Il superamento dei combustibili fossili

tra attualità e prospettive

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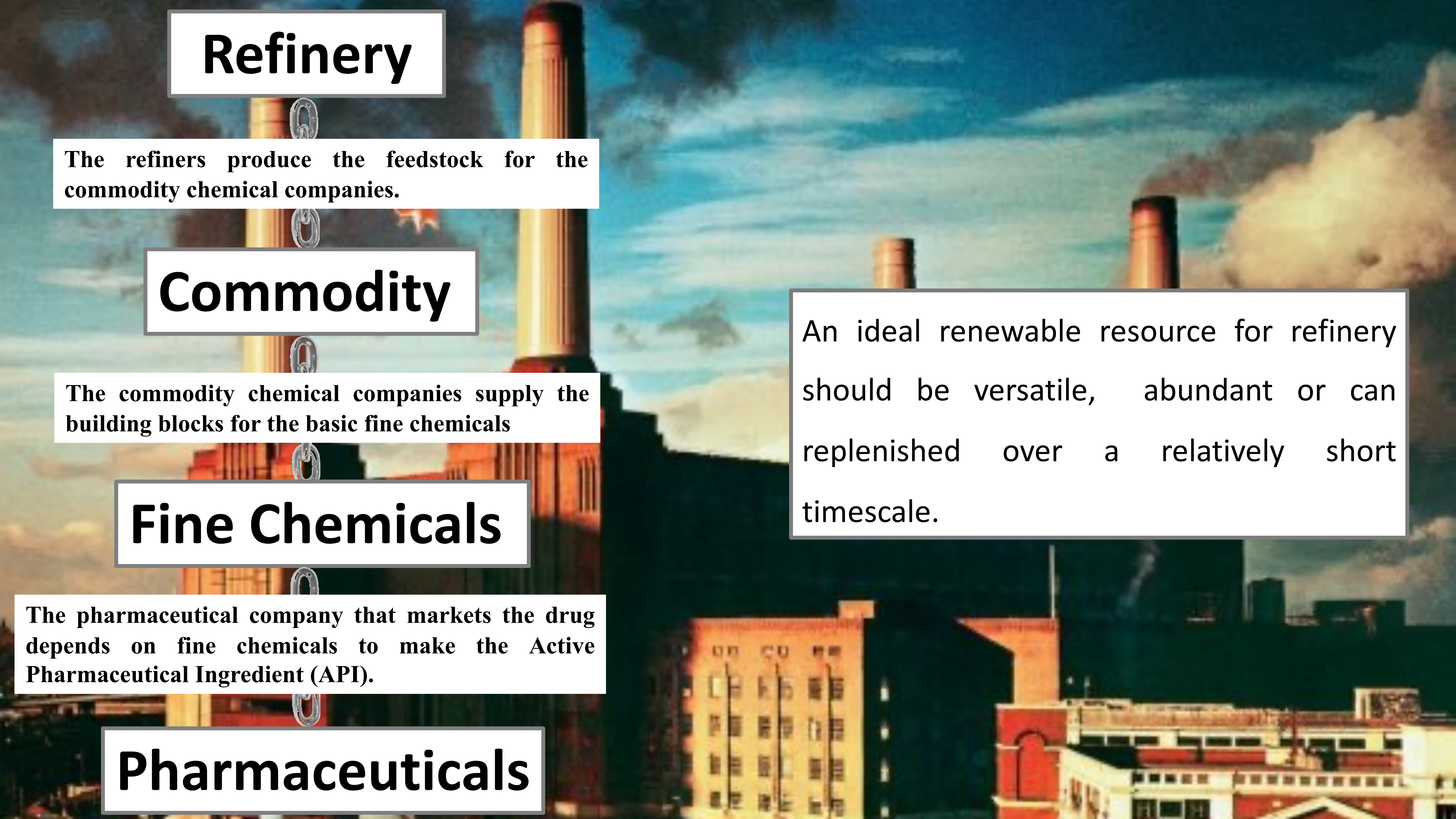
Refinery

A refinery is a production facility composed of a group of chemical engineering unit processes and unit operations refining certain materials or converting raw material into products of value. Most of a refiner's margin comes from higher-value "light products" (i.e. gasoline) that it makes. However, refineries also produce some lower-value products (such as fuel oil, kerosene) in the process. Some refineries also generate incremental value from producing some small-volume specialty products. The refiners produce the feedstock for the commodity chemical companies.



Refinery

The refiners produce the feedstock for the commodity chemical companies.

Commodity

The commodity chemical companies supply the building blocks for the basic fine chemicals

Fine Chemicals

The pharmaceutical company that markets the drug depends on fine chemicals to make the Active Pharmaceutical Ingredient (API).

Pharmaceuticals

An ideal renewable resource for refinery should be versatile, abundant or can replenished over a relatively short timescale.

The Whale Refinery

Fuels

Cosmetics

Materials

Food

Lubricants

Detergents

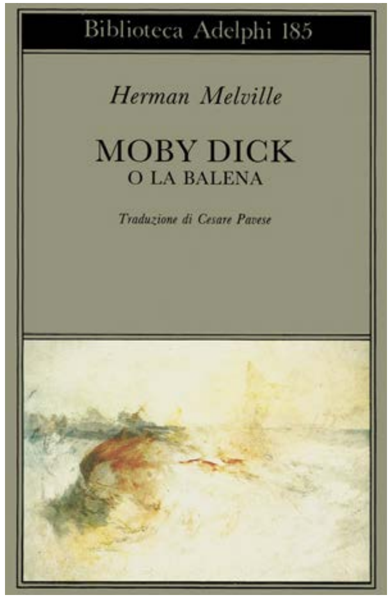
Early whaling records and old legends converge at 10,000 B.C. with the oldest graphical depiction of whaling in Scandinavian rock carving. Many tribes, when found by European explorers in the early 17th century, showed a sophisticated mastery of whaling. The whale, in its many forms and species, provided food, fuel, light, cordage, tools, and building materials.

Heart of the Sea
(R. howard)

Crude Oil as a sustainable resource

(in the XIXth century)

700 Basque Whaling monopoly begins
1100 Basque whalers reach Iceland
1200 Basque whalers reach Greenland
1500 Basque whalers send hundreds of boats to Newfoundland and Labrador
1630 Dutch send 400 ships & 20,000 men to Spitzbergen
1690 Commercial whaling begins in U.S. by non-Native Americans
1760 Americans deplete North Atlantic stocks
1773 Boston Tea Party aboard Nantucket whaler
1775 Whale oil prices soar 900% due to Revolutionary War shortages
1790 First Nantucket whaler returns from Pacific Ocean-a new era begins
1800 First battery producing electricity
1843 Largest sperm oil production: 166,685 barrels
1851 Largest whale oil production: 328,483 barrels
1851 industry worth $10 MM



The American whaling Industry rose from humble beginnings off Long island to become an international giant. In its peak year (**1846**), **735 ships and 70,000 people** served the industry.

Nonrenewable Resources, **1995**, *4*, 273–288.

Una Scelta sostenibile (per il XIX secolo)

1858 Electricity first used in lighthouses

1859 Subsurface oil discovered at Titusville, Pennsylvania

1861 U.S. Civil War begins

1865-1870 Standardized kerosene introduced by J.D. Rockefeller

1871 Arctic ice crushes 33 whalers

1888 Petroleum all but replaces whale oil as primary fuel and lubricant

1906 Spring steel replaces whalebone

1916 Last voyage by a ship of the largest American whaling fleet

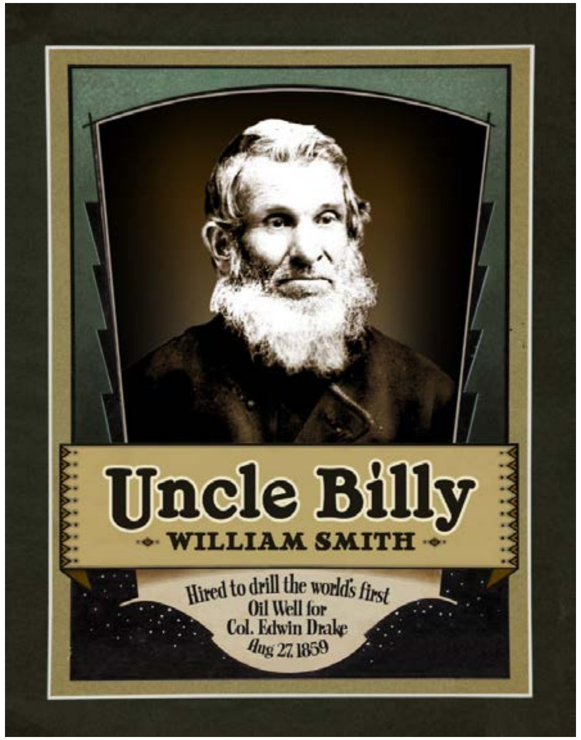
As whale stocks and reserves decreased, whalers were forced to go farther and farther from their New England home ports. Many ships returned empty, if at all. in 1871, most of the Arctic whaling fleet was crushed by early winter ice and lost. This calamity, in conjunction with the long-term diminishing whale stocks, the diversion of investment capital to more profitable ventures, and the discovery, development, and refinement of abundant petroleum crude oil, struck the death blow to the American whaling industry.

By **1890**, only **200 whaling vessels** were at work, and by 1971, no American commercial whaling ship sailed the world's oceans.

In the early 1850s a New York lawyer named George Bissell came across a sample of petroleum from Titusville, Pennsylvania. Bissell noted its resemblance to coal oil, and he and his partner, Jonathan Eveleth, sent an agent to investigate its source. The agent gave a favorable report, and the two lawyers proceeded to organize the Pennsylvania Rock Oil Company. Investors were slow to buy stock in the new company until a favorable report written by Benjamin Silliman, Jr., (Yale University) concluded that the company possessed "*a raw material from which, by simple and not expensive process, [it] may manufacture very valuable products*."

Edwin Drake is famous for drilling the first oil well in 1859. Drake was in his late 30s when he started his research in oil, having spent much of his adult life working for railroads. The invested $200— his total life savings — in the Pennsylvania Rock Oil Company (then Seneca Oil Company). In May 1858 Drake moved to Titusville, did some more scouting around, and decided to drill a well.

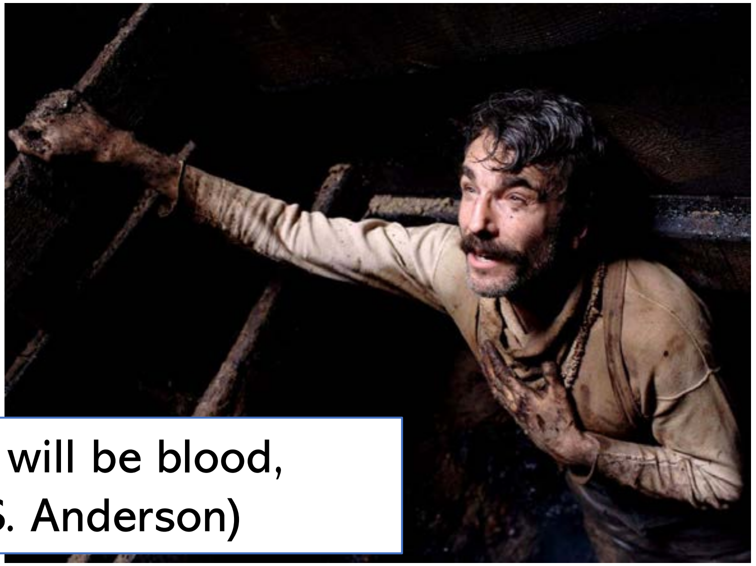
He spent several months in 1858-59 trying to find a driller. Potential recruits thought Drake "crazy" to drill for oil.



Uncle Billy” Smith agreed to work for $2.50 a day, make his own tools, and throw in the services of his 15-year-old son. Smith arrived in Titusville in May, 1859, and found that Drake’s men had been digging a hole 150 feet from Oil Creek. Smith discovered that the hole kept filling with water. He tried pumping out the water, with little success. Finally, Drake and Smith obtained cast iron pipe which they drove about 32 feet into the bedrock — past the water — using a white-oak battering ram. In mid-August Smith began drilling his well with steam power, through the pipe, averaging about three feet a day. On Saturday, August 27, with the drill at a depth of 69 feet, work stopped. The next day, “Uncle Billy” inspected the well and saw fluid at the top of the pipe and he realized it was oil. Ironically, Drake had drilled in the only spot in the region where oil could be found at such a shallow depth as 69 feet.

In 1860 wells in northwestern Pennsylvania produced several hundred thousand barrels and by 1862 production reached **three million barrels**. On contrast, Colonel Drake failed to act quickly to control production and he had not bought much land in the area. He died poor and a pensioner, never having benefitted from “discovering” oil in Titusville, Pennsylvania, on August 27, 1859

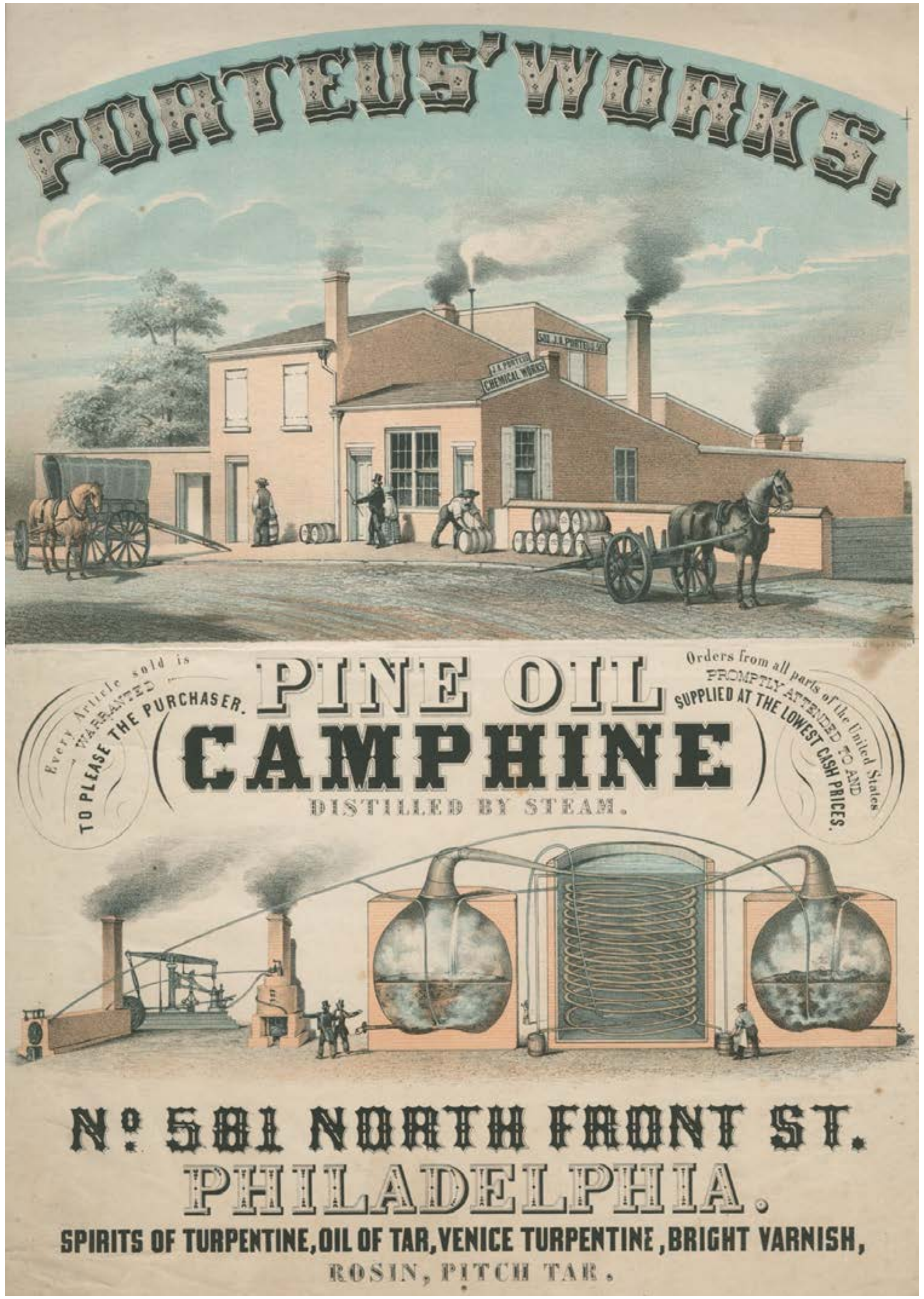
Judah Ginsberg, American Chemical Society, 2019



There will be blood,
(P. S. Anderson)

Even before petroleum became a major source of lamp fuel in the 1860s, by the 1850s kerosene from coal was widely available. Camphine and burning fluid, both plant based energy sources, were also common and fairly inexpensive. Likewise, fats from domestic animals (e.g., lard and tallow), which can be used as lamp fuel, to make candles, as lubricant, and to make soap, were abundant. In the twentieth century, the age of abundant fossil fuels and electric lighting, the slaughter of whales reached a new zenith. […] The factory ship and its fleet could not exist without fossil fuels, which powered the whole operation and allowed for long-duration storage of whale products by running freezers (for meat) and processing whale oil so it would not become rancid.

Socius, 2017. DOI :10.1177/2378023117739217



Radical innovations in the methods of whaling began in the 1860s on the Finnmark coast in northern Norway, led by S. Foyn, which ultimately transformed the entire industry, marking the emergence of modern whaling. One major change was the switch away from sail to coal-fired steamships (and later to diesel-powered ships) […] modern whaling techniques were developed shortly after petroleum, a potential substitute for whale oil. There is however a tension between supply and demand here, where fossil fuels offered the potential to suppress whaling by providing a substitute for whale oil while at the same time allowing for modern whaling techniques to increase the capacity to kill whales .

Grand Ball given by the Whales in honor of the discovery of the Oil Wells in PA

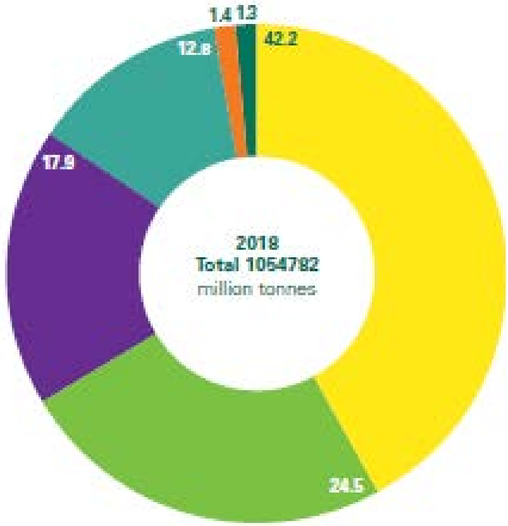
Socius, 2017. DOI :10.1177/2378023117739217

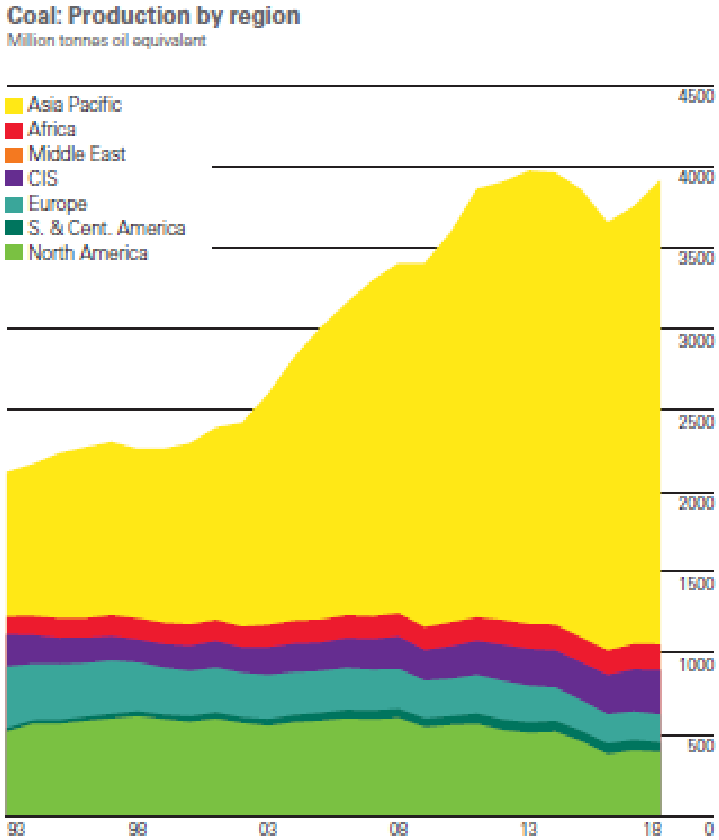
Fossil fuels: Coal

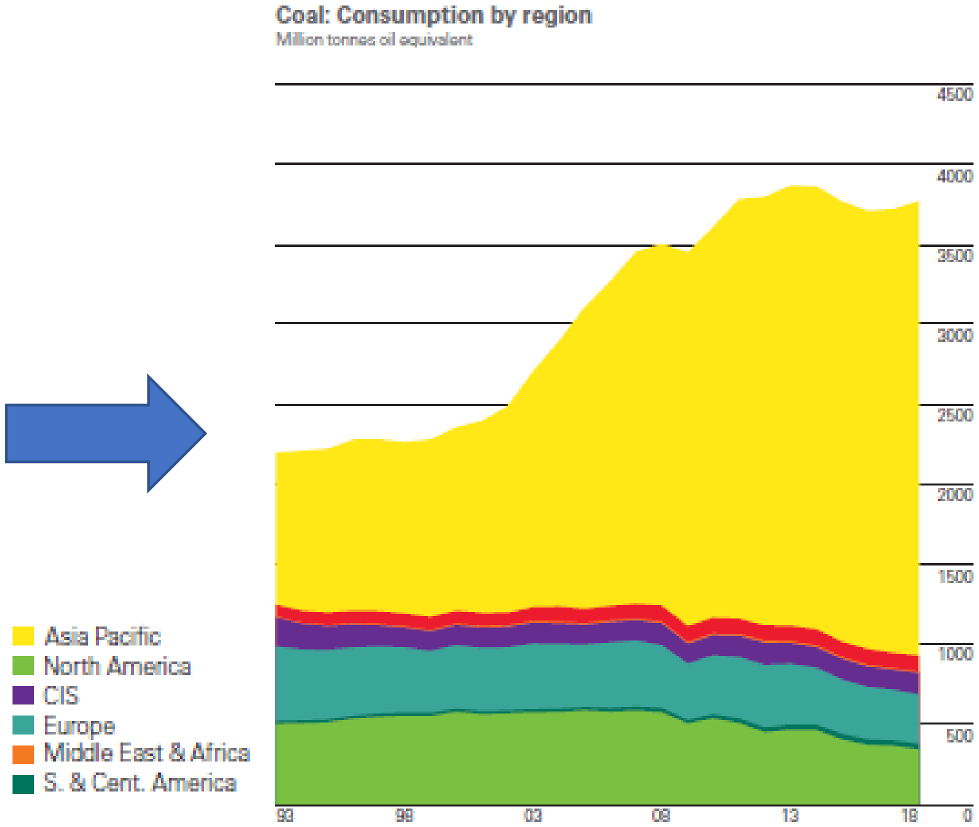
Anthracite, or **hard coal**, has the highest carbon content, the fewest impurities, and the highest energy density of all types of coal.

Lignite, or **brown coal**

Proved Reserves



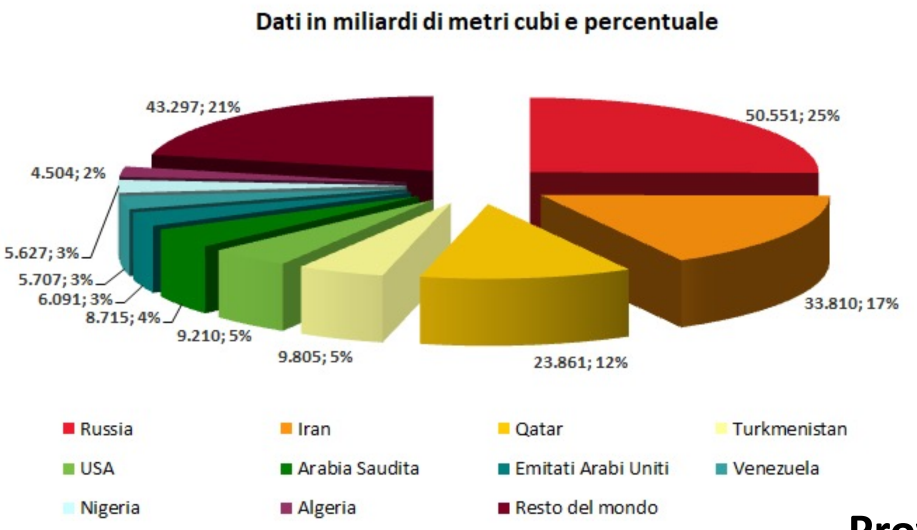




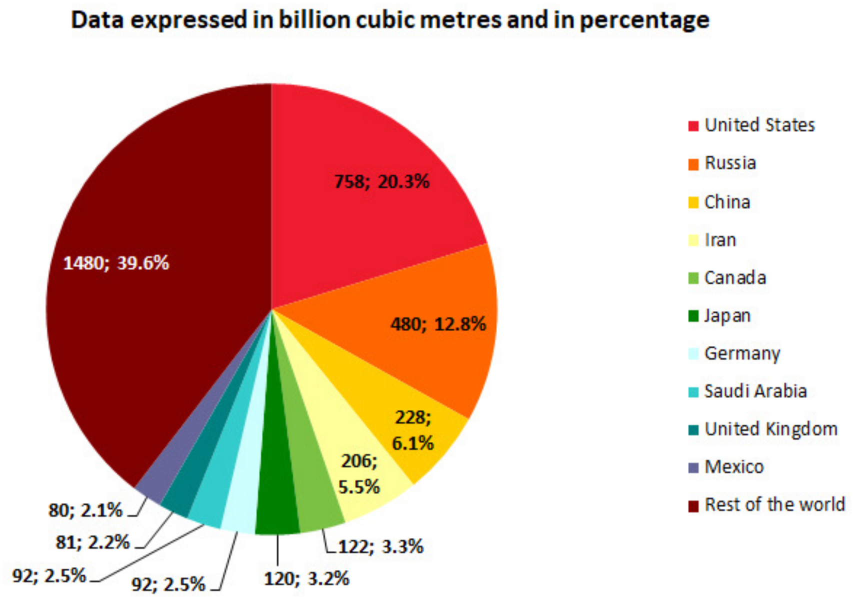
BP Statistical Review of World Energy 2019

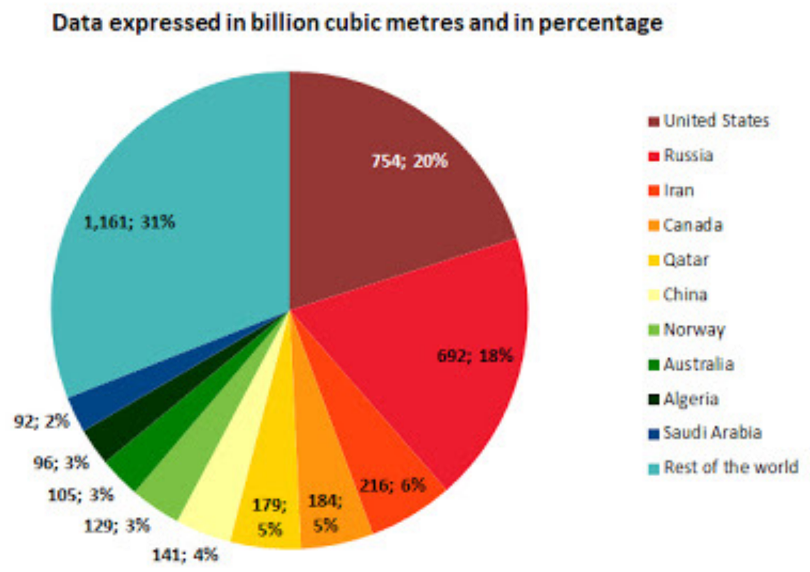
Fossil fuels: Natural Gas

The second large fossil fuels resource (low cost) available today is natural gas (NG). Its direct use as compressed or liquefied gas has not been accepted as a transportation fuel in a large scale. Over long distance NG is exclusively transported as liquefied natural gas (LNG) in cryo-tanks at –162°C. This is expensive and requires costly installations.



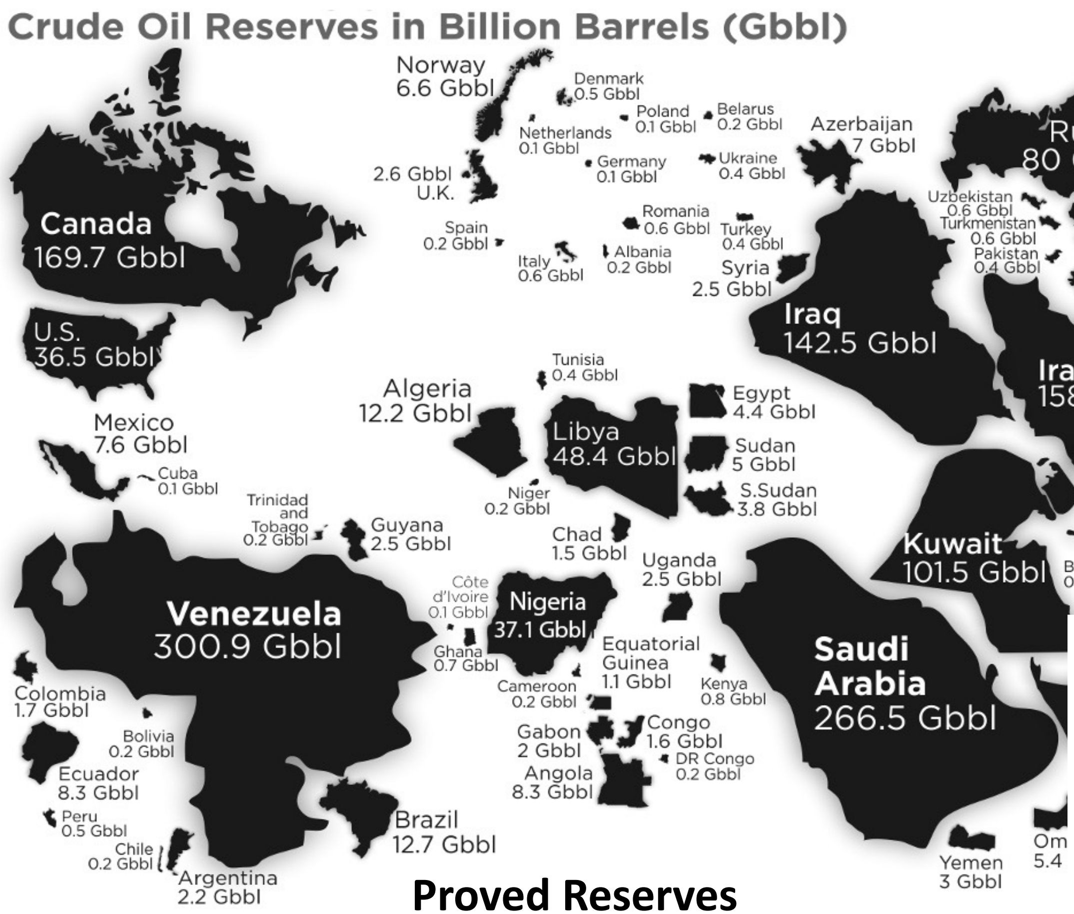
Proved Reserves



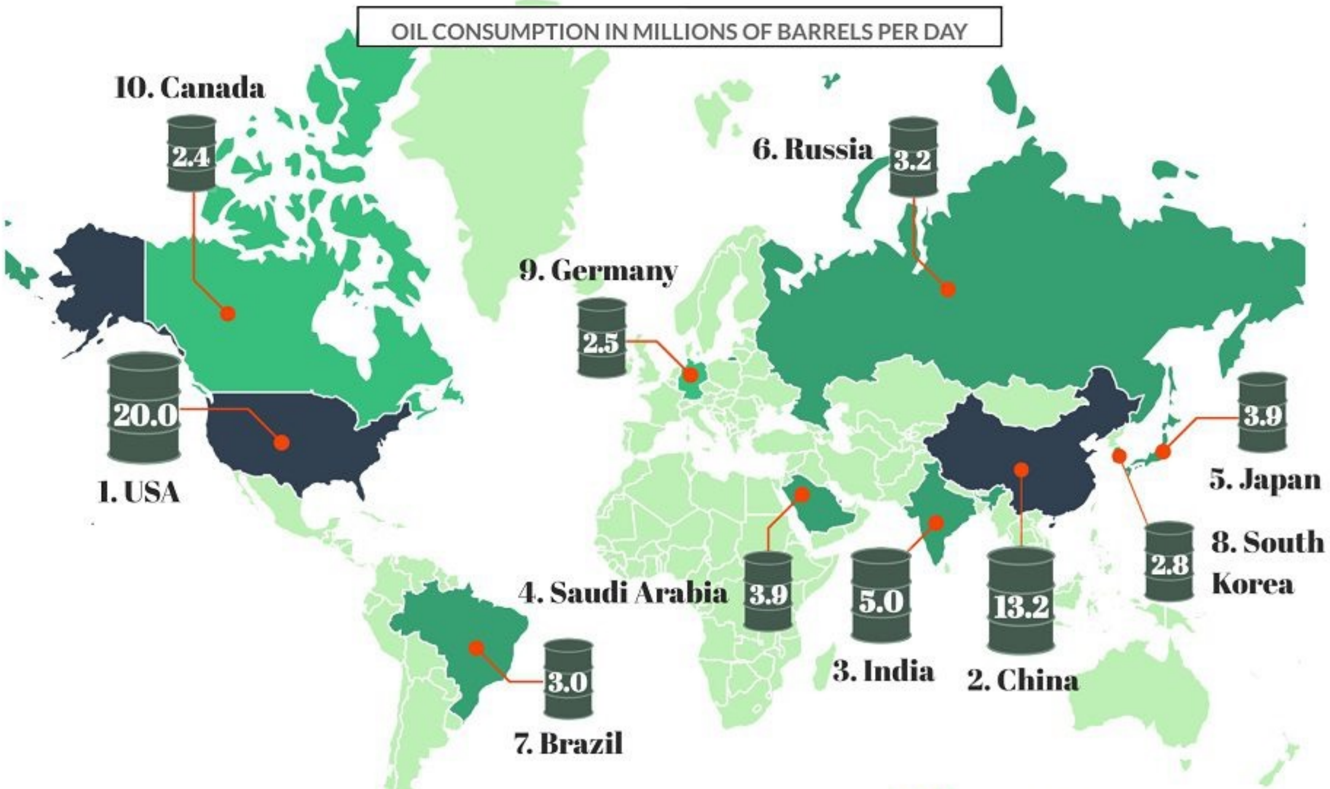


http://www.eniscuola.net/

Fossil fuels: Oil



Proved Reserves



Conventional oil is a term used to describe oil that can be produced (extracted from the ground) using traditional drilling methods. It is liquid at atmospheric temperature and pressure conditions, and therefore flows without additional stimulation. In some cases, water or gas is pumped to facilitate extraction. Thus, water, solid impurities or mineral salts should be eliminated by decantation or other physical methods before the refinery step.

Oil shale is an organic-rich fine-grained sedimentary rock containing significant amounts of kerogen (a solid mixture of organic chemical compounds) from which technology can extract liquid hydrocarbons (shale oil) and combustible oil shale gas. (U.S. 4800 to 5000 Mbarrels)

Oil sands consist of extra heavy crude oil or crude bitumen trapped in unconsolidated sandstone.

Oil Refinery

Oil

Fuels

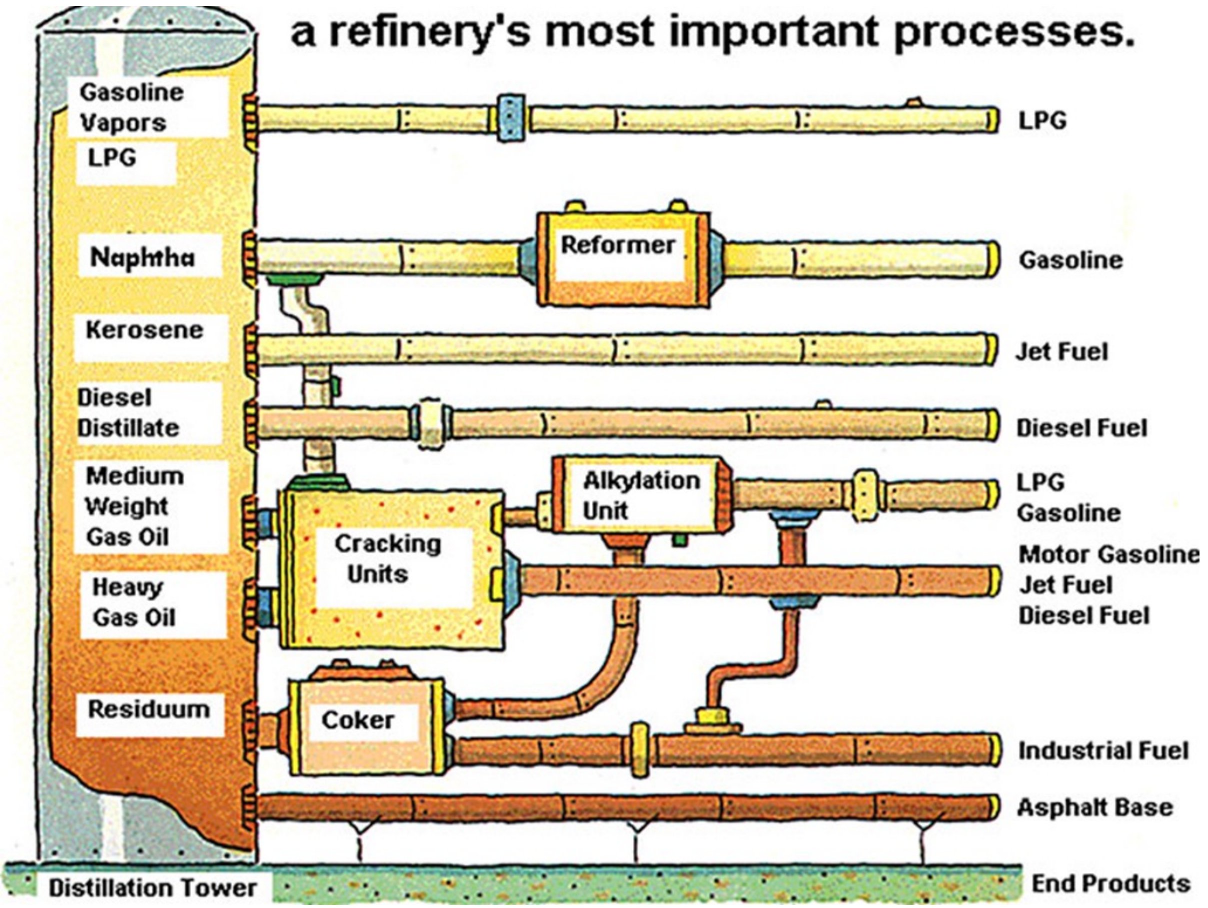
Solvents, Bulk chemicals

Polymers

fibers

Lubrificants

Detergents



Processes related with refinery industry

a) Minimization of Sulfur and Nitrogen contents

b) Feedstocks transports

c) Waste disposal

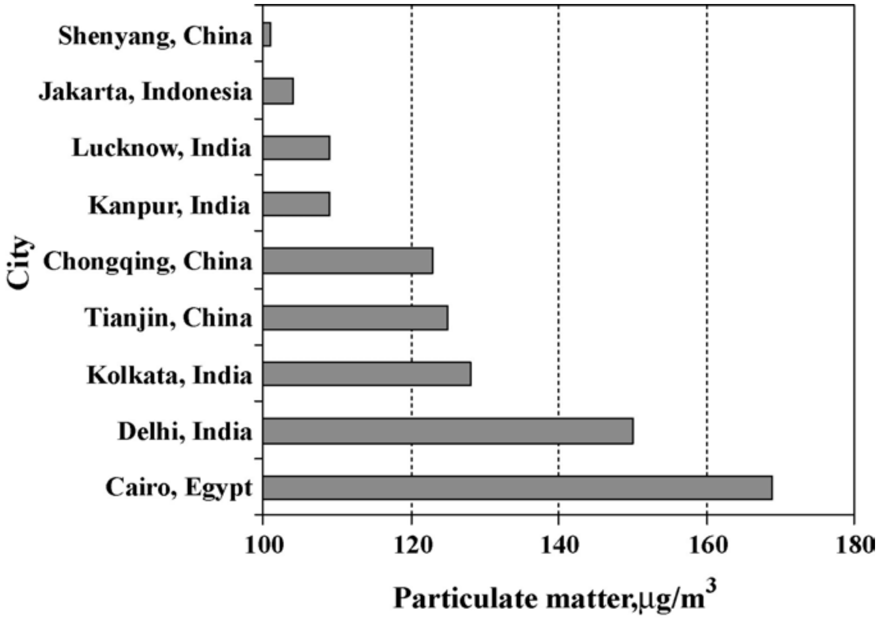
The typical composition of **gasoline** hydrocarbons (% volume) is as follows (4-12 carbon atoms).

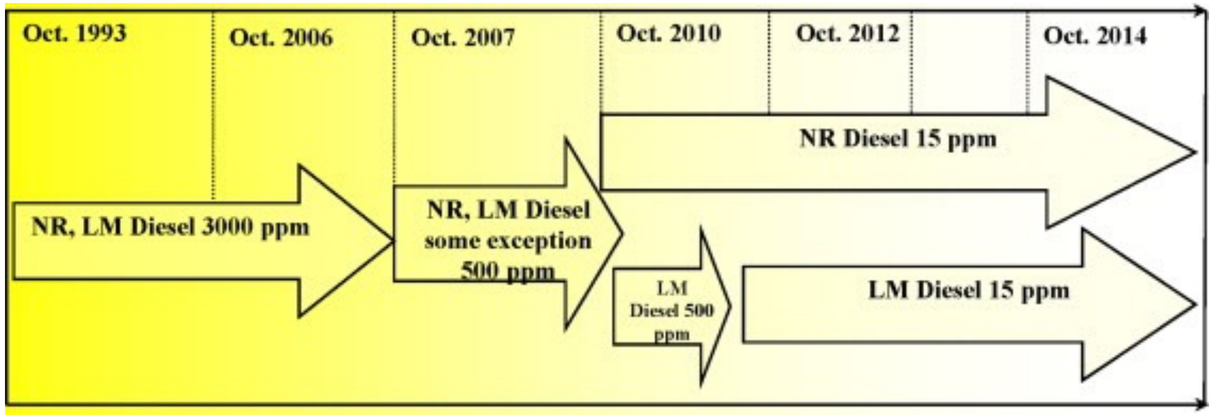
4-8% alkanes; 2-5% alkenes; 25-40% isoalkanes; 3-7% cycloalkanes; 1-4% cycloalkenes; and 20-50% total aromatics (0.5-2.5% benzene)

Diesel is a mixture of carbon chains that typically contain between 9 and 25 carbon atoms per molecule.

Ultra low sulfur diesel (ULSD)

Diesel engines are 25–40% more fuel-efficient than comparable gasoline engines. Nevertheless, they suffer from associated particulate, NOx and SOx emissions that are harmful to human health. Sulfur, a natural part of the crude oil from which diesel fuel is derived, is one of the key causes of particulates or soot in diesel. The main drivers of ULSD production in the petroleum refineries are the **environmental problems and health hazards caused by exhaust emissions** from the diesel powered vehicles, the strong influence of sulfur in enhancing the formation of harmful components of the emission (e.g. particulate matter (PM), NOx, SOx and CO), and the environmental legislations on diesel fuel sulfur level and air quality standard. Another important driver that encourages refiners to favor ULSD production over gasoline is the **continued increase in the demand** of ULSD.





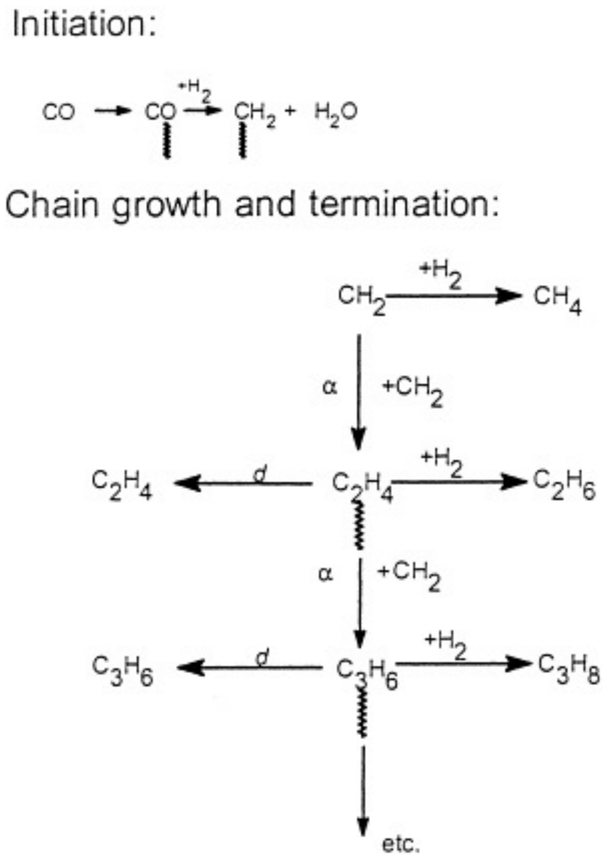
Catalysis Today 2010, 153, 1

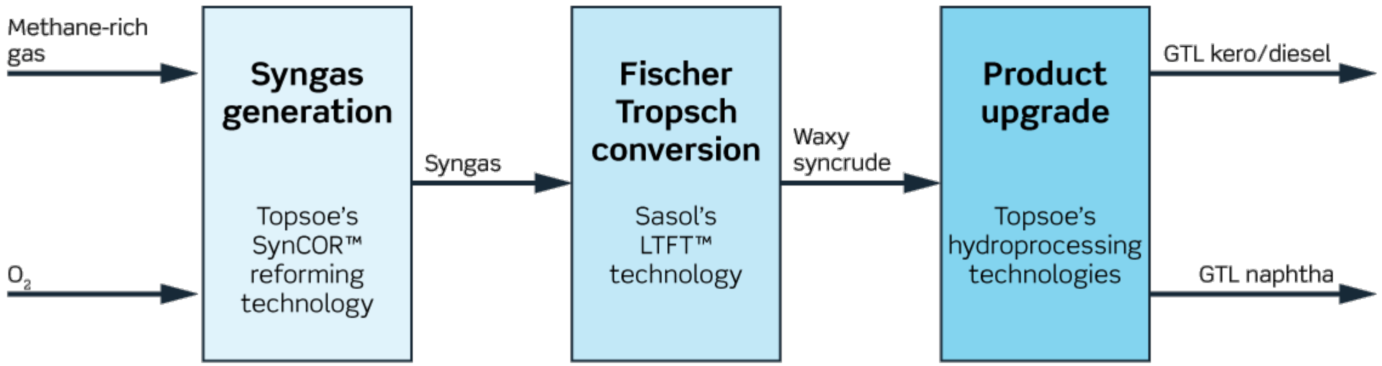
$CO + H_2$

Fischer Tropsch synthesis

Syngas, or synthetic gas, is a fuel gas mixture consisting primarily of hydrogen, carbon monoxide.

The industrial application of the FT process started in Germany and by 1938 there were nine plants in operation having a combined capacity of about 660×103 t per year. Even though these plants ceased to operate after the second world war, interest in the FT process remained because at that stage there was the persistent perception that the reserves of crude oil were very limited.

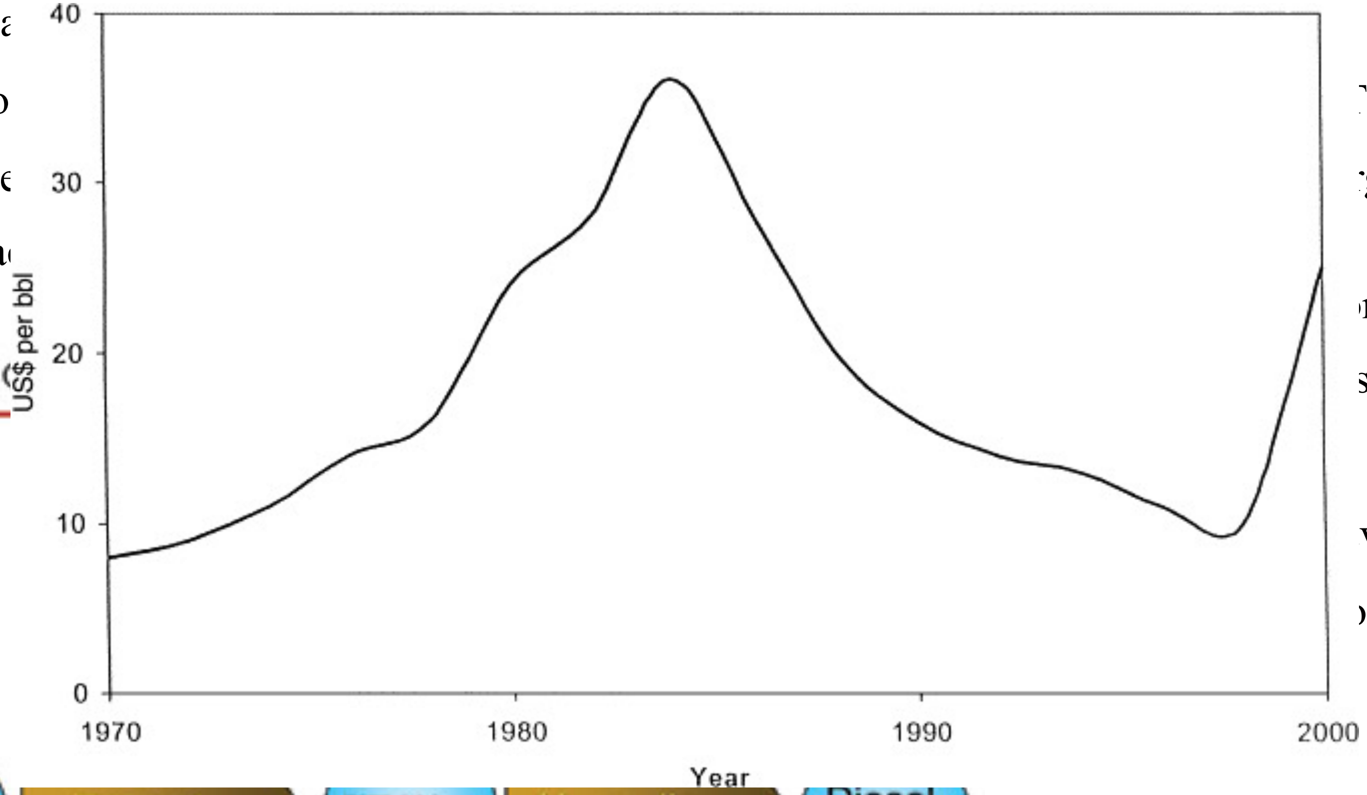




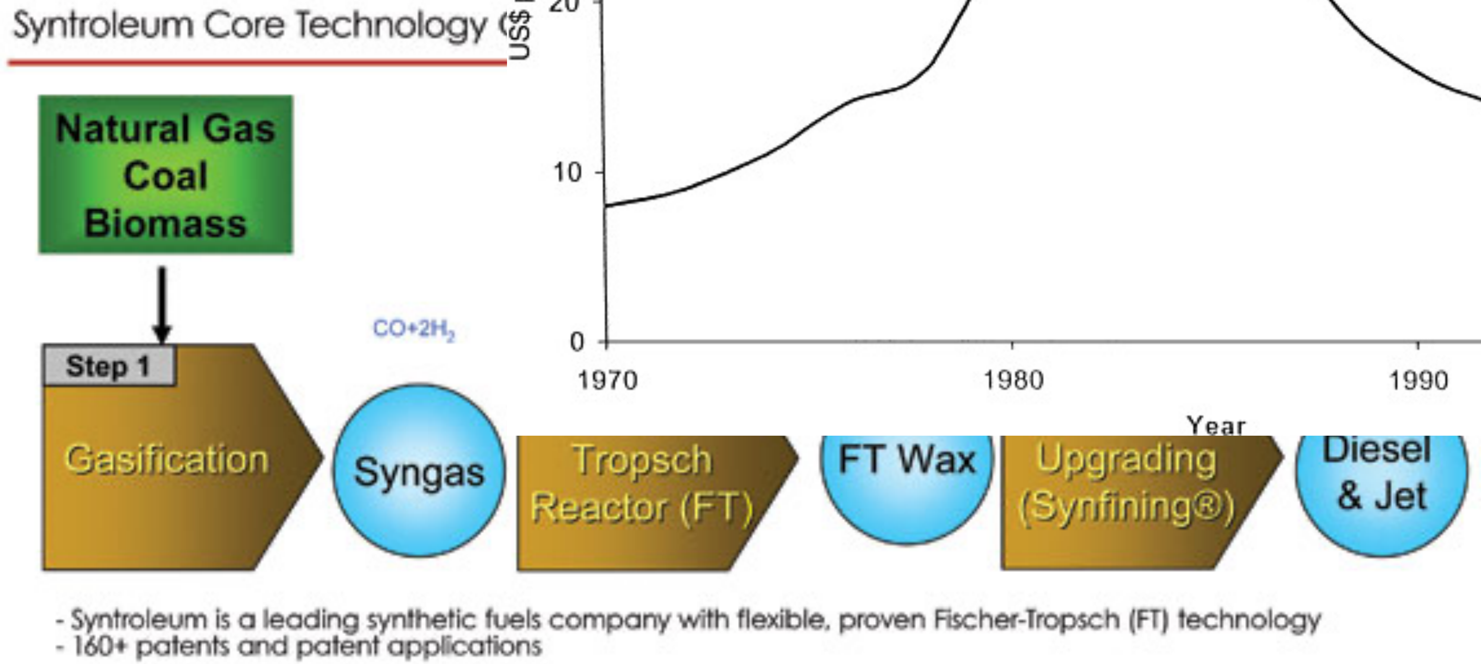
In an FT complex the production of purified syngas typically accounts for 60–70% of the capital and running costs of the total plant. Given its availability, methane is preferred to coal for syngas production. Not only is the capital cost of the methane conversion plant about 30% lower but the process is more efficient. In methane reforming about 20% of the carbon is converted to CO_2, whereas with coal gasification the figure is about 50% due to coal's much lower hydrogen content.

Cat. Today 2002, 227

In the 1955-1970 years period (the so called 'oil age') the world energy scene was governed by a plenty and cheap oil supply In consequence, only marginal interest in **Fischer Tropsch** synthesis survived with a few scientifically interested groups continuing their research, the exception being the South African FT industry at Sasol, relying on extremely cheap domestic coal and the particular state policy. Currently, the reserves of natural gas ha ... like a vessel on the cliffs. Such 'stranded gas' from remote lo ... synthesis. Due to energy saving policies and CO_2-emissions be ... ged with taxes, and it might even be of negative value at the pla...



...n to build a Fischer–Tropsch ... s still fraught with risk because ... based on the perceived future ... vailability of petroleum crude ... ocal politics.



Applied Catalysis A: General 1999, 186, 3

Syncrude (from FT) vs (crude) oil

Table 1 Comparison of syncrude and crude oil composition

Property	HTFT[a]	LTFT[b]	Crude oil
Paraffins	>10%	major product	major product
Naphthenes	<1%	<1%	major product
Olefins	major product	>10%	none
Aromatics	5–10%	<1%	major product
Oxygenates	5–15%	5–15%	<1% O (heavy)
Sulfur species	none	none	0.1–5% S
Nitrogen species	none	none	<1% N
Organometallics	carboxylates	carboxylates	phorphyrines
Water	major by-product	major by-product	0–2%

The absence of sulfur and nitrogen compounds in syncrude is immediately apparent. Much energy and effort is expended to remove these heteroatoms from crude oil. Syncrude contains oxygenates, and although not all oxygenates are desirable, there are also useful oxygenates in syncrude, such as lubricity-giving long chain carboxylic acids and high octane motor-gasoline components like ethanol.

Conversion process	Environmental considerations	Syncrude	Crude oil
C_4 hydroisomerisation	Clean	No	Yes
Aliphatic alkylation	H_2SO_4 or HF	No	Yes
C_5/C_6 hydroisomerisation	Clean[a]	Yes	Yes
Etherification	Clean	Possibly	Possibly
SPA olefin dimerisation	Clean	Yes	Possibly[b]
Hydrotreating	Clean	Yes	Yes
Reforming (Pt/Al_2O_3)	Chloroalkanes	No	Yes
Reforming (non-acidic Pt/L)	Clean	Yes	No
Aromatic alkylation	Clean	Yes	No

[a] Clean with Pt/ zeolite catalyst ; chloroalkanes needed with Pt/Al_2O_3. [b] Only if olefins cannot be sold as chemicals or processed differently.

Residues have to be upgraded, not only because the market for residue products is declining, but also because dumping of residue is environmentally unacceptable.

Green Chem., 2007, 9, 560

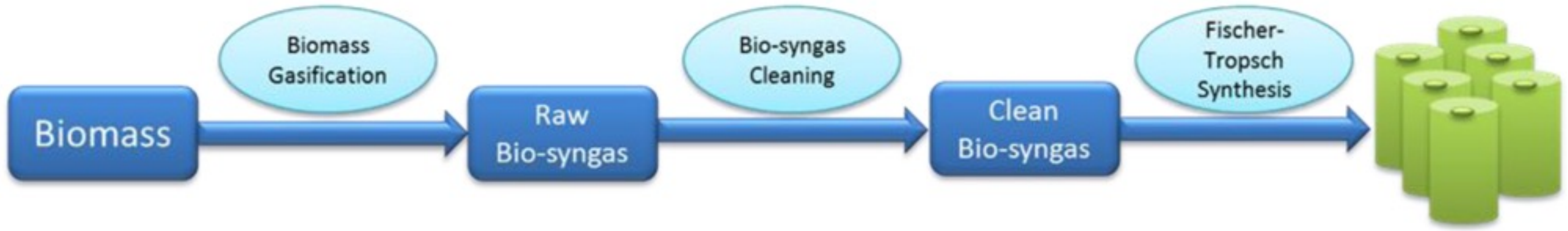
(a) Syncrude has inherently better properties than crude oil for the production of transportation fuel.

(b) The carbon number distribution of HTFT syncrude is such that it is the easiest feed material to refine.

(c) Motor-gasoline production from syncrude and crude oil derived naphtha has similar refinery complexity, but crude oil refining is less environmentally friendly.

(d) Distillate refining from syncrude and crude oil is of comparable complexity and environmental impact.

(e) The conversion of crude oil residue requires significantly more effort than the conversion of syncrude residue.



The most common sources for biosyngas production are lignocellulosic materials derived from agricultural and agroforestry activities due to their high thermal conversion into hydrogen and carbon monoxide. Sugarcane bagasse, rice straw, corn straw, and soybean straw are important raw materials for the biosyngas production

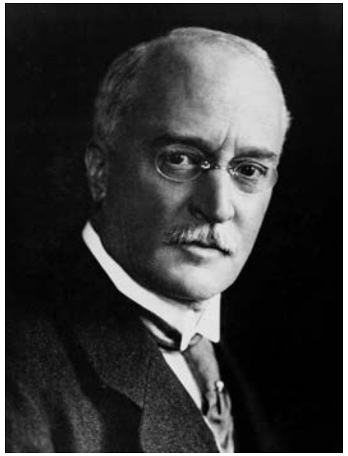
Int. J. Hydrogen Energy 2020, 18114

The fuels are evaluated either by their abilities to be blended with petroleum-based fuel for use in internal combustion engines or by their utility in alternative vehicle technology such as natural gas vehicles or flexible fuel vehicles.

Several points must be considered in the evaluation of edible biomass to produce biofuel. These are (a) the biomass chemical composition, (b) energy balance, (c) avail ability of croplands and the contribution to biodiversity and crop land value losses, (d) competition with food needs, (e) cultivation practices, (f) emission of pollutant gases, (g) impact of mineral absorption on water resources and soil, (h) use of pesticides, (i) cost of the biomass and its transport and storage, (j), soil erosion, (k) economic evaluation considering both the coproducts and feedstocks, (l) creation or maintenance of employment, and (m) resource availability such as water.

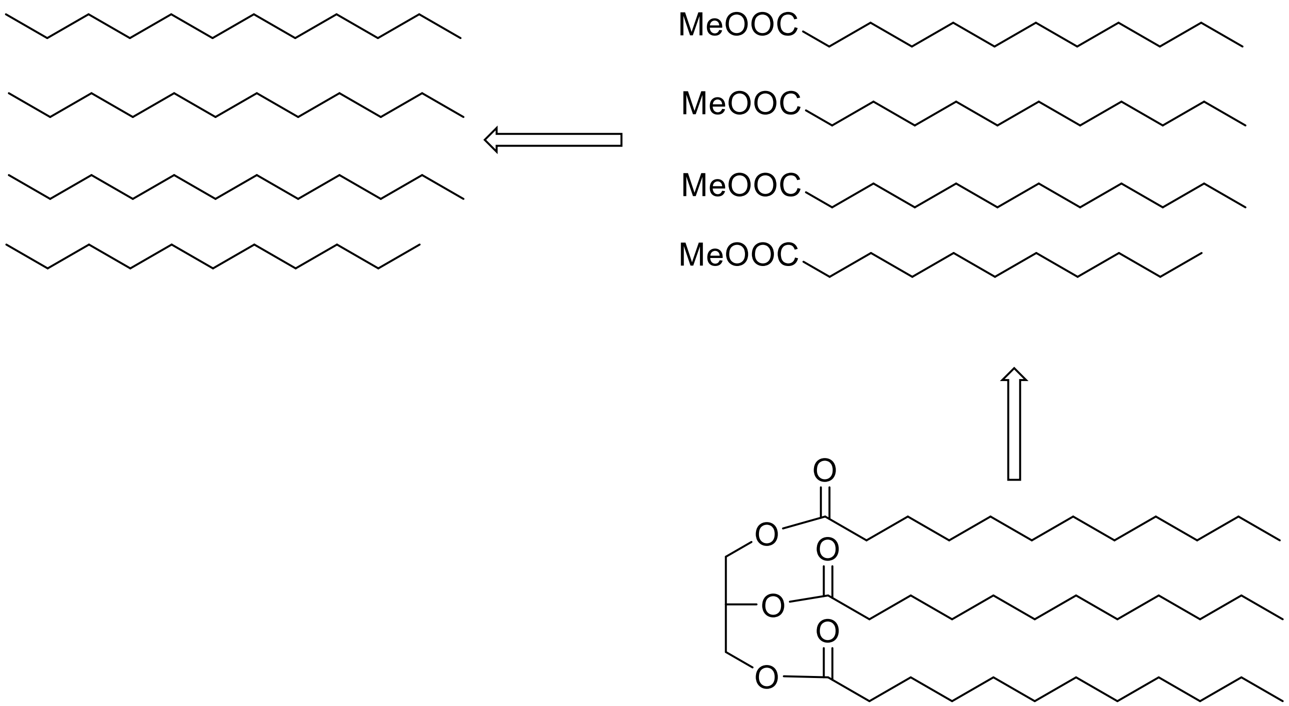
Renewable Energy Focus

From fuels to first generation biofuels

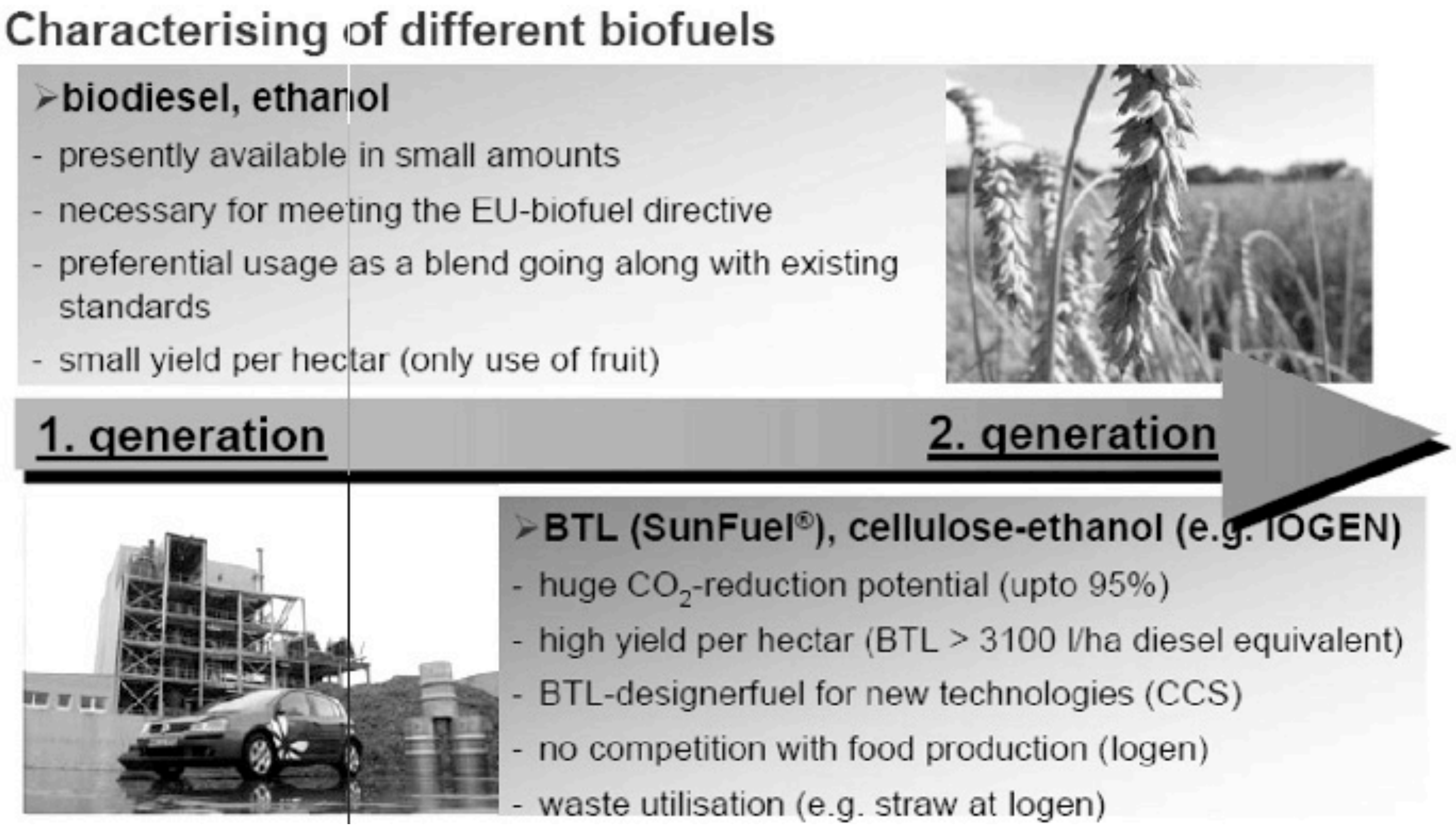


"The use of vegetable oils as engine fuels may seem insignificant today but the such oils may become, in the course of time, as important as petroleum and the coal tar products of the present time."

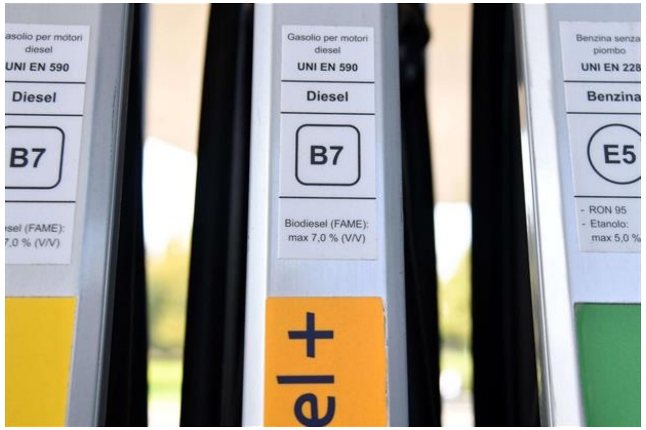
Rudolf Diesel, 1912



Although biofuels can be obtained from over 2000 various plants, only a few have found application due to various limitations and barriers. The first barrier in using biofuel (biodiesel and bioethanol, above all) is insufficient quantities. The second barrier is of economy nature namely the low yield and availability of cultivated soil. Biofuel production cost (with lower tax) is twice as high as the cost of mineral fuel.

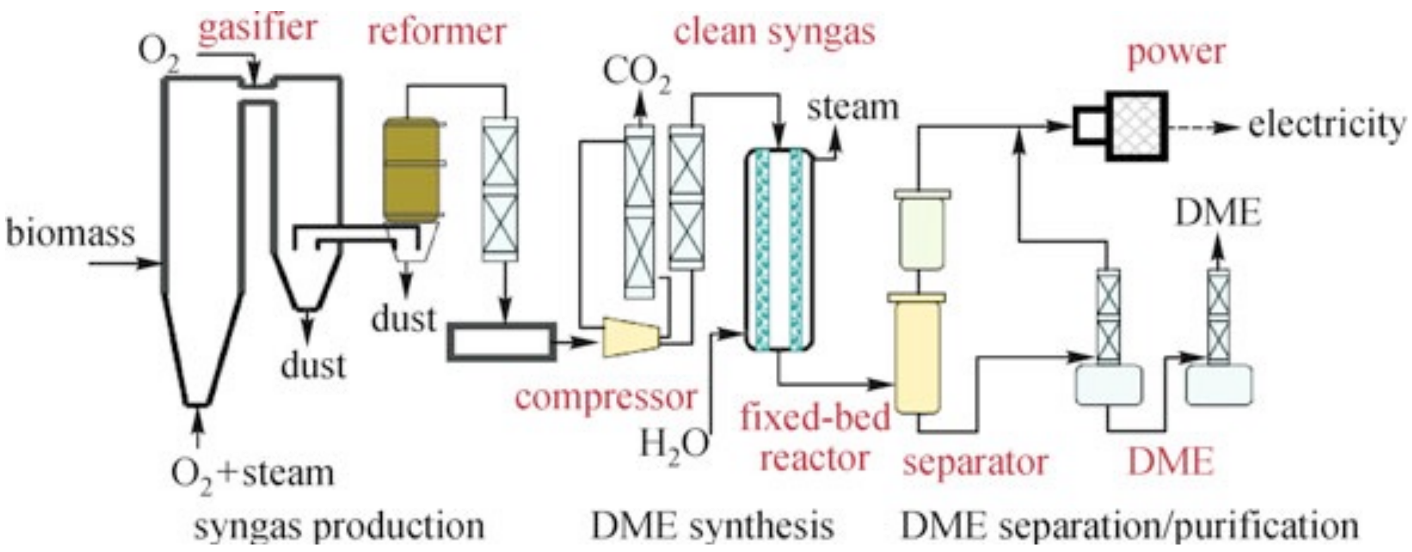


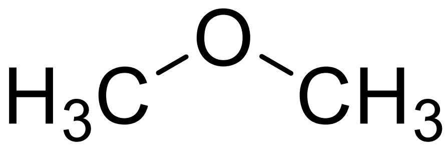
In the United States, the standard ASTM D7467 for blends of biodiesel with petrodiesel in the range of 6-20% biodiesel in petrodiesel was established in 2008.

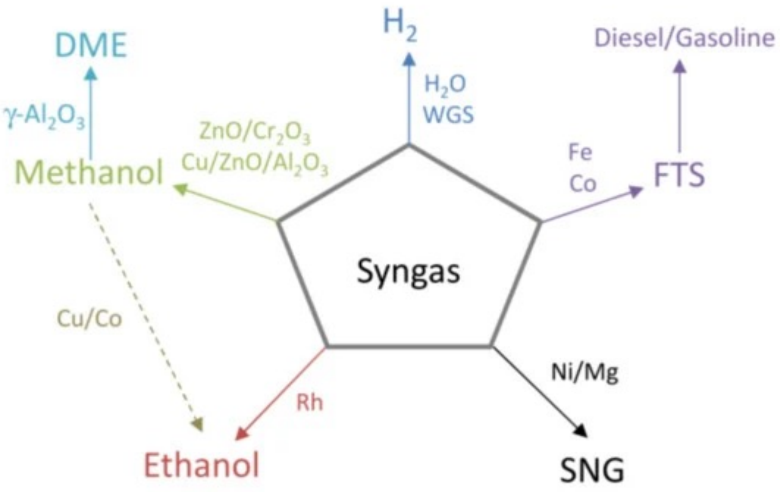


Thermal Science, 2009, 12, 175

Dimethyl ether (typically abbreviated as DME), also known as methoxymethane, wood ether, dimethyl oxide or methyl ether, is the simplest ether. It is a colourless, slightly narcotic, nontoxic, highly flammable gas at ambient conditions, but can be handled as a liquid when lightly pressurized. The properties of DME are similar to those of Liquefied Petroleum Gas (GPL). DME is degradable in the atmosphere and is not a greenhouse gas.







Front. Energy 2011, 5, 330

Bio Refinery

Biomass

Fuels

Solvents, Bulk chemicals

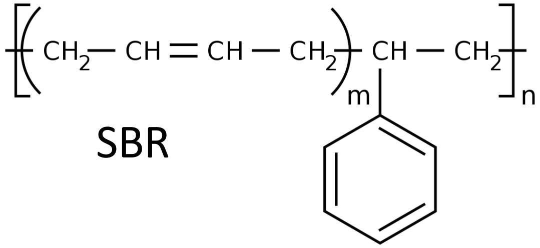
Polymers

fibers

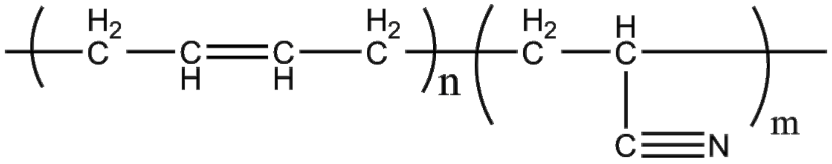
Lubrificants

Detergents

SBR



NBS



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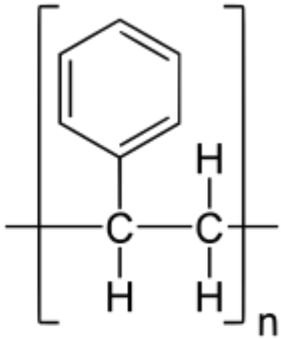
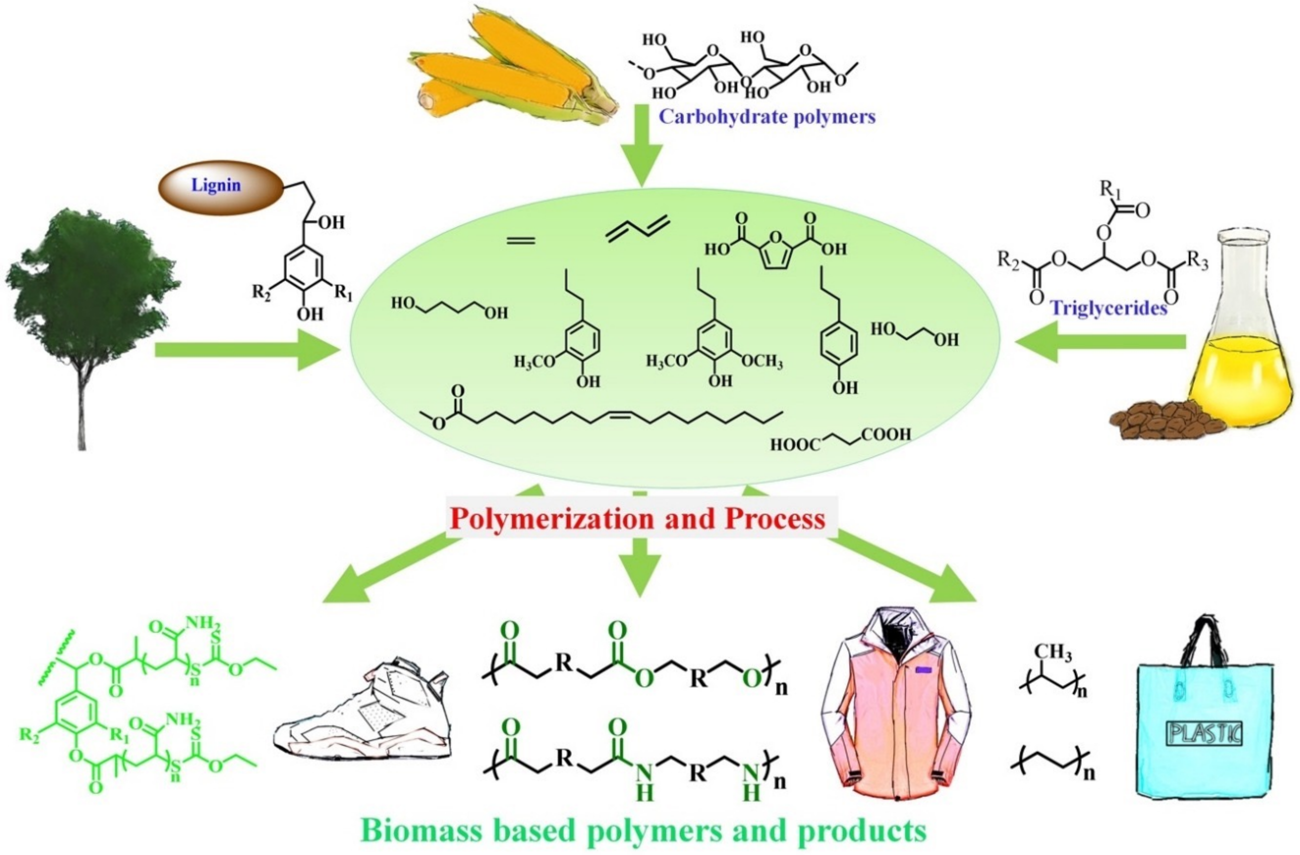


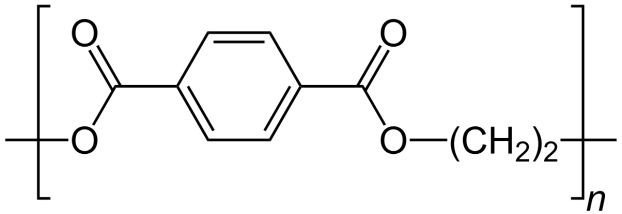
Over 99% of plastic is made from chemicals sourced from fossil fuels, and the fossil fuel and plastic industries are deeply connected

The Lancet, DOI: 10.1016/S2213-8587(20)30116-9

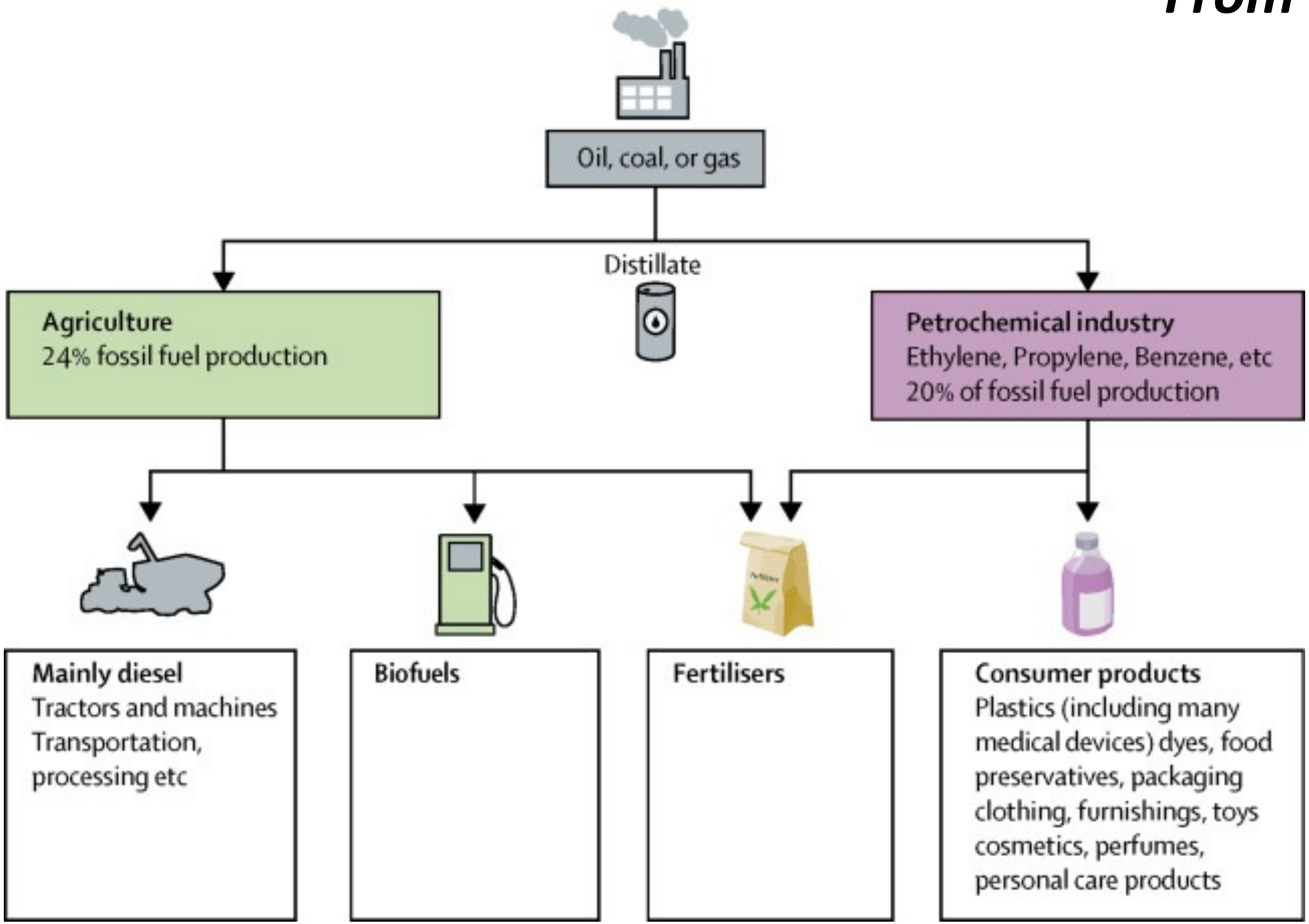
From Oil to Bio Refinery (?)

Renewable natural resources, such as plant oils, fatty acids, cellulose, and lignin, have been widely pursued as precursors for manufacturing sustainable polymers. There are many challenges in the production of biobased plastics



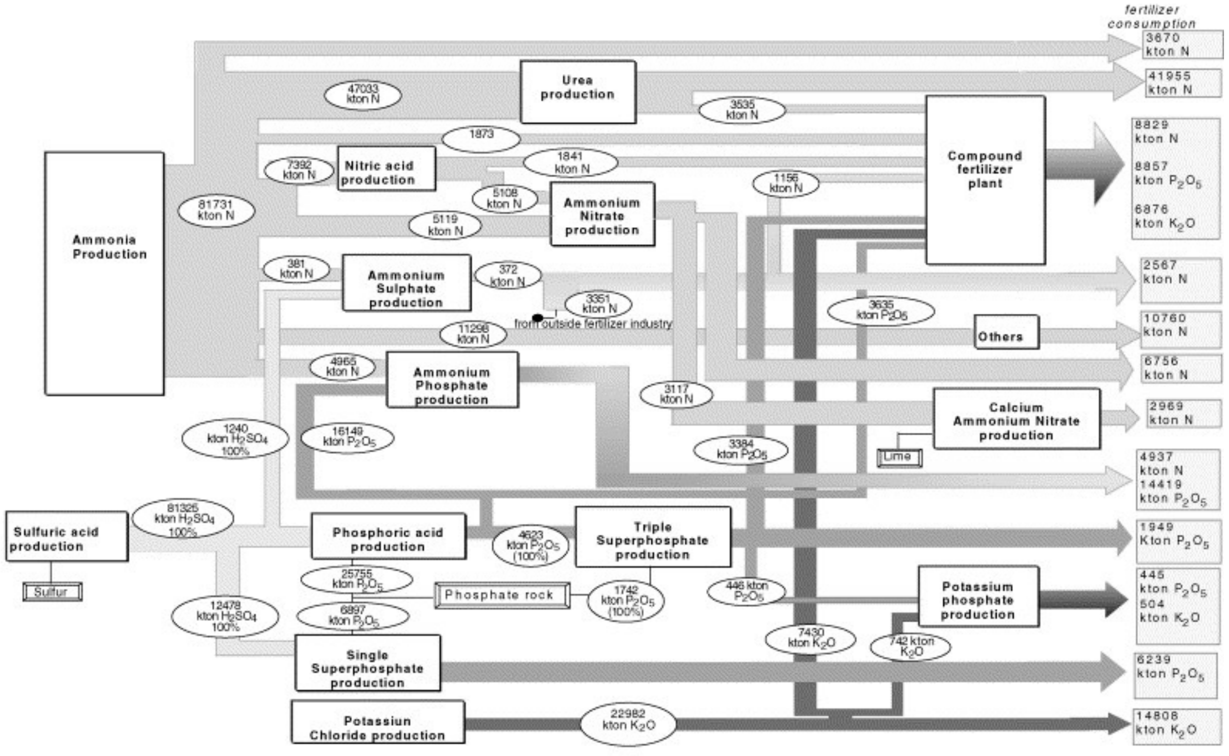


From Oil to Bio Refinery (?)



The Lancet, DOI: 10.1016/S2213-8587(20)30116-9

From Oil to Bio Refinery (?)



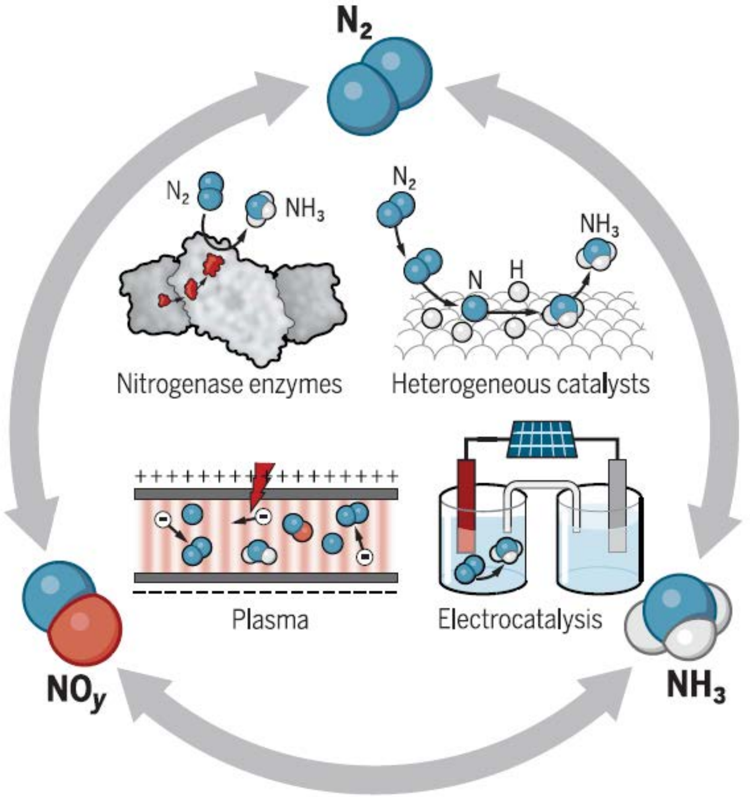
Note: This balance does not include the following fertilizer categories: basic slag, ground phosphate rock, Fused magnesium phosphate, dicalcium phosphate, phosphoric acid (applied direct), potassium magnesium sulphat and crude potash salts. They account for about 2% of the total nutrient consumed in the year 2001. The category named "other" include: nitrogen solutions, calcium nitrate, sodium nitrate, ammonium chloride, calcium cyanamide, ammonium bicarbonate.
We have assumed the following routes for the processing of compound fertilizers: 40% based on ammonium nitrate, phosphoric acid and potassoim chloride, 40% from urea, triplesuperphosphate and potassium chloride and 20% is based on Amonium sulphate, diamonnium phsophate and potassium chloride.We also asummed that only 10% of the Ammonium sulfate is produced in the fertilizer industry, the rest is a by-product of caprolactam production and gas scrubbing.

Product	Description	Main reactions
Ammonia (NH_3)	Produced by the reaction between hydrogen and nitrogen at high pressure (Haber process). There are two main stages: the reforming stages (first and second reformer) and the converting stage (ammonia synthesis). Between these two stages, carbon monoxide is converted into carbon dioxide and removed from the process	$CH_4 + H_2O \rightarrow CO + 3H_2$ } $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$ $2CH_4 + O_2 \rightarrow 2CO + 4H_2$ } $CH_4 + O_2 \rightarrow CO_2 + 2H_2$ $CO + H_2O \rightarrow CO_2 + H_2$ } $N_2 + 3H_2 \rightarrow 2NH_3$ }
Urea (NH_2CONH_2)	Produced by reacting ammonia and carbon dioxide	$2NH_3 + CO \rightarrow NH_4COONH_2$ $NH_4COONH_2 \rightarrow NH_2CONH_2 + H_2O$

Resources, Conservation and Recycling, 2006, 46, 75

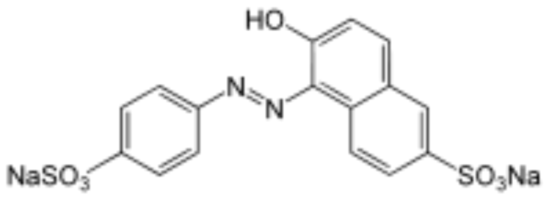
From Oil to Bio Refinery (?)

Nitrogen is fundamental to all of life and many industrial processes. The interchange of nitrogen oxidation states in the industrial production of ammonia, nitric acid, and other commodity chemicals is largely powered by fossil fuels. A key goal of contemporary research in the field of nitrogen chemistry is to minimize the use of fossil fuels by developing more efficient heterogeneous, homogeneous, photo-, and electrocatalytic processes or by adapting the enzymatic processes underlying the natural nitrogen cycle.

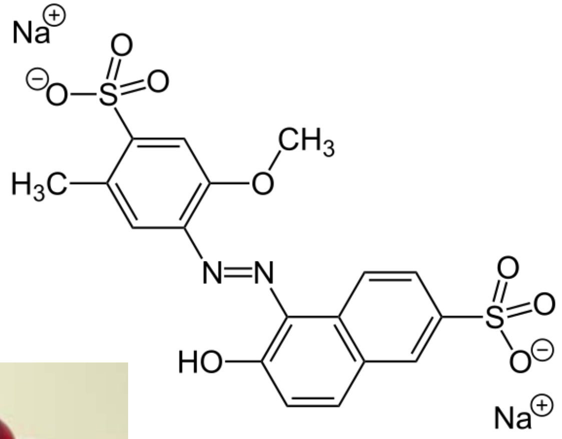


Science **360**, 873 (2018)

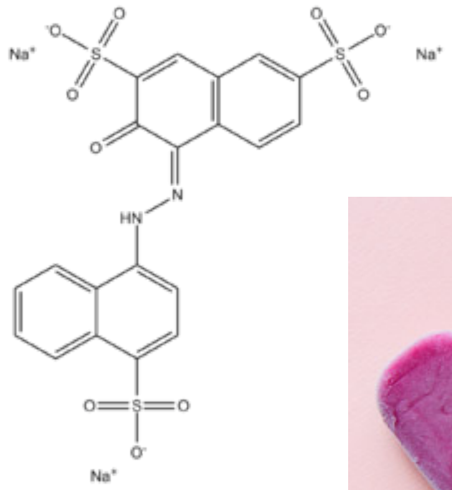
Food Additives from petroleum



Sunset yellow (E110)

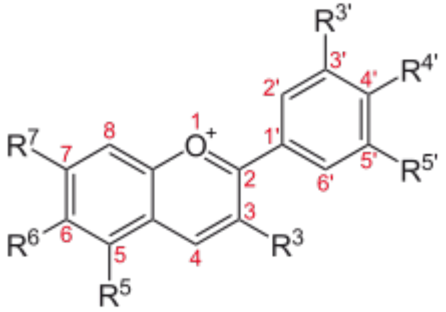


Allura Red AC

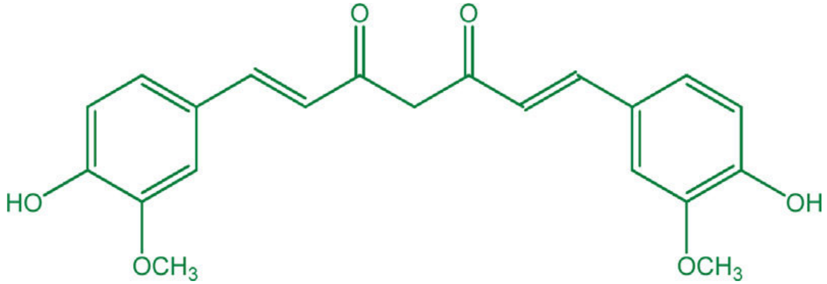


Amaranth

From Oil to Bio Refinery (?)



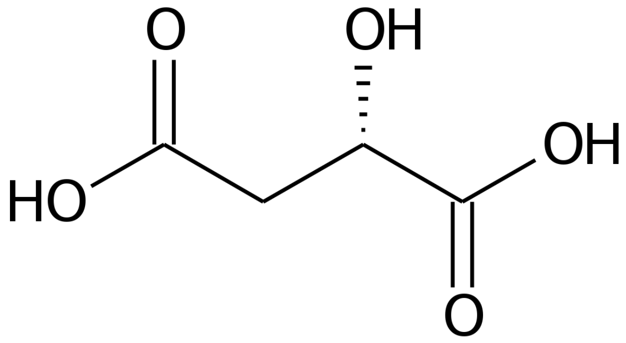
Elderberry juice



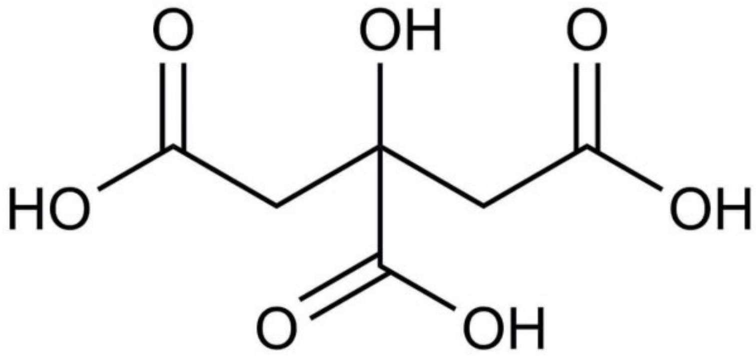
Curcumin

Paprika

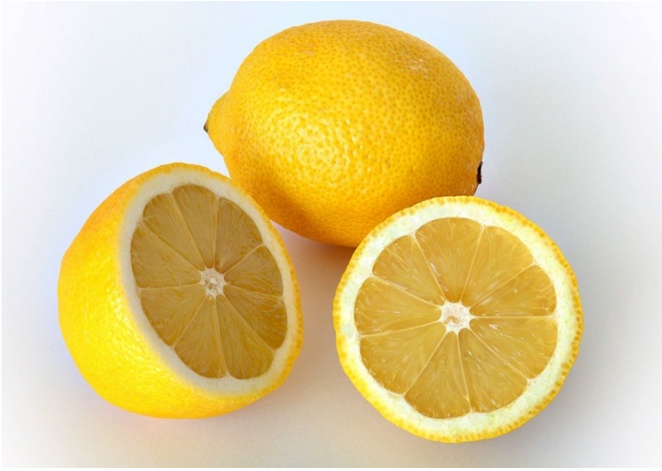
Caramel color



2-hydroxybutanedioic acid (Malic acid) is an organic compound that exists in its two stereoisomeric forms (L- and D-enantiomers), though only the L-isomer is found in nature. The salts of malic acid are known as malates. Applications: (a) low calorie beverages -its biggest advantage is that as compared to citric acid, the amount of malic acid required to be added to achieve the same level of sourness, is significantly lower .



Citric acid can be derived from natural sources (e.g. lemon, lime and orange) or synthetic sources (e.g. chemical reaction and microbial fermentation).



Petroleum and Health Care: Evaluating and Managing Health Care's Vulnerability to Petroleum Supply Shifts

Petroleum is used widely in health care (primarily as a transport fuel and feedstock for pharmaceuticals, plastics, and medical supplies) and few substitutes for it are available. This dependence theoretically makes health care vulnerable to petroleum supply shifts, but this vulnerability has not been empirically assessed.

Plastics. Plastics are central to the antiseptic model of modern health care and are used in a wide range of medical devices, supplies, and packaging.

Approximately 3% of petroleum production is used for pharmaceutical manufacture, but nearly 99% of **pharmaceutical** feedstocks and reagents are derived from petrochemicals.

American Journal of Public Health, 2011, 101

Analisi | in europa i rischi maggiori

Petrolio e Covid: così gli aerei a terra minacciano le raffinerie

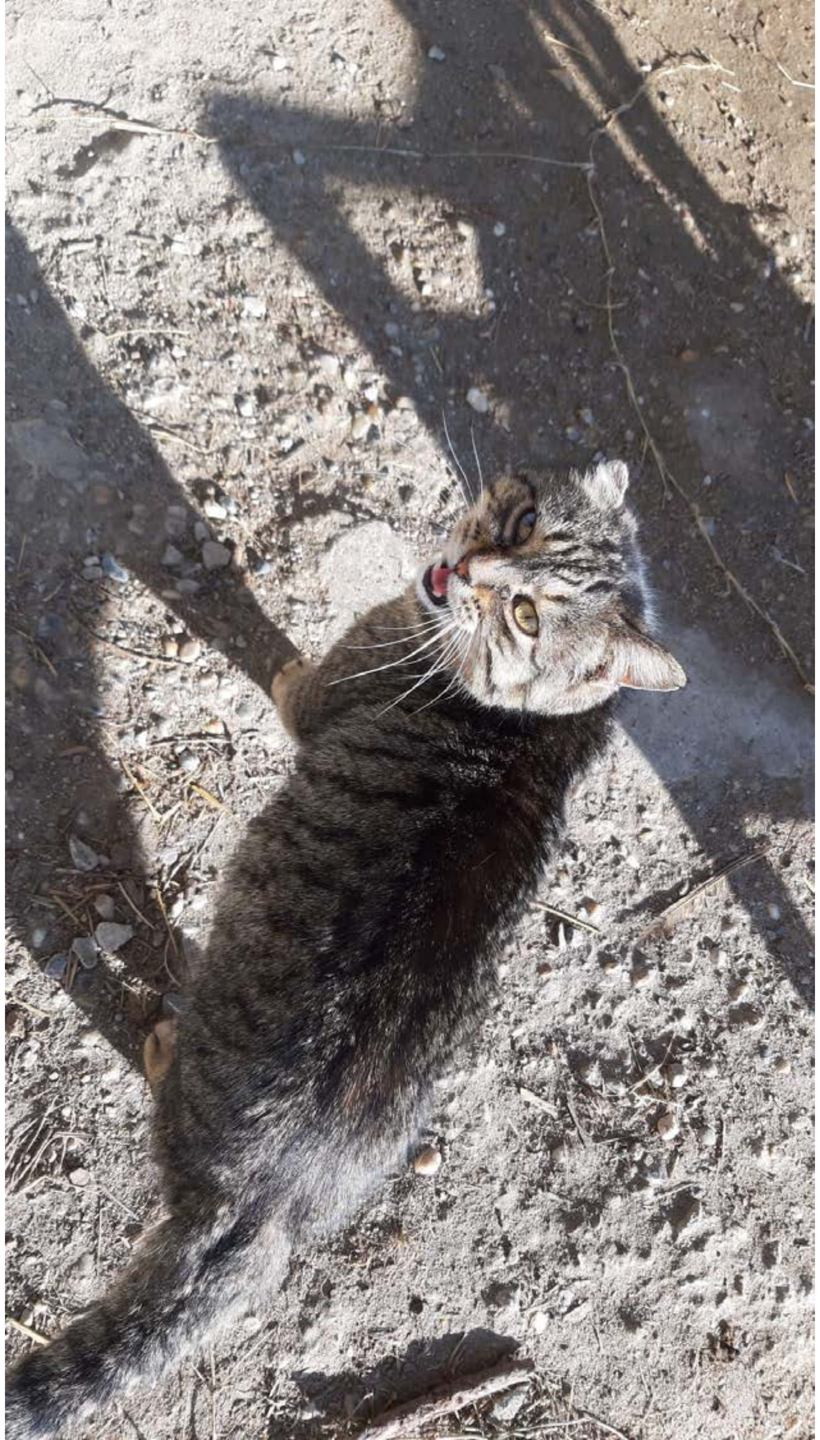
Lo stop prolungato dei voli rischia di essere una condanna a morte per molti impianti. Soprattutto in Europa, dove il settore in crisi da anni potrebbe non avere più tempo

In 1871, most of the Arctic whaling fleet was crushed by early winter ice and lost. This calamity, in conjunction with the long-term diminishing whale stocks, the diversion of investment capital to more ... elopment, ... rude oil, ... whaling

It is apparent that no single event caused the final, rapid decline. However, a single calamity, in an already stressed industry, that was self-insured and commercially interlinked, precipitated the end. Today's American petroleum industry, although adopting some principles of the American whaling industry, also has embraced other activities such as work process reengineering and customer alliances, which may preempt, or postpone, a similar catastrophic demise.

James L. Coleman, Jr

Grazie dell'attenzione



Refinery

The refiners produce the feedstock for the commodity chemical companies.

Commodity

The commodity chemical companies supply the building blocks for the basic fine chemicals

Fine Chemicals

The pharmaceutical company that markets the drug depends on fine chemicals to make the API.

Pharmaceuticals