Roots and Highlights of the Dutch School of Catalysis

Herman van Bekkum and John W. Geus

The Very Beginning of Heterogeneous Catalysis

- The "Hollandsche Scheikundigen"
- Five gentlemen, among which J.R. Deiman and A. Paets van Troostwijk studied at the end of the 18th century catalytic ethanol dehydration over alumina to "gaz oléfiant" (ethylene)
- First heterogeneously catalyzed reaction
- Alcohol dehydration still important, *e.g.*, step in Shell's SMPO process

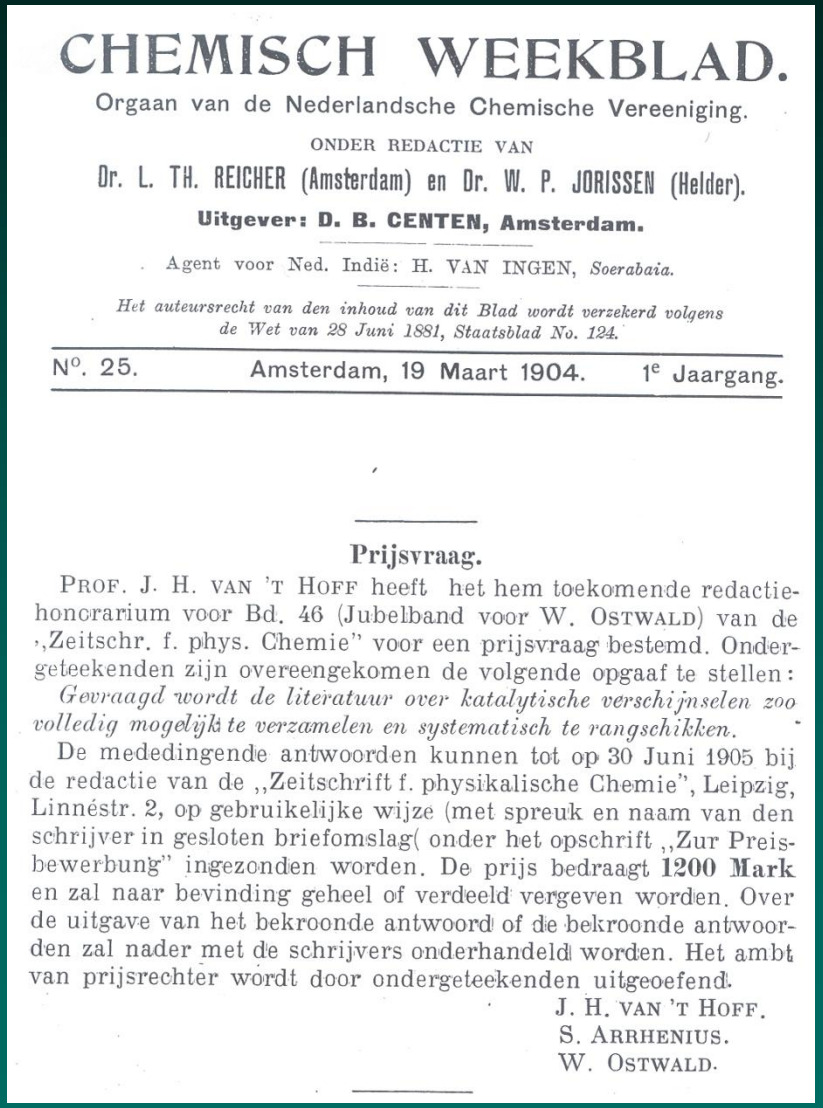
Early Homogeneous HO^--Catalysis Rec.14 (1895) 203

- **Action des alcalis sur les sucres. II.**
  Transformation réciproque des uns dans les autres des sucres glucose, fructose et mannose

  par M.M. C.A. Lobry de Bruyn et
  W. Alberda van Ekenstein

- Laboratory of the Navy, Amsterdam
  Laboratory of the Ministry of Finance
- Nowadays large-scale enzymatic (USA)
  glucose $\leftrightarrows$ fructose
- HO^--catalysis still applied in
  lactose $\leftrightarrows$ lactulose
  Solvay Pharmaceuticals

Early Interest in Catalysis in The Netherlands



CHEMISCH WEEKBLAD.

Orgaan van de Nederlandsche Chemische Vereeniging.

ONDER REDACTIE VAN

Dr. L. TH. REICHER (Amsterdam) en Dr. W. P. JORISSEN (Helder).

Uitgever: D. B. CENTEN, Amsterdam.

Agent voor Ned. Indië: H. VAN INGEN, *Soerabaia.*

N°. 25. Amsterdam, 19 Maart 1904. 1e Jaargang.

Prijsvraag.

PROF. J. H. VAN 'T HOFF heeft het hem toekomende redactie-honorarium voor Bd. 46 (Jubelband voor W. OSTWALD) van de „Zeitschr. f. phys. Chemie" voor een prijsvraag bestemd. Ondergeteekenden zijn overeengekomen de volgende opgaaf te stellen:

Gevraagd wordt de literatuur over katalytische verschijnselen zoo volledig mogelijk te verzamelen en systematisch te rangschikken.

De mededingende antwoorden kunnen tot op 30 Juni 1905 bij de redactie van de „Zeitschrift f. physikalische Chemie", Leipzig, Linnéstr. 2, op gebruikelijke wijze (met spreuk en naam van den schrijver in gesloten briefomslag(onder het opschrift „Zur Preisbewerbung" ingezonden worden. De prijs bedraagt **1200 Mark** en zal naar bevinding geheel of verdeeld vergeven worden. Over de uitgave van het bekroonde antwoord of de bekroonde antwoorden zal nader met de schrijvers onderhandeld worden. Het ambt van prijsrechter wordt door ondergeteekenden uitgeoefend.

J. H. VAN 'T HOFF.
S. ARRHENIUS.
W. OSTWALD.

Dutch School of Catalysis

- Important characteristics :

International character

Cooperation between academia and industry

Focus of this Lecture

- Cooperation between academia and industry
  - *Model from Finland cooperation between universities and industry (NRC/Handelsblad)*
  - *Complaint by chairman VNO-NCW (Chemisch Weekblad)*
  - *Achievements in The Netherlands not appreciated and apparently completely ignored*
- Not possible to deal exhaustively with the cooperation, which lasted more than fifty years, concentration on examples from the experience of the authors

Usual Dutch Modesty

- Jacques Schraven,
  voorzitter VNO-NCW :
  NRC/Handelsblad discussion with Piet Borst
- Economy based on knowledge
- Model of Finland, fruitful co-operation between academia and industry
- Model much earlier realized in catalysis in The Netherlands
- Managers of Dutch industry and Dutch government apparently less aware of achievements in The Netherlands than of performances outside the country

Dutch Industries involved in Catalysis

- Koninklijke/Shell
  - *Petroleum and Petrochemical Processes*
- Unilever
  - *Fat hardening; production of margarine*
- Nederlandse Staatsmijnen, presently DSM
  - *Initially ammonia synthesis, subsequently range of processes around production of caprolactam, acrylonitrile, range of other processes, presently biocatalysis (Gist)*
- Gist and Spiritus Fabriek, presently DSM
  - *Enzymatic catalysis; yeast, penicillin*
- DOW Chemical Terneuzen
  - *Very large production of monomers and range of other products mainly based on steam-cracking*

Dutch Industries involved in Catalysis

- Production of flavors and fragrances
  - *I.F.F. (Polak & Swarz), Quest International (Naarden), Polak's Frutal Works*
- Pharmaceutical industry
  - *Akzo-Nobel Biosynth Organon*
  - *Solvay Pharmaceuticals (Solvay Duphar and earlier Philips Duphar)*

Production of Solid Catalysts

- AKZO-Nobel (Zwavelzuurfabriek v/h Ketjen)
  - *F.C.C. and H.D.S. catalysts*
- Criterion (Koninklijke/Shell)
  - *H.D.S., ethylene oxide, styrene catalysts, range of other catalysts*
- Engelhard
  - *Chemical catalysts (De Meern)*
  - *Fat hardening catalysts*
- Synetics (Unilever, I.C.I., Johnson & Matthey)
  - *Fat hardening catalysts, nickel hydrogenation catalysts*

Activities of Dutch Universities in Catalysis

- Initially Technische Hogeschool Delft, H.I. Waterman
  - *Fat hardening*
  - *Alkylation processes*
- J.H. de Boer from Philips; surface science background
  - *Cooperation with Ketjen determination of porous structures of catalysts*
  - *Later on : Supports for fat hardening catalysts (Unilever)*

Fat Hardening

- Based on work by Waterman and the developments in the determination of the texture of porous catalysts, members of the group of De Boer developed in Vlaardingen excellent nickel hydrogenation catalysts
- Important features :
  - *Transport properties dominating; suspended catalyst bodies smaller than about 10 μm*
  - *Slight poisoning of nickel with sulfur improves selectivity*

Relationships between Academia and Industry dealing with Heterogeneous Catalysis

- Eindhoven, G.C.A. Schuit, from Koninklijke/Shell
- Leiden, W.M.H. Sachtler, from Koninklijke/Shell
- Delft, L.L. van Reijen, H. van Bekkum Koninklijke/Shell
- Nijmegen, J.W.E. Coenen, from Unilever
- Twente, P. Mars from DSM
- Utrecht, J.W. Geus from DSM

Relationships between Academia and Industry

- Initially academic people as consultant of industrial companies
- Subsequently bilateral co-operations, industry with academia
- Larger, governmental cofinanced projects
  - *I.O.P. Catalysis (chairman J. Oelderik)*
  - *ACTS (advanced catalytic technology for sustainability)*
    - Hydrogen as energy carrier
    - Fine Chemicals

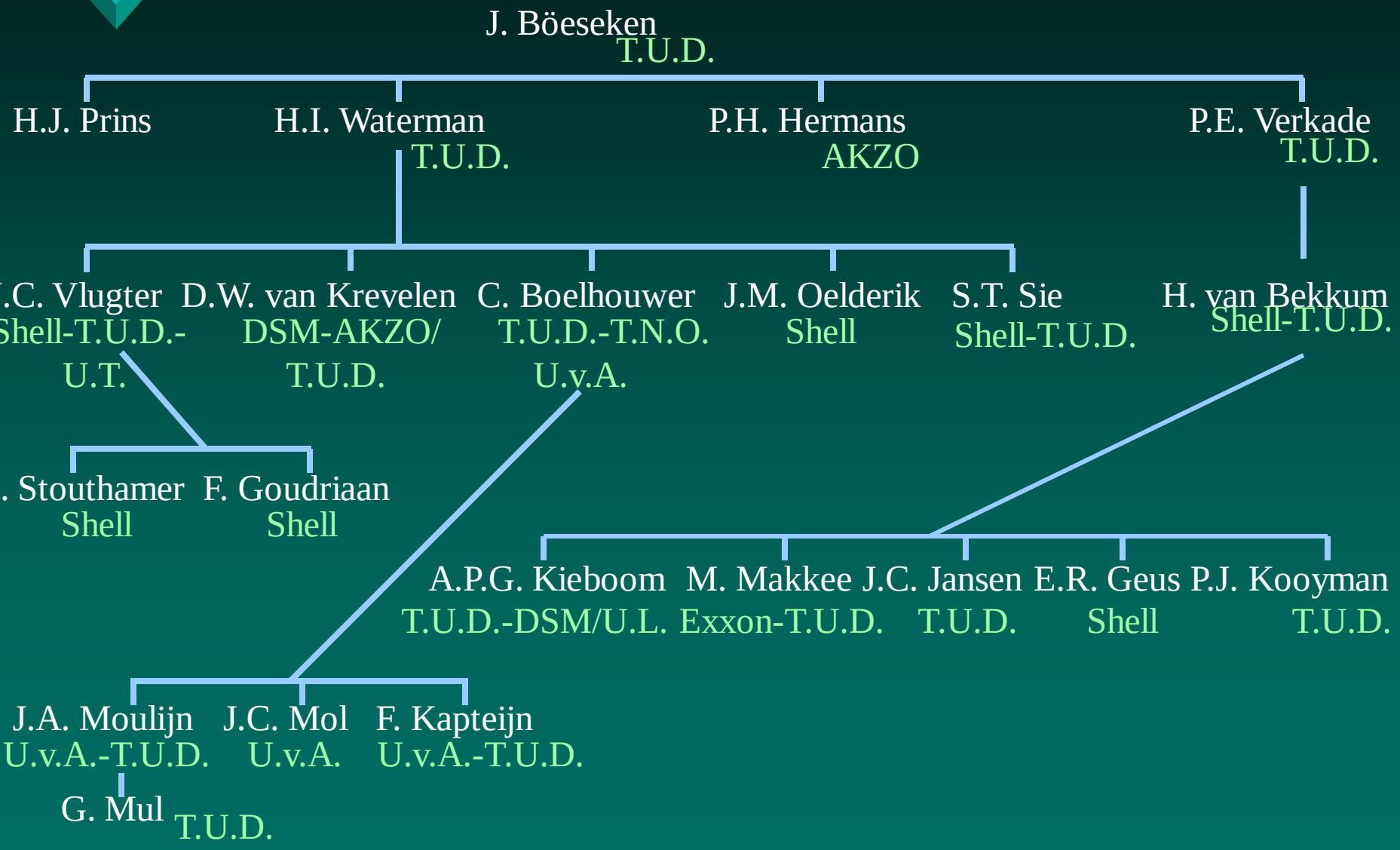
Relationships between Academia and Industry

- During the past years :
- Interaction increasingly intensive

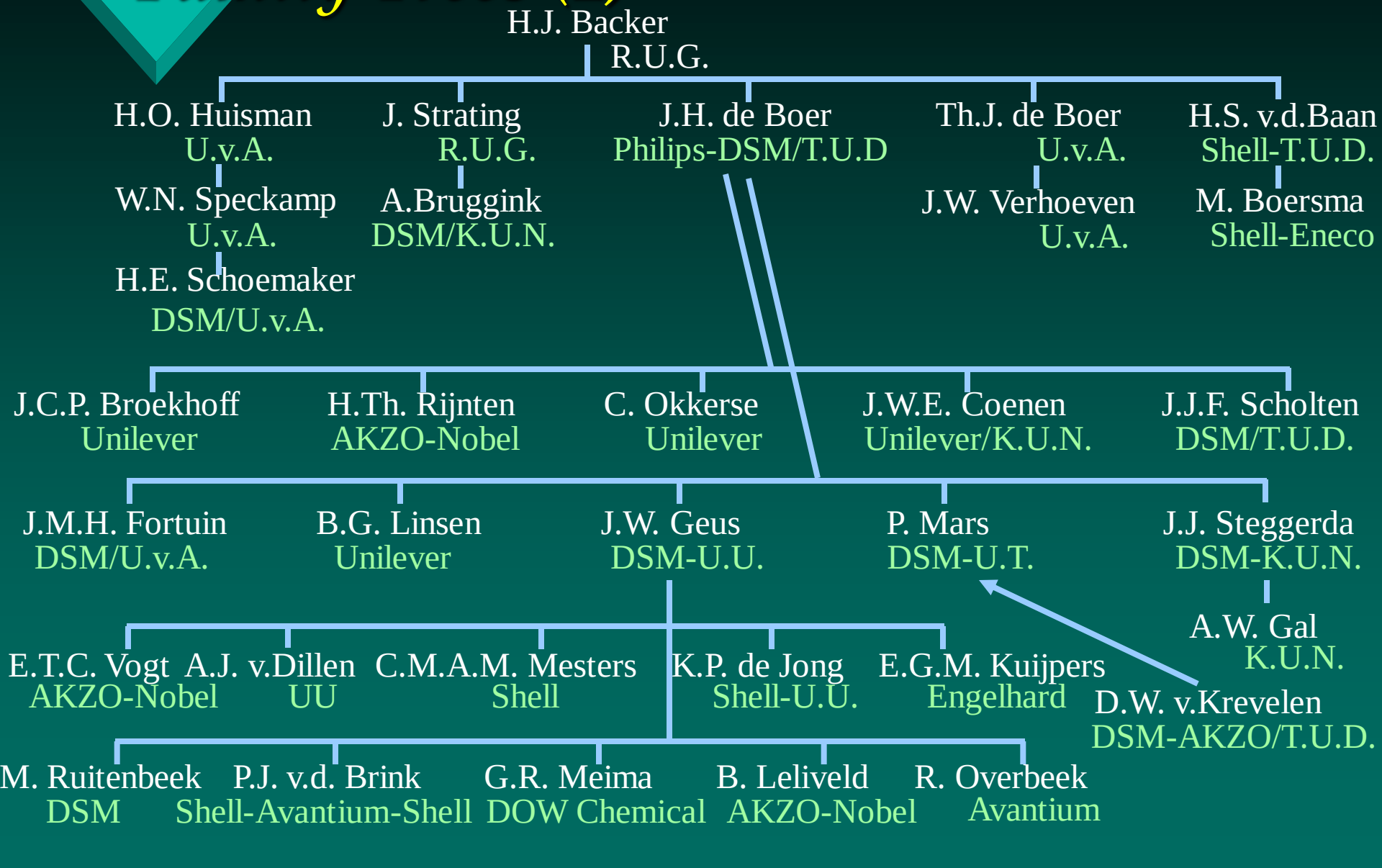
Relationships between Academia and Industry

- Intimate relation evident from "traffic" between universities and industries
- Ph.D.'s and graduates in catalysis very well represented in Dutch chemical industry
- People from industry returning to university (-) or being shared between industry and university (/)

Family Trees (1)



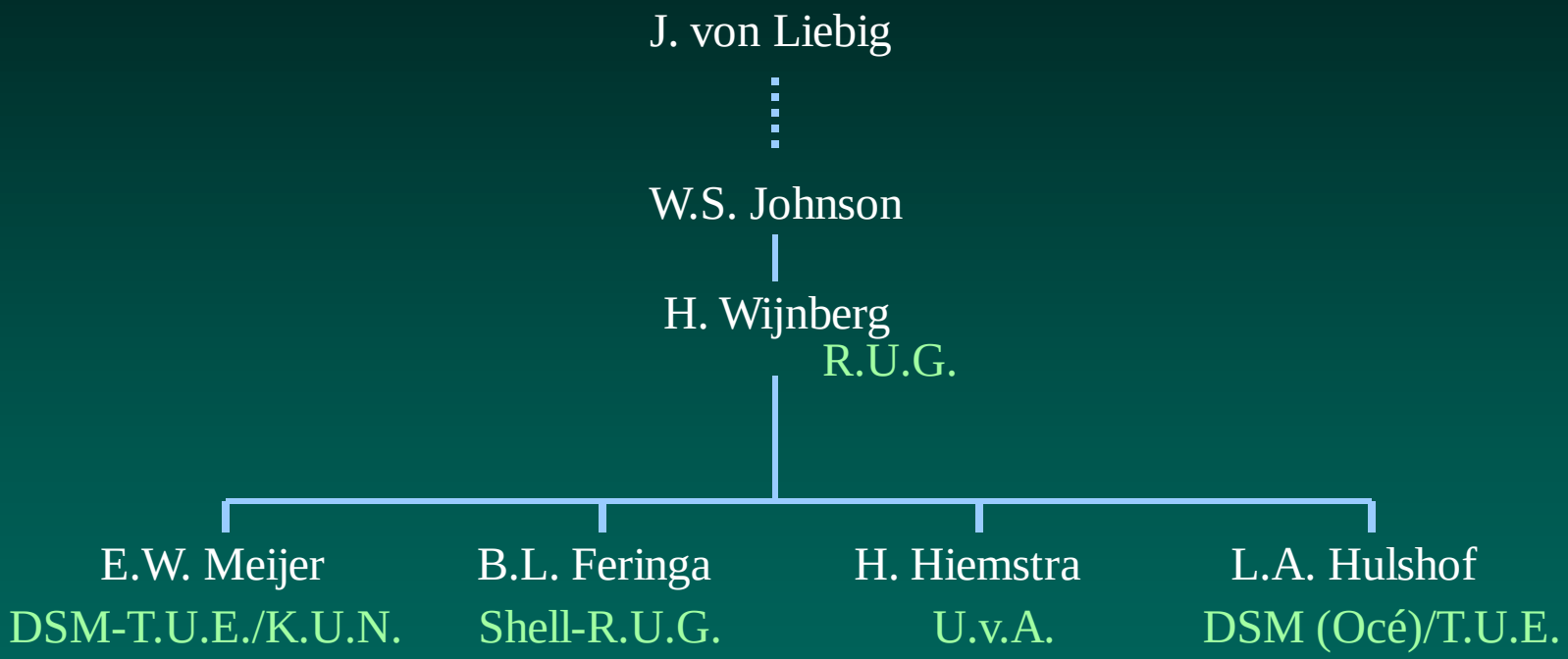
Family Trees (2)



Family Trees (3)

Family Trees (4)

Family Trees (5)



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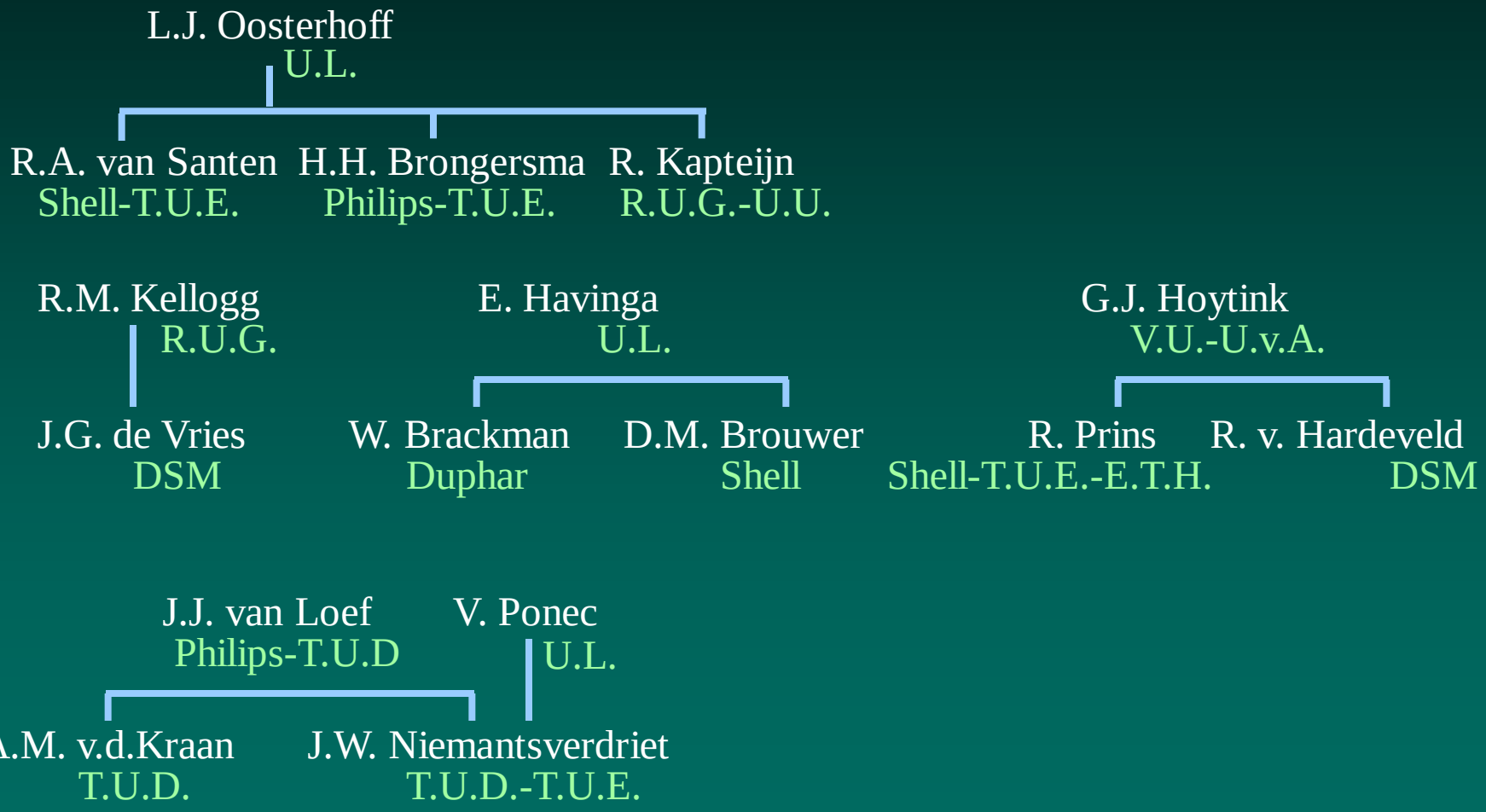

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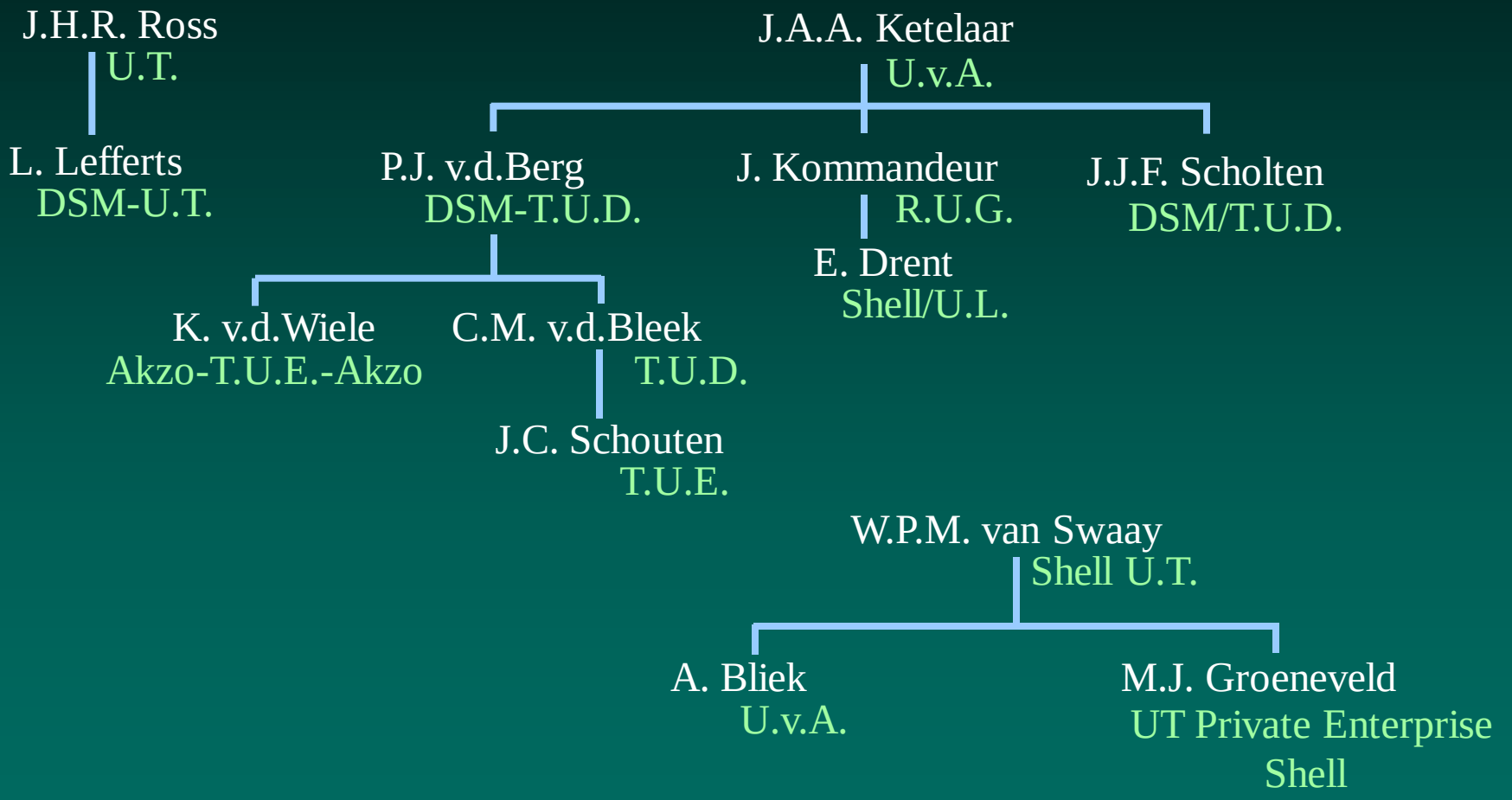

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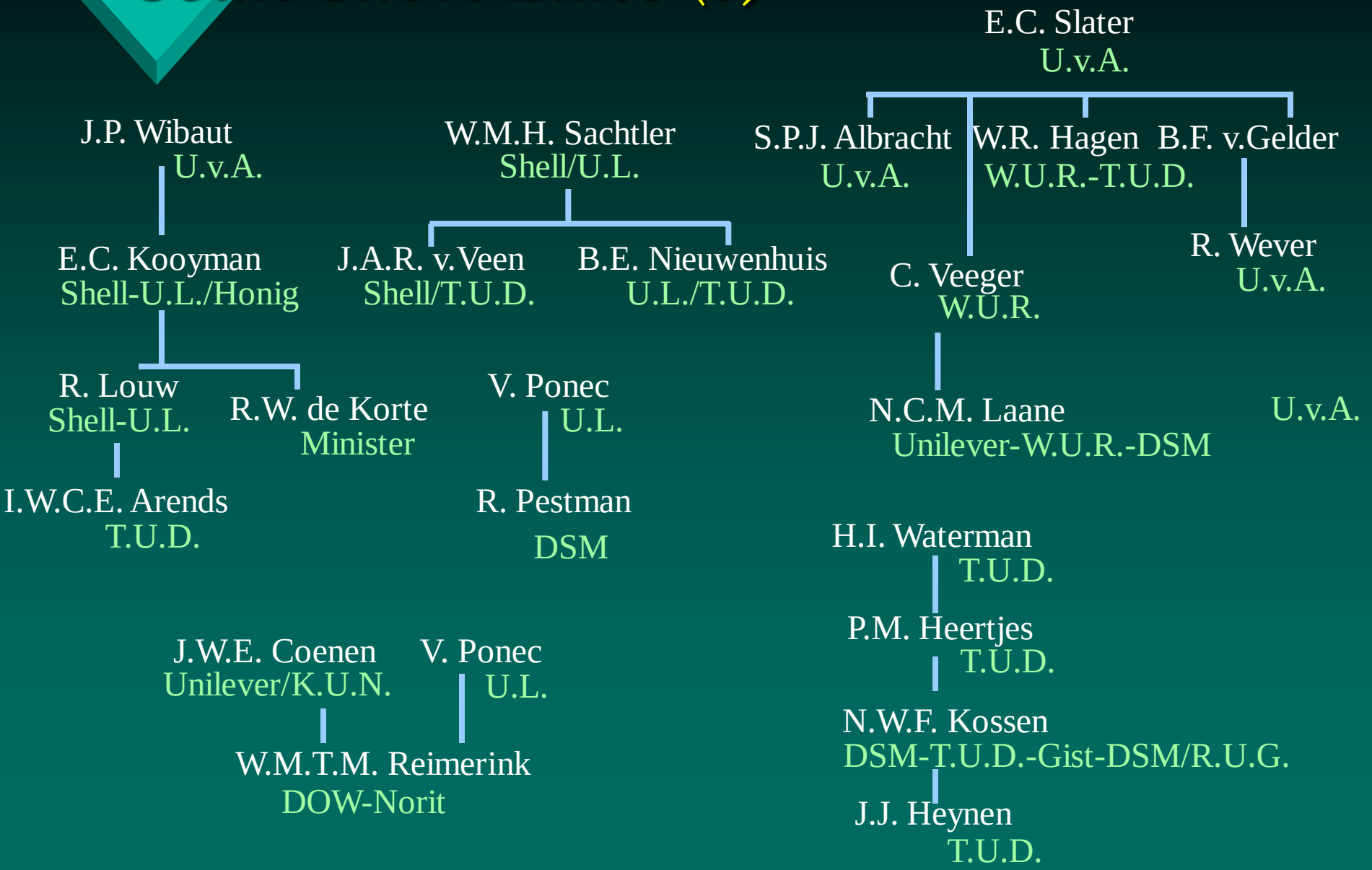


International Transfers in the Dutch Catalysis Society

Imported :

R. Oppenauer
W.M.H. Sachtler
V. Ponec
J.H.R. Ross
R.A. Sheldon
K. Seshan
J. Lercher
D. Vogt
Th. Maschmeyer
B.M. Weckhuysen

Exported :

R. Prins
M. Lok

Some Dutch Achievements in Homogeneous Catalysis (1)

- Oppenauer oxidation Organon/U.v.A.
- Ni(II)-catalyzed isocyanide polymerization U.U.
- Metathesis
  U.v.A.-Koninklijke/Shell-Solvay (Duphar)
  SHOP process of Koninklijke/Shell
- Hydroformylation Ligand design
  Koninklijke/Shell U.v.A.
- Dendrimeric catalysts
  DSM .-T.U.E. -U.U

Some Dutch Achievements in Homogeneous Catalysis (2)

- Cu-, Fe-, and Mn-enzyme mimics in various oxidation reactions
  Unilever Research-U.L.-R.U.G.-K.U.N.
- Cu-catalyzed 2,6-diMe-phenol polymerization
  General Electric/U.L./R.U.G.
- TEMPO-catalyzed oxidations
  T.N.O.-S.C.A.(Sweden)-T.U.D.
- Chiral Catalysis
  DSM-R.U.G.-T.U.D.-U.v.A.
- Supramolecular catalysis
  T.U.E.-K.U.N.

Catalysis in Dutch Polymers

- Poly-L-lactate *A. Pennings*
  PURAC-R.U.G.-U.T.
- Polyketone *E. Drent*
  Koninklijke/Shell
- Nylon 4,6 (Stanyl) *R.J. Gaymans*
  U.T.-DSM
- Dyneema *A.Pennings, P. Smith, P. Lemstra*
  DSM-R.U.G.
- M5 fibre *D. Sikkema*
  AKZO-Nobel
- Glare *B. Vogelesang*
  T.U.D.-Fokker Aerostructures (Stork)

Some Highlights in Dutch Heterogeneous Catalysis

- New processes in oil refining and petrochemistry
- Use of zeolites in petrochemistry and fine chemistry
- Characterization of catalyst texture
  - *Pore structure/Infrared spectroscopy/EXAFS/ 3D-TEM/Mössbauer/TEM and SEM*
- Monoliths in multiphase catalytic applications
- Several world-wide accepted mechanisms

Mechanisms of Heterogeneous Catalytic Reactions

- Catalytic oxidations : Mars-Van Krevelen DSM/T.U.D.-U.T.
- Cossee-Arlman propene polymerisation Koninklijke/Shell
- Zeolite synthesis, catalysis, diffusion, adsorption, reaction mechanisms T.U.E.-T.U.D.-U.T.-Shell-U.v.A.-U.U.
- Hydrogenation and hydrogenolysis mechanisms K.U.N.-U.L.-U.U.
- Fischer-Tropsch process U.L.-I.R.I.-Shell-T.U.E.-T.U.D.-U.U.

Successful Dutch Biocatalytic Processes and Products

- New enzyme production processes
  - *Chymosine (Unilever, DSM)*
  - *Phytase (DSM, T.N.O., I.D.-D.L.O.)*
- Aspartame (DSM)
- Zendium tooth paste (Akzo-Nobel)
- New 7-ADCA and Cephalexin processes (DSM-Universities)
- Anammox process (DSM-T.U.D.-Paques-K.U.N.)
- Biopaq and Thiopaq processes (Shell-T.U.D.-W.U.R.-Paques-Budelco)

Cooperation with DOW Chemical

- Carbon nanofibers
- Most spectacular result
  Complete absorption of radar waves by skin of aircraft; Stealth technology
- Silver catalysts for ethylene oxide
- Supported iron oxide-potassium oxide catalysts for dehydrogenation of ethylbenzene to styrene

Patent obtained by DOW Chemical

United States Patent
Geus, et. al.

4,855,091
Aug. 8, 1989

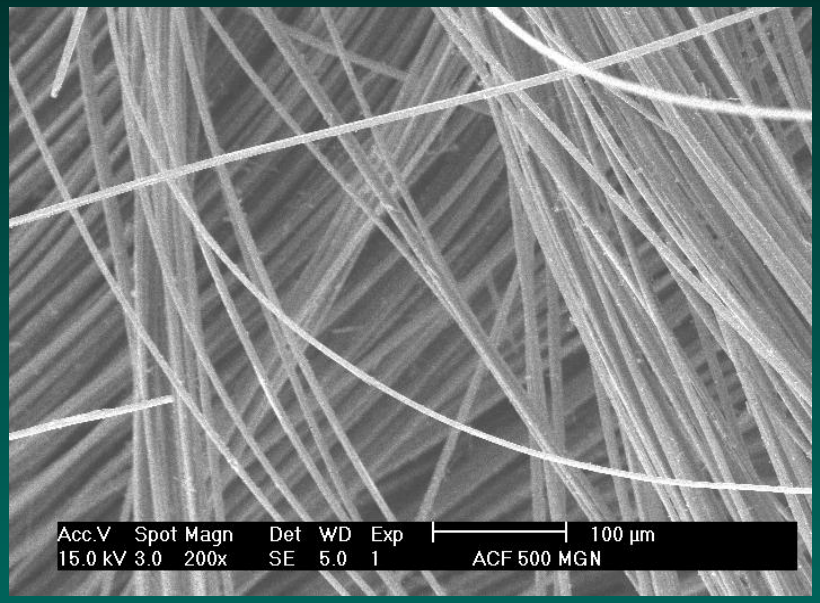
Method for the preparation of carbon filaments

Abstract

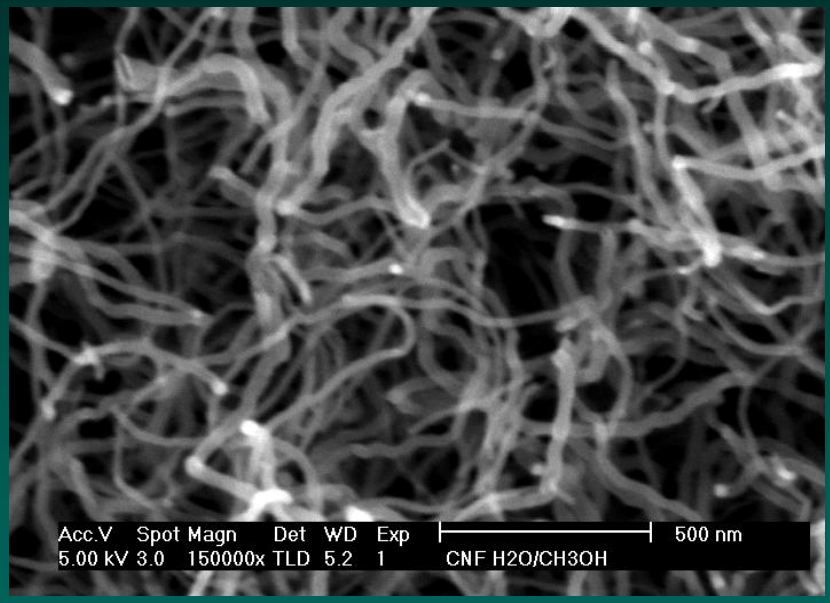
A method of preparing carbon filaments which comprises exposing a suitable thermostable substrate which is covered with reduced monocrystalline metal particles with a diameter of at least 5 nanometers to a carbon containing gas mixture at temperatures of about 250 *deg.* up to about 700 *deg.* C., for a period of time sufficient to form filaments of the desired length, and thereafter removing the substrate and/or the metal particles. The filaments are characterized by a crystalline graphitic structure and a morphology defined by a fishbone-like arrangement of the graphite layers along the axis of the filaments. A high carbide content is a prerequisite for the nucleation of the filamentous carbon with a fishbone like structure.

Inventors: **Geus; John W.** (GJ Bilthoven, NL); **Linowski; John W.** (Midland, MI).
Assignee: **The *Dow Chemical* Company** (Midland, MI).
Appl. No.: **723,123**
Filed: **Apr. 15, 1985**

Different Carbon Fibers



Usual carbon fibers



Carbon nanotubes (Carbon fibrils)

Dutch Desulfurization Know-How

- Fossil fuels
  - *Organic sulfur to H_2S*
    AkzoNobel-Shell (Criterion)
- Separation of H_2S from gas flows
  - *Koninklijke/Shell*
- Processing of H_2S
  - *Shell-Comprimo-GasTec-Engelhard*
- Aqueous streams
  - *$SO_4^{2-} \rightarrow S^{2-} \rightarrow S_n$ ThioPaq Process*
    Biotechnology
    Shell-T.U.D.-W.U.R.-Paques-Budelco

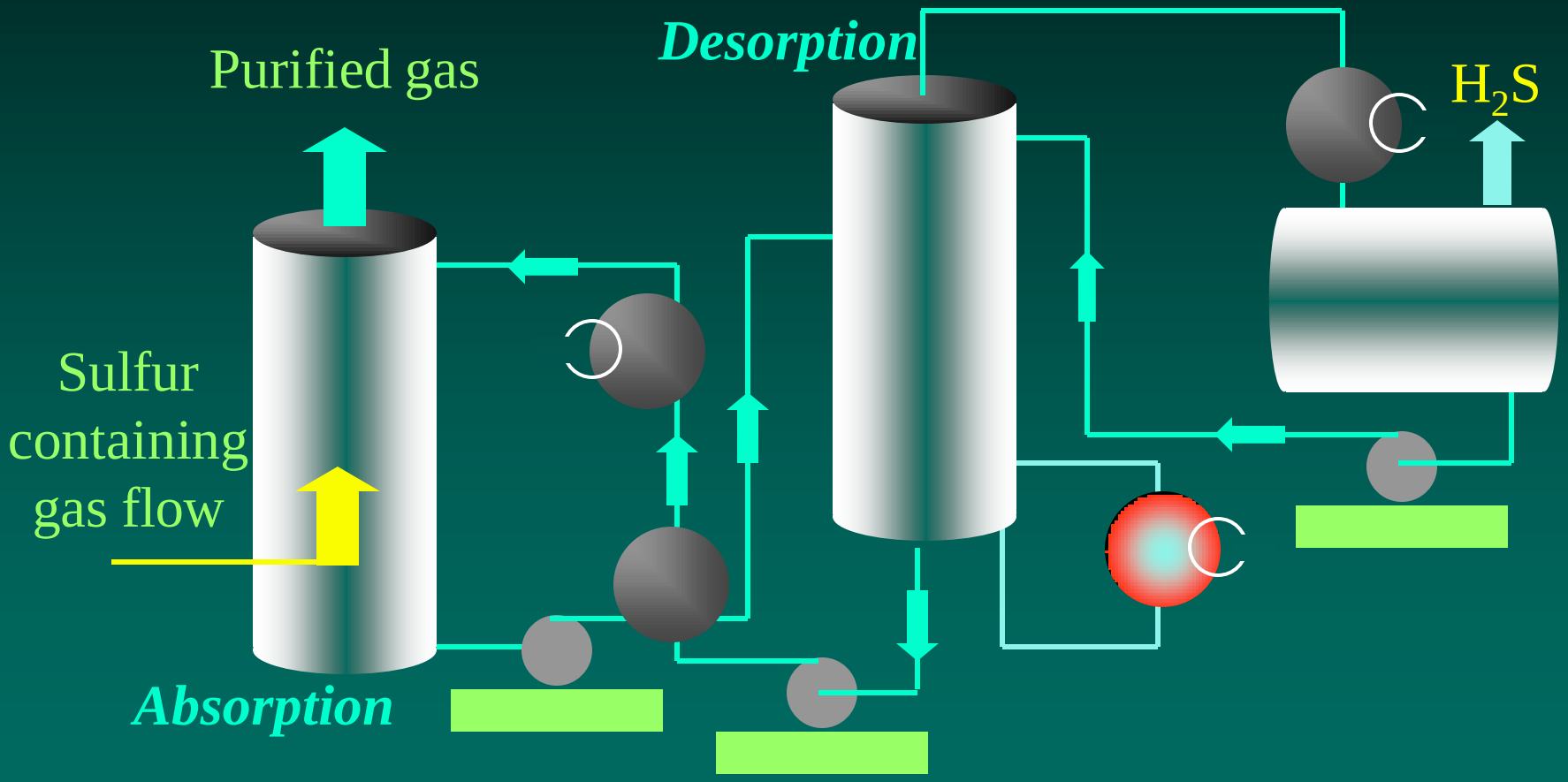
Extensive Research on Hydrodesulfurization Catalysts

- Eindhoven, G.C.A. Schuit, V.H.J de Beer, R. Prins, D.C. Koningsberger, J.A.R. van Veen J.W. Niemantsverdriet
- Amsterdam, J.A. Moulijn
- Delft, IRI, A.M. v.d.Kraan
- Utrecht, EXAFS D.C. Koningsberger
- Highly improved hydrodesulfurization catalysts produced by AKZO-Nobel and Criterion (Koninklijke/Shell)

Dealing with Pollution of Gaseous Sulfur Compounds

- In The Netherlands most advanced technology for dealing with environmental pollution of sulfur available
- Koninklijke/Shell know-how about absorption of hydrogen sulfide in regenerable liquids
- Koninklijke/Shell developed SCOT process, Shell Claus Offgas Treating process
- Comprimo designed plant based on Shell technology and commercialized Shell know-how
- Comprimo entered co-operation with Utrecht University and Gas Institute to develop new process for dealing with Claus tail gas

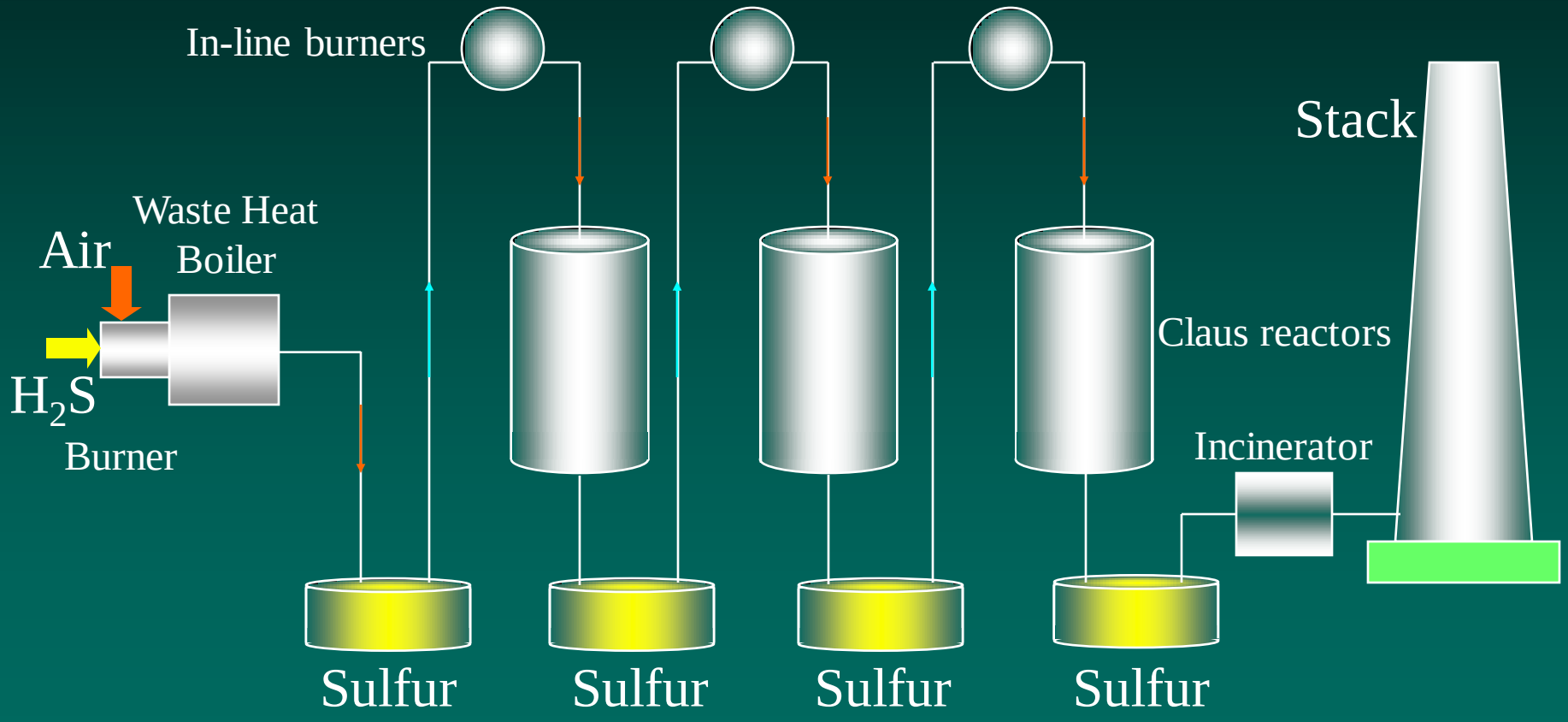
Separation of Hydrogen Sulfide



Claus Process

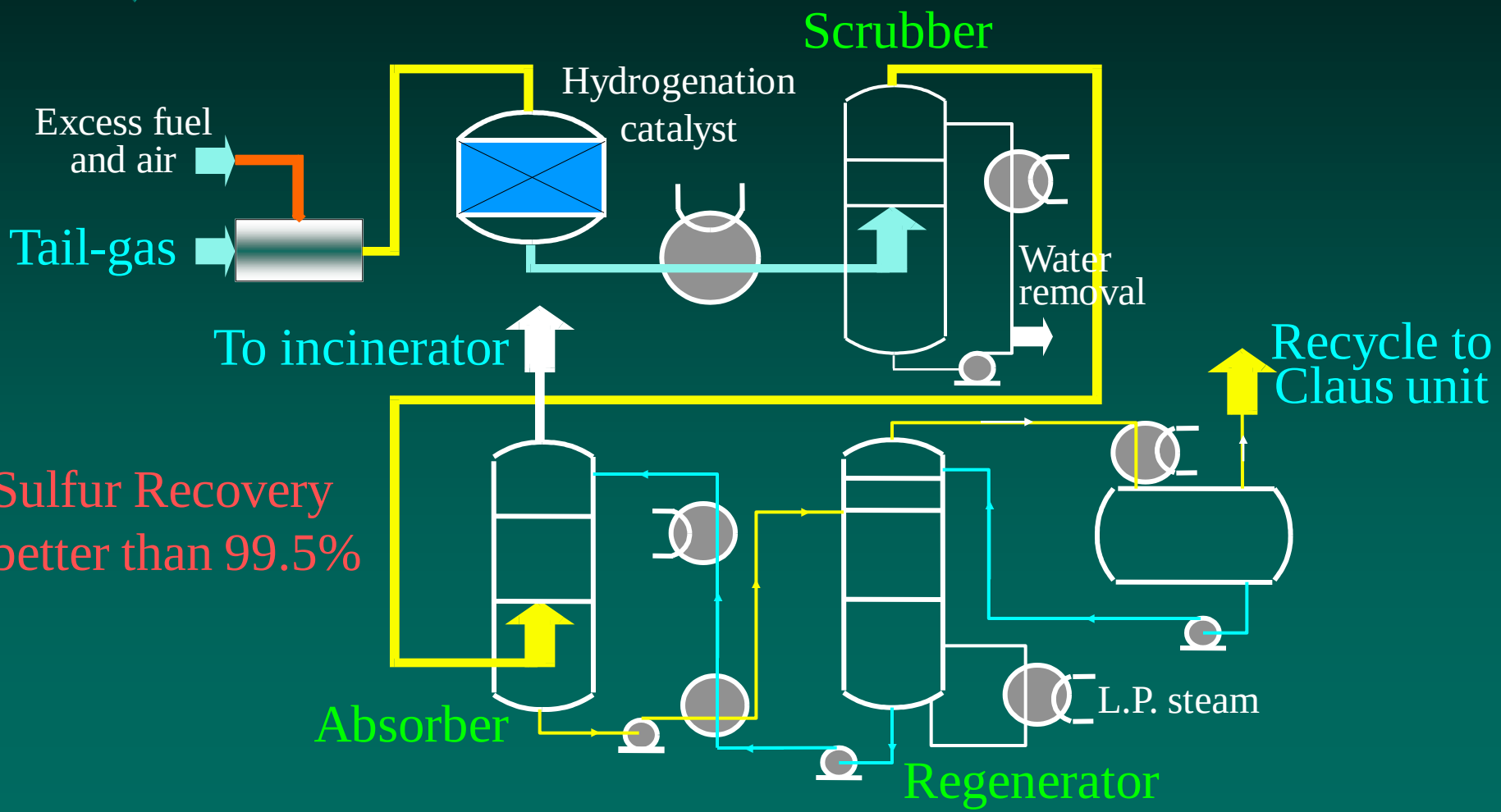
- Claus process
  - *1/3 of hydrogen sulfide oxidized to sulfur dioxide; equilibrium always on right-hand side*
    $2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$
  - *Subsequent reaction of hydrogen sulfide with sulfur dioxide*
    $2H_2S + SO_2 \leftrightarrows 3/nS_n + 2H_2O$
    Equilibrium reaction; at temperatures where reaction sufficiently rapid equilibrium not completely at right-hand side

Schematic Representation of Claus Process

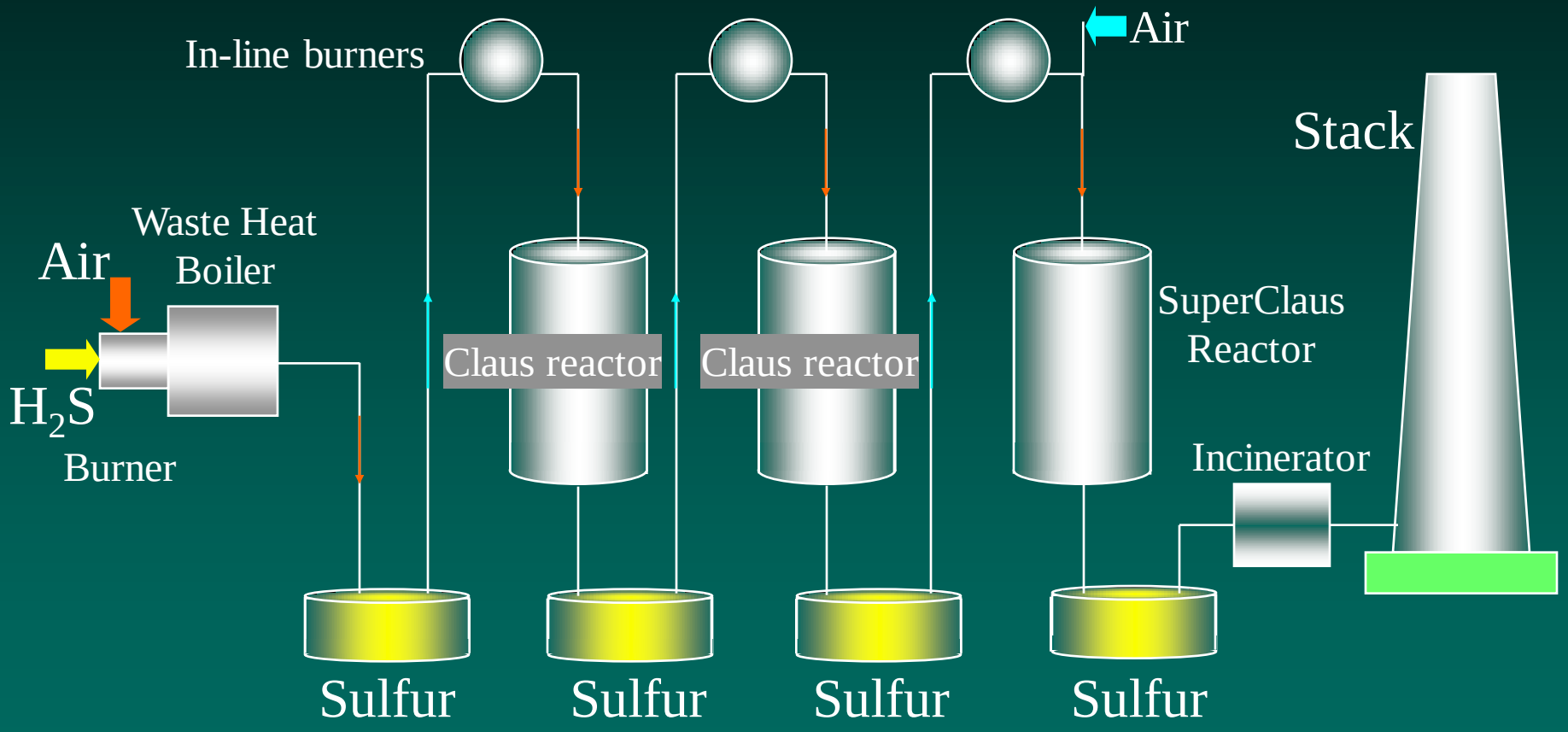


Sulfur recovery 96 - 97%

SCOT Process



SuperClaus Process



Sulfur recovery 99.2 - 99.4 %

Constraints

- Selective oxidation of hydrogen sulfide to elemental sulfur $2H_2S + O_2 = 2H_2O + n/2S_n$
- No condensation of elemental sulfur within catalyst bed
- High selectivity in the presence of 30 vol.% of water vapor $2H_2S + SO_2 \leftrightarrows 3/nS_n + 2H_2O$
- Excess of oxygen to deal with fluctuations in hydrogen sulfide flow $1/n\ S_n + O_2 = SO_2$
- Elevated selectivity within a wide range of temperatures

Earlier Russian Developments

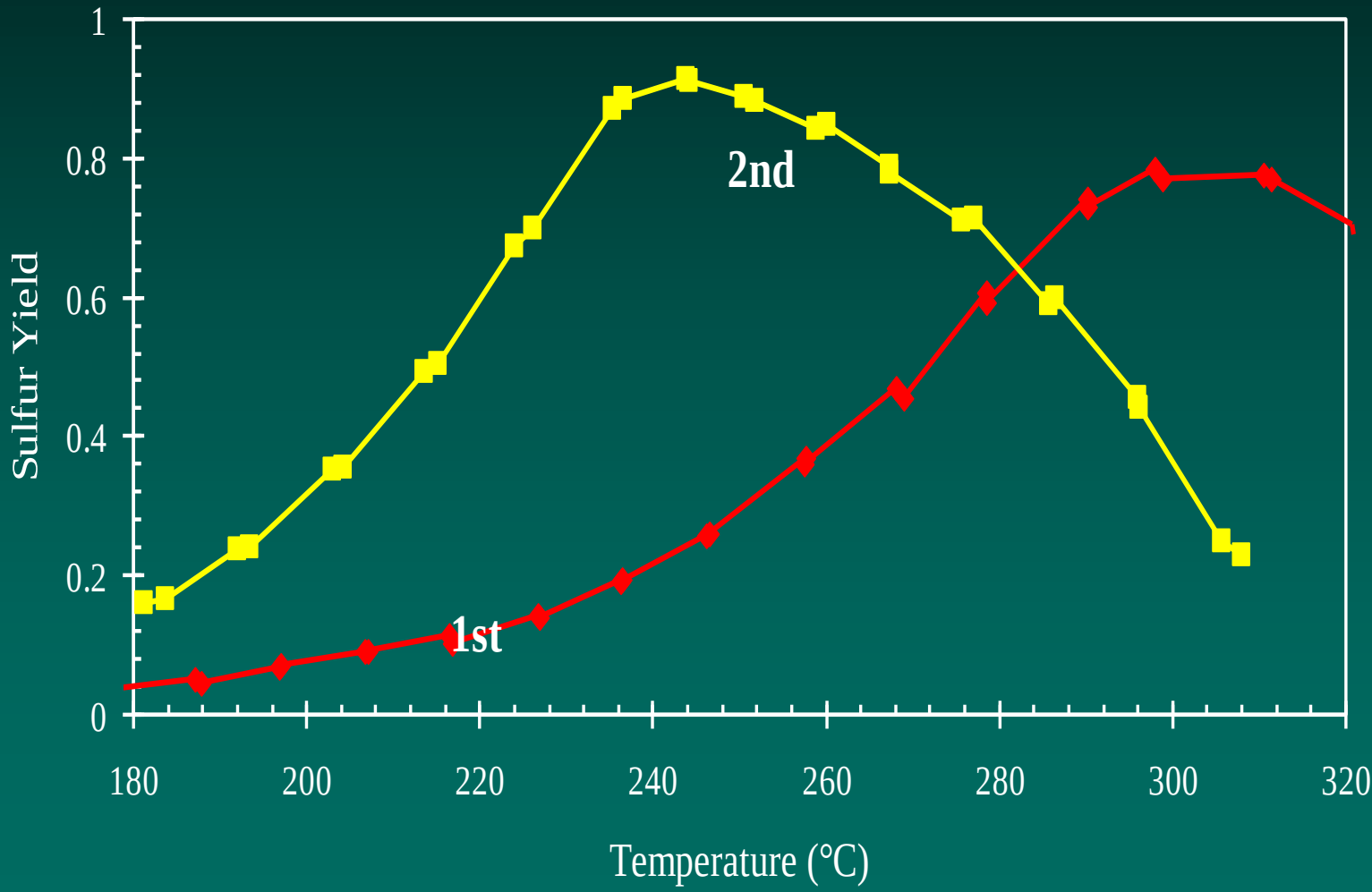
- Comprimo contact with Russian Institute
- Highly porous catalysts : promoting oxidation of elemental sulfur to sulfur dioxide
- Catalyst supports alumina or titania, active in the reaction $2H_2S + SO_2 \rightarrow 3/nS_n + 2H_2O$
- Performance of catalysts thus bad that process was not viable

Successful Utilizing Catalytic Knowledge

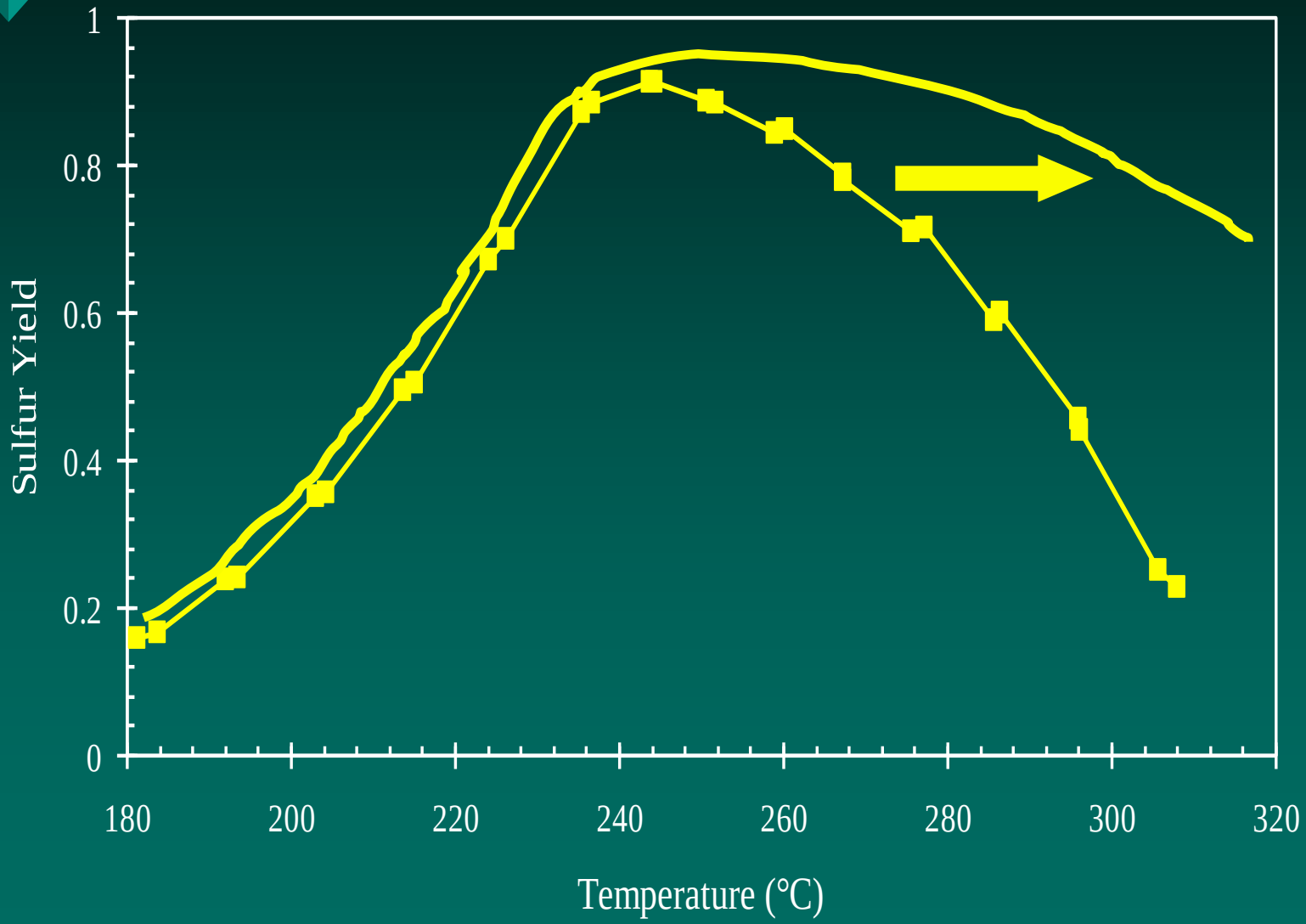
- Utrecht University :
  - *Oxidation of H_2S to elemental sulfur facile reaction not asking for highly active catalyst*
    Mild oxidation catalyst Fe_2O_3
  - *Rapid transport of elemental sulfur out of catalyst structure : Catalyst of low surface area having wide pores*
  - *Catalyst support not catalyzing Claus reaction*
    α-Al_2O_3 BET surface area about 10 m^2/g
    No narrow pores generated by active component
  - *H_2S/SO_2 ratio slightly higher than two*

Two generations of Superclaus catalysts

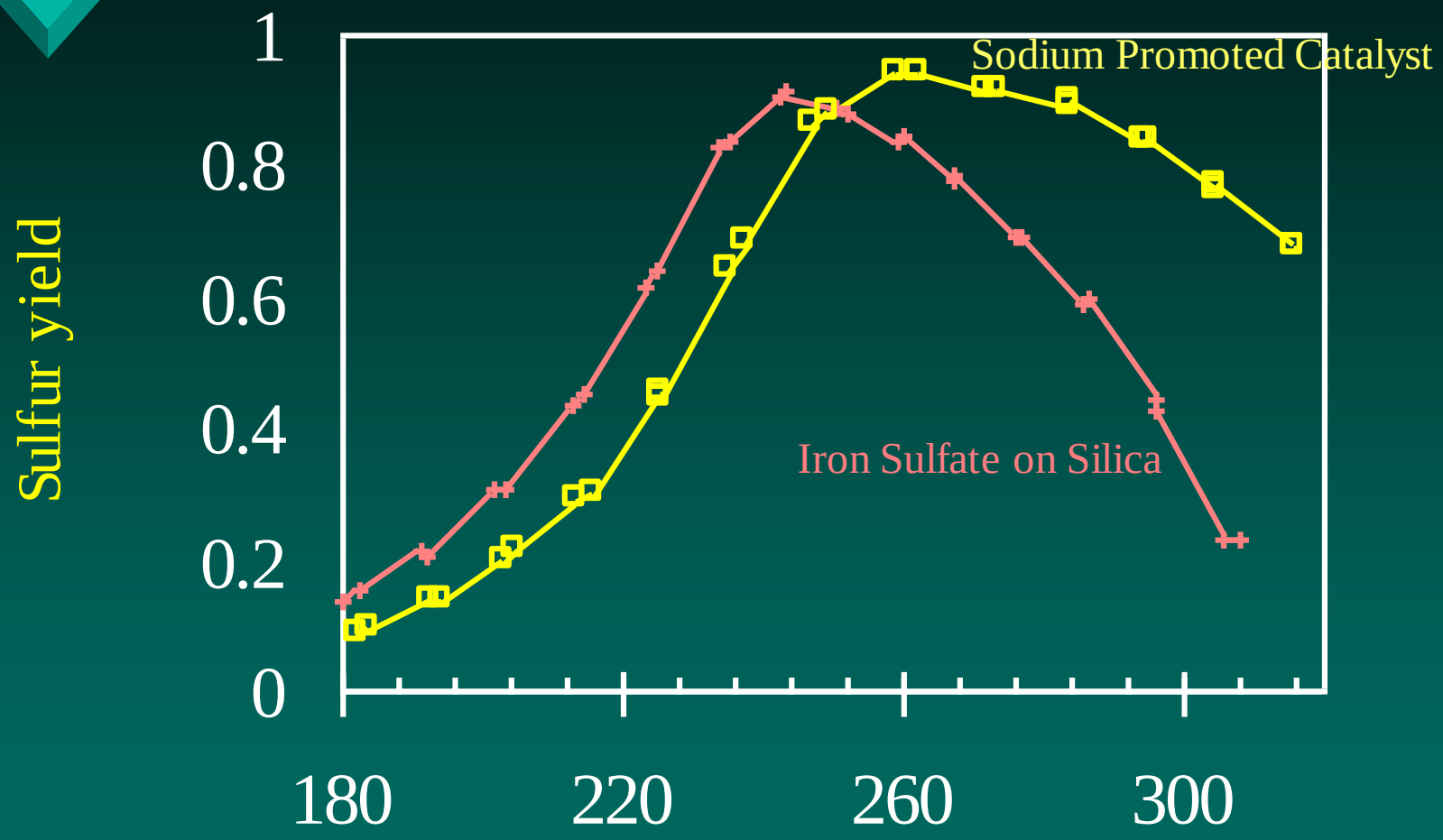
P. Berben P.J. v.d.Brink



Broader Temperature Window

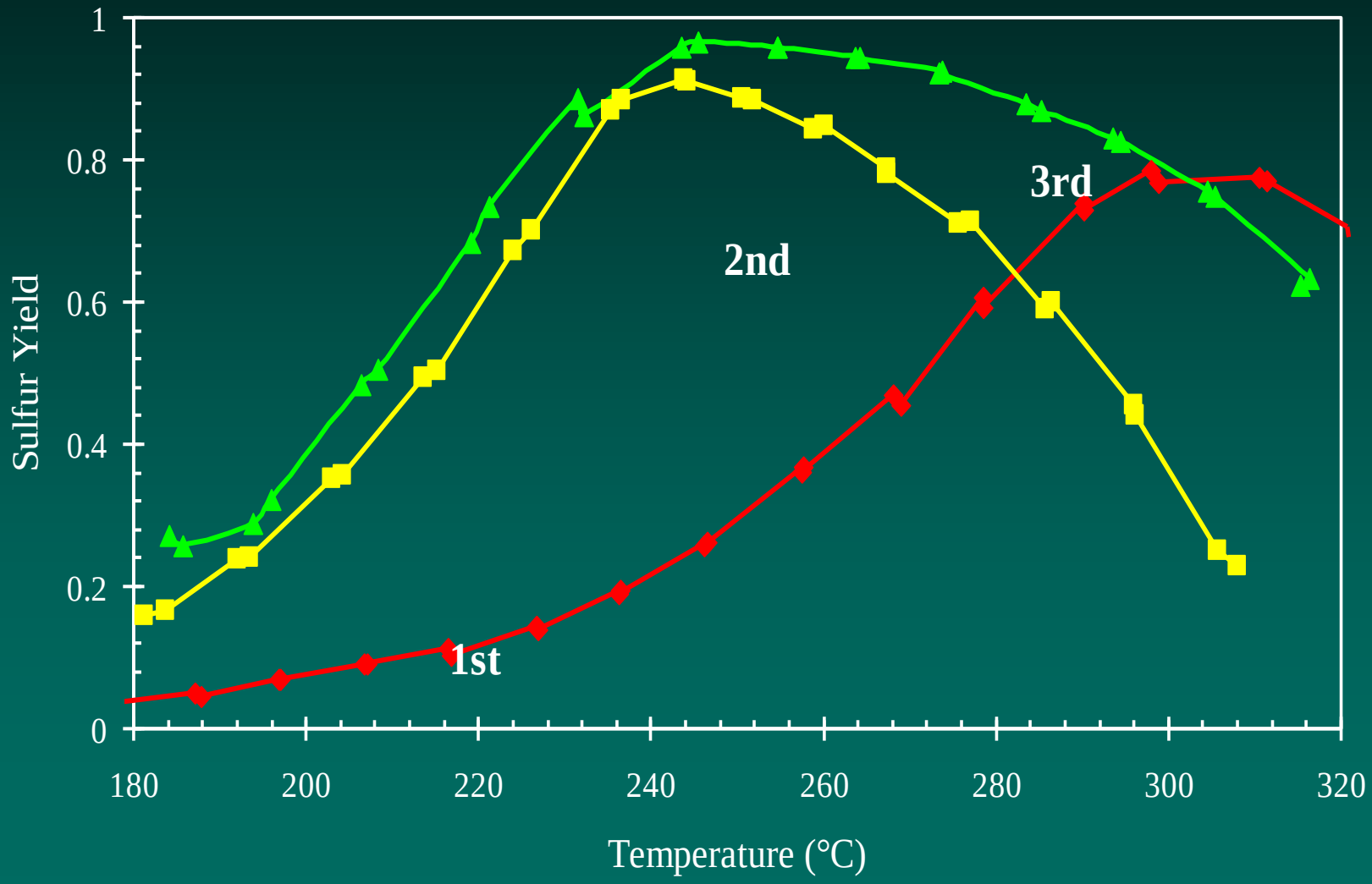


Sodium Promoted Catalyst



R. Terörde

Three Generations of SUPERCLAUS catalysts



From Laboratory to Industrial Scale of Operation

Final Results

- SuperClaus process presently employed worldwide in more than 100 plants
- Start-up of SuperClaus plants very smoothly due to fundamental knowledge of employees of Comprimo
- However, development has taken 12 years, which is much longer than business unit managers are feeling to be viable

Co-operation between Academia and Industry

- Universities are able to perform industrially relevant research for "out of pocket" costs
- Within one company time at which results are available decisively important
  - *Market*
  - *Means to invest in new technology*
  - *Availability of feedstock*
  - *Prof. E. Drent scientifically very impressive development of Carilon*
- University can contact number of different companies to commercialize research results

Conclusions

- The Dutch school of Catalysis is flourishing due to intense industry-academia interactions
- Part-time professors, alumni and joint projects provide efficient bridges between universities and industry
- DSM is practising the combination with universities most extensively
- Many talented Dutch students entered the field of catalysis
- The Dutch school of catalysis also attracts excellent young and senior people from abroad
- The reduced number of industrial catalysis workers is thus far compensated for by a larger number of university workers

Conclusions

- Still many challenges ahead :
  - *Learning from nature*
  - *Catalyst design; integration of catalyst and reactor*
  - *Cascade catalysis*
  - *Greening of chemistry*
- Strong international position of the Dutch school of catalysis is worthwhile to maintain
- Break-down can be performed within a very short period of time, whereas build-up research tradition and co-operation is very time-consuming