

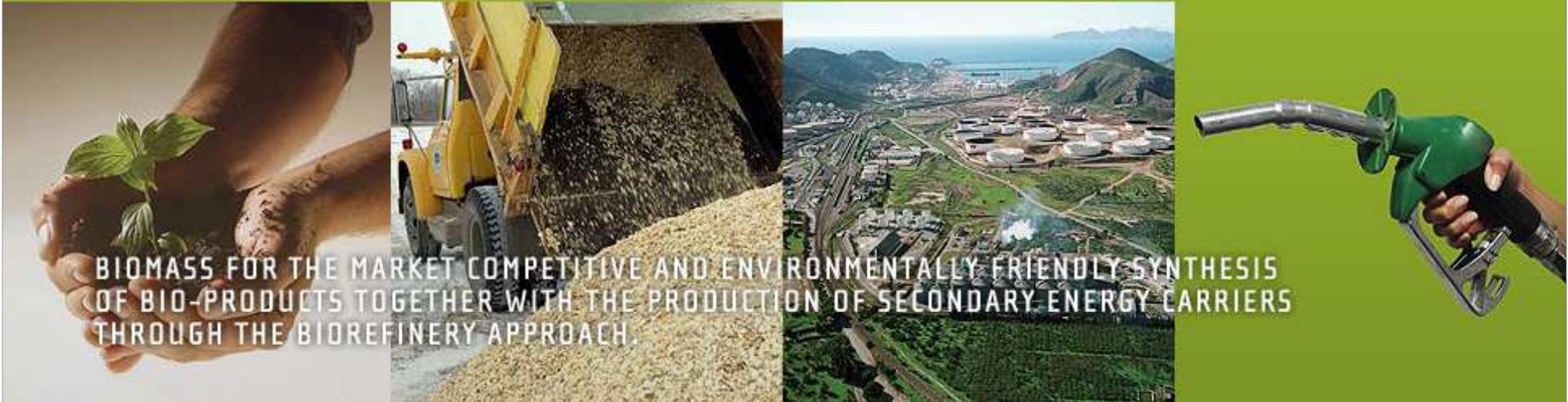
Kinetic Assessment For Selective Production of FURFURAL from C₅ sugars contained in Biomass

Gianluca Marcotullio

Delft University of Technology - The Netherlands



Marie Curie Actions
INECSE project



BIOMASS FOR THE MARKET COMPETITIVE AND ENVIRONMENTALLY FRIENDLY SYNTHESIS OF BIO-PRODUCTS TOGETHER WITH THE PRODUCTION OF SECONDARY ENERGY CARRIERS THROUGH THE BIOREFINERY APPROACH.

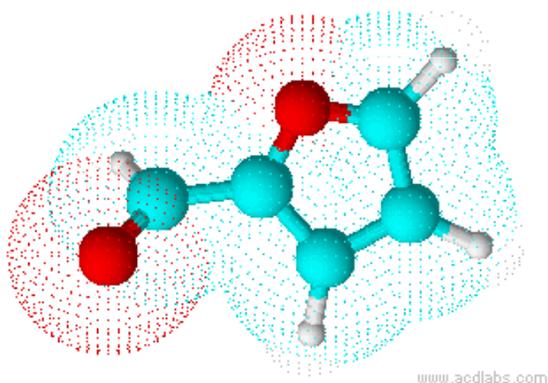
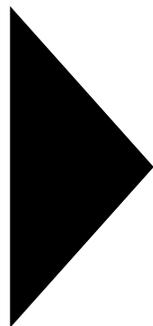
The BioSynergy project is supported by the European Commission through the Sixth Framework Programme for Research and Technological Development (2002 – 2006) with a **grant up to 7.0 million €**.

**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 C₅ sugars**.

FURFURAL



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

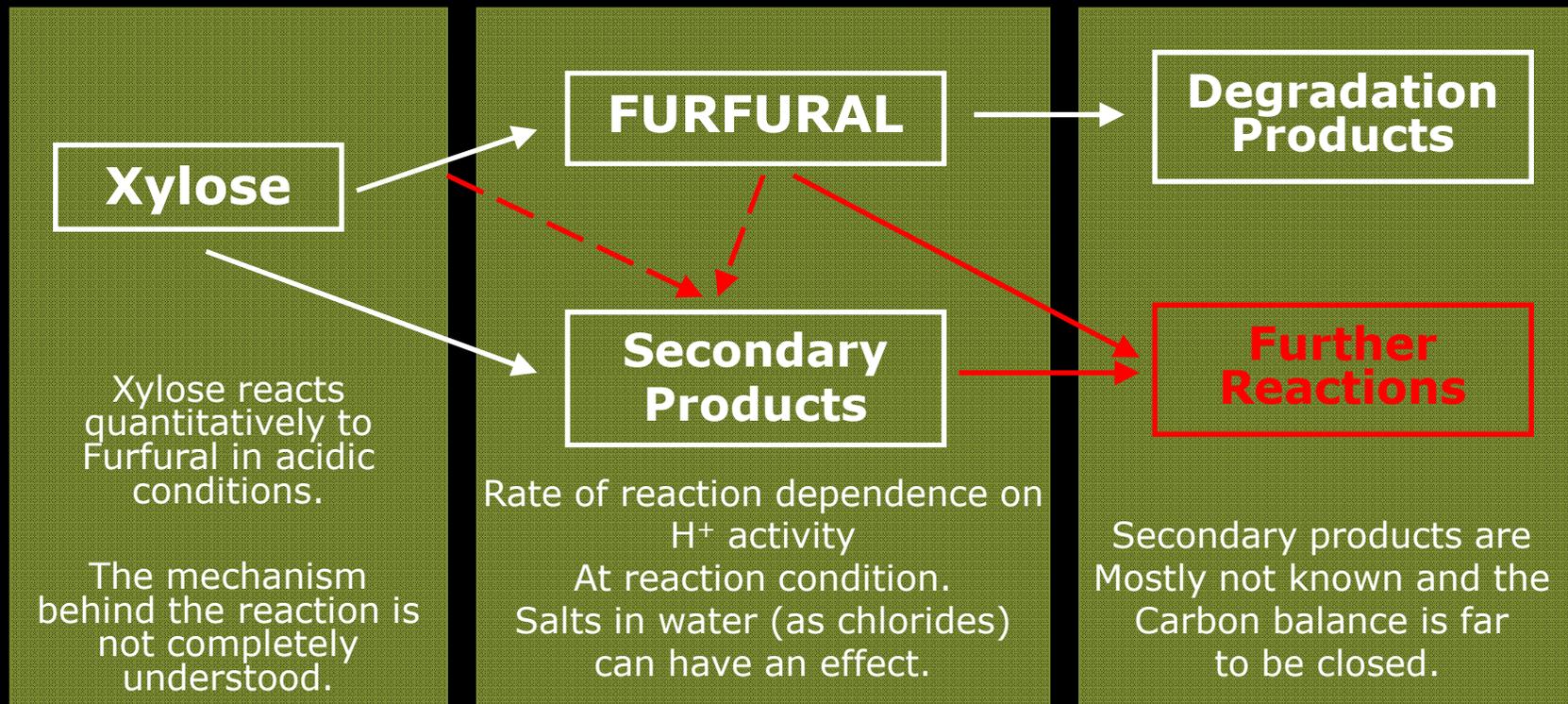
Furfural market is around 300,000 ton/y

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

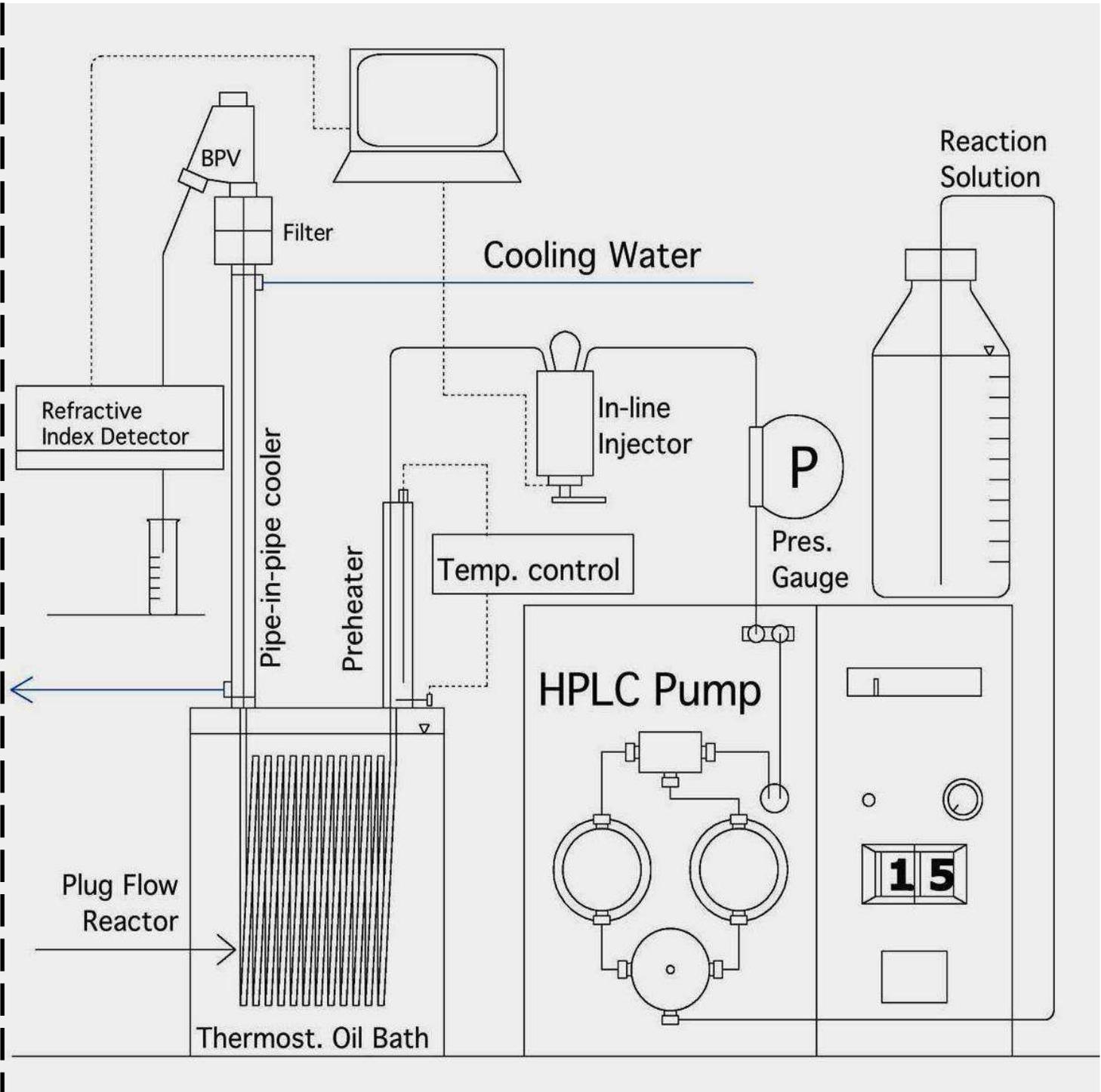


Most of the knowledge about kinetics of these reactions refers to the work of A.P.Dunlop (1948); D.F.Root et al. (1959); E.R.Garret and B.H. Dvorchik (1969); L.J.Antal Jr. et al. (1991)

Kinetic studies of the main reactions governing the FURFURAL production process



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



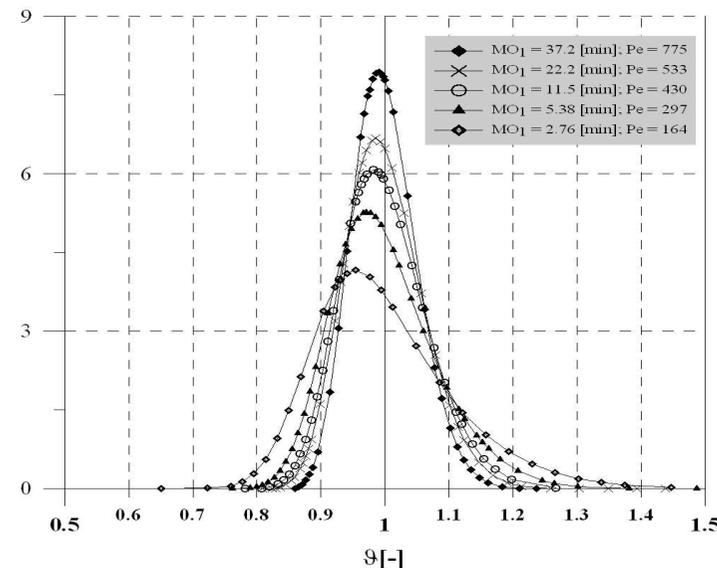
EXPERIMENTAL ACTIVITY



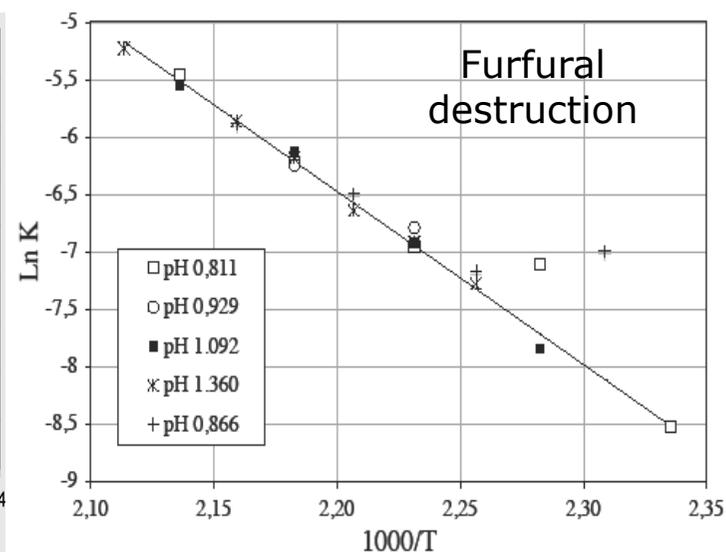
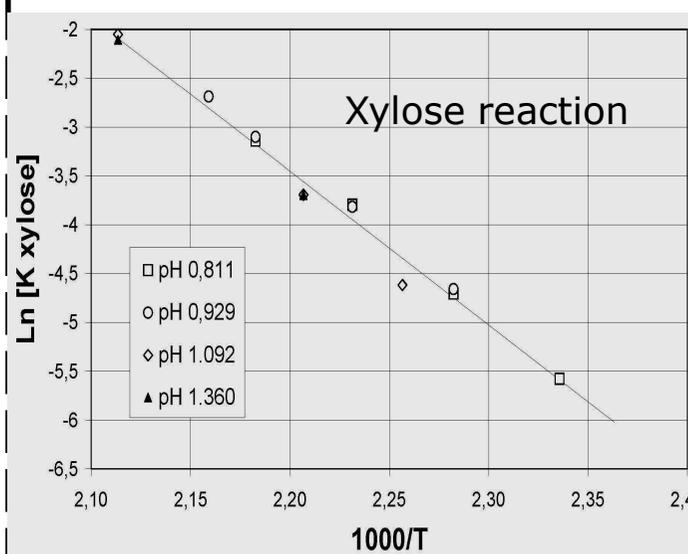
Experiments were carried out at temperature in the range 150-200 °C and pH from 0.81 to 1.36 (H₂SO₄)

Reactor validation

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



Both Xylose and Furfural follow a **1st order reaction** rate in aq. H₂SO₄. **H⁺ 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 **1st 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⁺ 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