Tribal Communities Care about Effluents:
Tracking Extractives, Inhibitors & Reaction Products in Bisulfite Processing

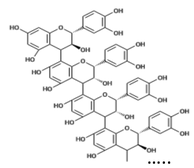
Karl R. Oleson and Daniel T. Schwartz
Chemical Engineering, University of Washington, Seattle, Washington 98195, USA

Background

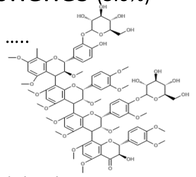
Traditional pulping studies show that the most toxic effluents arise from the extractive components of the feedstock [1], though carbohydrate and lignin degradation products can be important as well. The extractive components are typically 4-10% of wood feedstocks [2]. Some of the most important extractives in the effluents include tannins, resin acids, and sterols. Tannins can be 50% of the total Chemical Oxygen Demand in wastewaters [3]. Resin acids are the most toxic of extractives and are lethal to fish at ppm levels [4]. Sterols are endocrine disruptors in higher organisms [5]. To the best of our knowledge, no forest-residue-based biofuel process analysis has tracked the flow of extractives with this level of molecular specificity. We also track lignin and carbohydrate degradation products.

Quantifying Extractives in Douglas Fir

Tannins and Phlobaphenes (3.0%)

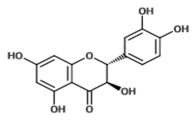


Condensed Tannin (1.9%)

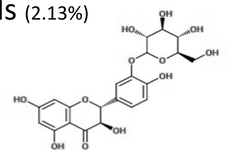


Phlobaphenes (1.1%)

Flavonoids (2.13%)

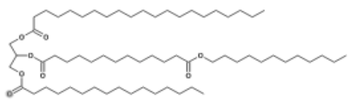


Dihydroquercetin (Taxifolin) (1.06%)

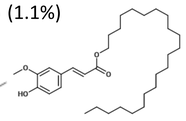


Dihydroquercetin -3'-O-β glucopyranoside (1.07%)

Fats and Waxes (1.1%)

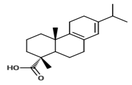


Triglycerides (.9%)



Ferulic Acid Esters (.2%)

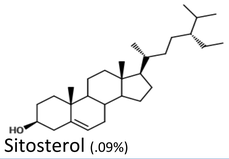
Diterpenes (.28%)



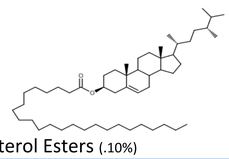
Palustric Acid (.17%)

Thunbergol (.1%)

Phytosterols (.19%)



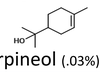
Sitosterol (.09%)



Sterol Esters (.10%)

Monoterpenes (.09%)

α-Pinene (.06%)



Terpineol (.03%)

P-cymene

* Quantities of components are reported on an o.d. weight and estimated from pulp and paper literature about Douglas fir spanning over 60 years [e.g. 6-9].

Bisulfite Process Modeling Methods

Aspen Plus V8.6

Douglas Fir Slash Model	Weight %
Cellulose and Hemicellulose	63.6%
Lignin	29.3%
Ash	0.2%
Protein	0.2%
Tannin	1.9%
Phlobaphene	1.1%
Dihydroquercetin-3'-o-glucoside	1.07%
Dihydroquercetin	1.06%
Triglyceride	0.9%
Ferulic Acid ester	0.2%
Palustric Acid	0.17%
Thunbergol	0.1%
Sitosterol Ester	0.1%
Sitosterol	0.09%
α-Pinene	0.06%
Terpineol	0.03%
Total Non-Carbohydrate Extractives	6.8%

100 kg o.d. biomass basis

Pretreatment Reactor

3:1 liquid to solids

Heat Exchanger

25° 1 bar

Pressing to remove SSL

Pretreated Pulp

40% solids

Enzymatic Saccharification

Spent Sulfite Liquor (SSL)

- Fermentation
- Incinerate
- Cement additive
- Waste

Aspen Component Data

Thermodynamics Properties

- NRTL used when parameters available
  - UNIFAC used to estimate data when NRTL data unavailable
- Water solubility data used when available
  - assumed to be either soluble or insoluble if data is unavailable.

Aspen Model Validation

- NRTL thermodynamics compared to thermodynamic data for monoterpenes and agreement was reasonable [10]
- Values for diterpenes and phytosterols in SSL consistent with observed concentrations leaving sulfite pulp mills

Reactions from Literature

Carbohydrate and Lignin Reactions:

- Carbohydrate conversions from Gao's 2013 Mild Bisulfite Paper [11]
- Lignin conversions yields from Leu's 2013 SPORL paper [12]

Extractives Reactions

* All extractive reactions assumed to go to 50% completion

1. Dihydroquercetin 3'-O-β glucoside + H_2O → Dihydroquercetin + glucose
2. 2 Dihydroquercetin + $2HSO_3^-$ → Quercetin + $S_2O_3^{2-}$ +3 H_2O
3. Condensed tannin or phlobaphene + HSO_3^- → Condensed Tannin + Epicatechin – (4 β) – sulphonate
4. Ferulic Acid ester + H_2O → Ferulic Acid + Lignoceryl Alcohol
5. Sitosterol Ester + H_2O → Sitosterol + Lignoceric Acid
6. α-Pinene + $2HSO_3^-$ → p-Cymene + $S_2O_3^{2-}$ + $3H_2O$

Aspen Stream Results

Components	Pretreated Pulp	SSL
Water	101.73	598.221
Cellulose	48.308	
Glucose	0.746	4.385
Mannose	0.635	3.732
Galactose	0.095	0.556
Xylose	0.176	1.032
Arabinose	0.014	0.079
Lignin	19.416	
Soluble Lignin	1.526	8.972
Furfural	0.068	0.397
HMF	0.162	0.953
Acetic Acid	0.27	1.588
Ash	0.2	
Protein	0.029	0.171
Tannin	0.138	0.812
Phlobaphene	1.1	
Epicatechin – (4 β) – sulphonate	0.138	0.812
Dihydroquercetin-3'-o-glucoside	0.078	0.457
Dihydroquercetin	0.102	0.602
Quercetin	0.681	0.023
Triglyceride	0.45	
Glycerol	0.005	0.031
Lignoceric Acid	0.067	0.392
Ferulic Acid ester	0.1	
Ferulic Acid	0.006	0.033
Behenyl Alcohol	0.009	0.056
Palustric Acid	0.159	0.011
Thunbergol	0.1	
Sitosterol Ester	0.117	
Sitosterol	0.001	0.001
α-Pinene	0.004	0.026
Terpineol	0.004	0.026
p-Cymene	0.004	0.026
Total Non-Carbohydrate Extractives	3.263	3.308

Conclusions

- Extractives propagate through bisulfite processes in different ways
  - Resin acids primarily follow the pretreatment pulp stream, but remain in the spent sulfite stream in toxic concentrations
  - Tannins and flavonoids leave in both streams
  - Phytosterols preferentially leave in the pulp
- Many thermodynamic parameters have not been reported for the extractives, thus requiring estimates based on molecular structure
- Bisulfite Processes will need to include ways to treat or utilize extractive as well as sulfite products

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