Agriculture and Agri-Food Canada | Agriculture et Agroalimentaire Canada

Green Technologies for the Conversion of Crop Residues to Biochemicals

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Canada

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Our Location

Pacific Agri-Food Research Centre, Summerland, British Columbia

Our Research

- **Fractionation of Crop Residues/Straw**
  -wheat, barley, triticale, oat, and flax straw and shives

- **Using Green Solvents**

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Composition of triticale straw and flax straw

(Results expressed as a percentage of the native, oven-dried basis).

Component	Triticale straw (Pronghorn)		Flax straw (Tieszen07Whole)	
	Native	H_2O-EtOH Extracted	Native	H_2O-EtOH Extracted
Total glycans	63.36 (0.01)[a]	63.88 (0.36)[a]	54.99 (0.51)[b]	54.37 (0.28)[b]
Glucan	39.05 (0.13)[b]	40.08 (0.30)[a]	33.35 (0.32)[c]	32.94 (0.06)[c]
Xylan	21.46 (0.04)[a]	21.37 (0.10)[a]	17.73 (0.20)[b]	17.51 (0.04)[b]
Galactan	0.81 (0.06)[c]	0.69 (0.01)[d]	1.52 (0.03)[a]	1.39 (0.05)[b]
Arabinan	2.03 (0.03)[a]	1.74 (0.04)[b]	0.47 (0.02)[c]	0.41 (0.03)[c]
Mannan	ND	ND	1.91 (0.03)[a]	2.13 (0.26)[a]
Total Lignin	21.01 (0.07)[c]	17.08 (0.08)[d]	28.23 (0.08)[a]	25.39 (0.06)[b]
Acid Insoluble Lignin	19.57 (0.07)[c]	15.95 (0.07)[d]	27.28 (0.08)[a]	24.63 (0.05)[b]
Acid Soluble Lignin	1.41 (0.00)[a]	1.14 (0.01)[b]	0.94 (0.01)[c]	0.76 (0.00)[d]
Ash	3.92 (0.03)[a]	0.74 (0.04)[d]	2.02 (0.10)[b]	1.18 (0.09)[c]
Extractives	NA	9.97 (1.01)[a]	NA	5.56 (0.82)[b]

Statistical difference; $p<0.05$ determined by Turkey test and Turkey-Kramer test (n=3); except total glycans, glucan, xylan, galactan, arabinan, mannan, total lignin, acid soluble lignin, and total of Triticale native (n=2).

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Green(er) Solvents of Interest

Supercritical CO2

Water

Ionic liquids

Green Processes

Being Investigated/Optimized

- Pressurized low polarity water (PLPW) extraction

- Supercritical CO2

- Ionic liquids

- Membrane-based separation

Pressurized Low Polarity Water (PLPW) Extraction Technology

Pressurized Low Polarity Water Extraction Technology

What is it ?

- **Pressurized low polarity water (PLPW) is a promising extraction and fractionation technique that uses low-to-moderate pressures to maintain water in the liquid state at temperatures above its normal boiling point.**

- **The higher temperatures decrease the polarity and viscosity and improve the mass transfer properties of water**

Pressure-enthalpy chart of water

5.17 MPa (750 psi or 52 bar)

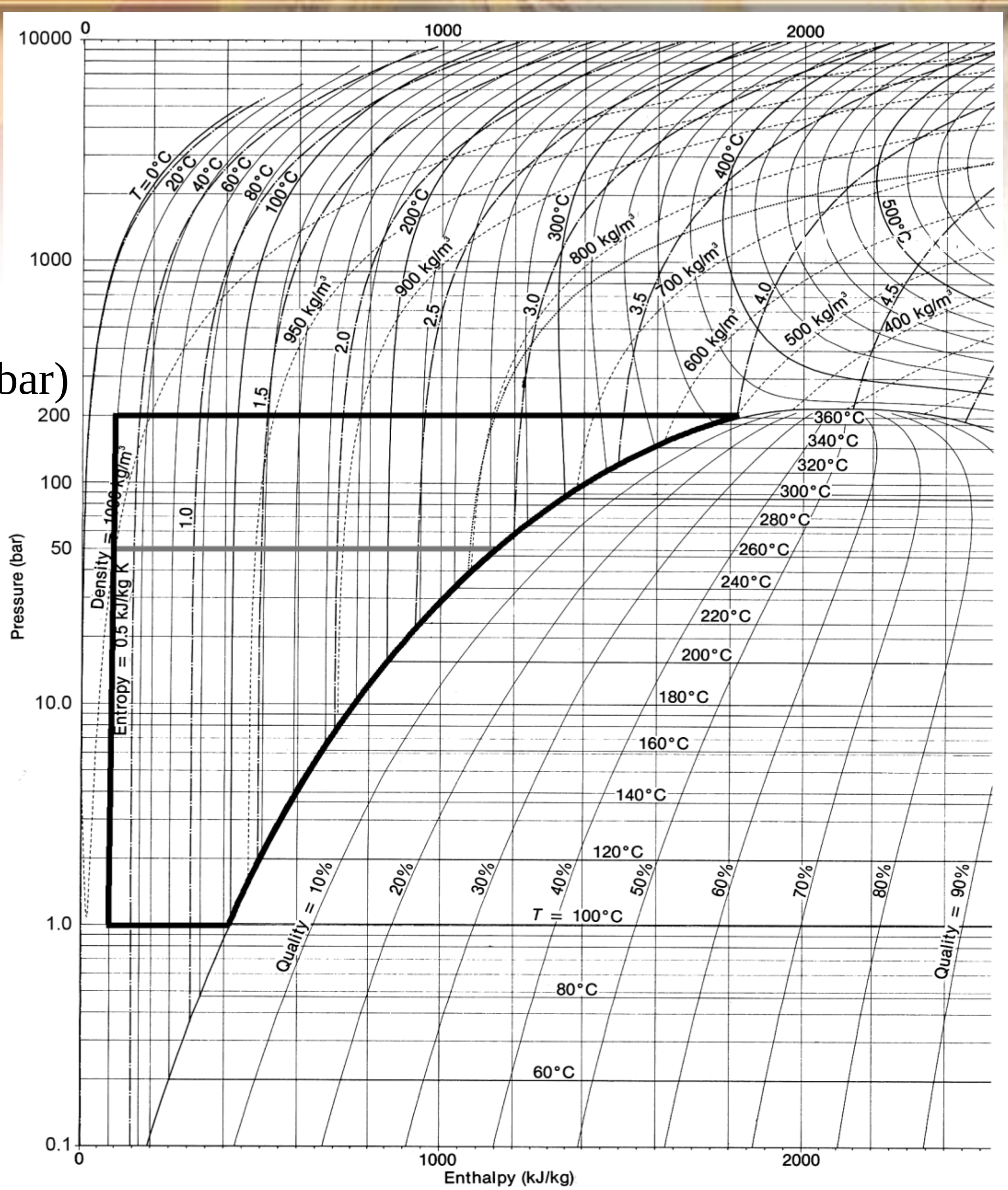
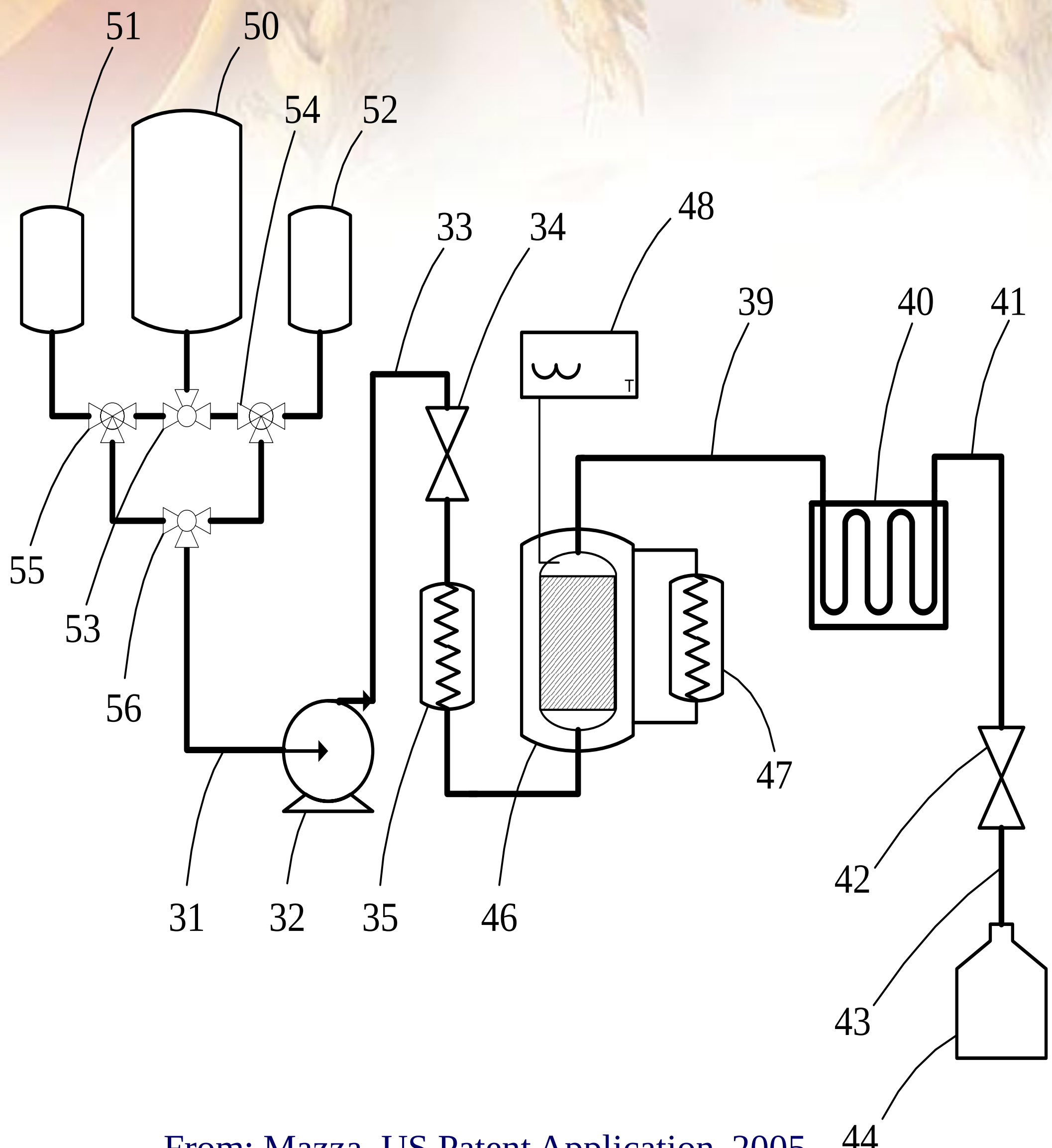


Diagram of Pressurized Low Polarity Water Extractor



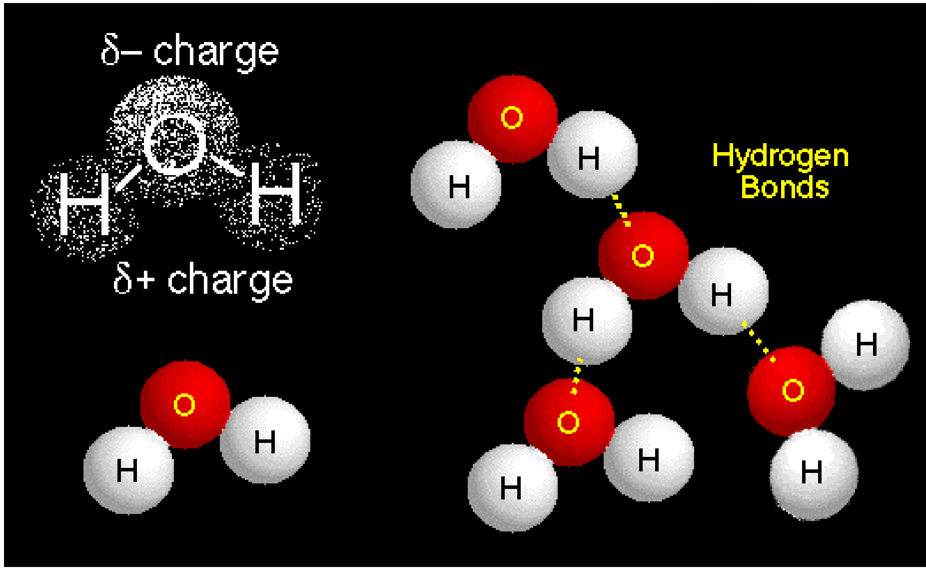
From: Mazza, US Patent Application, 2005

Pressurized Low Polarity Water Extractor

From: Mazza, US Patent Application, 2005

Changes in the Properties of PLPW

- **Temperature ↑**
- **Breakdown of H-bonded water structure**
- **Polarity/dielectric constant ↓**
- **Viscosity ↓**
- **Surface tension ↓**
- **Solubility of organic compounds ↑**



The solubility ↑ because of the ↓ polarity and the ↓ enthalpy of solution with the ↑ in temp

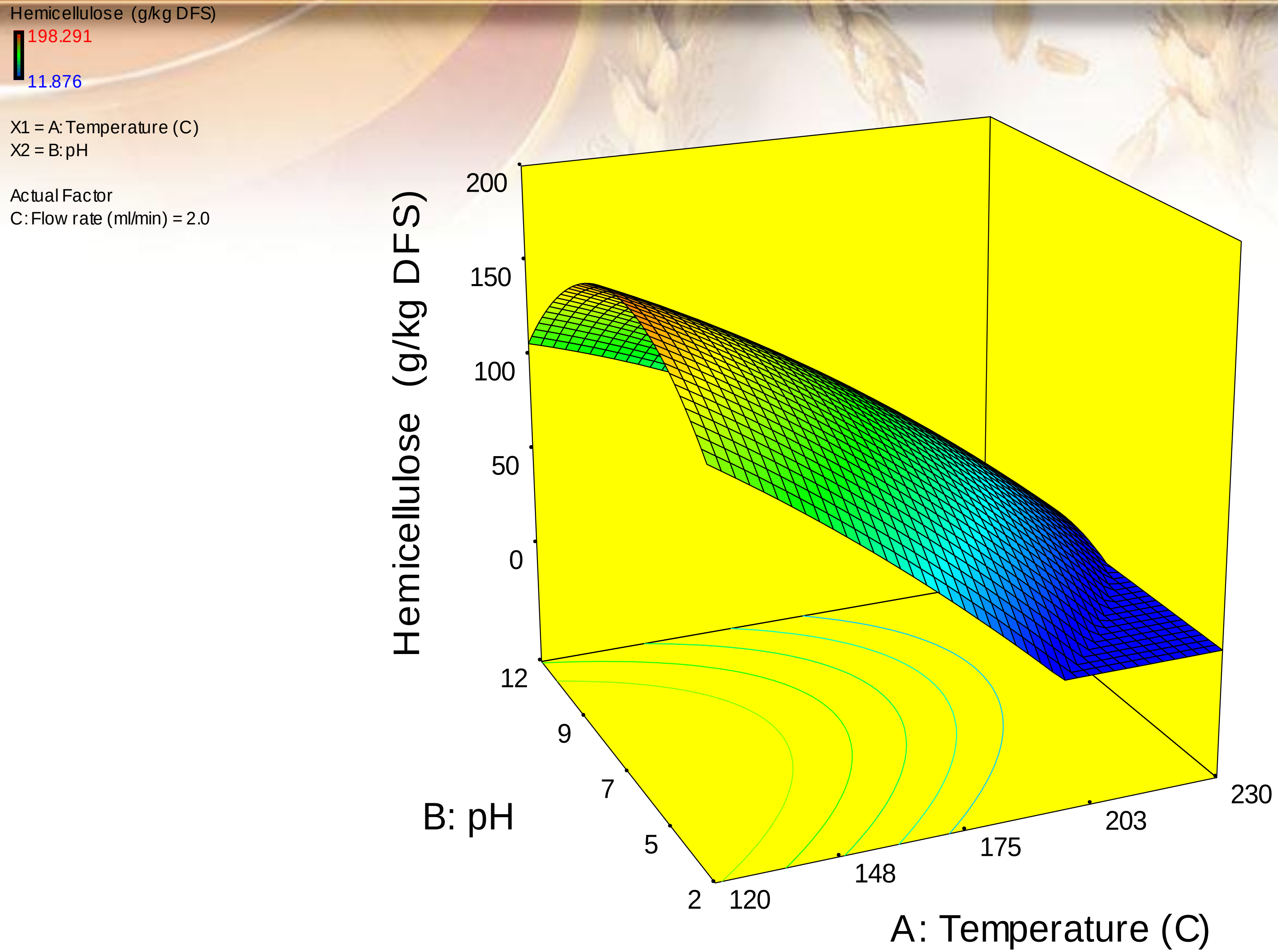
Phytochemicals of Interest

- Lignans from flaxseed and flaxseed meal
- Saponins from cow cockle seed

- Flavonoids from crop residues/culls
- Resveratrol and viniferin grape vines

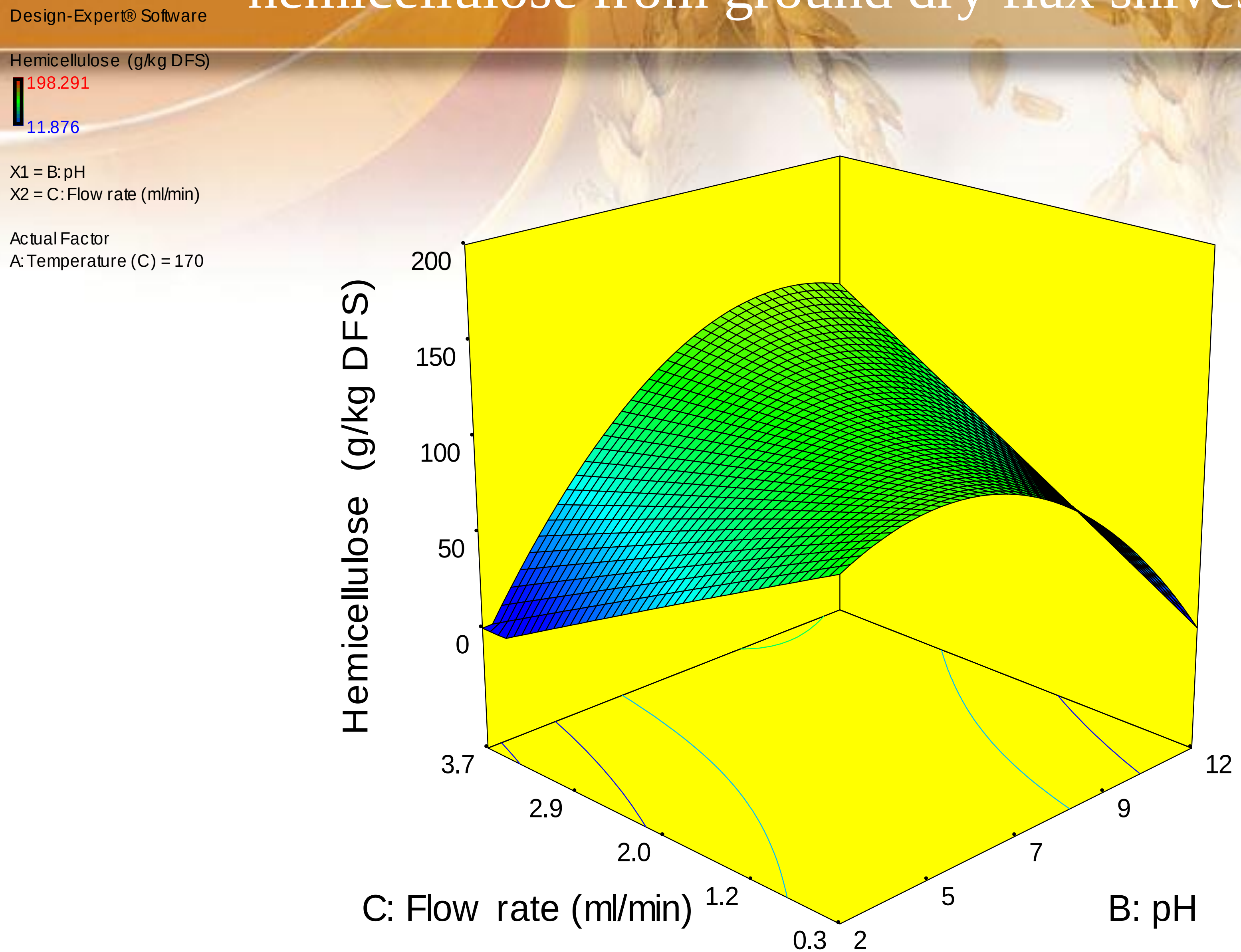
- Hemicelluloses/arabinoxylan from straw
- Lignins from straw
- Ferulic acid, vanillin and other phenolics from straw

Effects of temperature and pH on PLPW extraction of hemicellulose from ground dry flax shives



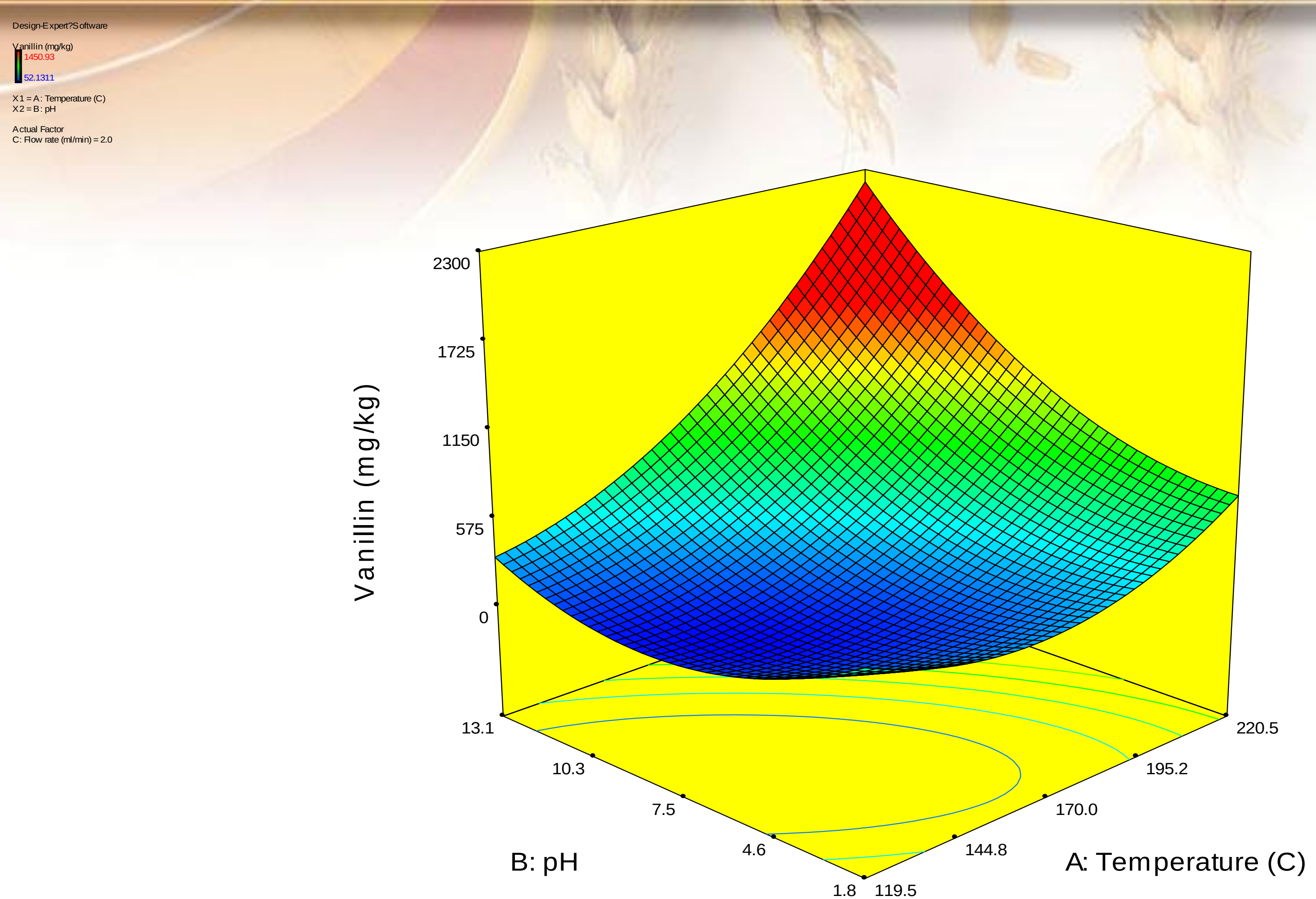
Hemicellulose in PLPW flax shive residues

Effects of pH and flow rate on PLPW extraction of hemicellulose from ground dry flax shives.



Hemicellulose in PLPW flax shive residues

Effects of temperature and pH on PLPW extraction of vanillin from ground dry flax shives



- in PLPW flax shives extracts

Green Processes Being Investigation

Supercritical CO_2

Supercritical CO_2

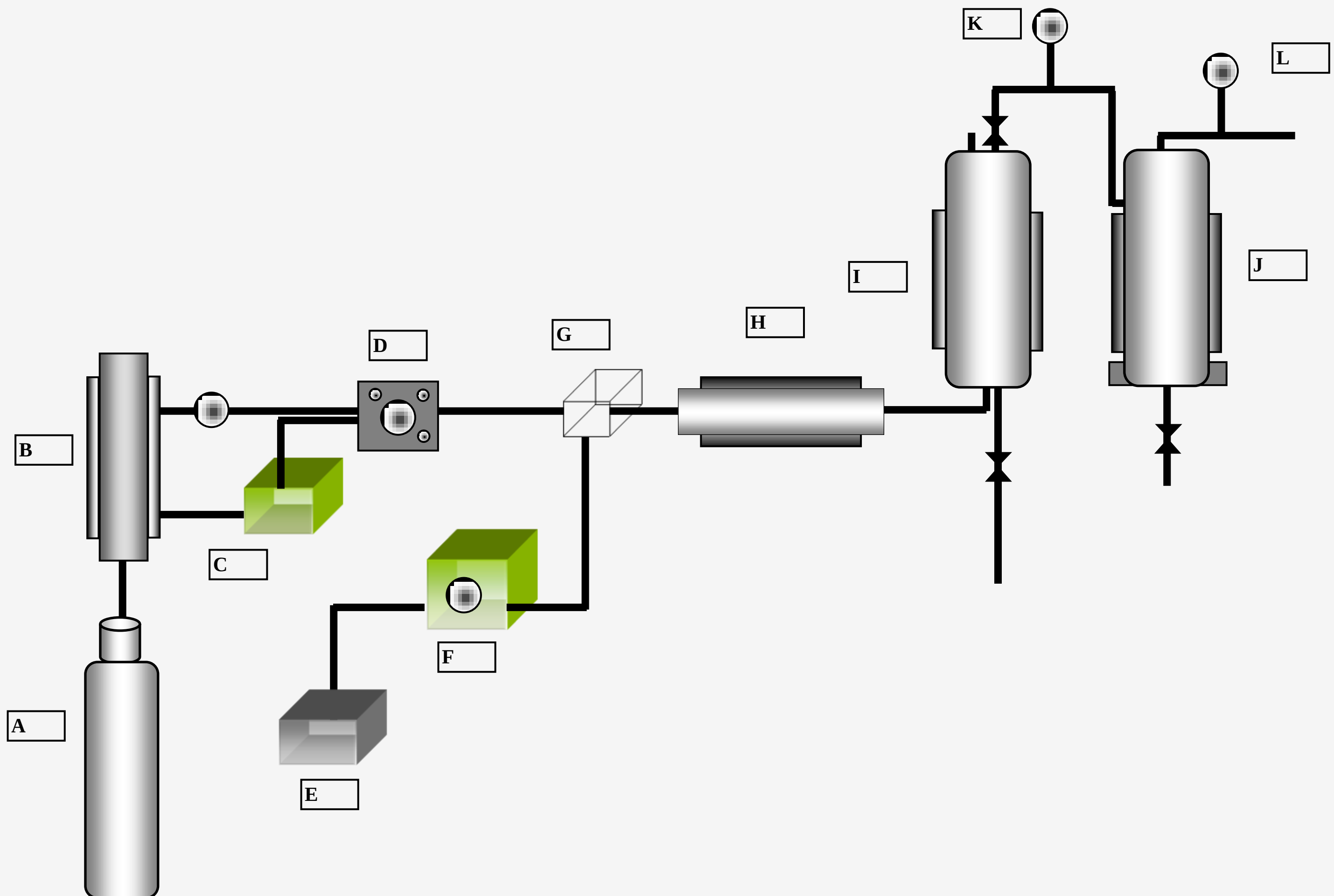
- **Moderate critical pressure (74 bar) and temperature (31° C)**
- **Non toxic**
- **Inert**
- **Non-flammable**
- **Easy removal: simple depressurization**

- **Its physical properties (polarity, etc.) can be tuned through pressure and/or temperature variations**

- **Replacement for organic solvents in extraction processes**

Extraction

Supercritical CO2



A: CO_2 cylinder, **B**: heat exchanger, **C**: cooling bath, **D**: CO_2 pump, **E**: solvent reservoir, **F**: co-solvent pump, **G**: mixer, **H**: heating exchanger, **I**: extraction vessel, **K**: automated back pressure, **J**: cyclone separator, **L**: gauge, M: heating bath

SC-CO2 Extraction/Fractionation

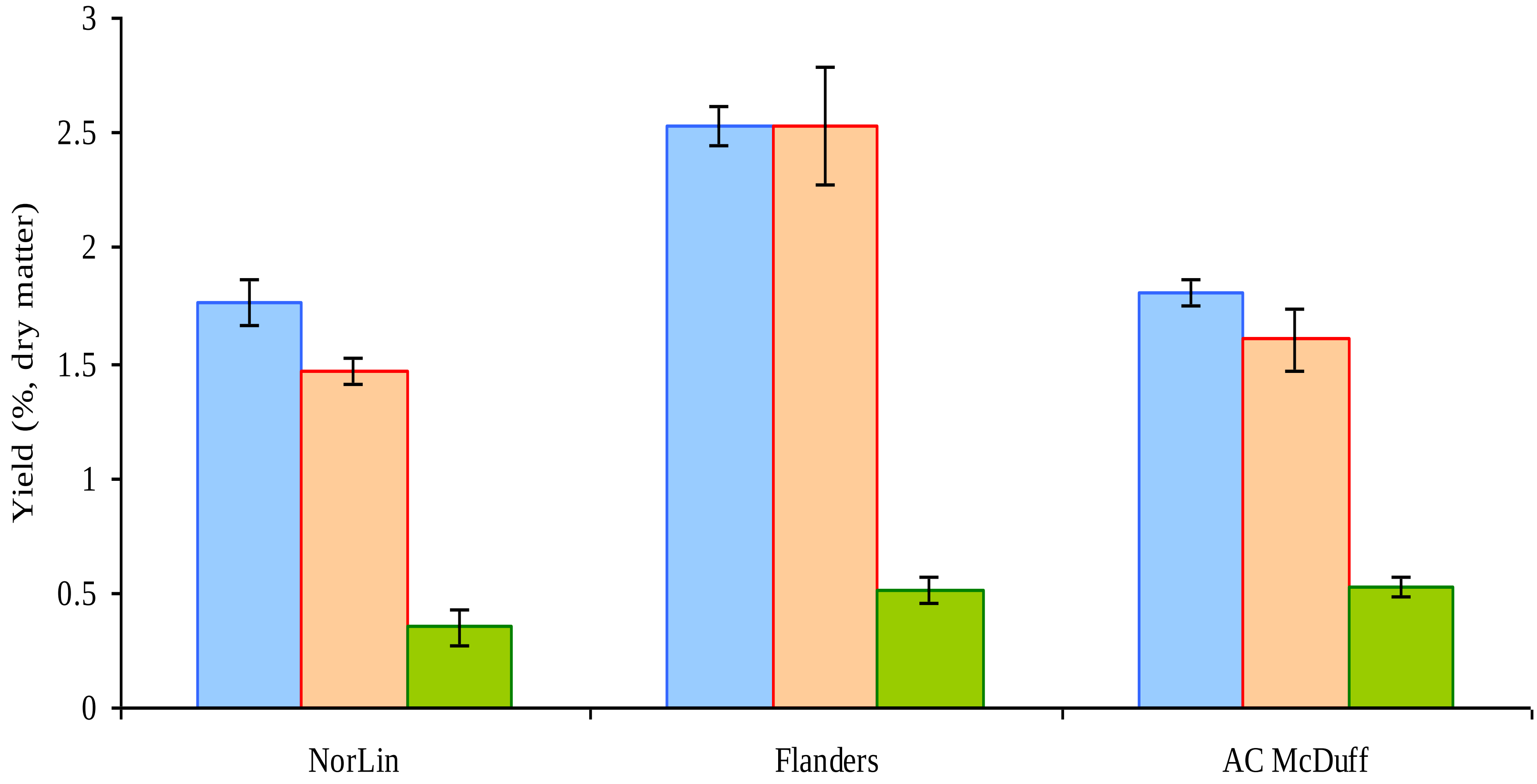
Waxes

Polycosanols—Fatty alcohols

Phytosterols

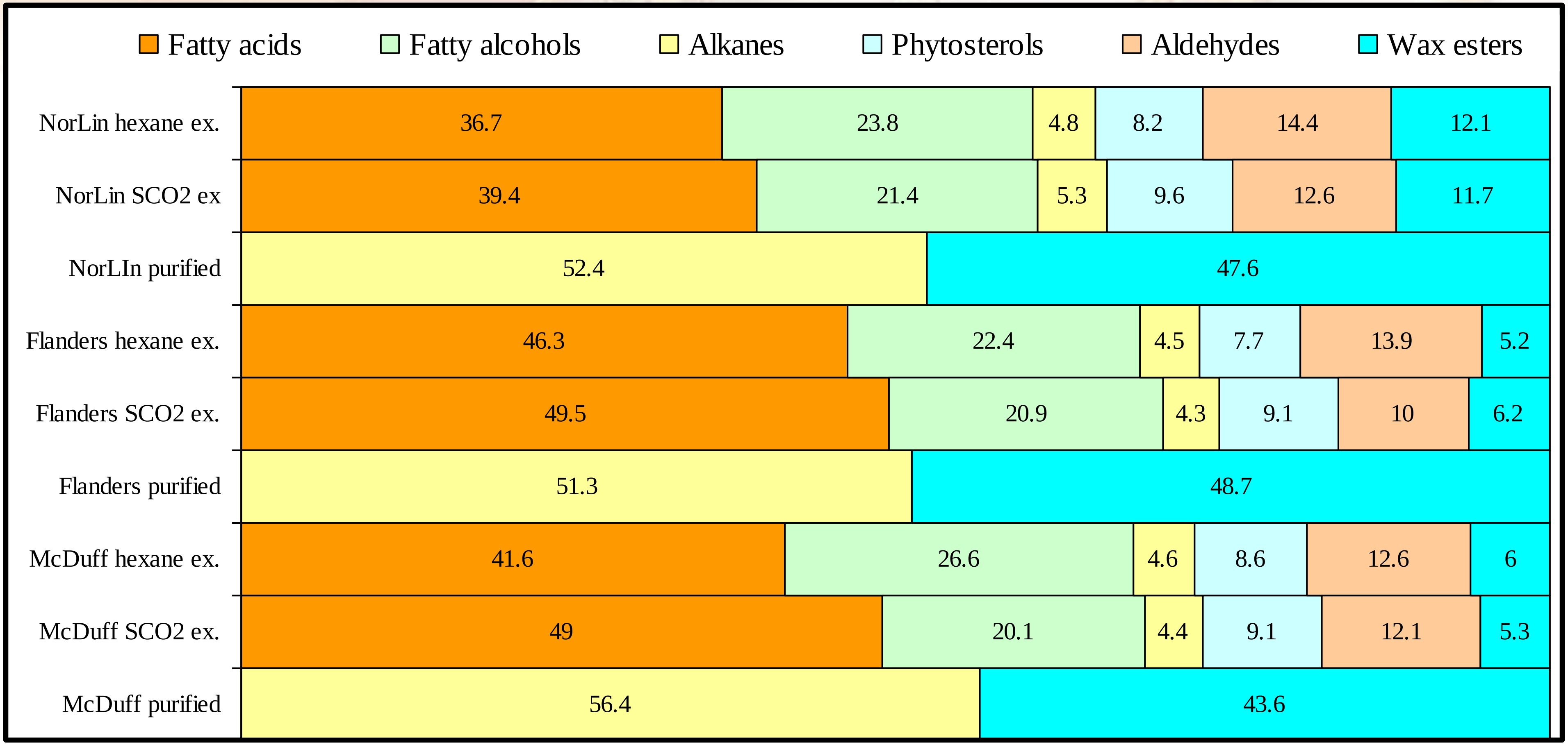
Alkylresorcinols--Phenolic lipids

Yield of wax from flax straw after SC-CO2 and hexane extraction



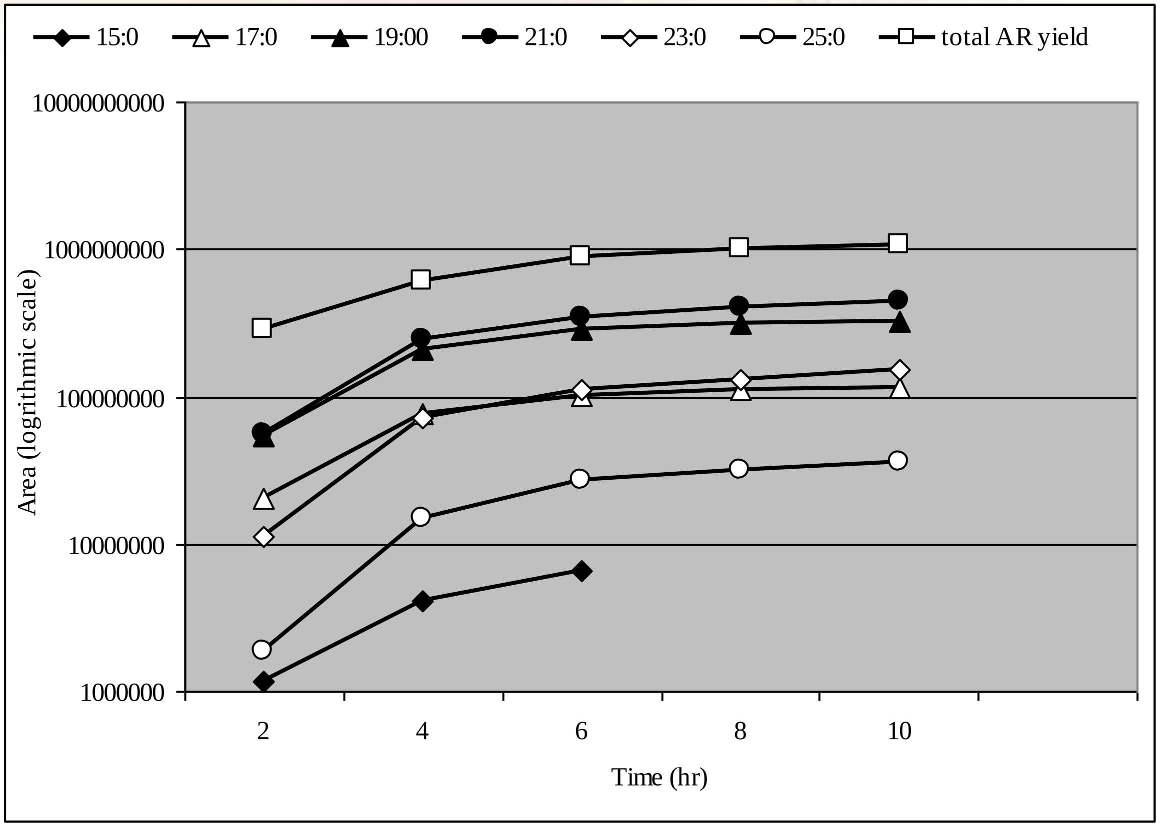
hexane extracted; SC-CO2 extracted; purified wax samples

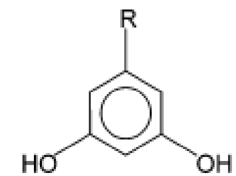
Major constituents in SC-CO2 and hexane extracts and in purified waxes from flax straw



Alkylresorcinols in triticale bran

Phenolic lipids reported to have anticancer, antimicrobial and antioxidant activity





R	Names	[CAS No.]
$C_{15}H_{31}$	**5-n-pentadecylresorcinol**, 5-pentadecyl-1,3-benzendiol, cardol (trivial) (C15:0)	[3158-56-3]
$C_{17}H_{35}$	**5-n-heptadecylresorcinol** 5-heptadecyl-1,3-benzendiol (C17:0)	[41442-57-3]
$C_{19}H_{39}$	**5-n-nonadecylresorcinol** 5-nonadecyl-1,3-benzendiol (C19:0)	[35176-46-6]
$C_{21}H_{43}$	**5-n-heneicosylresorcinol** 5-heneicosyl-1,3-benzendiol (C21:0)	[70110-69-7]
$C_{23}H_{47}$	**5-n-tricosylresorcinol** 5-tricosyl-1,3-benzendiol (C23:0)	[70110-60-0]
$C_{25}H_{51}$	**5-n-pentacosylresorcinol** 5-pentacosyl-1,3-benzendiol (C25:0)	[70110-61-1]

Green Processes Being Investigation

Ionic liquids

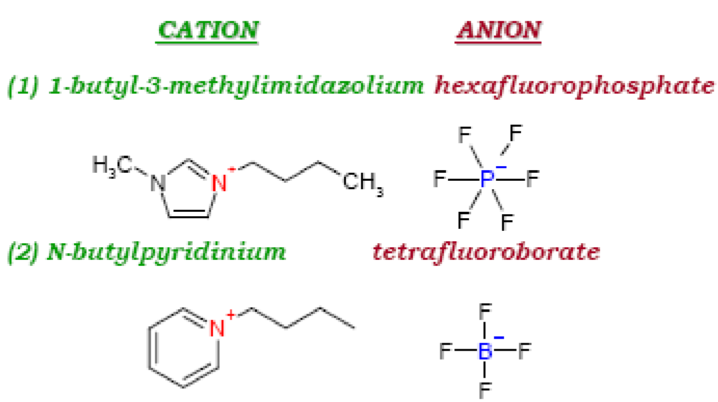
Green Solvents - Ionic Liquids (ILs)

- ILs are salts that melt below 100° C, composed wholly of ions.

- CATIONS such as substituted imidazoliums, substituted pyridiniums or others

- ANIONS such as borates, phosphates and halides and others

- Examples and structures



Green Solvents - Ionic Liquids (ILs)

Advantage

• No vapor pressure, thermally robust, liquid from -96° C up to 300° C

• Polarity and/or hydrophobicity can be tuned

•“Designer solvents” (1 million ionic liquids vs. 600 organic solvents)

Disadvantage

•High price

•Toxicity? Biodegradability?

•Recovery of the product and recycling of the catalyst?

Green Processes Being Investigation

Ionic liquid extraction of lignin from wheat, tritcale and flax straw

Ionic liquid pretreatment of straw

Enzymatic activity in N,N-dimethylethanolammonium alkylcarboxylate ionic liquids

Green Processes Being Investigation

In this study, we are examining the dissolution of straw lignin in several different ionic liquids, including:

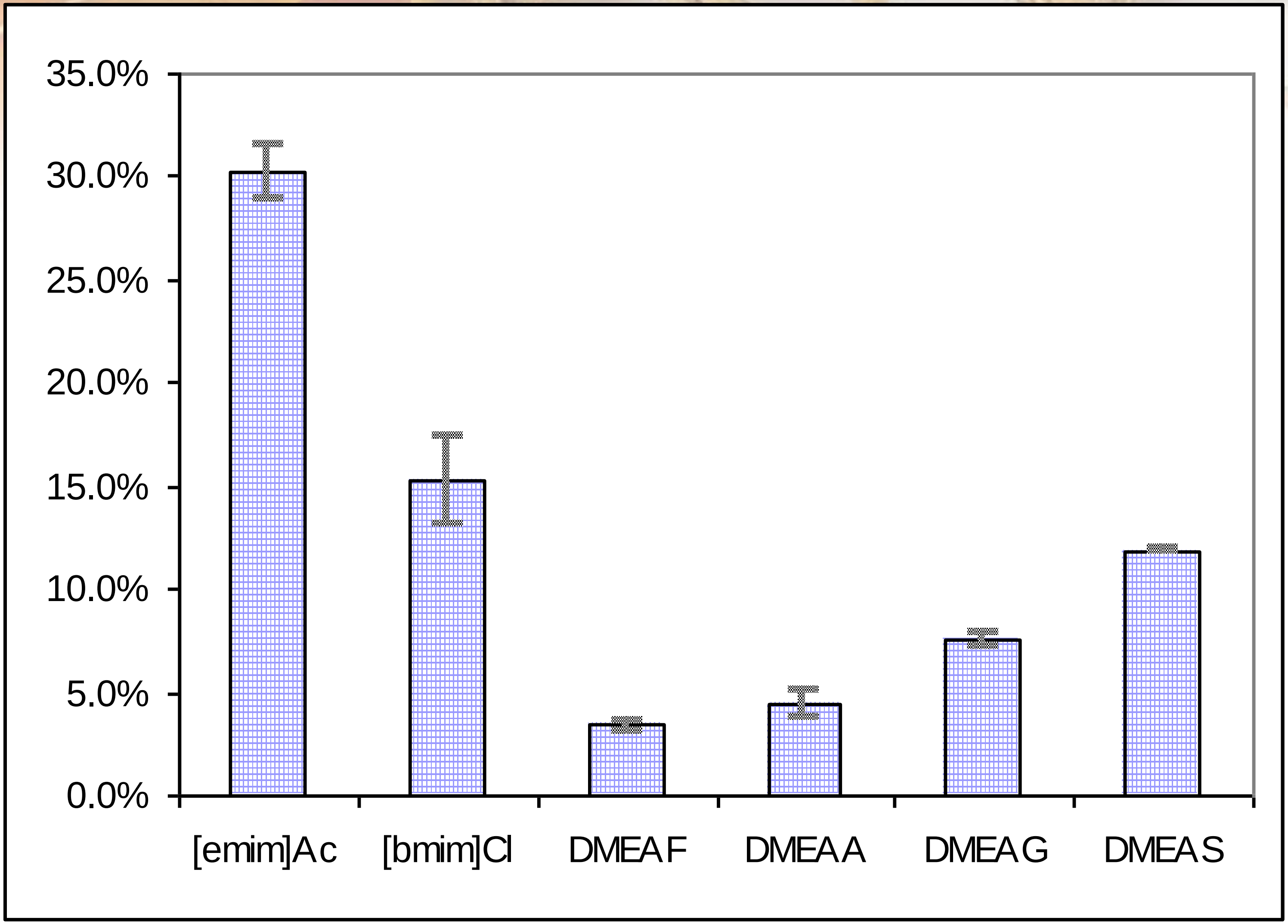
<u>Cations:</u>

1-ethyl-3-methylimidazolium acetate ([emim]Ac)
1-methyl-3-benzylimidazolium chloride ([bmim]Cl)

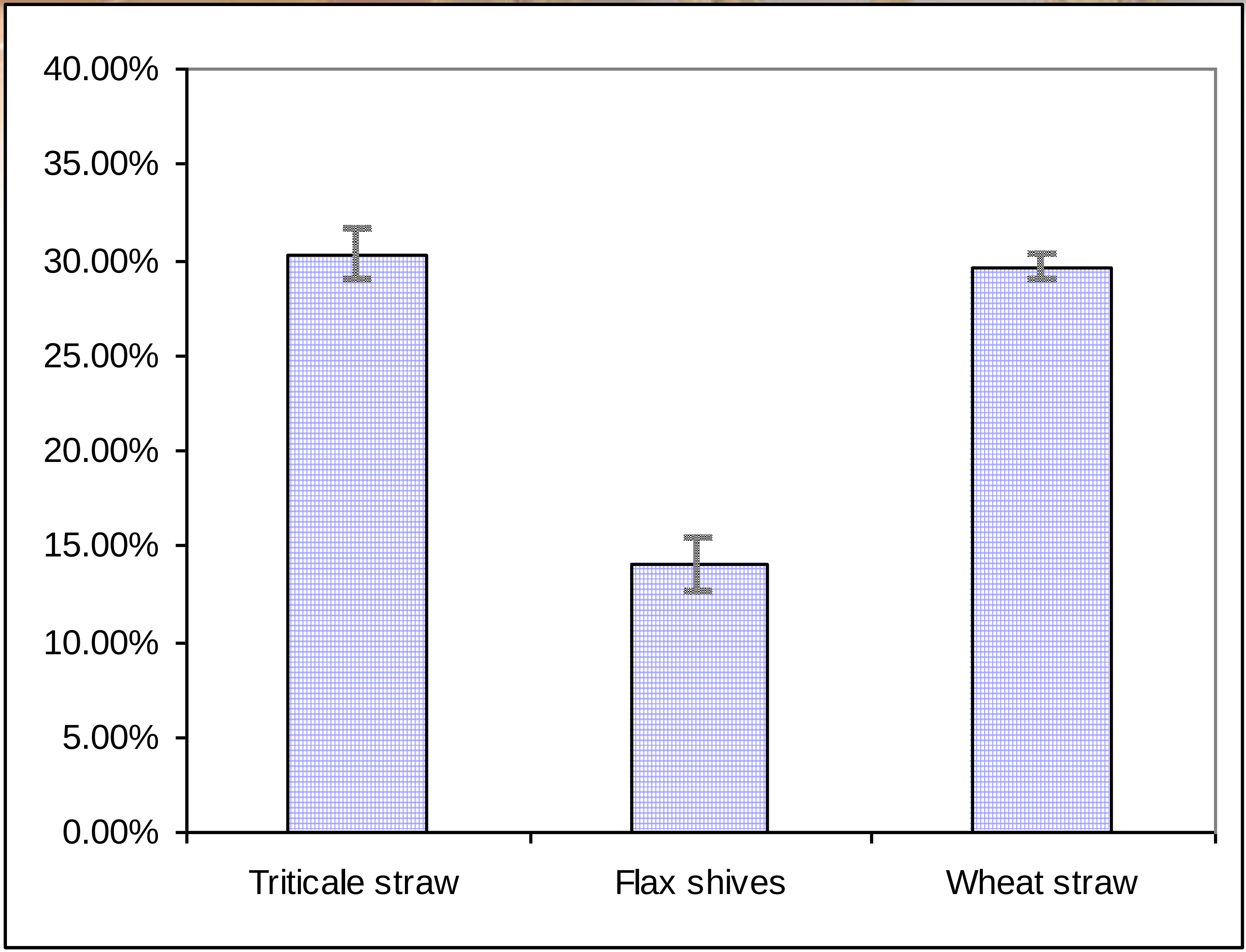
<u>Anions:</u>

dimethylethylammonium formate (DMEAF)
dimethylethylammonium acetate (DMEAA)
dimethylethylammonium glycolate (DMEAG)
dimethylethylammonium succinate (DMEAS)

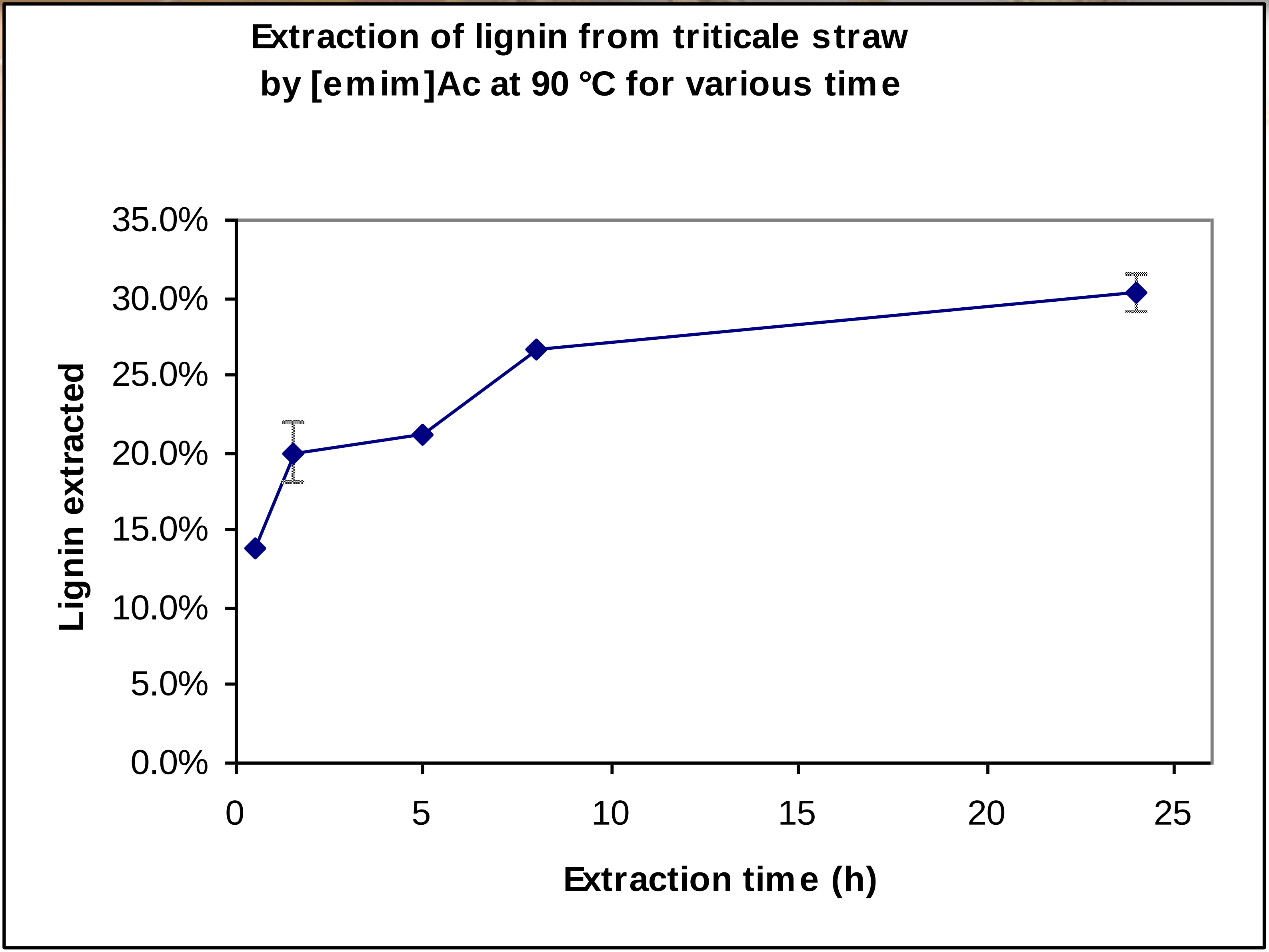
Extraction of Lignin From Tritcale Straw with Six Ionic Liquids at 90°C



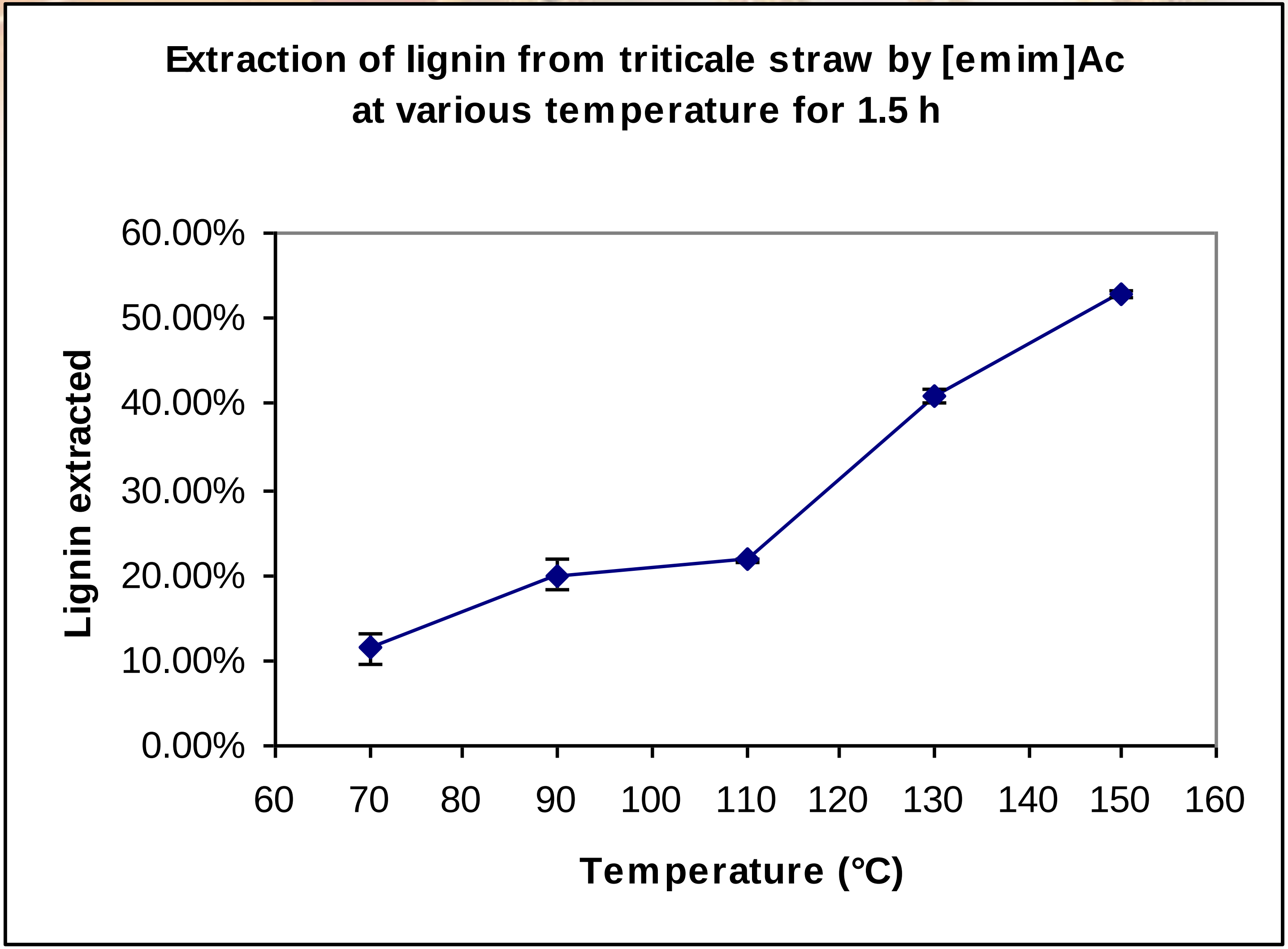
Ionic Liquid Extraction of Lignin From Wheat & Tritcale Straw & Flax Shives



Ionic Liquid Extraction of Lignin From Wheat & Tritcale Straw & Flax Shives



Ionic Liquid Extraction of Lignin From Wheat & Tritcale Straw & Flax Shives



Green Solvents - Ionic Liquids (ILs)

Rayne, S. and **G. Mazza**. 2008. Trichoderma reesei derived cellulase activity in three N,N-dimethylethanolammonium alkylcarboxylate ionic liquids. Nature Precedings. http://precedings.nature.com/documents/632/version/1.

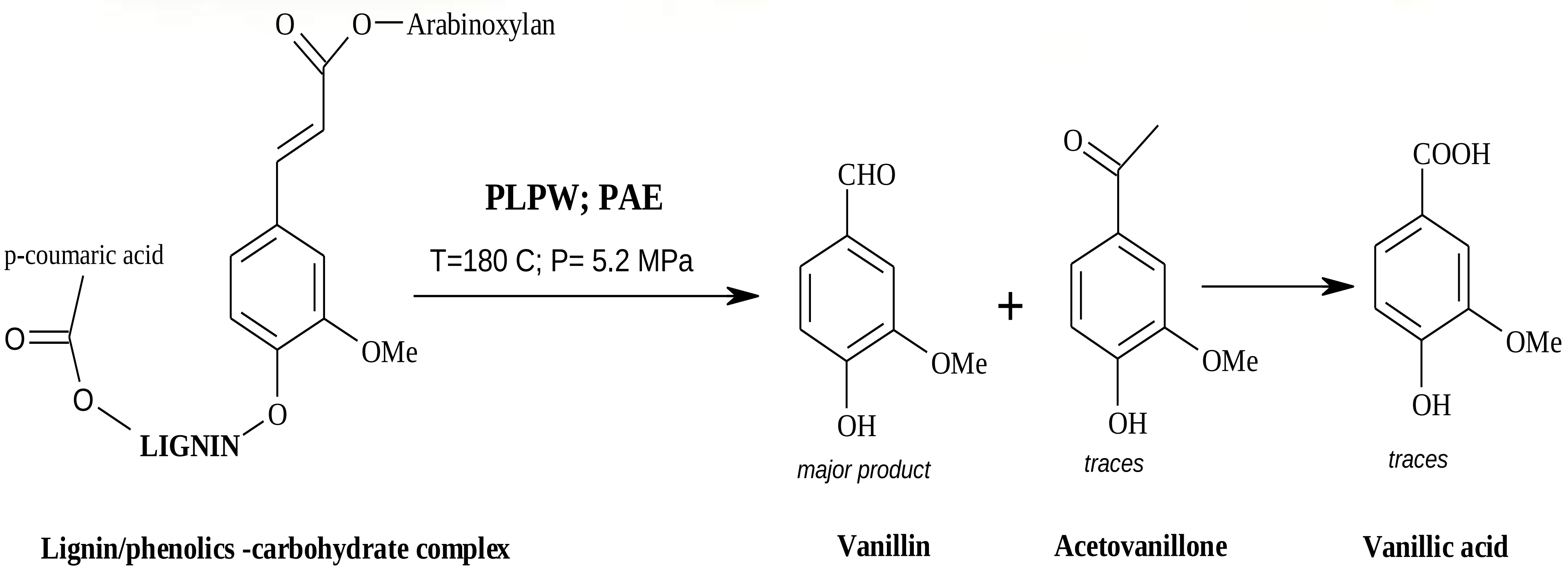
Conversion Processes

Thermo-chemical conversion

Bioconversion

Thermo-Chemical Conversion Processes

Extraction and conversion of ferulic acid from straw and bran by PLPW



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Thermo-Chemical Conversion Processes: Vanillin

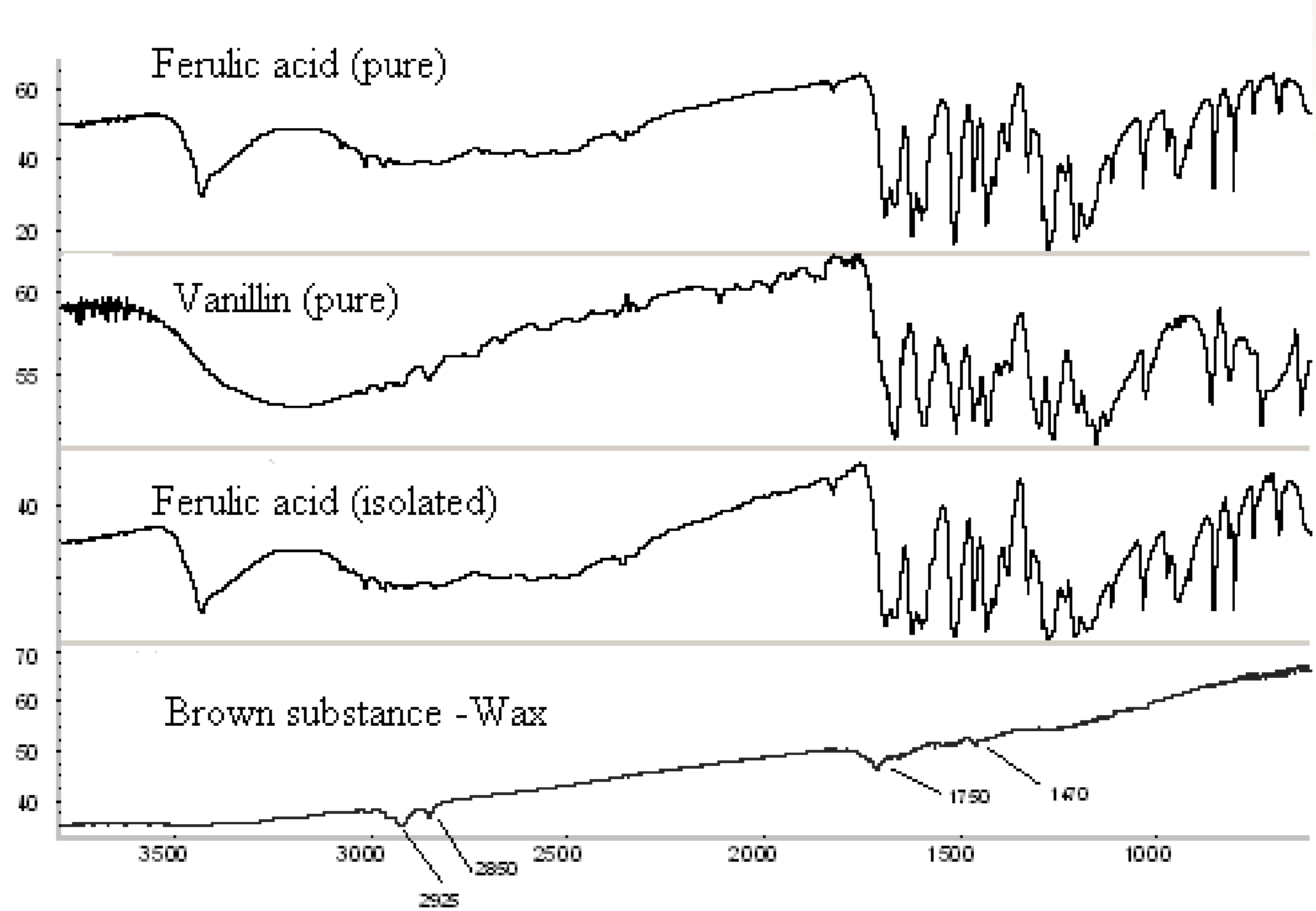
Vanillin is an important compound, widely used by the food industry for its aroma. Total consumption is estimated to be 12,000 metric tonnes/year.

Also used as raw material by the pharmaceutical industry for the synthesis of drugs such as L-dopa used for the treatment of Parkinson's Disease.

Commercial production of vanillin from lignosulfonates, formed during pulping processes, is no longer allowed due to environmental concerns.

The cost for “nature identical” vanillin from plant sources is ~$1000/kg.

FT-IR spectra of ferulic acid and wax fractions



Analytical Methods

RP-HPLC

Capillary gas chromatography (GC)

Fourier transform infrared (*FT-IR*) spectrometer

Capillary gas chromatography-mass spectrometry (GC-MS)

Differential scanning calorimetric (DSC)

Ion-moderated partition (*IMP*) *chromatography*

Size exclusion chromatography (SEC)

Pyrolysis-GC-MS

Liquid chromatography-mass spectrometry (LC-MS)

Scanning electron microscopy (SEM)

Confocal microscopy (CM)

Products of Interest

Products of Interest

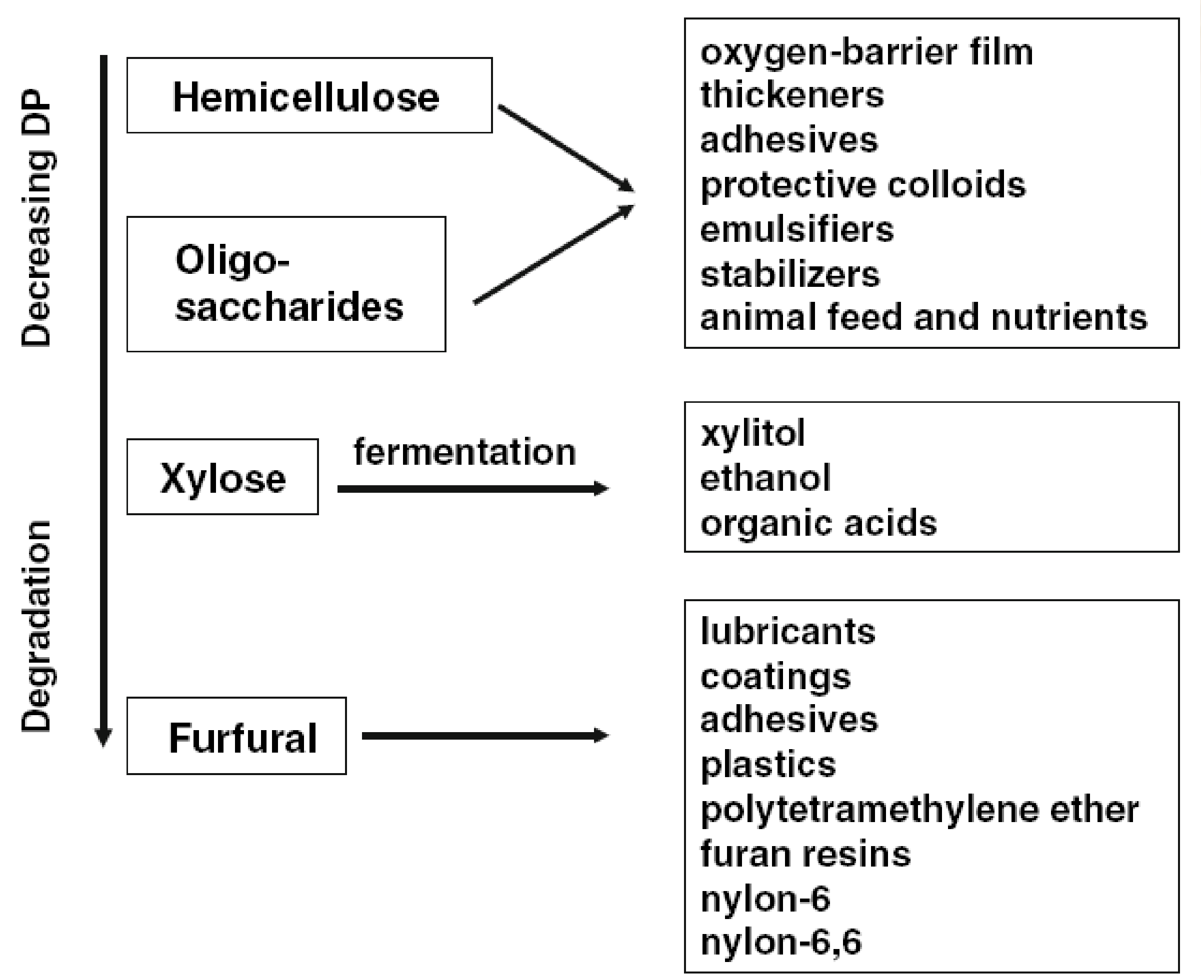
Nutraceuticals

Functional Food Ingredients

Cosmetics: Skin Care, Hair Care & Body Care

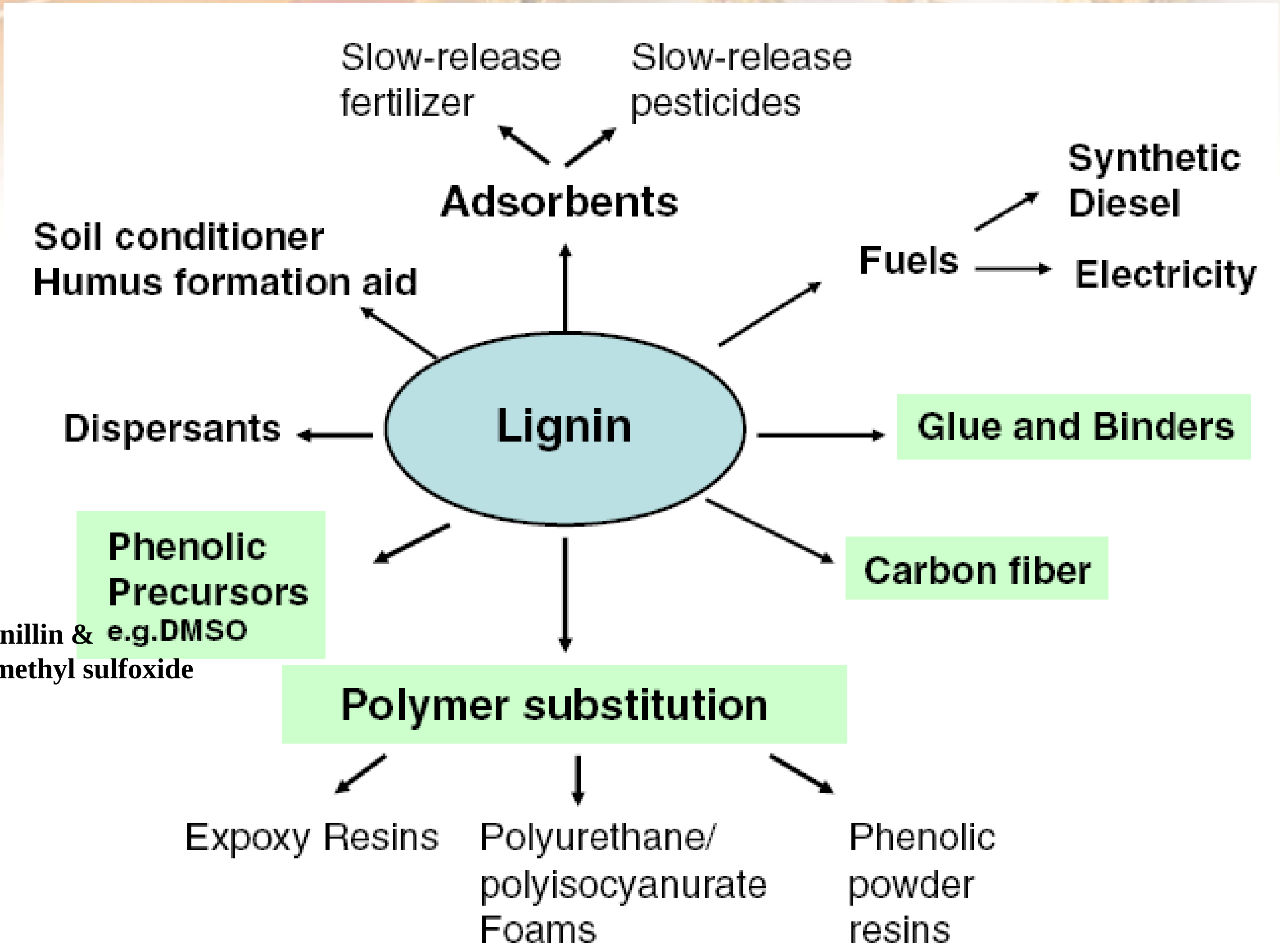
Medicinal, therapeutical & industrial products

A hemicellulose utilization tree



From: Y.-H. P. Zhang (2008). J Ind Microbiol Biotechnol

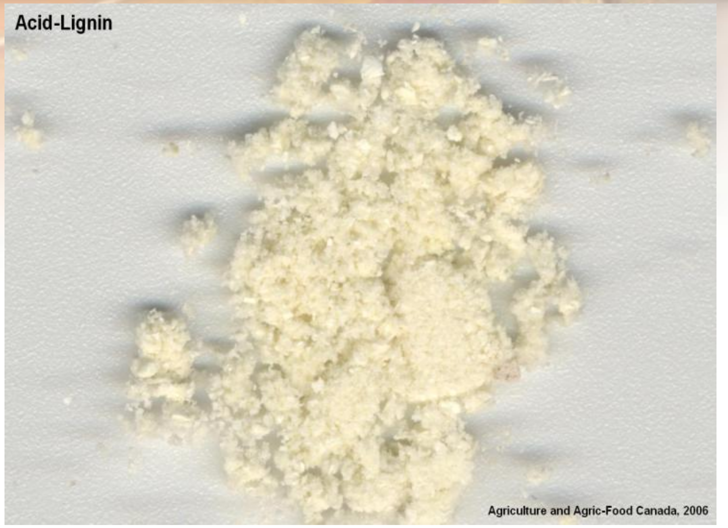
A lignin utilization tree

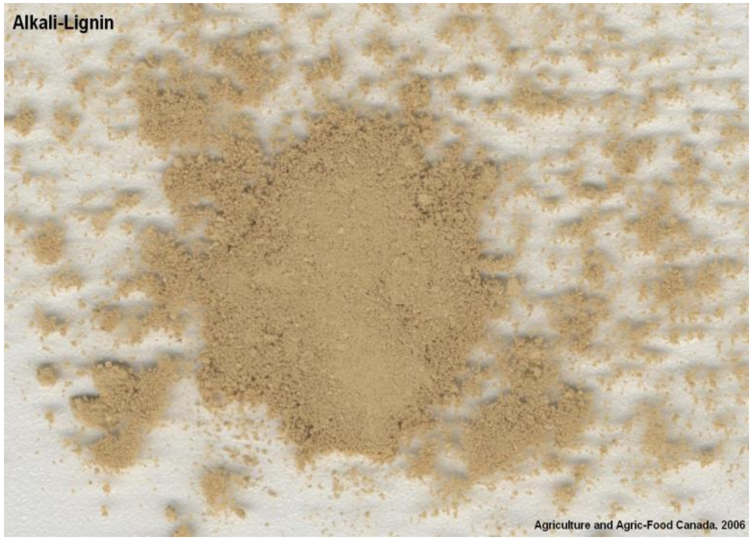


Vanillin & dimethyl sulfoxide

From: Y.-H. P. Zhang (2008). J Ind Microbiol Biotechnol

Biochemicals from Flax/Linseed Shives/Straw





Mazza 2007

Challenges

- **Developing sustainable green processes**
- **Chemical, physical and enzymatic modification**
- **Finding of specific functional/biological properties of components/molecules**

Conclusions

A variety of ‘green’ extractions and separation techniques are being investigated for manufacturing nutraceuticals, functional food ingredients, cosmetics, medicinal, therapeutical &/or industrial products

Selection and commercialization of the most appropriate technique(s) is being determined primarily by the raw material to be processed, phytochemical desired, and value of the finished product

Recent Scientific Publications

Pronyk, C. and **G. Mazza.** 2009. Design and scale-up of pressurized fluid extractors for food and bioproducts. Journal of Food Engineering. Article in Press, Corrected Proof . doi:10.1016/j.jfoodeng.2009.06.002

Kim, J-K.& **G. Mazza**. 2009. Extraction and separation of carbohydrates and phenolic compounds in flax shives with pH-controlled pressurized low polarity water. Journal of Agricultural and Food Chemistry 57, 1805 – 813.

Athukorala, Y., **G. Mazza** & B. D. Oomah. 2009. Extraction, purification and characterization of wax from flax (Linum usitatissimum) straw. European Journal of Lipid Science and Technology, *111*, 705–714.

Buranov, A. U. & **G. Mazza**. 2009. Extraction and Purification of Ferulic Acid from Flax Shives, Wheat and Corn Bran by Alkaline Hydrolysis and Pressurized Solvents. Food Chemistry, doi:10.1016/j.foodchem.2009.01.059

Hosseinian, F. S. and **G. Mazza.** 2009. Triticale bran and straw: Potential new sources of phenolic acids, proanthocyanidins, and lignans. Journal of Functional Foods 1, 5 7 –6 4.

Güçlü-Üstündağ, Ö. and **G. Mazza.** 2009. Effects of Pressurized Low Polarity Water Extraction Parameters on Antioxidant Properties and Composition of Cow Cockle Seed Extracts. Plant Foods Hum Nutr 64:32–38.

Karacabey, E. and **G. Mazza**. 2009. Optimization of antioxidant activity of grape cane extracts using response surface methodology. Food Chem. http://dx.doi.org/10.1016/j.foodchem.2009.06.029

Recent Scientific Publications

Karacabey, E. and **G. Mazza**. 2008. Optimization of Solid-Liquid Extraction of Resveratrol and Other Phenolic Compounds from Milled Grape Canes (*Vitis vinifera*). J. Agric. Food Chem. *56*, 6318–6325.

Buranov AU, Mazza G. 2008. Lignin in straw of herbaceous crops. Industrial Crops and Products 28, 237-259.

Kim, J-K.& **G. Mazza**. 2008. Optimization of phosphoric acid catalyzed fractionation and enzymatic digestibility of flax shives. Industrial Crops & Products 28:346-355.

Ho, C. H. L., Cacace, J. E. and **G. Mazza.** 2008. Mass transfer during pressurized low polarity water extraction of lignans from flaxseed meal. Journal of Food Engineering 89; 64–71.

Rayne, S., Karacabey, E., and **G. Mazza.** 2008. Grape cane waste as a source of trans-resveratrol and trans-viniferin: High-value phytochemicals with medicinal and anti-phytopathogenic applications. Industrial Crops and Products 27 (3): 335-340.

Rayne, S. and **G. Mazza**. 2008. Trichoderma reesei derived cellulase activity in three N,N-dimethylethanolammonium alkylcarboxylate ionic liquids. Nature Precedings. http://precedings.nature.com/documents/632/version/1.

Mazza, G. and T. Cottrell. 2008. Carotenoids and cyanogenic glucosides in saskatoon berries. Journal of Food Composition and Analysis 21:249–254.

Güçlü-Üstündağ, Ö. and **G. Mazza.** 2008. Extraction of Saponins and Cyclopeptides from Cow Cockle Seed with Pressurized Low Polarity Water. LWT - Food Science and Technology 41 (9):1600-1606.

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The research team

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Michael Parker
Miao Zhang
Robert Y. Nsimba

Pilot Plant South View

Mazza 2005

Pilot Plant North View