Funded by the Erasmus+ Programme of the European Union

ERASMUS + IESRES

TÜRKİYE ULUSAL AJANSI TURKISH NATIONAL AGENCY

INNOVATIVE EUROPEAN STUDIES on RENEWABLE ENERGY SYSTEMS

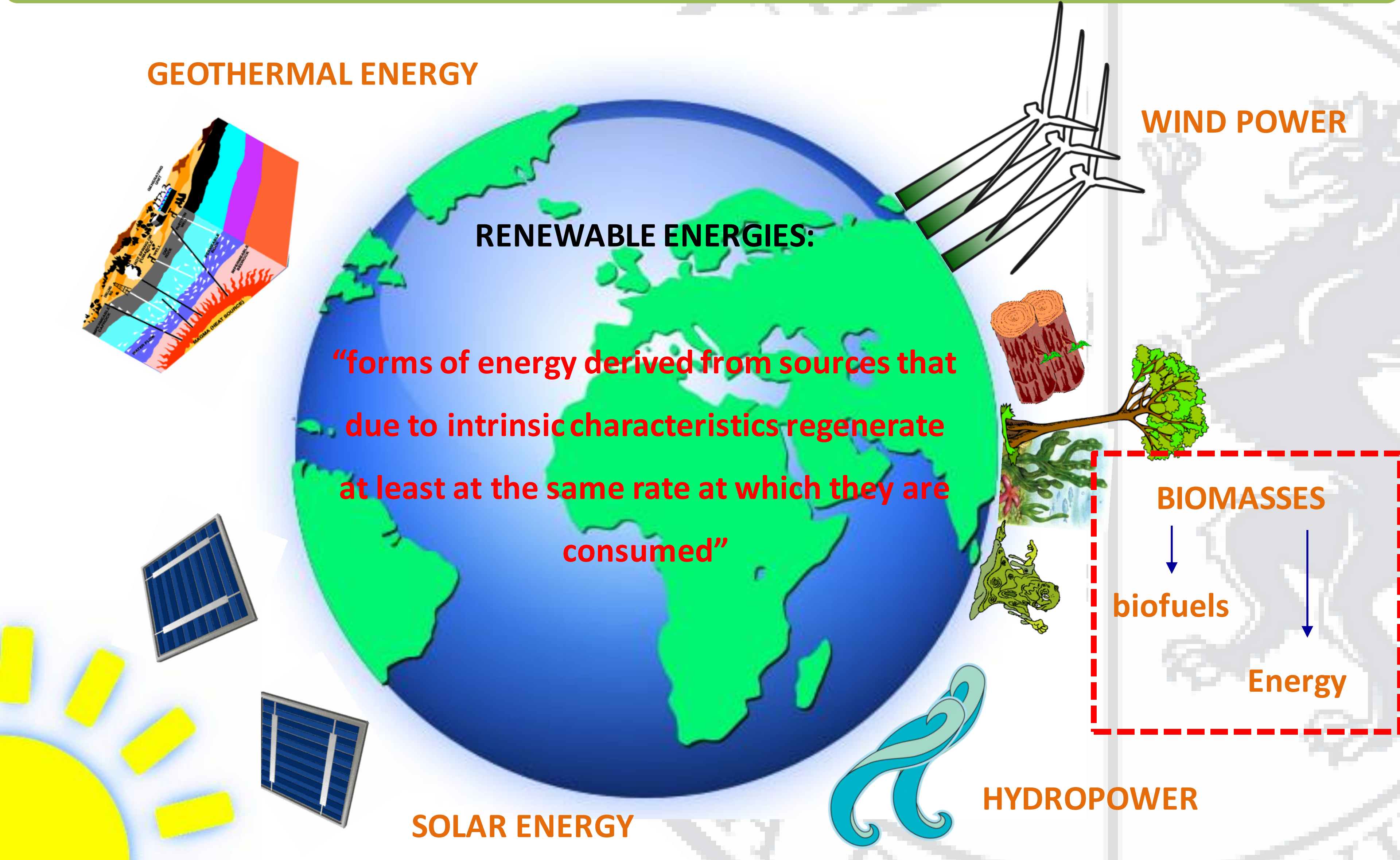
Energy from Waste (EfW) Renewable Technologies

Alessandro Di Michele

Dipartimento di Fisica e Geologia
Università degli Studi di Perugia

17th – 22st October 2016, PERUGIA, ITALY

CURRENT ENERGY SITUATION:



Y.Cengel, M.Boles. Thermodynamics. An Engineering Approach

European directives

- **The Renewables Energy Directive (2009/28/EC)**
  The Directive addresses a number of issues relating to renewable energies within the EU including the legally binding share of renewable energy in gross final energy consumption. **Renewable Energy share of energy mix to rise to 20% by 2020.**

- By 1st February, 2011 all 27 Member States submitted a National Renewable Energy Plan (NREAP).

- The ECN (Energy Research Network of the Netherlands) has collected all data from the NREAP documents

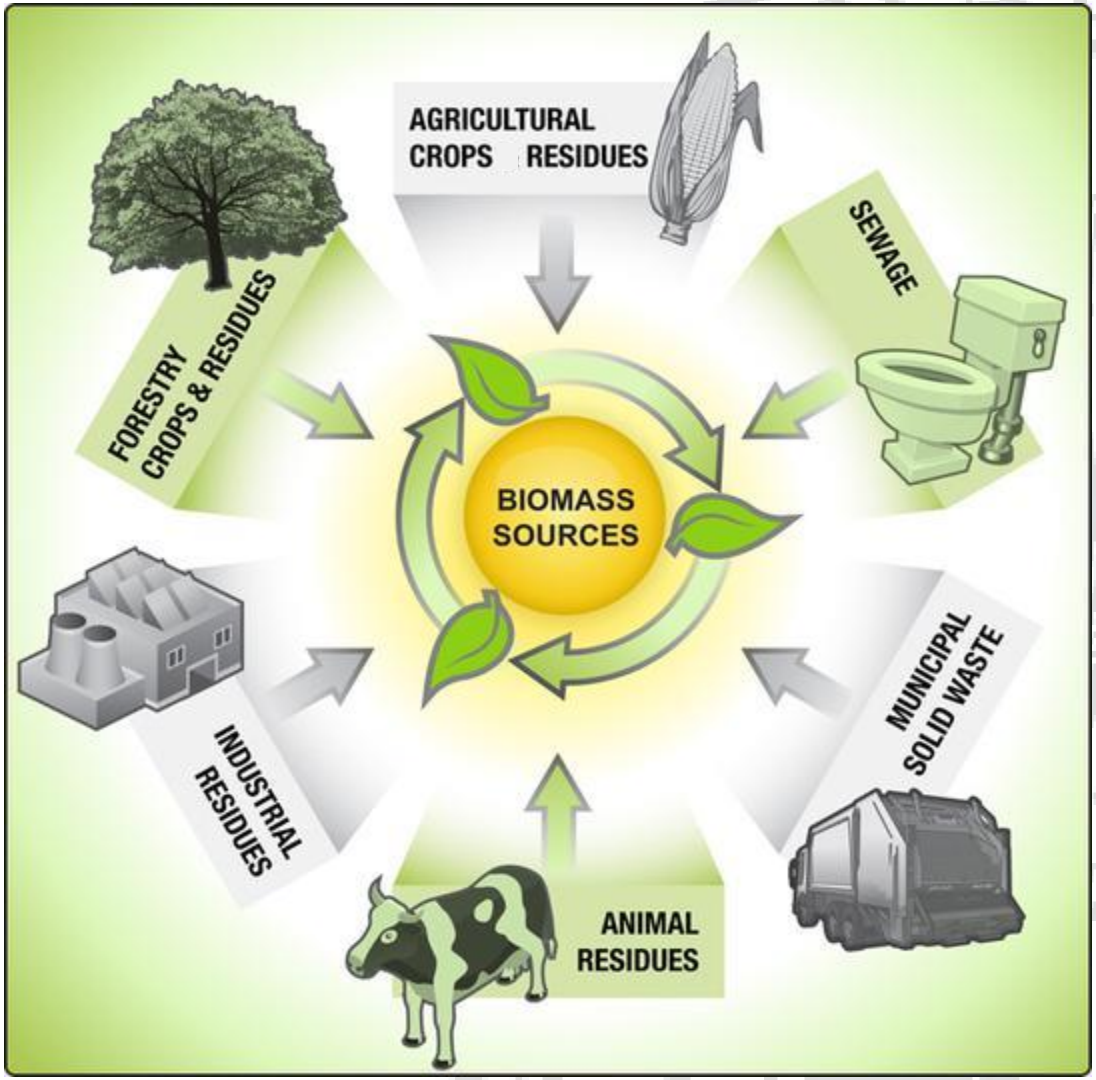
Sustainability criteria of biofuels in the European Union

The European Union has adopted a very ambitious plan to increase the share of renewables in their energy consumption to 20% by 2020, **including a 10% goal for the use of renewables in transport alone**.

Article 17 of the Directive defines two sets of sustainability criteria for biofuels. The two main sets of criteria, which must be fulfilled cumulatively, are **greenhouse gas (GHG) emission savings and land-use requirements**.

Article 3.4 Each Member State shall ensure that the share of energy from renewable sources in all forms of transport in 2020 is at least **10 % of the final consumption of energy in transport** in that Member State

Article 21.2. For the purposes of demonstrating compliance with national renewable energy obligations placed on operators and the target for the use of energy from renewable sources in all forms of transport referred to in Article 3(4), **the contribution made by biofuels produced from wastes, residues, non-food cellulosic material, and ligno-cellulosic material shall be considered to be twice that made by other biofuels.**



Biomass is biological material derived from living, or recently living organisms.

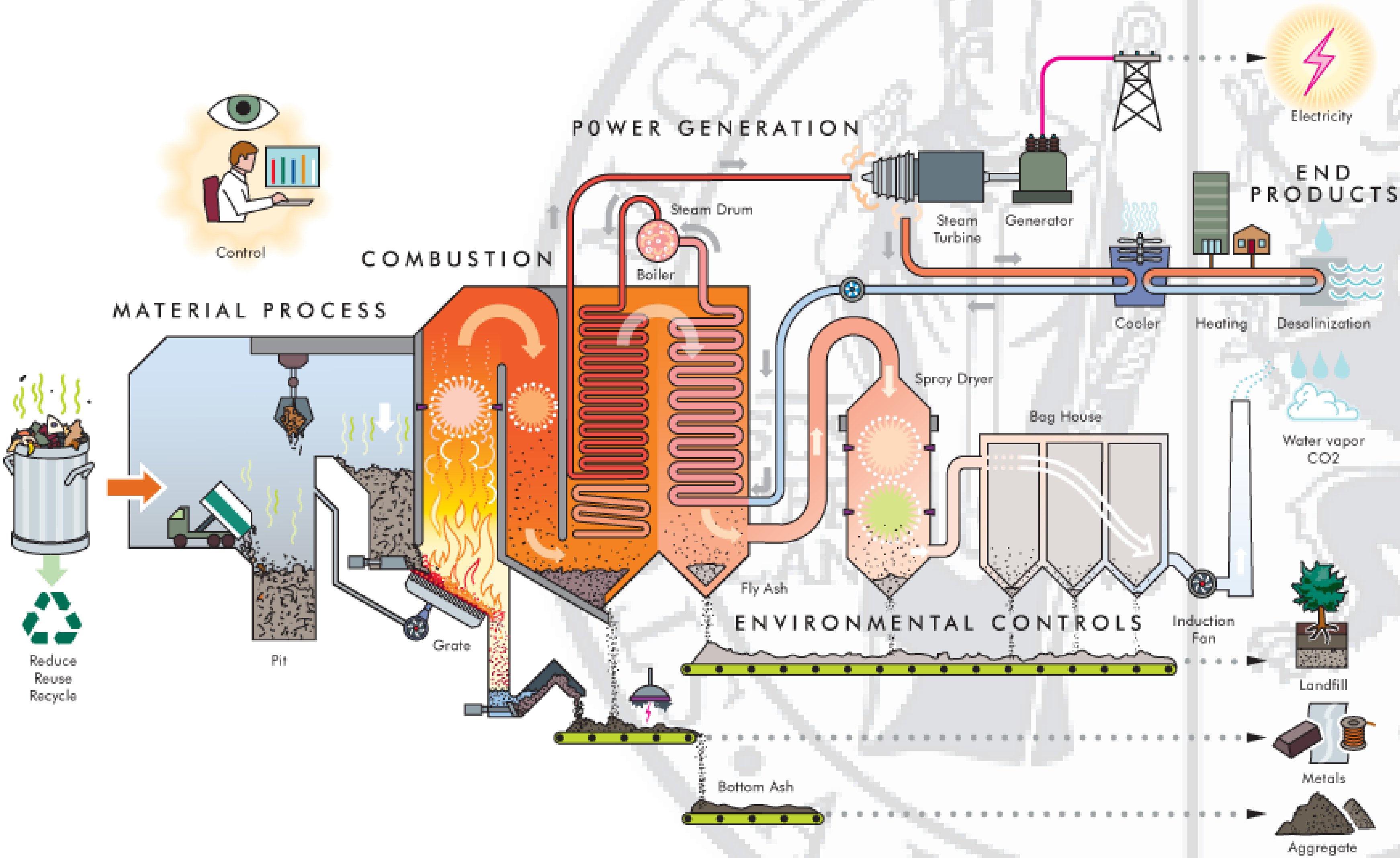
Biomass can equally apply to both animal and vegetable derived material

Energy from Waste technologies

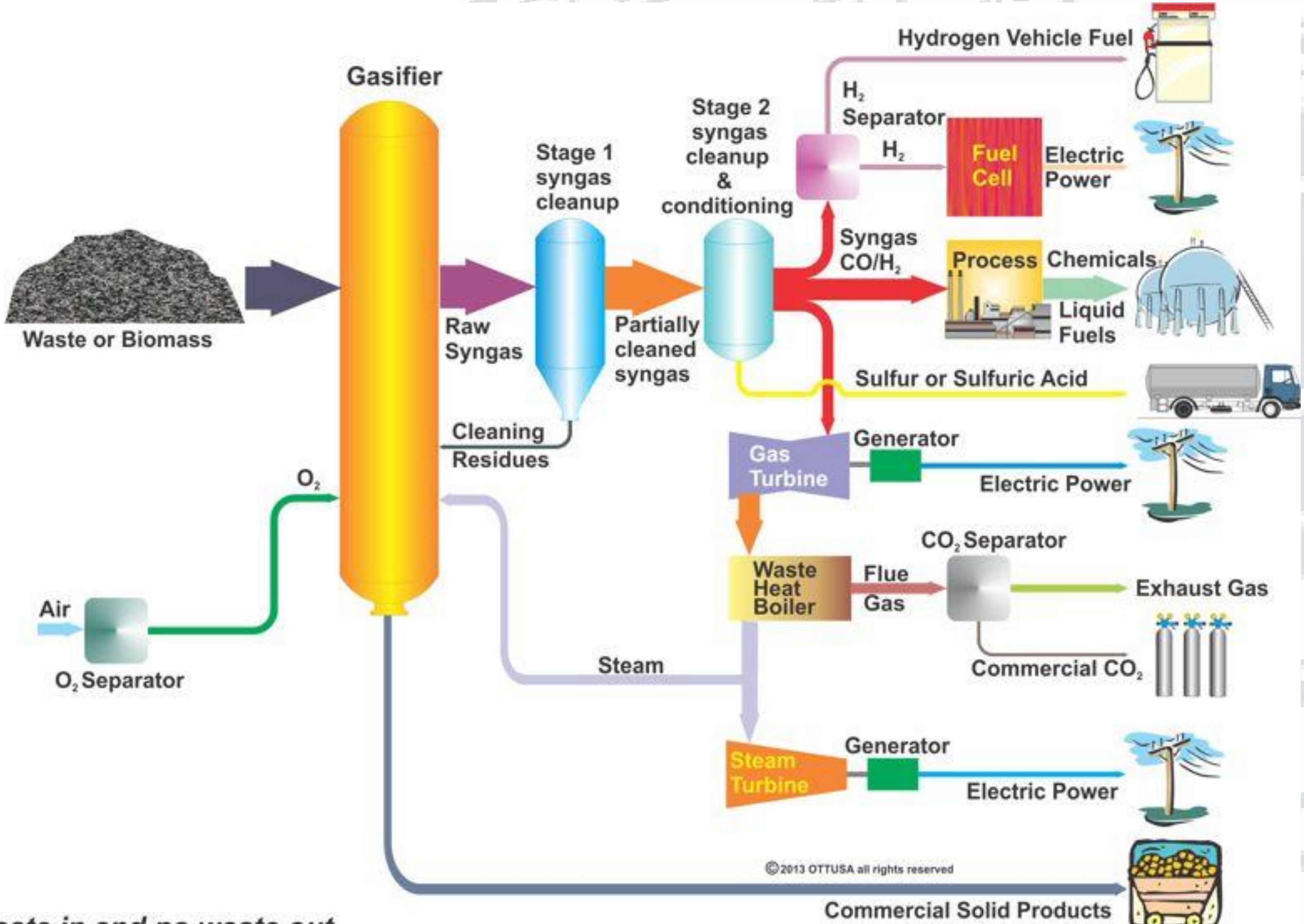
Energy can be recovered from waste by various (very different) technologies. It is important that recyclable material is removed first, and that energy is recovered from what remains, i.e. from the residual waste. Energy from waste (EfW) technologies include:

1. **Combustion**
2. **Gasification and Pyrolysis**
3. **Anaerobic Digestion**

1 Combustion in which the residual waste burns at 850°C and the energy recovered as electricity or heat



2 Gasification and pyrolysis, where the waste is heated with little or no oxygen to produce "syngas" which can be used to generate energy or as a feedstock for producing methane, chemicals, biofuels, or hydrogen (landfill gas)



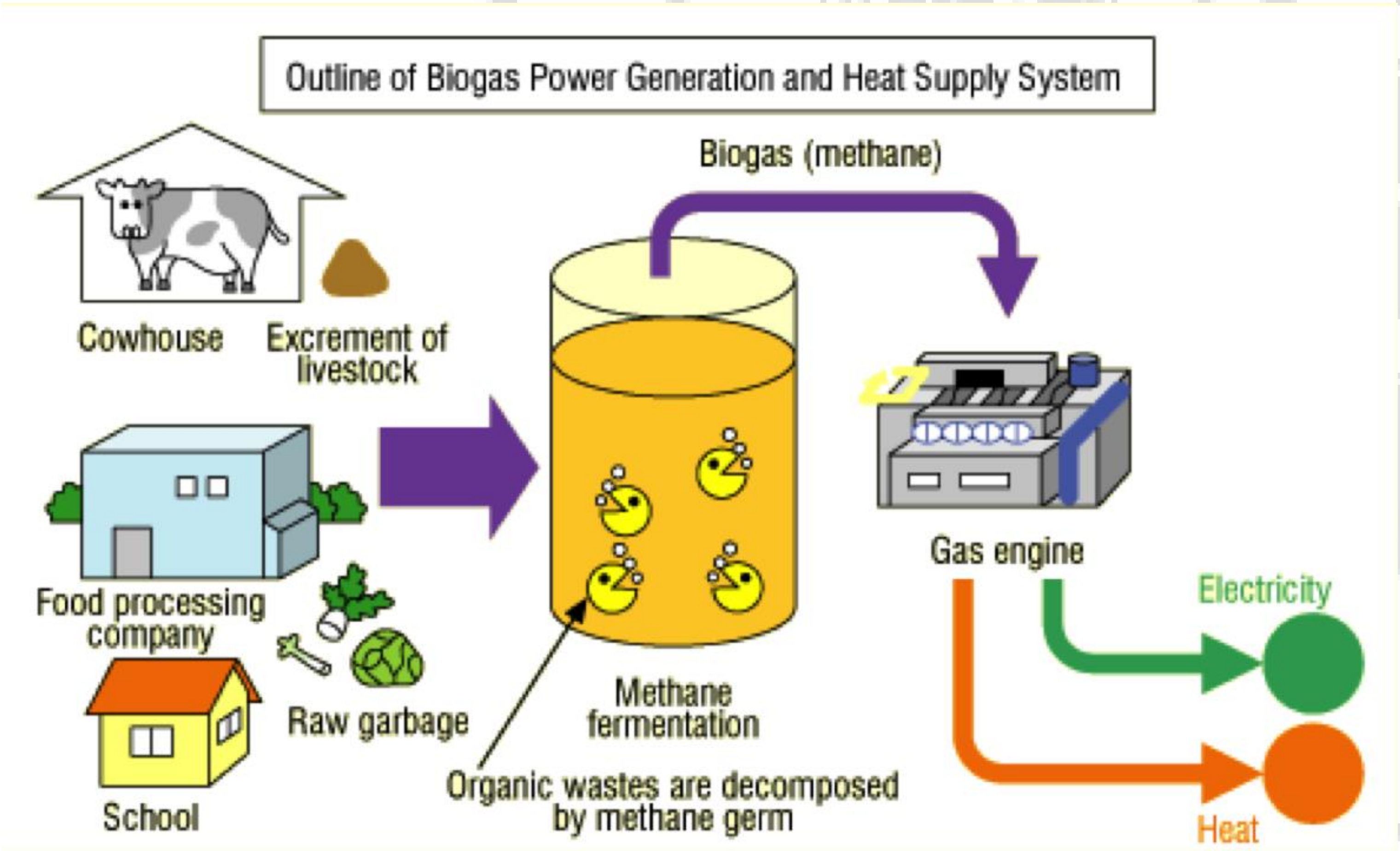
Waste in and no waste out

Gasification and Pyrolysis

Gasification, as applied to solid waste materials and biomass, is a relatively new application of this technology that is increasingly being used for the disposal of wastes. It is a thermo-chemical process in which wastes, including their biomass content is heated, in an oxygen deficient environment to produce a low-energy gas containing hydrogen, carbon monoxide and methane. The gas can then be used as a fuel in a turbine or combustion engine to generate electricity.

Pyrolysis is another emerging technology, sharing many of the characteristics of gasification. With gasification partial oxidation of the waste occurs, while with pyrolysis the objective is to heat the waste in the complete absence of oxygen. Gas, olefin liquid and char are produced in various quantities.

3 Anaerobic Digestion which uses microorganisms to convert organic waste into a methane-rich biogas that can be combusted to generate electricity and heat or converted to biomethane. This technology is most suitable for wet organic wastes or food waste. The other output is a biofertiliser



Anaerobic Digestion

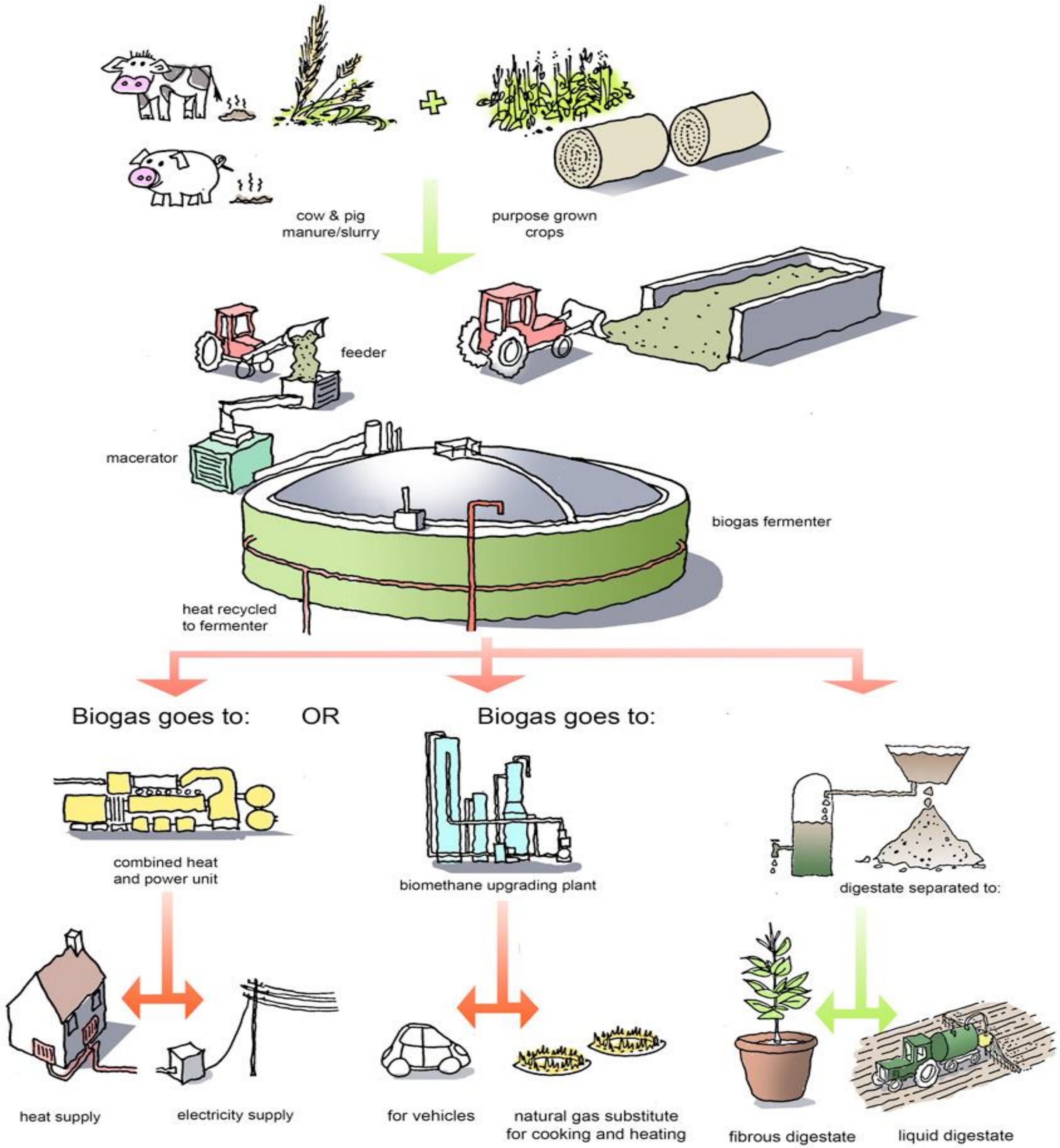
Anaerobic digestion (AD), as a renewable energy technology, is the harnessing of natural biological processes to use available biomass (e.g. food wastes, animal slurries and crop feedstocks) to produce renewable methane, which can then be used to produce electricity, heat or upgraded for vehicle fuel and injection to gas grid.

The methane produced can then be used in to generate renewable electricity and heat. Normally a biogas engine can gain an electrical conversion efficiency of up to 35% with the remainder being available as heat.

In addition to the production of power and heat, the left over organic material (digestate) is rich in nutrients and can be used as a substitute to chemical based fertilisers.

The energy in biogas can be used in several ways:

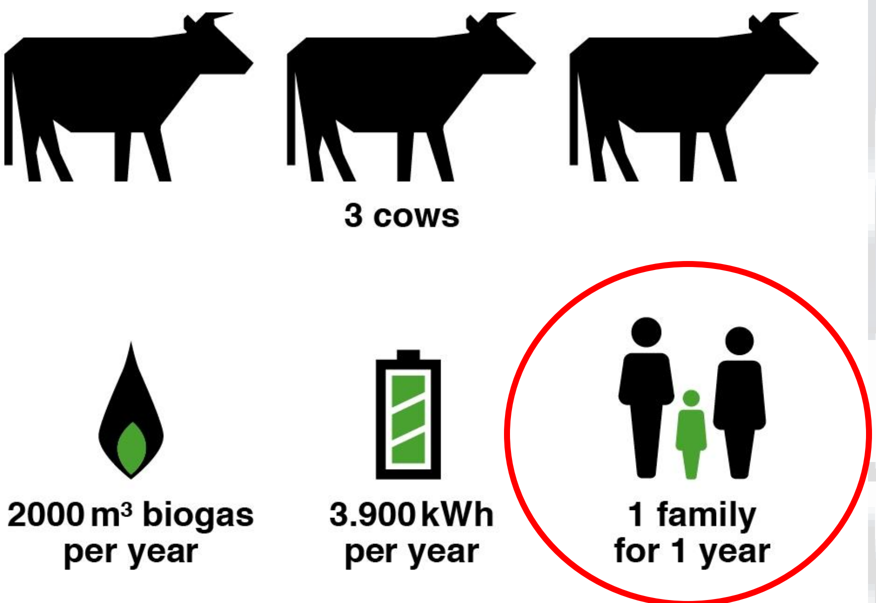
- Heat production
- Electricity production
- Combined heat and power
- Transport fuel
- Injection in to the main electricity or gas grid after upgrading
- Hydrogen production



cow & pig manure/slurry
purpose grown crops
feeder
macerator
biogas fermenter
heat recycled to fermenter
Biogas goes to:
OR
Biogas goes to:
combined heat and power unit
biomethane upgrading plant
digestate separated to:
heat supply
electricity supply
for vehicles
natural gas substitute for cooking and heating
fibrous digestate
liquid digestate

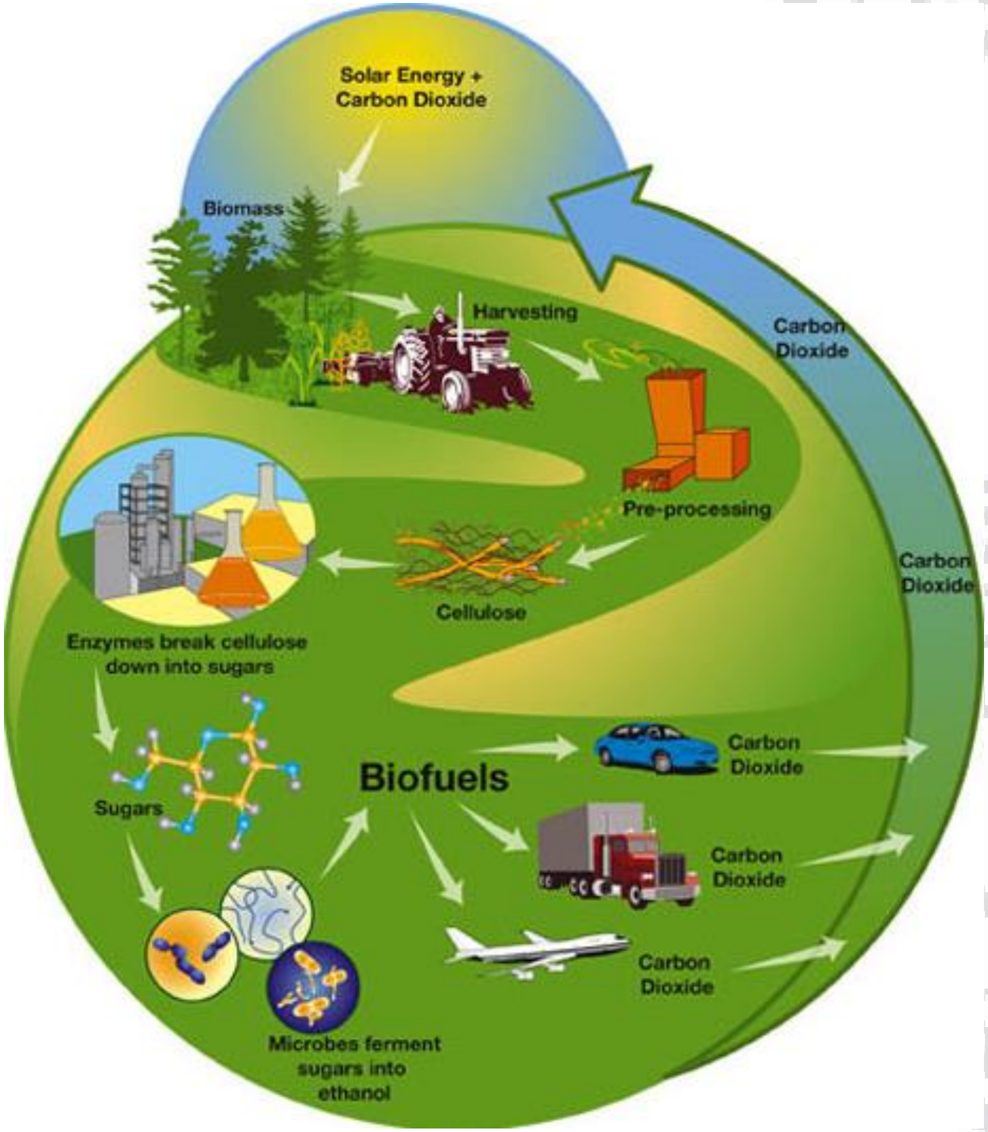
An example: **http://biolectric.ie/**

- A small scale Anaerobic Digester converts slurry from farm animals into usable energy .
- Slurry is digested in the reactor and produces methane as part of the digestion process.
- Methane is converted into electricity by combustion of gasses in the generator.
- The electricity is sold to the grid or used on the farm.
- A by-product of the process is hot water which can be used for heating or pre-heating.



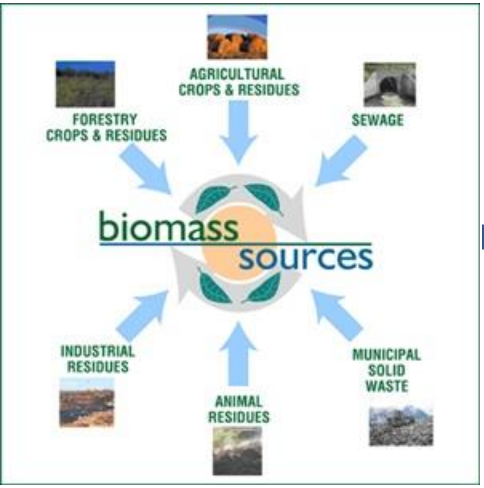
One year energy requirements for a family

Another technology: Biofuels from forest and agriculture residues (Cellulose and starch)



Bioethanol production

Summarizing…



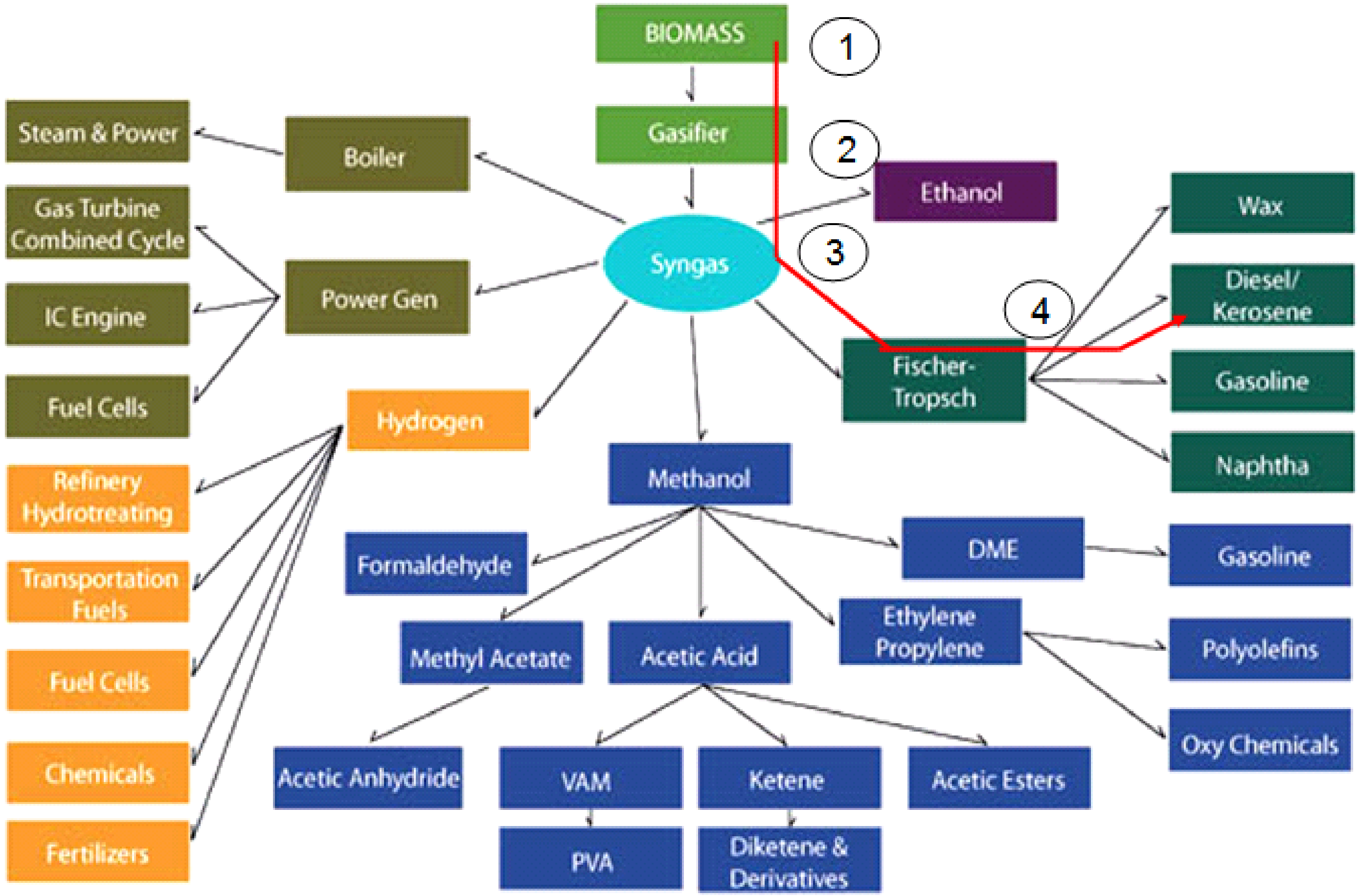
Pyrolisis & Gasification → SynGas **CO+H$_2$** → Electric Power

Anaerobic digestion → Biomethane **CH$_4$** → Electric Power

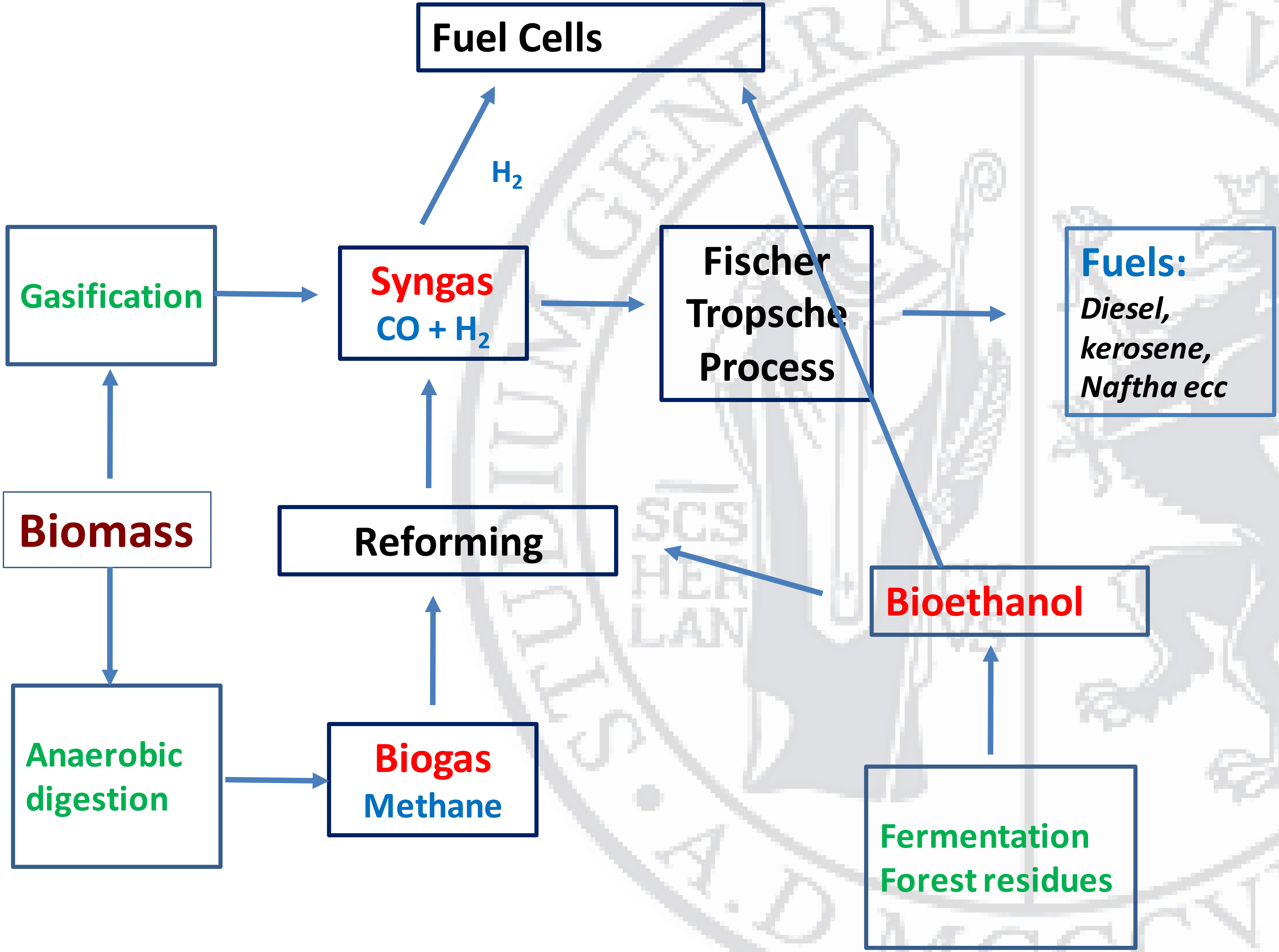
Fermentation → Ethanol **CH$_3$CH$_2$OH** → Biofuels; Ethanol → Electric Power

But……. → **Other technologic strategies**

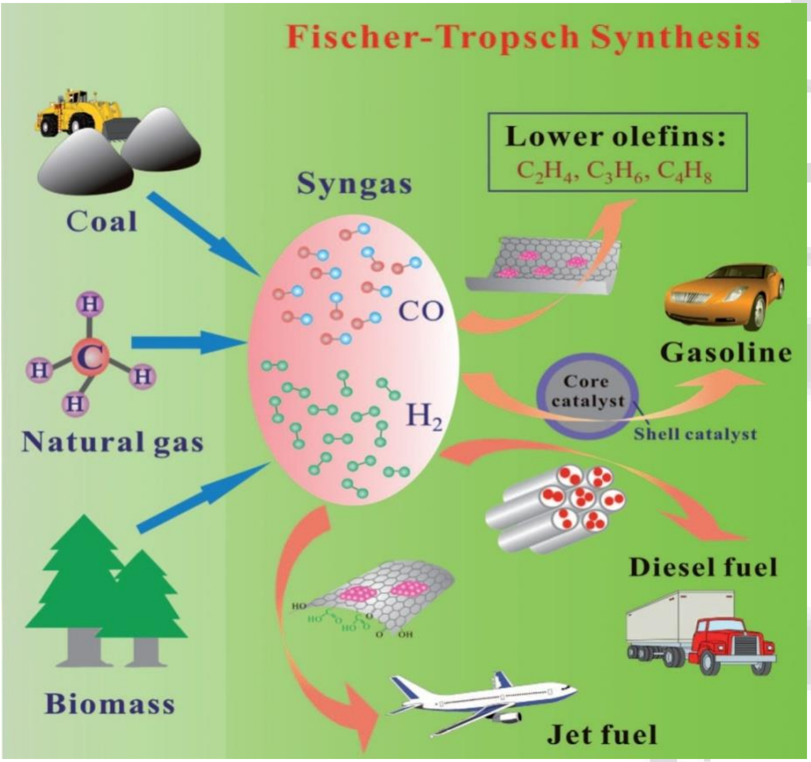
What can be done with syngas?



Waste to Liquid Technologies WTL


Fuel Cells
H_2
Gasification
Syngas
$CO + H_2$
Fischer
Tropsche
Process
Fuels:
Diesel,
kerosene,
Naftha ecc
Biomass
Reforming
Bioethanol
Anaerobic
digestion
Biogas
Methane
Fermentation
Forest residues

What is Fischer-Tropsch?



- FT is the conversion of so-called synthesis gas, composed mainly of carbon monoxide and hydrogen, to hydrocarbons through the influence of elevated temperatures and normal or elevated pressures in the presence of a catalyst.

- From a Chemist stand point this is simply:

$$CO + 2\ H_2 \longrightarrow \quad -CH_2- \quad + H_2O$$

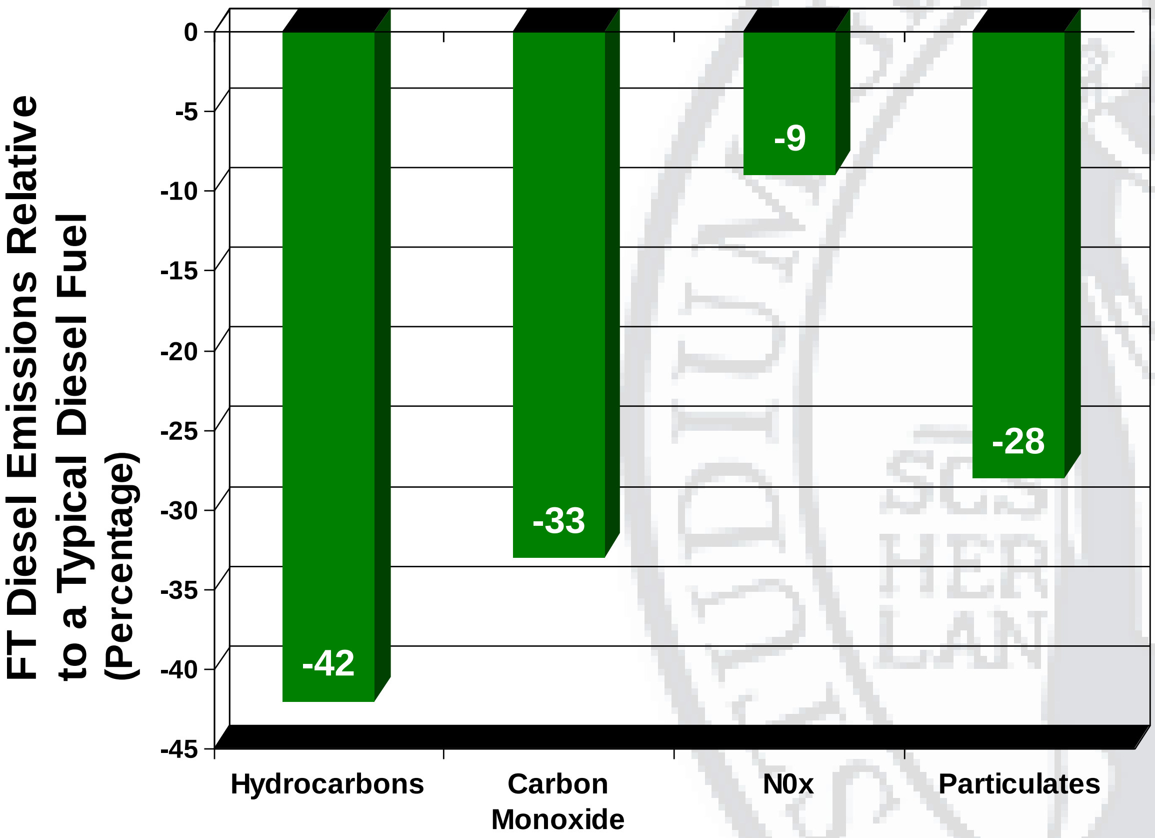
- This can simply be said – A process to convert gas into liquid fuels and various long chain carbons.

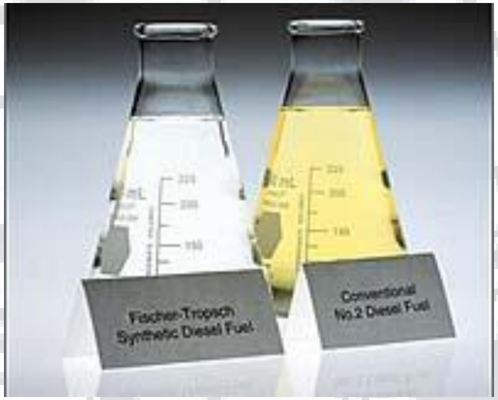
Franz Fischer

Hans Tropsch

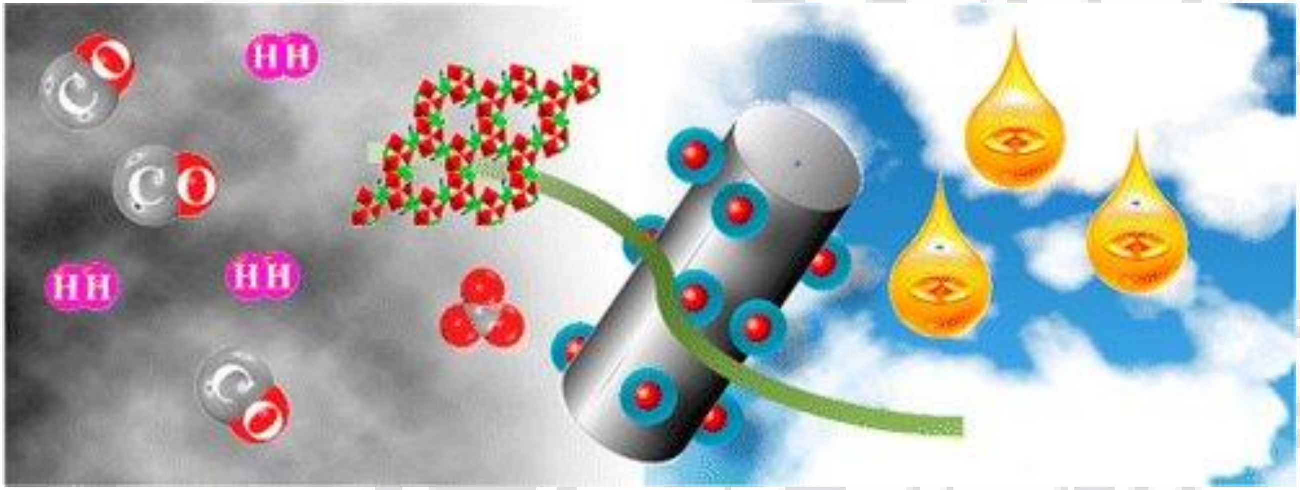
Q. Zhang, J. Kang, Y. Wang ChemCatChem 2010, 2, 1030 – 1058

Ultra Clean Diesel

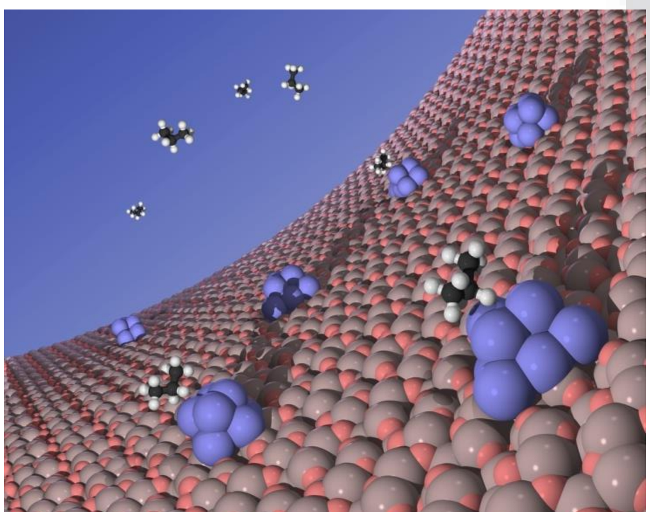


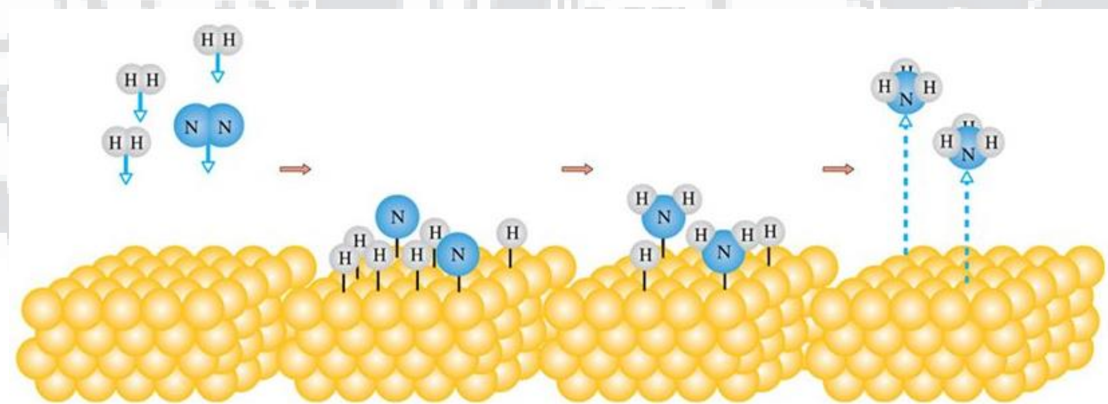


- No sulphur compounds
- No aromatics



Catalyst is substance that causes or accelerates a chemical reaction without itself being affected





Catalysts for FTS

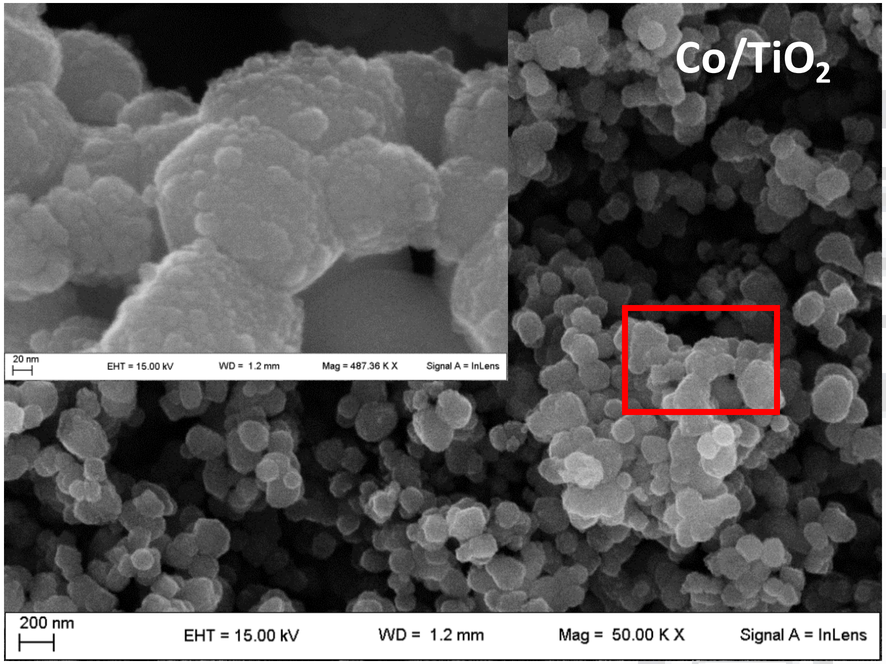
Iron Catalyst

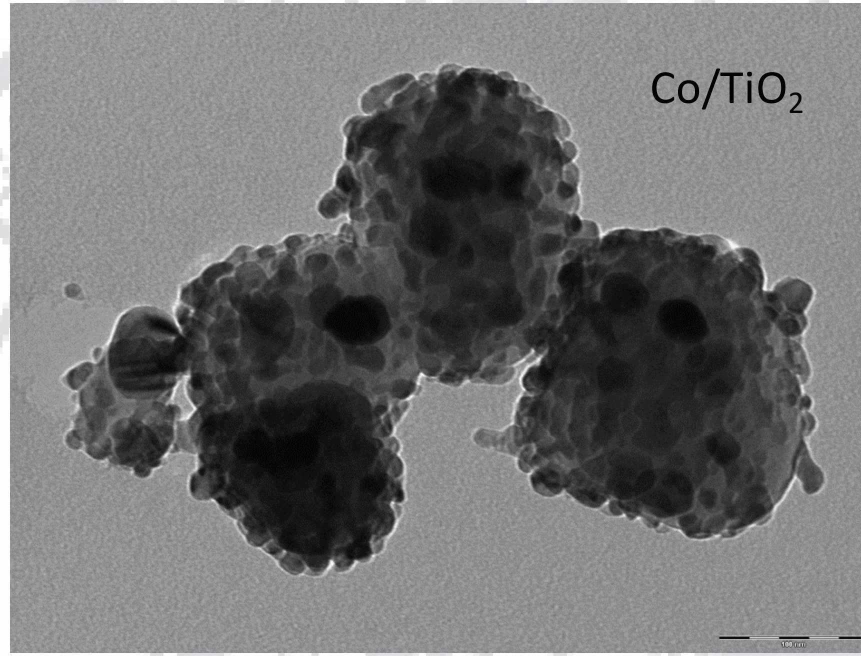
- Used for both Low Temperature and High Temperature process
- Low Temperature (200-240^{o}C)
- High Temperature (300-350^{o}C)
- Less Catalytically Active
- Promotes Water Gas Shift (requiring lower H_2:CO ratio which is ideal for Coal and Biomass)
- Olefins, shorter chains

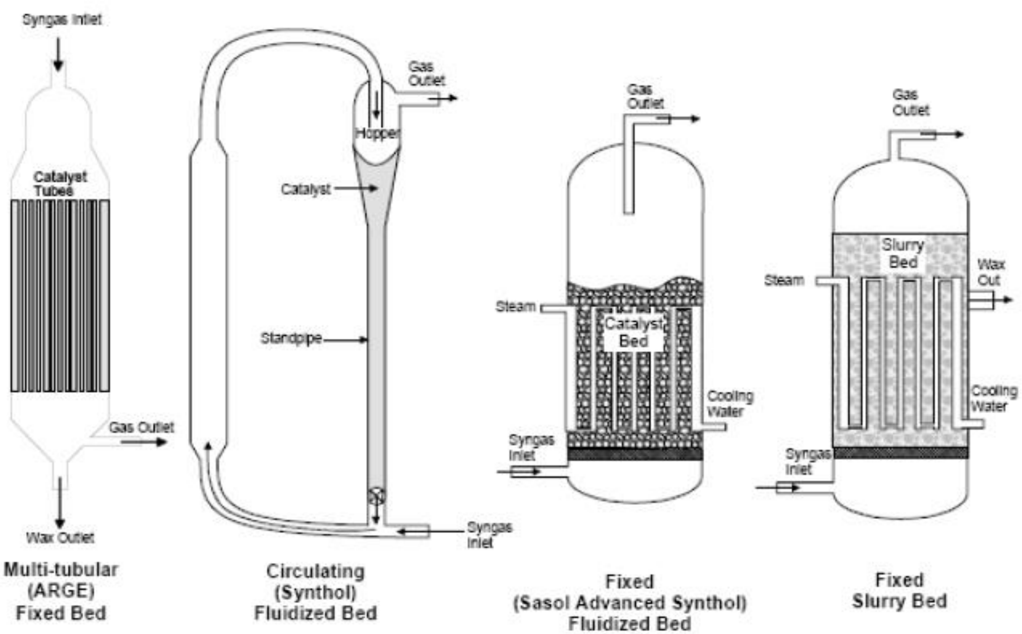
Cobalt Catalyst

- Much higher activity than Fe
- Used for Low Temperature (200-240^{o}C)
- Much more expensive than Iron based catalyst
- Does NOT promote water gas shift
- Has a much high sensitivity to sulfur deactivation
- Paraffins, higher chains

Khodakov, Wei Chu, Fongarlandl. Chem. Rev. **2007,** 107, 1692-1744







Reactor Design Types

PetroSA
StatoilHydro

Start up:	1992
Luogo:	South Africa
Capacità (bbl/g):	36'000
Catalizzatore:	Fe
Processo:	HTFT
Reattore:	CFBR

Start up:	1993
Luogo:	Malaysia
Capacità (bbl/g):	14'500
Catalizzatore:	Co
Processo:	LTFT
Reattore:	MTFBR

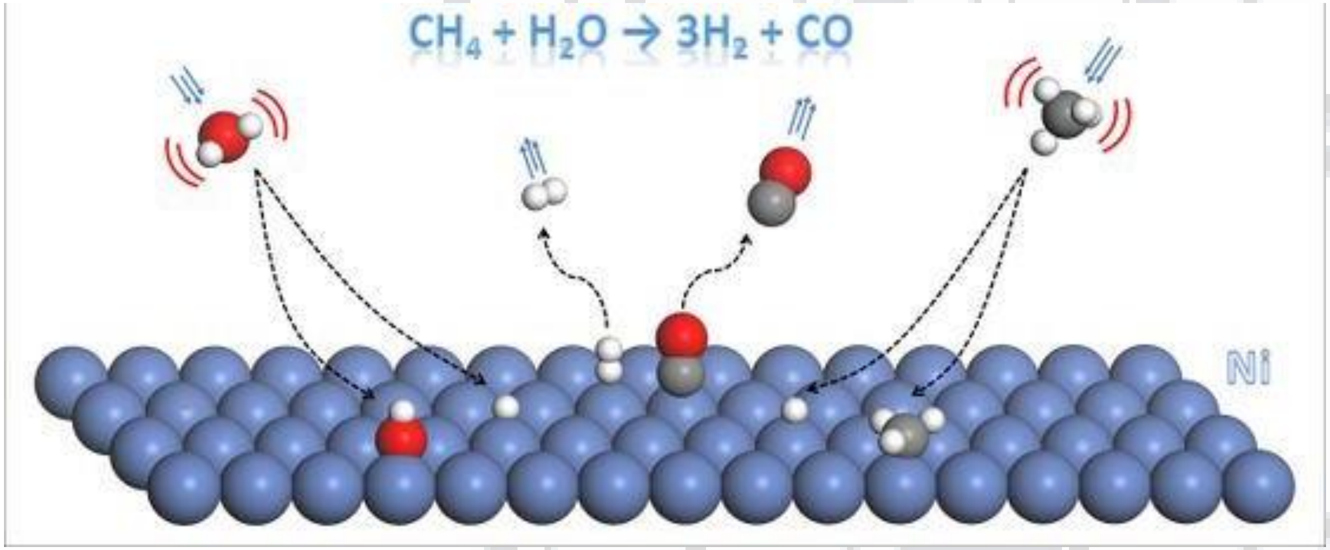
sasol
reaching new frontiers

قطر للبترول
Qatar Petroleum

Start up:	2007
Luogo:	Qatar
Capacità (bbl/g):	34'000
Catalizzatore:	Co
Processo:	LTFT
Reattore:	SBCR

Steam Reforming of (Bio)methane

Steam reforming is a method for producing hydrogen, carbon monoxide, or other useful products from hydrocarbon fuels



Nichel Based catalysts

The steam methane reforming is widely used in industry to make hydrogen

CH_4-reforming catalysts: requirements

- **Activity:** oxidation (CPO only), steam reforming (all technologies)

- **Thermal stability** – The process is characterized by high reaction temperatures (close to 1000-1200°C for ATR and CPO, close to 900°C for SR). Sintering, volatilization, metal inclusion are probable mechanisms of catalyst deactivation.
  They can be contrasted by proper selection of active element + supporting material
  Preferred supports: sintered oxides (α-Al_2O_3, ZrO_2) and oxide structures ($MgAl_2O_4$, spinels in general, perovskites)

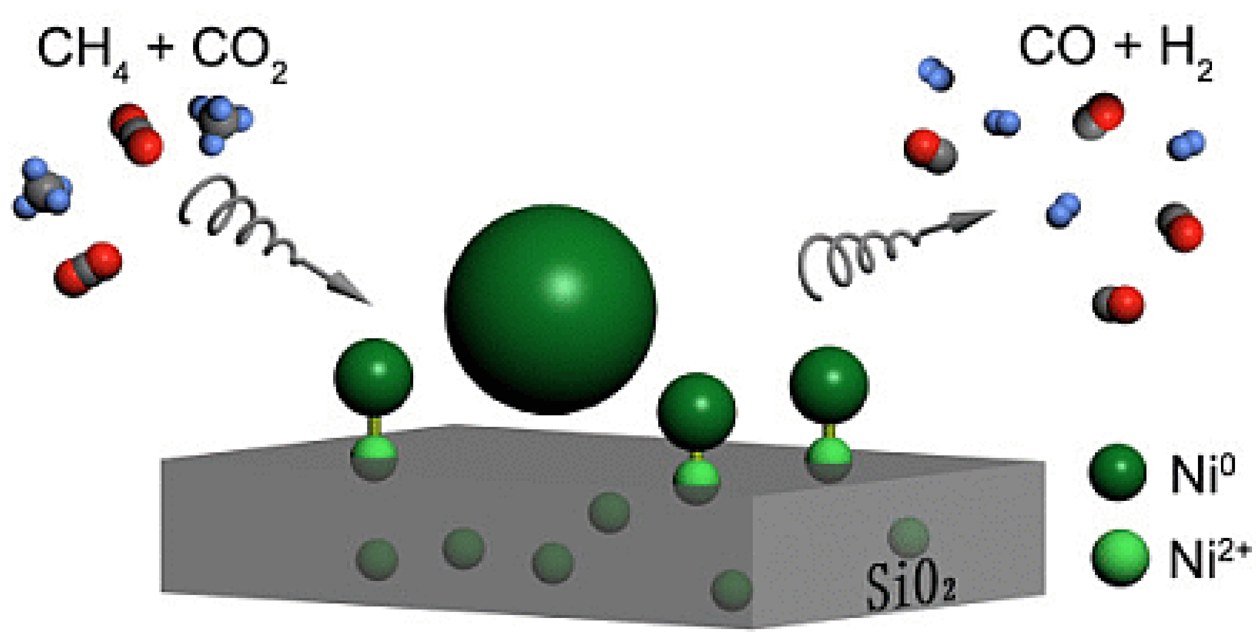
Metal	T_f, °C
Ni	**1455**
Co	1495
Fe	1539
Pd	1555
Pt	1773
Rh	**1966**
Ru	2500
Re	3170

- **Resistence to C-deposition**: methane activation consists of elementary steps of C-H bond breaking and C-O bond making whose relative rates need to be perfectly balanced to avoid C-accumulation on the surface.

Dry Reforming

Dry Refroming is a method of producing syngas from the reaction of carbon dioxide with methane.

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H_{298K} = 59.1\ \text{kcal.mol}^{-1}$$

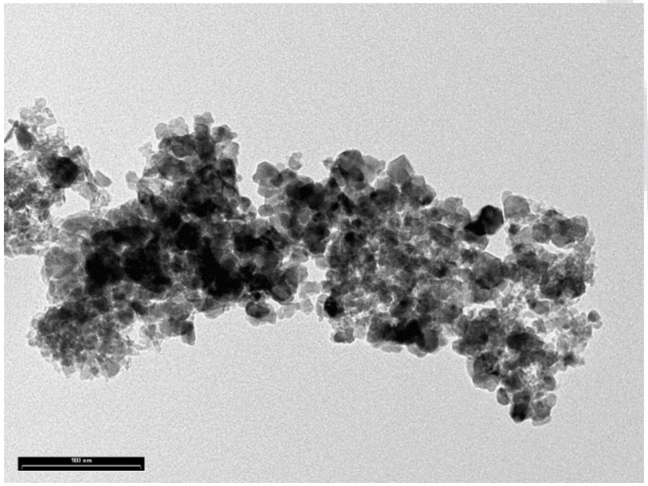


two greenhouse gases are consumed and useful chemical building blocks, hydrogen and carbon monoxide, are produced.

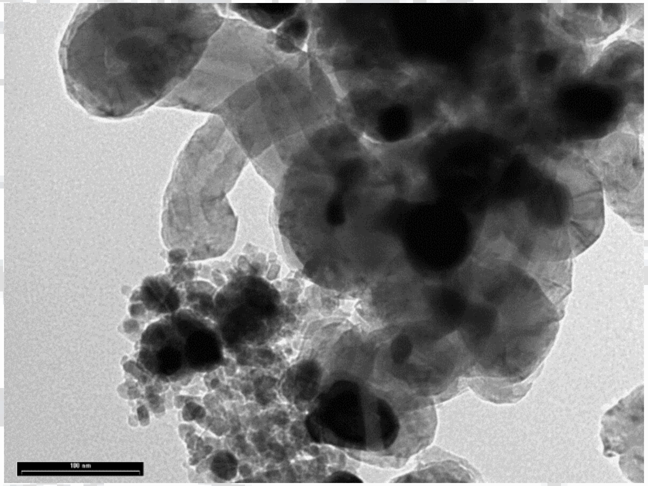
Required higher temperature and pressure
Thus, instability of catalysts and uneconomical

The main disadvantage of dry reforming of methane is the significant formation of structures (coke) that are subsequently deposited on the surface of the catalyst that is active in the reaction. **The deposition of coke** on the surface of the catalyst contributes to the reduction of its useful life.

Ni-Co/Al_2O_3



Before



After

Ethanol Steam Reforming

$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 6H_2$$

which may be seen as the sum of the syngas production and the water gas shift (WGS) reaction:

$$CH_3CH_2OH + H_2O \rightarrow 2CO + 4H_2$$

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

250-600°C

…An interesting alternative

- CO minimized
- Thermal duty reduced…
- No special steel alloys required

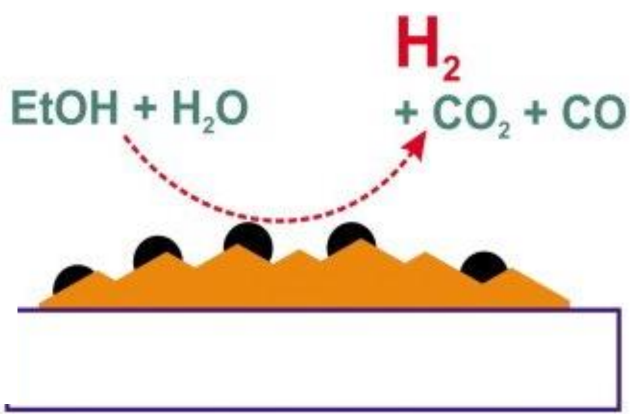
BUT

By-products (coke) more favoured

Catalyst deactivation

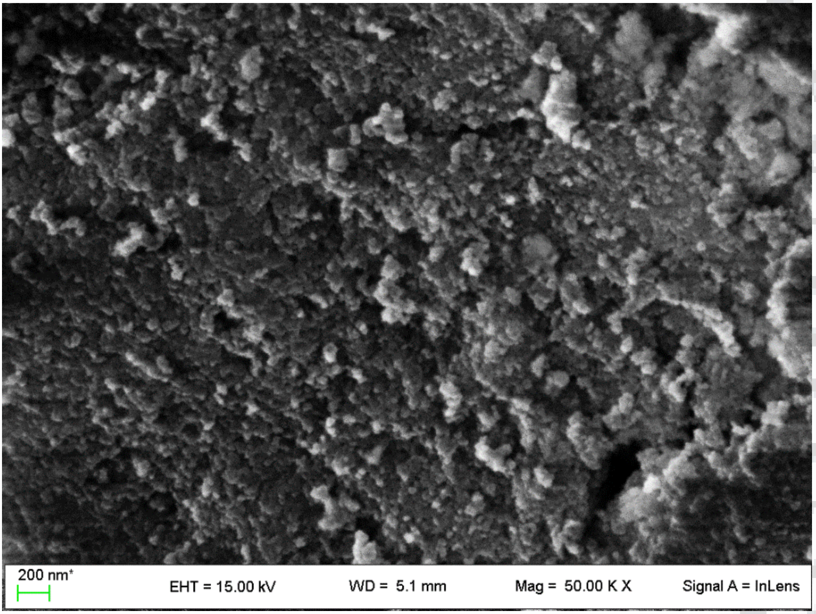
CATALYST Selection

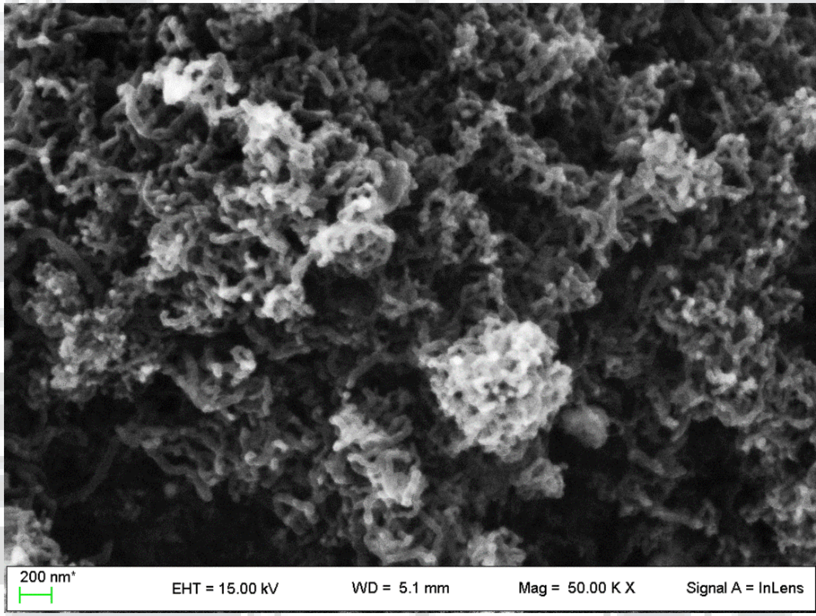
Ni



example

Ni/ZrO_2





Before

After

Ni/ZrO_2

Ni-Ca/ZrO_2

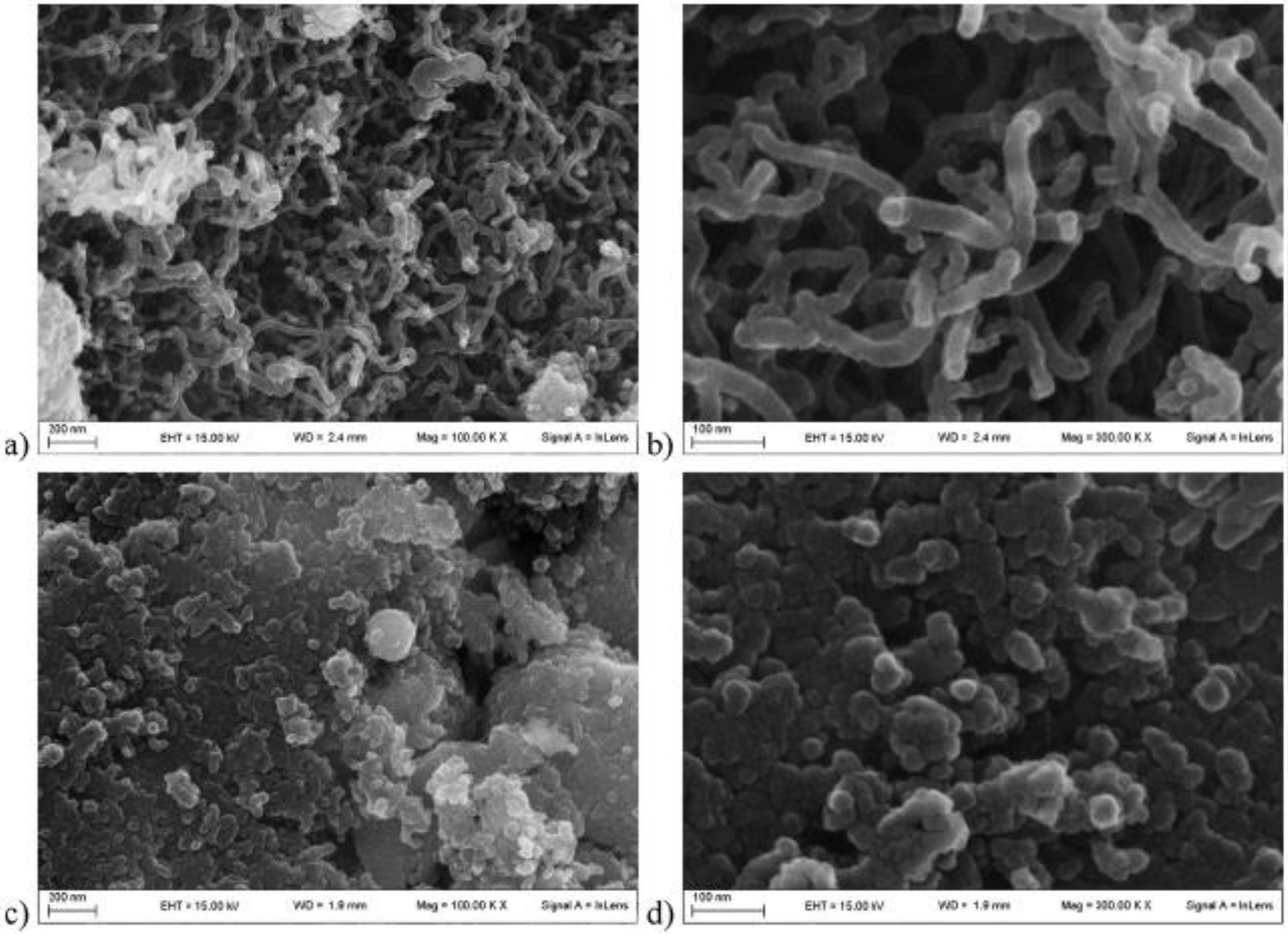
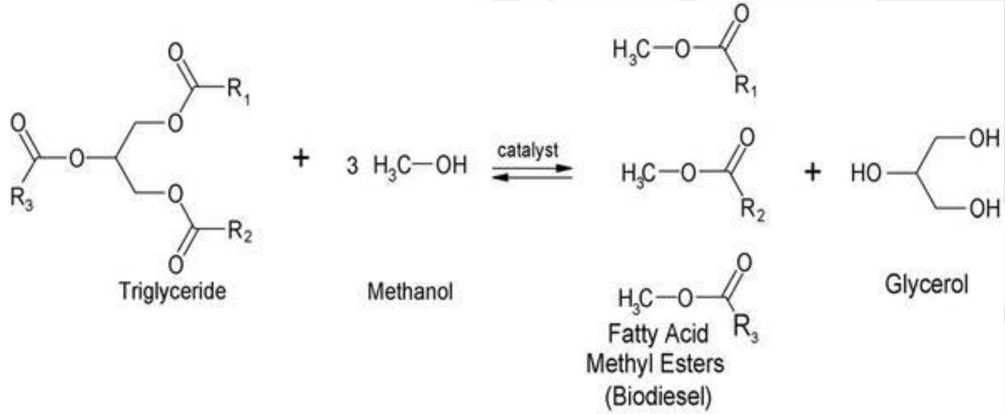


Fig. 9. FE-SEM images of spent samples ZNi (a and b) and ZCa_9Ni (c and d).

Glycerol Steam Reforming

- Glycerol is produced in mass quantity as by-product of biodiesel industries
- Glycerol is inedible, thus poses no direct competititon as in the case with food derivatives
- Glycerol has limited use, mainly in pharmaceuticals



coke deposition……….

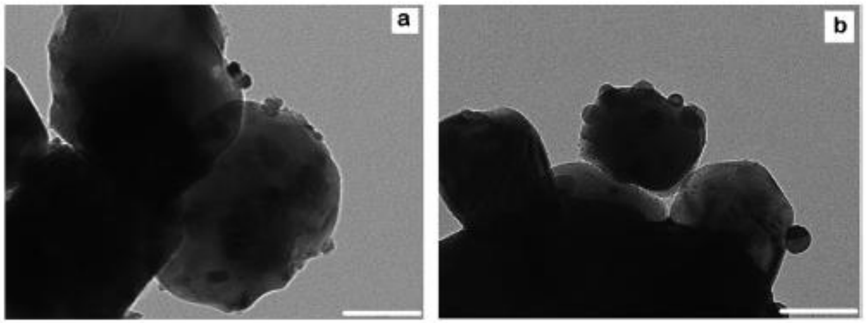
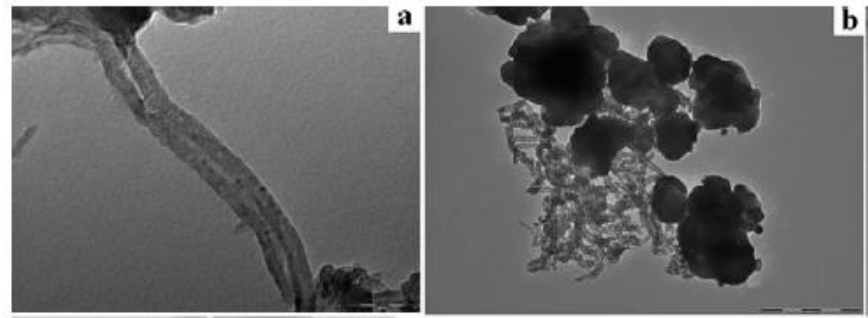
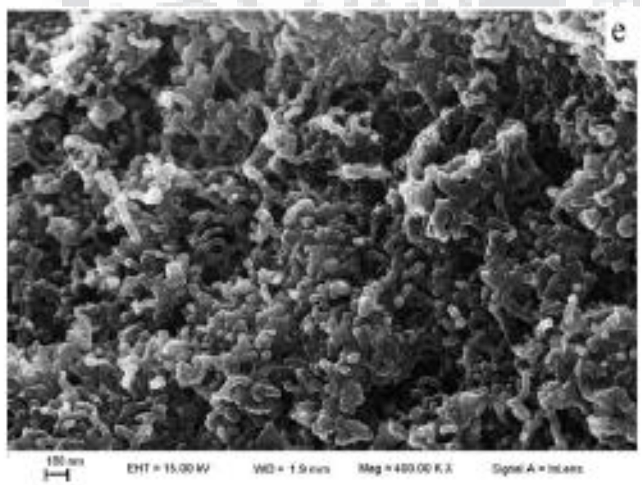


Figure 1. TEM analysis of the NiTiL sample a) as-prepared and b) reduced under 10 vol% H_2 flow at 700 °C for 1 h. Scale bars: 100 nm.





Research Purposes for Refoming process

- Synthesis of active catalysts
- Long time life of catalysts
- Improve resistance against coke deposition

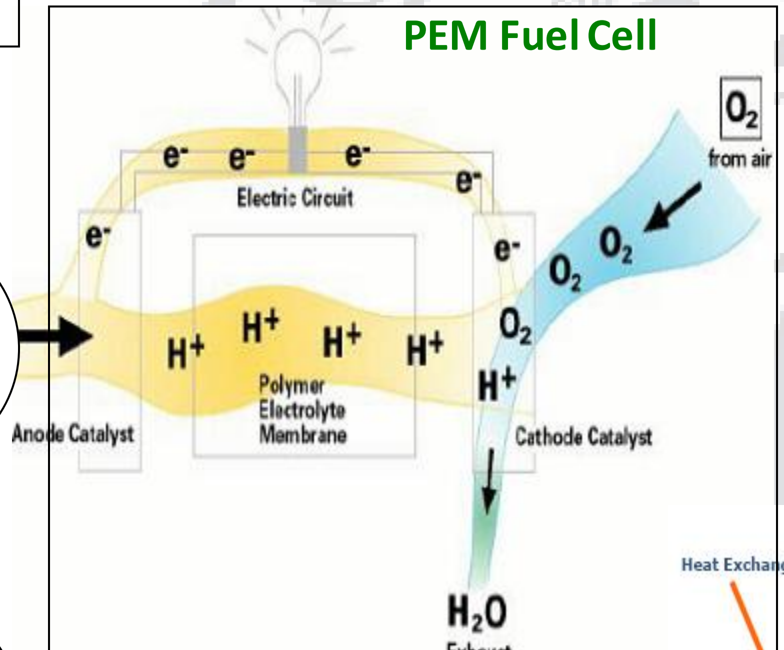

From biomass...
...to hydrogen!
H2

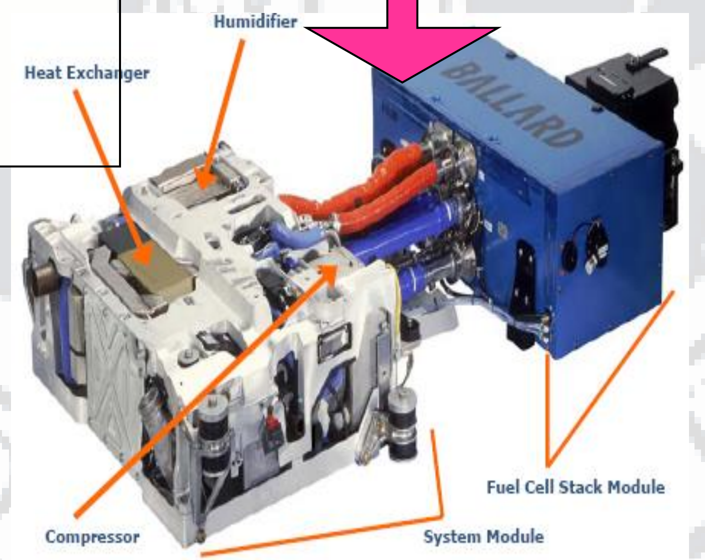

Hydrogen is the
future energy vector
Clean
No CO_2 emissions
High efficiency
Direct use
H2

Pure H_2 Supply

- Compressed H_2
- Liquid H_2
- H_2 Hydrid

H_2 Fuel



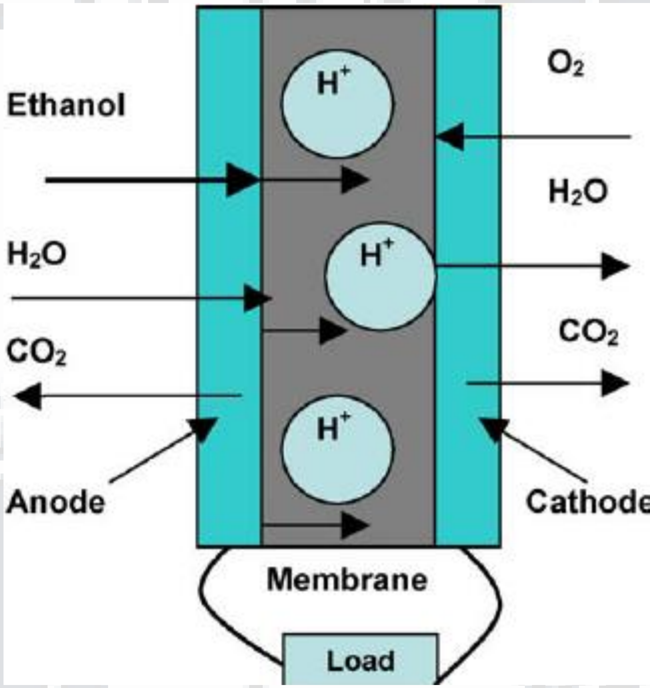


H_2 from Reformed liquid HC

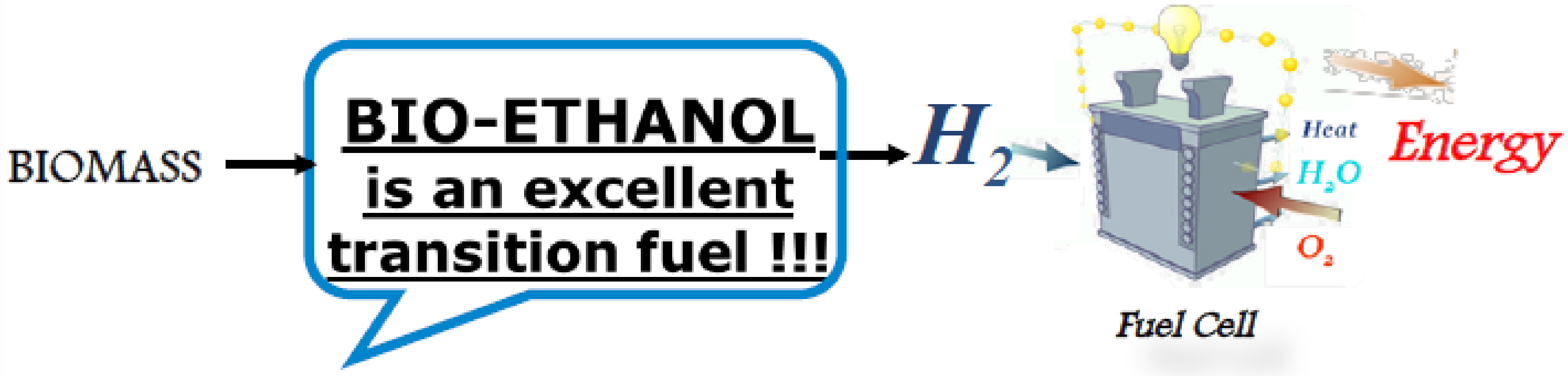
- Methanol
- Ethanol
- DME

Ethanol as Fuel for fuel cells

- High energy storage density
- High availability worldwide
  - existing distribution infrastrucuture
  - low demand to purity
- Low risks
  - Toxicity
  - Reaction to bullet impact
- Simple handling
- Reduce air pollution



A CLEAN AND ENVIRONMENTAL ROUTE FOR THE PRODUCTION OF HYDROGEN IS THE USE OF BIOETHANOL AS A TRANSITION FUEL:



- Easy to produce, handle, store and transport
- Reduction of CO_2, NO_x, SO_x... emissions
- Aqueous rather than anhydrous ethanol may be used

In Conclusion

- Reduce wastes
- Cleaner air and Reduction of GHG emissions
- New agricultural markets
- Energy security
- Reduction of municipal and industrial waste disposal
- Use of renewable low cost feedstocks
- Converting waste into ultra clean-diesel.
- Hydrogen production from Biomethane, Bioethanol and Glycerol

THANKS FOR YOUR ATTENTION