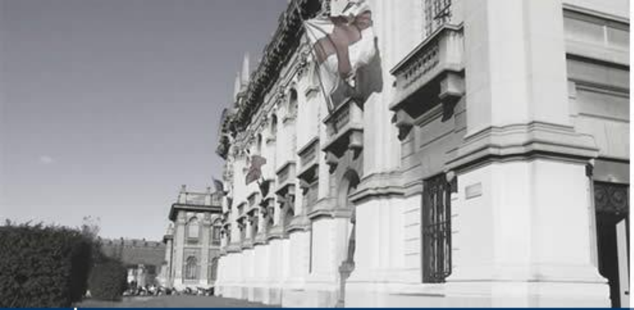


School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

GC-Focus: Inherent Hazards and Safety – Efficient Resource Uses.

Prof. Attilio Citterio

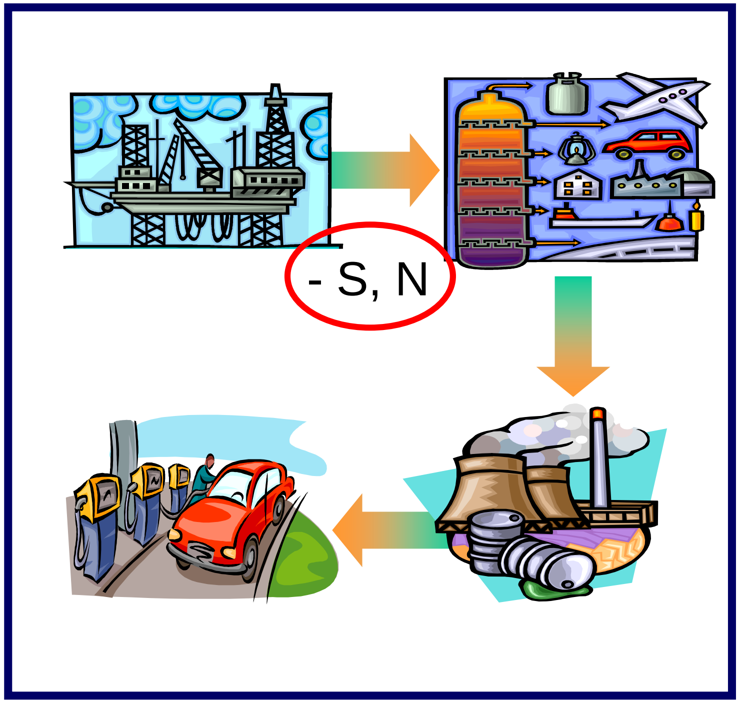
Dipartimento CMIC “Giulio Natta”

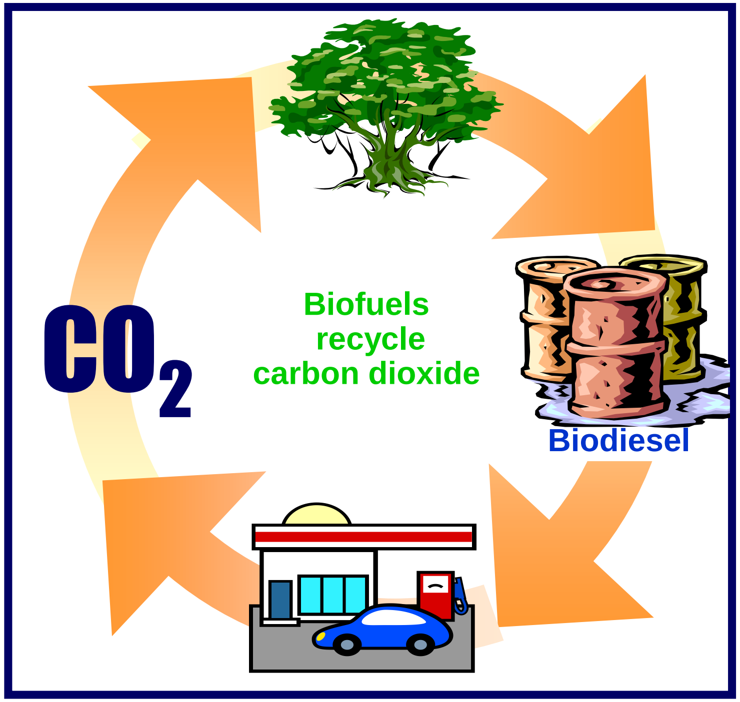
https://iscamapweb.chem.polimi.it/citterio/education/course-topics/

Examples of GC-proposed Solutions.

- Fuel/Biofuels Reformulation
- Environmental Programs
- Improvements of Processes
- Antibacterial Products
- Detergency
- Water Treatment
- Industrial cleaning agents

Fuel Reformulation and Biofuel.

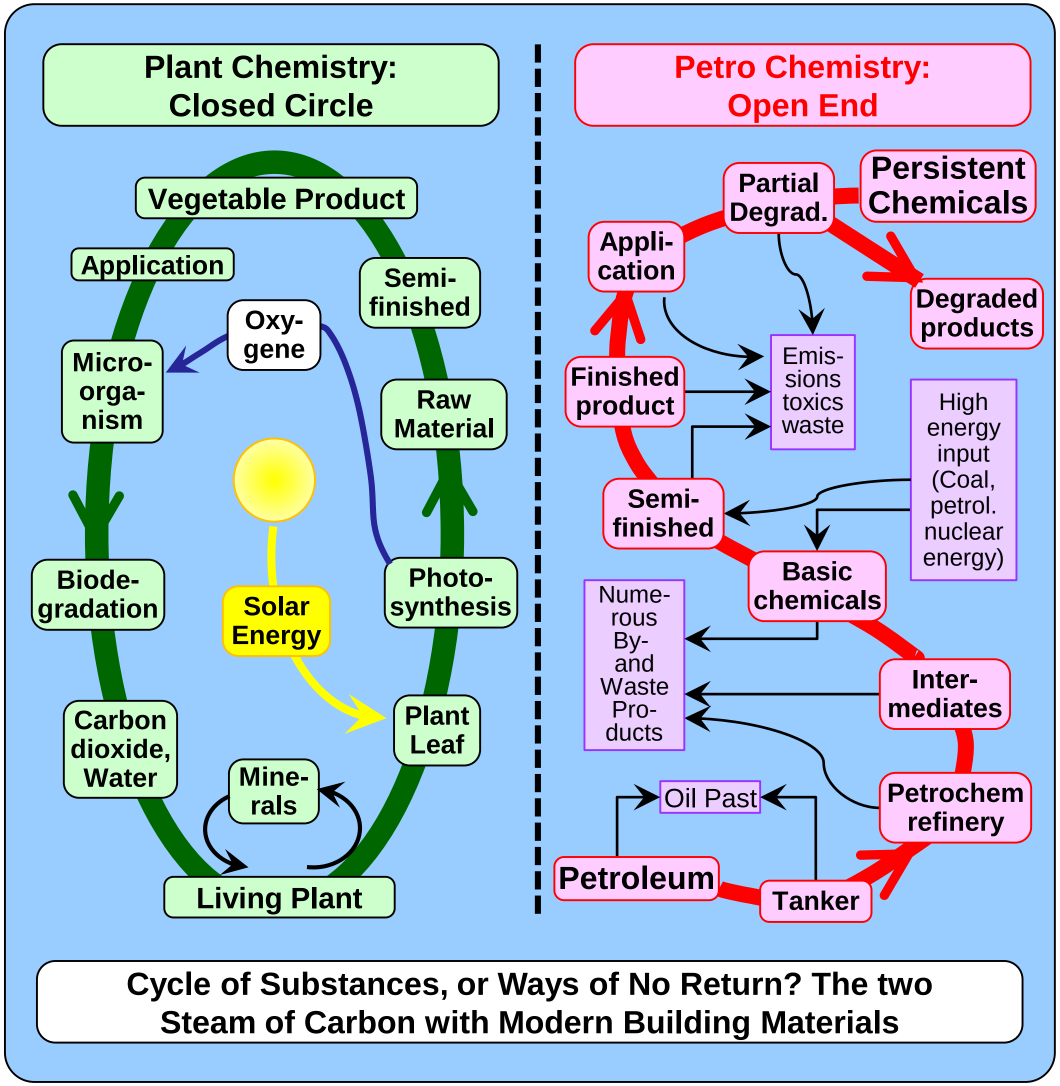




Reformulation of oil/gas

Fuels from biomasses

Plant Chemistry vs. Petro Chemistry: Quality of the 'Biosphere' System.



Also in respect to by-products generation the synthesis of vegetable raw material for the industry has advantages over today`s methods to synthesize matter in chemical retorts. Each product of the plant secondary metabolism has its natural function in the environment. None of these products are accumulated in the environment. The ecologically adapted creation of biomass has never damaged the basis for biomass production. in significant amounts.

Examples for Chemical Technical Products Based on Crude Oil - and Biogenic Alternatives.

Product range	Raw Material Petrochemical	Raw Material Biogenic	Examples for Raw Material	Example for Usage
Fiber reinforced material	Carbon fiber, GF, Polyamide	Plant fibers, Plant Resin	Hemp fiber Shellac resin	Machine Casting
Floor covering	PVC	Tree barks Plant oils Plant fibers Plant resins	Cork Linseed oil Jute Colophony	Linoleum
Textitles	Polyesters	Plant fibers	Linen	Upholstery
Wood glazes	Polyacrylates Glycoles	Plant resins Essential oils	Damar resin Citric oil	Natural resin glazes
Wood lacquers	Acid-drying lacquer	Plant wax Plant oil	Carnauba wax Linseed oil	Wax balm for wood
Artist's paints	Azo pigments	Plant Dye	Woad	Plant colors
Tensides	Alkylbenzol-sulfonate (LAS)	Plant Oil Carbohydrates	Coconut oil Sugar	Washing detergent
Hydraulics and lubricating oil	Mineral oils	Plant oils	Castor oil	Chain saw oil
Insulating material	Polystyrene	Straw Protein glue	Linseed straw Casein glue	Insulation mat
Packages	Polyethylene	Polysaccharides	Bipol	Shampoo

Fuel Specification: UE Legislation Trend.

Gasoline		1999	2000	2005	2010§	2018
Sulfur	ppm, max	500	150	50	10	10
Aromatics	%v, max	-	42	35	35	➔ 10
Olefins	%v, max	-	18	18	18	18
Benzene	%v, max	5	1	1	1	➔ 0
TVR Est.	kPa, max	70/90#	60/70#	60/70#	60/70#	60/70#

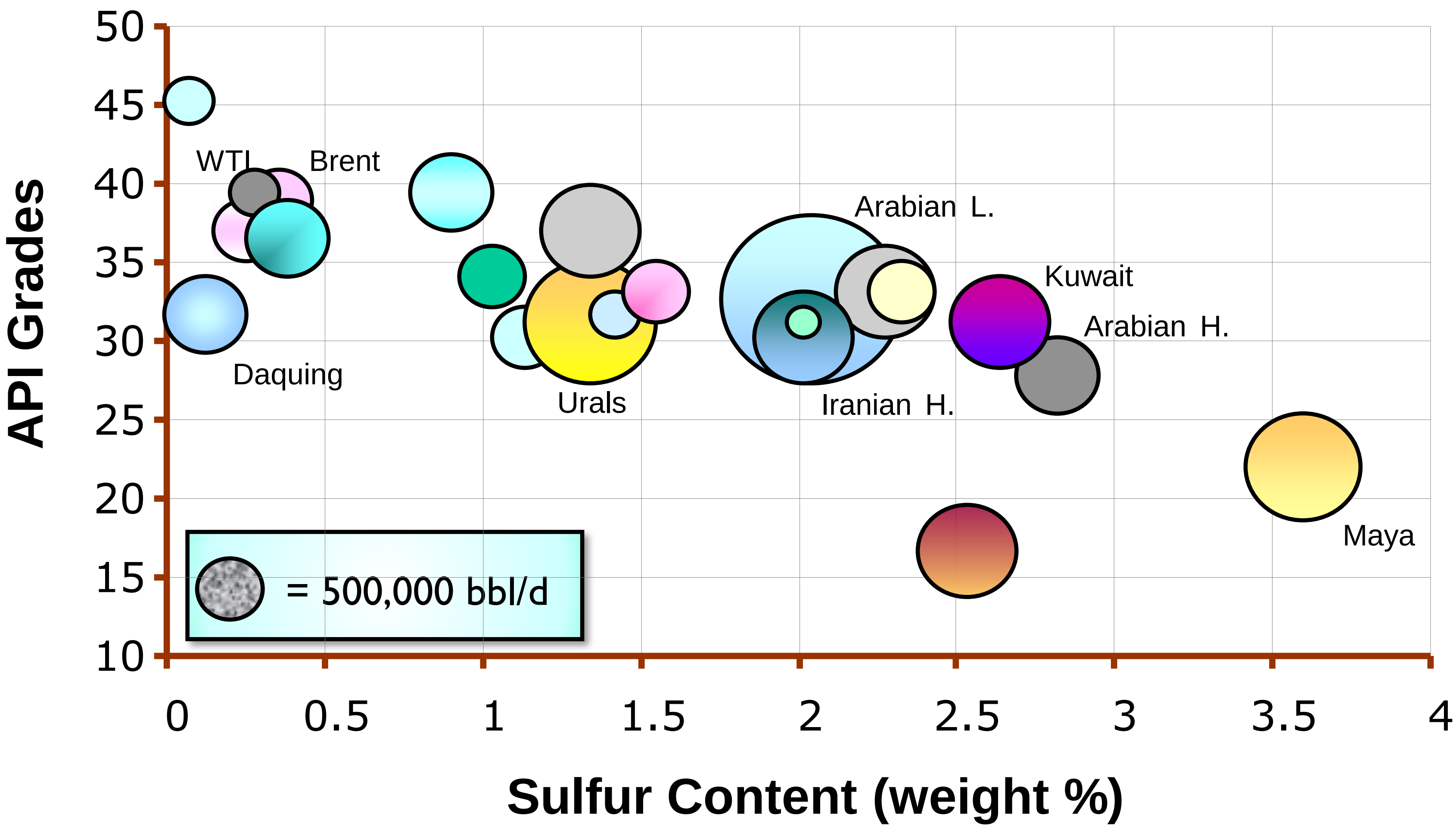
#: artic climate

DIESEL		1999	2000	2005	2010§
Sulfur	ppm, max	500	350	50	10*
Density,	kg/m^3, max	860	845	845	845
Cetane N.	min	49	51	51	51
T95	°C, max	370	360	360	360
PAH	%p, max	-	11	11	11

* Marine 50

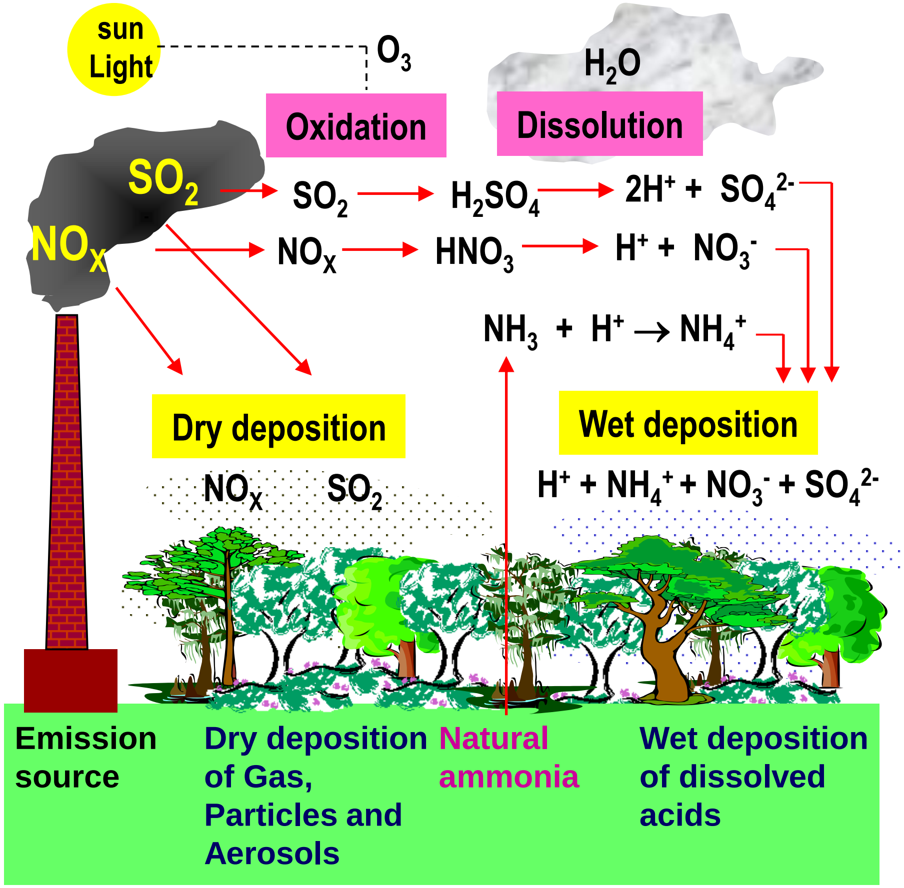
§ https://eur-lex.europa.eu/legal-content/EN/TXT/?qid=1522063005973&uri=CELEX:32009L0015

Production Volumes and Quality of Main Crudes.



Solutions: Sulfur Reduction in Fuels – to Reduce Acid Rain.

- Air emission of sulfur oxides SO_2 and SO_3 generates sulfuric acid (H_2SO_4) starting a process known as acid rain.
- Sulfur produced in combustions can be trapped using FGD (Flue-gas desulfurization) processes by conversion into harmless and reusable by-products.
- Alternatively, the fuel can be desulfurized at the origin in order to limit the problem.



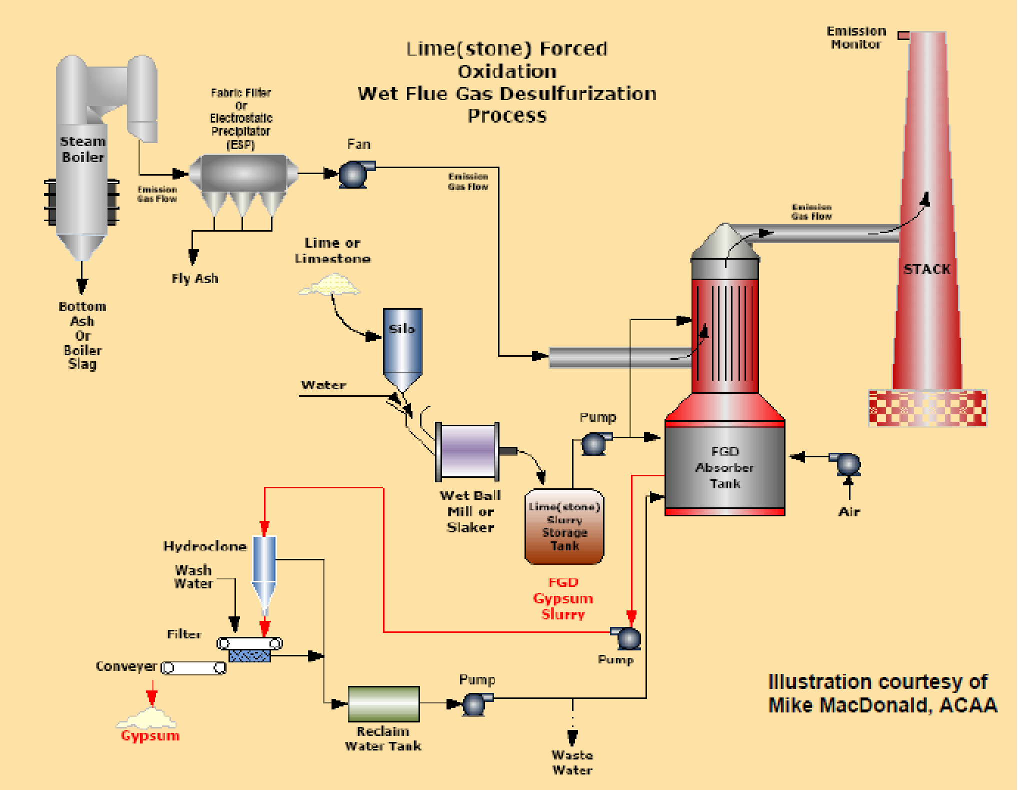
FGD Types: Wet and Dry.

Wet FGD is the preferred method in several coal based plants (~ 90% use this method).

There are two primary forms of wet FGD:

a) the systems which use a wet absorber, and

b) the systems which use the natural oxidation.



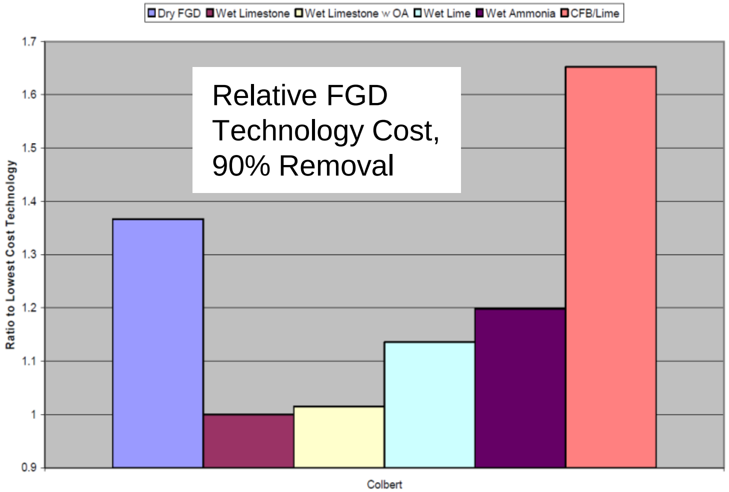
a) $SO_2 + Ca(OH)_2 \rightarrow CaSO_3 + H_2O$ — $CaSO_3$ calcium sulfite

b) $SO_2 + Ca(OH)_2 + ½\ O_2 \rightarrow CaSO_4 + H_2O$ — $CaSO_4$ calcium sulfate

Wet FGD Processes.

- Using a wet scrubber, an aqueous solution of limestone ($CaCO_3$) o lime ($Ca[OH]_2$) is added to the waste gas in a wide Tower Spraying.
- The solution capture SO_2 giving a by-product known as absorption mud, a matter of composition and structure similar to wet cement.

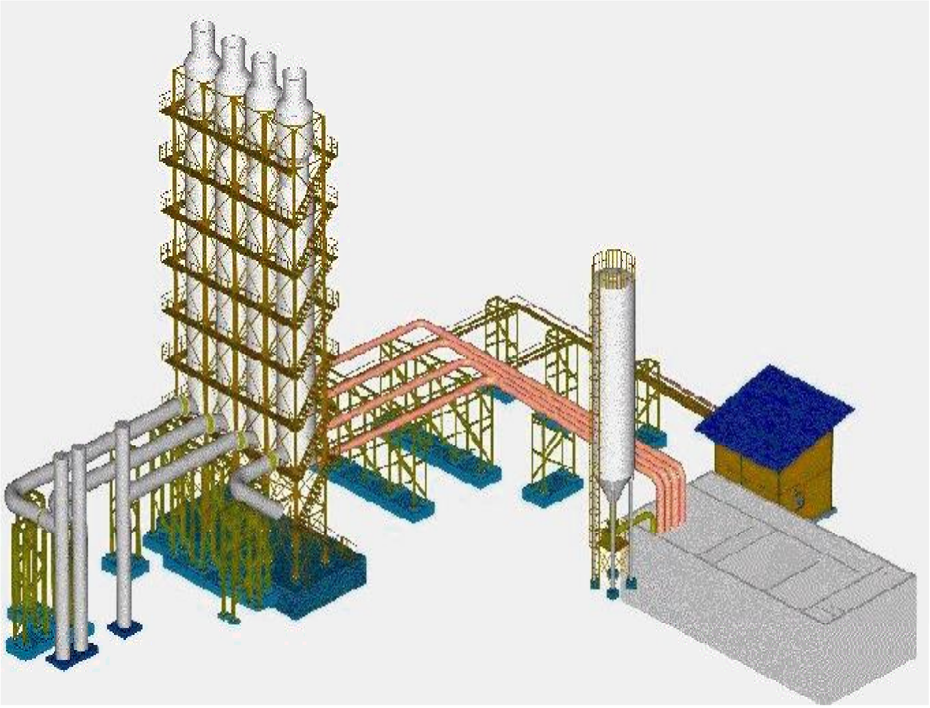
- By using natural oxidation, only natural oxygen in injected into the gas, producing as by-product calcium sulfite ($CaSO_3$).
- If the forced oxidation is used with the aid of fans to enter an excess of oxygen, the by-product calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) or gypsum is generated.



The Best Available Method (BAT).

The more used and efficient method is the forced oxidation, because gypsum has a variety of commercial uses much wider than calcium sulfite and does not need to be disposed in landfill.

Moreover, it is easier to confer in landfill, if necessary.



Wet FGD plant

Advantages of Wet FGD.

- There is no need to use demineralized water. It is possible to use hard water or wastewater.
- Water consumption is low. The used water is recycled, only the amount of evaporated water must be added.
- The consumption of chemicals is low.
- With a special design of scrubber it is possible to prevent the head loss, therefore the use of fans is prevented and the electricity consumption is reduced.
- Specially designed spiral nozzles are used to prevent obstructions.
- Nozzles are cleaned, controlled and substituted without stop the system.
- Total costs are minimized.
- Deviation tower are not necessary.

Dry FGD Process.

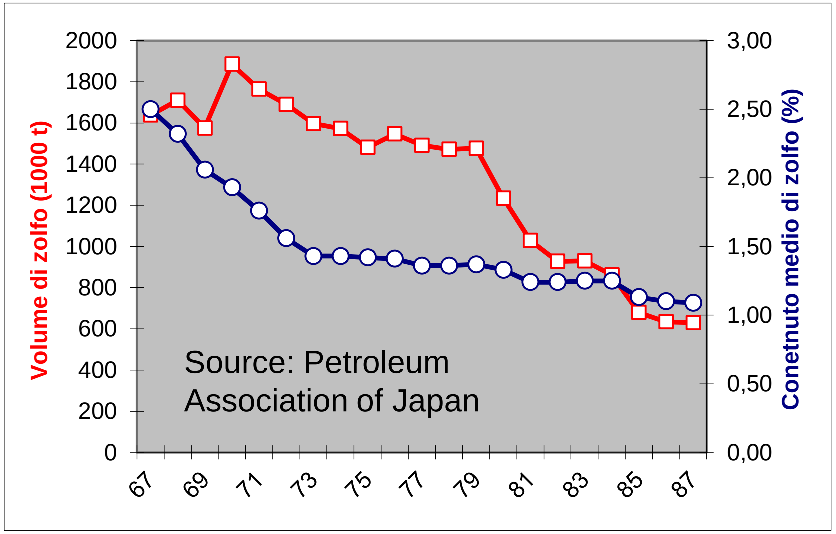
- Dry FGD systems use less water than the wet and produce a dry by-product.
- The most used dry FGD model is the spray dryer, in which a suspension of lime id sprayed in the gas flow. The heat of gas dry the by-product, normally $CaSO_3$ or fly ash.
- The main part of these by-products goes to landfills, but applications in building are also known.

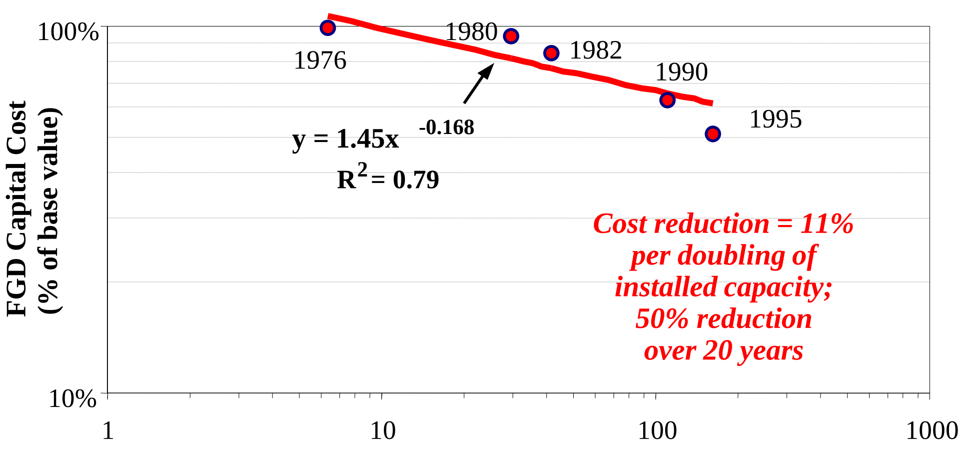
Advantages of Dry FGD.

- No waste is formed, therefore no waste treatment is necessary.
- Only see water and air are required.
- No other chemical is used.
- Capital and Operational Costs are lower than the wet systems.
- The absorbed SO_2 is oxidized to sulfate ion, a natural constituent of see water.
- Obstruction of scrubbers are strongly reduced.
- High reliability.

Evidences of FGD Effectiveness.

- Graph 1: trend of the "Volume of sulfur" and "Mean Content of Sulfur" in Combustible Oils for Domestic use in 20 years.
- It is evident a significant progressive decrease of total sulfur amount in the atmosphere with decrease of degenerative acid rains.
- Graph 2: parallel 10-15% reduction of plant costs, making the technology affordable.

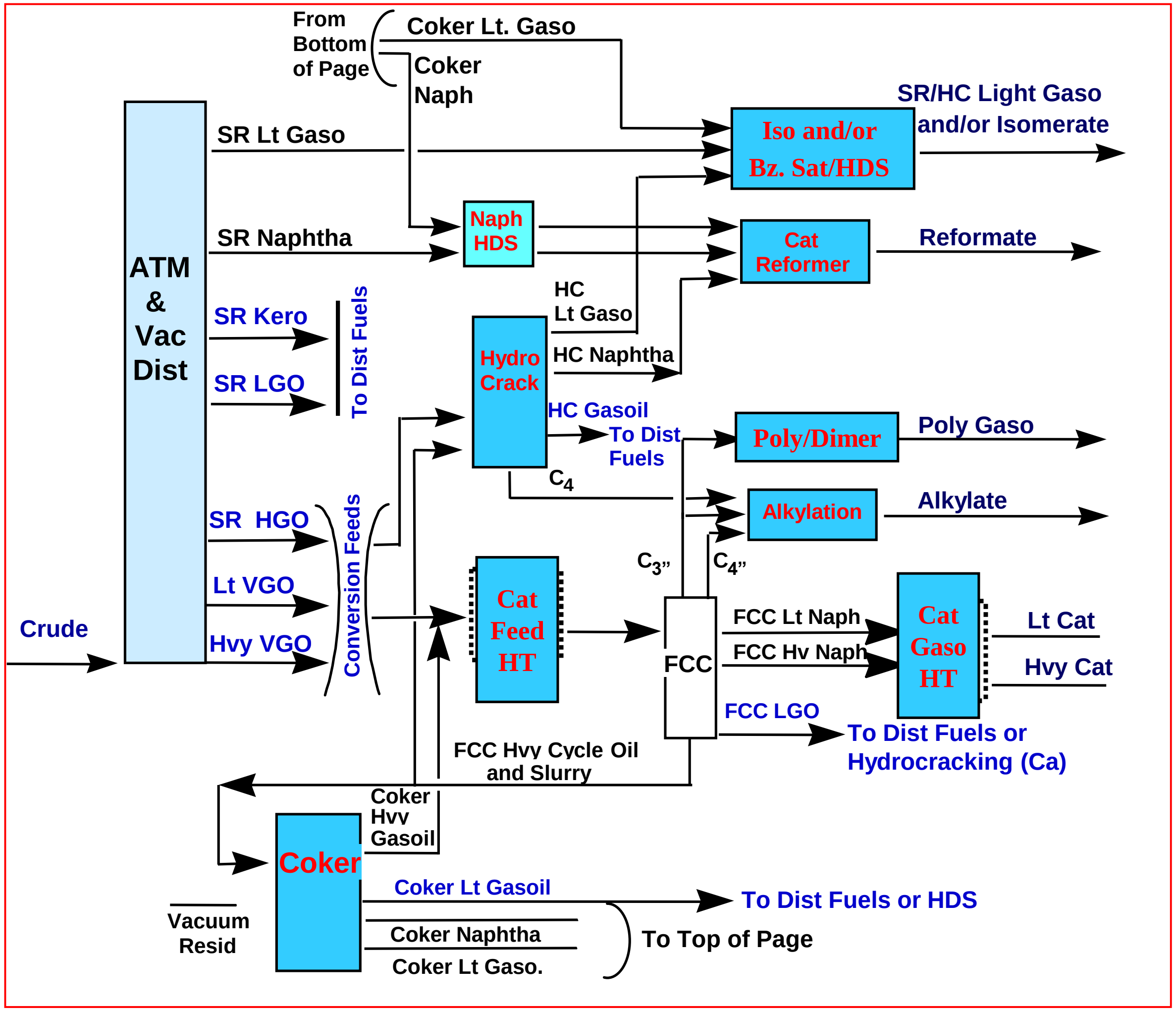




Sulfur Reduction in Natural Fuels.

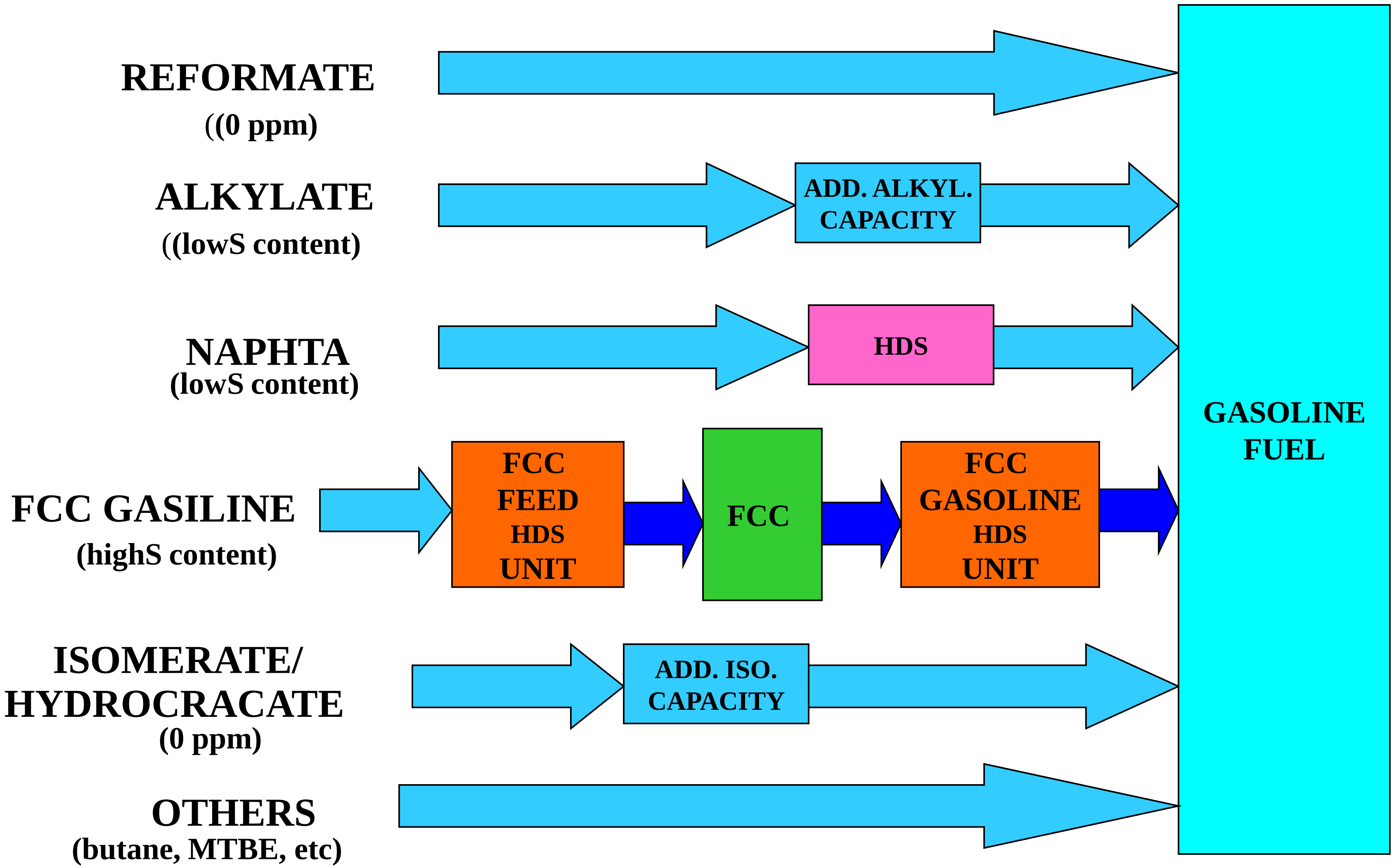
- “Sulfur free” fuels: their max. content of sulfur is 10 ppm
- The limit allowed in EU in 2004 was between 50 e 100 ppm for oil and diesel, respectively
- From 2005, both values were decreased to less than 10 ppm
- New technologies of oil refining by heterogeneous catalysis are now available, which use desulfuration via hydrogen to reach the limit of 5-15 ppm of sulfur.

Sulfur Reduction Strategies.



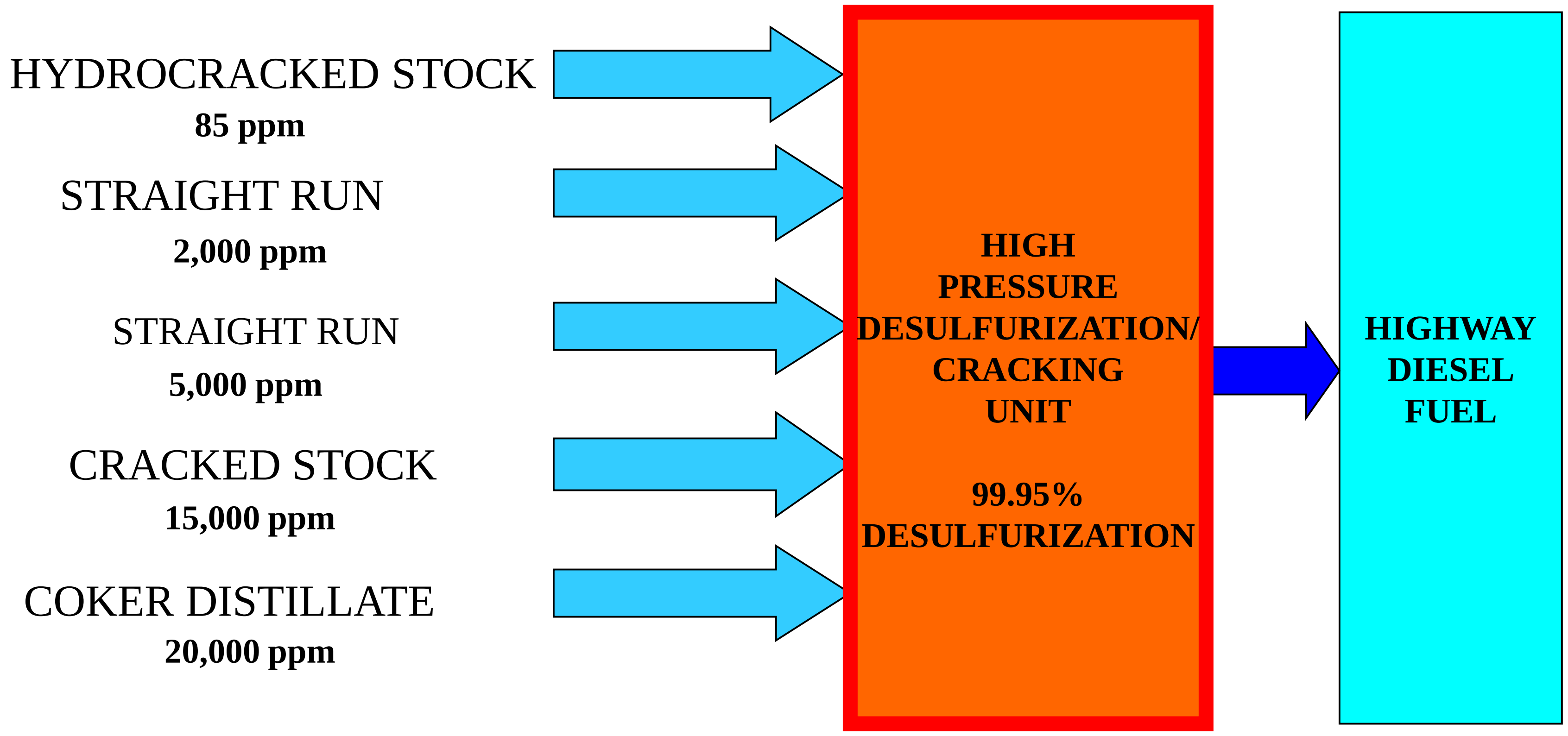
Refinery Block Flow Diagram

Gasoline Production (50 *ppm* / 10 *ppm*).



Diesel Production (10 *ppm*):

Very High Cost to Maintain Volume.



The Problem of Particulate Matter (PM_{10}) - Diesel Emulsions and DPF Filter.

Diesel Fuel

+

10%

Water

Surfactant and other additives

GECAM
il gasolio bianco

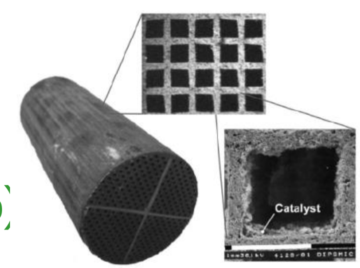
Approved as new fuel in 2001 in Italy and EU

production

Cam Tec

Commercially available

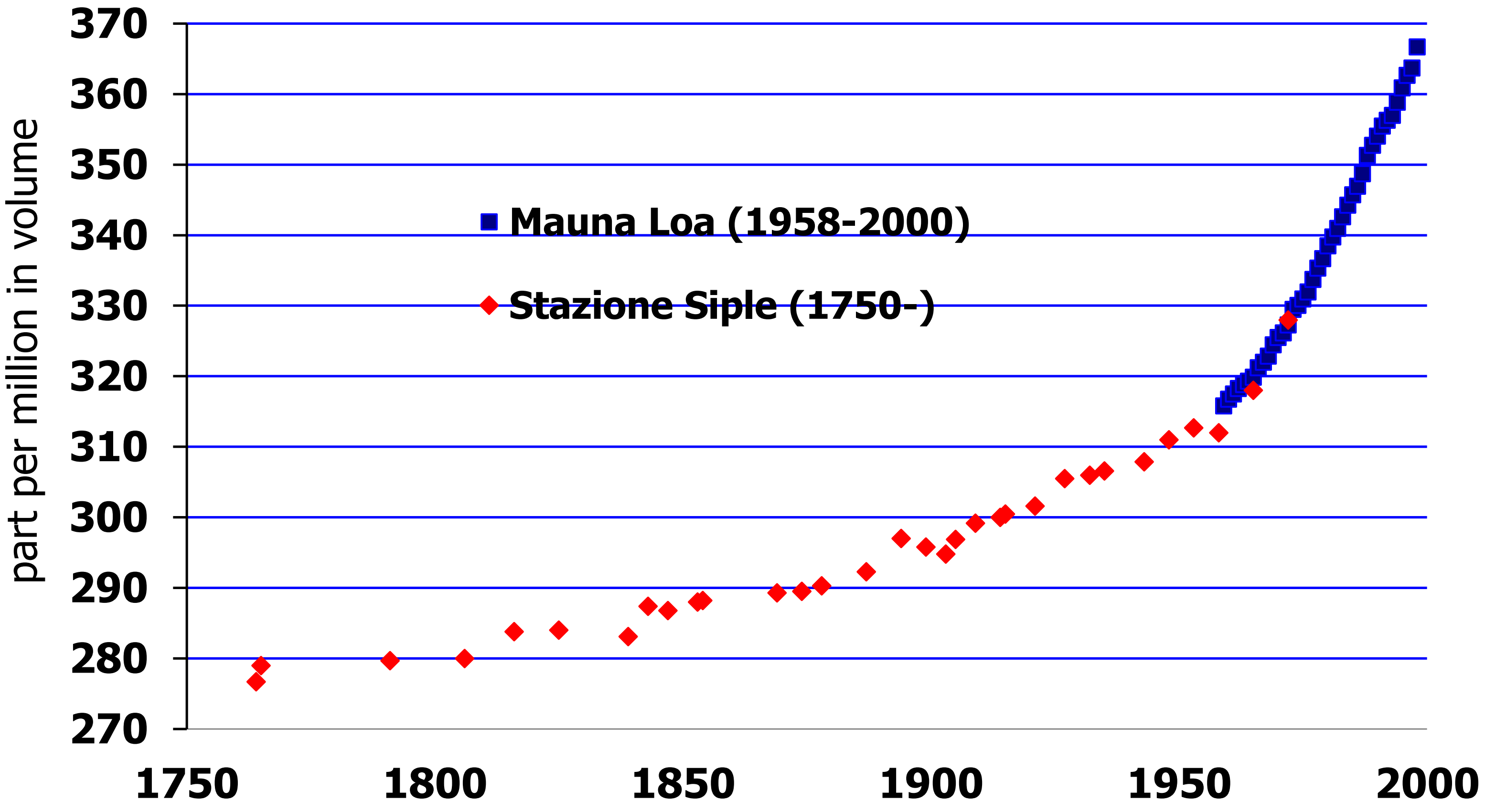
Ceramic filter with catalytic regeneration



Eco-target:

- PM_{10} (30-70%)
- NO_x (10%)
- CO and Hydrocarbons (~0%)

Greenhouse Effect: Atmospheric Carbon Dioxide Concentrations (1750 to present).



Sources: C.D. Keeling and T.P. Whorf, Atmospheric CO_2 Concentrations (ppmv) derived from in situ air samples collected at Mauna Loa Observatory, Hawaii, Scripps Institute of Oceanography, 1998. A. Neftel et al, Historical CO_2 Record from the Siple Station Ice Core, Physics Institute, University of Bern, Svizzera, 1994.

Biofuels.

Fuels obtained from biomass derived from organic material (frequently as solid, gaseous or liquid mixtures).

Types:

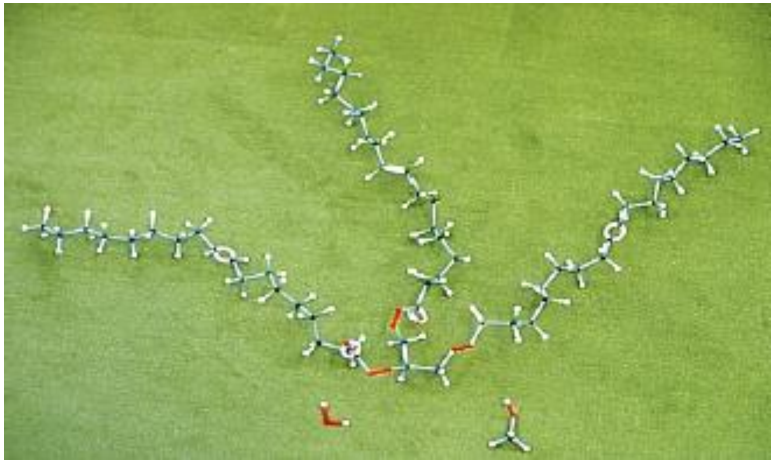
- **Solid biomass** (mainly cellulosic – wood, pyrolitic carbon, etc.)
- **Liquid Biofuels**:
  - Biodiesel (esters of fatty acids from oils and vegetable fats)
  - Bioalcohols (bioethanol and biomethanol)
- **Biogas** (gas from elaboration of organic residues by bacteria mainly anaerobic, specifically CH_4 and syngas)

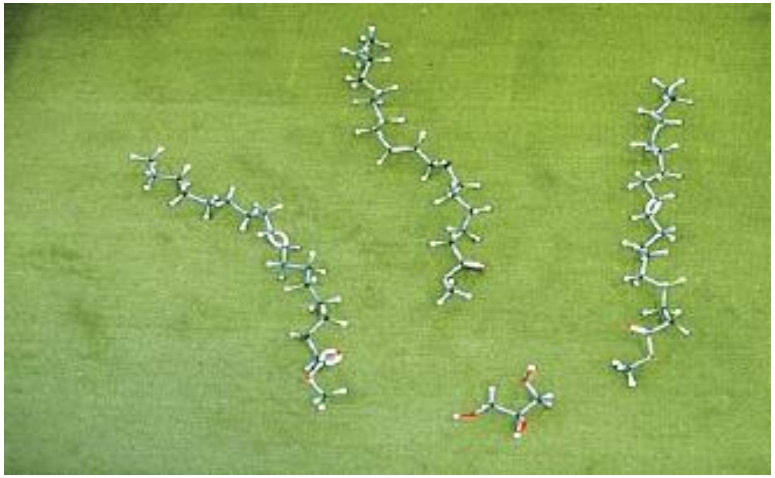
Biofuels have been used by man in the past but in a less elaborated form (wood, oils).

Oil or Fat to Biodiesel (FAME).

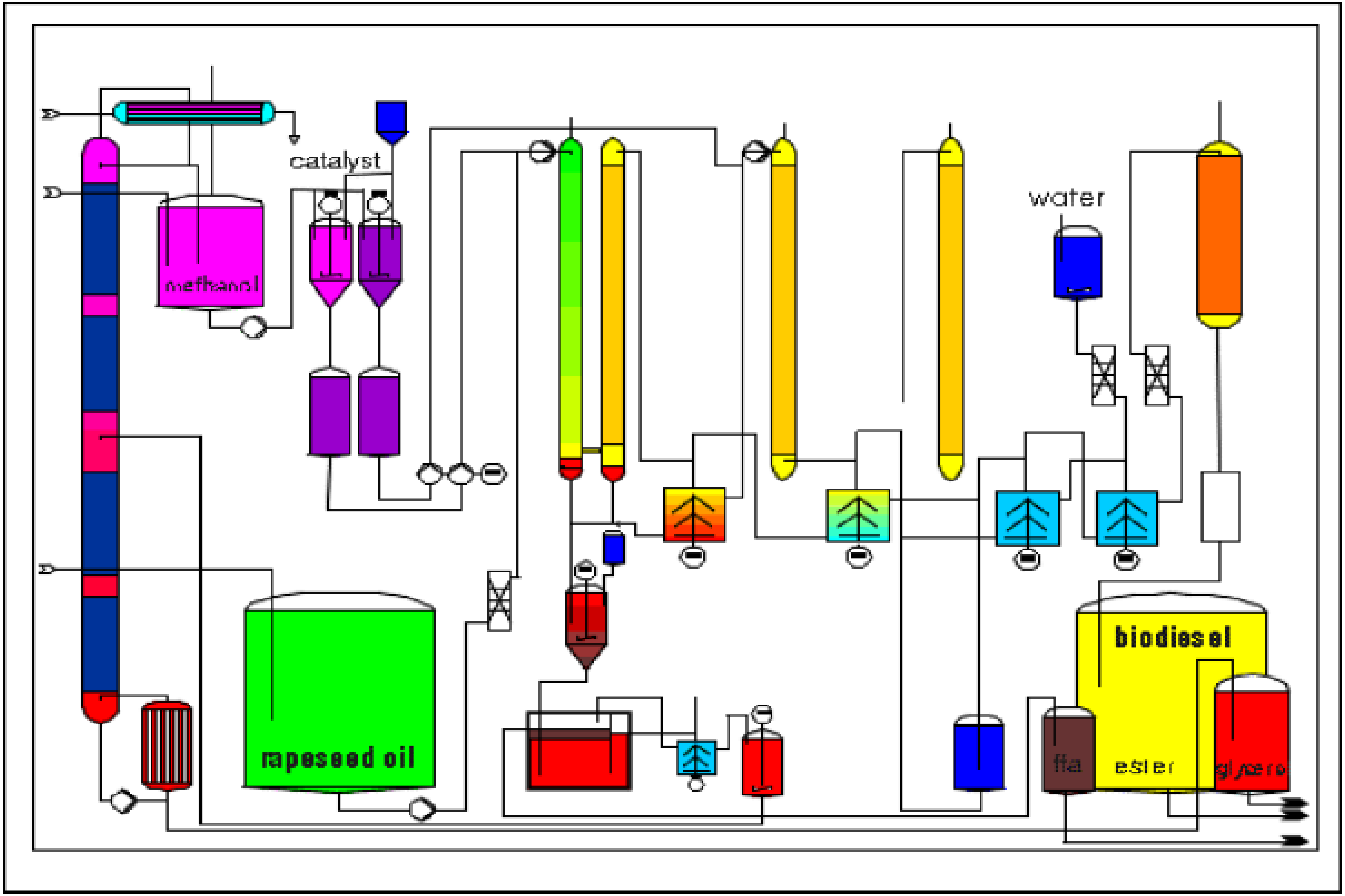
- Triacylglycerol +
  - methanol (from biomass?)
  - + catalyst gives
  - ester + glycerol
- The hooked tripod molecule
  - is changed to slippery ester chains, thus
- Viscosity is reduced from 60 to 4 cSt (like diesel fuel)

FAME = Fatty acid methyl esters





Biodiesel Process:
Biogenic Oils and Fats Transesterification.



Bio-Refinery.

Wheat

Fuels

Solvent

Plastics

Bulk chemicals

Fine Chemicals

Fibres

Oils

Petroleum Refinery.

Petroleum feedstock

→ Fuels

→ Solvents

→ Bulk chemicals

→ Plastics

→ Fibres

→ Fine chemicals

→ Oils

Industrial Voluntary Programs.

Voluntary initiative of the global chemical industry. Responsible Care is the commitment by chemical companies to demonstrate continuous improvement of their health, safety & environmental performance in a manner which is responsive to the concerns of the public

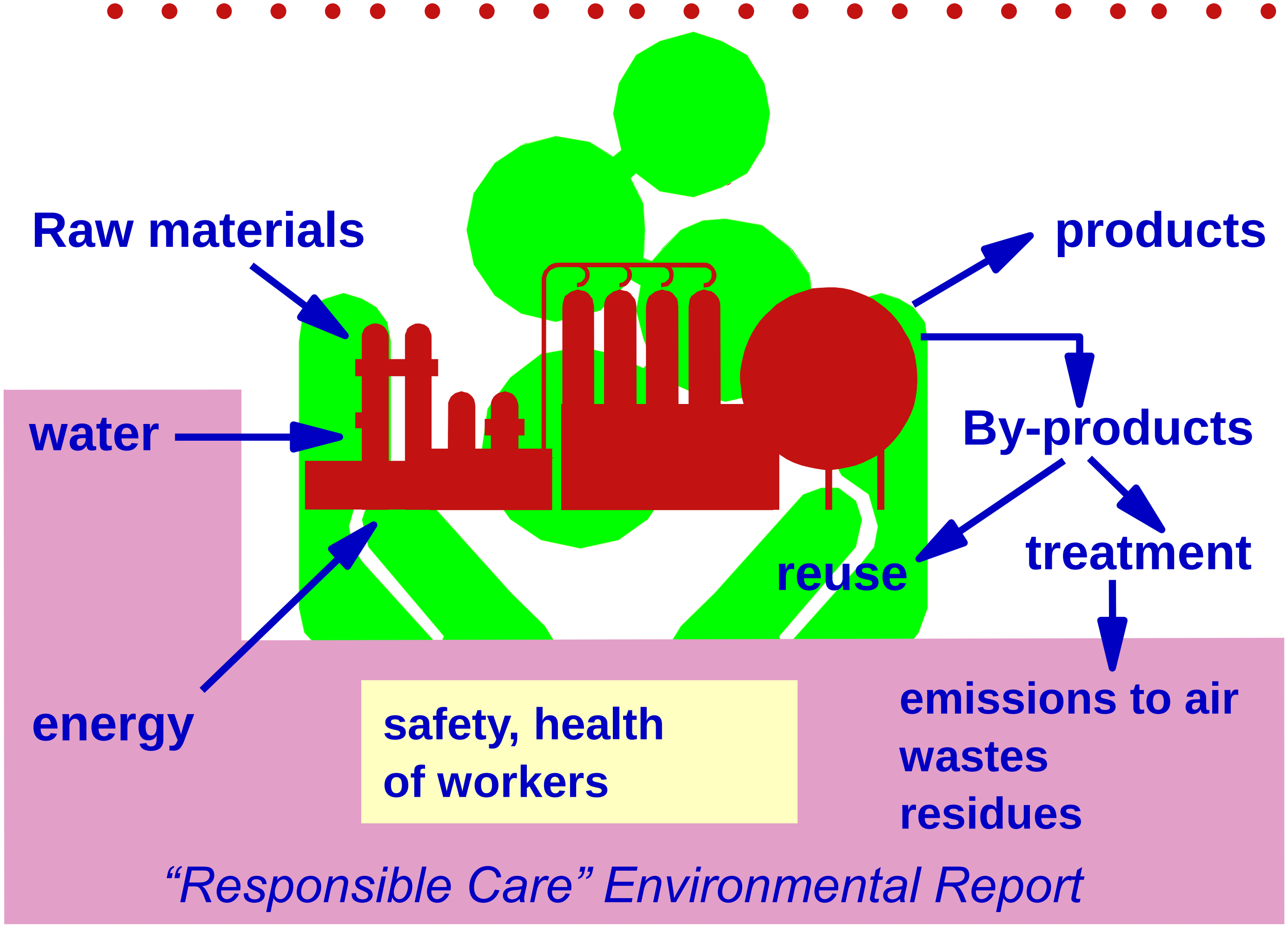
Responsible Care®

- Started in USA in 1988 following the relevant industrial accident of Bhopal, India – “No accidents, injuries or harm to the environment”

Long-range Research Initiative

- Aim to provide the essential research to improve on scientific basis the practices and the policies of measurements for new chemicals, processes, applications and the risk assessment

“Responsible Care®” Program.



“Responsible Care®” Program 1988-2018.

C A E R

Pollution prevention

Process Safety

Distribution

Workers Health and Safety

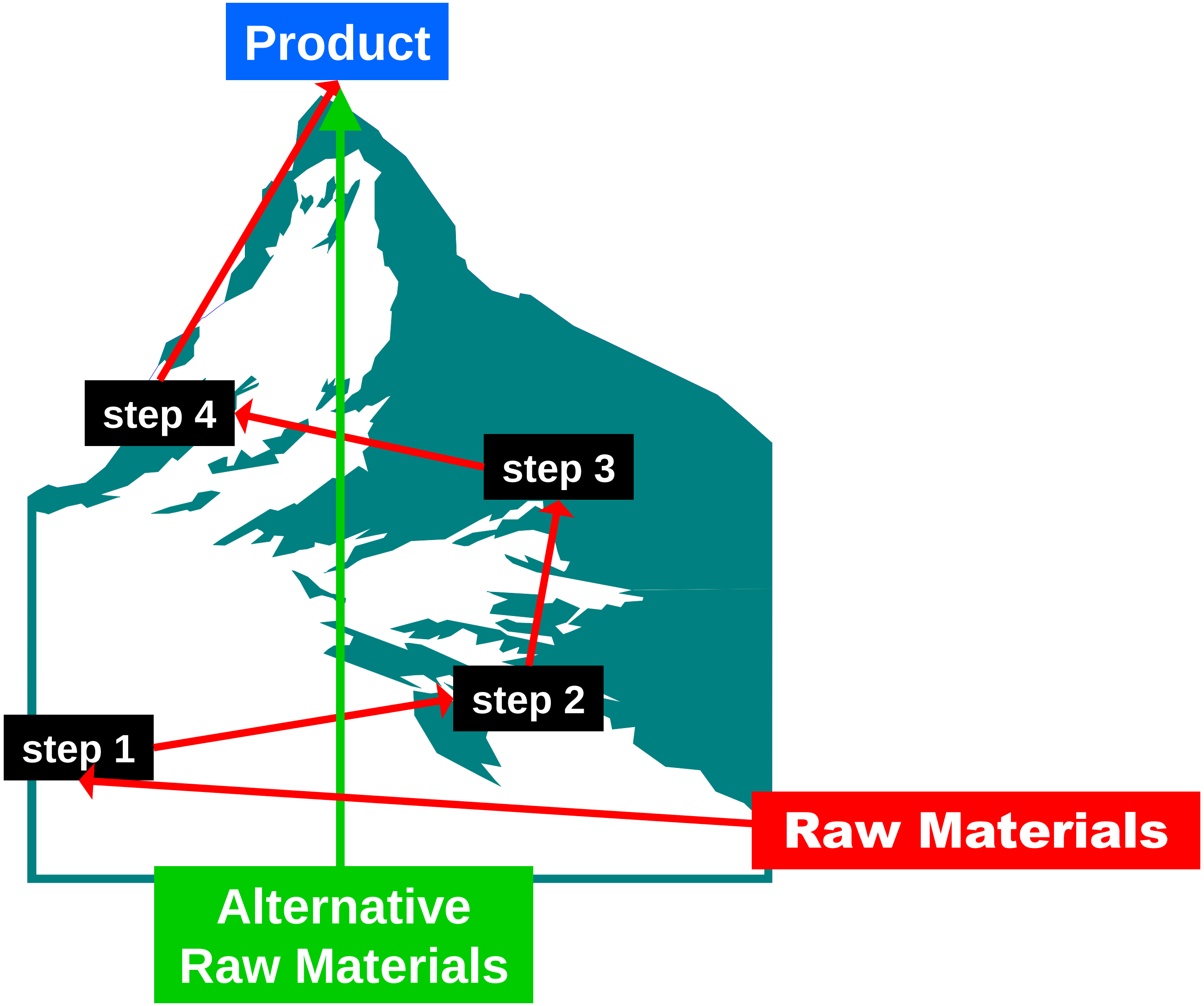
Product Stewardship

Environmental Program 3M & 3Ps.

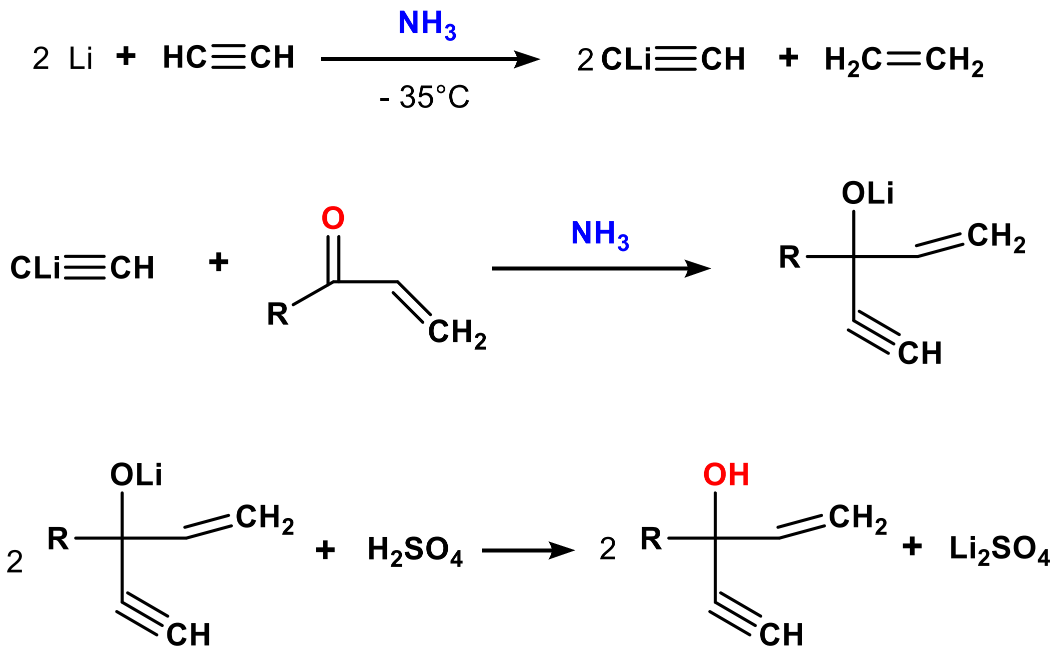
- 3M 1975 - Pollution prevention pay
- Reduce the need for end of pipe treatments
  - Product development
  - Engineered design
  - Process optimization
- 1.5 billion m^3 of wastes p.a. eliminated
- Emissions to air reduced by 100,000 ton. p.a.

- Examples: process in water, energy recovery from waste solvents, substitution of dangerous cleaning agents.

Process Improvement:
(route and optimization selection).



Synthesis of Etinol (Hoffmann La Roche).



Input: 3 kg of raw materials
output: 1 kg of product

Etinol Key Issues.

- Expensive due to loss of 67% of raw material
  - Ethene production
  - Significant resin formation in stage 2
  - Li atom lost with resin
- Improvements
  - R&D - vinyl ketone is unstable in ammonia – the yield improve by 15%, by addition in organic solvent. Li excess reduced, resins eliminated.

- Li could be recovered (not lost with resin), water used in stage 3 to recover LiOH - (off site conversion to Li)
- Engineering improvements to recycle acetylene & ammonia
- Use ethene as a fuel
- Acetylene use reduced by 50%, ammonia by 25%.

Greener Antibacterial Products.

- **Environmentally benign antibacterial agents**
  - Alternatives to traditional chlorine or tin containing antibacterial agents
- **Applications**
  - Bandages, sutures, hospital gowns, acne medication, toothpastes, air filters, antiviral agents

Magnesium hydroperoxyacetate

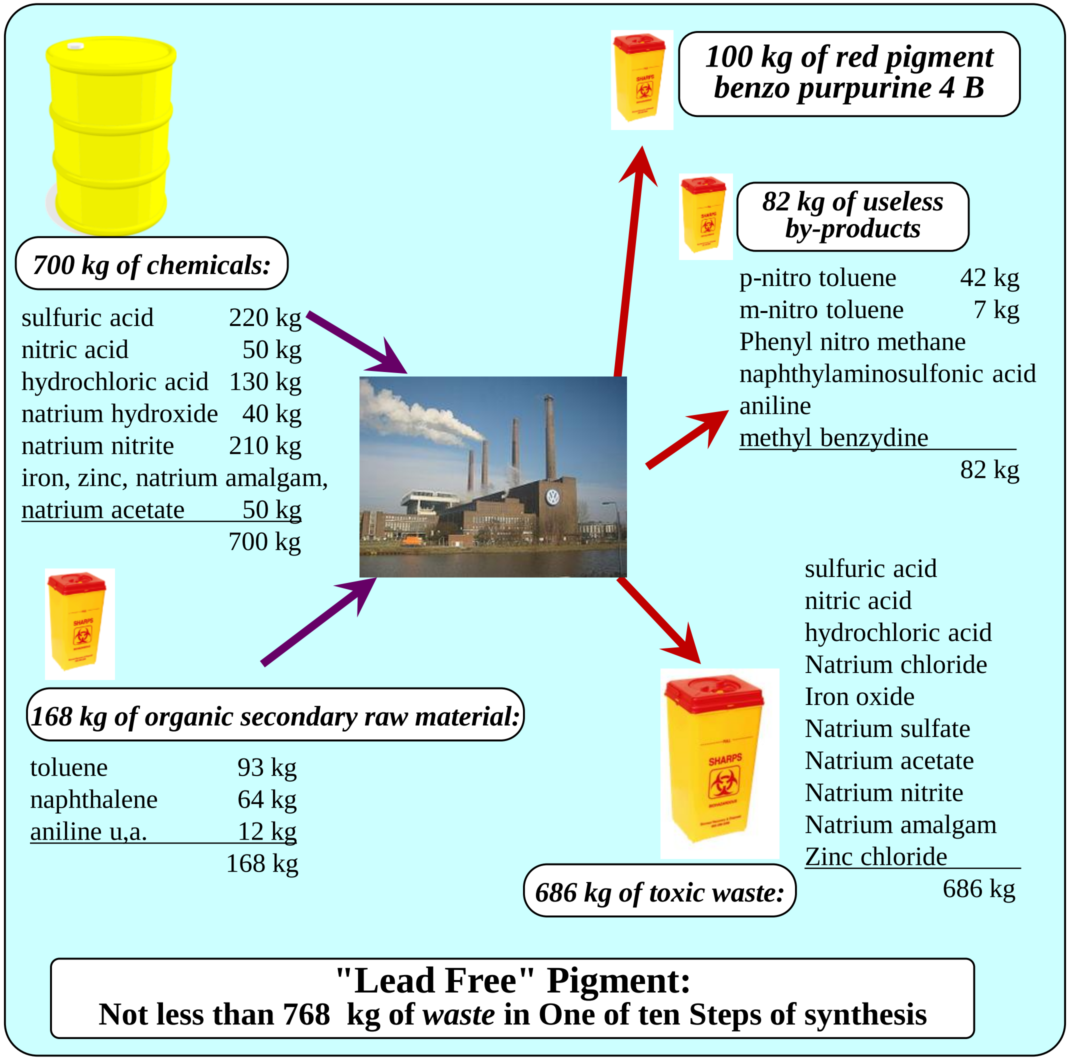
HO-O-Mg-OAc

Magnesium dihydroperoxide

HO-O-Mg-O-OH

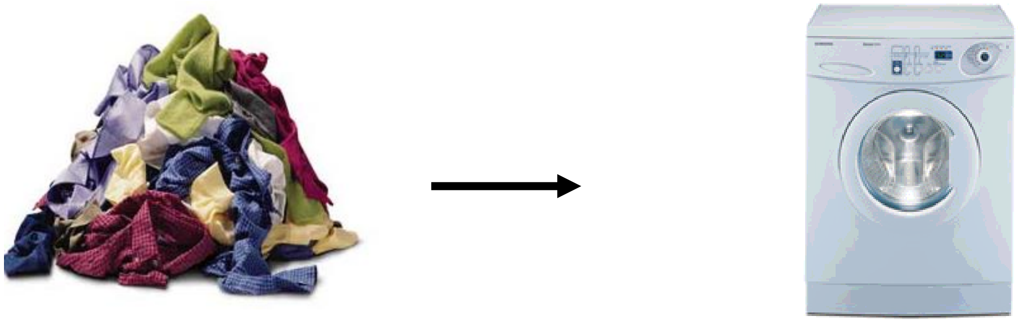
USDA

Material Flow at the Production of 100 kgs of Red Pigment "Benzo Purpurine 4 B“.



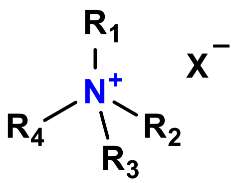
However, not all alternatives proposed are really well designed!

Dry Cleaning.

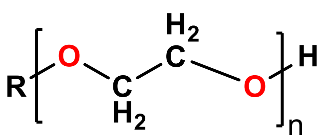


Use of surfactants to decrease the surface tension and favor the detergence in water and oxidants to eliminate colored compound

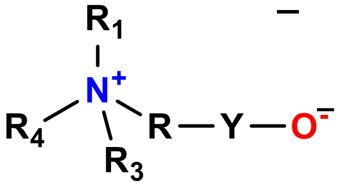
- Anionic $R-Y-O^{-}\quad X^{+}$
- Cationic



- Non ionic



- Amphiphilic

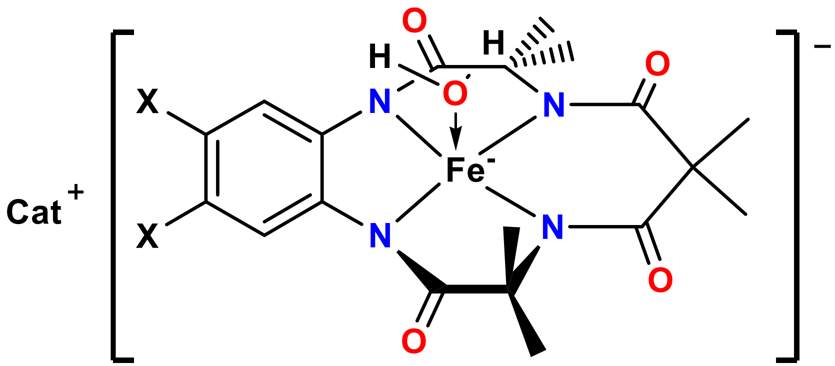


- Peroxides (H_2O_2)
- Peroxy salts ($NaBO_3$)
- Oxidant systems

Greener TAMIL Additive for Clothes Cleaning

Catalysts for activation of H_2O_2 (TAML)

- **Inhibit discoloration**
- **Potential additives for cleaners with a lower use of water**



Collins, Carnegie Mellon University

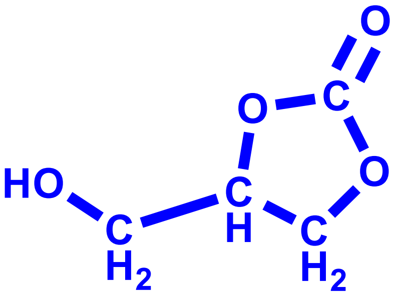
Cat^+ = Li^+, $[Me_4N]^+$, $[Et_4N]^+$, $[PPh_4]^+$
X = Cl, H, OCH_3

- **Total Impact Program (TIP®)**
  - Chemistry + application knowledge + product stewardship
  - Laundry formulation incorporates neutral pH detergent, enzymes, surfactants, oxygen bleach, and biodegradable softeners
- **Benefits**
  - Avoids high pH detergents, chlorine bleach, acid neutralization, poorly degradable surfactants

Alternative Clothes Cleaning.

- **CO_2 for Dry Cleaning**
  - current process uses perchloroethylene, a suspected carcinogen and groundwater contaminant
  - new process uses liquid carbon dioxide, a nonflammable, nontoxic, and renewable substance

- **Stain remover with glicerol carbonate**
  - Instead of hydrocarbons or haloorganics, the totally biodegradable glycerol carbonate is used as efficient water soluble cleaning agent. The compound is odorless, safe to use and fully miscible with water and other polar solvent..



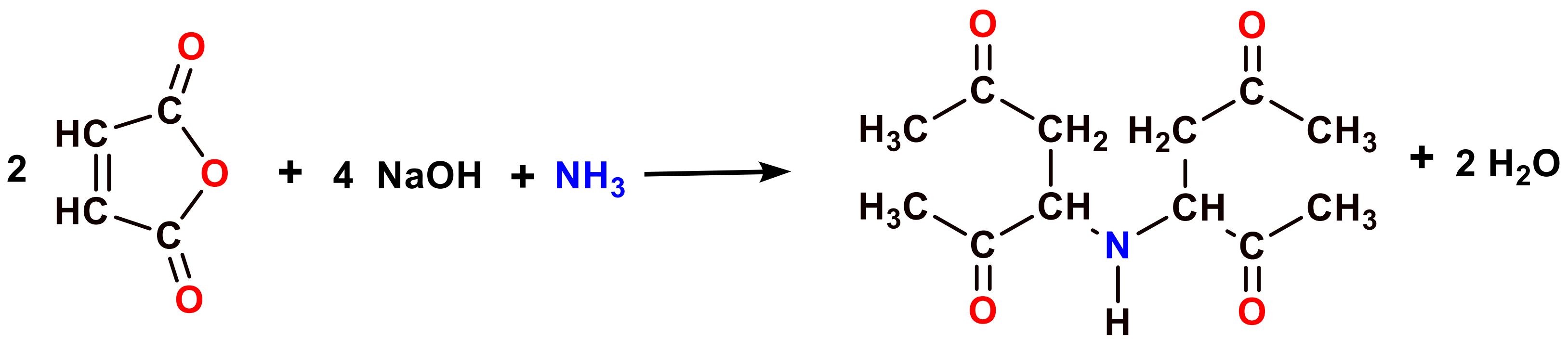
Clothes Cleaning – Chelating Agent.

Sodium iminodisuccinate -

- Biodegradable, environmentally friendly chelating agent (substitute of EDTA, typical toxic chelating agent)
- Synthesized in a waste-free process
- Eliminates use of hydrogen cyanide

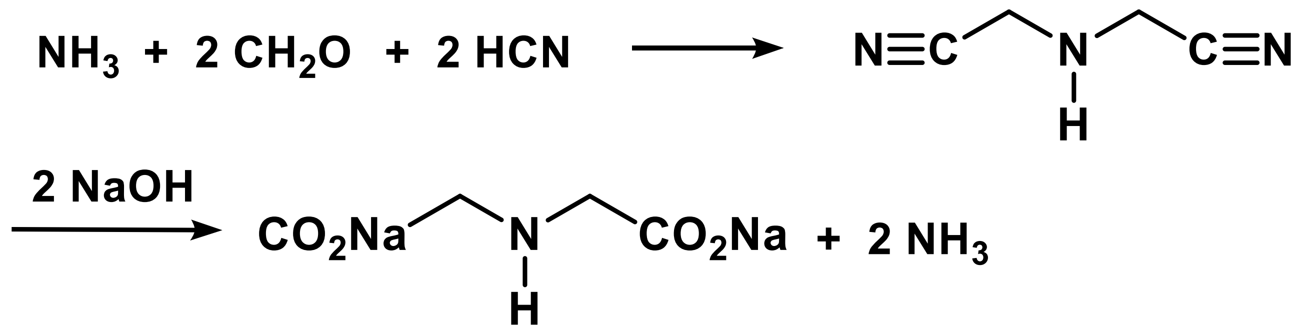
Bayer Corporation and Bayer AG

2001 Alternative Synthetic Pathways Award Winner



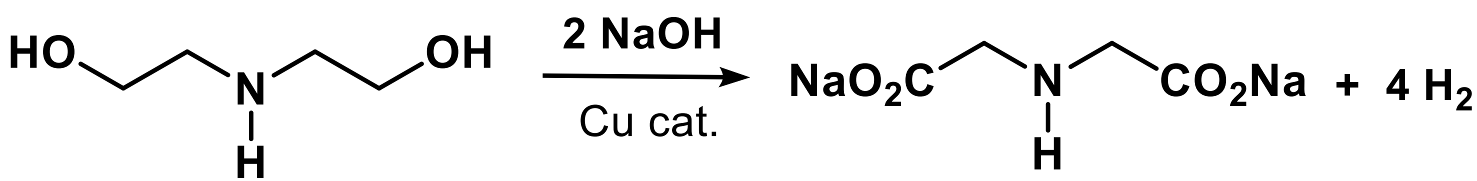
Alternative Synthesis of Disodium Iminodiacetate.

Traditional Synthesis of Disodium Iminodiacetate (Strecker Process)



Disodium Iminodiacetate

Alternative Synthesis of Disodium Iminodiacetate (catalytic dehydrogenation)



Diethanolamine

Disodium Iminodiacetate

Ref. Anastas & Warner, 1998

Industrial Cleaning – Detergents.

- **Printed circuit boards assembled using Surface Mount Technology (SMT)**
  - Lead/tin solder paste stenciled onto substrate
  - Stencils cleaned before reuse
    - CFC solvents
    - Aqueous solvents (high temperature, high pH)

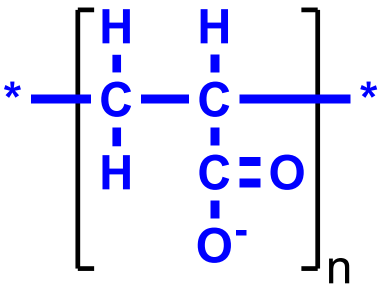
- **440-R SMT Detergent**
  - Aqueous-based, contains no VOCs
  - Ultrasonic technology

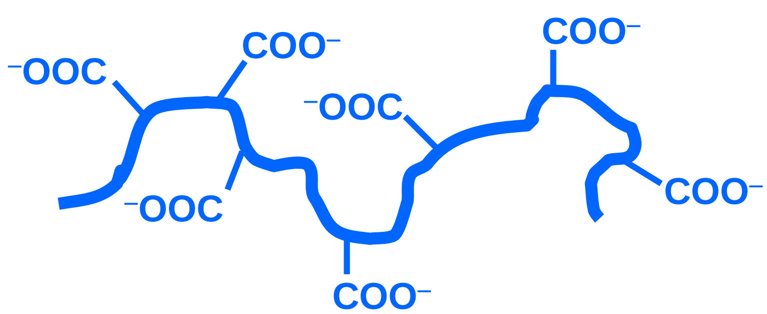
Smart Sonic Corporation

Biodegradable Scaling Agents.

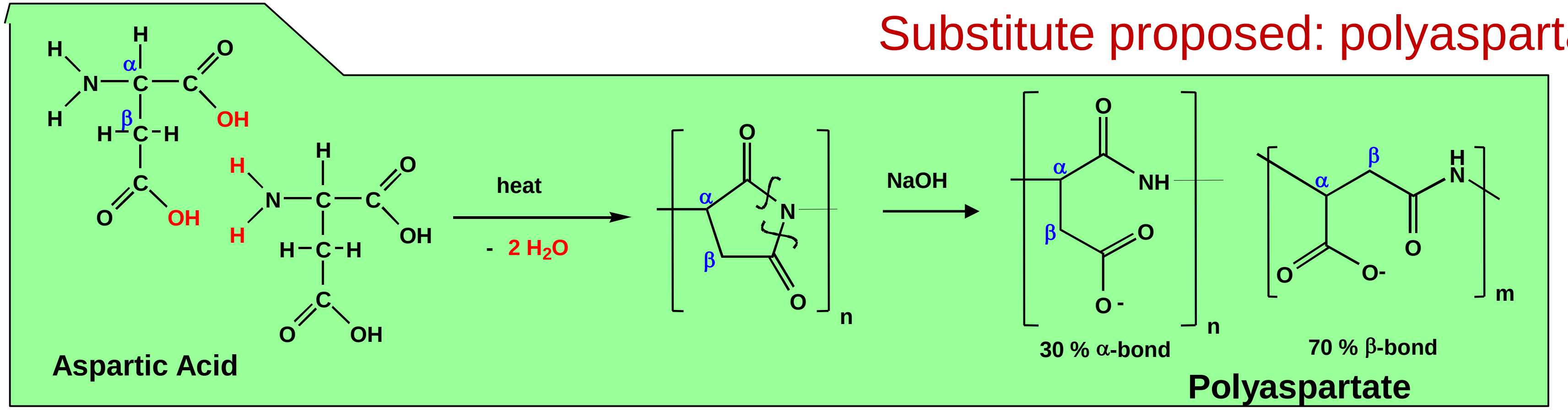
Polyacrylate (PAC) is a common antiscale and fluidizing agent.

- PAC is a polyanion, i.e. a polyelectrolite.



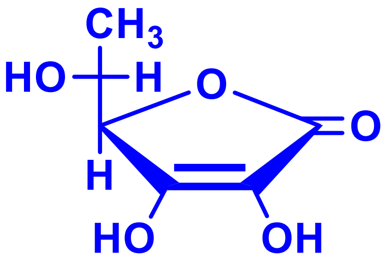


Substitute proposed: polyaspartate



Disinfection with Chlorine

- Important to prevent diseases
- Toxic for aquatic life
- Sulfur based compounds are used to neutralize chlorine



Vitamin C (Ascorbic Acid)

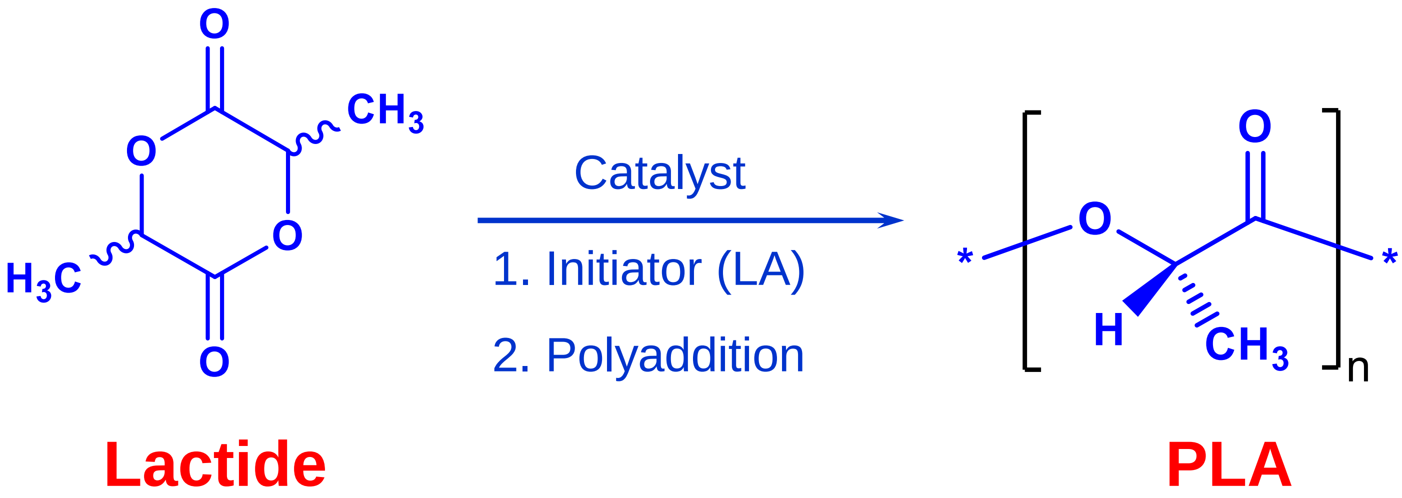
- More safe, efficient alternative for the neutralization
- Strengthen the immune system of aquatic organisms

Ultimer™ Polymer Technology

- manufacture of high molecular weight, water soluble polymers in aqueous salt solution
- eliminates use of oils and surfactants in manufacture and use
- uses ammonium sulfate, a waste by-product from the manufacture of caprolactam
- eliminates need for expensive mixing equipment required for water-in-oil emulsions

Nalco Chemical Company

Biodegradable Polymers with Properties Linked to Stereochemistry.



- Control of molecular weight on lactic acid concentration.
- Control of optical composition on the feeded lactide composition.

Interested Areas.

Transportation	Air, Water, Waste	Renewables	Energy Storage	Smart Power	Energy Efficiency	Green Building
Fleet management Mass trans. routing/ data solutions Logistics mgmt Carpooling Hybrid motors PHEV Fuel cell vehicles Biodiesel Intermodal tracking NOX/SOX reductions Cold-ironing systems Diesel particulate matter filters Combustion Fuel blends Flex fuel apps Drive train conversion Exploiting GPS and location information Monitoring and control of driver behavior	Water monitoring Cooling solutions Wastewater recycling Adv. water metering Storm-water and flood control, rain harvesting Smart irrigation On-site water disinfection Membranes for water treatment Advanced filtration Produced water (from oil exploration) Water pumping Reverse osmosis Advanced filtration Emissions controls Scrubber technology Carbon and GHG monitoring and control Carbon sequestration Carbon Capture/ storage Technology enablers for carbon markets VOC Reduction Waste cleanup DI water supply Agricultural waste Recycling Microbial water treatment Bio based packaging Methane capture/storage Soil technology Natural pesticides	C-Si Solar CIGS Thin film solar CPV PV Coatings F… F… E… Biobased fuels Tidal energy Wave energy Landfill gas Agricultural waste energy Hydropower Turbine blade design Advanced fluid flow designs Wind power	Batteries Battery chemistry Ni-metal hydride Hydrogen storage … for batteries Flywheels Grid hardware/ infrastructure Power storage for renewables	Advanced metering Network arch. for power mgmt Cloud computing, applied to grid … Flywheels Grid scale hardware and infrastructure Monitoring renewables Transmission efficiency Elec. controls for power distribution Novel metals and alloys for power Superconducting power trans. Real-time power monitoring	Pumps for water/ material Industrial process improvements Natural gas monitoring … HVAC solutions Heat pumps Waste heat mgmt Efficient heat transfer Utility scale natural gas controls Display systems for energy management Materials use in microelectronics mfg Deposition and sputtering processes Alternatives to heat intensive processes Cooling solutions Glass materials mfg	Insulation materials Cement/alternative Cement production BIPV Indoor air filtration systems Modular housing Disaster relief housing Architectural Designs for thermal mgmt Office environment Low VOC carpeting and flooring Water saving toilets, showers, plumbing Residential heat pumps Recycled materials Design improvements to commercial environment

Renewable Generation & Energy Storage → Intelligent Control → Reduced Consumption