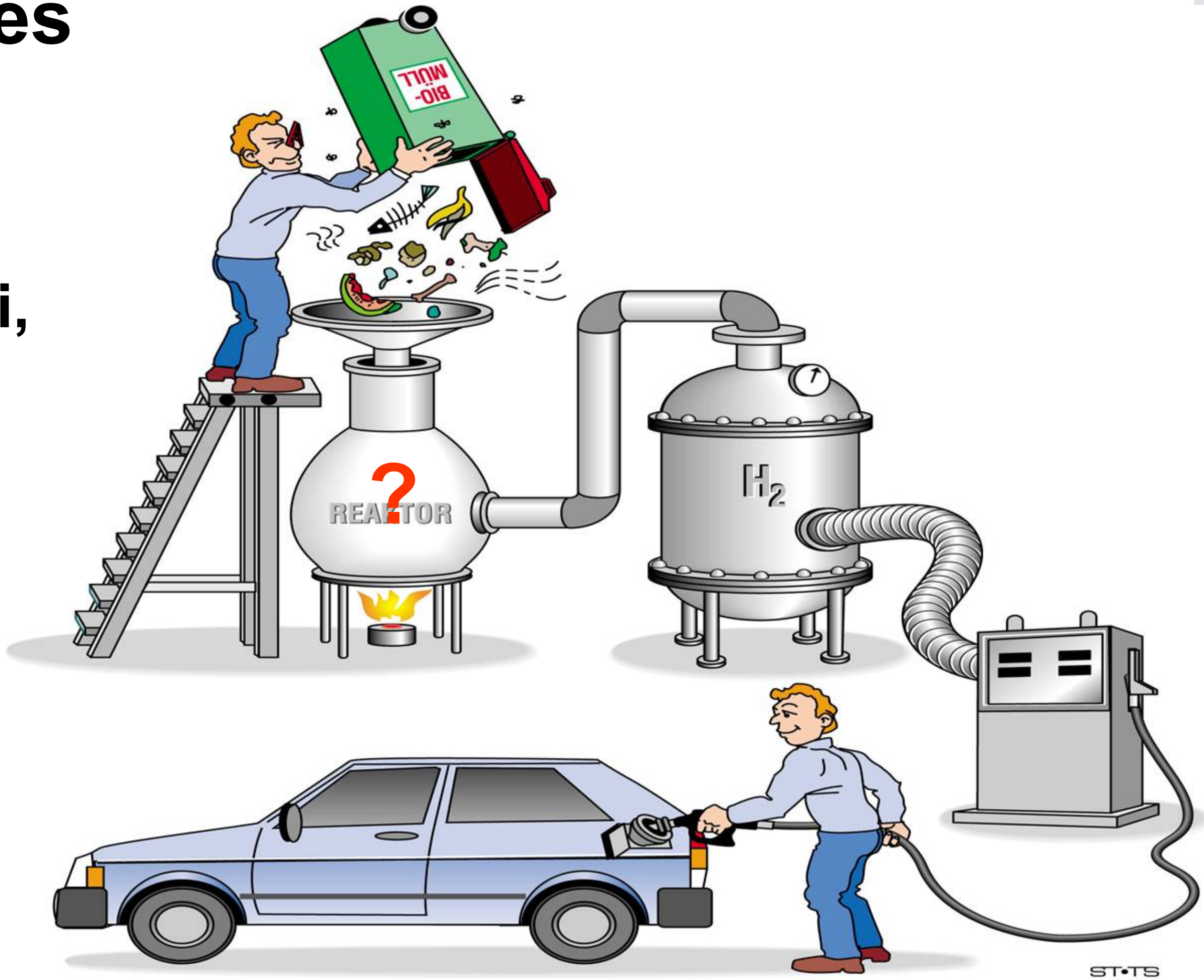
Supercritcal water gasification of biomass residues



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Use of Biomass – Why?

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

CO_2-neutral; United Nations Kyoto Protocol for the reduction CO_2-emissions.

Po

2/3 of the unused biomass in Germany is wet (> 50 %, often 80 – 95 % water content)

ption

*FZK; **Climate Change 1995, Watson et al

Outline: Process development

- What is supercritical water gasification of biomass?
- Advantages
- Basic investigations
  - Influence of
    - - salts,
    - - proteins.
- Bench scale plant
- Summary and conclusion
- Main challenges

The process

Wet (green) biomass is heated up to
≥ 600 °C and ≥ 30 MPa.

Because of thermodynamic reasons

No coke
at optimized conditions

Nearly complete gasification to H_2, CO_2
and lower amounts of CH_4

Advanges

- No drying of „wet biomass“ necessary
- Very low amounts of tar and (no) coke
- High H_2-yield, low CO content
- H_2 under pressure
- Easy CO_2-separation under pressure
- High space-time-yield
- Inorganic ingredients are not volatile

Role of water

Water is reactant:

- H_2 and CO_2 is formed instead of Syngas

  Very low CO content

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

- Fast hydrolysis of Cellulose → Homogenous reaction

Water is solvent:

Intermediates are dissolved

→ Less polymerization reactions

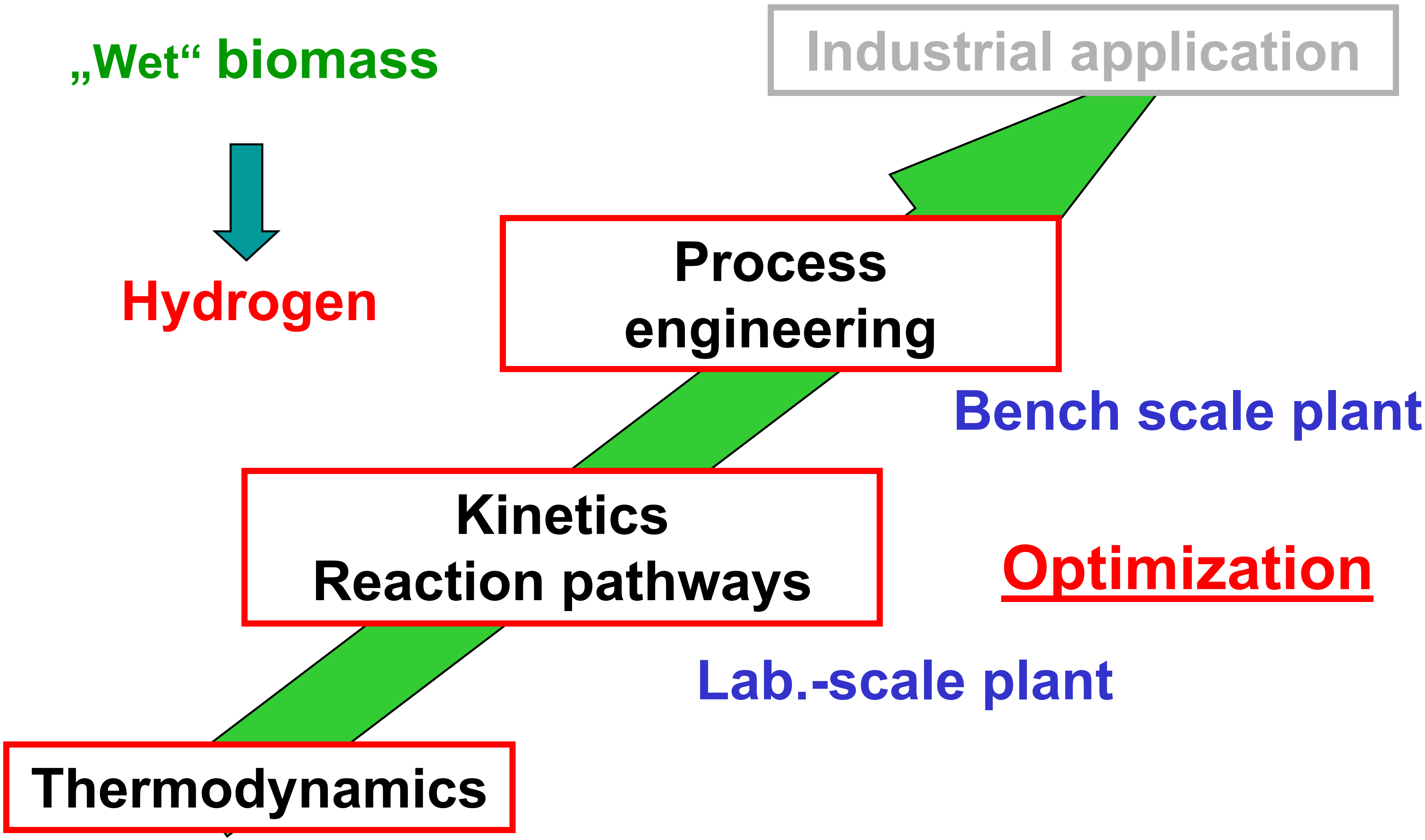
→ Less tar and coke

Disadvantage?

- Heating up of a large amount of water is a disadvantage ?

↕

- Heat exchange is necessary and very efficient (no evaporation in the heat exchanger)


„Wet“ biomass
Hydrogen
Industrial application
Process engineering
Bench scale plant
Kinetics
Reaction pathways
Optimization
Lab.-scale plant
Thermodynamics

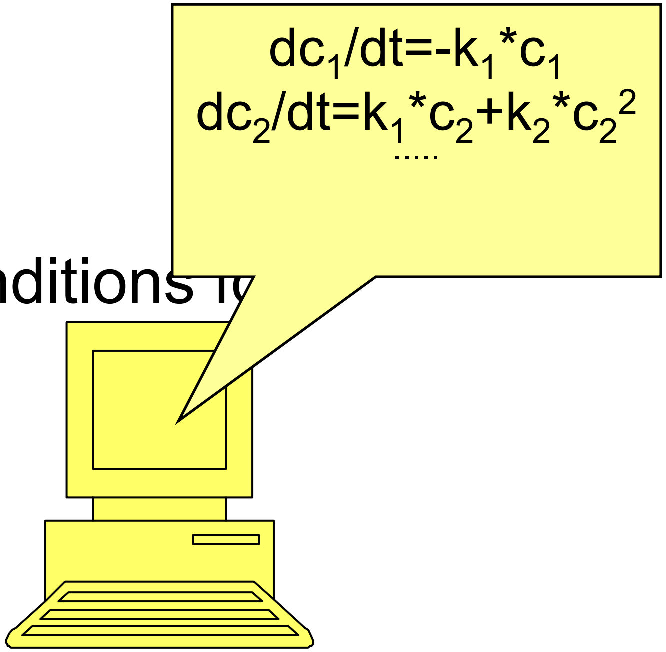
Goals of basic research

Investigation of the influence of

- process parameters (T, p, c, reactor type)
- biomass ingredients (salts, proteins, lignin)

Identification of optimized reaction conditions fo
large variety of biomass feedstock.

Kinetic model of the reaction.



KIT – die Kooperation von
Forschungszentrum Karlsruhe GmbH
und Universität Karlsruhe (TH)

Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

Lab-scale plants

Continuous stirred tank reactor (CSTR)

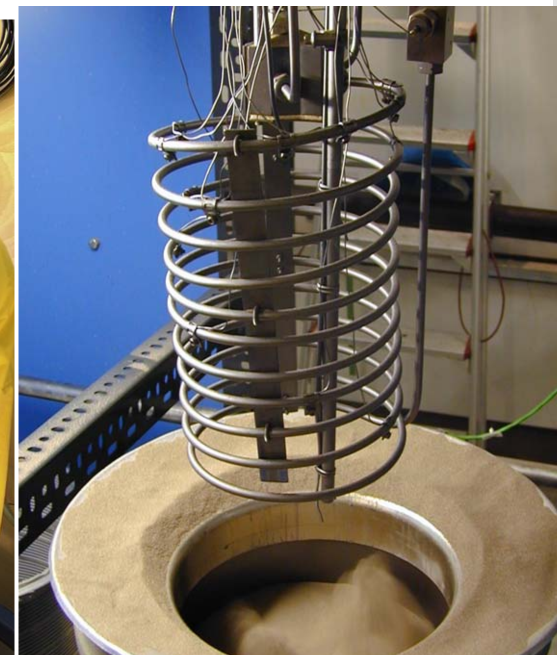
600 °C, 100 MPa, 190 mL

Tumbling batch reactor

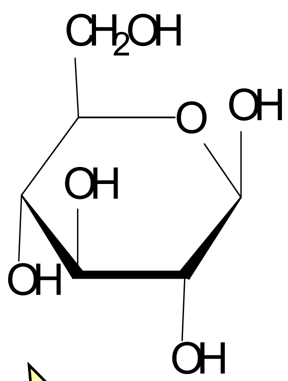
500 °C, 50 MPa, 1 L

Tubular reactor

600 °C, 30 MPa, 20 mL, 6 m long.

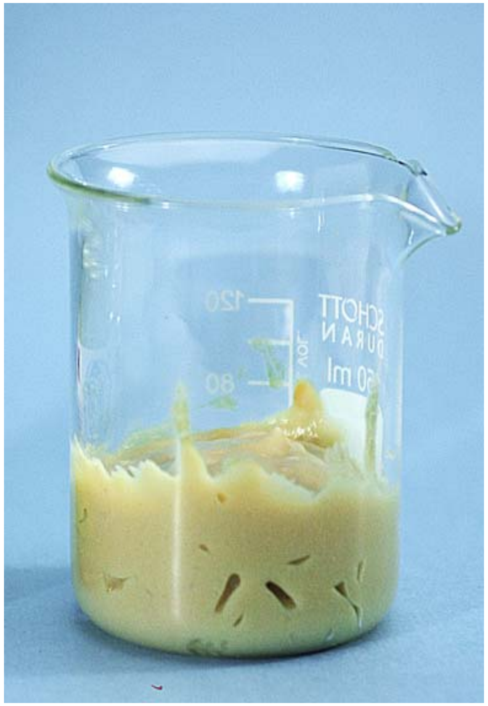


Model Systems



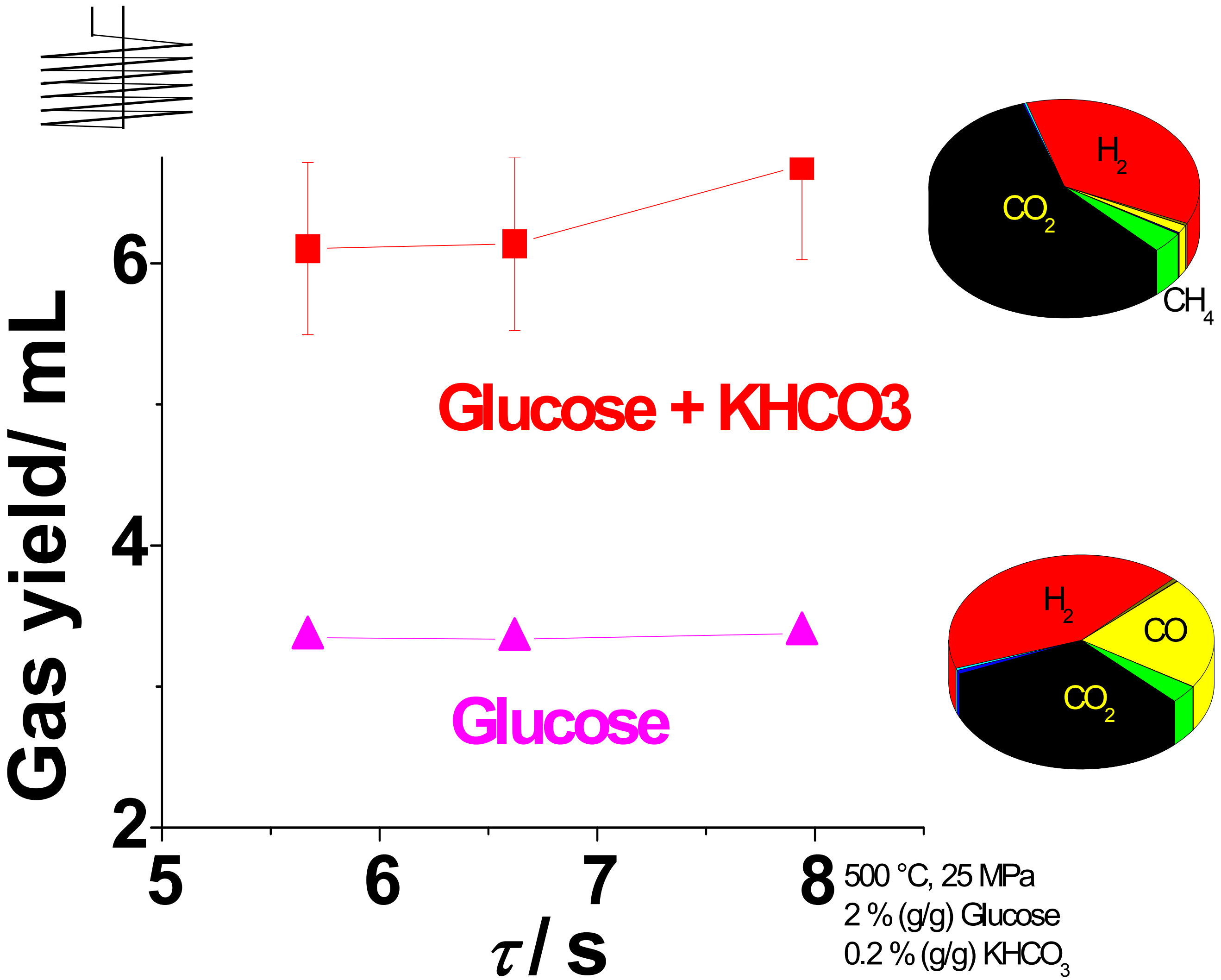
+ Salts
+ Amino acids
....

Phytomass:
carrots, potatoes



Zoomass:
chicken, rice

Influence of Salts



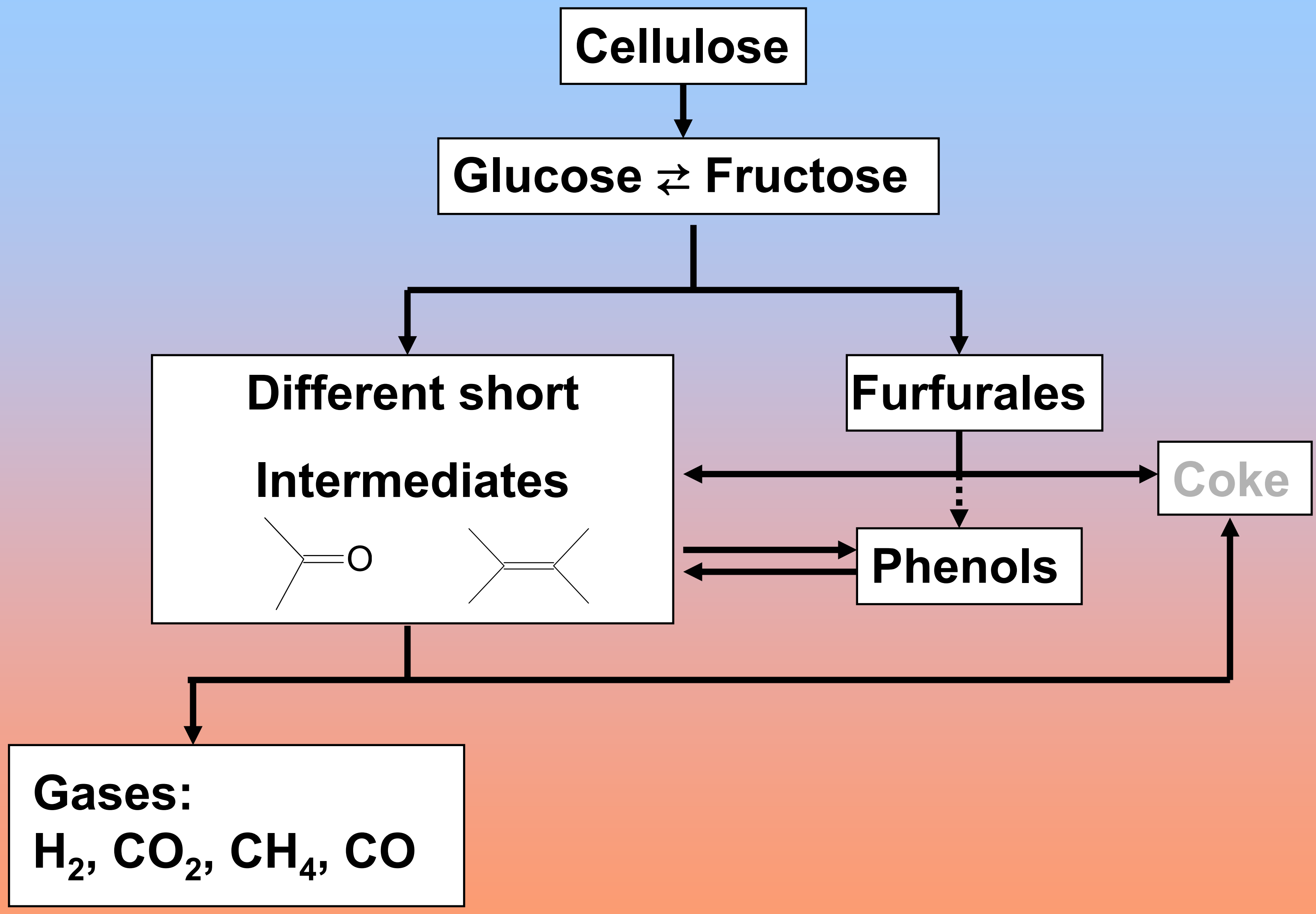
500 °C, 25 MPa
2 % (g/g) Glucose
0.2 % (g/g) $KHCO_3$

Alkali salts catalysis of the water-gas shift reaction

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

Formation of active hydrogen

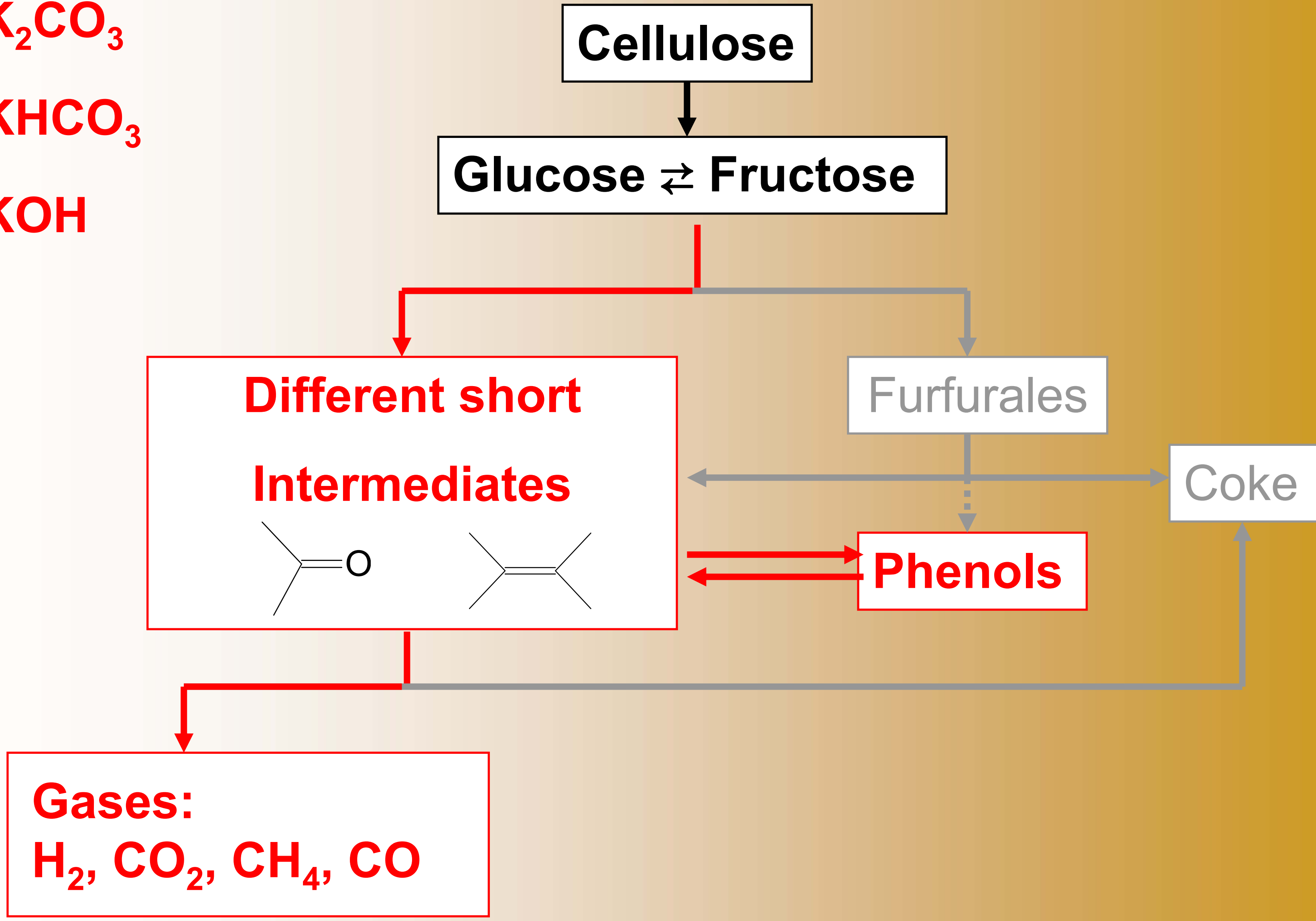
D. C. Elliott, L. J. Sealock, Ind. Eng. Chem. Prod. Res. Develop. 22, 1983, 426-431


Cellulose
Glucose ⇄ Fructose
Different short
Intermediates
O
Furfurales
Coke
Phenols
Gases:
H_2, CO_2, CH_4, CO

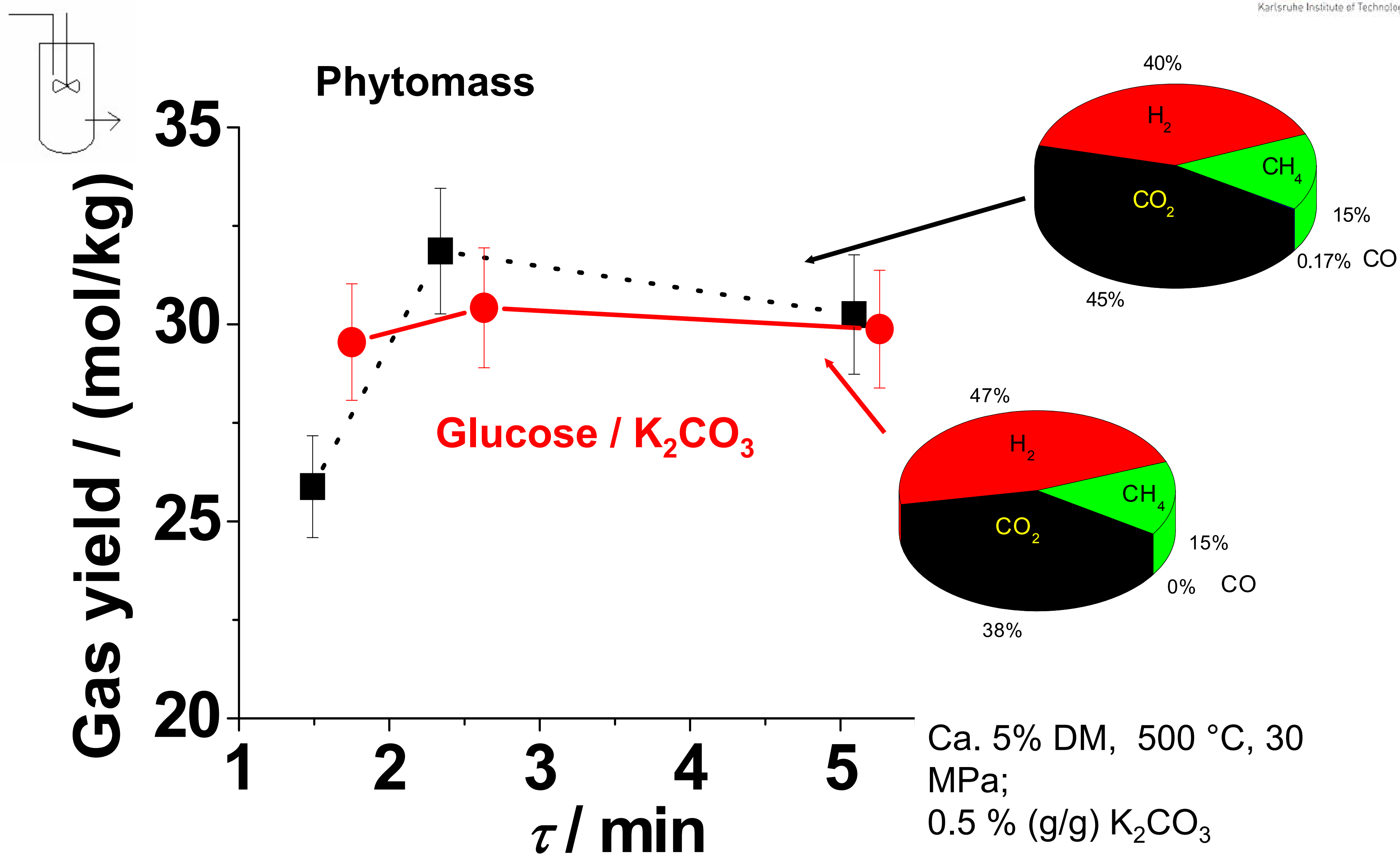
K_2CO_3

$KHCO_3$

KOH



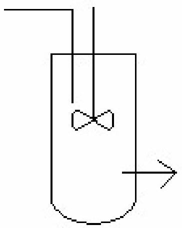
Biomass: Gas yield and gas composition



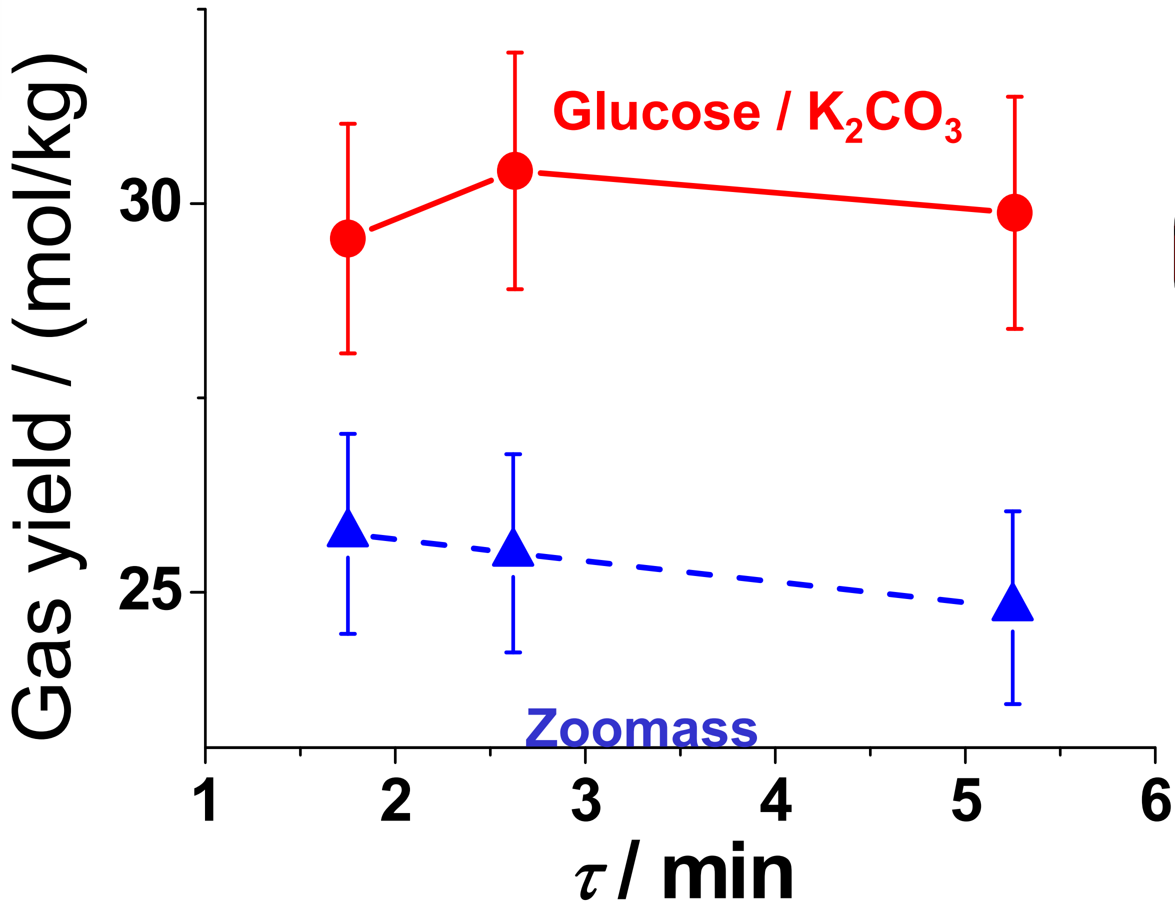
Ca. 5% DM, 500 °C, 30 MPa;
0.5 % (g/g) K_2CO_3

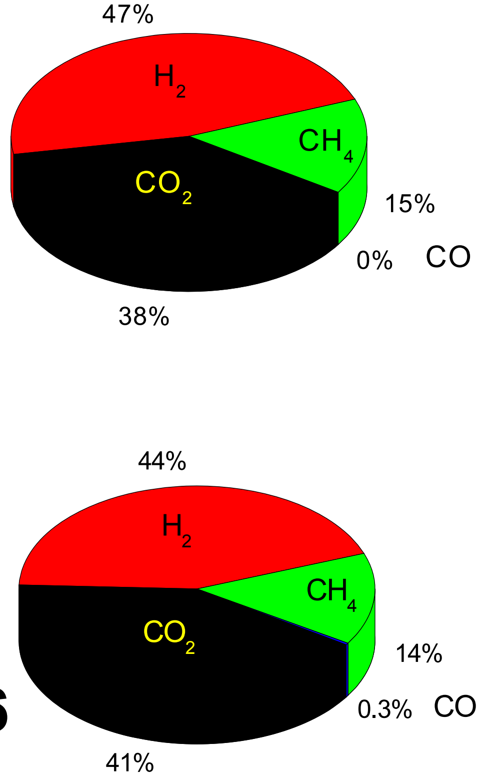
A. Kruse et al., *Ind. Eng. Chem. Res. 44*, **2005**, 3013.

Influence of proteins



Gas yield and gas composition



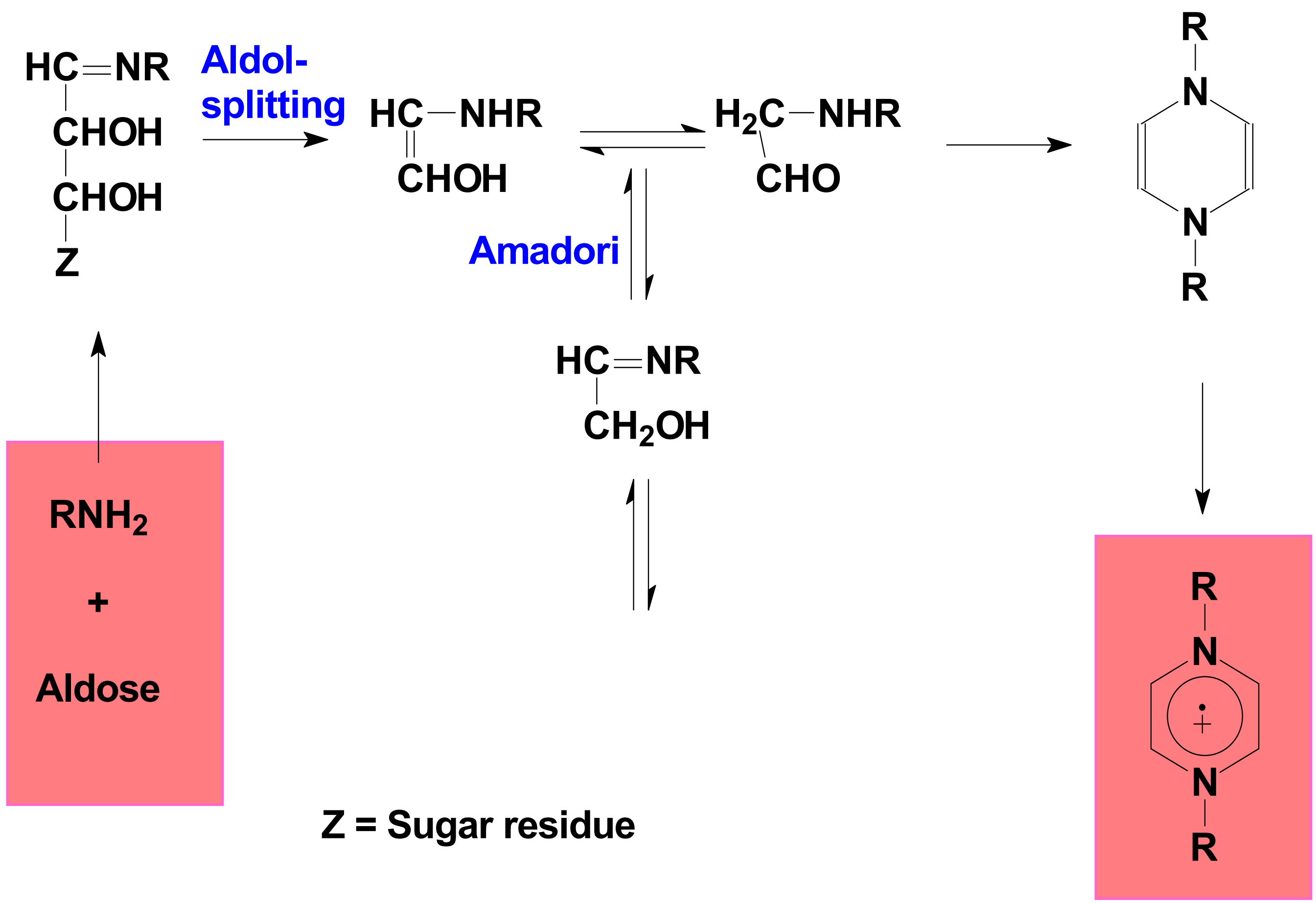


A. Kruse et al., *Ind. Eng. Chem. Res. 44*, **2005**, 3013.

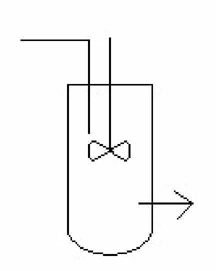
Ca. 5 % DM, 500 °C, 30 MPa;
0,5 % (g/g) K_2CO_3

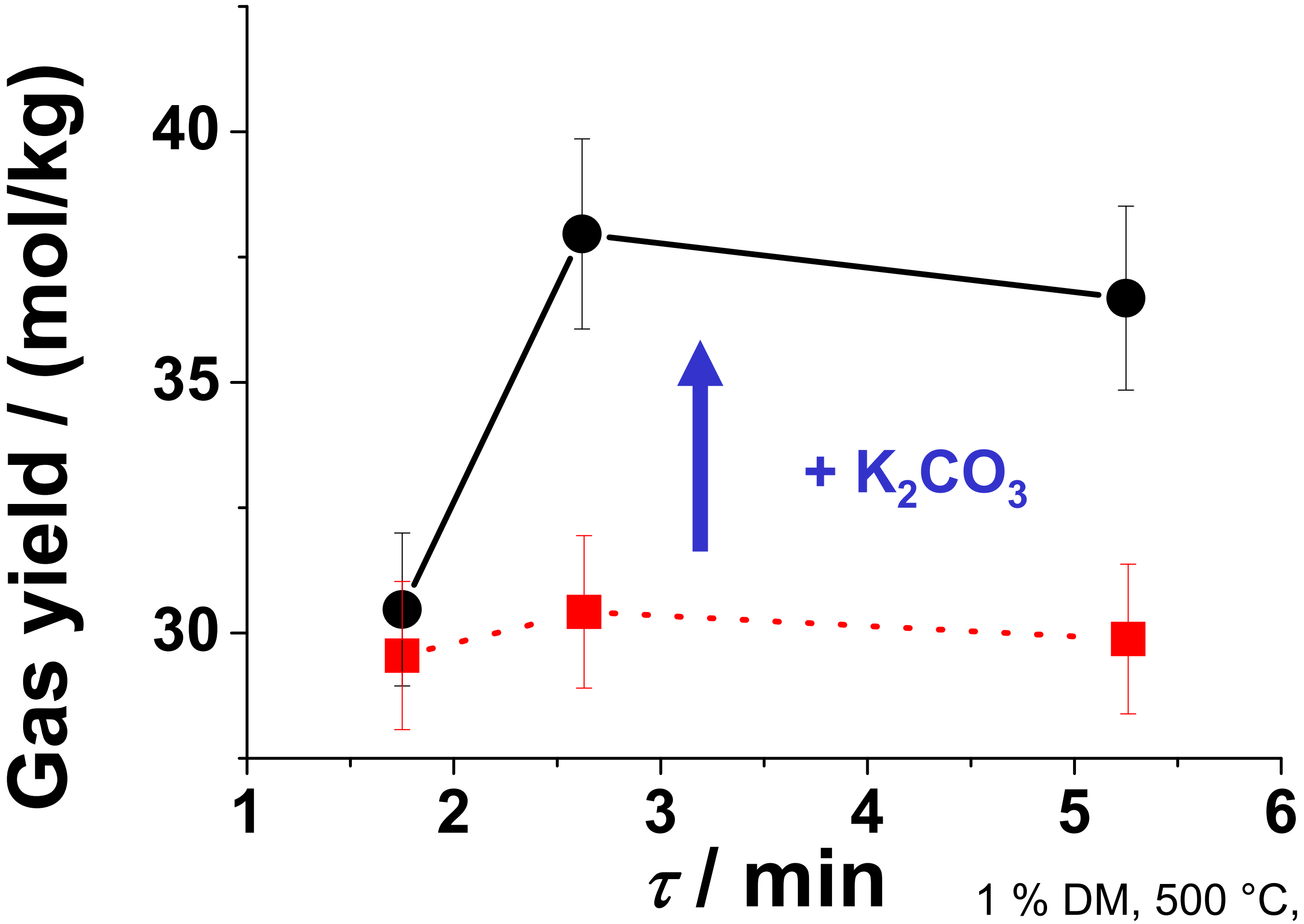
Formation of free-radical scavengers

Maillard-Reaction



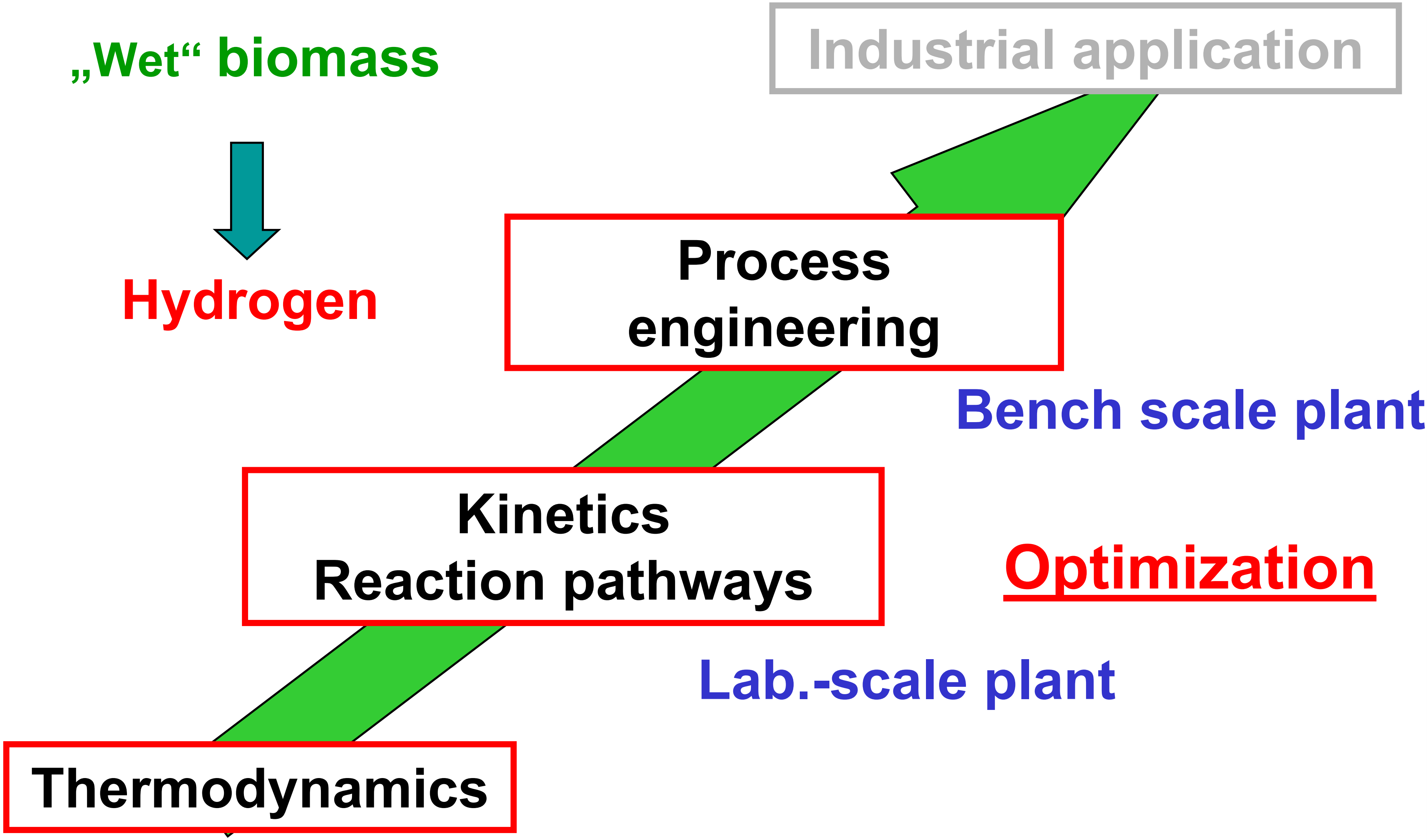
Compensation of the protein influence





1 % DM, 500 °C, 30 MPa;
0,5 % (g/g) K_2CO_3

A. Kruse et al., *Ind. Eng. Chem. Res. 44*, **2005**, 3013.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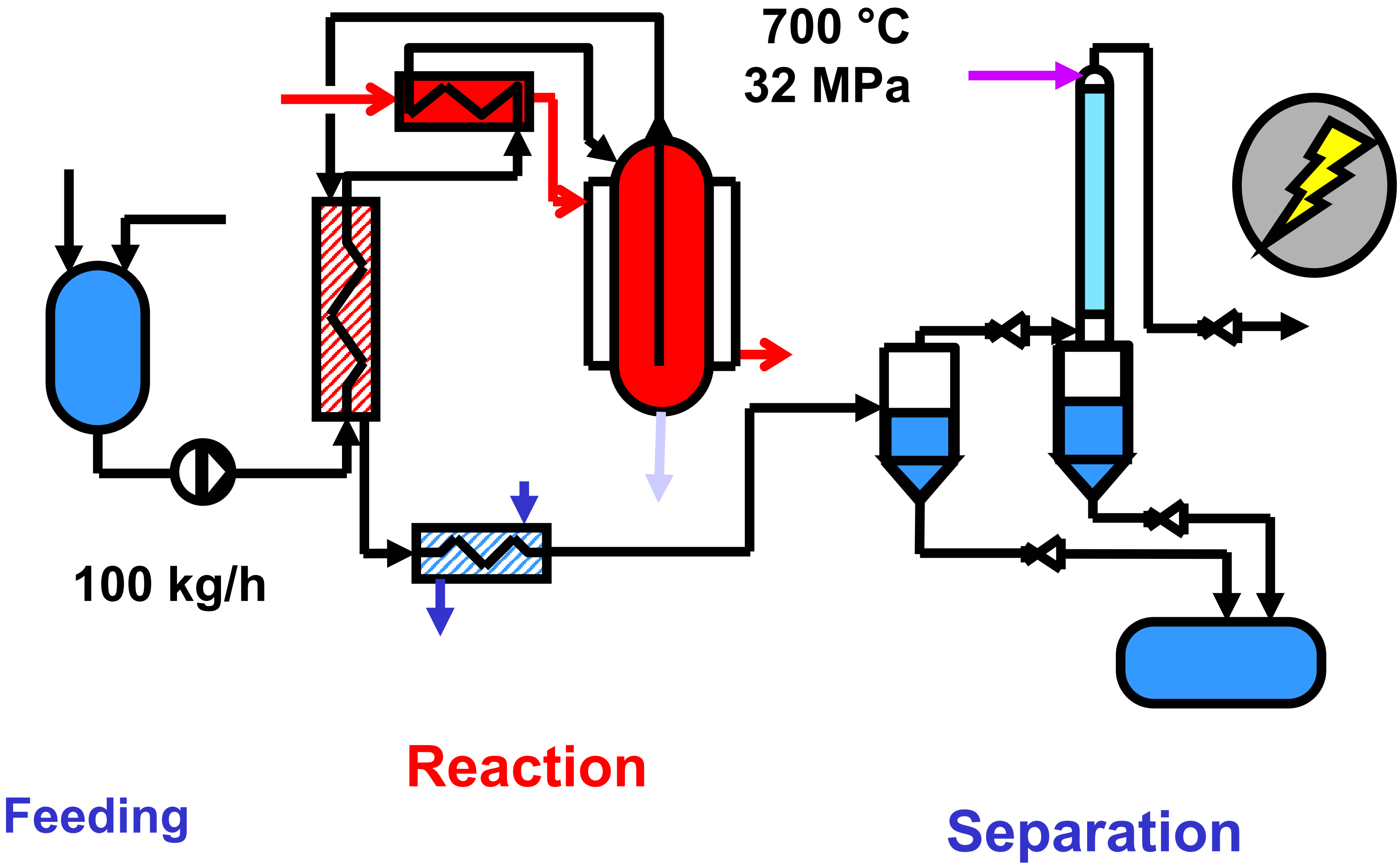
Pilot plant VERENA



Pilot plant VERENA

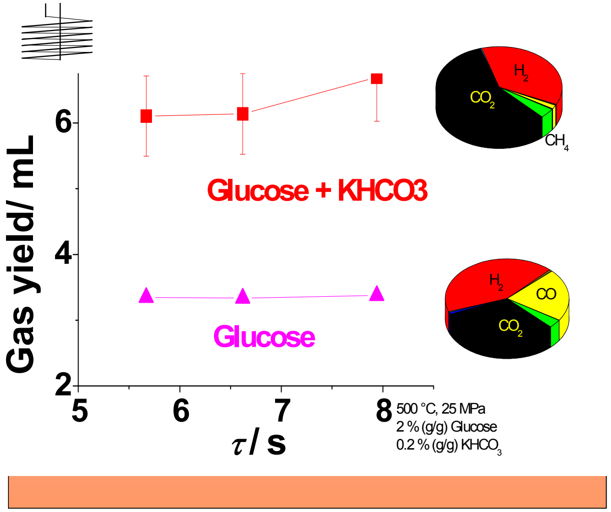
100 kg/h, 5-20 % DM

35 L, 600 °C, 30 MPa

Experiments in the VERENA-Plant

Materials tested : maize silage, greens, residues from wineries and breweries, such from bioethanol and biogas-production, but also biocrude oil, glycerol from biodiesel production …

Summary / Conclusion

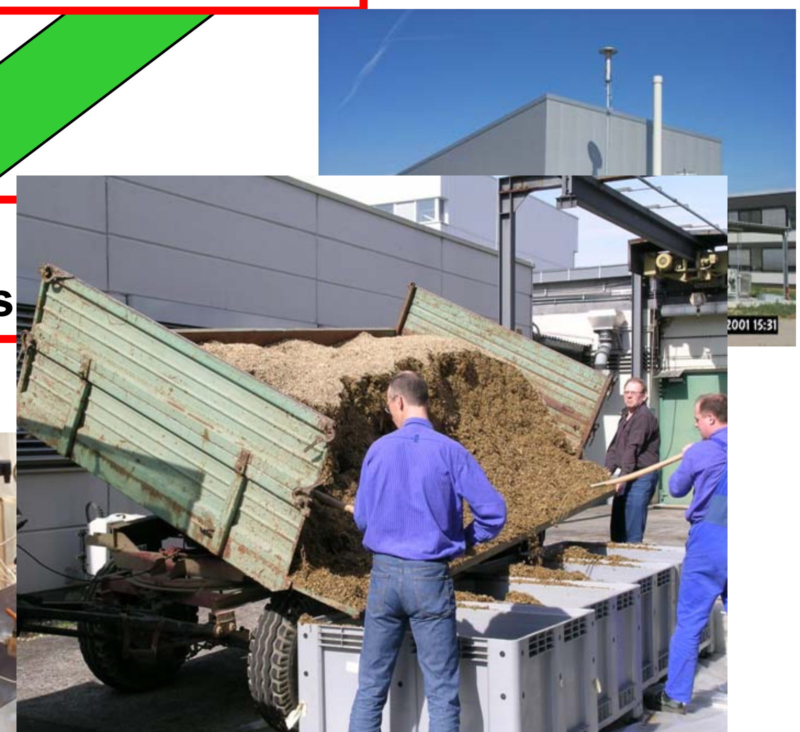


Industrial application

Process engineering

Kinetics
Reaction pathways

Thermodynamics



Main Challenge

- Salt separation to close the nutrition cycle
- Transformation of research results to a plant in technical scale.

Very suitable for biomass residues from other biomass conversion processes (biochemical, biological, chemical or thermochemical conversions)

→ Part of a biorefinery

Thanks!