

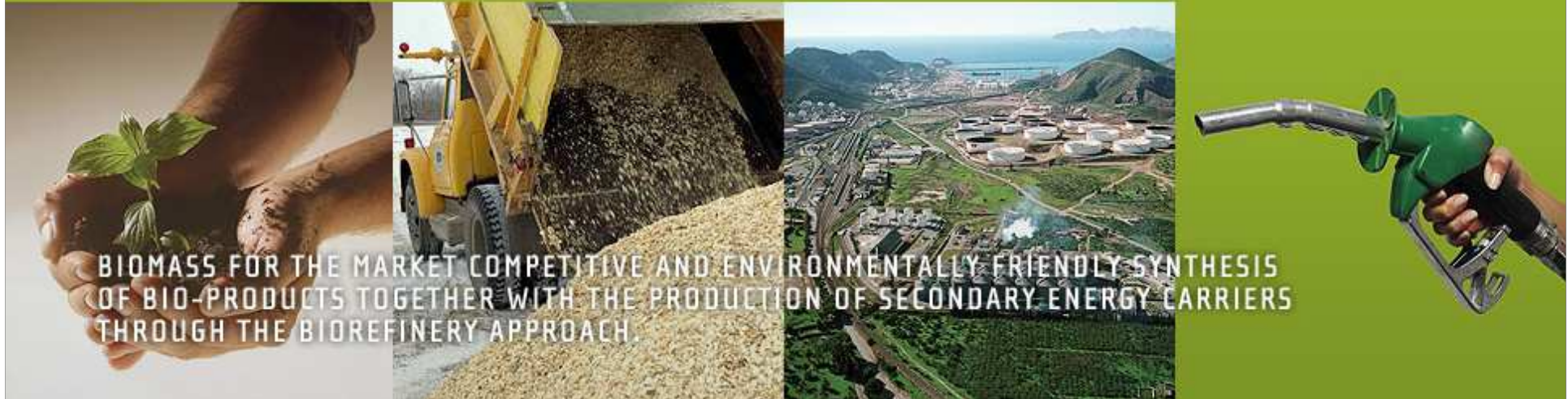
# Kinetic Assessment For Selective Production of FURFURAL from C<sub>5</sub> sugars contained in Biomass

Gianluca Marcotullio

Delft University of Technology - The Netherlands



Marie Curie Actions  
INECSE project



The BioSynergy project is supported by the European Commission through the Sixth Framework Programme for Research and Technological Development (2002 – 2006) with a **grant up to 7.0 million €**.

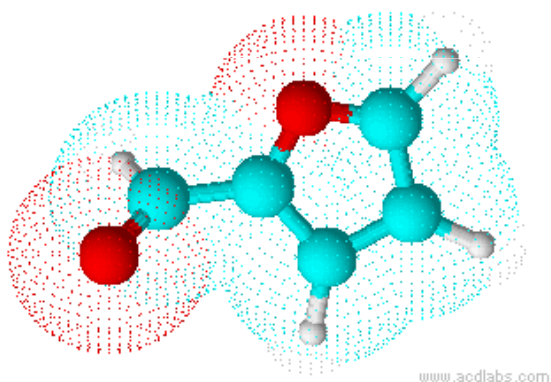
**17 partners around Europe  
1st of January 2007 for 48 months.**

The BIOSYNERGY project aims to use BIOMass for SYNthesis processes (transportation fuels, platform chemicals) and enERGY production (power, CHP) by **application of innovative, fully integrated, synergetic biorefinery concepts**, using advanced fractionation and conversion processes, and combining biochemical and thermochemical pathways.

**Delft University of Technology** is involved in dilute acid fractionation of the hemicellulose and **selective production of FURFURAL from C<sub>5</sub> sugars**.



# FURFURAL



It boils at 162 °C but forms a low-boiling azeotrope with water

Furfural market is around 300,000 ton/y

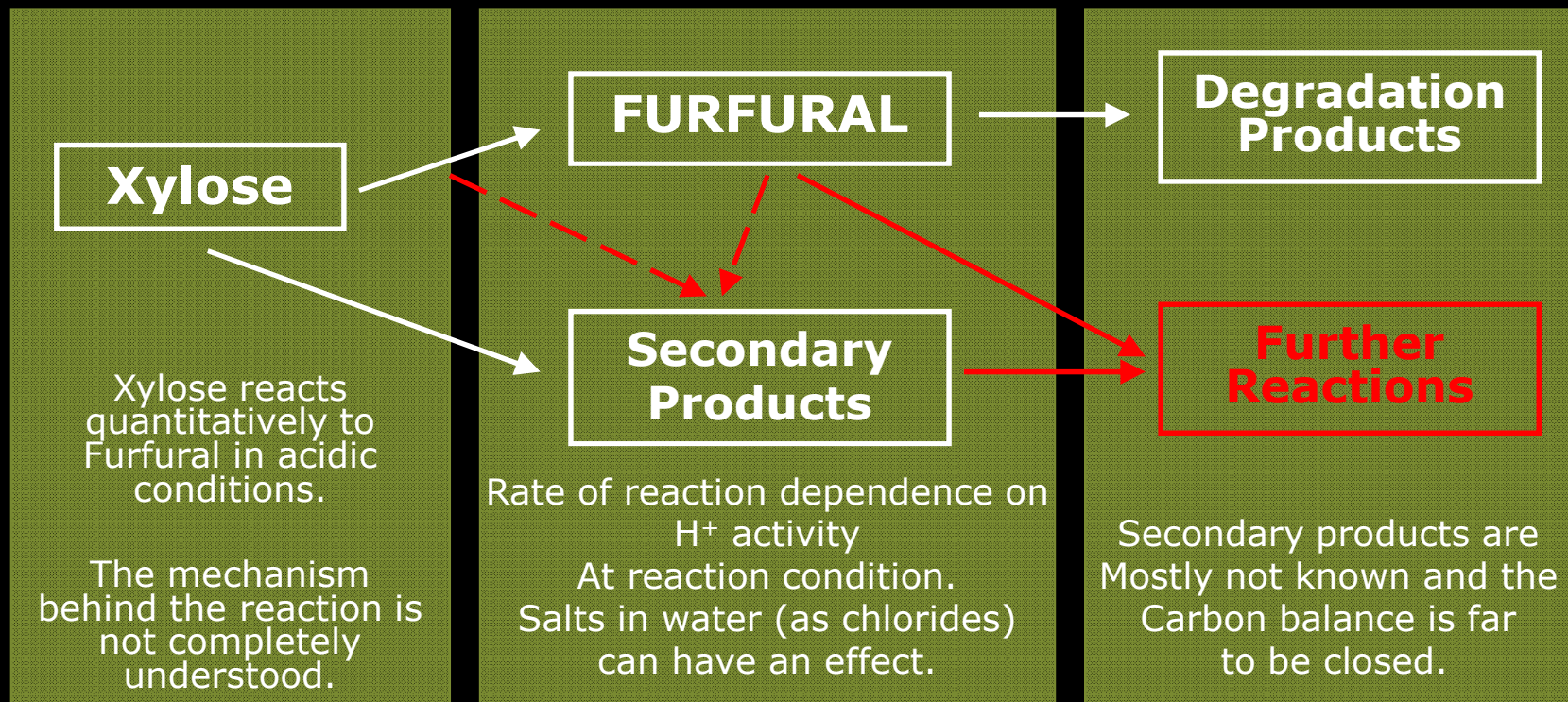
**Current processes** are based on cooking of biomass in acid conditions with continuous stripping (Furfural recovered as 6% solution in water).

**Energy intensive** production: from 15 to 50 ton of high pressure steam per ton of Furfural are used.

Total **yields are around 60%** of the theoretical yield.  
(Less than 10%wt of dry biomass)



# Furfural formation mechanism

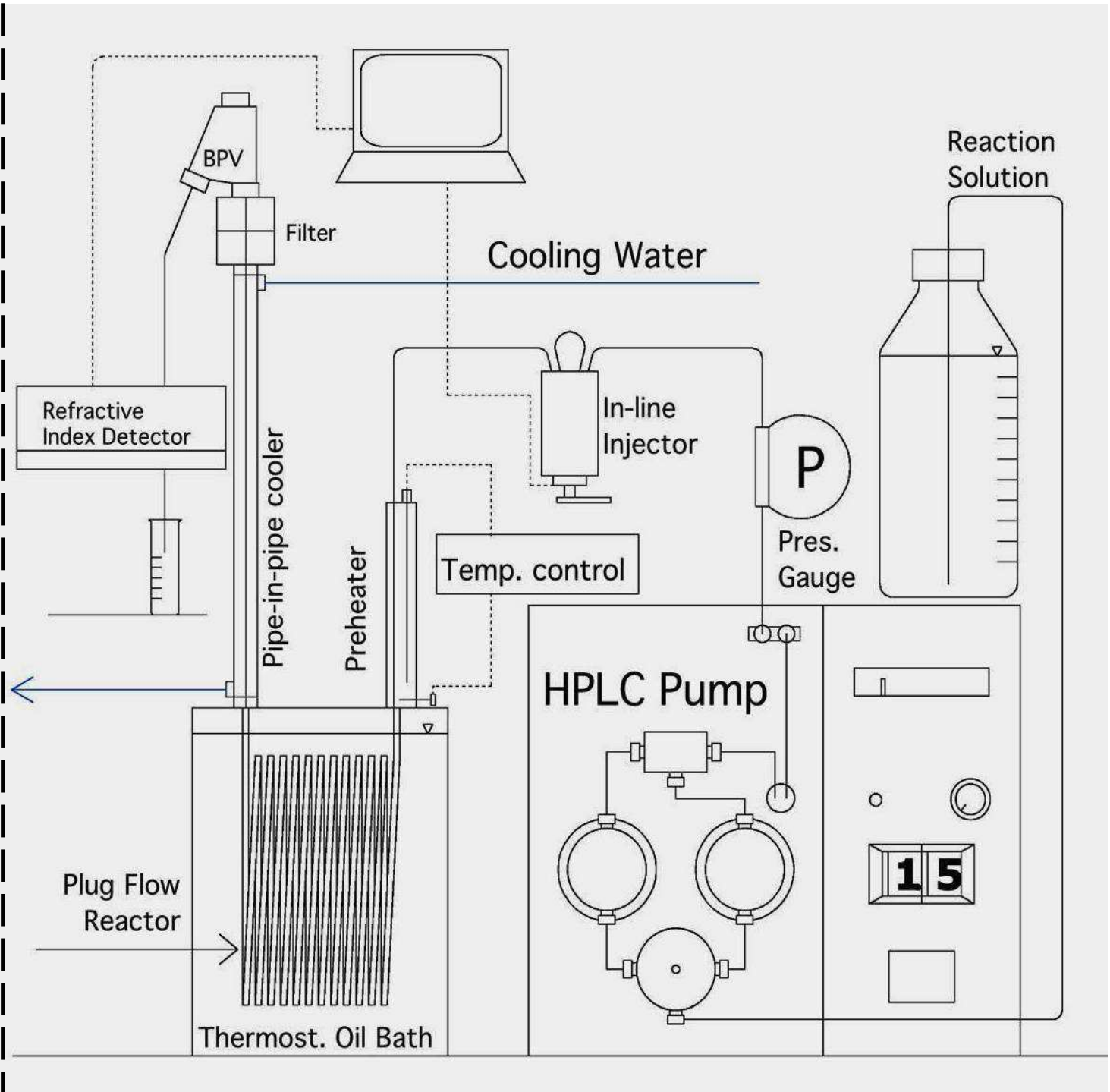


Most of the knowledge about kinetics of these reactions refers to the work of A.P.Dunlop (1948); D.F.Root et al. (1959); E.R.Garret and B.H. Dvorchik (1969); L.J.Antal Jr. et al. (1991)

**Kinetic studies of the main reactions governing the FURFURAL production process**



**Analysis is carried out by means of HPLC – UV – RI**



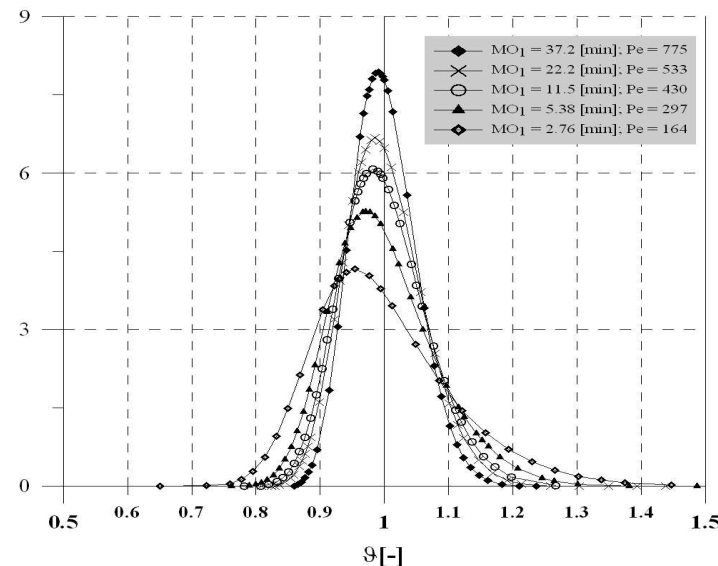
## EXPERIMENTAL ACTIVITY



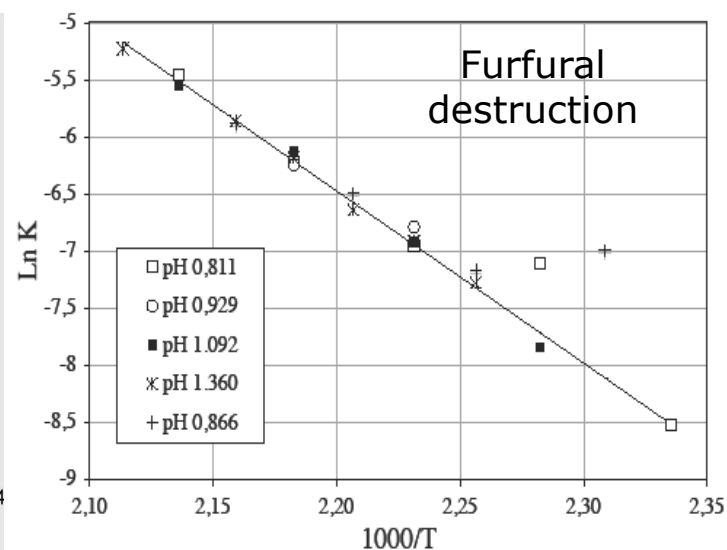
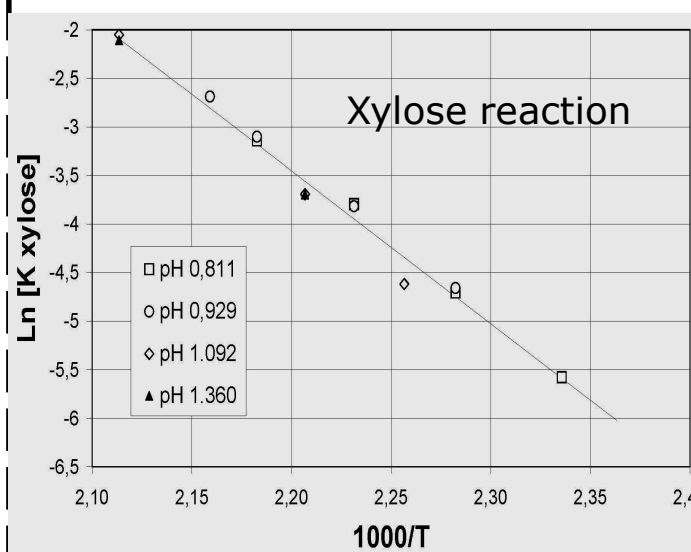
Experiments were carried out at temperature in the range 150-200 °C and pH from 0.81 to 1.36 (H<sub>2</sub>SO<sub>4</sub>)

## Reactor validation

Residence Time Distribution was assessed to validate the Plug Flow reactor assumption.



Both Xylose and Furfural follow a **1<sup>st</sup> order reaction** rate in aq. H<sub>2</sub>SO<sub>4</sub>. **H<sup>+</sup> activity** is considered for the kinetics, which is estimated through the eNRTL model. Reaction rate is then:  $r = -k \cdot a_{H^+} \cdot C_0$   
Xylose reaction is **20-25 times faster** than Furfural destruction.



## RESULTS AND DISCUSSION



G. Marcotullio et al.,  
*Furfural destruction kinetics during sulphuric acid-catalyzed production from biomass*, submitted for publication to IJCRE, Feb. 2009

### Paper submitted to the IJCRE about Furfural destruction kinetics

Furfural destruction takes place in aqueous sulphuric acid media following a **1<sup>st</sup> order** rate (no self-condensation reactions).

**Furfural destruction velocity** is significantly slower than Xylose reaction in the same conditions of acidity and temperature

Reaction rate is proportional to **H<sup>+</sup> activity** even though anion have shown to have an influence.

**Reaction products** from this reaction are not known and formic acid doesn't appear to be formed in relevant amounts.



## OUTLOOK AND CONCLUSIONS



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### Kinetics of Furfural production from biomass

**Major losses in furfural production** in aqueous acid solutions are represented by side reactions more than by furfural destruction in the same media.

**Side reaction products** haven't been clearly identified yet, and the kinetics of side reaction need more investigation. Work is being done in that direction.

Kinetics studies are likely to provide tools for optimization: **acid nature, dilution of the reactants and temperature** influence will be crucial for future processes.

**Laboratory yields up to 70% have been achieved so far from pure D-Xylose without ANY simultaneous furfural removal.**

**THANK YOU FOR THE ATTENTION**