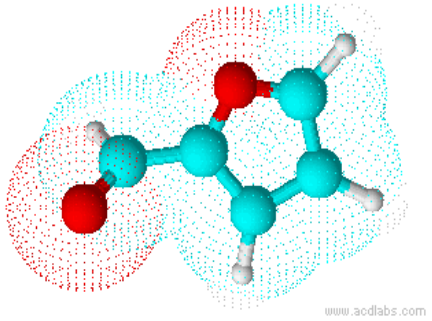
Furfural
the sleeping beauty



Furfural production in modern lignocellulose-feedstock biorefineries

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UNECE/FAO Workshop St. Petersburg – 22-24/05/2013

A network of knowledge for Furfural technology

Process and Energy Department - Delft, NL

Academic research on furfural formation and biorefineries

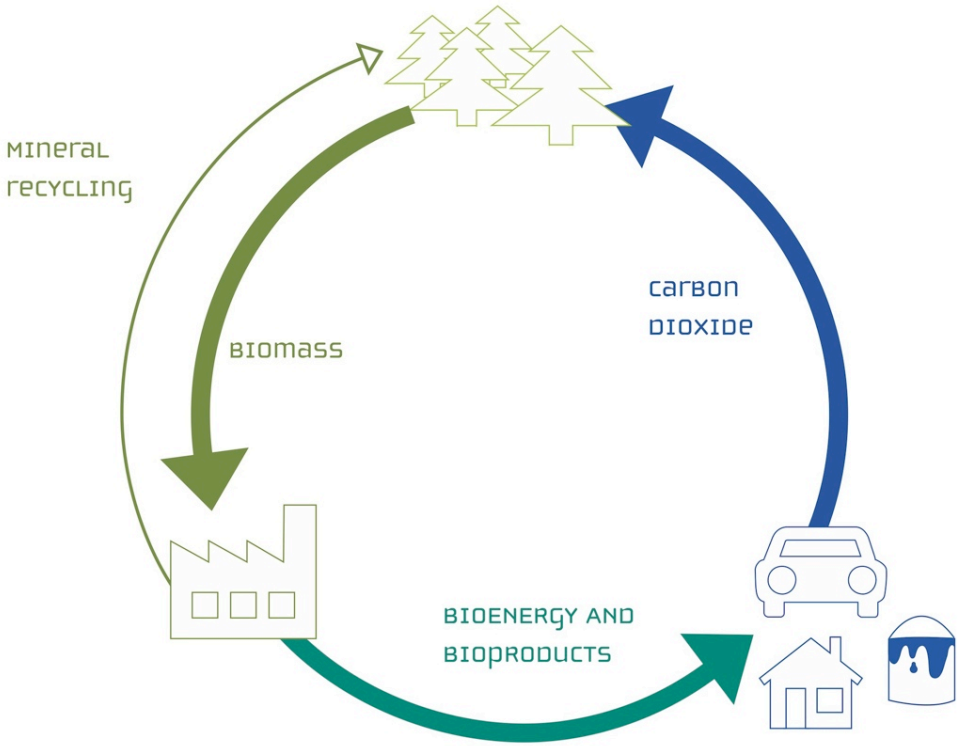
Durban, SA

Business development and technology transfer furfural industry

L'Aquila, IT

Energy Service Company (ESCo) and engineering in industry.

BIOREFINERY

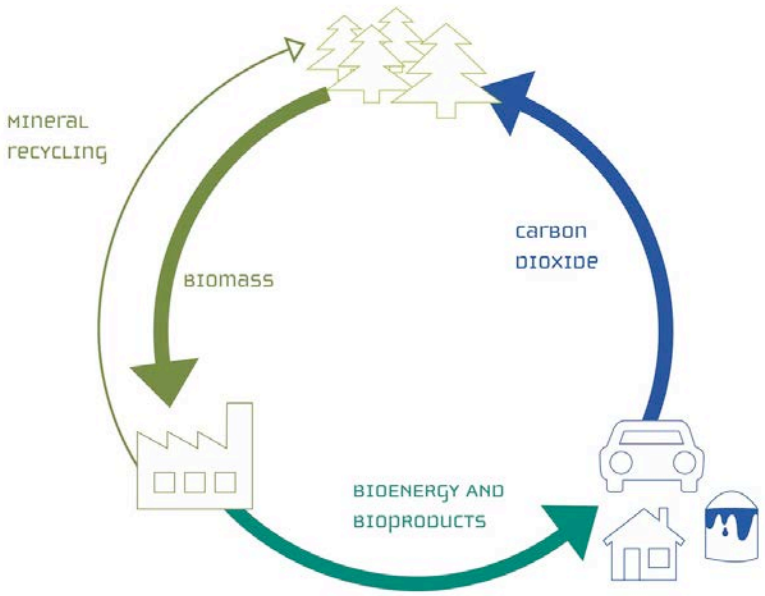


BIOREFINERY:

A complex system able to process different biomass feedstock, via different technologies, in order to produce a multiplicity of products.

Lignocellulose feedstock biorefineries

In a modern lignocellulose-feedstock biorefinery, every fraction of the biomass should be used possibly for added value productions, minimizing the wastes and the environmental footprint.



Chemical composition (dry basis) of common lignocellulose feedstock

LCF	Cellulose (%)	Hemicellulose (%)		Lignin (%)
		Hexoses	Pentoses	
Softwood	40-48	12-15	7-10	26-31
Hardwood	30-43	2-5	17-25	20-25
Cereal straw	38-40	2-5	17-21	6-21
Maize straw	35-41	2	15-28	10-17
Rape straw	38-41	-	17-22	19-22
Recovered paper	50-70	-	6-15	15-25

Bio-based chemical production is challenged by an overabundance of possible products

The US Department of Energy produced a systematic study aimed at **selecting the most promising building-blocks** based on 9 selected criteria

J.J. Bozell, G.R. Petersen, *Green Chem*, 12:539-554, ***2010***

Table 3 New top chemical opportunities from biorefinery carbohydrates, criteria for their inclusion and resulting technology needs

Compound	Criteria for inclusion	Illustrative general biorefinery technology needs
Ethanol	1, 2, 3, 4, 5, 6, 7, 8, 9	Selective alcohol dehydrations; improved biochemical production of alcohols from biomass (rate, yield, titer, product, pH, inhibitor tolerance); engineering of optimal fermentation organisms
Furans	Furfural: 1, 2, 7, 8, 9 HMF: 1, 2, 5, 8 FDCA: 1, 4, 5	Selective dehydrations of carbohydrates; new catalysts and reaction media for dehydration; reactive separations; selective oxidations of alcohols; improved oxidation and dehydration catalysts; catalytic systems for reactions in aqueous solution
Glycerol and derivatives	1, 2, 3, 4, 5, 6, 7, 8, 9	Reactions in aqueous solution; selective reductions and oxidations of polyols; improved biological conversions of polyols
Biohydrocarbons	Isoprene: 1, 2, 3, 4, 6, 7 Biohydrocarbons: 1, 2, 6	Improved biohydrocarbon production; engineering of organisms to convert sugars to hydrocarbons; optimizing rate, yield, titer, product tolerance
Lactic acid	1, 2, 4, 7	Optimization of bioconversion of carbohydrates; bioprocesses with high rate, yield, titer, product, pH and inhibitor tolerance; engineering of organisms to produce single materials
Succinic acid	1, 2, 5, 6	Bioconversion of carbohydrates; optimization of yield, rate, titer, separation; engineering of organisms for optimal production of target
Hydroxypropionic acid/aldehyde	1, 3, 4, 5	Optimization of bioconversion of carbohydrates; bioprocesses with high rate, yield, titer, product and inhibitor tolerance; engineering of organisms to produce single materials; selective dehydrations of alcohols; selective reductions of carbonyl groups, new selective hydrogenation catalysts; chemical processes in aqueous solution
Levulinic acid	1, 2, 3, 5, 6, 8	Selective dehydrations of carbohydrates; improved separations of products; utility of co-product schemes by biorefinery; improved catalysts for selective carbohydrate conversion processes
Sorbitol	1, 2, 3, 4, 5, 6, 7, 8, 9	Selective hydrogenolysis of polyols; new catalysts for reduction of carbohydrate derivatives; selective dehydrations of polyols; comparative assessment of chemical and biochemical conversion technology; selective bond breaking/bond making technology for polyols
Xylitol	1, 2, 5, 8, 9	Selective hydrogenolysis of polyols; new catalysts for reduction of carbohydrate derivatives; selective dehydrations of polyols; comparative assessment of chemical and biochemical conversion technology; selective bond breaking/bond making technology for polyols

Furfural Important dates

1821 –

1922 ---

1923 ----

1941 ------

1949 --------

1953 ----------

1961 -----

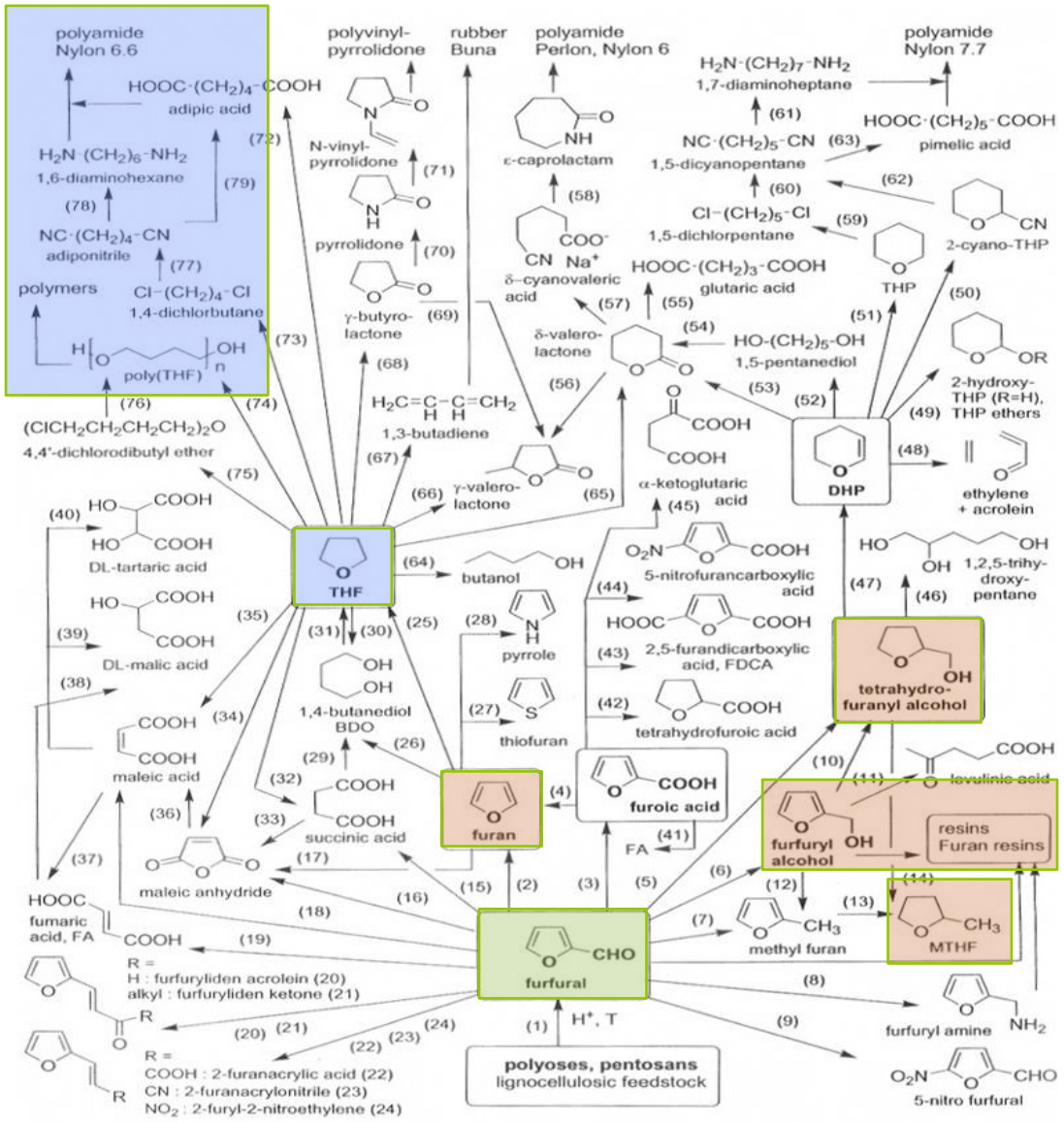
1990s ---

2000 -----

- Döbereiner first isolated a milky distillate during the preparation of formic acid from sugars. The molecule was given the name furfural (C5H4O2), and in 1840 Emmet observed that it can be produced from most vegetable substances.
- The Quacker Oats company start the industrial production of furfural from oats hulls in Iowa, USA, *rapidly distilling the aldehyde from the reaction chamber during the period of its formation.*
- Durite Plastics Inc. is the first manufacturer of phenol-furfural resins.
- Furfural derivatives are tested as automotive fuel in blends with gasoline.
- Du Pont starts the production of adiponitrile for the manufacture of nylon 6.6 from furfural and THF.
- A.P.Dunlop, F.N.Peters, The Furans, ACS Mon. series published. Commercial availability of furfuryl alcohol.
- Du Pont abandons the furfural-THF-adiponitrile process opting for oil derivatives as starting materials.
- Furfural market around 270 kton/year, mainly to furfuryl alcohol and furan resins.
- Karl J. Zeitsch writes a very successful book: *The chemistry and technology of furfural and its many by-products*

Furfural

what for?



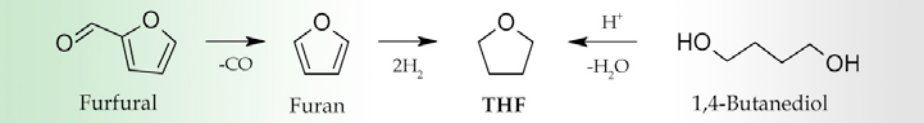
Furfural

what for?

MOST PROMISING APPLICATIONS

THF production

In the last years furfural based route is being rediscovered.



Furfuryl-alcohol resins

NON-TOXIC “furfurylation” gives to wood improved dimensional stability, hardness, moisture barrier, and resistance to microbial decay, making EU wood species comparable to tropical teak.

Agricultural nematocide

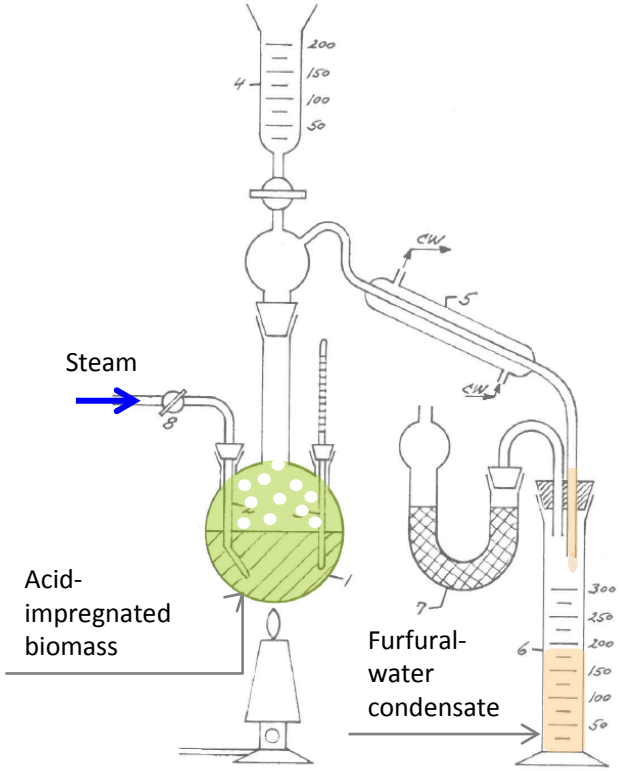
In view of methyl-bromide phasing out. Furfural is proven to control nematodes in a biological fashion, is non-systemic, has low acute toxicity, and safely applicable to soils via water solution. Already used in SA and being evaluated in USA.

Furan as building blocks for copolymers

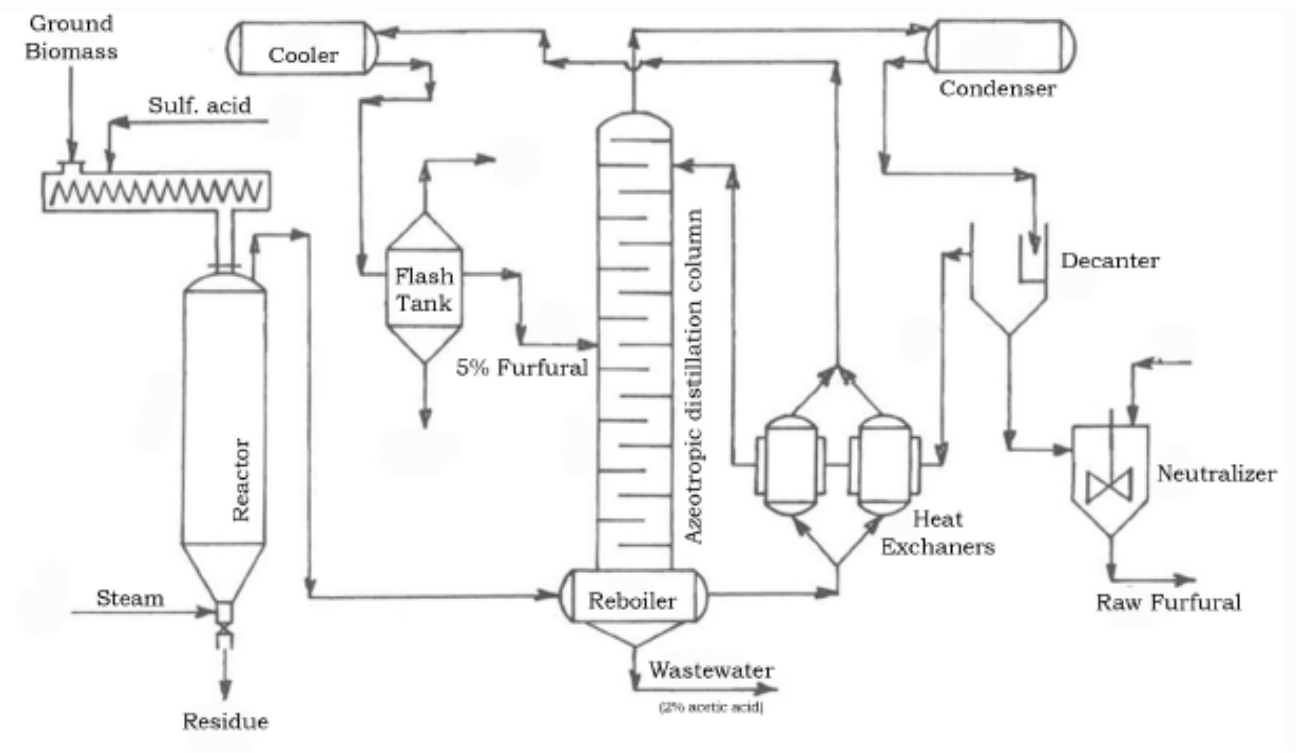
Synthetic fuels (furanics)

Biorefineries based on Furfural production

- Lab setup for furfural preparation



Present-day production processes



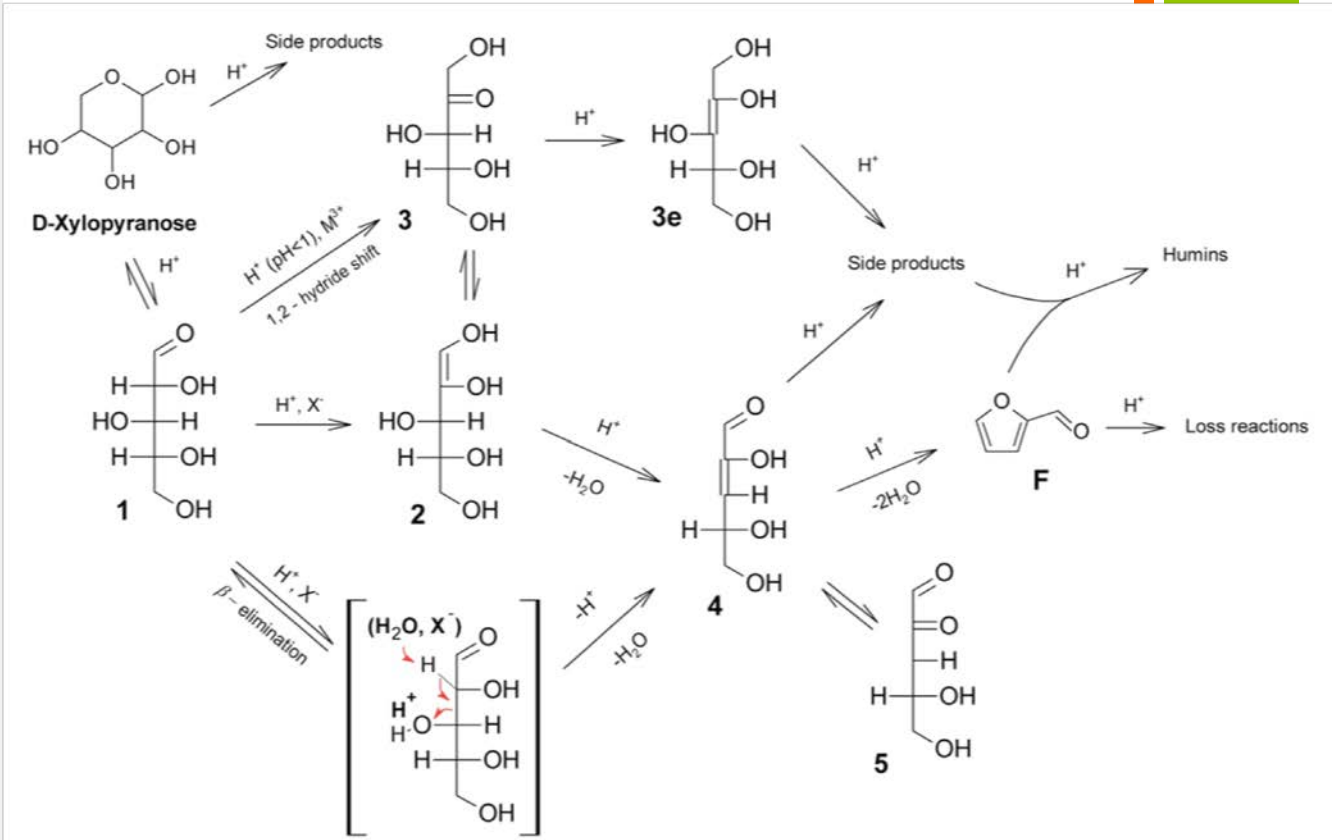
- **Low yields,** approximately 50% of theoretical.
- **High energy use.** 20-50 ton of steam per ton of furfural.
- **High (sulfuric) acid usage**, roughly 20%wt of furfural output.
- **No integration** apart from residues incineration.

New processes of this type are no longer manufactured. This process is fundamentally unsuitable nowadays.

Main results of the research at TU Delft

A significant evolution in the furfural industry cannot prescind from a deeper understanding of the mechanistic aspects of furfural formation.

- *Clarifying the critical steps of furfural formation mechanism is crucial for planning an appropriate catalytic strategy in the furfural industry.*
- **General acid-base catalysis** rather than specific acid catalysis applies.
- **95% yield obtained!**
- New mechanism of reaction proposed deriving from experimental results on xylose dehydration.

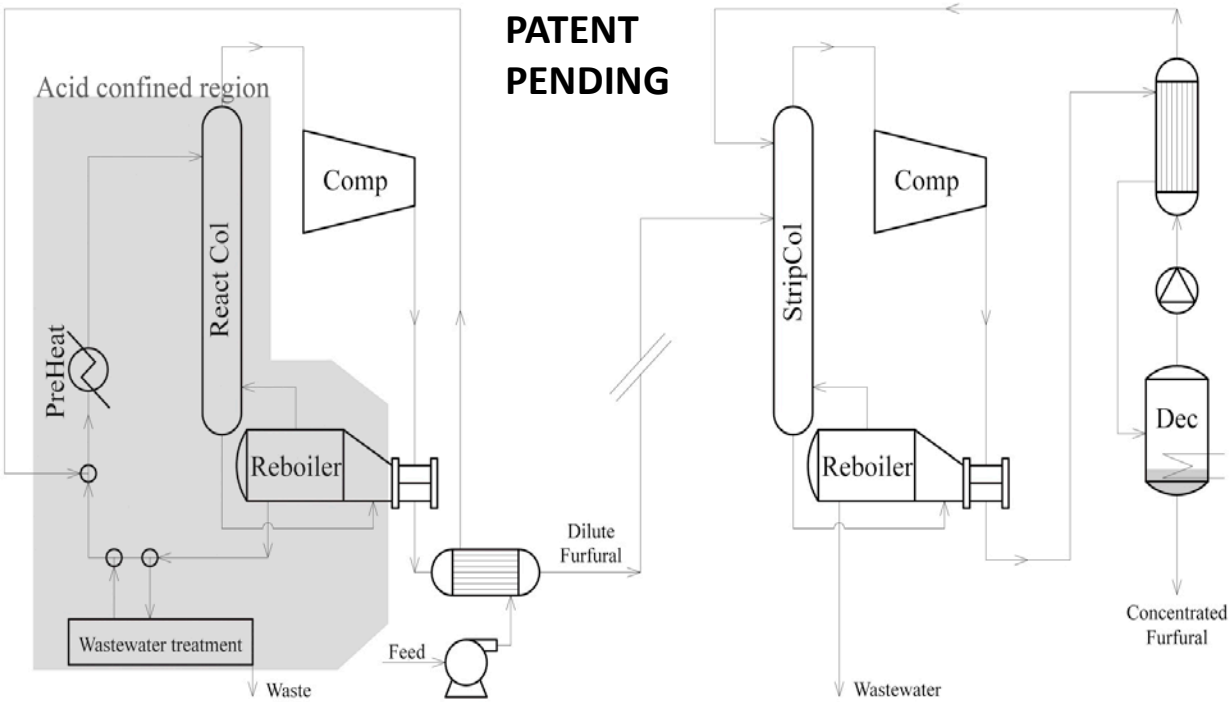


TU Delft Delft University of Technology

Main results of the research at TU Delft

Working with a major EU power/utility industry in a project aimed at furfural production from 2nd generation biomass (2 post-docs involved), duration: 2012-2014

- **Simple vapor recompression** allows abundant steam stripping with very low **energy expense.**
- **High yields** due to the catalyst mix and good separation
- Drastic **reduction of specific acid consumption** thanks to recirculation.
- Integration with modern **biorefineries** such as cellulosic ethanol.
- **Low cost** of production (around 800 US$/ton)



TU Delft Delft University of Technology

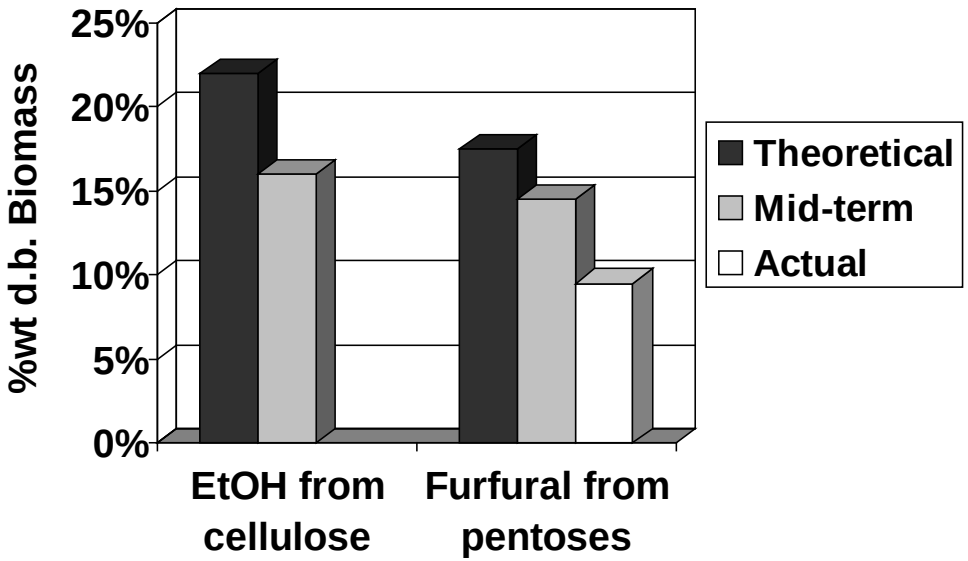
Furfural integration in a EtOH based biorefinery

- **Combined production of EtOH and Furfural** could yield around 30%wt material containing almost 50% of the initial calorific value of the biomass.

  Filling this gap is the objective of our work.
  By:

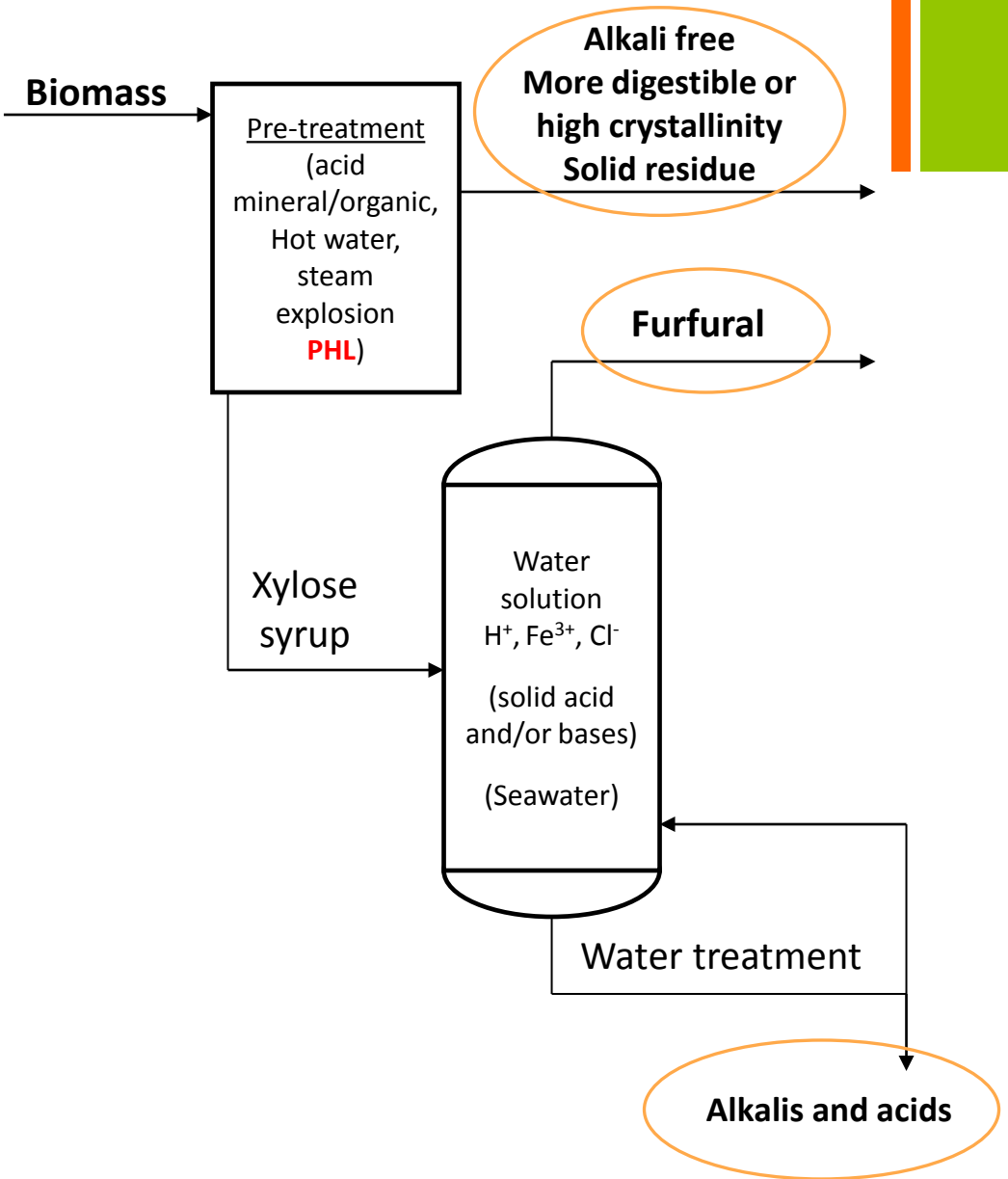
1. Optimizing pentoses production

2. Maximizing furfural yield from pentoses



Furfural integration in a biorefinery

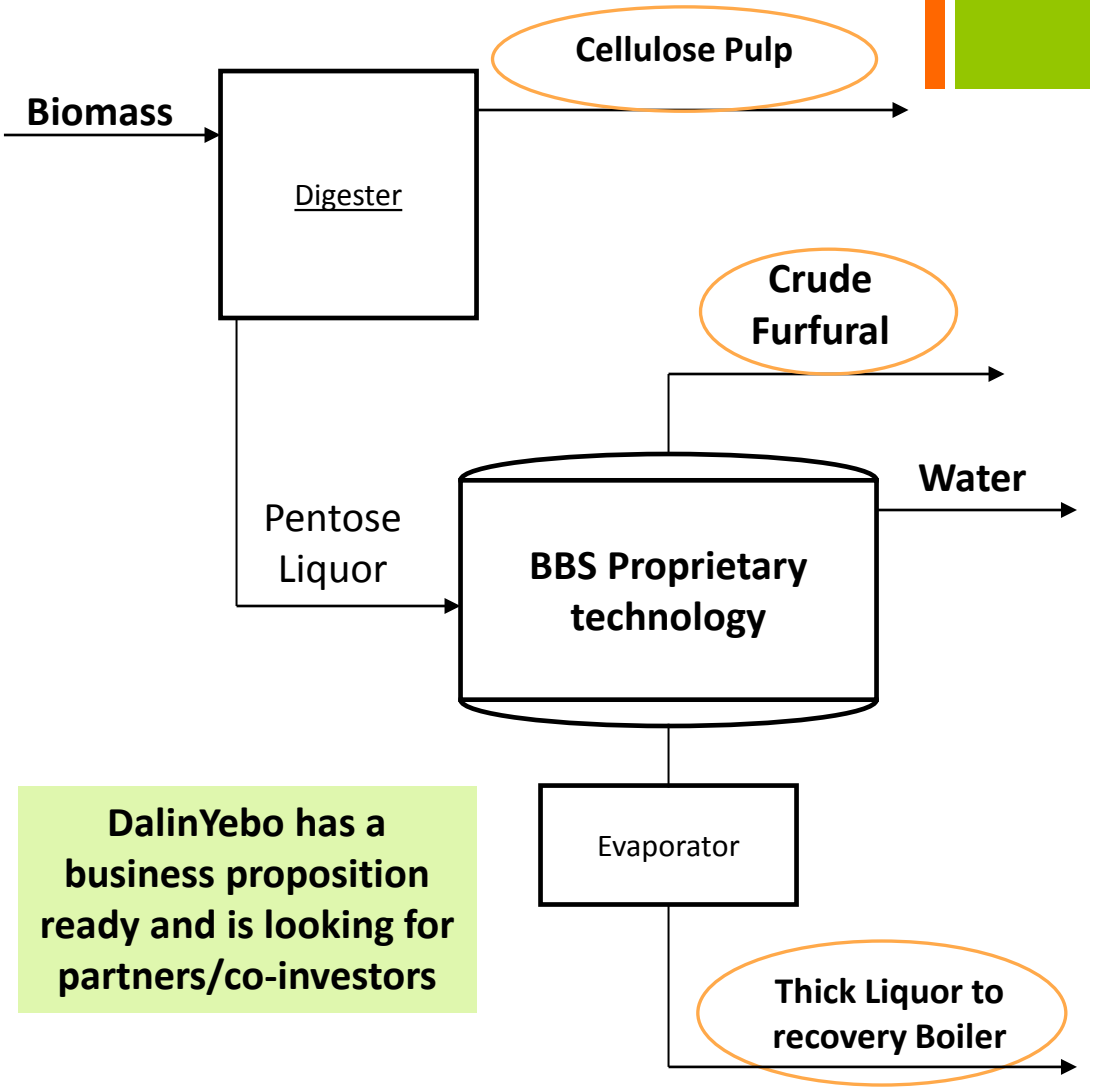
- In many pre-treatment processes **hemicelluloses derived carbohydrates normally end up in an aqueous stream** together with other water-soluble impurities.
- Mild hydrolysis processes are able to easily separate the hemicelluloses and water extractives from a **cellulose-rich residue with high crystallinity**.
- This process is of particular interest for the integrated furfural production within **pulp&paper and cellulose fibers industries.**



TU Delft Delft University of Technology

Furfural integration in Pulp & Paper
The *BBS plug-in*

- **Benefit of pentose removal:** reduced evaporation load, improved calorific value of black liquor,
- **Pentose readily available** from the sulphite mills or as Pre-Hydrolysis-Liquor from converted Kraft mills.
- **Novelty based on proven technologies**
- **Ideally suited** for pentoses removal from pulp mills or Cellulosic Ethanol liquors.



DalinYebo has a business proposition ready and is looking for partners/co-investors

DalinYebo

The µ-Biorefinery concept

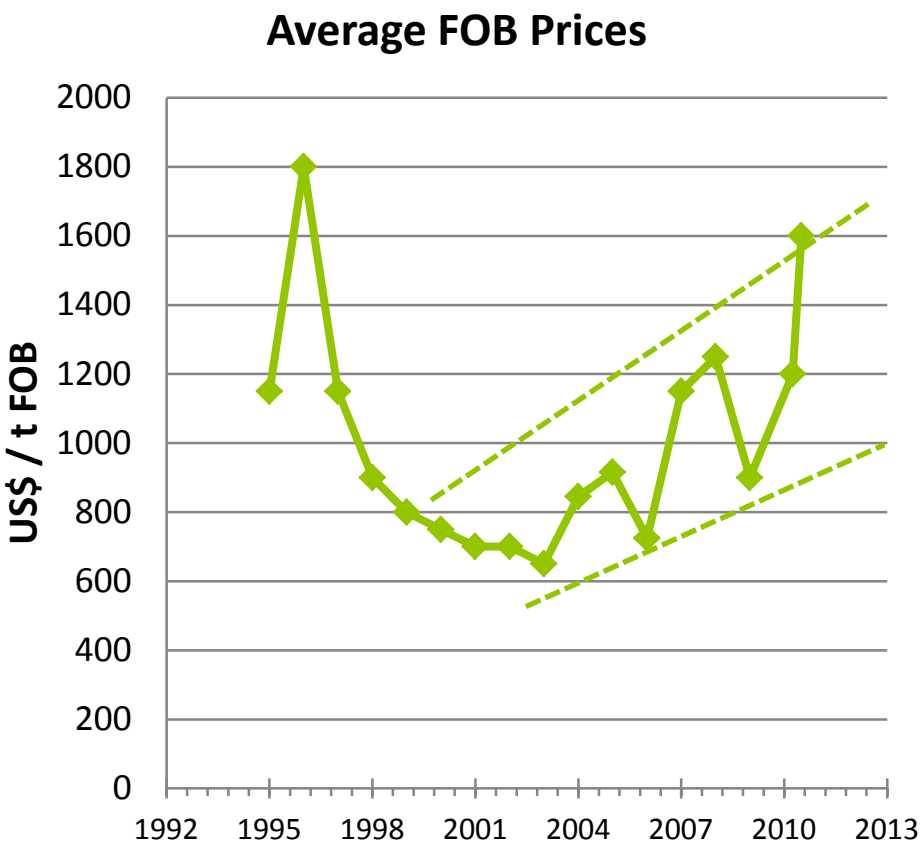
- DY has US$ 45 million pa of orders (LOI), which is unable to supply, due to lack of own production. Market demand is strong. Supply is sluggish.
- 20-25% growth pa due to demand of "green" or "biobased" products.

- **µ-BioRefinery™** makes use of simple, fit-for-purpose processing equipment that is installed close to the biomass source to produce bio-renewable chemicals and biobased electricity
- It is based on a **smart down-scaling** and integration of proven existing technologies (and their mass and energy balance)

DalinYebo

Furfural market overview

- **Furfural demand:** projected to grow at a substantial rate from the actual 300 kton/year due to demand of *green* and *bio-based* products. 1 Mton/a is easily achievable by 2020.
- **Steady price increase from early 2000** due to shortage of corncobs in China, environmental pressure on old mills, growth of Chinese domestic demand, Indian market increasing.
- **High prices are containing the emerging markets.** (Wood treatment alone has a gigantic potential market of about US$ 5bn).



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Conclusions

1. **Biorefineries represent the future of biomass** beyond biofuels and bioenergy.

2. Hemicellulose conversion to furfural has a **high-potential** to be unlocked.

3. Furfural production is facing a huge **renovation challenge** to meet new environmental and energy standards. Current technologies are unsuitable.

4. The challenge is in the hands of **innovative furfural producers** willing to implement novel and disruptive technologies.

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Thank you