Biomass gasification in supercritical water

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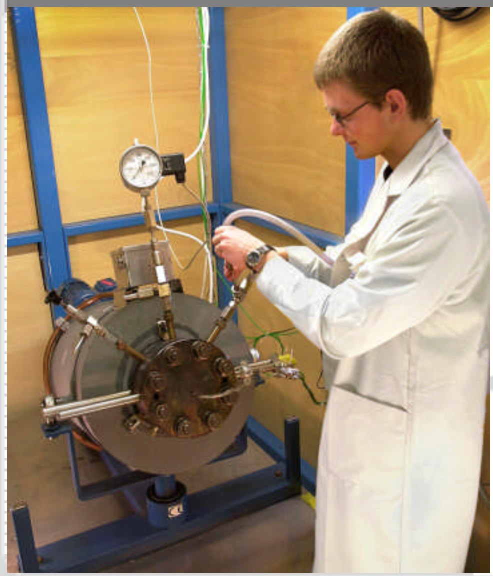
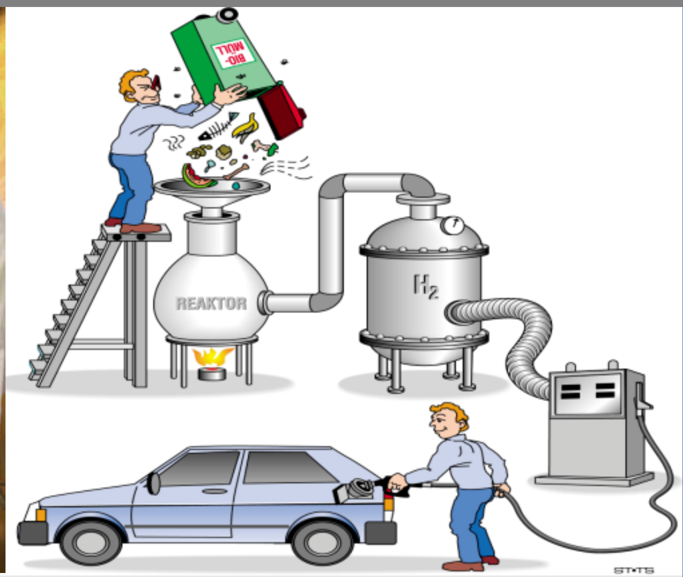
Insitute for Technical Chemistry, Chemical-Physical Processes





Goal:

Development and optimization of hydrothermal biomass conversion processes.

Use of Biomass – Why?

The loss and increase in the price as well as a heavy, uncertain access to fossil resources.

CO_2-neutral; EU strategies for the reduction of CO_2-emissions.

Thermochemical gas formation from biomass

Wet Biomass

H_2, CH_4

Fuell cells

Gas engines

……

$C_6H_{12}O_6 + 6\ H_2O \rightarrow 6\ CO_2 + 12\ H_2$

Dry Biomass

CO, H_2

Fischer-Tropsch

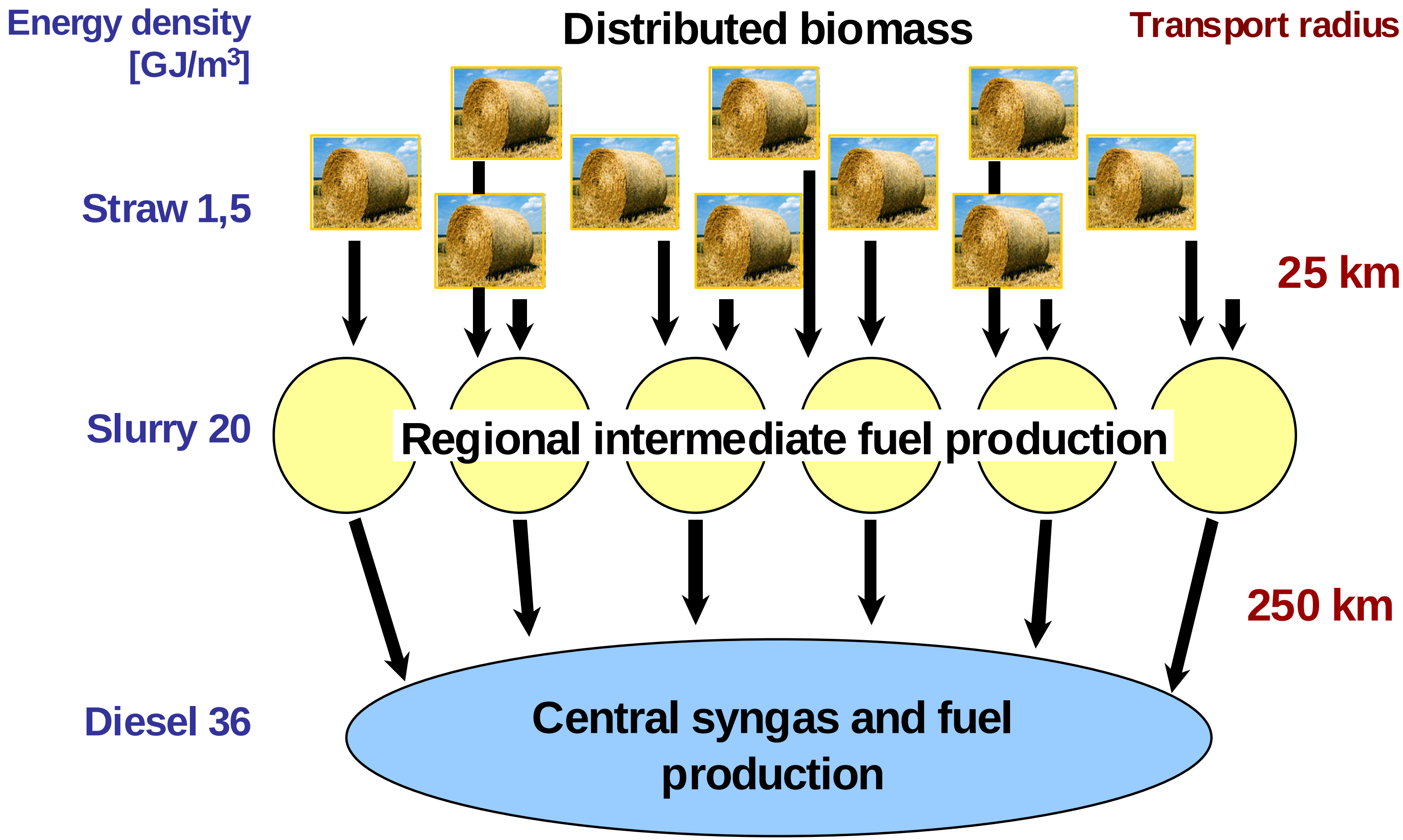
Methanol

DME .....

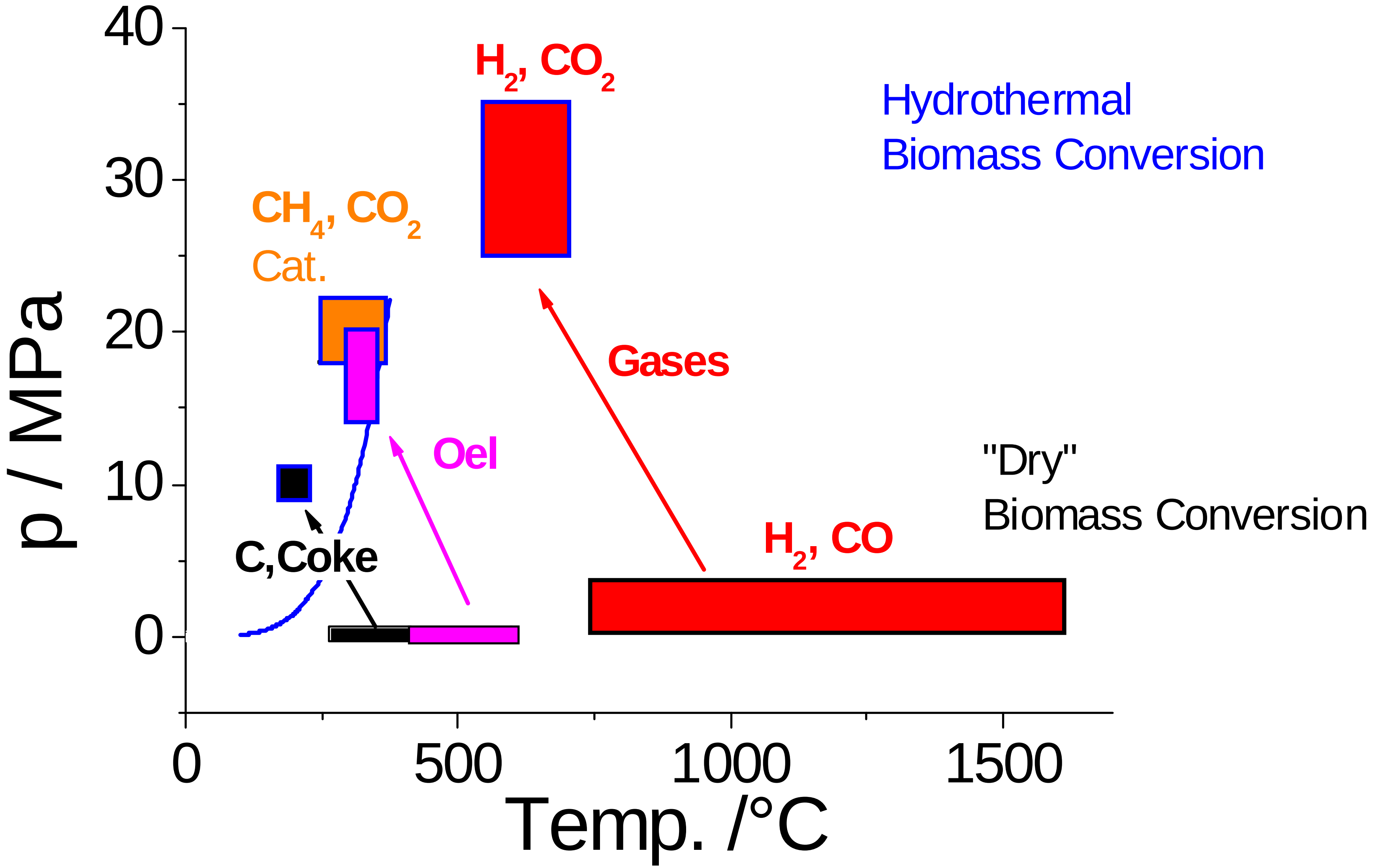
$C_6H_{12}O_6 \rightarrow 6\ CO + 6\ H_2$

$6\ CO + 6\ H_2O \rightarrow 6\ CO_2 + 6\ H_2$

The bioliq - slurry gasification concept



Hydrothermal Biomass Conversion Processes



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DME .....

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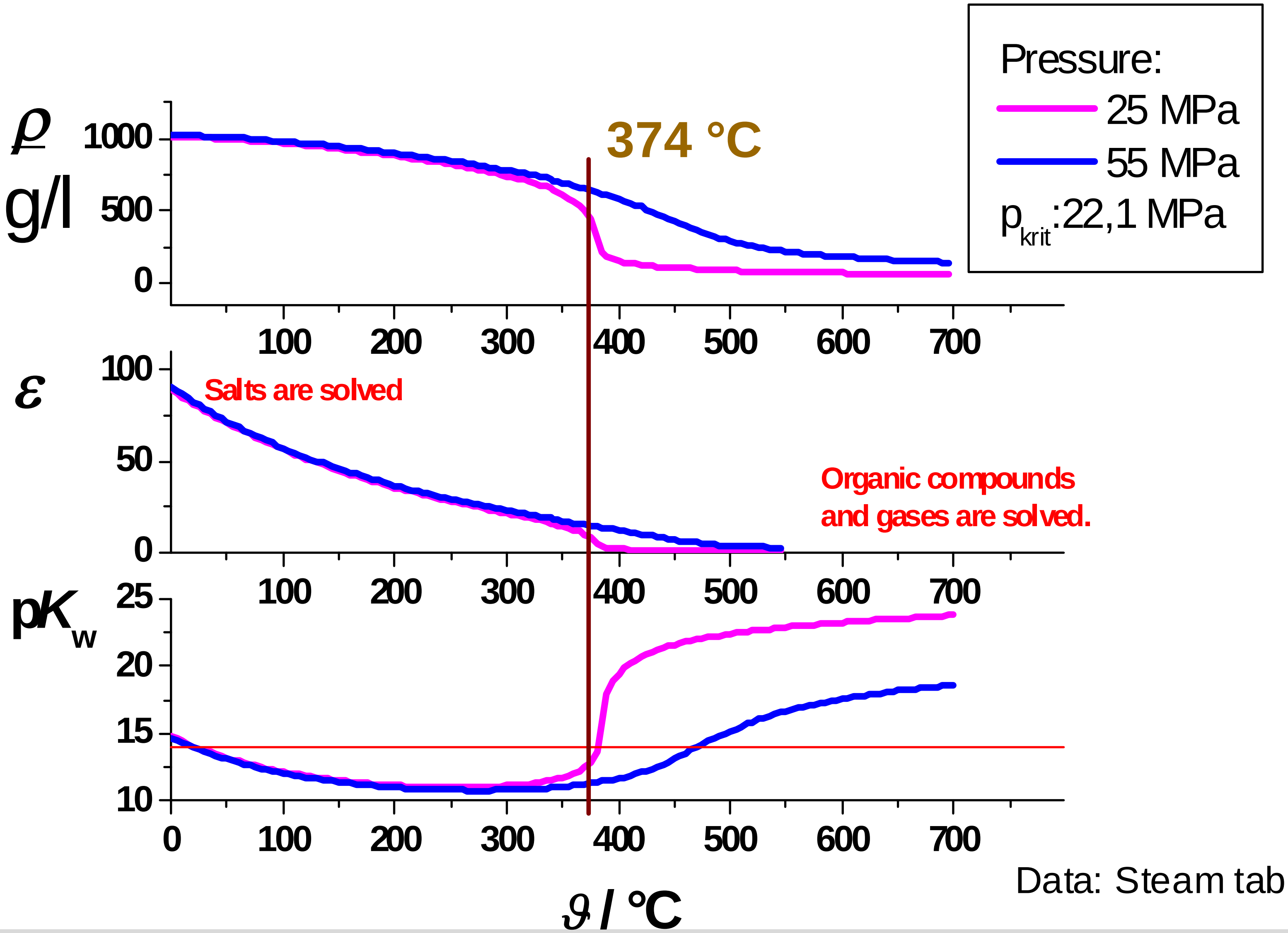
Properties of Water



Data: Steam tables

Gasification in supercritical water

Water is solvent:

Intermediates are dissolved

$\rightarrow$ Less polymerization reactions

$\rightarrow$ Less tar and coke

Water is reactant:

- H_2 and CO_2 is formed instead of Syngas

Very low CO content

$$(C_6H_{12}O_6) + 6\,H_2O \rightarrow 6\,CO_2 + 12\,H_2$$

+ CH_4

- Fast hydrolysis of Cellulose $\rightarrow$ Homogenous reaction

Hydrothermal biomass conversion

Relative low temperature

-> highly kinetically driven reaction system

Influence of salts

Influence of proteins / amino acids

Influence of Lignin / phenols

Influence of the reactor type

Hydrothermal biomass conversion

Temperature Increase

200 °C
300 °C

Critical Temp.: 374 °C

400 °C

600 °C

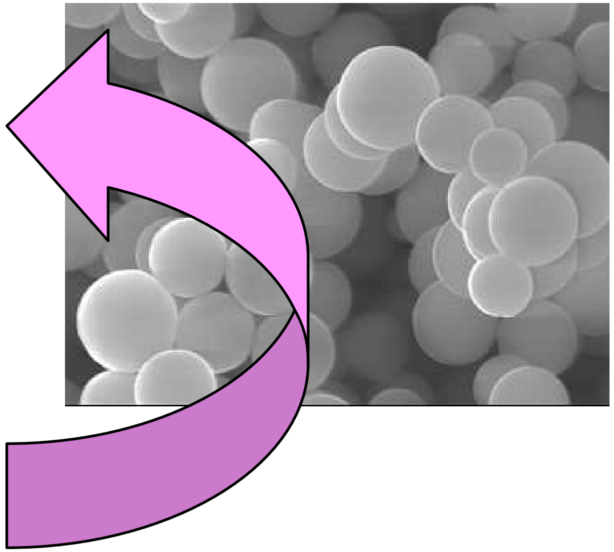
Biomass

"Artificial Coal"

„Oil", biocrude

Gases:

CO, CO_2, CH_4, H_2



Alkali salts catalysis of the water-gas shift reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Formation of active hydrogen

D. C. Elliott, L. J. Sealock, Ind. Eng. Chem. Prod. Res. Develop. 22, 1983, 426-431

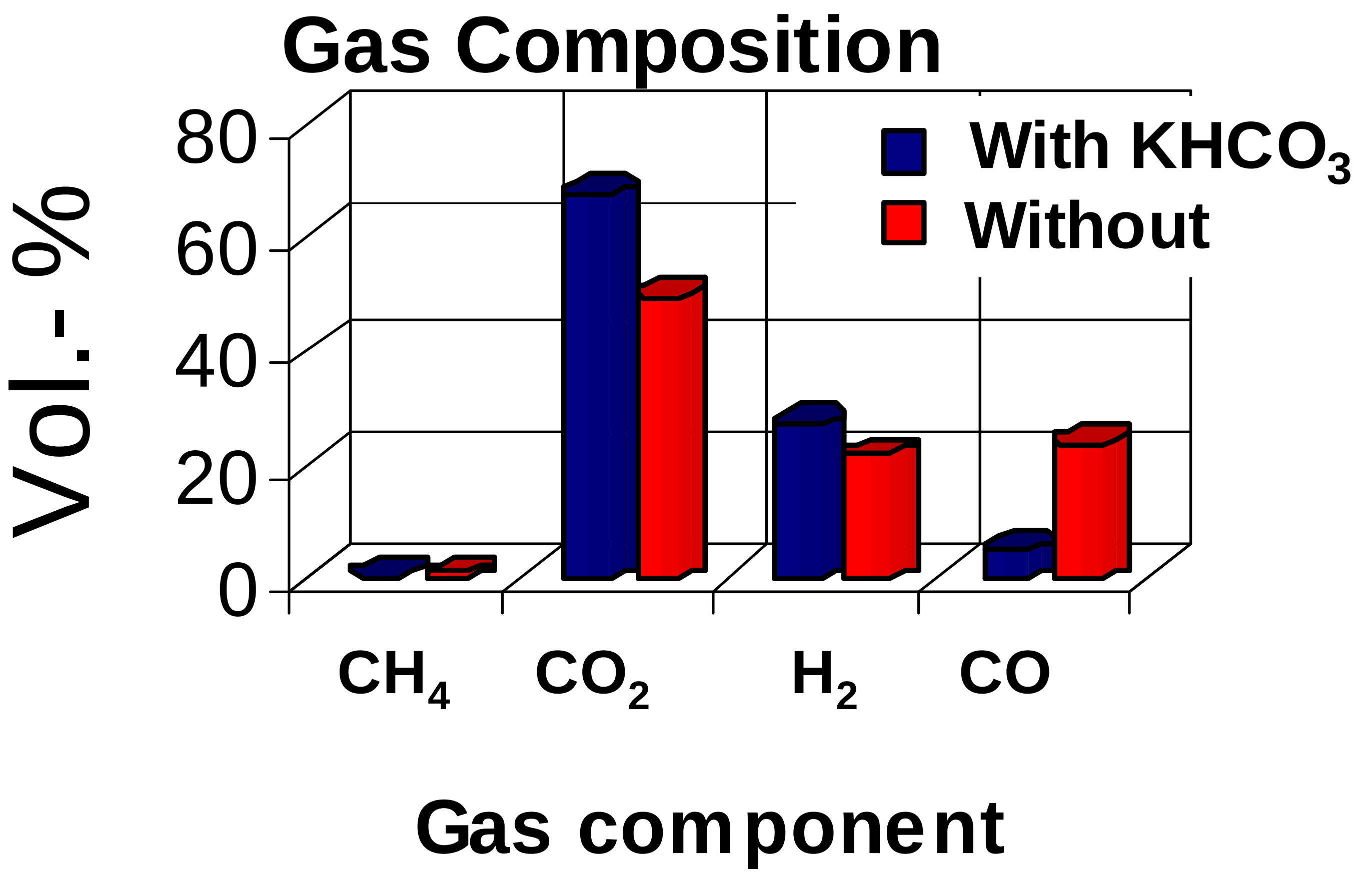
Influence of salts on gas compositon:

Glucose

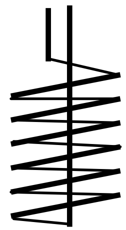
400 °C ↓

Gases,

..

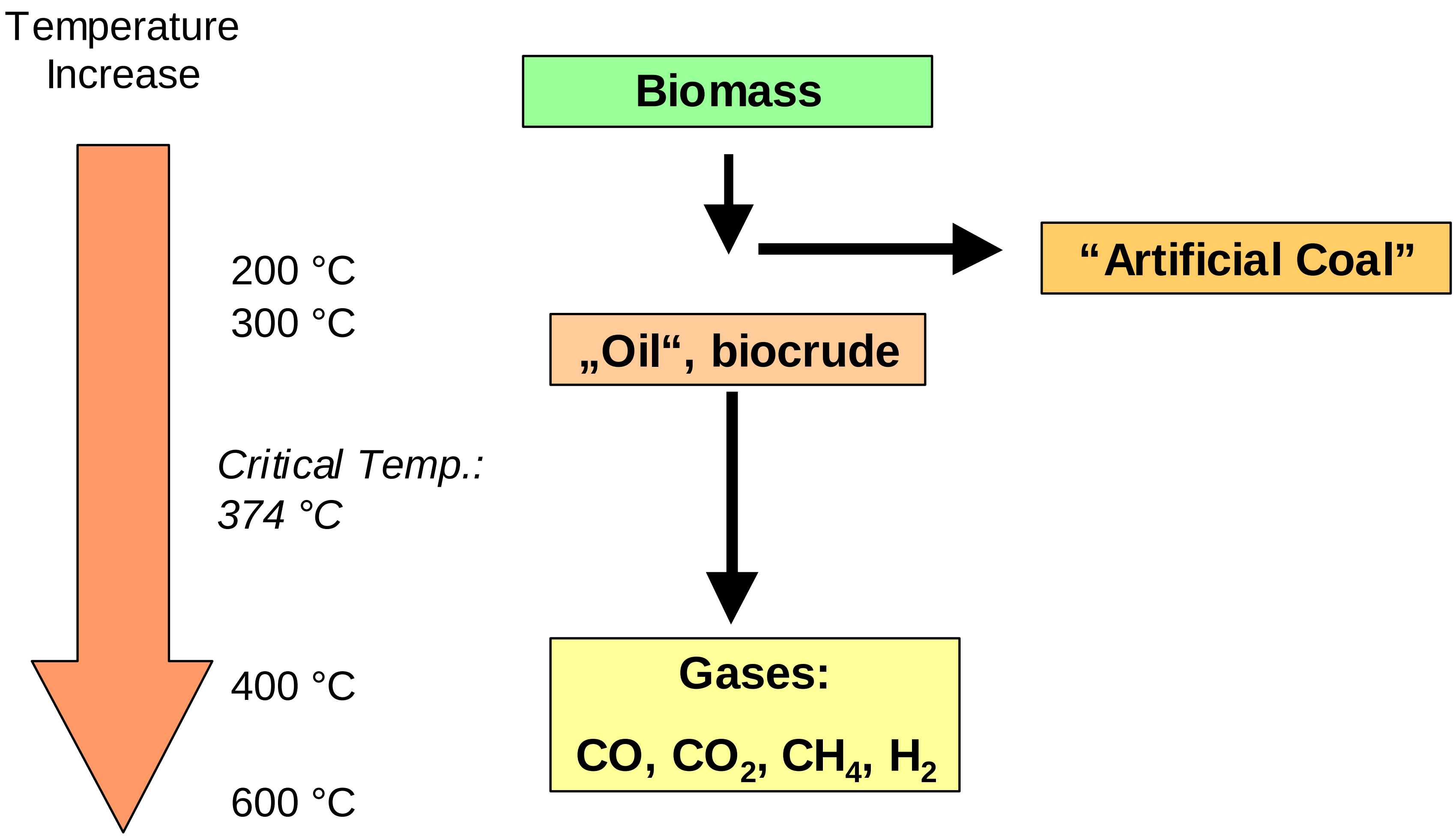


1,5 % (g/g) Glucose; 0,2 % (g/g) $KHCO_3$



A. Sınağ, A. Kruse, V. Schwarzkopf, *CIT 75*, **2003**, 1351-1355.

Hydrothermal biomass conversion



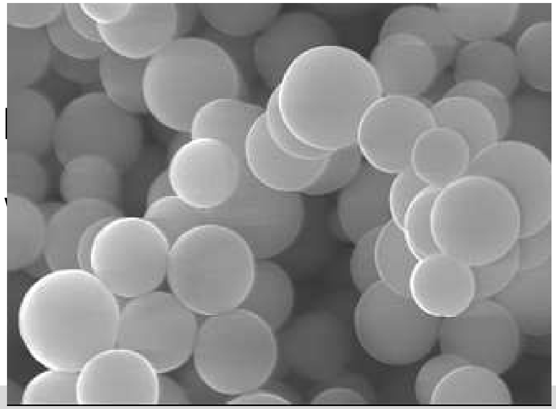
Influence of „active hydrogen“ on the formation of HMF

Glucose

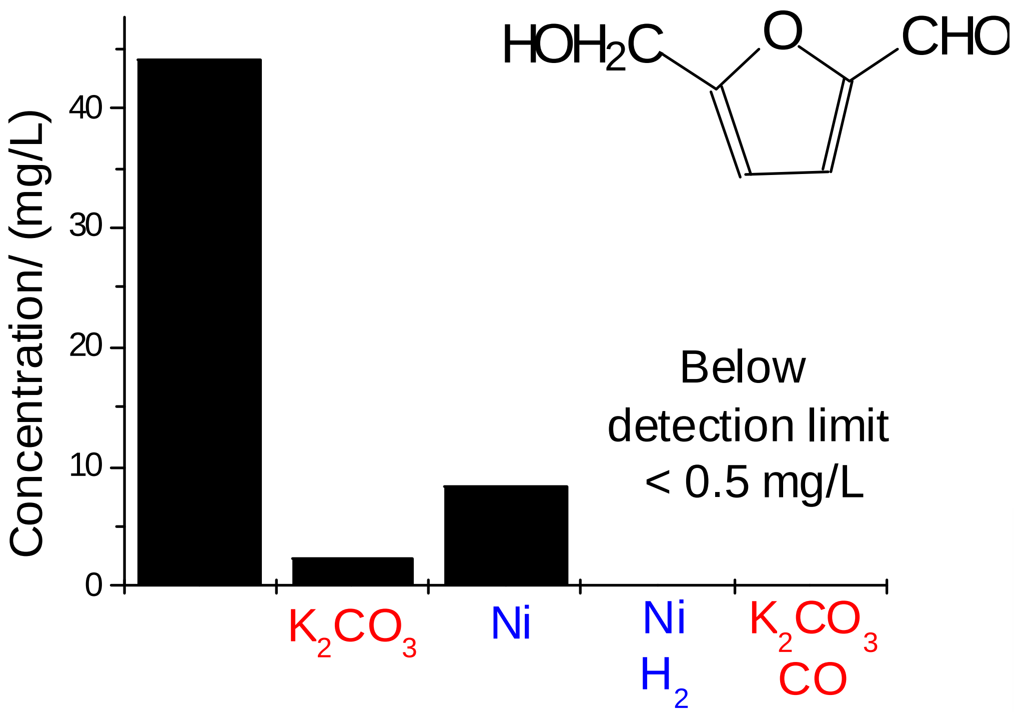
500 °C
32 MPa

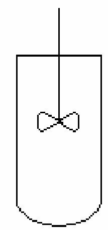
Furfurals,
..

1
5



Hydroxymethylfurfural





Influence on the formation of phenols

Glucose

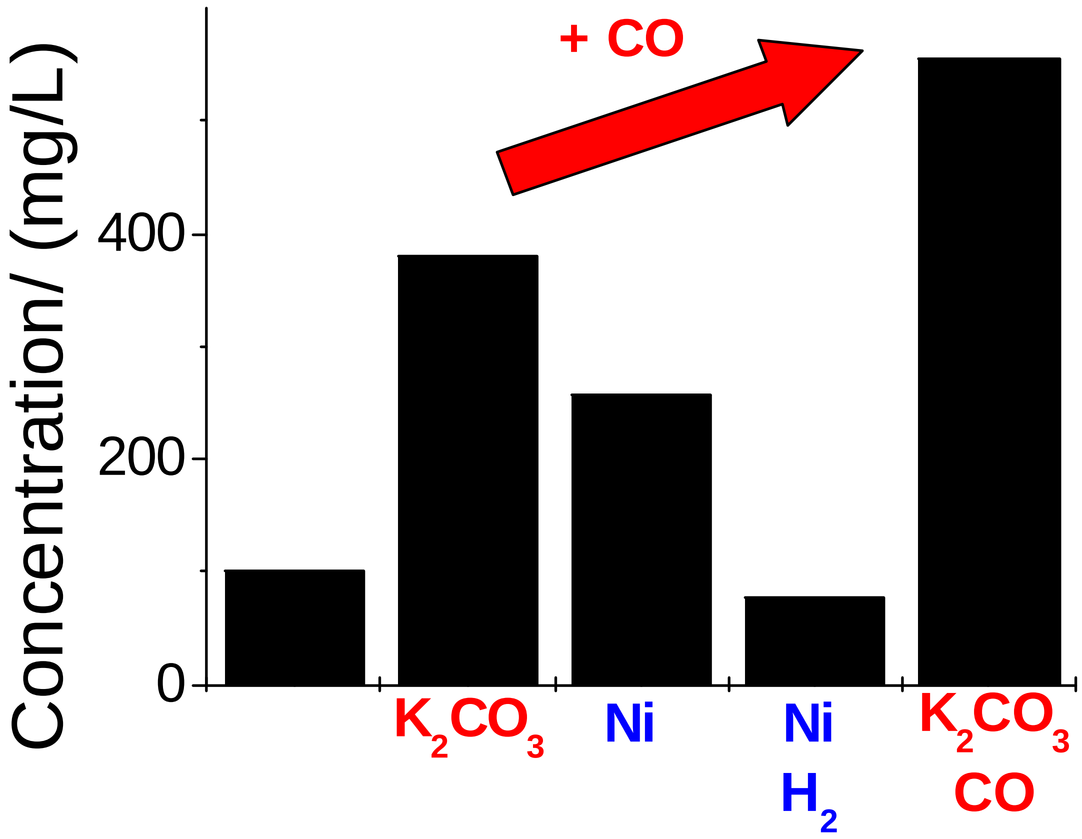
500 °C
32 MPa

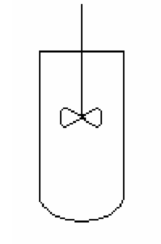
Phenols.

3 K/min heating rate

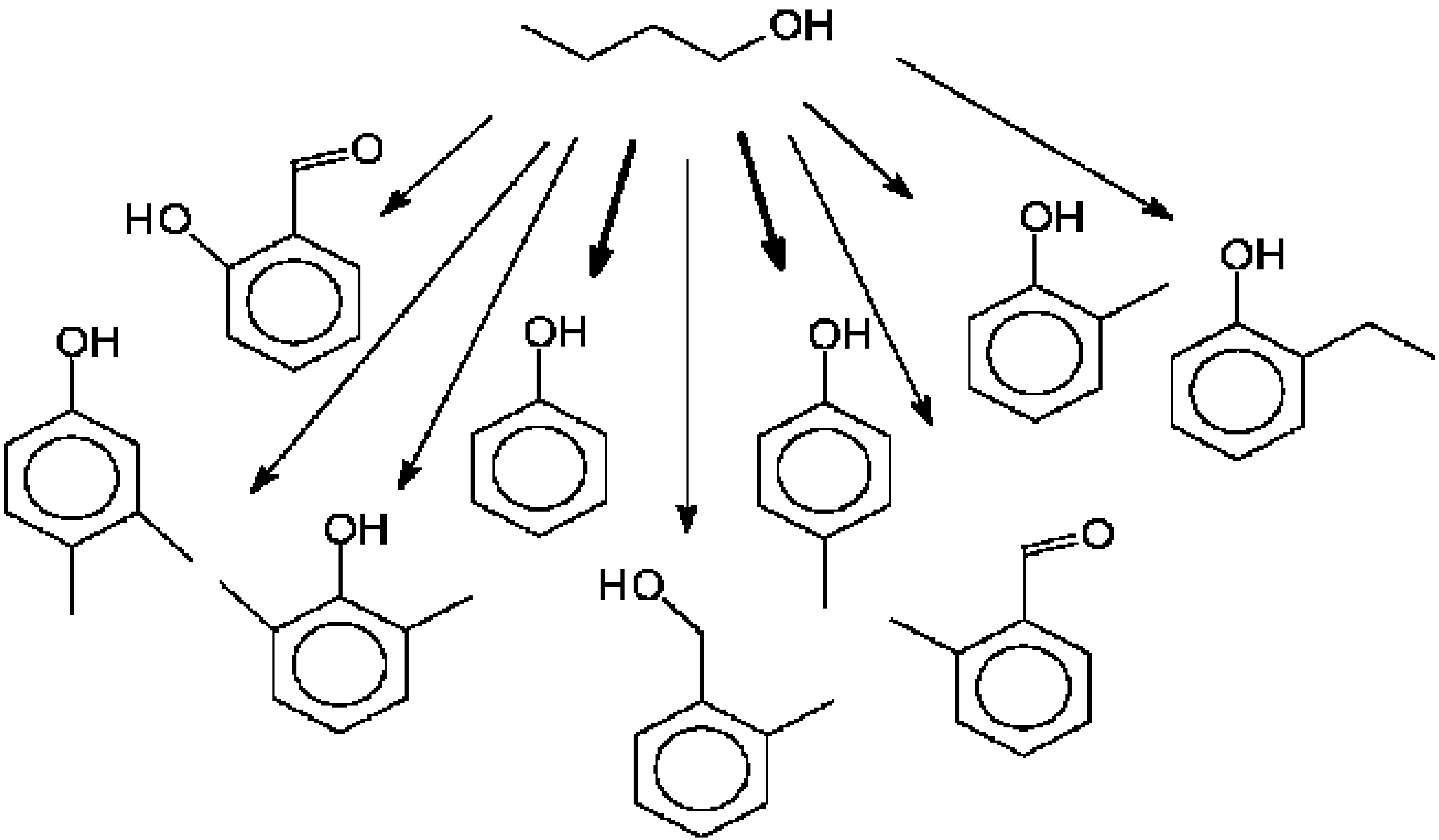
5 wt.% Glucose

Phenols





Phenols formation



A. Kruse, P. Bernolle, N. Dahmen, E. Dinjus, and P. Maniam, Hydrothermal gasification of biomass: consecutive reactions to long-living intermediates, Energy & Environmental Science, 3 (2010) 136-143.

Conclusion I

- The catalysis of the water-gas shift reaction and the formation of „active hydrogen“ has an impact on hydrothermal biomass gasification.
- The formation of Hydroxymethylfurfural, a coke precursor, is depressed by active hydrogen.
- No positive effect on phenols formation!

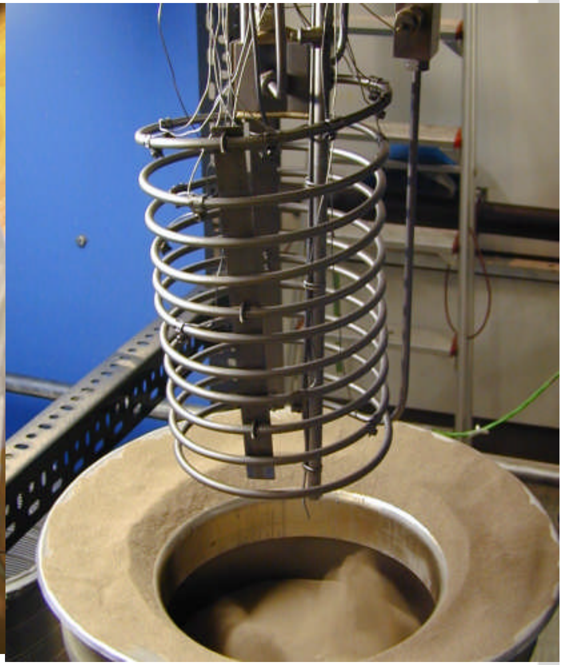
Different reactor types:

Tumbling batch reactor

500 °C, 50 MPa, 1 L

Tubular reactor

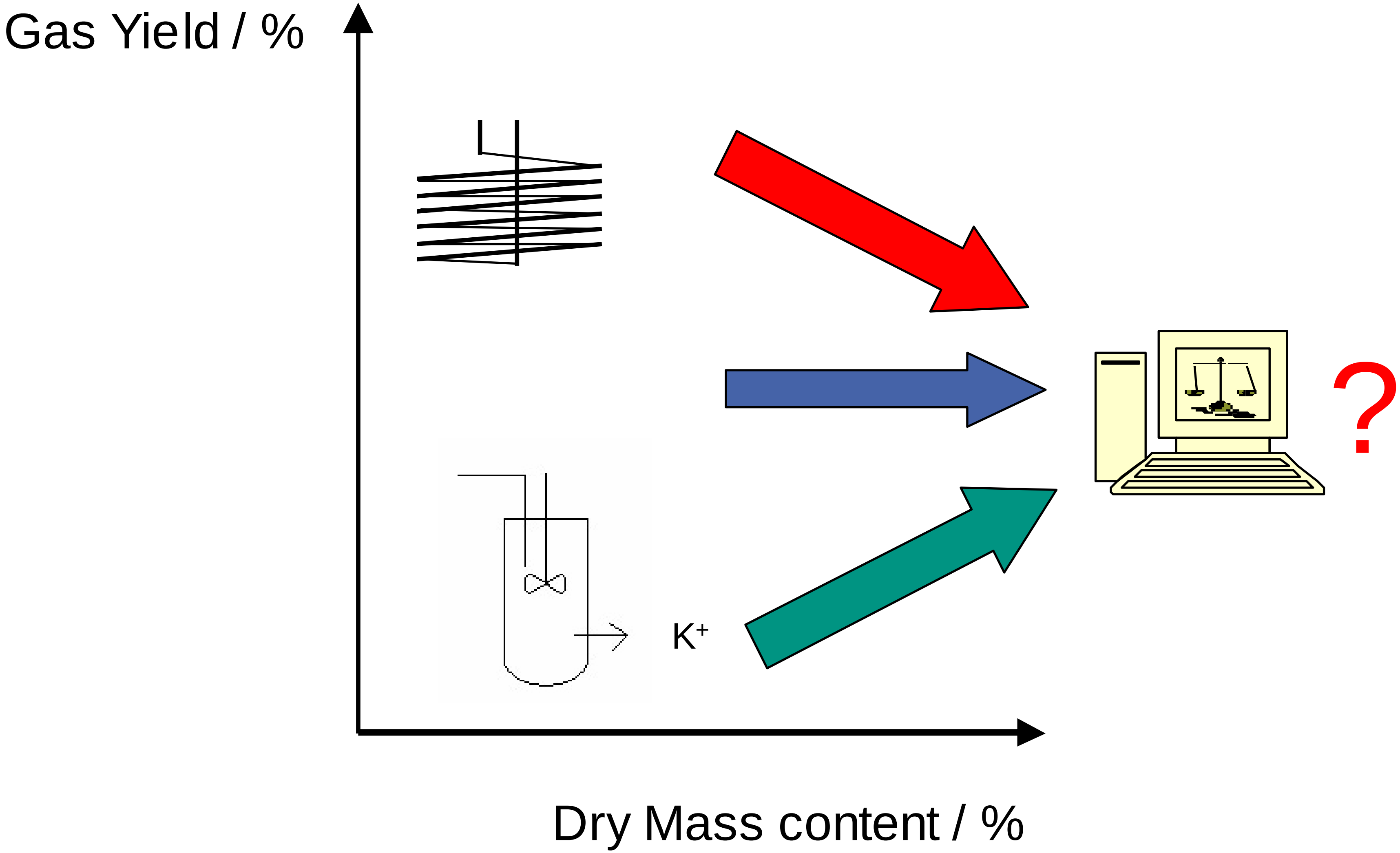
600 °C, 30 MPa, 20 mL, 6 m long.



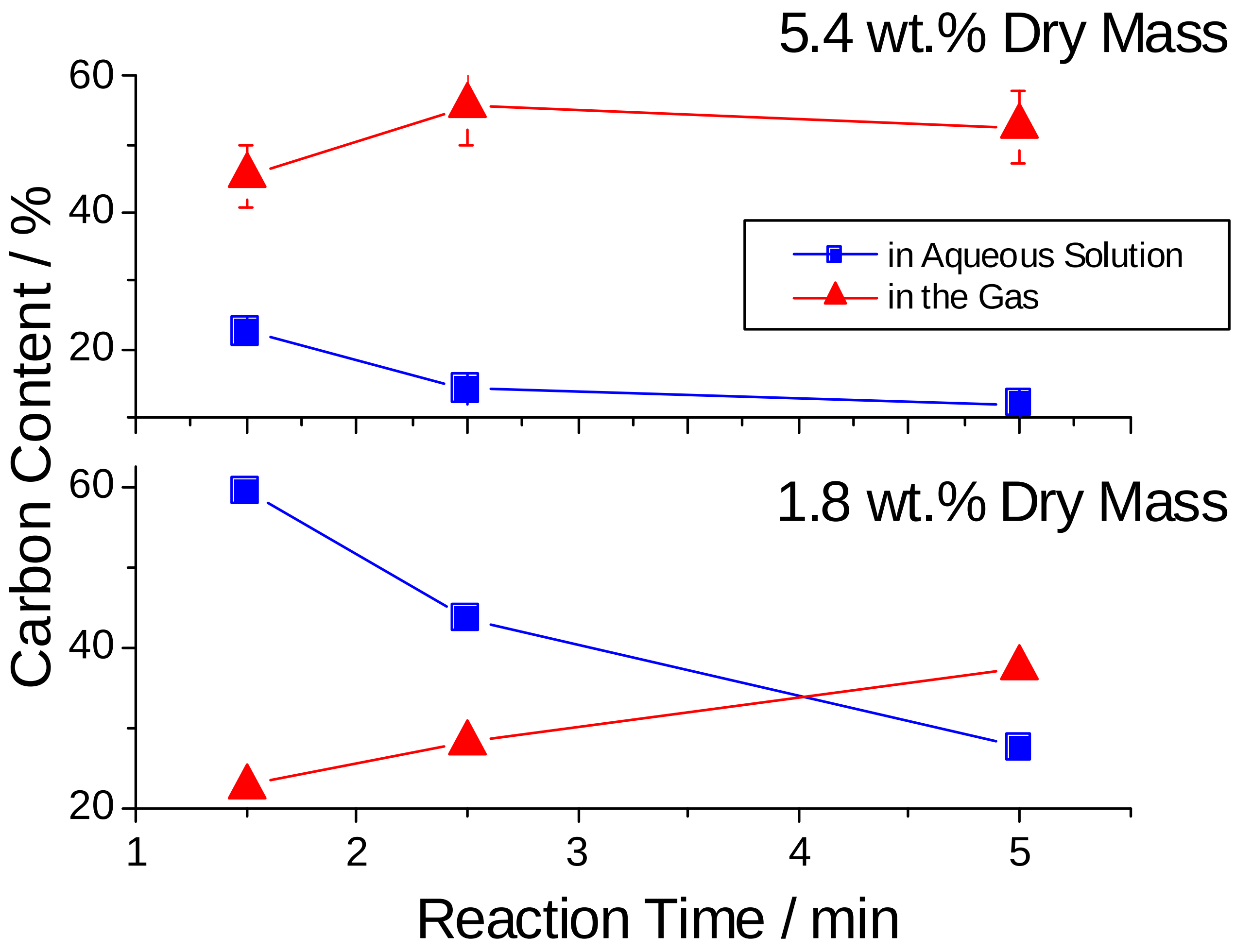
Continuous stirred tank reactor (CSTR)

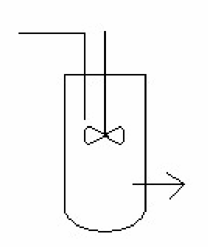
600 °C, 100 MPa, 190 mL

Relative gas yield dependence on dry mass



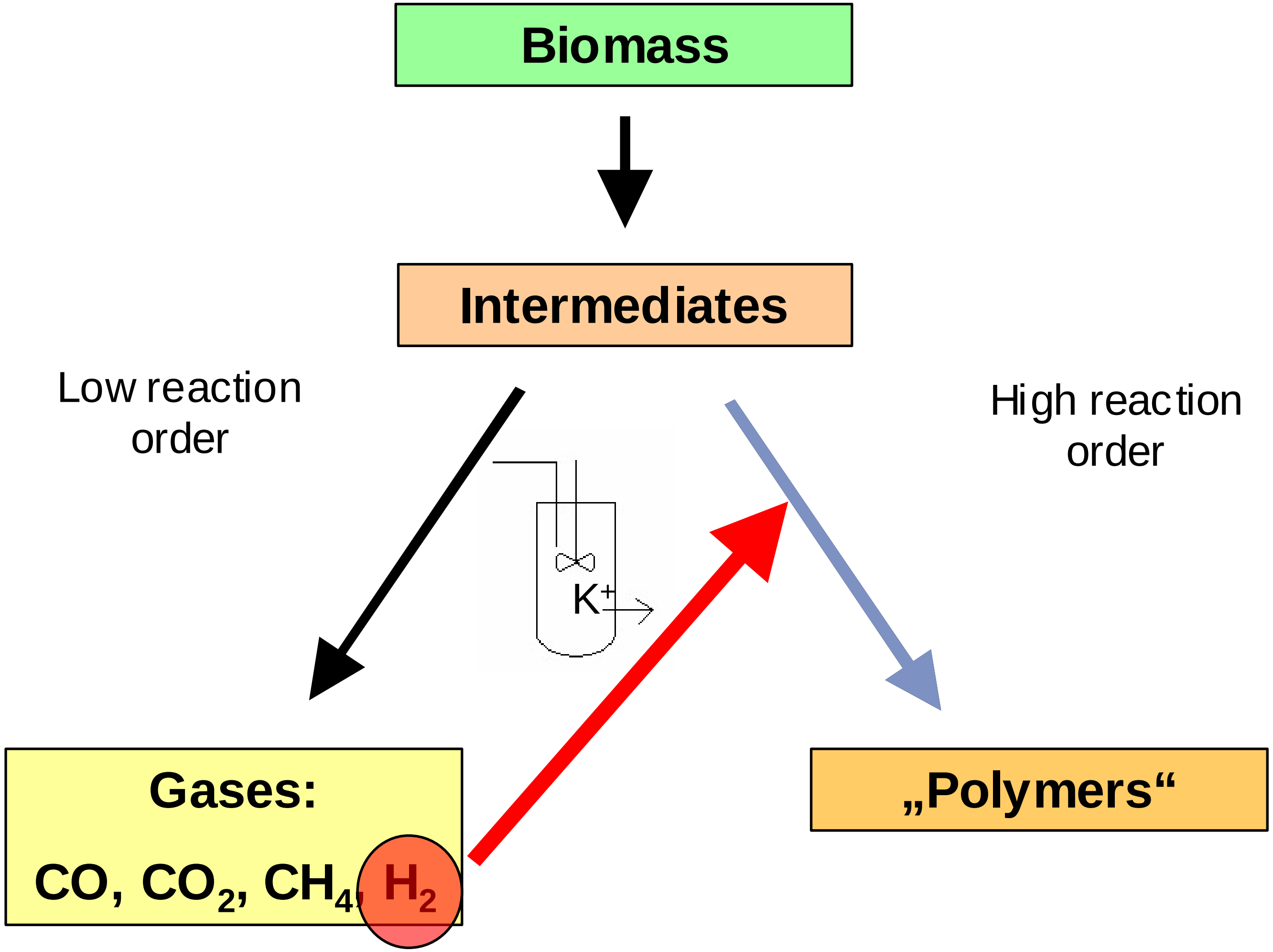
Carbon Content in the Gas and Liquid





A. Kruse and M. Faquir, Hydrothermal Biomass Gasification - Effects of Salts, Backmixing and Their Interaction, Chemical Engineering & Technology, 30 (2007) 749-754.

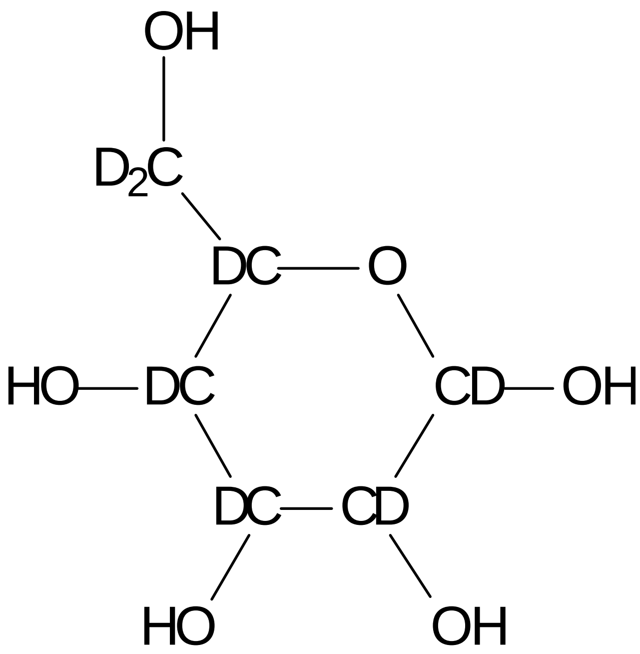
Possible explanation: Simple reaction model



Experiments with deuterated glucose in normal water:

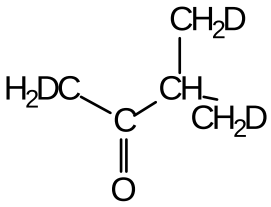
Tumbling batch reactor

500 °C, 50 MPa, 1 L



H_2O

Deuterated products:



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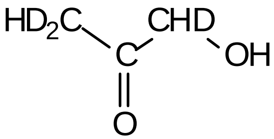

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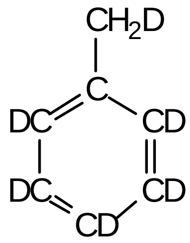

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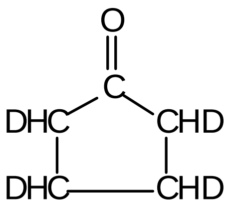

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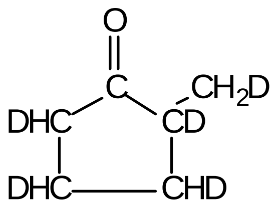

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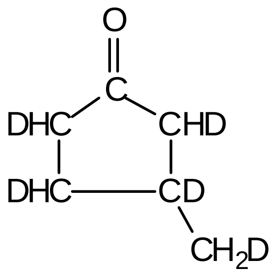

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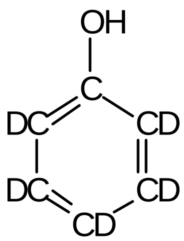

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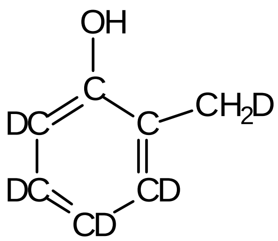

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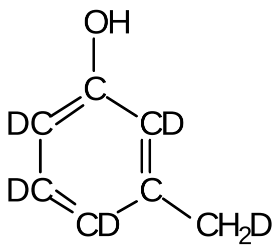
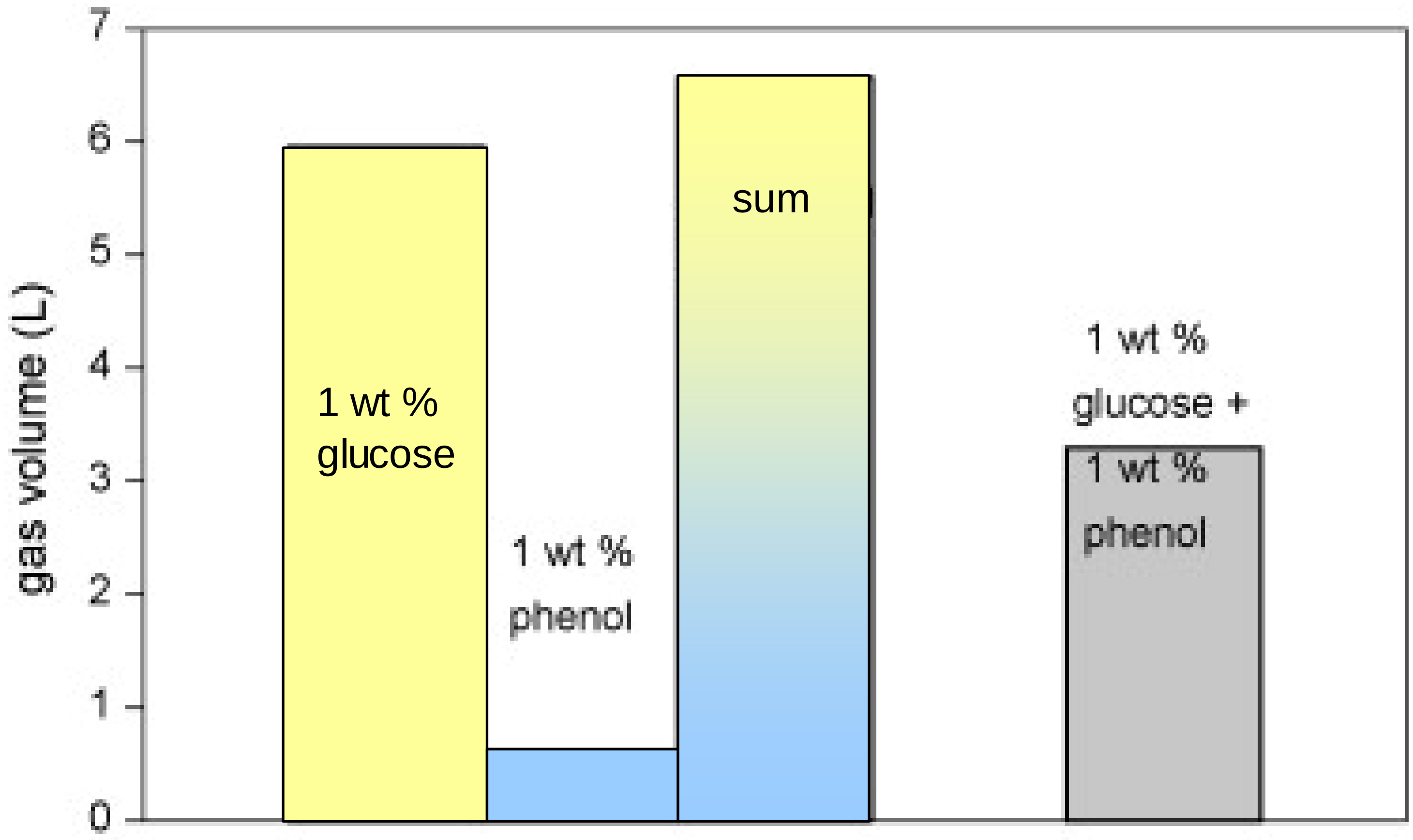
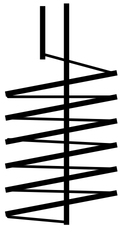


(9)

Gasification of Glucose/Phenol mixtures

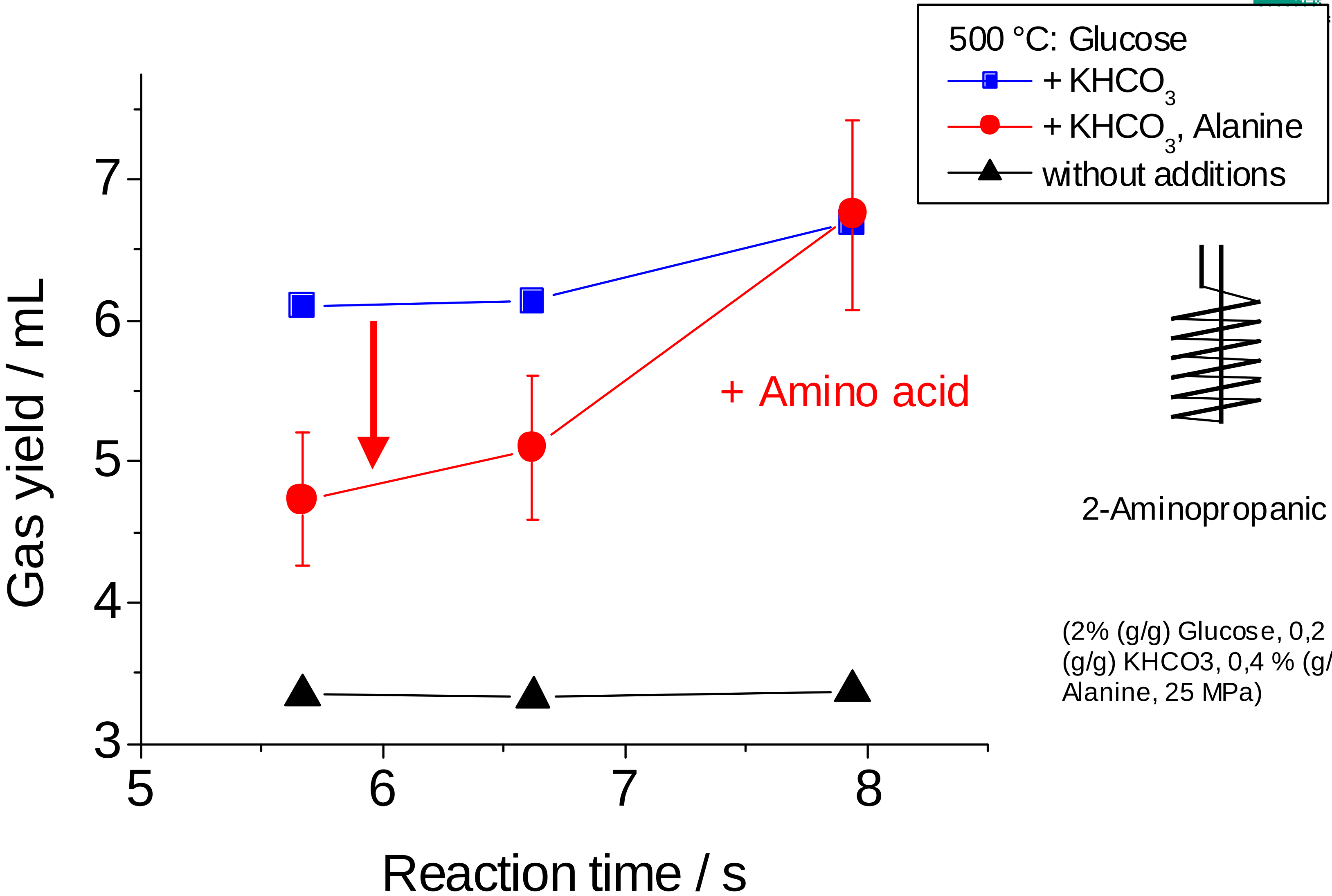
p = 25 MPa,
T = 500 °C





E. Weiss-Hortala, A. Kruse, C. Ceccarelli, and R. Barna, Influence of phenol on glucose degradation during supercritical water gasification, The Journal of Supercritical Fluids, 53 (2010) 42-47.

Influence of Alanine:



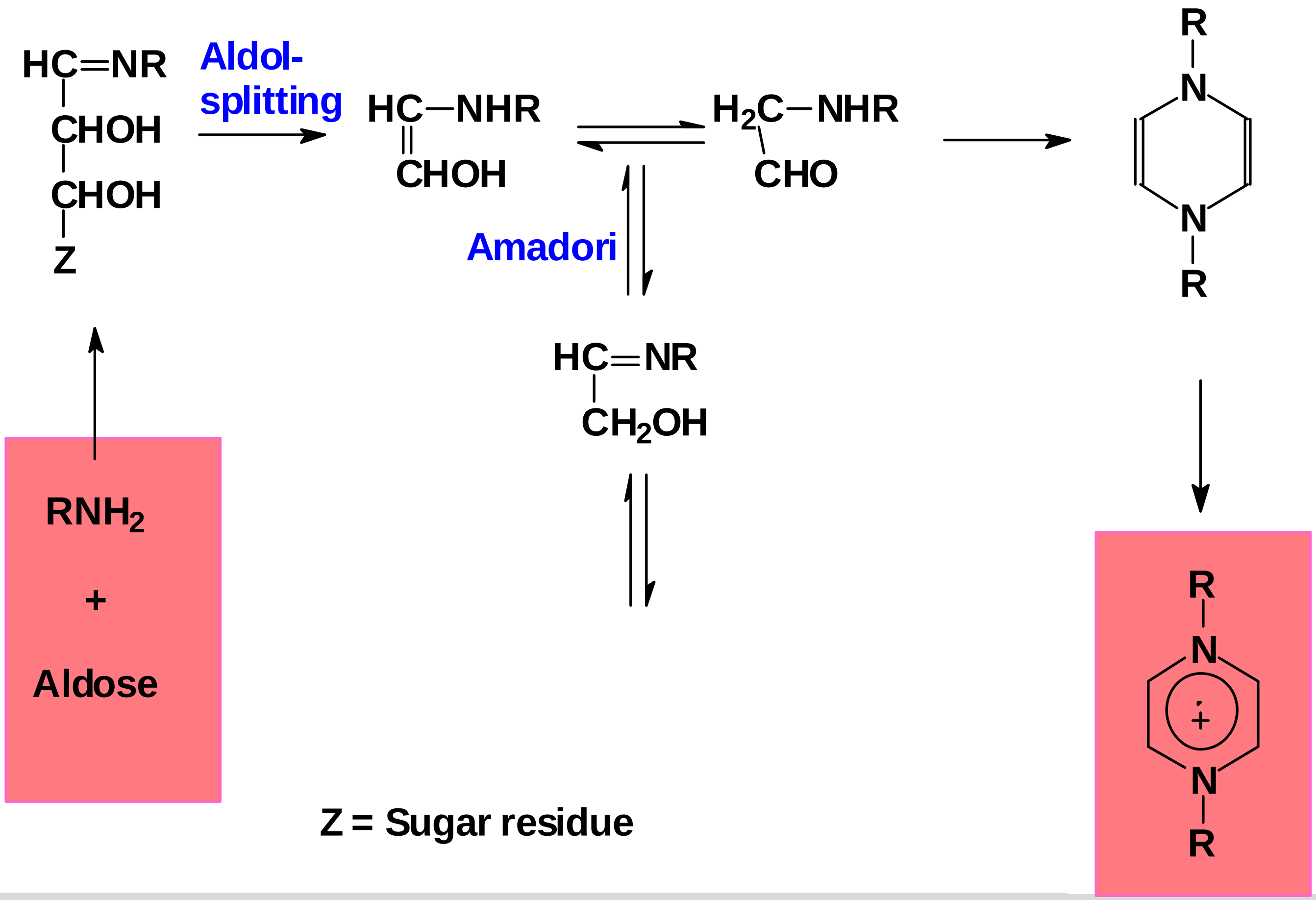
2-Aminopropanic acid

(2% (g/g) Glucose, 0,2 % (g/g) $KHCO_3$, 0,4 % (g/g) Alanine, 25 MPa)

A. Kruse, P. Maniam, F. Spieler, Ind. Eng. Chem. Res *46,* 2007, 87*.*

Formation of free-radical scavengers

Maillard-Reaction



Z = Sugar residue

G. P. Rizzi, Free radicals in the Maillard reaction. *Food Rev. Int. 19*, 375. **2003.**

Summary and Conclusion

Intermediates reactions

Positive Influence:

- Salts
- Continuous stirred tank reactor / Back mixing
- CO addition

Negative Influence:

- Proteins
- Lignin / Phenols
- Slow heating up

Understanding leads to optimization.

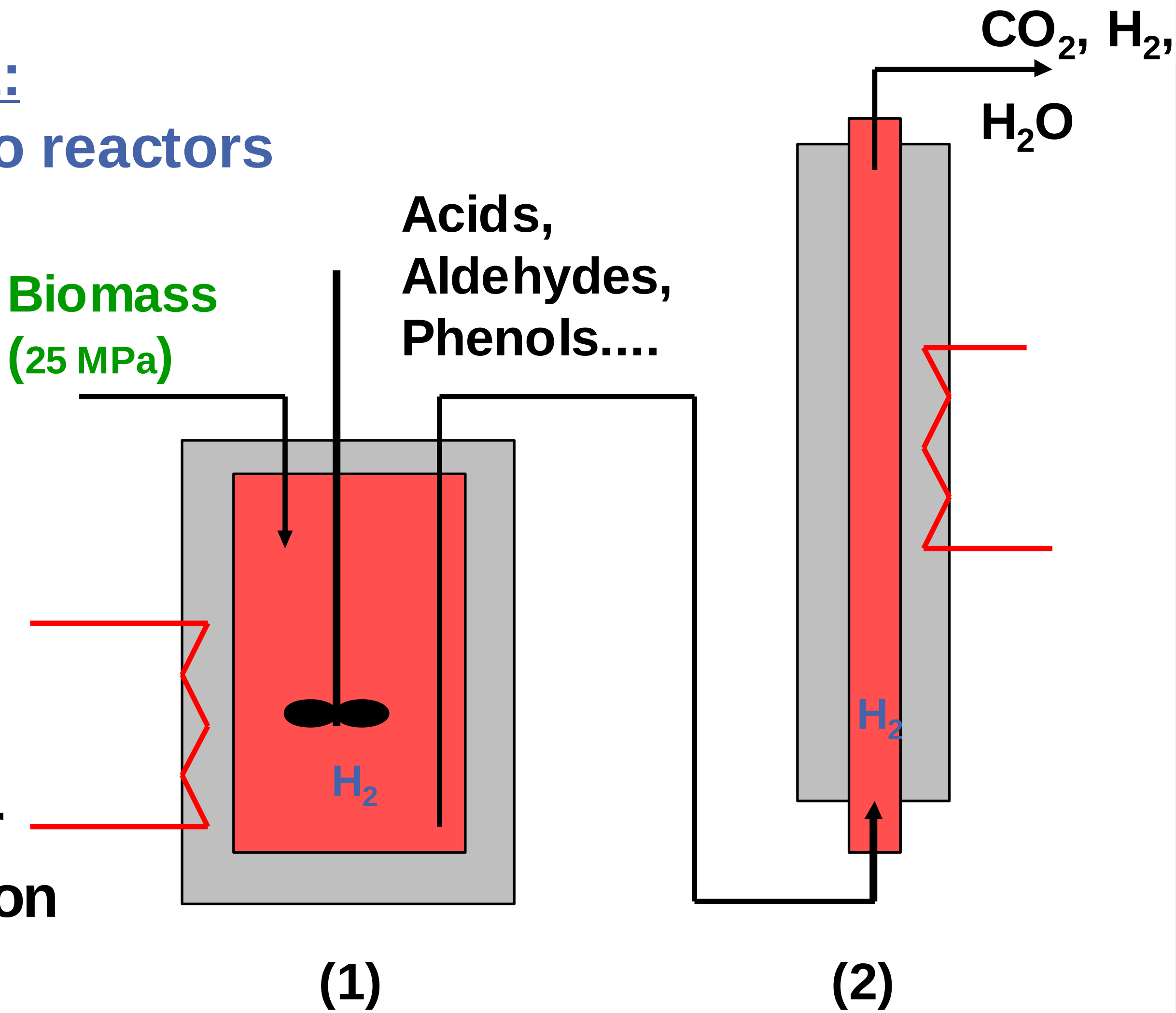
Consequence:

In a lab-scale plant:
Combination of two reactors

1. CSTR:

- **Fast heating up**
- **Hydrogenation conditions**
- **Less phenols**

2. Tubular reactor for „complete“ conversion



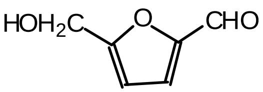
N. Dahmen, E. Dinjus, A. Kruse, DE 10259928 (20.12.02); published 22.6.04.

Conclusion and summary

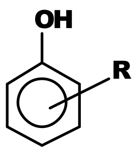
Water as reactant:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

Reaction pathways are influenced:



H_2 / CO



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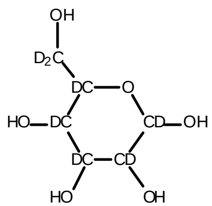
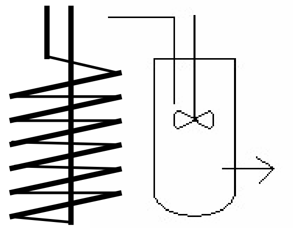
Experiments with deuterated glucose:



Reactor type influence:



Thank you very much!