The Emergence and Evolution of Atom Efficient and/or Environmentally Acceptable Catalytic Petrochemical Processes from the 1920s to the 1990s

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Abstract

The emergence and evolution of "Green / Sustainable Chemistry" began decades earlier than the 1990s. Beginning in the 1920s and 1930s, atom efficient catalytic processes for producing simple organic compounds started to be discovered and commercialized. In the 1940s and 1950s, oil refining processes using new catalytic methods dramatically increased the carbon efficiency of and usable variety of downstream products produced by oil refining processes, and simultaneously and dramatically decreased the waste residues and the pollution they produced. After World War II, new catalytic processes for producing a wide variety of increasingly atom efficient and/or "environmentally acceptable" downstream petrochemical products proliferated. This article will briefly recount multiple examples of those pre-1990s evolutionary developments in the petrochemical industries which produced new and highly atom efficient or environmentally acceptable catalytic processes for producing multitudes of petrochemical products that both changed modern societies, and also lead toward the modern conceptions of "Green / Sustainable Chemistry".

Keywords
Green Chemistry, Green Engineering, History, Atom Economy, E-Factor, Environmental Quotient, Catalysis, Interdisciplinary Research, Evolution, Industry, Sustainability

1. Introduction

Since the late 1990s, widely published but wildly incomplete "narratives" about the origins of "Green Chemistry" have widely propagated in the English-speaking Academic and Governmental literature, and also in the English-speaking trade and popular press, to the effect that "Green Chemistry originated during the 1990s from the efforts of the US Government, US EPA and Academia", and/or from the "12 Principles of Green Chemistry" published in 1998."[1,2,3]

Over the last several years this author (who conceived (in 1984) the BHC Ibuprofen Process that won one the earliest US Presidential Green Chemistry Challenge Awards, in 1997 [4]), has thoroughly documented and argued that "Green Chemistry" was in fact a narrow subset of, and evolved from and renamed, the much earlier and much broader international, interdisciplinary, and initially Industrial "Pollution Prevention" efforts during the 1970s and 1980s [5, 6].

However, even the purposely environmentally oriented industrial "Pollution Prevention" efforts of the 1970s and 1980s were preceded by the semi-independent emergence of multiple examples of increasingly "atom efficient"[7,] and/or "environmentally acceptable" [8, 9, 10] catalytic Industrial processes for producing commodity petrochemicals, beginning in the 1920s.

2. Early Atom Efficient Petrochemical Processes

The early industrial organic chemistry of the 1800s, typically based on treating chemicals isolated from coal with stochiometric reactants and/or reagents, was not environmentally friendly. Oil drilling and refining (by simple distillation) began in the 1850s but was also not environmentally friendly. But after cars and airplanes were invented in the early 1900s and their uses exploded, demand for more and better petroleum products also exploded. This article will focus on the early inventions, emergence and continuing evolution of increasingly environmentally friendly petrochemical processes and products, beginning in the 1920s, which then continued to emerge and evolve, well into the 2000s.

2.1. Early Industrial Organic Chemistry

As many have noted, prior to WWII most home heating was based on wood or coal, and lighting in the city streets was based on coal gas (flammable mixtures of carbon monoxide, hydrogen, and other gases produced by coal gasification). Most organic chemicals were derived from the coal tar byproduct of coal gasification. As Sheldon has described [8,10], industrial organic chemistry began with William Henry Perkin's 1856 serendipitous synthesis of "Aniline Purple" dye, via chromic acid oxidation of a mixture of aniline and toluidine's (derived from benzene and toluene isolated from coal tar), to form one of the first

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[1] See Anastas, PT., and Warner, J. C., (1998)
[2] See Anastas, P.T. and Beach, E.S., (2009)
[3] See Linthorst, J.A. (2010)
[4] Murphy, M.A, (2018)
[5] Murphy, M.A., (2020)
[6] Murphy, M.A., (2021)
[7] Trost, B.A., (1992)
[8] Sheldon, R.A., (1992a and 1992b)
[9] Murphy, M.A., (2023)
[10] Murphy, M.A., (2025a)

synthetic dyes for fabrics. That industrial process, like most of the synthetic organic reactions and industrial processes that followed over the next 100 years, typically employed multiple stoichiometric reagents comprising inorganic heteroatomic groups, groups which ultimately produced stoichiometric quantities of unwanted waste products and pollution in the environment, and too often continued the use of such inherently waste and pollution generating methods in the fine chemical and pharmaceutical chemical industries for decades. Change began in the 1920s however, when industrial chemists and engineers began to invent and develop catalysts capable of inducing “atom economical” and/or “environmentally acceptable” organic reactions that did not produce stoichiometric quantities of wastes, hazardous or otherwise.

2.2. “Atom Economy” and “Environmental Acceptability”

The concepts of “atom economy” and “environmental acceptability” were first described in the peer-reviewed scientific literature in the early 1990s by Trost[11] and Sheldon[12], though both men conceded that the use of “atom economical” catalytic reactions had already been in commercial use in the commodity chemicals industry for decades.[13] Trost’s Abstract had simply defined “atom economy” as the “maximum number of atoms of reactants appearing in the product”. Slightly later, Sheldon similarly described “atom utilization” as “the ratio of the molecular weight of the desired product to the sum of all the materials (excluding solvents) used.”

Sheldon then defined another concept related to “atom economy”, i.e. the “kg of waste to kg of desired product”, which is now known as the “Environmental Factor” or “E-Factor”.[8,13] The “E-factor” concept has since become a very well-known and widely used metric in Green Chemical research, for both contemplating conceptual chemical reactions, and also for evaluating the final commercial processes.

Sheldon also pointed out that simply calculating the total quantity of chemical waste for a given reaction or final process was not adequate, and that the “nature” of the wastes, i.e. the toxicities and/or dangers of the particular materials should also be considered, and then articulated a general concept of “unfriendliness”. Sheldon admitted the concept of “unfriendliness” is difficult to precisely define and is “debatable and will vary from one company to another, being partly dependent on the ability to recycle a particular waste stream”. As will be seen below, these generic concepts were not new to the industrial chemists of the time, but Sheldon was certainly correct to articulate his concepts in the peer-reviewed literature, give them a name, and point out the importance of those concepts to those Academics unfamiliar with them.

Sheldon also formulated and published another yet broader concept and terminology to include the importance of considering <u>both</u> the “E-Factor” and “unfriendliness”, by formulating a conceptual “equation” relating both the E-Factor and “unfriendliness” and used the “equation” to define a new terminology for “environmental acceptability”.

“Environmental Acceptability” Quotient”	=	**E** “Environmental factor”	**x**	x	**Q** “Unfriendliness

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[11] See Trost, B.M., (1991)

[12] See Sheldon, R.A., (1992a) and (1992b).

[13] See Murphy, M.A., (2023)

(kg waste / kg product)

While Sheldon's conceptual definition for "environmental acceptability" was not genuinely mathematical (because of the difficulties in rigorously defining "unfriendliness"), it can serve as a useful "conceptual framework" for contemplating the environmental impact of either a new chemical reaction, or a new commercialized process based on that chemical reaction.

As will be seen below in many examples, chemists in the commodity chemicals industry had already been quietly using these concepts, to discover, develop, and commercialize "atom economical" and/or "environmentally acceptable" petrochemical processes for about five prior decades. Furthermore, in 1992 Sheldon pointed out, and has continued to point out since, the importance of catalytic reactions to develop commercial processes that produce little waste and thereby achieve good "atom economy", "E-Factors" and "environmental acceptability".

To document that point, in Table 1 of his (1992a) publication Sheldon listed multiple already commercialized "Environmentally Acceptable" catalytic processes for making a variety of large volume commodity petrochemicals. Included on Sheldon's list were existing processes for making terephthalic acid, styrene, methanol, formaldehyde, ethylene oxide, acetic acid, phenol, propylene oxide, acrylonitrile, and vinyl acetate monomer. Below, we will provide more details about most of the already "Environmentally Acceptable" products and processes listed in Sheldon's Table I and provide additional examples of the downstream products and polymers produced from those early "building block" petrochemical products. Those examples will illustrate the long-term evolutionary processes that began and then progressed for decades before the 1990s.

3. Early "Environmentally Acceptable" Organic Products and Processes

The use of catalysts to invent, develop, and commercialize increasingly "atom efficient" and/or "environmentally acceptable" processes in the international oil refining and/or commodity chemicals ("Petrochemical") Industries began in the 1920s after WWI, about 100 years ago. For an even more detailed and technical description of Industrial Organic Chemistry as of the 1990s, see Weissermel and Arp (1997).

3.1. Methanol Synthesis

The following short summary of the history of methanol and its production and uses is based on the detailed description provided by D. Sheldon (2017). Methanol was a component of embalming fluid used by the ancient Egyptians, produced by the destructive pyrolysis of wood. The pure compound was first isolated by Robert Boyle by distillation in 1661, but the pure compound only became available in commercial quantities in the 1920s, after WWI. Mixtures of carbon monoxide and hydrogen were readily available from coal gasification, via treatment of hot coal with steam. In 1923 BASF commercialized a catalytic process developed by Mathias Pier (see U.S. Patent #1,569,775) using an iron-free Zinc Chromite catalyst previously developed Alwin Mittasch.

Scheme I, Methanol Synthesis

$$CO + 2\,H_2 \xrightleftharpoons[\substack{300 - 400\ C \\ > 300\ atm}]{Cr_2O_3\text{-}ZnO} CH_3OH \qquad (I)$$

$$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O \qquad (II)$$

$$CO + 2\,H_2O \rightleftharpoons CO_2 + H_2 \qquad (III)$$

The methanol synthesis reaction, Equation 1, Scheme I, is perfectly atom economical on paper, but practice was considerably more difficult for about four decades. The BASF process required very high pressures and temperatures to achieve the equilibrium state illustrated by the three reactions in Scheme I. All three reactions are exothermic, but entropically disfavored, and under those harsh conditions only small conversions to methanol were obtained. Accordingly, multiple passes over the catalyst were required, as were large and energy and high capital cost recycle streams, so the BASF process could hardly be called “Green” by today’s standards. But the BASF process did provide commercial quantities of methanol for the first time, which allowed for the development of many downstream uses, such as the formaldehyde synthesis process discussed below.

Major improvements followed in the 1950s and 1960s. Oil drillers began to capture natural gas that had previously been vented or flared, which provided a cheap source of methane. Methane can be reacted with very hot steam over supported Nickel catalysts to make synthesis gas (mixtures of CO and H_2) reasonably cleanly, atom efficiently, and very economically (see Scheme II, Eqn 1). Some of the CO can also react with water to make CO_2 and H_2 (the well-known “Water-Gas Shift Reaction, Scheme II Equation 2, and see also Scheme I Equation 1). This “Methane Reforming” process can produce syngas mixtures very efficiently and is also used to make most of hydrogen used in modern Industrial processes (such as ammonia synthesis).

Scheme II

$$CH_4 + H_2O \xrightarrow[800\text{-}900\ C]{Ni} CO + 3H_2 \qquad (I)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (2)$$

Engineering and equipment issues are very important in both the synthesis of the syngas and in the methanol synthesis reaction, as described in detail by Sheldon (2017). In 1963 Davies and Snowdon of ICI applied for patents (see U.S. Patent #3,326,956) that described catalysts comprising copper, zinc, and chromium which dramatically improved conversions, and lowered pressures (30-120 atm) and temperatures (200-300 C), at a methanol selectivity of 99.5%, an industrial scale production process that can reasonably be called “Green”. Refinements in both the catalysts and engineering / process design and equipment have continued since. In 2022, global methanol production was estimated to be 111 million metric tons.

3.2. Formaldehyde Production and Uses

Formaldehyde is ubiquitous in Nature and in biological systems at low concentrations but was first conclusively identified by August Wilhelm von Hofmann in 1868 after passing air / methanol mixtures over incandescent platinum. Pure formaldehyde is a colorless gas with a pungent odor, but it has many condensed and/or aqueous physical forms depending on its degree of hydration and/or polymerization.

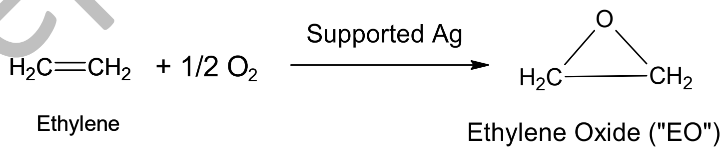
$$CH_3\text{-}OH + 1/2\ O_2 \xrightarrow{\text{Catalysts}} CH_2{=}O + H_2O$$

Very small-scale production via air oxidation began in Germany in the 1880s for use in embalming and preservatives, and then slowly spread and grew with time. Early catalysts used supported silver, but modern air oxidation processes typically use supported combinations of iron and molybdenum (or some other) oxides. The reaction is very exothermic, and heat and mass transfer issues are important to the results, and the N_2 gas from the air serves as a diluent to keep the reacting gases from reaching flammable conditions. Modern industrial processes achieve methanol efficiencies approaching 95%, but because formaldehyde is odiferous and considered a human carcinogen and a risk to workers exposed to higher concentrations over long periods, careful engineering and control of the purification, distillation and transport processes is important.

In 1907, Dr. Leo Baekeland, a Belgian chemist, invented a hard and moldable phenol-formaldehyde resin called “Bakelite”, which many regard as the first synthetic polymer. Today the biggest use for formaldehyde is in binding wood products such as plywood, particle boards, and fiberboards, using urea-formaldehyde, melamine modified urea formaldehyde, or phenol-formaldehyde. There are ppm levels of formaldehyde emissions from those wood products, and they are subject to governmental regulations in most countries, but their use enables inexpensive production of otherwise “Green” wood products. In 2022, formaldehyde production volumes were estimated to be 23 million tons.

3.3. Ethylene Oxide

In 1931, Theodore Lefort, a French chemist, filed a French patent application for the air oxidation of ethylene to produce ethylene oxide, (which was eventually granted in many countries, see US Patent #1,998,878).



LeFort’s air oxidation was perfectly atom economical on paper, and was commercialized in 1936 by Union Carbide, and initially had a Real-World selectivity to Ethylene Oxide of about 70%. The reaction is extremely exothermic, and technical details such as support, catalyst pellet characteristics, and reactor design and operation are all very important. Today, after evolutionary improvements, the selectivity to Ethylene Oxide is about 90%, and worldwide production was estimated to be about 32 million tons in 2022.

EO is an easily liquifiable gas, and moderately toxic. Most of the EO is hydrolyzed to make ethylene glycol, which is primarily used to make polyethylene terephthalate polyester, and as anti-freeze. Due to the high reactivity of EO, it is also used to efficiently make a wide variety of other downstream commercial products, many of which are non-toxic, bio-compatible and bio-degradable.

4. Use of Catalysts for "Greener" Oil Refining

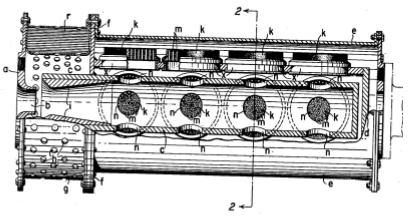
Prior to WWI, oil refining was conducted by simple atmospheric distillations of crude oil, primarily to produce kerosine for lighting and heating purposes. Before WWII, most industrial organic chemicals were derived from coal. But starting just before WWII, and over subsequent decades, multiple inventions and/or improvements in the oil drilling and refining industry occurred which steadily increased the proportion of salable products produced and decreased the amount of waste residues from oil refining. Those evolutionary developments were both economically and environmentally beneficial, though economic motivations may have been primary. This author previously described these developments in more detail[14], but will very briefly recount some of them here, because they dramatically increased the supply and decreased the price of several small downstream organic compounds that soon became feedstocks for increasingly "Green" petrochemical products and processes.

In the 1920s, French engineer Eugene Houdry experimented with natural zeolite clays as catalysts for cracking heavy coal oil waste residues, to provide lighter hydrocarbons useful as fuels, and Houdry developed a method for regenerating the quickly fouling zeolite catalysts. In 1930, Houdry moved to the U.S. and began collaborating with the Socony Vacuum and Sun Oil companies, to use the zeolite catalysts to crack heavy residues from the distillations of crude oil.

In 1937, a commercial "Houdry" cracking unit using a fixed bed catalyst opened at a refinery in Pennsylvania and dramatically increased the production of high-octane gasoline-range hydrocarbons from the heavy waste residues, as well as other valuable small hydrocarbons such as ethylene, propylene, and butanes and butenes. Several other "Houdry" fixed-bed cracking units were built before the U.S. entered WWII. Then in 1942 Houdry and Standard Oil of New Jersey opened a new fluidized bed cracking unit using zeolite catalyst powders that eliminated the need to shut down the cracking units for catalyst regeneration, and also dramatically decreased the amount of waste residues from oil refining. The "Houdry" high-octane aviation fuels gave US pilots a significant power advantage over Axis airplanes during the War and then proved very valuable for gasoline blending after the War as demand for high octane gasolines rose dramatically, especially when lead additives were banned from gasolines in the 1970s.

Furthermore, in 1950 Houdry filed a patent application for a catalytic converter for automobile exhaust gases, which oxidized the residual hydrocarbons in exhaust gases to CO_2 and H_2O! See U.S. Patent #2,647,521, and Figure I from that patent below.

Figure I from US Patent #2,674,521, "Catalytic Converter for Exhaust Gases"



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[14] See Murphy (2020), Murphy (2021), Murphy (2023), and Murphy (2025a)

Houdry's catalytic converter contained supported noble metal catalysts for air oxidizing the unburned hydrocarbons. Unfortunately the lead additives in gasolines during those times quickly fouled the precious metal oxidation catalysts, so Houdry's converters were not used in commercial practice until the 1970s when lead additives were banned from gasolines. Nevertheless, this author would nominate Eugene Houdry for the hypothetical title of "World's First Green Engineer"!

Also during and after WWII, oil refineries continued to develop additional new processes that chemically manipulated the organic compounds found in oil, to increase the yield of useful and salable products, decrease the waste residues, and improve the economic results.[15] Those new processes included 1) catalytic "alkylation" of propylene, butenes, and pentenes with isobutane, to form highly branched and high octane heptanes, octanes, and nonanes for gasoline blending; 2) catalytic reforming processes which convert napthas from early oil distillations into branched alkanes and aromatics; 3) catalytic hydrocracking which converts heavy distillation fractions (diesels, kerosines, and heavy gas oils) to lighter and more valuable napthenes and paraffins, and other gasoline-range hydrocarbons; and 4) olefin metathesis, which is sometimes used to upgrade low molecular weight olefins to higher molecular weight olefins. As a long-term result of these long-term evolutionary developments in oil refining, in 1992 Sheldon estimated that oil refineries were only producing about 0.1 kg of waste products per kg of useful and salable products.[16]

But importantly for purposes of this paper, the evolution of catalytic cracking processes in oil refineries generated large quantities of small organic building block molecules, such as ethylene, propylene, butenes, etc., which would stimulate the development and evolution of many downstream petrochemical products and processes, as discussed below.

5. The Post-War Evolution of Atom Efficient and/or Environmentally Acceptable Petrochemical Products and Processes

After WWII, the oil refining and organic chemical industries began to boom worldwide, as the international economies rebounded. The growing and cheap availability of small organic molecules from the proliferating oil refineries motivated research for new uses of those small organic molecules, and multiple inventors in multiple countries began to invent, develop, and commercialize a growing number of new petrochemical products made by new catalytic processes that were atom efficient and/or environmentally acceptable on paper, though considerable evolution was needed in some cases in order for those processes to become genuinely "Green" in Real-World practice. We describe some major examples below.

5.1. Olefin Hydroformylation

In 1938, Otto Roelen of Ruhrchemie was investigating Fisher-Tropsch reactions of CO/H_2 mixtures, as potential a source of synthetic fuels for Germany, and reacted ethylene with CO/H_2 at several thousand psig in the presence of heterogeneous Cobalt catalysts. Aldehydes were produced, and Roelen investigated further[17]. Despite the physical and political difficulties of WWII, Roelen and Ruhrchemie

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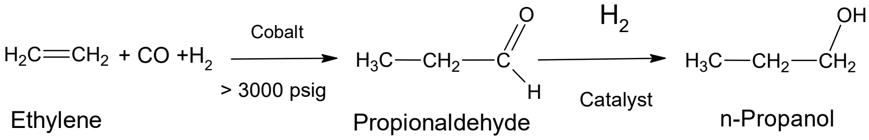
[15] See Leffler, W.L., (2008), Murphy (2020), and Murphy (2021)

[16] See Sheldon (1992a) and Sheldon (1992b)

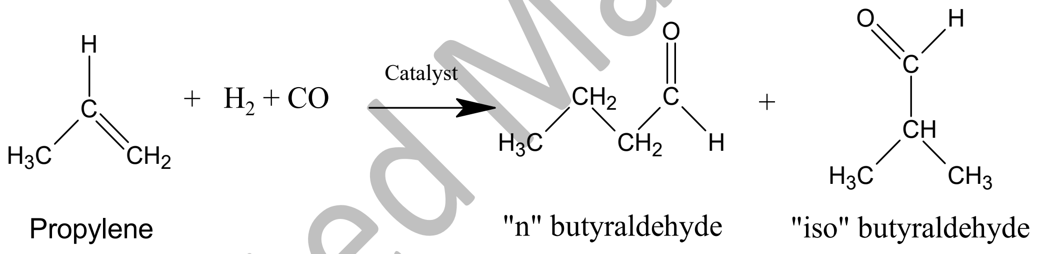
[17] See Cornils et.al., (1994)

managed to build a small functioning plant to hydroformylate ethylene to n-propionaldehye (at pressures well over 3000 psig), and then in a second step catalytically hydrogenated the propionaldehyde give n-propanol.



Both the two catalytic reactions shown above were perfectly Atom Economical on paper and gave good Real-World yields. After the War, the US “commandeered” Roelen’s original 1938 German patent application, see US Patent #2,327,066. Roelen apparently believed the Cobalt catalyst was heterogeneous, but in 1960-1961, Heck and Breslow of Hercules Corporation identified $HCo(CO)_4$ as the active homogeneous catalyst and explored the mechanism of the hydroformylation reaction. [18]

Many uses of hydroformylation have subsequently evolved and been commercialized to make a variety of important industrial products.[19] The biggest volume application is the hydroformylation of propylene to make n-butyraldehyde (see equation below). The annual production volume of n-butyraldehyde was estimated to be 7 million tons per year in 2017.



When a substituted olefin is hydroformylated, the carbon monoxide insertion can potentially occur at either end of the double bond, to produce either the “n”-aldehyde or an “iso”- aldehyde. In many (but not all) applications, the n-aldehyde is more commercially valuable. The propylene hydroformylation to give n-butyraldehyde was first commercialized by BASF / Ruhrchemie in 1960, using $HCo(CO)_4$ catalyst, at pressures well above 3000 psig. Unfortunately, the “n/iso” isomer ratio was only about 3:1, so the Real-World cobalt catalyzed propylene hydroformylation was not yet particularly atom efficient, or “environmentally acceptable”.

But in the late 1960s, Shell added trialkyl phosphines to the Cobalt catalysts, which significantly lowered the required pressures, increased the activity and stability of the Cobalt catalysts, and improved the n/iso ratio, to about 7:1. Shell and some other companies still use the Co/PR_3 catalyzed processes to manufacture some higher molecular weight aldehydes.

In 1968, Evans, Osborne, and Wilkinson of Imperial College of London described the use of Rh-triphenylphosphine complexes as catalysts for the homogeneous hydrogenation of olefins, and then the propylene hydroformylation reaction[20], part of the work that won Wilkinson a Nobel Prize in 1973. In

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[18] See Heck and Breslow, (1961)
[19] See Zhang et. al., (2022)
[20] See Evans, Osborn, and Wilkenson, (1968)

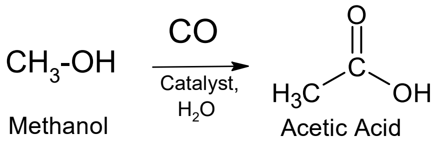
the 1970s Union Carbide (and other companies) rapidly commercialized the Rhodium / Triphenylphosphine catalyzed processes for propylene hydroformylation, which operate at much lower pressures (400 psig) than the Cobalt processes and produce much better n/iso ratios around 12:1. The Rh/PPh_3 catalyzed processes are also continuous and operate without added organic solvents, the product aldehyde (and a hydrocarbon oil that slowly builds up from condensation and hydrogenation of the aldehydes) are the only solvents. In this author's opinion, those processes had evolved into economically successful, truly atom efficient, and environmentally acceptable commercial petrochemical processes by the 1970s.

But further evolution of hydroformylation processes continued. In 1976, Emile Kuntz of Rhone-Poulenc developed a process for hydroformylation of olefins using Rhodium / tri-sulfonated triphenylphosphine catalysts dissolved in water, see US Patent #4,248,802. In 1984 Rhone Poulenc and Ruhrchemie commercialized a process for making n-butyraldehyde in which the catalyst is dissolved in water, and the sulfonated water-soluble phosphines have since been used for a variety of other catalytic processes. In the 1980s, researchers at several corporations explored and commercialized hydroformylation processes using sterically hindered bi-dentate phosphite complexes which produce very high n-iso ratos.[19] Readers will hopefully recognize the long-term evolutionary changes in hydroformylation chemistry which eventually resulted in "Green" commercial processes, decades before the 1990s.

An interesting spin-off from Wilkinson's work on Rh / phosphine complexes occurred when William S. Knowles of Monsanto modified Wilkenson's Rhodium catalysts to employ optically active bi-dentate phosphine ligands[21] and subsequently used them to invent a commercial process for making l-Dopa by asymmetric hydrogenation, see U.S. Patent #4,005,127. Knowles work was the first commercialization of the use of asymmetric metal complexes as catalysts for organic reactions, work for which he shared a Nobel Prize in 2001 with Ryöji Noyori and K.B. Sharpless (for their subsequent uses of metal complexes with optically active ligands as catalysts for many other asymmetric hydrogenation and epoxidation reactions).

5.2. Processes for Making Acetic Acid and Its Derivatives

Acetic Acid has been known and used by humans since Antiquity, in the form of fermented vinegars. It was first synthesized in pure form in 1845 by Hermann Kolbe. Before WWII, pure acetic acid was available on small commercial scales, by hydrolysis of calcium carbide, or from treatment of "pyroligneous liquor" from charcoal production with inorganic bases, processes which produced stoichiometric salt wastes. Around 1913, researchers at BASF discovered a Cobalt / Iodide catalytic process for making acetic acid by "methanol carbonylation", the reaction shown below, but the methanol feedstock was not yet available in commercial quantities, and the required pressures were very high.



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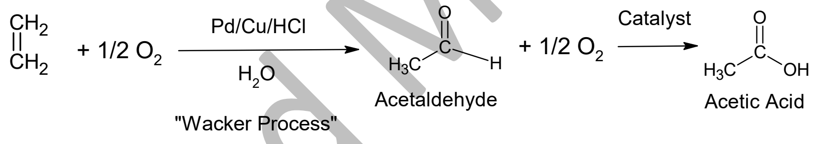
[21] See Knowles and Sabacky, (1968)

After commercial quantities of methanol became available in the 1920s, several companies began to investigate the reaction, and it was piloted at British Celanese in 1925, but the lack of sufficiently corrosion-resistant metals delayed commercialization for decades.[22]

However, after WWII, the oil-drilling and refining industries boomed, as did the use of oil cracking technologies. N-Butane became cheap and plentiful, and in the early 1950s several companies (including Celanese, Union Carbide, Standard Oil, Eastman, Huls, and AKZO) commercialized plants for cobalt catalyzed air oxidation of n-butane, which produced acetic acid as a major product, accompanied by smaller amounts of several other low molecular weight organic oxygenated organics.[4] Those catalytic processes were certainly not atom efficient, and they emitted considerable gaseous carbon dioxide and carbon monoxide, but they did eliminate the stoichiometric production of inorganic salt wastes that had been produced by prior processes. The complex mixture of oxygenated organic products required an energy-intensive separation by complex distillation processes, but nevertheless remained economically viable until the 1990s, when they finally became both technically, economically, and environmentally obsolete.

The price of ethylene and propylene were also decreasing dramatically, and many companies began to research potential applications. In 1956 Schmidt, Hafner, and Jira at Wacker Chemie discovered the "Wacker Process" for the air oxidation of ethylene to produce acetaldehyde[23], using a homogeneous Palladium / Copper / HCl catalyst, dissolved in water solvent (see equation below).



The "Wacker" catalyst solutions were however extremely corrosive, so commercialization was delayed until corrosion-resistant alloys became available several years later. The Wacker oxidation of ethylene was followed by a catalytic air oxidation of the acetaldehyde (over supported transition metal catalysts) to give acetic acid. Both these reactions are perfectly atom efficient on paper, and the Real-World yields are high, so together the two reactions represented a highly economically attractive and atom efficient and environmentally acceptable process for making acetic acid. Multiple plants were built by several companies in the 1960s, and they remained economically competitive until the 1990s.

Meanwhile, the development of corrosion-resistant alloys in the 1950s also enabled commercialization of methanol carbonylation processes for producing acetic acid, already briefly mentioned above. In 1960, BASF built a small plant for manufacturing acetic acid by methanol carbonylation, catalyzed by CoI_2. But the methanol selectivity was only about 90%, the carbon monoxide efficiencies were only about 70%, the required pressures were over 9,000 psig, and considerable byproducts were produced.[22] Two more plants were eventually built, but the Cobalt-catalyzed methanol carbonylation process was only marginally economically competitive with and/or "Green" as compared to the Wacker process.

Methods for methanol carbonylation improved dramatically in 1968, when Paulik, Hershman, Coeur, and Roth of Monsanto invented a new homogeneous Rh/I- catalyzed methanol carbonylation process, see US

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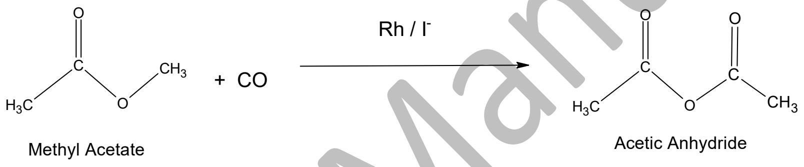
[22] See Wagner, F., and LookChem online Chemical Encyclopedia

[23] See Jira (2009) and U.S. Patent #3,080,425

Patent #3,769,329. The Monsanto Process was continuous, required only about 400 psig pressure, gave greater than 99% selectivity to acetic acid (based on methanol), gave carbon monoxide efficiencies in the low 90% range, and used the product acetic acid as solvent. Therefore, the Monsanto process constituted a new highly efficient, economically superior, and “Green” process for making acetic acid. Monsanto built a first plant in 1970, then licensed the process to Celanese (who built a plant in 1975), and later also to British Petroleum.

Although it was little recognized or understood for years, the acetic acid solvent used in the original “Monsanto” processes also <u>had</u> to contain at least about 8 mole % of water, in order to prevent rhodium precipitation during the isolation of the acetic acid product. The high water content also promoted a water-gas shift side reaction that significantly lowered the carbon monoxide efficiencies.

During the 1970s, multiple companies attempted to adapt the “Monsanto” Rh / I catalysts to carbonylate methyl acetate to produce acetic anhydride, in the complete absence of water, as shown in the equation below. But those early efforts were not commercialized because of poor rates, rhodium catalyst instability, and the formation of tarry byproducts.



But in the early 1980s, Larkins, Polichnowski, Tustin, and Young of Eastman Chemical developed a successful catalytic carbonylation of methyl acetate to acetic anhydride, which was commercialized in the mid-1980s at Eastman’s plant in Kingsport Tennessee. The secret to Eastman’s success (in the absence of water) was the addition of lithium iodide co-catalyst and deliberate inclusion of a modest partial pressure of H_2 in the carbon monoxide feed, see U.S. Patent #4,374,070. The new Eastman process for acetic anhydride was nearly perfectly atom economical on paper, and in practice, and was a commercial success.

In 1983, a small team at Celanese in Corpus Christi Texas, aware of the Eastman work and patents, successfully and dramatically lowered the water content required for commercial “Monsanto” methanol carbonylation, from 8 mole % to about 2 mole %, by the addition of lithium iodide and re-optimization of some other process variables.[24] The benefits from this “low water” methanol carbonylation were excellent Rh catalyst activity and stability, a large increase in plant capacity, lowered purification costs and energy usage (because of the much reduced water loads) and a significant increase in carbon monoxide efficiency (because of much lower rates for byproduct production via the water-gas shift side reaction). That even more efficient and Environmentally Acceptable Celanese “AO™” methanol carbonylation process was commercialized at Clear Lake Texas in the late 1980s, and two more Celanese plants were subsequently built and further improved. Furthermore, this author was working (on a part-time basis) on the early Celanese AO™ product team at the time (1984) he first conceived the BHC Ibuprofen Process (which used a carbonylation reaction for its final key step) that won one of the first U.S. Presidential Green Chemistry Challenge Awards.[25]

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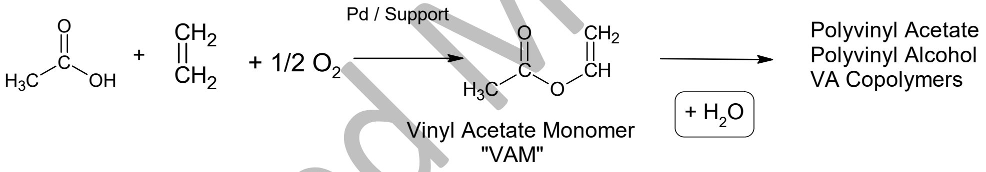
[24] See Smith et.al., (1987)

[25] See Murphy (2018)

The innovations at Celanese did not stop later innovation and evolution at Celanese’s competitors. In August 1994, Garland, Giles, and Sunley of BP Chemicals Ltd filed for a patent (see U.S. Patent #5,672,743, and Jones (2000)) for a methanol carbonylation process using Iridium / Ruthenium catalysts, which also runs under ‘‘low water’’ conditions. Several commercial BP plants for manufacturing acetic acid using Ir / Ru catalysts are now in commercial operation internationally. Global acetic acid production was estimated to be 18 million metric tons in 2018.

This author hopes that readers will recognize the evolutionary process that eventually produced the modern and highly atom efficient and “Green” acetic acid technologies actually began in 1913, followed by a long-term sequence of unpredictable evolutionary improvements carried out by a series of largely independent inventors and companies, wherein each improved on the technology of their predecessors and/or competitors.

Acetic Acid has many commercial uses, but the largest is the production of vinyl acetate monomer (“VAM”). It was discovered in 1912 by Fritz Klatte, who reacted acetylene with acetic acid in the presence of mercury salts, and who discovered VAM could be polymerized (sometimes violently) in the presence of various radical initiators. See U.S. Patent #1,241,738. For decades VAM was produced commercially by variations of Klatte’s method, but when ethylene from petroleum cracking processes became cheap and available, a new method of synthesizing VAM was discovered and commercialized by a number of companies, i.e. by catalytic air oxidation of ethylene and acetic acid over supported Palladium catalysts, as illustrated by the chemical equation below.



The continuous catalytic oxidation process uses atmospheric oxygen as a cost-free oxidant and converts it to water. Some over-oxidation of the ethylene to CO_2 occurs in practice, and Real-World efficiencies are in the range of 80-90%, and VAM is relatively non-toxic to humans. Accordingly, the VAM production process can be considered favorably “environmentally acceptable”. Global production volume for VAM was estimated at 9 million tons per year in 2023.

VAM is used to prepare a wide variety of polymers and copolymers. VAM can be homo-polymerized in solutions, water suspensions, and/or emulsions to form polyvinyl acetate emulsions (“Wood Glue”). Polyvinyl acetate is bio-degradable and is used in a wide variety of film and packaging applications, including the production of plywood and particle boards. Polyvinyl acetate production volumes were estimated to be 3.4 million metric tons in 2020.

Polyvinyl acetate can be hydrolyzed under basic conditions to produce polyvinyl alcohol (“PVA”), with the liberation of acetic acid, which can be recovered and recycled. PVA is a water-soluble and bio-degradable polymer with many uses in adhesives, papermaking, textiles, coatings, 3D printing, food and pharmaceuticals, wound dressings, and contact lenses, and for making water-soluble polymer blends. Worldwide production volumes are estimated to be about 650,000 tons per year.

VAM is also widely co-polymerized with other vinylic monomers, including ethylene and various acrylic acid esters, often for use in paint and coatings applications. Hopefully readers will recognize that the commercial availability of VAM has resulted in the evolution of a large downstream family of useful and relatively environmentally acceptable polymeric materials and products.

5.3. Ziegler-Natta Olefin Polymerization

The 1963 Nobel Prize in Chemistry was awarded to two bitter competitors, Karl Ziegler of the Max-Planck-Institut für Kohlenforschung (coal research), and Giulio Natta of the Institute of Technology in Milan Italy, for their discoveries related to the polymerization of ethylene and propylene to high molecular weight polyethylene and polypropylene respectively, polymeric plastics which are still produced today in massive commercial quantities worldwide.

To oversimplify an interesting and complex story (told more fully on the website of the Max Planck Institute[26], and by Sivaram (2017)), Ziegler and Natta both had prior relationships and research agreements with the Italian company Montecatini. Ziegler (who had a bent toward Academic research) and his graduate students pursued a tortuous multi-year research effort directed toward the catalytic polymerization of ethylene to produce high molecular weight polyethylene. In the Fall of 1953, Ziegler and his graduate students discovered an increasingly effective series of catalysts comprising mixtures of Group IV metal chlorides (especially $TiCl_4$) and aluminum alkyls, which successfully polymerized ethylene being bubbled through a solvent in a canning jar and produced 400 grams of (dry) high molecular weight polyethylene. Ziegler and his students rapidly submitted a German patent application (Patentschrift No. 973,626) for the polymerization of ethylene.

Natta, aware of Ziegler's catalysts and patent applications through both formal and informal channels, was inclined towards the practical applications of Scientific research, and began investigating use of Ziegler's catalysts for the polymerization of propylene and other substituted (and prochiral) olefins. To oversimplify, Natta's work led to the discovery (and ultimate commercialization) of stereoregular, crystalline, isotactic polypropylene, as well as the recognition of its crystalline, helical structure. Montecatini submitted a patent application naming Natta an inventor for the polypropylene polymerizations, without notifying or consulting Ziegler.

Over 40 years of bitter patent litigations resulted between the Max Planck Institute, Montecatini, and several other major petrochemical companies. The litigations were eventually won by the Max Planck Institute on the basis a "first-to-invent" feature of American patent law that is now legally defunct. In 2022, global production of polyethylene was estimated to be 110 million metric tons, and the global production of polypropylene was estimated to be 79 million metric tons.

Years afterwards, Ziegler compared his research path to "a hiking tour through a new country…but one on which one never did know just where the journey was really headed. For decades, I never even remotely thought that my path would also include technological successes." Now we recognize that the Ziegler-Nata polymerization reactions are atom efficient, and therefore "Green" in some respects. But it also seems safe to assume that neither Ziegler nor Natta foresaw the huge technical and economic importance of their discoveries, or the ecological problems that result from the lack of bio-degradability

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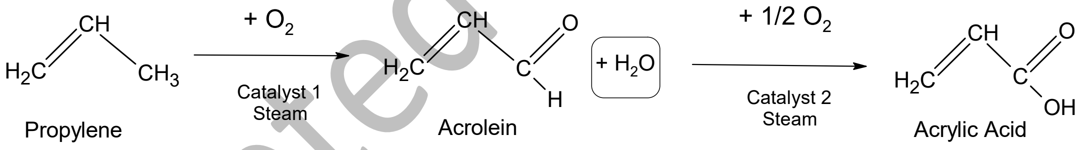
[26] See Max-Planck-Gesellschaft website, (2014)

of the huge volume of the commercial polyolefin plastics we now produce and use, an issue which we still struggle with today.

5.4. Acrylic Acid, Acrylic Esters, Methods for their Production, and Their Polymers

Acrylic acid was first prepared in 1847 by air oxidation of acrolein. The polymerization of acrylic acid and its esters was first reported in 1901 in a PhD thesis entitled “Polymerization products of Acrylic Acid” by Otto Röhm. In 1907 Otto Röhm and Otto Hass founded a German company to manufacture leather products, but in the 1920s Röhm began new research efforts directed toward polymers, especially polymers derived from acrylic acid, methacrylic acid, and their esters. In 1927, Röhm & Hass commercialized its first product, which used an acrylic polymer layer sandwiched between glass layers to form a shatter-proof glass, and in the 1930s commercialized PLEXIGLAS which used a polymethylmethacrylate layer between the glass sheets. The many commercial applications of acylates and methacrylates grew rapidly thereafter.

Until the 1950s, acrylic acid was typically produced by various methods from acetylene, which was typically produced from calcium carbide, which in turn was produced from coal, an expensive and dirty process that produced many waste salts and products. In the later 1950s, as the supply of propylene from refinery catalytic crackers increased and the price dropped, many researchers and/or companies began to investigate methods for the air oxidation of propylene to produce acrylic acid.[27] Although many variations of processes and catalysts have been reported since, modern commercial processes for producing acrylic acid from propylene typically operate continuously in two stages, as shown by the chemical equations below:[28]



In the first stage, air is used to oxidize propylene to acrolein, in the presence of a first supported catalyst and significant excess of steam (which acts as a moderator which also dilutes the gas mixture to below flammable limits) while oxidizing the propylene and reducing the oxygen to produce water as a non-toxic byproduct. Then in a second stage, conducted over second supported catalyst, another half mole of oxygen is injected which further oxidizes the acrolein to acrylic acid. A small amount of over-oxidation occurs, producing relatively small amounts of CO_2 and acetic acid byproducts. The hot 2nd stage product gas mixture is then immediately quenched by absorption into liquid water, and thereby easily separated from the gases. The aqueous acrylic acid is then extracted from the quench water into an organic solvent, and the organic phase is separated by distillation, to isolate the acrylic acid product and recycle the solvent. An instructive process flow diagram can be found in Turton’s article.

Acrylic acid monomer is toxic but is biodegradable in both air and water. The chemical oxidation reactions are not technically atom efficient (because of the water byproduct produced), but they are economically attractive and reasonably environmentally acceptable. Multiple companies use these

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[27] See for example Campbell et.al., (1970)

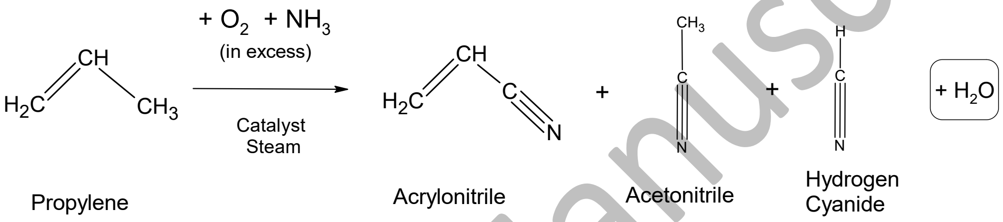
[28] See for example Turton, R., “Acrylic Acid Production via the Catalytic Partial Oxidation of Propylene”

oxidation processes commercially, and the global acrylic acid production volume was estimated to be about 8 million metric tons in 2022.

Acrylic acid monomer is used in many polymer and co-polymer applications, including superabsorbent polymers, cosmetics, skin care, and in adhesives, coatings, and sealants. Many acrylic acid esters are made and sold commercially, the choice of the particular alkyl group for the ester being dependent on the particular polymer or co-polymer application. The biodegradability of the polymer products depends on the characteristics of the particular polymer or copolymer.

5.5. Acrylonitrile

Acrylonitrile was first synthesized in 1893 and is produced today by the Sohio Process developed in the 1950s[29], via catalytic amoxidation of propylene with sizeable excesses of air, ammonia, and steam.



The Sohio process is carried out continuously in a single reactor over a bismuth phospho-molybdate catalyst, for short residence times. It is believed that the first step of the reaction is the oxidation of propylene to acrolein (similar the acrylic acid processes discussed above), and that the acrolein condenses with the ammonia (in an equilibrium step) to form an imine of the acrolein, which is then further oxidized in-situ to produce the highly valuable acrylonitrile monomer. Some over-oxidation also occurs, to produce substantial amounts of acetonitrile and hydrogen cyanide co products, which are also purified and sold commercially. Unfortunately, large excesses of ammonia and steam are required, and the process produces large gaseous and aqueous waste streams and high energy usage. Because the acrylonitrile monomer and hydrogen cyanide co-products are highly toxic, the current "Sohio" catalytic process can hardly be termed either atom economical or environmentally acceptable.

The acrylonitrile monomer is however very valuable commercially for producing polyacrylonitrile and multiple kinds of co-polymers, including styrene-acrylonitrile, acrylonitrile-butadiene-styrene, acrylonitrile-styrene-acrylate, and acrylonitrile-butadiene. The acrylonitrile is also a useful intermediate for making some types of nylons. The global annual production volume of acrylonitrile was estimated to be 8.6 million tons in 2022.

Various researchers have been investigating potentially "Greener" methods for producing acrylonitrile, including from bio-mass starting materials such as glycerol, but those methods are not economically competitive as yet.

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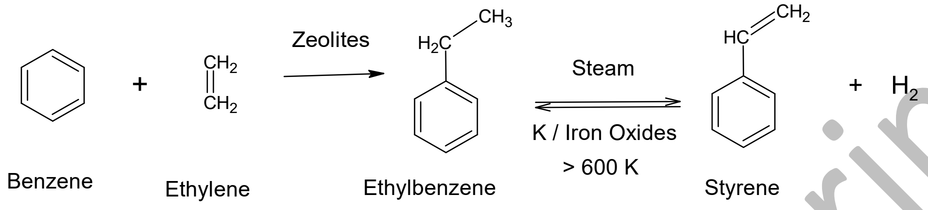
[29] See American Chemical Society, (2007), "The Sohio Acrylonitrile Process"

5.6. Styrene

Styrene was first isolated in 1839 by Eduard Simon and occurs in nature at low concentration levels. Although other modern processes exist and still operate, most styrene is derived from a continuous catalytic reaction over zeolite catalysts between benzene and ethylene to form ethylbenzene. The ethylbenzene is then thermally dehydrogenated over potassium promoted iron oxides in the vapor phase.



The dehydrogenation of ethylbenzene was discovered in the 1930s and was used during WWII to produce styrene for making styrene-butadiene rubber during the War. Styrene production expanded dramatically after WWII and continued to grow and evolve afterwards. In modern processes, ethylbenzene and steam are passed over potassium promoted iron oxide catalysts at temperatures over 600 K, at low pressures, to produce equilibrium mixtures of styrene and H_2. These processes have been recently described in considerable detail by Behr.[30] Although operation at high ethyl benzene conversions is possible, byproduct formation causes most modern plants to operate at lower conversions, using steam injection through multiple reaction stages, to produce conversions of 50-70% with recycle of unreacted ethylbenzene, but at overall yields of 88-95%. Behr provided worthwhile process flow diagrams.

The dehydrogenation of ethylbenzene to produce styrene is reasonably atom economical, but requires significant energy expenditure, and the benzene and styrene are both considered to be human carcinogens and toxic. The production process is nevertheless conducted on a large commercial scale. Global styrene production was estimated to be about 37 million tons in 2022.

Styrene is a low-cost monomer used in many polymer / co-polymer / plastic applications for packaging, construction, household goods, transportation and safety products and military applications. It is worth noting that the very first U.S. Presidential Green Chemistry Award, in 1996, was given to the Dow Chemical Company, for an invention entitled ‘‘100 Percent Carbon Dioxide as a Blowing Agent for the Polystyrene Foam Sheet Packaging Market”. See U.S Patent #5,250,577 to Gary C. Welsh, filed August 2, 1989.

Polystyrene is non-toxic but non-bio-degradable, though some polystyrene products can be recycled under some circumstances. The biodegradability and/or recyclability of the many co-polymers made from styrene vary depending on the exact nature of the copolymer and its particular application. The recyclability and/or lack of biodegradability of many polymers and co-polymers is of course these days a major issue and/or research topic in modern “Green” chemical research in the petrochemical industries.

5.7. Terephthalic Acid Production

Terephthalic Acid is a major industrial product used for condensation with glycols to produce polyesters. The predominant process for producing terephthalic acid was discovered by Saffer and Barker of Mid-

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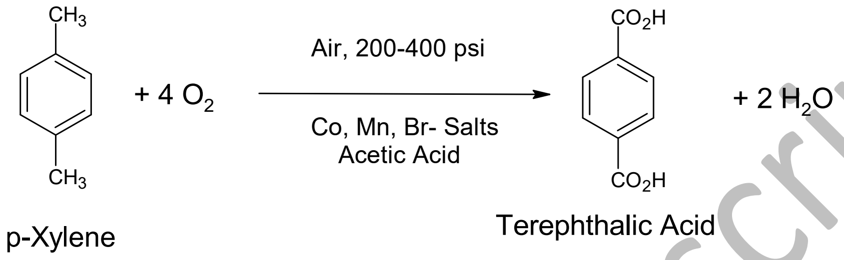
[30] See Behr, (2019), “Styrene Production from Ethylbenzene”

Century Corporation in the mid 1950s, see U.S. Patents #2,833,816 and #3,089,906. In this process, p-Xylene provided by reforming processes in refineries is continuously air oxidized to terephthalic acid in acetic acid solvent containing cobalt, manganese, and bromide ions as catalysts, see the equation below. On paper the reaction is not perfectly atom economical but is reasonably environmentally acceptable, because water is the only stoichiometric co-product and the terephthalic acid is biodegradable by microorganisms.



The Mid-Century process was developed and commercialized in the late 1950s in collaboration with Amoco and ICI, using the highly corrosion resistant alloys that became commercially available then. In practice, excess atmospheric O_2 reactant is used, and some minor over and under oxidation occurs, but the conversion of p-Xylene is reportedly around 98% with about 95% selectivity to terephthalic acid. A significant quantity of the acetic acid solvent does get combusted to CO_2 and H_2O during the process and must be replenished. Accordingly, the Mid-Century / Amoco process is reasonably environmentally acceptable, but research work continues to develop improved and/or "Greener" methods. [31] It has been estimated that the global production of terephthalic acid was 84 million metric tons in 2022.

The biggest uses for terephthalic acid is polymerization with various glycols to form polyesters. By far the biggest use is condensation polymerization with ethylene glycol to make polyethylene terephthalate ("PET"). The first synthesis of high molecular weight PET suitable for polymer application was in 1941 by J.R. Whinfield and J.T. Dickson of the Calico Printer's Association of England (see Canadian Patent Application CA 490196). PET polymers and processes for making them were developed and commercialized by DuPont in the early 1950s.

In most commercial processes, terephthalic acid is heated with ethylene glycol and the water produced by the polyesterification is removed by distillation, so the process is not technically atom efficient, but it is reasonably environmentally acceptable. A minority of commercial processes use a multi-step polymerization procedure in which the terephthalic acid is first esterified with methanol to eliminate water and make and isolate dimethyl terephthalate. The dimethyl terephthalate is then polymerized with ethylene glycol in a two-step polymerization procedure. Global production of PET was estimated to be about 25 million metric tons in 2022.

PET is widely used in food and drink packaging applications, textiles, electronic components, and many other applications. PET polymer is not very bio-degradable but is readily recycled to reusable resin in situations where the PET waste can be economically separated from the other materials in a waste

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[31] See Tomás, Bordado, and Gomes (2013) and Lapa, Luisa, and Martins (2023)

stream.[32] It is also sometimes possible to economically depolymerize PET with methanol or ethylene glycol to produce high quality monomers that can be re-polymerized.

6. Evolution in the Chemically Related Industries, "Green Chemical" Research, and Broader Societies

The historical examples described above demonstrate that after WWII, decades before the words and "Principles" of "Green Chemistry" were coined, many oil and petrochemical companies and their scientists and engineers (working in interdisciplinary teams with many different motivations) invented and commercialized multiple atom economical and/or environmentally acceptable catalytic processes for making low-priced but high-volume commodity petrochemicals.

After WWII, in the 1950s and 1960s, the Societies and/or economies in many countries recovered and then boomed, as did oil drilling and refining in response to booming demand for fuels. Economic recovery and the political and strategic imperatives of the developing Cold War dominated many Societies' concerns, and the understanding of ecological issues was still rudimentary. Technical, economic, and political motivations certainly outweighed environmental concerns during those years, but the discovery and development of efficient catalysts provided the technical tools /means that enabled much more efficient conversion of oil into low cost and readily available organic building block molecules, and growing profits, even though the companies and their scientists, and engineers kept many of their strategies, motivations, and technical details secret.[33] The building block molecules were then used generate a widening and evolving downstream network of downstream petrochemical products and polymers. Those atom efficient catalytic processes and resulting products improved people's lives in many ways, though little direct attention was being paid to environmental issues. Environmental regulations were typically lax and there was little immediate cost if toxic products, waste and/or pollutants were released into the biosphere.

Nevertheless, a wide variety of other motivations were also important in many individual cases, and they varied tremendously with time, the country, the company, and the individual people and circumstances. At least some of the industrial scientists and engineers involved had some internal environmental motivations, as was clear from Houdry's 1950s invention of a catalytic converter for exhaust gas emissions.

Other smaller segments of the chemically-related industries, including fine chemicals and pharmaceuticals, also did much to improve people's lives, but most continued to use the reactions of traditional organic chemistry that inherently produced stoichiometric wastes and/or pollution. In those industry segments, the proportion of waste produced per pound of product was orders of magnitude higher, but did not have much economic impact in the absence of environmental regulations, with the result that the environmental issues were neglected by many for many years by many companies in those industry segments.[34] Similarly, in many down-steam consumer products industry segments, the economic costs of waste disposal were modest and were mostly ignored for decades by too many companies.

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[32] See Joseph et.al., (2024)

[33] See Murphy (2025 b)

[34] See Sheldon (1992a), (1992b), and Murphy (2023)

But things began to change rapidly in the 1960s and 1970s as Society, the chemical industries, and the resulting pollution, grew rapidly[35], The Environmental Movement grew quickly in reaction against the pollution, and politicians in many countries also reacted. Legally inspired "Command and Control" environmental statutes and regulations were passed by the governments in many countries which dictated "end-of-the pipeline" methods for controlling and treating the wastes that were being created. But as the international industries attempted to implement the legally mandated "end-of-the-pipeline" controls, the industries quickly encountered poor effectiveness and spiraling costs, especially as the emission limits were lowered.

In the 1970s, in response to the rise of the Environmental Movement and "Command and Control" statutes, many industrial inventors in many countries began to work to creatively improve their individualized pollution problems. Those sorts of individualized solutions first coalesced into an organized "Pollution Prevention" organized (and publicized) program at the 3M Corporation in 1975, led by Dr. Joseph T. Ling, and those semi-independent efforts coalesced into a "movement" of very broad scope and approaches in 1976, at a United Nations multi-disciplinary seminar entitles "Non-Waste Technology and Production" published in 1978.[36]

Then in the 1980s many additional companies in many countries began to adopt the explicitly environmentally conscious 3M approaches and began to quietly commercialize many such "Pollution Prevention" projects, aided by slowly growing support from many national governments in the 1980s and 1990s.

Then, as this author has previously argued, the predominantly Academic / Governmental "Green Chemistry Movement" of the 1990s and 2000s evolved out of, but was only a narrow subset of, the earlier mostly industrial Pollution Prevention efforts of the 1970s and 1980s.

Furthermore, the importance of the mostly parallel and semi-independent emergence of modern bio-technology, not addressed by this paper, has clearly and rapidly accelerated and evolved, especially in recent years. But it also appears that much remains to be done to evolve both the "chemical" and "bio-technological" and downstream consumer products and achievements toward better economic and environmental outcomes.

This author believes that it is important to recognize the evolutionary nature of the long-term historical developments described here, and in this author's prior papers. In particular, this author has previously argued that:[37]

> …Real-World Industrial "Green Chemistry" emerged as a holistic final outcome from an extremely varied and complex set of parallel evolutionary "random tinkering" sub-processes that began about the time of World War II, and that evolutionary process accelerated in the 1970s …. That overall evolutionary process was the product of very complex interactions of very many internal and external events, carried out by many human investigators from multiple disciplines and countries, who were individually driven by many different goals, motivations, influences and input factors, including customer / societal needs and desires, economics, the environment, the legal / statutory /

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[35] See Murphy (2018), (2020) and (2021)

[36] See Murphy (2020) and Murphy (2021)

[37] See Murphy (2020)

> regulatory pressures, as well as the constantly evolving state of the underlying sciences of Chemistry, Biology, and Engineering, over decades. Many of the resulting individual inventions were also the direct product of individual human creativity, thought, and logic, as aided by intercommunications between the investigators, as well as the constraints of the laws of Nature, local circumstances, and elements of chance.

While contemplating such broad and long-term evolutionary phenomena, it seems worth re-considering a comment by Professor Giuseppi Bruni (the teacher and mentor of Guilio Natta), who said that "the only difference between theoretical (fundamental) and industrial (applied) problems is that the latter is more difficult to resolve because you have to take into account lot of factors that you can neglect in the former."

Fortunately, in the last 10 years or so, the "Green Chemistry Movement" appears to be evolving and broadening back again, to encompass the much earlier, broader, international, and interdisciplinary concepts of "Pollution Prevention", "Sustainability", "Systems Thinking", and/or a "Circular Economy".[38] In this author's opinion, those broader, international, interdisciplinary, and evolutionary approaches will be an important key to successfully addressing and resolving the sometimes conflicting needs and contributions of individuals, Industry, Society, the Economy, the various branches of the Sciences and Engineering with the Environment.

In 1997, Professor Jared Diamond of UCLA published his Pulitzer Prize winning book, "Guns, Germs, and Steel – The Fates of Human Societies." Diamond explored the influence and effect of very many external physical, biological, technological, and social factors on the evolution of, and births and deaths of multiple human societies, from many causes over thousands of years, beginning with the pre-historic hunter-gatherers, then up to the modern technological age. Surely, we should all occasionally take the time to consider and learn about and from all those factors and history, during our current and future attempts to further harmonize Man's constantly evolving technologies with the still growing population and its needs, and with the physical, biological, and cultural constraints of the Earth and its ecosystems.

Mark A. Murphy Ph.D., J.D. is a retired industrial chemist and patent attorney, writing "Pro-Bono." He thanks his many prior colleagues from Science, Engineering, and Law, and the authors of the references cited herein, and his wife Mary Bertini Bickers (a woman of many very unusual talents in her own right) for her many forms of support. The opinions stated in this article are solely those of the author and were not induced or financially supported in any way by any other person, business, or legal entity.

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[38] See Murphy (2023) and Murphy (2025a)

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