The methanol synthesis

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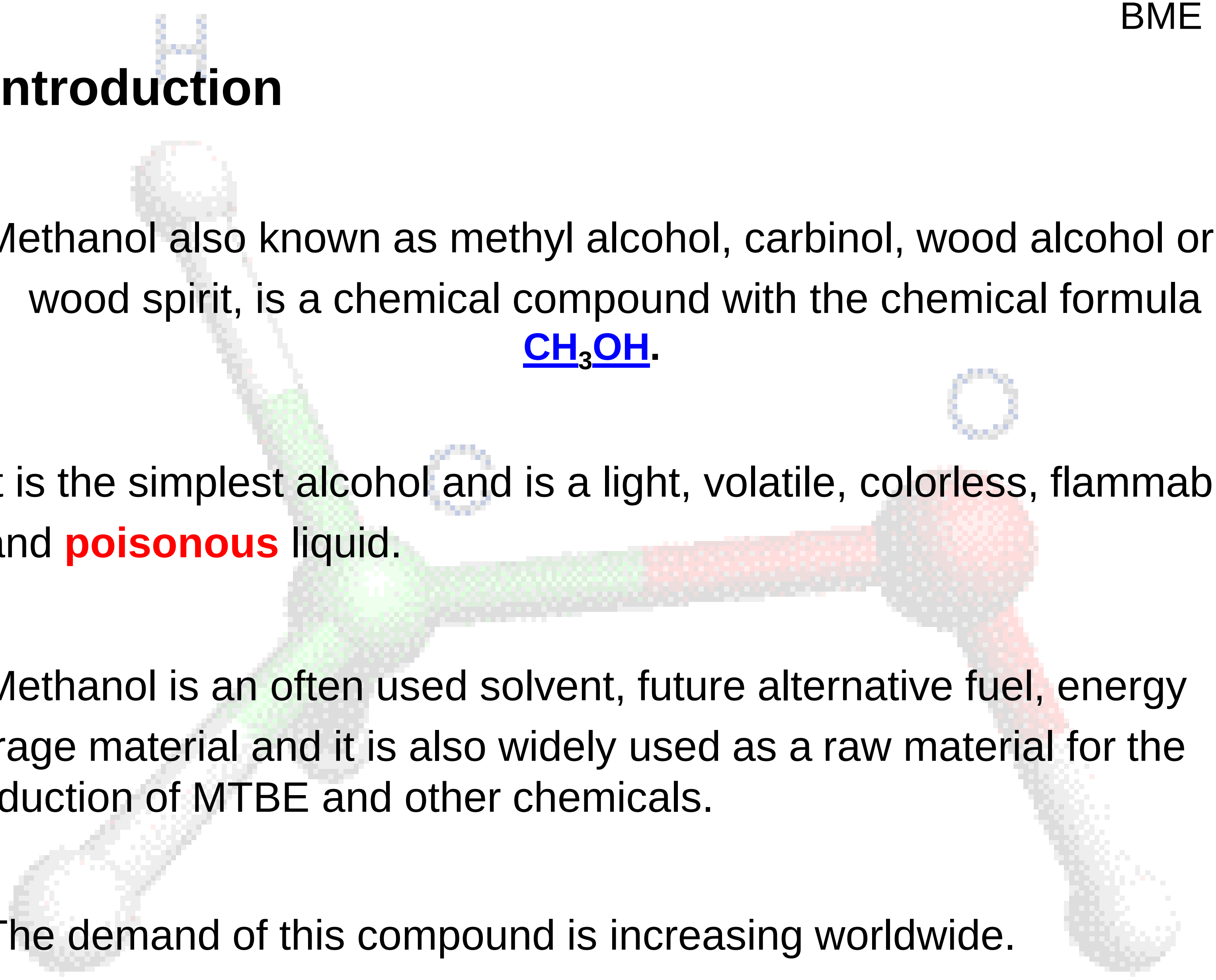
Introduction



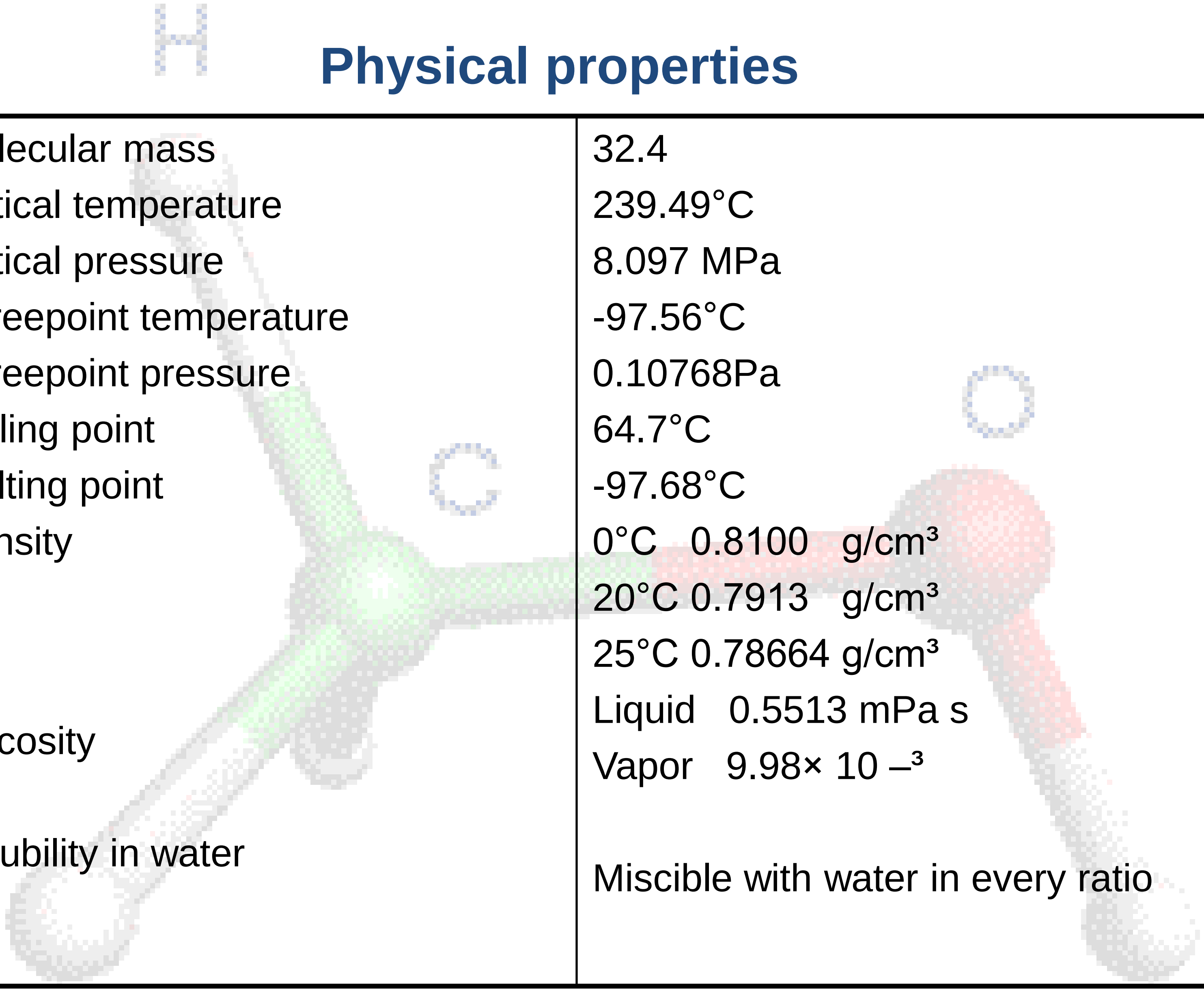
- Methanol also known as methyl alcohol, carbinol, wood alcohol or wood spirit, is a chemical compound with the chemical formula CH_3OH.

- It is the simplest alcohol and is a light, volatile, colorless, flammable and **poisonous** liquid.

- Methanol is an often used solvent, future alternative fuel, energy storage material and it is also widely used as a raw material for the production of MTBE and other chemicals.

- The demand of this compound is increasing worldwide.

Physical properties



Molecular mass	32.4
Critical temperature	239.49°C
Critical pressure	8.097 MPa
Threepoint temperature	-97.56°C
Threepoint pressure	0.10768Pa
Boiling point	64.7°C
Melting point	-97.68°C
Density	0°C 0.8100 g/cm^3
	20°C 0.7913 g/cm^3
	25°C 0.78664 g/cm^3
Viscosity	Liquid 0.5513 mPa s
	Vapor 9.98× 10^{-3}
Solubility in water	Miscible with water in every ratio

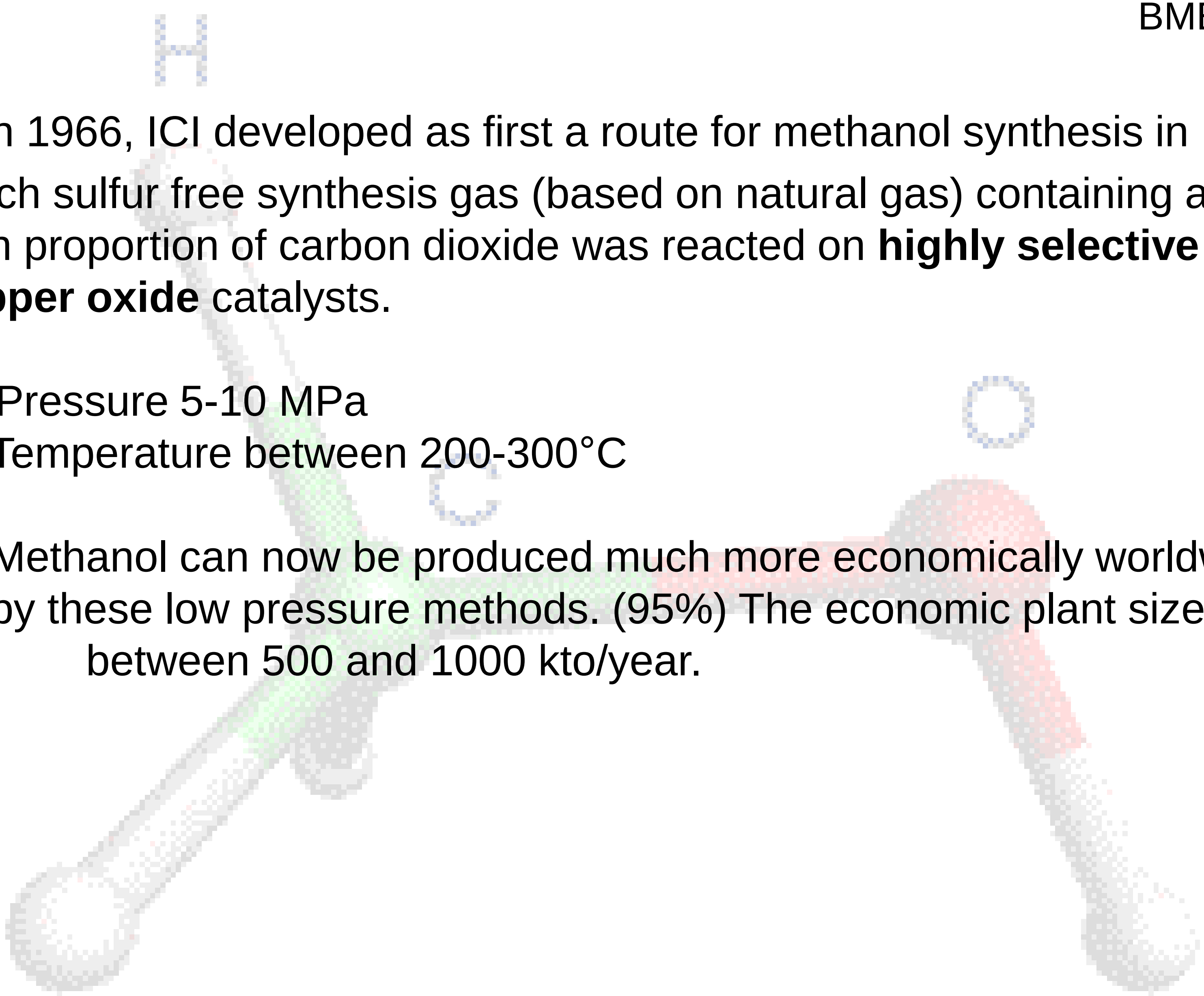
History of the methanol

- Pure methanol, was first obtained in 1661 by Robert Boyle, who called it spirit of box, because he produced it via the distillation of boxwood.

- Mittasch and his coworkers prepared a methanol containing mixture from synthesis gas(CO+H_2) with Fe catalyst in 1913 at BASF.

In **1923**, the German chemist Matthias Pier, working for BASF also, developed a highly selective catalytic reaction to convert synthesis gas (a mixture of carbon monoxide and hydrogen derived from coke and used as the source of hydrogen in synthetic ammonia production) into methanol.

Pressure 25 – 35 MPa
Temperatures of about 400°C.
Catalyst ZnO/Cr_2O_3 on alumina



- In 1966, ICI developed as first a route for methanol synthesis in which sulfur free synthesis gas (based on natural gas) containing a high proportion of carbon dioxide was reacted on **highly selective copper oxide** catalysts.

Pressure 5-10 MPa
Temperature between 200-300°C

Methanol can now be produced much more economically worldwide by these low pressure methods. (95%) The economic plant size is between 500 and 1000 kto/year.

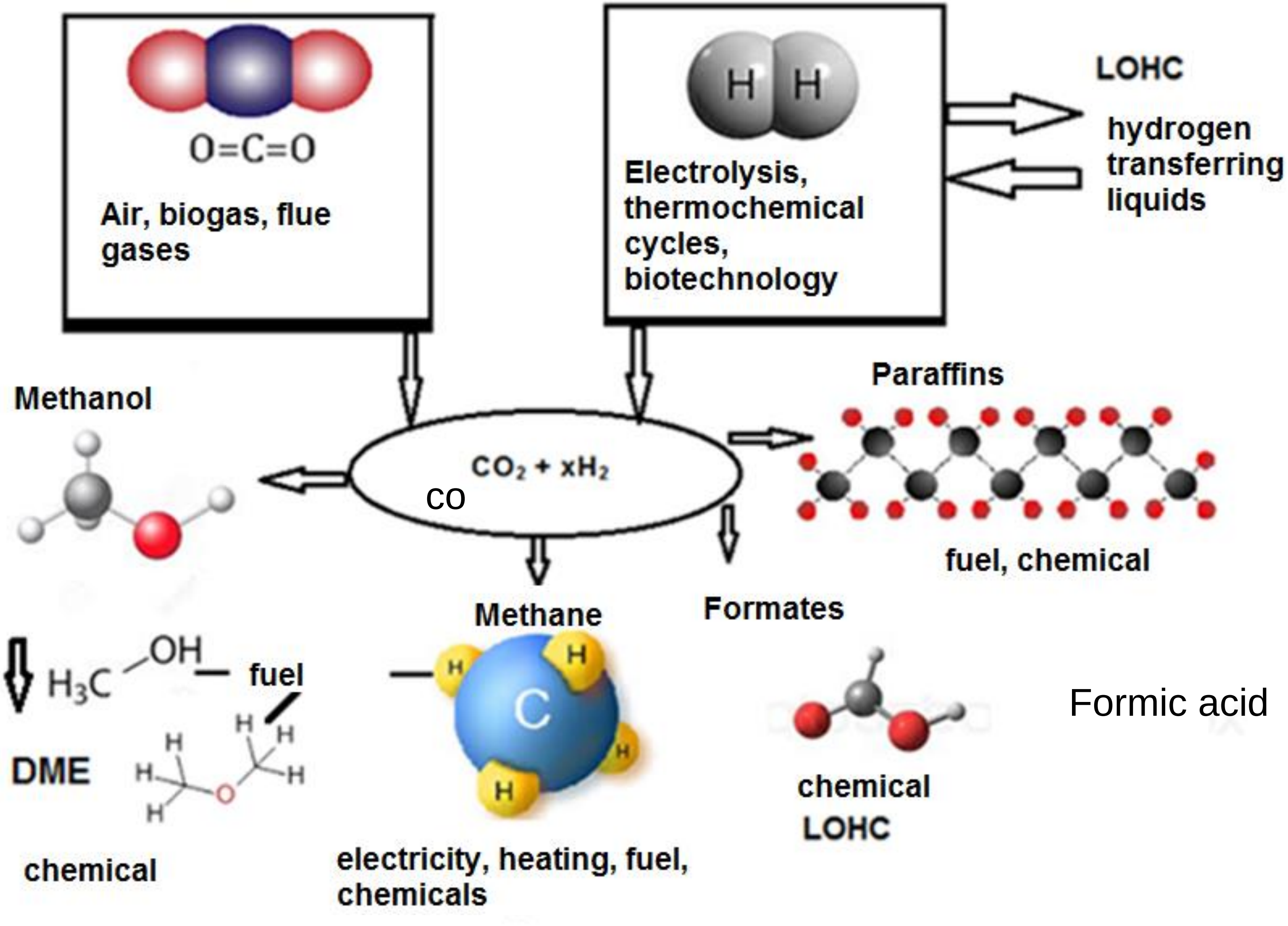
The methanol, as energy storage material

The output of renewable energy production (wind turbines, photovoltaics) changes significantly with time (exceptions are biogas and geothermal energy), therefore storage capacities are needed to overcome the low production periods in order to ensure the continuous electric energy supply. The feasible solution for energy storage is the use of diverse methods and capacities.

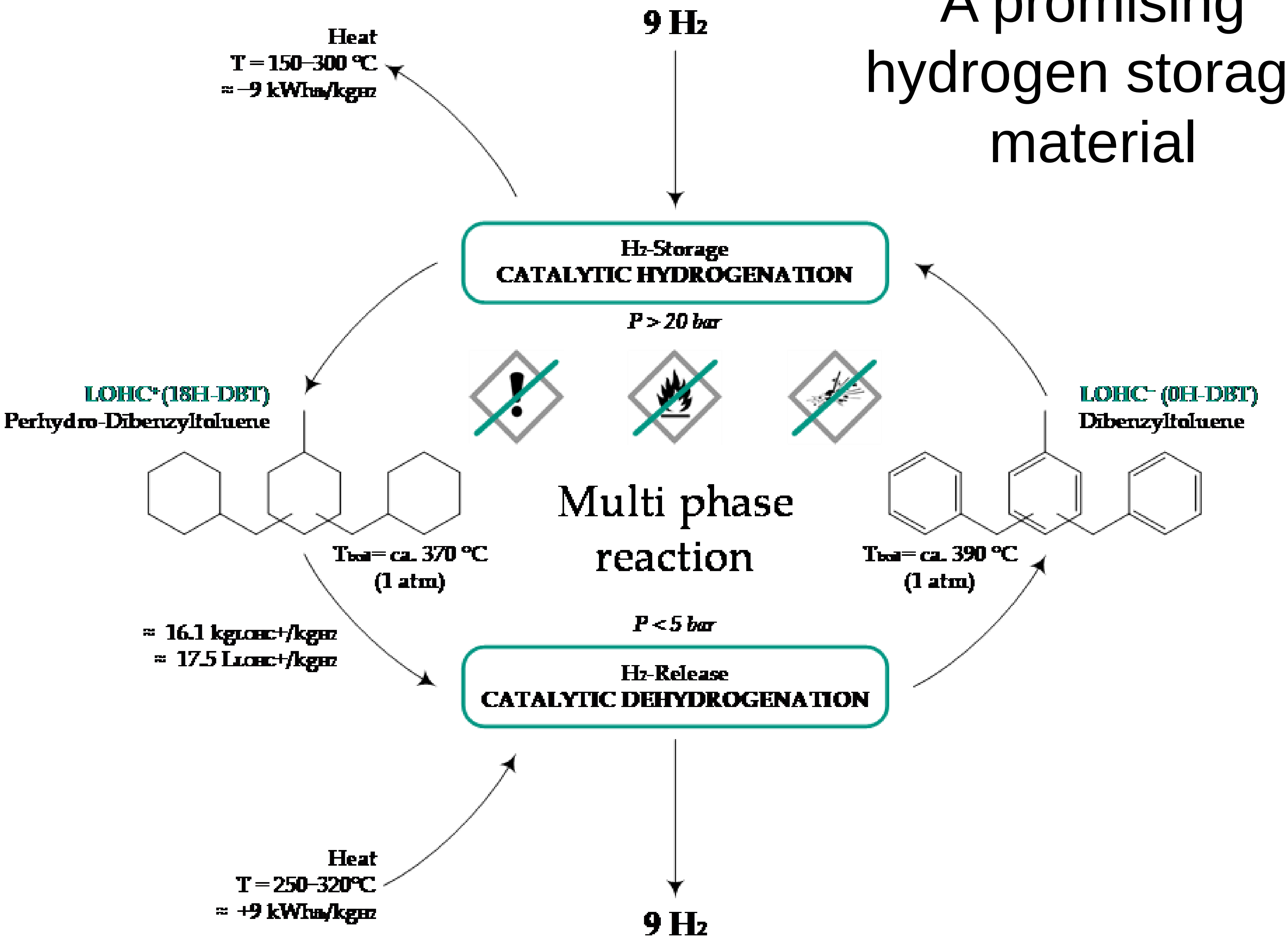
George Olah (Nobel prize winner 1994) and his coworkers, in their book about „Methanol Economy" discuss the options and vote for methanol as fuel and energy storing material.

According to their opinion methanol can be the alternative of hydrogen!?

Energy storing materials



A promising hydrogen storage material



$9\ H_2$

Heat
$T = 150–300\ °C$
$\approx -9\ kWh_{th}/kg_{H2}$

H_2-Storage
CATALYTIC HYDROGENATION

$P > 20$ bar

LOHC⁺(18H-DBT)
Perhydro-Dibenzyltoluene

T_{boil}= ca. 370 °C
(1 atm)

Multi phase reaction

LOHC⁻ (0H-DBT)
Dibenzyltoluene

T_{boil}= ca. 390 °C
(1 atm)

$\approx 16.1\ kg_{LOHC+}/kg_{H2}$
$\approx 17.5\ L_{LOHC+}/kg_{H2}$

$P < 5$ bar

H_2-Release
CATALYTIC DEHYDROGENATION

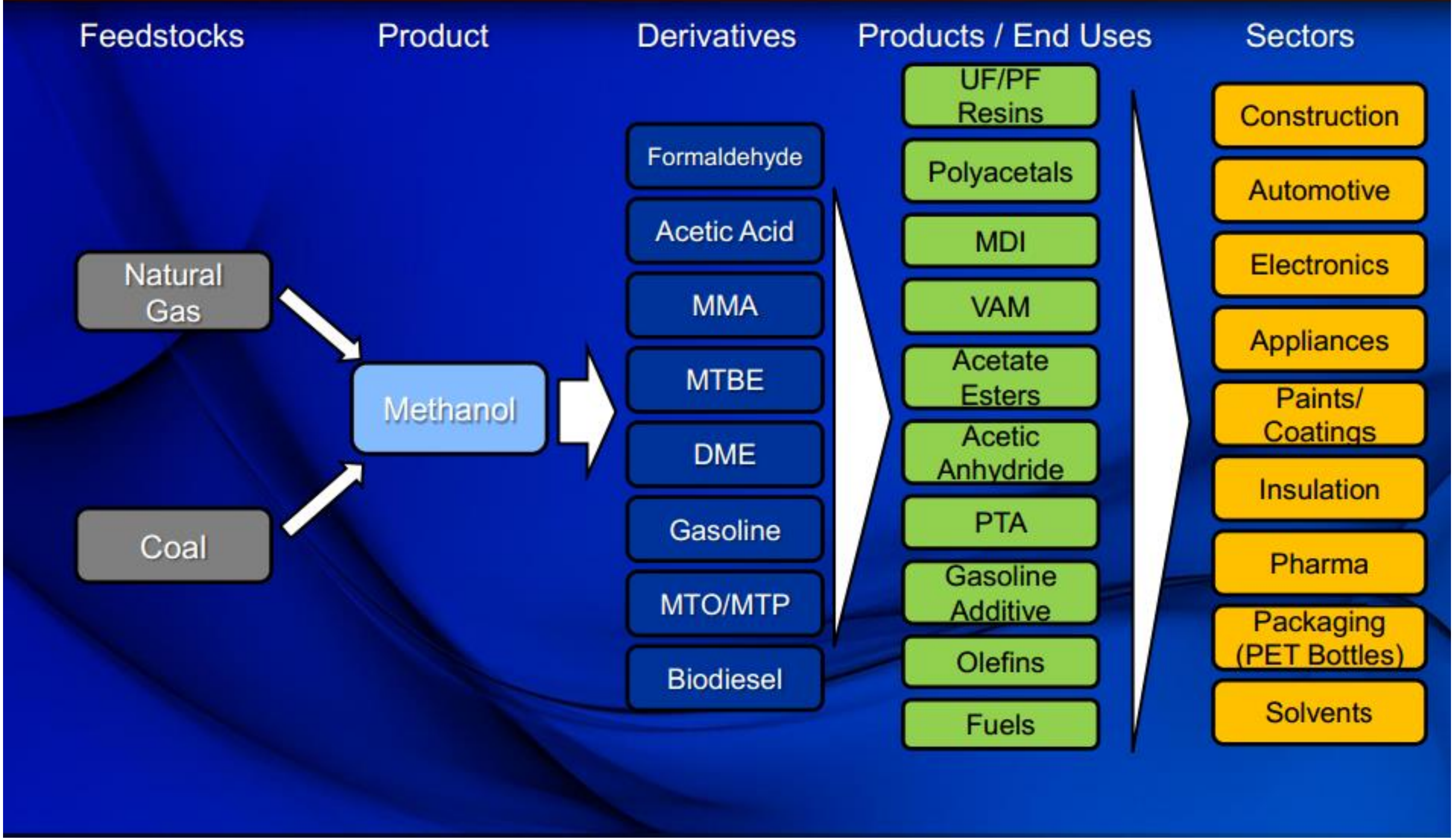
Heat
$T = 250–320°C$
$\approx +9\ kWh_{th}/kg_{H2}$

$9\ H_2$

Uses of the methanol

- As a solvent and as an antifreeze in pipelines.
- About 40% of methanol is converted to formaldehyde, and from there into products as diverse as plastics, plywood, paints, explosives and permanent press textiles.
- Large amounts of methanol is used to produce the gasoline additive octane enhancer methyl tert-butyl ether (MTBE).
- Other chemical derivatives of methanol include dimethyl ether, which has replaced chlorofluorocarbons as the propellant in aerosol sprays, and another main product is acetic acid.

Value Chain - Methanol



Feedstocks

- Natural Gas
- Coal

Product

- Methanol

Derivatives

- Formaldehyde
- Acetic Acid
- MMA
- MTBE
- DME
- Gasoline
- MTO/MTP
- Biodiesel

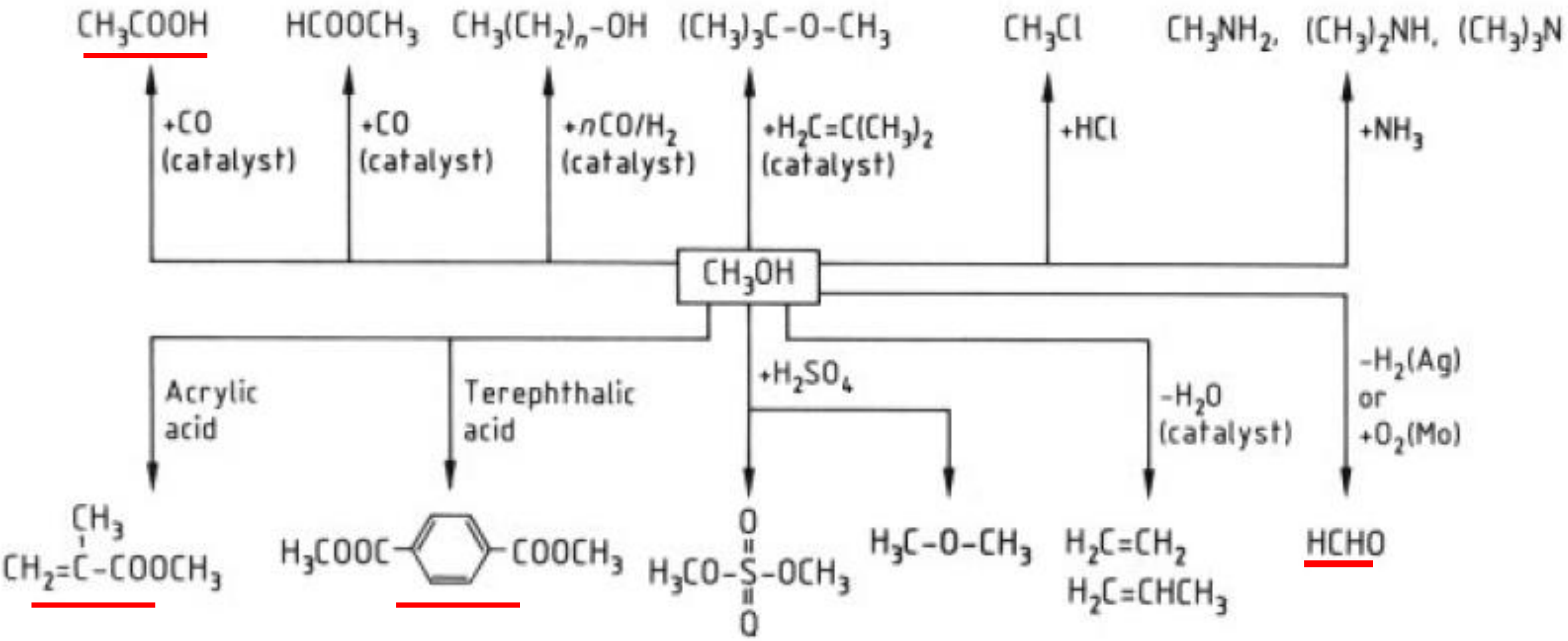
Products / End Uses

- UF/PF Resins
- Polyacetals
- MDI
- VAM
- Acetate Esters
- Acetic Anhydride
- PTA
- Gasoline Additive
- Olefins
- Fuels

Sectors

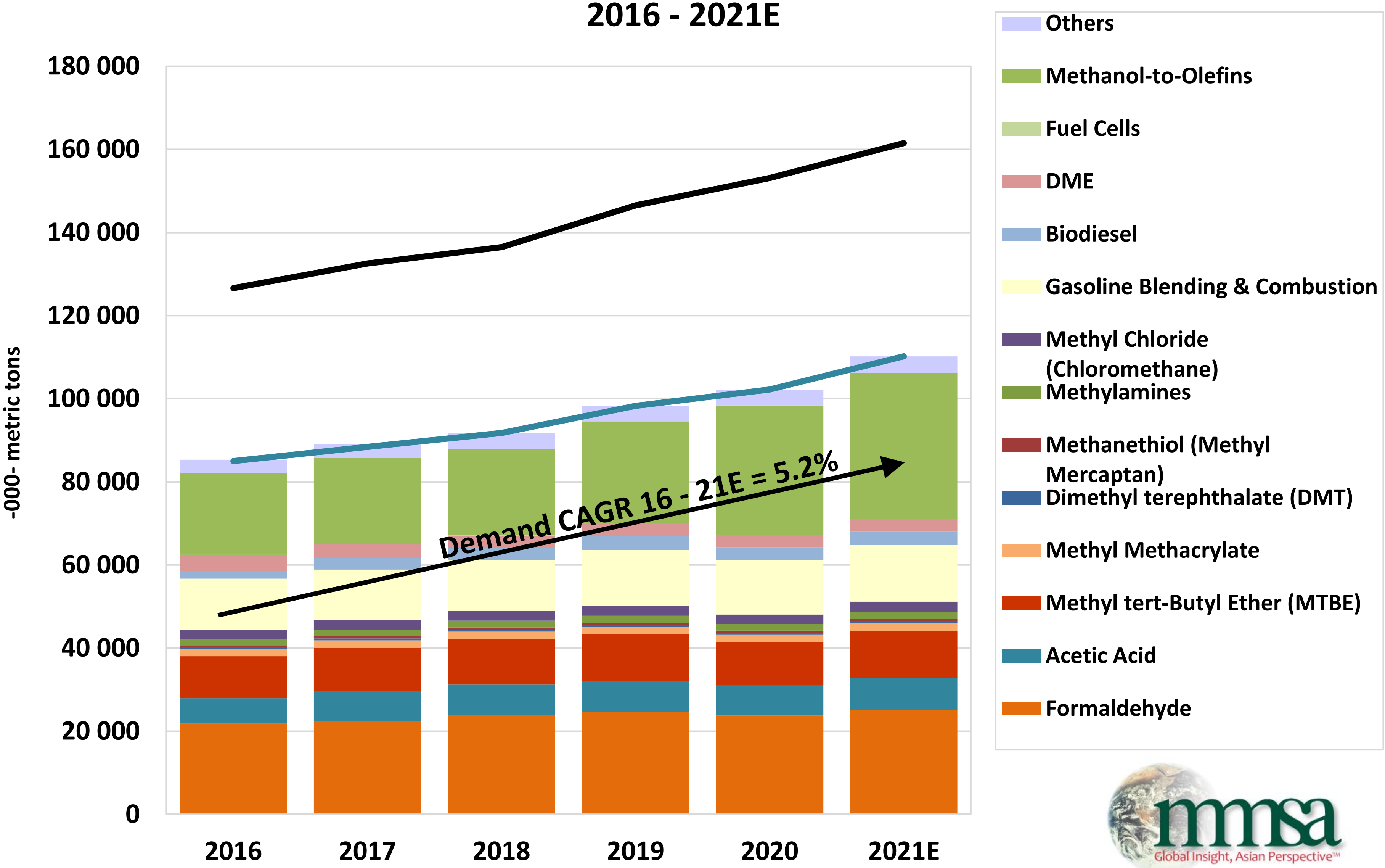
- Construction
- Automotive
- Electronics
- Appliances
- Paints/ Coatings
- Insulation
- Pharma
- Packaging (PET Bottles)
- Solvents

The use of methanol for synthetic purposes



MMSA Global Methanol Supply and Demand Balance

2016 - 2021E



mmsa
Global Insight, Asian Perspective™

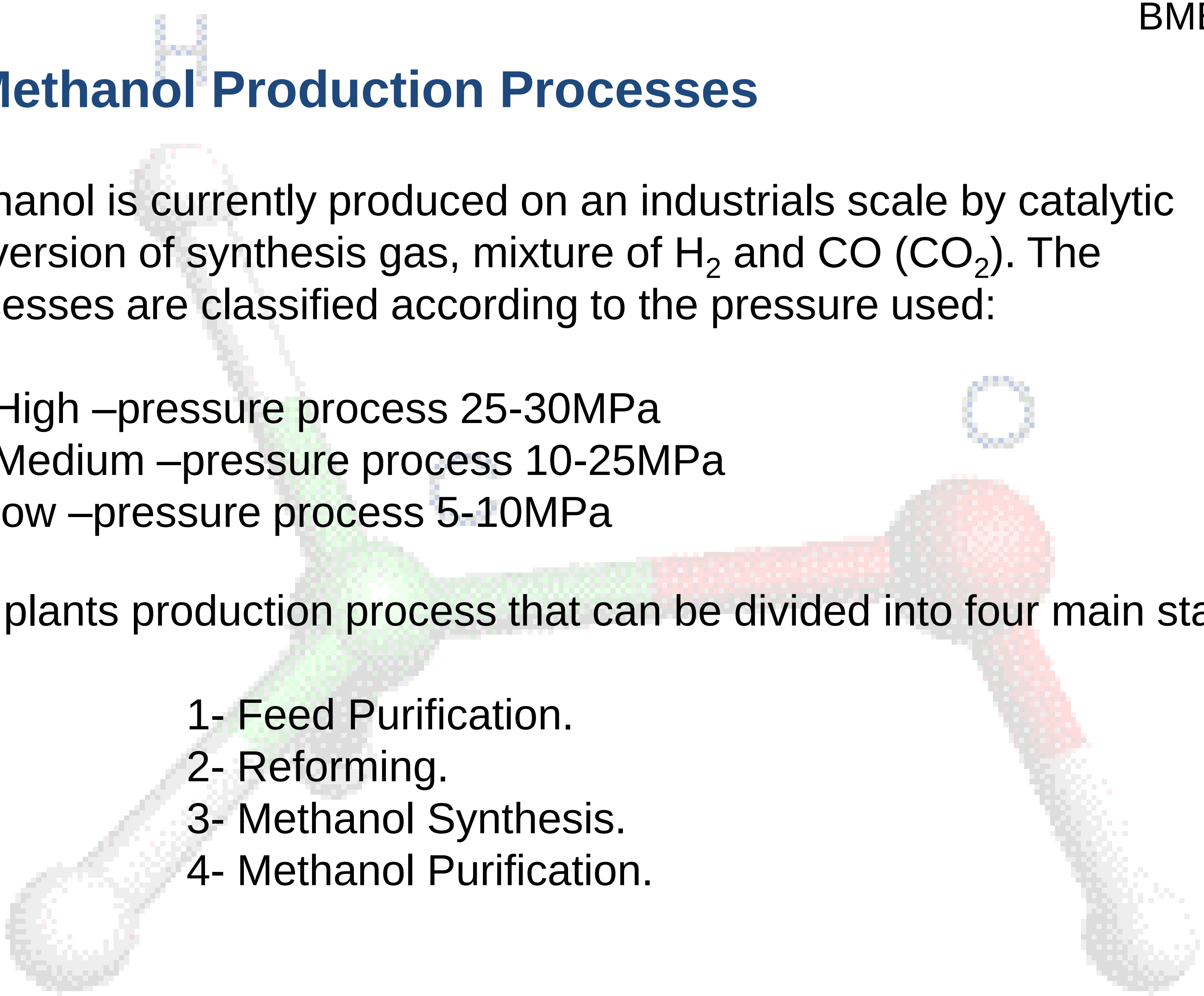
Main parts of methanol production plants

1- Purification of raw materials.

2- Steam Reforming of methane.

3- Methanol synthesis.

4- Methanol purification



Methanol Production Processes

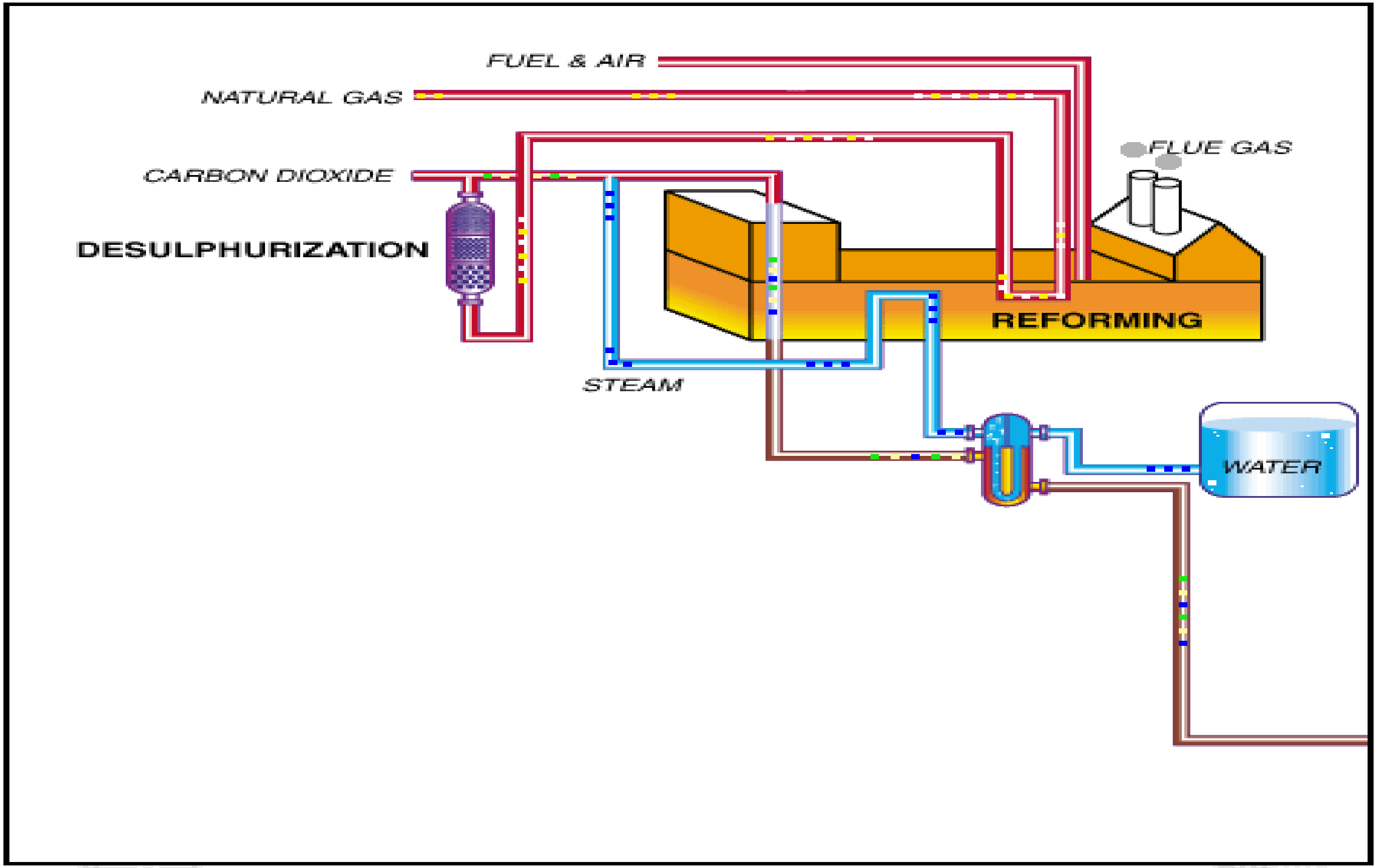
Methanol is currently produced on an industrials scale by catalytic conversion of synthesis gas, mixture of H_2 and CO (CO_2). The processes are classified according to the pressure used:

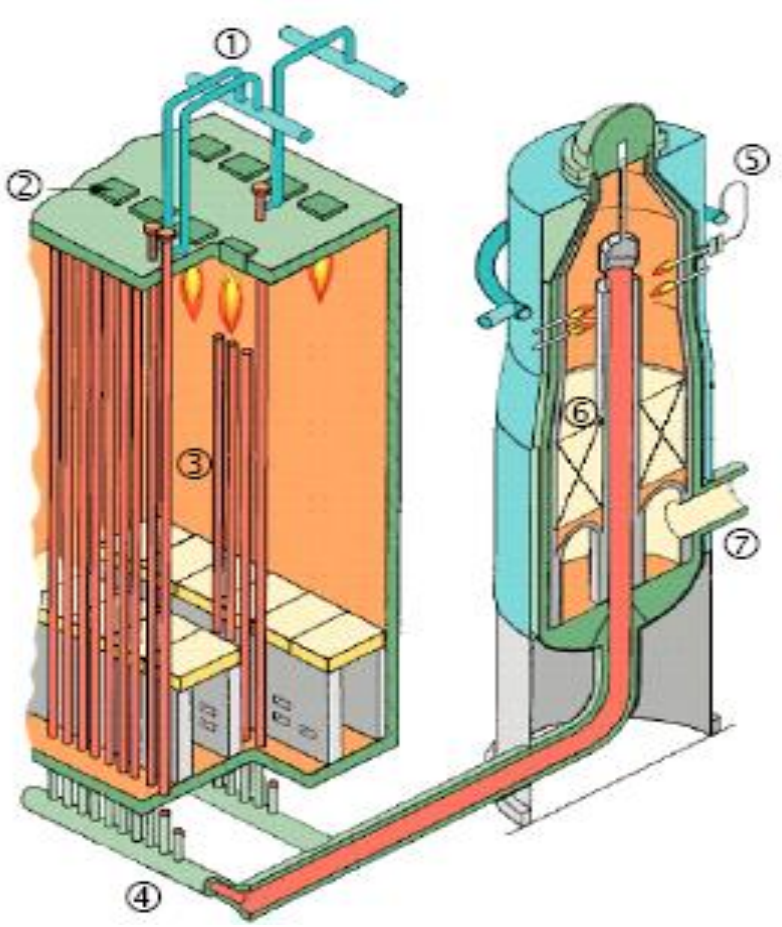
1- High –pressure process 25-30MPa
2- Medium –pressure process 10-25MPa
3- low –pressure process 5-10MPa

The plants production process that can be divided into four main stages:

1- Feed Purification.
2- Reforming.
3- Methanol Synthesis.
4- Methanol Purification.

Feed Purification and Reforming (1, 2)



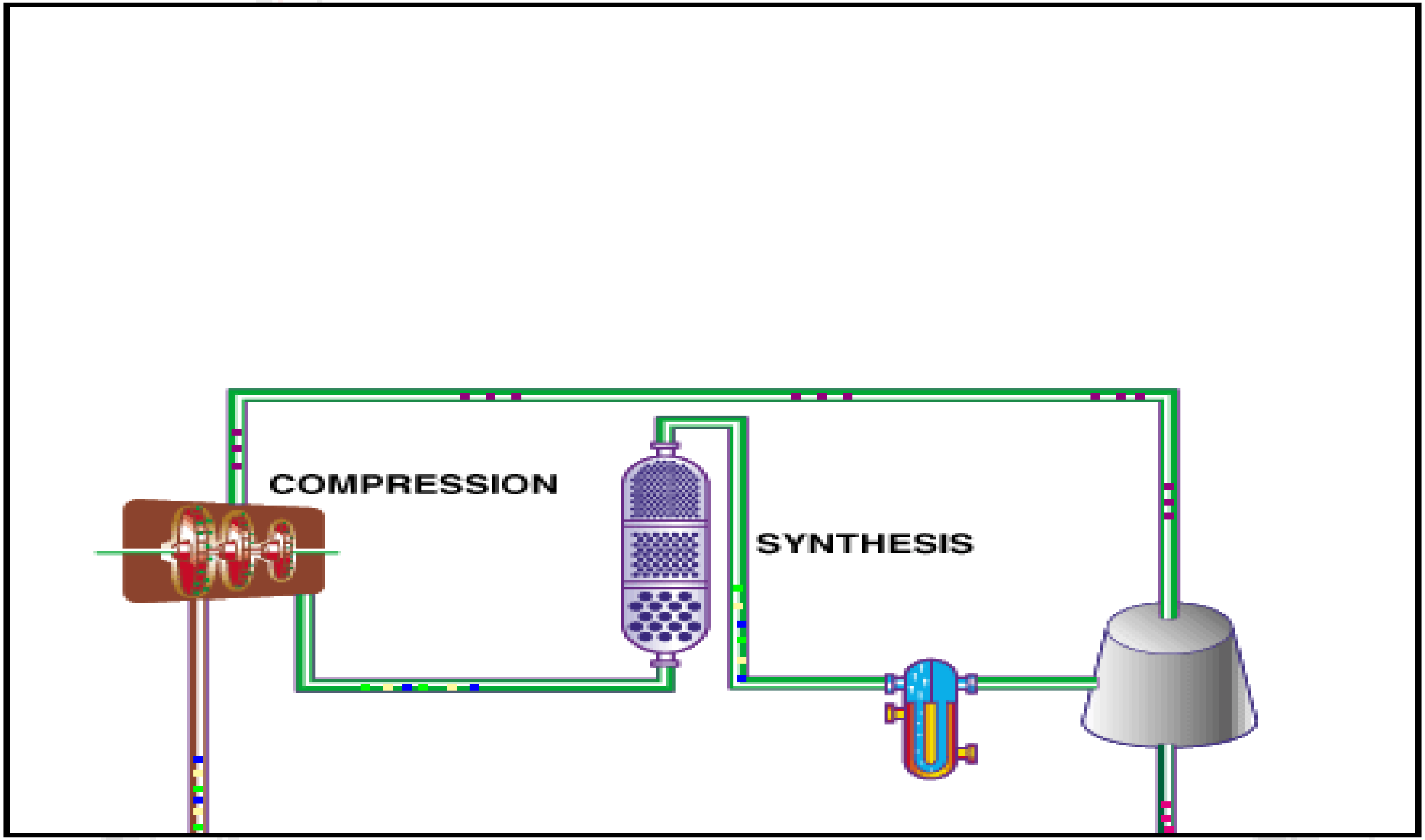


Uhde radiation and secondary water-gas shift reformer

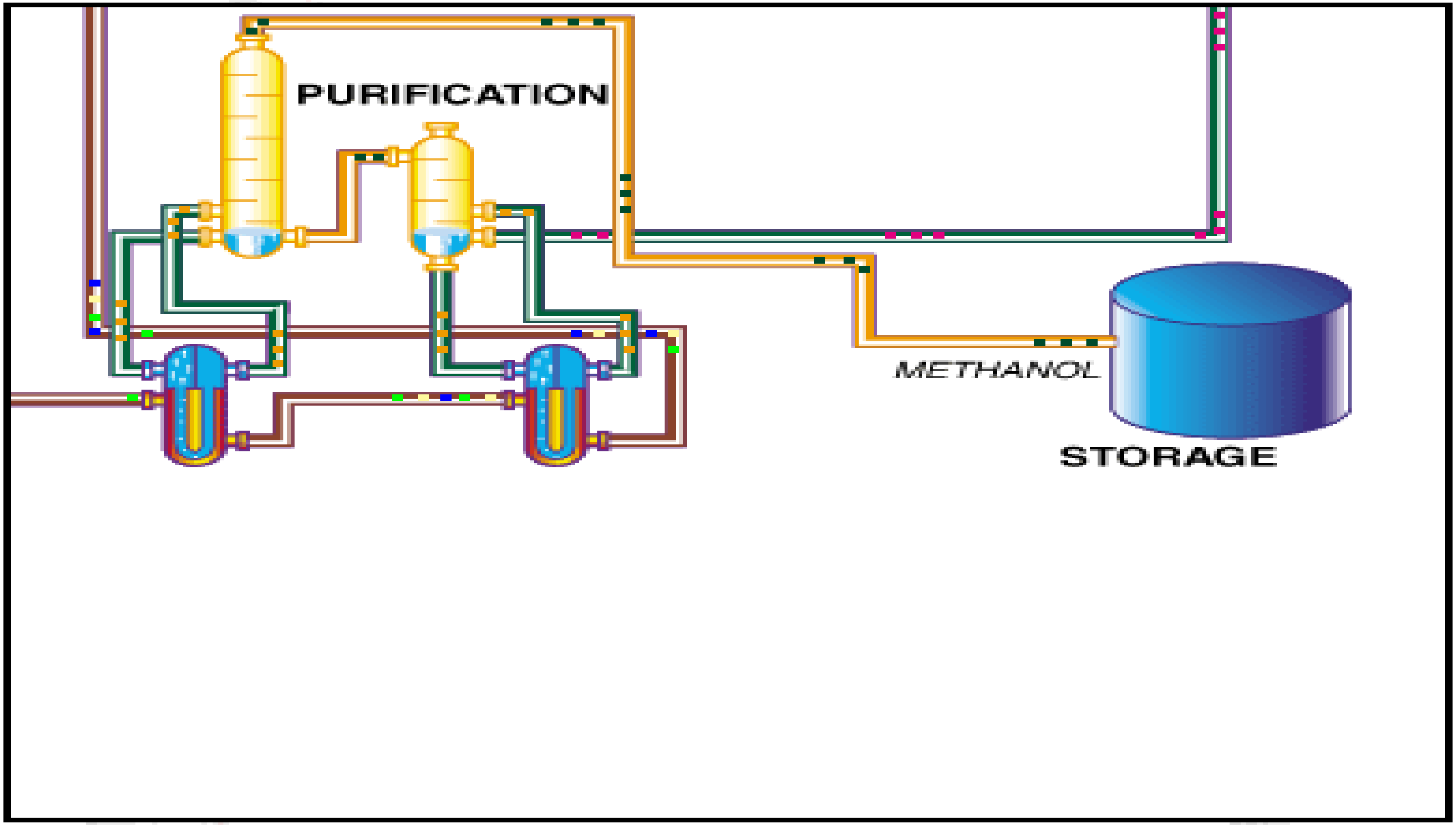
1) Gas introduction 2) burners, 3) reforming tubes, 4) outlet 5) air introduction, 6) catalyst bed 7) gas outlet

Reforming tubes contain Ni catalyst, pressure 10-20 bar, temperature ~850^{o}C

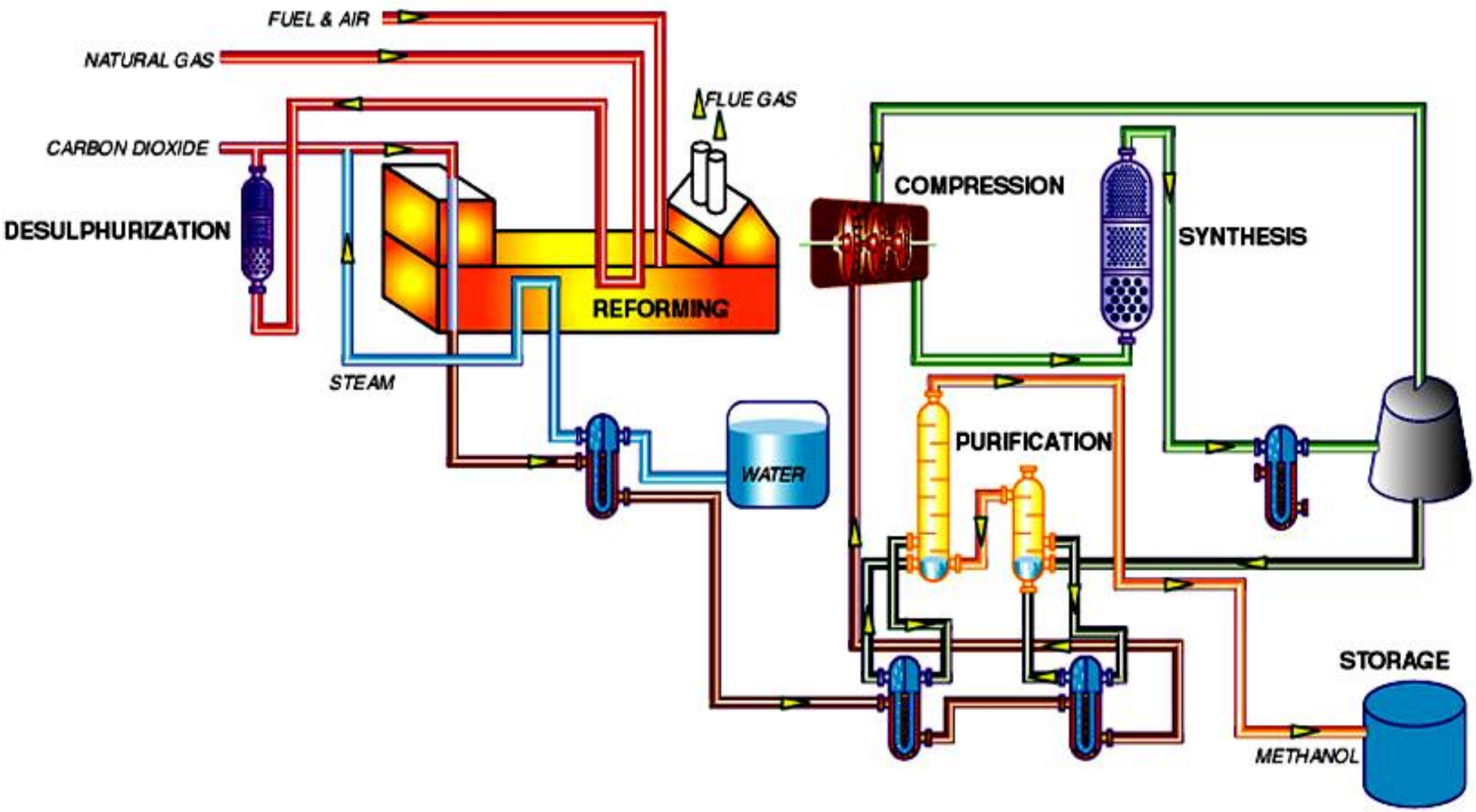
Methanol Synthesis (3)



Methanol Purification (4)



Methanol Production Processes



Synthesis Gas Generation

Today, synthesis gas is most commonly produced from methane, from natural gas rather than from coal.
At moderate pressures of 1 to 2 MPa (10–20 atm) and high temperature (around 850 °C), methane reacts with steam on a nickel catalyst to produce synthesis gas according to

$$CH_4 + H_2O = CO + 3H_2$$

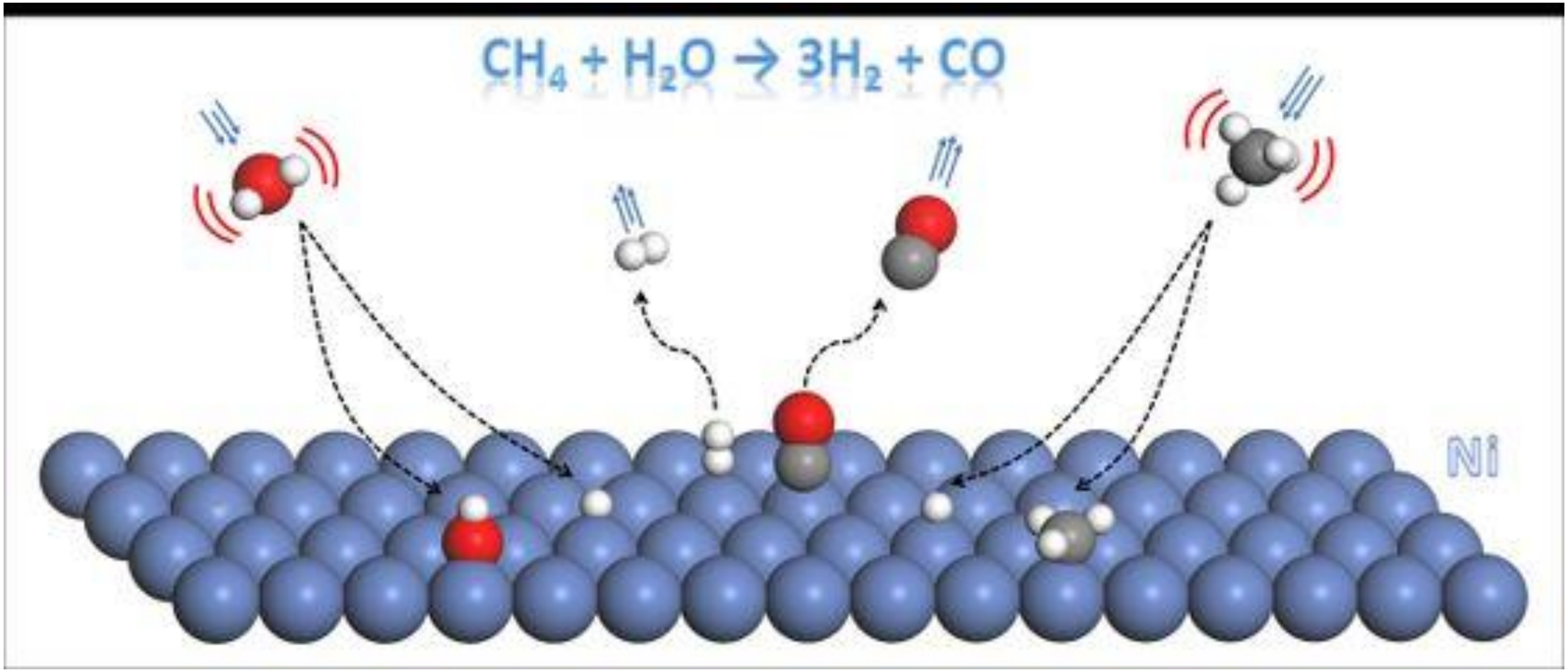
This reaction, commonly called steam-methane reforming or SMR, is endothermic.

The next step can be the CO conversion:

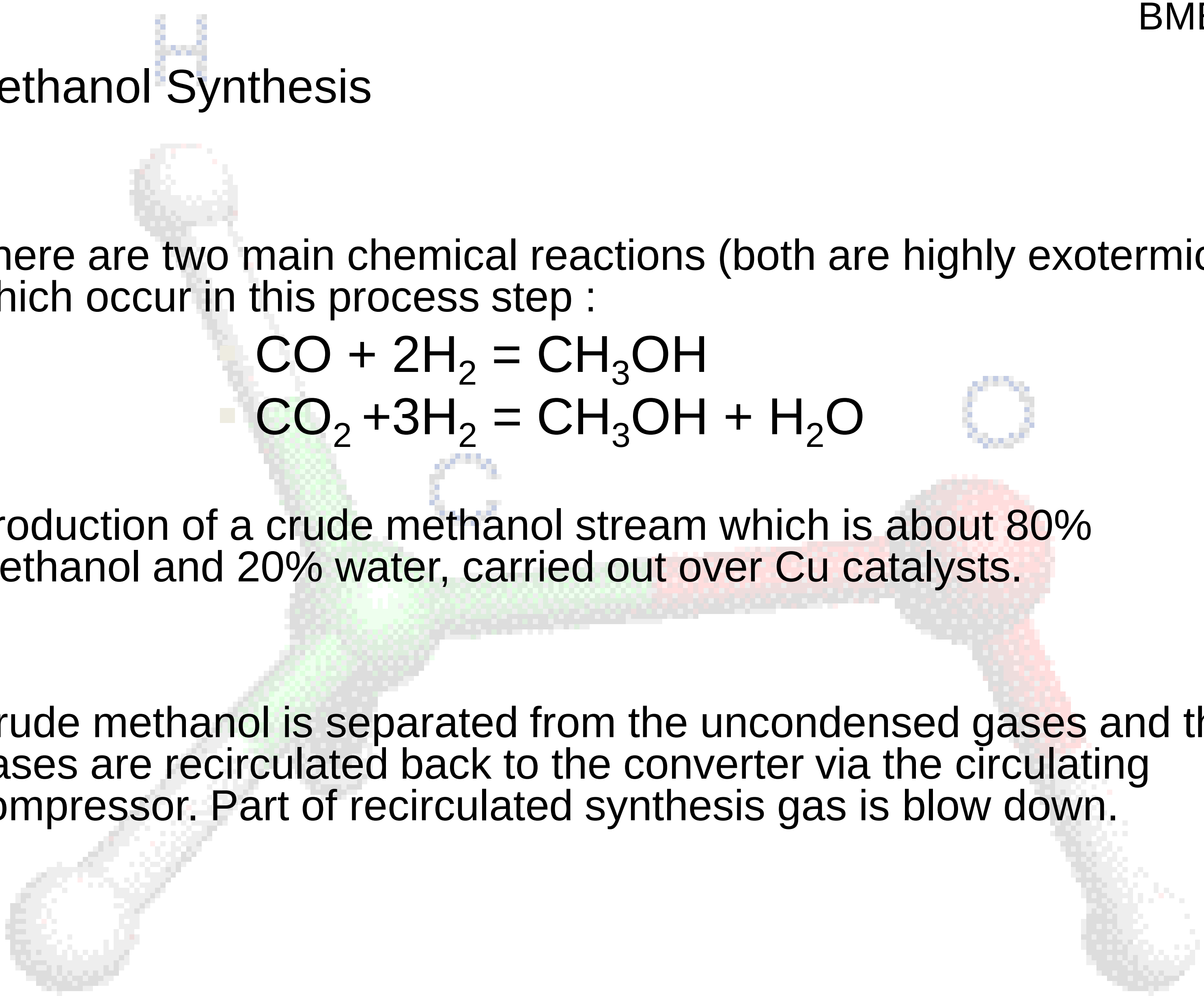
$$CO + H_2O = CO_2 + H_2$$

This is exothermic reaction.

No. 2. Water gas-shift reaction of methane on Ni catalyst

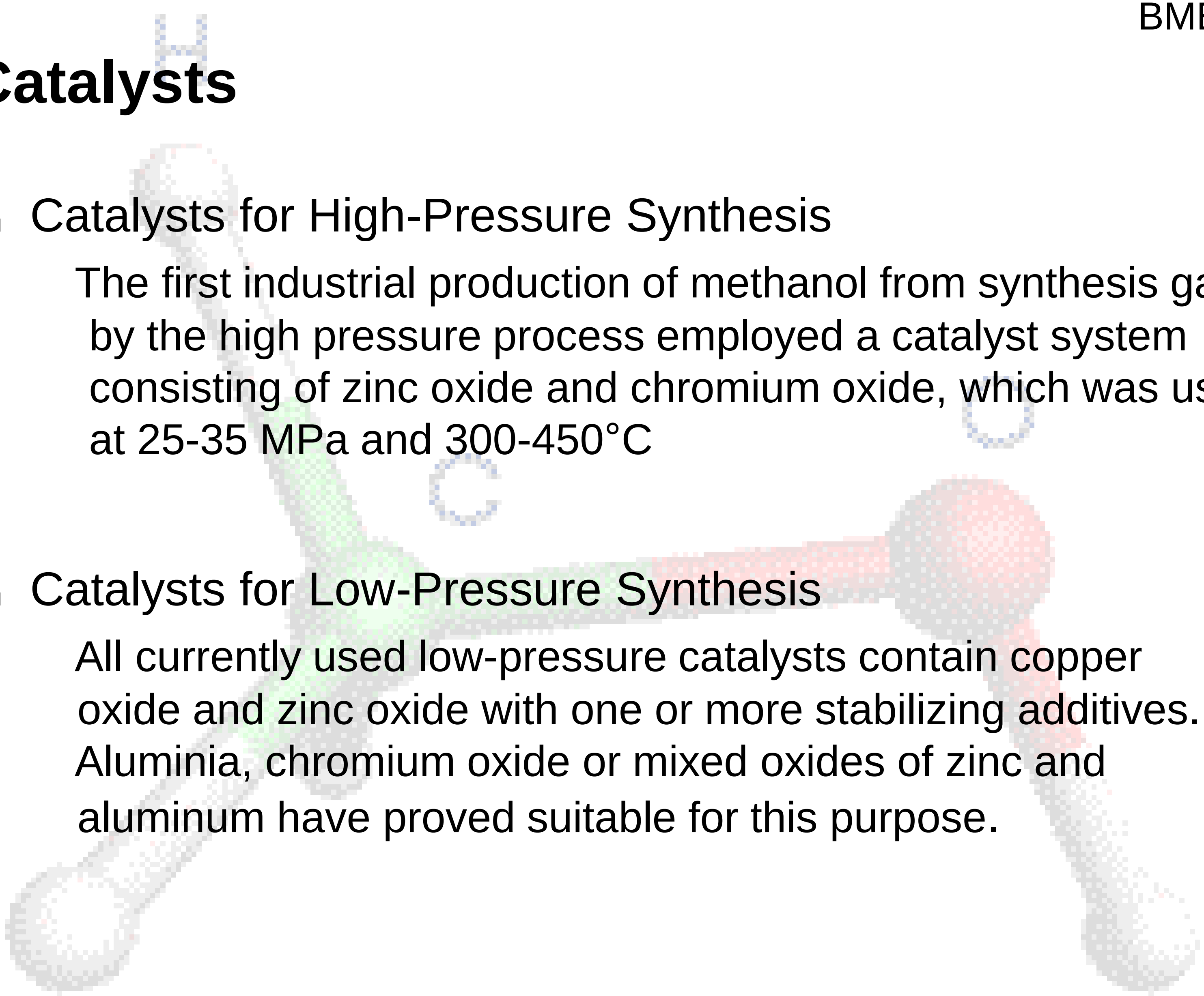


Methanol Synthesis



- There are two main chemical reactions (both are highly exotermic) which occur in this process step :
  - $CO + 2H_2 = CH_3OH$
  - $CO_2 + 3H_2 = CH_3OH + H_2O$
- Production of a crude methanol stream which is about 80% methanol and 20% water, carried out over Cu catalysts.
- Crude methanol is separated from the uncondensed gases and the gases are recirculated back to the converter via the circulating compressor. Part of recirculated synthesis gas is blow down.

Catalysts



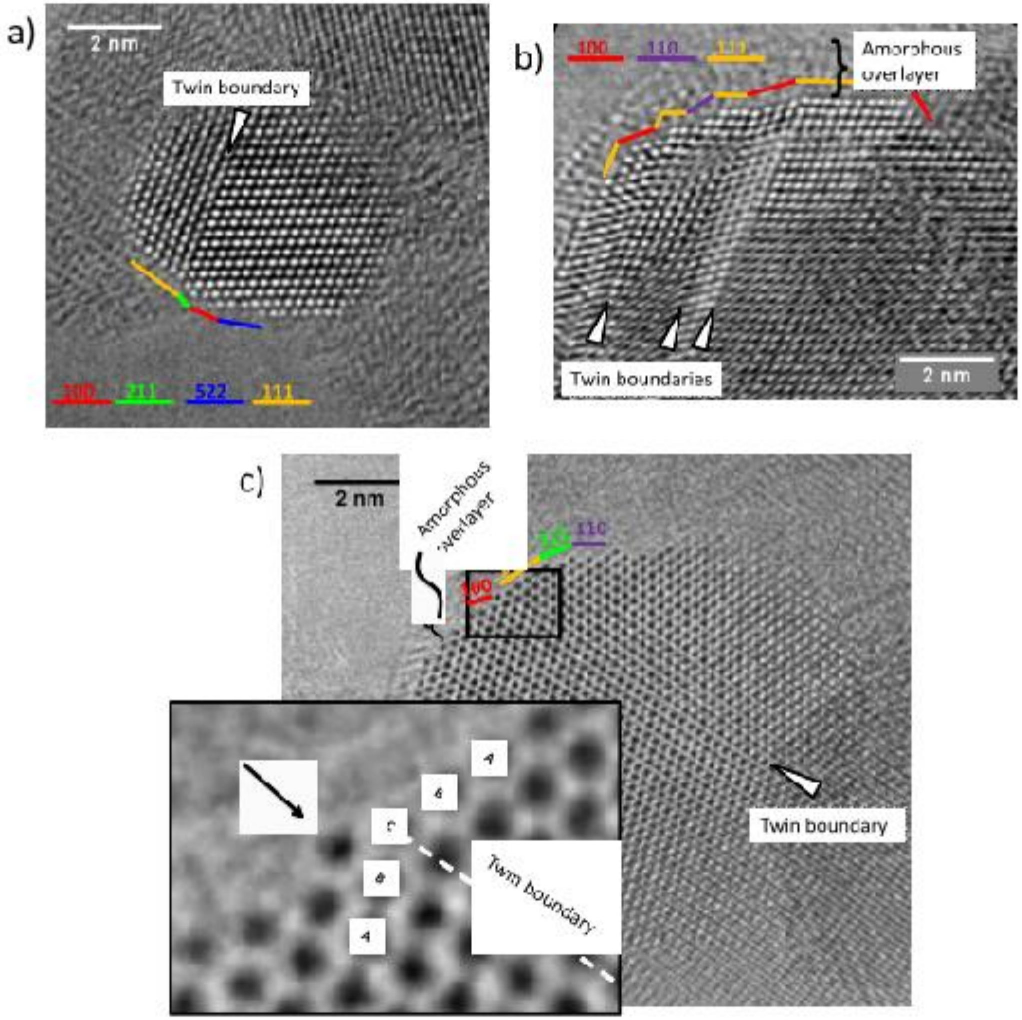
- Catalysts for High-Pressure Synthesis

  The first industrial production of methanol from synthesis gas by the high pressure process employed a catalyst system consisting of zinc oxide and chromium oxide, which was used at 25-35 MPa and 300-450°C

- Catalysts for Low-Pressure Synthesis

  All currently used low-pressure catalysts contain copper oxide and zinc oxide with one or more stabilizing additives. Aluminia, chromium oxide or mixed oxides of zinc and aluminum have proved suitable for this purpose.

The industrial catalyst Cu/ZnO/Al_2O_3 consists of active sites with Cu steps, decorated with Zn atoms and defects which stabilize these steps.

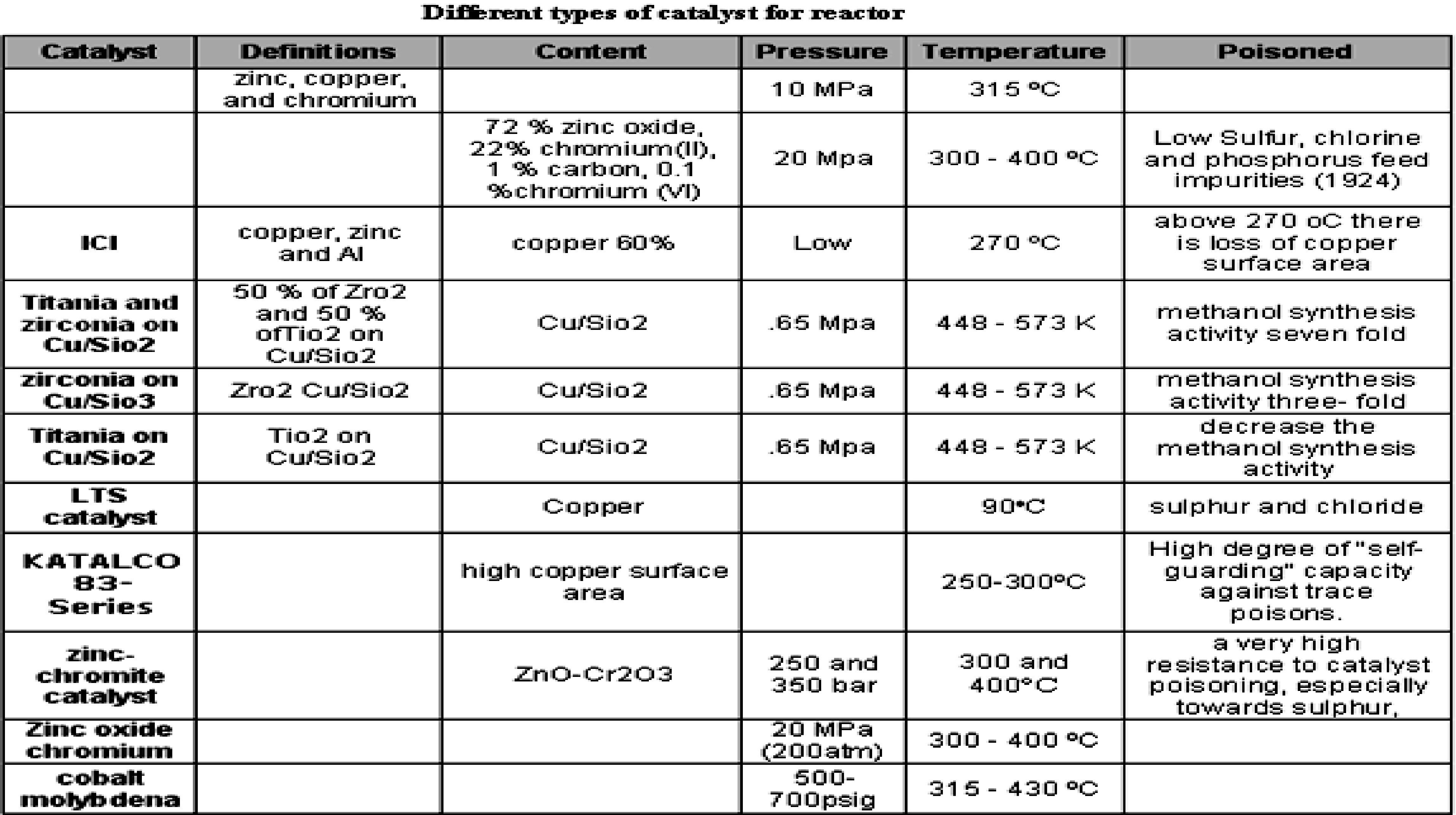


HRTEM pictures about the catalyst surface, with steps, decorating ZnO layer and at the meeting points of regular lattice planes there are the defects.

Catalyst Selection

BME

- Catalyst is an important item, its activity and poison resistance:
- the pressure and temperature of the reactor depends on the properties of the catalyst.



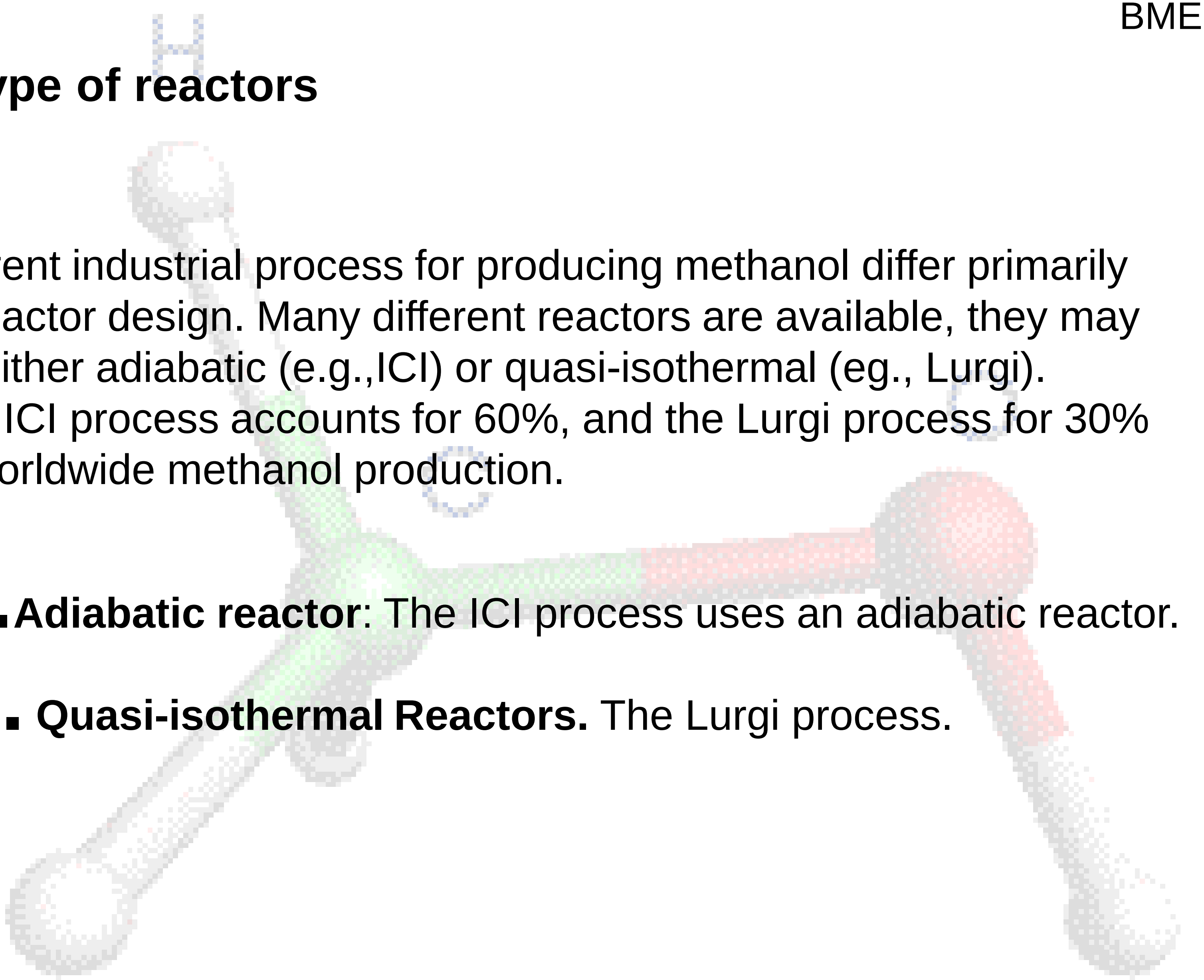
Different types of catalyst for reactor

Catalyst	Definitions	Content	Pressure	Temperature	Poisoned
	zinc, copper, and chromium		10 MPa	315 °C	
		72 % zinc oxide, 22% chromium(II), 1 % carbon, 0.1 %chromium (VI)	20 Mpa	300 - 400 °C	Low Sulfur, chlorine and phosphorus feed impurities (1924)
ICI	copper, zinc and Al	copper 60%	Low	270 °C	above 270 oC there is loss of copper surface area
Titania and zirconia on Cu/Sio2	50 % of Zro2 and 50 % ofTio2 on Cu/Sio2	Cu/Sio2	.65 Mpa	448 - 573 K	methanol synthesis activity seven fold
zirconia on Cu/Sio3	Zro2 Cu/Sio2	Cu/Sio2	.65 Mpa	448 - 573 K	methanol synthesis activity three- fold
Titania on Cu/Sio2	Tio2 on Cu/Sio2	Cu/Sio2	.65 Mpa	448 - 573 K	decrease the methanol synthesis activity
LTS catalyst		Copper		90•C	sulphur and chloride
KATALCO 83-Series		high copper surface area		250-300°C	High degree of "self-guarding" capacity against trace poisons.
zinc-chromite catalyst		ZnO-Cr2O3	250 and 350 bar	300 and 400°C	a very high resistance to catalyst poisoning, especially towards sulphur,
Zinc oxide chromium			20 MPa (200atm)	300 - 400 °C	
cobalt molybdena			500-700psig	315 - 430 °C	

Table 1—Commercial methanol synthesis catalyst formulations

Manufacturer	Cu	Zn	Al	Other	Patent date
	(atom%)	(atom%)	(atom%)		
IFP	45-70	15-35	20-Apr	Zr-2-18	1987
ICI	20-35	15-50	20-Apr	Mg	1965
BASF	38.5	48.8	12.9		1978
Shell	71	24		Rare Earth oxide –5	1973
Sud Chemie	65	22	12		1987
Dupont	50	19	31		none found
United Catalysts	62	21	17		none found
Haldor Topsoe	> 55	21-25	10-Aug		none found
MK-121					

Source: P.L. Spath and D.C. Dayton, Preliminary screening—technical and economic assessment of synthesis gas to fuels and chemicals with emphasis on the potential for biomas-derived syngas, National Renewable Energy Laboratory, NREL/TP-510-34929, December, 2003.



Type of reactors

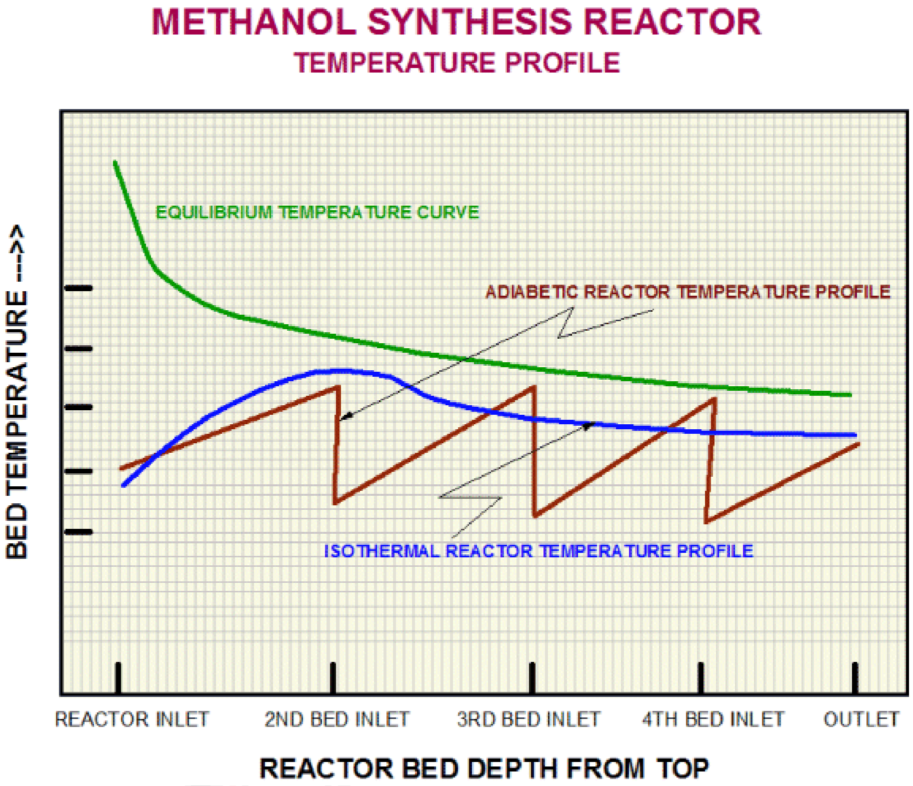
Current industrial process for producing methanol differ primarily in reactor design. Many different reactors are available, they may be either adiabatic (e.g.,ICI) or quasi-isothermal (eg., Lurgi).
The ICI process accounts for 60%, and the Lurgi process for 30% of worldwide methanol production.

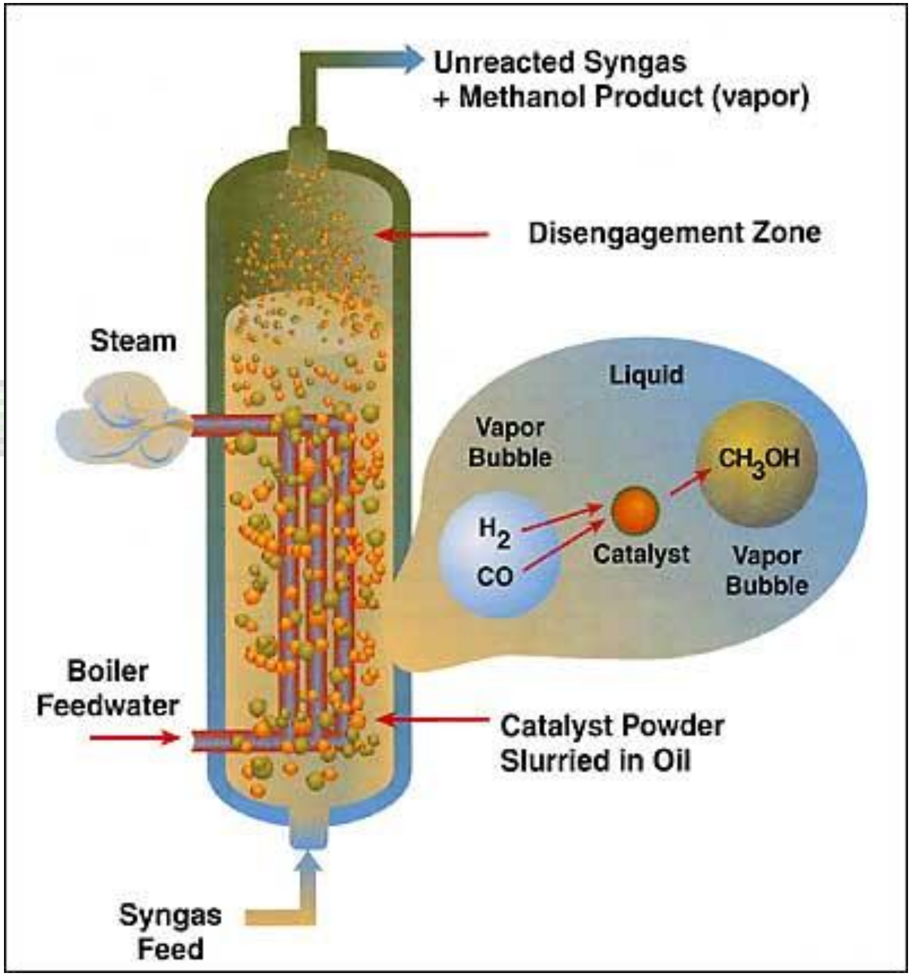
- **Adiabatic reactor**: The ICI process uses an adiabatic reactor.
- **Quasi-isothermal Reactors.** The Lurgi process.

Reactor types

Stepwise adiabatic reactor

Quasi isotherm reactor Lurgi process





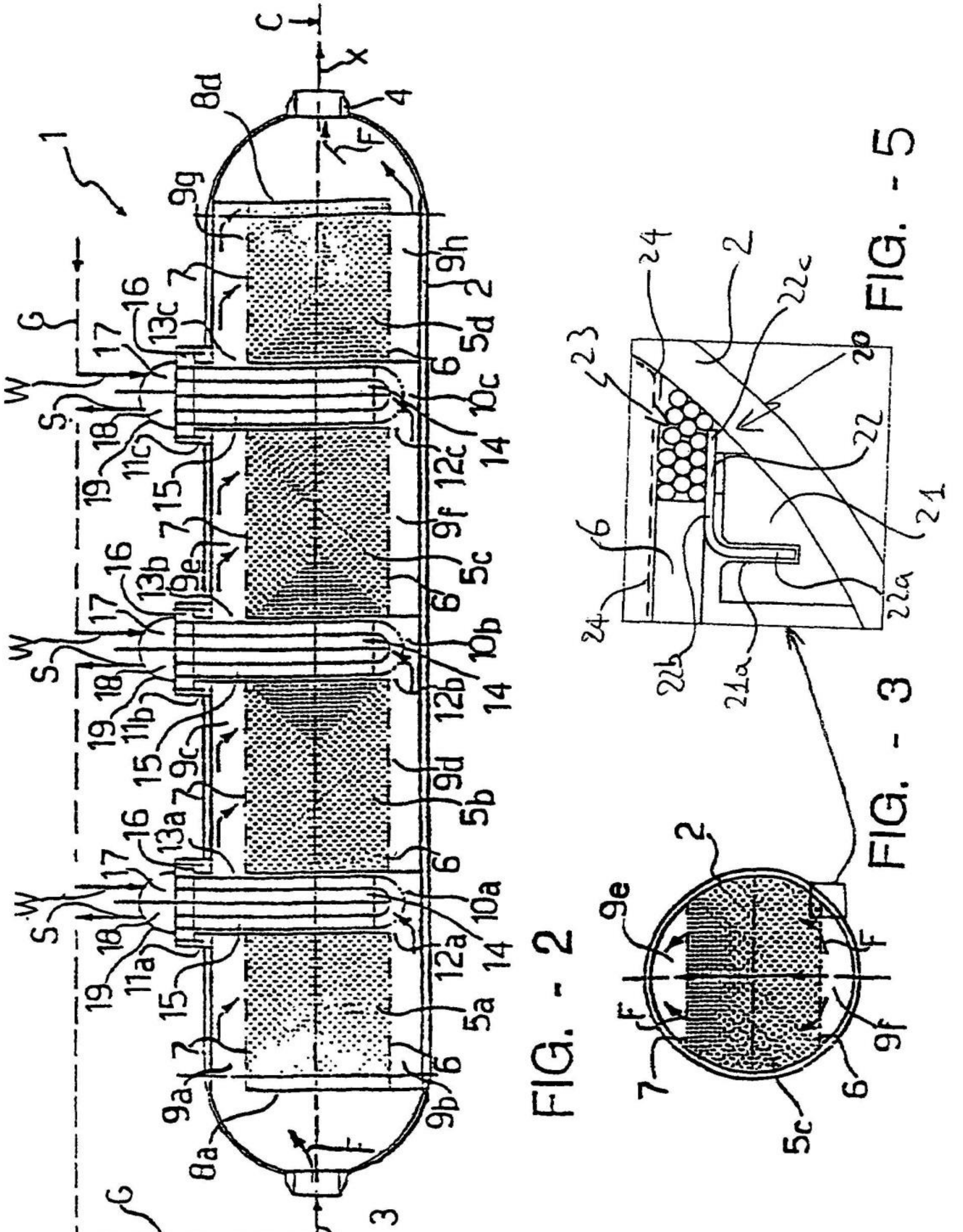


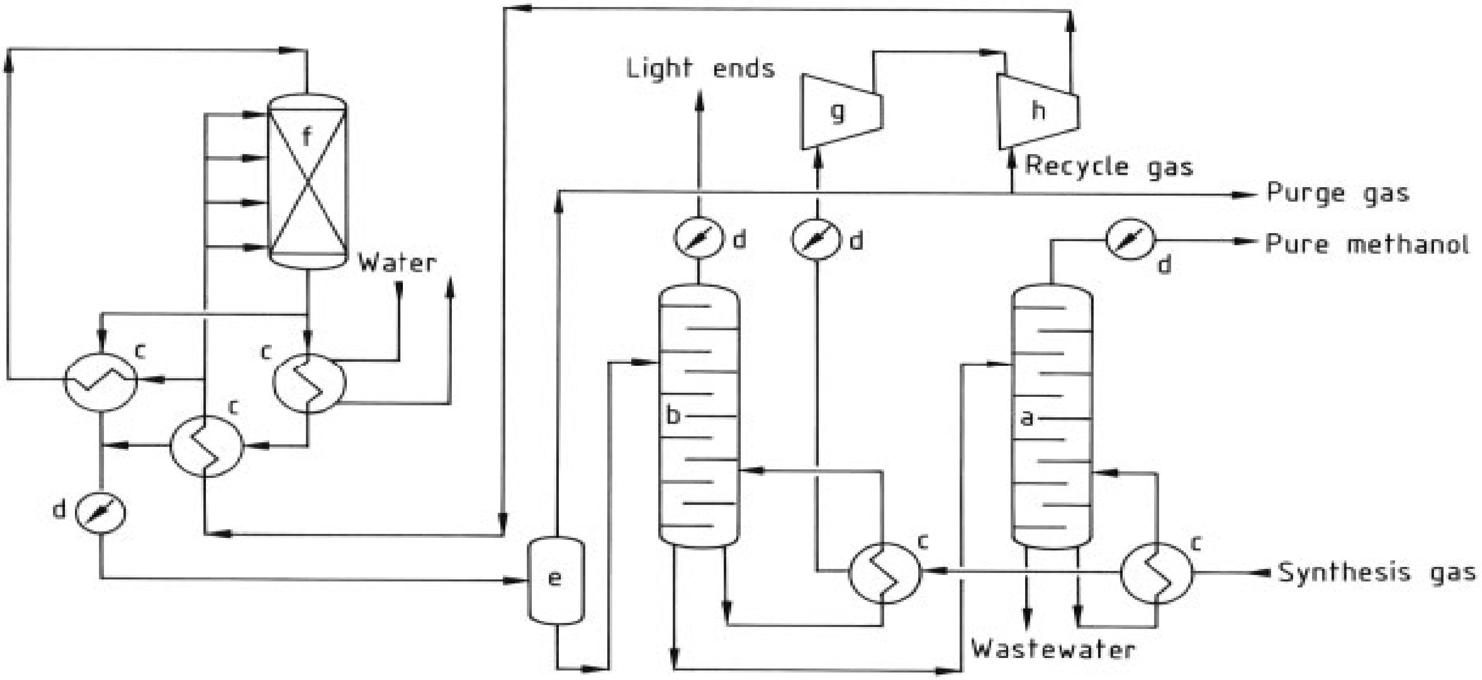
FIG. - 2

FIG. - 3

FIG. - 5

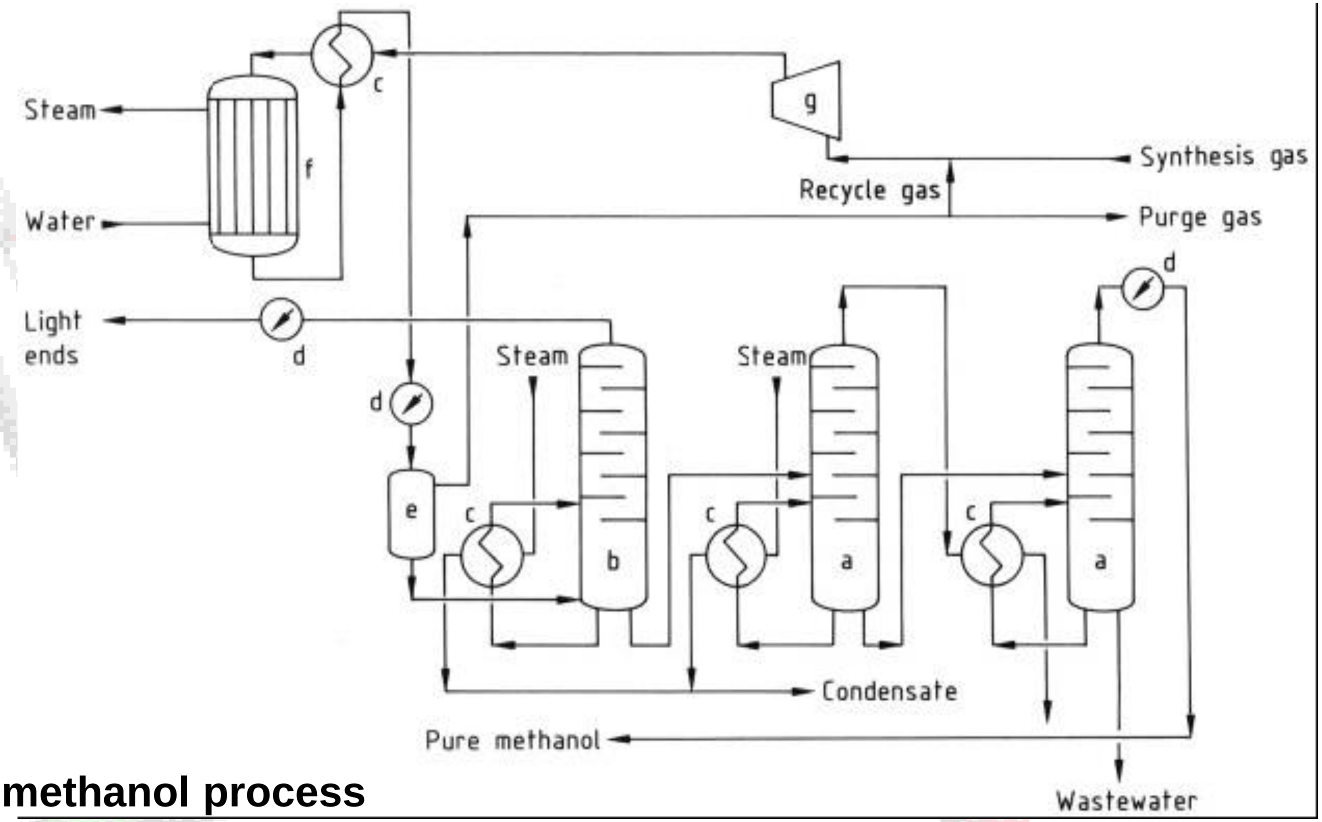
Quasy adiabatic reactor

Two solutions:
quenching (cold gas feed at intermediate points)
Catalyst bed sections with cooling in between



The ICI low-pressure methanol process

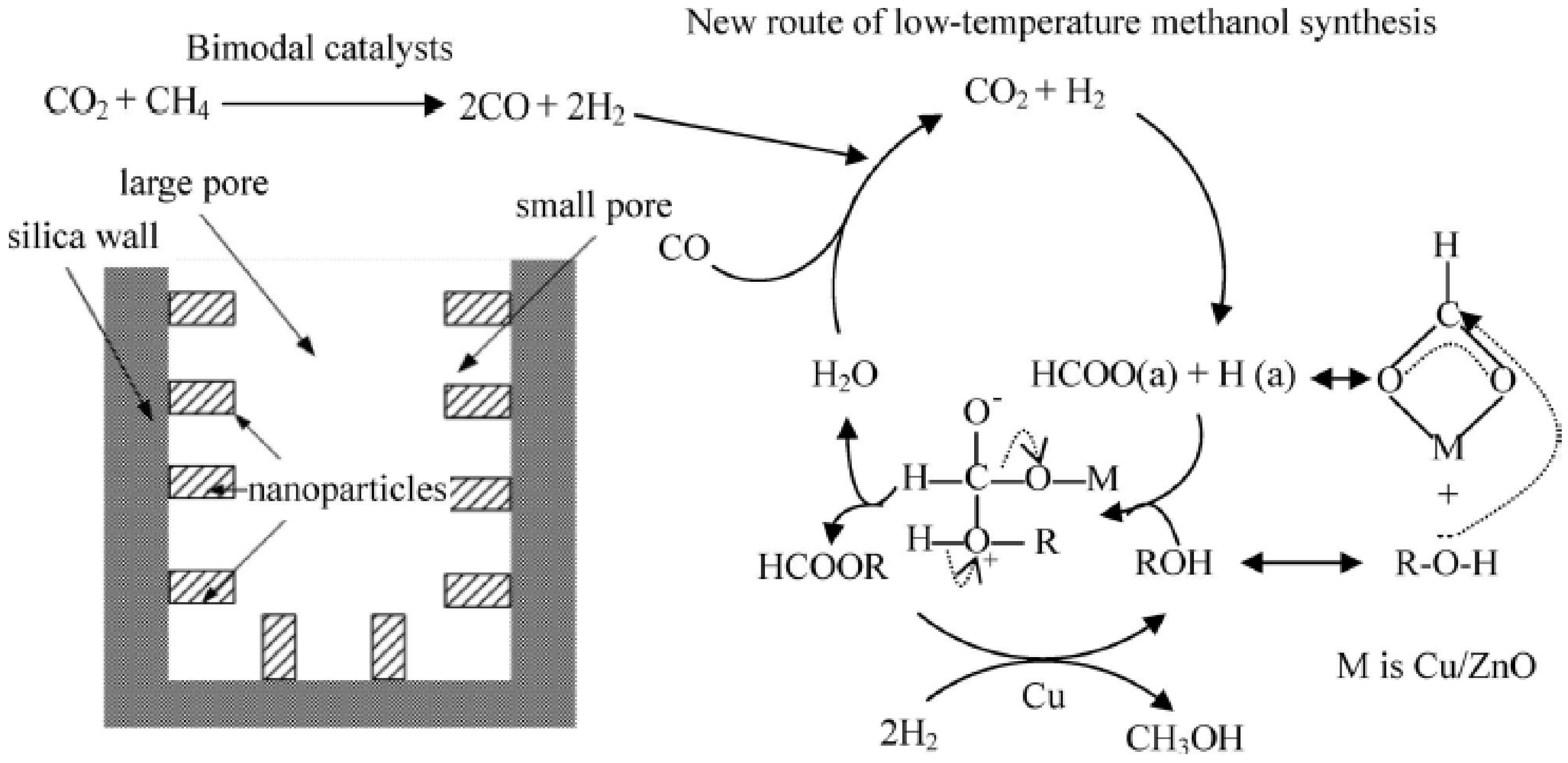
a) Pure methanol column;
b) Light ends column;
c) Heat exchanger;
d) Cooler;
e) Separator;
f) Reactor;
g) Compressor;
h) Compressor recycle stage



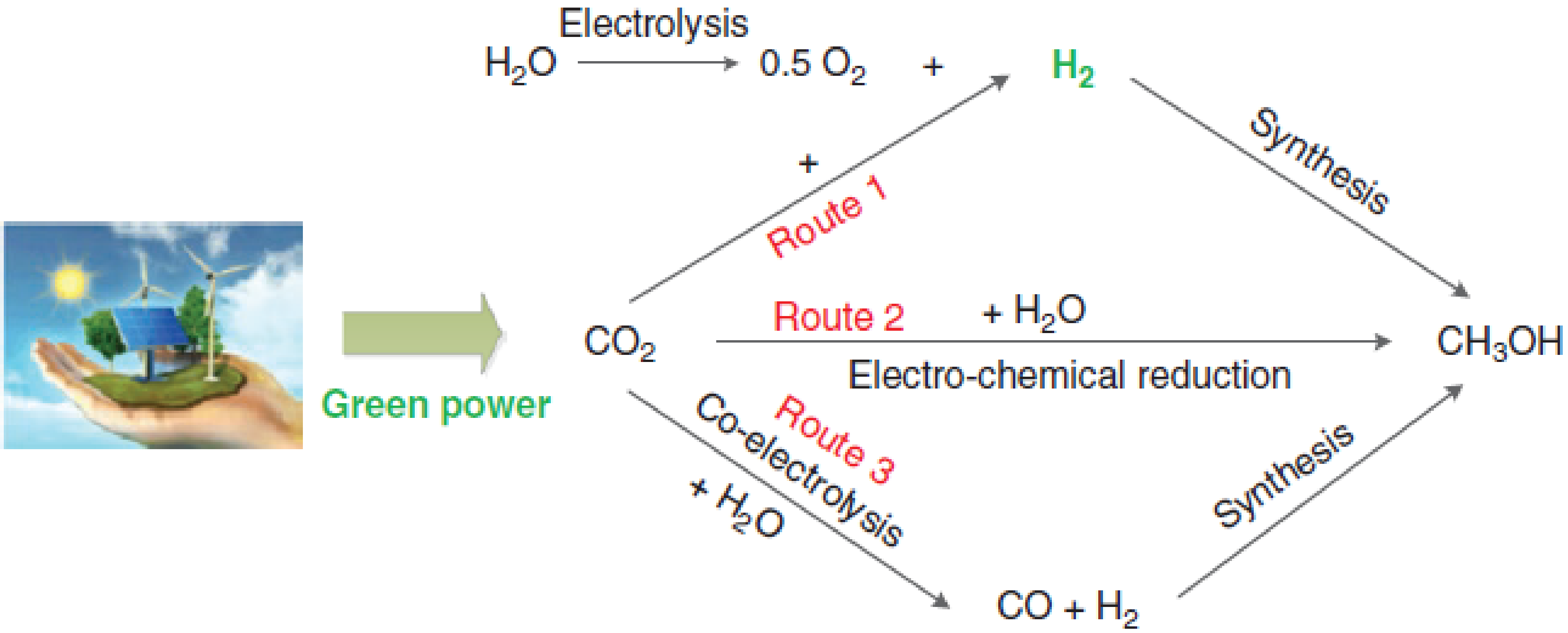
Lurgi low-pressure methanol process

a) Pure methanol columns;
b) Light ends column;
c) Heat exchanger;
d) Cooler;
e) Separator;
f) Reactor;
g) Compressor recycle stage

A new route: low pressure methanol synthesis, the feed is from the dry+wet-reforming of biogas, the hydrogenation has two steps, with addition of an aliphatic alcohol



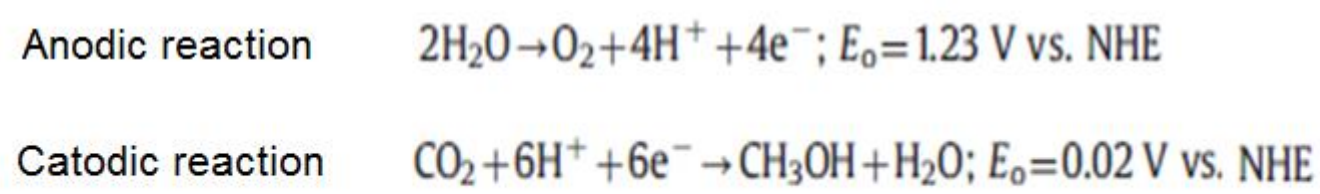
Methanol production possibilities from carbon dioxide



New possibilities of methanol synthesis

The conversion of CO_2 to methanol with **homogeneous catalytic reactions with Ru complexes**, among mild conditions (40 bar, 80°C) with promising reaction rates.

Electrochemical reduction, with low selectivity and effectiveness

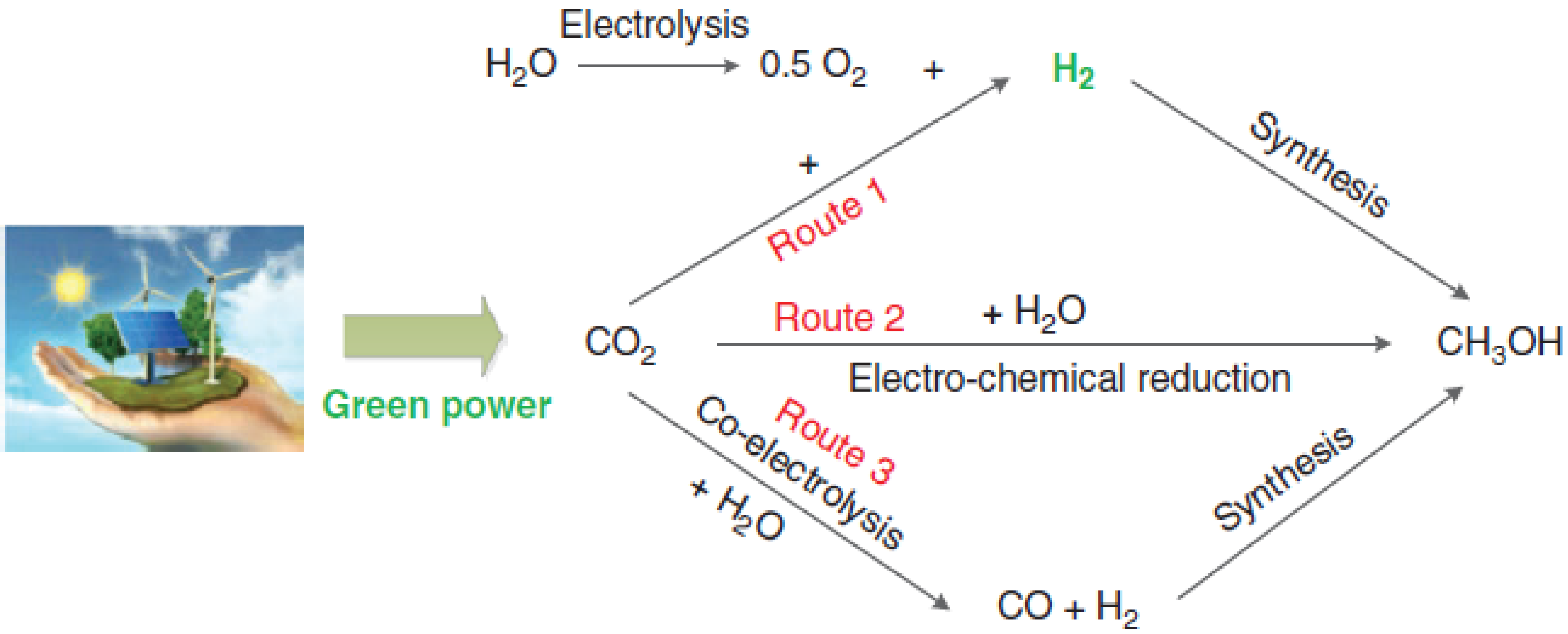


Anodic reaction $2H_2O \rightarrow O_2 + 4H^+ + 4e^-; E_o = 1.23$ V vs. NHE

Catodic reaction $CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O; E_o = 0.02$ V vs. NHE

Combination of **electrochemical and photochemical catalytic methods can be promising!**

Electrochemical conversion possibilities of carbondioxide into methanol



Pourbaix diagram for carbon dioxide reduction reaction at 25˚C

$2H^+ + 2e^- \rightleftharpoons H_2$ $E_o = 0.0$ V vs. SHE (1.1)

$CO_2 + 12H^+ + 12e^- \rightleftharpoons C_2H_4 + H_2O$ $E_o = 0.079$ V vs. SHE (1.2)

$CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + H_2O$ $E_o = 0.169$ V vs. SHE (1.3)

$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O$ $E_o = -0.103$ V vs. SHE (1.4)

$CO_2 + H^+ + 2e^- \rightleftharpoons HCOO^- + H_2O$ $E_o = -0.225$ V vs. SHE (1.5)

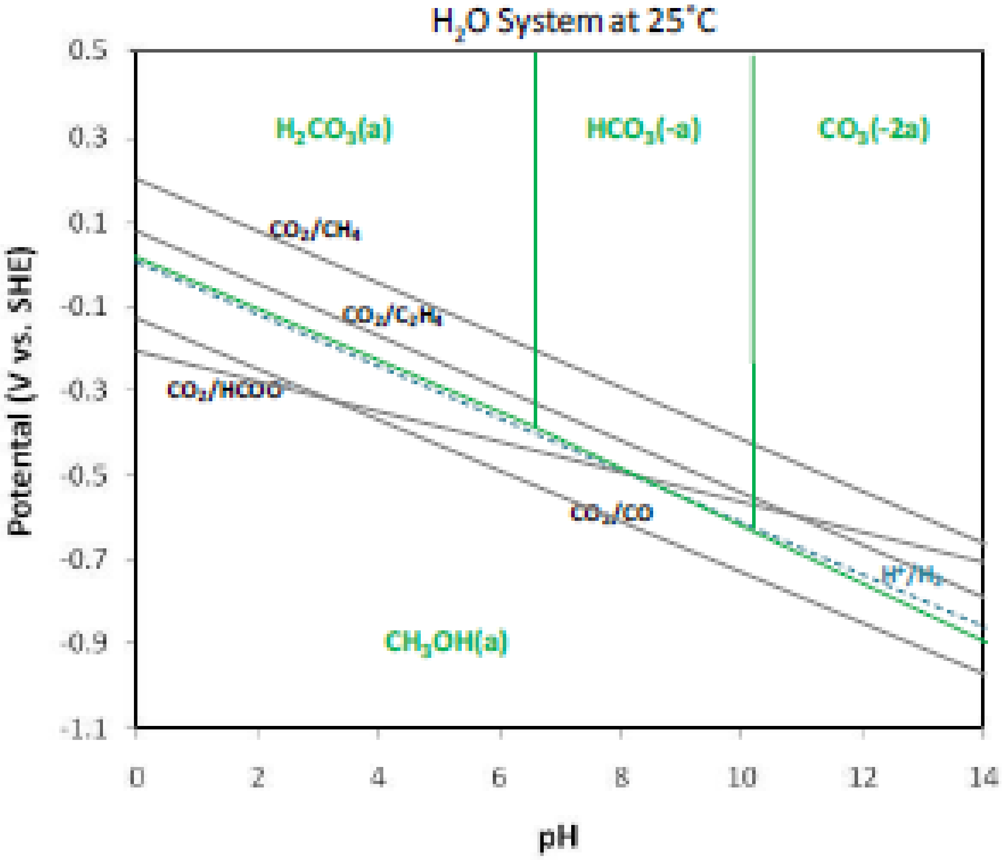
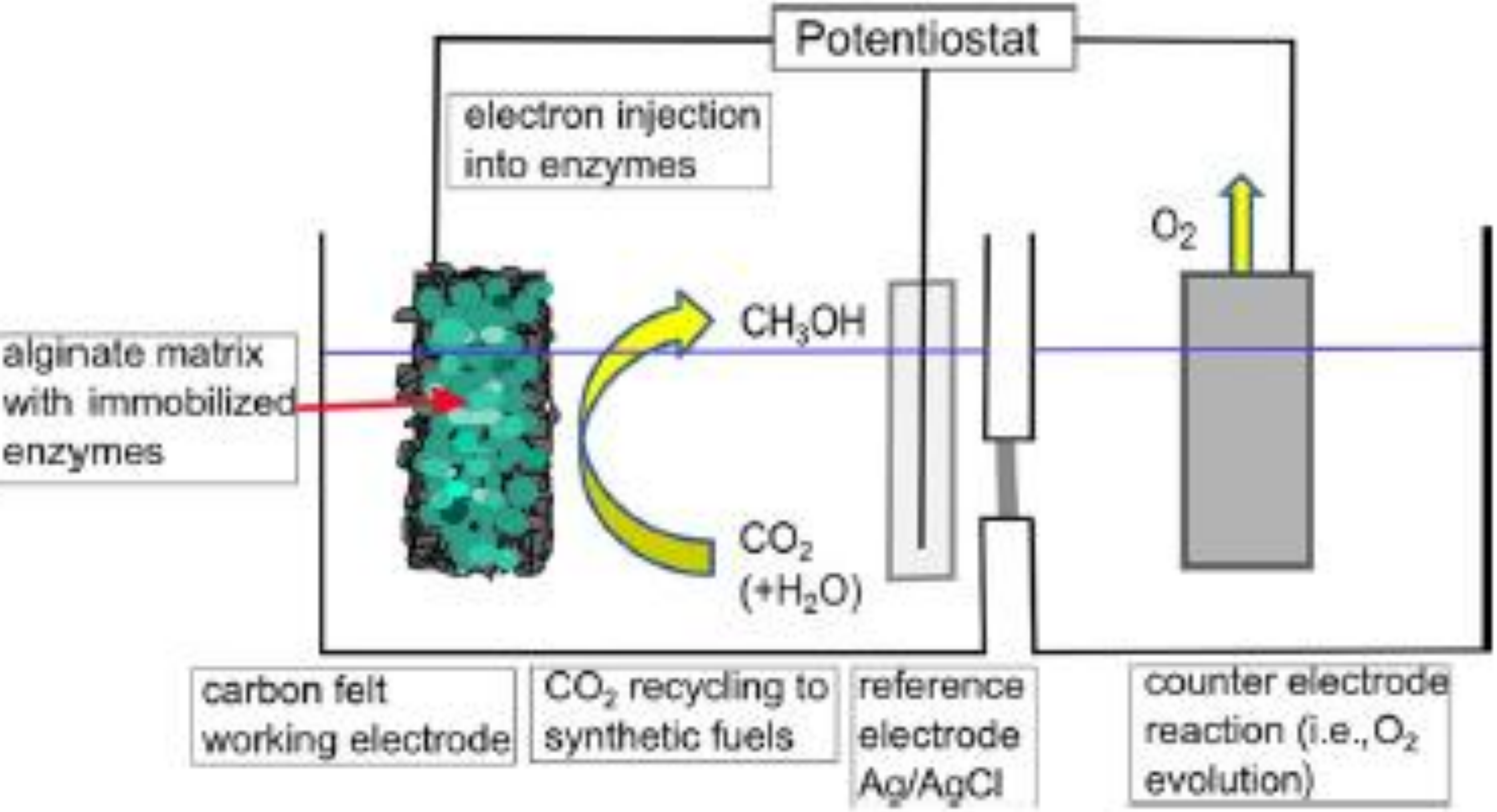
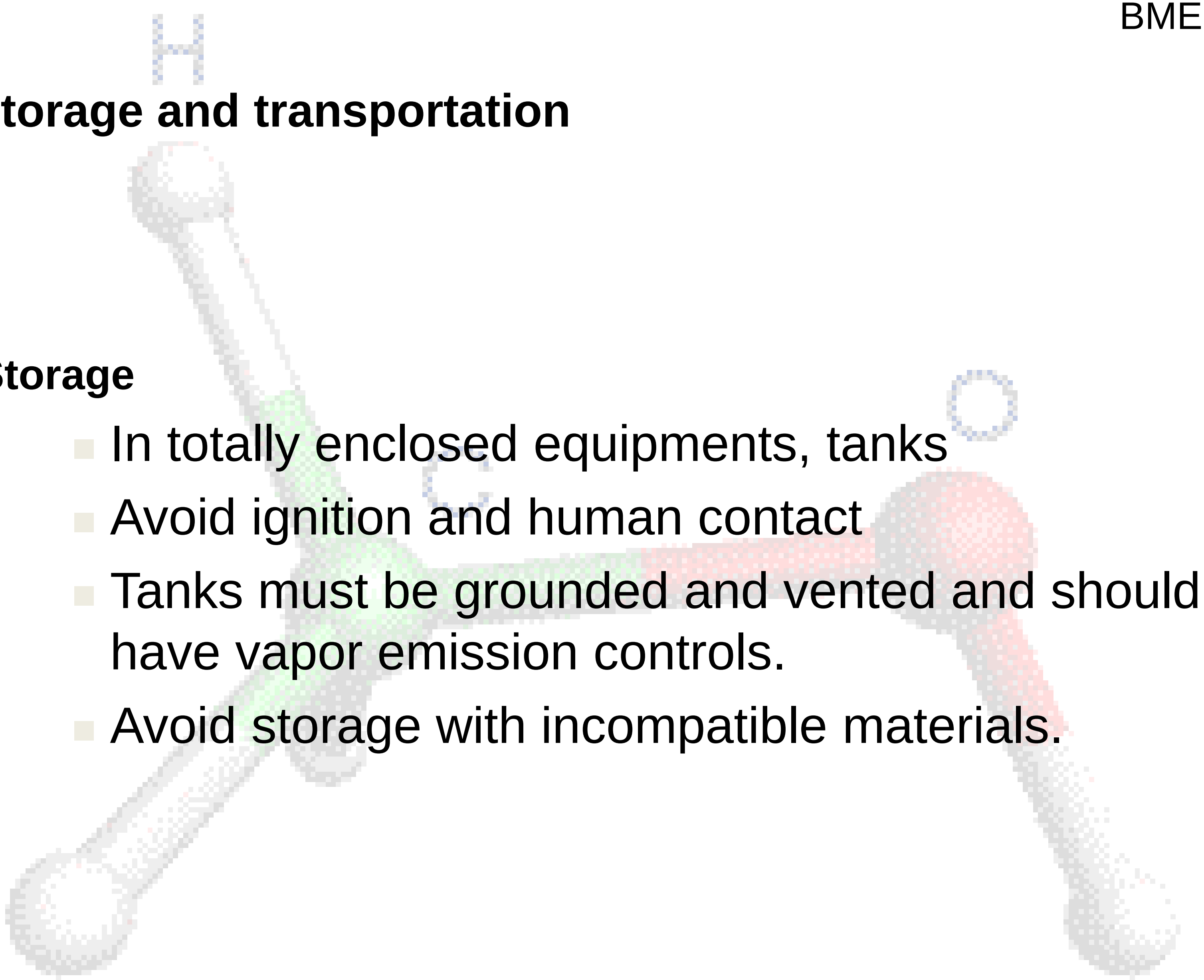


Figure 1. Representation of the electrochemical CO_2 reduction using enzymes. Electrons are injected directly into the enzymes, which are immobilized in an alginate–silicate hybrid gel (green) on a carbon-felt working electrode. CO_2 is reduced at the working electrode. Oxidation reactions take place at the counter electrode.

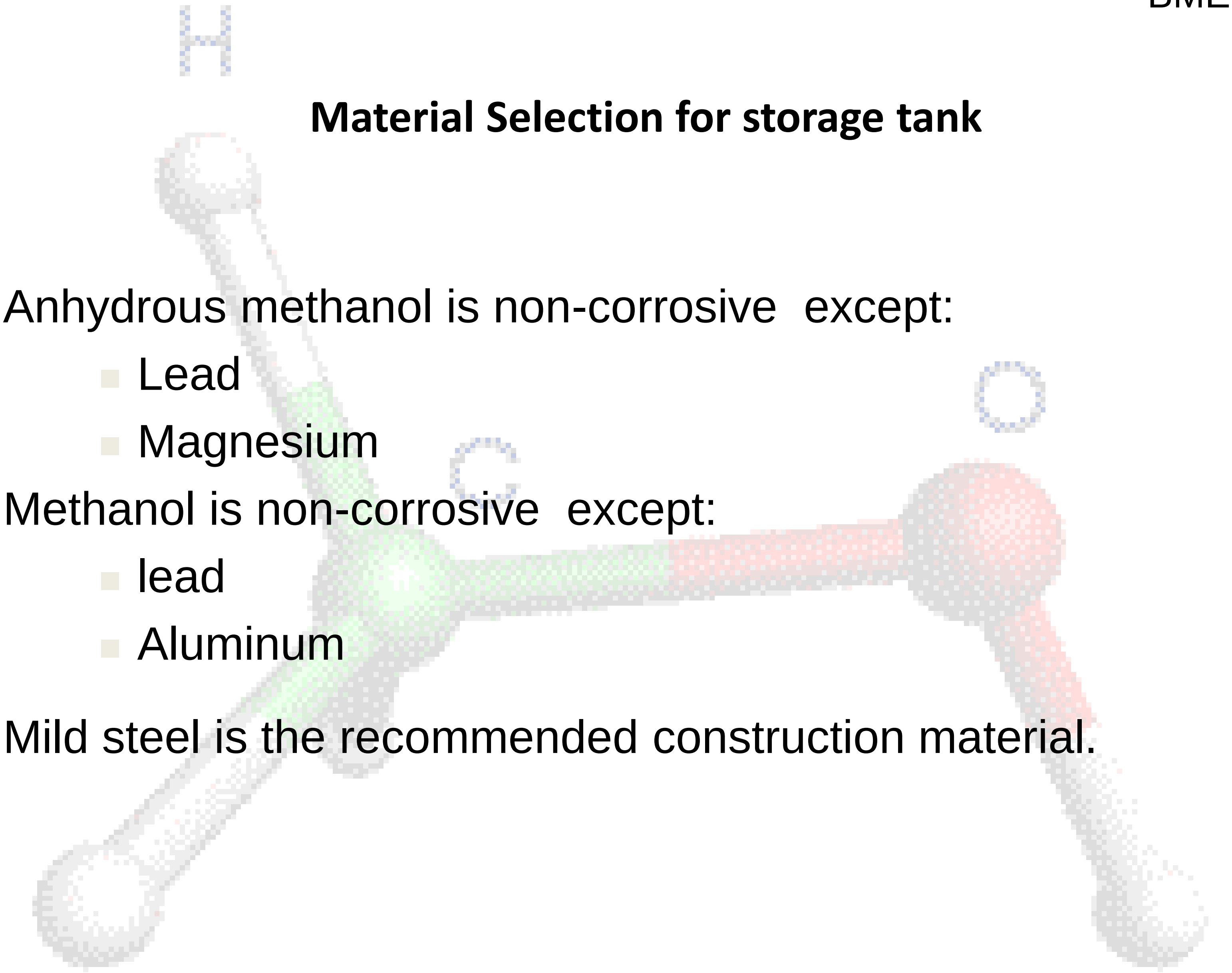


Storage and transportation



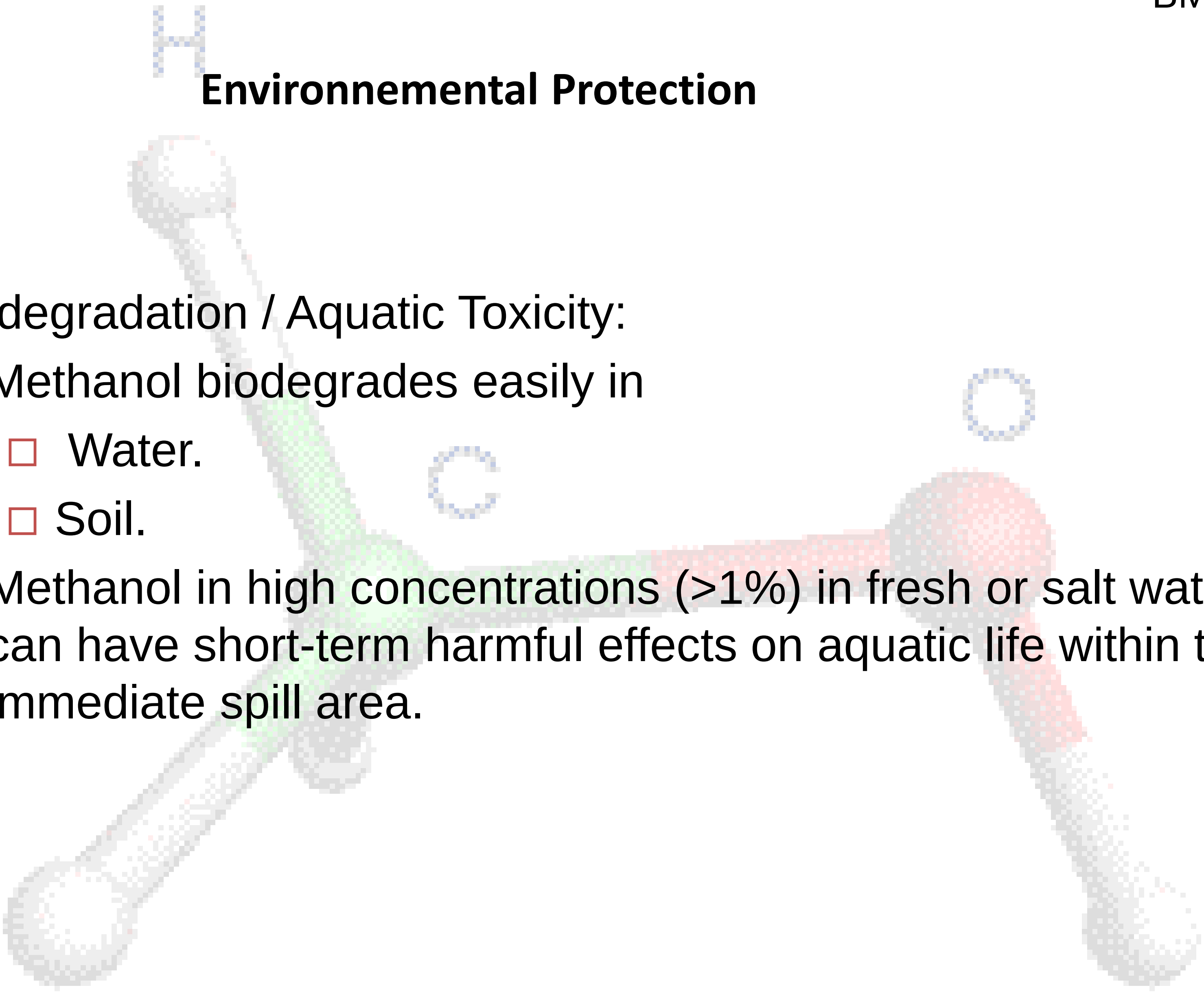
- **Storage**
  - In totally enclosed equipments, tanks
  - Avoid ignition and human contact
  - Tanks must be grounded and vented and should have vapor emission controls.
  - Avoid storage with incompatible materials.

Material Selection for storage tank



- Anhydrous methanol is non-corrosive except:
    - Lead
    - Magnesium
- Methanol is non-corrosive except:
    - lead
    - Aluminum
- Mild steel is the recommended construction material.

Environnemental Protection



Biodegradation / Aquatic Toxicity:

- Methanol biodegrades easily in
  - Water.
  - Soil.
- Methanol in high concentrations (>1%) in fresh or salt water can have short-term harmful effects on aquatic life within the immediate spill area.

Thank you for your attention!