



Fakultet kemijskog inženjerstva i tehnologije
Sveučilište u Zagrebu

Diplomski studij

Kolegij:

VODIKOVA ENERGIJA I EKONOMIJA

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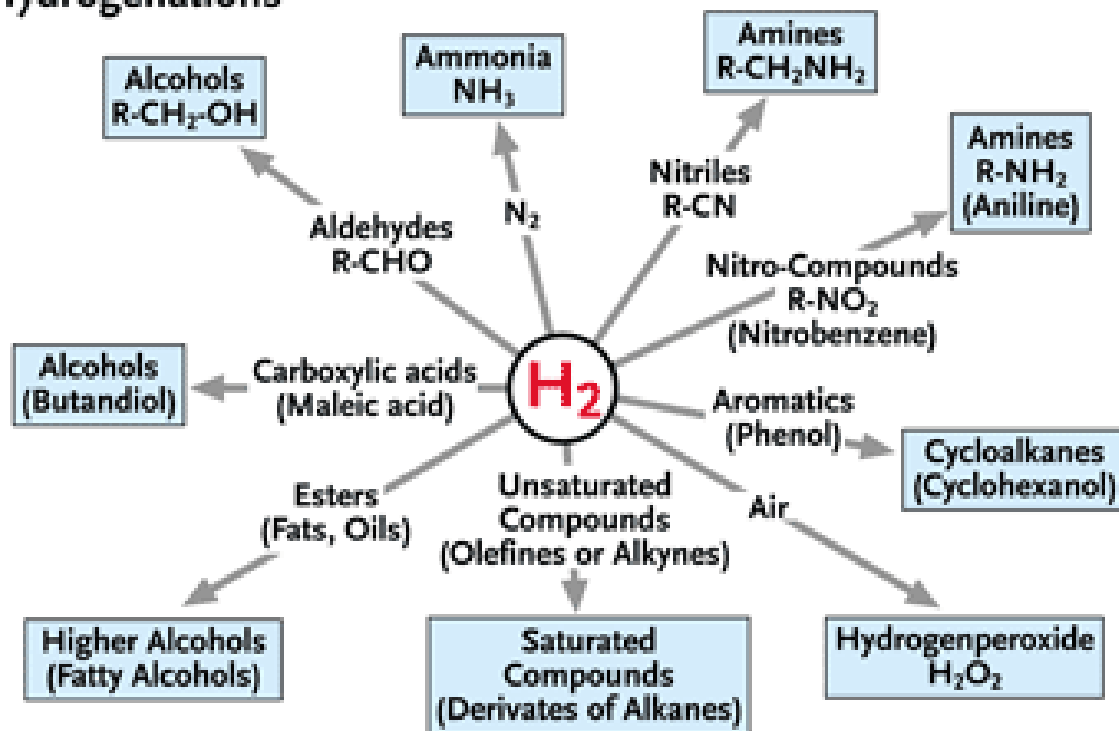


Akademsko godina: 2010-2011

Hydrogen Applications in Petrochemical Industry

Hydrogen is widely used in the production of bulk chemicals, intermediates and speciality chemicals.

Hydrogenations



Mixtures of hydrogen and carbon monoxide, known as **syngas**, are fed to processes for large-scale production of methanol and various so-called oxo-products like higher alcohols and aldehydes.

Proizvodnja sinteznog plina / vodika

Sintezni plin (synthesis gas, syn-gas) - smjesa ugljikova monoksida i vodika u raznim omjerima, najčešće $\text{CO} / \text{H}_2 = 1 / 2$.

Naziv potječe od njegove uporabe u brojnim sintezama kemijskih proizvoda.

Izravno najviše služi za dobivanje metanola ($\text{CO} / \text{H}_2 = 1/2$), zatim, u procesima *hidroformilacije* (okso-alkoholi, $\text{CO} / \text{H}_2 = 1/1$) kao i za dobivanje smjesâ ugljikovodika, Fischer-Tropschovom sintezom ($\text{CO} / \text{H}_2 = 2/1$).

Također, može se razdvojiti u sastavnice, vodik i ugljikov monoksid.

Vodik najviše služi za proizvodnju amonijaka ($\text{N}_2 / \text{H}_2 = 1/3$) i u rafinerijskoj preradbi nafte, dok se izdvojeni ugljikov monoksid najviše upotrebljava u procesima *karbonilacije* (octena kiselina, polikarbonati, diizocijanati).

Procesi dobivanja

Sastav sinteznog plina izravno ovisi o sirovini, s tim da je najveći prinos na vodik u pri preradbi metana. Tri su temeljna postupka dobivanja:

a) *Parno reformiranje*

Katalitički proces, jednostavan i ekonomičan, samo "lake" sirovine, ponajprije CH₄ i u manjem obimu primarni benzin:



Sirovini je potrebno prethodno ukloniti katalitičke otrove ($S < 1 \text{ mg kg}^{-1}$).

b) *Djelomična (parcijalna) oksidacija*

"Teške" sirovine: loživo ulje, ostatci destilacije nafte, nafta; sadrže velike udjele sumporovih spojeva pa njihovo prethodno uklanjanje nije ekonomično. Stoga se postupak provodi bez katalizatora, pri visokim temperaturama.

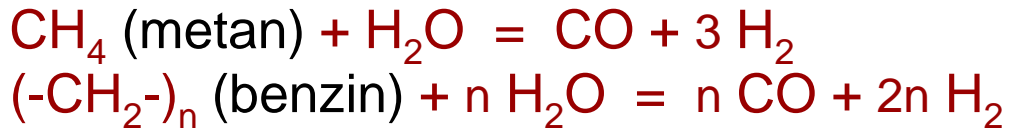
c) *Uplinjavanje ugljena*

Reakcijom ugljena s vodenom parom pri visokim temperaturama nastaje tzv. *vodeni plin*.

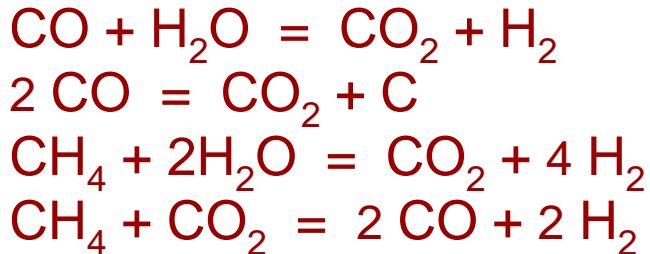
1. Proces parnog reformiranja

- danas najvažniji postupak dobivanja sinteznog plina od nižih ugljikovodika (metan, benzin) i vodene pare, endotermnom reakcijom uz heterogene katalizatore, Ni / Al₂O₃ + MgO, pri visokoj temperaturi 700...800 °C i tlaku oko 20 bara.

Temeljna reakcija



Sporedne reakcije



Ukupni proces parnoga reformiranja sastoji se od dvije cjeline:

- a) *uklanjanje sumporovih spojeva iz sirovine,*
- b) *pretvorba u sintezni plin.*

2. Proces djelomične oksidacije (nepotpunog izgaranja)

- gotovo sve ugljikovodične sirovine – metan, plinsko ulje, sirova nafta. Najčešće plinska - loživa ulja (jeftina u usporedbi s prirodnim plinom).
- sadrže veće udjele sumporovih spojeva (3····4 %) - prihvatljivi su samo nekatalitički procesi.

Temeljne reakcije:

1) djelomična oksidacija ($\Delta H = -$)



2) reakcija hidratacije ($\Delta H = +$)



Sporedne reakcije:

1) nastajanje koksa



2) potpuno izgaranje



Procesni uvjeti: 1200····1500 °C, 30····80 bar.



RAZVITAK TEHNOLOGIJA

Proces djelomične oksidacije (nepotpunog izgaranja)

- uporaba zraka umjesto O₂

3. Uplinjavanje ugljena

- nekad najzastupljeniji proces dobivanja sinteznog plina (do 1960.)
- dio ugljena (30...40 %) u potpunosti izgara (zato se postupak provodi uz smjesu $O_2 / H_2O = 1 / 1$) što osigurava reakcijsku toplinu za endotermnu reakciju nastajanja smjese CO / H_2 .

Temeljne reakcije:



Endotermna reakcija uplinjavanja ugljena zahtijeva veliki utrošak energije potrebne za temeljnu reakciju (1), a također je potrebna i vrlo visoka temperatura (900...1000 °C) za odgovarajuću ukupnu brzinu reakcije, što se osigurava spaljivanjem ugljena, reakcija (2).

Premda je cijena sirovine, ugljena, prema drugim sirovinama razmjerno niska, postupak je ekonomičan samo uz vrlo velike proizvodne kapacitete i istodobne primjene “na licu mjesta”

(uz nuklearne elektrane, ugljenokopi u Južnoj Africi - “Sasol proces”).

Sastav sinteznog plina u ovisnosti o vrsti sirovine i procesu

Sirovina (proces)	Sastav sinteznog plina					
	H ₂	CO	H ₂ / CO	CO ₂	N ₂ + Ar	CH ₄
Metan (parno reformiranje)	75,7	15,5	5	8,1	0,2	0,5
Teško plinsko ulje (djelomična oksidacija)	46,7	47,3	1	4,3	1,4	0,3
Ugljen (uplinjavanje)	31	68	0,5	1,0	-	-

NH₃ - P r o c e s

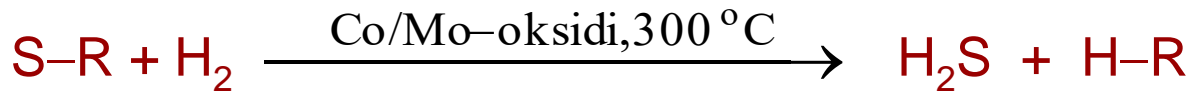
Proces proizvodnje amonijaka sastoji se od šest temeljnih, međusobno povezanih stupnjeva:

- (1) odvajanje sumporovih spojeva iz prirodnog plina,
- (2) parno reformiranje metana,
- (3) oksidacija ugljikova monoksida,
- (4) uklanjanje ugljikova dioksida,
- (5) metanacija ostatnog CO i CO₂
- (6) izravna sinteza amonijaka.

(1) Odvajanje sumporovih spojeva iz prirodnoga plina

Prirodnom plinu uklanjaju se sumporovi spojevi do udjela sumpora manjeg od 1 mg kg^{-1} , a proces se provodi u dva stupnja:

1.a. Hidrodesulfurizacija metana



Reakcijski uvjeti: tlak oko $20\cdots 40 \text{ bar}$ i temperatura $350\cdots 400^\circ\text{C}$.

1.b. Odvajanje H_2S

Sumporovodik, nastao reakcijom hidrodesulfurizacije, odvaja se najčešće reakcijom s krutim ZnO ili oksidacijom do elementarnog sumpora.

(2) Parno reformiranje metana (proizvodnja vodika)

Dobivanje sinteznog plina endotermnom reakcijom metana s vodom:



Proces reformiranja odigrava se u dva stupnja:

2.a. Primarno reformiranje

Smjesa metana i vodene pare (u molnom omjeru 3,6 / 1) predgrijava se izmjenjivačem topline s izlaznim dimnim plinom do 400 °C, zatim zagrijava u cijevnom reaktoru s Ni-katalizatorom pri 800 °C; postiže se konverzija od oko 90 %.

2.b. Sekundarno reformiranje

Reakcijska se smjesa u sljedećem cijevnom reaktoru, također uz Ni-katalizator miješa sa zrakom u omjeru s kojim se oslobađa stehiometrijski udjel N₂ u reakcijskom plinu (N₂ + 3 H₂):

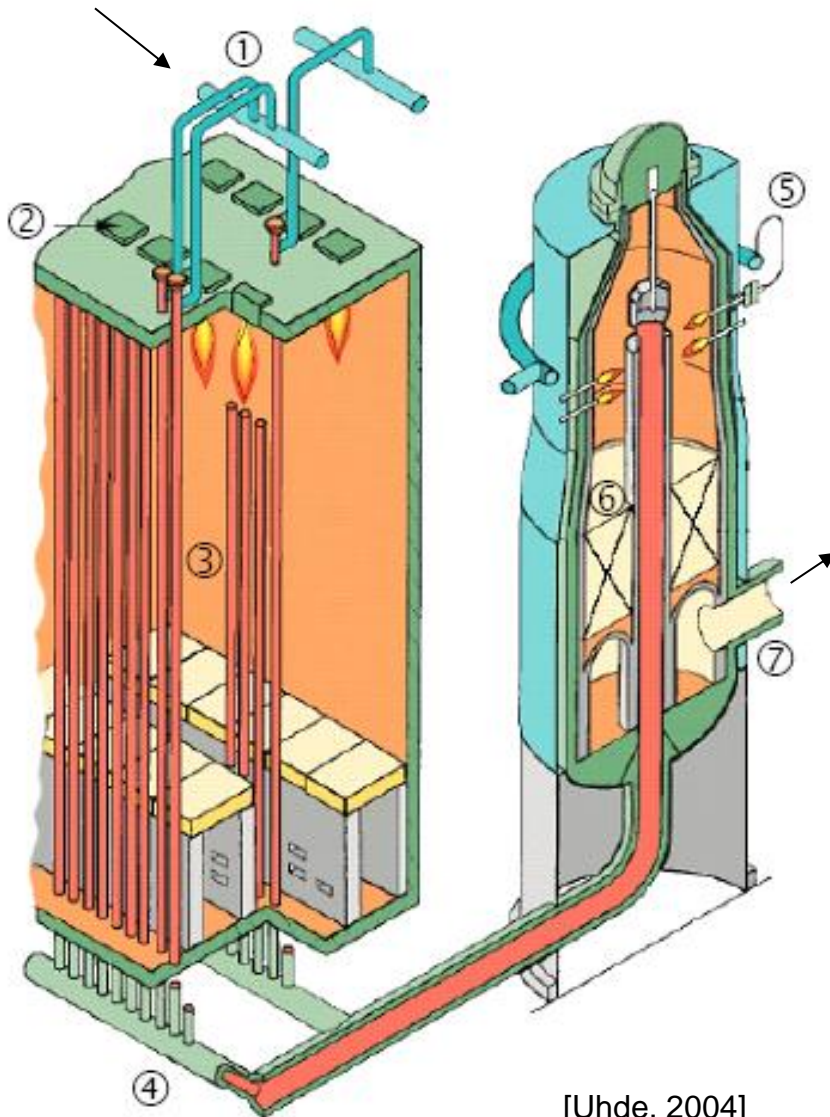


Istodobno se nastavlja reakcija metana i vode do potpune konverzije CH₄ (99,6 %).

Toplina izgaranja upotrebljava se i za proizvodnju vodene pare neophodne za pogon visokotlačnih kompresora.

Example of a reformer radiant section and a secondary reformer

- (1) inlet manifold, (2) burners, (3) reformer tubes, (4) outlet manifold, (5) process air inlet, (6) catalyst bed, (7) gas outlet



Primjer radijalne sekcije primarnog reformera i sekundarnog reformera:

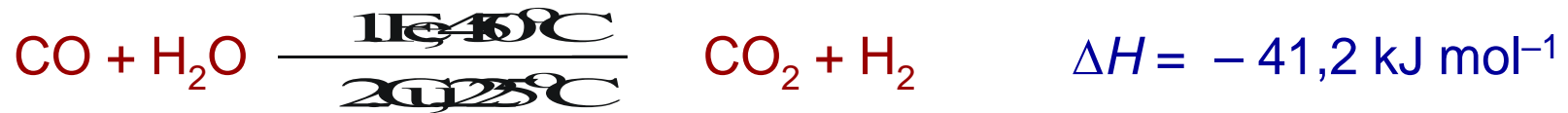
- (1) ulazni sabirnik, (2) plamenici, (3) reakcijske cijevi, (4) izlazni sabirnik, (5) ulaz procesnog zraka, (6) sloj katalizatora, (7) izlaz plina

The applied steam to carbon molar ratio (S/C ratio) is typically around 3.0; although the actual optimum ratio depends on several factors, such as the feedstock quality, purge gas recovery, primary reformer capacity, shift operation, and the plant steam balance.

In new plants, the optimum S/C ratio may be lower than 3.0.

(3) Oksidacija ugljikova monoksida

Reakcija u prethodno opisanom procesu nastalog CO, uz dobivanje dodatne količine vodika:



Proces se također provodi u dva stupnja:

3.a. Visokotemperaturna pretvorba (konverzija)

Nakon hlađenja reakcijske smjese parnog reformiranja, pretvorba CO provodi se visokotemperaturnim procesom pri oko 450°C uz Fe-katalizator, do vrlo visoke konverzije od 97 % odnosno volumnog udjela CO manjeg od 3 %.

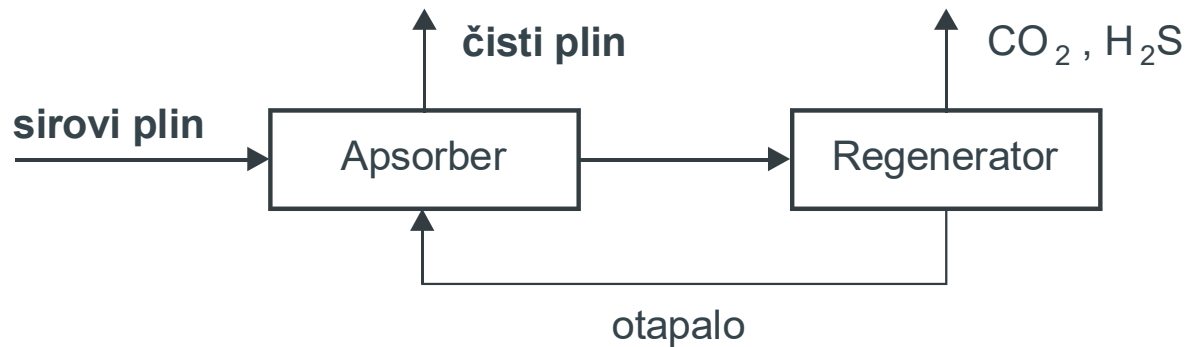
3.b. Niskotemperaturna pretvorba (konverzija)

Temperatura u reaktoru je oko 225°C , a uz Cu-katalizator volumni udjel CO se smanjuje na vrijednost manju od 0,2 %.

(4) Uklanjanje ugljikova dioksida

Izlaznim plinovima iz reaktora niskotemperaturne konverzije (CO_2 , H_2 , N_2), uklanja se CO_2 u protustrujnim kolonama s vodenom otopinom K_2CO_3 ili monoetanol-amina.

Desorpcijom se dobiva i čisti CO_2 , koji se najviše upotrebljava za proizvodnju uree.



Overview of some CO₂ removal processes

[European Commission, 2000]

Process name	Solvent/reagent + additives	CO ₂ in treated gas (ppm)
Physical absorption systems		
Purisol (NMP)	N-methyl-2-pyrrolidone	Less than 50
Rectisol	Methanol	Less than 10
Fluorsolv	Propylene carbonate	Function of pressure
Selexol	Polyethylene glycol dimethyl ether	Function of pressure
Processes with chemical reagents		
MEA	Water/monoethanolamine (20 %)	Less than 50
Promoted MEA	Water/MEA (25 – 30 %) + amine guard	Less than 50
Benfield	Water/K ₂ CO ₃ (25 – 30 %) + DEA, etc.	500 – 1000
Vetrocoke	Water/K ₂ CO ₃ + As ₂ O ₃ + glycine	500 – 1000
Catacarb	Water/K ₂ CO ₃ (25 – 30 %) + additives	500 – 1000
Lurgi	Water/K ₂ CO ₃ (25 – 30 %) + additives	500 – 1000
Carsol	Water/K ₂ CO ₃ + additives	500 – 1000
Flexsorb HP	Water/K ₂ CO ₃ amine promoted	500 – 1000
Alkazid	Water/K ₂ -methylaminopropionate	To suit
DGA	Water/diglycolamine (60 %)	Less than 100
MDEA	Water/methyl diethanolamine (40 %) + additives	100 – 500
Hybrid systems		
Sulfinol	Sulphones/DIPA	Less than 100
TEA-MEA	Triethanolamine/monoethanolamine water/sulpholane/MDEA	Less than 50

(5) Metanacija ostatnog CO i CO₂

Plinska smjesa, nakon apsorpcije ugljikova dioksida, još sadrži oko 0,2 % CO i do 500 mg kg⁻¹ CO₂, pa se procesom metanacije pri oko 300 °C uz Ni-katalizator kvantitativno reducira u metan:



(6) Proces izravne sinteze amonijaka

Izravnom sintezom amonijak se dobiva reakcijom stehiometrijske smjese dušika i vodika, uz odvajanje nastalog amonijaka.

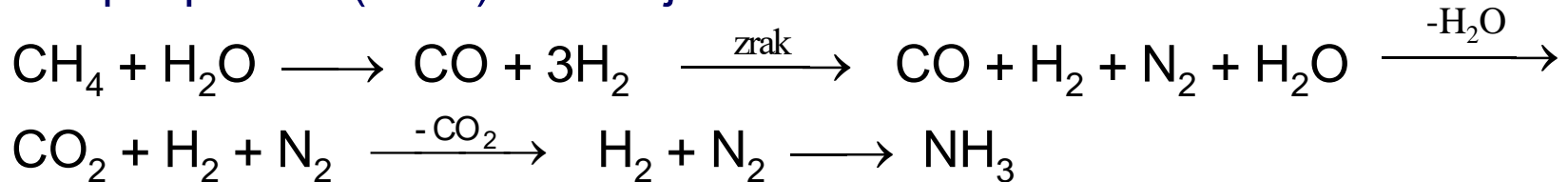
Prvi reaktori bili su izrađeni od čeličnih topovskih cijevi otpornih na visoke tlakove, ali su bili male trajnosti.

Pri visokom tlaku vodika i visokoj temperaturi procesa dolazi do redukcije ugljika u čeliku ($C + 2 H_2 \longrightarrow CH_4$) i gubitka njegovih mehaničkih svojstava. Rješenje je našao C. Bosch izradbom reaktora po načelu "cijev-u-cijevi".

Unutarnji dio izradio je od mekoga čelika s malim sadržajem ugljika i zato neosjetljivog na vodik.

Vodik je djelomice difundirao do drugoga sloja izrađenog od posebnoga, legiranog čelika, koji osigurava mehanička svojstva reaktora. Zbog blagih uvjeta, između dvaju slojeva ne dolazi do redukcije ugljika, a bočnim prolazima osiguran je izlaz nakupljenog vodika. Po tom se načelu i danas izrađuju reaktori za sintezu amonijaka.

Ukupni proces (1...6) i reakcija:



Output from ammonia production

1. Ammonia

A typical size for a single stream ammonia production plant is 1000 – 1500 tonnes/day (300000 – 500000 tonnes/year) [1, EFMA, 2000].
The product is stored if not utilised.

Commercial anhydrous ammonia has two grades of purity:

- anhydrous ammonia min. 99.7 wt-%, water content approximately 0.2 wt-%
- anhydrous ammonia min. 99.9 wt-%.

Output from ammonia production

2. Carbon dioxide

Carbon dioxide is produced in accordance with stoichiometric conversion and can be recovered for **further use** as feedstock in a **urea** plant, for use in **fertiliser production** (ODDA process) and/or **methanol** production or **liquefaction**, in the **beverage industry** or as a **coolant gas** in nuclear reactors.

There is, however, an inevitable excess of CO_2 which is released as an emission from the process.

The carbon dioxide production in the ***steam/air reforming*** of natural gas is **1.15 – 1.40 kg / kg NH_3** , dependent on the degree of air reforming (the figures do not include carbon dioxide in the combustion gases).

A CO_2/NH_3 mole ratio of 0.5 (weight ratio 1.29), the stoichiometric ratio for urea production, is obtainable in the heat exchange reformer concepts.

In ***partial oxidation*** of residual oils, CO_2 production is **2 – 2.6 kg / kg NH_3** , dependent on the feedstock C/H ratio.

Output from ammonia production

3. Sulphur

In partial oxidation, **87 – 95 % of the sulphur** content of the gasifier feed **is recovered** in a Claus unit.

4. Steam

Modern steam reforming processes can be designed with no steam export or with some export if this is favourable for the site energy balance of low/medium pressure steam.

Surplus steam is usually produced in reforming processes where the process air compressor is driven by a gas turbine and in cases when electric power is used for the main compressors and can be used as export.

Processes with gas heated primary reforming may be designed for zero steam export even though some power import or gas turbine drive steam input is needed.

The partial oxidation process will have a steam deficit if all of the compressors are driven by steam.

Razvitak procesa

Currently, about 80 % of the ammonia production capacity worldwide is provided by the well-developed steam reforming process.

High level process integration, innovative equipment design and improved catalysts are the main characteristics of ammonia plants today.

Applied processes and feed stocks in the production of ammonia

The third column shows the related share of world capacity (1990)

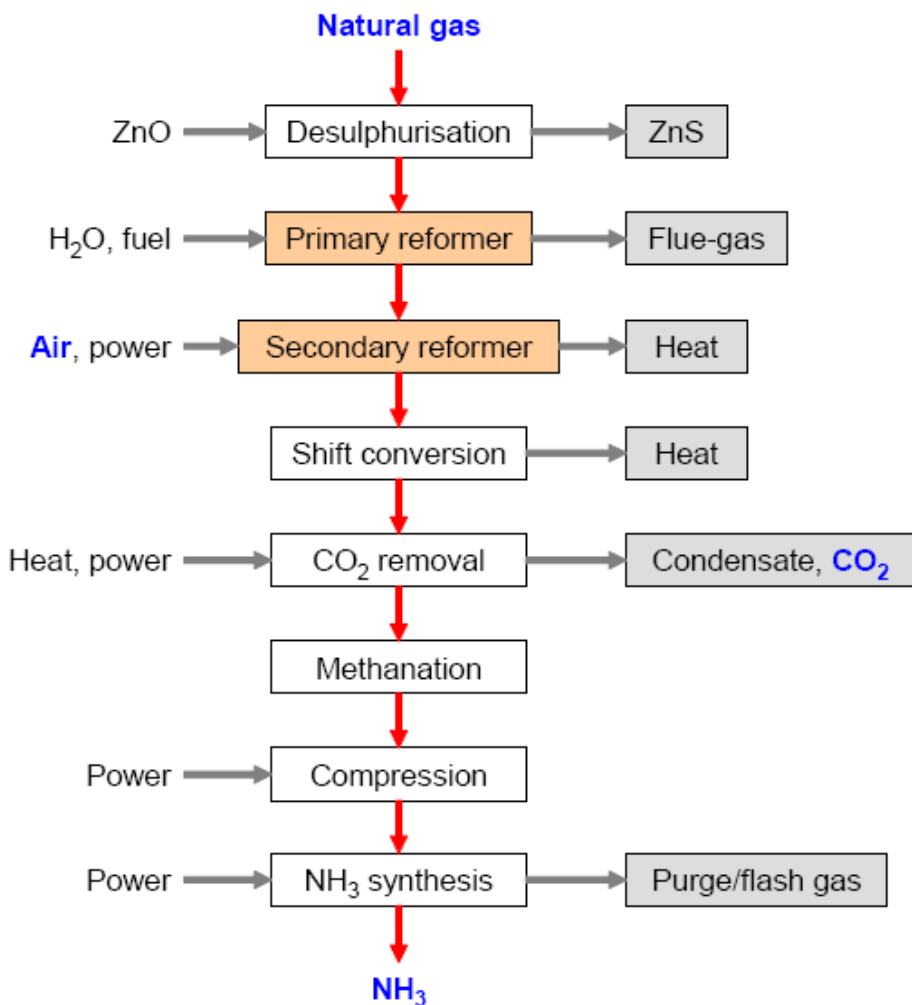
Feedstock	Process	% of world capacity
Natural gas	Steam reforming	77
Naphtha, LPG, refinery gas	Steam reforming	6
Heavy hydrocarbon fractions	Partial oxidation	3
Coke, coal	Partial oxidation	13.5
Water	Water electrolysis	0.5

Cost differences and total energy demands for ammonia production

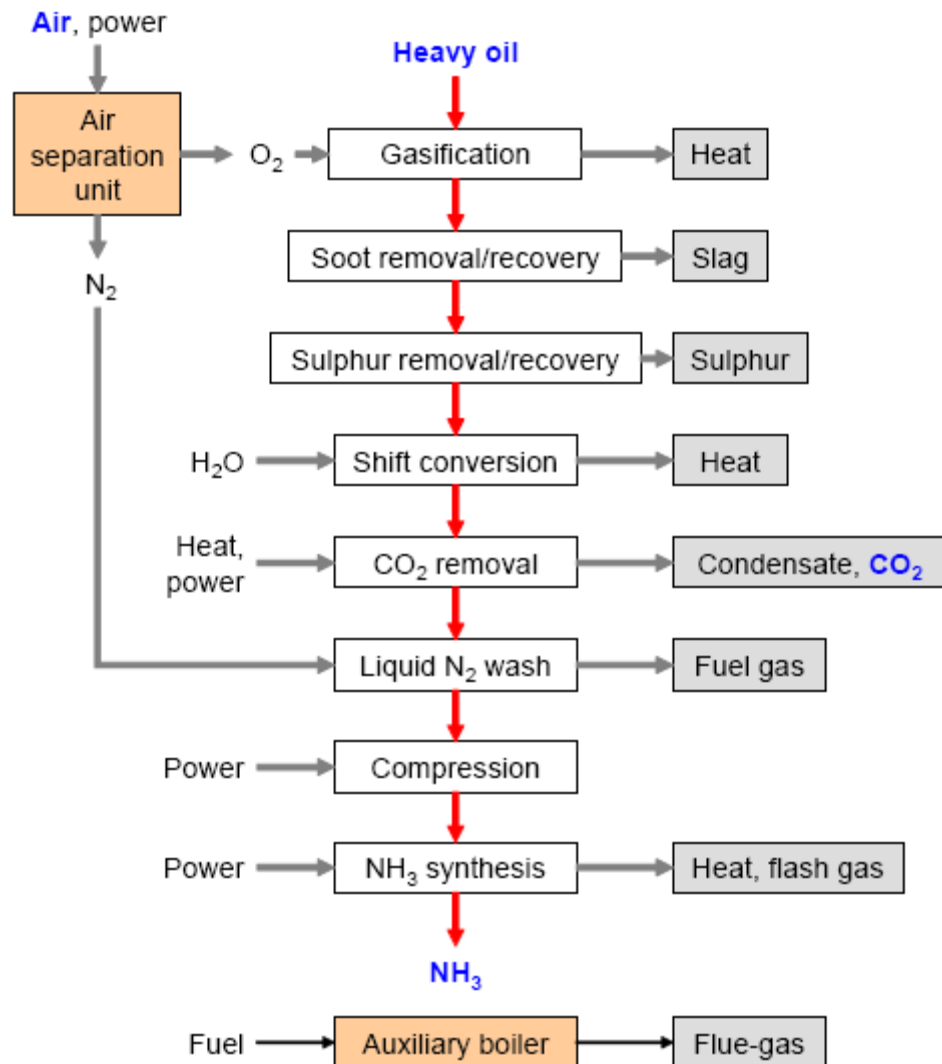
[European Commission, 1997]

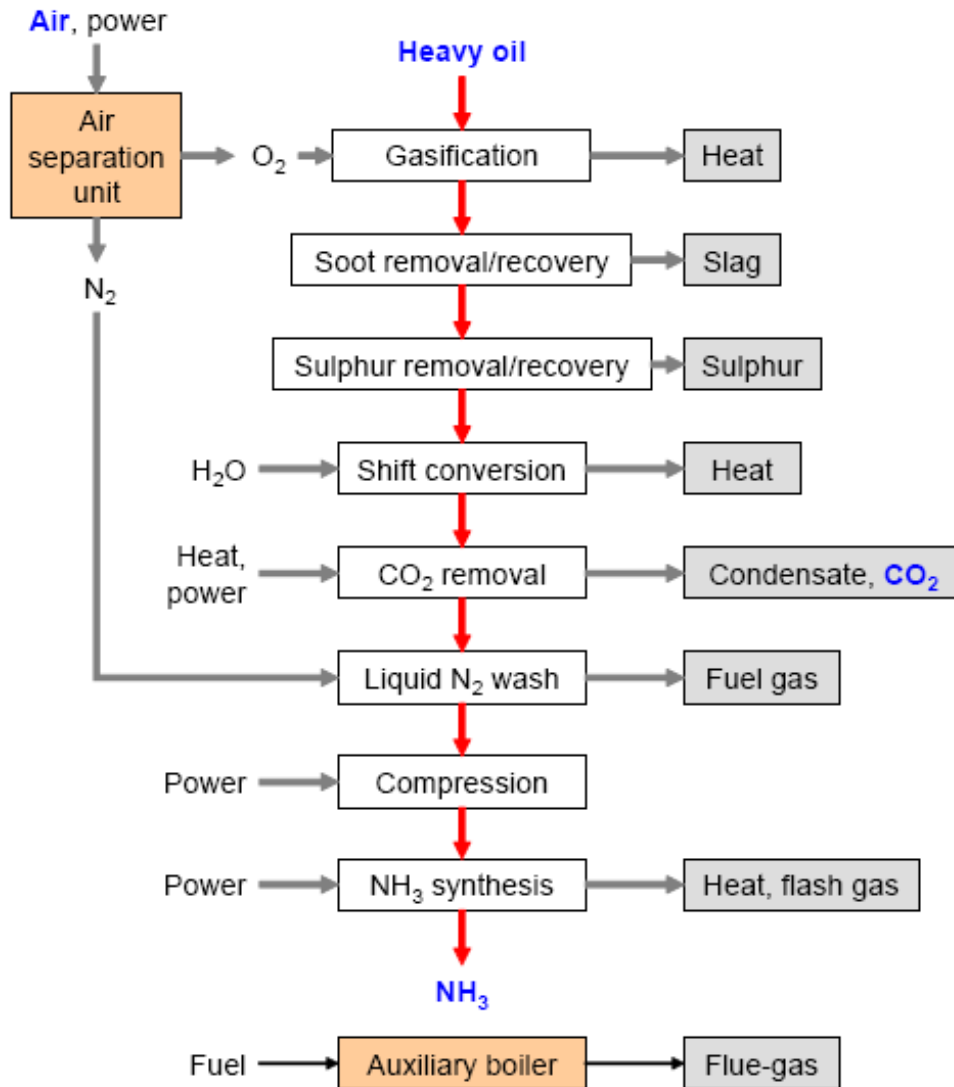
Feedstock	Process	Net primary energy consumption GJ/t NH₃ (LHV)	Relative investment
Natural gas	Steam reforming	28 ^x	1
Heavy hydrocarbons	Partial oxidation	38	1.5
Coal	Partial oxidation	48	2 – 3
^x Best achieved data			

NH₃ production by conventional steam reforming



NH₃ production by partial oxidation



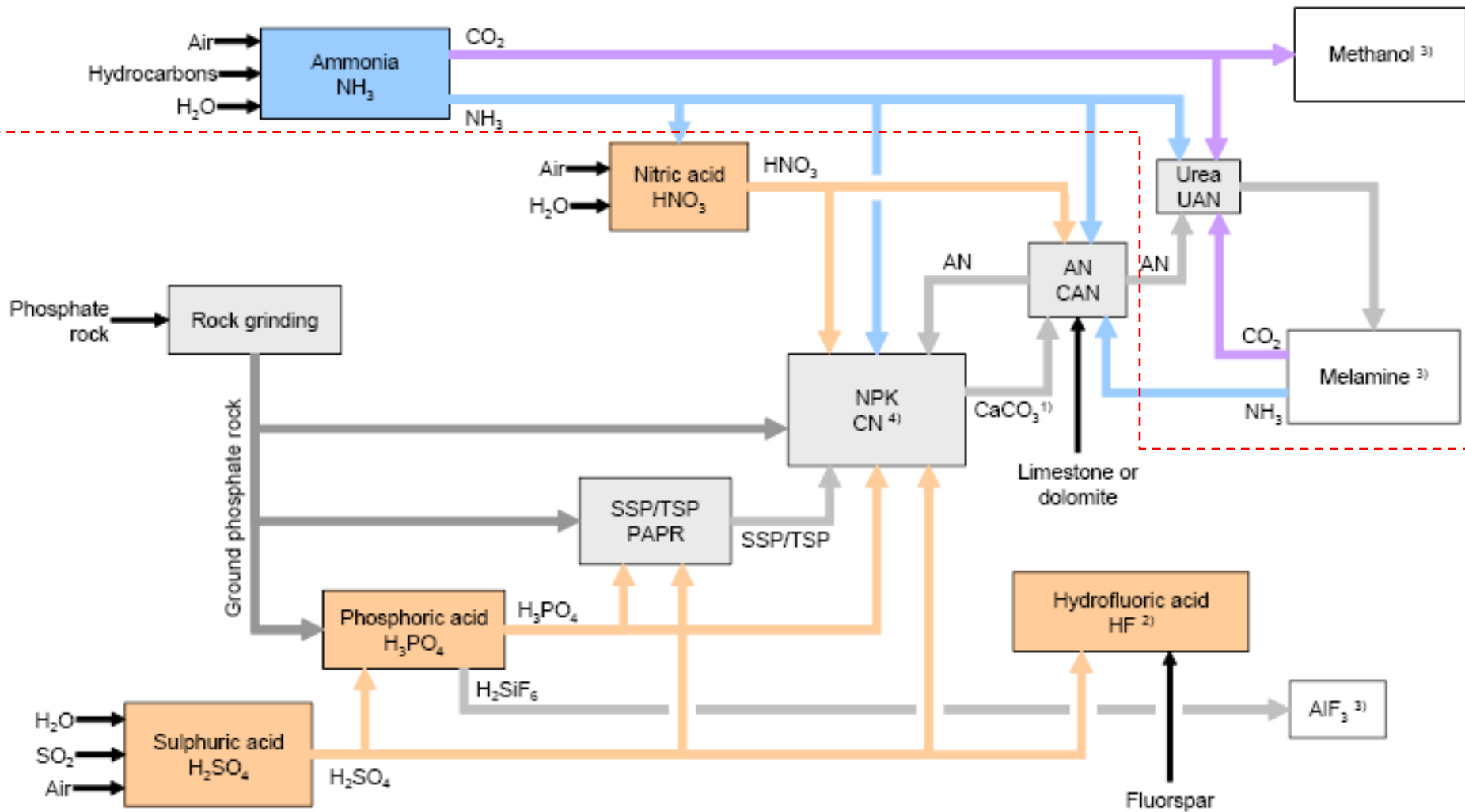


The **partial oxidation** process is used for the gasification of *heavy feedstocks* such as **residual oils** and **coal**.

Figure gives an overview of the process steps.

The process is **very flexible** and can handle the full range of hydrocarbon feedstock, **from natural gas up to the heaviest asphalt** including **waste materials** such as **plastics**.

Ammonia plants which incinerate waste require compliance with the waste incineration Directive 76/2000/EC and the **emissions of dioxins** **may be a concern**.



Overview of boundaries and links between the **Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilisers / LVIC-AAF** industries

(1) only with NPK production using the nitrophosphate route (2) not typically produced on fertiliser sites

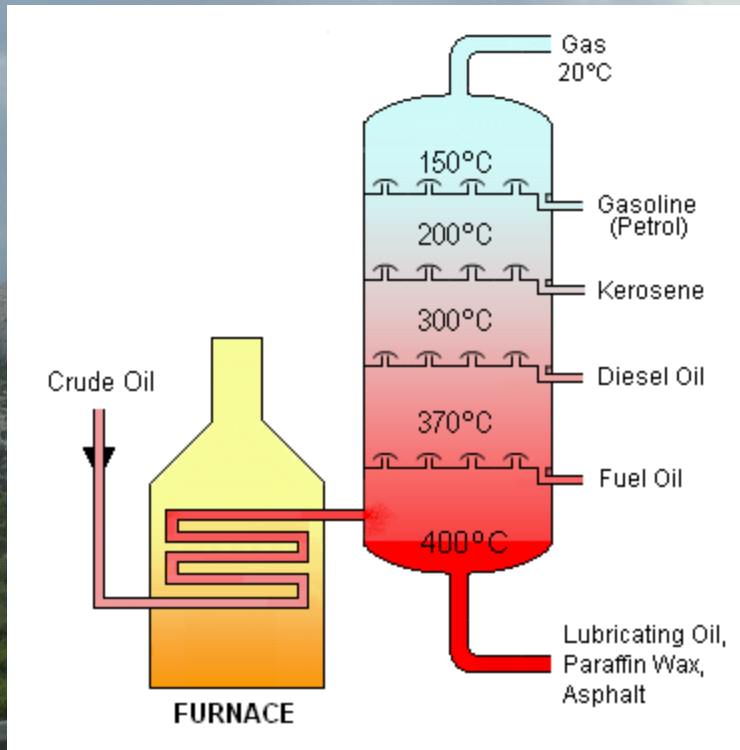
(3) not described in this document (4) CN is Ca(NO₃)₂, and is alternatively produced by neutralisation of HNO₃ with lime

Gasoline, Diesel, and LPG Technologies

In this section we will be describing the different refining technologies relating to Gasoline, Diesel and LPG. Although these are labeled as conventional technologies, refineries today have become increasingly more efficient and efforts across the globe are being made to invest in better performing technologies and processes that save energy and decrease each refineries environmental impact whilst meeting increasingly more stringent fuel product specifications.

As can be seen below a basic refinery typically produces a variety of products including: LPG; petrochemicals; gasoline; jet fuel; paraffin for lighting and heating; lubricating oils, waxes and polishes; heavy fuel oil, and bitumen for roads and roofing.

Products Produced by Refineries



Different Refining Configurations Related To Automotive Fuel Qualities

A refinery's configuration refers to the type, size, number of process technologies and facilities employed, and the flow sequence.

Refinery configurations depend on what crude oil quality, product mix and quality, and environmental, safety, economic or other constraints were specified with its design. No two refineries are exactly alike, but refineries can be characterized into generic groups defined by the availability of the technologies.

A refinery's complexity is typically referred to within four configurations. These configurations are listed in the table below together with their available process technologies and their yields.

Refining Configurations and Their Yields

Configuration Group & Process Technologies	Product & Yield (vol %)				Comments
	Gas	Gasoline	Diesel	Fuel Oil	
Topping <ul style="list-style-type: none"> • Crude Distillation 	2	32	30	37	<ul style="list-style-type: none"> • Product quality and volume is dependent on crude oil source. • Distillate contains lots of heavy products. • Gasoline has low octane value.
Hydroskimming <ul style="list-style-type: none"> • Crude distillation • Hydrotreating • Reforming 	3	28	30	37	<ul style="list-style-type: none"> • Product quality and volume is dependent on crude oil source. It allows refiners to adjust product slate (gasoline instead of naphtha). • Provides new possibilities to improve fuel quality, especially for gasoline. • Sulphur removal.
Conversion <ul style="list-style-type: none"> • Crude distillation • Hydrotreating • Reforming • FCC • Some upgrade units 	3	49	30	17	<ul style="list-style-type: none"> • Flexibility in final production. • High quality products.
Deep Conv/Complex <ul style="list-style-type: none"> • Crude distillation • Hydrotreating • reforming • FCC • Many upgrade units 	3	47	43	4	<ul style="list-style-type: none"> • Addition of coking allows minimal production of low valued fuel oil.

Refineries are comprised of a number of individual technology based processing facilities with varying objectives, and integrated as necessary to meet product targets.

The types, size, number and flow sequence of a specific refinery (i.e., refinery configuration) will vary depending on crude oil quality, required product mix and quality, and environmental, safety, economic or other constraints.

The major refinery processing steps or technologies can be categorized into six functional areas: separation, conversion or cracking, combination, reformulation, treating and other specialty or support operations.

All these steps and technologies are included in the figure below that illustrates a complex refinery configuration.

Processing units used in refineries

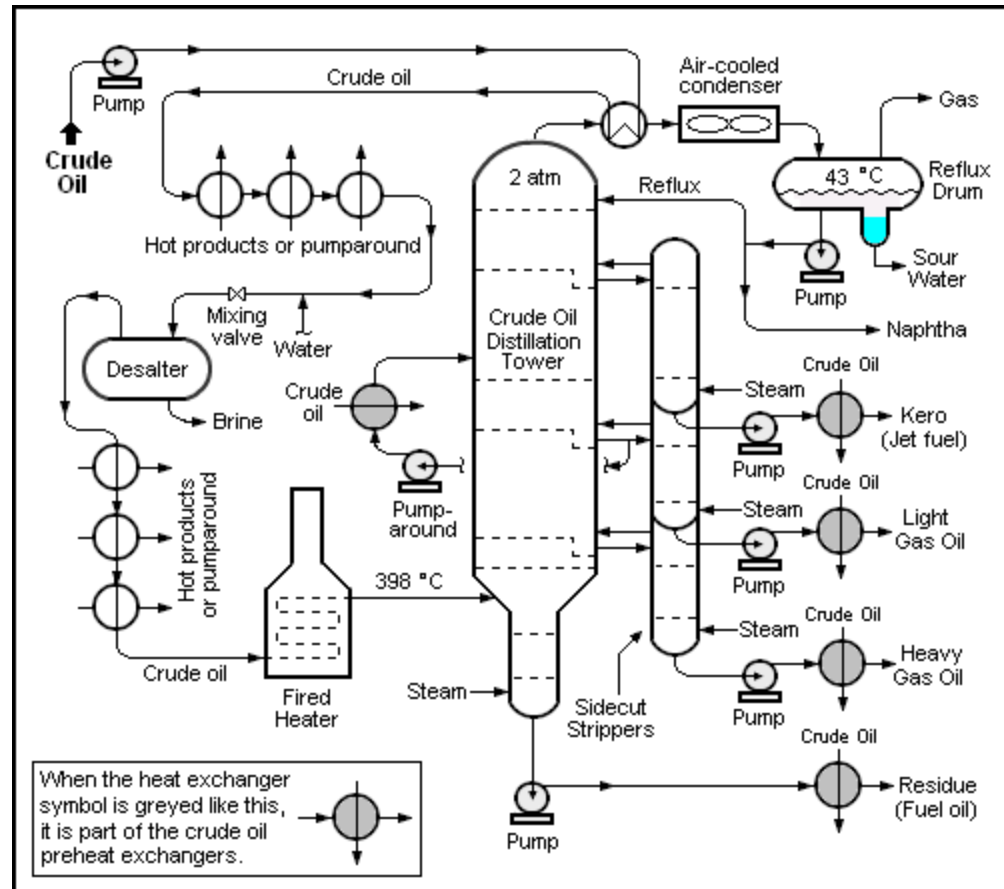
- [Crude Oil Distillation unit](#): Distills the incoming crude oil into various fractions for further processing in other units.
- [Vacuum Distillation](#) unit: Further distills the residue oil from the bottom of the crude oil distillation unit. The vacuum distillation is performed at a pressure well below atmospheric pressure.
- [Naphtha Hydrotreater](#) unit: Uses [hydrogen](#) to desulfurize the [naphtha](#) fraction from the crude oil distillation or other units within the refinery.
- [Catalytic Reforming](#) unit: Converts the desulfurized naphtha molecules into higher-octane molecules to produce *reformate*, which is a component of the end-product gasoline or petrol.
- [Alkylation](#) unit: Converts isobutane and butylenes into *alkylate*, which is a very high-octane component of the end-product gasoline or petrol.
- [Isomerization](#) unit: Converts linear molecules such as normal pentane into higher-octane branched molecules for blending into the end-product gasoline. Also used to convert linear normal butane into isobutane for use in the alkylation unit.
- [Distillate Hydrotreater](#) unit: Uses hydrogen to desulfurize some of the other distilled fractions from the crude oil distillation unit (such as diesel oil).
- [Merox](#) (mercaptan oxidizer) or similar units: Desulfurize LPG, kerosene or jet fuel by oxidizing undesired [mercaptans](#) to organic [disulphides](#).
- [Amine gas treater](#), [Claus unit](#), and tail gas treatment for converting [hydrogen sulphide](#) gas from the hydrotreaters into end-product elemental sulphur. The large majority of the 64,000,000 metric tons of sulphur produced worldwide in 2005 was byproduct sulfur from petroleum refining and [natural gas processing](#) plants.
- [Fluid catalytic cracking](#) (FCC) unit: Upgrades the heavier, higher-boiling fractions from the crude oil distillation by converting them into lighter and lower boiling, more valuable products.
- [Hydrocracker](#) unit: Uses hydrogen to upgrade heavier fractions from the crude oil distillation and the vacuum distillation units into lighter, more valuable products.
- [Visbreaker](#) unit upgrades heavy residual oils from the vacuum distillation unit by thermally cracking them into lighter, more valuable reduced viscosity products.
- [Delayed coking](#) and [Fluid coker](#) units: Convert very heavy residual oils into end-product petroleum coke as well as naphtha and diesel oil by-products.

Auxiliary facilities required in refineries

- [Steam reformer](#) unit: Converts natural gas into hydrogen for the hydrotreaters and/or the hydrocracker.
- [Sour water stripper](#) unit: Uses steam to remove hydrogen sulfide gas from various wastewater streams for subsequent conversion into end-product sulfur in the Claus unit.
- Utility units such as [cooling towers](#) for furnishing circulating cooling water, [steam generators](#), instrument air systems for pneumatically operated [control valves](#) and an [electrical substation](#).
- Wastewater collection and treating systems consisting of [API separators](#), [dissolved air flotation](#) (DAF) units and some type of further treatment (such as an [activated sludge](#) biotreater) to make the wastewaters suitable for reuse or for disposal.^[9]
- Liquefied gas (LPG) storage vessels for propane and similar gaseous fuels at a pressure sufficient to maintain them in liquid form. These are usually spherical vessels or *bullets* (horizontal vessels with rounded ends).
- Storage tanks for crude oil and finished products, usually vertical, cylindrical vessels with some sort of vapour emission control and surrounded by an earthen berm to contain liquid spills.



Schematic flow diagram of a typical crude oil distillation unit as used in petroleum crude oil refineries





Hydrogen Applications in Refineries

Hydrogen demand will increase in the upcoming years as a result of stricter environmental legislation, more extensive processing of residues and higher diesel demand compared with gasoline.

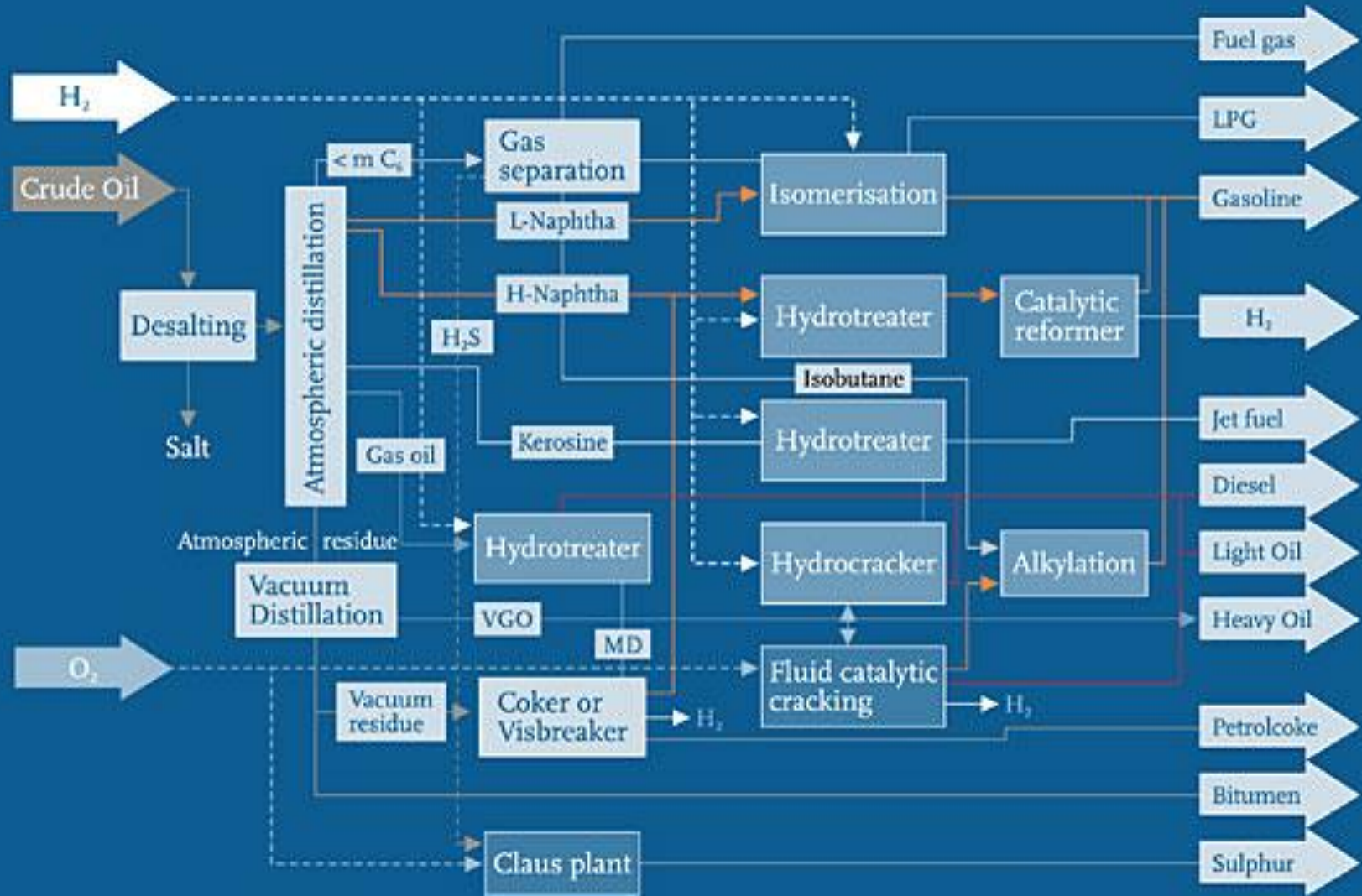
There are various hydrotreating processes in a refinery.

To name only a few of them:

- **Hydrodesulfurization**: sulfur compounds are hydrogenated to hydrogen sulfide H_2S as feed for Claus plants
- **Hydroisomerization**: normal paraffins are converted into iso-paraffins to improve the product properties (e.g. RON)
- **Dearomatization**: aromatics are hydrogenated to cycloparaffins or alkanes
- **Hydrocracking**: long-chain hydrocarbons are cracked to shorter chains in the gasoline range

Hydrogen Applications in Refineries

Basic flow diagram of a refinery

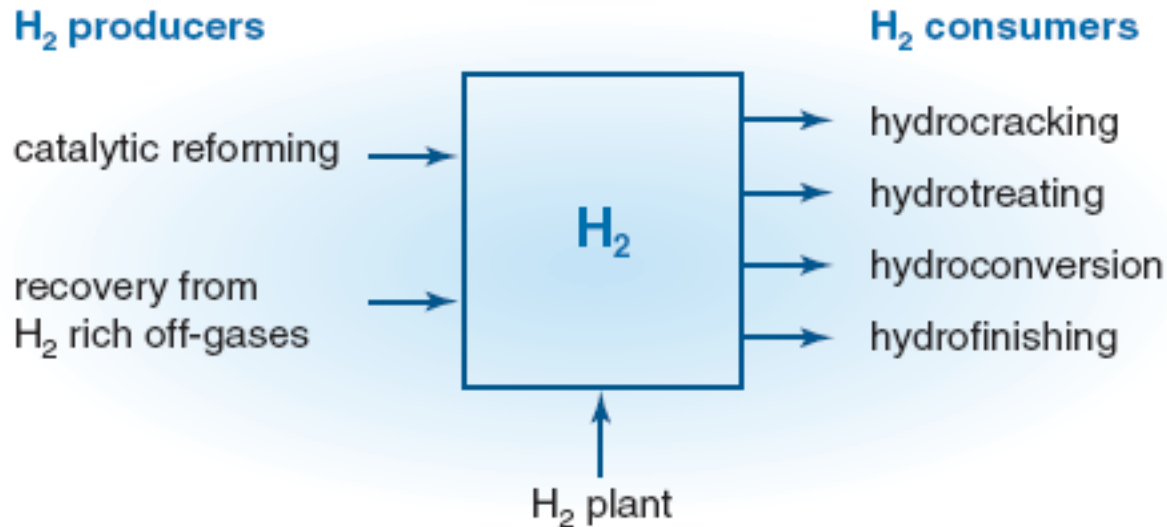


Hydrogen Applications in Refineries

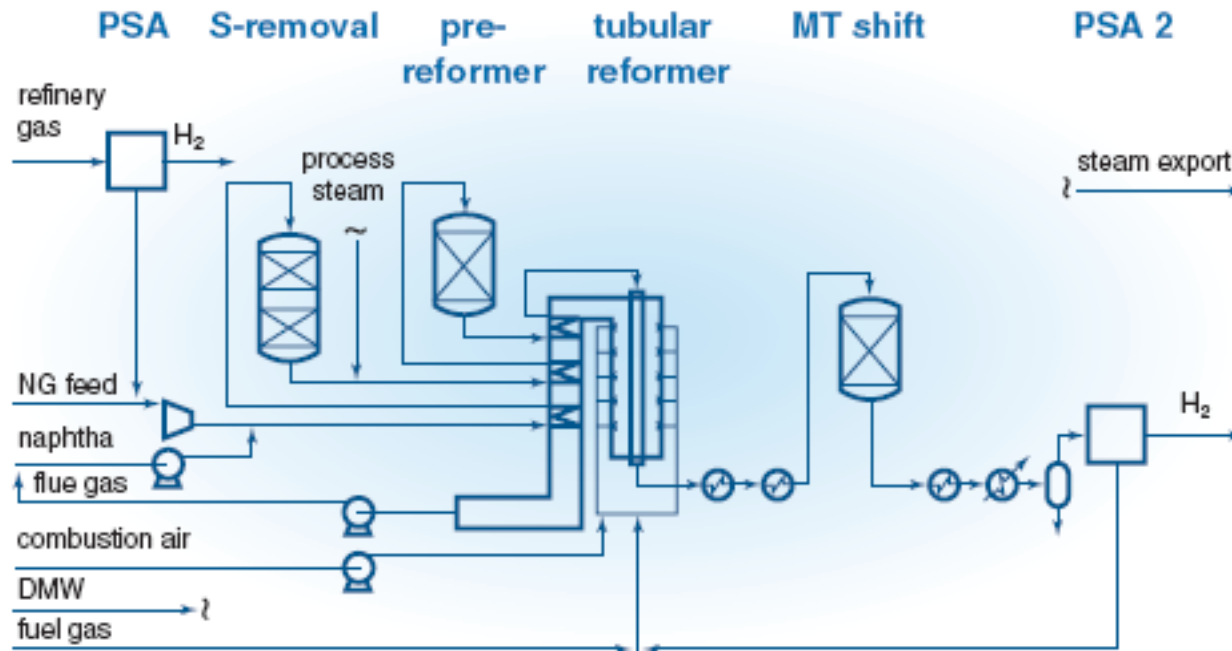
Hydrogen volumes consumed increasingly exceed those produced in a platformer (reformiranje) and have to be supplemented by other sources.

Main processes for hydrogen on-site supply:

- Steam reforming of methane or other hydrocarbons
- Recovery from refinery off-gases
- Recovery from syngas
- Gasification of oil refining residues



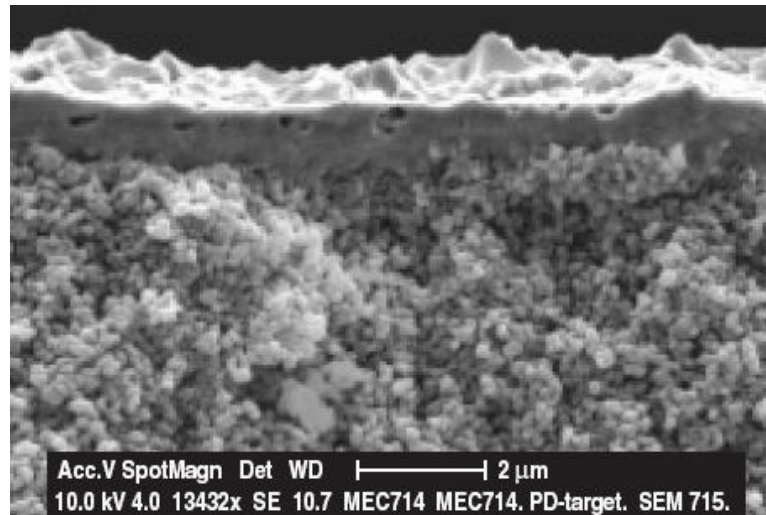
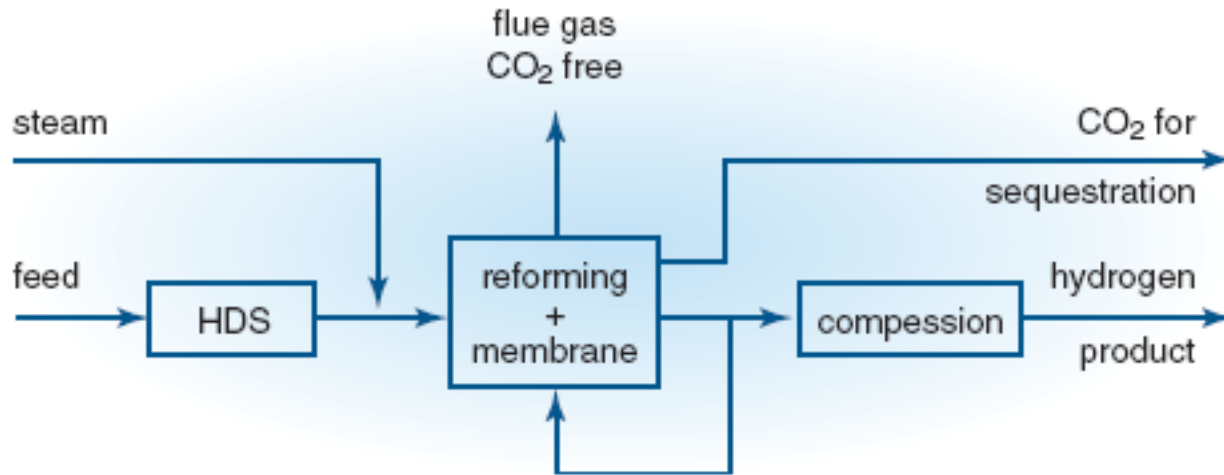
Schematic of refinery hydrogen balance.



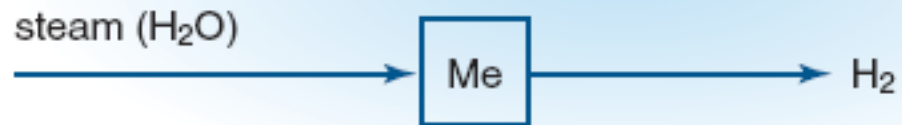
Process lay-out of a typical multi feedstock H₂-plant (Haldor Topsoe).

A typical *process lay-out* of a feedstock flexible hydrogen plant operating at 25 bar on refinery gas, natural gas and naphtha. Refinery gas, containing large amounts of hydrogen, is sent to a **PSA unit** where pure hydrogen is extracted. The off-gas from the PSA, containing non-converted methane, is compressed and used as feed in the hydrogen plant. In this way, low grade refinery gas is used as feed to a hydrogen plant and thereby substituting more expensive natural gas or naphtha. PSA off-gas is mixed with natural gas or vaporized naphtha, and the gas mixture is preheated, **desulfurized** (over **CoMo-catalyst and ZnO**), mixed with process steam and further heated before entering the adiabatic prereformer. Typical inlet temperatures are in the range 450–550 °C, depending on feedstock and the steam to carbon ratio. The prereformed gas is then heated to 650 °C before entering the **tubular reformer** where final conversion to equilibrium of methane into hydrogen, carbon monoxide and carbon dioxide takes place at 850–950 °C, depending on lay-out. The reformed gas is cooled by producing steam before entering the **shift converter**, typically containing a **medium temperature shift (MTS)** (210–330 °C). Over the **copper-based shift catalyst**, more hydrogen is produced by the conversion of carbon monoxide and steam to carbon dioxide and hydrogen. The shifted gas is cooled to ambient temperature before entering the **second PSA unit**. The off-gas from this PSA unit is used as fuel in the tubular reformer supplemented with fuel gas.

Membrane reforming hydrogen plant with CO₂ sequestration.



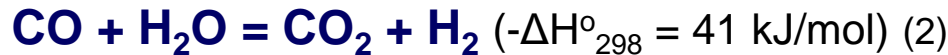
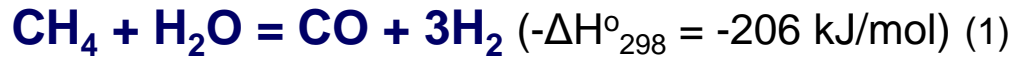
Palladium Membrane. A micron thin palladium film is deposited on a functionally designed ceramic support tube.



Cyclic process for CO₂-free hydrogen.
Me = metal.

Partial oxidation

For very large grass root hydrogen plants (in excess of about 200,000 Nm³ H₂/h), the different economies of scale with respect to tubular reformers and oxygen plants may favor the use of oxygen for partial oxidation of the hydrocarbon feed as practiced in the *autothermal reforming process*:



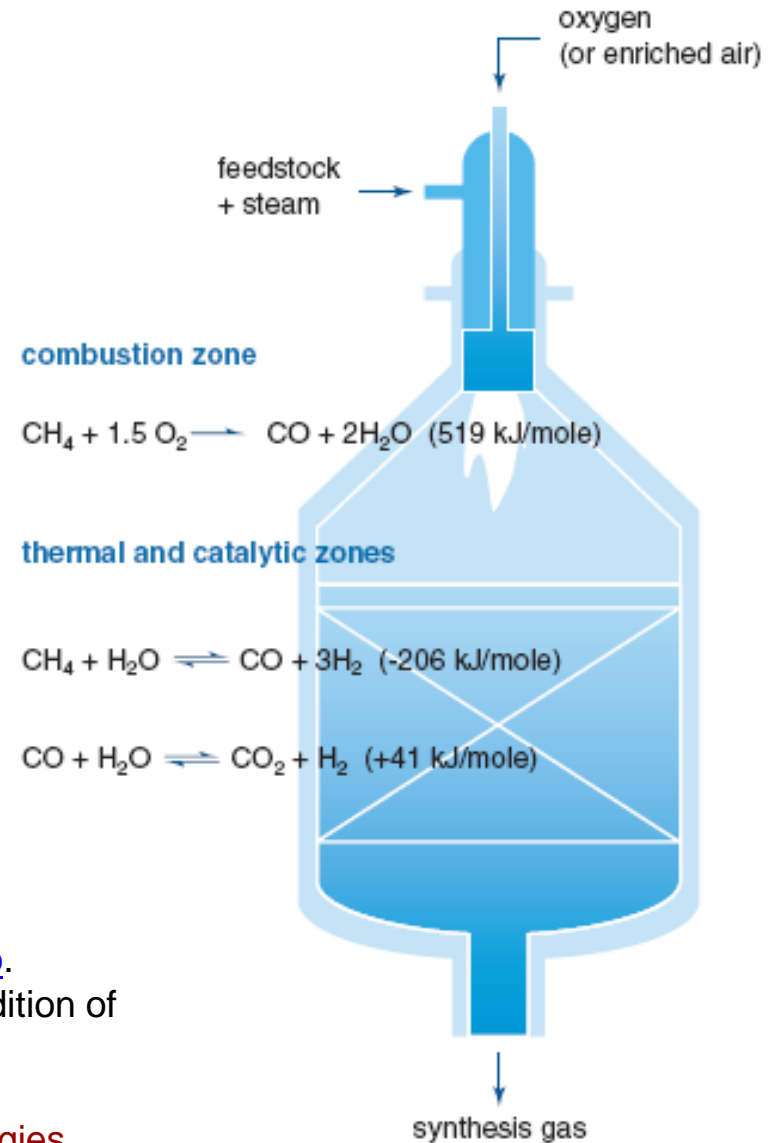
In the autothermal reforming process, the feedstock is reacted with a mixture of oxygen and steam by the use of a burner and a fixed nickel catalyst bed for the equilibration (reactions (1) and (2)) of the gas.

This results in a **lower oxygen consumption**, O₂/CH₄ = 0.5–0.6, than used in non-catalytic routes.

With the addition of steam, it is possible to adjust the H₂/CO ratio.

This cannot be achieved by non-catalytic routes because the addition of steam results in a reduction of temperature and soot formation.

On the other hand, the non-catalytic routes are the only technologies available for gasification of resid and at the non-distillate fuels.



Research Focuses on Overcoming Challenges

Although the technology for distributed natural gas reforming is advancing rapidly, several challenges remain. Capital equipment costs, as well as operation and maintenance costs, must be reduced, and process energy efficiency must be improved in order to meet hydrogen cost targets.

In order for hydrogen to be successful in the market place, it must be cost-competitive with the available alternatives. In the light-duty vehicle transportation market, this means that hydrogen needs to be available untaxed at \$2–\$3/gge (gasoline gallon equivalent). This would result in hydrogen fuel cell vehicles having the same cost to the consumer on a cost-per-mile-driven basis as a comparable conventional internal-combustion engine or hybrid vehicle.

Key research areas:

- 1. Intensifying the process (combining steps into fewer operations)**
- 2. Developing better designs to lower equipment manufacturing and maintenance costs**
- 2. Improving process efficiency by using better catalysts and better heat integration.**



Hydrogen Processes in Refineries

Hydrodesulfurization (HDS) is a *catalytic chemical process* widely used to remove sulfur (S) from natural gas and from refined petroleum products such as gasoline or petrol, jet fuel, kerosene, diesel fuel, and fuel oils.

The purpose of removing the sulfur is **to reduce the sulfur dioxide emissions** that result from using those fuels in automotive vehicles, aircraft, railroad locomotives, ships, gas or oil burning power plants, residential and industrial furnaces, and other forms of fuel combustion.

Another important reason for removing sulfur from the naphtha streams within a petroleum refinery is that **sulfur**, even in extremely low concentrations, **poisons the noble metal catalysts** (platinum and rhenium) in the *catalytic reforming units* that are subsequently used to upgrade the octane rating of the naphtha streams.

The industrial hydrodesulfurization processes include facilities for the capture and removal of the resulting hydrogen sulfide gas. In petroleum refineries, the hydrogen sulfide gas is then subsequently converted into byproduct elemental sulfur or sulfuric acid.

An HDS unit in the petroleum refining industry is also often referred to as a hydrotreater.

Hydrogen Processes in Refineries

Hydrodesulfurization (HDS)

The process chemistry

Hydrogenation is a class of chemical reactions in which the net result is the addition of hydrogen (H). **Hydrogenolysis** is a type of hydrogenation and results in the cleavage of the C-X chemical bond, where C is a carbon atom and X is a sulfur, nitrogen (N) or oxygen (O) atom. The net result of a hydrogenolysis reaction is the formation of C-H and H-X chemical bonds.

Thus, hydrodesulfurization is a hydrogenolysis reaction.

Using ethanethiol (C₂H₅SH), a sulfur compound present in some petroleum products, as an example, the hydrodesulfurization reaction can be simply expressed as



Hydrogen Processes in Refineries

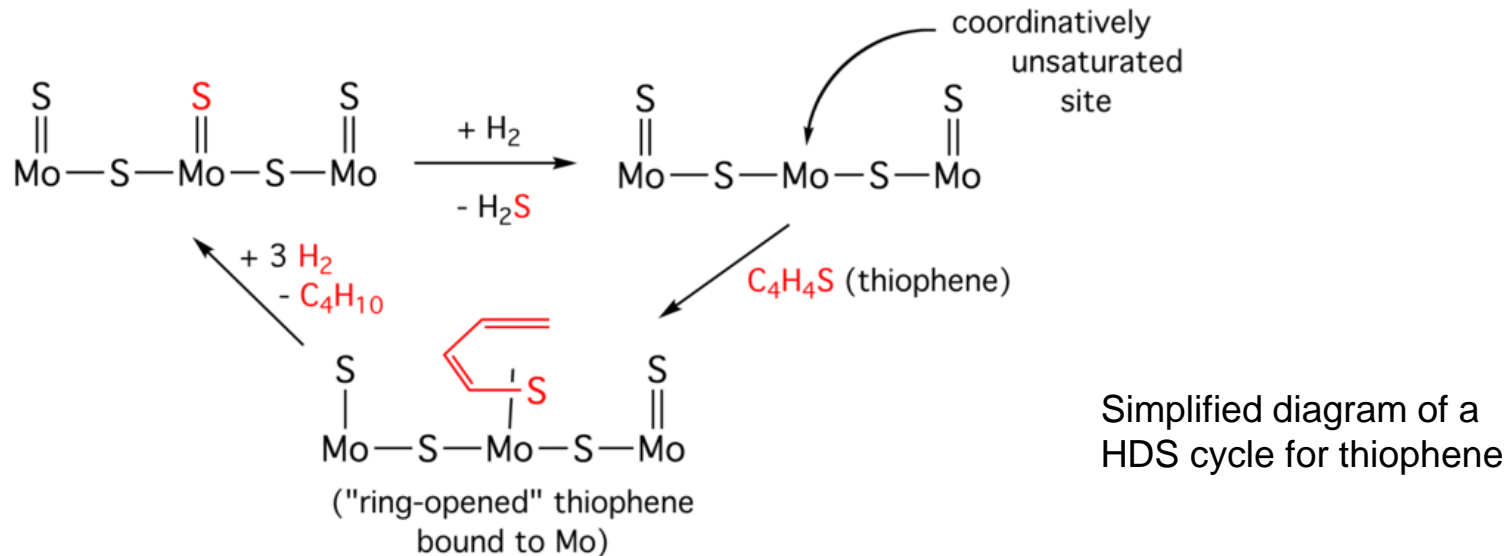
Hydrodesulfurization (HDS)

Catalysts and mechanisms

The main HDS catalysts are based on molybdenum disulfide (MoS_2) together with smaller amounts of other metals.

At the edges of the MoS_2 crystallites, the molybdenum centre can stabilize a coordinatively unsaturated site (CUS), also known as an anion vacancy.

Substrates, such as thiophene, bind to this site and undergo a series of reactions that result in both C-S scission and C=C hydrogenation. Thus, the hydrogen serves multiple roles - generation of anion vacancy by removal of sulfide, hydrogenation, and hydrogenolysis. A simplified diagram for the cycle is shown:



Simplified diagram of a HDS cycle for thiophene

Most metals catalyse HDS, but it is those at the middle of the transition metal series that are most active.

Ruthenium disulfide appears to be the single most active catalyst, but binary combinations of **Co-Mo** are also highly active. Aside from the basic cobalt-modified MoS_2 catalyst, nickel and tungsten are also used, depending on the nature of the feed. For example, **Ni-W** catalysts are more effective for hydrodenitritication (HDN).

Metal sulfides are "supported" on materials with high surface areas. A typical support for HDS catalyst is γ -alumina.

The support allows the more expensive catalyst to be more widely distributed, giving rise to a larger fraction of the MoS_2 that is catalytically active. The interaction between the support and the catalyst is an area of intense interest, since the support is often not fully inert but participates in the catalysis.

Hydrogen Processes in Refineries

Hydrodesulfurization (HDS)

Hydrodenitrogenation

The hydrogenolysis reaction is also used to reduce the nitrogen content of a petroleum stream in a process referred to as hydrodenitrogenation (HDN). The process flow is the same as that for an HDS unit.

Using pyridine (C_5H_5N), a nitrogen compound present in some petroleum fractionation products, as an example, the hydrodenitrogenation reaction has been postulated as occurring in three steps:

Pyridine + Hydrogen \rightarrow Piperidine + Hydrogen \rightarrow Amylamine + Hydrogen \rightarrow Pentane + Ammonia

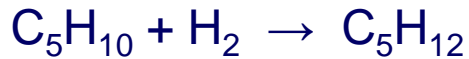


Many HDS units for desulfurizing naphthas within petroleum refineries are actually simultaneously denitrogenating to some extent as well.

Saturation of olefins

The hydrogenolysis reaction may also be used to saturate or convert olefins (alkenes) into paraffins (alkanes). The process used is the same as for an HDS unit.

Pentene + Hydrogen \rightarrow Pentane



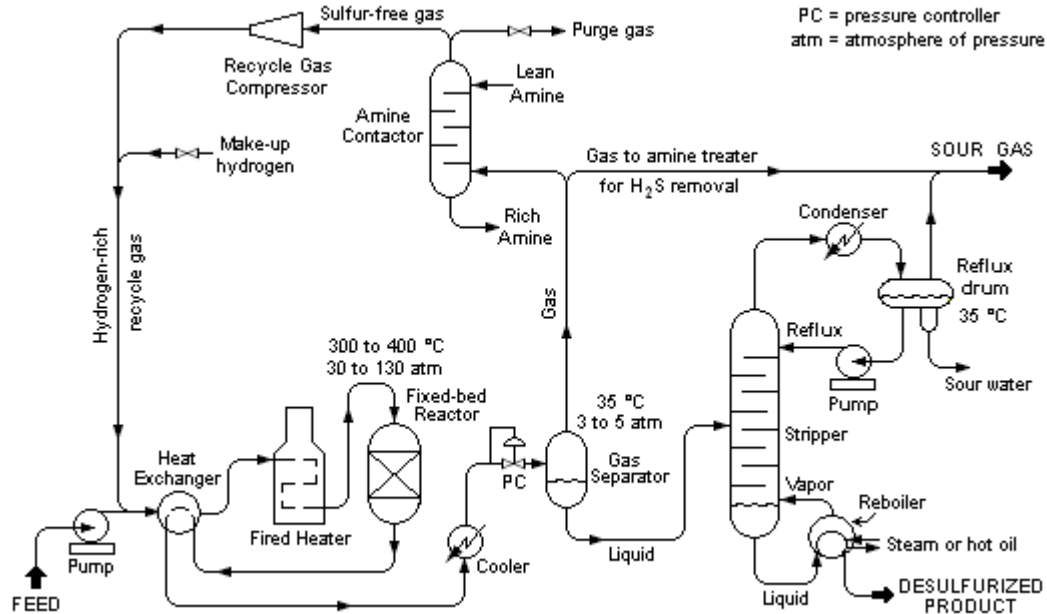
Some hydrogenolysis units within a petroleum refinery or a petrochemical plant may be used solely for the saturation of olefins or they may be used for simultaneously desulfurizing as well as denitrogenating and saturating olefins to some extent.

Hydrogen Processes in Refineries

Hydrodesulfurization (HDS)

Process description

In an industrial hydrodesulfurization unit, such as in a refinery, the hydrodesulfurization reaction takes place in a fixed-bed reactor at elevated temperatures ranging from 300 to 400 °C and elevated pressures ranging from 30 to 130 atmospheres of absolute pressure, typically in the presence of a catalyst consisting of an alumina base impregnated with cobalt and molybdenum (usually called a CoMo catalyst). Occasionally, a combination of nickel and molybdenum (called NiMo) is used, in addition to the CoMo catalyst, for specific difficult-to-treat feed stocks, such as those containing a high level of chemically bound nitrogen.



Schematic diagram of a typical Hydrodesulfurization (HDS) unit in a petroleum refinery

Hydrogen Processes in Refineries

Hydrodesulfurization (HDS)

Process description

The liquid feed (at the bottom left in the diagram) is pumped up to the required elevated pressure and is joined by a stream of hydrogen-rich recycle gas. The resulting liquid-gas mixture is preheated by flowing through a heat exchanger. The preheated feed then flows through a fired heater where the feed mixture is totally vaporized and heated to the required elevated temperature before entering the reactor and flowing through a fixed-bed of catalyst where the hydrodesulfurization reaction takes place.

The hot reaction products are partially cooled by flowing through the heat exchanger where the reactor feed was preheated and then flows through a water-cooled heat exchanger before it flows through the pressure controller (PC) and undergoes a pressure reduction down to about 3 to 5 atmospheres. The resulting mixture of liquid and gas enters the gas separator vessel at about 35 °C and 3 to 5 atmospheres of absolute pressure.

Most of the hydrogen-rich gas from the gas separator vessel is recycle gas, which is routed through an amine contactor for removal of the reaction product H_2S that it contains. The H_2S -free hydrogen-rich gas is then recycled back for reuse in the reactor section. Any excess gas from the gas separator vessel joins the sour gas from the stripping of the reaction product liquid.

The liquid from the gas separator vessel is routed through a reboiled stripper distillation tower. The bottoms product from the stripper is the final desulfurized liquid product from hydrodesulfurization unit.

The overhead sour gas from the stripper contains hydrogen, methane, ethane, hydrogen sulfide, propane, and, perhaps, some butane and heavier components. That sour gas is sent to the refinery's central gas processing plant for removal of the hydrogen sulfide in the refinery's main amine gas treating unit and through a series of distillation towers for recovery of propane, butane and pentane or heavier components. The residual hydrogen, methane, ethane, and some propane is used as refinery fuel gas. The hydrogen sulfide removed and recovered by the amine gas treating unit is subsequently converted to elemental sulfur in a Claus process unit or to sulfuric acid in a wet sulfuric acid process or in the conventional Contact Process.

Note that the above description assumes that the HDS unit feed contains no olefins. If the feed does contain olefins (for example, the feed is a naphtha derived from a refinery fluid catalytic cracker (FCC) unit), then the overhead gas from the HDS stripper may also contain some ethene, propene, butenes and pentenes, or heavier components.

It should also be noted that the amine solution to and from the recycle gas contactor comes from and is returned to the refinery's main amine gas treating unit.

Postrojenje za odsumporavanje lakog plinskog ulja i kerozina procesom hidrodesulfurizacije



Hydrogen Processes in Refineries

Hydrodesulfurization (HDS)

Amine gas treating

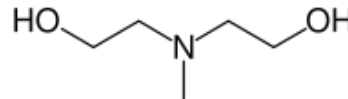
Amine gas treating, also known as gas sweetening and acid gas removal, refers to a group of processes that use aqueous solutions of various alkylamines (commonly referred to simply as amines) to remove hydrogen sulfide (H₂S) and carbon dioxide (CO₂) from gases. It is a common unit process used in refineries, and is also used in petrochemical plants, natural gas processing plants and other industries.

Processes within oil refineries or chemical processing plants that remove hydrogen sulfide and/or mercaptans are commonly referred to as sweetening processes because they result in products which no longer have the sour, foul odors of mercaptans and hydrogen sulfide.

There are many different amines used in gas treating:

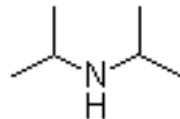
- Monoethanolamine (MEA) $\text{HO-CH}_2\text{-CH}_2\text{-NH}_2$

- Diethanolamine (DEA)

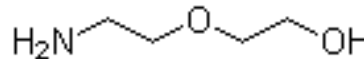


- Methyldiethanolamine (MDEA)

- Diisopropylamine (DIPA)



- Aminoethoxyethanol (diglycolamine) (DGA) $\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OH}$



The most commonly used amines in industrial plants are the alkanolamines MEA, DEA, and MDEA.

Amines are also used in many oil refineries to remove sour gases from liquid hydrocarbons such as liquified petroleum gas (LPG).

Hydrogen Processes in Refineries

Hydrodesulfurization (HDS)

Amine gas treating

Gases containing H₂S or both H₂S and CO₂ are commonly referred to as sour gases or acid gases in the hydrocarbon processing industries.

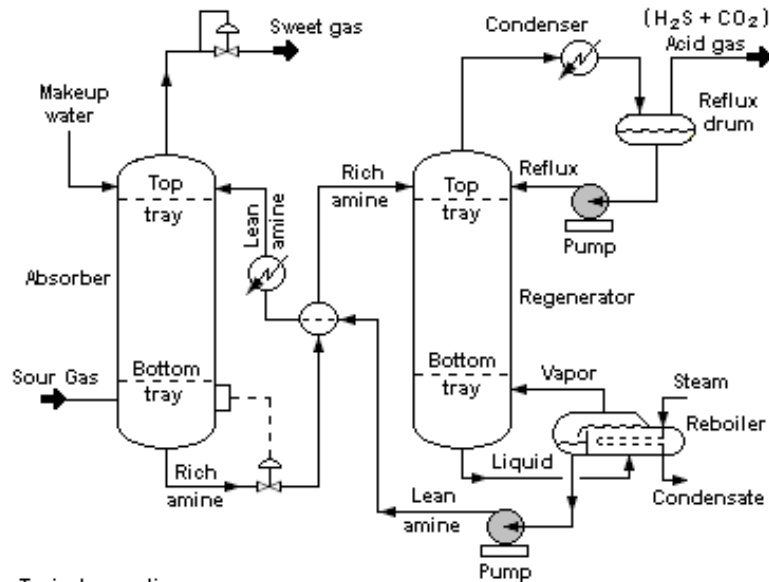
For one of the more common amines, methanolamine (MEA) denoted as RNH₂, the chemistry may be simply expressed as:



Hydrogen Processes in Refineries

Hydrodesulfurization (HDS)

Amine gas treating



Typical operating ranges

Absorber : 35 to 50 °C and 5 to 205 atm of absolute pressure
Regenerator : 115 to 126 °C and 1.4 to 1.7 atm of absolute pressure
at tower bottom

A typical amine gas treating process includes an absorber unit and a regenerator unit as well as accessory equipment.

In the absorber, the downflowing amine solution absorbs H_2S and CO_2 from the upflowing sour gas to produce a sweetened gas stream (i.e., an H_2S -free gas) as a product and an amine solution rich in the absorbed acid gases. The resultant "rich" amine is then routed into the regenerator (a stripper with a reboiler) to produce regenerated or "lean" amine that is recycled for reuse in the absorber. The stripped overhead gas from the regenerator is concentrated H_2S and CO_2 .

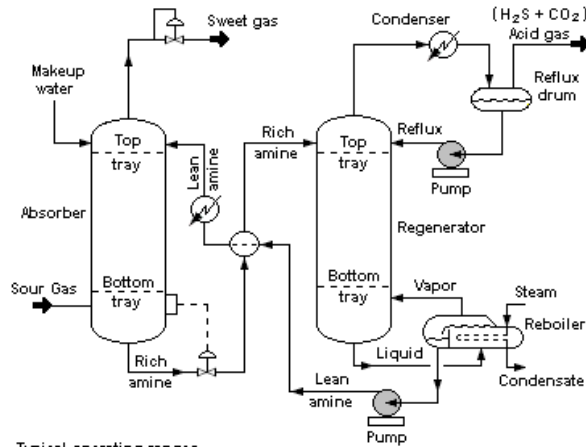
In oil refineries, that stripped gas is mostly H_2S , much of which often comes from a sulfur-removing process called hydrodesulfurization. This H_2S -rich stripped gas stream is then usually routed into a Claus process to convert it into elemental sulfur.

Another sulfur-removing process is the WSA Process which recovers sulfur in any form as concentrated sulfuric acid. In some plants, more than one amine absorber unit may share a common regenerator unit.

Hydrogen Processes in Refineries

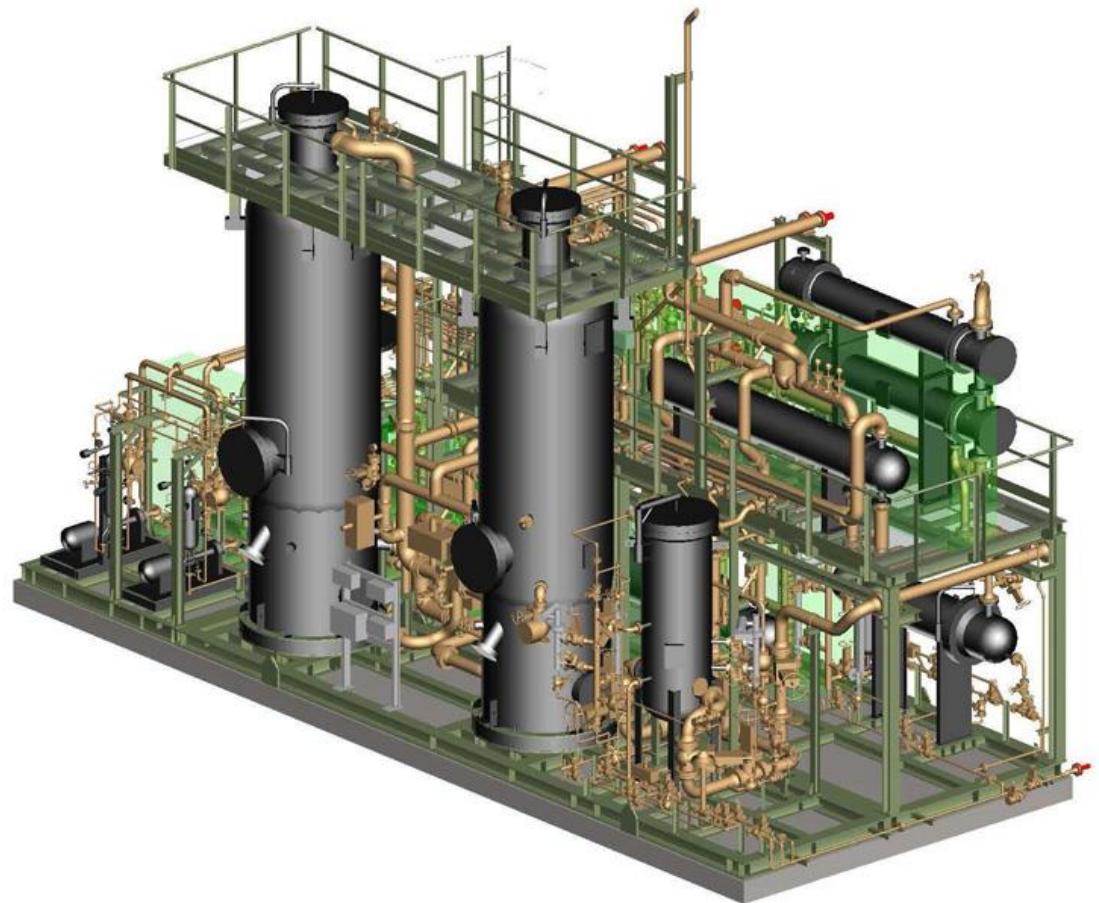
Hydrodesulfurization (HDS)

Amine gas treating



Typical operating ranges

Absorber : 35 to 50 °C and 5 to 205 atm of absolute pressure
Regenerator : 115 to 126 °C and 1.4 to 1.7 atm of absolute pressure
at tower bottom



Hydrogen Processes in Refineries

Hydrodesulfurization (HDS)

Claus process

The Claus process is the most significant gas desulfurizing process, recovering elemental sulfur from gaseous hydrogen sulfide. First patented in 1883 by the scientist Carl Friedrich Claus, the Claus process has become the industry standard.

The multi-step Claus process recovers sulfur from the gaseous hydrogen sulfide found in raw natural gas and from the by-product gases containing hydrogen sulfide derived from refining crude oil and other industrial processes. The by-product gases mainly originate from physical and chemical gas treatment units (Selexol, Rectisol, Purisol and amine scrubbers) in refineries, natural gas processing plants and gasification or synthesis gas plants. These by-product gases may also contain hydrogen cyanide, hydrocarbons, sulfur dioxide or ammonia.

Gases with an H₂S content of over 25% are suitable for the recovery of sulfur in straight-through Claus plants while alternate configurations such as a split-flow set up or feed and air preheating can be used to process leaner feeds.

Hydrogen sulfide produced, for example, in the hydro-desulfurization of refinery naphthas and other petroleum oils, is converted to sulfur in Claus plants. The overall main reaction equation is:



In fact, the vast majority of the 64,000,000 metric tons of sulfur produced worldwide in 2005 was byproduct sulfur from refineries and other hydrocarbon processing plants. Sulfur is used for manufacturing sulfuric acid, medicine, cosmetics, fertilizers and rubber products. Elemental sulfur is used as fertilizer and pesticide.

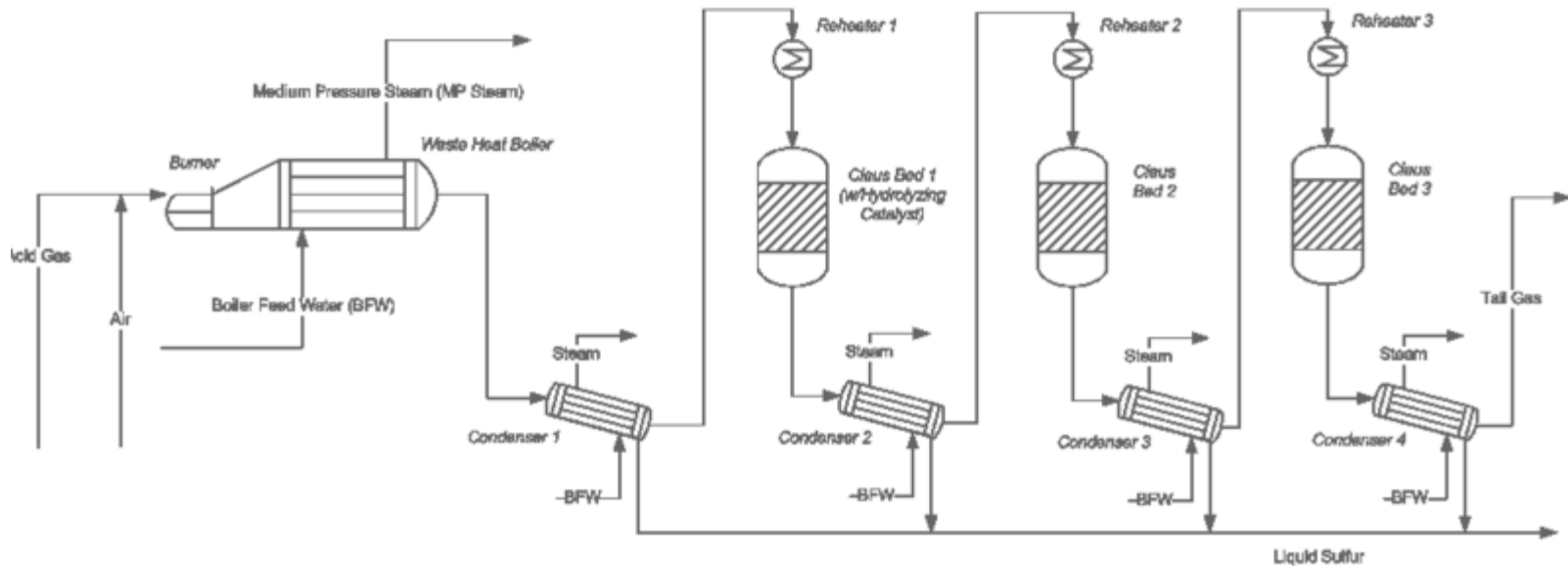
Hydrogen Processes in Refineries

Hydrodesulfurization (HDS)

Claus process

Process description

Sulfur Recovery Unit
Straight-Through 3-Bed Claus Plant



The Claus technology can be divided into two process steps, thermal and catalytic.

Hydrogen Processes in Refineries

Hydrodesulfurization (HDS)

Claus process

1. In the thermal step, hydrogen sulfide-laden gas reacts in a substoichiometric combustion at temperatures above 850 °C such that elemental sulfur precipitates in the downstream process gas cooler.



This is a strongly exothermic free-flame total oxidation of hydrogen sulfide generating sulfur dioxide that reacts away in subsequent reactions. The most important one is the Claus reaction:



The overall equation is:



This equation shows that in the thermal step alone two-thirds of the hydrogen sulfide is converted to sulfur.

Gases containing ammonia, such as the gas from the refinery's sour water stripper (SWS), or hydrocarbons are converted in the burner muffle. Sufficient air is injected into the muffle for the complete combustion of all hydrocarbons and ammonia.

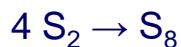
The air to the acid gas ratio is controlled such that in total 1/3 of all hydrogen sulfide (H_2S) is converted to SO_2 .

This ensures a stoichiometric reaction for the Claus reaction in the second catalytic step.

The separation of the combustion processes ensures an accurate dosage of the required air volume needed as a function of the feed gas composition. To reduce the process gas volume or obtain higher combustion temperatures, the air requirement can also be covered by injecting pure oxygen.

Usually, 60 to 70% of the total amount of elemental sulfur produced in the process are obtained in the thermal process step.

The sulfur forms in the thermal phase as highly reactive S_2 diradicals which combine exclusively to the S_8 allotrope:

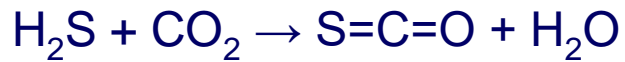


Hydrogen Processes in Refineries

Hydrodesulfurization (HDS)

Claus process

Other chemical processes taking place in the thermal step of the Claus reaction are:



Hydrogen Processes in Refineries

Hydrodesulfurization (HDS)

Claus process

2. The Claus reaction continues in the catalytic step with activated aluminum (III) or titanium (IV) oxide, and serves to boost the sulfur yield. More hydrogen sulfide (H_2S) reacts with the SO_2 formed during combustion in the reaction furnace in the Claus reaction, and results in gaseous, elemental sulfur.



This sulfur can be S_6 , S_7 , S_8 or S_9 .

The catalytic recovery of sulfur consists of three substeps: heating, catalytic reaction and cooling plus condensation. These three steps are normally repeated a maximum of three times. Where an incineration or tail-gas treatment unit (TGTU) is added downstream of the Claus plant, only two catalytic stages are usually installed.

The typically recommended operating temperature of the first catalyst stage is 315°C to 330°C (bottom bed temperature). The high temperature in the first stage also helps to hydrolyze COS and CS_2 , which is formed in the furnace and would not otherwise be converted in the modified Claus process.

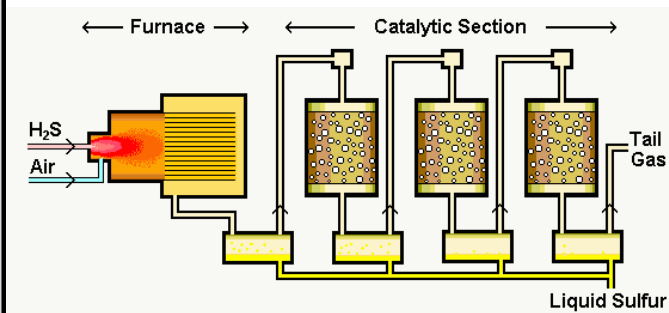
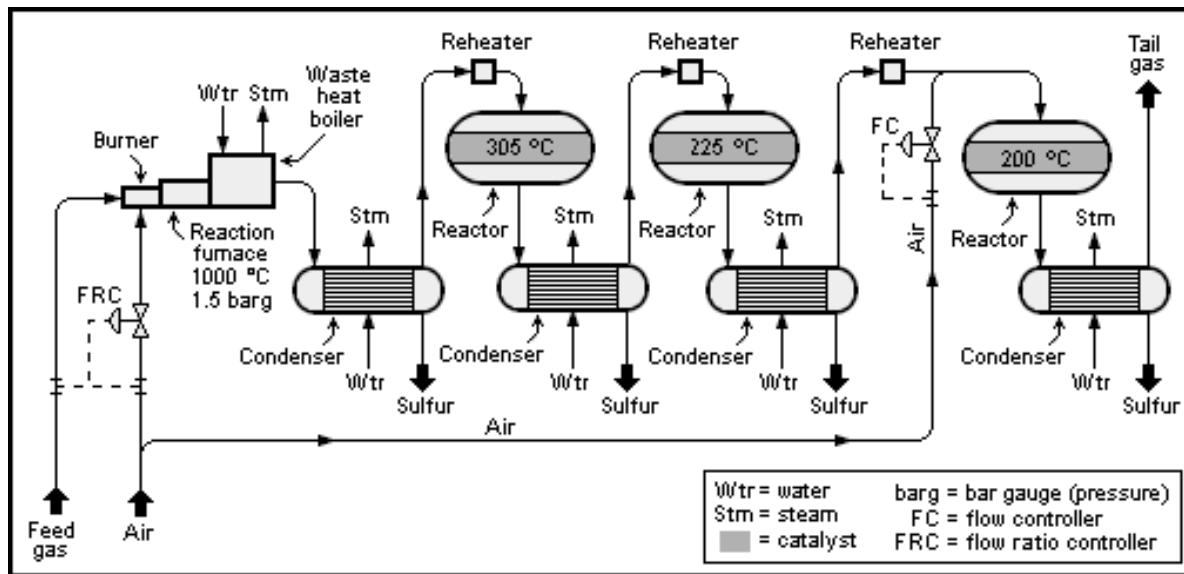
The catalytic conversion is maximized at lower temperatures, but care must be taken to ensure that each bed is operated above the dew point of sulfur. The operating temperatures of the subsequent catalytic stages are typically 240°C for the second stage and 200°C for the third stage (bottom bed temperatures).

In the sulfur condenser, the process gas coming from the catalytic reactor is cooled to between 150 and 130°C . The condensation heat is used to generate steam at the shell side of the condenser.

Before storage, liquid sulfur streams from the process gas cooler, the sulfur condensers and from the final sulfur separator are routed to the degassing unit, where the gases (primarily H_2S) dissolved in the sulfur are removed.

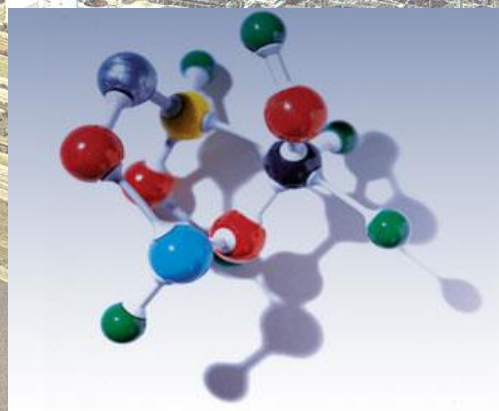
The tail gas from the Claus process still containing combustible components and sulfur compounds (H_2S , H_2 and CO) is either burned in an incineration unit or further desulfurized in a downstream tail gas treatment unit.



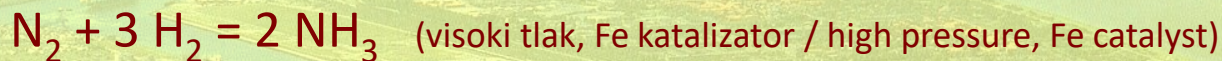


Catalyst developing trends – Industrial catalysis

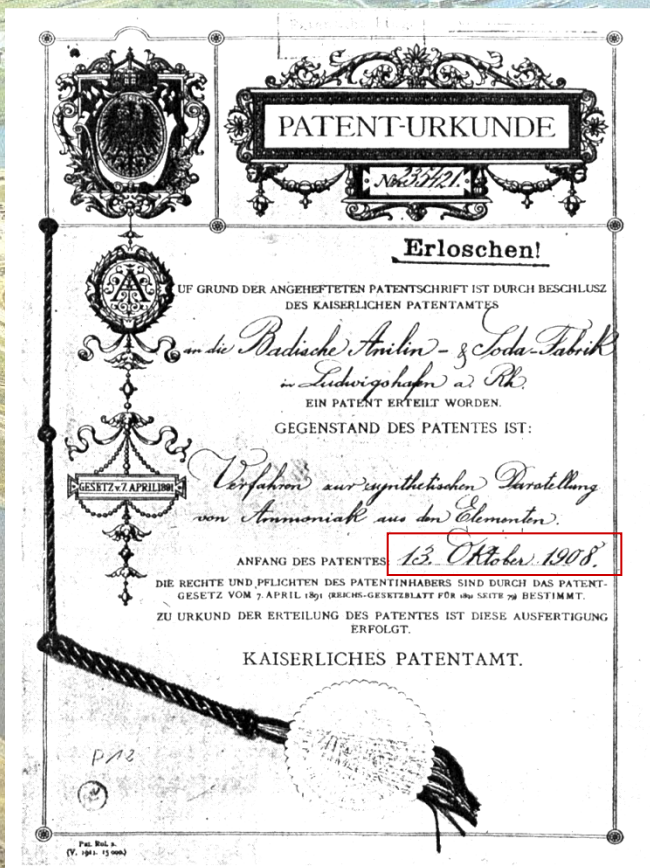
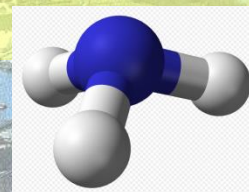
- about 90 % of all chemical processes use catalysts
- 15 - 20 % of GNP in industrially developed countries depends on catalysts
- essential for environmental protection, fuel upgrading and supply of chemicals
- many types of catalysts: metals, alloys, oxides, sulfides, zeolites etc.



Industrijska proizvodnja amonijaka / 1913. g., BASF, Oppau, Ludwigshafen:



2010: 150 000 000 t



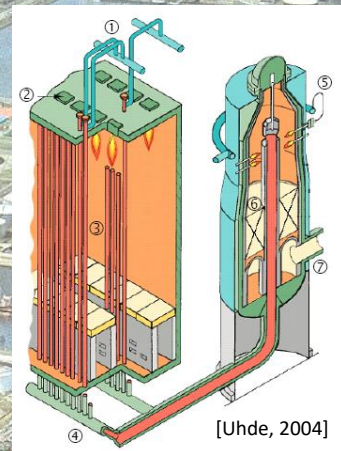
Fritz Haber
Nobelova nagrada za kemiju /
Nobel Prize in Chemistry **1918**



Carl Bosch
Nobelova nagrada za kemiju /
Nobel Prize in Chemistry **1931**



Gerhard Ertl
Nobelova nagrada za kemiju /
Nobel Prize in Chemistry **2007**
- "for his studies of chemical processes on solid surfaces"



Example of a reformer radiant section and a secondary reformer:
(1) inlet manifold, (2) burners, (3) reformer tubes, (4) outlet manifold, (5) process air inlet, (6) catalyst bed, (7) gas outlet
[Uhde, 2004]

Refinery

- catalysis is more important than ever:

high crude oil prices - small profit margin

(economic environment, EU refinig overcapacity, technology, maintenance, volume of products...)

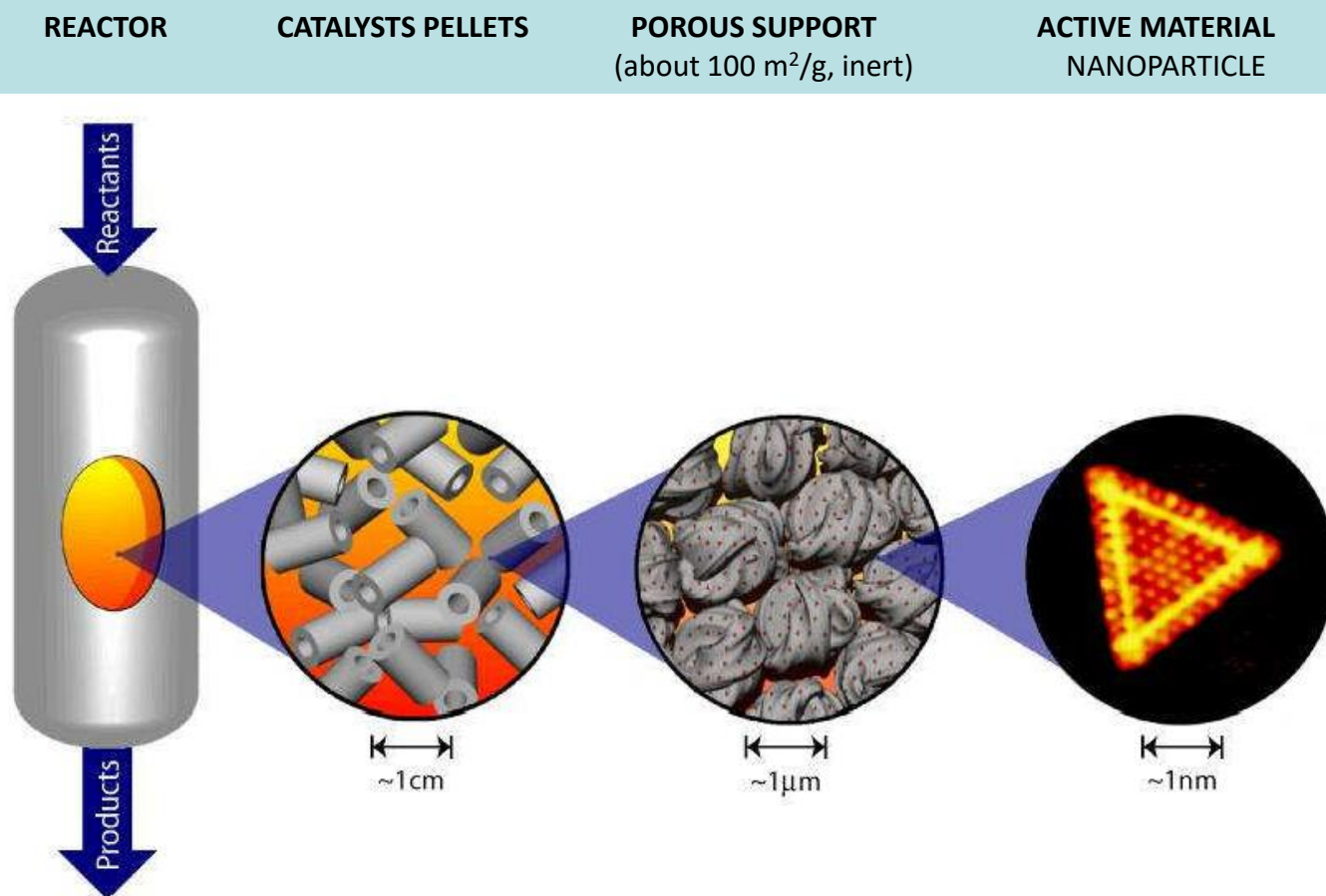
- industrial catalysts are at the heart of refining processes and determine the way they will evolve in the future
- from the standpoint of value, refinig catalysts account for about 33 % of the world market, coming just after environmental protection catalysts (40 %)
- refinery of the 21st century – high-performance non-poluting processes
- more active, selective and stable catalysts with lower production cost



Neste Oil reference margin
(USD/bbl)

Nanocatalysis

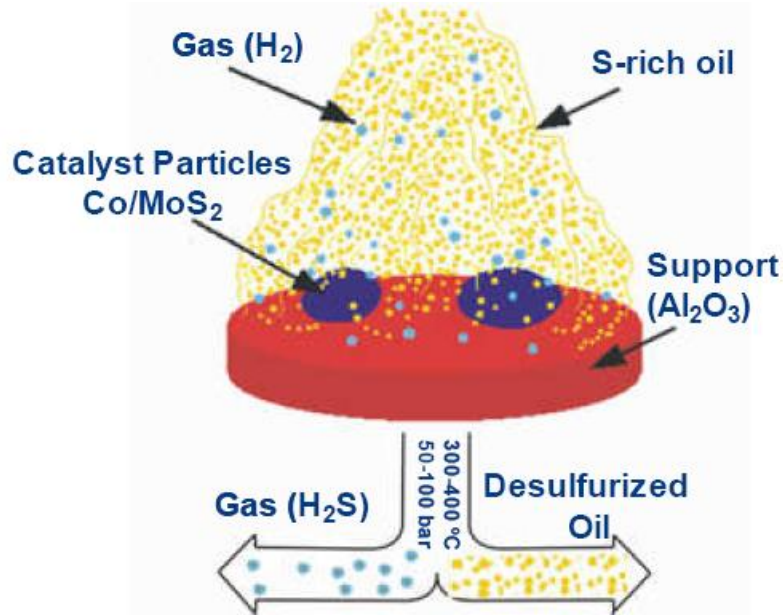
- it is expected to revolutionize the way catalysts are developed and prepared
- ability to design and characterize new nano-materials and predict their catalytic capabilities
- nanoparticles have a large surface to volume ratio



The structure of a heterogeneous catalyst illustrating the length scales and complexity involved in a heterogeneous catalyst

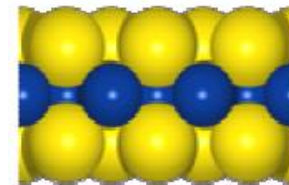
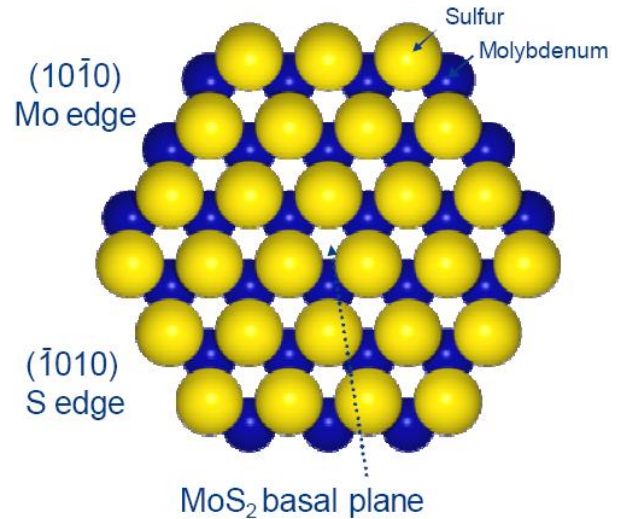
HydroDeSulfurization Process (HDS)

Regulatory push sulphur in diesel requires more hydrotreating

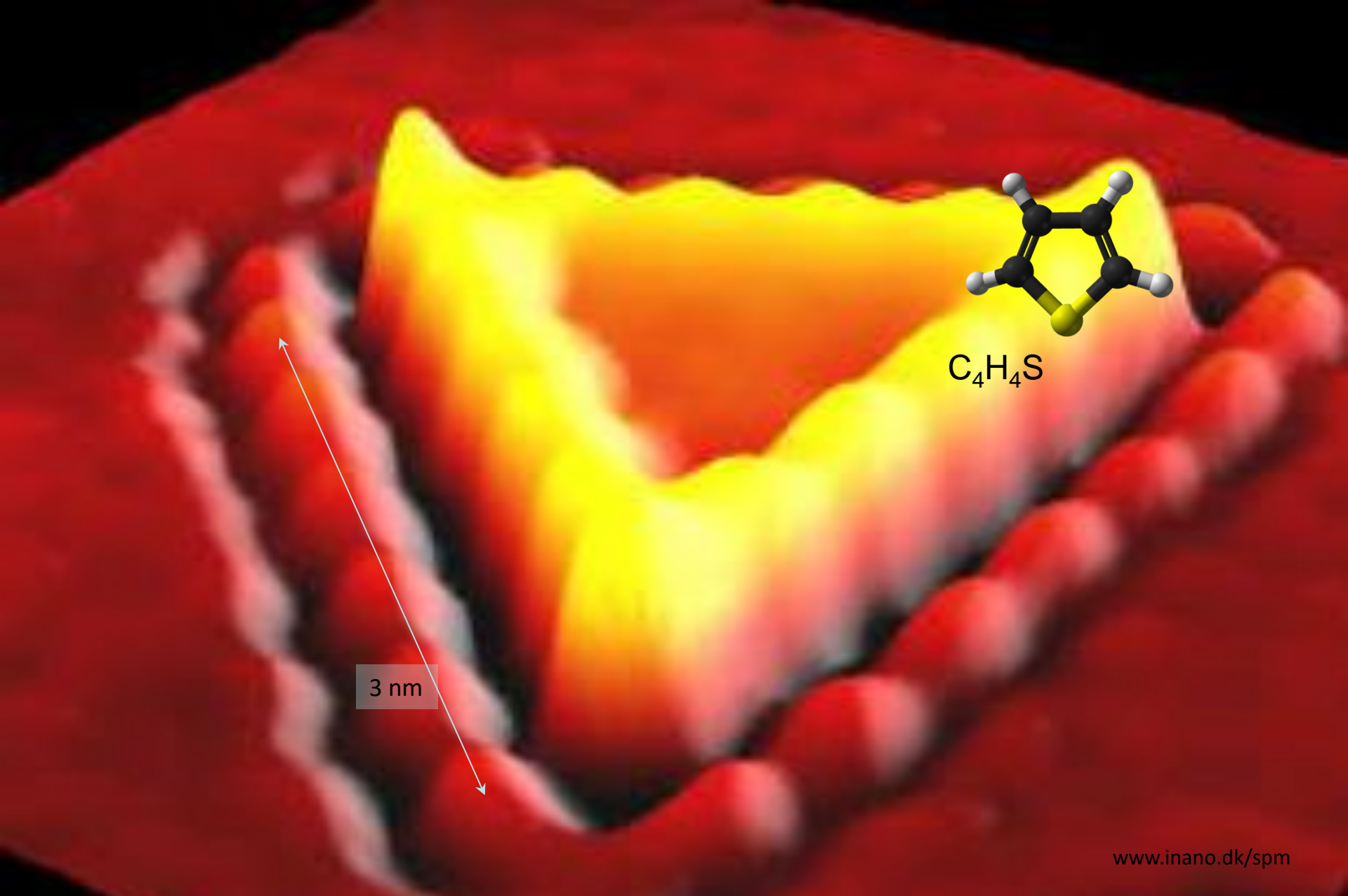


In-situ EXAFS measurements:
single-layer MoS₂-like, ~10-20 Å at 400 °C

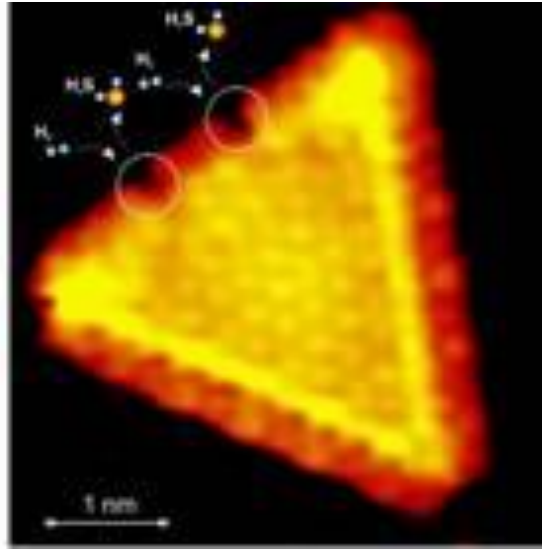
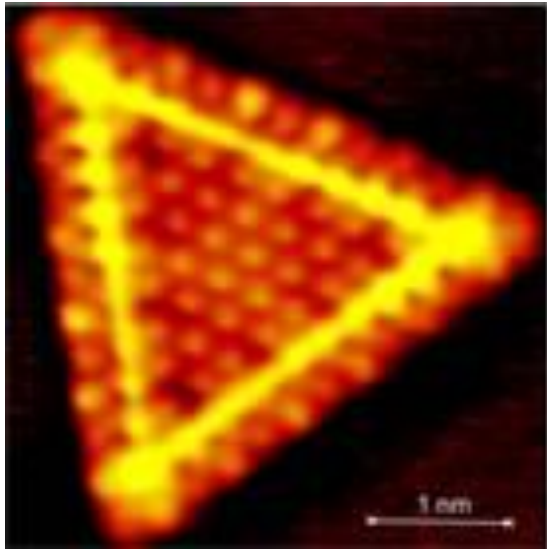
Nano-clusters of MoS₂



Mo-edge
(0%)



Thiophene adsorption on MoS_2 nanoclusters



Left: Atom-resolved STM image of an MoS₂ nanocluster which is active as catalyst for removal of S from crude oil.

The cluster is 3 nm wide and consists of 78 Mo atoms and 204 S atoms.

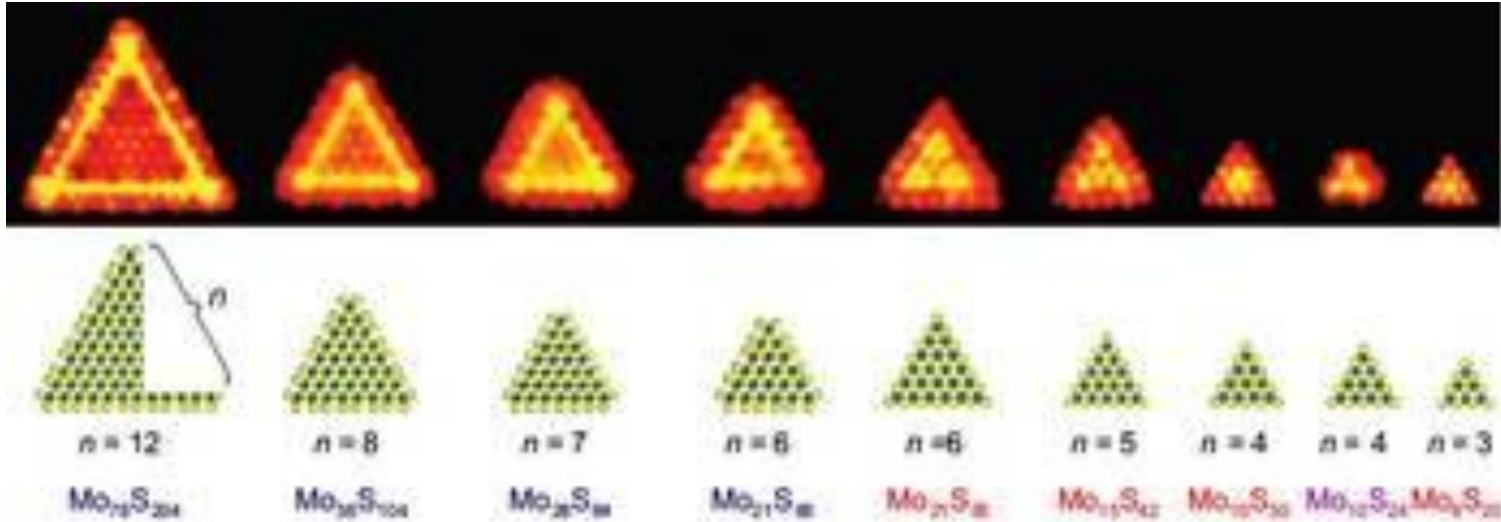
Right: An STM image of the MoS₂ particle in its catalytically active state. Circles indicate single S atoms that have been removed by reaction with hydrogen gas.

The illustration shows an atom-resolved STM image of a triangular ~3 nm wide MoS₂ particle supported on a Au support. Only the edges of the nanoparticles are reactive. The STM studies have revealed the exact atomic structure of the edges, and have shown that sulfur vacancies form on these edges. Using the STM it has been possible directly followed the first step of a hydrodesulfurization reaction occurring on the edges of the triangular MoS₂ nanoclusters, which showed that the sulfur vacancies on the edges have the ability to bond S-bearing molecules and subsequently cleave C-S bonds in a catalytic process.

Additionally, the studies have revealed the surprising catalytic importance of so-called metallic brim states of MoS₂, which are one-dimensional edge states present only on the edges of MoS₂.

The metallic character of the brim states present adjacent to the cluster edges can catalyze the hydrogenation and then C-S scission of sterically hindered molecules, and **by optimizing the effect of the brim states it has been possible to make the hydrotreating catalyst more active.**

This is an example on how nanotechnology discoveries performed under controlled laboratory conditions can successfully assist the development of real technical catalysts operating in industrial plants.



A sequence of STM images of MoS_2 nanoparticles with a varying size

The control of nanoparticle size in $\text{Mo}(\text{Co}, \text{Ni})\text{S}_2$ -based catalyst may also offer **new opportunities to optimize the catalytic reactivity**;

the structure (and in particular the edge structure and therefore the reactivity) changes as the size of the MoS_2 nanoparticles.

Current efforts are aimed at elucidating the optimum nanoparticles size for hydrotreating reaction of severely sterically hindered molecules.

Hydrogen production

steam reforming of natural gas: $\text{CH}_4 + \text{H}_2\text{O} = (\text{Ni catalyst}) = \text{H}_2 + \text{CO}$

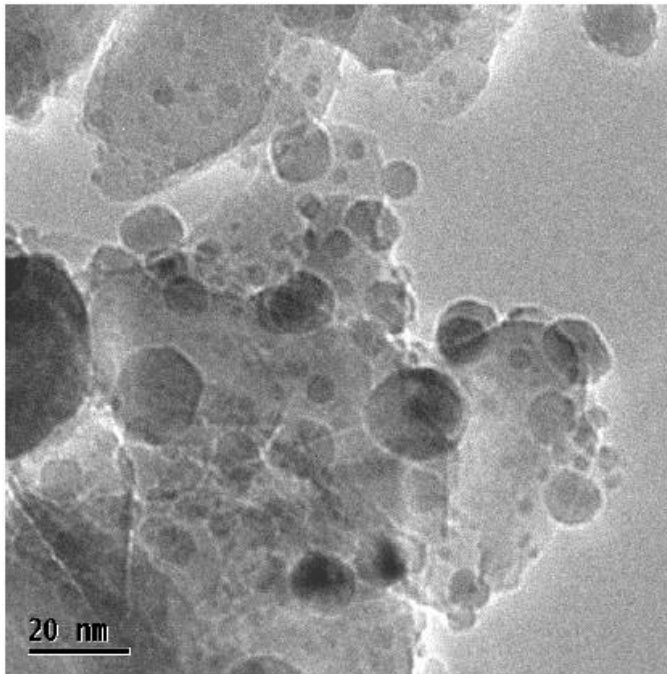
water-gas shift: $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$

carbon forming side reactions: $2\text{CO} = \text{C} + \text{CO}_2 / \text{CH}_4 = \text{C} + 2\text{H}_2$

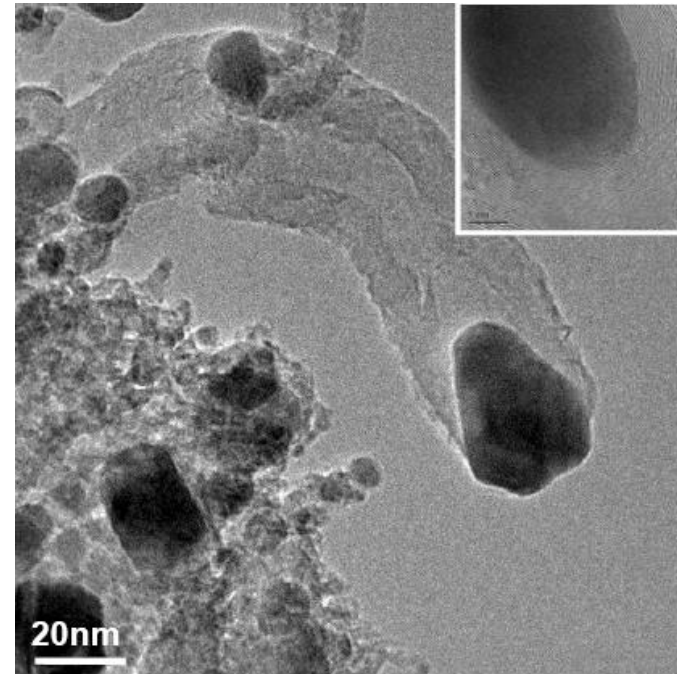
- carbon filaments in Ni-based catalysts



Haldor Topsøe A/S



reduced catalyst



deactivated catalyst

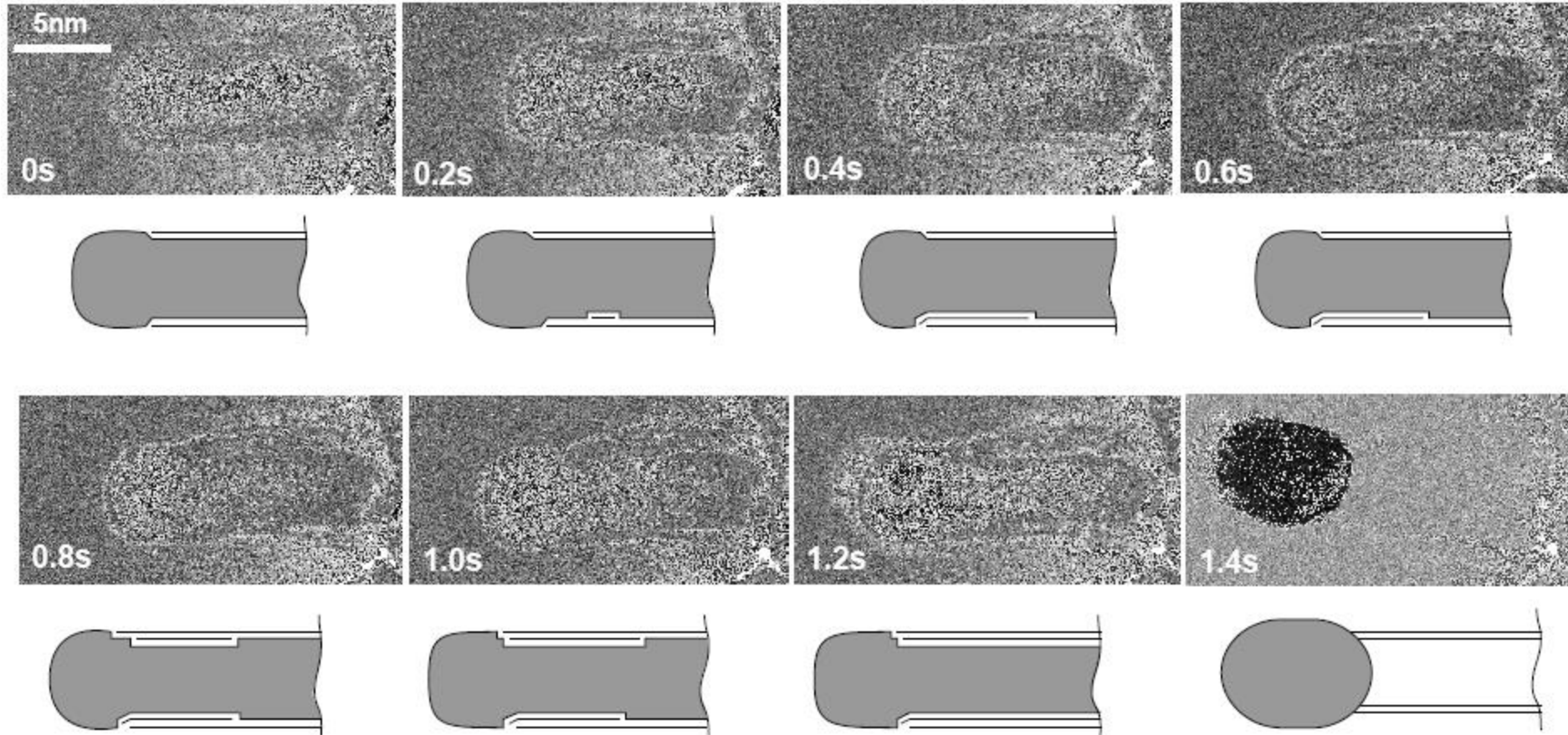
Dynamic reshaping of Ni nanocrystals



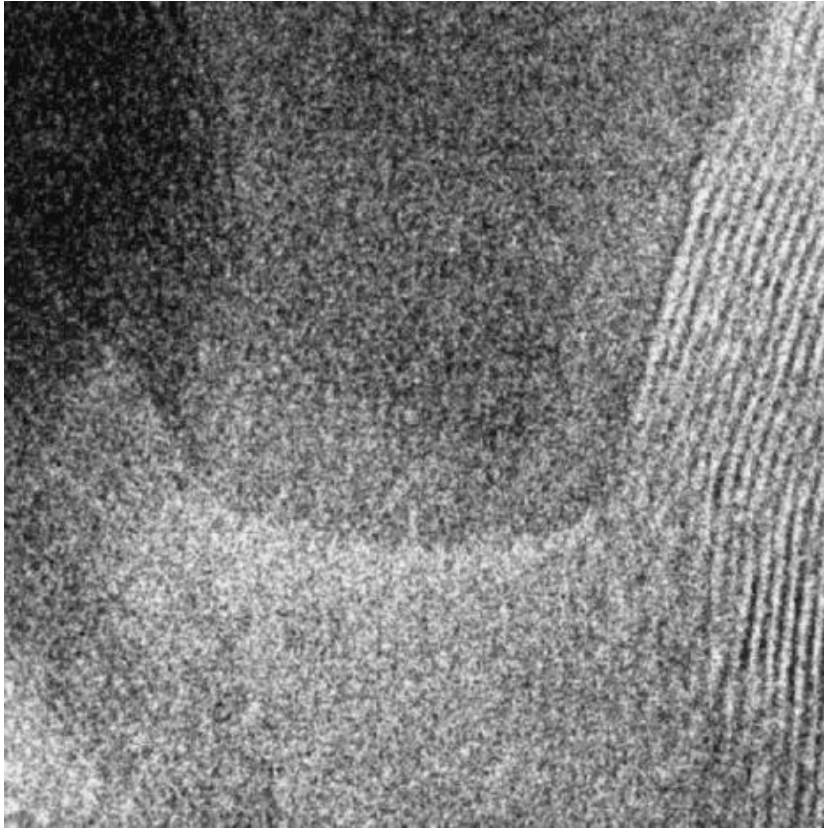
- elongation of Ni \sim more C sheets forms
- C sheets aligned along Ni surface
- growth ceases if C encapsulates Ni
- continuous elongation/contraction
- $\text{CH}_4 : \text{H}_2 = 1 : 1$, 2.1 mbar, 536 °C
- images acquired (displayed) with 10 (25) frames/s
- image size 21.3 x 21.3 nm²
- growth rate \sim 1 nm/s

Graphene formation from Ni atomic steps

- spontaneous formation of mono-atomic Ni step sites
- transport of C and Ni atoms



Ni step-edge dynamics at C-Ni interface



- reshaping of Ni is size-dependent
- whisker-type structures
- step-edge dynamics on Ni surface assist growth of graphene
- transport of C towards and Ni atoms away from C-Ni interface
- CH₄:H₂=1:1, 2.1 mbar, 525 °C
- images are acquired (displayed) with 10 (25) frames/s
- image size: 21.3 x 21.3 nm²

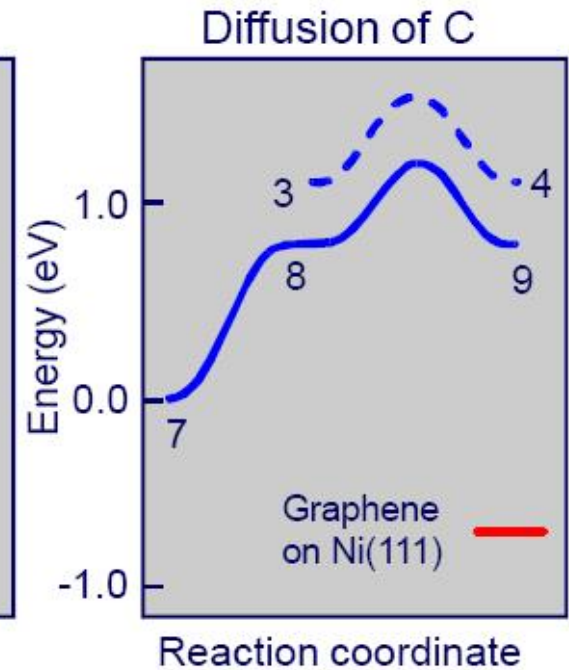
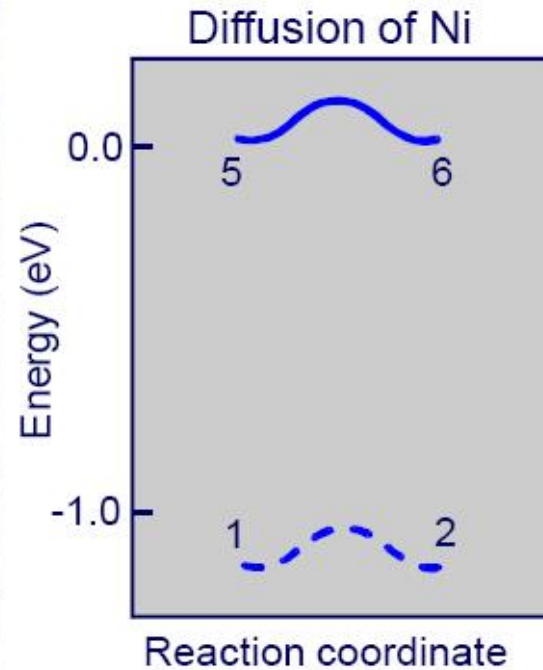
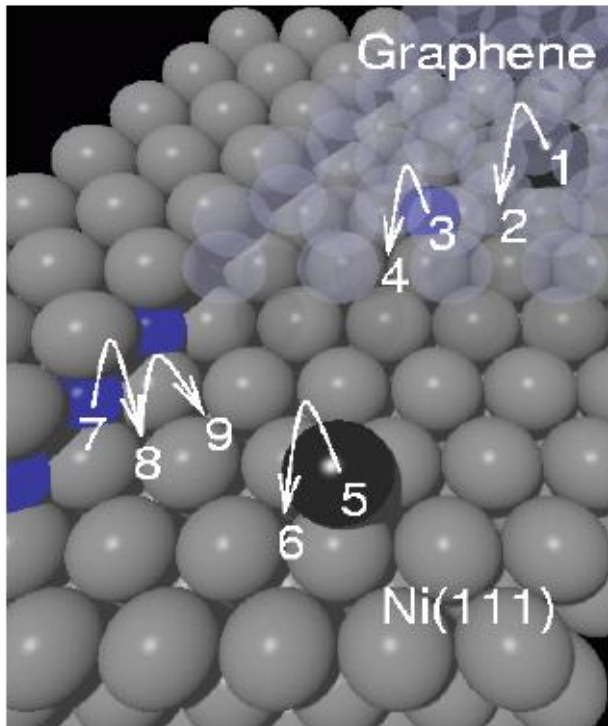
The synthesis of carbon nanotubes with predefined structure and functionality plays a central role in the field of nanotechnology, whereas the inhibition of carbon growth is needed to prevent a breakdown of industrial catalysts for hydrogen and synthesis gas production. The growth of carbon nanotubes and nanofibres has therefore been widely studied.

Recent advances in *in situ* techniques now open up the possibility of studying gas–solid interactions at the atomic level.

Here we present time-resolved, high-resolution *in situ* transmission electron microscope observations of the formation of carbon nanofibres from methane decomposition over supported nickel nanocrystals. Carbon nanofibres are observed to develop through a reaction-induced reshaping of the nickel nanocrystals. Specifically, the nucleation and growth of graphene layers are found to be assisted by a dynamic formation and restructuring of mono-atomic step edges at the nickel surface.

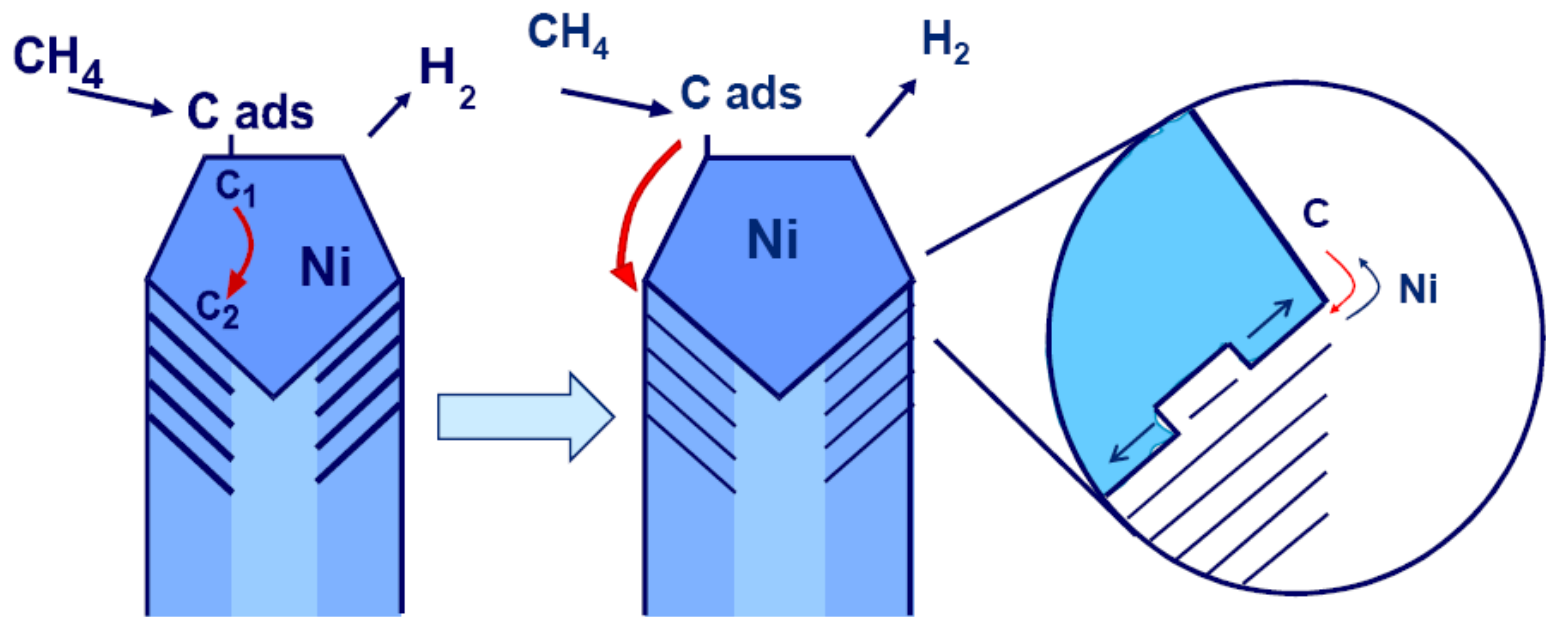
Density-functional theory calculations indicate that the observations are consistent with a growth mechanism involving surface diffusion of carbon and nickel atoms. The finding that metallic step edges act as spatiotemporal dynamic growth sites may be important for understanding other types of catalytic reactions and nanomaterial syntheses.

Surface transport – DFT calculations



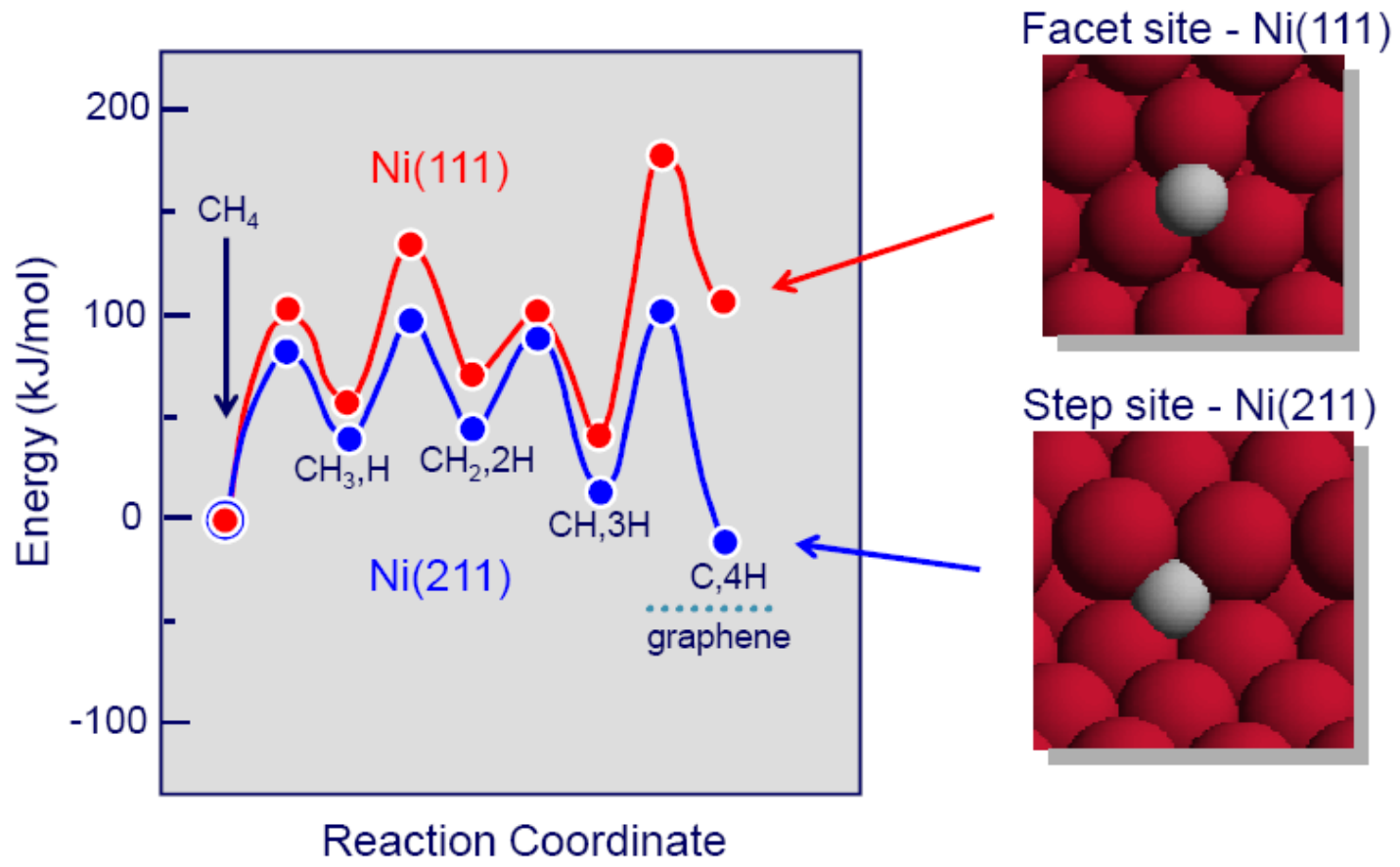
Surface diffusion of C: 1.6 eV
Exp. growth barrier: 1.3 - 1.5 eV

Proposed carbon fiber growth mechanisms;
bulk vs. surface diffusion



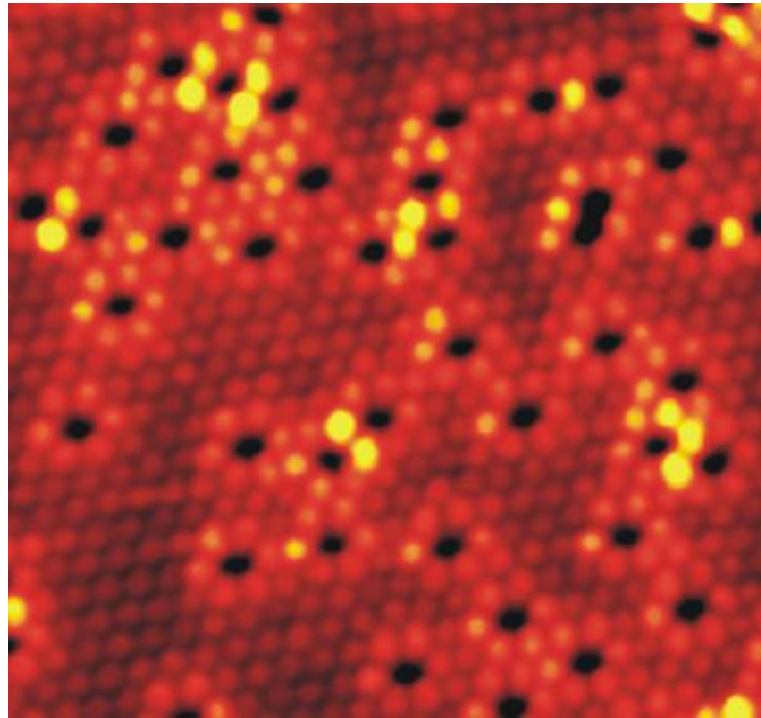
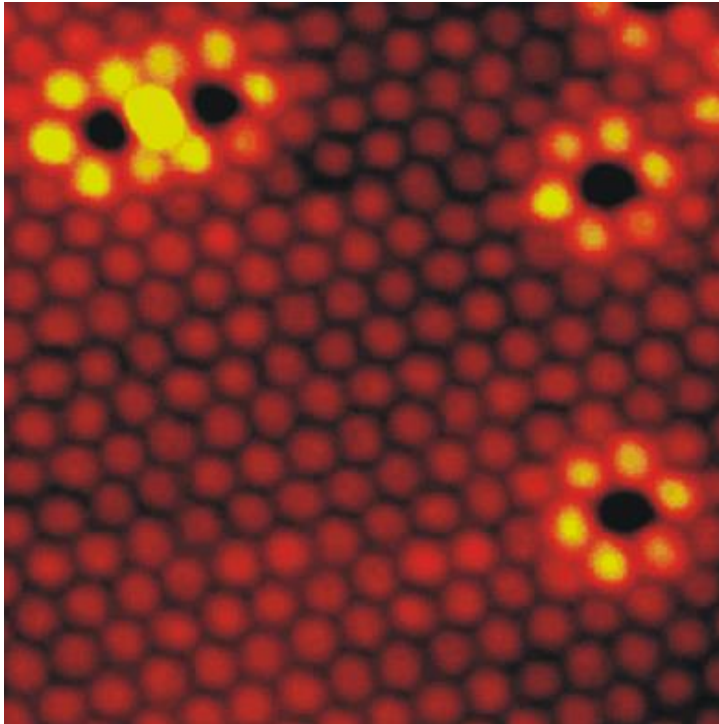
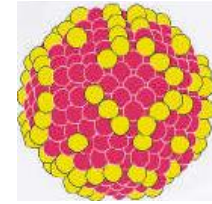
graphite fiber (whisker)

CH₄ decomposition – DFT calculations



Design of a new steam reforming catalyst based on nanoscience

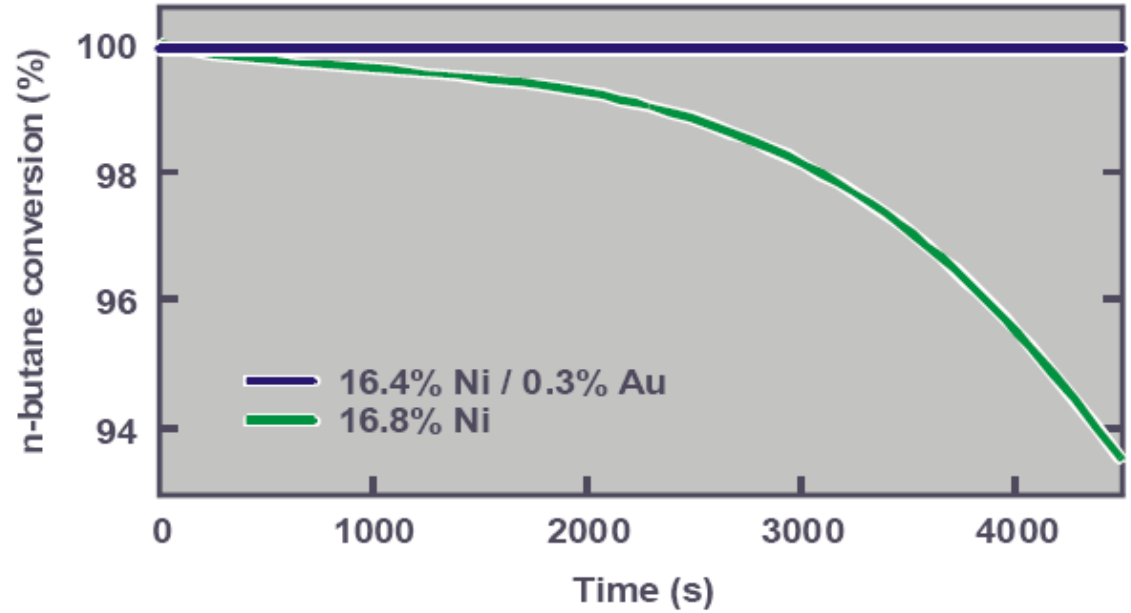
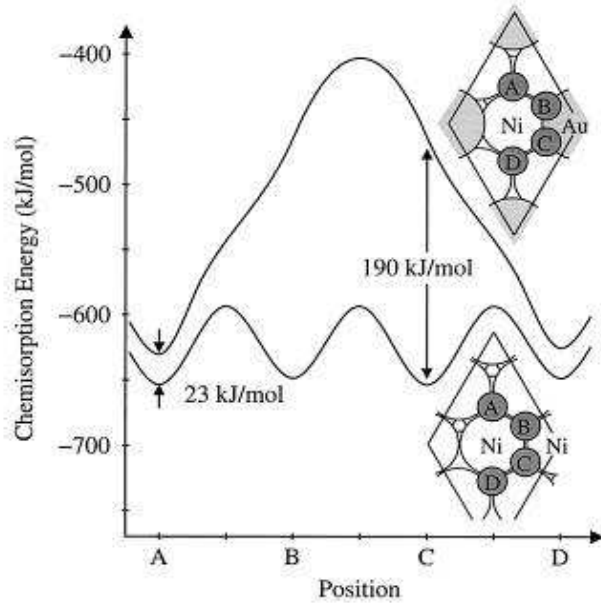
- Au-Ni surface alloy



F. Besenbacher, et al., Design of a Surface Alloy Catalyst for Steam Reforming, *Science* 279 (1998) 1913

Design of a new steam reforming catalyst based on nanoscience

- Au-Ni surface alloy



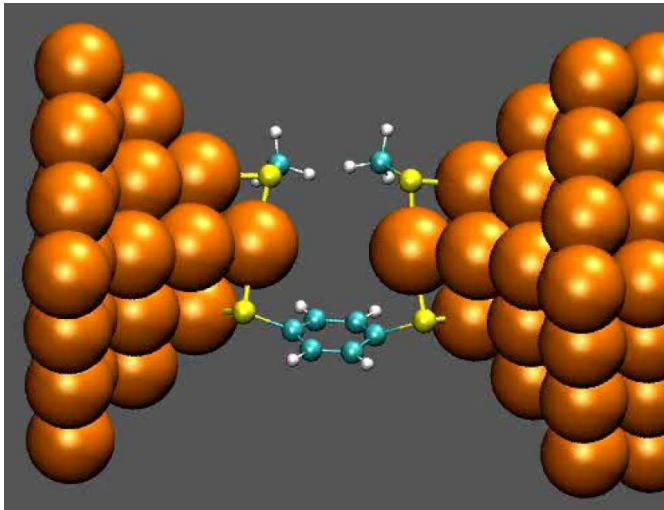
F. Besenbacher, et al., Design of a Surface Alloy Catalyst for Steam Reforming, *Science* 279 (1998) 1913

Au nanoparticles

- interesting catalysts for selective oxidation (e.g. low temperature CO oxidation) and hydrogenation reactions
- catalytic properties depend on the support, the preparation method, and the Au particle size/morphology (structure sensitive reaction)

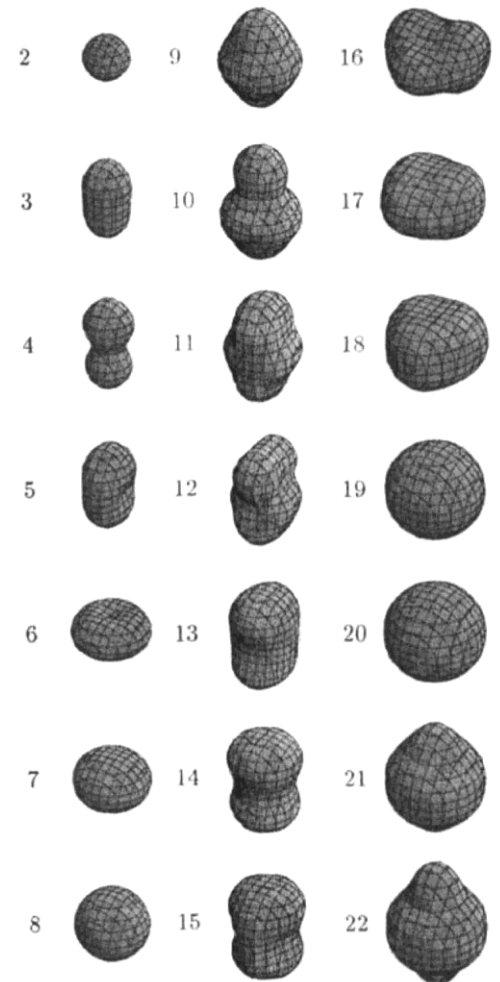
Proposals for high catalytic activity:

- Sites at interface between Au and support (Haruta)
- Low-coordinated Au atoms (Nørskov, Baiker)
- Supply of reactive oxygen from support (Muhler)
- Charge transfer between the support and the Au (Heiz, Landman)
- Strain in Au particles (Mavrikakis, Nørskov)
- Quantum size effects; metal-to-nonmetal transition (Goodman)

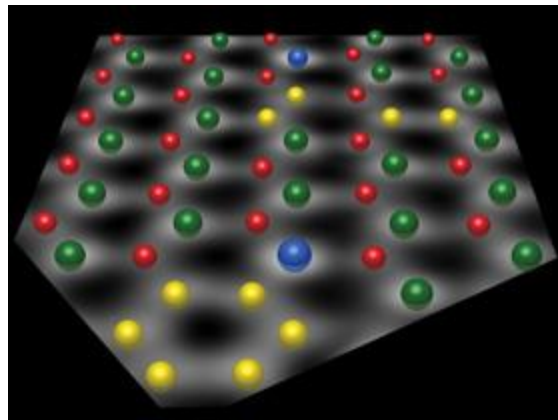
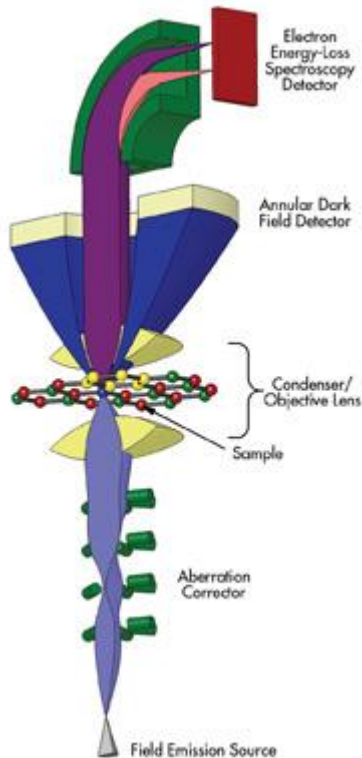
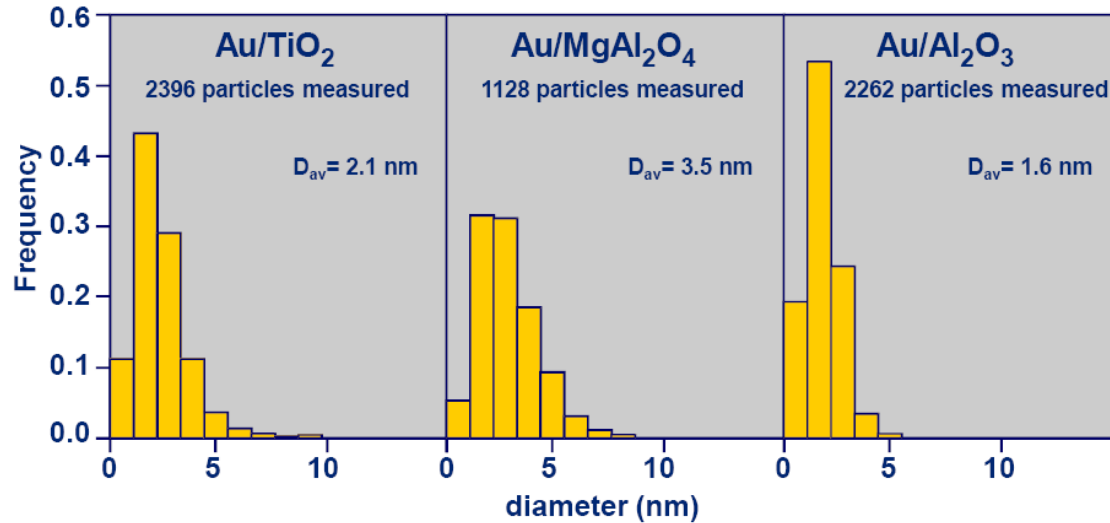


From atoms to nanoscale /
gold clusters:

- gold has nearly free electron character *and* covalent bonding (planar structures)
- ligand protection – “divide and protect”
- chemically produced in large quantities



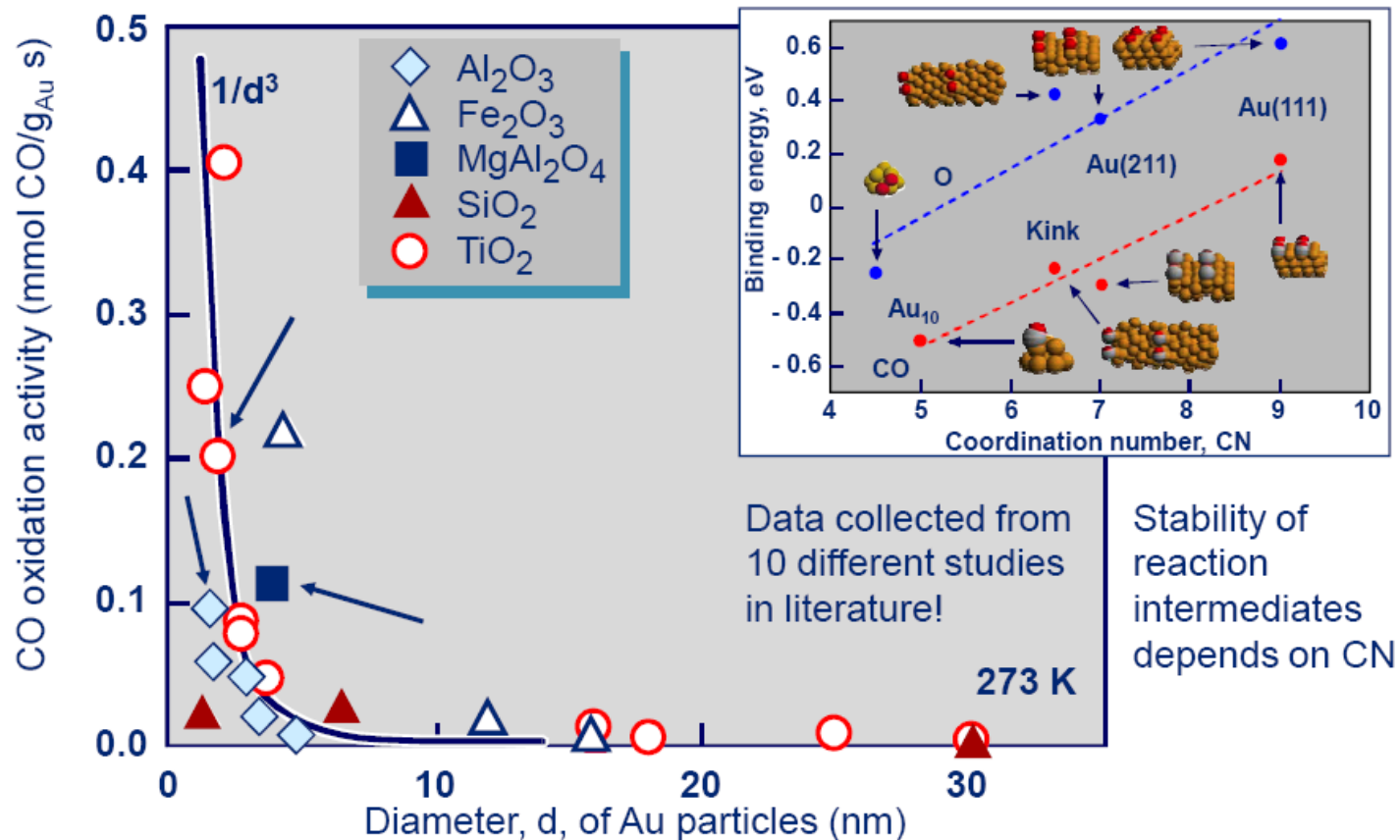
Au particle size distributions from STEM



STEM - Scanning Transmission Electron Microscopy - technique maps all the atoms in any molecule

Using aberration-corrected annular dark-field electron microscopy (left), researchers for the first time have located and identified all atoms in a nonperiodic sample of boron nitride with substitutional impurities. Shown is an experimentally determined model superimposed on the image, with boron (red) and nitrogen (green), along with impurities carbon (yellow) and oxygen (blue). Courtesy of Ondrej L. Krivanek, Nion Co.

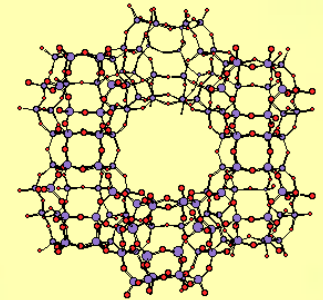
Au nanoparticles - CO oxidation activity



Conclusion

Major drivers in the development of new and improved catalysts:

- nanoscience & nanotechnology
- electronic structure of materials and density functional theory
- new / *in situ* / experimental techniques (AFM, STM, TEM...)
- new and improved synthesis methods for a 'tailor-made catalysts' – composition, structure, pore size distribution, morphology...



FKITMCMXIX



Fakultet kemijskog inženjerstva i tehnologije
Sveučilište u Zagrebu

Objedinjavanje rafinerijske preradbe nafte i petrokemijske industrije

Ante Jukić

Zavod za tehnologiju nafte i petrokemiju

HR-10000 Zagreb, Savska cesta 16, p.p. 177 / Tel. +385-1-4597128 / E-adresa: ajukic@fkit.hr

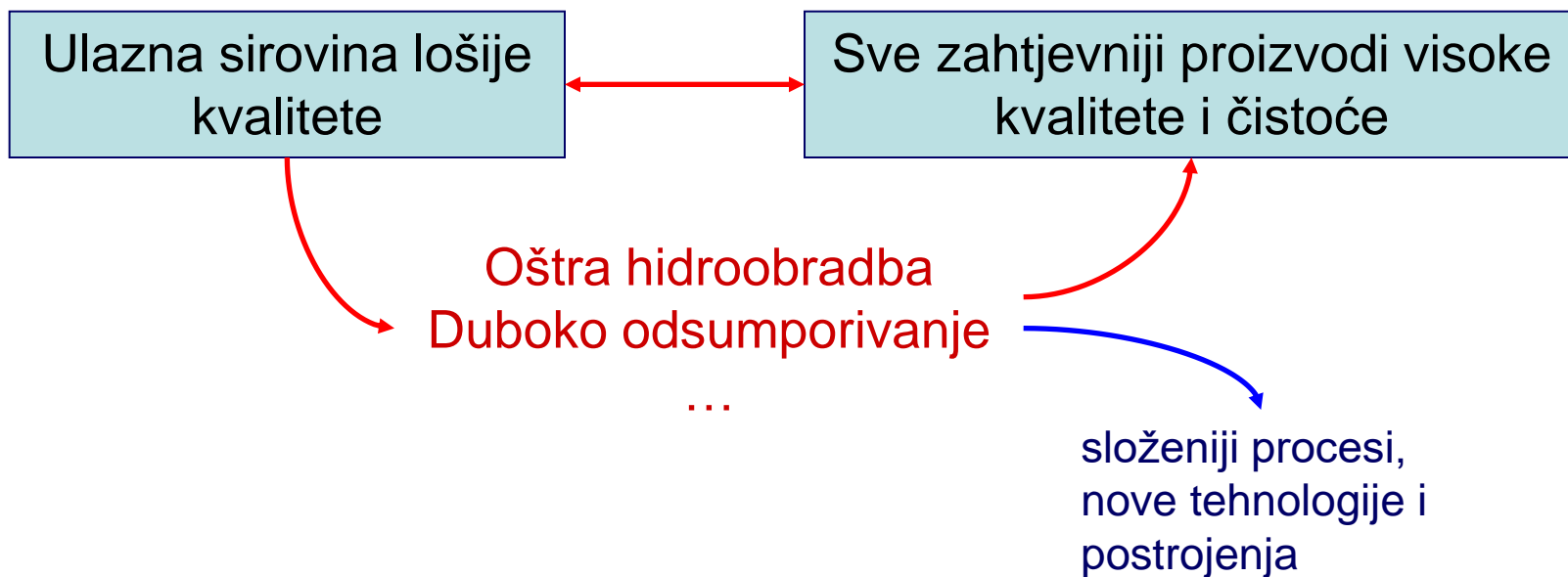
U Zagrebu, 27. studenoga 2009.

Rafinerije nafte danas:

- nesigurnost opskrbe
- velike promjene u cijeni sirovine
- strogi zahtjevi za svojstvima proizvoda (ultra niski sadržaj sumpora)
- sirovina lošije kvalitete - teže i korozivnije sirove nafte, većeg udjela S (2020. udjel nafte s TAN > 1: 20 %)
- strogo zakonodavstvo o utjecaju na okoliš
- jaka konkurencija.

Svi ovi čimbenici potiču na **snižavanje operativnih troškova** gdje god je to izvedivo, i razmatranje **ulaganja u tehnološka poboljšanja postojećih postrojenja** (e. retrofitting), kao i **izgradnju novih**.

Pri tome je temeljni cilj proizvodnja većeg udjela i obima vrlo čistih goriva, te drugih proizvoda veće dodane vrijednosti (petrokemikalije).



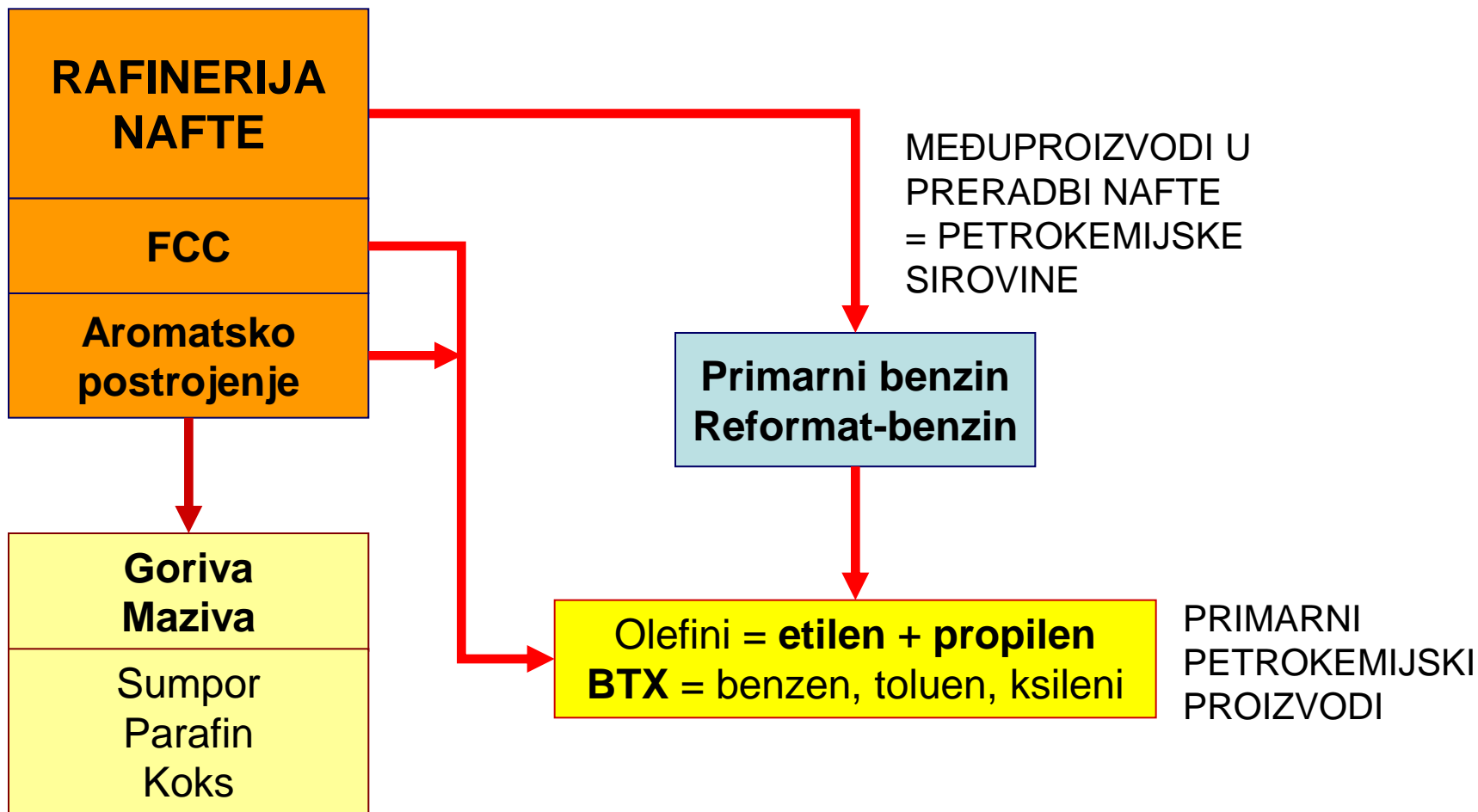
Rezultat:

- nadogradnja u smjeru nadzora i kontrole procesa (katalizator, p , T) više nije isplativa bez promjena glavnih dijelova opreme, npr. kapaciteta i konfiguracije reaktora
- nedostatak i odgađanje isporuke glavnih dijelova opreme (reaktori za hidroobradbu, kompresori, turbine)
- visoka cijena novih tehnologija (uključujući materijale i rad) (400.000 bpd rafinerija (~20 mil. t / g.) / očekivana cijena: 6,5 mlrd. USD, najniža ponuda 15 mlrd. USD; Kuwait, 2008.)

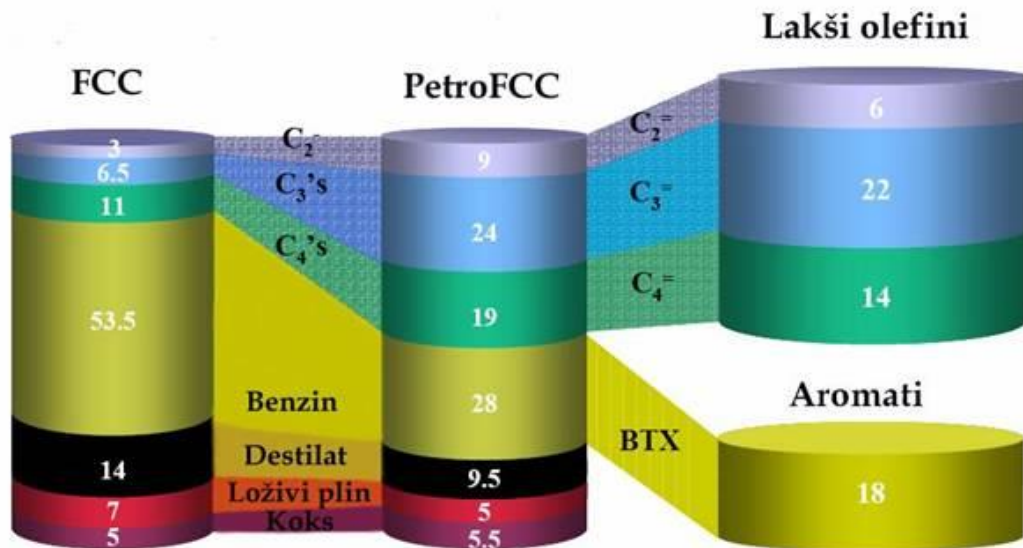
Tradicionalna povezanost PETROKEMIJSKE i INDUSTRIJE PRERADBE NAFTE



sirovinska i tehnologijska sinergija omogućava veću dobit ostvarenjem veće radne učinkovitosti, smanjenjem troškova i dobivanjem proizvoda veće vrijednosti



Rast godišnje potražnje za $C_{2=}$ i $C_{3=}$ u sljedećih pet godina 5 – 6 %
 (propilen iz FCC > 30 %)



PetroFCC
 SuperFlex
 DCC
 Maxofin
 Flexicracking IIR

Granični kapacitet:
 30.000 bpd sirovine
 (~1,5 mil. t / g.)

Exxon Mobil Chemical / 4 mlrd USD / 2011 / Singapur
rafinerija teške nafte + parno krekiranje (piroliza) primarnog benzina

kapaciteta 1 mil tpy Et =

650.000 tpy PE

450.000 tpy PP

300.000 tpy **specijalni elastomeri**

340.000 tpy B

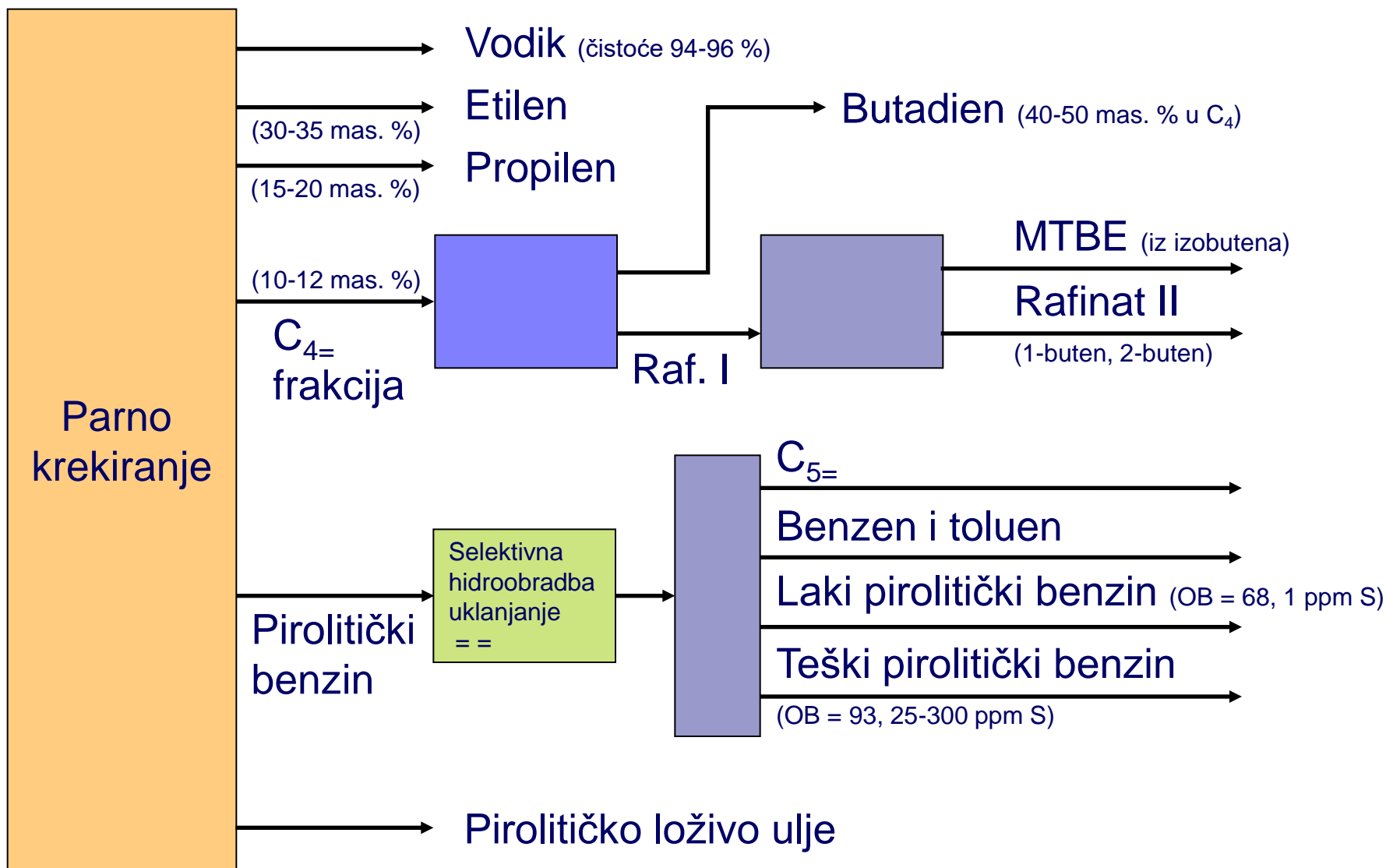
120.000 tpy **oxo-alkoholi**

220 MW **električne energije** iz kogeneracijske elektrane

Objedinjavanje preradbe nafte i petrokemijske proizvodnje u modernim rafinerijama

PARNO KREKIRANJE primarnog benzina:

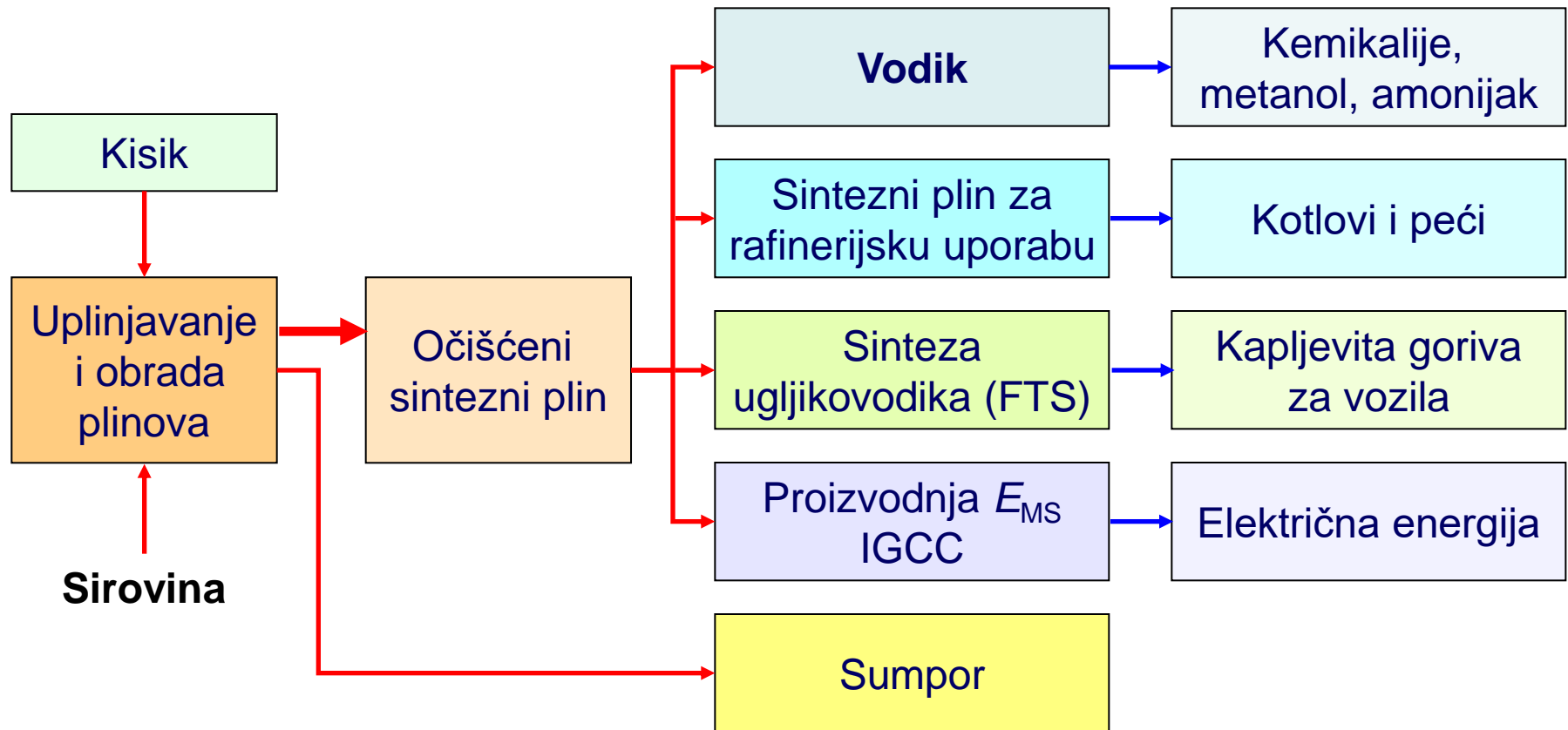
vodik, MTBE, benzin, C₄ sirovina za alkilaciju



Objedinjavanje preradbe nafte i petrokemijske proizvodnje u modernim rafinerijama

UPLINJAVANJE

sintezni plin (H_2+CO), petrokemikalije (CH_4 , NH_3 ,...),
sintetski benzin i diesel, toplinska (para) i električna energija



Objedinjavanje preradbe nafte i petrokemijske proizvodnje u modernim rafinerijama

Tehnologije za proizvodnju sinteznog plina

	SMR	ATR	CAR	Uplinjavanje ulja
Tlak, bar	< 40	< 85	< 85	< 85
Temperatura, °C	~860	~1000	~550	~1350
Sirovina	prirodni plin, primarni benzin			kapljevita
H ₂ / CO	3-6	2-3,5	1,5-3	1,3-1,8
Katalizator	x	x	x	nema
Metan	2-7	0,3-1	0,3-1	< 0,3
O ₂ / sirovina, Nm ³ / Nm ³	-	~0,7	~0,6	~1
Jedinični kapacitet 1000 Nm ³ / h (H ₂ + CO)	500	500	70	150

SMR = Steam-Metane Reforming / parno reformiranje metana

ATR = Autothermal Reforming / autotermalno reformiranje

CAR = Combined Autothermal Reforming

Odabir tehnologije za proizvodnju sinteznog plina:

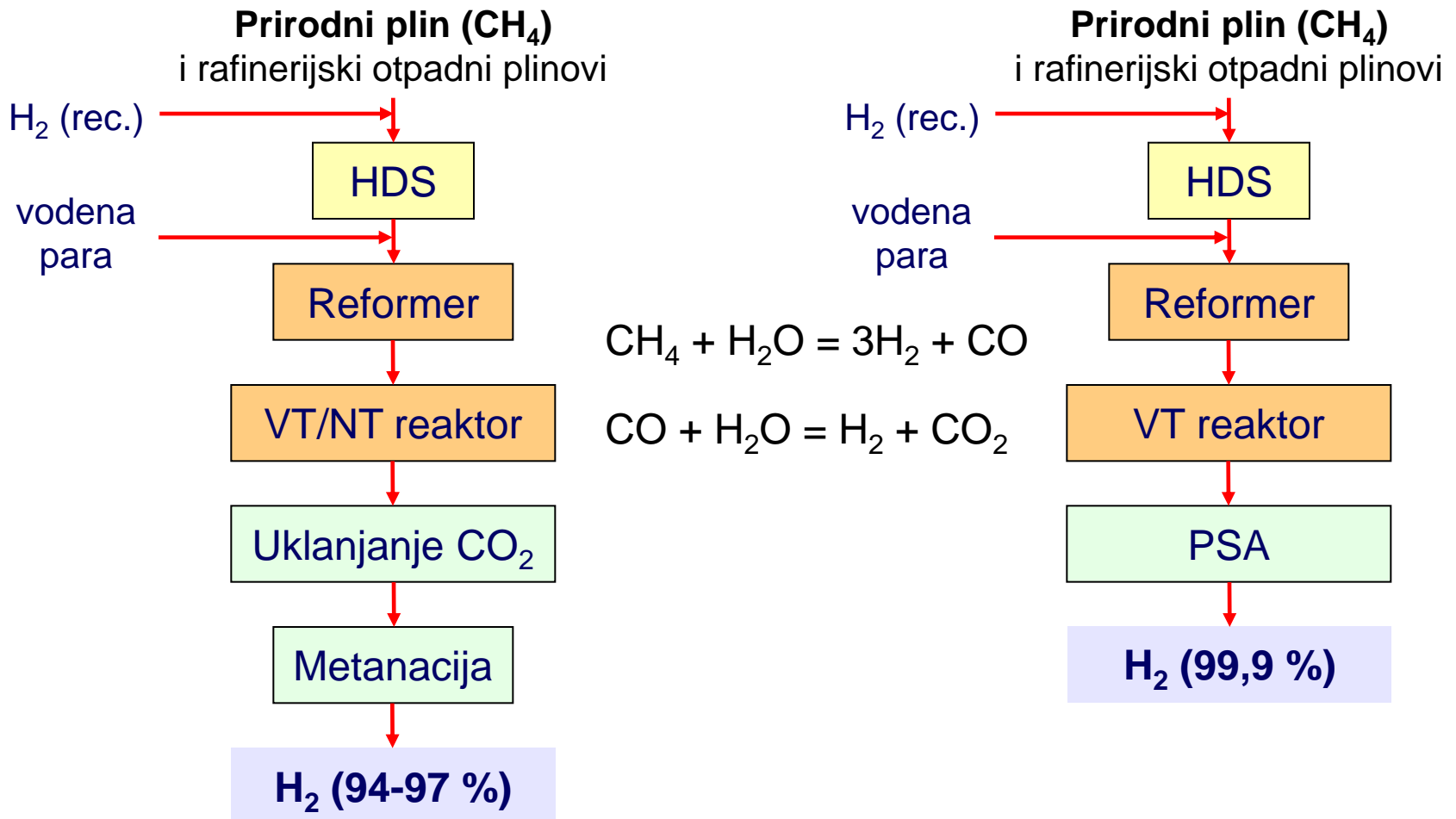
1. željeni omjer H_2 / CO
2. vrsta sirovine, dostupnost i zalihe
3. čistoća sirovine (sadržaj sumpora)
4. katalizator
5. procesno iskustvo (npr. uplinjavanje ugljena)
6. ... (zbrinjavanje CO_2)

Katalizatori:

Metal	Jedinična cijena	Metal	Jedinična cijena
Fe	1	Ru	35000
Ni	55	Pt	190000
Co	325	Rh	320000

Objedinjavanje preradbe nafte i petrokemijske proizvodnje u modernim rafinerijama

PROIZVODNJA VODIKA PARNIM REFORMIRANJEM



Ključni momenti procesa:

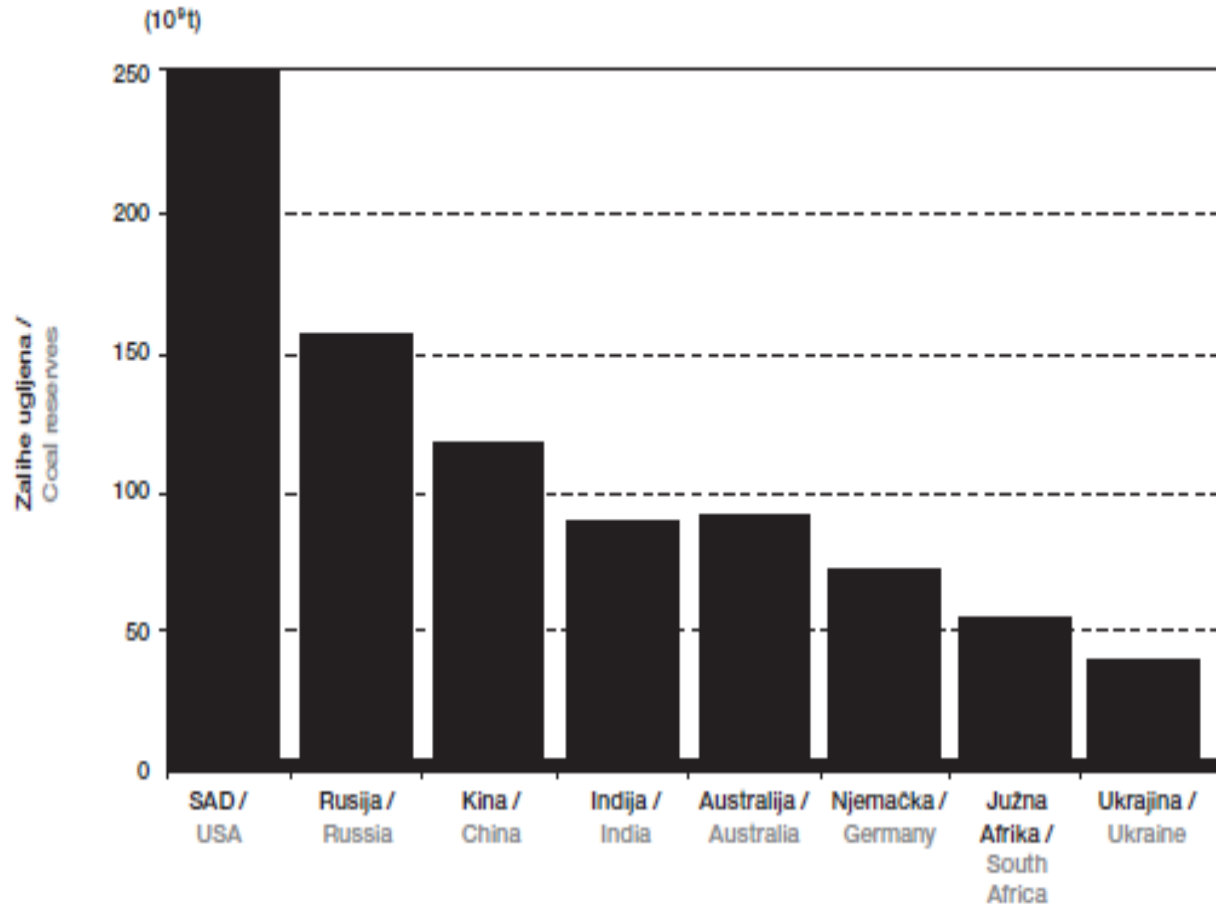
objedinjena bilanca vodika na razini rafinerije, sirovina (otpadni plinovi), postojanost i aktivnost katalizatora, energijska bilanca, zbrinjavanje CO₂, sigurnost

IGCC

- zrelost tehnologije nije postignuta (komercijalna postrojenja od 1990-tih)
- visoka početna ulaganja
- nepouzdanost - neispunjena očekivanja učinkovitosti i ekonomičnosti (prevladavaju državna ulaganja; S.A.D. DOE Clean Coal program)
- standardizacija dizajna postrojenja; sirovina, poligeneracija: H₂, E, kemikalije
- zbrinjavanje CO₂
- 2015. - 2025. drugi naraštaj IGCC; > 500 MW_e (iz koksa)

Ugljen je u svijetu najraširenije fosilno gorivo. Otprilike 25 % potreba za primarnom energijom te 40 % za električnom energijom namiruje se iz ugljena.

Izgaranjem ugljena proizvodi se i ispušta u atmosferu oko 10 milijardi tona CO₂, a 70 % od toga iznosa odnosi se na proizvodnju električne energije.



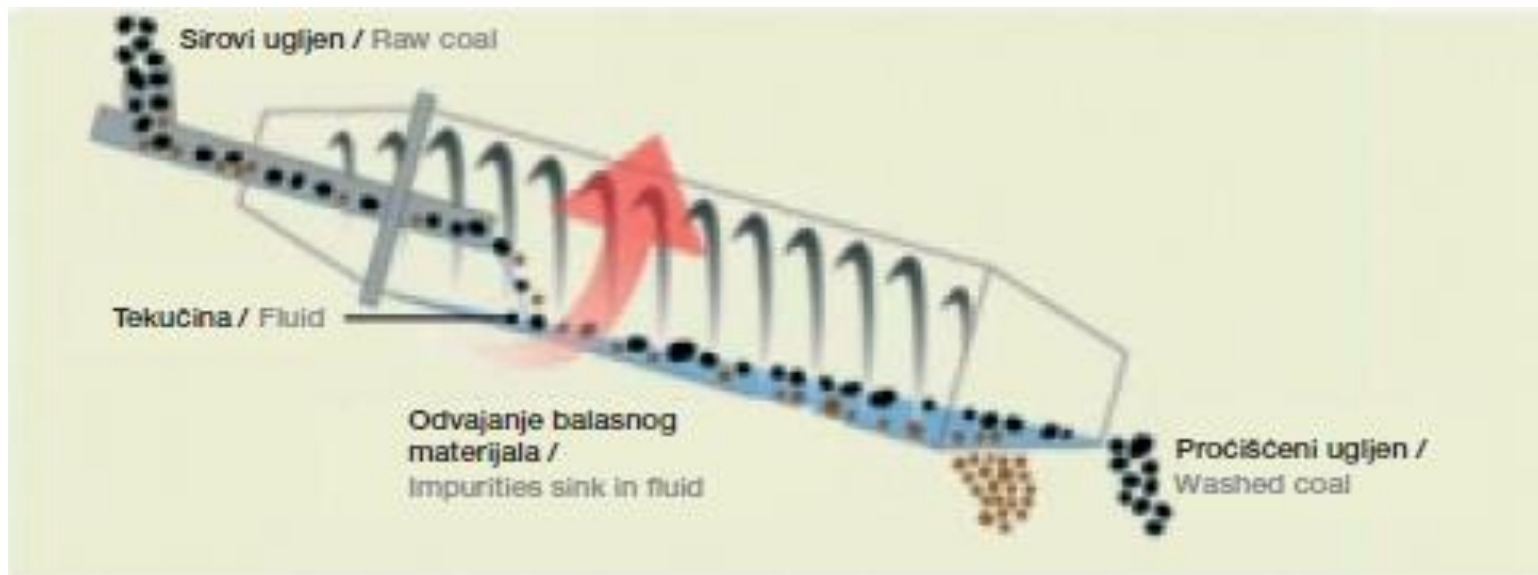
Zemlje s najvećim rezervama ugljena

Povijesno, tehnologije čistog ugljena bile su usmjerene na smanjenje emisija sumporovih i dušikovih oksida te krutih čestica. Danas, u svjetlu zabrinutosti zbog klimatskih promjena, pažnja se sve više usmjerava prema smanjenju ugljikovih, **CO₂ emisija**.

U1. Ispiranje ugljena

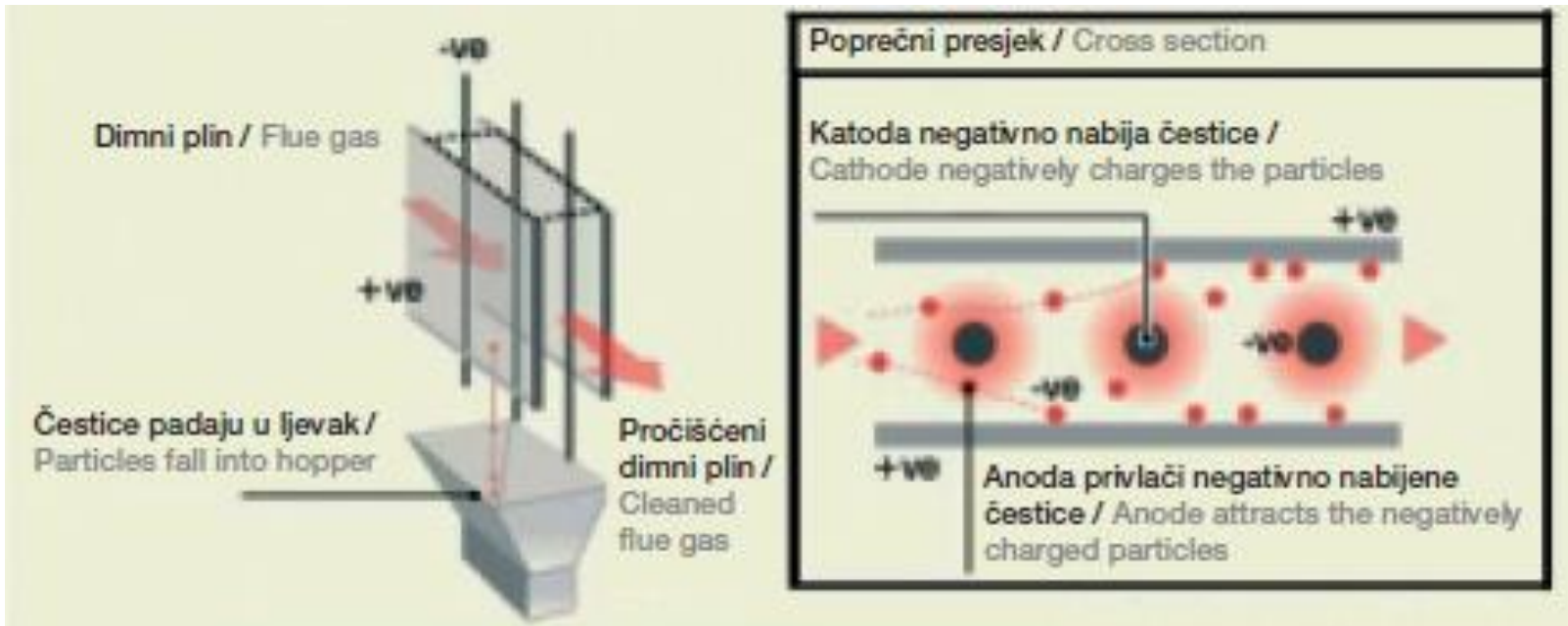
Čišćenje ugljena ispiranjem uobičajena je praksa u razvijenim zemljama - **smanjuju se emisije pepela i SO_x, a povoljno djeluje i na proces izgaranja**.

Ugljen se transportira do termoelektrane zajedno s mineralnim sadržajem koji je nesagorljiv, a može sadržavati i štetne sastojke (poput žive). Ugljen se usitnjava i uvodi u sporo rotirajući bubanj u kojemu se nalazi tekućina veće gustoće, tako da ugljen pluta dok teži, mineralni materijal tone i sa dna se odvodi iz bubnja. Pročišćeni se ugljen zatim melje u finu prašinu pogodnu za izgaranje.



U2. Odvajanje krutih čestica

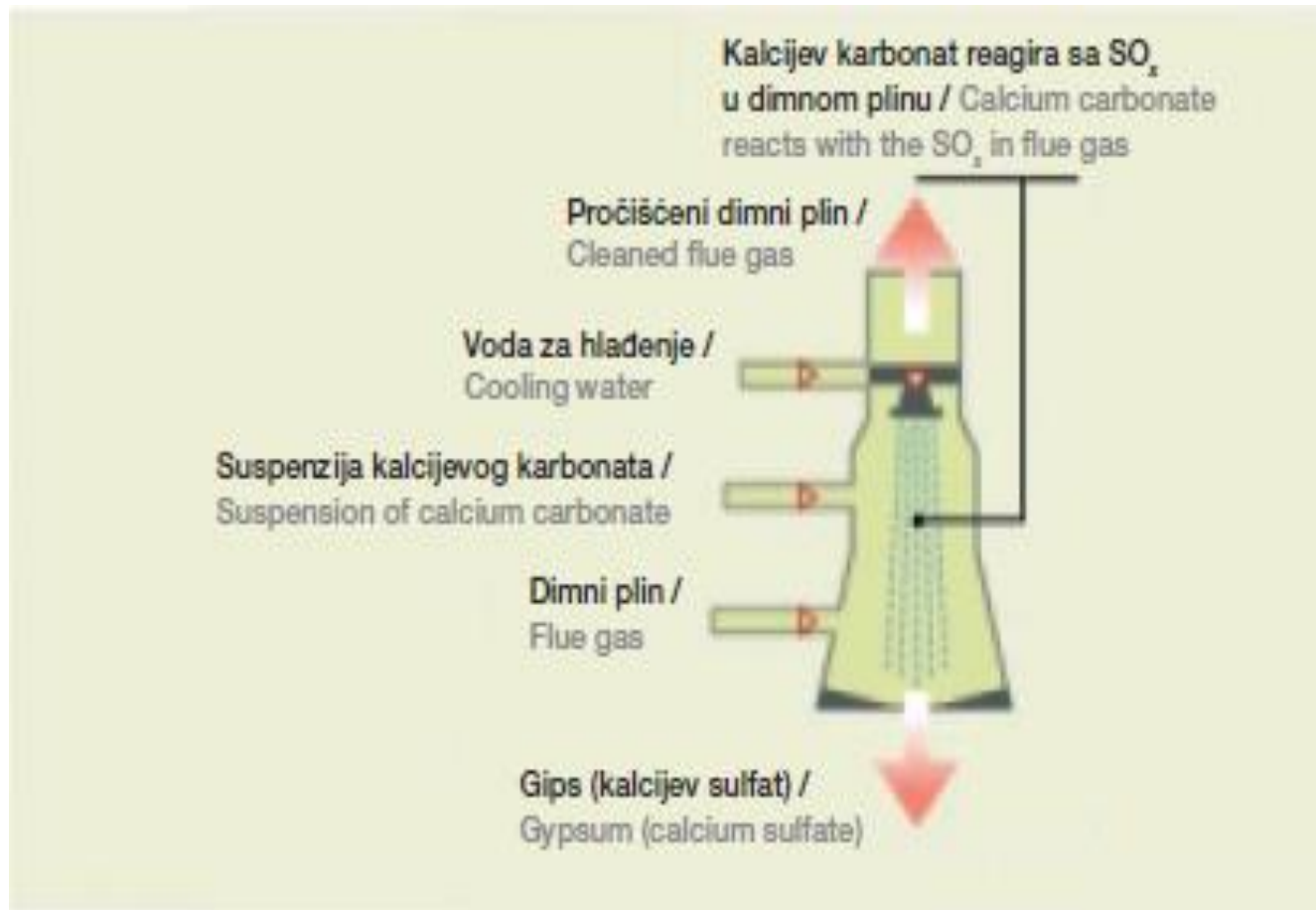
Korištenjem elektrostatskih filtara, može se iz dimnih plinova **odstraniti do 99,7 % pepela**. Rade na principu elektrostatskog polja u kojemu se čestice električki nabijaju i sakupljaju na anodi. Osim **elektrostatskih filtara** koji su u najširoj uporabi, koriste se i **vrećasti filtri**.



U3. Redukcija sumporovih oksida (odsumporavanje)

Sumporovi oksidi (SO_x) nastaju tijekom procesa izgaranja goriva koje sadrži sumpor.

Za odstranjivanje sumporovih oksida u konvencionalnim se termoenergetskim postrojenjima najčešće koristi mokri postupak odsumporavanja, kojim se iz dimnih plinova **odstranjuje do 95 % SO_x** . Dimni plinovi reagiraju s raspršenom smjesom kalcijevog karbonata (vapnenac) i vode, pri čemu se stvara gips (kalcijev sulfat) koji se odstranjuje i upotrebljava u građevnoj industriji.



U4. Redukcija dušikovih oksida (NO_x)

Znatno smanjenje emisije dušikovih oksida može se ostvariti već primarnim mjerama, tijekom izgaranja, što se postiže odgovarajućom *konstrukcijom plamenika* i *stupnjevitim dovodenjem zraka i goriva*. Time se smanjuju maksimalne temperature u jezgri plamena i smanjuje se koncentracija kisika u zoni izgaranja.

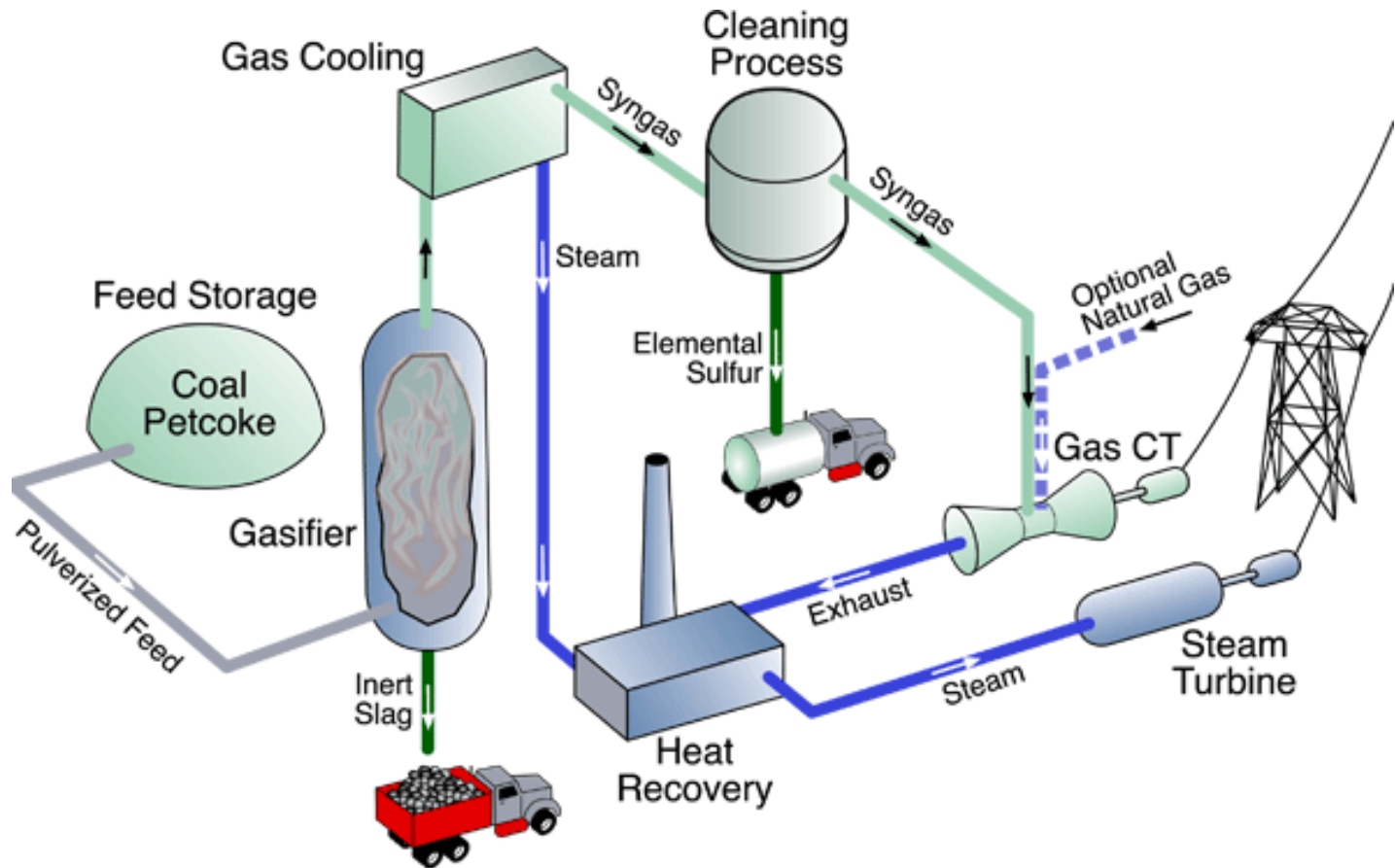
Količinu nastalog NO_x na taj način može se smanjiti na vrijednost manju od 300 mg/m³ (do 40 %). Sekundarne mjere za smanjenje emisije NO_x, koje se primjenjuju iza zone izgaranja, uključuju selektivnu nekatalitičku redukciju (SNCR) kojom se amonijak / urea uvodi u generator pare na mjestu gdje vladaju temperature dimnih plinova od 850 °C do 900 °C. Time se postiže smanjenje emisije od oko 70 %. Uvođenjem katalizatora ostvaruje se selektivna katalitička redukcija (SCR) kojom se može ostvariti smanjenje emisije NO_x do 90 %.



Uplinjavanje objedinjeno s kombiniranim ciklusom plinske i parne turbine (Integrated gasification combined cycle, IGCC)

1. Proizvodnja sinteznog plina uplinjavanjem ugljena: H_2 , CO , CO_2 i CH_4 .
2. Uklanjanje kiselih plinova.
3. Proizvodnja električne energije kombiniranim ciklusom plinske i parne turbine.
(proizvodnja vodika / sintetičkih kapljevutih goriva)

IGCC postrojenja prihvatljiva su rješenja za centraliziranu proizvodnju vodika i električne energije uz niske troškove stlačivanja i skladištenja vodika.



1. High thermal efficiency

- Air-blown gasifier with lower auxiliary power than oxygen-blown gasifier is adopted.
- The net thermal efficiency of commercial plants with 1500 °C class gas turbine is about 20 % higher than conventional coal-fired plants.

2. High environmental performance

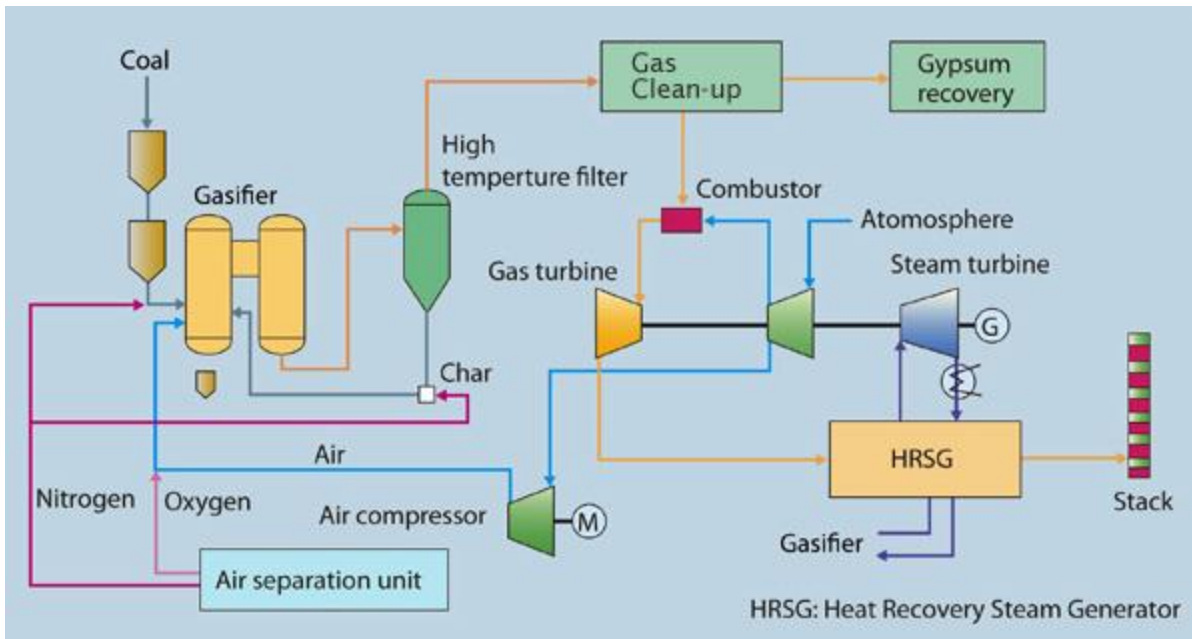
- Emission of CO₂, NO_x, SO_x, and dust is reduced due to high thermal efficiency.

3. Coal flexibility

- Even low rank coal which is unacceptable for usual conventional coal-fired boilers because of its low ash melting temperature and high moisture content is suitable for IGCC.

4. Better coal ash disposal

- Coal ash is discharged in a form of slag whose volume is half of fly ash from conventional coal-fired plants. It has no leaching characteristics of trace element.



Clean Coal Power R&D Co., Ltd. in Nakoso, Iwaki City, Fukushima

IGCC – očišćeni sintezni plin učinkovitije je gorivo u odnosu na ugljen - sintezni plin izgara pri višim temperaturama.

Iskorištenje plinske turbine kreće se u rasponu od 25 % do 35 %. Toplina plinova izgaranja se zatim koristi za stvaranje pare za parnu turbinu. Para se stvara u generatoru pare, gdje obična voda prolazi kroz seriju izmjenjivača topline kako bi se prenijela toplina ispušnih plinova na vodu. Voda isparava do prezasićenja, ulazi u parnu turbinu, te ju pokreće i preko generatora se dobiva električna energija. Iskorištenje parne turbine je u rasponu od 40 % do 45 %.



IGCC elektrana od 250 MW u Nakosu, Japan

- 2015. - 2025. drugi naraštaj IGCC; > 500 MW_e (iz koksa)

PRIRODNI PLIN
(natural gas)
UGLJEN
(coal)
BIOMASA
(biomass)

**PROIZVODNJA
SINTEZNOG
PLINA, CO + H₂**

reformiranje
djelomična oksidacija
uplinjavanje

**FISCHER-
TROPSCHOVA
SINTEZA**

oligo/polimerizacija

**NADOGRADNJA
PRODUKTA**

hidrokreiranje
hidroobradba
/-izomerizacija
/-alkilacija
/-reformiranje

GTL
(gas-to-liquid/plin-u-kapljevinu)
CTL
(coal-to-liquid/ugljen-u-kapljevinu)
BTL
(biomass-to-liquid/biomasa-u-kapljevinu)
sintetska goriva i maziva
(bazna ulja)

Izazovi
LNG
/ UPP

GTL – nadomjesne tehnologije



INO
NOGATE
 PROJECTS OF
 EUROPEAN INTEREST
 FOR NATURAL GAS PIPELINES
 December 2003

Izazovi Širenje mreže plinovoda



an Union. The contents of this publication are the sole responsibility of the contractor, ENI AG/IGDF/EL, and can in many instances reflect the views of the European Union.

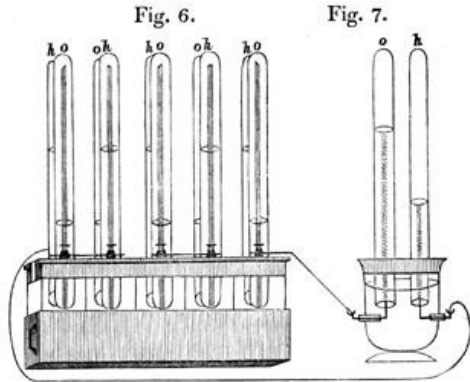
Izazovi

Biomasa (tehnologije 2. naraštaja / kemijske i biokemijske)



Izazovi

Elektrokemijski motori (gorivni članci) i baterije

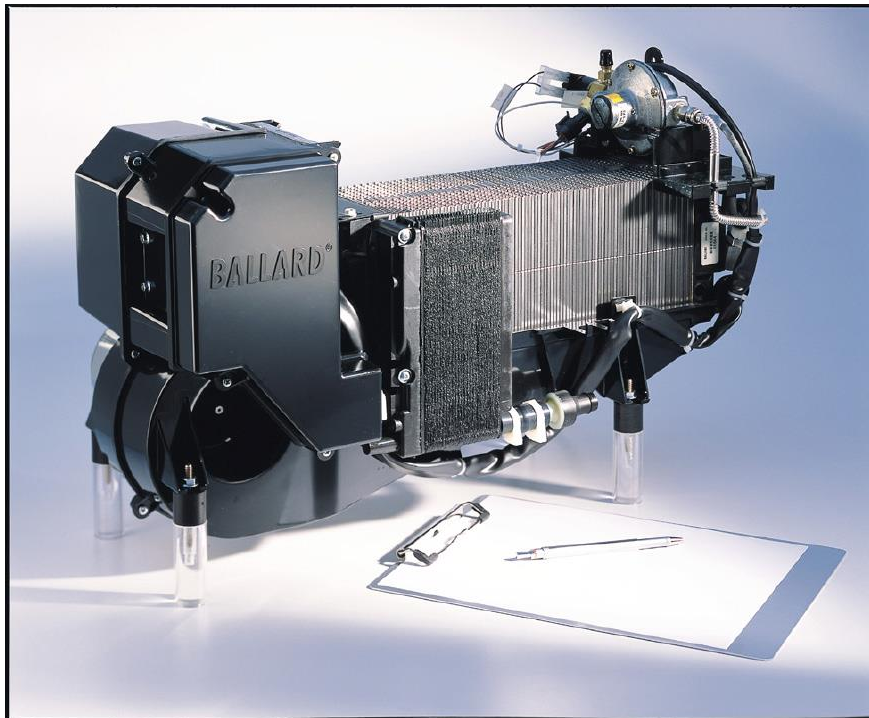


Groveova "plinska baterija" – prvi gorivni članak.

W. Grove:

"On the Gas Voltaic Battery",

Philosophical Magazine and Journal of Science (1843), str. 272.



Nexa™

Rated net power: 1200 W, 46 A, 26 V

Operating lifetime: 1500 h

Weight: 13 kg

Emission: max. 0.87 liters H₂O per hour

Supply H₂ pressure: 10 to 250 PSIG

Consumption: ≤ 18.5 SLPM

(standardna litra po minuti)

ZAKLJUČAK

Mogućnosti povezivanja petrokemijskih i tehnologija preradbe nafte vrlo su brojne, a sama primjena ovisi o složenosti i posebnostima pojedine rafinerije i pripadajućeg tržišta.

Za očekivati je da će zakonodavstvo o zaštiti okoliša i kvaliteti proizvoda poticati daljnje objedinjavanje ovih industrija.



MODERNE TEHNOLOGIJE ZA VISOKOVOLUMNU PROIZVODNJU VODIKA

Centralizirana visokovolumna proizvodnja vodika znatno je jeftinija u odnosu na proizvodnju vodika u malom obujmu, onda kad postoji tržište velikih potrošača.

Dvije su glavne tehnologije koje velika postrojenja čine ekonomski isplativima:

1. Parno reformiranje i oksidacija; uplinjavanje.

2. Dobivanje vodika upotrebom električne energije proizvedene iz topline nastale u nuklearnim elektranama. Najvažniji pravci razvitka ove tehnologije s ciljem poboljšanja njene učinkovitosti:

tradicionalna elektroliza (električna energija + $\text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_2 + \text{O}_2$);

visoko-temperaturna elektroliza (električna energija + $\text{H}_2\text{O} (\text{g}) \rightarrow \text{H}_2 + \text{O}_2$);

hibridni (mješoviti) ciklusi

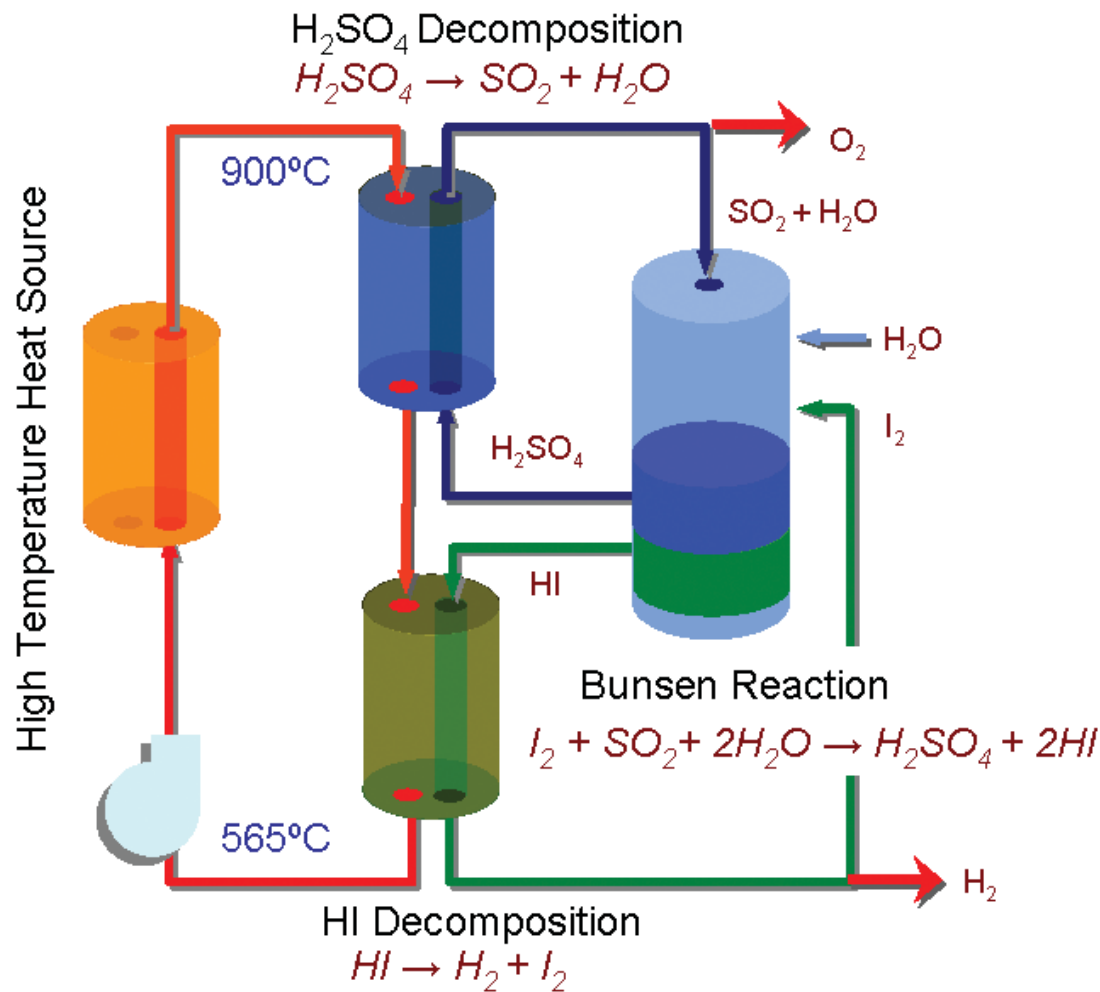
(električna energija + toplina + $\text{H}_2\text{O} \rightarrow [\text{cikličke kemijske reakcije}] \rightarrow \text{H}_2 + \text{O}_2$);

i termokemijski ciklusi

(toplina + $\text{H}_2\text{O} \rightarrow [\text{cikličke kemijske reakcije}] \rightarrow \text{H}_2 + \text{O}_2$).

Uplinjavanje uz kombinirane turbinske cikluse, a kojima se vodik proizvodi u velikom obujmu, razvijaju se u isplativi oblik centralizirane suproizvodnje vodika i električne energije, uz niske troškove stlačivanja i skladištenja vodika.

Jedna od temeljnih **termokemijskih reakcija za proizvodnju vodika** je **sumporojodični (S-I) ciklus cijepanja vode**, koji koristi toplinsku energiju iz izvora topline visoke temperature kao što su nuklearni reaktor ili *solarni toranj*. Ciklus se sastoji od tri dijela: Bunsenove reakcije, raspada sumporne kiseline te raspada HI. Toplinske je djelotvornosti od 47%, što ga čini jednim od gospodarski najpoželjnijih za industrijsku visokovolumnu proizvodnju vodika. Prednosti S-I ciklusa: odsutnost otpadnih voda, laki prijenos reaktanata u tekućem ili plinovitom obliku. Glavni problem: korozivna priroda kemikalija koje su uključene u reakciju.



ELEKTROLITIČKI PROCESI

PROIZVODNJA VODIKA ELEKTROLIZOM VODE

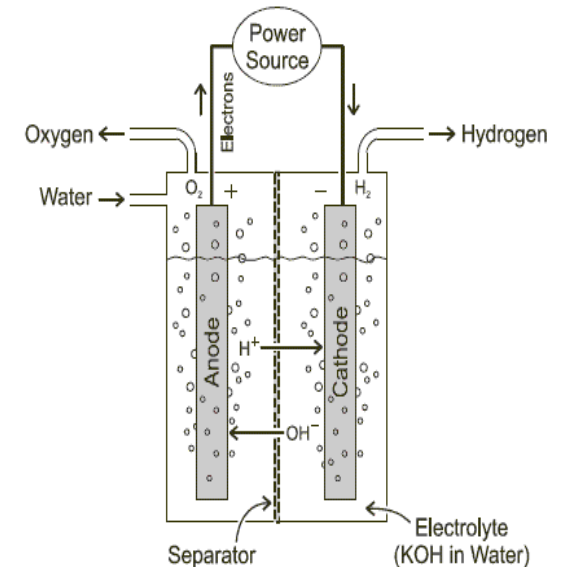
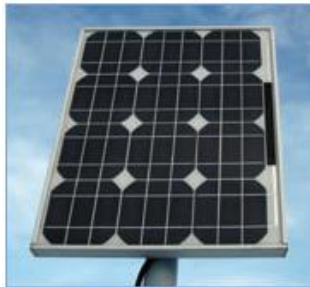
Katodna reakcija (+): $2 \text{H}_2\text{O} (\text{l}) + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g}) + 2 \text{OH}^- (\text{aq})$

Anodna reakcija (-): $4 \text{OH}^- (\text{aq}) \rightarrow \text{O}_2 (\text{g}) + 2 \text{H}_2\text{O} (\text{l}) + 4 \text{e}^-$

$$E^0 = -1,23 \text{ V}$$

Elektrolit: KOH

Elektrode (elektrokatalizator): Ni



Elektroliza je elektrokemijski proces razdvajanja vode na vodik i kisik upotrebom električne energije. Zbog visoke cijene električne energije, učinkovitost je vrlo važan parametar kod elektrolize.

Visoka učinkovitost postiže se provođenjem elektrolize pri višim temperaturama i pri višim tlakovima. Iako je elektroliza skup proces, cijena dobivenog vodika može biti znatno niža ako je korištena vršna električna energija i ako su postrojenja visokovolumna.

ELEKTROLITIČKI PROCESI

PROIZVODNJA VODIKA ELEKTROLIZOM VODE

Anoda (oksidacija): $2 \text{H}_2\text{O} (l) \rightarrow \text{O}_2 (g) + 4 \text{H}^+(aq) + 4e^-$ $E^\circ_{\text{ox}} = -1.23 \text{ V}$ ($E^\circ_{\text{red}} = 1.23$)

Katoda (redukcija): $2 \text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$ $E^\circ_{\text{red}} = 0.00 \text{ V}$

Standardni potencijal = -1.23 V na 25°C ($\Delta G = -z F E > 0$).

(potencijal polučlanka/elektrode - redukcijski)

$$E_{\text{red}} = E_{\text{red}}^\ominus - \frac{RT}{zF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}}}$$

$$E = E^0 - \frac{0.05916 \text{ V}}{z} \log_{10} \frac{a_{\text{Red}}}{a_{\text{Ox}}}$$

(potencijal članka = elektromotorna sila)

$$E_{\text{cell}} = E_{\text{cell}}^\ominus - \frac{RT}{zF} \ln Q$$

ELEKTROLITIČKI PROCESI

PROIZVODNJA VODIKA ELEKTROLIZOM VODE



Visokotlačni PEM elektrolizer
(PEM – proton exchange membrane)

- izlazni tlak vodika oko 120-200 bar na 70 °C
- nema potrebe za vanjskim kompresorom



Hvala na pažnji !