A century of petrochemical advances

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Abstract

The beginnings of the petrochemical industry date back more than 150 years. The first chemicals produced were aniline and dyestuffs and other derivatives from coal starting in the mid-1800s. Then, scientists in Germany led major advances, starting from acetylene production via Reppe's chemistry. This presentation gives an overview from these early beginnings to modern day cracking for ethylene and propylene production and modern aromatics complexes, derivatives, and the like, to next generation technologies on the horizon, such as those based on natural gas or on coal to olefins via syn gas and methanol intermediates.

Historical perspective

We think it is fair to claim that the petrochemical industry was born and developed as a result of the dyestuff industry, or rather from the quest for synthetic dyes, in particular synthetic indigo, a naturally occurring blue dye extracted from a number of plants in SE Asia, and in Central and South America. While natural indigo was used throughout the XIX century, today all indigo-type dyes are synthetic.

The main precursor of all modern synthetic dyes was aniline, the simplest aromatic amine. The following was liberally abstracted from a Wikipedia contribution on “aniline”:

> Aniline was first isolated from the destructive distillation of indigo in 1826 by Otto Unverdorben, who named it *crystalline*. In 1834, Friedrich Runge (Pogg. Ann., 1834, 31, p. 65; 32, p. 331) isolated from coal tar a substance that produced a beautiful blue color on treatment with chloride of lime, which he named *kyanol* or *cyanol*. In 1841, C. J. Fritzsche showed that, by treating indigo with caustic potash, it yielded an oil, which he named *aniline*, from the specific name of one of the indigo-yielding plants, *Indigofera anil*, anil being derived from the Sanskrit nīla, dark-blue, and nīlā, the indigo plant. About the same time N. N. Zinin found that, on reducing nitrobenzene, a base was formed, which he named *benzidam*. August Wilhelm von Hoffmann investigated these variously-prepared substances, and proved them to be identical (1855), and thenceforth they took their place as one body, under the name *aniline* or *phenylamine*.
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> Its first industrial-scale use was in the manufacture of *mauveine*, a purple dye discovered in 1856 by Hoffmann's student William Henry Perkin (for whom the Perkin medal was later named by the Society of Chemical Industry to honor outstanding contributions in the field of industrial chemistry). The great German chemist von Hoffmann (whose name is variously spelt Hoffman or Hofmann) had been brought over to England by queen Victoria’s prince consort, Albert, to teach at the Royal College of Chemistry in London. At the time of *mauveine*'s discovery, aniline was an expensive laboratory compound, but it was soon prepared "by the ton" using a process

previously discovered by Antoine Béchamp. The synthetic dye industry grew rapidly as new aniline-based dyes were discovered in the late 1850s and 1860s.

On this basis, we can place the birth of the petrochemical industry in the mid-1800s. However, a parallel chemical or "petrochemical" industry had derived in parallel in the meantime based on the recovery of fractions from coal tar distillation, principally in Germany and around Manchester, in Lancashire. Before we proceed we must give credit to Peter H Spitz for his volume "Petrochemicals – The rise of an Industry," published by John Wiley and Sons in 1988. From here onwards, any quotations or references derived from this book will be simply denoted by (*).

Coal tar and coke oven gases had been used to produce chemicals in Lancashire as early as 1817 (*), A number of compounds were separated and identified. In addition to the basic aromatics, from benzene to naphthalene and anthracene, other derivatives were produced: nitrobenzene, phenol, picric acid, and others. Subsequent efforts, however, centered on the synthesis of dyestuffs, and in this area, the German chemical industry soon took an undisputed leadership. After beating Perkin's patent application for the synthesis of alizarin by one day (*) the German chemists proceeded to commercialize symtheses for methylene blue, scarlet red, benzopurpurin, etc. Not surprisingly, the three larger German chemical firms that formed the huge I.G.Farbenindustrie chemical combine all had names associated with dyestuffs : Badische **Anilin** und Soda Fabrik, **Farb**werke Hoechst, and **Farben**fabriken Bayer, as did the combine itself (I.G. **Farben**).

In reality, then, the petrochemical industry derived from coal and is thus aptly named. It evolved along a number of semi-independent branches, not all simultaneously. Most of the early processes were developed by industrial chemists ("chemical engineering" as such did not yet exist) in Germany and were based on the use of acetylene and benzene (and the other aromatics). Although known, ethylene at the time was far from being an industrial commodity.

Over and over again we come to realize that the petrochemical industry largely developed in Germany and was based on coal. The petrochemical industry that developed in the Unite States in the 1930s and 1940s had the advantage of having virtually unlimited supplies of petroleum and natural gas in the US Gulf Coast and thus gave the US a significant edge in the war effort over Germany. Although a lot was known about the prowess of the German petrochemical industry, it was only at the end of World War II that its full vastness, inventiveness, and creativity were revealed when the CIOS (Combined Intelligence Objectives Subcommittee) teams carefully described the products and technologies at the many German plants, principally at I.G. Farben (BASF, Hoechst, Bayer, and others), Chemische Werke Hüls, etc

The first large-scale synthetic petrochemical was acetylene. Production of acetylene by the hydrolysis of calcium carbide had been shown by a French scientist, Moissan, in 1892. Calcium carbide was produced by the high-temperature processing of coal and limestone mixtures in an electric furnace. This technology was widely used in Germany and other countries (e.g. Union Carbide in the United States); its current use is pretty much obsolete and discontinued, but at least only a few years ago (in the early 1990s) a plant was still operational in Guizhou, China.

Table 1

Historical dates of the first commercial production of some important organic chemicals (*)

phenol	F Raschig (Germany)	1901
	Hoffmann-LaRoche (Switzerland)	
carbon tetrachloride	Griesheim-Elektro (Germany)	1903
trichloroethylene	Wacker (Germany)	1908
ethylene	Griesheim-Elektro (Germany	1913
ammonia	BASF (Germany)	1913
acetic acid	Wacker (Germany)	1916
ethylene oxide	BASF (Germany)	1916
acetaldehyde	Hoechst (Germany)	1916
acetone	Hoechst (Germany)	1917
	Weitzman (UK)	
	Standard Oil of NJ (US)	
vinyl acetate	Shawinigan Chemicals (Canada)	1920
methanol	BASF (Germany)	1923
butanol	BASF (Germany)	1923
vinyl chloride	Wacker (Germany)	1930

As early as 1863 another French chemist, Berthelot, had discovered that acetylene can be produced by passing methane gas across an electric arc. This technology was finally incorporated into the industrial production of acetylene in Germany in the mid-1920s and early 1930s, and, in a more modern version, is the technology used by Chemische Werke Hüls and its successor companies (Oxeno, etc.) in Marl, Germany. In the United States a similar technology was commercialized By the Standard Oil Company (New Jersey) (now Exxon-Mobil) in co-operation with I.G. Farben.

Acetylene was primarily used to produce acetaldehyde using a mercury-sulfuric acid catalyst (still in use at Guizhou) that could be converted to acetic acid. More importantly, however, was the alkaline aldol condensation of acetaldehyde followed by hydrogenation to butylenes glycol over a copper-chrome catalyst (*). Dehydration to butadiene was effected over a phosphate catalyst supported on coke. Butadiene is the main component in the production of synthetic rubber of vital importance in the war effort.

Ethylene could be recovered as a byproduct from the production of acetylene or by the selective hydrogenation of ethylene. Ethylene was alkylated with purified coke-oven benzene in the liquid phase with $AlCl_3$ catalyst (*) and the resulting ethylbenzene dehydrogenated to styrene over zinc oxide.

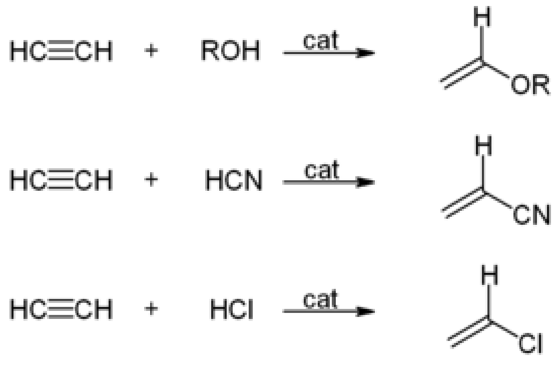
Interestingly, olefins were also produced in Germany by the Fischer Tropsch technology from CO/H_2 mixtures (synthesis gas or syn gas) obtained from a Winkler coal gasifier (*). These olefins ranged from ethylene to the C_{11} to C_{17} fraction and were use for the production of alcohols (and detergents) in what was probably the first Oxo unit ever built. This work was based on the discoveries of Franz Fischer and Hans Tropsch who in 1925 had demonstrated that syn gas could be converted into mixtures of liquid oxygenates and hydrocarbons at relatively mild operating conditions and, even today, is the best solution for a petrochemical and fuels industry that can become relatively independent from petroleum consumption. The first commercial Fischer-Tropsch unit was built by Ruhrchemie in Holten in 1934 (*).

Although not a petrochemical as such, ammonia plays a critical role in the petrochemical industry, Here too the contributions of German industrial chemists were fundamental. The ideas developed by Fritz Haber and the reactor design by Carl Bosch resulted in the commercialization of the so-called Haber-Bosch ammonia synthesis process that first came on stream in 1913. Perhaps lesser known are the catalyst discoveries contributed by Alwin Mittasch (*) (who had first synthesized methanol from syn gas as early as 1913) who supposedly tested over 20,000 different catalytic materials (an early version of combinatorial chemistry!) to finally arrive at a catalyst composed of magnetite with a few percent aluminum and a small amount of potassium.

In all of the above, German industrial chemists made great strides at understanding and developing the role of catalysts in chemical syntheses. This also contributed to the development of technologies for the production of a large variety of chemicals: phthalic anhydride by the liquid-phase oxidation of naphthalene with a mercury catalyst (only later replaced by the vapor-phase oxidation over vanadium pentoxide); sulfuric acid by the direct oxidation of sulfur dioxide with air; production of hydrocarbon fuels by the direct hydrogenation of coal; the synthesis of methanol and higher alcohols from synthesis gas using a zinc-chromium catalyst; high-pressure urea synthesis; various applications of carbonylation and hydroformylation reactions; hydroforming of paraffins to aromatics (a precursor of later catalytic reforming technologies), etc. First and foremost was perhaps the development of the so-called “Reppe chemistry” after Walter Julius Reppe (1892-1969) that exploited a number of interesting applications based on acetylene. The following is copied from Wikipedia:

The high pressure reactions catalysed by heavy metal acetylides, especially copper acetylide, or metal carbonyls is called Reppe Chemistry. Reactions can be classified into four large classes:

- Vinylization according to the equation:

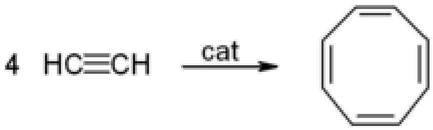


- Preparing ethynyldiols from aldehydes according to the equation:

- Reactions with carbon monoxide:

This simple synthesis was used to prepare acrylic acid derivatives for the production of acrylic glass.

- Cyclic polymerization of acetylene



This reaction provided an unusual route to benzene and especially to cyclooctatetraene, which was difficult to prepare otherwise.

Products from these four reaction types proved to be versatile intermediates in the syntheses of lacquers, adhesives, foam materials, textile fibers, and pharmaceuticals that could now be produced.

Not to be overlooked also were the early developments of plastics and synthetic fibers: nylon 6,6 from adipic acid and hexamethylenediamine (HMDA) developed by Wallace Hume Carothers at DuPont (1935), or nylon 6 from the self-polymerization of caprolactam developed by Paul Schlack at I.G. Farben (1938), or the early polyesters (also by Carothers although initially dismissed by him as impractical), polyurethanes (initially from hexamethylene-di-isocyanate and 1,4-butanediol), and many others ranging from poly-vinyl chloride to chloroprene or neoprene.

Today's petrochemical industry

Today's petrochemical industry is perhaps better viewed as families of compounds derived from a starting feedstock. The main starting feedstocks are olefins and aromatics. An alternative starting feedstock is synthesis gas or "syn gas" (mixtures of H_2 and CO) that can be obtained from any hydrocarbonaceous material ranging from methane to coal.

While the early petrochemical industry was based on acetylene, modern petrochemicals are derived from olefins. Although still very reactive, olefins are much less energetic than acetylene and, thus, more stable, safer, and economic to produce. Invariably, most olefins are produced by the cracking of hydrocarbon feedstocks, whether thermal or catalytic. An alternative route, still not fully commercialized, produces olefins by the catalytic conversion of methanol (from syn gas). A relatively obsolete route (for economic reasons) is the production of ethylene by the dehydration of ethanol from bio sources.

Thermal cracking of hydrocarbons in the presence of dilution steam (steam cracking)is by far the largest source of olefins. If the hydrocarbon is ethane, the product olefin is ethylene obtained in high yield. If the feed hydrocarbon is heavier – propane, butane, naphthas, or even gas oil – the product olefins range from ethylene to C_5s and aromatics. Typically, the yield of ethylene decreases with increasingly heavier feedstocks, while the yield of propylene remains fairly uniform. Because of the variety of valuable coproducts and byproducts obtained from steam cracking, this type of unit invariable is the focal point of very large industrial complexes. While the first steam cracking units built in the early 1940s had relatively small ethylene capacities (6000 to 10000 t/year), modern large-scale complexes routinely produce in excess of 500,000 t/year ethylene. The major coproducts and byproducts include:

- propylene
- 1,3-butadiene
- Isobutylene
- 1-butene (and perhaps 2-butene)
- py gas – a C_5+ cut rich in olefins and aromatics from which various olefins and diolefins (e.g., isoprene) can be recovered, as well as BTX (benzene, toluene, and xylenes) and heavier aromatics

Ethylene and propylene (and, if recovered, 1-butene) are routinely upgraded to polymer-grade quality (at least 99.95% purity in the case of ethylene) by means of fractionation . The products are usually shipped to separate polymerization facilities but such facilities are sometimes integrated within the complex. All the products from s steam cracker find use in a myriad of petrochemical derivatives. To name but a few:

- from ethylene
    - ethylene oxide – by direct catalytic oxidation
    - ethylene glycol – by the hydration of ethylene oxide
    - ethylene dichloride/vinyl chloride – via chlorination and oxychlorination
    - acetaldehyde – by ethylene oxidation in either a one-step or a two-step process
- from propylene
    - propylene oxide – by propylene epoxidation, either via the chlorohydrins process or by means of a hydroperoxide (isobutane hydroperoxide to yield *tert*-butanol or MTBE as a coproduct, or, more importantly, ehylbenzene hydroperoxide to yield styrene as a coproduct)
    - propylene glycol – via propylene oxide hydration
    - acrylonitrile – via the ammoxidation of propylene; acetonitrile and hydrogen cyanide are major valuable coproducts; acrylonitrile can also be dimerized to adiponitrile via an electrochemical or a chemical process
    - acrolein and acrylic acid – by direct catalytic oxidation; methionine is also an important derivative of acrolein
- from butenes
    - *tert*-butanol or MTBE from isobutylene; methacrylayes can be prepared from *t*-butanol
    - *sec*-butanol and methyl ethyl ketone (MEK), usually from 2-butene
    - maleic anhydride, currently mostly obtained by the catalytic oxidation of n-butane and an intermediate in the production of 1,4-butanediol
    - high-octane motor fuel alkylate by the alkylation of 2-butene with isobutane
    - high-octane motor fuel gasoline by the condensation of isobutylene with itself or with other butenes, followed by hydrogenation of the resulting products
    - 1,3-butadiene for the production of various synthetic rubbers and polymers (polybutadiene, acrylonitrile-butadiene-styrene, etc.)
    - adiponitrile from 1,3-butadieneby hydrocyanation; adiponitrile can be used to produce hexamethylene diamine (HMDA)
- from benzene
    - ethylbenzene and styrene
    - cumene (isopropyl benzene) phenol and acetone (acetophenone is a byproduct)
        - from acetone – methacrolein, methacrylic acid, and methacrylates
        - from acetone – ketene and acetic anhydride
        - from acetone and phenol – bisphenol A and polycarbonates
        - from phenol –aniline (alternative route)
        - from phenol – cyclohexanol and cyclohexanone (alternative route)
    - cyclohexane
        - cyclohexanol and cyclohexanone, intermediates for the production of caprolactam (and nylon 6)

        - adipic acid (also from phenol and other sources); my be used in theproduction of adiponitrile, 1,6-hexanediol, 6-hydroxycaproic acid, etc.
    - nitrobenzene and aniline (also from phenol); also diamines; anilne and formaldehyde can be condensed to 4,4'-diaminodipheylmethanes which, once phosgenated, yield MDI (methylene diamino diphenyl isocyanateor diphenyl methane 4,4'-diisocianate)
    - maleic anhydride – currently mostly produced by n-butane oxidation; intermediate in the production of 1,4-butanediol, tetrahydrofuran, *gamma*-butyro lactone, fumaric acid, etc.
- from toluene
    - benzoic acid
    - nitrotoluene, dinitrotoluene, and trinitrotoluene (TNT)
    - tolylene diamines and tolylene diisocyanate (TDI) for the production of polyurethanes
    - terephthalic acid via toluene carbonylation (alternative scheme)
- from o-xylene
    - phthalic anhydride and many plasticizers, alkyd resins, unsaturated polyester resins, etc.
    - terephthalic acid (alternative scheme)
- from p-xylene
    - terephthalic acid (TPA and PTA) (and dimethylterephthalate, DMT)

The above summary provides a bird's eye view of the major petrochemicals derived from steam cracking. Steam cracking, however, is not the only source of petrochemicals. Others are:

- fluid catalytic cracking (FCC) is major source of propylene
- catalytic reforming of naphthas is the main source of BTX aromatics
- hydrocyclodimerization of propane and butanes is an alternative source of BTX aromatics
- methanol derived from syn gas is the main source of acetic acid and derivatives

Syn gas (blends of hydrogen and carbon monoxide, CO) is a very versatile, though indirect, source of petrochemicals

- syn gas can be used to produce olefins and saturated hydrocarbons via the Fischer-Tropsch reaction
- syn gas is required for the synthesis of methanol and derivatives (e.g., formaldehyde)
- methanol from syn gas can be used for the production of olefins (mostly ethylene and propylene) and aromatics (gasoline and heavy aromatics like durene)
- hydrogen from syn gas is absolutely necessary for all hydrogenation reactions, desulfurization reactions, etc.
- carbon monoxide, CO, from syn gas is required for carbonylation reactions: carbonylation of methanol to acetic acid, carbonylation of toluene to p-toluic aldehyde (and terephthalic acid)
- carbon monoxide and hydrogen in the hydroformylation of olefins to aldehydes (and to alcohols or acids)
- carbon monoxide for the production of phosgene for the synthesis of isocyanates

No matter how comprehensive we try to make this list, there are always other compounds that are hard to fit in a logical sequence of feedstocks and products. For example,

- polyether polyols – from the reaction of an epoxide with a polyol (a glycol or glycerin, for example)
- 1,3-propanediol – a novel polymer intermediate to compete with ethylene glycol or 1,4-butanediol in the production of polyesters
- various specialty isocyanates – hydrogenated diphenylmethane 4,4'-diidocyanate (HMDI), hexamethylene diisocyanate (HDI), xylylene diisocyanate (XDI), hydrogenated xylylene diisocyanate (HXDI), naphthalene diisocyanate (NDI), etc.
- 2,6-naphthalene dicarboxylic acid – a naphthalene-based analogue of terephthalic acid
- 1,4-dimethylol cyclohexane – a naphthenic glycol for polyester manufacture
- 1,4-butanediol by the Reppe reaction between acetylene and formaldehyde to 1,4-diol-2-butyne; 1,4-butanediol by the acetoxylation of 1,3-butadiene
- laurolactam for the manufacture of nylon-12 (usually from cyclododecane by butadiene cyclotrimerization)

Although this article concerns "petrochemicals" we should not forget that other non-petrochemical compounds are often required in the petrochemical industry. The two most important ones are perhaps

- ammonia – urea, nitric acid, NPK fertilizers, etc.
- chlorine – caustic an related compounds
- sulfuric acid and derivatives
- hydrogen peroxide – as used in several epoxidation reactions

A discussion of these separate industries is beyond the scope of this article.

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