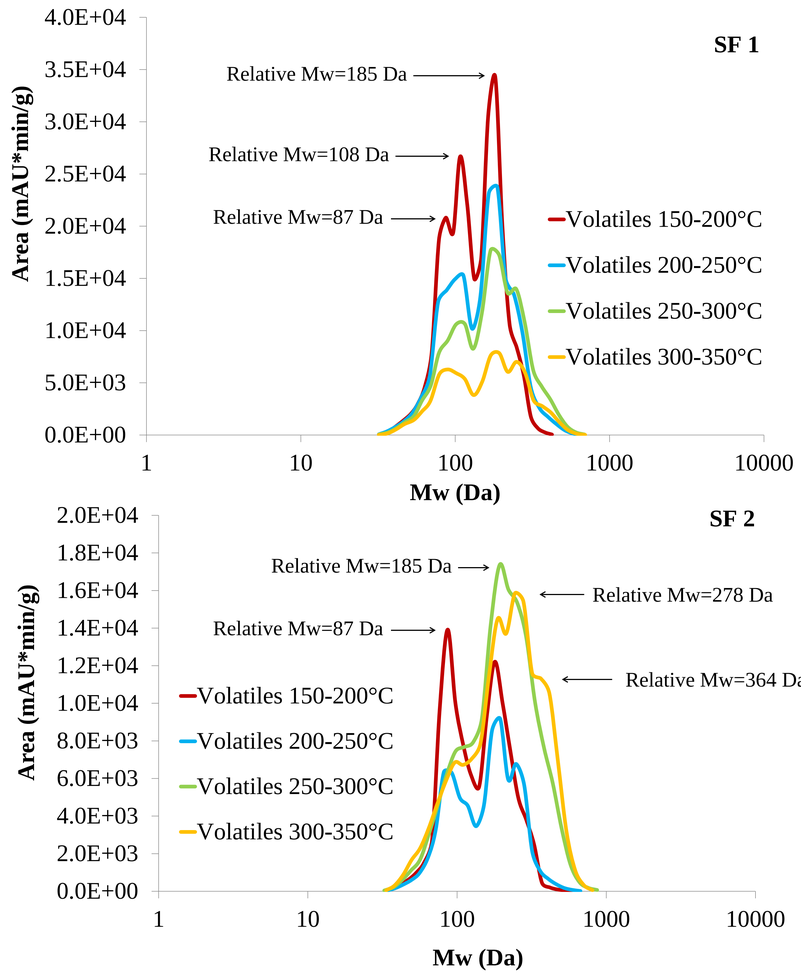
Temperature Range (°C)	SF 1 Residue Remaining (wt%)	Temperature Range (°C)	SF 2 Residue Remaining (wt%)
33 - 57	90.5	31 - 56	91.7
58 - 108	80.3	57 - 108	83.5
108 - 155	70.4	108 - 152	77.3
153 - 201	59.7	152 - 201	67.8
201 - 251	51.8	201 - 253	58.1
251 - 301	44.8	252 - 302	46.3
302 - 352	39.5	304 - 353	39.2
352 - 402	35.7	355 - 403	35.5

SF 1 and SF 2 Raffinate Relative Molecular Weight Distribution





Relative Molecular Weight of Raffinate Volatiles SF 1 and SF 2



Conclusions

1. SF 1 and SF 2 contain 44-47 wt% phenolics (22-24 wt% g/g whole bio-oil).
2. SF 2 phenol oligomeric raffinate appears to be more stable than SF 1
   - Dramatic increase in molecular weight does not occur until 200°C, whereas SF 1 occurs at 150°C.
   - The 300°C SF 1 raffinate sample was not soluble in THF while SF 2 raffinate was.
3. SF 2 raffinate is comprised of larger molecular weight species versus SF 1.

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. Mullen CA, Boateng AA. Characterization of water insoluble solids isolated from various biomass fast pyrolysis oils. *Journal of Analytical and Applied Pyrolysis* (2011).

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

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