

Literature Review

Synthetic Methods

Industrial Feedstock Chemicals

July 25th, 2013

■ **Topics Covered:**

- Basic overview of “fossil fuel” supply chain
- Industrial production of fundamental gases (hydrogen, CO, ethylene, propylene)
- Industrial production of BTX chemicals (benzene, toluene, xylenes)
- The CO economy (acetic acid, methanol, etc.)
- The ethylene economy (ethanol, ethylene oxide, etc.)
- The benzene economy (styrene, cumene, cyclohexane, etc.)
- Sources of miscellaneous chemicals

- Will not cover much of the ingenious engineering and separation science that goes into production
- Will not cover historical syntheses – economics dramatically changes the processes used – industrial chemistry is amazingly flexible!

■ From the Earth:

conventional sources

gas deposits
(desirable composition) → *extraction, processing*

natural gas



"unconventional" sources

← *fracking, horizontal drilling, etc.*
("shale gas")

oil deposits
(desirable composition) → *drilling, processing*

crude oil



← *extraction ("bitumen")* oil sands
← *fracking, extraction ("tight oil")*

impermeable rock formations

synthetic crude



← *extraction, pyrolysis*

oil shale
(kerogen)



← *mining* shale deposits (many types)

coal deposits
(desirable composition) → *mining, processing*

coal



Gas: 3,360 trillion L/a worldwide in 2011, ~39% between USA and Russia

Oil: ~4.9 trillion L/a worldwide in 2010, 35% between Russia, Saudi Arabia, and USA

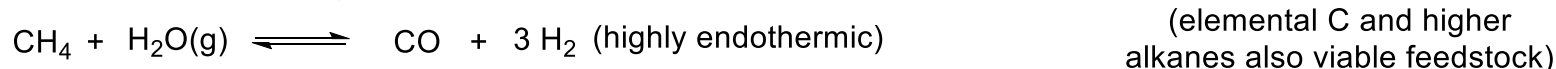
Coal: 7,700 Mt/a worldwide in 2011, ~50% of China

■ Statistics:

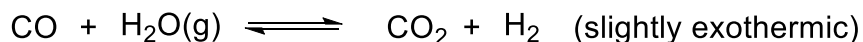
Since hydrogen escapes the atmosphere into space, all hydrogen used is synthetic. The actual worldwide production and consumption of hydrogen gas is difficult to quantify since it is typically immediately consumed or burned as it is generated. Worldwide production was estimated at 45 Mt/a in 2006.

■ Relevant Synthesis Reactions:

Alkane steam reforming:



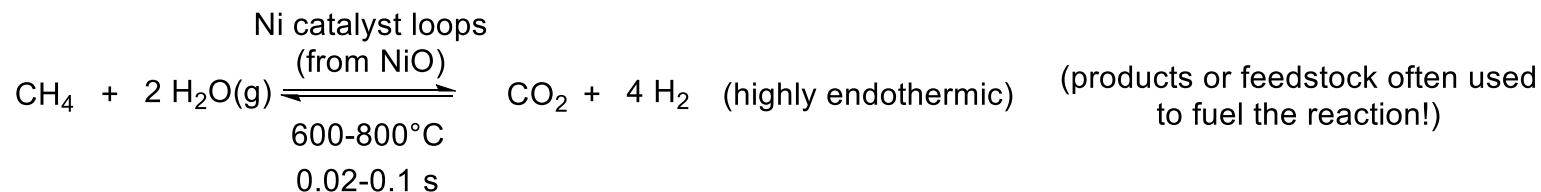
Water-gas shift reaction:



Boudouard reaction:



Overall steam-reforming process:



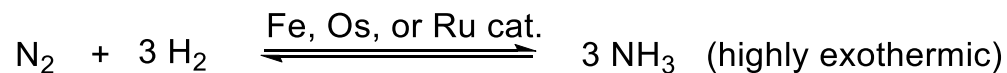
Note that these equilibrium reactions can be pushed in many different directions by the concentrations of fuel, CO, H₂, H₂O, CO₂, and O₂ (to form CO).

Coal, oil, wood, and waste gasification (by partial oxidation) can feed this reaction, although natural gas is often most economical. Water splitting produces 4% of the world's H₂ only as a byproduct of the chlor-alkali process for Cl₂ production.

■ Some Downstream Coupled Reactions:

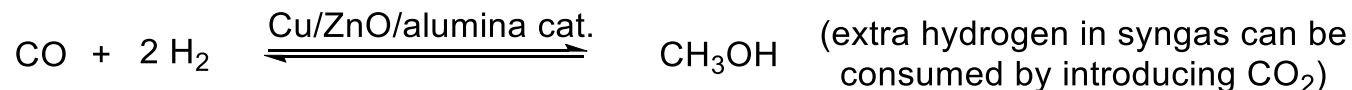
Most hydrogen generated is used in the Haber-Bosch process to produce ammonia (~60%). Global ammonia production consumes an estimated 1% of the world's entire energy consumption and an estimated 3-5% of the world's entire natural gas consumption.

Haber-Bosch process:



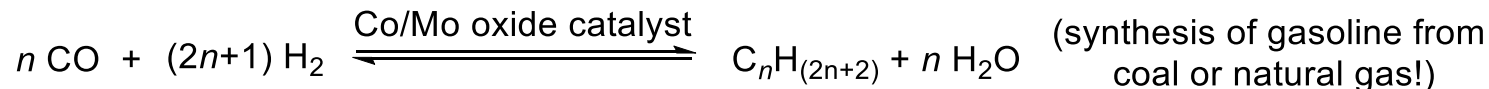
Methanol production accounts for ~10% of hydrogen use, while other petrochemical processes such as hydrotreating, hydrodesulfurization, hydrocracking account for ~25% of hydrogen use. Other minor industrial processes make up the remainder 5%. The cost to produce hydrogen is approximately \$0.10 per 1000 L.

Methanol synthesis:

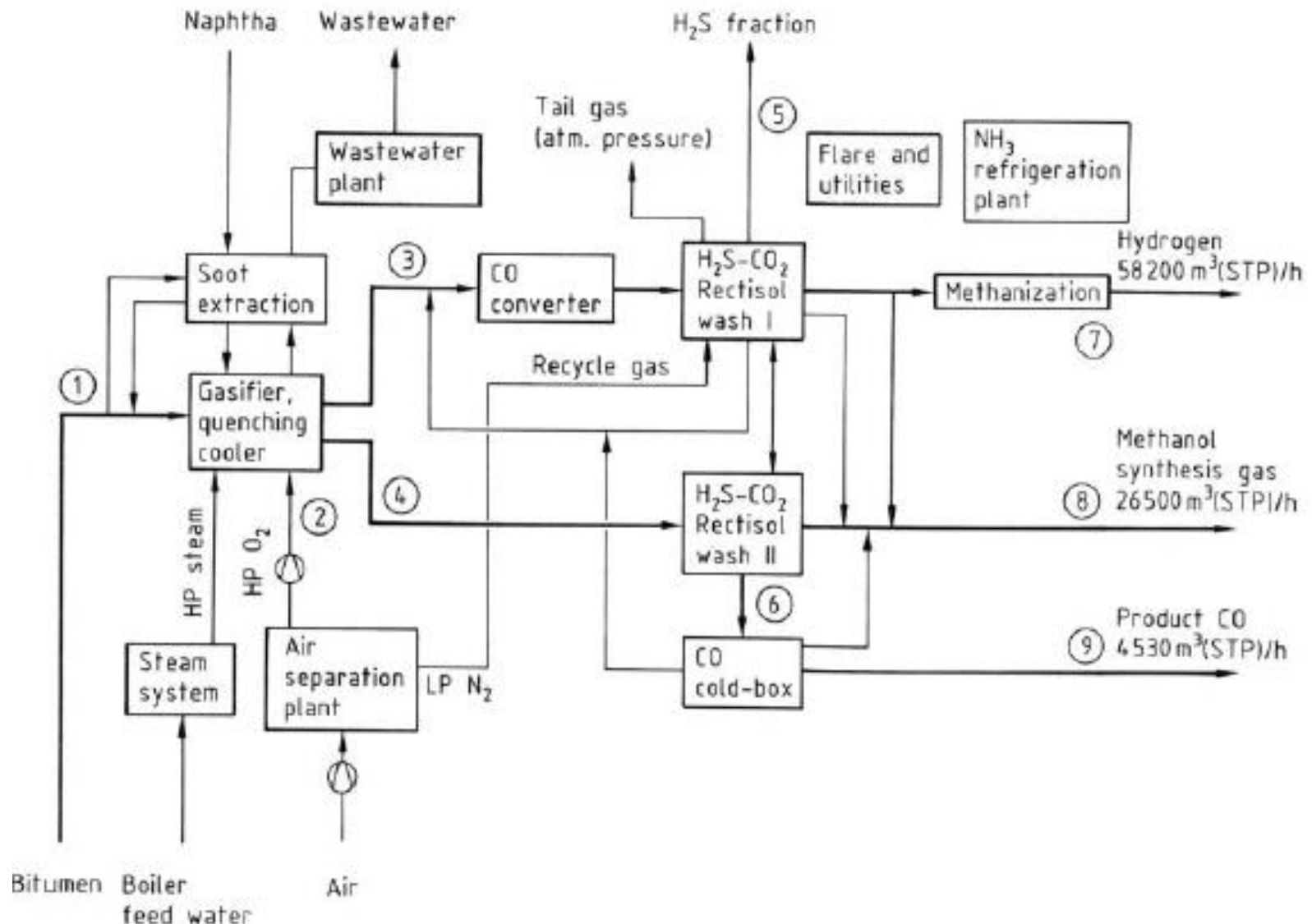


The Fischer-Tropsch alkane synthesis from CO and hydrogen (the reverse of steam-reforming) is used in South Africa (SASOL) to produce petroleum, though this is more expensive currently than cracking processes. Note that this chemistry enables the synthesis of gasoline from any combustible carbon source – the world's fuel oil supply is *literally* inexhaustible!

Fischer-Tropsch process:



■ Example Syngas Generator Employing Bitumen Feed:



Product gas for producing	Typical process stages*	Typical H ₂ O/C ratio, mol/mol	Typical pressure at reformer tube outlet, MPa	Typical reformed gas temperature, (primary reformer), °C
CO	desulfurization, tubular reforming with recycled CO ₂ , CO ₂ scrubbing, CO separation (e.g., low-temperature separation, CoSorb, PSA, or membranes)	2 – 3	1 – 3	850 – 900
H ₂	desulfurization, tubular reforming, HT and LT conversion, CO ₂ scrubbing, methanation (standard arrangement)	4 – 5	1.5 – 3	800 – 900
	desulfurization, tubular reforming, HT conversion, PSA, or membranes	3	2 – 2.5	800 – 900
Oxosynthesis gas	desulfurization, tubular reforming, CO ₂ scrubbing, partial separation of hydrogen by PSA, addition of imported CO ₂ upstream of reforming if necessary	2.5	1 – 2	850 – 950
Methanol synthesis gas	desulfurization, tubular reforming, or additional secondary reformer	2.5 – 2.8	2 – 3	850 – 900 700 – 800
NH ₃ synthesis gas	desulfurization, tubular reforming (primary reformer), secondary reforming, HT and LT conversion, CO ₂ scrubbing, methanation	3.5	3 – 4	780 – 830
Town gas	desulfurization, tubular reforming, HT conversion, CO ₂ scrubbing	3.0	1 – 2.5	650 – 750
Reduction gas	desulfurization, tubular reforming, or top gas recycling upstream of tubular reforming	1.25 – 1.5 0.65	0.2 – 0.3 0.15 – 0.2	850 – 1000 900 – 1000

*PSA = pressure swing adsorption; HT = high temperature; LT = low temperature.

■ Statistics:

Second-largest volume petrochemical produced worldwide, after NH_3 – 113,000,000 tons per annum (t/a) capacity in 2005, with actual demand of 105,000,000 tons per annum (t/a) in 2005

Ethylene is typically produced and consumed on-site at the center of “*world-scale*” petrochemical complexes – a typical ethylene generator has a capacity of 1,500,000 t/a

■ Production Plant Example:

Shell's Singapore-based Eastern Petrochemical Complex, an ethylene-based refinery, employs an 800,000 t/a ethylene cracker which feeds the production of 750,000 t/a monoethylene glycol, most of which is used for polyester

5 years to build, operational in May, 2010



■ Steam Cracking:

Most ethylene has been produced by steam pyrolysis (steam cracking) over the last 50 years

Either gas feedstock (i.e. ethane, propane, butane) or liquid feedstock (e.g. full-range naphtha, b.p. = 35-180°C) can be used

Feedstock is mixed with steam at 500-680°C and then heated to 750-875°C for 0.1-0.5 seconds by a radiant coil – cracking occurs in this flash of time

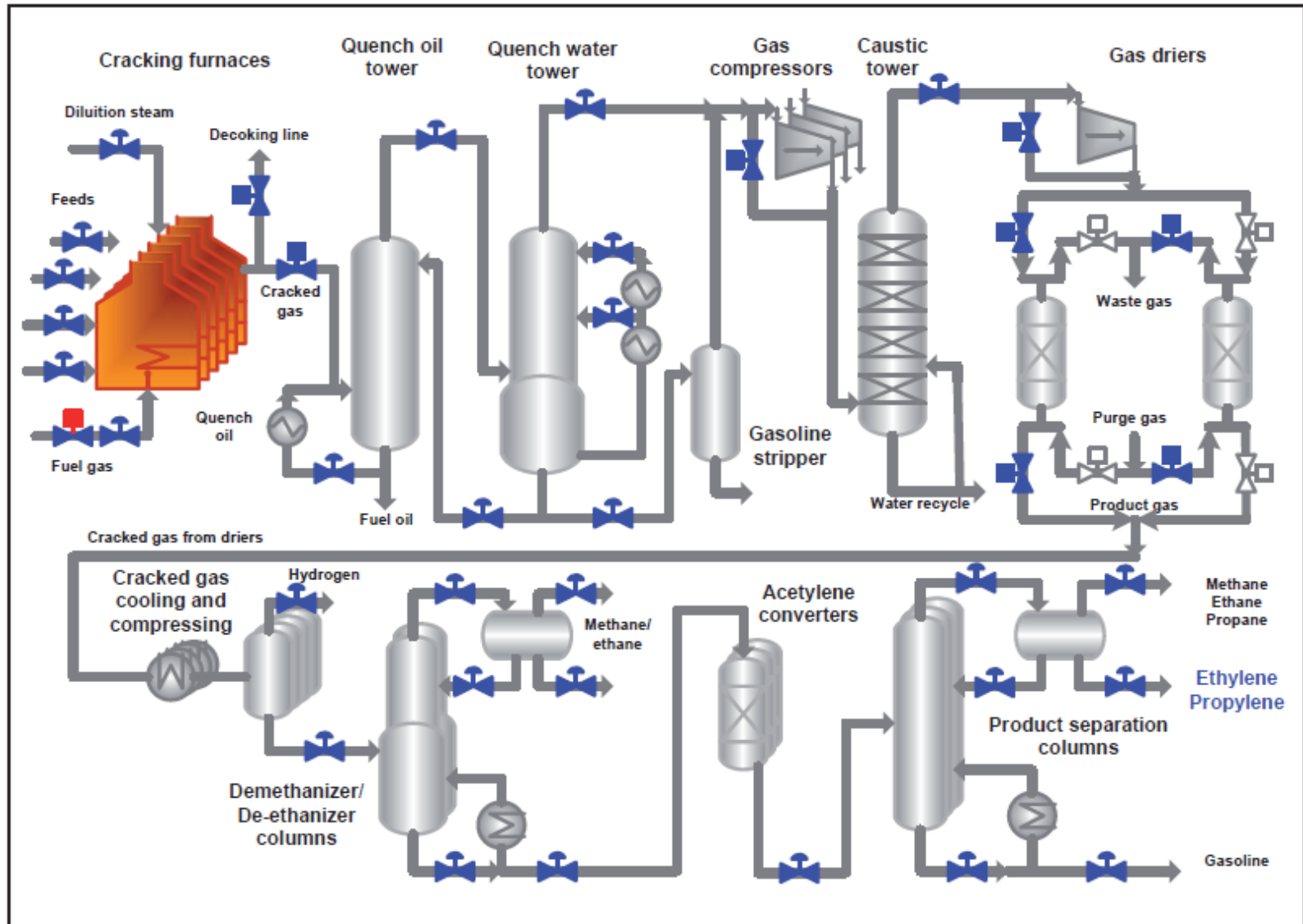
Resulting gas is cooled again to 550-650°C within 20-100 ms to prevent degradation – a complex analysis and separation process provides the products

Free radical mechanism initiated by homolysis of C-C bond – results in large, concentration-sensitive and feedstock-dependent distribution of products




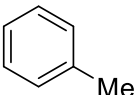
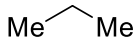
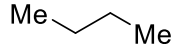
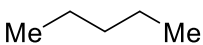
Steam is used to dilute the reaction gas (good ol' O-H bond) to prevent oligomerization of feedstock and polymerization of aromatic impurities resulting in tar, although some coke inevitably forms over time

Counterintuitively, 20 ppm dimethyl sulfide is deliberately added to sulfur-free feedstock to poison Ni-active sites on cracking coil which would otherwise catalyze coke-”cleaning” (water-gas shift reaction turning $C + H_2O$ into CO and H_2) resulting in less pure gas. De-coking is instead deliberately done once every few months instead with an air/water purge.

■ Modern Steam Cracker Schematic (Metso):



■ Steam Cracking:


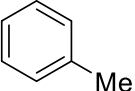
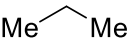
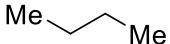
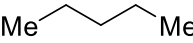
		from ethane (wt %):	from naptha (wt %):	
		H ₂	4%	0.8%
		CH ₄	4%	14%
		H ₂ C=CH ₂	52%	25%
		Me-Me	35%	5%
			1%	16%
			2%	5%
			0.6%	6%
			0.08%	3%
Me-Me or  or  or  + isomers and higher analogs	$\xrightarrow[\text{0.02-0.1 s}]{\text{H}_2\text{O(g)}, \text{750-875}^\circ\text{C}}$			

The distribution of products is highly sensitive to the source of feed and the conditions used – this can have massive-scale economic implications

In 2008, when crude oil jumped from \$60/bbl (159 L) to \$140/bbl, gas feeds became more economical than liquid (naptha) feeds, resulting in refineries burning mostly gas

Lower yield of butadiene byproduct from gas resulted in a massive butadiene shortage affecting the asphalt, rubber, and many other industries

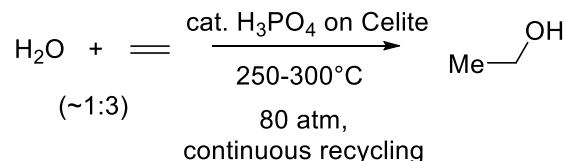
■ Steam Cracking:

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Me-Me or  or  or  + isomers and higher analogs	$\xrightarrow[\text{0.02-0.1 s}]{\text{H}_2\text{O(g)}, 750-875^\circ\text{C}}$			

Many feedstock chemicals are produced in large quantities as byproducts of naptha-based ethylene production including but not limited to: acetylene (0.4 Mt/a), propylene, butadiene, isoprene, styrene, pentadiene, cyclopentadiene, and random aromatics

■ Ethylene Economy:

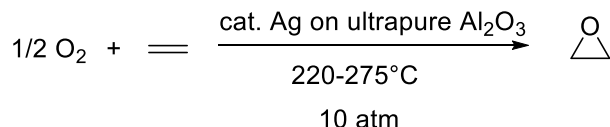
Ethanol synthesis:



worldwide: 58 Mt/a in 2009

conversion of ethylene-proton pi-complex to carbocation is rate-determining step

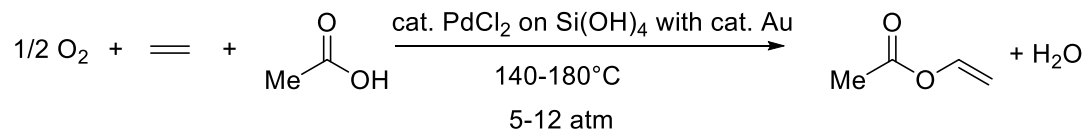
Ethylene oxide synthesis:



worldwide: 15 Mt/a in 2000

mechanism controversial - believed to be Langmuir-Hinshelwood-type (both ethylene and oxygen adsorbed first) with atomic oxygen as the oxidant - >90% selectivities possible now vs. combustion to CO₂ and H₂O, stainless steel reactor walls needed to prevent rust-catalyzed isomerization

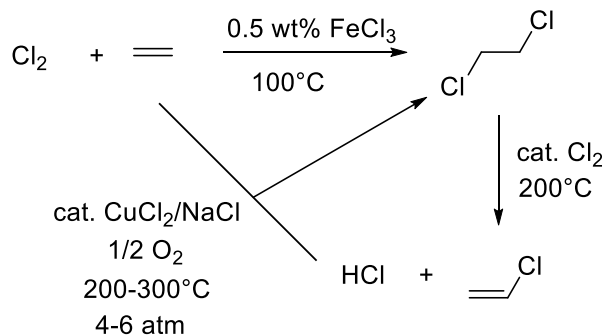
Vinyl acetate synthesis:



worldwide: ~4 Mt/a in 1994

80% worldwide production is from ethylene, 20% from acetylene, caution must be used due to the formation of flammable gas mixtures

1,2-Dichloroethane and vinyl chloride:

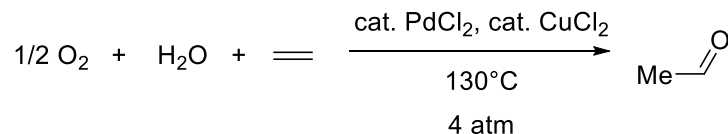


worldwide: ~20 Mt/a in 2004

highly efficient coupled process, dichloroethane cracking occurs by radical mechanism promoted by chlorine

■ Ethylene Economy (cont'd):

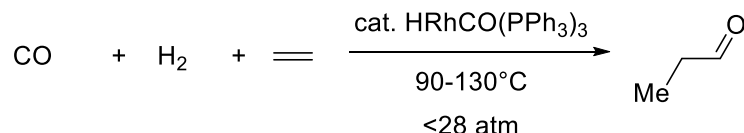
Acetaldehyde synthesis:



worldwide: >2 Mt/a in 1970s

acetaldehyde synthesis is losing value due to new processes circumventing its use

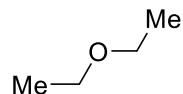
Propionaldehyde ("oxo-") synthesis:



worldwide: ~0.2 Mt/a in 2000

this is a general aldehyde synthesis from olefins

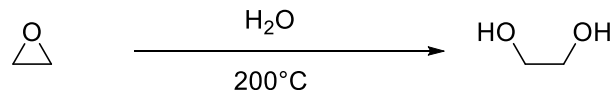
Diethyl ether synthesis:



worldwide: ~12 Mt/a in 1991

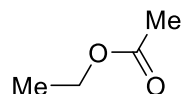
diethyl ether is produced as a significant byproduct of ethanol synthesis (2-3%) - this is more than enough to meet world demand as of 2007

Ethylene glycol synthesis:



worldwide: ~6.7 Mt/a

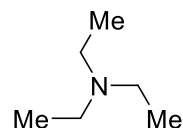
Ethyl acetate synthesis:



worldwide: ~1.3 Mt/a in 2004

from acetic acid and ethanol, liquid phase

Ethylamines:



worldwide: ~0.08 Mt/a in 2000

redox alkylation with ethanol and ammonia and Ni/Co/Fe/Cu catalysts and hydrogen, mixtures produced with triethylamine as the minor component

■ Statistics:

In 2002, global propene production was ca. 53,000,000 t/a, with 36 Mt/a as a byproduct from ethylene-targeted cracking, 15 Mt/a as a byproduct from gasoline-targeted catalytic cracking, and 1.6 Mt/a from propane dehydrogenation and olefin metathesis.

Texas, Louisiana, and Belgium possess extensive propene pipelines for transport between refineries and factories. Elsewhere, propene must be transported by road, rail, or ship as a pressurized liquid or at -47°C .

Recent contract lists chemical-grade propene: \$0.715/lb, polymer-grade propene: \$0.73/lb

■ Production Plant Example:

Petrologistics started the world's largest propane dehydrogenation plant in 2010. It is the first of seven such PDH plants to go into operation in North America, made economically feasible by the shale gas boom.

This plant will employ Catofin chromia-based technology, with a capacity of 0.5 Mt/a propene production (~1% of world demand).



■ Propene Synthesis:

Propene synthesis and isolation hinges on excellent separation science. High-pressure-distilled C3's fraction from cracking processes is selectively hydrogenated with Pd catalysts to remove allene and propyne gases before being further distilled under high pressure to separate propane and propene.

The remaining 3% of worldwide propene production is made by propane dehydrogenation or olefin metathesis by several competing processes.

The Oleflex process employs a proprietary Pt on alumina catalyst doped with Sn and alkali metals between 500-700°C. Dehydrogenation is highly selective, resulting in >90% yields! This process was based on the Pacol process, used to dehydrogenation C10-C14 alkanes to olefins for detergent manufacture.

The Phillips Steam Active Reforming (STAR) process uses a 0.2 to 0.6 wt% Pt on Al₂O₃ catalyst doped with Zn and Sn to dehydrogenate propane diluted with steam. The catalyst is importantly water-stable, allowing the steam-dilution to drive the equilibrium towards dehydrogenation.

The Catofin and Linde-BASF processes employ Cr-based catalysts. The Linde catalyst is composed of 18% Cr₂O₃ and 0.25% ZrO₂ on alumina with trace K⁺. The active site structure is controversial, but the catalytic cycle involves Cr(IV) and Cr(III). The catalyst lasts up to 3 years with *in situ* regeneration.

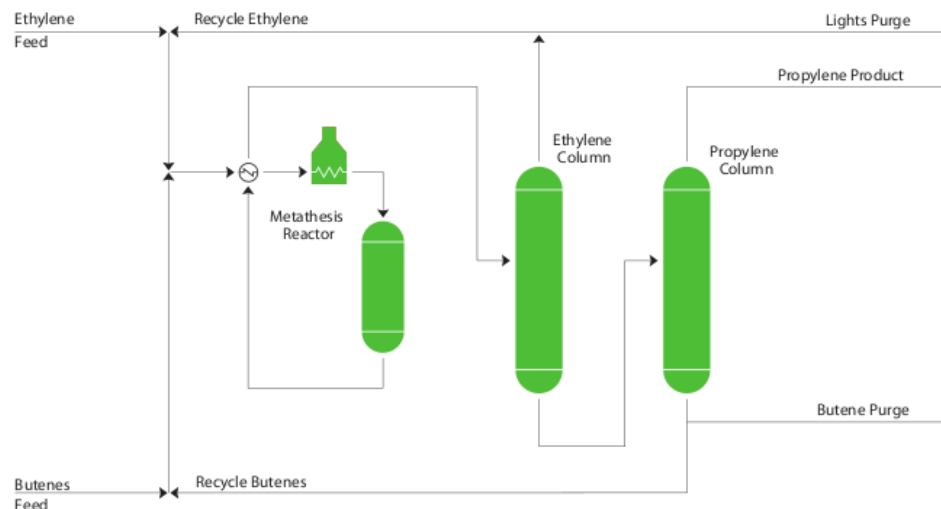
■ Propene Synthesis:

The remainder of industrial propene comes from olefin metathesis.

The propene and ethylene/butene equilibrium reaction was originally discovered in 1964 by scientists at Phillips, who employed $\text{Mo}(\text{CO})_6$ or $\text{W}(\text{CO})_6$ on alumina at 90-315°C. Back then, propene was less desirable than ethylene and butane.

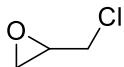
Today, WO_3 on silica is used to catalyze the reverse reaction forming propene from ethylene and butene. This reaction can be coupled to ethylene dimerization and butene isomerization processes to produce propene with >90% selectivity. Lummus licenses this technology to refineries. LyondellBasell operates the largest metathesis plant, with an estimated capacity of 0.5 Mt/a.

*Process Flow
Diagram*



■ Propene Economy:

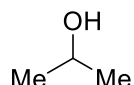
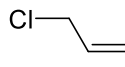
worldwide: ~0.8 Mt/a in 1997



epoxy resins

>90%

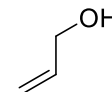
worldwide: 0.8 Mt/a in 1997



worldwide: 0.87 Mt/a in 2003
1-propanol produced
by hydroformylation of ethylene

polystyrene-supported
sulfonic acid or supported
WO₃, H₂O

worldwide: 0.05 Mt/a in 1990,
also from allyl chloride



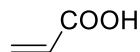
glycerol

worldwide: ~18 Mt/a
also from other
isobutene sources
MTBE

Li₃PO₄, ~300°C

styrene

+ t-BuOH or methylbenzylalcohol



Mo and Te oxides

O₂

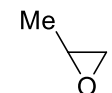
worldwide: ~3.8 Mt/a in 2002

acrylate esters, then polymers



2-step via chlorohydrin/substitution or

1-step coupled to t-BuOOH or ethylbenzene
hydroperoxide (from alkane + O₂)



worldwide: 8.6 Mt/a
economics of synthesis
depend greatly on byproduct values

NH₃, 3/2 O₂ cat. Bi₉PMo₁₂O₅₂, 400-510°C
Sohio process



+ MeCN (~3-4%)
worldwide: ~0.02 Mt/a in 1986

worldwide: ~5 Mt/a in 2000

acrylonitrile-butadiene-styrene (ABS) polymer,
acrylamide polymers

~60-75%

polyurethanes

■ Statistics:

In 2010, the global consumption of benzene was ~40 Mt/a.

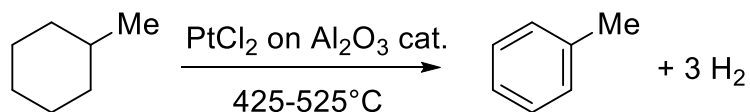
While benzene, toluene, and xylenes (BTX) are found in crude oils, they are present in such small quantities that they are not worth isolating

While historically much of BTX was isolated as byproducts of coal refining (e.g. for production of hard coke for the steel industry), most of the world's BTX today comes as the byproducts of catalytic reforming of "heavy" low-octane naphtha to high-octane naphtha and as the byproducts of ethylene production.

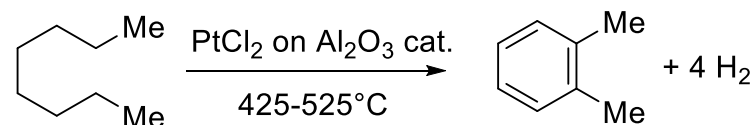
■ Catalytic Reforming:

Catalytic reforming employs noble metal (Pt/Re) catalysts to dehydrogenate and isomerize C₆-C₈ alkanes, leaving higher ratios of desired branched products and C₉+ components as well as BTX byproducts

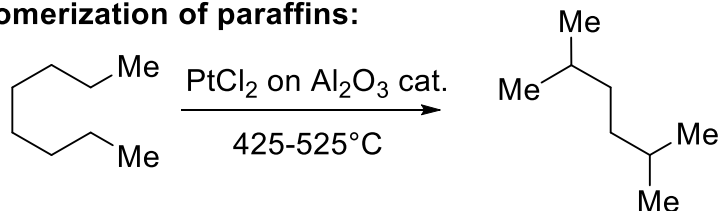
Dehydrogenation of naphthenes:



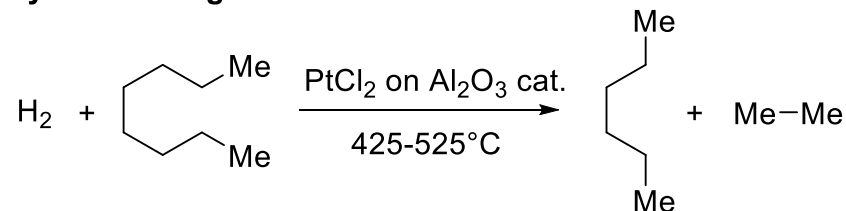
Cyclodehydrogenations:



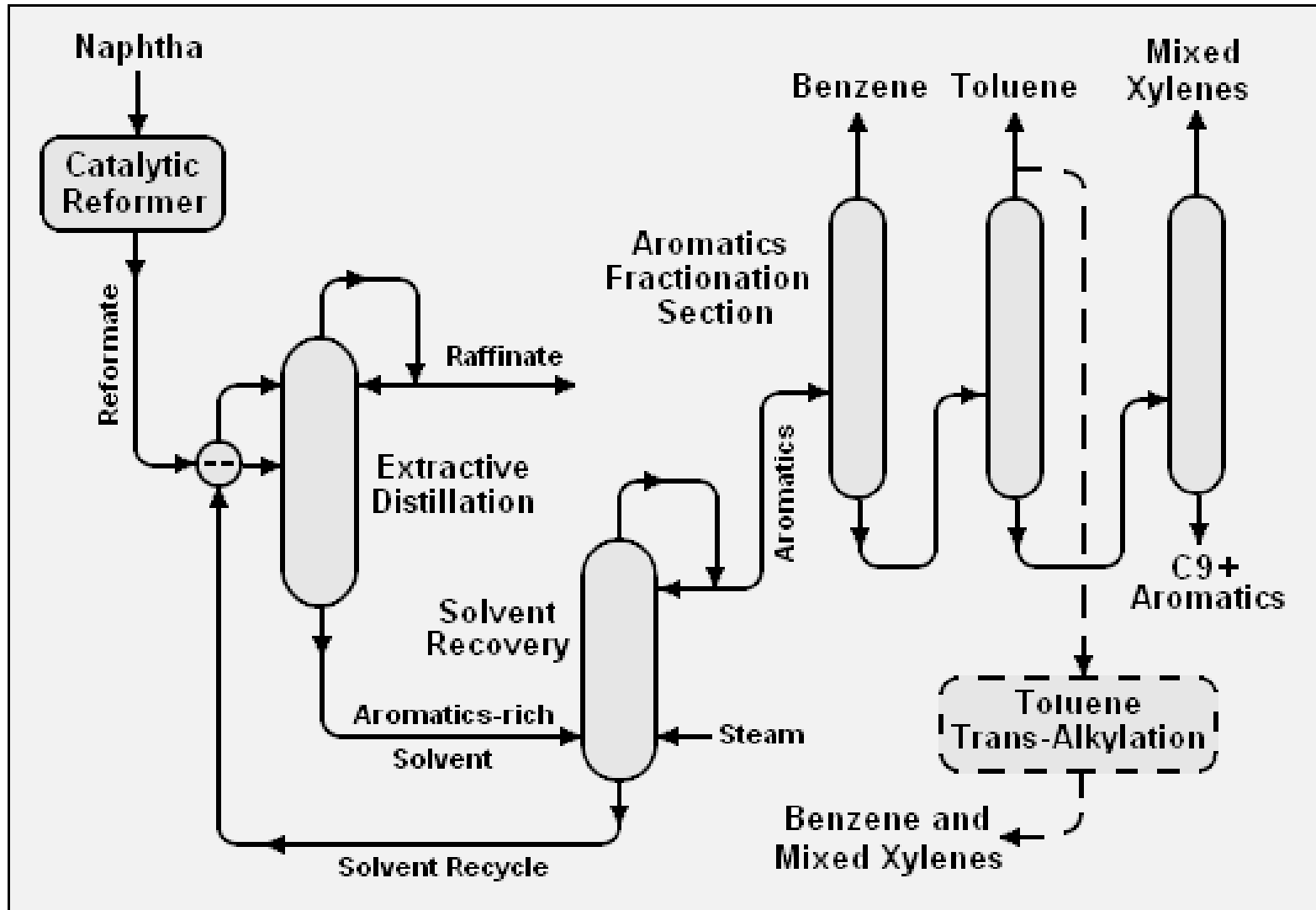
Isomerization of paraffins:



Hydrocracking:



■ Simplified Process Overview:



■ Separation of Aromatic Components:

Since BTX is produced as a byproduct, the most important part of benzene, toluene, and xylene production is the actual isolation of the fractions. In different processes, different heavy solvents are used to extract the BTX. BTX is then distilled from the heavy solvent, providing highly pure benzene, toluene, and xylenes.

Process	Solvent
Edeleanu	sulfur dioxide
Udex	diethylene glycol and others
Sulfolane	sulfolane
Arosolvan	1-methyl-2-pyrrolidone
IFP	dimethyl sulfoxide
Formex	<i>N</i> -formylmorpholine
Morphylane	<i>N</i> -formylmorpholine

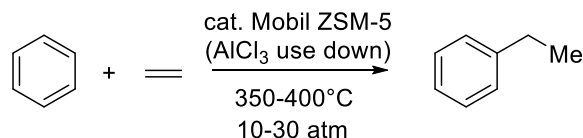
The sulfolane process, developed by Shell, is the most widely used extraction process today.

■ Catalytic Reforming:

Often, toluene and xylenes are converted to benzene since benzene is in much greater demand. This is accomplished by two common methods: hydro-dealkylation with hydrogen gas (toluene + H₂ to benzene + methane), or catalytic disproportionation (2 toluene to 2 benzene + ethane).

■ Benzene Economy:

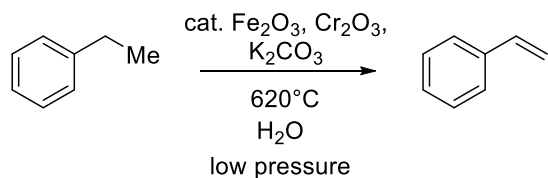
Ethylbenzene synthesis:



worldwide: 25 Mt/a in 2009

AlCl₃ use is being phased out due to waste concerns, old factories still operational but new factories all use zeolite

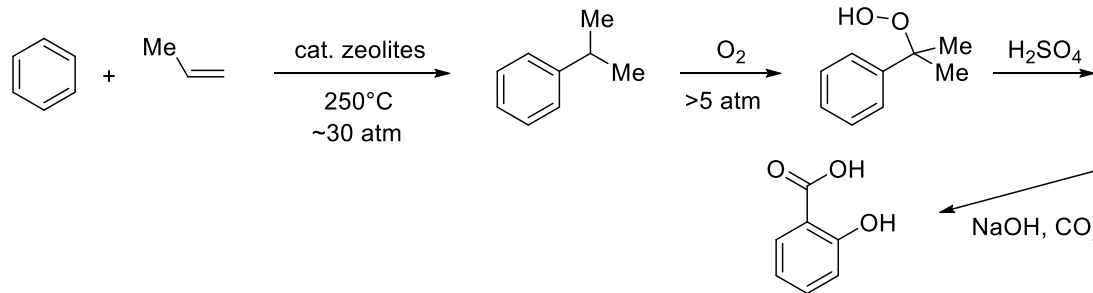
Styrene synthesis (steam cracking):



worldwide: 18 Mt/a in 2009

hydrogen gas is recycled to other parts of petrochemical complex - alkali helps catalyze de-coking to keep catalyst alive

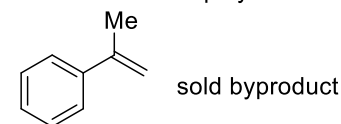
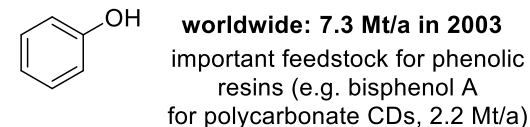
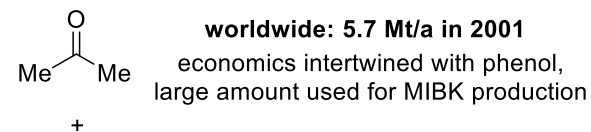
Cumene (Hock) process:



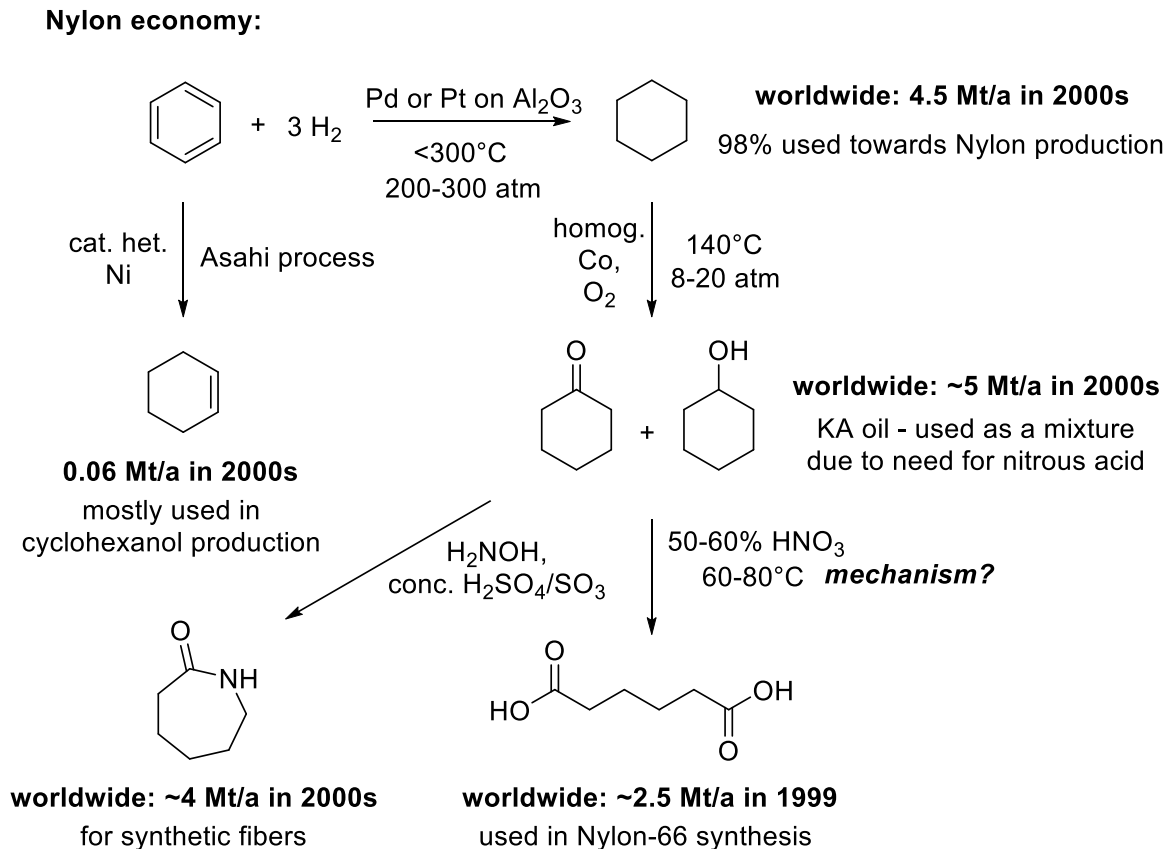
worldwide: 0.06 Mt/a in 2001



ketones (e.g. MVK)

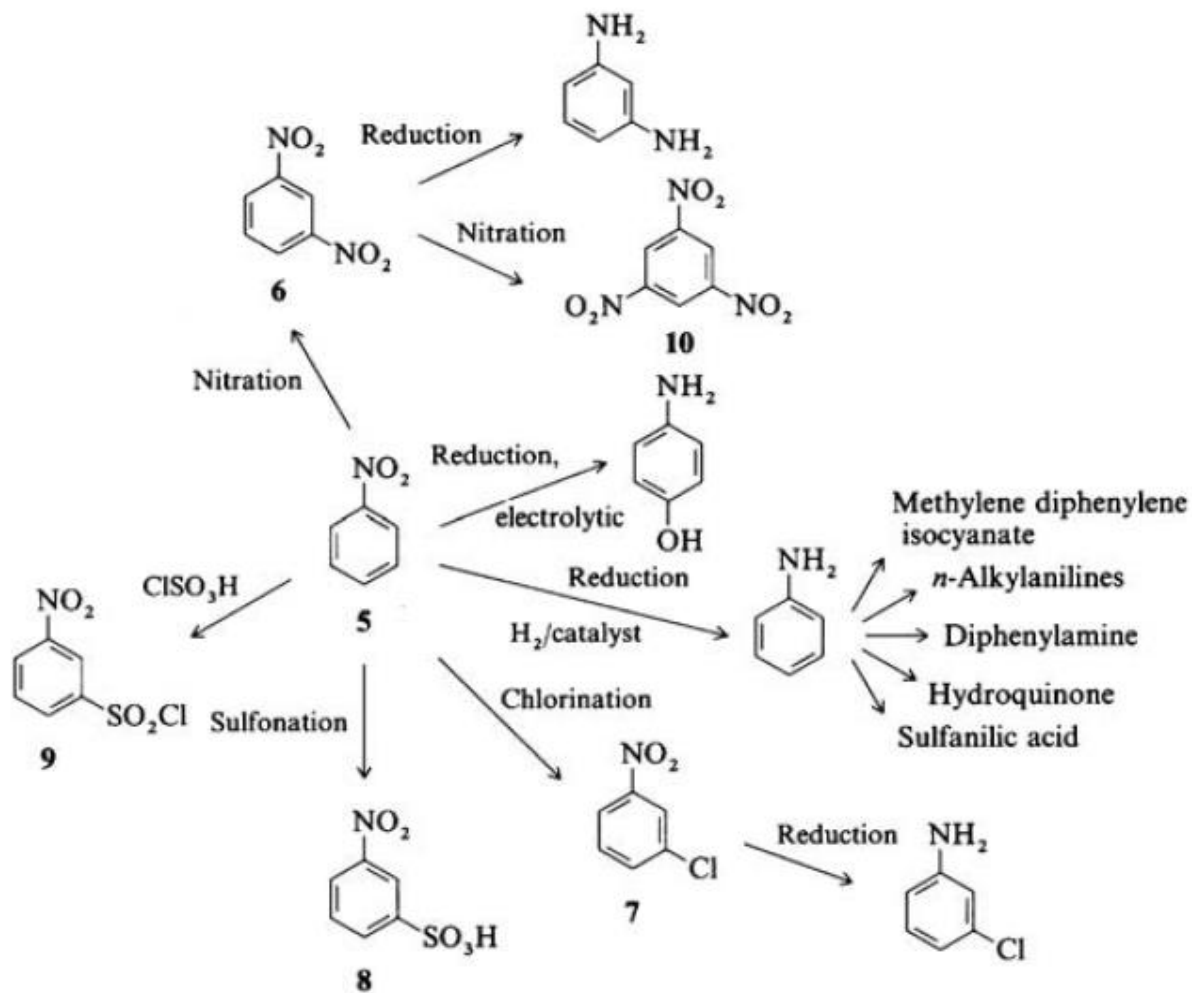


■ Benzene Economy:



Chlorobenzene, bromobenzene, nitrobenzene, anthraquinone, maleic anhydride also derived from benzene, although maleic anhydride is now primarily being produced from *n*-butane due to rising cost of aromatics

■ Benzene Economy:



■ Statistics:

Global production capacity exceeds 7 Mt/a. Most of this is used in the production of vinyl acetate (for latex emulsion resins in paints, adhesives, paper coatings, and textiles treatment) and acetic anhydride (acetylating agent for cellulose-based materials)

Vinegar is still made by the 5000-year-old process of wine fermentation.

Chloroacetic acid, acetoacetic esters, malonates, glycine, etc. all derived from acetic acid

■ Production:

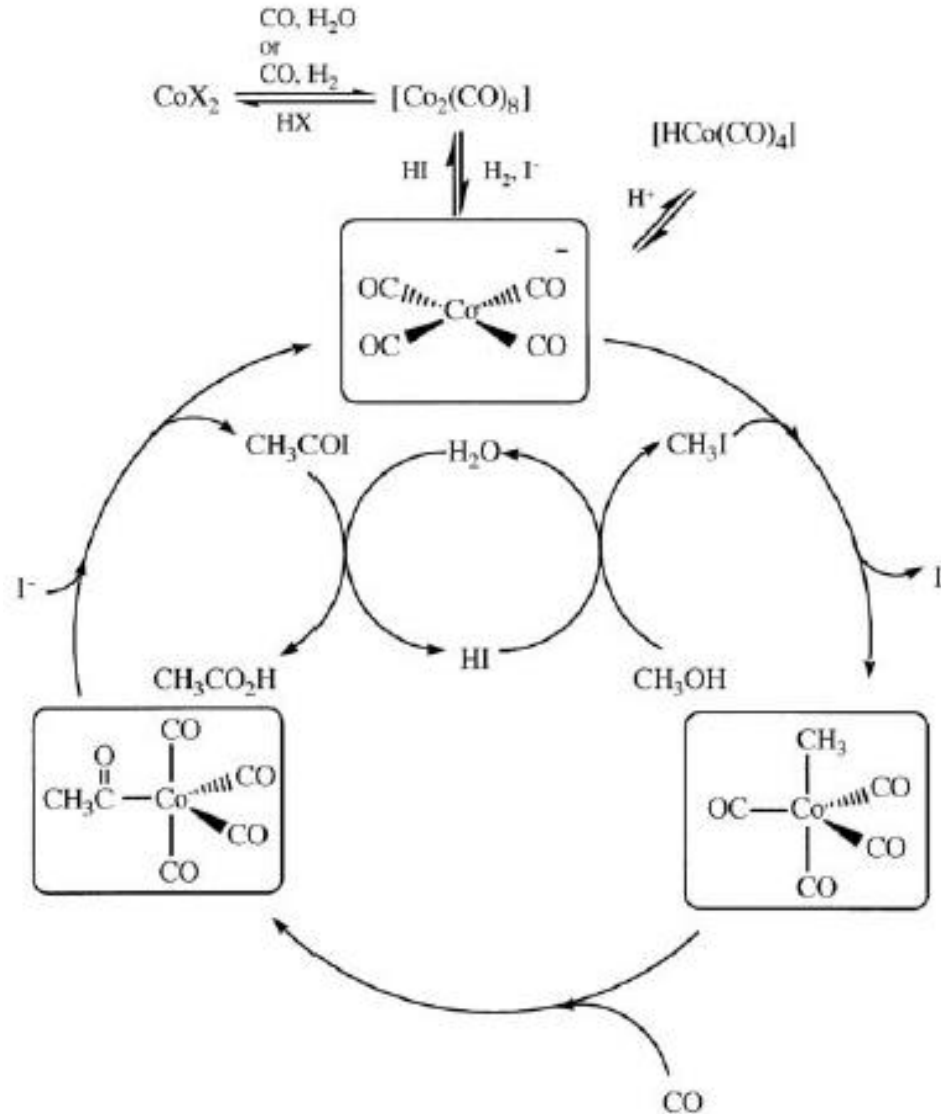
Acetic acid is predominantly synthesized by catalytic methanol carbonylation. This reaction was known as early as 1913 by scientists at BASF. A cobalt catalyst was discovered by Reppe in BASF in the 1940's and the process commercialized in the 1960's.

In the 1960's, Monsanto developed a rhodium iodide catalyzed process operable at atmospheric pressure with yields of 99% and 90% from methanol and CO, respectively.

While Monsanto scientists found that iridium also catalyzed the reaction, this didn't become optimized and commercially deployed until the 1990's, after the rights to the carbonylation process was bought by BP Chemicals. This Cativa process currently dominates the synthetic acetic acid market.

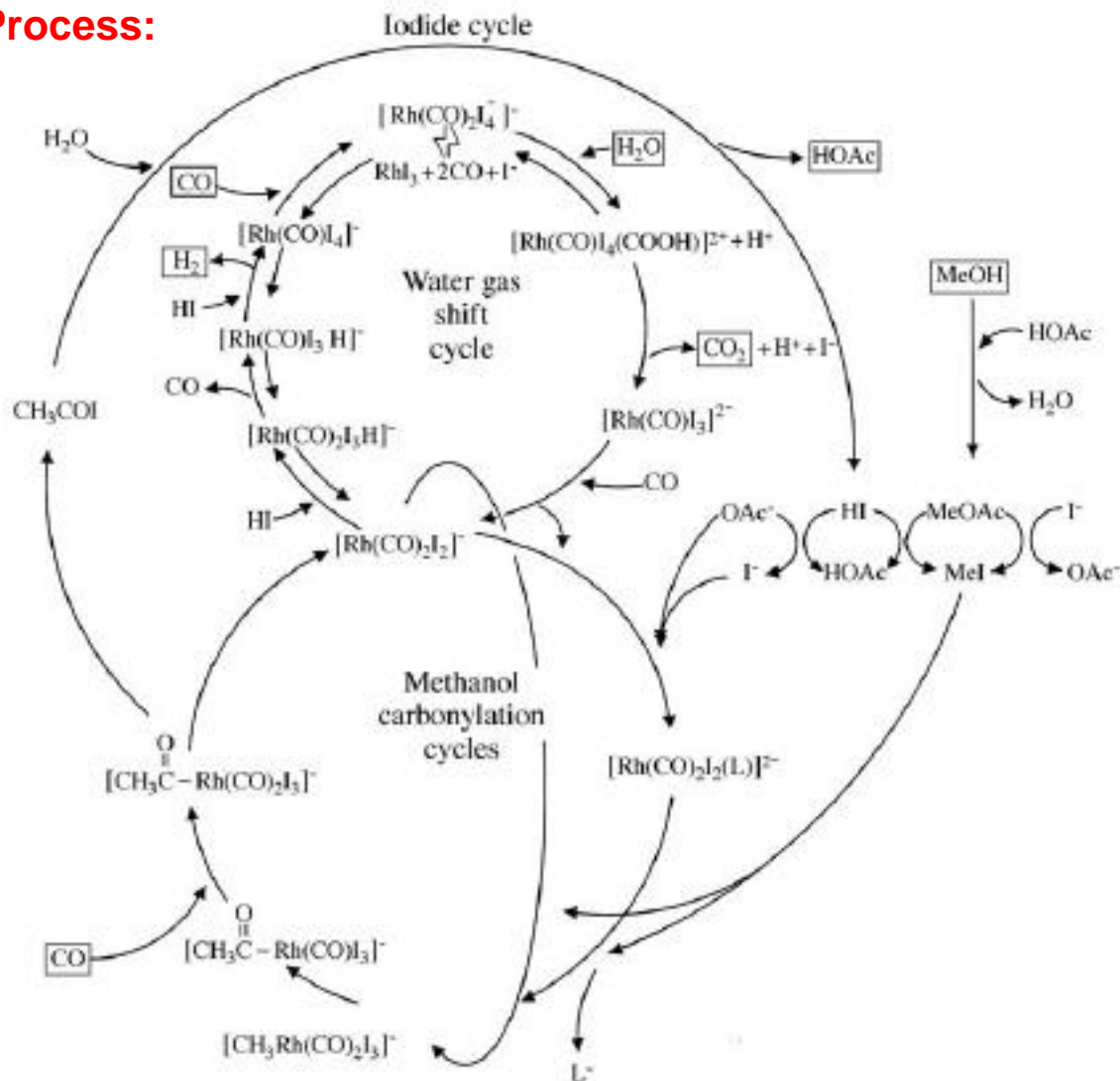
In the 1980's Eastern Chemical developed an acetic anhydride synthesis using methyl acetate and lithium iodide instead of methyl iodide. This process was not covered by the Monsanto patents.

■ BASF Process



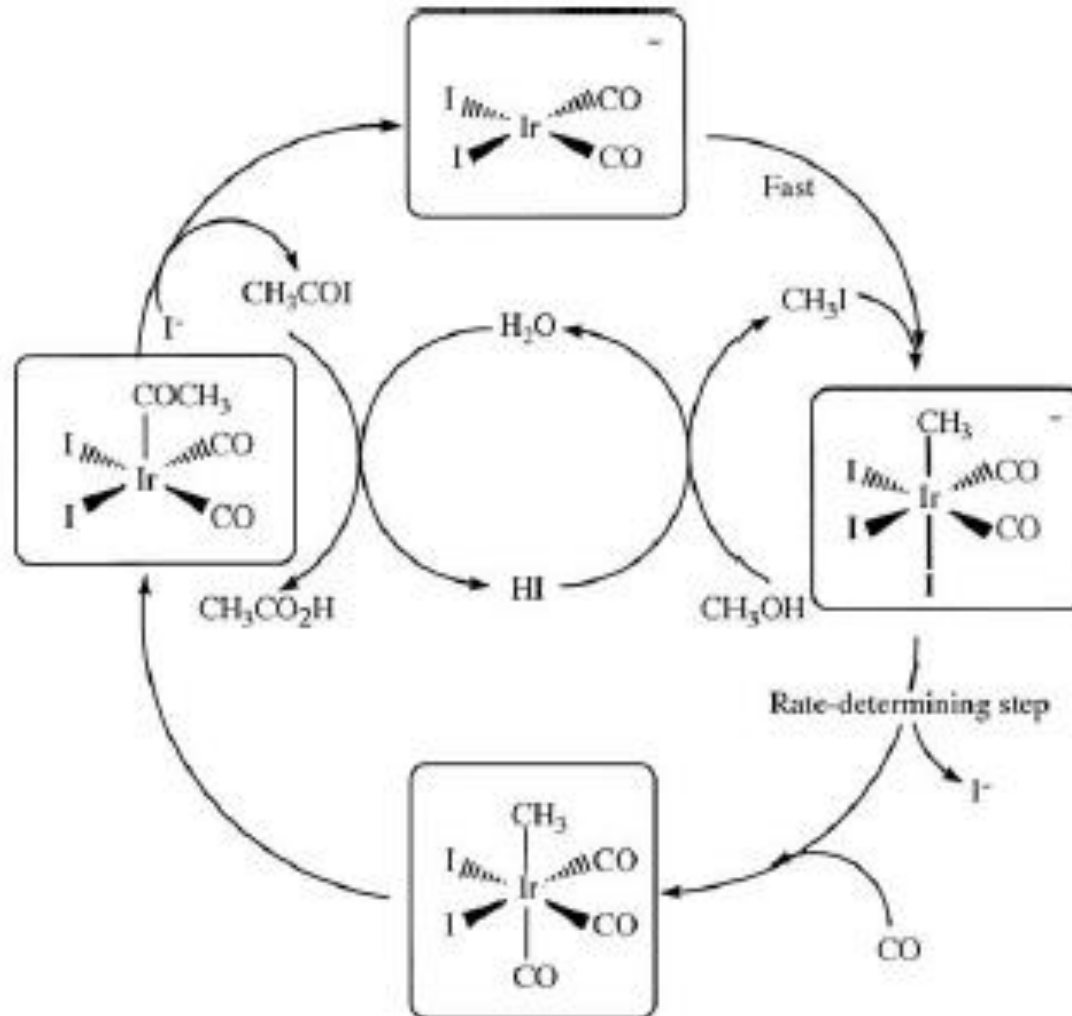
Water-gas shift reaction produces significant amounts of hydrogen, resulting in byproducts like methane and propionic acid.

■ Monsanto Process:



Inorganic iodide addition dramatically improves selectivity and rates. RDS is proposed to be the oxidative addition of methyl iodide due to a direct rate dependence on MeI conc. H_2 from water-gas shift reaction is needed to re-reduce dead $\text{Rh}(\text{III})$ species.

■ Cativa Process:



Rate-determining step is proposed to be Me-group migration to form acyl complex.

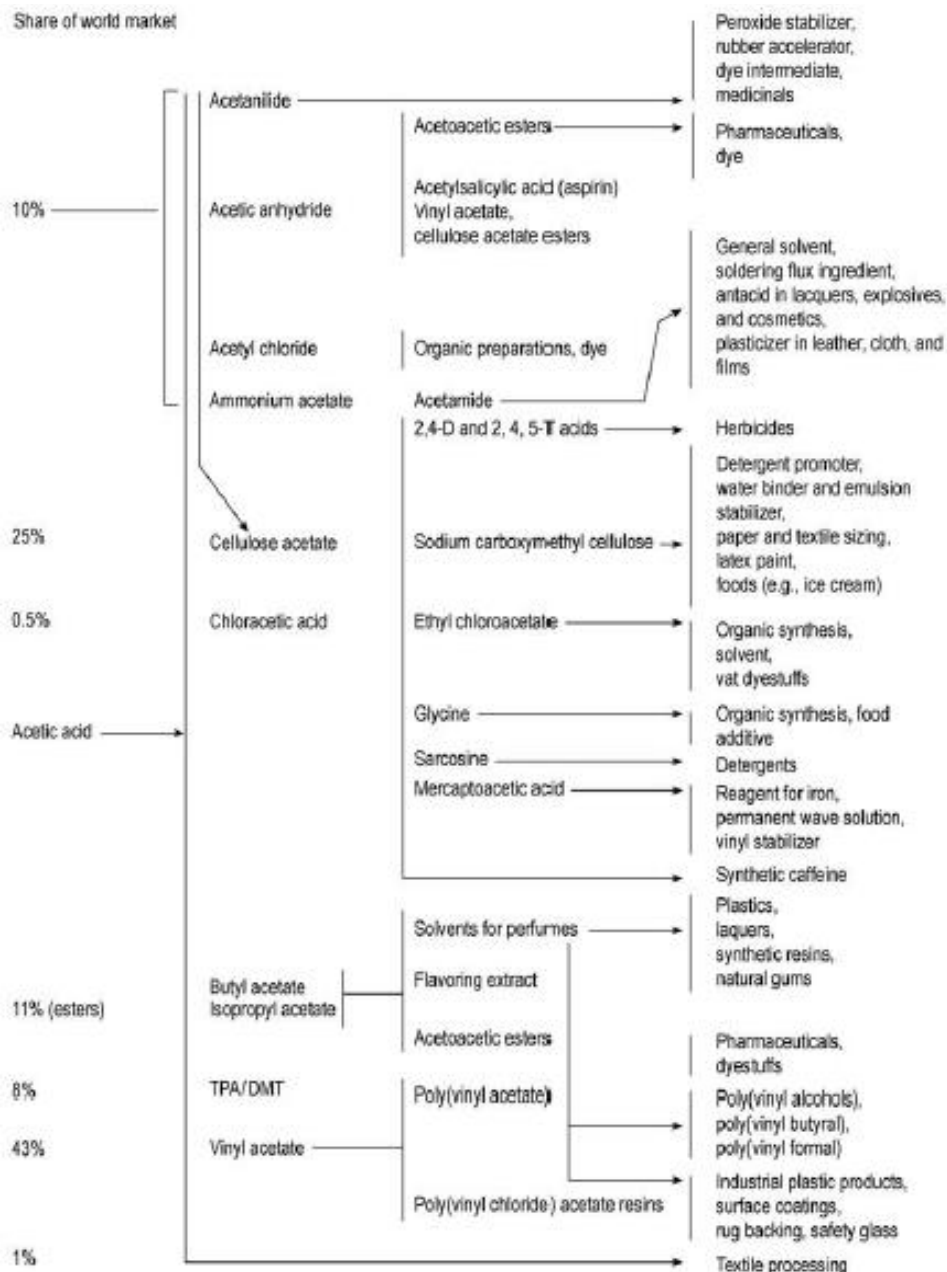


Figure 8. Uses of acetic acid

■ Miscellaneous Chemicals:

Cyclopentadiene is isolated from cracking processes (40 kg per ton of naphtha), further refined to chemicals such as cyclopentene and fluorobenzene

Cyclooctadiene and cyclododecatriene are produced by Ni-catalyzed cyclooligomerizations of butadiene and hydrogenated to their respective mono-enes. Cyclooctene is used for ring-opening metathesis polymerization and cyclododecene is used to make lauro lactam.

Vinyl cyclohexene is a byproduct of cyclooctadiene manufacture

Catechol comes from the destructive distillation of plant catechin, a byproduct of wood processing – this is further converted to guaiacol and vanillin (0.01 Mt/a)

Dimethyl sulfide is a byproduct of H₂S-based wood pulping (paper industry, sulfide used to decompose lignin) – this is used to make DMSO and other sulfur-containing compounds

Dichloromethane, chloroform, and carbon tetrachloride come from the radical chlorination of methyl chloride by chlorine gas.

TiCl₄ is an intermediate in TiO₂ synthesis (>2 Mt/a) for pigments

For comparison, a “large-scale” synthesis of Naproxen in 1970s would be ~500 kg/a! This is even at a ~500 mg/tablet dosage level.

■ Chiral Pool:

Sourcing for the pharmaceutical industry is different – since the value of a drug is very time-dependent, 3-5 years developing a fermentation route to a chiral building block may not be worth the time, even if its cheaper than a synthetic process! (3 month delay could mean \$150 million in lost sales!) A low dosage drug may only require 10 kg of a chiral building block for the entire synthesis.

L-tartaric acid from wine is produced on a 30,000 t/a scale in France, Spain, and Italy – it is a major byproduct of distillation, isolated as the calcium salt and re-acidified. DL-tartaric acid, from which the D-isomer is resolved, is made from the epoxidation of maleic anhydride (one plant in South Africa...)

L-Phenylalanine is fermented on a 12,000 t/a scale for aspartame. D-phenylalanine is only used on a ton scale and is produced by chemoenzymatic resolution. L-aspartate is produced on the same scale by chemoenzymatic synthesis from maleic anhydride.

D-glucose, D-sorbitol, D-fructose, D-mannitol are all widely available. Protection and oxidative cleavage provide smaller chiral fragments.

Alpha-Pinene is isolated from pine trees in ~91% ee and upgraded to 99.5% ee by formation and decomposition of $(\text{Ipc})_2\text{BH}$.

D, L, and DL-limonenes are isolated from fruit oils.

Menthol is available from the Takasago synthesis.

■ Chiral Pool:

L-Carvone is prepared from limonene by NOCl oxidation.

Camphor is produced from pinene through an acid-catalyzed rearrangement followed by oxidation (~25,000 t/a).

Merck selectively crystallizes L-DOPA on a scale of ~500 t/a.

D-proline is produced from dynamic crystallization of DL-proline in the presence of D-tartaric acid. D-tartaric acid is recycled.

~700 tons/a of cinchona alkaloids are isolated from bark.

Phenethylamine and cyclohexane-diamine are resolved with tartaric acid.

■ Conclusions:

For “world-scale” chemicals, most of what we pay in the laboratory is for quality control, shipping, and packaging (e.g. ethylene lecture bottles) – some chemicals themselves are not even worth selling at less than 500,000 ton per annum rates!

Changes in the economic environment can have enormous consequences on the world’s chemical supply chains: think 2008

The cost of raw materials and the amount of waste is truly trivial for the pharmaceutical industry when compared to the energy, textiles, metals, plastics, dyes, agricultural, etc. industries! The pharmaceutical industry could really be thought of more as a service industry.

What is our role in academia? Arguably to discover new chemical entities, properties, and to understand and predict chemical phenomena.

A lot of ingenious engineering is taken for granted by chemists – have confidence that if what you make is truly useful, process chemists and engineers will figure out a great way to make it!

Selectivity is often more important than conversion – recycling is used to drive reactions to completion (even unfavored equilibrium reactions!) and separation/purification processes are much more intensive than the actual reactions.

Chemists and chemical engineers will always be in demand – if not in abundance in the pharmaceutical industry, in virtually any other product-based industry in the world.