Hybrid shrub-willow biomass as potential raw material for platform molecules

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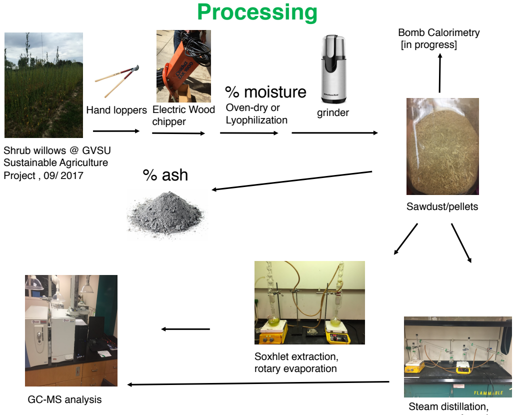
Overview

- **Shrub-willow** is a fast growing woody biomass that is native to the Mid-West region of the United States. It is adapted to the local environment and, therefore, does not need agricultural inputs (fertilizers, pesticides, water,) or arable land. Due to its fast growth rates, it also rapidly sequester atmospheric carbon. These qualities have made it the subject of recent research as a source of biomass for platform molecules and biofuels in the Mid-West region (http://www.esf.edu/willow).
  - shrubs develop ~10-20 small branches from a single seeding stick and reach 20+ ft. after 3 year of growth (https://doubleavineyards.com/sx64).
  - willows are harvested in 3 year cycles for 5+ harvesting cycles (15 years!) (https://doubleavineyards.com/sx64)
- **Research goal**:
  - explore the potential of shrub-willows as a competitive source of biomass, compared to corn and sugarcane in the mid-west region of the United States, and areas of similar climate.
  - understand the physical and chemical characteristics of the willow-shrubs, to potentially increase the efficiency of refining this biomass into value-added products, and, thereby, making them cheaper and more competitive with corn and sugarcane.
- **Physical characteristics** determined in this project:
  - % moisture & % ash: two essential considerations in large-scale biorefinery processes. Ash can be a major byproduct and the water can interfere with the conversion of the biomass into value-added products
  - heat of combustion, currently under investigation, is critical for understanding the energetic potential of willow biomass for producing biofuels (ethanol, butanol, furan derivatives), or being used as fuel.
- **Chemical composition** of the extractable mix was explored with GC-MS and UV-Vis spectroscopy. Extractions solvents included: hexanes, acetone, dichloromethane (DCM), and ethanol (EtOH). Ethanol was selected as the best solvent for its high % extractable value and its benign toxicological qualities.

Processing



Experimental

Processing

- Sample of sticks & branches, ~½-1 inch thick, were chipped into ~4 inch long chips with a Lescha-Zak 1800 electric chipper and manually trimmed afterwards to ~½-1 x ~⅓ inches. Chips were dried and moisture content determined. Dry chips were processed in a 'Kitchen Aid' coffee grinder to a uniform sawdust material.

% moisture

- **Oven drying:** Thermo Scientific oven, at 80°C, for 3 days. The moisture content was determined for the mass of the sample before and after drying.
- **Lyophilization (freeze drying):** A 1-liter Labconco Freezone Lyophilizer equilibrated at ~0.01 mBar and -50ºC, for 3 days. The change in the sample mass, before and after the process, allow % moisture calculations

% ash

- Platinum crucibles were heated in a muffle furnace at 575°C for ~1½ hours. After cooling, they were loaded with ~5 grams of the ground dry sample, and placed in the oven at 575°C for ~2¾ hours, and then weighed. The % ash content was determined form the ash collected.

Steam distillation

- 10-11g of ground dry sample in 250 mL of HPLC-grade water was heated and stirred while distilling, for 1 hour. The distillate was separated with a separatory funnel, with additional solvent, either hexanes or ethyl acetate, and 2-3 scoopfuls of NaCl. The resulting organic fractions were dried with $MgSO_4$ and the solvent evaporated with a stream of N_2 gas.

Soxhlet extraction

- ~12g of ground/dried samples, in a cellulose thimble, and 250mL of solvent, either hexanes, acetone, ethanol (EtOH), or Dichloromethane (DCM), were refluxed in a Soxhlet apparatus for 6 hours (~ 70 reflux-cycles). Extracts were concentrated via rotary evaporation. The mass of sample added to the thimble was compared against the mass of the post-extraction sample to determine the % extractable. Although acetone and ethanol extracts are quantitatively similar, the composition of the ethanol extract was more easily identifiable on GC-MS, hence EtOH was used for all subsequent extractions.

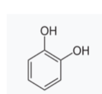
GC-MS

- Thermo Focus DSQ-II GC-MS
  Column: 15 meter DB-5 MS, Restek
  Flow rate: 1 mL per minute of Helium gas
  Temperature profile: 2 min. @ 40ºC, 12°C/min. to 325°C, 2 min. @ 325°C.

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

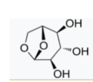
Compound / Sample	(2E)-3,5-dimethyl-2-Hexene	cis-Aconitic anhydride	Catechol	Salicylic alcohol	2-hydroxy-Aceto-phenone	Levoglucosan	(E)-Coniferol	Palmitic acid	Salicin	Hepta-cosane	β-Sito-sterol	α-Amyrin	Asta-xanthin
SX-64	3.78	2.65	7.33	2.95	8.99	7.37	3.61		19.99		9.53		
Fish creek	2.17		2.74	1.85		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

*Standards have not yet been used.

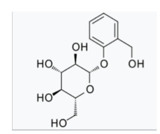


Catechol

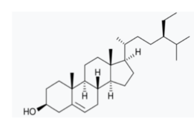
Palmitic acid



Levoglucosan



Salicin



β-Sitosterol

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	% Ash dehydrated samples	% Extractable dehydrated samples: Ethanol	% Extractable dehydrated samples: DCM Hexane
New[1]–1 New –2	50.77 49.35	2.90 2.72	11.05	1.69 3.69
Fish Creek (*Salix purpurea*)	44.8 ± .3[2] 42.4[3] T-test[4]: 12	1.5 ± .4[2] T-test[4] : 2.24	4 ± 4[2] 11.05[3] T-test[4]: 2.8	
Fabius (*Salix viminalis* x *Salix miysbeana*)	53.7 ± .2[2] 53.6[3] T-test[4]: 0.67	2.5 ± .6[2] T-test[4]: 0	10 ± 2[2] 9.2[3] T-test[4]: 0.73	
SX-64 (*Salix miyabeana*)	51 ± 2[2] 50[3] T-test[4]: 0 .72	2.5 ± .6[2] T-test[4]: 0.076	12.2 ± .3[2] 9.6[3] T-test[4]: 12.7	
Millbrook (*Salix purpurea* x *Salix miyabeana*)	52.2 ± 0.9[2] 51.1[3] T-test[4]: 1.8	2.8 ± .9[2] T-test[4] : 0.35	7 ± 6[2] 12[3] T-test[4]:1.0	

[1] New-1,2 are different processing batches from the same harvest of a wild willow shrub that was growing near the cultivated samples. They were both oven-dried.

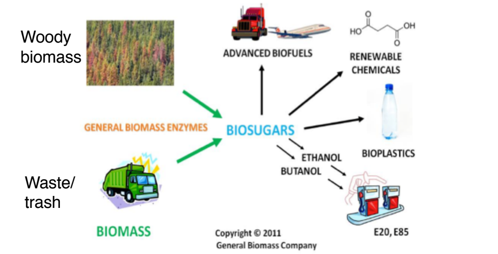
[2] Averages and standard deviations of the samples grown at the GVSU Sustainable Agriculture Project. 2 trials of each sample were conducted, with the exception of 3 trials for the % extractable for the Fishcreek willow variety.

[3] Lyophilized (freeze-dried) trials.

[4] Test of differences conducted between the oven-dried and the lyophilized samples. The T-tests for % ash were conducted between each sample and the % ash for Fabius, used as the standard.

Background

Although any biomass, with a neutral carbon foot print, is preferable to fossil fuels, a complete lifecycle analysis should be used to distinguish between different biomass sources.



Human cultivated biomass: corn, soybeans, and sugarcane are currently the *largest utilized* sources of biomass for the production of bioethanol and biodiesel (http://www.eesi.org/topics/bioenergy-biofuels-biomass/description). However,

- they are food crops that redirect food from people
- they require arable farmland and agricultural inputs: fertilizers, pesticides, water, labor.
  - eutrophication, a problem from fertilizers run-off.
  - fresh water demands – an estimate of water footprint, in m^3 of fresh water required per liter of biofuel produced, for corn, soybean, and sugarcane respectively is 2.01, 15.63, and 1.47 (Yang et al.). That is a lot of fresh water!
  - the nutritional requirements for growing these crops can be taxing for the soil, especially in the monoculture farming model that populates many national farms.

Native woody biomass *largest existent* globally (https://www.nrel.gov/workingwithus/re-biomass.html) is the ideal source of biomass because it

- does not displace food from people
- does not diminish the nutritive quality of top soil
- provides a temporary habitat for local wildlife
- does not require agricultural inputs
- can be cultivated globally

Value-added compounds/materials currently produced from biomass

- Lignin, the most prevalent aromatic polymer in nature: phenol; carbon fibers; activated carbon; resins; **electrolytic polymer** (Zhu *et al.).*
- Cellulose, the most abundant polymer on Earth: **levulinic acid** (Wang *et al.*); **5-hydroxymethyl furfural**; **ethanol**; butanol; xylitol; 2,3-butandiol; organic acids; furfural; biohydrogen; chitosan; xylo-oligosaccharides; ferulic acid; vanillin.
- Hemi-cellulose, an irregular polymer of pentose and hexose sugars: **ethanol** and others (see cellulose)

Future work

- Degradation og lignocellulose (the non-extractable component of willow biomass that constitutes ~85% of dry mass) into lignin, cellulose, and hemicellulose.
- Kraft process, used industrially to convert lignocellulosic wood into paper via treatment with hydroxide, will be the primary separation method to degrade lignocellulose into cellulose and the 'black liquor' byproduct (lignin, hemicellulose, and ash). Further processing of 'black liquor' will be explored.

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