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Thermochemical and Catalytic Upgrading Biomass into Industrial Bioproducts

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Forest Biorefinery

NSERC/FPInnovations
Industrial Research Chair (IRC)
Program in Forest Biorefinery
"maximizing the values of trees"

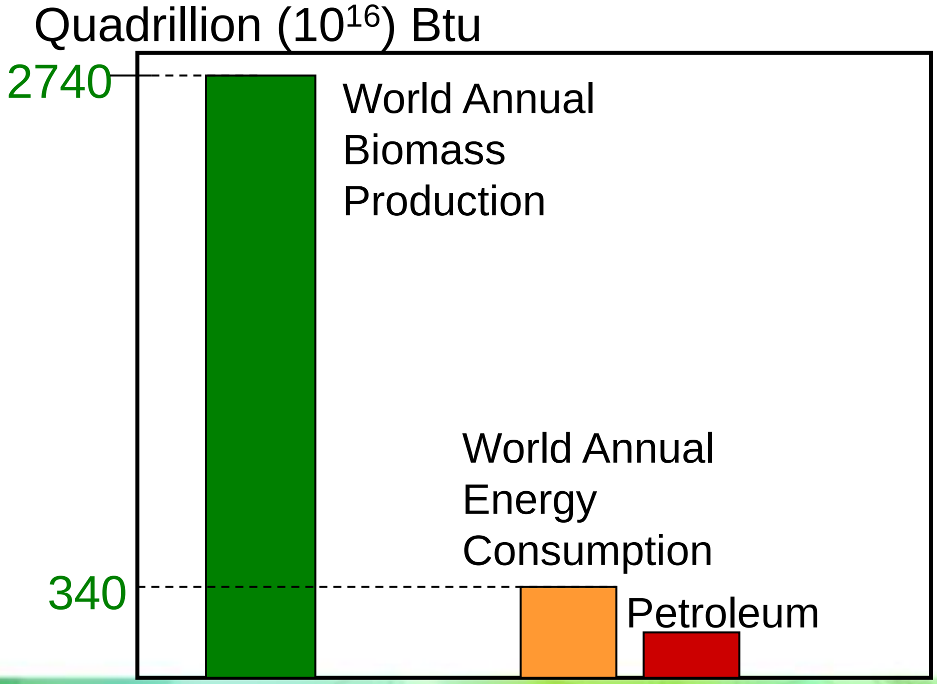
Seminar at WISE – Waterloo Institute for Sustainable Energy June 6, 2012

Outline

- ❑ **Introduction of Industrial Bioproducts**
- ❑ **Agricultural and Forestry Biomass Resources**
- ❑ **Biomass Conversions Technologies**
- ❑ **A Showcase of Dr. Xu’s Research on Thermochemical and Catalytic Upgrading Biomass into Industrial Bioproducts**

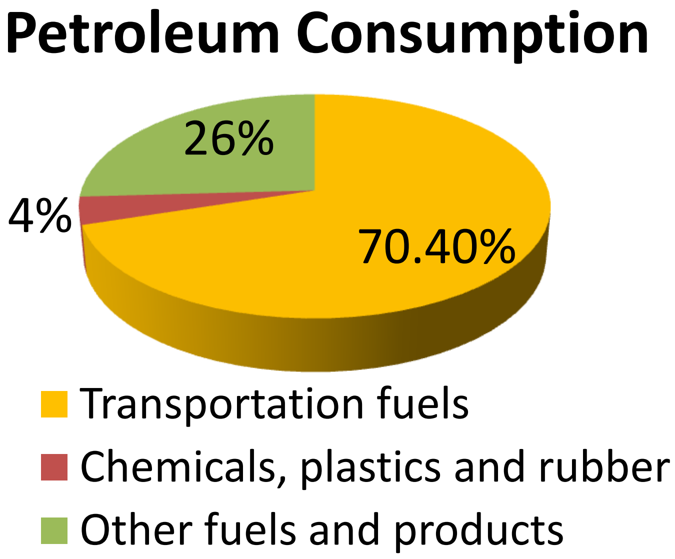
What are Industrial Bioproducts

- Today the world economy is heavily relying on fossil energy (petroleum, coal, natural gas) to produce power, fuels, chemicals and materials.
- The world fossil resources are depleting fast.
- Biomass (terrestrial or aquatic vegetation, agricultural or forestry residues and industrial or municipal waste) presents an immense renewable resource that could provide an alternative to fossil resources.
- The **bio-based chemical and materials products** derived from biomass are called **industrial bioproducts**.

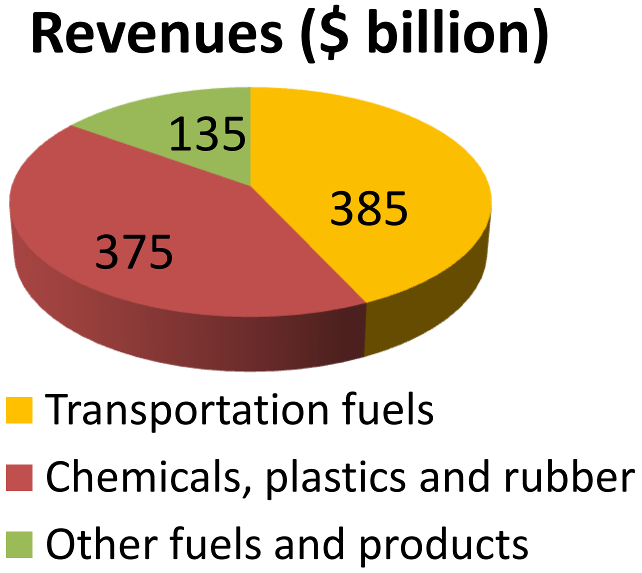


Why not Fuels, but Chemicals/Materials?

Chemicals and materials much more valuable than fuels – a lesson learnt from the petroleum industry …



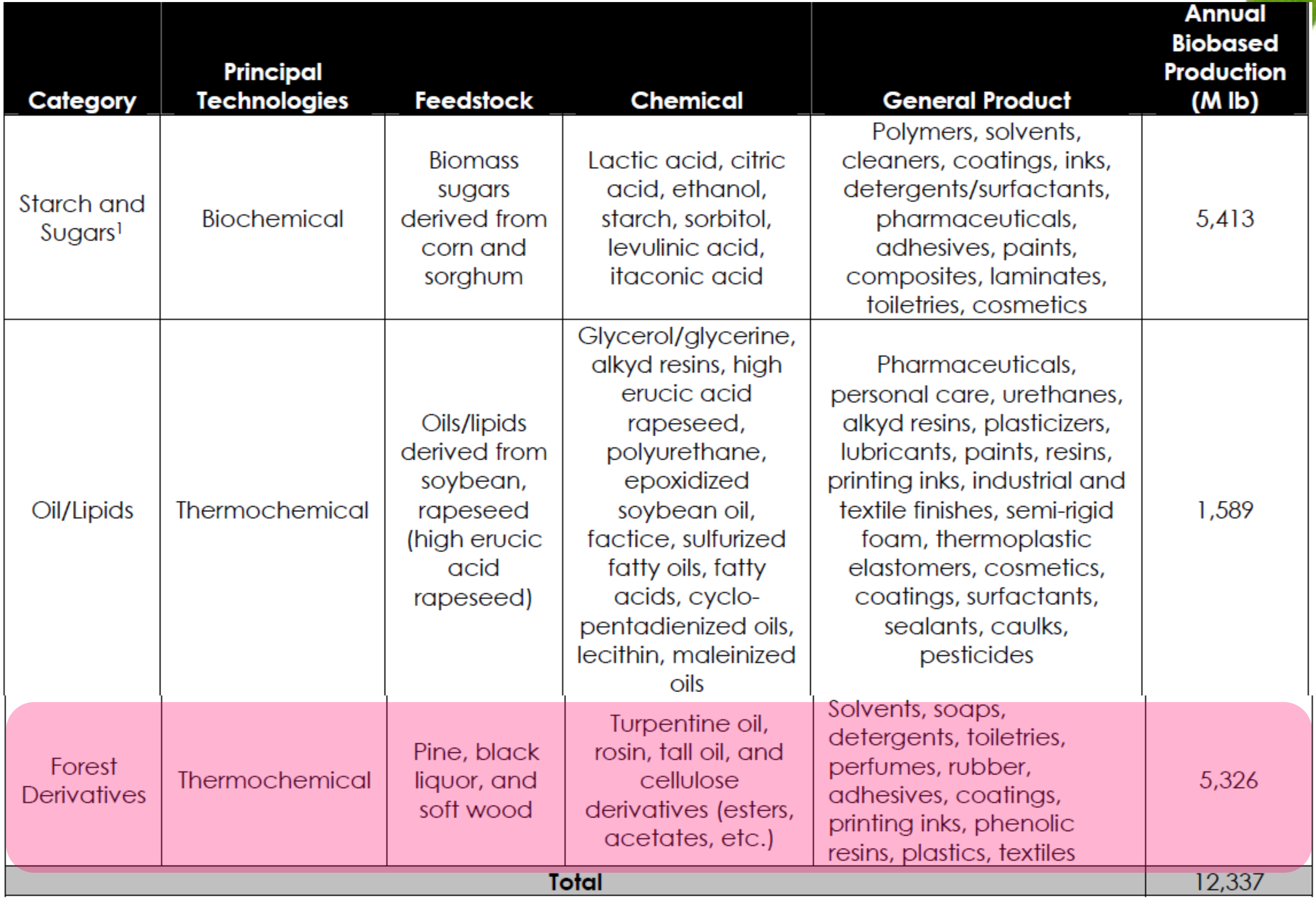
Petroleum Consumption



Revenues ($ billion)

From presentation by John Schmidt, the NSERC Strategic Biomaterials and Chemicals Network Overview Workshop, April 12, 2010, Toronto.

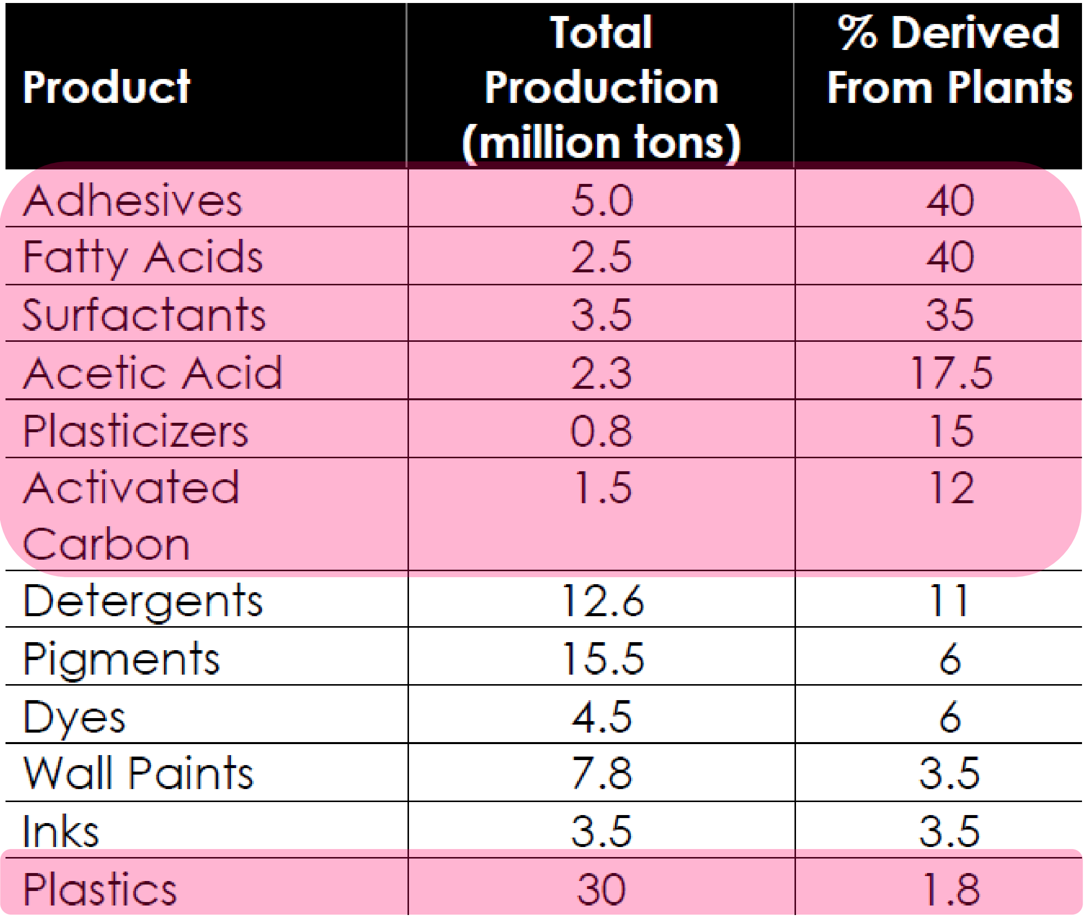
Current Industrial Bioproducts Production in the US



Category	Principal Technologies	Feedstock	Chemical	General Product	Annual Biobased Production (M lb)
Starch and Sugars[1]	Biochemical	Biomass sugars derived from corn and sorghum	Lactic acid, citric acid, ethanol, starch, sorbitol, levulinic acid, itaconic acid	Polymers, solvents, cleaners, coatings, inks, detergents/surfactants, pharmaceuticals, adhesives, paints, composites, laminates, toiletries, cosmetics	5,413
Oil/Lipids	Thermochemical	Oils/lipids derived from soybean, rapeseed (high erucic acid rapeseed)	Glycerol/glycerine, alkyd resins, high erucic acid rapeseed, polyurethane, epoxidized soybean oil, factice, sulfurized fatty oils, fatty acids, cyclo-pentadienized oils, lecithin, maleinized oils	Pharmaceuticals, personal care, urethanes, alkyd resins, plasticizers, lubricants, paints, resins, printing inks, industrial and textile finishes, semi-rigid foam, thermoplastic elastomers, cosmetics, coatings, surfactants, sealants, caulks, pesticides	1,589
Forest Derivatives	Thermochemical	Pine, black liquor, and soft wood	Turpentine oil, rosin, tall oil, and cellulose derivatives (esters, acetates, etc.)	Solvents, soaps, detergents, toiletries, perfumes, rubber, adhesives, coatings, printing inks, phenolic resins, plastics, textiles	5,326
Total					12,337

Energetics, Industrial Bioproducts: Today and Tomorrow, July 2003

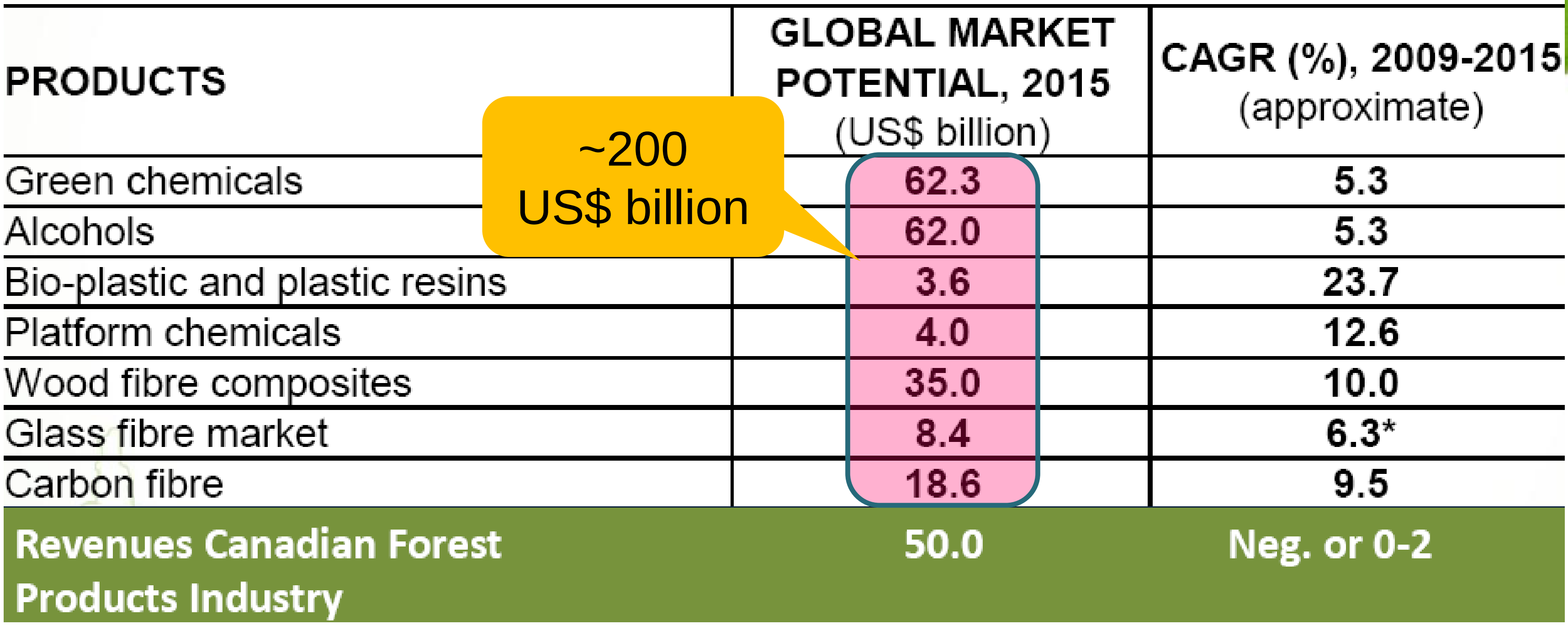
The Market Share of Industrial Bioproducts in the US



Product	Total Production (million tons)	% Derived From Plants
Adhesives	5.0	40
Fatty Acids	2.5	40
Surfactants	3.5	35
Acetic Acid	2.3	17.5
Plasticizers	0.8	15
Activated Carbon	1.5	12
Detergents	12.6	11
Pigments	15.5	6
Dyes	4.5	6
Wall Paints	7.8	3.5
Inks	3.5	3.5
Plastics	30	1.8

Morris, David, and Ahmed, Irshad. 1992. *The Carbohydrate Economy: Making Chemicals and Industrial Materials from Plant Matter. Institute for Local Self-Reliance. Washington, D.C*

Bioproducts Market Outlook



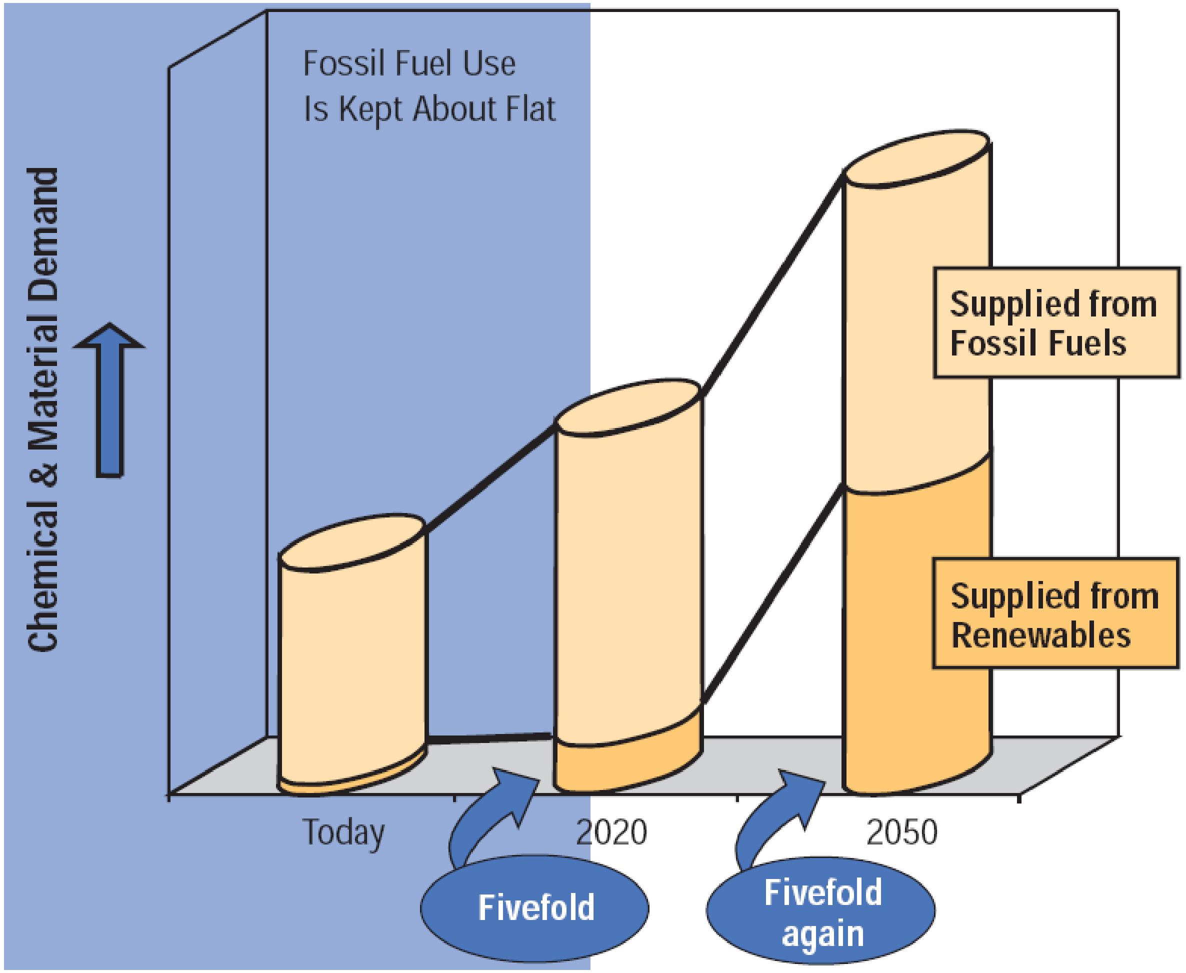
PRODUCTS	GLOBAL MARKET POTENTIAL, 2015 (US$ billion)	CAGR (%), 2009-2015 (approximate)
Green chemicals	62.3	5.3
Alcohols	62.0	5.3
Bio-plastic and plastic resins	3.6	23.7
Platform chemicals	4.0	12.6
Wood fibre composites	35.0	10.0
Glass fibre market	8.4	6.3*
Carbon fibre	18.6	9.5
Revenues Canadian Forest Products Industry	**50.0**	**Neg. or 0-2**

~200
US$ billion

The Canadian forest industry is poised to be a dynamic contributor to the new bio-age

(Canadian Bio-Pathway, Forest Products Association of Canada)

Bioproducts Market Outlook (Cont'd)



RENEWABLES VISION 2020, EXECUTIVE STEERING GROUP, "THE TECHNOLOGY ROADMAP FOR PLANT/CROP-BASED RENEWABLE RESOURCES 2020": http://www1.eere.energy.gov/biomass/pdfs/technology_roadmap.pdf

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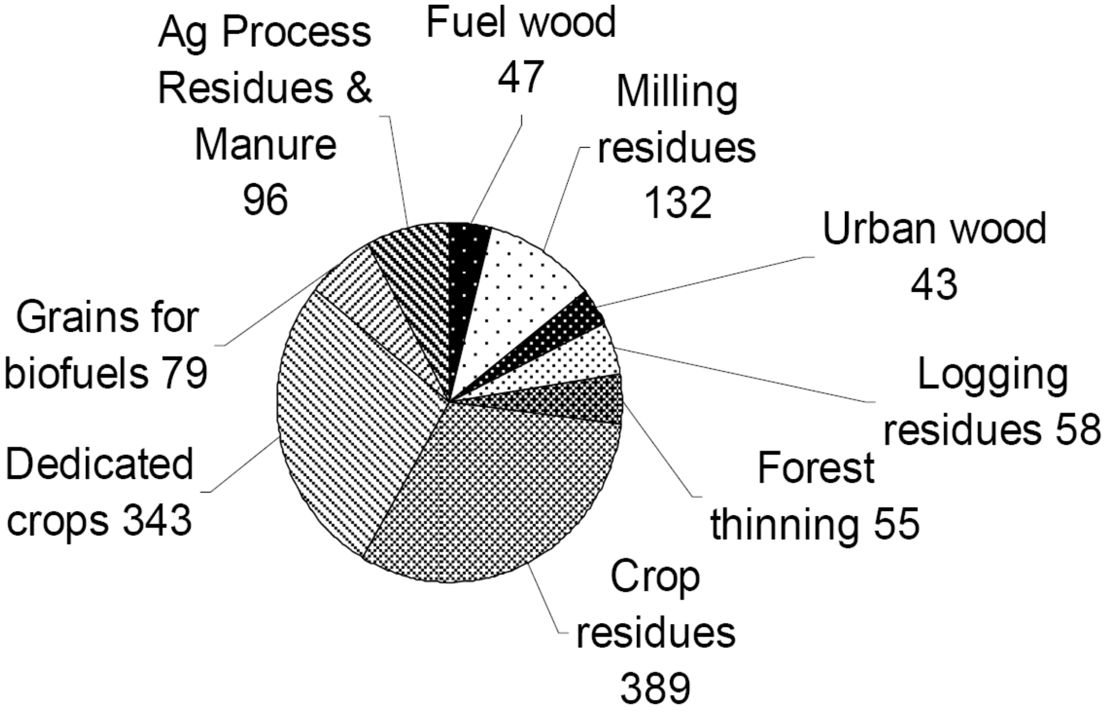
Agricultural and Forestry Biomass Resources in the US

- The US DOE and the US Department of Agriculture demonstrated that 1.3 billion metric tons of biomass can be produced exclusively for bio-fuel production in the US each year (NREL, 2006), which could supply 21% of U.S. energy demand, or 33% of U.S. transport fuels.



Unit: millions of metric tons

Agricultural & Forestry Biomass Resources in Canada

- The amount of potential agricultural residues in Canada has been estimated at **29.3 Mt oven dried** (OD) biomass per year, among which **17.8 Mt OD** biomass/year may be available for energy and chemical production (Wood and Layzell, 2003)
- Canada is blessed with **401.9 million hectares of forest** (approximately 10% of the world's total forest), producing ~15 million tonnes of pulp annually.
- A **vastly large amount** of **forestry residues are available for energy and bioproducts production**.

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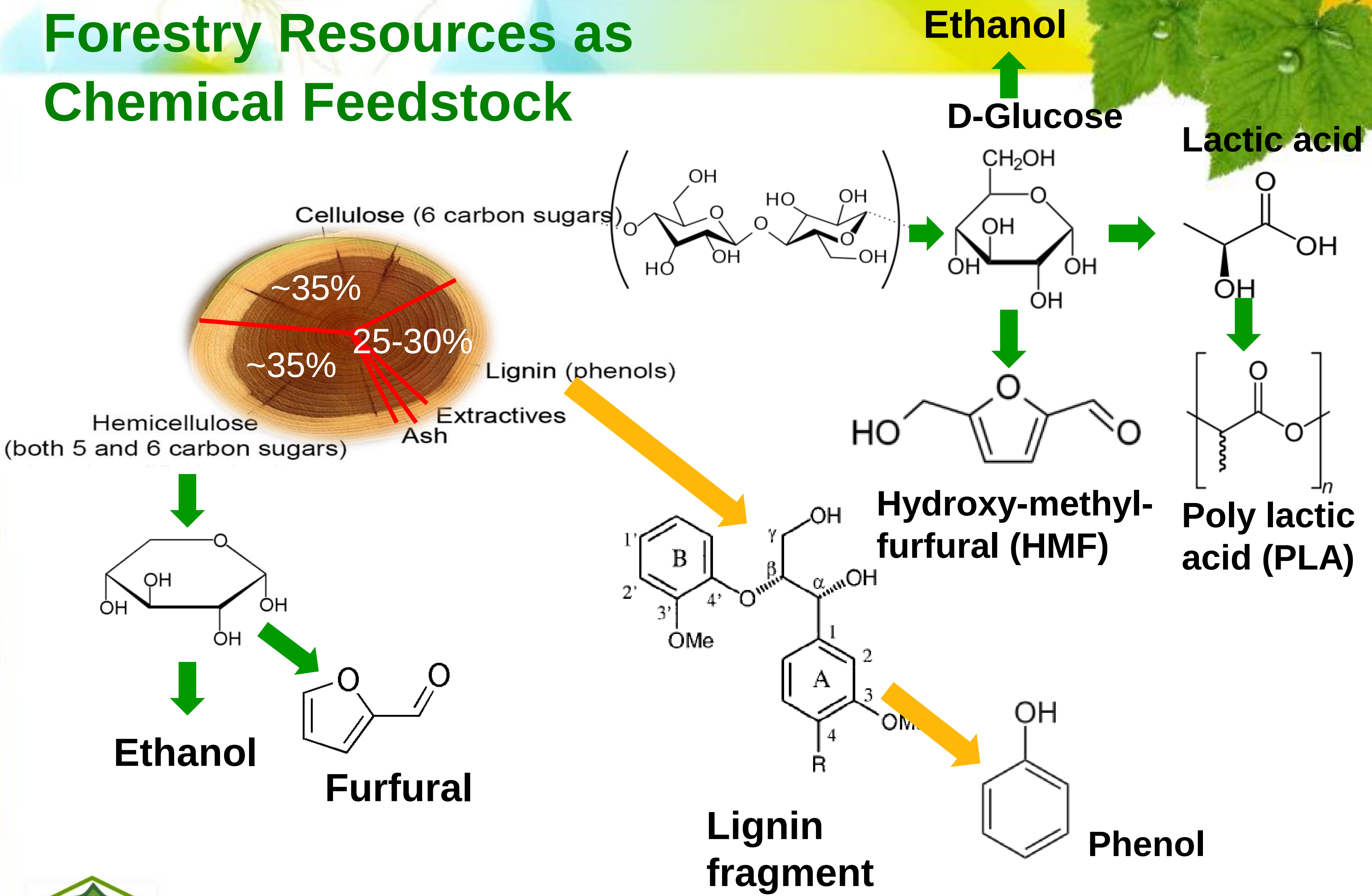
Forestry Resources as Chemical Feedstock



Ethanol

D-Glucose

Lactic acid

Hydroxy-methyl-furfural (HMF)

Poly lactic acid (PLA)

Ethanol

Furfural

Lignin fragment

Phenol

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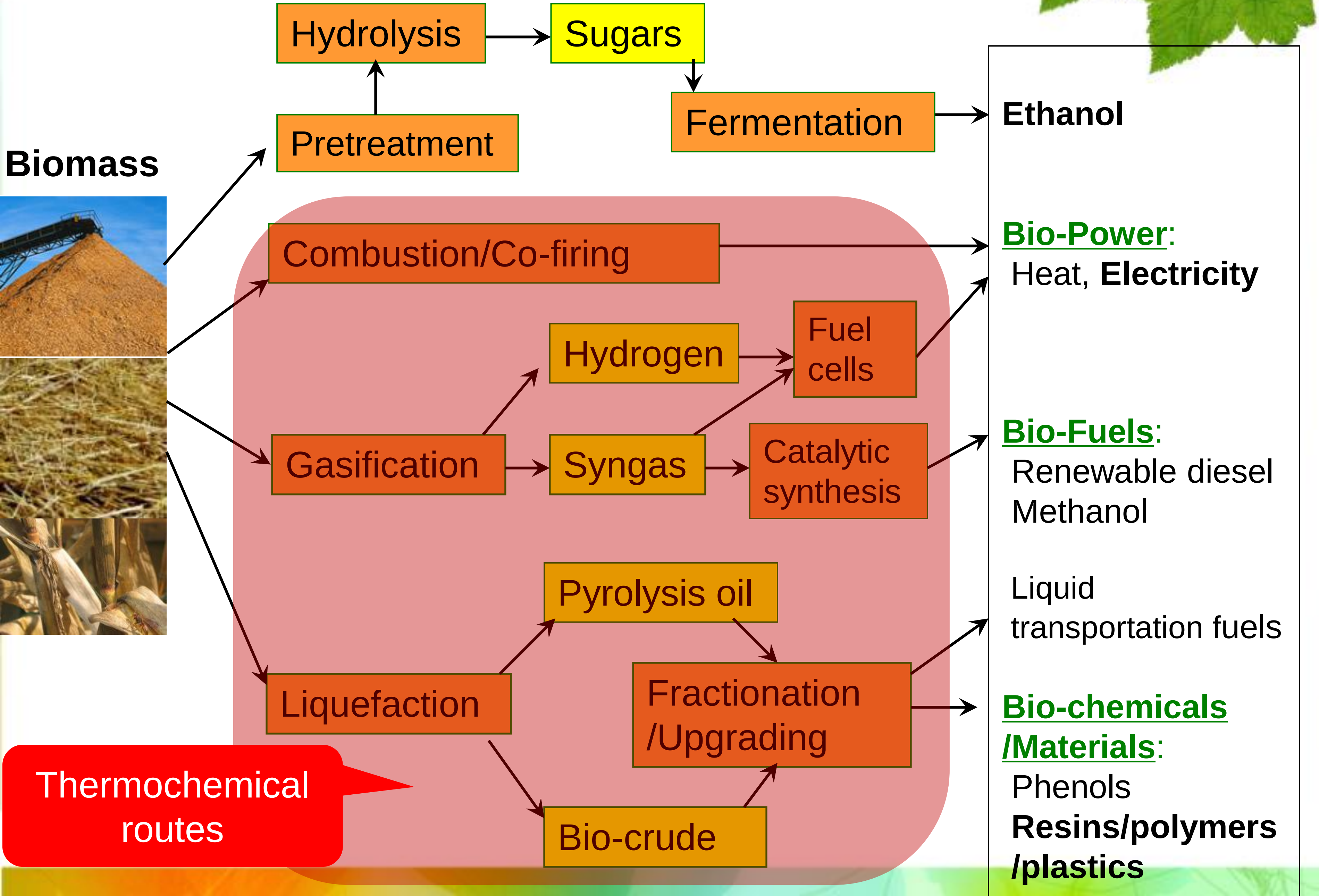


Biomass

Hydrolysis

Sugars

Pretreatment

Fermentation

Combustion/Co-firing

Hydrogen

Fuel cells

Gasification

Syngas

Catalytic synthesis

Pyrolysis oil

Liquefaction

Fractionation /Upgrading

Bio-crude

Thermochemical routes

Ethanol

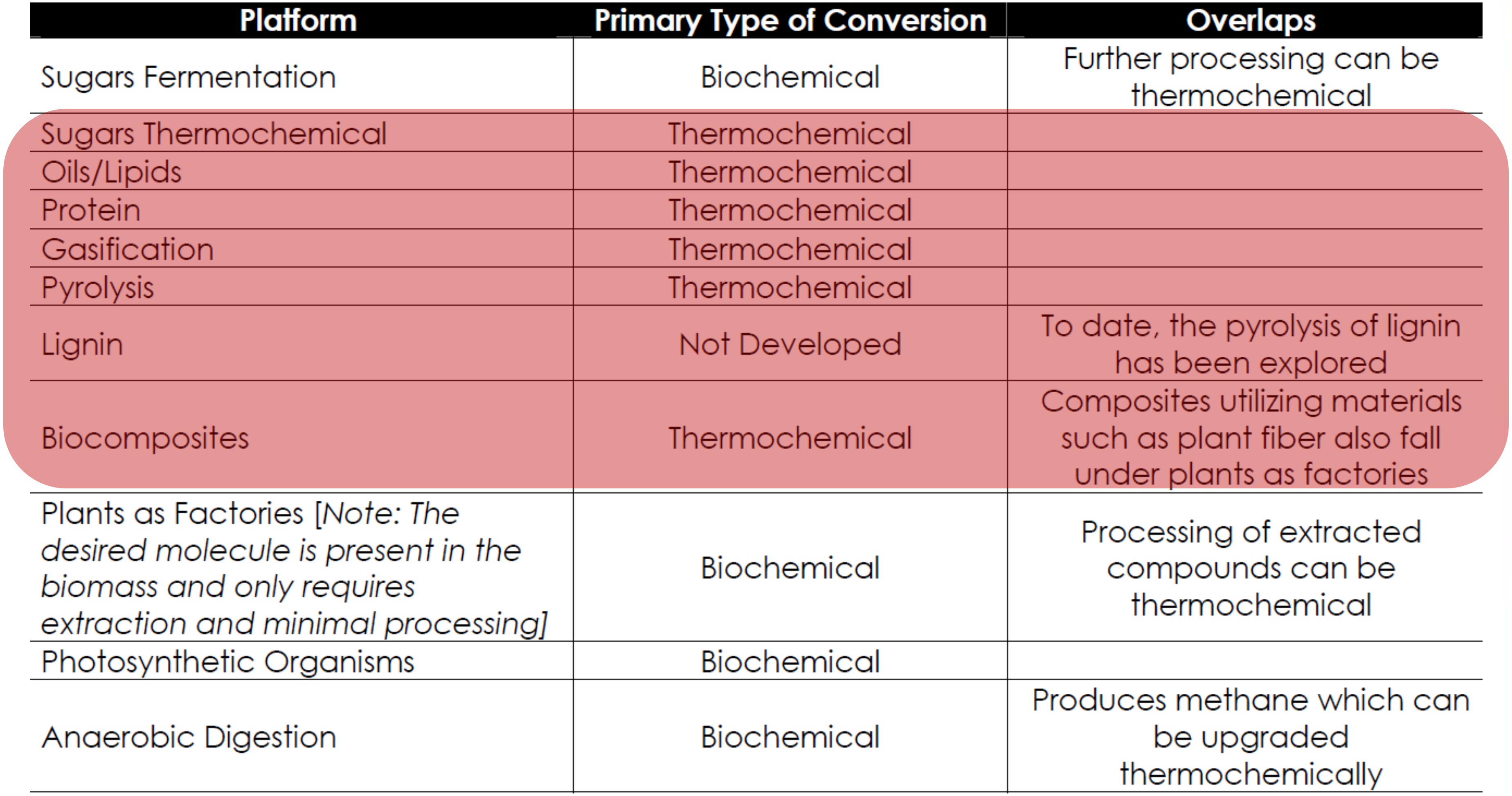
Bio-Power: Heat, **Electricity**

Bio-Fuels:
Renewable diesel
Methanol

Liquid transportation fuels

Bio-chemicals /Materials:
Phenols
Resins/polymers /plastics

Biorefinery technology platform and Types of Biomass Conversion



Platform	Primary Type of Conversion	Overlaps
Sugars Fermentation	Biochemical	Further processing can be thermochemical
Sugars Thermochemical	Thermochemical	
Oils/Lipids	Thermochemical	
Protein	Thermochemical	
Gasification	Thermochemical	
Pyrolysis	Thermochemical	
Lignin	Not Developed	To date, the pyrolysis of lignin has been explored
Biocomposites	Thermochemical	Composites utilizing materials such as plant fiber also fall under plants as factories
Plants as Factories [*Note: The desired molecule is present in the biomass and only requires extraction and minimal processing]*	Biochemical	Processing of extracted compounds can be thermochemical
Photosynthetic Organisms	Biochemical	
Anaerobic Digestion	Biochemical	Produces methane which can be upgraded thermochemically

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  - Esterification of Starch for the Production of Biodegradable Materials
  - Production of Bio-phenols and Green Resins/Adhesives from Forestry Residues
  - Novel One-step Catalytic Process to Produce 1-Butanol and Fuel Additives from Bio-ethanol

Esterification of Starch for the Production of Biodegradable Materials

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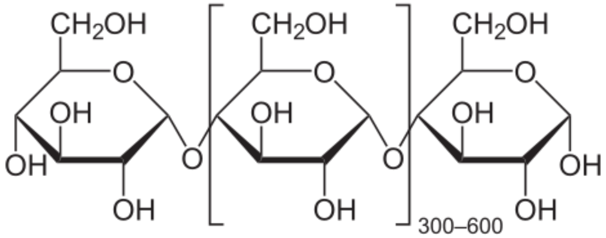
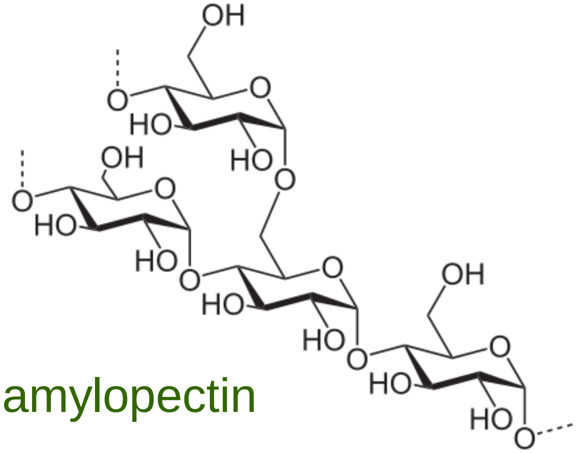
Starch

- The most important digestible carbohydrate in human and animal diets;
- A major constituent of traditional foods found in many crops and most plant seeds;
- A polymer of glucose composed of linear amylose and highly branched amylopectin with approximately three hydroxyl groups in each glucose unit.



amylose



amylopectin

Why Use Starch as a Raw Material for Biopolymer/Biomaterials

- **Abundant/renewable resource**: Canada produces approx. 50 million tonnes (Mts) of grains annually (Agriculture and Agri-Food Canada , 2009);
- **High purity**
- **Biodegradable**
- **Low cost**

Why biopolymer/biomaterials

- ○ Renewable/Biodegradable
- ○ Environmentally benign and non-toxic
- ○ Inexpensive
- ○ A rapidly growing market: the global market for biodegradable polymers will rapidly grow at a compound average growth rate of more than 17%/year through 2012 (BCC Research)

Modification is Needed

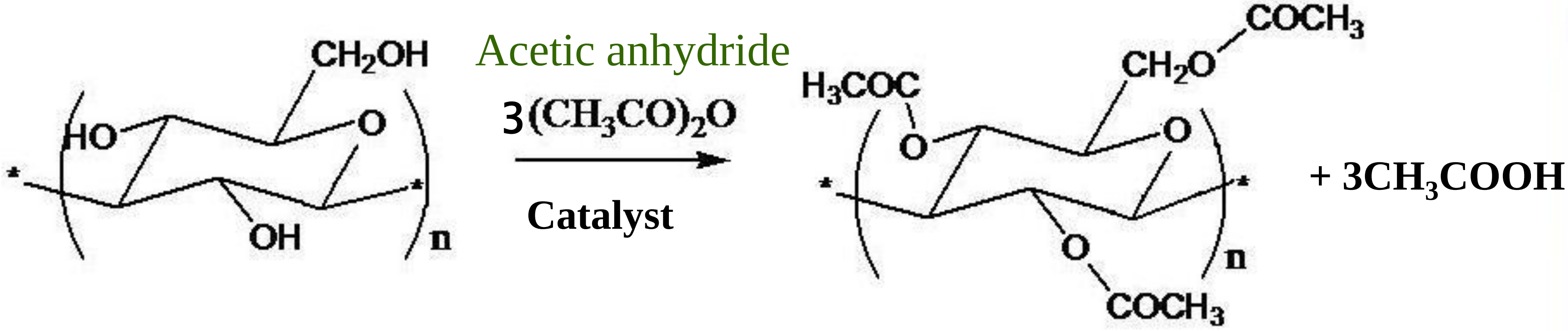
- **Starch**
  - High polarity, not compatible with other materials, insoluble in organic solvent
  - High crystallinilty, hard to melt and process
  - Strong intra-molecular interaction (hydrogen bonds), no strength
- After Modification to **Starch Acetates** (by esterification)
  - Low polarity, compatible with other materials, soluble in organic solvent
  - Low crystallinilty, can melt and ease processing
  - Weaker intra-molecular interaction, improved strength

Applications Starch Acetates (SA)

- Food and medicinal industry
- Hot melt adhesives
- Coatings
- Cigarette filters
- Biodegradable packaging materials
- Metal ion absorbents
- Films
- Foams or plastic parts
- Composite with synthetic materials to form biodegradable materials

Biodegradable Plastics

Starch Modification by Esterification



Original starch polymer

Starch triacetate with DS of 3

- SA of lower degrees of substitution (DS) – food and medicinal applications
- SA of high DS – biomaterials products

Conventional methods for synthesis of Starch Acetates

	Year	Reactant	Catalyst	Precipitation Method	Product
Mullen and Pacsu	1942	Fatty anhydrides	Pyridine		Fully-substituted fatty acid esters of starch
Mark and Mehltretter	1972	Acetic anhydride	50% NaOH solution for 2 – 5 hr	Water	Starch triacetates
Shogren	1992	Acetic anhydride	NaOH solution in 10-50 min	Water	Starch triacetates of DS 1.5-2.5

Conventional methods for synthesis of Starch Acetates (Cont'd)

	Year	Solvent	Catalyst	Precipitation Method	Product
Billmers and Tessler	1994	Anhydride	25% NaOH for 4 h at 0 – 40 °C	water	Starch acetates of DS 1-2
Lammers, Tiitola, Vuorenpaa	1998	Anhydride	NaOH at higher T of 130 – 180 °C at 0.1 – 50 bar	water	Starch acetates of Medium-high DS 1-2.5
Runkel, Stoye	1999	Acetic anhydride	No catalyst at high T of 180 °C and 5 bar	water	Starch acetates of DS 1.2-2.6
Volkert, et al.	2010	Acetic anhydride	Potassium carbonate at 95°C for ≤0.75 hr	water	Starch acetates of DS 2.9, yield of 89%

Common Problems of the Conventional Methods for SA Synthesis

- Low DS: 1-2 or <3
- Large quantities of sodium (or potassium) acetate by-products, with a low market value.
- Reaction conditions (difficult to control)
  - High T/P was used in some processes
- Loss of yield from hydrolysis of acetic anhydride by water and sodium hydroxide

Synthetic Procedure

Dry cornstarch (8.1g, 0.05 mol)

acetic anhydride

50 mL acetic acid

Three-neck flask reactor (100mL) in an oil bath

catalyst of type A, B, or C

Reflux for 2h at 120 °C

Cool down and precipitate the SA products in ethanol or isopropanol

Filtration

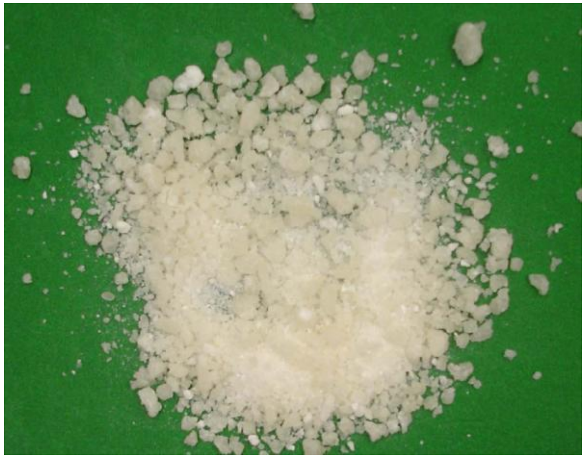
SA products

Solvent for recovery

Cornstarch-derived SA Products

Soluble in acetic acid and other organic solvents

Insoluble in acetic acid



(a)

SA of DS of 3

(b)

SA of DS of 2

(c)

Original cornstarch

SA Products Yields

- Catalysts A and C produced highest yields at an average of 79 – 85 %; Catalyst A was selected because of its price, activity and better product quality (lighter color SA products);
- Increase of catalyst amount did not affect the products yields;
- Increase of acetic anhydride/starch ratio could substantial increase the product yields from 36 to 85%;
- The SA products yields can be improved by optimizing the precipitation conditions (precipitating solvent and conditions).

Type A Catalyst

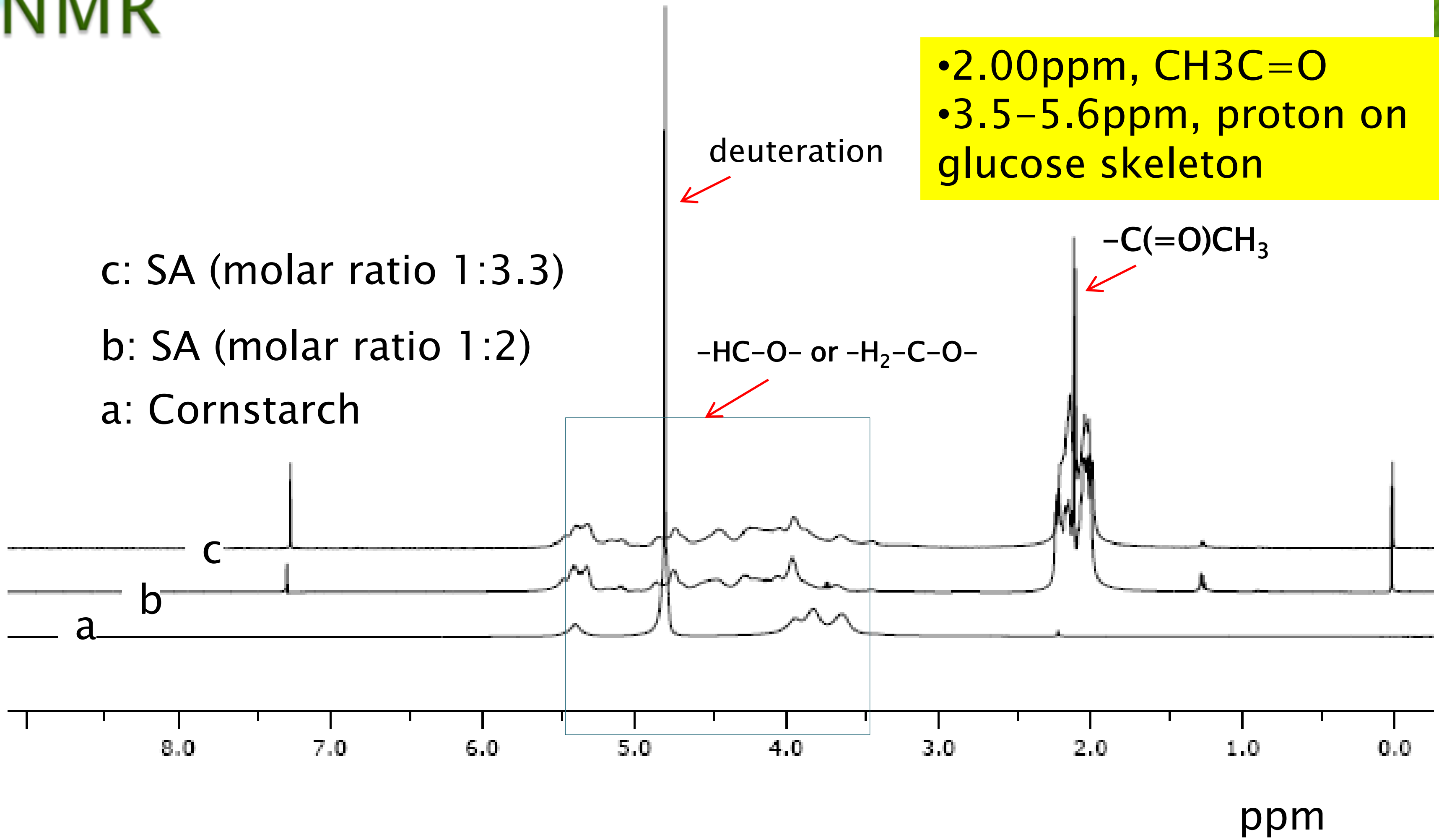
Type B Catalyst

Type C Catalyst

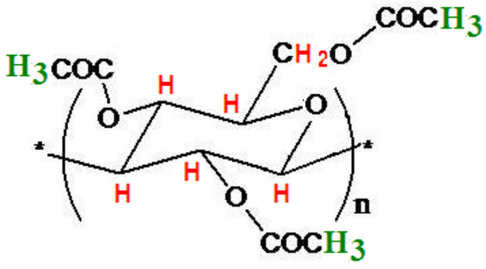
No catalyst

NMR

- 2.00ppm, $CH3C=O$
- 3.5-5.6ppm, proton on glucose skeleton



For DS=3, the peak area ratio of 2.0ppm to 3.5 - 5.6 ppm is 1.4, slightly higher than 9/7(=1.3) for a theoretical DS=3, showing high degree of substitution.



Production of Bio-phenols and Green Resins/Adhesives from Forestry Residues

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Phenol-formaldehyde (PF) resins

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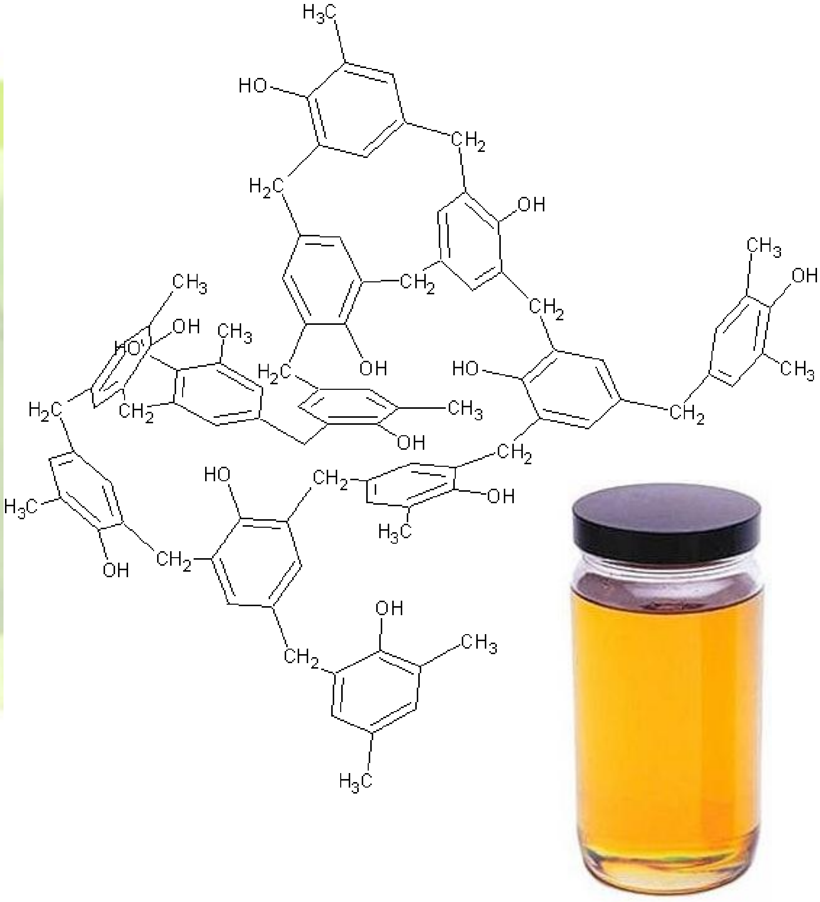
- The global production and consumption of PF resins in 2009 were approximately **3.0 Mt**. It is expected an average growth of 3.9% per year from 2009 to 2014, and 2.9% per year from 2014 to 2019 (SRI Consulting, 2010).
- The PF resin manufacture is an important industry valued approx. **$10 billion in the world, and $ 2.3 billion in North America.**

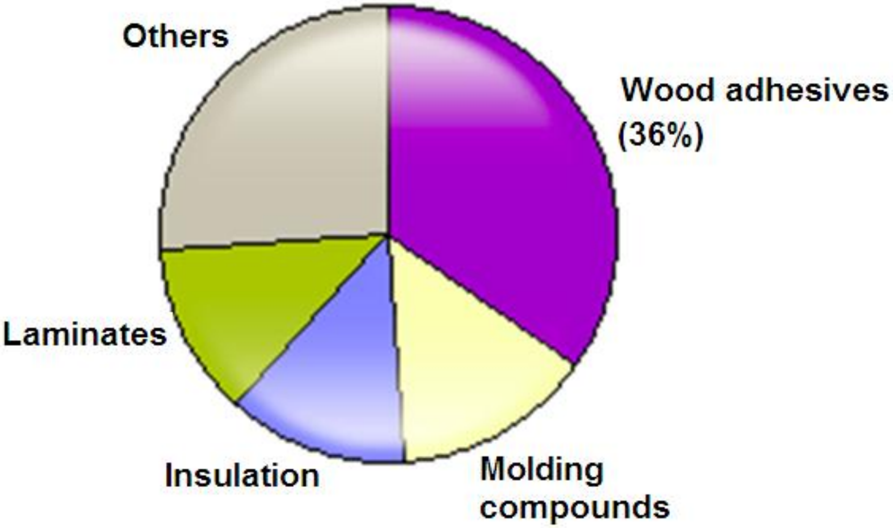


SRI consulting, World Petrochemical (WP) report on PF Resins, January 2010. *http://www.sriconsulting.com/WP/Public/Reports/pf_resins/ (retrieved Jan 14, 2011)*

Phenol-formaldehyde (PF) resin (Cont'd)

- PF resins are most widely used as **wood adhesives**.
- The cost of PF resins varies from **US$ 1,500 to US$ 2,000** per metric ton, mainly due to the high and fluctuating cost of phenol.

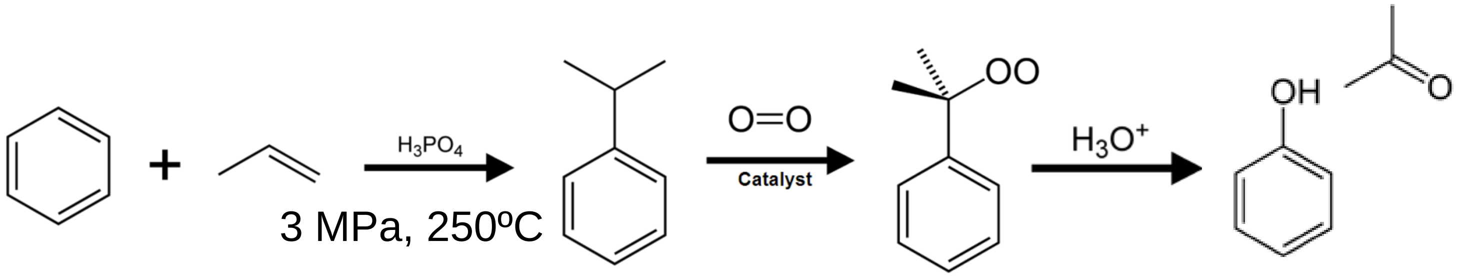
World consumption of phenol-formaldehyde resins in 2009



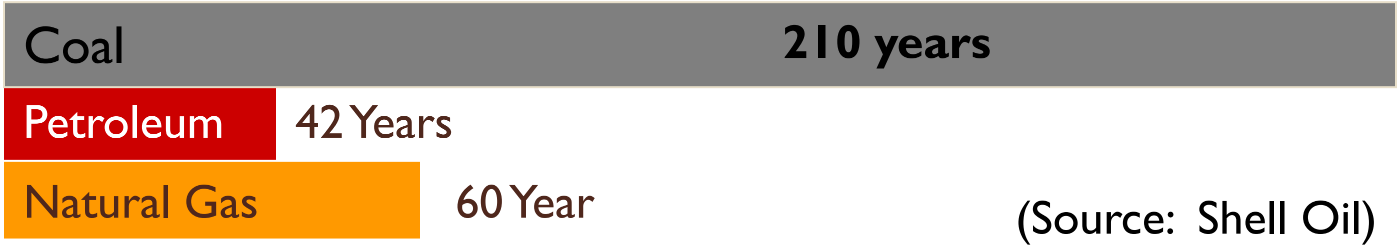
SRI consulting, World Petrochemical (WP) report on PF Resins, January 2010. http://www.sriconsulting.com/WP/Public/Reports/pf_resins/ (retrieved Jan 14, 2011)

Phenol

- Phenol is mainly consumed for the production of PF resins. In USA, PF resins manufacture consumes **35-40% of the phenol** produced.
- **The global production of phenol is about 10.7 Mt/y at a cost of $700-1,500/t**. Expected growth is **4.5%** per year 2010-2015.
- More than 95% of phenol is produced from petroleum-derived benzene by the cumene process



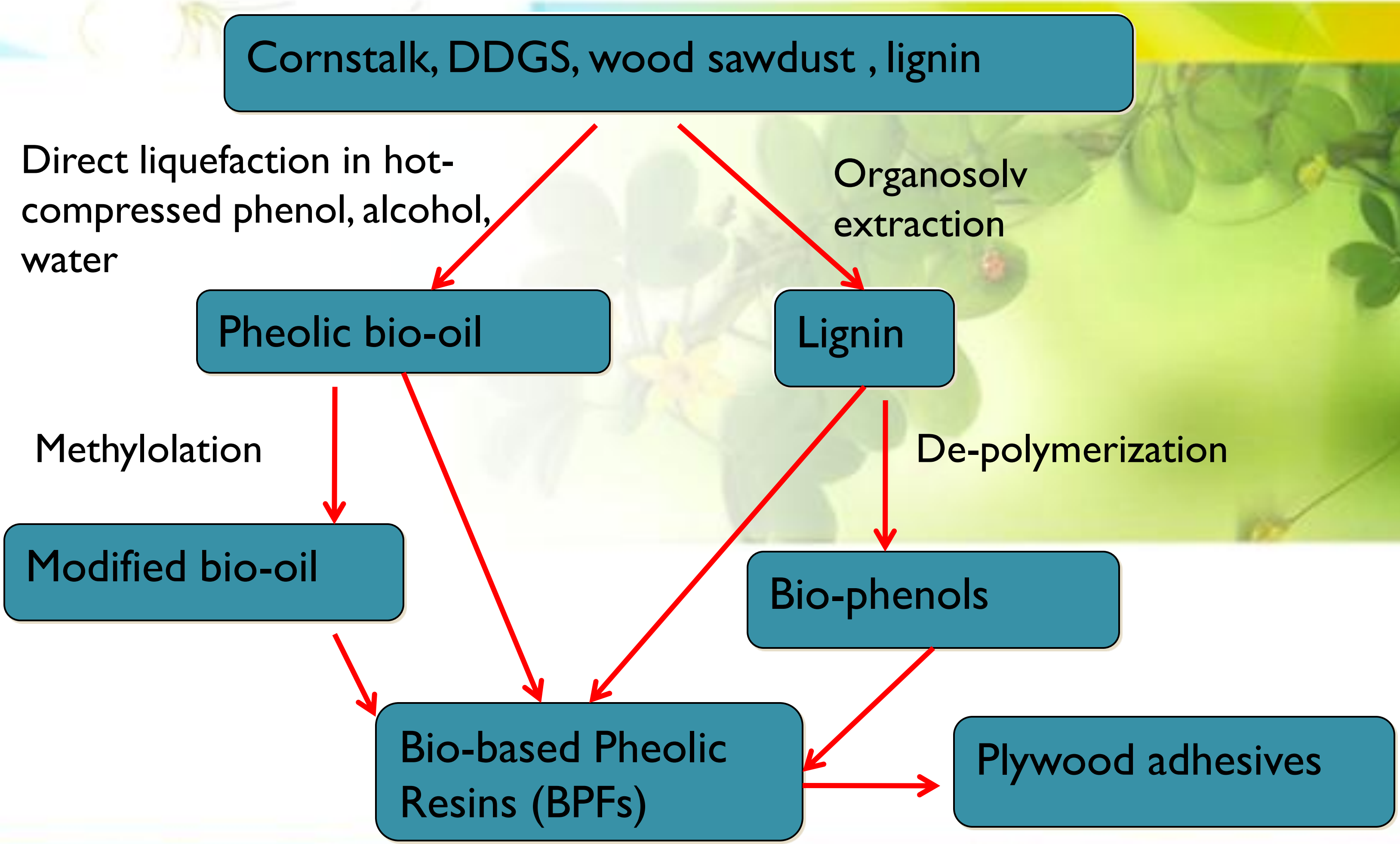
benzene propylene cumene cumene hydroperoxide **phenol**



(Source: Shell Oil)

Phenol and PF resins from renewable resources (biomass)?

Methodologies/ Approaches



Cornstalk, DDGS, wood sawdust , lignin

Direct liquefaction in hot-compressed phenol, alcohol, water

Organosolv extraction

Pheolic bio-oil

Lignin

Methylolation

De-polymerization

Modified bio-oil

Bio-phenols

Bio-based Pheolic Resins (BPFs)

Plywood adhesives

Key Results

Reductive De-polymerization of Alkali Lignin (M_n ~10,000) in Hot-compressed Alcohol

De-polymerization conditions	**Solvents**	**DL[1] / %**	**SR[2] / %**	**GP[3] / %**	**GPC results[4]**		
					M_n	**M_w**	**M_w/M_n**
300 °C, 240min, 5 MPa H_2, lignin-to-solvent ratio of 1:10 (w/w)	100% water	48.6 (±4.4)	41.7 (±2.6)	1.6 (±0.3)	NA[5]	NA	NA
	25% water-75% ethanol	48.6 (±1.7)	35.7 (±1.8)	8.0 (±0.1)	NA	NA	NA
	50% water-50% ethanol	**87.8 (±2.7)**	**5.7 (±3.3)**	**6.4 (±0.7)**	**415**	**1010**	**1.95**
	75% water-25% ethanol	52 (±3.8)	34.3 (±1.5)	6.5 (±2.6)	NA	NA	NA
	100% ethanol	**15.3 (±1.6)**	**64.1 (±0.8)**	**3.6 (±0.7)**	**260**	**631**	**2.43**

1: DL– De-polymerized lignin products; 2: SR – Solid residue; 3: GP – Gaseous products; 4: The GPC results were from the THF-soluble portion of the DLs; ; 5: NA – not analyzed.

Catalytic lignin de-polymerization

5 MPa H_2 (cold pressure) for 2 hr in 50% ethanol,
300°°C

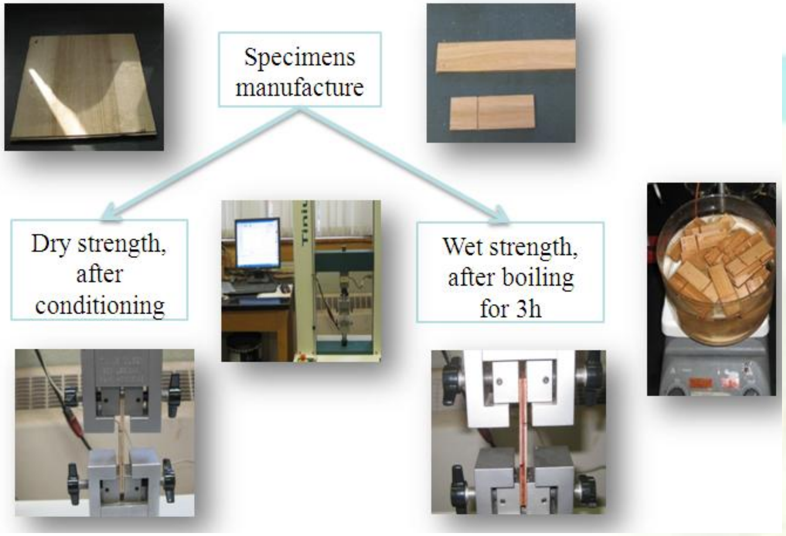
Catalyst	Yield/%			GPC results of DLs[1]			
	DL	SR1	Gas	Solubility in THF/%	M_n	M_w	M_w/M_n
None	**87.8 (±2.7)**	**5.7 (±3.3)**	**6.4**	**~70**	**415**	**1010**	**1.95**
RA	66.3 (± 0.4)	22.1 (± 0.6)	1.1	~90	370	869	2.35
RC	89.4 (± 1.9)	6.1 (± 1.6)	3.9	~70	396	927	2.34
NC	84.1 (± 5.7)	8.8 (± 1.3)	1.5	~70	356	846	2.38
NM	80.5 (± 3.0)	19.9 (± 0.1)	0.5	~90	431	1060	2.46
KOH	91.3 (± 1.1)	19.7 (± 2.3)	0.1	~90	389	815	2.09

[1] For the THF soluble fraction of DL

The optimum catalyst appears to KOH, RC, NC, with respect to DL yields, THF solubility and molecular weights.

Summary of Key Results (Cont'd)

- **Application of bio-based phenolic resins to plywood adhesives**



Specimens manufacture

Dry strength, after conditioning

Wet strength, after boiling for 3h

Note:

- **Yellow birch veneer, conditioned 10-12% MC;**
- **Adhesive application (250 g/m^2) ;**
- **Press, 140^{o}C, 2500 psi, 4 min**

[1] Each value represents an average of 20 specimens.

[2] Test after conditioning.

[3] Test after boiled for 3h.

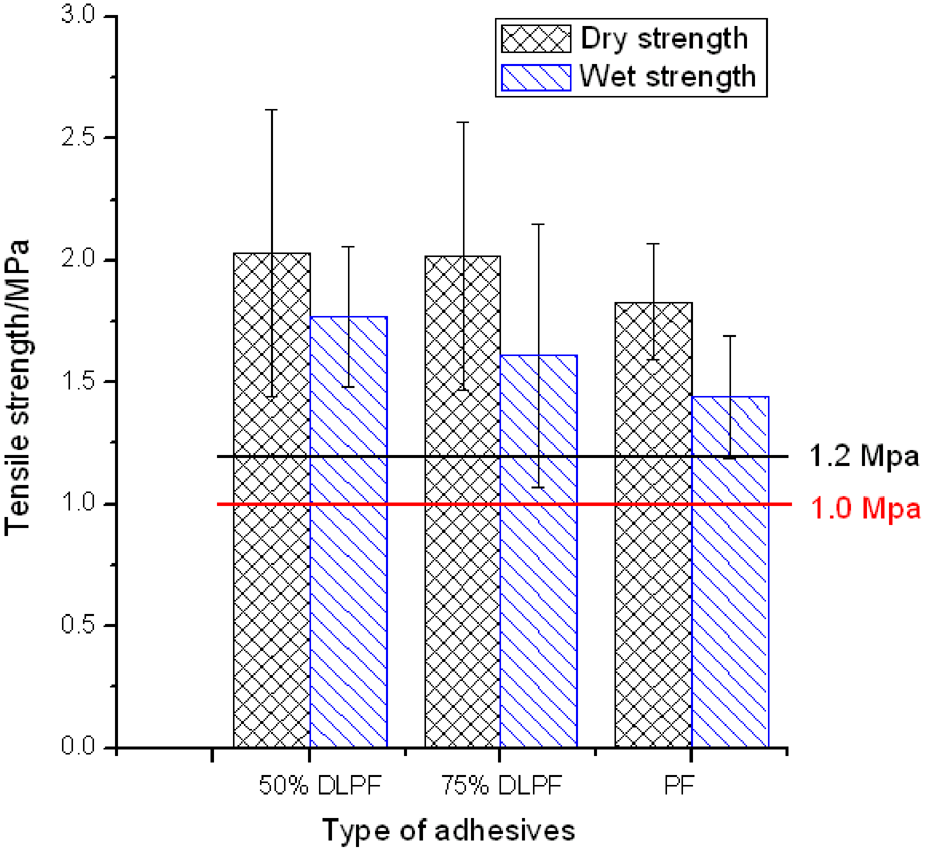


Figure Tensile-strength profile of plywood glued by the DLPFs and pure PF adhesives. The horizontal lines indicate the minimum requirement of the tension shear strength specified by the JIS K-6852 standard (1.2 MPa for dry strength, and 1.0 MPa for wet strength) for resole-type plywood adhesives.

Novel One-step Catalytic Process to Produce 1-Butanol and Fuel Additives from Bio-ethanol

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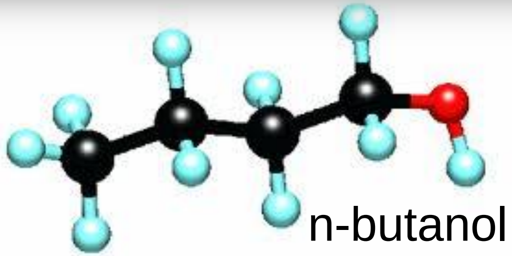
Properties of Common Liquid Transportation Fuels

Fuel	Energy density (MJ/L)	Air-fuel ratio	Specific energy (MJ/kg air)	Heat of vaporization (MJ/kg)	RON	MON
Gasoline and biogasoline	32	14.6	2.9	0.36	91–99	81–89
Butanol fuel	29.2	11.1	3.2	0.43	96	78
Ethanol fuel	19.6	9.0	3.0	0.92	107	89
Methanol fuel	16	6.4	3.1	1.2	106	92

Butanol

1. Molecular formula of C_4H_9OH



2. As an intermediate in chemical synthesis (isobutyl acetate or isobutyl esters).

3. As a solvent

4. As a potential fuel to substitute for gasoline or fuel additive (gasoline additive)

According to the US's Renewable Fuels Standard, the US production of bio-butanol will reach 57 billion liters by 2022, which is mainly derived from corn-starch and agricultural residue (The US Energy Independence & Security Act of 2007).

Butanol vs. Ethanol

- Butanol contains 25% more energy than ethanol.
- Butanol is safer because it is evaporated six times less than ethanol and 13.5 times less volatile than gasoline.
- Butanol has a much higher compatibility with gasoline than ethanol.
- Butanol can be blended with gasoline at a ratio up to 100%.
- Butanol is clean as it does not produce sulfur and nitrogen oxides at combustion.
- **Butanol is much more valuable than ethanol** (Current iso-butanol and n-butanol prices are around $1400 and $1500 per tonne, compared to corn ethanol which sells at around $700 per tonne)

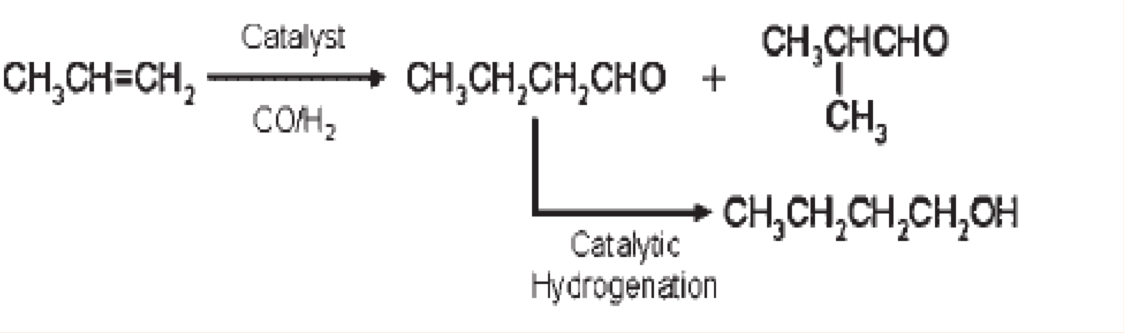
Khimicheskaya Promyshlennost (2008)85, 203–208.

Industrial Chemical Synthesis of Butanol

Biotechnology and Bioengineering, (2008)101;209-228

A

Oxo synthesis (hydroformylated to butyraldehyde)

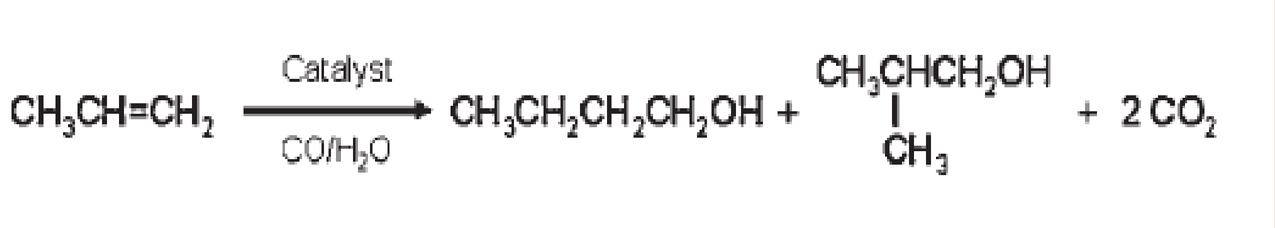


$$CH_3CH{=}CH_2 \xrightarrow[CO/H_2]{\text{Catalyst}} CH_3CH_2CH_2CHO + \underset{\displaystyle CH_3}{CH_3\overset{}{C}HCHO}$$

$$CH_3CH_2CH_2CHO \xrightarrow[\text{Hydrogenation}]{\text{Catalytic}} CH_3CH_2CH_2CH_2OH$$

B

Reppe synthesis

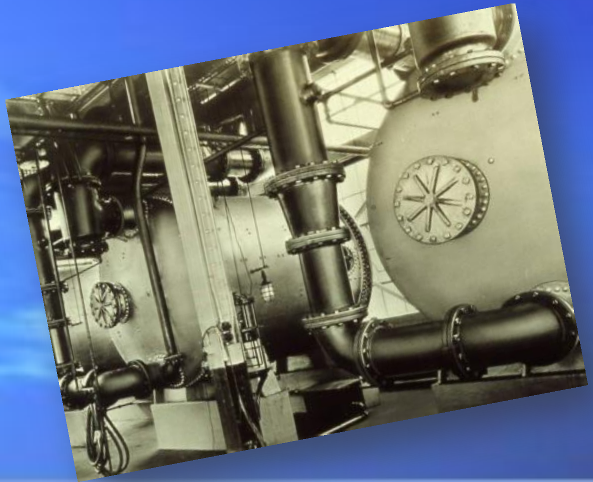


$$CH_3CH{=}CH_2 \xrightarrow[CO/H_2O]{\text{Catalyst}} CH_3CH_2CH_2CH_2OH + \underset{\displaystyle CH_3}{CH_3CHCH_2OH} + 2\,CO_2$$

Biological Production of Butanol

Lee, et al., (2008). Biotechnology and Bioengineering 101: 209-228

- Pasteur in 1861
- Weizman in 1914
- Industrial producing of butanol began in 1916
- **ABE fermentation** (acetone, butanol and ethanol) in during World War II, using Bacteria Clostridia Acetobutylicum

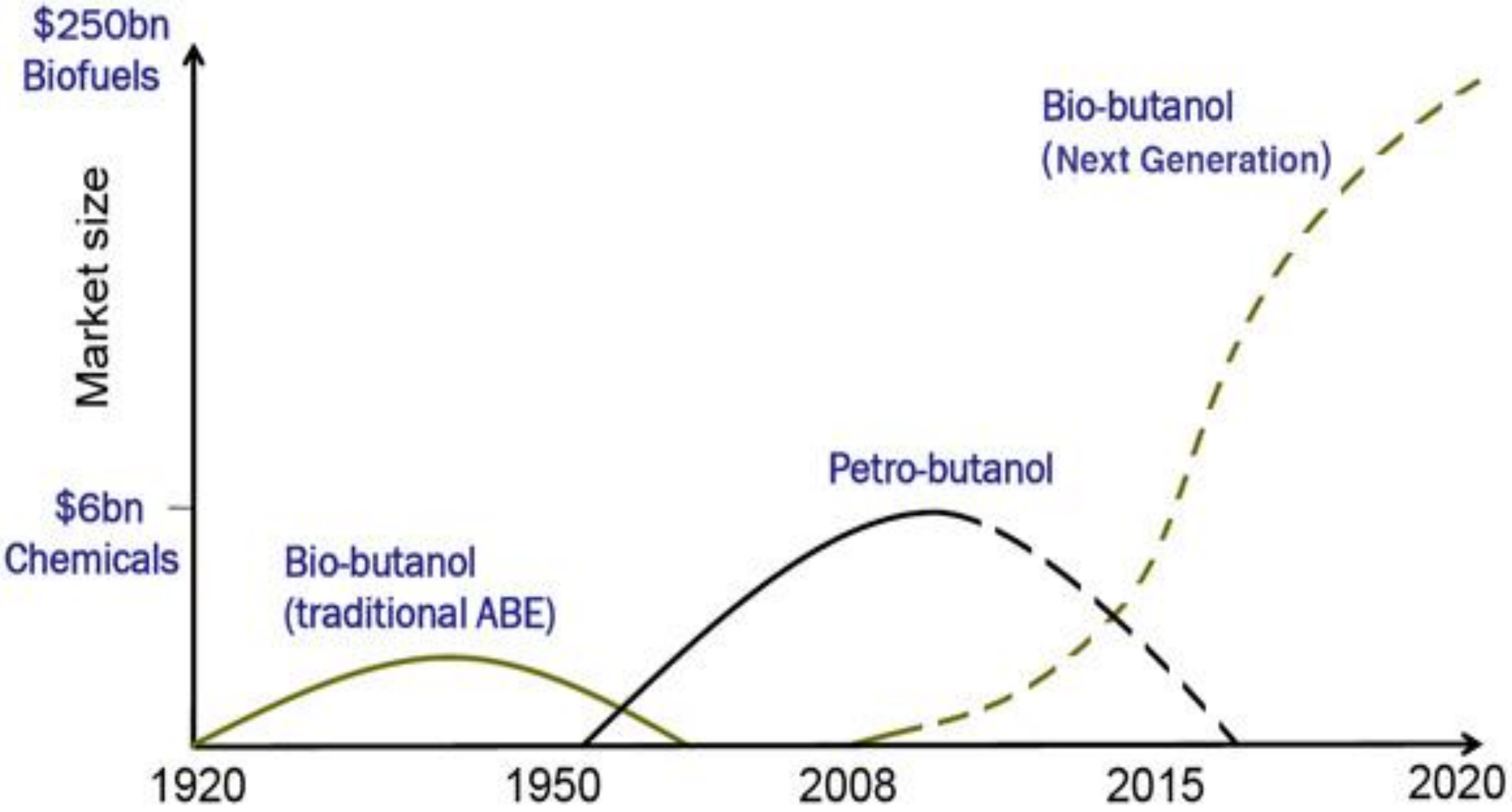


Problems of Traditional ABE Process

- ABE products toxicity to the bacteria strain
- Low product concentrations
  (concentration below 2.0% at productivity of 4.46 g/L/h)
- Low yield
  (butanol yield of less than 25% on the glucose weight)

Biotechnology and Bioengineering, (2008)101;2209-228

Outlook of World Butanol Production



Research Objectives

We aim to develop a one-step continuous catalytic process to convert bio-ethanol into 1-butanol, 1-hexanol, and some other compounds that are useful as fuel additives.

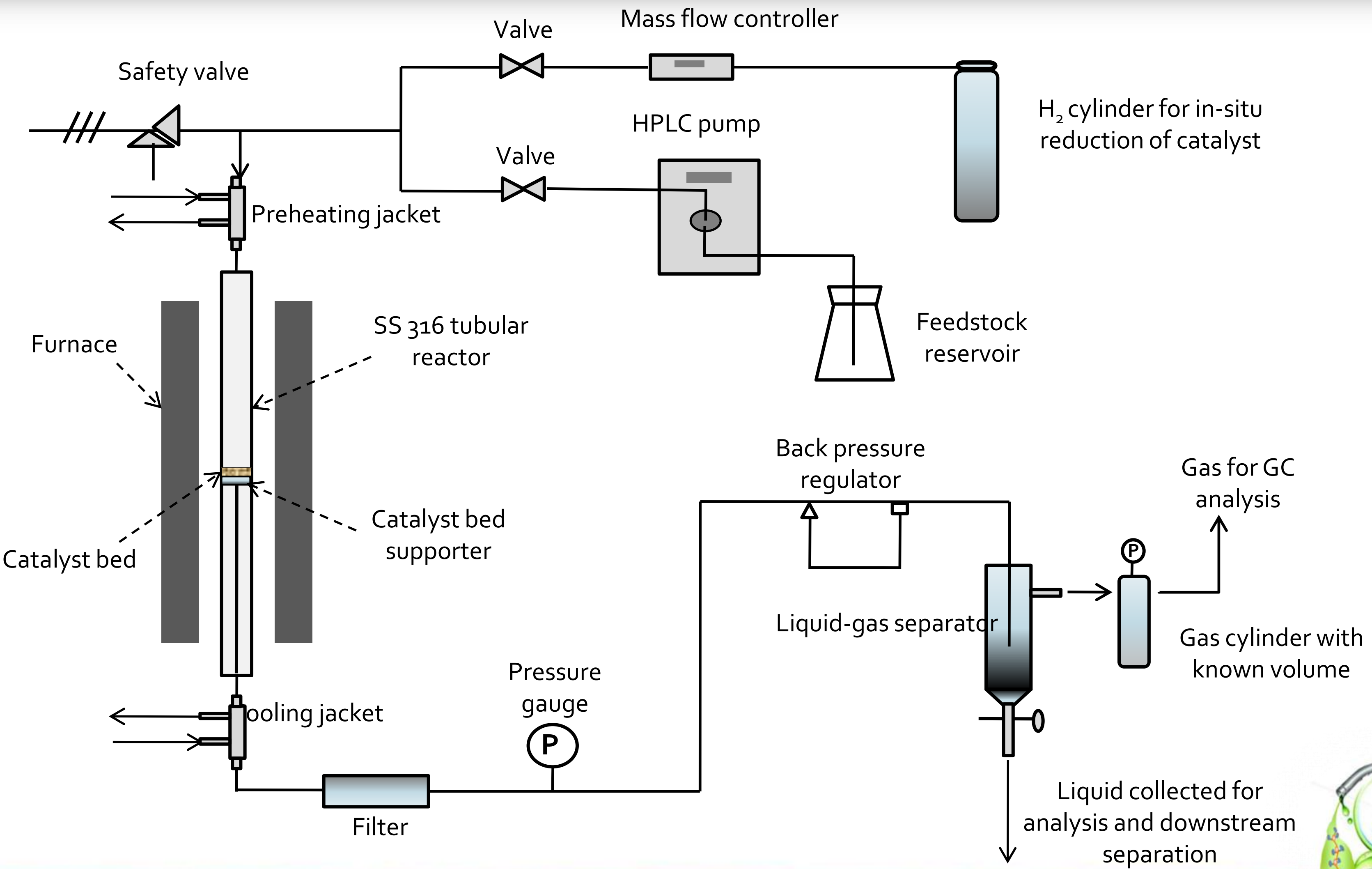
$$2\ C_2H_5OH \rightarrow C_4H_9OH + H_2O$$

Molecular weight (g/mol):	92	74	18
Theoretical yield:	1 kg (basis)	0.8 kg	0.2 kg

Materials

- Commercial anhydrous ethanol (purity>99%) from Commercial Alcohols (GreenField Ethanol)
- Self-prepared less expensive supported metallic catalysts

Experimental Setup



Valve

Mass flow controller

Safety valve

H_2 cylinder for in-situ reduction of catalyst

HPLC pump

Valve

Preheating jacket

Furnace

SS 316 tubular reactor

Feedstock reservoir

Back pressure regulator

Gas for GC analysis

Catalyst bed supporter

Catalyst bed

Liquid-gas separator

Gas cylinder with known volume

Pressure gauge

P

ooling jacket

Filter

Liquid collected for analysis and downstream separation

Different catalysts performance in bioethanol conversion to 1-butanol

Catalyst	1-Butanol Yield (%)	Ethanol Conversion (%)	1-Butanol Selectivity (%)
8NA	21.2	59.6	71.1
17NA	19.6	56.7	69.1
27NA	Complete gasification of bioethanol		
27NiA[1]	8.2	23.3	70.4
MOA & 27NA[1]	12.0	19.5	>100?
Neat MO & 27NA[1]	8.1	19.8	81.8

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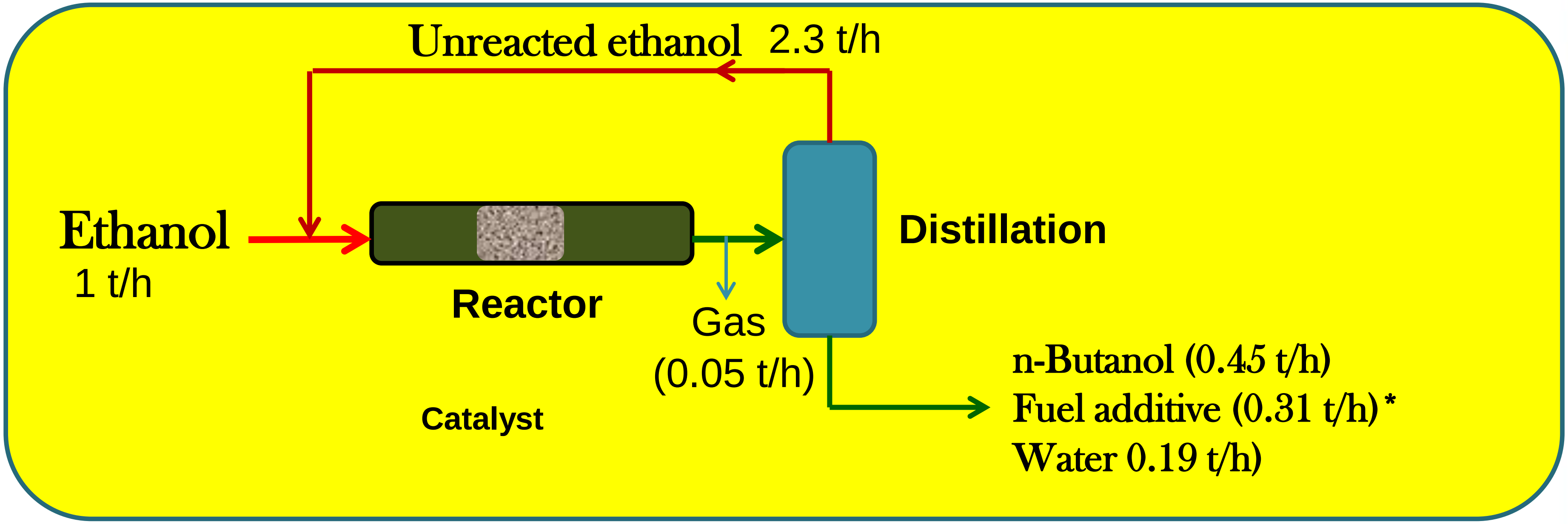
[1] Catalyst was diluted with crushed Pyrex glass beads of 20-50 mesh (1:3 w/w).

An schematic of process flow diagram for producing n-butanol and fuel additive



Unreacted ethanol 2.3 t/h

Ethanol
1 t/h

Reactor

Catalyst

Gas
(0.05 t/h)

Distillation

n-Butanol (0.45 t/h)
Fuel additive (0.31 t/h)*
Water 0.19 t/h)

$2\ C_2H_5OH \rightarrow C_4H_9OH + H_2O$

Acknowledgements

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THANK YOU!