Efficacy of shrub willow biomass as a chemical feedstock

Andrew Freiburger,[1] Dalila G Kovacs,[1] James J Krikke,[1] Erik Nordman[2]

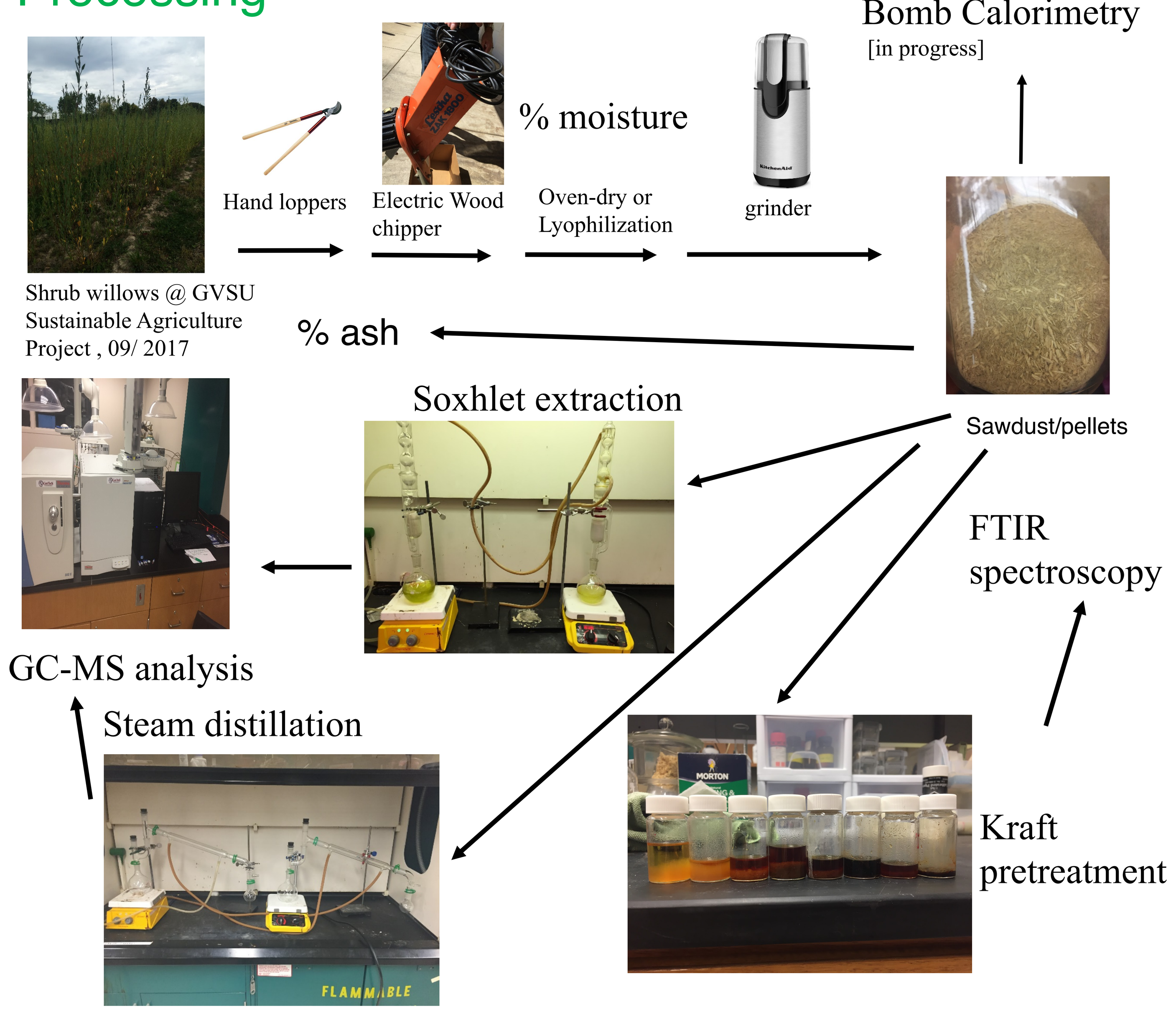
[1]Chemistry, [2]Natural Resource Management, Grand Valley State University, Allendale, Michigan 49401

GVSU Green Chemistry

Overview

- Contemporary sources of biomass – e.g. corn, soybeans, and sugarcane – bear substantial carbon footprints, which diminish the sustainable nature of the feedstocks.
  - **Water:** Per L of biofuel produced from corn, soybean, and sugarcane, 2.01, 15.63, and 1.47 m^3, respectively, are required [Yang et al., **2009**].
  - **Fertilizers:** Corn requires 302 lb of fertilizer per year [USDA, **2016**].
  - **Food**: Using these crops for biomass diverts food from the estimated 810 million hungry people globally [*World Health Organization,* **2018**].
- By contrast, woody biomass requires no deliberate watering or fertilizer application to optimally grow.
  - **Shrub willow** is a fast-growing woody biomass that is native to temperate deciduous environments, and has thus been recently investigated by groups in New York [Volk et al., **2005**], Finland [Dou et al., **2016** and **2019**], Sweden [Mola-Yudego et al., **2008**], and the UK [Vincent et al., **2018**], to name a few studies. There are, however, few studies of willow biomass in Michigan.
- To expand the literature pertaining to willow biomass – a promising alternative feedstock – this interdisciplinary research project was created between the chemistry and biology departments of GVSU.
  - **Research goal:**
  - Characterize 4 varieties of shrub willows and compare with literature values
  - Explore pretreatment methods for future applications in valorization of the willows towards high-value chemical.
  - Create undergraduate, laboratory-scale, procedures for analysis of alternative feedstocks
- The willows were **physically examined** for % moisture & % ash, which are two essential considerations in large-scale biorefinery processes. Ash specifically can pose a major problem for biomass processing techniques, especially pyrolysis, where deposits or corrosive complexes can degrade machinery.
  - The enthalpy of combustion is currently under investigation and may bear importance for understanding the energetic potential of willow biomass.
- The willows were **chemically examined for** % extractable – via steam distillation and Soxhlet extraction (using DCM, hexanes, ethanol, and acetone) – extractable composition – via Gas Chromatography Mass Spectrometry – and lignified matter by the Kraft process and Soxhlet extraction – via Infrared Spectroscopy.

Processing



Experimental

Acquisition of sample

- Branches, ~½ in - 1in thick, were cut and subsequently chipped to ~4 inch long with a Lescha-Zak 1800 electric chipper. The chips were then manually trimmed to ~1in x ~⅓ in x ~⅓ in. Dried chips were ground in a 'Kitchen Aid' coffee grinder.

% moisture

- **Oven drying:** *Thermo Scientific oven*, @ 80°C for 3 days.
- **Lyophilization (freeze drying):** *1 liter Labconco Freezone Lyophilizer,* @ ~0.01 mBar and -50°C for 3 days.
- $\% \, moisture = \frac{initial\ mass - final\ mass}{initial\ mass}$

% ash

- Platinum crucibles were cleaned in a muffle furnace for ~1 ½ hours @ 575°C. ~5 grams of the ground dry sample were tested for ~2 ¾ hours @ 575°C.
- $\% \, ash = \frac{initial\ mass - final\ mass}{initial\ mass}$

Steam distillation

- 250 mL of HPLC-grade water with ~11g of ground dry were distilled for 1 hour. 100mL of distillate was separated from aqueous via liquid-liquid extraction, using hexanes or ethyl acetate and NaCl. The organic fractions were dried with $MgSO_4$ and evaporated with N_2 gas.

Soxhlet extraction

- Cellulose thimbles were filled with ~12g of ground/dried samples and extracted with ~275mL of solvent (hexanes, acetone, ethanol, or dichloromethane) for 6 hours (~55 reflux cycles). Concentrated extracts were examined via GC-MS and UV-Vis spectroscopy. Although acetone and ethanol extracts are quantitatively similar, ethanol qualitatively outperforms acetone, and was thus used for comparative analysis of each willow variety.
  - Thermo Focus DSQ-II GC-MS
    - Column: 15 meter DB-5 MS, Restek
    - Flow rate (He): 1 mL per minute
    - Temperature profile:
      - 2 minutes @ 40ºC
      - 2ºC per minute to 325ºC
      - 2 minutes @ 325ºC
- $\% \, extraction = \frac{initial\ mass - final\ mass}{initial\ mass}$

Kraft Pretreatment

- 5%, 10%, and 10% sodium hydroxide solutions were heated to boiling. 10.00mL were pipetted while hot into vials containing ~1.5g of dried and Soxhlet extracted sample. The samples were either heated @ ~80°C or only stirred for an addition few days. Undigested wood was filtered and the solution was examined via IR spectroscopy
  - Precipitates of the solutions were additionally filtered and examined via IR spectroscopy.

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Results

Table 1: % moisture, % ash, and % extractable (via Soxhlet). A further description of the trials is located below the data table.

Wood sample	% moisture total biomass oven-dried (except were noted)	% Ash dehydrated samples	% Extractable dehydrated samples (Ethanol, Acetone, DCM, Hexanes)
New[1] Old[2]	50.06 ± 0.71 19.76 ± 0.26	2.862 ± 0.037 2.44 ± 0.27	11.05, —, 3.54, 1.69 12.3, 10.5, 3.87, 1.99
Fish Creek (*Salix purpurea*)	43.6 ± 1.6 42.3[3]	1.51 ± 0.24	9.8 ± 1.1
Fabius (*Salix viminalis* x *Salix miysbeana*)	52.2 ± 2.0 53.6[3]	2.39 ± 0.37	11.22 ± 0.90
SX-64 (*Salix miyabeana*)	50. ± 2.2 50.4[3]	2.53 ± 0.67	12.42 ± 0.40
Millbrook (*Salix purpurea* x *Salix miyabeana*)	51.6 ± 1.2 51.1[3]	2.72 ± 0.53	10.72 ± 0.70

[1] "New" denotes wild shrub willows which were found growing in a ditch near the cultivated plot at GVSU. These are a wild comparison to the cultivated varieties.

[2] "Old" denotes an amalgamation of cultivar cuttings which were left beside the farm house for ~5 months.

[3] Lyophilized sample

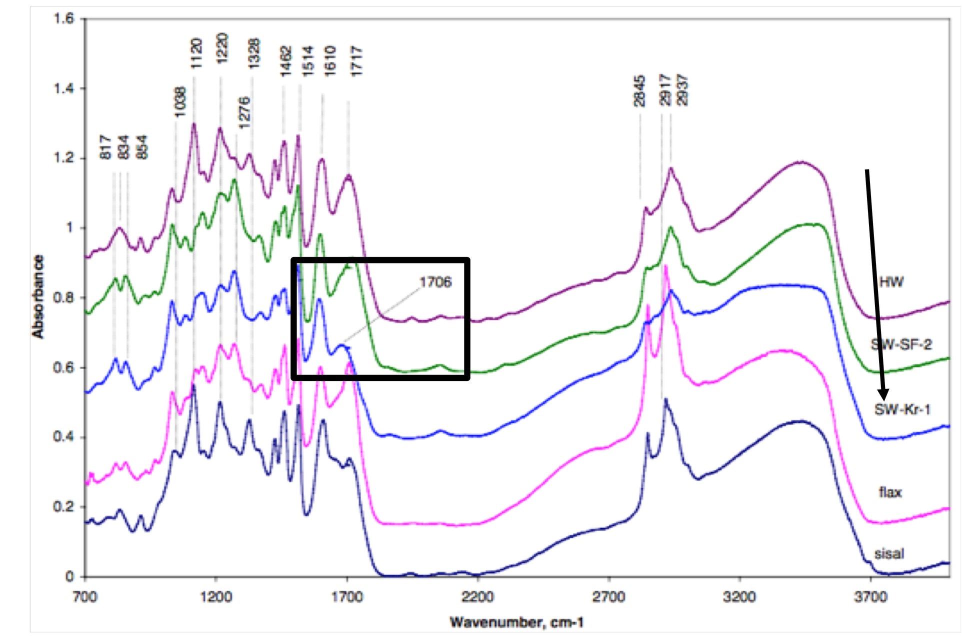


Figure 2 (left): Literature IR spectra for pretreated wood samples [Boeriu et al., **2004**]. The SW-Kr-1 trial is soft wood treated via the Kraft process. The boxed 1706 cm^{-1} peak matches an observed peak in willow kraft delignified sample (figure 3 below).

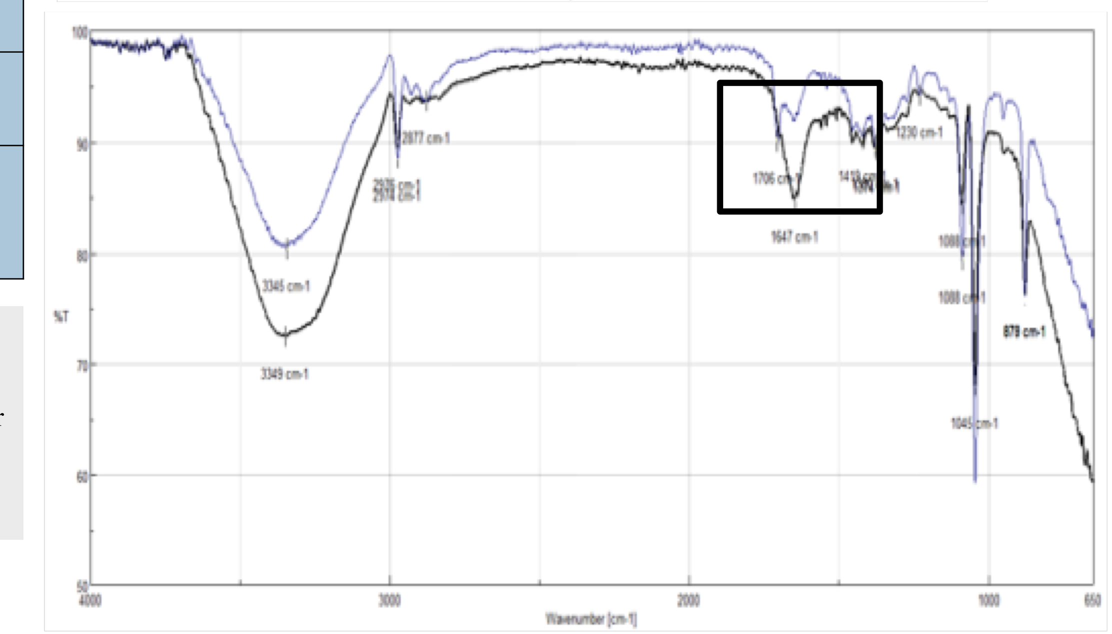
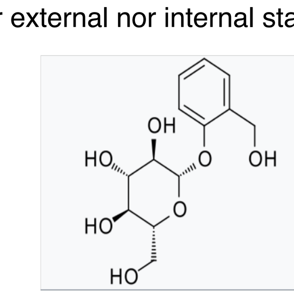


Figure 3 (left): IR spectra of 10% Kraft trial – heated sample on top and the stirred-only sample on bottom. The boxed 1706 cm^{-1} peak matches the literature peak (figure 2) and suggests that willow is depolymerized with ≥ 10% hot sodium hydroxide.

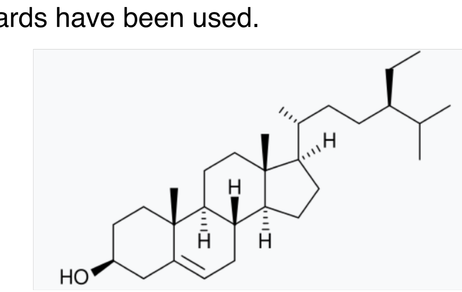
Table 2: Selected Compounds (identified via MS library) with area % GC integration* for each willow species.

Compound / Sample	(2E)-3,5-dimethyl-2-Hexene	cis-Aconitic anhydride	Catechol	Salicylic alcohol	2-hydroxy-Aceto-phenone	Levoglucosan	(E)-Coniferol	Palmitic acid	Salicin	Hepta-cosane	b-Sito-sterol	a-Amyrin	Asta-xanthin
SX-64	3.78	2.65	7.33	2.95	8.99	7.37	3.61		19.99		9.53		
Fish creek	2.17		2.74	1.85		7.15			**43.29**	3.73	10.2		2.46
Millbrook	2.35	1.75	4.83	2.75	3.11	5.19		**11.06**	27.17	2.17	7.87	3.28	3.02
Fabius		2.51	**22.26**			**13.15**	4.95	2.22	11.56		**13.24**	2.23	2.29

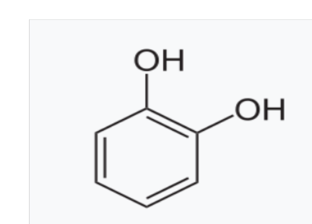
*Neither external nor internal standards have been used.



Salicin

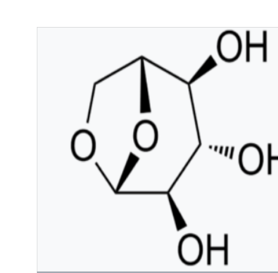


b-Sitosterol



Catechol

Palmitic acid



Levoglucosan

Conclusions

- Fishcreek possesses the lowest quantity of ash and moisture, and the highest proportion of Salicin, which qualities suggest that it may be the most promising willow variety for biorefinery applications.
- Air-drying specimens significantly reduces the % moisture without changing the % extractable, and may be a cost effective method drying biomass.
- Continuously heated solutions of ≥ 10% sodium hydroxide solutions are supported to delignify willow biomass.
- Undergraduate experimental procedures were developed for the characterization and pretreatment of alternative feedstocks.

Future Work

- Complete enthalpy of combustion experiments and calculations.
- Explore other methods of degrading lignocellulose – e.g. pyrolysis, sulfuric acid treatment – and derivatize high value chemicals.