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Co-products from Algae Biorefinery and Lignocellulosic Biomass

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Biorefinery

Feedstock

- Lignocelluloses
- Algae

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Co-products from Algae Biorefinery

Approach for concomitant extraction of bio-oil and co-products.

Approach A

1. Screen different high oil content algae
2. Identify the value added products present in those algae
3. Develop a method to extract them along with oil

Approach B

1. Use any conventional biofuel method and upgrade it for the concomitant production of oil and co-products.
2. Identify the value added products that can be isolated by that method
3. Screen the algae which are fit for such method .

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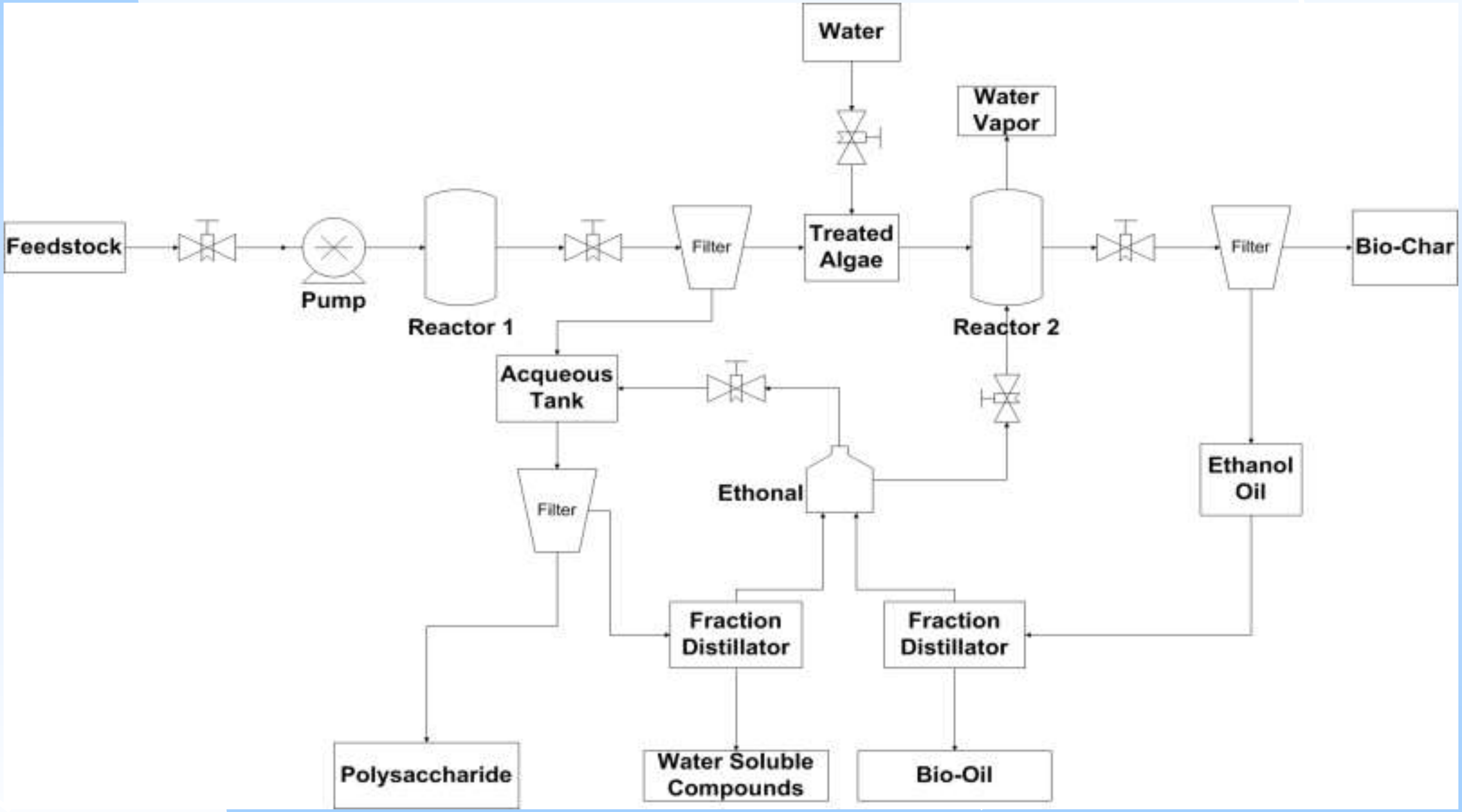
Sequential Subcritical Hydrothermal Extraction (SSHTE)



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Advantages of the SSHTE method

Advantages

- Along with bio-oil this method is capable of efficiently removing the valuable algal polysaccharides and antioxidant compounds.
- Comparative analysis of the bio-oil produce by conventional direct hydrothermal liquefaction (DHL) showed that removal of polysaccharides is not significantly influencing the yield of bio oil
- Comparative analysis of the DHL and the invented method showed DHL method lead to the high production of bio char. But in SSHTE method production of bio char is very less.
- This method isolated products of non-oil origin therefore, not effecting the yield of bio oil.

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Plan of work to develop algal polysaccharides as a Co-products to reduce the biofuel cost

Approach

To identify the use of polysaccharides for the targeted industry :

Work should be divided into two broad groups:

1. Characterization of the isolated polysaccharides to identify the targeted industry for which it can be developed.

2. Screening of different valuable algal polysaccharides which can be extracted along with the bio oil by our method

Targeted Industry

1. **Food industry**
   - Bio-emulsifier
   - Edible coating
   - Food Packaging

2. **Cosmetic Industry**
   - Tooth paste, Shaving cream
   - Antioxidants , antibacterial cream
   - Other skin enhancement lotion

3. **Pharmaceuticals**
   - Formulation of vaccines
   - Healing agent for burning as used in bandage
   - Immunomodulatory agents, anti inflammatory agents

Potential value added co-products from Algae

Market estimations for micro algal products

Product group	Product	Retail value (US $\$x10^6$)	Development
Biomass	Health food,	1250-2500	Growing
	Functional food	800	Growing
	Feed additive	300	Fast-growing
	Aquaculture	700	Promising
	Soil Conditioner		
Coloring substances	Astaxanthin	>150	Growing
	Phycocyanin	<10	Stagnant
	Phycoerythrin	>2	Stagnant
Antioxidants	β-carotene,	>280	Promising
	Tocopherol,	100-150	Stagnant
	Antioxidant extract	20	Growing
	ARA,	1500	Fast growing
	DHA,	10	
	PUFA extracts		
Special products	Toxins	1-3	
	Isotopes	>5	

Market evaluation of macro algal polymers (From McHugh 2003)

Product	Production	Algae harvested ($t\ y^{-1}$)	Value (US$/ Mio)	Comments
Carrageenan	33,000	168,400	240	Mainly *Eucheuma* and *Kappaphycus*
Alginate	30,000	126,500	213	*Laminaria*, *Macrocystis*, *Lessonia*, *Ascophyllum* and other.
Agar	7,630	55,650	137	Mainly *Gelidium* and *Gracilaria*
Extracts			10	
Nori	40,000	400,000 (wet only in Japan)	1500	*Porphyra*

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Products yield

Product	Temperature	SSHTE	DHL
Polysaccharide	160˚C	26%	/
	180˚C	14%	
Bio-oil	300˚C	27%	34%
Bio-char	300˚C	2.40%	14.60%

1. Polysaccharide extracted from SSHTE total account for 40% based on dry algae weight and DHL is 0.
2. Crude bio-oil yield is decreased from SSHTE compared with DHL.
3. Bio-char amount from SSHTE is fairly less than it from DHL.

- **Elemental Analysis**

Bio-Oil	C%	O%	N%	S%	HSV(MJ/kg)
SSHTE	76	11	0.78	0.16	40.8
DHL	72	11	1.14	0.14	43.7

1. Crude oil elemental composition from two different methods are similar;
2. oil from SSHTE shows higher carbon amount and less nitrogen amount compared with DHL method;

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Chromatographic Characterization of Crude bio oil

- **GC Analysis for Bio-Oil**

Retention Time	Compound(DHL)	Compound(SSHTE)
8.7148	2-Cyclopenten-1,one,2-methyl-	/
14.442	2-Cyclopenten-1-one,2,3-dimethyl	/
15.057	Benzene,butyl-	Benzene,butyl-
16.799	2-Cyclopenten-1-one,2,3,4-trimethyl-	/
19.7	Benzene,pentyl-	Benzene,pentyl-
24.406	/	Benzene,hexyl-
28.484	/	Naphthalene,1,2-dihydro-1,1,6-trimethyl-
34.335	9-octadecenal [z]-	Hexa-hydro-farnesol
46.677	Pentadecanoic acid	Pentadecanoic acid
47.243	1-Dodecanol,3,7,11-trimethyl-	1-Dodecanol,3,7,11-trimethyl
49.195	13-heptadecyn-1-ol	13-heptadecyn-1-ol
49.918	Pentadecanoic acid,14-methyl-methylester	Pentadecanoic acid,14-methyl-methylester
50.646	9-Hexadecenoic acid	9-Hexadecenoic acid
50.694	/	Hexadecenoic acid,Z-12-
51.6	Palmitic acid	Palmitic acid
53.3	Heptadecanoic acid	Heptadecanoic acid
57.1	Oleic acid	Oleic acid
59.1	Linoleic Acid	Linoleic Acid
62.5	Lioleic Acid ethylester	Lioleic Acid ethylester
62.7	9-Octadecanamide,[z]-	9-Octadecanamide,[z]-

Fatty acid	Structure	Control % FA	Control mg/g	SSHTE % FA	SSHTE mg/g	DHL % FA	DHL mg/g
Palmitic	C16:0	21.17	57.48	28.33	148.50	30.02	167.49
Hexadecenoic	C16:1n9	5.34	14.50	4.87	25.53	4.47	24.94
Stearic	C18:0	1.90	5.17	2.37	12.40	2.51	14.02
Hexadecatrienoic	C16:3n4	0.00	0.00	7.35	38.51	7.84	43.72
Hexadecatrienoic	C16:3n3	27.53	74.76	22.29	116.83	23.46	130.89
Linoleic	C18:2n6	30.93	84.00	9.48	49.68	8.92	49.77

1. Fatty acid are the major composition in crude bio-oil. Palmitic acid and Hexadecatrienoic acid are the major component of Crude Bio-Oil;
2. Crude oil from SSHTE and DHL do not have too much qualitative difference but with some quantitive difference;
3. The oil amount from both extraction methods were improved highly compared with the control group

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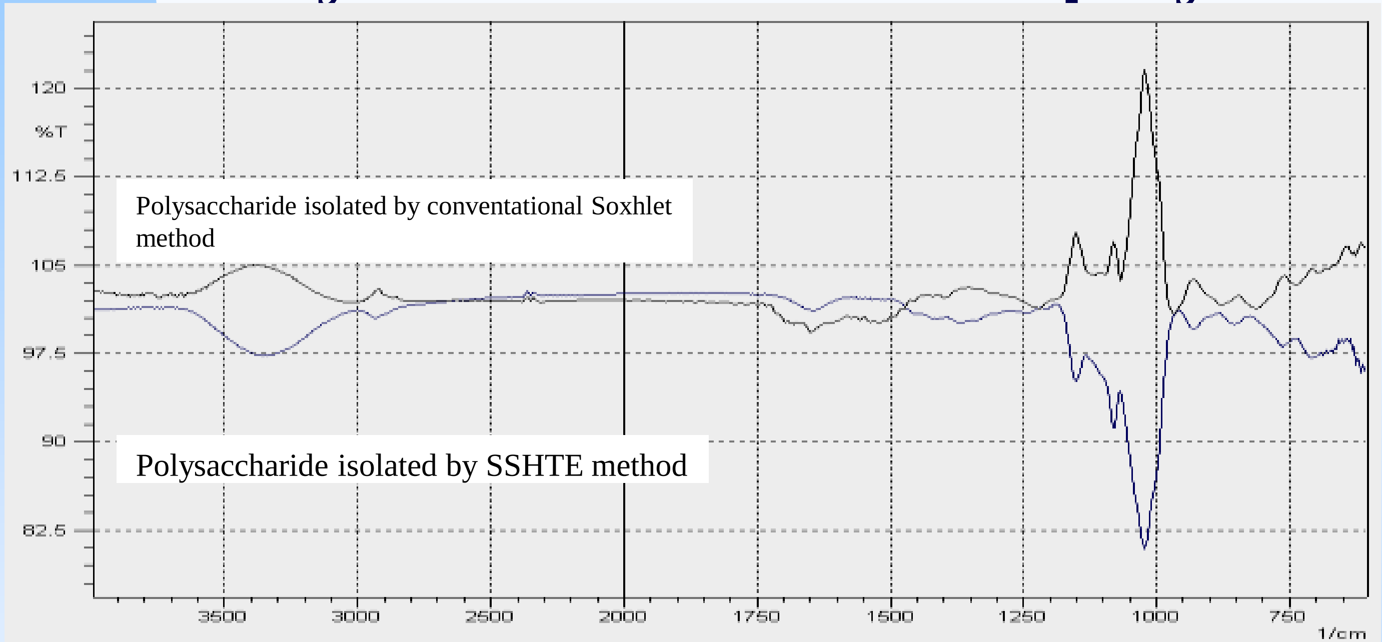
FT-IR analysis of the extracted polysaccharide



Region Assignments

3300-2700 1/cm – C-H stretching vibrations
1800-1500 1/cm – Characteristic bands for proteins
1700-1600 1/cm – Amide-I bands (due to C-O stretching)
1600-1500 1/cm – Amide-II bands (due to N-H bending)
1200-900 – C-O, C-C, C-O-C stretching vibration of polysaccharides

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Characterization of the isolated polysaccharides to identify the targeted industry for which it can be developed.

- Characterization has been divided into 4 groups

1. Identifying the polysaccharides as suitable bio emulsifier by testing their rheological and emulsifying properties under different condition (pH, NaCl concentration, different concentration of polysaccharides and temperature)

2. Testing the bio surfactant property of the polysaccharides by evaluating the effect of this compound in minimizing the surface tension of distill water

3. Characterization different bio material property like the storage modulus, loss modulus and material hardening , tensile property to evaluate its probable use of the compounds as a industrial polymer.

4. Evaluation of the bio activity and further purification of the crude polysaccharides to develop finer compounds for pharmaceutical uses.

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Emulsifier

Emulsifier is a substance which can be used to produce an emulsion out of two liquids that normally cannot be mixed together (such as oil and water).Surfactants and emulsifiers are indispensable components of daily life.

Use of emulsifier

- Pharmaceutical
- Cosmetic
- Petroleum
- Food industries

Market Value

- The surfactant industry now exceeds US$ 9 billion per year (Desai and Banat, 1997).

Source of emulsifier

- Most of these compounds are of petroleum origin, which are not easily biodegradable and their manufacturing processes and by-products can be environmentally hazardous.

Drawback of petroleum originated emulsifier

Increased environmental awareness and strict legislation has made environmental compatibility of surfactants an important factor in their applications for various uses .

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Bio emulsifier

- Several different microbial products that exhibit surface-active properties have been identified in the past.
- These biosurfactants are produced by certain bacteria and by a number of yeasts and filamentous fungi.
- They include low-molecular-weight glycolipids, lipopeptides and high-molecular-weight lipid-containing polymers such as lipoproteins, lipopolyssacharide-protein complexes and polysaccharide-protein-fatty acid complexes .
- These are readily biodegradable and can be produced in large amounts by microorganisms and thus are not dependent on petroleum-derived products.
- The success of biosurfactant production depends on the development of cheaper processes and the use of low cost raw materials, which account for 10-30% of the overall cost.

Formation of emulsion

Corn oil Benzene Hexane

Percentage of Emulsion (E 24)	Solvent
60.1 %	Corn oil
61.5 %	Benzene
75.0 %	Hexane

Future Goal

- Screening of algae containing more new relatively temperature resistant co-products, that have higher value when used as functional compounds than merely as biofuel molecules.
- Further standardization of the SSHTE method for cost effective separation of those compounds from algae biomass.
- Alteration of the concentrations and compositions of those compounds through species selection and varying culture conditions.
- Product development for targeted industry

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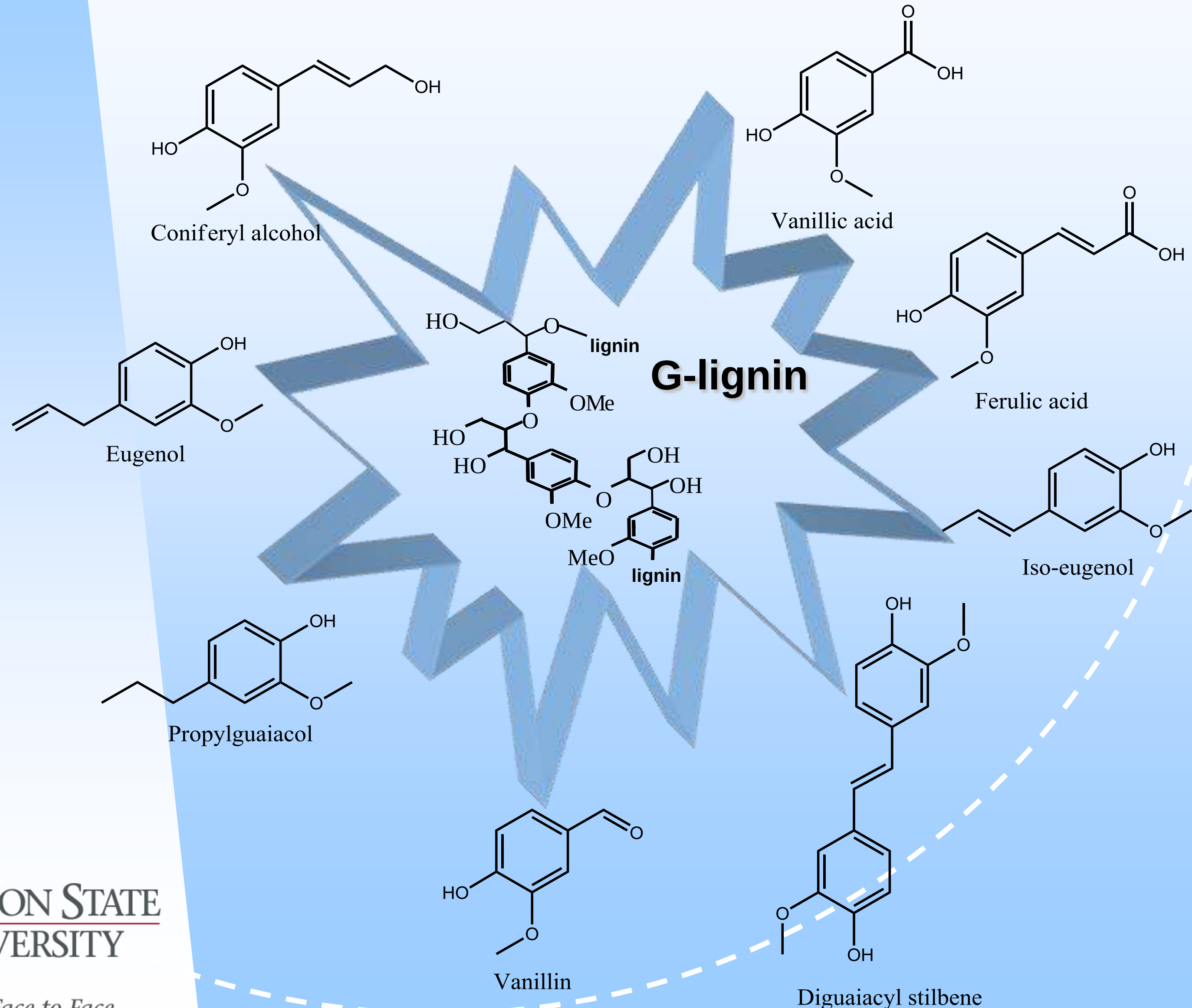
High Value Lignin-derived Co-products

Research Work Plan

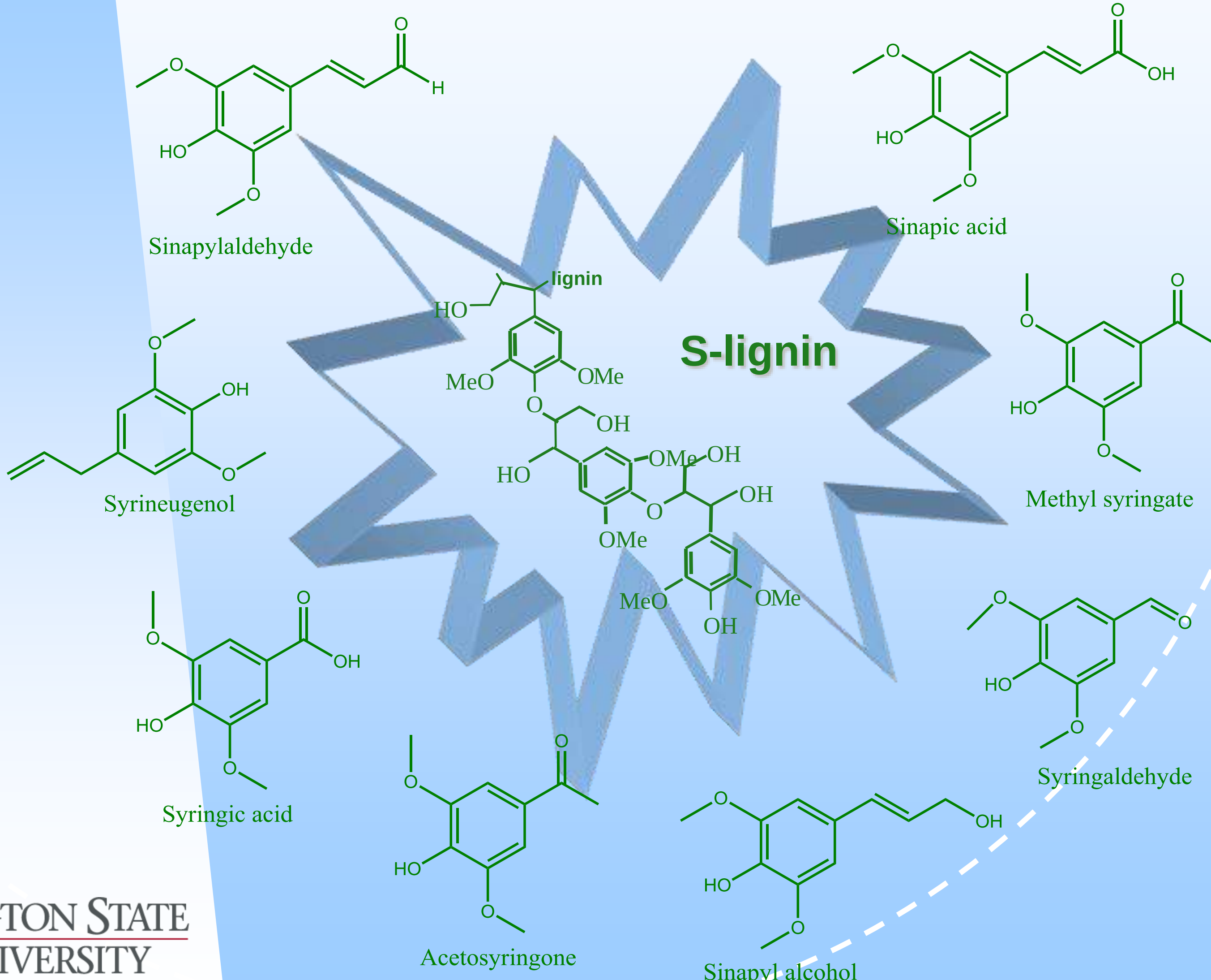
- Chemical characterization of the bio-degraded lignin and metabolites released during chemical and biological pretreatment to the ascertain structural relationship with the native lignin macromolecular assembly

- Investigate physical, chemical and biological properties of the lignin derived co-products to evaluate potential application as fine chemicals, antioxidant and high valued products

Degradation product of G-Lignin



Degradation product of S-Lignin



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Bacterial Species of Interest for Lignin Deconstruction and Bio-degradation

S. Viridosporus – ATCC 39115 - $255
•BSL 1 – Grows in Yeast Malt Extract Agar, 26 C

P.Putida – ATCC 33015 - $205
•Grows in Benzoate Medium, 30 C

Rhodococcus sp. 43230 – unavailable
•Study obtained from Dr. Eltis, UBC, Canada

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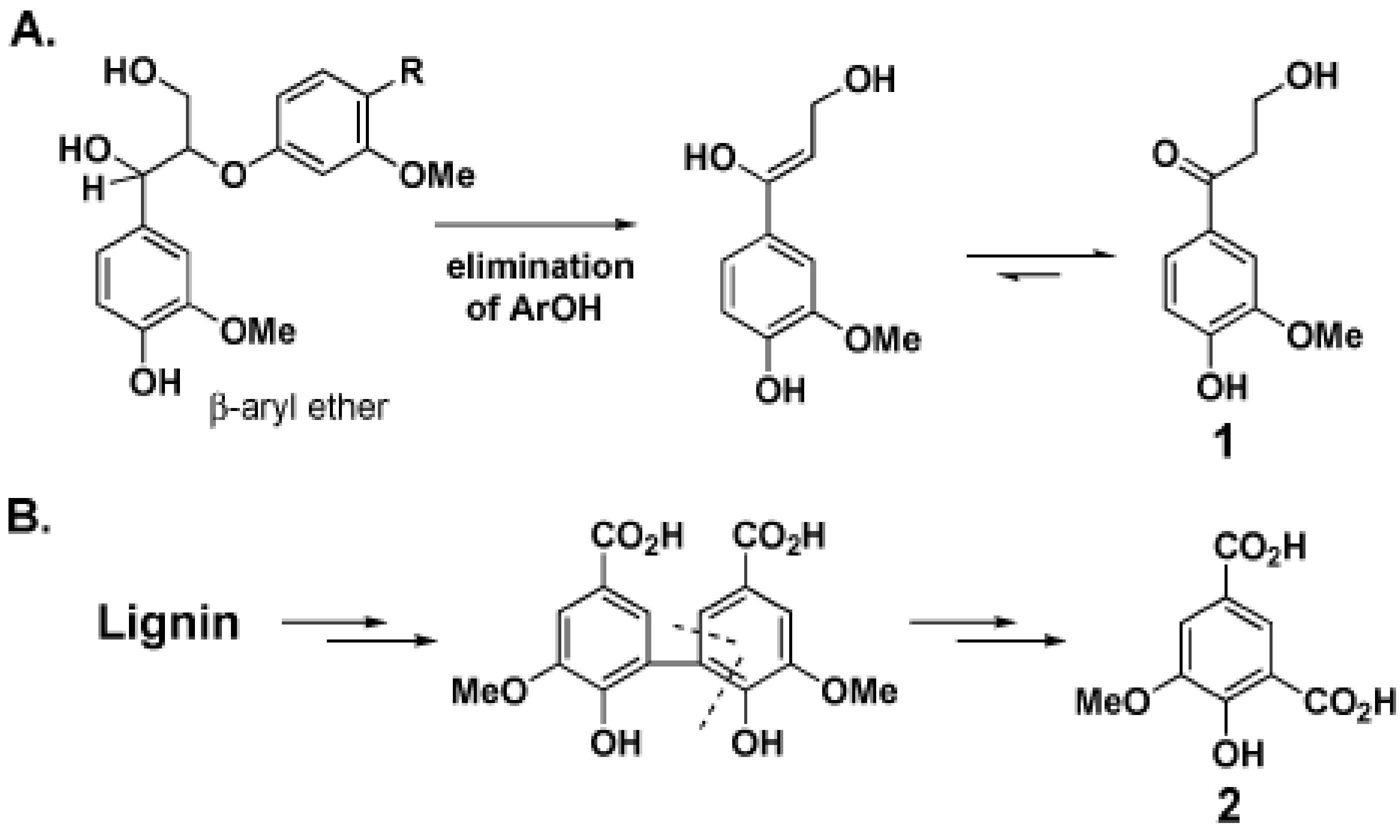
Proposed Pathway for Microbial degradation of Lignin



Possible pathways for the formation of breakdown products

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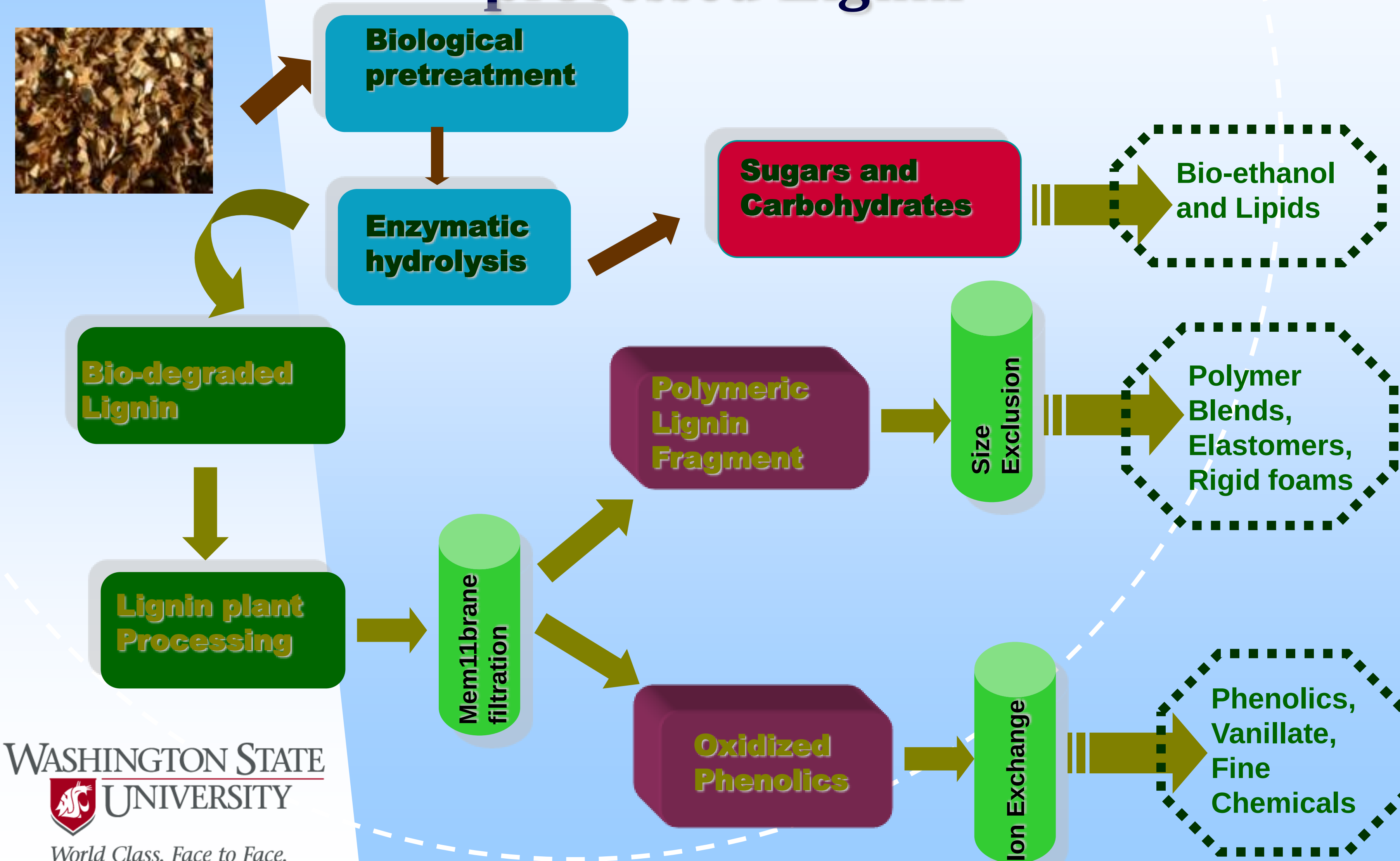
Adapted from: Ahmad et al., 2010, *Molecular Biosystems*, 6, 815-821

Proposed Integrated Process for Producing Biopolymers and Fine Chemicals from Bio-processed Lignin



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