Production of furfural from corn residue through catalytic fast pyrolysis using $ZnCl_2$ in a fluidized bed reactor

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Paths from Biomass to Bioenergy

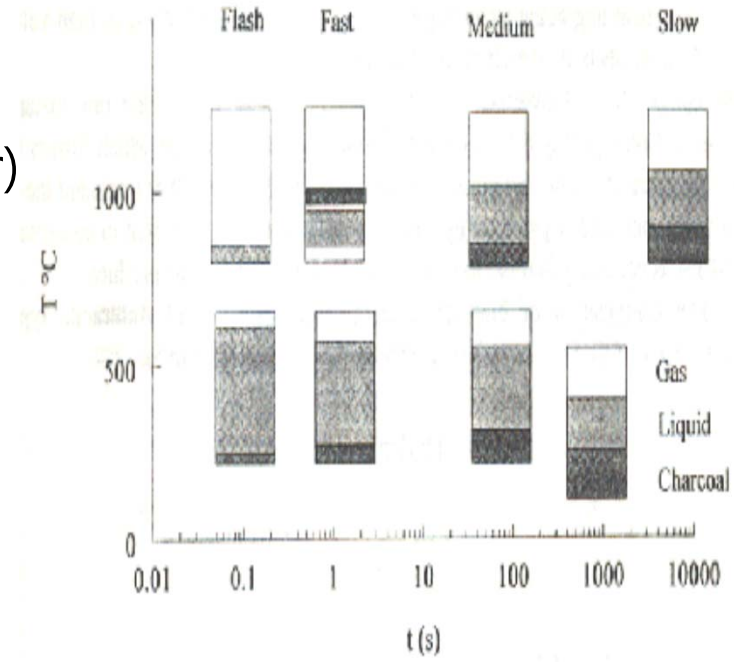
- Thermal (or thermochemical) conversion:
  - Direct combustion ⇒ heat
  - Pyrolysis (slow- or fast pyrolysis) ⇒ bio-oil, biochar
  - Gasification (air, O_2, H_2O) ⇒ syngas
- Biochemical conversion:
  - Alcoholic fermentation ⇒ bioethanol
  - Anaerobic digestion ⇒ biogas
- Physicochemical conversion:
  - Organic oils ⇒ biodiesel

Pyrolysis

Definition: A thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen

<u>Pyrolysis of biomass</u>

- Slow pyrolysis
  - a.k.a. carbonization
  - used for producing charcoal (or biochar)
- Fast pyrolysis
  - high heating rates
  - low retention times in reactors
  - greater liquid, i.e. 'bio-oil' yield
  - coproducts
    - ✓ biochar
    - ✓ combustible gas



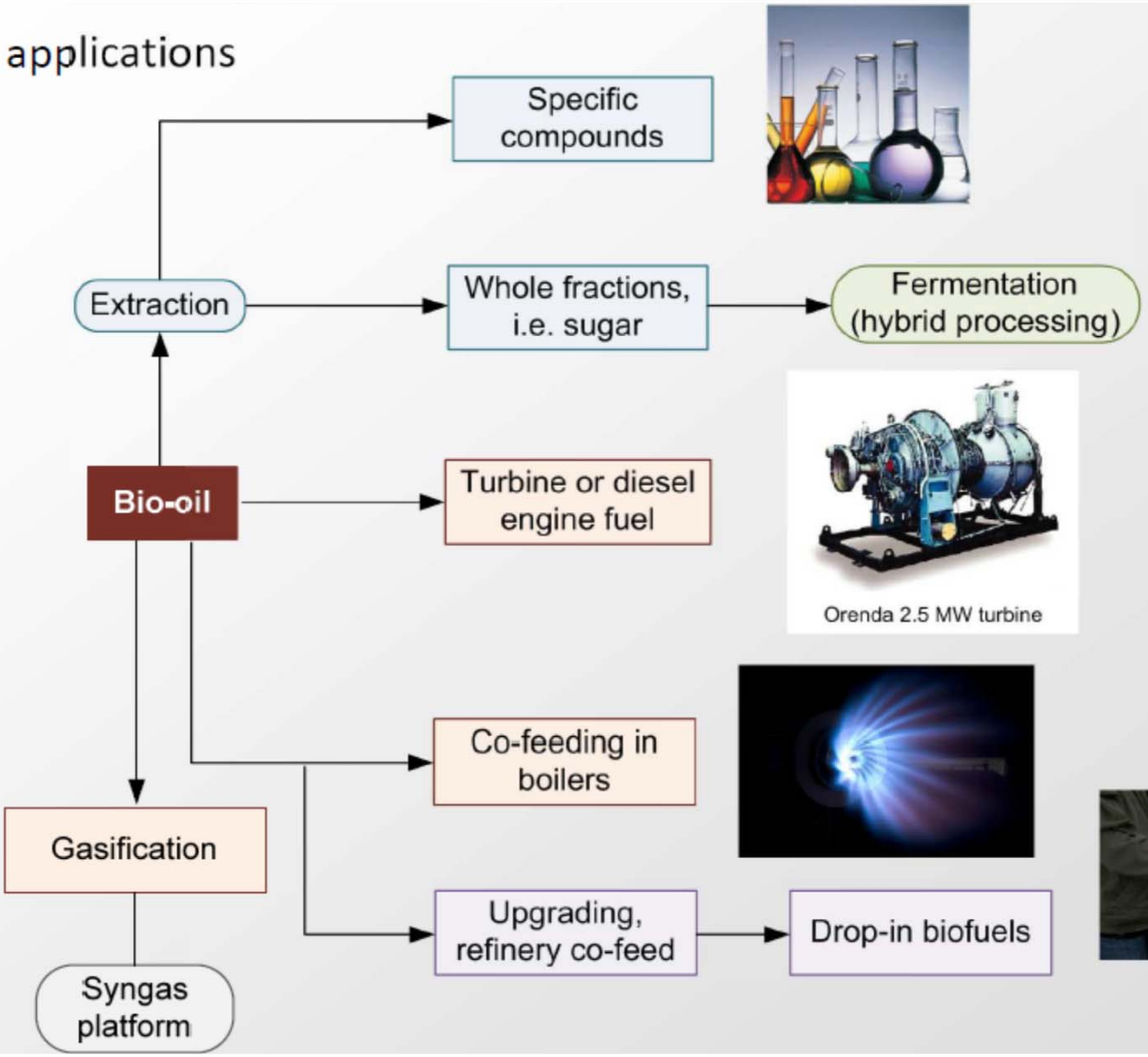
Bio-oil Properties

	bio-oil	heavy fuel oil	
vol. energy density	21	39	GJ/m^3
density	1220	963	kg/m^3
viscosity at 50 °C	13	351	mm^2/s
acidity	3	7	pH
water content	20	0.1	wt.%
ash content	0.02	0.03	wt.%
C	52	86	wt.%
H	7	10	wt.%
O	40	0.5	wt.%
N	0.1	0.6	wt.%
S	< 0.1	2	wt.%

1 MJ Feedstock 1 MJ Product

Applications of Bio-oil

- Bio-oil applications

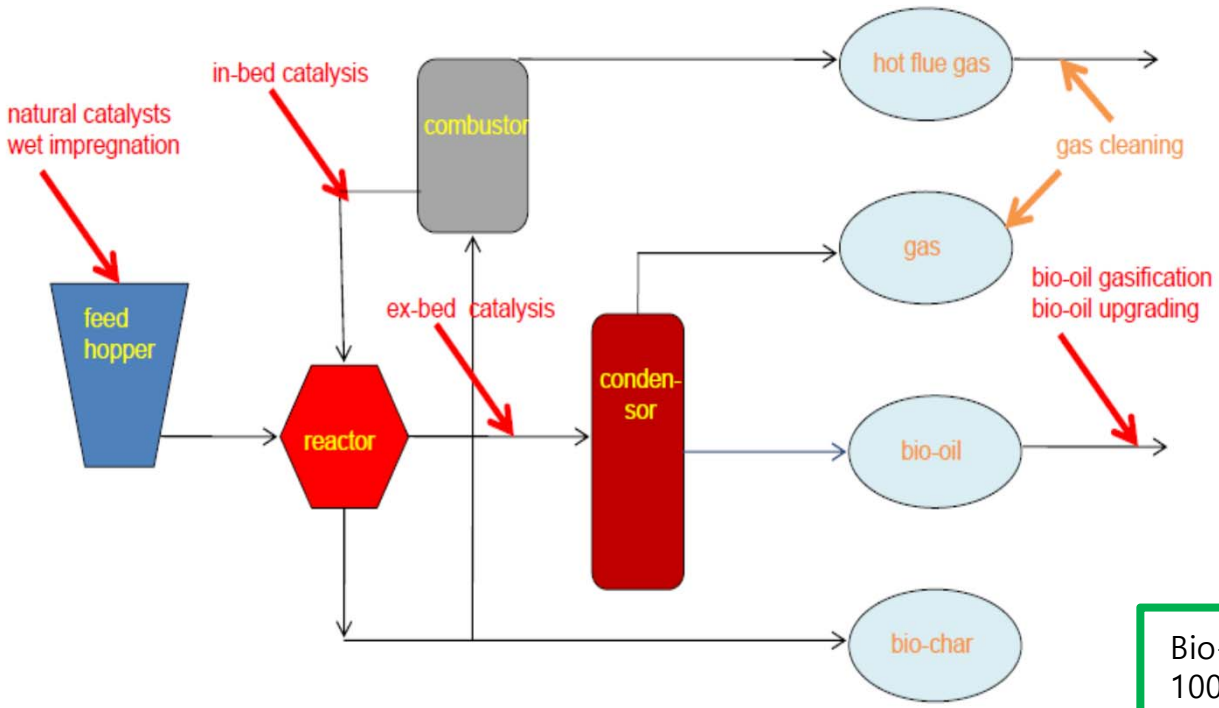


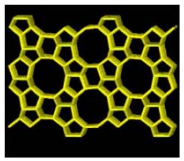
Bio-oil Upgrading

Attribute	Problem	Solution
Low pH	Corrosion	Adequate Materials
		Neutralization
		Hydroprocessing
High viscosity	Handling, pumping	Add water or solvent
		Hydroprocessing
Instability	Storage, phase separation, polymerization, viscosity increase	Avoid heat
		Catalytic Stabilization
		Add Water or Diluents
Solids content	Combustion problems, equipment blockage, erosion	Liquid filtration
		Hot gas filtration
Alkali metals	Deposition of solids in boilers, engines, and turbines	Biomass pretreatment
		Hot gas filtration
		Catalytic upgrading
Water content	Complex effect on heating value, viscosity, pH, homogeneity, etc.	Optimization of water content according to application

- Physical upgrading
  - Solvent addition
  - Filtration
  - Separation
- Chemical/catalytic upgrading
  - Esterification/Transesterification
  - Zeolite or Hydrodeoxygenation (HDO)

Catalytic Upgrading of Bio-oil: Zeolite





Zeolite

Bio-oil
100 wt%

CO, CO_2, H_2O
50 wt%

Coke on Cat.
20-30 wt%

Hydrocarbons
15-30 wt%

Catalytic Upgrading of Bio-oil: HDO

- Hydrodeoxygenation (HDO) : commercial sulfided CoMo and NiMo and new catalysts like Ru/C and CuNi/δ-Al_2O_3

Pyrolysis oil → (+ H_2; **HDO**; Final T: 230-340 °C; P: 290 bar)

Oil Phase
dry yield: 47-50 wt.%
Energy yield: 55-68 %
(MJ HDO oil / MJ PO+H_2)

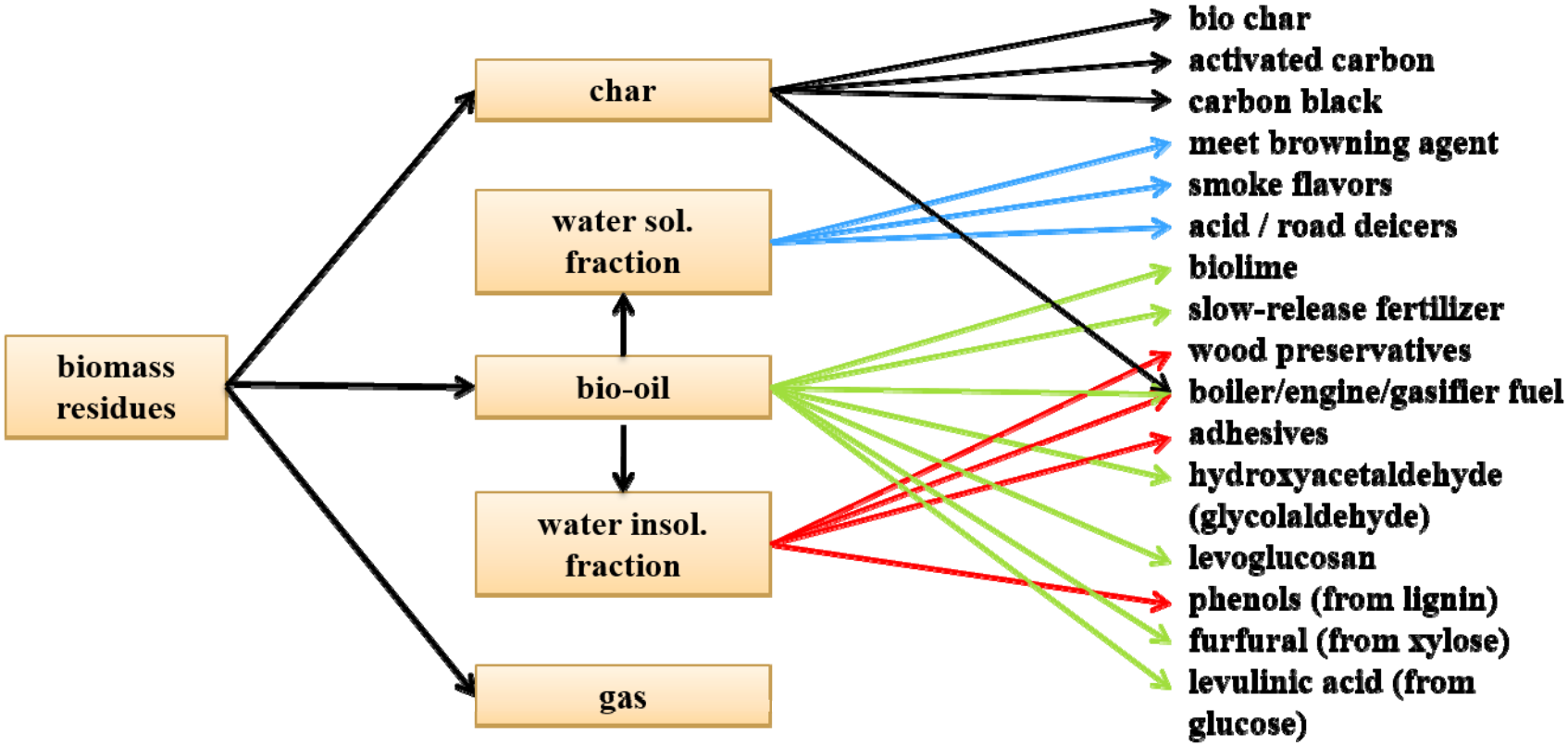
Aqueous Phase
dry yield: 39-14 wt.%

Gas Phase
dry yield: 3-9 wt.%

Produced water
dry yield: 9-19 wt.%

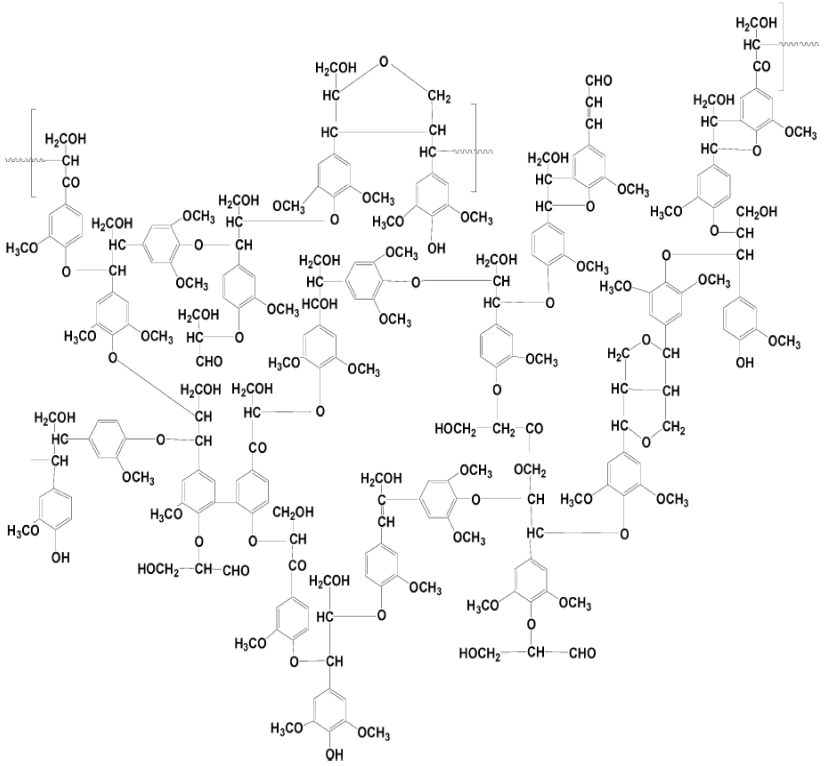
F. De Miguel Mercader et al. Applied Catal. B 96 (2010) 57-66

Biomaterials and Biochemicals from Bio-oil

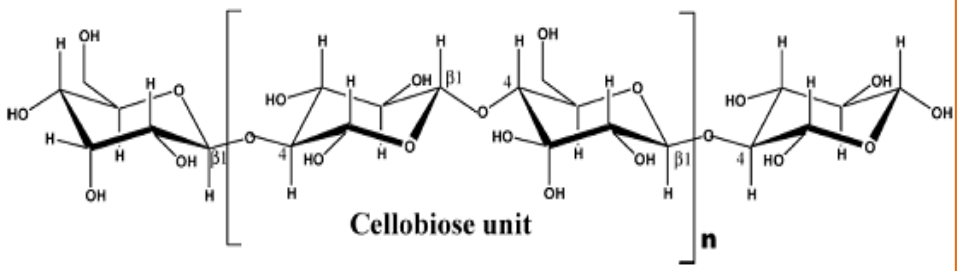


Chemical Structure of Lignocellulosic Biomass

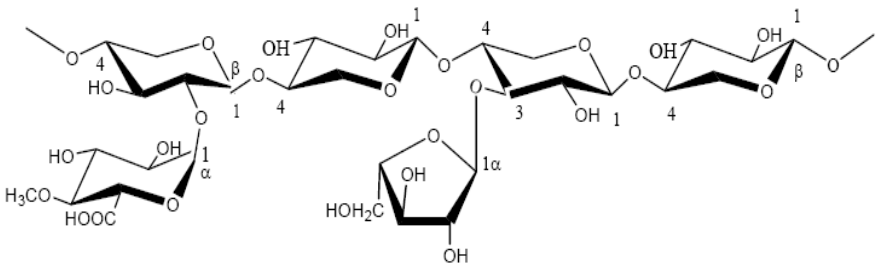
Lignin



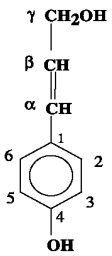
Cellulose



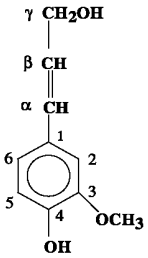
Hemicelluloses



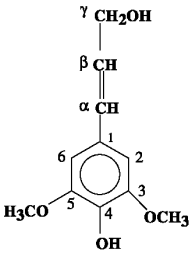
p-coumaryl alcohol



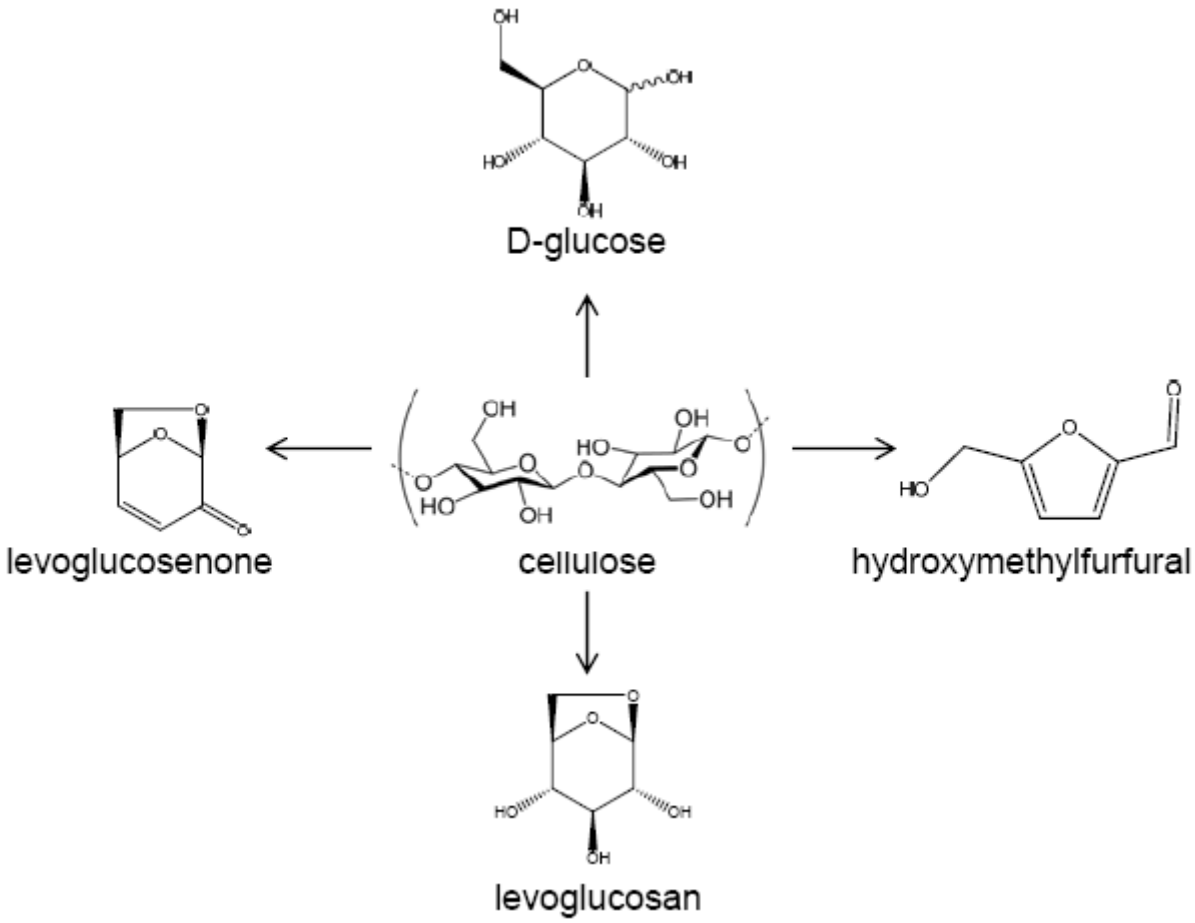
coniferyl alcohol



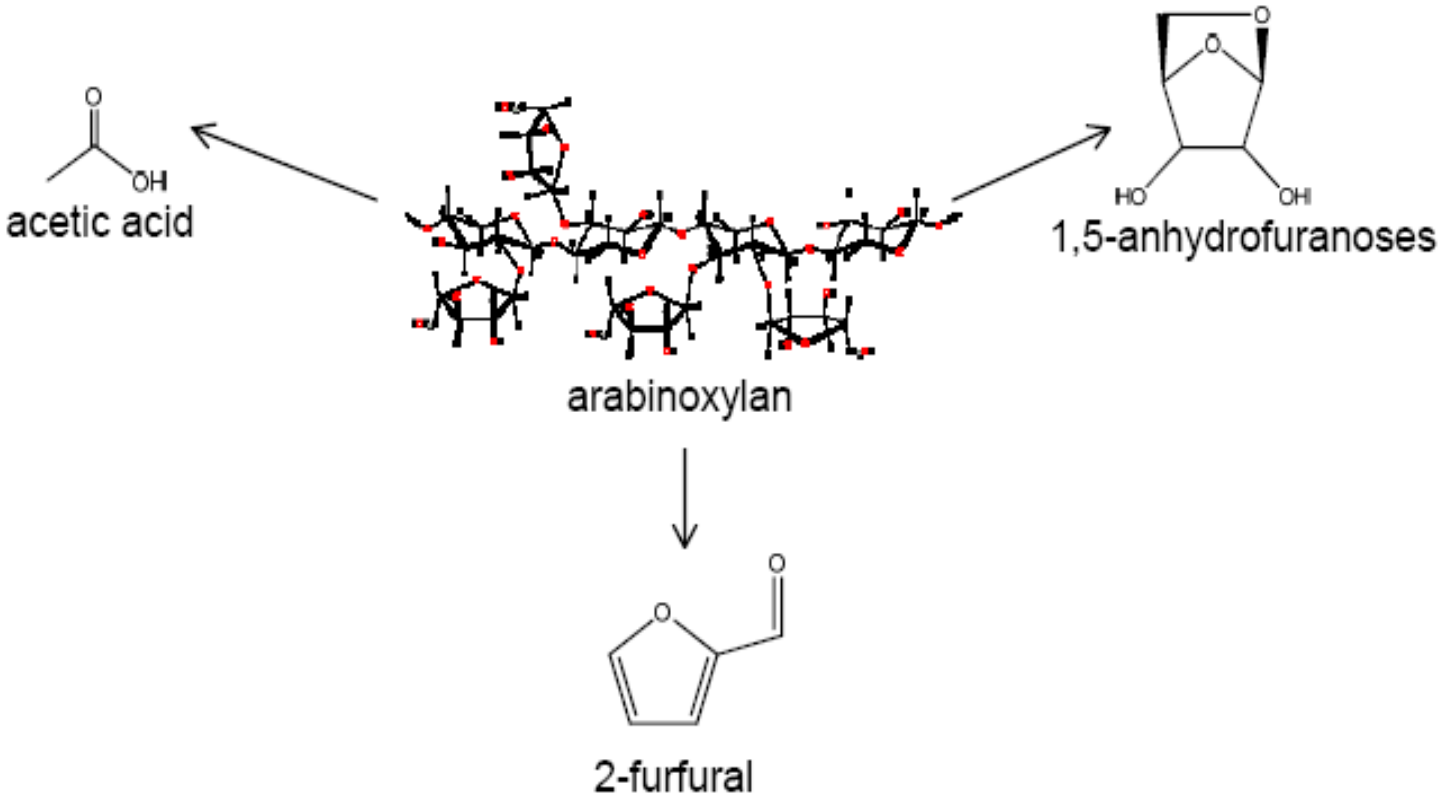
sinapyl alcohol



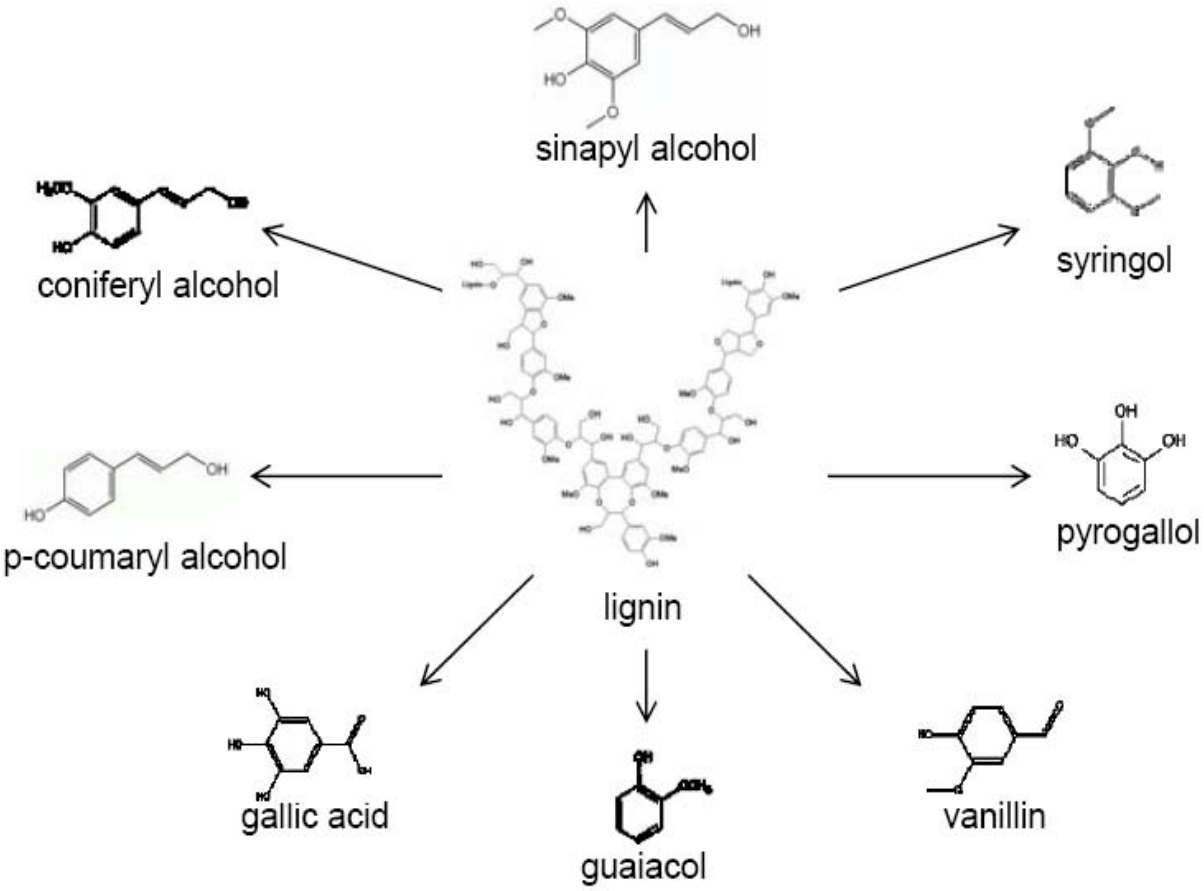
Products of Cellulose Pyrolysis



Products of Hemicellulose Pyrolysis



Products of Lignin Pyrolysis

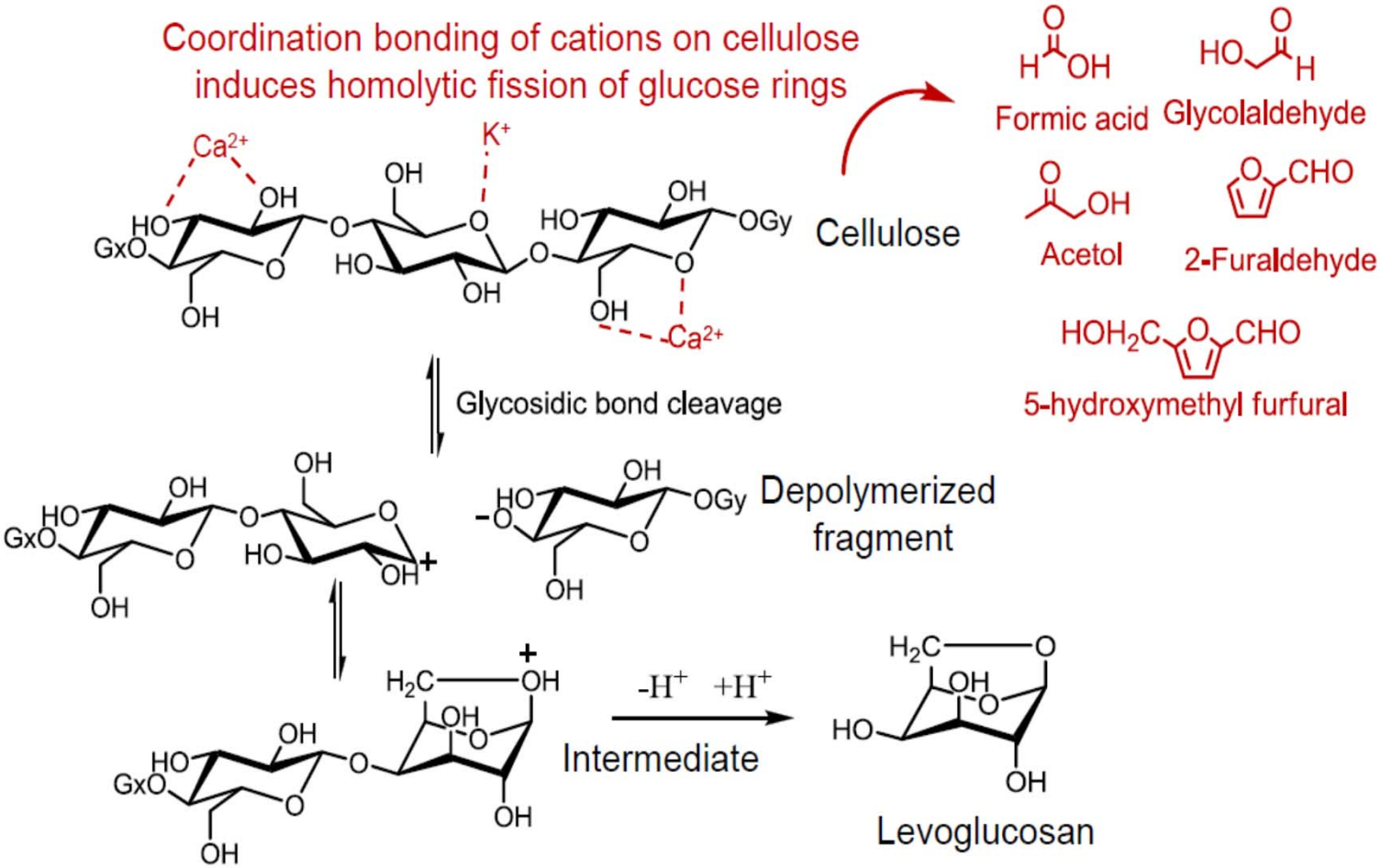


Maximal Contents of Chemicals in Bio-oil(Reported)

Market price: 250$/100g

levoglucosan	30.4	wt%	**furfural**	**1.1**
hydroxyacetaldehyde	15.4		formaldehyde	2.4
acetic acid	10.1		phenol	2.1
formic acid	9.1		propionic acid	2.0
acetaldehyde	8.5		acetone	2.0
furfuryl alcohol	5.2		methylcyclopentene-ol-one	1.9
catechol	5.0		methyl formate	1.9
methyl glyoxal	4.0		hydroquinone	1.9
ethanol	3.6		acetol	1.7
cellobiosan	3.2		angelica lactone	1.6
1,6-anhydroglucofuranose	3.1		syringaldehyde	1.5
			methanol	1.4

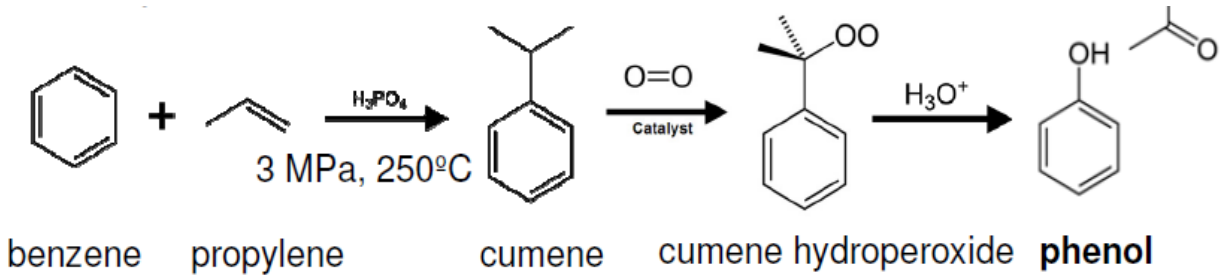
Levoglucosan



Market applications: glucose, polymers, antibiotics

Ponder et. al., *J Anal. App. Pyrolysis*, 1991: Yang et al. *Chem. Res. Chinese U.* 2006

Biomass-derived Phenolic Resin

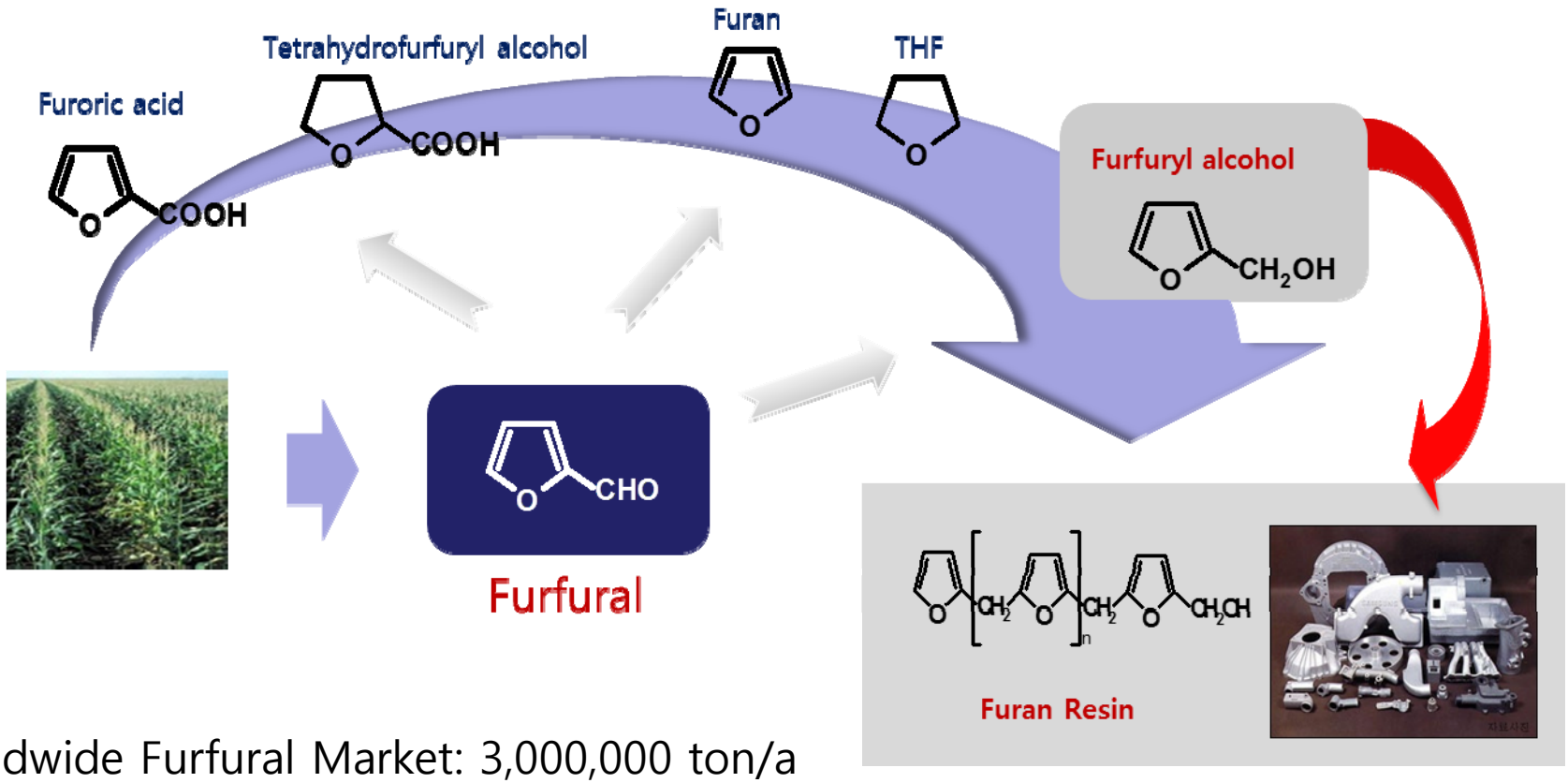


Most phenol is produced from petroleum-derived benzene by the cumene process

Cleavage of the weak β-O-4 ether bonds in lignin yields phenols and derivatives.

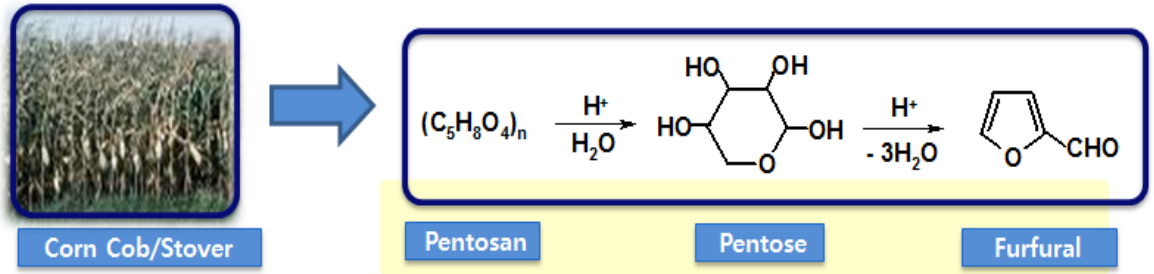
Used mainly as adhesives for plywood and oriented strand board (OSB), circuit boards, molded products, and fire proof/retarding materials

Application of Furfural

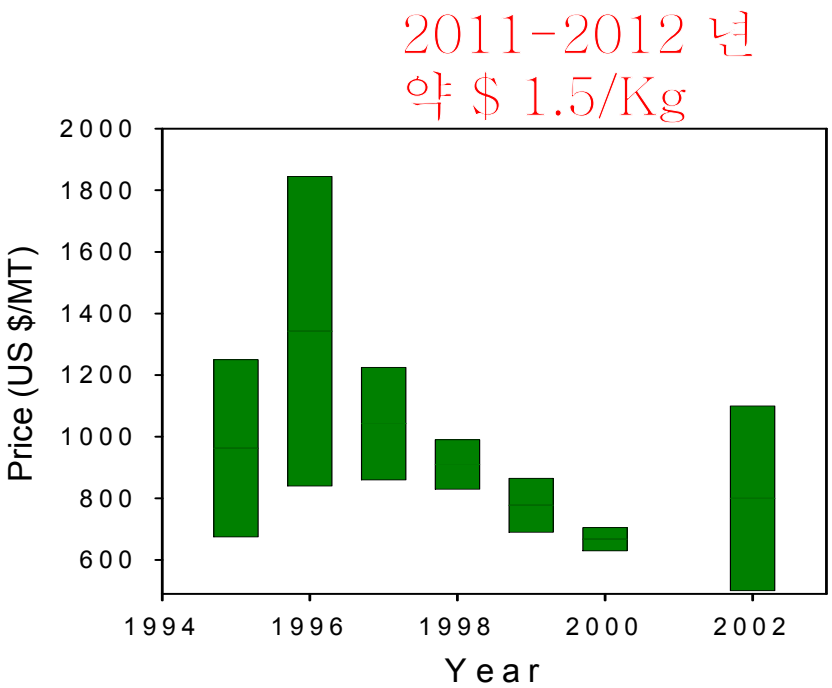


Worldwide Furfural Market: 3,000,000 ton/a

Commercial Production of Furfural

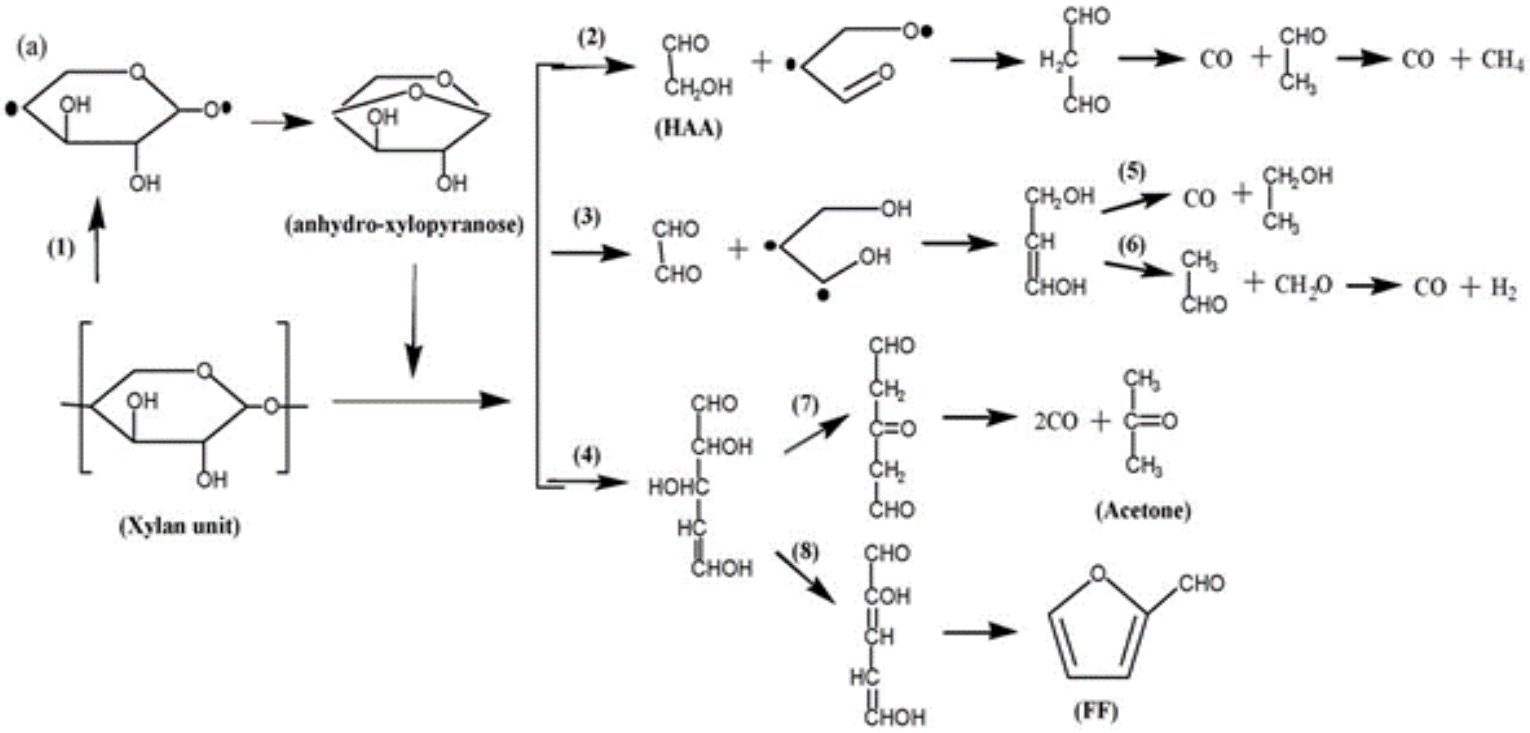


o Acid hydrolysis followed by dehydration
- Huge amount of wastewater
- Batch process



Nation (2001 year)	Main source	Furfural and furfural intermediate [MT/year]
China	Corncobs	200,000
India	-	10,000
Thailand	Corncobs	8,500
Republica Dominicana	Bagasse	32,000
Republic of South Africa	Bagasse	20,000
Spain	Corncobs	6,000
Others	Corncobs/Bagasse	15,000
Russia	Corncobs	5,000
Total		296,500

Furfural from Hemicelluloses (ex. Xylan)



Furfural formation by non-catalytic pyrolysis

Experimental- Feed material (Corncob)

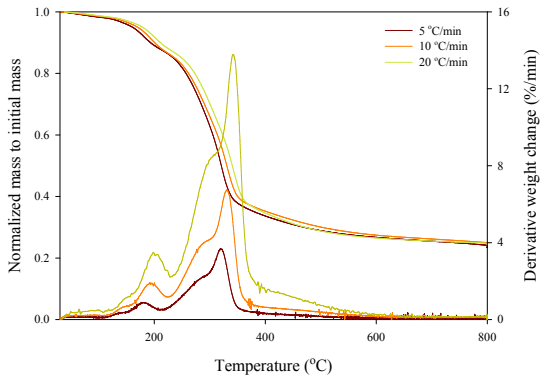
Characteristics of corncob

Feed size (mm) :
0.250-0.425, 0.425-1

Proximate analysis

Corncob	wt %
Volatile matter	88.1
Fixed carbon	1.1
Ash	8
Moisture	2.8

Thermogravimetric analysis



Ultimate analysis

Corncob	wt %
Carbon	43.3
Hydrogen	5.5
Nitrogen	0.9
Sulfur	-
Oxygen[a]	50.3

Chemical composition

Corncob	wt %
Cellulose	27.5
Hemicelluloses	33.6
Lignin	19.6

Thermal degradation range

Cellulose : 240 – 350 °C
Hemicelluloses : 200 – 260 °C
Lignin : 280 – 500 °C

Experimental-Feed material (Corn stover)

Characteristics of corn stover

Feed size (mm) : 0.425-1

Proximate analysis

Corn stover	wt %[a]	wt %[b]
Volatile matter	75.7	82.9
Fixed carbon	12.2	12.9
Ash	6.7	3.6
Moisture	5.4	0.6

a: before soaking, b: after soaking

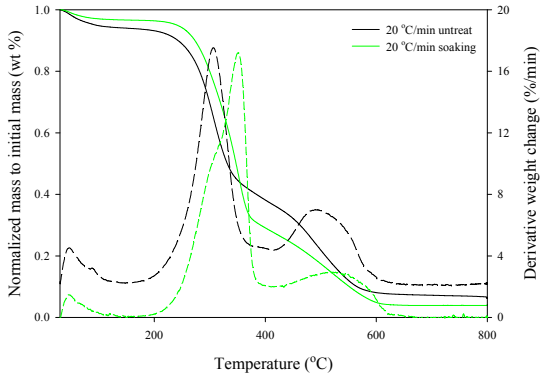
Ultimate analysis

Corn stover	wt %
Carbon	44.3
Hydrogen	6.28
Nitrogen	0.8
Sulfur	0.23
Oxygen[a]	41.8

Chemical composition

Corn stover	wt %
Cellulose	38.8
Hemicelluloses	29.6
Lignin	22.1

Thermogravimetric analysis



Thermal degradation range

Cellulose : 240 – 350 °C
Hemicelluloses : 200 – 260 °C
Lignin : 280 – 500 °C

Experimental-Corn stover Pretreatment

Soaking
80 °C, 3hr

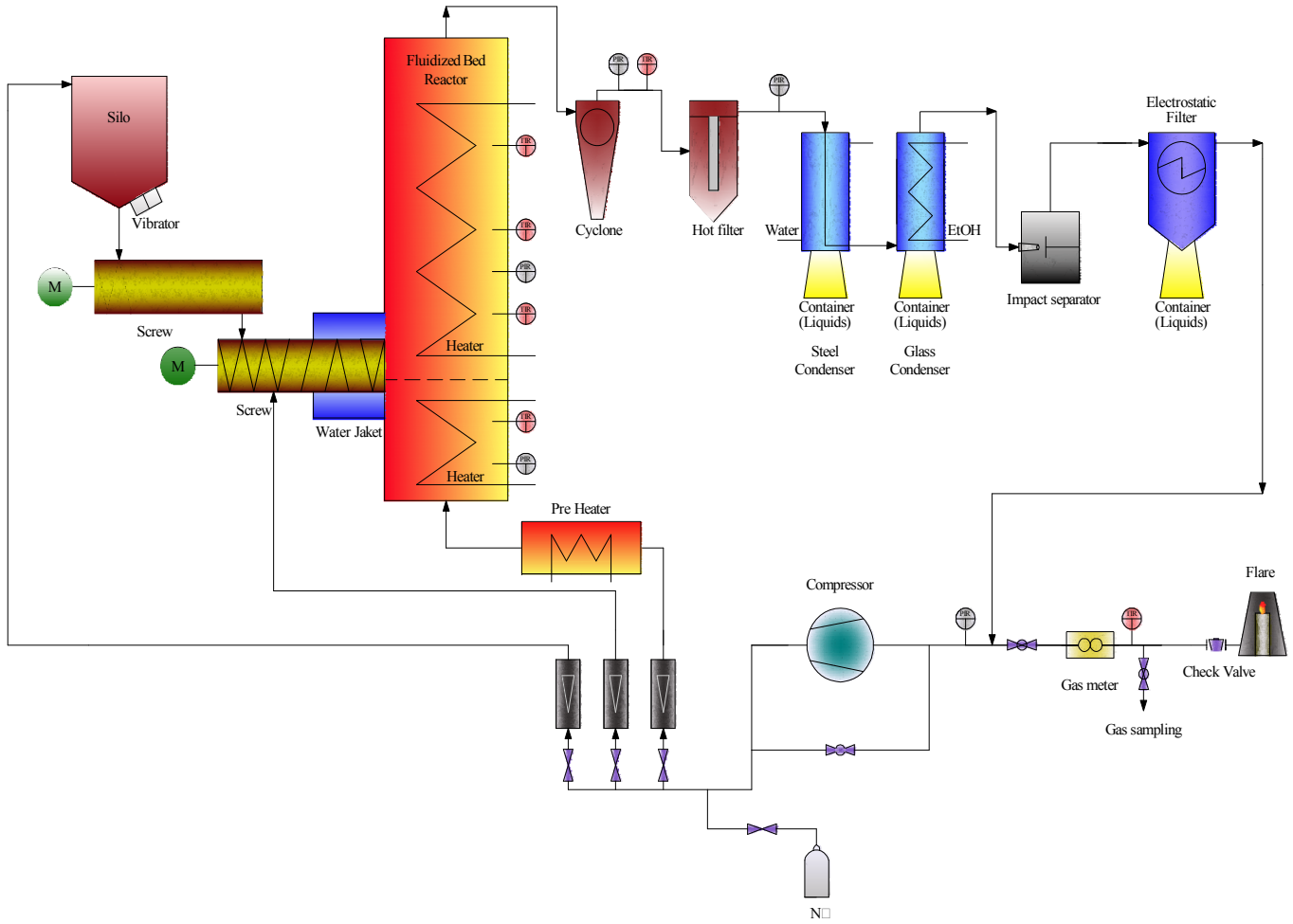
Corn stover
0.425-1 mm
400-600 g

+ **Distilled water** (~6 L)

Washing

Drying
75 °C, 24hr

Experimental-Fluidized bed Reactor



Experimental-Reaction conditions (Corncob)

Flow rate (NL/min): 38-46
Feed amount (g): 100

Parameters	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Rum 9	Run 10
Reaction temperature (°C)	311	357	411	356	358	355	353	347	345	351
Feed rate (g/min)	2						4			
Feed size (mm)	0.425-1					0.250-0.425	0.425-1	0.250-0.425		
$ZnCl_2$ content (wt%)	0			10 [a]	20 [a]	20 [a]	0	10 [b]	20 [b]	20 [a]

a : Mechanical mixing, b : Impregnation

Experimental-Reaction conditions (Corn stover)

Flow rate (NL/min): 38-46
Feed rate (g/min): 5
Feed size (mm) : 0.425-1
Feed amount (g): 300

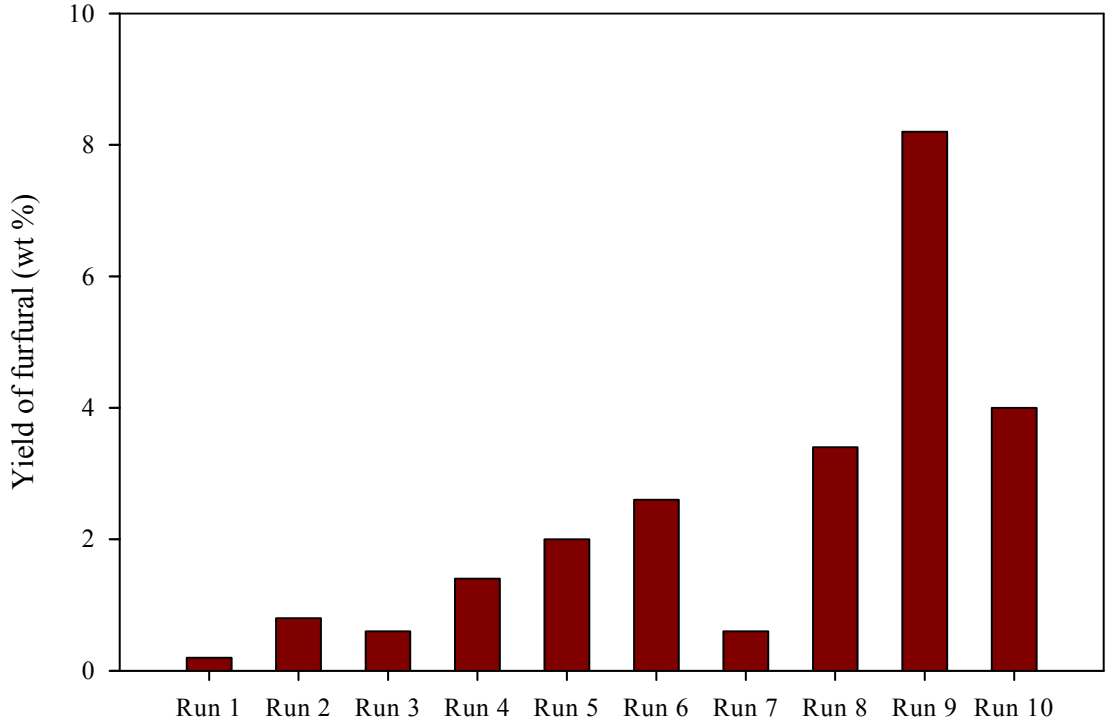
Parameters	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
Reaction temperature (°C)	343	370	430	337	346	337	335
Pretreatment	No			Washing			No
$ZnCl_2$ content (wt%)	-				7.6	18.5	18.5

Results-Mass balances (Corncob)

Products (wt %)	Run 1 311 °C	Run 2 357 °C	Run 3 411 °C	Run 4 356 °C	Run 5 358 °C	Run 6 353 °C	Run 7 355 °C	Run 8 347 °C	Run 9 345 °C	Run 10 351 °C
Oil	48.2	52.7	58.3	46.3	29.8	46.6	59.0	60.0	48.1	47.8
Gas	17.7	21.5	24.3	16.8	14.9	15.3	17.7	10.0	10.1	11.4
Char	34.1	25.8	17.4	36.9	55.3	38.1	23.3	30.0	41.8	40.8

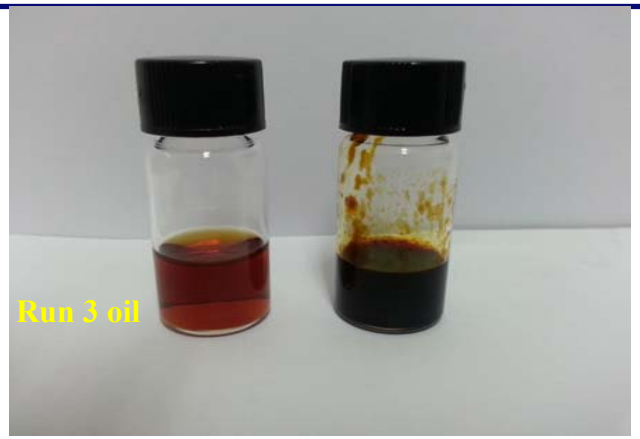
Run 4, 5, 6 and 10: Mechanical mixing
Run 8 and 9: Impregnation

Results-Furfural yield (Corncob)



	Run1	Run2	Run3	Run4	Run5	Run6	Run7	Run8	Run9	Run10
Furfural	0.2	0.8	0.6	1.4	2	2.6	0.6	3.4	**8.2**	4

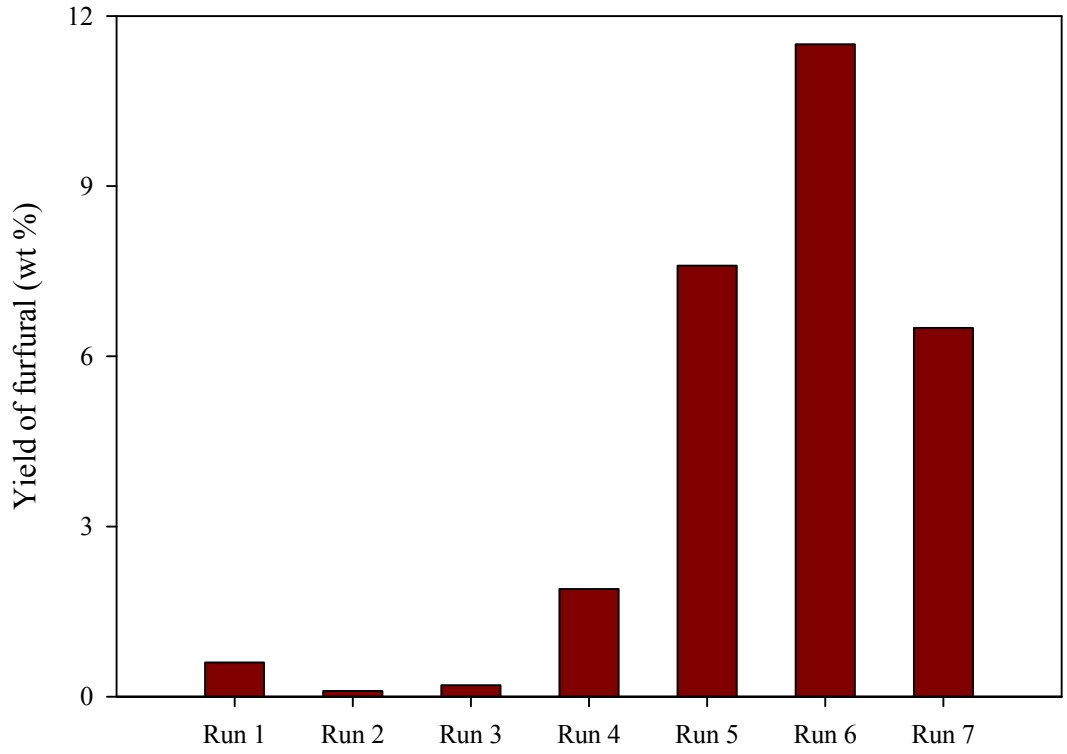
Results-Mass balance (Corn stover)



Products (wt %)	Run 1 343 °C	Run 2 370 °C	Run 3 430 °C	Run 4 337 °C	Run 5 333 °C	Run 6 346 °C	Run 7 335 °C
Oil	46.84	46.27	48.21	53.08	49.44	42.34	36.2
Gas	20.58	20.25	23.56	18.79	11.54	10.9	14.6
Char	36.77	34.34	31.43	28.13	39.03	46.76	49.2

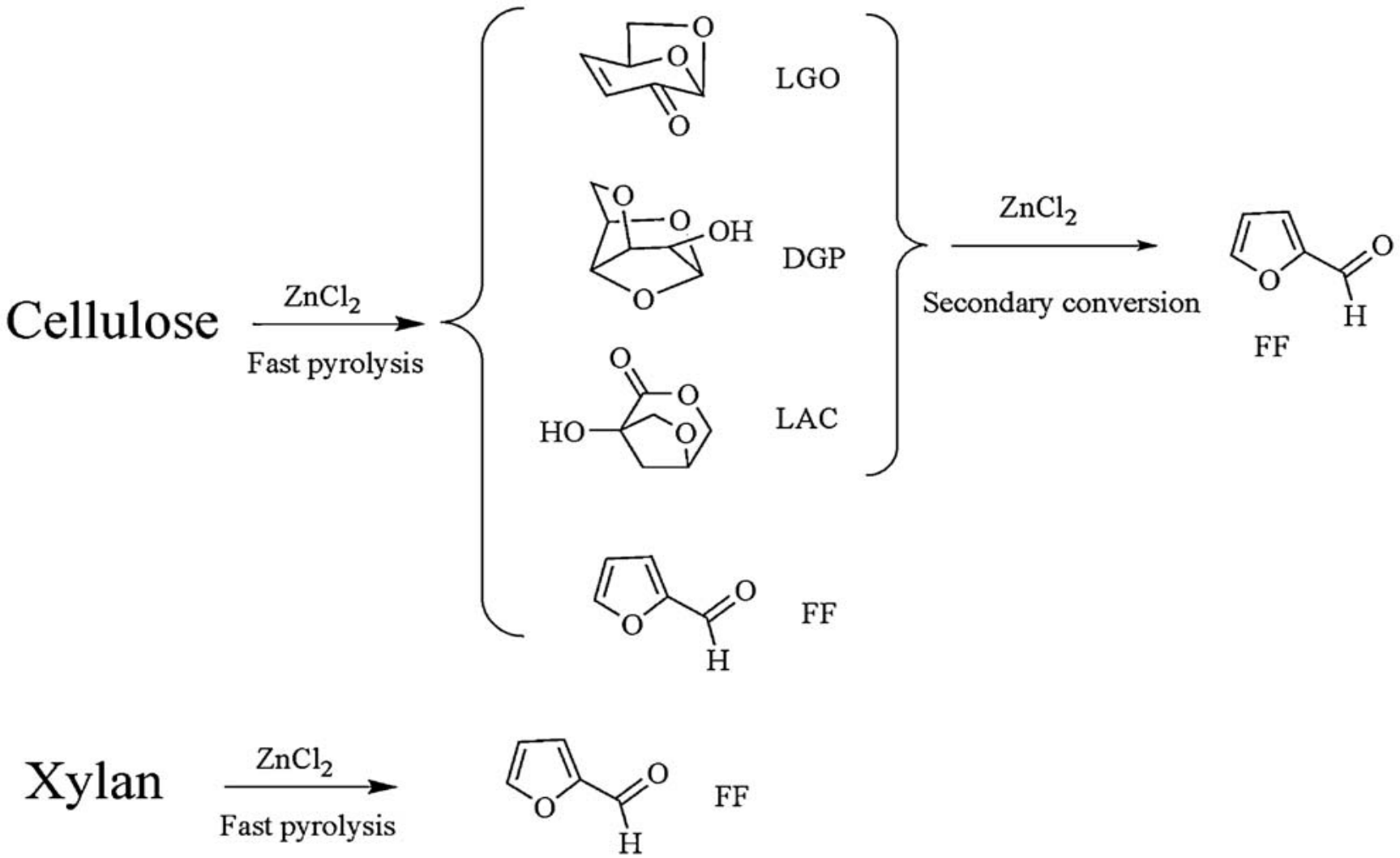
Run 4, 5, and 6 : Soaking
Run 5, 6, and 7 : $ZnCl_2$ impregnation

Results-Furfural yield (Corn stover)

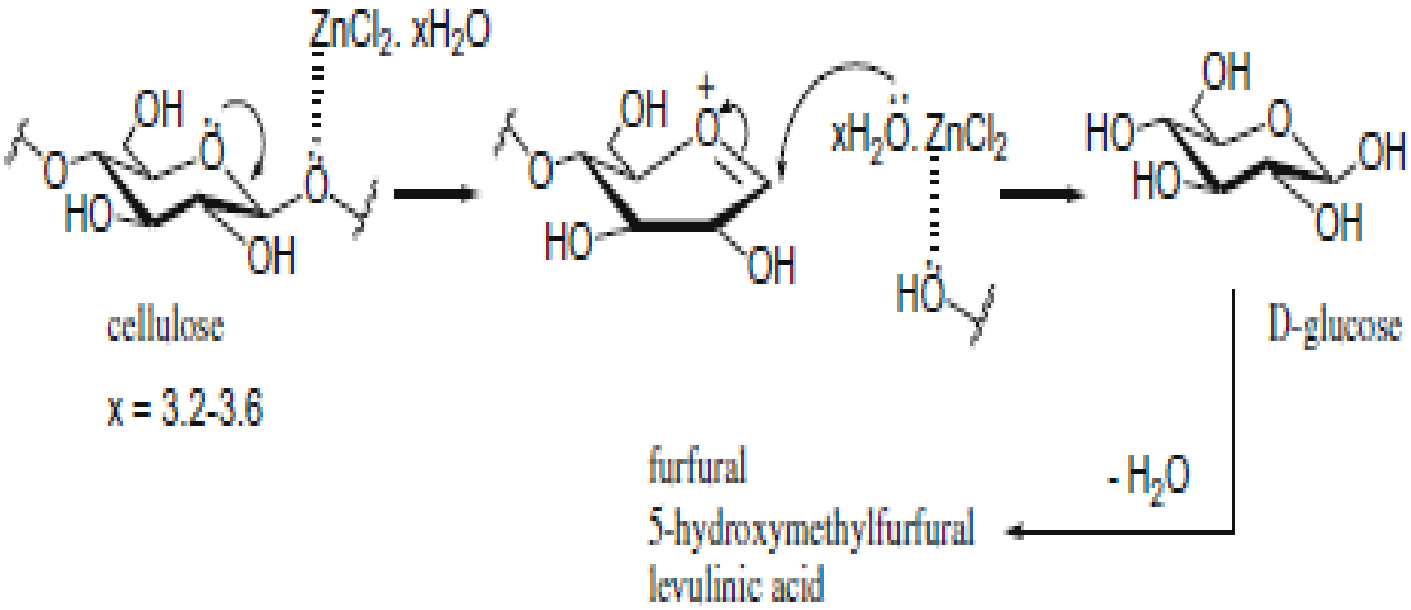


	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7
Furfural	0.6	0.1	0.2	1.9	7.6	**11.5**	6.5

Results-Furfural from cellulose and hemicellulose via $ZnCl_2$

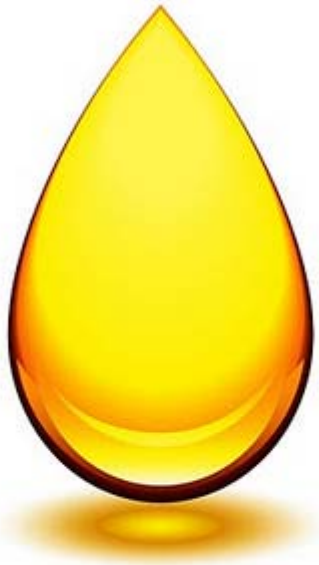


Results-Furfural from cellulose via $ZnCl_2$



Conclusion

1. Maximum bio-oil yield: about 60 wt%
2. Maximal furfural yield: 11.5 wt%
3. $ZnCl_2$ was effective for the production of furfural
4. Washing led to the increase in bio-oil and furfural yields
5. Economical separation method for furfural should be found (ex. Extraction).



Thank you for your atention