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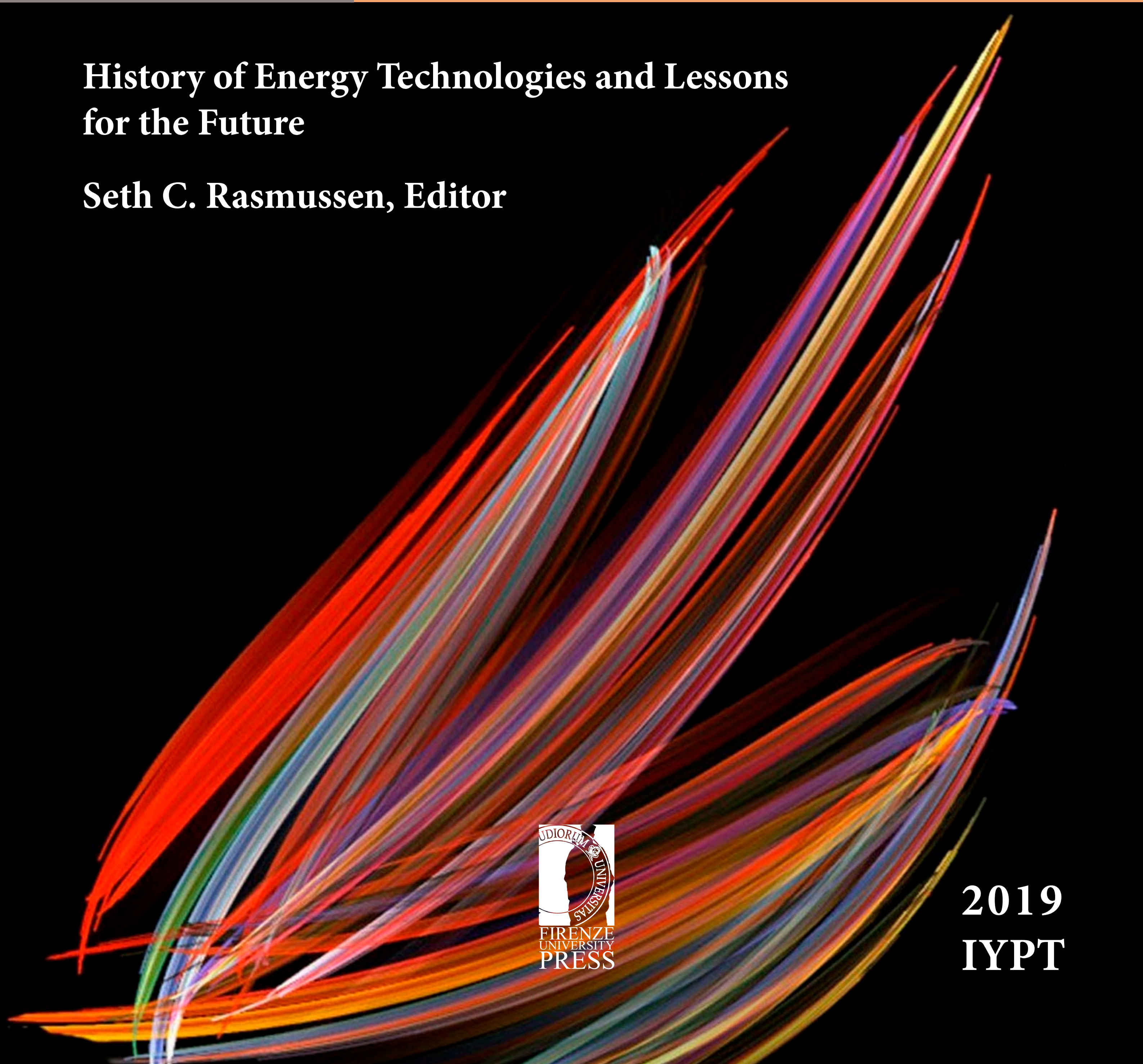
History of Energy Technologies and Lessons for the Future

Seth C. Rasmussen, Editor



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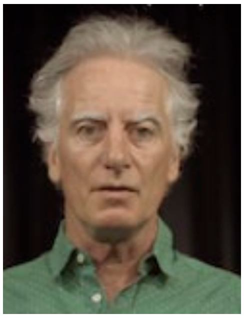

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Preface

It is a great honour for me to write these few lines of preface to the special issues of *Substantia* dedicated to the 150th anniversary of the Periodic Table by Dmitrij Mendeleev. In 2019 there are other important anniversaries besides that of the periodic table. One of these is the centenary of Primo Levi's birth. I believe these two anniversaries are strictly related, in fact *The Periodic Table* by Levi has been considered by the *Royal Institution of Great Britain* as the "best book of science ever written". It would be sufficient to recall an impressive excerpt from "Iron", a tale of the *The Periodic Table*, to acknowledge the uniqueness of this literary work:

> "*We began studying physics together, and Sandro was surprised when I tried to explain to him some of the ideas that at that time I was confusedly cultivating. That the nobility of Man, acquired in a hundred centuries of trial and error, lay in making himself the conqueror of matter, and that I had enrolled in chemistry because I wanted to remain faithful to this nobility. That conquering matter is to understand it, and understanding matter is necessary to understand the universe and ourselves: and that therefore Mendeleev's Periodic Table [...] was poetry ...*".

When we designed the project related to these special issues, we had in mind Levi's work and in particular his wonderful tales that belong to *The Periodic Table*. I like to recall this homage to a chemist-writer-witness to introduce the six topics that are associated to the special volumes of *Substantia*.

As President of the University of Florence which is the owner of the publisher *Firenze University Press*, I am truly grateful to the Editors – Marc Henry, Vincenzo Balzani, Seth Rasmussen, Luigi Campanella, Mary Virginia Orna with Marco Fontani, and Brigitte Van Tiggelen with Annette Lykknes and Luis Moreno-Martinez – for accepting the invitation made by the Editor-in-Chief Pierandrea Lo Nostro and for the extraordinary work for the preparation of these special issues. Of course the choice of the six subjects was not accidental: we tried to identify some features of the chemistry realm, related for several reasons to the periodic table. They are strikingly associated to the great challenges for our future: these are water, sustainability, energy, open chemistry, the history and the educational perspectives of the periodic table.

During its long path of progress and civilisation mankind has strongly modified nature to make our planet more comfortable, but at present we must be very careful with some dramatic changes that are occurring in our Earth. Science and technology, and chemistry primarily, can help mankind to solve most of the environmental and energy problems that emerge, to build a radically different approach from that that has prevailed in the last two centuries. It is a fantastic challenge, since for the first time we can consider nature not as a system to simply exploit, but a perfect ally for improving life conditions in the whole planet. Chemistry has already engaged and won a similar challenge when, understanding the pollution problems generated by a chaotic and rapid development, succeeded in setting up a new branch, green chemistry, that turned upside down several research topics. Now is the time to develop sustainable chemistry: the occurring events demand that chemists propose new routes and innovative approaches. In the last two centuries we have transformed immense amounts of matter from nature into waste without thinking that we were using non renewable energy sources. We have been acting as our natural resources were unlimited, but knowing that they are instead limited. Now we are realizing that it is not possible to continue along this road. Our planet and our atmosphere are made of finite materials and their consumption during the last two centuries has been impressive. Some elements that are crucial for current and future industrial countries are known to be present on Earth crust in very small amounts and their recycling from waste cannot be a choice anymore, but it is rather an obligation.

Climate is another big problem associated to the terrific changes occurring in some equilibria, both as a consequence of the violent industrial development and energy consumption. We need, and we will always need more and more, an immense amount of energy. The only solution to secure wellness to future generations is the conversion to renewable energy sources. In this view, food and water, due to the strong increment in the demographic indices, could become the true emergencies for billions of individuals. Looking at the picture I tried to draw in this short preface it becomes more clear why we selected those topics for our special issues.

I am optimistic, and I have the strong confidence that chemistry, that studies matter and its transformations, will give mankind the picklock to overcome those challenges.

We will definitely need insightful minds, creativity, knowledge and wisdom.

Luigi Dei
President of the University of Florence

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Editorial

Sustainability and Energy
Knowledge of the Past is Critical for our Future

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Sustainability and Energy – two fundamental topics that are key to the past, and future, of humanity. Of these two, however, energy has long been the primary focus and the contribution of sustainability has been a secondary concern. Our preoccupation with energy via chemical means can be traced back to the initial taming of fire, dating to at least 500,000 BCE[1]. By 300,000 BCE, mankind was beginning to use fire to cook their food and, by 100,000 BCE, the use of fire as a source of heat and light had become well-established, permanently changing the future of humanity[2]. Throughout these time periods, mankind was dependent on carbon as the singular source of fuel for energy production via combustion. As the carbon sources consisted of wood and other plant matter, this earliest energy technology could at least be viewed as renewable. As such, it could be considered sustainable, providing that the consumption of wood and plant matter did not outpace the regrowth of new trees and plants to take their place.

Of course, as civilizations developed and population centers grew, the desire for more effective fuels grew. By the first millennium BCE, coal had emerged as a more concentrated fuel for combustion, with Theophrastus (c. 371–287 BCE) referring to the use of coal as fuel in his geological treatise *On stones*[3]. During the 18th century it was found that coal could also be used to produce a combustible gaseous product, known as *coal gas*, via its destructive distillation. This gas went on to become the initial fuel for gas lighting. Methane, originally known as either *firedamp* or *marsh gas*, was also first studied in the 18th century and was later determined to be the primary component of coal gas[4]. In the modern day, methane from natural deposits is

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[1] S. C. Rasmussen in *Chemical Technology in Antiquity* (Ed.: S. C. Rasmussen), ACS Symposium Series 1211, American Chemical Society, Washington, D.C., **2015**, p. 7.

[2] R. Shahack-Grossa, F. Bernab, P. Karkanasc, C. Lemorinid, A. Gophere, R. Barkaie, *J. Archaeol. Sci.* **2014**, *44*, 12.

[3] E. R. Caley, J. F. C. Richards. *Theophrastus On Stones. Introduction, Greek Text, English Translation, and Commentary*. The Ohio State University, Columbus, OH, **1956**, p.48.

[4] S. C. Rasmussen. *Acetylene and Its Polymers. 150+ Years of History.* Springer Briefs in Molecular Science: History of Chemistry, Springer, Heidelberg, **2018**, pp. 5-6.

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more commonly known as natural gas, which can also contain some higher alkanes and small amounts of other gaseous impurities. The discovery of other hydrocarbon gases such as ethylene and acetylene then followed in the 19th century, although coal gas still remained the primary gaseous fuel for applications such as lighting until the large-scale production of acetylene from calcium carbide at the end of the 19th century[5].

During this same time period, another commonly used fuel was whale oil, particularly for use as a lamp oil for lighting. The demand for whale oil was high during the 18th century and reached its peak in the 19th century. It was only with the development of the petroleum industry that the use of whale oils declined considerably as it was replaced by cheaper and more effective fuels. Although descriptions of the distillation of crude oil by Islamic philosophers date back to the 9th century[6], the modern history of petroleum began with the development of kerosene by Abraham Gesner (1797-1864) in 1846[7]. Even though kerosene was first produced from coal, it was soon found that it could be produced more easily from petroleum. Other products were also isolated during the fractional distillation of kerosene from petroleum, but these initially found little use. It wasn't until the invention of the automobile in the late 19th century that one of these products, gasoline or petrol, was recognized as a valuable fuel. By 1916, the production of gasoline grew to surpass that of kerosene and petroleum fuels rapidly became the primary source of energy throughout the industrialized world.

While we were able to view the early use of wood for combustion as sustainable, at least under specific limiting factors, the same cannot be said for these later carbon fuels. Coal, natural gas, and petroleum are all fossil fuels resulting from the anaerobic decomposition of organic matter. While initially abundant, the natural deposits of these materials are thought to have taken millions of years to accumulate and cannot be replenished within a reasonable timeframe. Whale oil, too, is anything but sustainable and the hunting of whales for this fuel is said to have nearly brought about their extinction.

Beyond carbon, the ability to obtain energy from other elements on the periodic table was not really an option until the beginning of the 19th century. It was in 1800 that energy via non-combustion methods was primarily introduced with the discovery of the Voltaic Pile (i.e. the first battery) by Alessandro Volta (1745-1827)[8]. Electricity via static generation had been previously known since the Roman era, but could only be stored in an early form of capacitor and could not be released or applied in a controlled fashion. It was Volta's invention of the battery that really began the electric age. Although Volta's initial battery utilized combinations such as copper and zinc, a variety of other metal combinations were also found to successfully generate current and modern battery technology now exhibits a plethora of chemical combinations. Other electrochemical variants of the classical battery followed, most notably the fuel cell introduced by William Grove (1811-1896) in 1839[9].

It was also in the 19th century that interest began to turn to the potential of electrical energy from light, beginning with the first report of photovoltaic effects by Edmond Becquerel (1820-1891) in 1839. Of course, mankind had always relied on the sun for both heat and light, but the possibility of harvesting electricity from sunlight ushered in the development of solar cells in the pursuit of solar energy. Although initial progress was slow, the first practical silicon solar cells were developed in 1954 by Bell Labs[10], which only further increased interest in this nascent technology. Since then, great advances have been made in the development of silicon solar cells, as well as the introduction of a wide variety of other solar cell devices, including the recent focus on solar cells from semiconducting organic materials in the last couple of decades.

Of course, another powerful source of energy in the form of uranium (specifically uranium-235) resulted as a consequence of the Manhattan Project during World War II. The first nuclear reactor was constructed in November 1942 by a group led by Enrico Fermi (1901-1954), with a self-sustaining nuclear reaction successfully demonstrated in December of the same year[11]. This was followed with the construction of an experimental breeder reactor in Idaho, which generated the first electricity from nuclear energy on December 20, 1951. The first commercial plant to generate electricity by nuclear energy was located in Shippingport, Pennsylvania and reached its full design power in 1957, after which the US nuclear power industry grew rapidly in the 1960s.

As can be seen from the discussion above, mankind's love-affair with energy is long and varied. This is

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[5] S. C. Rasmussen. *Acetylene and Its Polymers. 150+ Years of History.* Springer Briefs in Molecular Science: History of Chemistry, Springer, Heidelberg, **2018**, pp. 30-35.

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[8] A. Volta, *Philos. Trans. R. Soc. London* **1800**, *90*, 403.

[9] A. E. Becquerel, *C. R. Acad. Sci.* **1839**, *9*, 145.

[10] J. Perlin. *The Silicon Solar Cell Turns 50* (NREL Report No. BR-520-33947). National Renewable Energy Lab., Golden, CO, **2004**.

[11] U.S Department of Energy (DOE/NE-0088). *The History of Nuclear Energy.* Office of Nuclear Energy, Science and Technology, Washington DC.

especially true as the current discussion has been limited to those fuels and technologies based on chemical processes. As such, physical/mechanical energy technologies such as hydroelectric power and wind energy could also be added to those previously discussed. Still, considering the varied sources of energy at our disposal, the industrialized world still relies primarily on fossil fuels to meet its energy needs. This is especially concerning due to the finite nature of these fuels, as well as the toll our historic dependence on combustion technologies has inflicted upon the environment. While a hot-button topic within the general public, the vast majority of actively publishing climate scientists – ca. 97%[12] – agree that global warming and climate change are the result of such human activities[13]. Furthermore, if something is not done to change our energy habits, things will only get worse. In fact, it is believed that even if we completely stopped emitting greenhouse gases today, global warming would continue for at least several more decades, if not centuries. Still, it is believed that it is not be too late to avoid or limit some of the worst effects of climate change.

Due to these various factors, it is clear that future energy technologies must be both sustainable in practice and shift away from our current emphasis on combustion. At the same time, there are various factors that actively inhibit such paradigm shifts, be it economic, political, limits in current technology, or simple inertia. It is only with a clear knowledge of the past that we can completely understand how mankind came to the current cross-roads. At the same time, such knowledge can also highlight factors that prohibited the development of alternate technologies that might have served us better in the long run. Thus, to better serve the future, it is worthwhile to review the past in greater detail. It is with this viewpoint that I am proud to present the following special issue on *Sustainability and Energy* that highlights the histories of various energy technologies, particularly those that might provide potential paths forward to a better future. The fact that this issue is part of *Substantia*'s celebration of the *International Year of the Periodic Table* is also very fitting, as the various energy technologies discussed above have not been limited to any one element or periodic block, but have originated in chemistry based upon elements from across the periodic table.

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[12] J. Cook, D. Nuccitelli, S. A. Green, M. Richardson, B. Winkler, R. Painting, R. Way, P. Jacobs, A. Skuce. *Environ. Res. Lett.* **2013**, *8*, 024024.
[13] N. Oreskes. *Science* **2004**, *306*, 1686.

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Watt's in a name? Units of power and energy

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Abstract. The origins and adoption of the units of power and energy, watt and joule, are examined, along with their relationships to the achievements of their namesakes, James Watt and James Prescott Joule. The watt and joule came about as part of a group of practical electrical units named and defined in the second half of the nineteenth century. The development of that system and its relationship to the French revolutionary metric system and the current Système International (SI) are outlined. William Thomson (later Lord Kelvin) and the Siemens brothers had important parts in the story; their roles and the units named after them are also described.

Keywords. Nomenclature, units, watt, electricity.

INTRODUCTION

Scientists are accustomed to eponyms, terms derived from the names of people.[1] Often the terms refer to laws, chemical reactions, or other discoveries, named for the putative discoverer of the phenomenon.[2] Fourteen chemical elements have been named directly for scientists, and another two indirectly (named after minerals which had been named after scientists). All 14 of the elements directly named for scientists are synthetic elements, discovered and named only in the years after the Second World War. The scientists so immortalized include some who were themselves important discoverers of elements, such as the Curies, Glenn Seaborg, and most recently Yuri Oganessian; others, such as Copernicus, Einstein, and Mendeleev, discovered no elements, but are honored for other epochal scientific contributions. Constants and units are also often named for scientists. As with elements, so with constants, the connection between the constant and the eponymous scientist is sometimes more direct, sometimes less. The Planck constant, for example, is named for Max Planck, the first scientist to use it in a physical problem.[3] Planck gave the constant the symbol still used for it (h) and a value smaller by just over 1% than the currently fixed value. The Avogadro constant, or its numerical value better known to chemists as Avogadro's number, on the other hand, is a quantity that Amedeo Avogadro never knew, even approximately. Avogadro is best known for proposing that equal volumes of gas contain equal numbers of molecules, but he had no idea of what that number might be. Jean Perrin named the quantity in Avogadro's honor early in the 20th century.[4]

Names of units are the focus of this paper, in particular units of energy and closely related physical quantities such as power and force. The paper was motivated by curiosity over when and under what circumstances the current units of power and energy in the international system of units (Système international, SI) came to be proposed and adopted. As the title suggests, the watt and James Watt are prominently featured. In the course of researching the watt, I learned that the tendency toward eponymy in physical units is more recent than I had expected, dating from the middle to later nineteenth century; that Watt thought more about units than I had realized; that the path from the French revolutionary metric system to the twentieth-century SI was far from straight; and that the watt was first defined as an electrical unit.

The origins of the watt and the joule are so inextricable from the establishment of electrical units and standards in the nineteenth century that the main narrative in the paper (although not its main concern) is how those units and standards came to be. In service of the main focus on eponymy, though, digressions from that narrative include glimpses at aspects of the scientific careers of Watt and Joule and of two other eponyms prominent in the establishment of electrical units, namely William Thomson (later Lord Kelvin) and the Siemens brothers. And in order to round out the main narrative, the relationship of the electrical units to the metric system of units and to the current SI will also be outlined.

ELECTRICAL UNITS CIRCA 1860

Well before 1860, important force laws for electricity and magnetism had been discovered, and the fact that the two apparently different kinds of phenomena were in fact related was also known. The relationship between electricity and magnetism has implications for the units chosen to describe electromagnetic phenomena. For the purpose of understanding the origins of various electrical units, we may take Coulomb's electrostatic force law or Ampère's electromagnetic force law as foundational. Force is a mechanical property with dimensions of $M\ L\ T^{-2}$, where M represents the dimension mass, L the dimension length, and T the dimension time. The choice of one or the other force law as fundamental is arbitrary; however, the choice of either amounts to defining an absolute set of electrical and magnetic units. The set is absolute in the sense that all of the electrical and magnetic units within it would be related to already existing mechanical units.

Choosing Coulomb's law to be fundamental amounts to a choice of electrical units called *absolute* electro*static* units in which electrical charge has dimensions $L^{3/2}\ M^{1/2}\ T^{-1}$; the dimensions of current, then, would be charge per unit time or $L^{3/2}\ M^{1/2}\ T^{-2}$. However, if one takes Ampère's law to be fundamental, different dimensions result. Absolute electromagnetic units have charges of dimension $L^{1/2}\ M^{1/2}$ and currents $L^{1/2}\ M^{1/2}\ T^{-1}$. (For more detail, see the Appendix.)

Within an absolute system of units, further choices are needed before units are defined: one must also select the defining mechanical or dynamical units (that is, of length, mass, and time). The system favored in Britain for scientific work at this time and eventually adopted more widely was the cgs system, in which lengths are specified in centimeters, masses in grams, and time in seconds. (Later scientists would say simply that the centimeter, gram, and second are the *base units* of the cgs system; however, the term base unit was not yet coined.[5] Base unit is a useful term, and I will use it anachronistically in what follows.) The cgs electrostatic unit of charge is therefore 1 $\mathrm{cm}^{3/2}\ \mathrm{g}^{1/2}\ \mathrm{s}^{-1}$. The corresponding unit of current, then, is 1 $\mathrm{cm}^{3/2}\ \mathrm{g}^{1/2}\ \mathrm{s}^{-2}$. In Germany, the preferred set of mechanical base units was the millimeter, milligram, and second;[6] call it mms. Under this system, the electrostatic unit of charge is 1 $\mathrm{mm}^{3/2}\ \mathrm{mg}^{1/2}\ \mathrm{s}^{-1}$ and that of current 1 $\mathrm{mm}^{3/2}\ \mathrm{mg}^{1/2}\ \mathrm{s}^{-2}$. Obviously, electrostatic units have different magnitudes in the cgs and mms systems, even though they are both based on the same fundamental equation. And these units are different than the absolute units based on the electromagnetic force law.

Neither cgs nor mms electrostatic or electromagnetic units were of convenient magnitude for the practical electrical or magnetic applications of the time, such as telegraphy. Submarine telegraph cables were laid in the 1850s, and the first attempt at a transatlantic cable also took place in that decade.[7]

Not surprisingly, a desire for electrical and magnetic units such that a typical laboratory or commercial measurement was comparable in size to the unit (as opposed to many orders of magnitude greater or smaller) emerged around this time. Such units were described as "practical." As we will see below, practical units could be defined in terms of absolute ones (such as the ohm defined as 10^{10} mms units of resistance) or they could be based on arbitrary standards (such as Werner Siemens's mercury standard for resistance). In the later nineteenth century, "practical" and "absolute" were often but not always used as though mutually exclusive, for the term absolute was often applied only to units whose relationship to other units in the system had a numerical factor of 1. Thus, a unit defined as 10^{10} mms units of resistance might be called absolute in the sense that it is defined in terms of specified non-electrical units, although it is not itself "the" absolute unit of resistance in the mms system.

Whether absolute or practical, international units and standards were required for science, industry, and commerce, and they would be much discussed over subsequent decades.

NAMES AND UNITS

Just before the start of the formal and organized efforts to define electrical units and standards outlined below, two engineers on the Atlantic Submarine Telegraph project floated a proposed system of practical electrical units. Latimer Clark and Sir Charles Bright made a presentation at the 1861 British Association for the Advancement of Science (BAAS) meeting and published their paper in *The Electrician* shortly thereafter. "The science of Electricity and the art of Telegraphy have both now arrived at a stage of progress at which it is necessary that universally received standards of electrical quantities and resistances should be adopted," they begin. They go on to propose four practical units, not connected to absolute mechanical units. And to illustrate the relationships among these arbitrary units, they suggest "for this temporary purpose let us derive terms from the names of some of our most eminent philosophers, neglecting … all etymological rules".[8]

Quantity	**Name**	**Definition**
Tension (i.e., electromotive force)	Ohma	1 Daniell cell
Quantity (i.e., charge)	Farad	Charge induced by 1 Ohma across 1 m^2 plates separated by 1 mm dry air
Current	Galvat	1 Farad per second
Resistance	Volt	Passes 1 Galvat under 1 Ohma tension

The paper by Clark and Bright appears to be the beginning of eponymy in scientific units. Later committees charged with describing electrical units followed their example, sometimes explicitly,[9] although the names on their list were eventually attached to different quantities than they proposed. Clearly, eponymy in other aspects of electrical research was already well established: Clark and Bright refer to Daniell's cells and to a galvanometer without remarking upon those terms.

At the same 1861 conference in Manchester where Clark and Bright made their proposal of electrical units, the BAAS at the behest of William Thomson[10] appointed a committee to report on standards of electrical resistance.[11] The committee initially included several scientists who would become eponyms: Alexander Williamson (whose name is attached to a synthesis of ethers) and Charles Wheatstone (best known for the Wheatstone bridge electrical circuit), as well as Thomson (the Thomson in the Joule-Thomson effect of cooling a gas by letting it expand through a porous plug, later to become Lord Kelvin). The committee rather quickly expanded its purview beyond standards of resistance, noting that such a resistance unit ought to be part of a coherent system of electrical units. The unit of resistance, and indeed, the other units of the system, ought to "bear a definite relation to the unit of work, the great connecting link between all physical measurements".[12]

They advocated basing those electrical units on the "French metrical system" rather than the units in common use in Britain. As might be inferred from their preference for the metric system, the committee was not insular or provincial. Indeed, they solicited opinions from scientists throughout Europe and as far afield as the United States (in the person of Joseph Henry, then Secretary of the Smithsonian Institution and now an eponym for a unit of electrical inductance).[12]

In 1865, the Committee specified a practical standard of electrical resistance. By now the Committee had expanded to 12 members, including such eponymous luminaries as James Clerk Maxwell (equations of electricity and magnetism), James Prescott Joule (unit of energy; see below), and Charles William Siemans (unit of conductivity; see below).[13] The resistance unit was intended to be equal to 10^{10} mm s^{-1}. (An absolute electromagnetic unit of resistance would have dimensions of L T^{-1}, so mm s^{-1} would be the electromagnetic unit of resistance preferred by Germans such as Wilhelm Weber, who had done important work in this area.) The committee wanted their new standard to have "a distinctive name, such as the B. A. unit, or, as Mr. Latimer Clark suggests, the 'Ohmad'".[10] This name was later changed to ohm, which became the first of yet another set of electrical and magnetic units, eventually to be known widely as the practical system. The committee had chosen its unit because it wanted a decimal multiple of a unit already in use (i.e., not something completely arbitrary or unrelated to existing systems) and because a physical standard of approximately this magnitude had already been developed and found convenient.

Members of the Committee threw around ideas for names of units as well as for ways of indicating decimal multiples or submultiples of units, for it was clear that at least some of the units of any coherent system would be of inconvenient size for at least some practical uses. C. F. Varley, one of the committee members, wrote a letter to Thomson in 1865 describing unit names he had discussed with Latimer Clark and Fleeming Jenkin. The letter tells Thomson that Clark had proposed the names Galvad for potential, Ohmad for resistance, Voltad for current, and Farad for quantity (or charge as we would say). The names for one million units would be Galvon, Ohmon, Volton, and Faron respectively. In effect, the multiple 10^6 was proposed to be represented by a suffix, -on. Jenkin objected that denoting magnitude by an ending would lead to confusion, particularly in the case of unclear ("indiscreet") writing, to which Jenkin said he was prone; Varley said that that problem also applied "to me and to you [Thomson]." Varley would like to see a French name on the list, perhaps Ampère for the magnetic pole, but he objected to Galvad "because Galvani discovered next to nothing[14]." We see in Varley's letter the same four scientists that Clark and Bright had in mind four years earlier, now associated with different quantities, but still not with the quantities that would eventually "stick" to their names. We also see an attempt, albeit not adopted, to conveniently refer to multiples of a unit, recognizing that no system would have magnitudes convenient for all applications.

The BAAS Committee on Standards of Electrical Resistance continued to meet and report until 1869, investigating such matters as the relationship between electromagnetic and electrostatic units.[15] In 1872 the BAAS appointed another committee, this one "for reporting on the Nomenclature of Dynamical and Electrical Units." Included on the new committee were four members of the earlier committee: Thomson, Maxwell, Siemens, and Jenkin.[16] The following year, that committee reported a preference for the cgs system for both electrical and dynamical units. It proposed a terminology for expressing decimal multiples by appending the cardinal number of the appropriate power of ten to the name of a unit (for example centimeter-nine = 10^9 cm) and for expressing submultiples by prefixing the ordinal number of the absolute value of the relevant power of ten to the name of a unit (for example, ninth-second = 10^{-9} s). This suggestion came from committee member G. Johnstone Stoney, who was the lone dissenting voice against selecting the centimeter as a base unit of the recommended system. His argument that the base unit ought not to include a multiplicative prefix was apparently less persuasive than Thomson's favoring a system in which the density of water was unity. This report proposed names for the cgs units of force (dynamy, dynam, or dyne), work (ergon or erg), and power (ergs per second).[17] Looking back from the twenty-first century at the development of eponymy in units, this report appears to be a pause. It mentions the ohm, volt, and farad, practical electrical units previously defined by a BAAS committee that included several of the same members. But for dynamical units, the committee selects names based on Greek roots, a classical language still influential in British higher education.

INTERNATIONAL UNITS

Although the BAAS consulted widely, expressed a preference for the "French metrical system," and proposed an international menu of eponyms, it was a national and not an international body. The 1870s and 1880s would see international bodies and international agreements concerning weights and measures.

Seventeen nations signed the Convention du Mètre in 1875, thereby establishing the Bureau international des poids et mesures (BIPM, International Bureau of Weights and Measures) to be directed by an international committee (CIPM, Comité international des poids et mesures) which itself is under a general conference (CGPM, Conférence générale des poids et mesures) consisting of delegates of the member states. The initial signatories were mainly from countries of Europe or Eurasia (i.e., the Russian and Ottoman Empires), along with a few from the Americas. The principal nation that persists in employing non-metric units in domestic commerce, the United States, was among the original signatories. The United Kingdom, was represented at the 1875 conference that led to the treaty, but it declined to sign until 1884. The BIPM was initially charged with maintaining prototypes of the meter and kilogram, and thermometry and geodesy were also included within its purview. In 1921, coordination of electrical units and standards was added to its range of responsibilities.[18]

The birth of the metric system in revolutionary France during the 1790s is a remarkable story, summarized here in only the briefest outline. The revolution's wholesale overthrow of feudal institutions enabled a widespread centralizing and rationalizing reform of weights and measures to replace a patchwork of regional units. In 1790 Talleyrand, then Bishop of Autun and a member of the National Assembly, brought up reform of weights and measures in that Assembly. After receiving a favorable report, that body decreed in May 1790 that a new set of uniform weights and measures be drawn up. The decree directed the king to "beg His Majesty of Britain to request the English Parliament to concur with the National Assembly in the determination of a natural unit of measures and weights." Louis XVI, still King of France at the time, sanctioned the decree in August.[19] The British declined to participate in the project. The decision to define the meter as the 1/10,000 of a quadrant of the earth's circumference and to determine its value by measuring an arc of a meridian from Dunkirk to Barcelona is described, along with the epic execution of the survey, in *The Measure of All Things* by Ken Alder.[20] Reform of weights and measures continued as the revolutionary government changed (to the Convention), decreed a new calendar, suppressed the Académie des Sciences, and purged the Commission of weights and measures. A law of 18 Germinal, year III, (known elsewhere on the continent as 7 April 1795), defined the new units: the meter, the are (an area of a square with a 10-m edge), the stere (a meter cubed), the liter (the capacity of a cube with side 1/10 m), and the gram (mass of a cube of water with side 1/100 m at the melting point of ice).[21] In 1798, another attempt was made to give the new system international standing by inviting European scientists to participate in the final stages of defining its standards. Invitations were issued by Foreign Minister Talleyrand to nearby countries neutral in the ongoing European hostilities or allied to France (such as the short-lived Batavian, Cisalpine, Helvetian, Ligurian, and Roman Republics).[22] Platinum standards were made for the meter and the kilogram in 1799, and a law of that year defined the units in terms of the standards. The new system was widely used by savants and bureaucrats and taught in the centralized schools, but it did not displace older units in the marketplace for more than a generation afterwards.[21]

At the time of our principal narrative in the 1860s, metric units were widely used in science throughout Europe, but the units considered basic were typically neither the meter (but the centimeter or millimeter) nor the kilogram (but the gram or milligram). In 1869, the French government (Second Empire under Napoleon III) invited representatives from European, Eurasian, and American countries to take part in an International Commission of the meter with an eye toward propagating the use of the metric system in international commerce and constructing new international prototypes of the 1799 standards. This commission, which met in 1870 (just after the start of the Franco-Prussian war) and in 1872, led to the Convention of the Meter in 1875 and the permanent international institutions established therein.[23]

Not long afterward, in 1881, the first International Electrical Congress was held in Paris under the auspices of the French government and in conjunction with an international electrical exposition. It would be the first of many such international electrical meetings in the late nineteenth and early twentieth centuries held at international commercial expositions. Members of this Congress came predominantly from Europe, but Japan was also represented as well as several countries from the Americas.

Among the actions taken was the adoption of a set of practical electrical units. The Congress's commission on electrical units passed seven resolutions, including: to base its units on a cgs foundation; to keep the practical units ohm and volt with their current definitions of 10^9 cgs units of resistance and 10^8 of electromotive force respectively; to define an ampère as the current produced by one volt through one ohm resistance; to define a coulomb as the quantity (charge) such that an ampère is one coulomb per second; and to define a farad as the capacity such that a coulomb in a farad yields a volt.[6]

These extensions to the practical system of electrical units came after some drama inside the conference chamber. They were adopted after the Congress had been adjourned without conducting any business on the previous day, September 20. On that day, the French Minister of Posts and Telegraphs, presiding, opened the meeting and immediately presented his colleague, the Foreign Minister. The latter told the assembly that a telegram had just announced the death of US President Garfield. "He thought that considering the bereavement that fell upon a friendly nation the assembly would wish to show its deep sympathy by immediately adjourning the meeting".[24]

Apparently, some drama regarding the units in question took place behind the scenes at the conference as well. Éleuthère Mascart was secretary of the section of the Congress that dealt with electrical units. He described the delegates enjoying the spectacle of Thomson and Hermann Helmholtz (himself an eponym in thermodynamics) debating heatedly in French, each with his own distinctive pronunciation. The section got bogged down on the standard for the ohm. On the next day, an unofficial group consisting of Mascart, Thomson, William Siemens, Helmholtz, Gustav Kirchhoff (Kirchhoff's laws of circuits), Rudolf Clausius (Clausius-Clapeyron equation), Gustav Wiedemann and Werner Siemens agreed on the definitions of ohm and volt and on appointing an international commission to define the dimensions of the mercury column that was to be the ohm standard. Still later Mascart and Thomson worked out the definitions of ampère, coulomb and farad over a hot chocolate with Lady Thomson (born Frances "Fanny" Blandy). When Mascart read the definitions to the section on September 21, some members were surprised, but after Thomson and Helmholtz spoke in their favor, the group adopted them.[25]

Several more international electrical congresses gathered in various European cities in the 1880s and 1890s, frequently in Paris. At the Paris congress of 1889, practical units of work and of power were adopted. The unit of work was called the joule, defined as 10^7 cgs units of work, the energy dissipated by one ampere through one ohm of resistance. The unit of power was called the watt, defined as 10^7 cgs units, equal to one joule per second. It was also decided that the output of industrial machines would be expressed in kilowatts rather than in horsepower.[26] Here we finally meet our featured units, defined as practical electrical units.

WATT AND JOULE,
THE SCIENTISTS AND THE UNITS

James Watt (1736-1819) is well known as an engineer whose improvements to the steam engine powered the industrial revolution in Britain. That aspect of Watt's life and work is well documented elsewhere[27] and will not be discussed here except to note that Watt's name is a particularly appropriate eponym for a unit of power, even though electrical power was outside his expertise. Watt is also known to historians of chemistry for his interest in that discipline, including important work on the composition of water.[28] Watt's interest in units, though, is what will occupy our attention here.

The unit closely associated with Watt during his lifetime, the horsepower, was to be displaced by the kilowatt, at least for electrical generators and other electrical machines if the International Electrical Congress of 1889 was to have its way. The horsepower survives, though, as a unit for rating engines, especially automobile engines. The horsepower was the first important unit of power. Units for power and energy arose before the physical concepts themselves, and they were developed largely in response to industrial and commercial needs. Those who sold energy or heat (in the form of coal, for example) needed a rational basis for pricing their wares. Thomas Savery (1650-1717), who patented a "fire engine" before Watt was born, suggested around 1700 that the rate at which a horse does work would make an appropriate measure of power. Watt made a quantitative estimate of the unit considerably later. Horses were, of course, used as draft animals in agriculture at the time, but they were also used for mechanical power in factories. In that application, they usually walked around a circular track, pulling one end of a lever attached to a shaft, whose gears or other linkage ran a pump or other machine. Watt estimated the average force and speed of a horse pulling a 12-ft capstan lever, and arrived at 33,000 ft lb/min or 550 ft lb/s. This is the definition of the horsepower unit.[29]

Perhaps less well known is Watt's interest in international units and in multiples of 10 to simplify their use. In 1783 Watt wrote to the Irish natural philosopher Richard Kirwan (1733-1812) after experiencing considerable difficulty in converting the weights and measures used by Lavoisier and Laplace to the English weights and measures to which he was accustomed. In the letter, he proposed to define a "philosophical" pound consisting of 10 (philosophical) ounces or 10,000 grains, a philosophical ounce consisting of 10 drachms or 1000 grains and a philosophical drachm consisting of 100 grains. He also advocated "the ounce measure of water" for the measure of elastic fluids, avoiding cubic inches of different sizes. "If all philosophers cannot agree on one pound or one grain, let everyone take his own pound or his own grain," he added, seeing that the simplicity of decimal conversions would at least apply to relative measures, whatever the base unit. But it would be better, he noted, if all agreed on the same pound.[30]

James Prescott Joule (1818-1889) is likewise a celebrated figure. He is best known in the history of physics for quantifying the "mechanical equivalent of heat" and for contributing to the emerging concept of energy as a key physical quantity. Thus, he is a fitting scientist to honor with the name of a unit of energy. Unlike Watt, Joule did important electrical experiments. In the 1840s, he investigated electrical heating and found that electricity gave rise to heat in proportion to the resistance and the square of the current. Indeed, over the course of his career, he explored equivalences among thermal, electrical, chemical, and mechanical effects.[31]

As we have seen, Joule served on the BAAS Committee on Standards of Electrical Resistance. Indeed, he carried out experiments on the resistance of the BAAS unit.[32] Joule also served on the later BAAS Committee for the Selection and Nomenclature of Dynamical and Electrical Units. It is worth noting that Joule was still alive, albeit only for a few more weeks, when the International Congress adopted his name as a unit.[33]

SIEMENS AND THOMSON/KELVIN,
THE SCIENTISTS AND THE UNITS

The joule and the watt were adopted internationally in 1889, but they had been proposed earlier in an address by William Siemens, President of the BAAS, at its annual meeting in 1882.[34] The matter of units, both mechanical and electrical, takes up several pages of

Siemens's address. He regrets that the UK "still stands aloof" from the metric system, and he would like the BAAS to ask the government to join the "International Metrical Commission" (BIPM, established by the Meter Convention in 1875). Moving from mechanical to electrical units, he notes with some satisfaction the past work of the BAAS on this matter and acknowledges that their practical system was largely adopted by the previous year's International Electrical Congress. He ventures to suggest two additions to the practical electrical system, one of "magnetic quantity or pole" and one of power. For the former, he suggests the name weber[35] and for the latter he proposes watt. Two further units "may have to be added" before too long, he adds, one for magnetic field and one for "heat in terms of the electro-magnetic system." For the former, he follows Thomson in suggesting the name gauss[36] and for the latter he proposes joule, to be defined as an ampère flowing through an ohm. Both Weber and Joule were still alive at this time when Siemens proposed their names as units.

Siemens's own name is now an electrical unit, although whether the unit is named for him or his older brother Werner is not clear. Werner von Siemens was born Ernst Werner Siemens in Prussia in 1816. In the 1840s, he went into the field of telegraphy. He investigated insulation for laying underground telegraph wires, finding that gutta percha served admirably. He and Johann Georg Halske formed a partnership for manufacturing electrical equipment, including, eventually, electrical generators and motors, electric elevators and railways. A successful inventor and entrepreneur, Siemens maintained a strong interest in basic science. He devised an instrument for measuring alternating current, for example, and helped to fund the German metrology lab, Physikalisch-Technische Reichsanstalt.[37]

William Siemens was born Karl Wilhelm Siemens, also in Prussia, in 1823. Wilhelm went to London in 1843 to try to market an electroplating patent of Werner's. He stayed in England, where he invented a water meter that earned him quite a bit of money. Working with his younger brother August Friedrich (1826-1904), he developed an open hearth method of steel manufacture that used otherwise wasted heat from flue gases to burn off impurities from molten iron and to pre-heat incoming air entering the combustion zone. In 1859, William married Anne Gordon and became a British citizen the same year.[37] Before long, as we have seen, he took an active part in the BAAS, serving on its committees on standards of electrical resistance and on nomenclature of dynamical and electrical units, and eventually serving as President. William became Sir William shortly before his death in 1883, and Werner Siemens became Werner von Siemens in 1888, a few years before his death in 1892.

The Siemenses enter our story of electrical units shortly after the BAAS committee on standards on electrical resistance began its work. In the first report of that committee (1862), we see Werner Siemens among the foreign scientists consulted and we find his letter to the committee included as an appendix.[38] Elsewhere in the proceedings of that year's BAAS conference, we see William ("C. W.") Siemens among the six British scientists added to the committee.[39] Werner's letter calls the committee's attention to a paper he had published in 1860 in Poggendorff's *Annalen* in which he had proposed using a meter-long column of mercury of one square millimeter cross section at 0°C as a unit of resistance, and goes on to describe the advantages of using mercury for such a standard. "Should the adoption of the mercury unit be deemed advisable, I would place at the service of the British Association any further information or assistance in my power".[38] Preliminary measurements relating "Siemens's unit" to other resistance measurements available suggested that the former was very close to 10^{10} times the absolute electromagnetic resistance unit (mms system) defined by Weber. Although the mercury standard was not, in the end, adopted to define the BAAS ohm, the 1881 International Electrical Congress chose a mercury standard (length to be determined) as its standard for the ohm.[40]

When the International Electrotechnical Commission (IEC) acted in 1935 to adopt the MKS (meter, kilogram, second) system of units that later became the SI, the siemens was included as the unit of conductivity, the reciprocal ohm. Which Siemens is the eponymous one (if there is only one), was left unspecified.[41] The name siemens displaced an unofficial name for the reciprocal ohm, namely the mho,[42] which was coined by Sir William Thomson in 1883.[43] Thomson has crossed our path so often that we ought to pause to focus on him and his eponymous unit.

William Thomson (1824-1907) is well known to physicists and chemists, although not necessarily by that name. He is better known as Lord Kelvin, more formally Baron Kelvin of Largs. He was elevated to the peerage in 1892, the first scientist recognized in that way.[44]

Scientists know him for his work on thermodynamics in the 1850s,[45] and if they do not know Kelvin the scientist they know kelvin (K), the unit of thermodynamic temperature. Much of his work in thermodynamics was highly abstract and mathematical; however, he also engaged in practical applications of the science of his day, particularly in electricity and magnetism[46]. "There cannot be a greater mistake, than that of looking superciliously upon practical applications of science," he told an audience at the Institution of Civil Engineers in 1883. Much of the progress he saw in electrical and magnetic measurement over the previous 20 to 30 years, he attributed to the demands of commercial applications such as telegraphy and more recently lighting.[47] During his lifetime, he was celebrated for his role in the transatlantic telegraph cable, and he was knighted soon after its completion in 1866. One later writer even calls Thomson the "ruling spirit behind the work" and deems his work on electrical units and standards "his greatest contribution to science".[48] He invented several instruments for electromagnetic measurements and worked on many committees involving units and electrical standards.[49]

As Thomson's interest in units, standards, and nomenclature suggests, he was a strong advocate for internationally adopted units. During a lecture in the United States in 1884 on the wave theory of light, he made a digression on the virtues of the metric system and the evils of the English system of units. "You, in this country, are subjected to the British insularity in weights and measures," he observed; so he employed feet and inches in the lecture, but he apologized for using such inconvenient measures. He lamented the action of an English government official who had rescinded a recently introduced mandate to teach the metric system in English schools. "I look upon our English system [of weights and measures] as a wickedly brain-destroying piece of bondage under which we suffer," he observed. "The reason why we continue to use it is the imaginary difficulty of making a change and nothing else; but I do not think in America that any such difficulty should stand in the way of adopting so splendidly useful a reform."[50]

As a member of the British House of Lords, Kelvin spoke in favor of a bill on weights and measures in 1904 that would have made metric measures mandatory. After recounting how adoption of metric measures in other countries was achieved without hardship, Kelvin appealed to British self-regard. He said that while the UK might be grateful to France for inventing it and pleased to see how well it has worked in other European countries, it was interesting to note that the idea was born at home: "James Watt laid down a plan which was in all respects the system adopted by the French philosophers seven years later, which the French Government suggested to the King of England as a system that might be adopted by international agreement. James Watt's objects were to secure uniformity and so establish a mode of division which should be convenient as long as decimal arithmetic lasted".[51]

In 1892, the year Thomson was made Baron Kelvin, the British Board of Trade, which had worked with Thomson on practical and legal electrical standards, proposed the name kelvin in place of kilowatt-hour for "the energy contained in a current of 1000 amperes flowing under an electromotive force of one volt during one hour." Kelvin demurred, pointing out that meters manufactured by other instrument makers reading in kelvins would be confusing for users since he had also designed electrical instruments (albeit no supply meters). Kelvin suggested "supply unit" instead. The proposal was revived shortly after Kelvin's death in December 1907. The revived proposal noted that "Board of Trade Unit" could be confusingly abbreviated as BTU, which already stood for British Thermal Unit.[52] As anyone who has seen a household electric bill recently can attest, the kilowatt hour (kWh) is still the standard unit for supply of electrical energy.

Where the kelvin has taken root as a unit name is as the unit of thermodynamic temperature. This is entirely appropriate, for Thomson devised the thermodynamic temperature scale in very nearly its current form in 1848.[53] During his lifetime, it was known as Thomson's absolute scale or Lord Kelvin's absolute scale. In 1948, the ninth CGPM adopted, in principle, the Kelvin scale. It stated that the Kelvin scale "is recognized as the basic thermodynamic scale to which any temperature measurement must eventually be able to relate",[54] an acknowledgment that the scale and its name were well established in practice. Six years later, the tenth CGPM defined the Kelvin scale by fixing the triple point of water at 273.16 degrees Kelvin.[55] And in 1960, the degree Kelvin was listed among the six base units of the newly launched SI.[56] The alert reader may notice the phrase "degree Kelvin," which is not the current name of the unit; the unit and symbol were changed from "degree Kelvin" (°K) to "kelvin" (K) in 1967.[57] The definition of the unit was changed recently; it is now defined in terms of the Boltzmann constant.[58]

FROM INTERNATIONAL ELECTRICAL UNITS TO THE INTERNATIONAL SYSTEM OF UNITS

When we last met the watt and the joule, they had been proposed as units by BAAS President William Siemens and adopted at the International Electrical Congress of 1889. The International Electrical Congress of 1893, held in Chicago, defined a set of "international" units based on cgs electromagnetic unit but defined in terms of practical standards. For example, the international ohm was "based upon the ohm equal to 10^9 units of resistance of the c. g. s. system of electromagnetic units" and "represented by the resistance offered to an unvarying electrical current by a column of mercury at the temperature of melting ice 14.4521 grammes in mass, of a constant cross-sectional area and of the length of 106.3 centimetres." Similarly, the international ampere was described in terms of cgs electromagnetic units (10^{-1} such units of current) and given a realization in terms of a rate of deposition of silver from silver nitrate solution. The joule and the watt were approved essentially as in 1889, but relative to the international ampere and international ohm.[59] The Congress recommended that the nations represented there adopt the international units as legal units, that is, to which regulations would refer. Many nations did so, and that made changing the international electrical units more difficult thereafter, as many legal codes would have to be revised in the aftermath of such change.[60]

At the International Electrical Congress in St. Louis, Missouri, in 1904, no units or standards were defined, but a resolution was adopted to appoint an international commission on standardization and nomenclature for electrical apparatus. That resolution led to the founding, in 1906, of the International Electrotechnical Commission, an organization that continues more than 100 years later. The first president of the IEC was Lord Kelvin.[61] Although no action on units was taken at St. Louis, a proposal that would lead eventually to the SI made its international debut there. Moise Ascoli, head of the Italian delegation at the Congress, read a paper supporting the proposal of his countryman Giovanni Giorgi (1871-1950), and Giorgi's proposal was included in the printed proceedings of the Congress as an appendix to Ascoli's paper.[62]

Giorgi had noticed that the joule, equal to 10^7 cgs units of energy, was also equal to 1 MKS unit of energy, namely to 1 kg m^2 s^{-2}. So it (and the watt) would be natural units in a system whose mechanical foundations were the meter, kilogram, and second. That alone was not enough to bring the other practical electrical units into a coherent system. But if one defined one of the practical electrical units arbitrarily as a fourth base unit, then the other practical electrical units already defined would be part of the new coherent system. The system would be neither electrostatic nor electromagnetic in the sense described earlier in the paper: neither Coulomb's nor Ampère's force law was privileged. In the paper presented at St. Louis, Giorgi selected the ohm as the fourth base unit of the system. As eventually adopted, the ampere was the fourth base unit.[63]

Giorgi had first presented his proposal in Rome in 1901 to the Italian Association of Electrical Engineers, and he also presented it to the Physical Society of London in 1902. His system was little more than an academic exercise for more than 30 years until taken up by the IEC in the 1930s. David Robertson, Professor of Electrical Engineering at the Merchant Venturers' Technical College in Bristol, England, independently devised a similar system, proposing the name newton as the unit of force in the MKS system.[64]

In 1935, the IEC adopted the MKS system, leaving temporarily undecided the choice of the fourth base unit.[63] In the wake of that decision, L. Hartshorn and P. Vigoureux of the British National Physical Laboratory proposed newton as the name of the unit of force in the system: "The name of Newton is universally associated with the idea of impressed force, … and as Newton's name cannot but occur again and again throughout the teaching of even the most elementary mechanics, pronunciation should present no difficulty in other countries".[65] Giorgi was still very much alive at this time. In fact, he was a delegate from Italy in IEC meetings in 1935 and 1938.[66] (Robertson's name and ideas, though, appear to have been forgotten).

In the 1920s and early 1930s, the CGPM seemed to be heading in the opposite direction from the IEC. Having taken electrical matters into its purview in 1921, the CGPM set up a Consultative Committee on Electricity in 1927. (The CIPM operates using consultative committees of various specializations.) In 1933 the CGPM adopted in principle the substitution of absolute electrical units for the so-called international units; in effect, this endorsed cgs units over the practical international units.[67] The CGPM did not meet again until 1948. By that time, it had received requests to adopt a practical international system of units. The International Physical Union recommended development of an MKS system augmented by a practical electrical unit (but did not recommend that physicists drop the cgs system). At this meeting, CGPM instructed CIPM to begin consulting to make recommendations on a single practical system of units.[68] At its next meeting in 1954, the CGPM decided on six base units for its practical system of units, namely the meter, kilogram, second, ampere, degree Kelvin, and candela.[55] And when the CGPM unveiled the SI, newton, joule, and watt were listed among the derived units; they are the SI units of force, energy, and power respectively.[56] As we have already seen, degree Kelvin became kelvin in 1967.[57] The other eponym we have followed in this paper, the siemens, joined the SI as a derived unit in 1971, the same year, incidentally, that saw the mole added as a base unit.[69]

CONCLUSIONS

Although one of the foci of this paper is power (and its units) in the narrow physical sense, the narrative above is full of encounters of science with commercial and political power. We have seen Thomson attribute much of the progress in electrical measurement to demands from commercial applications such as telegraphy and lighting. Indeed, commercial technologies appear to be the driving force for practical electrical units from the telegraphic engineers Clark and Bright to the development of the SI. The international gatherings of electrical scientists and technologists coincided with great commercial expositions, such as the Paris International Exposition of Electricity (1881) and Universal Exposition (1889, which featured the Eiffel Tower), the Columbian Exposition in Chicago (1893), and the Louisiana Purchase Exposition in St. Louis (1904). And even on a side branch of the main narrative above, we have seen that Werner Siemens both practiced science and supported it using the wealth he earned from new electrical technologies.[70]

Over the course of this narrative, we see signs of the much-vaunted international character of science becoming institutionalized, and sometimes being caught up in hostilities that engulfed the wider world. Many international scientific bodies were formed in the early twentieth century, in the aftermath of the First World War. The International Union of Pure and Applied Chemistry (IUPAC) and the International Astronomical Union (IAU) celebrate centennials in 2019.[71] The International Union of Pure and Applied Physics (IUPAP) was founded in 1922.[72] As we have seen, the IEC was formed a few years earlier.

The turmoil of the French Revolution permitted a wholesale change of weights and measures in France. Indeed, that nation saw changes in its calendar, which were rescinded, and a proposed change in time units, which never took hold, as well as the reform of its weights and measures, which endured.[21] International repercussions of the French Revolution limited the active participation of other Europeans in the founding of the metric system mainly to states allied with France or neutral toward them.[19] Given the British reluctance to adopt the metric system even a century later, it seems doubtful that Britain would have accepted the invitation of the King of France to join in devising an international reform of weights and measures even in the absence of international tensions surrounding the French revolution; however, under the circumstances of the revolution, such an invitation was a non-starter.

The failure of the UK in the early twentieth century and the US still to adopt metric units exhibits a reluctance to change from a familiar system. The effort required to change is obvious, perhaps even exaggerated, while the benefits are less evident, particularly since the system already in place appears to work well enough. This sort of inertia is not confined to scientific matters, of course, but scientists are not immune from it. Cgs units were still used in physics courses on electricity and magnetism and in the textbooks used in such courses when I was a student in the 1980s.

Finally, I found it interesting to learn that the attachment of names to formal entities such as units did not arise until the second half of the nineteenth century, although names associated with inventions and apparatus were considerably older. Using Google's Ngram viewer, one can see that eponymous terms like Copernican system, voltaic pile, and Halley's comet were in use in the first half of the nineteenth century. Terms like Boyle's law, Hooke's law, and even Pythagorean theorem, however, only start to appear after 1860 or so.[73]

I have not been able to conclude, even tentatively, what prompted Clark and Bright to use eponyms for unit names in 1860. Their paper (Ref. 8) proposes names based on prominent scientists as if off the cuff, as an expedient for the sake of having names to illustrate relationships. Indeed, the more deliberative discussion of terminology in their paper concerns prefixes to denote multiples of units. I do not know what influenced them to use eponyms for their four proposed units. One of this paper's reviewers wondered whether the sheer quantity of new units that needed names was responsible, and I thank the referee for a plausible suggestion. Tapping a reservoir of names of scientists would have the advantage of furnishing multiple names in a short time—names, moreover, that would have at least some familiarity and association in the minds of the scientists and engineers who would use the names. I found no evidence either in favor or opposed to this plausible hypothesis, other than to note that the BAAS committee on the Nomenclature of Dynamical and Electrical Units opted not to use eponyms for a set of three dynamical cgs units.[17] Still, four names for a pair of authors preparing a conference paper is a large number compared to three names for a committee with time for extensive deliberation. It is clear that Clark and Bright's example of eponymy in units influenced the committees described above. It is not clear, though, that their example had any influence in the appearance of the eponyms Boyle's law, Hooke's law, and Pythagorean theorem that began widespread use in the 1860s.

APPENDIX[74]

Well before 1860, important force laws for electricity and magnetism had been discovered, and the fact that the two apparently different kinds of phenomena were in fact related was also known. The fact that the two phenomena are related has implications for the units chosen to describe electromagnetic phenomena. For the purpose of understanding the origins of various electrical units, we may take Coulomb's or Ampère's force law as foundational. Coulomb's law states that the electrostatic force, F_e, experienced by one point charge, q_1, in the presence of another, q_2, is proportional to the product of the charges and inversely proportional to the square of the distance, r, that separates them.

$$F_e = k_e \frac{q_1 q_2}{r^2} \tag{1}$$

If we take the proportionality constant, k_e, to be 1, a set of so-called *electrostatic* units results, based on the choice of making the fundamental law of electrostatics as simple as possible.

Ampère's force law is a special case of one of the first observed quantitative phenomena that connect electricity and magnetism. It gives the magnetic force, F_m, experienced by two long parallel wires carrying a steady current. In such an arrangement, the force per unit length, L, of wire is directly proportional to the product of the currents, I_1 and I_2, and inversely proportional to the distance, d, between the wires:

$$\frac{F_m}{L} = 2k_m \frac{I_1 I_2}{d} \tag{2}$$

If we take the proportionality constant, k_m, to be 1 (the factor of 2 that appears in the equation comes from this special case of two parallel wires), the result is a set of so-called *electromagnetic* units. The two constants in these laws are not independent: they are related by the relationship

$$\frac{k_e}{k_m} = c^2 \tag{3}$$

where c is the speed of light in a vacuum.[75]

At first blush, there appear to be two choices of units, but in fact, these two choices represent two *families* of electrical units. To specify a set of units requires a choice of a system of mechanical units, that is of units of length, mass, and time. The system favored in Britain for scientific work at this time and eventually adopted more widely was the cgs system. To see how this choice of mechanical units defines electrical units, let us derive some cgs electrostatic units. Coulomb's law, with k_e = 1, says that two unit charges separated by unit distance (that is, by 1 cm) experience unit force (1 dyne, or 1 cm g s^{-2}). By rearranging Coulomb's law to solve for two equal charges, one obtains the derived cgs electrostatic unit of charge as 1 $cm^{3/2}$ $g^{1/2}$ s^{-1}. The corresponding unit of current, then, would be one unit of charge per unit of time, or 1 $cm^{3/2}$ $g^{1/2}$ s^{-2}.

To obtain cgs electromagnetic units, rearrange equation 2 to solve for two equal currents with unit values for all other quantities, including the constant k_m. Never mind the numerical value: not even the dimensions are the same for the corresponding quantities in the two systems.

The cgs *electromagnetic* unit of current is $cm^{1/2}$ $g^{1/2}$ s^{-1} (compared to $cm^{3/2}$ $g^{1/2}$ s^{-2} in cgs *electrostatic* units); similarly the cgs *electromagnetic* unit of charge is $cm^{1/2}$ $g^{1/2}$ (compared to $cm^{3/2}$ $g^{1/2}$ s^{-1} in cgs electrostatic units). In the electromagnetic system, k_m = 1, so k_e must be equal to c^2.

In the SI, current has a base unit, namely the ampere, A, so the proportionality constant in Ampère's law also has units. Rearranging that law with unit currents, force, and distances shows that k_m has units of kg m s^{-2} A^{-2}. The numerical value of km in these units was taken to be exactly 10^{-7}, just the conversion factor that relates the MKS unit of energy to the cgs unit of energy. The constants k_m and k_e are still related, so

$$k_\mathrm{e} = k_\mathrm{m}c^2 \approx (10^{-7}\ \mathrm{kg\ m\ s^{-2}\ A^{-2}})(3.0\cdot10^8\ \mathrm{m\ s^{-1}})^2 = 9.0\cdot10^9\ \mathrm{kg\ m^3\ s^{-4}\ A^{-2}}$$

In the SI, the proportionality constants in Coulomb's and Ampère's laws are not expressed in terms of k_e and k_m. Their standard form in SI units are

$$F_e = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r^2} \text{ and } \frac{F_m}{L} = \left(\frac{\mu_0}{4\pi}\right)\frac{2I_1 I_2}{d} \tag{4}$$

Where did the factors of 4π come from? As Edward Purcell explains it in his textbook, "Separating out a factor of 1/4π was an arbitrary move, which will have the effect of removing the 4π that would appear in many of the electrical formulas, at the price of introducing it into some others, as here in Coulomb's law".[76] Equations of electricity and magnetism that use this convention with respect to 4π are said to be rationalized. The constants that appear in these equations are called the electrical permittivity (ε_0) and magnetic permeability (μ_0) of vacuum. Their values are[77]

$$\mu_0 = 4\pi\times10^{-7}\ \mathrm{kg\ m\ s^{-2}\ A^{-2}} \approx 1.257\times10^{-6}\ \mathrm{kg\ m\ s^{-2}\ A^{-2}}$$

$$\text{and } \varepsilon_0 = \frac{1}{\mu_0 c^2} \approx 8.854\times10^{-12}\ \mathrm{kg^{-1}\ m^{-3}\ s^4\ A^2}$$

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Taking the Earth's temperature:

200 years of research has established why the Earth is as warm as it is and how burning fossil fuels is making it warmer

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Abstract. Because of the threat of global warming due to the build-up of atmospheric carbon dioxide from burning fossil fuels, energy use is the central factor in creating a sustainable future. Anthropogenic climate change is real, but climate change deniers insist that carbon pollution is not a threat and that the science behind climate change is flimsy at best and a sham at worst. In fact, efforts to understand Earth's climate and why the planet's temperature is what it is date back to the early 19th century, and I review that history in this paper. Earth's atmosphere was first likened (inaccurately, as it turns out) to a greenhouse in the 1820s; CO_2 was first shown to be a greenhouse gas in the 1860s; the idea that burning fossil fuels could change the Earth's temperature was proposed in the late 19^{th} century; the concentration of CO_2 in the atmosphere was first shown to be inexorably rising in the 1950s. The science of climate change has a long and distinguished pedigree.

Keywords. Greenhouse gases, global warming, climate change, fossil fuels, carbon dioxide.

INTRODUCTION

Energy consumption is by far the most important factor in determining whether humanity can transition to a sustainable economic system in the 21^{st} century. Burning fossil fuels powered the Industrial Revolution and, in a mere 200 years, transformed civilization. Civilization as we know it is entirely dependent on burning fossil fuels—which are, in fact, fossilized sunshine—cheaply. Humans burn fossil fuels on the cheap because we treat the atmosphere as a free dumping ground for the waste products of combustion, primarily carbon dioxide (CO_2).

For many years, economists and others thought the supply of fossil fuels would place limits on economic growth. Books were written on "peak oil"—when the amount of petroleum extracted from the Earth would begin an inevitable decline as oil fields were depleted.[1] It turns out that that's probably not the case. Enough fossil-fuel resources—petroleum, natural gas, and coal—are left on Earth for us to keep the economic engines that have powered 200 years of exponential growth going for another 200 or 300 years or so.

Earth's climate, however, will not tolerate humans continued unrestrained fossil fuel use. The buildup of atmospheric CO_2—from 280 ppm at the beginning of the Industrial Revolution to more than 400 ppm today[2]—is already forcing the climate to change. Earth's temperature is increasing due to the buildup of CO_2 and other greenhouse gases, many of them associated with fossil fuel production and use.

Among scientists, there is no doubt that anthropogenic climate change is real. However, a determined cadre of climate change deniers insists that carbon pollution is nothing but propaganda, that climate scientists are engaged in an elaborate conspiracy to demonize fossil fuels and line their pockets with research grants. One persistent thread in the deniers' claims is the suggestion that climate change is a relatively new idea cooked up by left-leaning scientists and politicians bent on strangling economic growth. Nothing could be further from the truth. Scientists have been pondering the question of why the Earth's temperature is what it is for 200 years. That the Earth's atmosphere plays a role in regulating the planet's temperature was first proposed in the 1820s. Carbon dioxide was first shown to be a greenhouse gas—able to absorb infrared radiation—in the 1860s. The idea that burning fossil fuels could ultimately change Earth's climate was proposed in the late 19th century; the first calculation on the potential impact of CO_2 on climate was published in 1896. Climate change has a long and distinguished scientific pedigree.

It should be noted that while the terms "greenhouse gases" and "greenhouse effect" are now firmly embedded in the vernacular concerning climate change and that a number of 19th century scientists made allusions to a greenhouse or a blanket when discussing the influence of Earth's atmosphere on the planet's surface temperature, the term "greenhouse effect" was not used until 1901 by the Swedish scientist Nils Ekholm. Perhaps unfortunately, as will be discussed further, a greenhouse is not an accurate analogy for how gases like carbon dioxide are warming the Earth.

ENERGY BALANCE

Why is the temperature at the surface of the Earth what it is? The French mathematician and physicist Joseph Fourier (1768–1839) addressed the question in the early 1800s as part of his more general work on heat flow. Fourier is best known for his work on discontinuous functions, work that is the foundation of what is known today as the Fourier transform. He also made seminal experimental and theoretical contributions to our understanding of energy flow in various substances.

Fourier thought that there were three sources of energy that contributed to Earth's surface temperature: solar radiation, which is unevenly distributed across Earth's surface and gives rise to the diversity of climates; energy from interstellar space, essentially from the stars; and energy from Earth's interior, which he thought to be relatively minor.[3,4,5] The most important energy source was the sun. When the light from the sun strikes the Earth and warms it, why doesn't the planet just keep getting hotter? Fourier reasoned that the Earth must be radiating invisible heat—infrared radiation—back into space to achieve a net energy balance.

Treating the Earth as a black body being heated by sunlight, Fourier calculated that its temperature would be significantly lower than it is. Fourier thought, incorrectly, that the difference was likely made up by energy from interstellar space. However, he also speculated that the atmosphere might be transparent to sunlight impinging on the planet but that it somehow impeded the outward flow of heat from the planet back into space. In one analogy, he compared the heating of the atmosphere to the action of a heliothermometer, an instrument designed and used by Horace Benedict de Saussure (1740–1799) in the 1770s to study the variability of the intensity of solar radiation with altitude. The device consists of a small wooden box lined by a layer of

Figure 1. Joseph Fourier (1768–1830); Credit: www.bridgemanimages.com.

blackened cork and fitted with three panes of glass separated by air spaces. The similarity of a heliothermometer to a greenhouse and Fourier's reference to it are what gives rise to the suggestion that Fourier was the first to liken Earth's atmosphere to a greenhouse, although he never used that term.

In fact, it's a little bit tricky to unearth Fourier's precise thinking about this subject. Fourier's 1827 disquisition "Mémorie sur les temperatures du globe terrestre et des espaces planétaires" ("Memoir on the temperature of the earth and planetary spaces"), often cited to support the link between Fourier and the greenhouse effect, may well have been a public presentation rather than a formal scientific paper. It contains no equations or formal calculations. As James R. Fleming points out in "Joseph Fourier, the 'greenhouse effect', and the quest for a universal theory of terrestrial temperatures,"[6] the 1827 article "has been mentioned repeatedly as being the first reference in the literature to the atmospheric 'greenhouse effect.' Here I will review the origins of this practice and demonstrate that most of these citations are unreliable, misdirected and anachronistic. While there are indeed greenhouse analogies in Fourier's writings, they are not central to his theory of terrestrial temperatures, nor are they unambiguous precursors of today's theory of the greenhouse effect." Nevertheless, Fourier clearly stimulated others to investigate the factors that determined the Earth's temperature.

One such scientist was Claude S. M. Pouillet (1790–1868), who in the 1830s developed a pyrheliometer and made the first quantitative measurements of the solar constant. In his 1838 article,[7,8] "Mémoire sur la chaleur solaire, sur le pouvoir rayonnants et absorbants de l'air atmosphérique, et sur la temperature de l'espace" ("Memoir on solar heat, on the radiating and absorbing powers of the atmospheric air, and on the temperature of space"), Pouillet credits Fourier as being "the first who has had the idea of regarding the unequal absorption of the atmosphere as exercising an influence on the temperature of the soil."

Pouillet regarded light rays and heat rays to be fundamentally different—"the rays of heat and of light may derive their origins from the same source, be emitted at the same time, and coexist in the same pencil of rays, but they preserve a distinctive character"—and as such could be thought of differently in how they interact with matter. This allows him to view the atmosphere as being "diathermanous," meaning that light rays can pass through the atmosphere without heating it while heat rays are absorbed by it and warm it. Thus, he writes:

> *With regard to the solar heat no doubt exists: we know that in traversing diathermanous substances it is less absorbed than the heat which is derived from different terrestrial sources, the temperature of which is not very high. It is true that we have been able to make the experiment only upon liquid or solid diathermanous screens; but we regard it as certain that the atmospheric stratum acts in the manner of screens of this kind, and that consequently it exercises a greater absorption upon the terrestrial than upon the solar rays.*

That is, some component of the atmosphere absorbs heat emanating from the Earth's surface resulting in an overall warming of the planet. Neither Fourier nor Pouillet had any idea what that component of the atmosphere might be.

OF GLACIERS AND ICE AGES

Questions about the Earth's temperature also were stimulated in the first half of the 19th century by the then radical idea that the Earth had experienced numerous ice ages during its history. Geologists had taken note of large boulders scattered across much of Europe far from the mountains from which they had originated. How did they get there? One explanation was Noah's Flood. Another was violent volcanic activity. Jean de Charpentier (1786–1855), a German-Swiss mining engineer and geologist who studied Swiss glaciers, proposed that these so-called erratics had been carried to their locations by glaciers that had once been much more extensive than at that time.[9] He did not know how the glaciers had formed, moved, or what had happened to them.

Credit for the idea of ice ages is somewhat controversial.[10] The German botanist Karl Friedrich Schimper (1803–1867) studied mosses growing on erratics and, like Charpentier, wondered where the boulders had come from and concluded that they had been carried by ice. Schimper spent the summer of 1836 in the Swiss Alps with his former university friend Louis Agassiz (1807–1873) and Charpentier and together they developed the theory of successive glaciations covering much of northern Europe, Asia, and North America. Schimper coined the term "ice age" ("eiszeit" in German) in 1837. The same year, Agassiz, already renowned for his work in paleontology, presented the theory to the Helvetic Society. The theory was not well received as it conflicted with then current ideas about Earth's climate history. In 1840, Agassiz published a two-volume work "Études sur les glaciers" ("Studies of Glaciers").[11]

The question, of course, was, if the idea of global ice ages was correct, what could possibly have caused the Earth's climate to shift so drastically to allow such massive ice sheets to form? It is a question that has still not been completely answered.

John Tyndall (1820-1893), an Irish chemist and physicist, had a keen interest in glaciers and in heat flow. He was a careful and precise experimenter who had made his reputation with his studies of diamagnetism in the early 1850s.[12] He was also an accomplished mountaineer who had made close studies of glaciers. In addition to a number of papers on glaciers—he coauthored "On the Structure and Motion of Glaciers" with Thomas Huxley in 1857—he wrote "Glaciers of the Alps: Being a narrative of excursions and ascents, an account of the origin and phenomena of glaciers, and an exposition of the physical principles to which they are related" in 1860.

Tyndall began his experiments on the absorption of heat by gases in early 1859. His biographer, Roland Jackson, writes:

> *His interest had a long gestation. … He had considered the topic for several years; he read Macedonio Melloni's work on the absorption of heat by liquids and solids around 1850, and frequently discussed the issue with friends. His work on glaciers rekindled that interest. He had explored the existence of air bubbles in ice, the conduction of heat through ice, and the formation of flower-shaped structures in ice by a focused beam of light. Now his attention turned to the atmosphere, to examine its interaction with solar and terrestrial radiation, and to investigate the remarkable condition of temperature in mountain regions. His aim was to do for gases what Melloni had done for liquids and solids. There was further motivation. He was convinced that not only the physical but also the chemical composition of substances—and specifically their molecules—played a part previously unrecognized in radiation and absorption. He would be probing the nature of molecules themselves using radiation.*[13]

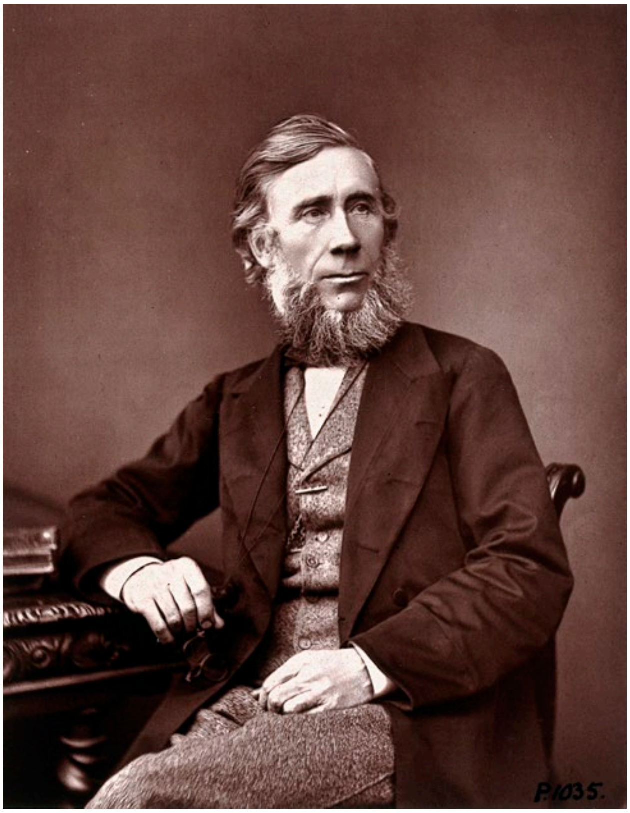


Figure 2. John Tyndall (1820–1893). Credit: Wellcome Collection, CC BY.

Tyndall's skill as an experimentalist allowed him to succeed where Melloni had failed in measuring how different gases interacted with heat radiation. Tyndall built the first differential spectrometer.[14] It consisted of a long tube that he filled with the gas under study. The ends of the tube were capped with slabs of rock salt, which is transparent to infrared radiation. A precision heat source emitted radiation that traversed the tube and interacted with the gas before entering one cone of a differential thermopile. Another heat source emitted exactly the same amount of radiation directly into the other cone of the thermopile. The thermopile was connected to a galvanometer, which measured small voltage differences. A voltage measurement indicated that the gas under study had attenuated the passage of radiation down the tube.

Tyndall quickly discovered that dry air is transparent to heat radiation and that both water vapor and carbon dioxide absorbed it. He announced his results to the Royal Society and followed with a "Discourse" to the Royal Institution, "On the transmission of heat of different qualities through gases of different kinds."[15] He had demonstrated that a number of gases absorbed heat, although the only one he specified in his report was "coal gas," a mixture of carbon monoxide and methane. He concluded: "Thus the atmosphere admits of the entrance of the solar heat; but checks its exit, and the result is a tendency to accumulate heat at the surface of the planet."

Tyndall continued his research on gases into the 1860s.[16] He showed that water vapor, CO_2, and numerous hydrocarbons absorbed heat radiation and that absorption was proportional to density for small amounts of a gas. Why were oxygen and nitrogen such poor absorbers of radiant heat? As Jackson summarizes:

> *Tyndall thought that this might be due to their existence as single atoms—although we now know them to be diatomic—and that the far stronger power of other substances, such as water, carbon dioxide, and coal gas, was*

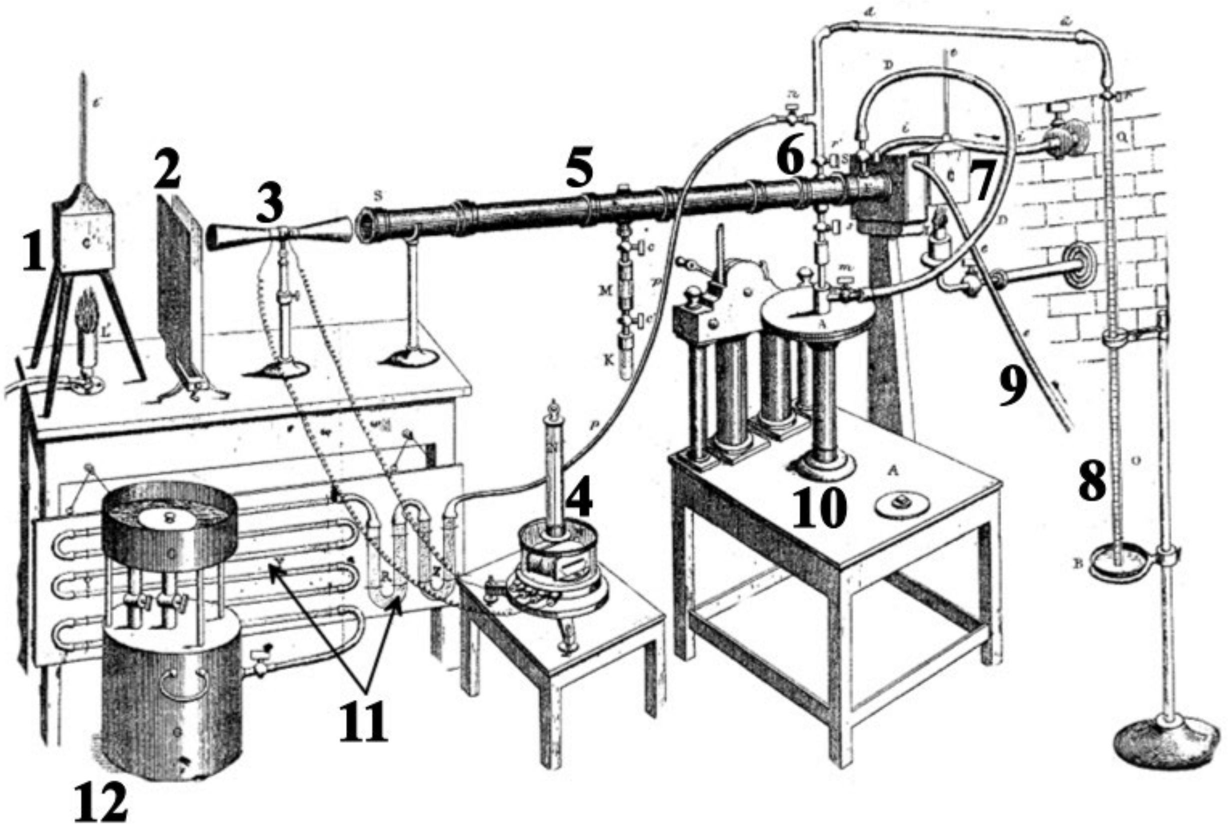


Figure 3. 1: Heat source. 2: Heat screen. 3: Thermopile, with conical reflectors. 4: Galvanometer. 5: Brass tube with rock salt plugs at each end. The tube contains the gas that is under study. 6: Gas enters tube. 7: Heat source. 8: Manometer. 9: Circulating cold water solves a heat conduction issue. 10: Vacuum pump. 11: The gas or gas mixture can pass through some filtration process beforehand. 12: Container of gas or gas mixture to be studied.

> *due to their molecular structure as oscillating systems of atoms. These compound molecules, Tyndall imagined, 'present broad sides to the ether,' unlike the simple individual spherical atoms. They have more sluggish motions, so tend to bring the period of oscillation into synchrony with the slower undulations of radiant heat compared to those of visible light.*[17]

Tyndall realized that water vapor, because of its relatively high atmospheric concentration compared to other trace gases, was the most influential absorber of heat radiation in the atmosphere. In an 1863 Royal Institution Discourse "On radiation through the earth's atmosphere," he stated: "This aqueous vapor is more necessary to the vegetative life of England than clothing is to man. Remove for a single summer night the aqueous vapor from the air which overspreads this country and you would assuredly destroy every plant capable of being destroyed by a freezing temperature."[18]

Tyndall went on to probe the nature of heat radiation, which he referred to as "black" or "obscure" heat, beginning to break down the idea that visible light and heat are fundamentally different phenomena. He showed that heat radiation could be focused, that it could set paper ablaze, and that it could make metal glow with visible light, a phenomenon he referred to as "calorescence," a counterpoint to "fluorescence." In a presentation to the Royal Society in 1865, he showed that the maximum heat in the spectrum of an electric lamp was beyond the visible red.[19]

Interestingly, although Tyndall's work has long been recognized as seminal in our understanding of the interaction of the atmosphere and solar radiation, he was not the first person to show experimentally that a trace constituent of the atmosphere could absorb infrared radiation. In 2010, Raymond P. Sorenson, a retired petroleum geologist, discovered the work of Eunice Foote (1819–1888), an American scientist who in 1856 reported that water vapor and carbon dioxide absorbed heat radiation and in doing so warmed the atmosphere.[20] Foote speculated that a higher concentration of CO_2 could have been the cause of a much warmer climate earlier in Earth's history. Foote's paper, "Circumstances affecting the heat of the sun's rays," was presented in August 1856 at the 10th annual meeting of the American Association for the Advancement of Science by John Henry, the founding director of the Smithsonian Institution. Foote subsequently published a paper, "On the heat of the Sun's rays" in the November 1856 issue of the *American Journal of Science & Arts* with a note that it had been presented at the AAAS meeting.[21]

Foote's experimental apparatus, only vaguely described in her paper, was crude compared to Tyndall's. Unlike Tyndall, Foote did not expose gases only to long-wavelength radiation, which is the basis of the greenhouse effect. Nevertheless, in a recent paper, Jackson concludes that Foote "does seem to have been the first person to notice the ability of carbon dioxide and water vapour to absorb heat, and to make the direct link between the variability of these atmospheric constituents and climate change. For that she deserves proper recognition, even if she was not able to explore, and perhaps did not recognize, the distinction between solar radiation and radiated heat from the earth".[22]

HOW COLD? HOW WARM?

Tyndall had concluded that Earth would be a frozen wasteland without the greenhouse warming provided by water vapor, but he didn't calculate what the Earth's temperature would, in fact, be without that cloak. Nor did he try to calculate what change in atmospheric CO_2 levels could bring on an ice age.

The Swedish chemist, physicist, and mathematician Svante Arrhenius (1859–1927) is primarily remembered for his research on the conductivities of electrolytes, work for which he won the 1903 Nobel Prize in chemistry; and the concept of an activation energy, an energy barrier that must be overcome before two molecules will react.

However, as with Tyndall and many other 19th century natural philosophers/scientists, Arrhenius' intellect ranged widely. It was this diversity of talents and interests that led him to embark on what some now view as his greatest achievement, the mathematical analysis of the influence of CO_2 on the Earth's energy budget as detailed in his now-famous paper, "On the influence of carbonic acid [carbon dioxide] in the air upon the temperature on the ground."[23] While the work is now regarded as a seminal contribution to climate science, it was not recognized as such when it was published or for many years thereafter.

Arrhenius was a founding member of Stockholm Physics Society, which drew a wide range of scientists to its fortnightly meetings to discuss topics ranging from physics to chemistry, meteorology, geology, and astrophysics, including the ice ages and what caused them.[24] It was through meetings of the society that Arrhenius formed a close collaboration with Arvid Högbum (1857–1940), a geologist who studied the geochemical carbon cycle of the Earth, especially how atmospheric CO_2 is influenced by the oceans, vegetation, and formation of carbonates. Högbum believed that atmospheric CO_2 levels varied widely over geologic time and likely influenced climate.

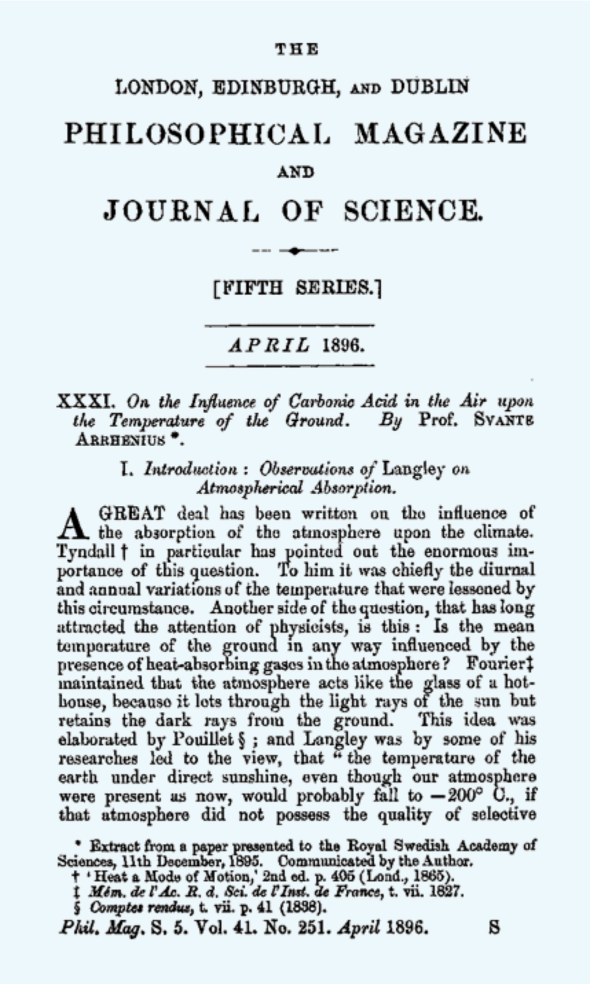
Why focus on CO_2 when water vapor is much more prevalent in the atmosphere and a much more influential greenhouse gas? Arrhenius realized that Earth is a wet planet. Water cycles in and out of the atmosphere continuously. CO_2, by contrast, remains in the atmosphere

Figure 4a. Svante Arrhenius (1859–1927). Credit: University Archives, Universität Würzburg.

for centuries. It acts as a "control knob" that sets the level of atmospheric water vapor. If atmospheric CO_2 levels dropped substantially, Earth's temperature would fall only slightly at first. But this lower temperature would result in less water vapor in the atmosphere, further lowering the Earth's temperature.

Arrhenius embarked on the laborious effort to develop equations to quantify how much atmospheric CO_2 would have to vary to bring about changes, both warmer and colder, that could explain the ice ages. As Thomas R. Anderson, Ed Hawkins, and Philip D. Jones point out in their paper "CO_2, the greenhouse effect and global warming: from the pioneering work of Arrhenius and Callendar to today's Earth System Models": [25]

> *The calculations involved balancing the radiative heat budget (thereby assuming a state of equilibrium), namely solar radiation arriving at the Earth's surface (including the effects of albedo from clouds and the Earth's surface) and the subsequent absorption of re-emitted infrared radiation by the atmosphere. Calculating this absorption required integration across the different wavelengths that encompass the absorption spectrum of CO_2 and water vapor, as well as integrating across different zenith angles … and the corresponding path lengths associated with incoming and outgoing radiation.*



THE
LONDON, EDINBURGH, AND DUBLIN
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AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

APRIL 1896.

XXXI. *On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground. By* Prof. SVANTE ARRHENIUS *.

I. *Introduction: Observations of* Langley *on Atmospherical Absorption.*

A GREAT deal has been written on the influence of the absorption of the atmosphere upon the climate. Tyndall † in particular has pointed out the enormous importance of this question. To him it was chiefly the diurnal and annual variations of the temperature that were lessened by this circumstance. Another side of the question, that has long attracted the attention of physicists, is this: Is the mean temperature of the ground in any way influenced by the presence of heat-absorbing gases in the atmosphere? Fourier‡ maintained that the atmosphere acts like the glass of a hot-house, because it lets through the light rays of the sun but retains the dark rays from the ground. This idea was elaborated by Pouillet §; and Langley was by some of his researches led to the view, that "the temperature of the earth under direct sunshine, even though our atmosphere were present as now, would probably fall to −200° C., if that atmosphere did not possess the quality of selective

* Extract from a paper presented to the Royal Swedish Academy of Sciences, 11th December, 1895. Communicated by the Author.
† 'Heat a Mode of Motion,' 2nd ed. p. 405 (Lond., 1865).
‡ *Mém. de l'Ac. R. d. Sci. de l'Inst. de France*, t. vii. 1827.
§ *Comptes rendus*, t. vii. p. 41 (1838).

Phil. Mag. S. 5. Vol. 41. No. 251. *April* 1896. S

Figure 4b. First page of Arrhenius' groundbreaking paper.

By his own admission, the calculations were laborious, taking up a year of his time. In his 1896 paper, he wrote: "I should certainly have not undertaken these tedious calculations if an extraordinary interest had not been connected with them." It is possible that he immersed himself in the work as an emotional escape from personal problems. That year, he went through a painful divorce after only two years of marriage from Sofia Rudbeck, a former student, losing not only his wife but custody of their young son.

Arrhenius made calculations for six scenarios, with CO_2 levels at 0.67, 1.0, 1.5, 2.0, 2.5, and 3.0 times the levels in the atmosphere at that time. His work showed that doubling or halving the amount of CO_2 would result in warming or cooling the Earth by 5–6 °C. To lower the temperature the 4–5 °C needed to bring on an ice age, he wrote, would require CO_2 to drop to 0.62–0.55 of its 1896 level.

What of global warming? Arrhenius wasn't too concerned because he thought it would require 3,000 years for humans burning coal to double the atmospheric level of CO_2. Nor did he necessarily consider global warming such a bad outcome. In his 1908 book "Worlds in the Making," which was written for a nontechnical audience, Arrhenius wrote:

> *We often hear lamentations that the coal stored up in the earth is wasted by the present generation without any thought of the future. … We may find a kind of consolation in the consideration that here, as in every other case, there is good mixed in with the evil. By the influence of the increasing percentage of carbonic acid in the atmosphere, we may hope to enjoy ages with more equable and better climates, especially as regards the colder regions of the earth, ages when the earth will bring forth much more abundant crops than at present, for the benefit of rapidly propagating mankind.*[26]

Arrhenius' friend and collaborator, the Swedish meteorologist Nils Ekholm (1848–1923), expressed a similar sentiment, saying that if "the present burning of pit-coal continues for some thousand years, it will undoubtedly cause a very obvious rise in the mean temperature of the earth," and that, with this impact, coupled with humans tapping other sources of CO_2, "it seems possible that man will be able efficaciously to regulate the future climate of the earth and consequently prevent the arrival of a new ice age".[27]

As it turns out, the temperature changes that Arrhenius calculated are somewhat higher than the currently accepted range of 1.5–4.5 °C of warming that would result from doubling atmospheric CO_2.[28] Nevertheless, his accomplishment was remarkable given the tools and data at his disposal.

One argument raised against Arrhenius' conclusions on the effects of atmospheric CO_2 is important because it was widely accepted at the time and because it is still raised by climate change deniers. Not long after Arrhenius published his results, another Swedish scientist, Knut Ångström (1857–1910), who published the first infrared absorption spectrum of CO_2, argued that his work showed that the infrared absorption bands of the gas were completely saturated in the lower atmosphere. That is, the trace CO_2 already in the atmosphere was absorbing all of the infrared radiation that it was capable of absorbing, and that, therefore, adding more CO_2 could not change the Earth's energy balance.[29]

Arrhenius strongly rejected Ångström's argument,[30] but many other influential scientists of the day did not. As a result, practically no one took seriously Arrhenius' idea that burning coal and other fossil fuels could eventually result in a warmer Earth, and no one paid much attention to the concentration of CO_2 in the atmosphere. The fallacy in Ångström's reasoning is that it treats the atmosphere with regard to infrared radiation as a single slab, much like the panes of glass in a greenhouse. In point of fact, this is where the greenhouse metaphor as an explanation of global warming breaks down.

For the purposes of absorbing infrared radiation, the atmosphere must be viewed as consisting of many layers which get thinner, drier, and colder at higher and higher altitudes. Earth's temperature is controlled by these thin upper layers where radiation escapes easily into space. Adding CO_2 to these layers does change the planet's energy balance. As infrared radiation leaving the surface of the Earth moves up through the layers of the atmosphere, some of it is absorbed at each layer. The layer of air radiates some of the energy back toward Earth's surface and some toward higher layers. In the topmost layers where heat radiation from lower layers slips easily through into space, adding CO_2 means the layer will absorb more radiation and warm, thus shifting to even higher layers where radiation escapes into space. Adding greenhouse gases to the atmosphere effectively increases the pathlength infrared radiation takes before escaping into space, changing the equilibrium of energy arriving and departing the planet. Instead of the metaphor of a greenhouse, a more accurate analogy is that adding CO_2 and other infrared absorbers to the atmosphere has the effect of placing a thicker blanket around the Earth. (Which, like all metaphors for atmospheric dynamics, isn't entirely accurate, either.)

THE OCEANS AS A CO_2 SINK

There were other substantive objections to Arrhenius' argument that CO_2 could influence Earth's climate. One was related, in a way, to Ånström's objection that the CO_2's infrared absorption was saturated in the lower atmosphere. CO_2 absorbs infrared radiation in a few narrow bands while water vapor's infrared absorption bands are broad and largely overlap those of CO_2. Thus, this reasoning went, more CO_2 in the atmosphere could not affect the absorption of radiation already entirely absorbed by water vapor. This argument, although widely accepted, fails for the same reason Ångström's objection fails: what is critical is the CO_2 in the dry, cold upper layers of the atmosphere. Moreover, in the thin upper atmosphere the absorption lines of both molecules narrow and become better defined, and here the overlap between the two spectra is not complete.

Yet another argument raised against Arrhenius was that the oceans would absorb the vast majority of CO_2 released by all sources. It was known that there is 50 times more CO_2 dissolved in the oceans than is present in the atmosphere. However, the dynamics of the equilibrium between atmospheric CO_2 and CO_2 dissolved in ocean water are complicated and were not well understood. Most scientists simply assumed that ocean water represented an essentially infinite reservoir for the CO_2 humans were pouring into the atmosphere from burning fossil fuels. Earth's climate, the argument went, was a self-regulating system that naturally remained at equilibrium.

These objections to the notion of anthropogenic climate change mitigated against research into the field for most of the first half of the 20th century. There simply didn't seem to be much point in probing what was an inherently complex system because the consensus was that there wasn't anything to discover. Scientists are loath to waste their time on questions that have already been answered.

Guy Stewart Callendar (1898–1964) did not subscribe to the consensus view and developed data to challenge it. A British steam engineer with a lifelong passion for a wide variety of scientific topics, Callendar took up meteorology and climatology as a hobby.[31] Callendar compiled temperature records from the late nineteenth century through the 1930s and detected a warming trend over a 50-year period. He also evaluated old measurements of atmospheric CO_2 concentrations and, although these were crude, concluded that the concentration of the gas had increased by 6% between 1880 and 1935 and that this could account for the observed warming. The increased atmospheric CO_2, he argued, was consistent with combustion of fossil fuels which had added about 150 billion tons of the gas to the atmosphere, about three quarters of which, he estimated, remained there. He published his findings in a 1938 paper "The artificial production of carbon dioxide and its influence on temperature".[32]

The opening paragraphs of Callendar's paper neatly summarize the then-accepted consensus and his own challenge to it:

> *Few of those familiar with the natural heat exchanges of the atmosphere, which go into the making of our climate and weather, would be prepared to admit that the activities of man could have any influence upon phenomena of so vast a scale.*
> *In the following paper I hope to show that such an influence is not only possible, but is actually occurring at the present time.*

Figure 5. Guy Stewart Callendar (1898–1964). Credit: Copyright University of East Anglia, used by permission.

> *It is well known that the gas carbon dioxide has certain strong absorption bands in the infra-red region of the spectrum, and when this fact was discovered some 70 years ago it soon led to speculation on the effect which changes in the amount of the gas in the air could have on the temperature of the earth's surface. In view of the much larger quantities and absorbing power of atmospheric water vapor it was concluded that the effect of carbon dioxide was probably negligible, although certain experts, notably Svante Arrhenius and T.C. Chamberlin, dissented from this view.*

Callendar did not accept the idea that the oceans would absorb most of the CO_2 being produced by burning fossil fuels. He felt that the relatively shallow surface waters of the oceans would become rapidly saturated with CO_2 and that it would take thousands of years for the ocean water to turn over and be fully exposed to the atmosphere.

Callendar published numerous papers on climate change, infrared radiation, and the carbon cycle between 1938 and his death in 1964. His ideas, however, were not taken seriously throughout much of that time by mainstream climate scientists. But his model was surprisingly accurate, given the resources he had at hand. A 2016 analysis of Callendar's work by Anderson, Hawkins, and Jones asked, "What, then, would Callendar have projected for global temperature rise during the twentieth century if he had correctly anticipated the increase in atmospheric CO_2, as well as taking into consideration the other greenhouse gases and aerosols?" Using Callendar's equations, they showed that he would have predicted an increase in heating of "0.52 °C which is somewhat on the low side compared to the observed rise of 0.6 °C … a consequence of Callendar's model … not taking account of climate feedbacks (other than water vapour) that amplify warming. … Nevertheless, we conclude that Callendar's model, in conjunction with realistic forcing, performs remarkably well when used to project climate warming during the twentieth century". [33]

As Anderson, Hawkins, and Jones note in their paper, a source of uncertainty in Callendar's calculations was the role of the ocean as a reservoir for CO_2. Callendar believed that the oceans did not absorb all of the CO_2 being produced by burning fossil fuels, but he had not demonstrated it. That task fell to one of the seminal figures of twentieth century climate science, Roger Revelle (1909–1991), director of the Scripps Institute of Oceanography in San Diego, and his Scripps collaborator, Hans Seuss (1909–1993).

Before moving to Scripps to work with Revelle in 1956, Seuss worked at the U.S. Geological Survey in Washington, D.C. No one at the time knew whether CO_2 from burning fossil fuels was adding to the total amount of CO_2 in the atmosphere. Suess, working in collaboration with Harold Urey's laboratory at the University of Chicago, undertook a study of the concentration of ^{14}C in wood harvested in the early 1950s compared to wood from the nineteenth century, prior to the advent of the industrial revolution. ^{14}C is continuously being produced in the atmosphere by cosmic rays interacting with ^{14}N. Plants absorb the ^{14}C and incorporate it into their tissues. Because ^{14}C has a half-life of only 5,730 years, however, fossil fuels contain an undetectable amount of the isotope. If CO_2 from burning fossil fuels were accumulating in the atmosphere, it should be reflected as a relative decrease in the amount of ^{14}C in the modern wood compared to the nineteenth century wood.

Seuss' work showed that this was, indeed, the case. The ^{14}C concentrations in four nineteenth century wood samples varied only slightly, not more than 0.12%, Seuss reported. By contrast, results for the modern wood "showed marked variations, always in the direction of a lower ^{14}C content," suggesting to Seuss "relatively large local variations of CO_2 in the atmosphere derived from industrial coal combustion".[34]

At Scripps, Revelle and Seuss worked to determine the average lifetime of a CO_2 molecule in the atmosphere. Their 1957 paper, "Carbon Dioxide Exchange Between the Atmosphere and Ocean and the Question of an Increase of Atmospheric CO_2 during the Past Decades," in a sense, marks the beginning of the modern age of climate science. The paper's abstract concisely summarizes the situation humans faced:

> *From a comparison of C^{14}/C^{12} and C^{13}/C^{12} ratios in wood and in marine material and from a slight decrease of the C^{14} concentration in terrestrial plants over the past 50 years it can be concluded that the average lifetime of a CO_2 molecule in the atmosphere before it is dissolved into the sea is of the order of 10 years. This means that most of the CO_2 released by artificial fuel combustion since the beginning of the industrial revolution must have been absorbed by the oceans.*
> *The increase in atmospheric CO_2 from this cause is at present small but may become significant during future decades if industrial fuel combustion continues to rise exponentially.*[35]

Revelle had studied ocean chemistry throughout his career. He realized that absorption of CO_2 by sea water was a complex process buffered by the various species the molecule adopts when it goes into solution—carbonate ion (CO_3^{2-}), bicarbonate ion (HCO_3^-), and protonated carbonic acid ($H_3CO_3^+$)—and that the combination of dissociation constants limits how fast CO_2 can enter the ocean.

Revelle and Seuss were very aware of the implications of their work. They pointed out in their paper that the United Nations had estimated in 1955 that during the first decade of the 21st century fossil fuel combustion could produce CO_2 equal to 20% of that then in the atmosphere, which they estimated was something like two orders of magnitude greater than the rate of CO_2 production from volcanoes. The scientists famously wrote:

> *Thus human beings are now carrying out a large scale geophysical experiment of a kind that could not have happened in the past nor be reproduced in the future. Within a few centuries we are returning to the atmosphere and oceans the concentrated organic carbon stored in sedimentary rocks over hundreds of millions of years. This experiment, if adequately documented may yield a far-reaching insight into the processes determining weather and climate.*

THE KEELING CURVE

Revelle and Seuss concluded their paper with a focus on some of what still needed to be understood to know whether humans were changing earth's climate:

> *Present data on the total amount of CO_2 in the atmosphere, on the rates and mechanisms of CO_2 exchange between the sea and the air and between the air and the soils, and on possible fluctuations in marine organic carbon, are insufficient to give an accurate base line for measurement of future changes in atmospheric CO_2. An opportunity exists during the International Geophysical Year to obtain much of the necessary information.*

The opportunity did indeed exist and Revelle would set in motion a profoundly important set of measurements to answer what seemed to be a fundamental question: Was the concentration of atmospheric CO_2 increasing because of use of fossil fuels?

In fact, an even more fundamental question needed to be answered: What was the atmospheric concentration of CO_2? The literature stated that the concentration was about 300 ppm by volume, but published values ranged from 250 to 550 ppm. Atmospheric scientists had even proposed using CO_2 concentrations as tags to track different air masses.[36]

Revelle was one of the founders of the International Geophysical Year (IGY) in 1957–58, an international effort involving 67 countries collaborating to make geophysical measurements over an 18-month period in 11 earth sciences, including meteorology and oceanography. Revelle hired a young California Institute of Technology postdoc, Charles David Keeling (1928–2005), to nail down the atmospheric concentration of CO_2 and monitor it over time to establish whether humans were changing the composition of Earth's atmosphere.

Keeling was an ideal choice for the work. He had received his Ph.D. in chemistry with a minor in geology from Northwestern University in 1953. His thesis had been in polymer chemistry and he had received job offers from a number of chemical companies on the East Coast, which, to his thesis advisor's consternation, he had turned down. In a charming 1994 extended autobiographical sketch,[37] Keeling wrote: "I had trouble seeing the future this way. I wrote letters offering my services as a Ph.D. chemist exclusively to geology departments west of the North American continental divide. In general, I received back polite declining letters, but I got two offers." He accepted one of them, an invitation from Harrison Brown (1917–1986) to become his first postdoctoral fellow in the newly established geochemistry department at Caltech.

At Caltech, Keeling developed instrumentation and carried out field observations to test an idea of Brown's: that the concentration of carbonate in ground water could be estimated by assuming that the water is in equilibrium with both limestone ($CaCO_3$) and atmospheric CO_2. He did the field work in the pristine environment of Big Sur on the central California coast. Keeling quickly discovered that the water in the stream he was monitoring was supersaturated with CO_2 and therefore not amenable to Brown's equilibrium hypothesis. He focused his attention on measurements of CO_2 in air because they showed an intriguing diurnal pattern: the air contained more CO_2 at night than during the day and the $^{13}C/^{12}C$ ratios in night and day air suggested that, during the day, plants at some sites reabsorbed CO_2 previously released into the air locally the night before. He also found that air in the afternoon always had nearly the same amount of CO_2, about 310 ppm, while concentrations at night were quite variable and always higher than during the day.

Keeling's studies eventually resulted in job offers from the Weather Bureau in Washington, D.C., and from Revelle at Scripps. Once again, he chose the west and work in open spaces to the east and a cramped basement office. He moved to Scripps in August 1956.

In the year leading up to the advent of the IGY in July 1957, Keeling established CO_2 monitoring stations at the weather observatory on Mauna Loa in Hawaii at an altitude of about 3,000 meters and at a U.S. weather station on the coast of Antarctica. The measurements were made with a highly precise, continuously recording infrared gas analyzer. Keeling had insisted on instrumentation with a precision of 0.1 ppm, which some critics thought unnecessary as they anticipated that atmospheric CO_2 concentrations would be highly variable.

A number of issues arose at Mauna Loa in the fall of 1957 that prevented data from being collected. Data collected in 1958 were somewhat patchy due to electrical outages and other issues, but a clear trend was evident: CO_2 concentration increased from January until May and then

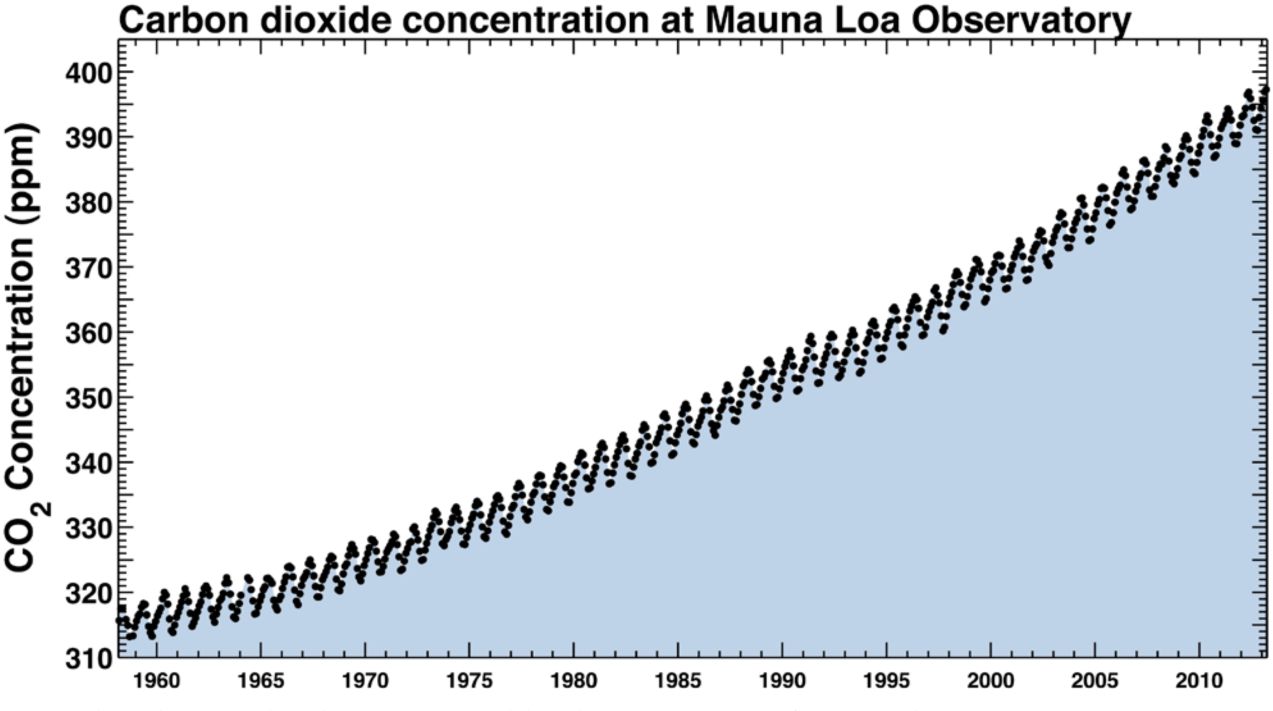

Figure 6. The Keeling Curve through 2019. Courtesy Ralph Keeling, Scripps Institute of Oceanography.

began a steady decrease that lasted until late September when the trend reversed and the concentration began to increase once again. The variation was not insignificant, on the order of 6 ppm from the summer peak to the winter minimum. As Keeling writes: "The maximum concentration at Mauna Loa occurred just before the plants in temperate and boreal regions put on new leaves. At Mauna Loa the regular season pattern almost exactly repeated itself during the second year of measurements. … We were witnessing for the first time nature's withdrawing CO_2 from the air for plant growth during the summer and returning it each succeeding winter."

One other trend was immediately clear from the data: the atmospheric concentration of CO_2 was steadily increasing at a rate of 0.7 ppm per year.[38] Human beings, through their ravenous thirst for energy, were slowly but surely changing the chemical makeup of the atmosphere.

Keeling would continue measuring CO_2 at Mauna Loa for the remainder of his career, despite regular threats by various government agencies to cut his funding. Since Keeling's death in 2005, the work has been supervised by Ralph Keeling, one of Keeling's five children, who is the principal investigator for the Scripps Atmospheric Oxygen Research Group and the director of the Scripps CO_2 Program. The sawtooth, steadily rising plot of the CO_2 data is now known as the "Keeling Curve," and has been called by many the single most important environmental data set of the twentieth century. On May 9, 2013, the CO_2 concentration on Mauna Loa passed 400 ppm for the first time, a dire milestone in human history.[39] In the long quest to understand why earth's temperature is what it is and whether human beings could affect earth's climate, two things were now clear: CO_2 is a potent greenhouse gas and burning fossil fuels was inexorably increasing its concentration in earth's atmosphere. One critical question remained: was Earth's climate heating up?

THE HOCKEY STICK

Accurate thermometer readings of Earth's temperature extend back only to the 1880s. In the 1930s, Callendar believed that he had detected a slight increase in Earth's temperature over the 50-year period covered by that temperature record. Many critics thought that Callendar was simply wrong in this conclusion. Others argued that, even if there had been an increase, it was part off the natural fluctuations one would expect of Earth's complex climate system.

By the 1970s, the temperature record suggested a slight cooling trend over the previous several decades, and many observers declared that concerns about the buildup of CO_2 in the atmosphere were overblown. In 1975, Wallace Broecker (1931–2019), a distinguished climate scientist at Columbia University's Lamont-Doherty Earth Observatory, published what would come to be recognized as a groundbreaking paper in *Science*, "Climate Change: Are We on the Brink of a Pronounced Global Warming?" that strongly challenged this view. Broecker wrote:

> *The fact that the mean global temperature has been falling over the past several decades has led observers to discount the warming effect of CO_2 produced by the burning of chemical fuels. In this report I present an argument to show that this complacency may not be warranted. It is possible that we are on the brink of a several-decades-long period of rapid warming. Briefly, the argument runs as follows. The ^{18}O record in the Greenland ice core strongly suggests that the present cooling is one of a long series of similar natural climatic fluctuations. This cooling has, over the last three decades, more than compensated for the warming effect produced by the CO_2 released into the atmosphere as a by-product of chemical fuel combustion. By analogy with similar events in the past, the present natural cooling will, however, bottom out over the next decade or so. Once this happens, the CO_2 effect will tend to become a significant factor and by the first decade of the next century we may experience global temperatures warmer than any in the last 1000 years.*[40]

Broecker's paper proved to be prophetic, as global temperatures almost immediately began to climb and have continued to do so ever since. As his 2019 obituary in the *New York Times* pointed out, however, Broecker based his predictions "on a simplified model of the climate system, and he later realized … that some of his analysis had been flawed. He would later write a follow-up paper stating that, as accurate as his prediction turned out to be, 'It was dumb luck.'"[41] Nevertheless, Broecker's paper earned him the sobriquets "grandfather of climate science" and "father of global warming."

Broecker's analysis was theoretical. In his paper, he observed that, "Meteorological records of the mean global temperatures are adequate only over the last century. … From this record alone little can be said about the causes of climatic fluctuations. It is too short and may be influenced by pollution." But was the temperature record really so inconclusive?

The National Aeronautics & Space Administration's Goddard Institute for Space Studies (GISS) published its first global temperature analysis in 1987.[42] GISS scientist James Hansen (1941–) and coauthor Sergei Lebedeff analyzed surface air temperature data from meteorological stations from 1880–1985 and found that the temperature changes at mid- and high-latitude stations were highly correlated. "We find that meaningful global temperature change can be obtained for the past century, despite the fact that the meteorological stations are confined mainly to continental and island locations. The results indicate a global warming of about 0.5°–0.7 °C in the past century, with warming of similar magnitude in both hemispheres." They continued that a strong warming trend between 1965 and 1980 "raised the global mean temperature in 1980 and 1981 to the highest level in the period of instrumental records."

Hansen and Lebedeff updated their analysis a year later, reporting that, "Data from meteorological stations show that surface air temperatures in the 1980s are the warmest in the history of instrumental records. The four warmest years on record are all in the 1980s."[43]

On June 23, 1988, Hansen and other climate scientists testified on the possibility of anthropogenic climate change before the Senate Committee on Energy & Natural Resources. Hansen was more emphatic than any other witness, stating:

> *I would like to draw three main conclusions. Number one, the earth is warmer in 1988 than at any time in the history of instrumental measurements. Number two, the global warming is now large enough that we can ascribe with a high degree of confidence a cause and effect relationship to the greenhouse effect. And number three, our computer climate simulations indicate that the greenhouse effect is already large enough to begin to affect the probability of extreme events such as summer heat waves.*[44]

While stressing that global climate models needed improvement, Hansen drew particular attention to the correlation between the observed warming in the temperature record and warming predicted by computer models of the climate. "Since there is only a one percent chance of an accidental warming of this magnitude, the agreement with the expected greenhouse effect is of considerable significance," he told the committee.

Although scientists had been discussing the possibility that CO_2 from burning fossil fuels could impact Earth's climate for decades, Hansen's Senate testimony marked a turning point in the public perception of the

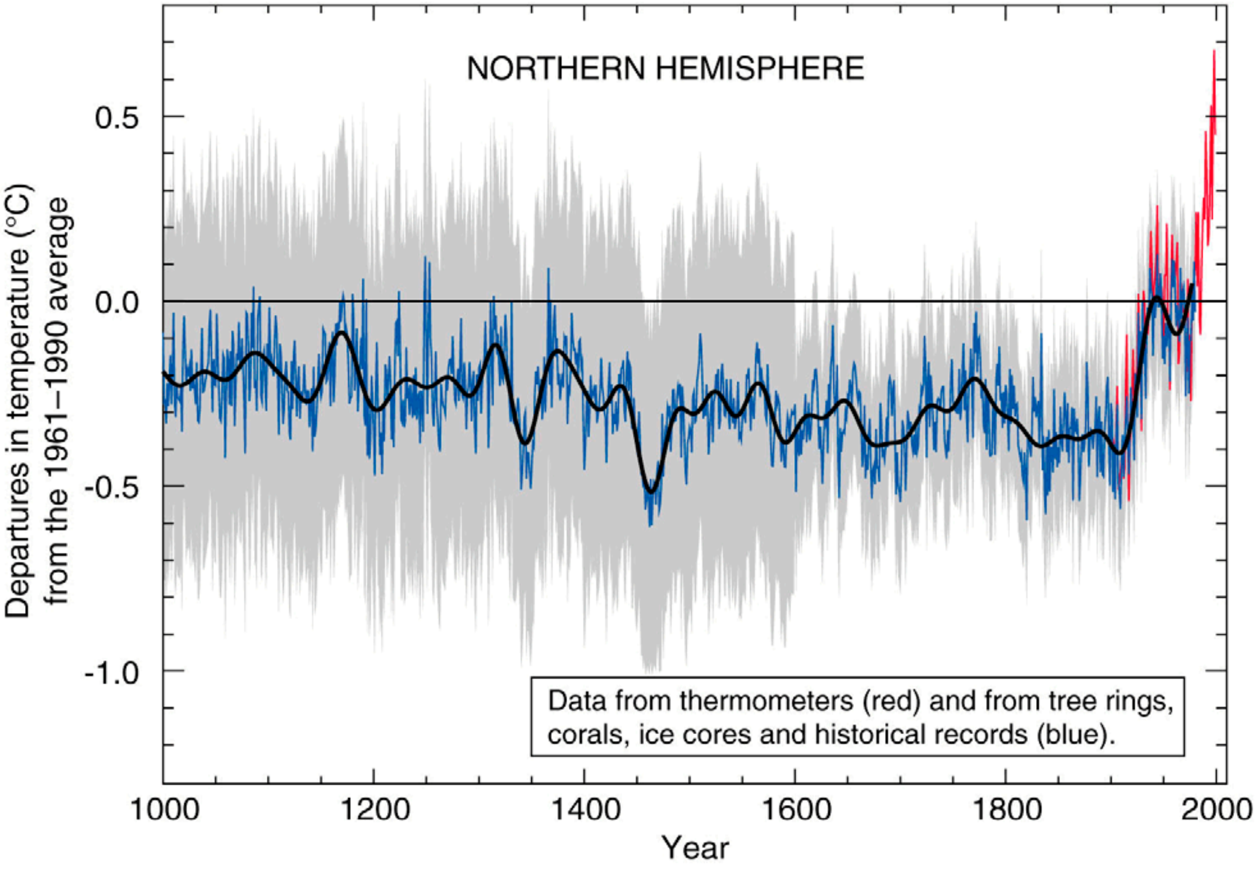

Figure 7. The Hockey Stick—time reconstructions (blue) and instrumental data (red) for Northern Hemisphere mean temperature. In both cases, the zero line corresponds to the 1902-80 calibration mean of the quantity. Courtesy Michael Mann.

issue. NASA was 99% certain, Hansen had testified, that a warming trend was occurring and that humans were responsible. The June 24, 1988, front-page story in the New York Times on Hansen's testimony was entitled "Global Warming Has Begun, Expert Tells Senate."[45]

Temperature records go back only about 140 years. Climate change skeptics insisted that the changes Hansen was seeing were not, in fact, indicative of a long-term trend. Other scientists, however, were working to extend our understanding of the temperature of the Earth over much longer time spans, over hundreds and even thousands of years into the past. The field of paleoclimatology uses indirect evidence provided by "proxy climate data"—oxygen isotope ratios from ice cores, tree rings, deep ocean sediments, corals, and other natural data—to estimate temperature changes in the past.

In 1998, Michael E. Mann and Raymond S. Bradley of the Department of Geosciences at the University of Massachusetts and Malcolm K. Hughes of the Laboratory of Tree-Ring Research at the University of Arizona published "Global-Scale Temperature Patterns and Climate Forcing over the Past Six Centuries," in which they used proxy data networks to reconstruct Earth's temperature from 1400 to the present.[46] A year later, they extended the analysis over the entire past millennium in "Northern Hemisphere Temperatures During the Past Millennium: Inferences, Uncertainties, and Limitations."[47]

In his book "The Hockey Stick and the Climate Wars,"[48] Mann describes the data set that resulted from this work:

> *Despite the uncertainties, my coauthors and I were able to draw certain important conclusions. We deduced that there had been a decline in temperature from a period running from the eleventh century through the fourteenth—a period sometimes referred to as the medieval warm period—into the colder Little Ice Age of the fifteenth to the nineteenth centuries. Think of this as the shaft of a hockey stick laid on its back. This long-term gradual decline in temperature was followed by an abrupt upturn in temperatures over the past century. Think of this as the blade.*

Mann and his colleagues used actual temperature measurements to fill in the plot from 1980 through 1999 as relatively few long-term proxy records had been updated since the early 1980s.

"Thus was born the hockey stick—though the term itself was actually coined later by a colleague in Prince-

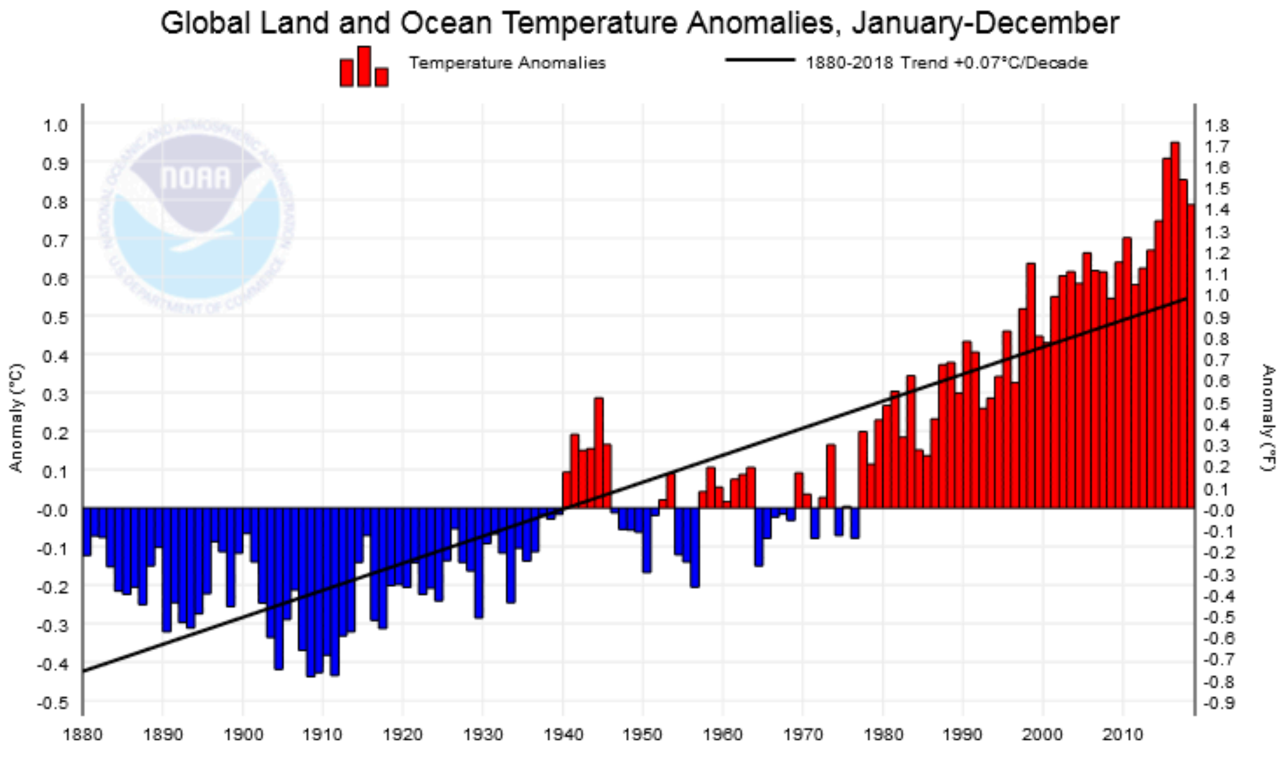

Figure 8. Graph of average annual global temperatures since 1880 compared to the long-term average (1901-2000). The zero line represents the long-term average temperature for the whole planet; blue and red bars show the difference above or below average for each year. National Oceanic & Atmospheric Administration.

ton," Mann writes. "It didn't take long for the hockey stick to become a central icon in the climate change debate. It told an easily understood story with a simple picture that a sharp and highly unusual rise in atmospheric warming was occurring on Earth."

CONCLUSION

For 20 years, the hockey stick has drawn the scorn of climate change deniers. They insisted the blade of the hockey stick flattened in the 2000s as Earth's temperature increase seemed to pause, albeit at an elevated level. Then the temperature began to increase again around 2010 and the blade still looks very much like a blade.

When James Hansen testified before the Senate, he pointed out that the 1980s were the warmest years in the historical record.

Those days are long gone. According to NOAA, 18 of the 19 warmest years on record have occurred in the twenty first century—the only outlier is 1998—and the past five years have been the warmest ever (Figure 8).[49] Ocean levels are rising because the oceans are being warmed and are expanding and the Greenland and Antarctic icecaps are melting; oceans are also acidifying as they absorb excess CO_2. The large-scale geophysical experiment that Revelle and Seuss pointed to in 1957 is now well underway and climate change denial is both intellectually indefensible and morally reprehensible.

Any notion of a sustainable economy in the 21st century must center on energy, specifically weaning humanity from fossil fuels. Other Earth resources are under stress and must also be attended to, but Earth's climate is not just under stress. It is careening toward catastrophe. A sustainable world requires many adaptations, but chief among them is for humans to learn to power civilization with energy sources other than fossil fuels, primarily the Sun. Humans will have to learn how to live off the sun in real time.

There is much work left to be done before Earth's climate is fully understood, but two hundred years of path-breaking research has made our dilemma clear.

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Historical Article

From Aqua Vitae to E85: The History of Ethanol as Fuel

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Abstract. Ethyl alcohol, or ethanol, is one of the most ubiquitous chemical compounds in the history of the chemical sciences. The generation of alcohol via fermentation is also one of the oldest forms of chemical technology, with the production of fermented beverages predating the smelting of metals. By the 12th century, the ability to isolate alcohol from wine had moved this chemical species from a simple component of alcoholic beverages to both a new medicine and a powerful new solvent. The use of alcohol as a fuel, however, did not occur until significantly later periods, the history of which is generally presented as a separate narrative from its initial applications as intoxicating beverages, medicines, or chemical reagents. The current report aims to more firmly connect these two disparate historical accounts, presenting an overview of the history of ethanol from its initial isolation in the 12th century through its current application as a fuel additive for most automotive vehicles in the United States.

Keywords. Ethanol, distillation, combustion, spirit lamps, alcohol stoves, engine fuel.

INTRODUCTION

There is no doubt that ethyl alcohol (or ethanol, CH_3CH_2OH) can be considered one of the most ubiquitous chemical compounds in the history of the chemical sciences. In the chemical laboratory, it is commonly used as a quite versatile solvent that is not only miscible with both water and wide variety of other organic solvents, but can also solubilize a broad range of analytes. As such, it still remains one of the most common chemical media for a wide range of solution-based chemical processes. Historically, ethanol represents one of the earliest nonaqueous solvents and it is most certainly the very first such solvent of high polarity.[1] Beyond its laboratory use as both a solvent and chemical reagent, the antibacterial and antifungal properties of ethanol provide an effective medium for the preservation of organic matter and well as a highly useful disinfectant in medical applications.[1-4]

Of course, ethanol predates its eventual isolation in the 12th century[1-3,5-10] and dates back as far as ca. 10,000 BCE[2] as the psychoactive component of various fermented beverages (i.e. mead, wine, beer), resulting in euphoria and other mind-altering effects. As such, the alcohol content of such fermented beverages is one of the oldest known recreational drugs, and is still the most widely accepted of such drugs in most cultures. Ethanol has thus played, and continues to play, a central role in the history of society in general.[1,2]

More recently, the flammable nature of ethanol has led to its use as a fuel for a variety of applications. While such early uses were limited to sources of light and heating, ethanol has now become a common fuel or fuel additive for the combustion engine. In these latter applications, the ability to produce ethanol from the fermentation of biomass provides the attractive promise of renewable alternatives to our current dependence on petroleum fuels. As such, the current report aims to present an overview of the history of ethanol as a fuel, starting with its initial isolation from wine in the 12th century through its current application as a fuel additive for most automotive vehicles in the United States.

BRIEF HISTORY OF EARLY DISTILLATION

As discussed above, the production of alcoholic beverages via fermentation is thought to date back to sometime before 6000 BCE,[2,10-13] yet the isolation and application of ethanol as a distinct chemical species did not occur until the 12th century CE.[3,5-10] As such, it is natural to wonder why its isolation took so very long. The simple answer to this is that distillation, the primary method for the separation of alcohol from such fermented beverages, was not really developed until the 1st century CE[14-22]. Even so, it still took essentially another thousand years for ethanol's successful isolation. In order to understand this additional delay, we first need to briefly review the history of distillation before returning to its use in the isolation of alcohol.

Distillation is considered an ancient art and its physical apparatus, commonly referred to as a still, is thought to be the earliest known specifically chemical instrument.[14-16,21,22] Distilling equipment was first described by the late first century CE alchemist known as Maria the Jewess. As her writings already illustrated a fairly advanced state of development, she is generally given credit for its invention.[14-22] Unfortunately, very little is known about Maria other than writings ascribed to her, which survive only in quotations by the later alchemist Zosimos.[14,15,19,22]

As shown in Fig. 1, the early still consisted of three components: the distillation vessel (*cucurbit*), the still-head (*ambix*) with an attached delivery tube (*solen*), and the receiving vessel (*bikos*).[9,16-18,22,23] Such early stills were constructed from a mixture of materials, primarily earthenware (with a glazed interior), copper, and glass, that were fixed together using a plastic material known as a lute to seal the joints between the individual components.[6,16-18,22,24,25] Glass, however, was initially limited to just the receiving vessels,[6,15,16,18,22,23] where its transparency allowed the distiller to observe the collecting product. As glass technology evolved, glass later began to be also used for the ambix, and eventually for both the ambix and cucurbit.[6,16,22,23] A difficulty encountered with the early use of glass in such applications, however, was the instability of glass vessels under heat. This can be seen in instructions from Maria the Jewess as quoted by Zosimos:[15,19]

> *...place at the ends of the tubes glass flasks, large and strong so that they may not break with the heat coming from the water...*

Pliny the Elder later warned of similar issues, stating:[26]

> *Glass is unable to stand heat unless a cold liquid is first poured in.*

Up through the Roman period, early glasses primarily utilized a simple soda-lime-silica composition that varied depending on the specific raw materials applied.[22,27,28] Here, the calcium of the lime acted as a stabilizer to counteract the high solubility of the sodium contained within the glass. Unfortunately, however, lime was not intentionally added as a major constituent before the end of the 17th century and all calcium content prior to that time was a result of impurities in either the sources of silica (SiO_2) or soda (Na_2CO_3).[22,27-31] Because of this, early glasses consisted of a high soda

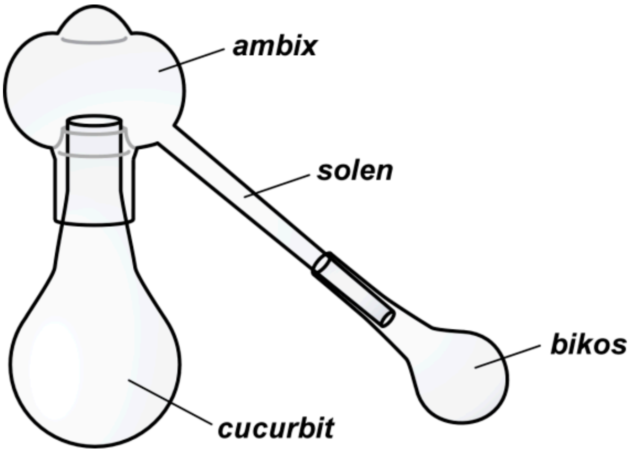

Figure 1. Basic components of the early still [*reprinted from reference 22 with permission from Springer Nature*].

and low calcium content which resulted in overall poor chemical resistance.[16,23,32,33] Furthermore, the thermal expansion of the such glasses increases with soda content,[34] so the high soda content coupled with the physical defects common in early glass caused high thermal expansion and low thermal durability, which had a tendency to break under rapid heating.[22,23,34] In an effort to overcome the limited stability of glass vessels under heat, heavy-walled flasks were typically used, the exterior of which was then coated with clay (layers up to 2-3 fingers width). [6,16,17,22, 23,35] This helped reduce breaking, but the poor heat transmission of the clay coatings resulted in long preheating periods and limited control of the cucurbit temperature, which when combined with the inefficient cooling of early still heads, made it difficult to distill volatile liquids such as alcohol.[16,22,24]

As the knowledge of distillation apparatus was transmitted to Islamic philosophers during the 7th-8th centuries CE, the term ambix was transformed through the addition of the Arabic article *al-* to become *al-anbîq*, which eventually became *alembicus* and *alembic*.[15-18,20,22,23] By the 10th century, the terms ambix and alembic were commonly used to refer to both the still-head and the still as a whole.[6,15-18,20,22] Because of the Arabic contribution to the word alembic, some authors have mistakenly attributed the discovery of distillation methods to Islamic philosophers.[10]

As discussed above, distillation efforts prior to the 12th century were limited by both the poor quality of glass and ineffective cooling methods for the collection the condensing material.[7] Initial methods to improve cooling were to cool the delivery tube (solen) with wet sponges or rags. As this tube was now generally cooler than the still-head, condensation would occur primarily in the solen rather than collecting the condensate within the still-head. As such, the typical medieval alembic no longer contained an inner rim to collect and transfer the collecting liquid to the solen.[6,16,22,23] As one of the earliest references to distilled alcohol is found in the writings of Magister Salernus,[6,9,22,24] it is believed that he may have pioneered the cooling of the solen to effect condensation outside the still-head[22,23,25].

Beginning in the 13th century, the prospering Venetian glass industry began blending Roman and Syrian glassmaking methods to produce a significantly improved glass.[23,36-39] This improvement in glass technology was largely due to a change in the soda source used, as well as the introduction of new processes for the purification of both silica and soda sources prior to their use in glassmaking.[39] The soda utilized exclusively by the Venetians was a plant ash imported from the Levant that contained large amounts of magnesium and calcium in addition to the desired Na_2CO_3 and its use in glassmaking resulted in a new glass that exhibited both higher chemical durability and reduced thermal expansion.[32-34,39] Furthermore, the Venetians' innovative purification methods removed insoluble, non-fusible components from the resulting glass, which would have acted as stress points during heating. With the introduction of the improved Venetian glass, both glass cucurbits and alembics then became more common.[6,16,23]

The common fabrication of still components from glass then allowed the investigation of more versatile approaches to still design, particularly for improved cooling. However, the most revolutionary and critical of these advances, the modern cooling coil, was initially fabricated from copper.[40] This design was introduced during the late 13th century by Taddeo Alderotti of Florence (ca. 1210-1295, Fig. 2), who is commonly viewed to be its inventor[3.,6,16,18,22-24] In his *De virtutibus aquae vitae*, Alderotti describes the distillation of wine using an alembic with an elongated solen consisting of a *canalem serpentinum* ("serpentine channel"), along with a cooling trough and regular supply of fresh cooling water.[24,40] The earliest known pictorial representation of this new cooling method (Fig. 3A) was not given until ca. 1420 by Johann Wenod, a physician in Prague.[6,16,41-43] Unfortunately, Wenod provides very little detail and only gives the notation *vas cum aqua* (vessel with water) above the cooling tub.[43] Based on Alderotti's description of a serpentine channel, however, it was thought that his cooling

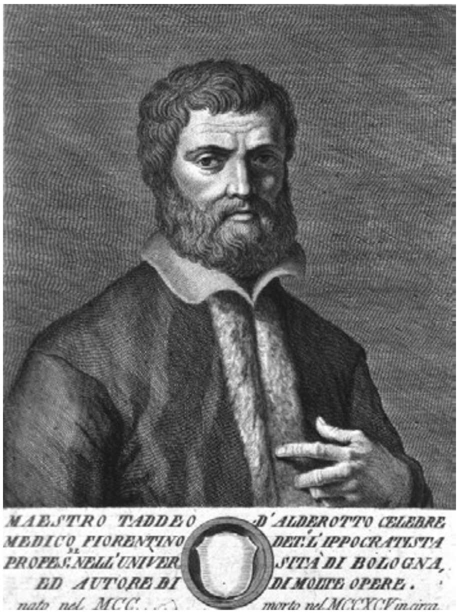

Figure 2. Engraving of Taddeo Alderotti of Florence (ca. 1210-1295) [*The National Library of Medicine*].

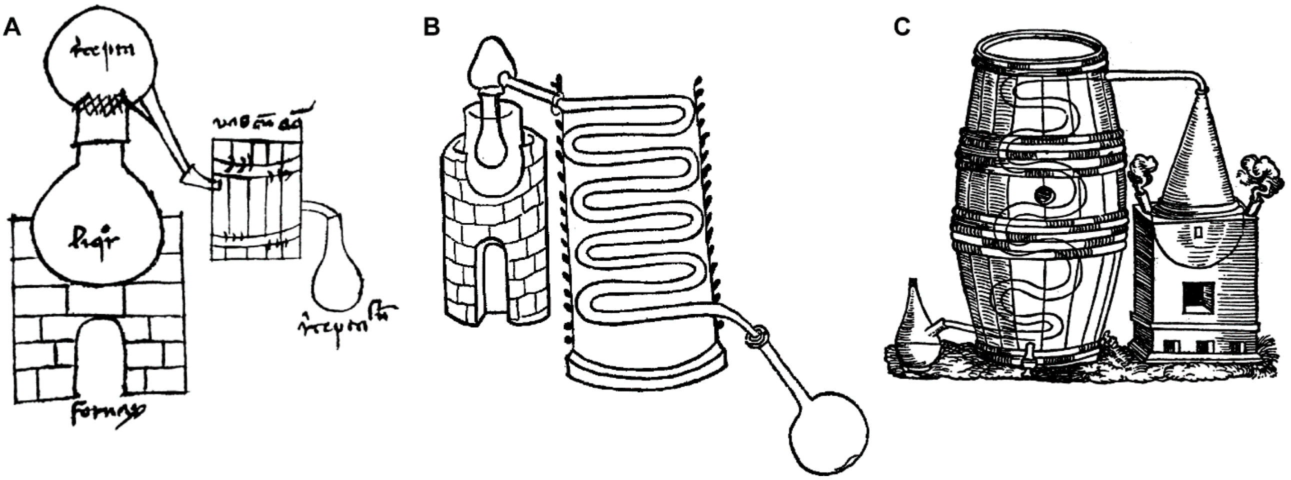

Figure 3. External cooling trough as depicted in the treatise of Johann Wenod (A) and illustrations of the worm-like nature of the "wormcooler" cooling coil from: (a) Philipp Ulstadt's *Coelum Philosophorum seu De Secretis Naturae Liber,* 1525 (B) and Walter Ryff's *Neu Gross Destillierbuch*, 1556 (C).

apparatus wound 'worm-like' through the cooling trough as shown by many later pictures (Fig. 3B & 3C)[6,8] and is thus commonly referred to as a "wormcooler".

The impact of the improved Venetian glass and the growing glass industry on the evolution of distillation apparatus led not only to the development of new, improved glass-based components, but also to new stills fabricated completely from glass.[16] As it became more common to utilize all-glass distillation apparatus, the cucurbit and alembic were eventually combined into a single piece. This new form of still (Fig. 4) was called the *retort* (from Latin *retortus*, "bent back") and was introduced in the early 14th century.[6] The retort was especially well-suited for high temperature distillations when the lute sealing together a typical multi-component alembic would begin to fail.[42] Distillation via a retort was often referred to as *destillatio ad latus* ("sidewards distillation").[6]

Two later still designs both focused on the still-head, rather than the solen, in order to increase effective cooling during distillation[6,48,45]. The Rosenhut (German) or Rozenhoed (Dutch, both literally meaning "rose hat") (Fig. 5A) is thought to be the earlier design, as it was illustrated in its fully developed form in 1478,[6] but essentially disappeared by the end of the 16th century.[44] The still consisted of a high conical, air-cooled alembic and was a common form used for making early liqueurs.[6,45] This modified alembic was typically fitted to a wide-mouthed cucurbit and, although never shown in illustrations, is thought to have been built with an inner rim to collect the distillate.[6] While glass was now the commonly utilized for distillation components, the Rosenhut was often constructed from metals such as lead and copper as the high thermal conductivity of the metals resulted in superior air cooling.[6,45]

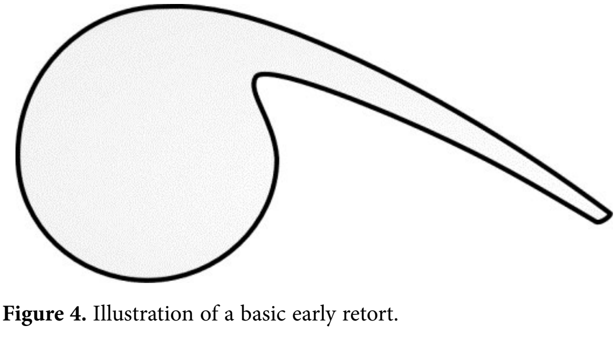

Figure 4. Illustration of a basic early retort.

In contrast, the Mohrenkopf ("Moor's head") enclosed the still-head in a basin or container which was filled with cooling water (Fig. 5B). The Moor's head was typically made of glass (although pottery is also said to have been used) and is thought to be an invention of the later 15th century.[6,45] It has been suggested that it may have been influenced by the Chinese still, which also utilized a water-cooled head,[3] and was viewed to give lower quality distillates than those obtained via the wormcooler.[46]

EARLY ISOLATION OF ETHANOL

Based on available evidence, the current view is that the initial isolation of alcohol occurred in southern Italy during the 12th century, most likely at the School

Figure 5. Illustrations of the Rosenhut from Michael Puff von Schrick's *Hienach volget ein nüczliche materi von manigerley ausgepranten wasser,* 1478 (A) and the Moor's head from Hieronymus Brunschwyck's *Liber de arte distillandi de Compositis*, 1512 (B).

of Salerno.[3,5-10,14,22,24,47] Some authors argue for an earlier discovery by Muslim philosophers and it is possible that the alcohol could have been isolated prior to the 12th century.[48] However, while it is believed that Arab alchemists distilled wine prior to the 12th century,[3,48] no convincing evidence has been presented that they isolated ethanol prior to that of the known western sources.[6,49] In fact, the common view is that the Arabs did not find the distillates obtained from wine very interesting,[3] which would make sense if the distillates still contained high water content, as would be expected from the ineffective isolation of the volatile alcohol products.

This assignment to 12th century Italy is supported by the fact that one of the earliest direct recipes for the isolation of alcohol is found in the writings of Magister Salernus.[5-7,24] Earlier School of Salerno treatises from 1100-1150 CE discuss the preparation of "beneficial waters" by distillation,[3,6,9] but his writings were the first to directly mention alcohol.[6] Another recipe from the same time period is found in the *Mappae Clavicula*, which may predate that of Salernus.[3,5,7,47] This Medieval Latin text is thought to date to ~820 CE, but only later 10th and 12th century versions are currently available and the alcohol recipe is only found in the 12th century version.[3,7,47] A third recipe is also said to have been found in a 12th century parchment recovered from Weissenau, a south German monastery. Further recipes for preparing alcohol are frequently found in the available literature after the 13th century.[7]

The late discovery of alcohol is viewed to be primarily due to inefficient cooling during distillation coupled with the use of materials with poor heat transmission, thus requiring long preheating periods and limited temperature control.[22] Some authors have linked the dependence of alcohol's isolation on improvements in cooling methods[3] and the evolution in still design most certainly improved the ability to isolate alcohol. Unfortunately, none of the early recipes discussed above include details on the distillation methods used, particularly the nature of any cooling methods. As such, it is unknown if these initial successes utilized any methods for cooling the solen. It has been proposed that it could have been possible to distill alcohol in the ancient cucurbit and alembic without cooling the solen, but only if the heating could be carefully regulated.[6] However, such temperature control would not have been possible through the common use of earthenware or clay-coated glass curcurbits, which usually resulted in long digestion periods before distillation and excessive temperatures that drove off the low boiling fractions, thus making it difficult to isolate volatile liquids such as alcohol.[6,16,22,23,25] As such, the successful distillation of alcohol would necessitate either more effective cooling or curcurbits constructed of materials with more effective heat transmission, with the best results involving a combination of the two. If not, alcoholic distillates separated by the early stills would contain so much water that they would not burn, thus making it difficult to differentiate such distillates from normal water.[3,6]

Another factor that contributed to the success of these early isolations was the addition of a variety of salt substances (NaCl, potassium tartrate, K_2CO_3, etc.) as detailed in the recipes discussed above. These added salts acted by absorbing some of the water content of the wine, thus increasing the alcohol concentration and making it easier to isolate via distillation.[6,7] It is thought that this practice may have been influenced by the view of Islamic philosophers that something to absorb one nature should be added in attempting to purify another nature.[7] Distillations of such wine-salt mixtures gave solutions referred to as either *aqua ardens* (burning water)[3,7,9,50,51] or *aqua flamens* (flaming water), which typically had such low alcohol content that they burned without producing significant heat.[3,5,6,8,50] The combination of pretreatment with salts along with more efficient cooling methods ultimately produced alcoholic distillates containing less than 35% water and repetitive fractional distillation was said to allow the isolation of "absolute" alcohol.[6] After the introduction of Aderotti's wormcooler, the use of the salt pretreatments were no longer necessary and it is thought that it should have been possible for him to obtain 90% alcohol by fractional distillation.[3,6,18] Strong alcohol distillates were referred to as *aqua vitae* (water of life)[3,7] by authors such as Aderotti[40] and Arnald of Villanova (ca. 1240-ca. 1312)[6,8,52], the latter who stated:

> *This name is remarkably suitable, since it is really a water of immortality. It prolongs life, clears away ill-humours, revives the heart, and maintains youth.*

It should be stressed that although the description of aqua vitae is sometimes given as absolute alcohol, the highest alcohol concentration that can achieved by the simple distillation of aqueous solutions is 95%. This is due to the fact that the 95% ethanol:5% water mixture represents a minimum-boiling azeotrope that cannot be separated by distillation. Such an azeotrope has a fixed composition, a fixed boiling point, and in all respects acts as a pure liquid. In order to generate true absolute (99-100%) alcohol, the ethanol needs to be distilled from an ethanol-benzene-water mixture, or the water must be removed though the use of a dehydrating agents such calcium oxide (CaO). [53]

FROM AQUA VITAE TO ETHYL ALCOHOL

As introduced above, the original names for ethanol were aqua ardens, aqua flamens, and aqua vitae, with the last of these terms still surviving in the modern words *aquavit* (Scandinavian), *eau-de-vie* (French), *whiskey* (Scottish), and *vodka* (Slavic). An additional later reference to ethanol was *spirit of wine*, as the separation of alcohol from wine was viewed to be analogous to the separation of the soul from an impure body. Thus, alcohol was viewed to be the "spirit" of the wine and the remaining residue was called the *caput mortum* (dead body). [22] This is also the origin of the term *spirits* to refer to various forms of strong alcoholic beverages. The modern term *alcohol*, however, was not used to refer to these distillation products until the 16th century, with the development of the word an amazing example of the complexities of etymology.

The word alcohol finds its origin in the word *kohl* (or *kuhl*), which referred to a finely powdered form of the mineral stibnite, or antimony trisulphide (Sb_2S_3). [5,6,54-56] Kohl can vary in color from dark-grey to black and was used in antiquity as a cosmetic, particularly to color the upper eyelid in Egypt. Its use has been documented back to at least the 15th century BCE.[56] As Greek and Roman knowledge was eventually transmitted to the Islamic Empire, kohl was modified with the Arabic prefix *al-* to become *al-kohl* (or *al-kuhl*) in a similar fashion to alembic as discussed above.[5-7,53,54,56] The meaning of the word then changed over time, first transitioning from the simple black powder of kohl to refer to any very fine powder[6-8,53,54,56] and then further extended to mean the most fine or subtle part of something.[5,6,55] As a result, al-kohl

Figure 6. Philippus Aureolus Theophrastus Bombastus von Hohenheim (1493-1541), commonly known as Paracelsus [*Edgar Fahs Smith Collection, University of Pennsylvania Libraries*].

or *al-kohol* became generally used for any substance refined by pulverization, distillation, or sublimation.[57] By the 16th century, Paracelsus (Fig. 6) in his *Von Offenen Schaden* and other writings referred to aqueous solutions distilled from wines as *alcool vini* or *alkohol vini* (i.e. the subtle part of wine). Over time, *vini* was then eventually dropped to become first *alkohol* and then finally the modern *alcohol*.[5,7,56] Even into the 18th century, alcohol was still often defined first as powders of the finest form and only secondly as the spirit of wine.[54]

The use and meaning of the term alcohol then changed again, beginning with the discovery of methyl alcohol (CH_3OH) in 1834 by Jean Baptiste Dumas (1800-1884) and Eugène Peligot (1811-1890). [58,59] As a result, Jöns Jacob Berzelius (1779-1848) proposed alcohol as the general name for these compounds, with ethanol referred to as wine alcohol (*wein-alkohol*) and methanol as wood alcohol (*holzalkohol*).[58] Shortly thereafter, Dumas and Peligot revealed that a compound previously discovered by Michel Chevreul (1746-1889) was cetyl alcohol ($C_{16}H_{33}OH$)[58,59] and the fact that the family now consisted of three known examples suggested that a series of such alcohols were waiting to be discovered. For the discussion herein, any use of the general family name alcohol will refer specifically to ethyl alcohol, the modern name of which had become accepted, and was in formal use, by the second half of the 19th century.

INITIAL APPLICATIONS IN HEAT AND LIGHTING

The combustible nature of alcohol was discovered almost as soon as it was first isolated in the 12th century, as evidenced in its initial names aqua ardens and aqua flamens. Such early studies revealed that although it looked like water, alcohol burned with a blue, gemlike flame, a perplexing contradiction for the time as everyone knew that the nature of water was to extinguish fire. Given this early knowledge, however, there is no evidence that alcohol was used to any extent as a fuel in its first 500 years.[60] This may have been due to the fact that it was too highly prized as a consumable and medicine, as well as for its various uses in the chemical and medical arts to solubilize other reagents.[61] By at least the end of the 15th century, however, high-alcohol mashes could now be produced via the fermentation of a wide variety of common crops (grains, potatoes, corn, sugar beets, etc.).[53,60,62] This wide variety of potential sources, coupled with the previously discussed advances in distillation methods by this period, should have thus allowed the production of ethanol on large enough scales that additional applications were only a matter of time.

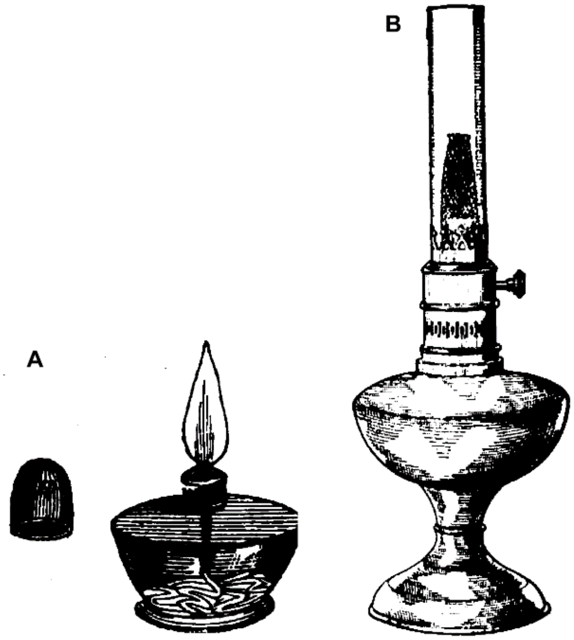

Figure 7. A simple spirit lamp, circa 1830 (A) and an incandescent alcohol lamp, circa 1900 (B).[63,64]

The earliest such use referenced are for alcohol-based spirit lamps, which consisted of small burners that could be used to heat food or other objects. It is thought by some that the use of such spirit lamps date as far back as the 17th century, but they were most certainly in widespread use by the beginning of the 19th century. By the 1830s, such alcohol-fueled sprit lamps (Fig. 7A) were an important laboratory device for the application of heat and served as a useful alternative to more powerful heating sources such as gas flames, fires, or furnaces.[63] Such lamps were popular in France and Germany, where alcohol was inexpensive. In England, however, the taxes on alcohol made its use for this purpose cost prohibitive such that labs were typically forced to rely on oil lamps.

At the same time, the 1830s witnessed the introduction of high-proof alcohol as a solvent for illumination. In 1833, Augustus Van Horn Webb introduced a substitute in the United States (US) for the existing candles and whale-oil commonly used throughout the country.[64] Webb called this substance "*spirit gas*," which consisted of a mixture of alcohol and spirits of turpentine. Subsequent experiments resulted in the additional ingredients, whereupon he changed the name of the mixture to "camphorated gas". A limitation, however, was that the spirits of turpentine were too resinous and thus he worked to further refine it, the product of which was given the name *camphene* (also known as *camphine*[65]).[64] This led to his final composition of what was now called "burning fluid", consisting of one-part camphene and 4.5 parts 95% ethanol.[64] From 1840 to 1860, camphene and burning fluid were emphatically the "lights of the world," the former for fixed lamps, the latter for portable lamps. From 1850 to the outbreak of the Civil War the business of distilling alcohol and camphene, and the manufacture and sale of burning fluid, became a distinct and very extensive business, with the market for alcohol-based solvents and fuels exceeding 25 million gallons per year by 1860.[65] The dominance of burning fluid in the US was short-lived, however, due to the introduction of low-cost kerosene from refined petroleum in the early 1860s, coupled with increased taxes on alcohol in 1861.[64,65]

The introduction of the incandescent alcohol lamp (Fig. 7B) at the end of the 19th century then led to a resurgence of alcohol for lighting.[64] The success of this lamp was the incandescent mantle developed by Carl Auer von Welsbach (1858-1929) in the mid-1880s.[66] In attempts to maximize the emission of rare earth elements, Welsbach had conceived of the idea of saturating a cotton fiber with a solution of the rare earth salts, after which he burned out the cotton, leaving behind a structure of metal oxides (originally a mixture of magnesium, lanthanum, and yttrium).[64,66,67] This mantle would incandesce brightly when a flame was applied to it to emit a soft, intensely white light[66,67] and its adaptation for use with alcohol lamps marked a notable improvement in the efficiency of the lamp such that it no longer required camphene or burning fluid to produce a luminous flame and simple alcohol alone was all that was needed.[64,68] Furthermore, comparative tests on the illuminance of alcohol in the new lamp showed that it outperformed kerosene by more than a factor of two.[53,64,67] From this point, alcohol found widespread use for both indoor and outdoor lighting.[64,67]

In addition to lighting, the initial simple spirit lamps eventually developed into an assortment of more specific alcohol-fueled devices. This included a wide range of more sophisticated stoves for the heating and cooking of food, as well as hot water heaters, tea kettles, coffee percolators, coffee roasters, and flatirons.[67,68] This last is particularly interesting, as such alcohol-fueled flatirons (Fig. 8) appear to be the first example of a "self-heating" flatiron in comparison to a device that needed to be heated on an external heat source such as a stove or fire. As a result, this should have provided more consistent temperature control.

Lastly, various alcohol-burning stoves had also been developed for heating internal living spaces. A limitation here is that the alcohol flame itself radiates very little heat outward, with nearly all of the heat traveling upward from the tip of the flame. Thus, in order to heat a room with an alcohol stove, the heat of the alcohol flame needed to be reflected out into the room. This was usually accomplished with a curved sheet of copper, as shown in the heaters depicted in Fig. 9.[67,68] The fluted arrangement of these sheets would further enhance the ability of the stove to throw out the heat in the largest possible quantities into the room.[68] This is only one of the various types of heaters used for this purpose[67,68] and other designs utilized a piece of non-combustible material, such as asbestos, which could be rendered red-hot by the flame. Germany in particular had developed many such alcohol-fueled heaters, where they were in common use by the early 20th century.[67]

DENATURED ALCOHOL

A primary issue that limited the use of alcohol as fuel was the frequent taxes and duties levied by governments upon distilled spirits. In the US, taxes were imposed on distilled spirits in 1791 to discourage its use as an intoxicant.[65] These taxes were repealed in 1802,[65] but were then reinstated in 1861 when the Civil War

Figure 8. Alcohol-fueled flatirons, circa 1900.[67,68]

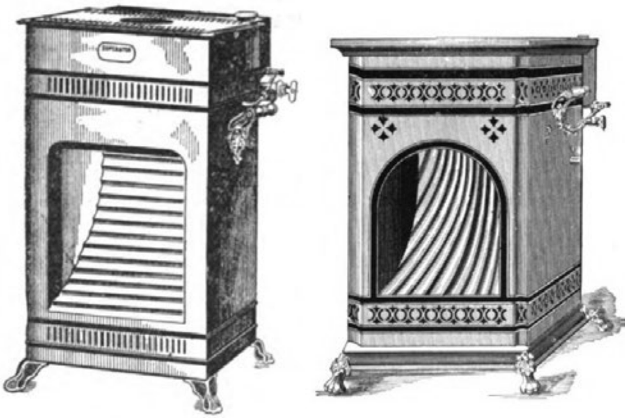

Figure 9. Alcohol-fueled space heating stoves, circa 1900.[67,68]

made it necessary to raise money by every means possible. As early as 1864, however, the US government wanted to relieve the tax burden on the industrial uses of alcohol, while retaining taxes on alcohol beverages, but a path towards this goal was unclear.[69,70]

The US was not the only country struggling with the fact that the high taxes typically placed on consumable alcohol was limiting its possible uses as a fuel.[60] As a potential solution, efforts began to produce a form of alcohol that could still be used for industrial uses, but would no longer be desirable to consume. This process of rendering alcohol unsuitable for drinking was referred to as "denaturing," and essentially consisted of adding a soluble substance to the alcohol that generated a bad taste or odor of such intensity that it would render it impossible or impracticable to use the modified alcohol as a drink.[62] Furthermore, the substance added should be something that was quite difficult to remove from the modified alcohol by distillation. This modified alcohol was then commonly known as *denatured alcohol* or *industrial alcohol*.[62,69,70] Proposed denaturing agents included camphor, turpentine, acetic acid, methanol, pyridine, acetone, methylene blue, aniline blue, naphthalene, castor oil, and benzene, among others.[62]

Great Britain was the first country to put the denaturing of alcohol into practice, with the duty-free use of denatured alcohol first authorized in 1855.[53,69,70] The denaturing was accomplished via a mixture containing 10% commercial wood alcohol (a mixture of methanol and wood naphtha) and 90% ethanol, the combination of which was then referred to as *methylated spirit*. The acetone and other constituents of the wood naphtha were so difficult to remove that methylated spirit was considered permanently unfit for consumption and thus not subject to duty.[69]

France then followed suit, with the permitted use of denatured alcohol under benefit of reduced taxes in 1872.[69] This was then revised in 1881 to make it impossible to use any methanol except that which possesses the characteristic odor to render any alcohol to which it has been added completely unfit for consumption. As with Great Britain, the French utilized commercial wood alcohol for the denaturing, although added benzene and either solid malachite or aniline green dye.[67,69] This latter additive then gave the denatured alcohol a pale-green color to easily distinguish it from consumable alcohol.[69]

In Germany, the use of tax-free alcohol was first permitted in 1879, using alcohol denatured with the addition of wood alcohol.[69] This was then modified in 1887[69-71] through the addition of pyridine bases in order to permit greater general use. These pyridine bases are exceedingly repugnant in both taste and smell and were obtained as byproducts from the destructive distillation of coal.[69] The German yearly consumption of denatured alcohol in 1904 was 26 million gallons.[71]

Figure 10. Solid alcohol cubes.[67]

Other countries soon followed suit, including Austria-Hungary (1888), Italy (1889), Sweden (1890), Norway (1891), Switzerland (1893), and Belgium (1896). A law permitting the tax-free, domestic use of denatured alcohol for general purposes in the US was finally approved on June 7, 1906[53,62,65,70] and enacted January 1, 1907.[69] In the US, denatured alcohol was required to consist of 100 parts ethanol (90% or greater), 10 parts methanol, and ½ part benzene.[62,67] In the first year following the introduction of its tax-free use, 1.5 million gallons of denatured alcohol were used in the US.[53] By 1918, this had grown to over 90 million gallons of denatured alcohol.[60]

SOLID ALCOHOL

In the beginning of the 20th century, another innovation was introduced in Europe, which was called *Smaragdin*.[67] This was a solid gel that came in small cubes about one-third inch in size. The cubes were made via the addition of a little ether to ethanol, after which a small amount of gun cotton was dissolved into the liquid mixture. This mixture would then set into a jelly-like solid, which would keep for a year or more in a closed vessel, with little loss due to evaporation. Fuel in this form could then be easily carried in small amounts and used as ordinary alcohol, leaving little residue. Furthermore, it could be used for heating where no alcohol burner was available, as it could be burnt in any non-combustible receptacle.[67] As of the 1920s, large quantities of industrial alcohol were used in the US in order to the make such solidified alcohol as a fuel for chafing dishes and small portable stoves.[60]

ALCOHOL IN INTERNAL COMBUSTION ENGINES

The use of alcohol as a fuel in internal combustion engines dates to their early development. In 1826, Samuel Morey (1762-1843) published and patented in the US an internal combustion engine prototype that utilized vapor from a liquid fuel.[72] Although this work originated with the application of a fuel consisting of a mixture of water and spirt of turpentine, he reported that both alcohol-turpentine mixtures and pure alcohol were also successful.[70,72]

In 1876, German engineer Nikolaus August Otto (1832-1891) then perfected his four-stroke engine with compressed loading, that became known as the Otto cycle engine. Such Otto engines were suitable for a range of fuels, including gasoline, kerosene, and alcohol.[73] In 1902, Deutz Gas-engine Works (Deutz AG), the company originally founded by Otto and Eugen Langen in 1864, began producing alcohol-fueled motors for portable uses in Germany. These were then used extensively in tractors, harvesters, and railway engines.[73]

In 1907, the Hart-Parr Company in the US then began adapting their gasoline traction engine for use with alcohol to be used as plowing-engines for agriculture[65,70,73]. At the time, it was viewed that the use of alcohol motors on the farm would become quite common as soon as such adaptations were completed. This included applications such as wagons, carriages, stationary Motors, water pumps. mowing machines, and plows.[68]

By the 1890s, horseless carriages (automobiles) could be found in both Europe and the US. In 1896, Henry Ford (1863-1947) completed his first automobile, which he called the *Quadricycle*, powered by an ethanol-powered, two-cylinder engine (Fig. 11).[74] When Ford later released the Model T in 1908, it ran on gasoline, but it was equipped with an adjustable carburetor that could be adapted to run on pure alcohol.[65,70,74,75] A competing manufacturer, the Olds Gas Power Company, soon followed suit to offer carburetor components that would allow their automobiles to run on either alcohol or gasoline.[70] Alcohol was then used to as an automotive fuel into the 1920s as efforts were made to build and sustain a US ethanol program.[65,75,76] As reported by Scientific American in 1921:[60]


Figure 11. Henry Ford (1863-1947) on his ethanol-powered Quadricycle (Wikimedia Commons).

> *The prospect is, indeed, that within the span of a very few years, alcohol or fuels with an alcohol base will largely or entirely replace gasoline as a fuel for motor cars.*

However, the US prohibition era then made it illegal to sell, manufacture, and transport alcohol, which made its use as automotive fuel nearly impossible.[65,74] Ethanol could still be sold when mixed with gasoline, but by the end of World War I, gasoline has become the most popular fuel in the US, as well as many other parts of the world.[74]

FROM GASOHOL TO E85

Although the use of pure alcohol never really found long-term success as an automotive fuel, decreases in the supply of gasoline, increasing fuel demand, and higher fuel prices all led to interest in replacing at least some of the gasoline in liquid fuel. The primary substitute in such efforts was alcohol, which had the benefits of lower cost and more efficient combustion, thus resulting in little formation of troublesome carbon deposits.[53] In the 1930s, such gasoline-alcohol blends became popular in the US Midwest, which grew the corn from which most US ethanol fuel was produced.[74] By 1938, a plant in Atchison, Kansas, was producing 18 million gallons of ethanol a year, supplying more than 2,000 service stations in the Midwest that sold alcohol blends (6-12% ethanol). [74,75]

During World War II, Brazil enacted a wartime law that automotive fuel must be comprised of at least 50% ethanol.[74] By the end of World War II, however, fuels from petroleum and natural gas became available in large quantities at low cost, thus eliminating any economic incentives for alcohol fuels from crops. Governments quickly lost interest in the production of alcohol fuels, resulting in the dismantling of many of the wartime distilleries.[75] A few countries such as Brazil, however, still continued the production and development of ethanol fuels.[74]

Interest in ethanol was renewed in the 1970s, when oil embargoes initiated in the Middle East resulted in limited supply and increased prices for petroleum products.[74,75,77] At the same time, the US began to phase out lead (an octane booster) from gasoline.[75] In 1976, Brazil then made it mandatory that gasoline contain ethanol.[74] In the US, the Energy Tax Act of 1978 introduced Federal tax exemption for gasoline containing 10% alcohol in an effort to decrease the nation's vulnerability to oil shortages.[74,75,78] This subsidy brought the cost of ethanol down to near the wholesale price of gasoline, making alcohol blends economically viable.[75] Amoco then began to market fuels containing ethanol as both an octane booster and gasoline volume extender in 1979.[75] Other major oil companies, including Texaco, Beacon, Ashland, and Chevron, all soon followed suit.[74,75] The resulting 10% alcohol blends were marketed as *gasohol* (now known as E10)[74,75,78] and were available at 1200 fuel stations across the Midwest by the end of 1979.[78]

By 1980, 25 states in the US had made ethanol at least partially exempt from gasoline excise taxes in order to promote consumption.[75] At the same time, the US government introduced guaranteed loans for prospective ethanol producers to cover up to 90% of construction costs and then placed a tariff on imported ethanol in an effort to ensure that only local sources of alcohol were cost-effective.[74] Federal and State tax incentives then made ethanol economically attractive in the Midwest, resulted in the production of 175 million gallons in 1980. The high cost and difficulty of transporting ethanol still limited consumption in other markets, however.[75]

Ethanol received a boost from the US Congress in 1990 with the passage of the Clean Air Act Amendments, which mandated the use of oxygenated fuels (minimum of 2.7% oxygen by volume) in specific regions of the US during the winter months to reduce carbon monoxide.[75] This was commonly achieved by blending gasoline with either methyl *tert*-butyl ether (MTBE) or ethanol. However, the higher oxygen content of ethanol made it attractive, even when more expensive than MTBE. The higher volatility of ethanol did limit its use in hot weather, where evaporative emissions could contribute to ozone formation, but its expanded role as a clean-air additive allowed alcohol-blended fuels to penetrate markets outside the Midwest.[75]

This was then followed with the Energy Policy Act in 1992, which made it mandatory for certain car fleets to start buying vehicles capable of running on alternative fuels such as E85 (ca. 85% ethanol:15% gasoline). Tax deductions are also given to promote the sale of such vehicles. However, the availability of E85 at this time was still low and generally limited to the Midwest.[74] Between 1997 and 2002, 3 million cars and light trucks capable of running on E85 are produced. Such vehicles, collectively known as *flex-fuel* vehicles, can run on gasoline or alcohol blends up to, and including, E85. Such vehicles strengthened the demand for alcohol fuels in Brazil[74] and by 2005, over 4 million flex-fuel vehicles are on the road in the US. By this time E85 was now available at ca. 400 fuel stations, primarily in the Midwest. After the EU adopted its first biofuels policy in 2003, ethanol blends have seen a steady increase, primarily as either E5 or E10 (5 and 10% ethanol, respectively), with E85 limited primarily to Sweden, France, Germany.[79] By 2012, the number of flex-fuel vehicles in the US had risen to over 6 million,[74] with more than 4600 stations offering E85 by 2019.[80]

CONCLUSION

The application of ethanol as a fuel for a variety of applications consists of a long history that dates back more than 200 years. Of course, this is brief in comparison to the much longer history of ethanol as a solvent, disinfectant, medicine, and most importantly, intoxicating beverage. In fact, it is not unrealistic to say that it was due to the highly valued nature of these earlier applications that ethanol's promise as a fuel was delayed by hundreds of years. Although ethanol has a number of significant benefits as a fuel, its use has been limited throughout its history by such factors as insufficient supply, the availability of less expense alternatives, excessive taxation, and, to some extent, its stigma as an intoxicant. Still, ethanol provides a promising alternative to petroleum fuels and its adaption as a standard, contemporary fuel seems to be on the rise.

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Biodiesel: History of Plant Based Oil Usage and Modern Innovations

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Abstract. The history of biodiesel dates back to mid-19th century when transesterification of vegetable oils was discovered. It took another half century for the world to realize its potential as fuel. Through the 20th century, two World wars and other regional turmoil increased the quest for energy security among nations. This chapter presents the history of biodiesels from the perspective of its development from vegetable oils, and animal fats. Usage of biodiesel and straight vegetable oil before World war, and how the energy crises sparked the intense development of these fuels around the globe towards the end of 20th century.

Keywords. Biodiesel, Biofuels, Vegetable oils, Transesterification, Energy policy, Food or Fuel.

INTRODUCTION

Modern society relies heavily on fossil fuel-based engines to achieve various tasks and work.[1] The rate of consumption of fossil fuels over the last two centuries has increased dramatically. A valuable alternative to diesel and related fossil fuels is Biodiesel: a liquid fuel derived from fats and oils of plants, animals, and other sources. Biodiesel can be produced from pure vegetable oil, algal cultures, oils from animal fats, tallow, grease, and waste cooking oil.[2]

The term vegetable oil covers a number of oil sources, such as nuts, seeds, vegetables and other plants.

This chapter will discuss the history of biodiesel, from conception and development to industrial scale production. Also detailed here is the historical use of plant oils and their adaptation to biodiesel. Over the past century, the global political climate, war, socio-economic conditions, government policies and various other factors have shaped the development and use of biodiesel. Generally, diesel is a C8 to C25 hydrocarbon mixture produced from the distillation of crude oil. Chemically, the term Biodiesel signifies mono-alkyl esters of fatty acids from oils and fats.[3] Although utilized since the late nineteenth century, the term Biodiesel wasn't used in the mainstream until the 1980s. In 1984, the word "Bio-Diesel" appeared in Power Farming magazine out of Sydney, Australia. The term has become more common in the literature subsequently. With the exception of a few nontechnical reports, most articles use the term “biodiesel” without the hyphenation.

The definition of biodiesel in the present day is often confusing. With US regulations differentiating biodiesel and Biomass Based Biodiesel, the EU regulatory requirements are based on meeting the standards outlined in the definition of biodiesel. Biodiesel’s fuel quality is measured by ASTM (USA) and designated as D6751 and in Europe (EU is EN 14214).[2] The qualities that define a biodiesel are completion of the transesterification reaction, complete removal of the catalyst, removal of glycerin, sulfur content, trace amounts of alcohol, and any free fatty acids present.[4]

The U.S. Department of Energy defines “biodiesel” as “renewable, biodegradable fuel manufactured from vegetable oils, animal fats of recycled restaurant grease. It is a liquid fuel often referred to as B100 or neat biodiesel in its pure form”.[5]

The process of obtaining fuel from fat is an ancient one. Several civilizations have used Straight Vegetable Oil (SVO) and oils derived from animal fat and other sources for fuels.[6] In the seventeenth and eighteenth century, whale oil was used as a major fuel source throughout Europe and the US. In 1853, E. Duffy and J. Patrick reported transesterification of oils.[7]

Transesterification is a process of using triglycerides in the presence of a base or acid to chemically break the molecule and produce methyl or ethyl esters of the fatty acids.[8] This was not utilized for production of biodiesel until 1937 however, when a Belgium engineer patented the use of this process for producing fuels. Several countries explored the opportunity to use vegetable oils as fuels for diesel engines, as it gave some self-sufficiency to countries that had access to oil producing crops and other feedstock materials.[9]

Modern day demands for alternative energy and fuel sources is high. SVO usage in biofuels has increased over the 20th century globally, with major producers such as the European Union, South East Asia and the Americas.[10] Biodiesel can be produced from a variety of feedstocks, including edible and non-edible oils. Different countries utilize different plant based oils, but more than 95% of the world’s biodiesel comes from edible oils. The popularity of some non-edible oils as feedstock is growing however, with easy to grow plants like Jatropha[11]. Multiple studies have been conducted on the use of biodiesel versus SVO outlining the cost-benefit to the consumer and the type of engine.[10–12] The use and production of SVO and biodiesels from edible oils has been shown to improve not only emissions and renewability, but can help local economies that are producing these fuels.[12]

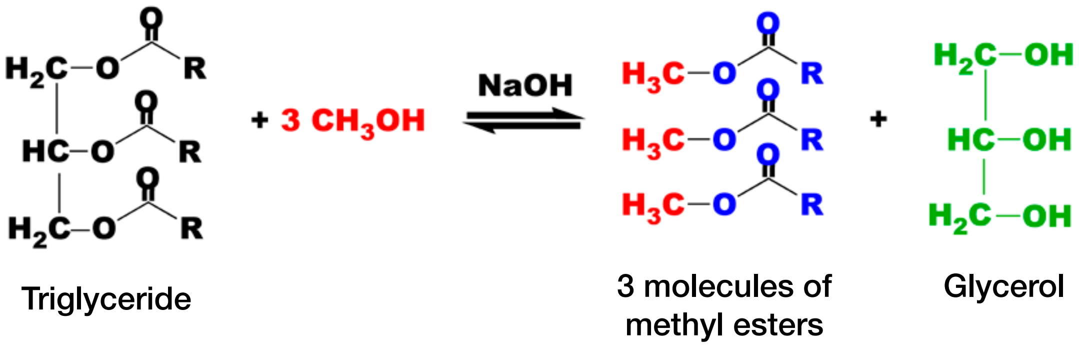
The use of biofuels and the evolution of biodiesel can be separated into four time periods:

1) Use of Straight Vegetable Oils (SVO) as a lamp fuel from times before antiquity to the mid-19th century; 2) The use of SVOs in internal combustion engines and esterification of SVOs to produce biodiesel during the 1930s and 40s 3) as replacement for petroleum during oil shortages in the 1970s; and 4) Present day need for alternative fuels including global energy needs, and sustainable agriculture and environmental impacts.

CHEMISTRY OF BIODIESEL TRANSESTERIFICATION OF OILS

In 1853, Irish chemists Patrick and Duffy reported transesterification of oils (**Scheme 1**).

Transesterification is an important reaction in industry, not only for biodiesel, but is crucial for the production of numerous household products, soaps and detergents. All biodiesel around the globe is produced through this process.[3,13,14] Triglycerides are molecules with a glycerol molecule head group and three fatty



Scheme 1. Transesterification of triglycerides with methanol.

acids attached to the three hydroxyl groups. In general, characteristics of the fat are determined by the chemical nature of the fatty acids attached to the glycerol. Vegetable and nut oils contain mostly triacyl glycerols or triglycerides, which is why they are often the precursors for biodiesels.[15]

When triacyl glycerols (triglyceride) are combined with a base and an alcohol (eg. methanol), they produce methyl esters of fatty acids and the byproduct glycerol. This class of reaction is known as transesterification.[8]

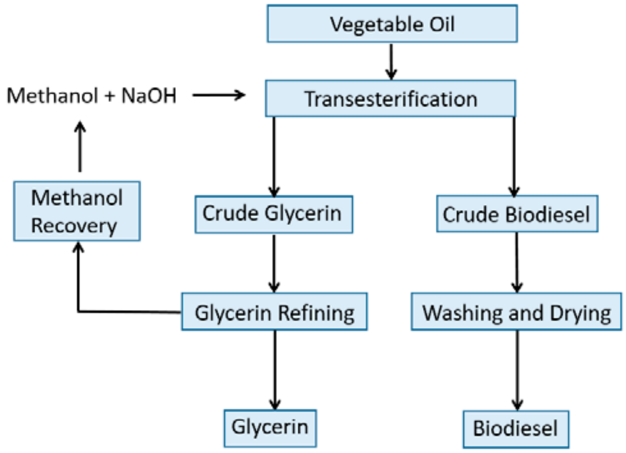
The previous scheme shows the chemical process for fatty acid methyl esters- biodiesel production. The reaction between the triglyceride and the alcohol is a reversible reaction, so the alcohol must be added in excess to ensure complete conversation of the reactants.[16] It was not until 1937, when Georges Chavanne patented the production of fuel through this process, that the utility of bio-diesel was realized.[2]

PRODUCTION AND PROPERTIES OF BIODIESEL

Biodiesel is produced from moisture-free vegetable oil. The oil is pre-heated to 60°C and sodium methoxide in methanol is added in a closed reactor. The reaction usually takes about two hours for completion.

The alcohol reacts with the fatty acids to form the mono-alkyl ester, the glycerol by-product of the reaction deposits on the bottom of the reactor due to its density and is removed. Industrial scale production of biodiesel is described in **Scheme 2**.

In most production, methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalyzed by either potassium or sodium hydroxide. Potassium hydroxide is more suitable for the ethyl ester biodiesel production, but either base can be used for methyl ester production.[14,16–18]



Scheme 2. Schematic representation of Biodiesel production process from vegetable oil.

Various research has been performed over the years on enhancing the chemical stability of biodiesel. As they are derived from fatty acids, the oxidative stability has always been of concern.[19] This has been addressed mainly by modifying the fatty acid composition of the feedstock oil. Usually polyunsaturated fatty acids are avoided in the production of biodiesel. Literature reports suggest that carbon chain-lengths up to C16 and C18 show good oxidative stability. In permitted situations, the biodiesel produced will be fractionally distilled to separate saturated and unsaturated fractions.[20,21] Other than a transesterification reaction, the alternate two ways to produce biodiesel include: hydro processing or deoxygenation and microemulsion or co-solvent blending. The biodiesel production facility at Amsterdam (**Figure 1**) in Netherlands, producing 150,000 tons of biodiesel annually along with 50,000 tons of pharma grade glycerin.[22]

Biodiesel is bio-renewable in all aspects: the feedstock, the product and the byproducts are all renewable. For this reason, it is often termed as carbon neutral. Properties of biodiesel such as biodegradability and its high flash points makes it safer in the event of crash or spills. The present technology enables the production of biodiesel from any plant or animal derived oil. However as discussed above, some oils produce benefits upon conversion to biodiesel compared to others.[8,23] Around the globe various vegetable oils and other fat sources have been used as feedstock materials for years. Ultimately there was a need for suitable starting material that provides a high-quality lipid for transesterification and subsequent biodiesel product. The source material is composed of triglycerides, which contain three long

Figure 1. Biodiesel Production facility at Port Amsterdam.

Table 1. Fatty acid composition of common oils and fats.

Fat or Oil	12:0	14:0	16:0	18:0	18:1	18:2	18:3	20:0	20:1	22:1
Soybean		.	8	5	25	55	11			
Corn		2	10	4	19-49	34-62	.			
Peanut		.	9	2-3	50-65	20-30	.			
Olive		.	10	2-3	73-84	10-12	.			
Cottonseed		0-2	23	1-2	23-35	40-50	.			
Butter		7-10	25	10-13	28-31	1-2.5	.2-.5			
Lard		1-2	30	12-18	40-50	7-13	0-1			
Tallow		3-6	26	20-25	37-43	2-3	.			
Linseed Oil		.	6	2-4	25-40	35-40	25-60			
Pongamina Pinnata		2	6	8	45-71	11-18		4	11	5
Coconut Oil	45-53	17-21	10	2-4	5-10	1-3	.			
Palm oil	.	.	44	5	39	10	.			
Palm kernel oil	48	16	8	.	15	3	.			

strings of fatty acids attached to a glycerin molecule. The fatty acids can differ in their length and degree of unsaturation. The overall fatty acid content differs in each oil source material.[15] **Table 1** shows the percentage composition of fatty acids in common oils used for biodiesel production.

The nomenclature of fatty acid is as follows, the number on the left represents the number of carbon atoms and the number after the colon represents the number of double bonds in the fatty acids. Based on the number of carbon atoms and number of double bonds, each fatty acid has different freezing point, ability to polymerize and overall energy content.[24] The fatty acid composition can also affect important physical properties of biodiesel such as viscosity (fluidity), ignition point and caking at low temperatures. Degree of unsaturation also effects the performance of biodiesel produced from vegetable oils.[22,25,26] The overall saturation levels of many biodiesel oils are given in **Table 2**.

Oils with maximum amounts of saturated fat content yield biodiesel that has a lower gel point. Biodiesels derived from oils with more unsaturation oxidize sooner than oils with less unsaturation. For example, biodiesel derived from walnut oil, poppy oil and linseed oil degrades relatively quickly.[25] Currently, biodiesels derived from cooking oils perform well comparatively to other source materials. Most of these oils contain one or two double bonds per fatty acid. This gives optimum shelf life for the biodiesel as well as desired properties.[15,26] Based on the performance, canola oil is reported to perform well when converted to biodiesel. Historically this has increased the cost of canola oil in the US market. Olive oil has also been an option for producing biodiesel. The advantage of canola oil is it is genetically modifiable to produce increased amount of polyunsaturated rather than saturated content. Hydrogenated vegetable oils have not been significant in biodiesel production as they yield a fuel with undesired qualities. Used cooking oils, especially the ones with high free fatty acids are attractive for biodiesel production.[13,22,23,27,28]

Waste Vegetable Oil (WVO), which is high in free fatty acids cannot be converted into biodiesel in the most preferred method of production: the base catalyzed. The use of base results in conversion of the free fatty acids to soaps. The acid catalyzed esterification process is better suited to WVO. The soaps formed as impurities from oils with high free fatty acid content during biodiesel conversion, can lead to accumulation of water due to the hygroscopic nature. This results in biodiesel with more water content than normal and an undesirable product.[16,29] The viscosities of SVOs are an order of magnitude higher than that of the biodiesels derived from them. The derivatives of SVO, methyl and ethyl esters also have different viscosities. Various biodiesel producing countries resort to methanol as the alcohol partner in transesterification, due to the low cost of methanol.[30] The viscosity of biodiesel is similar to petroleum diesel, in cases where biodiesel is mixed with petroleum diesel the lubricity of the fuel is increased.[8,26] Biodiesel and petroleum-based fuels are highly miscible and are available and utilized around the world in many markets. Biodiesel can be used as such in present day modified diesel engine vehicles (B100). Blends of 20% biodiesel with 80% petroleum diesel (B20) are used in unmodified diesel engines. Some drawbacks occur with the use of biodiesel, it will degrade natural rubber parts in vehicles manufactured

Table 2. Fatty acid nature (saturation) level in common oils and fats.

Oil	Saturated	Monounsat.	Polyunsat.
Butter	63%	26%	4%
Canola oil	7%	62%	31%
Coconut oil	90%	6%	2%
Camelina Oil	10%	33%	54%
Chufa oil	20%	67%	12%
Corn Oil	13%	24%	59%
Olive oil	14%	73%	11%
Soybean oil	16%	23%	58%
Peanut oil	17%	46%	32%
Cottonseed Oil	26%	18%	52%
Chicken Fat	30%	45%	21%
Lard	39%	45%	11%
Palm Oil	49%	37%	9%
Palm Kernal Oil	81%	11%	2%
Sunflower oil	10%	20%	66%
Safflower Oil	7%	14%	79%

* Note- The values are averaged. Actual values may vary based on the region of growth, genetic modification made, and method of extraction.

before 1992 and emissions of nitrogen oxide and ozone precursors are higher than in petroleum diesel. However, there are many benefits, the use of biodiesel has been found to breakdown the residues and deposits in fuel lines. Biodiesel burns cleanly with 80% less CO_2 emissions and 100% less sulfur dioxide than regular diesel. The octane number, measure of fuel's ignition quality for biodiesel is 100, for petroleum diesel it is 40. The energy content of biodiesel (average) is 35MJ per liter, close to petroleum diesel at 38.3MJ per liter.[31]

The US Federal Trade commission distinguishes biodiesel based on the starting material. Although it is not in the scope of the current report to discuss in detail regarding the differences and similarities between biodiesel and Biomass-Based Diesel (BBD). It is important to distinguish between the two.[32] The Federal Trade Commission defines BBD as "a diesel fuel substitute produced from non-petroleum renewable resources that meets the registration requirements for fuels and fuel additive established by the environmental protection agency under 42 U.S.C. 7545, and includes fuel derived from animal wastes, including poultry fats and poultry wastes and other wastes materials, or from municipal solid waste and sludge's and oils derived from wastewater and treatment of wastewater, except that the term does not include biodiesel". Whereas Biodiesel is simply defined as "the mono alkyl esters of long chain fatty acids derived from plant or animal matter that meet the ASTM standard D6751 requirement and registration requirements for fuel and fuel additive". [31–33]

Scheme 1 and **2** clearly shows that during the production of biodiesel, glycerol is produced as a byproduct. With the global increase in production of biodiesel, there has been an increase in crude glycerol production. For every 9 kilograms of biodiesel, about 1 kilogram of glycerol is produced as by-product. Although glycerol is a valuable material to produce industrial chemicals, intermediates, cosmetics and polymers, purifying this amount of crude glycerol poses a challenging problem from a sustainability standpoint. The average consumption of glycerol in the US in the past decade was 200 million kg. The amount of glycerol entering the US market was 20 billion kg in 2010. Since the early 2000s, methods for converting glycerol into other useful products have been explored. One approach is to convert glycerol to ethanol, CO_2 and hydrogen using *E.Coli*. In work from 2005, Dharmadi et al. reported the use of *E.Coli* to consume glycerol resulted in 75% theoretical yield ethanol. One drawback to this process is that it produced more than 50% carbon dioxide.

HISTORICAL USE OF VEGETABLE OILS

Plant and seed oils have documented use as far back as 1500 BCE. Oils and fats were not only historically used for light and heat fuel, but Ancient Egyptians used perfumed oils for beauty routines, religious ceremonies and medicine as well. Additionally, these oils have long been part of the food supply. Recent archeological work has shown that as early as 6000 BCE olive oil was being extracted for a food source in Galilee, Israel.[34,35]

Cultivation of olive trees dates to 3500 BCE in the eastern Mediterranean. Ancient Greeks utilized olive oil for food, religious ceremonies, fuel for oil lamps, and medicinal treatments. It was one of the regions chief exports and continues to be a commodity in modern Italy and Greece. Other ancient civilizations also utilized plant and natural oils in similar ways.[36]

The use of castor oil was extensive in ancient Egypt and is documented in the Ebers papyrus. The historic text outlines the use of multiple parts of the plant and extracted oil for headache, respiration, digestion, skin treatments, and hair growth. The oil was also used for fuel and ceremonies. Almond oil mixtures for skin and anti-aging treatments are also described in the Smith papyrus.[37,38]

Early Greece was also a consumer of plant oils, Herodotus recorded the use of castor oil for lamp light, and as a hair and skin treatment. The Greek expanded on the Egyptian knowledge of medicine that influenced care until the middle ages. The Greek physician Hippocrates recommended the use of olive oil for sports injuries and to warm the body[39]. As international exploration continued the varied uses of these oils spread to China and India. These societies also utilized plant oils for fuel, beauty, medicine and religious ceremonies.[38]

Linseed, or flax oil was used for waterproof clothing, luggage, carriages and shelter fabric in the 18th century, as documented by Louis Franquet, a French explorer. "They (Canadians) name prelart a large and heavy cloth, oil-painted in red, [...] to keep oneself from the rain" Louis Franquet, 1752.[40] Canvas or linen was boiled with a combination of oil and paint in order to achieve the waterproofing.[41] Oilcloth remained popular through the late 1950s, until rubberized and plasticized fabrics became more available. In the 1870s, Procter and Gamble endeavored to make individually sized bars of soap to sell. In order to achieve this, they revolutionized the use of palm and coconut oil rather than animal fat for soap. Around this time, the US cotton industry was producing tons of oil as byproduct from the industrial process. Consumption of the cottonseed oil eventually led to production at such high rates, that this byproduct was later industrialized and converted to a food product that is now highly consumed in the US.[42,43]

During the late 19th and early 20th centuries, the use of natural medicinal oils fell out of favor due to growing advances in synthetic pharmaceutical chemistry.[44] In recent history, there has been a renewed interest in natural, plant and essential oils for their use as homeopathic remedies and Eastern-based medicine. For example, a recent study tested the efficacy of lemongrass, pine and clove oil compared to DEET. These oils were found to be up to 98% as effective as the common insecticide.[45] As with ancient times, modern use of these plant oils includes food, beauty and medicinal purposes. They are also still used for heat and lamp oil in developing countries and in generators during emergencies.

During the mid-nineteenth these plant oils were being utilized as fuel for combustion engines. Diesel, Otto and other inventors of the time designed engines that would run off pure oil, mixed petroleum and plant oils or other combinations of fuels.[14] Biodiesel is also an effective cleanup solvent for petroleum based oil spills, as shown in lab tests with simulated shorelines.[46] Modern day awareness for the environment have re-invigorated international policies encouraging the use of alternative fuels like plant-based biodiesel.

THE TRANSITION TO A FUEL: NINETEENTH CENTURY UTILIZATION OF THE INTERNAL COMBUSTION ENGINE AND CHOICE OF FUELS

Internal Combustion engines played a crucial role in shaping up the development and use of biodiesel. Prior to the invention of the diesel engine there were many attempts throughout the seventeenth century to develop an internal combustion engine.[47] Historian Lyle Cummins recorded the detailed history of these attempts in his book. In 1893, Rudolf Diesel, a German engineer (**Figure 2**) wrote an essay on theory and construction of a heat motor. Historical reports indicate the first biofuel powered vehicle is Diesel's oil powered 10 iron cylinder with a flywheel in the base. This ran on peanut oil for the first time in Augsburg, Germany on August 10th, 1893.[48] Diesel had a strong desire to develop alternatives to conventional fuel engines.[49] In 1912, a year before his death, he gave a speech in which he mentioned that, "the use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time."

In the following years he filed a patent for his design. At the time of Diesel's invention, steam engines were common, even with a relatively low efficiency at only about 10%. Diesel's invention came as a breakthrough during this era. In his internal-combustion engine design, the combustion of the fuel and the piston movement occurred through an isothermal reaction. Although revolutionary to the field, the initial models of Diesel's engine were bulky and could not be moved easily, so were not ideal for automobiles or trains.[47,48]

Throughout the time that Diesel was working on his engine, other engines with alternative fuel sources were being developed despite low gasoline prices. Alcohol fueled engines, coal gas, kerosene and gasoline engines were all advanced during this time. Kerosene was of particular interest, as the byproduct of gasoline fractionation, but multiple alternative sources were being utilized and explored at this time.[2,3,13,50] These other alternative combustion engines were capable of running on different fuels and fuel mixtures. Prior to Diesel's invention, in 1860, German engineer Nicholas August Otto developed an engine utilizing ethanol. Just like vegetable oil used for burning lamps in eighteenth and nineteenth century Europe, ethanol lamps or spirit lamps were also common. Hence, Otto conceptualized an engine burning ethanol as fuel. With funding from Eugen Langen, owner of a sugar refining company, they launched the Otto & Langen company which produced stationary piston engines in the 1870s. These engines were powered

Figure 2. Early portrait of Rudolf Diesel.

by coal gas. Later in the1880s, he came out with a four-stroke "Otto-cycle" engine that used gasoline.[47,50]

In 1900, at the Paris Exhibition, the French Otto Company had four diesel engines including one from Diesel's own son Eugen Diesel. Out of the five engines, one engine ran entirely on peanut oil; although not many of the visitors realized this according to Diesel.[51] He mentions that, "*the engine was built for petroleum (mineral oil) and was used for the plant oil without any change. In this case also the consumption experiments resulted in heat utilization identical to petroleum*". The French Government did take notice of the engine running on peanut oil. Diesel notes that the French had interests in testing the efficiency of Arachide (earthnut or in this case peanut oil). The availability of large quantities of ground nuts and other sources of vegetable oils in the French African colonies prompted the French government to encourage the cultivation of these food sources.[47,50] Thus, using these vegetable oils as possible fuel source in engines. From an engineer's perspective, this was made possible mainly because diesel engines developed around 1900s had complex injection system to accommodate various fuels. From kerosene, coal dust, oils and petroleum mixtures early diesel engines ran on various fuels.

The major implementation of Diesel's internal combustion engine (or diesel engine) did not start until almost two decades after Diesel's patent expired in 1908. Numerous varieties of diesel engines were introduced, to the extent that Diesel felt he was not accredited properly for his invention. Even though in histories of biodiesel, the first use of a bio-fueled engine is mistakenly attributed to Rudolf Diesel in 1900 at the World Expo in Paris. While it is true that there was an engine displayed at World's expo that ran completely on peanut oil, it was demonstrated by Nicolas Otto.[47,48]

Diesel engines quickly gained attention in early the 20th century due to their power, reliability and fuel economy. Numerous versions of Rudolf Diesel's engine were developed within a short span during this time. From Diesel's statements and speeches, it is evident that he envisioned the use of reliable SVOs to assist the fuel power of developing and underdeveloped nations such as African and Asian countries where petroleum-based fuels did not reach. Diesel had interest in creating an efficient engine.[47,52] From his book *Die Entstehung des Dieselmotors* (translation: The Emergence of the Diesel Engine) in his own words he mentions his motivation, "*the desire to realize the ideal Carnot process determined my existence*". Rudolf Diesel died in 1913, before his vision of developing efficient engines that could utilize SVOs was realized. During the decade following Diesel's death, the petroleum industry developed a by-product that was able to power the modified diesel engine, they termed it "diesel fuel". It was around this time that the industry shifted towards petroleum-based fuels and the focus on alternative fuels was lost. Diesel engine manufacturers of the 1920s altered engines to better suit low viscosity fuels rather than the viscous fuels such as SVO or biodiesel. August 10, the day Rudolf Diesel demonstrated his internal combustion engine using SVO is presently observed as International Biodiesel day.[31,47]

The fluidity of SVOs creates problems in present day diesel engines that are made to run on less viscous diesel. Preheated peanut oil, animal fat and other oils have been successfully used to power diesel engines, but this requires modifications to the engine.[53] When the shortage of petroleum-based fuels occurred in 1970's, the existing engines were only able to run specifically on diesel and issues occurred when other fuels were attempted. Petroleum industries have monopolized the automobile industry, as they have been able to produce fuels at much lower costs compared to biomass derived fuels. This has resulted in a century of added pollution and increased carbon emissions from the use of petroleum fuels. The research, infrastructure and technological advancements of biomass-based fuels such as biodiesel were suppressed for many decades due to the monopoly of petroleum-based fuels.[54]

WORLD WARS AND THE EFFECT ON DEVELOPMENT

During World War II, the demand for biofuels increased, as importing petroleum-based fuels was becoming difficult. Germany was experiencing a fuel shortage, which led to another phase in alternative fuel engine development. Mixing gasoline with alcohol derived from potatoes came into practice.[55] Following Germany, the UK implemented the use of mixing grain alcohol with gasoline. At the same time, Brazil prohibited the export of cottonseed oil so that it could be utilized as a substitute for diesel. In China, Tung oil and other SVOs were used to produce a fuel similar in performance to kerosene.[50]

American automobile entrepreneur Henry Ford also had great interests in alternative fuels. His interest and the fact that up to World War II, soybean crops in the US were mainly used for oil production, he developed the "soybean car" in 1941. During World War II, Ford built a single experimental soybean car, but due to the war activities it never saw the production line. The Soybean car weighed 2,000 pounds; 1,000 pounds lighter than other cars in production in 1941. After World War II, the development of the soybean car did not resume.[56]

After World War I and II, America, France and the UK had the advantage of access to petroleum-based fuels, resulting in the common saying "they floated to victory on a wave of oil". Germany had become self-sufficient in ethanol-based fuels as early as 1910, as ethanol production was a major part of their economy.[57] In 1942, Germany reached a peak in synthetic fuel production at 1.7 billion liters from coal. In the same year, Germany produced 267 million liters of fuel grade ethanol from potatoes. In sum, Germany made 54% of their fuels from non-petroleum-based sources.[58]

The war in the western hemisphere created different pressures in India and China. Since much of the fuel was imported by the allied nations, it sparked an interest in substitutes for petroleum-based fuels in these areas. Vegetable oils were not readily available due to the large populations of these countries, which were dependent on the land. One crop that proved viable as an alternative fuel source however, was sugar cane. Molasses from sugar cane was used as raw material for alcohol production. In China, Benzonite, a mixture of 55% ethanol, 40% benzene and 5% kerosene was sold after World War I. Sugarcane plants demand huge volumes of water for growth, hence India and China slowly made their shift away from sugarcane bioethanol to alternative plant based biodiesel.[59] The plantations moved to cheaper and drought resistant crops such as Jatropha. There are also reports that indicate that the use of biodiesel produced from peanuts, tea leaves, tung, cotton seed and cabbage seed was implemented during this time.[53]

Despite all of international advancements in the biodiesel industry, when peace returned to much of the world, the oil prices from the middle east region dropped again reducing the demand for alternative fuel research.[13]

THE RISE AND FALL OF BIODIESEL INNOVATION, HOW THE GLOBAL MARKET SHAPED THE INDUSTRY FROM THE 1950S THROUGH 1970S

The 1950s was a prosperous time for the US, and petroleum-based fuel was readily available. In the 30 years following the end of World War II, consumption of oil on the global scale had grown six times[60]. At this time the US was a top producer of soybean oil and Europe produced large amounts of canola oil. Although demand for biodiesel was low, these crops determined the type of biodiesel that would be developed and used in these countries. In 1951, US researchers reported the efficient use of cotton seed oil as diesel fuel.[61]

In the 1970s, the unstable political situation of the Middle East shook the global availability of petroleum fuel. This lack of supply propelled countries to search for alternate fuel sources once again. In the US and Europe, a major consumer of petroleum fuel was agricultural machinery and heavy vehicles.[52,57] From the period of 1973 to 1979, a serious supply deficit occurred all around the globe due to the growing conflict in the Middle East. The OPEC (Oil Producing and Exporting Countries) nations reduced the supply of fuels to non-OPEC nations, which increased the motivation to develop biodiesel. A second energy crisis occurred in October 1978, when Iranian oil refineries were attacked, effectively shutting down five percent of the world's oil exports. The conflict lasted until January 1979, increasing the cost per barrel twice in a time span of six months.[32]

The oil crisis of the 1970s primarily impacted the United States. On October 6th, 1973, Egypt, Saudi Arabia and other Arabian countries attacked Israel in an attempt to regain lost land from the 1967 war. US aids were flown to Israel on October 17th, but on the same day Arab oil ministers met in Kuwait and signed an agreement for an oil embargo against the United States and its allies. The agreement pledged to reduce oil production by five percent every month, which had immediate effects on the US oil market. The price of crude oil went up by four times. After these conflicts were resolved, the supply of petroleum-based fuels was restored. Diesel production and the improvement of supply chain infrastructure increased the accessibility of petroleum fuels. With these shifts in petroleum fuel availability, the concept of biodiesel research, development and production was not actively pursued and fell by the wayside once again.[51]

The twenty first century has seen a bigger push for alternatives to petroleum based fuels as growing concerns over climate change, carbon emissions and sustainability push politics towards subsidies and incentives for the biofuel industry.[62] Biodiesel initiatives around the globe have been implemented in which blends of diesel and biodiesel are sanctioned.[63] However, using SVO as a diesel engine fuel hasn't experienced the same uptick. Multiple studies have reviewed the usage of SVO in diesel and combustion engines with overall mixed conclusions about engine performance.[12,64] While the future of biodiesel and SVO as alternative fuel sources is promising, there are still many challenges to overcome.

BIODIESEL PRODUCTION GLOBALLY, INTERNATIONAL ENERGY POLICY AND REGULATIONS: SHAPING THE HISTORY OF BIODIESEL

US

In the United States, biodiesel programs rapidly developed and commercialized after 1980. It was difficult for the advancement of biodiesel to gain traction, as US oil industries propagated myths about alternative fuels.[65] Some of which espoused that ethanol is an inferior fuel, which creates technical issues, and that blending biodiesel and gasoline creates inferior quality fuel that doesn't have the same power output as petroleum-diesel. In addition, the US automobile industry historically backed the oil industry claims. On the other hand, the farming industry which relied heavily on diesel for heavy equipment operations, supported biodiesel production. During the 1980s, the Brazilian Alcohol expansion program worked with the Nebraska Corn Products Utilization committee to initiate road tests with corn ethanol to prove that the efficiency and power claims were completely true.[66]

Following the Second World War, the United States faced a shortage of petroleum-based fuels for a short time. This inspired the start of the "Dual Fuel" project, at Ohio State University (Columbus, OH).[67] Extensive exploration was carried out on cottonseed oil, corn oil and various blended oils as a substitute diesel fuel. Although the use of vegetable oils has resulted in satisfactory performance with engines, the power output consistently remained lower than conventional petrol engines.

After the oil crisis of the 1970s, in 1978 US President Jimmy Carter created a 25-million-dollar program called 'Aquatic Species Program' to investigate high-oil from algae, focusing on biodiesel production. In 1980, he signed another bill giving a $0.54 per gallon ethanol tax incentive. This legislation sealed the developmental path of the US biofuel and biodiesel programs. The US biodiesel industry slowed to a crawl in the 1990s, due to lower costs of petroleum-based fuels.[51,55] Despite this, in 1996 Pacific Biodiesel, the nation's first biodiesel plant was established on the island of Maui, Hawaii. It focused on recycling cooking oil into biodiesel. This plant, through its waste conversion to biodiesel, produced over 49,000 liters of biodiesel per day as of 2016 and was certified as a "Sustainable plant" that same year.[54]

Legislation in the US regarding biofuels started in the early 1990s in an effort to reduce market demands for foreign oil. The Energy Policy Act of 1992 was one of the pieces of legislature aimed at increasing research on biofuels and how federal programs should be constructed to increase biofuel implementation. It was the first time that requirements were put on the Department of Energy to increase biofuel utilization in their own vehicle fleets and to collect data on the efficiency, use and supply of biofuels and environmental effects of biofuels.[68]

Oil prices rose following the events of 9/11/2001, which again renewed interest in biodiesel production ventures. The Energy Policy Act of 2005 introduced a biodiesel tax credit which allowed blended fuel producers to claim a one-dollar credit per gallon. It also expanded research and development of alternative fuels to include expanded agricultural supplies of biofuel and additional bio-power energy systems.[69] This furthered the production and growth of the biodiesel industry. In the same year, Minnesota became the first state to make it mandatory for all diesel fuels sold in the state to have a minimum of 2% biodiesel.

Additional legislation in 2007, 2008 and 2009 to help liberate the US market from dependence on foreign oil and crashes in commodities were put in place via presidential order, and stimulus packages from congress. These laws helped protect troubled assets and gave tax credits to biodiesel and incentivize environmentally friendly energy practices.[70] These policies helped grow the biofuel industry in the US, providing innovation and furthered the reach and implementation of these alternatives.

The use of biodiesel in the continental United States has increased over the past decade. In 2017, the US produced 7.38 billion liters of biodiesel and imported 1.1 billion liters.[71] Biodiesel has been increasingly used as the fuel of choice for university and college campus transportations across the US. Biodiesel is biodegradable, nontoxic, and has significantly fewer emissions than petroleum-based diesel when burned. This makes it the fuel of choice in delicate eco-systems. In 1995, Yellowstone National Park launched the "Truck-in-the Park" project in collaboration with the University of Idaho and several other partners. The project featured a pickup truck with a direct injected diesel engine that ran on canola ethyl ester. When an engine check was performed at 92,000 miles, the impact of emissions was far less than that of a regular diesel engine. Over the next decade, the National Park system started using solely biodiesel blends and by 2006 had completely converted to these blended fuels. As of 2016, a total of 163,000 liters of blended biodiesel had been consumed by trucks, graders, front-end loaders and other heavy vehicles utilized in the parks. This has reduced the carbon and sulfur dioxide emissions and particulate matter released into the air. Other pilot programs were introduced which utilized biodiesel for public transportation infrastructure, such as community buses and heavy equipment. The US made a pledge of achieving production of 120 metric tons of biofuels by 2022.[72]

Europe

Much of the present-day European biodiesel industry was developed in the 1980s. The fuel crisis that hit the US hard in the 1970s was also a detriment to supplies in Europe. In Europe and South Africa, pioneering work on biodiesel was conducted by researchers such as Martin Mittelbach who advanced the production processes and the storage stability of biodiesels.[73,74] This propelled the development of the biodiesel industry into the 1990s.

In 1990, France launched a program named "Diester" aimed at the production of biodiesel from rapeseed oil.[75] Specifically, the methyl ester derivative of rapeseed oil was sold as biodiesel in France, Austria, Germany, Sweden, Italy, Belgium, Hungary and the Czech Republic around 1988. Germany established specific criteria for rapeseed biodiesel to be sold using standards based on the density, viscosity, iodine value and residual catalyst.[57,65]

The European Union proposed a 90% tax reduction for biodiesel in 1997, leading to an increase in the production of biodiesel. The estimated amount produced was 660,000 tons per year in the following years. As of 2005, worldwide biodiesel production crossed 4.1 billion liters with the EU being the largest producer. The European legislation has had requirements in place since 2008 for the use and expansion of biofuel which has led to the production of over 10.6 billion liters of biodiesel as of 2017. Their work will continue into the 2020s, with directives to ban palm oil and increase energy efficiency in public transport and consumption.[76]

India, China and Southeast Asia

Shortly after World War II, India gained independence. In 1948, nine million liters of alcohol was produced for fuel and two million liters of alcohol blended fuel was used. Although there was a dire need for alternate fuels, the issue of "food vs fuel" prevented the use of grains for oil production. Hence, the expansion of biodiesel did not occur in these regions until after 1980. Since alcohol was also produced from sugar cane wastes, the Indian Alcohol Act of 1948 mandated the use of 20% alcohol blending in fuels.[77] This law was repealed in 2000, but an ethanol blending program was mandated in 2002. Unfortunately, it has been impossible to enforce this ethanol blended biofuel due to lack of supply and bureaucracy delays.[67]

In 1990, India established biodiesel production with a goal of reducing imported oil and improving energy security. Due to the vast amount of non-agricultural land available, the drought resistant Jatropha plant was chosen for biodiesel production. In 2003, the Indian government launched the National Biodiesel Mission in order to improve technology and extraction of biodiesel and to allocate land and the implementation of the industrialization of Jatropha to biofuel.[78] In 2011 and 2012, India's total biodiesel production was projected to grow to 3.6 million tons. Although economic development has made automobiles affordable for much of the population in India, it comes hand in hand with pollution, increased greenhouse gases and total carbon emissions.

In the Philippines the first use of biofuel dates to 1914, when alcohol was used as an engine fuel on Calamba Sugar Estate, an American-operated sugar plantation. On August 22nd 1922, The Philippine Motor Alcohol Corporation was founded, with a goal of experimenting with and producing alternative fuels. During World War II, ethanol production stumbled in the Philippines, but soon regained momentum and reached 30 million liters by 1950[79]. Again, the years to come provided cheap oil availability, and alternative fuel sources were abandoned. A Philippine representative spoke at the United Nations on this issue stating that *"the use of blended motor fuel was abandoned, for the simple reason that the gasoline interests fought hard to kill it. After such a very sad experience, we fully realize that proper legislation similar to that in India should be adopted in the Philippines"*.

Many Asian countries faced the dilemma of increasing availability of cheap Middle East petroleum-based fuels versus their alternative fuel programs. Due to this inexpensive, readily available petroleum fuel and lack of sustainability for the programs, biofuel initiatives were abandoned in these regions after the 1950s.

In 2006, the Philippines established a biofuel usage mandate that required 5% ethanol blended gasoline distribution. In 2007 legislation regarding biofuel use and consumption was enacted, the first of its kind in Southeast Asia.[80] Ethanol production in the region has continued to increase over the past ten years to current day. Nine percent ethanol blended fuel is the current standard in the country, with an aim of 20% ethanol by 2020, which isn't projected to succeed. Biodiesel production and consumption has stayed stagnant since 2009 at a 2.5% blend rate.

Brazil

Brazil made several efforts in 1931 to encourage the use of alternative fuels like ethanol, this trend continued and eventually lead to the nation's efforts in the field of biodiesel production. In 1933, Brazil established Instituto do Assucar e do Alcool for sugarcane ethanol production. During the global oil crisis in the 1970s, Brazil pushed the production of ethanol blended fuel as well as vehicles which required it. Legislation for the reduction in sales tax for the use of pure alcohol fuels and blended fuels was introduced. This set the stage for Brazil to be one of the global leaders in production and innovation in the biofuel and biodiesel industry. Brazil is the only country where the production of biofuel is profitable without tax incentives and subsidies.[81]

In 2005, based on the success of their ethanol biofuel, Brazil invested in biodiesel with legislation requiring replacement of two percent of the petroleum diesel and an increase over the next seven years to five percent. The feedstock material for biodiesel in Brazil is soy beans. Brazil also uses palm and castor beans as well. Unfortunately, the development of biodiesel production has come at the cost of the rain forests of Brazil. At the urging of the Brazilian government, drier regions of the country are encouraged to use other sources: like Jathropha in India.[65,67,82]

Biodiesel production in Brazil is projected to reach 4 billion liters. Unlike ethanol biofuel, Brazil's biodiesel production is not profitable for the country and like the rest of the international markets, requires subsidies and tax incentives. These government supports have helped maintain biodiesel production and demand, especially for local farmers and the region where the feedstock is produced.[83]

Other Biodiesel programs

In 1932, 30 industrial nations introduced tax incentives for an ethanol-petroleum fuel blending program. From these 30 nations only a few graduated to establishing sustainable methods for biodiesel production.[53]

Argentina was one of the pioneer nations to utilize biofuel from oils for diesel engines. The first diesel engine was imported to Argentina in 1916. The same year, R.J. Gutierrez of Buenos Aires University tested castor oil on the engine. Biofuel is produced in Argentina from soybeans, and despite a mandate in 2010 for five percent blended fuel, most of their biofuel is exported and isn't supported through tax reimbursements.[84]

Cuba and Panama have been able to produce 20% ethanol mixed gasoline since 1922. This is in part due to the fact that raw ethanol was cheaper than gasoline. Unfortunately, these nations efforts towards ethanol were not matched in their biodiesel efforts. Failure to subsidize biodiesel production, and political obstacles historically prevented these nations from cultivating biofuel production and consumption.[67]

Canada has gotten on board with the biofuel movement, the Canadian Renewable Fuels Association promotes the use of ethanol and biodiesel. In 2008, the production of ethanol for use as a biofuel was incentivized through the EcoEnergy for Biofuels Program. This tax reimbursement was decreased annually however, and there are few trade protections on biofuel as compared to the international market. This has resulted in the cost of blended biodiesel in Canada being 10 cents higher than the cost of petroleum diesel.[84]

BIODIESEL AN ETHICAL DILEMMA? FOOD V. FUEL AND THE ECOLOGICAL IMPACTS

In countries where fossil fuels are not available, biodiesel was found to be a practical and sustainable means to meet the fuel demands. Although numerous crops and plants have been added to the list of feedstocks for biodiesel production, it is important to realize that crops abundant in a specific region are likely needed for food supply rather than biodiesel demands.[85]

Currently, only a fraction of biodiesel comes from waste products. The majority of the biodiesel is produced from sources such as seed and other vegetable oil. This in combination with the production of other biofuels such as corn-ethanol has sparked a controversy of 'food vs fuel'. The diversion in the use of the crops from fuel purposes has added pressure to food prices. In 2007, this issue was raised at the UN Food and Agricultural Organization, with some reporters calling the use of food sources as fuel a "crime against humanity". [1] This 'feed, food and fuel' debate has raised serious question about the impact of biofuels such as biodiesel on climate change, sustainability and biodiversity.[86] Since the early 2000s, when this debate began, studies have shown differing results supporting opposing sides of the food or fuel argument: depending on how the studies are carried out and the statistical analysis methods utilized.

In addition to strains on the food supply, growing non-food biofuel feedstock can also have ecological and environmental implications. Clearing of forest lands to grow fuel in addition to rising food demands results in higher amounts of carbon dioxide being released into the atmosphere.[87] Presently, sugar cane is the largest cultivated crop along with soybean, palm and Jatropha for biofuel production. Palm oil is the infamous biodiesel crop held responsible for destroying large areas of tropical rain forests in the Amazon.[88] The growth of plants and trees for biodiesel production in South America has presented a large ecological concern. Although the growth of the biodiesel industry in countries such as Brazil will benefit the economy and lessen the dependence on fossil fuels, the land abuse has created environmental problems that reach beyond pollution caused by fossil fuel usage. Millennia-old rain forests continue to be destroyed since the push for biodiesel production in the 1980s. Palm oil is the most infamous source for biodiesel, as rain forest clear cutting in order to grow this crop has recently been publicized. For the same reason, rainforests in Indonesia and Malaysia are being destroyed and raising further concerns of sustainability.[89]

Despite the great risk to amazon forests, there is an argument that well planned palm oil use can replace pastureland and reduce the global threat on the extinction of rainforests. Compared to any biofuel, palm oil yields the highest amount of fuel per hectare. Brazil introduced a biofuels policy where 80% of the palm plantations land should count towards forest area. Following Brazil's example, smaller countries like Colombia and Ecuador are also growing the size of their palm plantations. These developing nations argue that palm plantations create more jobs compared to soy or cattle farming while sustaining biodiesel production.[90]

CONCLUSION:
WHAT DOES THE FUTURE HOLD FOR BIODIESEL?

Biodiesel's inception started with the discovery of transesterification of vegetable oils. German engineer Rudolf Diesel envisioned the efficient use of vegetable oils in his engines and was also well ahead of his time in his foresight into the challenges and potentials of renewable sources. In his 1912 book he talks about alternative power sources, *"In any case, they make it certain that motor-power can still be produced from the heat of the sun, which is always available for agricultural purposes, even when all our natural stores of solid and liquid fuels are exhausted"*.[51]

There is no recorded history of the use of mono alkyl esters of fatty acids from vegetable oils as fuels documented in the literature until George Chavanne's patent in 1937. Although not a major producer of the feedstock oil crops, countries like France, Belgium, and the UK showed great interests in biodiesel manufactured from vegetable and plant oil. This interest was primarily based on the availability of the raw materials from their colonies. As the global political environment changed, priorities and energy policies changed. Interest and investment into biofuel research and production ebbed and flowed depending on the global market until it gained real traction in the early 1970s when the industrial process for the production of biodiesel was developed. In 1977 Brazilian scientist Expedito Parente patented the production. It was over a decade later when the first commercial biodiesel plant started production in Austria in 1989.[47,48,50]

The success of the biofuel industry has always hinged on geography, political climate, economics of the feedstock material and regional regulations. Countries must navigate these obstacles in order to grow their alternative energy programs. The global petroleum fuel market has historically been the driving force behind nations' quest for energy security and the subsequent use of biodiesel and alternative fuels.

In order to drive the development and production of biofuels, petroleum-based fuels have historically needed to be scarce in the market, only recently have the challenges facing humanity been motivational for this industry. Challenges like species extinction, ecosystem collapse and resource sustainability have sparked debates on climate change, energy policy and food rights. Many of these debates are aimed at constructing an optimal and sustainable energy system. Biodiesel is a good candidate to lessen the world's reliance on fossil fuels and increase energy safety, with its clean emission profile. However, with minimal subsidies allocated to biodiesel and the long argued "food v. fuel" argument, the future of biodiesel will become increasingly unstable. Production of biodiesel will rely on an ideal situation where the world is able to produce renewable feedstocks such as plants and vegetables to meet the worlds food supply and keep the cost of biodiesel competitive to fossil fuels. Unlocking the potentials of renewable energy is not a choice but a need for the future generations to survive and sustain.

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Energy on demand: A brief history of the development of the battery

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Abstract. Portable, readily available electrical energy provided by batteries is ubiquitous in modern society and can easily be taken for granted. From the early Voltaic piles to modern lithium ion cells, batteries have been powering scientific and technological advancement for over two centuries. A survey of select notable developments leading to modern batteries commercially available today are presented, with emphasis on early technologies and also including some of the advancements made within the last few decades. A brief discussion of the chemistry utilized by battery technology is also included.

Keywords. Battery, electrochemical cell, Voltaic pile, Daniell cell.

INTRODUCTION

In the modern industrialized world, it can be difficult to imagine life without ready access to on-demand electricity. Massive electrical infrastructures have been built allowing for safe, reliable, and constant delivery of electrical energy to households, businesses, and industrial complexes throughout much of the globe. By 1950, electric power consumption in the United States was reported at 291 billion kilowatt hours.[1] By the mid 1990's usage topped 3,000 billion kilowatt hours, and demand has continued to increase with consumption of 3,946 billion kilowatt hours reported for 2018, the bulk of which is split between residential (37%) and commercial (35%) usage.[1]

While this infrastructure effectively provides fixed access to electrical energy within relatively easy reach in homes, workplaces, and other locations, batteries are used as a source of power for a myriad of devices. From cell phones to flashlights, wall clocks to children's toys, more and more electronic devices utilize battery power. Medical devices, whether implanted such as a pacemaker or external like an insulin pump, also require lightweight mobile power sources, as do fully electric automobiles on an even larger scale.

With a ready supply of electrical energy ubiquitous in industrialized society, it can be easy to take this valuable resource for granted without consideration for the process by which the development of the battery occurred, or the technological advancements that followed. A complete and exhaustive accounting of all these advances would be an undertaking beyond the scope of this work and may well be out-of-date prior to publication, as work currently continues to design and produce smaller, lighter, and longer lasting batteries for mobile electronics. As such, this work will focus on the earliest battery developments as well as the more significant general developments within the past several decades.

THE ELECTROCHEMICAL CELL

The term "battery" has several different meanings which may at first glance appear unrelated.[2] The common thread within these varied definitions is the reference to multiple parts working in concert, whether artillery pieces, a pitcher and a catcher in baseball, or a collection of electrochemical cells. Benjamin Franklin is attributed with one of the first uses of the term "Electrical Battery", included in a letter describing his work with static electricity using Leyden jars to English naturalist Peter Collinson in 1749:

> *Upon this We made what we call'd an Electric Battery, consisting of eleven Panes of large Sash Glass, arm'd with thin leaden Plates,...with Hooks of thick Leaden Wire one from each Side standing upright, distant from each other; and convenient Communications of Wire and Chain from the giving Side of one Pane to the receiving Side of the other; that so the whole might be charg'd together, and with the same Labour as one single Pane;...*[3]

Over time, the term "battery" has come to refer to both a collection of connected electrochemical cells and a single working cell, and will be generally used without specificity throughout this work.[4]

Batteries produce electrical energy through oxidation-reduction (redox) processes, wherein one substance loses electrons through oxidation while another substance gains electrons through reduction. It is sometimes convenient to examine the oxidation and reduction processes independently as half reactions, an example of which is shown below. However, it is important to note that oxidation cannot occur without a corresponding reduction process also occurring and vice versa, although the two processes do not necessarily need to occur at the same physical location.

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$
Reduction: $Cu^{2+}(aq) + 2\,e^- \rightarrow Cu(s)$

Overall: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

In simple electrochemical cells (Figure 1), these processes occur at the surface of electronic conductors, termed electrodes. These electrodes may be composed of a redox-active material or more electrochemically inert materials such as platinum, mercury, gold, or graphite.[5] Oxidation occurs at the anode, while the reduction process occurs at the cathode. Between the electrodes is an electrolyte, an ionic conductor necessary to reduce polarization and allow current to flow. Wire or another electrically conducting material connects the two electrodes to a load, completing the circuit, allowing the battery to discharge and work to be done. The overall system must remain charge-neutral in order to continue functioning. If a build up of charge occurs, polarization results and the electric current is reduced and ultimately stopped completely.

Batteries are often classified as either primary or secondary batteries. In both cases, chemical potential energy is converted to electrical energy. For primary batteries, the chemical reactants are consumed in a process which is not easily reversible, resulting in a battery which can only be discharged a single time. Examples of primary batteries include common alkaline batteries, silver button cells and watch batteries, and the homemade "lemon battery" consisting of pieces of iron and copper stuck into the flesh of the acidic citrus fruit.

Secondary batteries also convert chemical potential energy to electrical energy, but do so through reversible chemical process which render the resulting battery rechargeable. Application of electrical energy from an external source such as a generator or another battery can regenerate the initial chemical reactants, restoring the battery's charge and allowing repeated charge/discharge cycles. Because of this ability to store energy, these types of cells are also known as "storage batteries". Common examples of storage batteries include lead-acid

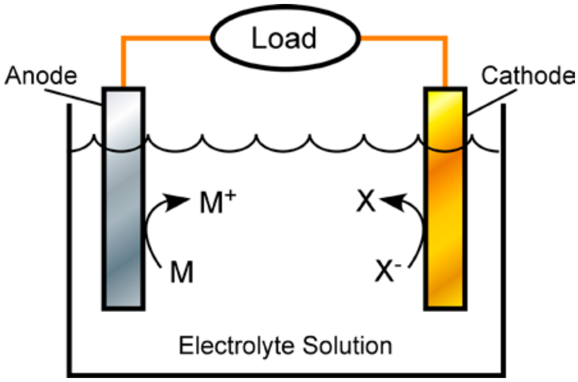

Figure 1. A simple electrochemical cell.

batteries used in most automobiles and lithium-ion batteries found in mobile consumer electronics.

THE VOLTAIC PILE

Prior to 1800, studies of electricity were limited to what could be achieved through collection and discharge of static electricity.[6–8] While arcs with rather large voltages could be achieved, their application was limited by the small current and extremely short duration of the discharge.[6] Despite this limitation, the study of electrical phenomenon spanned from attempts to split water through electrolysis, to studies with frogs predating Luigi Galvani's well-known work, to Franklin's famous lightning experiments.[9–13]

In March of 1800, Alessandro Volta (Figure 2), professor of natural philosophy at the University of Pavia in Lombardy, Italy, in a correspondence to Joseph Banks, President of the Royal Society of London, described a device which could provide a continuous supply of electrical power.[8,14] This apparatus (Figure 3), later known as the "Voltaic Pile" consisted of discs of tin or zinc paired with discs of copper, brass, or silver, with layers of water-soaked paper, fiber board, or leather between the disc pairs. Wire contacts with the discs on the top and bottom of the pile allowed the experimenter access to a constant electric current. Also included was a description of what Volta termed a "crown of cups", a series of what would modernly be described as simple wet cells.[14]

Discharging Volta's pile resulted in visible corrosion occurring on the zinc (or tin) discs, the result of oxidation of the anode. A slight corrosion was also sometimes noted on the silver (or copper) cathode discs, but not to the same extent as seen on the anode. At the time this led him to believe the current was solely the result of the anodic reaction. Considering it is now known that oxidation cannot occur without reduction, and with Volta and others noting problematic polarization resulting from bubbles of hydrogen gas adhering to the electrode surfaces, it seems evident that the corresponding reduction process in Volta's pile was the reduction of hydrogen from water, as seen in the overall electrochemical reaction below.

$$Zn_{(s)} + 2H_2O_{(l)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} + 2OH^{-}_{(aq)}$$

It should be noted that the reduction process is often incorrectly attributed to reduction of the cathode material (half reactions seen below for silver and copper). However, this would require ions of the cathode material to be already present in order to occur. While it is possible some advantageous oxidized cathode material may

Figure 2. Alessandro Volta (1745-1827) (public domain).

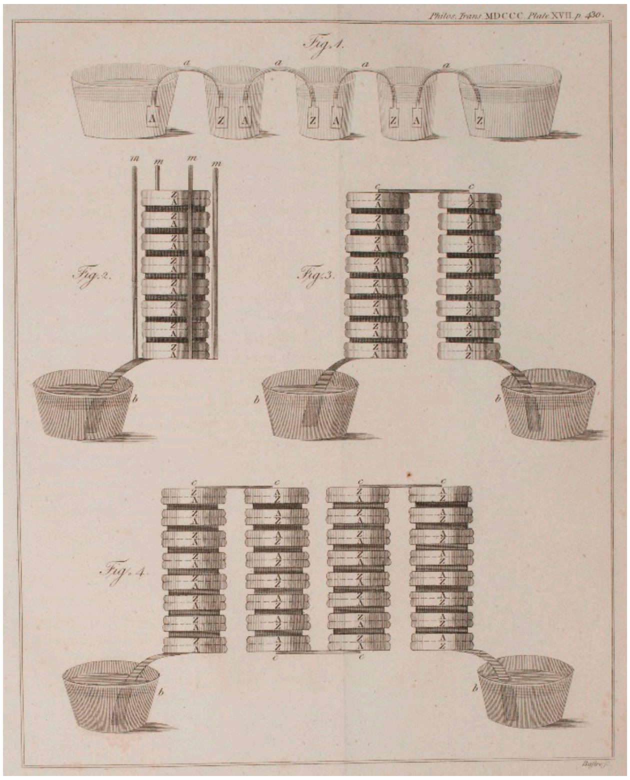

Figure 3. Volta's crown of cups and several piles (public domain).

have been present, it is unlikely there would be enough to support much electric current out of the device.

$$Cu^{2+}_{(aq)} + 2\,e^{-} \rightarrow Cu_{(s)}$$
$$Ag^{+} + e^{-} \rightarrow Ag_{(s)}$$

Volta's description of his pile was quite complete and its design was elegant yet simple, allowing experimentalists to very quickly build replicas in their laboratories for application to their own work. Volta in this same letter described experiments where he applied the leads from his pile to his lips and tongue, describing the results:

> *In fact, once the circuit is closed in a convenient manner, one will excite simultaneously...a sensation of light in the eyes, a convulsion on the lips and even in the tongue, a painful prick at the point of the tongue, finally followed by a sensation of taste.*[15]

IMPACT OF VOLTA'S PILE

This new development had an almost immediate impact on the study of electricity. Possibly due to hostilities between France and England at the time, Volta sent the first four pages of the letter to Banks in March, with the remainder sent several months later.[8] As a result, Volta's letter was not formally read into the Society until June 26, 1800.[14] However, Banks shared the contents of the first four pages with a number of the members of the Society, allowing them to build devices for their own work prior to the paper's reading. William Nicholson specifically mentions these circumstances in his accounts of this new "electrical or Galvanic apparatus" published in July, 1800, indicating he felt it proper to delay publication of his own work until Volta's entire paper had been read to the Society.[16]

In this same paper, Nicholson describes work he performed with Anthony Carlisle which included the electrolysis of water, with application of electric current for a period of 13 hours to produce 1.17 cubic inches of gas.[16] This was a significant improvement in both yield and efficiency from earlier works using static discharge. For comparison, George Pearson reported collecting one third of a cubic inch of gas utilizing over 14,600 static discharges.[9] While times for that specific experiment are not given by Pearson, based upon times given for other experiments in the same paper, the process likely took approximately 18 hours to complete. Later that same year, Humphry Davy produced isolated hydrogen and oxygen gases from samples of water in separate glasses using a Voltaic pile, completing the circuit through his own body by inserting a finger in each glass of water.[17]

Further advances rapidly followed. Electrodeposition of metals was reported by Nicholson and Carlisle along with William Cruickshank in England, and independently by J.W. Ritter in Bavaria in 1800.[18–20] In 1805, Ritter was reported to have developed a modified pile utilizing a single metal which could be charged, a precursor to the storage battery.[21] Humphry Davy confirmed that charcoal could substituted for the wires connected to the pile (a phenomenon originally reported by Volta), and is reported to have used charcoal to produce impressive sparks as early as 1802.[22] By 1808, Davy had used the Voltaic pile to discover and isolate several of the alkali and alkaline-earth elements, including sodium, potassium, barium, calcium, strontium, and magnesium.[23,24]

EARY IMPROVEMENTS TO THE BATTERY

While undoubtedly a monumental improvement over static discharge collecting devices of the time, the Voltaic pile was not without its imitations. The useful lifetime of the pile was limited, as corrosion of the metal discs, while a necessary result of the chemical processes driving the output, would occur quite rapidly and require the pile to be rebuilt.[25] In addition, polarization of the electrodes would result in a decrease in output over time. Within a year, numerous attempts to improve the Voltaic pile were made. One such modification was the trough battery developed by Cruickshank (Figure 4).[25] A grooved wooden trough was used, with soldered pairs of zinc and silver plates affixed in the grooves with rosin or wax to create a number of sealed chambers. These chambers were then filled with a solution of ammonium nitrate, effectively replacing the wetted paper discs of the pile with a fluid solution. This ensured a more ready supply of electrolyte at the surface of the plates, and allowed the plates to be more easily cleaned as corrosion occurred through treatment with hydrochloric acid solution.[25]

Charles Wilkinson modified Cruickshank's trough battery, using wooden partitions instead of metal plates, and attached wires to separated zinc and copper plates, allowing the plates to be removed at the conclusion of the battery's daily usage while leaving the electrolyte in the trough.[26] Wilkinson had previously noted the power of the device was not related to the contact area between the copper or silver plate and the zinc plate, and proposed an increase in available zinc surface area resulted in increased output.[27] With the zinc and copper plates completely separated, Wilkinson reported his plunge-type device with four inch plates was the equal of a Cruickshank-type trough battery with six inch plates.[26]

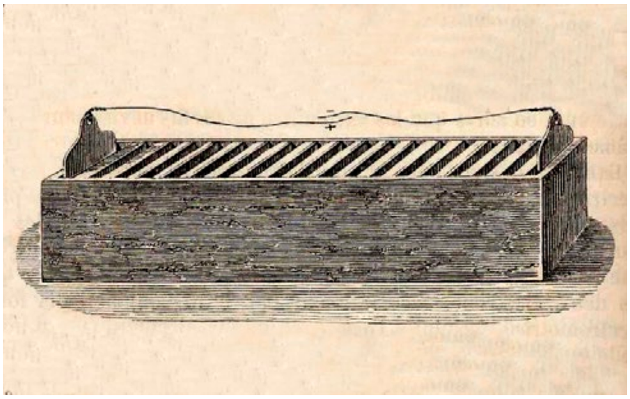

Figure 4. 19th Century illustration of a trough battery (public domain).

As previously mentioned, corrosion of the anode material was recognized to occur during discharge of a battery. However, corrosion would also occur, albeit more slowly, even when the battery was left idle or stored for a period of time. While removal of the anode metal from the electrolyte solution as seen in plunge-type batteries was an effective means to halt this secondary corrosion, the two-fluid cell would prove to be another approach with historical significance.[6]

THE DANIELL CELL

While aspects of a two-fluid cell had previously been described independently by Becquerel and Wach, the successful invention is generally credited to J. Frederic Daniell.[6,28] In letters to Michael Faraday, Daniell describes a cell composed of a copper cylinder with a membrane tube "formed of a part of the gullet of an ox" suspended by collars inside (Figure 5).[29–31] Within the membrane was contained a zinc rod as well as a solution of either sulfuric acid or zinc sulfate, with the copper cylinder filled with a copper(II) sulfate solution. Additionally, a siphon tube was included to allow removal of saturated zinc sulfate solution from the bottom of the membrane tube. Thus, fresh acid and copper(II) sulfate could be added as needed. Later other materials such as paper dividers or porous ceramic were used to separate the two solutions.[6,32,33] The presence of copper ions in the outer solution, and the need to occasionally add copper(II) sulfate to the cell, indicate the reduction reaction for the Daniell cell was not hydrogen reduction as seen in the Voltaic pile and the trough battery, but rather the reduction of copper ion, resulting in the following overall reaction.

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

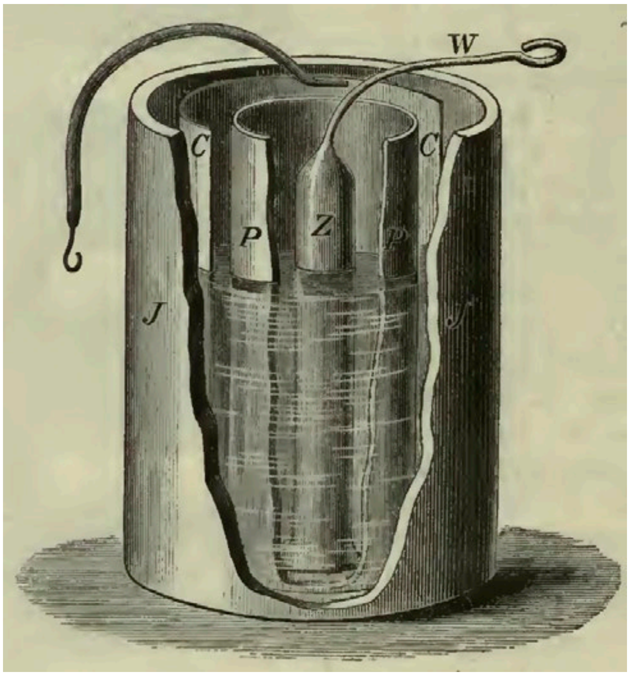

Figure 5. A drawing of a Daniell Cell. This later design utilizes a ceramic cell container and paper divider, with copper sheet and zinc rod electrodes.

One particularly noteworthy modification of the Daniell cell was developed by William Grove.[34,35] While investigating the action of a mixture of nitric and hydrochloric (muriatic) acids on gold foil, he discovered connecting the gold foil to an isolated pool of nitric acid via a wire resulted in the dissolution of the gold foil.[34] He also proposed that using nitric acid and an inactive cathode such as platinum in one chamber of a Daniell cell, with a zinc anode in the other, should produce a greater electric current than the standard configuration.[34] While nitric acid had been used as an electrolyte previously, this is believed to be the first time nitric acid was recognized as a cathodic reactant.[6] The half reactions, as well as the combined overall redox reaction, can be seen below.

Oxidation: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\,e^-$
Reduction: $2\,H^+_{(aq)} + 2\,HNO_{3(aq)} + 2\,e^- \rightarrow$
$2\,H_2O_{(l)} + 2\,NO_{2(g)}$

Overall: $Zn_{(s)} + 2\,H^+_{(aq)} + 2\,HNO_{3(aq)} \rightarrow$
$Zn^{2+}_{(aq)} + 2\,H_2O_{(l)} + 2\,NO_{2(g)}$

Further improvement of the Grove cell occurred through the inclusion of carbon as an inert electrode material.[6] While many investigators, including Volta and Davy, had already explored charcoal and graphite for charge collection or as electrical conductors, it is Robert Bunsen who is commonly credited with initiating its widespread use in batteries.[6] The replacement of the expensive platinum cathode with carbon helped reduce the cost of Grove-type batteries, which undoubtedly increased their usage. However, the disadvantages inherent to the use of nitric acid were still present, particularly the production of noxious nitrogen oxides (NO, N_2O_4). Eventually oxidants other than nitric acid were explored, including chromic acid, permanganate, and chlorates, and modified Grove cells were used for the next several decades for certain applications.[6] However, the greatest value in both the Daniell and Grove cells may have been in laying the groundwork for what would eventually become the modern dry cell battery.

TOWARD THE MODERN DRY CELL

One significant downside to the Cruickshank, Daniell, and Grove batteries, as well as their derivatives, was the need for liquid electrolytes, often times corrosive acid solutions. These solutions resulted in batteries that were quite heavy, prone to spillage if moved, and susceptible to messy leaks. This combination of factors was especially problematic for applications requiring a mobile source of power, such as on railroads, street cars, or eventually for carriage lighting.

A significant step toward a solution to this problem occurred with the design of a cell by Georges Leclanché, patented in France in 1866.[36] The Leclanché cell continued to utilize a zinc rod as the anode, but made use of a porous ceramic pot filled with a mixture of manganese(IV) oxide and carbon with a carbon rod current collector as the cathode (Figure 6). Reduction of the manganese from +4 to +3 occurred at the cathode, and can be seen below.[7] A solution of saturated ammonium chloride was used as the electrolyte.[6]

Oxidation: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\,e^-$
Reduction: $2\,H^+_{(aq)} + 2\,MnO_{2(s)} + 2\,e^- \rightarrow 2\,MnO(OH)_{(s)}$

Overall: $Zn_{(s)} + 2\,H^+_{(aq)} + 2\,MnO_{2(s)} \rightarrow Zn^{2+}_{(aq)} + 2\,MnO(OH)_{(s)}$

While still a wet cell, and thus still suffering from some of the same limitations of its predecessors, the elimination of acid served to improve the stability of the cell, and reduced the hazards associated with leaks and spills. Unfortunately, current outputs were limited under prolonged use, with only a slight improvement over the Daniell cell, possibly due to the limited redox availability of the MnO_2 residing in microdomains within the carbon matrix.[6] As with the Daniell and Grove cells, the Leclanché cell also served as an important stepping stone toward the eventual development of the dry cell battery.

Numerous attempts were made through the years to immobilize the electrolyte and create a "dry cell", thus reducing or eliminating risk of leaking or spillage. Volta's original pile immobilized the electrolyte by absorbing it in paper or leather.[14] Attempts with other materials were reported, including starch pastes, sand, asbestos, wool, and gelatin.[6,36] In 1887, Carl Gassner, Jr. filed a patent in the United States outlining the use of zinc oxide mixed with plaster surrounding a MnO_2/C cathode inside a zinc cylinder, which served as both anode and cell container for a battery.[37] While this approach was not particularly successful, likely due to extremely limited ion mobility within the solid plaster, it does bear a striking resemblance to the modern dry cell configuration.

Alkaline electrolytes were reported in a French patent in 1881, followed by a U.S. patent in 1883, by Felix de Lalande and Georges Chaperon, although it is likely the use of alkaline solutions was investigated far earlier.[38] Lalande and Chaperon used caustic potash or caustic soda with zinc anodes and copper oxide as the cathode material to good effect, and in 1889 a manufacturing plant was producing alkaline zinc and copper oxide cells in the United States.[38,39]

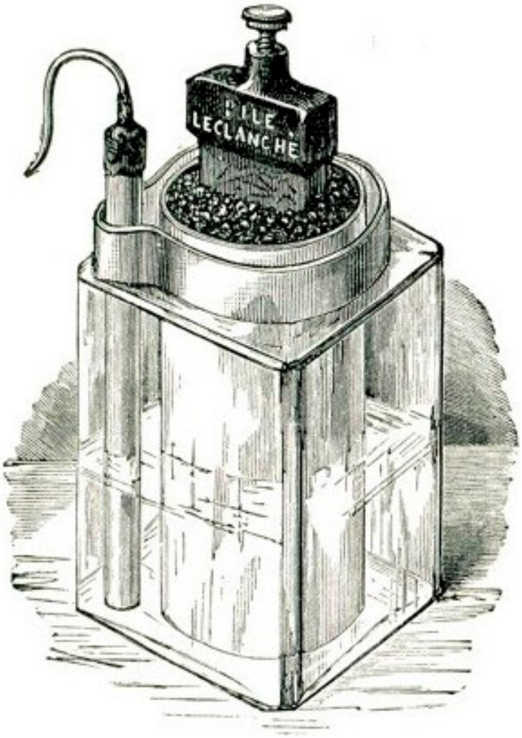

Figure 6. Leclanché wet cell (public domain).

The modern alkaline battery can be considered a culmination of many of the advances described above, although 50 years would pass before its invention. A zinc casing serves as the anode as used by Gassner. Contained within the cell is a cathode composed of the carbon rod collector made popular by Bunsen surrounded by a MnO_2/C paste similar to that found in the Leclanché cell. A caustic soda paste serves as the electrolyte as described by de Lalande and Chaperon. The alkaline electrolyte and the cathode materials are separated with a layer of paper, reminiscent of the separators used in Volta's original pile. Patents were granted for this configuration to Lewis Urry, Paul Marsal, and Karl Kordesch in 1947 in Great Britain, and in the United States over a decade later in 1960.[40] One additional development to improve safety was the use of small amounts of mercury to suppress hydrogen gas production inside the cell which could cause the cell to rupture.[41] Due to the toxicity of mercury, its use eventually fell out of favor, and there is now a worldwide ban on the use of mercury in commercial batteries.

LEAD-ACID BATTERY

While Ritter's "charging pile" should be recognized as the first storage battery, its application did not gain traction at the time.[21] The first widely utilized secondary battery was the lead-acid battery. The use of lead plates to store electrical charge was first described by W.J. Sinsteden in 1854.[42] However, it was Gaston Planté several years later who would develop a version which would be viable on a useful scale, although its usefulness was still limited and it could be considered to be ahead of its time.[43]

Sinsteden, for unknown reasons, used lead plates to connect batteries to a voltammeter instead of using silver, platinum, or copper wires as was commonly done.[42,43] He noted a small secondary current that could be measured, which increased with subsequent charge/discharge cycles. He also noted the formation of lead oxides on one of the plates. Planté looked at this phenomenon more closely, comparing the results of a number of different metals including aluminum, silver, copper, lead, iron, and gold.[43] He also compared electrolyte acidified with sulfuric acid to other options.

The modern lead-acid battery utilizes a series of cells, each containing a lead-alloy grid as one electrode, and a lead(IV) oxide-coated lead plate or grid as the other electrode (Figure 7). The overall redox process results in both oxidation and reduction of lead, as seen below.

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2\ H_2O_{(l)}$$

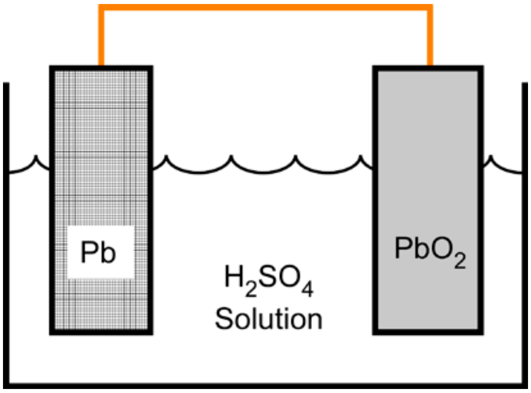

Figure 7. Diagram of a lead-acid battery.

The increased surface area of the lead grid allows for a greater current output than could be achieved using similar sized plates. A solution of 20-30% aqueous sulfuric acid serves as the electrolyte.

Although the battery was capable of being recharged, the technology needed to generate the current to efficiently charge it had not yet been developed, and as such the only way to recharge a lead acid battery was to exhaust a number of primary batteries such as Daniell or Grove cells. It wasn't until the 1880's when large scale electrical power production allowed storage batteries to flourish.[6] Even today, the lead-acid battery holds a worldwide market share of over $35 billion USD annually, with automotive batteries as the primary market.[44]

NICKEL STORAGE BATTERIES

While the lead-acid battery was (and continues to be) quite serviceable for many static applications, its weight and acidic electrolyte made it less-than-ideal for more portable purposes. The first secondary battery to successfully compete with the lead-acid battery was developed by E.W. Jungner. In a patent filed in his native Sweden, Jungner first described a nickel-iron cell in 1897, followed in 1901 by a patent replacing iron with cadmium.[45,46] In 1901, Thomas Edison also obtained a United States patent for a nickel-iron secondary battery.[47] It is unclear if Edison was aware of the work of Jungner at the time.

Owning to the lower density of nickel and cadmium (7.81 and 8.00 g/cm^3, respectively) versus that of lead (10.66 g/cm^3), these cells showed a significant decrease in weight when compared to their lead-acid counterparts.[48] Jungner also utilized an alkaline electrolyte rather than acid, which would eventually allow for dry cell development. However, mass production of NiCd (sometimes termed "nicad") batteries did not occur until the middle of the 20th century, upon development of a means of dealing with gases that can be produced during the redox processes, allowing for creation of a completely sealed battery.[49]

While quite popular in the second half of the 20th century, NiCd cells had several downsides. First, they were prone to memory effects, requiring a full discharge prior to recharging to avoid loss of charge capacity. Additionally, the toxic nature of the cadmium cathode was a disposal concern, and in 2009 the European Union prohibited their use in most applications.[7]

Improvements to NiCd batteries were investigated as early as the 1960's. Efforts to improve the capacity of the nickel hydroxide electrode through inclusion of didymium hydrate (a mixture of rare-earth oxides, primarily lanthanum and neodymium) were granted a United States patent in 1967.[50] Development of what would become known as nickel-metal hydride batteries occurred in the 1990's, when Stanford Ovshinsky and coworkers expanded the scope of additives to include many rare-earth and transition metals.[51,52] These additives allowed the cadmium cathode to be replaced with a nickel-metal alloy. These cathodes allowed for the storage and discharge of hydrogen (as hydride) through charge/discharge cycles, increasing the charge capacity and greatly reducing memory effects compared to standard NiCd batteries.[7] Having led the work that directly allowed commercialization of nickel-metal hydride batteries, Ovshinsky, a prolific inventor, is often referred to as the inventor of the nickel-metal hydride battery.[53]

THE RISE OF LITHIUM

While zinc was the predominant anode material for almost two centuries, potential was seen for lithium as a replacement. Lithium has a higher activity and a lower density than zinc, which would allow for lighter batteries with increased voltage output than zinc cells. Gilbert Lewis and Frederick Keys successfully measured the potential of the lithium electrode as early as 1913.[54] Unfortunately lithium, like the rest of the alkali metals, reacts with water, rendering it unusable with aqueous electrolytes. Additionally, lithium metal reacts readily with atmospheric nitrogen at ambient temperatures to produce a surface coating of lithium nitride, generally with some amount of lithium oxide as well, thereby requires inconvenient inert atmosphere conditions to successfully work with lithium metal.

In was not until 1965 when a patent for a secondary battery utilizing lithium (as well as sodium, potassium, magnesium, beryllium, and aluminum) was obtained, although the patent application was filed in 1961.[55] An organic solvent with salts of the anode material is specified, avoiding the problems associated with aqueous electrolyte solutions. Also mentioned are cathodes composed of redox-active organic polymers including polymers of quinones, sulfoxides, hydroxylamines, and azo compounds. Another approach was described by D.A.J. Swinkels in 1966, wherein a molten lithium chloride electrolyte was used.[56] Unfortunately, this system required a minimum operating temperature of 650 °C, making it impractical for widespread use.

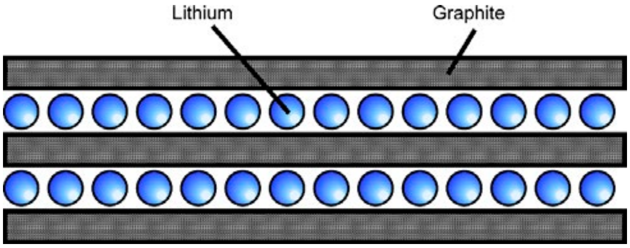

Figure 8. Intercalation of lithium ions.

One practical application of lithium metal anodes was the lithium-iodine battery.[57] Its development had a significant positive impact in medicine, improving the performance of pacemakers implanted in cardiac patients by decreasing the weight and increasing the battery life compared to previous battery options of the time.[58] While not necessarily a problem for pacemaker applications, the lithium-iodine battery was a primary battery, and could not be effectively recharged. With pure metal anodes, ions produced through oxidation upon discharge must be reduced and redeposited onto the anode when the cell is recharged. Unfortunately, for several reasons, lithium often does not redeposit evenly on the electrode surface but instead can form dendrites which can grow to sufficient length to short circuit the cell.[58]

In the mid 1970's, intercalation of ions, including lithium ions, into a host framework had been recognized and described.[59] Rather than relying upon a pure lithium metal electrode with the inherent risks associated with it, electrodes composed of materials capable of accepting lithium ion insertion within its solid structure (Figure 8) were explored. Attempts to develop cells based upon intercalating electrodes proceeded through the 1980's.[58] The most successful of these, which would form the basis for the lithium ion batteries now common, utilized a lithium cobalt oxide ($LiCoO_2$) material developed by J.B. Goodenough and coworkers in 1981.[60] Other materials were also found to support lithium ion insertion, including TiS_2, V_4O_{10}, and graphite.[61] Intercalating electrodes are now commonly used for both the anode and the cathode in lithium ion batteries, with lithium ions shuttled between them during charge or discharge processes.[62]

CONCLUSIONS

As society relies more and more on portable electric power, there is little doubt that significant effort will be expended to further improve battery technology. The desire for increased charge capacity, better thermal stability, longer functional lifetimes with more charge/discharge cycles, faster recharge rates, and decreased size and mass will continue to drive exploration and innovation. For example, efforts are currently underway to improve the performance of gel electrolytes in lithium ion batteries for mobile electronics and electric automobiles. It seems likely that increased efforts to develop ultra-high capacity, large scale stationary batteries to store renewable energy sources such as wind and solar to stabilize a greener energy grid is also on the horizon. One can only guess at what Alessandro Volta would think if he were to see the impact his device ultimately had on the world.

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Fuel Cells: A Challenging History

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Abstract. Professional and popular journals present fuel cells as the salvation of transportation and electric power infrastructures; the ultimate rechargeable battery. Engineers and investors alike find them attractive as a modern and elegant alternative to other electrical generators. On three occasions since W. R. Grove's initial research around 1840, widespread adoption of fuel cells seemed imminent. Each time, technical challenges in materials and systems integration, along with advances in other electrical technologies frustrated advocates' hopes. Despite successful development of several different types, commercialization remains limited to niche applications. After 180 years fuel cells remain outside the mainstream of power generation technology. This paper presents an overview of that history. The author discusses basic challenges that have faced developers, and suggests how present research may benefit from past experience.

Keywords. Fuel cells, gas batteries, electrochemical technology.

> *...we concluded that the economical production of powerful currents for commercial purposes ... did not seem to be a problem likely to be readily solved....*
> —Charles R. Alder Wright and Charles Thompson, 1889.[1]

INTRODUCTION

Fuel cells have captivated and frustrated researchers and investors since 1839. A device that quietly combines hydrogen and oxygen to produce electricity and water would solve many problems in a world dependent on electric power. Scientists spent decades learning how fuel cells generate electricity, and engineers built them into submarines, automobiles, a farm tractor, and other devices. Humans traveled to the moon with fuel cells. Yet after 180 years of work, Wright and Thompson's conclusion remains valid. Significant commercial adoption remains elusive due to high costs, intractable technical difficulties, and competition from other technologies.

The seeming simplicity and potential benefits of fuel cells nurtures optimism rarely deterred by persistent obstacles.[2] In the 1890s, the 1960s, and around 2000, technical journals and the popular press described fuel cells as nearing commercial viability.[3] On each occasion, development faltered and significant diffusion failed to occur. Encouraging test results and occasional high-profile successes obscured vital facts: fuel cells come in non-interchangeable types that must function within larger technical and economic systems. Today, a few are in low-rate production for automotive engines and stationary power. Though prototypes proliferate, fuel cells remain niche products. Perceived technical elegance does not convey success in the laboratory or in the marketplace.

Rather than a triumphal march from discovery to market, fuel cell history provides a sobering counter to progressive views of technology development. After a technical review, this article discusses four distinct periods of fuel cell work. Examining the past brings perspective to current events by highlighting recurring factors that hindered adoption. The situation of fuel cells as components in technological systems—requiring other devices in order to operate, while meshing with existing infrastructures—served as one factor.[4] Another is the influence of public and professional perceptions on expectations, including the persistent myth that fuel cells are simple devices on the verge of mass production. The article also presents important differences in socially- dependent contexts, such as differing economic and technical circumstances of each period, so as to avoid the fallacy of cyclical history. Setting the recurring factors in their changing contexts helps explain why fuel cells continue to fascinate despite many disappointments.[5]

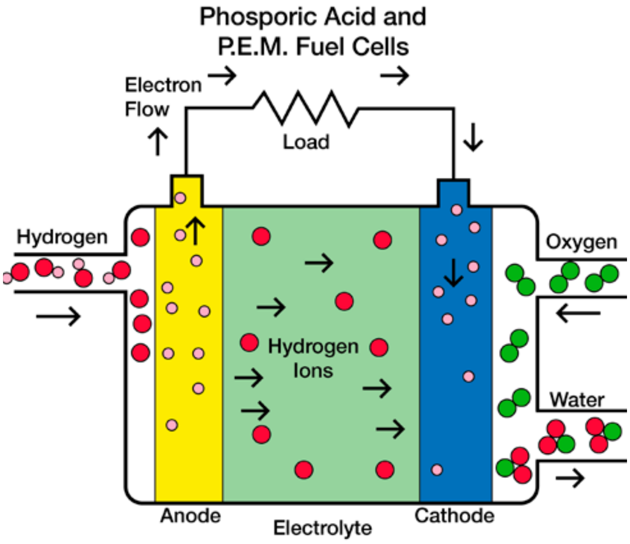

Figure 1. Diagram showing basic fuel cell components. Smithsonian image.

AN ELEGANT TECHNOLOGY

Engineers often refer to an especially efficient process or device as elegant. From the beginning, many admirers declared fuel cells (originally called gas batteries) elegant.[6] Like batteries, they generate direct current electricity through chemical action. Several types exist and their operational details vary in important ways. Figure 1 shows one type and depicts the general components and operating principle. Fuel cells contain two electrodes, an anode and a cathode respectively, each treated with a catalyst, often platinum. Hydrogen introduced at the anode and oxygen supplied to the cathode interact with the catalyst that facilitates the chemical action. An electrolyte separates the electrodes allowing passage of ions through the cell, while electrons routed externally provide electric power. Recombination of gases generates waste heat and water.

The operating process reverses electrolysis, in which an electric current separates water into hydrogen and oxygen. Pure hydrogen can be pumped into a fuel cell directly or extracted from a hydrogen-containing fuel by a reformer. Likewise, cells can use pure oxygen or air. Engineers must manage waste water and heat, control reaction products that can damage catalysts, and prevent the internal leakage of gases and electrolytes. Ideally cells emit no pollutants or greenhouse gases, though environmental challenges exist in mitigating the impact of cell fabrication and disposal, as well as in obtaining and delivering hydrogen fuel. Individual cells yield only a modest amount of electricity. Arranging cells in stacks boosts total output to as much as five megawatts. A power inverter changes the direct current to alternating current, if desired.

Fuel cells are typically classed by the form of their electrolyte. The principle types are: alkali, phosphoric acid, proton exchange membrane (PEM), molten carbonate, and solid oxide. Some types are more appropriate than others for certain applications, and each presents specific technical challenges. Molten carbonate and solid oxide cells operate at relatively high temperatures and are usually classed together. High temperatures reduce the need for expensive catalysts and pure fuels. But cells and auxiliary equipment tend to be large and immobile, and reuse of waste heat can be critical to overall system efficiency. Acid, alkali, and PEM cells operate at lower temperatures and can be more compact and portable. But fuel purity becomes an issue and the power output is reduced.[7]

Far from simple devices, each type's history grew ever more distinct through time though some common features emerge. Specific technical problems as well as general issues like making and distributing hydrogen fuel vexed generations of researchers.

Meanwhile, other researchers actively refined competing types of electrical generators.[8] In a world of limited resources, societies typically made choices based on economics rather than technical elegance with the result that fuel cells remain marginalized.

DISCOVERY OF A PUZZLE

In the 1790s, Alessandro Volta of Italy (1745-1827) stacked discs of alternating metals such as zinc and silver to create “piles” that produced a steady, continuous electric current. His work inspired experimenters worldwide who improved on his discovery.[9] Advances came rapidly and in 1838, Welsh jurist and scientist William Robert Grove (1811-1896, figure 2) devised an eponymous wet cell battery. He used a platinum electrode immersed in nitric acid and a zinc electrode in zinc sulfate. Grove cells proved popular with early telegraphers; American Samuel F. B. Morse (1791-1872) used them to power his 1844 “What Hath God Wrought” demonstration.[10]

While experimenting with his new batteries, Grove arranged two platinum electrodes such that one end of each was immersed in a container of sulfuric acid. He sealed the other ends separately in containers of oxygen and hydrogen, and then measured a constant current flowing between the electrodes. The sealed containers held water as well as the gases, and he noted that the water level rose in both tubes as the current flowed. Christian Schönbein of Germany (1799-1868) independently noted a current in his experiments with platinum and various gases about the same time.[11]

Figure 2. Portrait of William Robert Grove. Woodburytype by Lock and Whitfield. Smithsonian Institution Libraries.

Grove decided to “effect the decomposition of water by means of its composition” and assembled several sets of electrodes in series, as seen in figure 3. Energy lost as heat eventually stopped the process but Grove’s experiment attracted attention. He named the new device a gas battery and published several papers on his experiments.[12] He noted however, that “I have never thought of the gas battery as a practical means of generating voltaic power.”[13]

Grove’s discovery challenged a scientific community still defining basic principles of chemistry, electricity, matter, and energy. Gas batteries were, as Wilhelm Ostwald (1853-1932) of Germany wrote, “a puzzle” for those struggling to understand what caused current to flow from some substances but not others.[14] And it intensified a controversy between proponents of two competing theories. Contact theory, proposed by Volta to explain the pile and “defended” by Johann Poggendorff (1796-1877) and Christoph Pfaff, required physical contact between substances in order for current to flow.[15] A rival theory supported by Grove and Schönbein held that a chemical reaction generated electricity. Arguments between the two camps became quite acrimonious.[16]

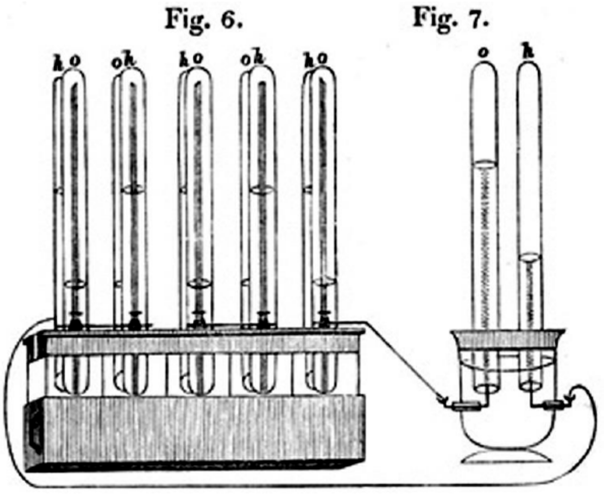

Figure 3. Grove’s apparatus for “the decomposition of water...by means of its composition.” W. R. Grove, *Trans. Roy. Soc.* **1843**, 133, plate V, p. 93.

The debate faded as knowledge advanced. Concluding that the gas battery was "of no practical importance," Ostwald recounted the solution of the puzzle. "The answer is contained in the fact that oxidizing agents are always substances that form negative ions or make positive ions disappear; the reverse is true of reducing agents. Oxygen and hydrogen are nothing more than oxidizing and reducing agents."[17] Ironically both theories held some truth. Later fuel cell researchers noted that chemical reactions in gas diffusion electrodes take place in "the contact zone where reactant, electrolyte and catalyst meet."[18]

The controversy's details are less important here than the fact of its existence. Ostwald was correct. No practical device emerged from that era, despite several attempts. The primary importance of the gas battery in the mid-nineteenth century lay in spurring research that refined scientific theory. As scientific understanding improved, researchers shifted to making something useful. While that focus contributed to basic science—there was certainly more to be learned—research turned to developing better materials and more efficient designs. But by century's end, Ostwald's countrymen Ludwig Mond (1839-1909) and Carl Langer (1859-1935) noted that "very little attention has been given by investigators to the [gas battery]."[19]

ENGINEERING AND EXPERIMENTS

Public and professional interest in fuel cells briefly surged in the years around 1900 as several researchers looked for novel ways to produce electricity. Mond and Langer worked to increase gas batteries' electrical output by means of an earthenware panel soaked with sulfuric acid and fueled with coal-derived "Mond-gas." But then they chanced to discover "the carbonyl process for refining and purifying nickel, and [their] attention was diverted away from fuel cells to the foundation of the great nickel industry."[20] This would not be the last time that fuel cell researchers turned to other work deemed more important or more amenable to success.

Englishmen Charles R. Alder Wright (1844-1894) and Charles Thompson (1861- 1892) developed a similar fuel cell about the same time. They made progress but reported that internal gas leaks interfered with attempts to increase voltage output, "even with only infinitesimal currents." They concluded,

> *our results were sufficiently good to convince us that* if the expense of construction were no object, *so that large coated plates could be employed, enabling currents of moderate magnitude to be obtained with but small current density, there would be no particular difficulty in constructing [cells] of this kind, competent to yield currents comparable with those derived from ordinary small laboratory batteries; although we concluded that the economical production of powerful currents for commercial purposes by the direct oxidation of combustible gases did not seem to be a problem likely to be readily solved, chiefly on account of the large appliances that would be requisite.*[21]

Their concern with "powerful currents for commercial purposes" reflected the increasing influence of industrial age goals and organizations on electrical research. Wright and Thompson worked during a period of rapid electrification. They understood that producing "currents of moderate magnitude" held little attraction for industrialists who wanted to electrify factories and whole cities.[22] After publishing their results, both turned to other work. Thompson led research at a soap manufacturer. Wright, a physician, is remembered as the inventor of heroin.[23] Neither returned to fuel cells.

A few others did take an interest in fuel cells however, even one industrialist. Steam research during the 1800s led to higher efficiencies in coal-fired electrical generating plants. A major driver of fuel cell development since the 1880s has been the desire to escape Carnot heat-cycle limits in electrical plants. Some researchers hoped that fuel cells might enable the direct conversion of coal into electricity. They pursued that goal vigorously, leading to a burst of research and publicity.

American Thomas A. Edison (1847-1931), sought many ways to cut costs and improve the efficiency of generating electric power for his new lighting system. He spent over two years investigating the direct conversion of coal and received several patents, but found himself facing "an insurmountable obstacle." He could not have been encouraged when the experiments resulted in "all the windows [being] blown out of his laboratory."[24] Edison rarely wasted time on inventions that showed little profit potential and soon moved on to other work.

In late 1894, the French team of Louis Paul Cailletet (1832-1913) and Louis J. E. Colardeau (?-?) described a gas battery that used "precious metals" in sponge form to absorb gases, but deemed the process impractical.[25] At the same time Wilhelm Borchers (1856-1925) of Germany described an apparatus for "direct production of electricity from coal and combustible gases."[26] American Charles J. Reed (1858-1943) critiqued Borchers' work, then wrote two papers of his own on this "most promising" use of gas batteries.[27] Economic questions persisted, however. One editorial noted that given the low price of coal, even if Borchers' system gave 100% conversion efficiency consumers would see less than a 10% reduction in electricity prices. "[Assuming] that the [technical] problem were really solved, it does not follow, as is often asserted, that a revolution in the electrical industry would result."[28]

That reminder of economic reality soon fell by the wayside. William W. Jacques (1855-1932), an American electrical engineer and chemist, "startled the scientific world and general public," in 1896, "by his broad assertion that he had invented a process of making electricity directly from coal." Jacques generated current via a "carbon battery" in which air injected into an alkali electrolyte reacted (or so he believed) with a carbon electrode. The apparatus, illustrated in a trade journal (figure 4) at the time, consisted of 100 cells arranged in series and placed on top of a furnace that kept the electrolyte temperature between 400-500 °C.

Jacques claimed 82 percent efficiency for his carbon battery, but critics soon pointed out that he had failed to account for the energy used heating the furnace or driving the air pump. They calculated an actual efficiency of only 8 percent. Further research indicated that the current generated by his apparatus came not through electrochemical action, but rather through thermoelectric action.[29] Even had Jacques' battery worked as well as claimed it left unanswered the economic question raised by Borchers' critics. Nonetheless, the desire to convert plentiful and inexpensive coal directly into electricity by way of an electrochemical process continued in the twentieth century.[30]

Around this time, the use of fuel stocks like coal and manufactured gas gave the fuel cell its modern name. A follow-on article labeled Borchers' device a "fuel battery," in recognition of the "combustible gas" he used.[31] Though the term gas battery remained in use for a time, newer generations came to call it a fuel cell. And experimenters in the years around 1900 found fuel cells to be far more complex than Grove's gas battery.

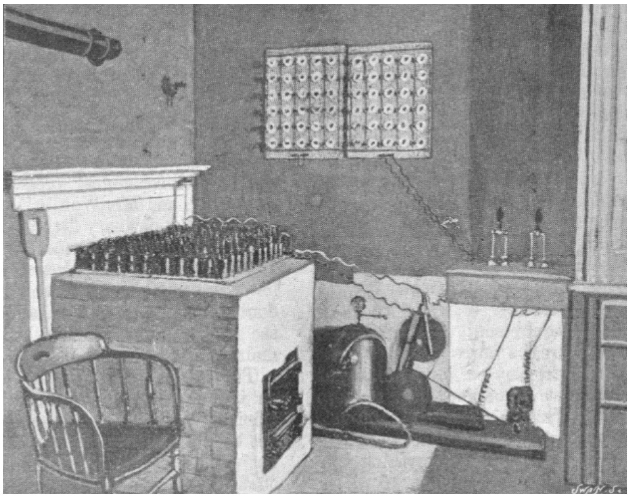

Figure 4. William Jacques' carbon battery apparatus showing the furnace at left with carbon cells on top, and air pump at center bottom. *Electr. Rev.* (London) **1898**, 42, 128.

Despite the flurry of work, fuel cells faded from the scene for reasons modern developers would recognize: costly materials and unfavorable economics.

COMPETITION

Ordinary batteries, for example, provided a less expensive alternative for important markets that needed low power devices. As with Morse's use of Grove's first battery, practical applications supported many battery producers, creating economies of scale. Aside from telegraphy, Alexander Graham Bell (1847-1922) and others used batteries to power telephone call stations and switchboards. The use of inexpensive materials like lead and the ease of refilling and refurbishing primary cell batteries also drove costs down.

Aside from single-unit applications such as telephones, electrical utilities in cities and towns connected large numbers of batteries into banks to buffer and regulate current on distribution grids. That application increased demand for batteries, attracted investment, and spurred research. In the larger scope however, most utilities required generators that produced bulk power, and neither batteries nor fuel cells could produce electricity at that scale.[32]

Nor could either efficiently produce the alternating current that many utilities wanted for their electric light and power systems. Though direct current proved useful for heavy motors and industrial applications, utility executives like Samuel Insull (1859- 1938) of Chicago's Commonwealth Edison pushed equipment makers to improve ac generator technology. In 1904, Insull opened Fisk Street Station that featured new steam turbine generators rated at 5 MW each.[33] The power industry's focus on steam and hydroelectric generators left little interest in low-power devices like fuel cells, although it did ultimately boost battery development in a roundabout way.

Utilities struggled in the early years to find customers for electricity generated outside of evening or morning hours when lighting demand peaked. Insull and others pushed daytime use of appliances like fans and irons, and equipment like pumps and elevators in order to keep generators spinning and improve return on invested capital. They identified automobiles as a potential market for so-called off-peak power. Early internal combustion engines were noisy, dirty, and unreliable, and many people saw battery-powered electric vehicles as the wave of the future. In the 1900s and 1910s, many utilities supported the idea of recharging electric vehicles overnight for urban use during the day.

Improvements in combustion engines and the creation of gasoline production and distribution infrastructures ultimately pushed electric vehicles aside, but that business model drove investment in battery research.[34] Edison developed his alkali batteries in hopes of entering the market via a route untapped by other inventors. Not for the last time, utilities or auto makers determined that component expense and the need for a continuous fuel supply made fuel cells an inferior choice compared to batteries. No mass market developed and fuel cells faded from the scene.

BACK TO THE LAB

Laboratory work continued during the early decades of the twentieth century. Karl Siegl (?-?) of Germany published a paper describing his gas battery work on the eve of the Great War. After the war, John G. A. Rhodin (1872-1941) of Britain returned to the idea of direct conversion of coal by asking, "Can the heat of combustion of coal be turned directly into electric energy?"[35] While fuel cells generated less interest outside the lab than in the 1890s, scientists explored several novel designs, leading to the diversification of fuel cell types.

Emil Baur (1873-1944) of Switzerland (with students at Braunschweig and Zurich) conducted wide-ranging research into different types of fuel cells during the first half of the twentieth century.[36] Baur and Hans Preis experimented with solid oxide electrolytes using such materials as zirconium, yttrium, cerium, lanthanum, and tungsten. Less electrically conductive than they hoped, their designs also experienced unwanted chemical reactions between the electrolytes and various gases, including carbon monoxide.[37] In the 1940s, Oganes K. Davtyan (1911-1990) of the Soviet Union added monazite sand to a mix of sodium carbonate, tungsten trioxide, and soda glass "in order to increase [electrolyte] conductivity and mechanical strength." This design also experienced unwanted chemical reactions and short life ratings, but work on high temperature devices by Baur, Davtyan and others paved the way for both molten carbonate and solid oxide fuel cells.[38]

Fuel cells in general, however, remained a solution in search of a problem. As Europe plunged toward the Second World War, a suitable problem suggested itself to British scientist Francis T. Bacon (1904-1992). Bacon suggested that fuel cells would be a good substitute for batteries on submarines, where hydrogen gas from damaged batteries could reach dangerous concentrations in the enclosed environment. Bacon set to work at King's College but after a short time the Royal Navy, battling German U-boats, reassigned him to a sonar project. Although promising, fuel cell research again gave way to other priorities.

No applications emerged during the war, but the research of Bacon and others set the stage for a resurgence of interest in fuel cells afterwards.[39] The onset of Cold War competition between the US and the USSR spurred increased investment in many technologies with potential military use, including fuel cells. During the 1950s and 1960s designers tested cells containing different electrolytes in a range of applications. At the same time, research investment in competing technologies reduced or eliminated other prospective fuel cell applications.

MANY POSSIBILITIES

After the war, Bacon moved to Cambridge and for the next twenty years experimented mostly with alkali electrolytes, settling on potassium hydroxide. KOH performed as well as acid and was less corrosive to the porous gas-diffusion electrodes he used.[40] Bacon's work showed good results, but nuclear energy better satisfied the power requirements for his original application. As demonstrated by USS *Nautilus* in 1954, compact nuclear reactors allowed submarines to stay submerged for extended periods without refueling. The new technology provided far more electric power than fuel cells and by 1960 the Navy deemed nuclear a superior alternative.

At the time, that seemed only an isolated example with little impact on fuel cell development. A post-war economic boom in the US unleashed a flood of ideas for civilian applications that leveraged Cold War military research. The popular press reported many fuel cell prototypes under development, from DeSoto's "Cella 1" concept car (figure 5) and Exide Battery's "Racer" to Electric Boat's submersible.[41] In 1959 Allis- Chalmers demonstrated a farm tractor powered by a stack of 1,008 alkali cells based on Bacon's work (figure 6). Generating 15 kW, the tractor could pull about 1400 kg (3000 lb.). Supported by the US Air Force, Allis-Chalmers pursued fuel cell research for some years, also testing a golf cart and a fork lift.[42]

Battery maker Union Carbide also experimented with alkali cells in this period. Karl Kordesch (1922-2011) and colleagues built on 1930s work by George W. Heise (1888-1972) and Erwin A. Schumacher (1901-1981), to make alkali cells with carbon gas-diffusion electrodes.

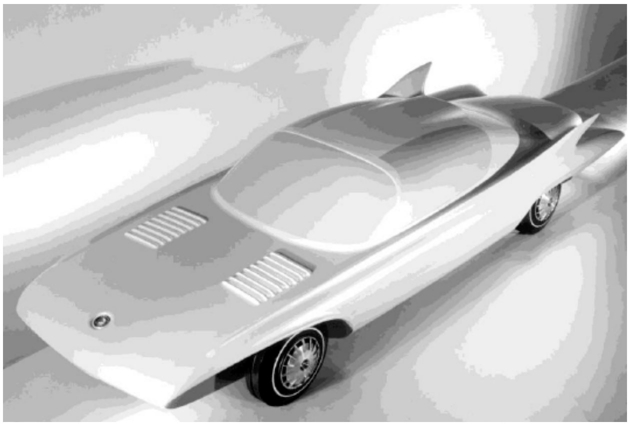

Figure 5. DeSoto "Cella 1" concept model, ca. 1959. From the Science Service Historical Images Collection, courtesy De Soto.

They demonstrated a mobile radar set for the US Army and designed fuel cells to run an undersea base. Kordesch turned heads in Cleveland, Ohio by driving around in a converted Austin A40 automobile powered by batteries and an alkali fuel cell.[43] Union Carbide also provided cells for General Motors' experimental "Electrovan" (figure 7).[44]

Amid the work on alkali cells researchers did not abandon acid electrolytes, and many turned to phosphoric acid. In 1961, Glenn V. Elmore (1916-2009) and Howard A. Tanner tested an electrolyte of 35 percent phosphoric acid and 65 percent silica powder pasted into a Teflon gasket. "Unlike sulfuric [acid]," they noted, "phosphoric acid is not reduced electrochemically under cell operating conditions."[45] The US Army explored the potential of phosphoric acid cells that ran common fuels like diesel as well as unusual fuels like hydrazine (figure 8). An industrial partnership known as the Team to Advance Research for Gas Energy Transformation, Inc. supported research in phosphoric acid cells for the electric power industry, and developed a series of power plants ranging from about 15 kW in 1969 to nearly 5 MW in 1983.[46] Unfortunately phosphoric acid proved a poor conductor of electricity. That among other issues slowed the pace of development.

Interest in high temperature fuel cells resurged after WWII due to their greater tolerance for fuel impurities.

Dutch scientists Gerard H. J. Broers (1920-2003) and Jan A. A. Ketelaar (1908-2001) began building on the prewar research of Baur and Preis, and Davtyan. They decided that limits on solid oxide conductivity and life expectancy made short-term progress unlikely so focused instead on electrolytes of molten carbonate salts. By 1960, they demonstrated a cell that ran for six months using an electrolyte "mixture of lithium-, sodium- and/or potassium carbonate, impregnated in a porous sintered disk of magnesium oxide." However, they found that the molten electrolyte was slowly lost, partly through reactions with gasket materials.[47]

Francis Bacon also began working with a molten cell, using two-layer electrodes on either side of a "free molten" electrolyte.[48] Other groups tested semisolid or "paste" electrolytes, and investigated diffusion electrodes rather than solid ones. Texas Instruments made molten carbonate cells for the Army that ranged in output from 100 W to 1 kW (figure 9). The promise of a cell with a stable solid electrolyte that could tolerate a variety of fuels sustained modest interest in solid oxides. Research-

Figure 6. Allis-Chalmers fuel cell tractor, 1959. From the Science Service Historical Images Collection, courtesy Allis-Chalmers

Figure 7. Sample Union Carbide KOH fuel cell for General Motors "Electrovan." NMAH catalog no. 2007.3061.01. Smithsonian Image.

Figure 8. A soldier refuels a 300 W hydrazine fuel cell, ca. 1964. Courtesy of the US Army Mobility Equipment R&D Center.

ers at Westinghouse experimented with a cell using zirconium oxide and calcium oxide in 1962.[49]

WHEN PRICE IS NO OBJECT

The post-WWII work produced prototypes and conference papers, but little in the way of practical devices. Fabrication costs continued to run high and substitute power sources existed for most potential applications. Only in the mid-1960s did an application emerge that took advantage of fuel cells: the US space program. Batteries sufficed for the first piloted spacecraft, the Soviet Union's Vostok and US' Mercury. But National Aeronautics and Space Administration (NASA) planners knew that batteries would be too heavy for lunar expeditions, and fuel cells gave the added advantage of producing potable water. When reaching the moon became a political priority, concerns about costs receded. NASA ultimately used two types of fuel cells, a novel design from General Electric (GE), and a derivative of Bacon's cell made by Pratt & Whitney.

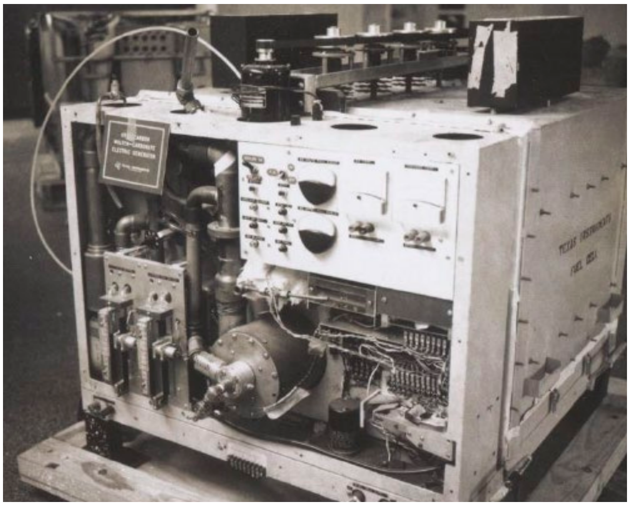

Figure 9. Texas Instruments 1 kW molten carbonate fuel cell. NMAH catalog no. 330031. Smithsonian image.

W. Thomas Grubb (1923-1994) and Leonard Niedrach (1921-1995) at GE developed a polymer electrolyte in the form of a thin, permeable sheet. In 1962, the company introduced the proton exchange membrane (PEM) fuel cell, proposing small units for the military. The unit ran on hydrogen made by mixing water and lithium hydride contained in disposable canisters. Though compact and portable, the cells' platinum catalysts were expensive.[50] The expense did not deter NASA officials who liked the compact size and chose PEM cells for Project Gemini. Missions lasting up to fourteen days would test in earth orbit equipment and procedures needed for lunar flights. Unfortunately for GE, their model PB2 unit experienced problems including internal cell contamination and oxygen leakage through the membrane. The first four short duration Gemini flights used batteries while GE hurriedly fixed the problems. Their new model P3 performed poorly in Gemini 5 but served adequately on six later flights.[51]

The PEM cells' problems boded ill for NASA's very fast schedule to reach the moon. Rather than risk additional delays, the agency chose Pratt & Whitney's alkali cells for Project Apollo's service module. The company had licensed Francis Bacon's patents in the early 1960s and moved into production (figure 10). The alkali cells performed well for Apollo, and a decade later space shuttle designers chose an updated version. Ultimately five shuttles made 135 flights between 1981 and 2011 with electrical power provided by alkali cells.

Powering spacecraft allowed researchers to gain operational experience with fuel cells. They could accept

Figure 10. Apollo fuel cell assembly at Pratt & Whitney. From the Science Service Historical Images Collection, courtesy Pratt & Whitney.

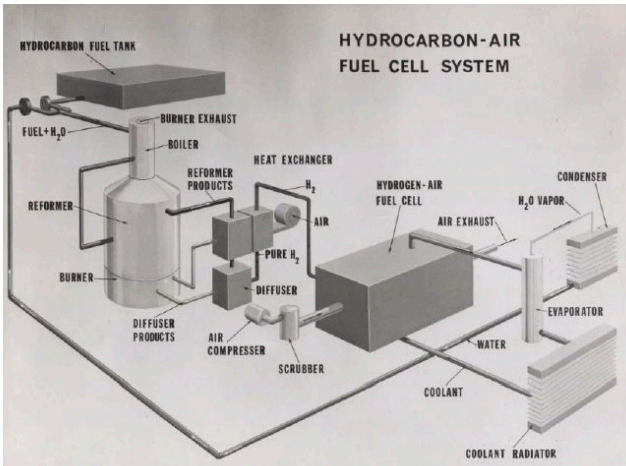

Figure 11. Diagram of fuel cell system. Courtesy of US Army Engineer Research & Development Laboratories.

high costs since few practical alternatives existed. Driven by politics, scientists and engineers spent the money needed to improve cell performance. But space applications proved too limited a market to support that level of research.

Technical hurdles remained intractable and researchers struggled to find a replacement for expensive platinum catalysts. Fuel cells still could not compete with other power sources in markets where costs mattered.

Another factor became clear during the post-WWII period: fuel cells were just one component in holistic power systems. Figure 11 shows a representative example. As Eisler points out, though Bacon and others chose to ignore this issue, fuel cells required ancillary equipment like reformers, hydrogen storage tanks, and inverters.[52] All those pieces, themselves complex, had to function compatibly when interconnected.

Modifications to one affected the others, increasing costs and complicating integration into the host device. If the application required the fuel cell assembly to function within a greater system, such as an electric power or transportation infrastructure, an external layer of compatibility issues arose. All power sources face these systems issues, but they add another disincentive to the high costs of adopting fuel cells.

In the 1960s, specialty markets proved too small to generate the economies of scale necessary to reduce fuel cell production costs. Potential mass markets took advantage of less expensive alternatives. Internal combustion engines could power cars, tractors, and motorbikes more economically than fuel cells. Gas turbine engines for aircraft were adapted for electric power stations; one was even displayed next to a fuel cell at the 1964 World's Fair (figure 12).[53] Propane engines could power fork lifts, batteries could run small submersibles and golf carts. Military users liked the idea of fuel cells but not well enough to add hydrogen fuels to their logistic supply chains.[54] They also grew wary of unfulfilled promises when technical and operational difficulties persisted.[55] Some companies (Allis-Chalmers, DeSoto), failed while others (Texas Instruments, Philco) ceased fuel cell research. Public and corporate interest waned and fuel cells' prospects again faded.

ENERGY & ENVIRONMENT

After the 1973 oil embargo, interest in new power sources rebounded and kept money flowing into fuel cell research. Two potential markets attracted significant investment: stationary electric power and automobiles. Utilities and auto makers faced the challenge of satisfying customers who demanded lower costs and less pollution.

Attempts to meet those demands led to another round of fuel cell prototypes and demonstrations during the 1990s and early 2000s. Press releases promised near term availability of commercial products, and indeed a few did emerge for backup and auxiliary power. However, as before, investment in competing technologies resulted in advances to alternatives that made fuel cells less attractive, hindering widespread adoption.[56]

Electric power utilities faced many difficulties beginning in the 1960s, including blackouts and soaring construction expenses.[57] High oil prices led utilities to abandon that fuel where possible but replacements often seemed no better. Nuclear technology faltered in the aftermath of the Three Mile Island meltdown and the Chernobyl disaster. Coal plants needed to install expensive equipment to control emissions that created acid rain and smog, offsetting the low cost of fuel. Renewable sources like solar and wind power were intermittent and expensive, while few acceptable sites remained for new hydroelectric plants.

Also, a backlash against large scale technical infrastructures led many people to question the basic concept of centralized power systems. Plans to expand high voltage transmission grids became politically contentious, especially near scenic or historically sensitive areas. Advocates of decentralized systems argued that small generating plants situated near users would reduce transmission losses, be less expensive to build, and limit the impact of malfunctions.[58] That idea came to be known as distributed generation.

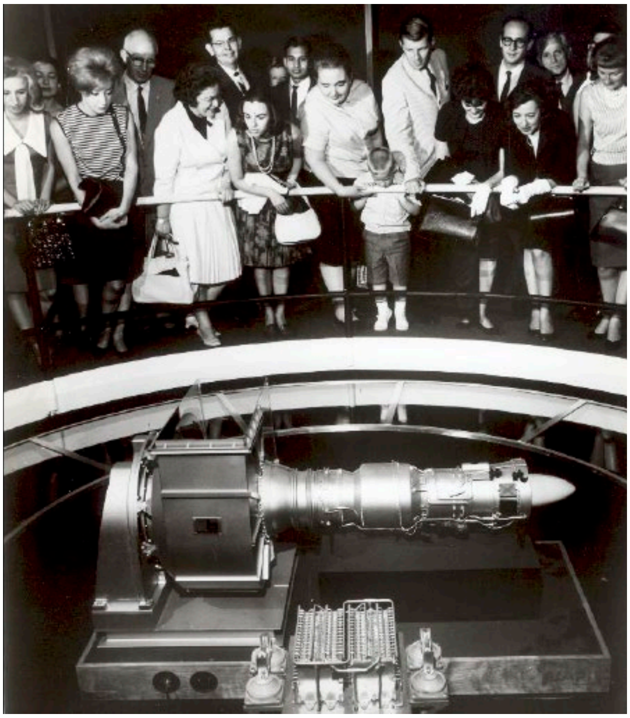

Figure 12. Fuel cell and gas turbine at the 1964 World's Fair. From the Science Service Historical Images Collection, courtesy American Gas Association.

Fuel cells held promise for distributed generation in two ways: as additions to localized power grids, and as stand-alone generators. Manufactured in relatively small, modular units, fuel cells' cleanliness made them especially attractive to pollution conscious urban planners. Nearly 200 fuel cells had been installed in Japan by 2001, including phosphoric acid units of up to 200 kW capacity, similar to the unit in figure 13.[59] In the late 1990s, the US Department of Energy worked with industry groups on several demonstration projects. One cogeneration unit coupled a solid oxide fuel cell with a microturbine, while a demonstration plant in Santa Clara, California, tested a molten carbonate stack.[60]

One urban plant demonstrated how non-technical problems could disrupt fuel cell adoption. Using mostly public and some private funding, Consolidated Edison built a 4.8 MW molten carbonate power plant in New York's Bedford–Stuyvesant neighborhood (figure 14). An extended period of inspections and reviews, spurred by local residents' fears about the underground storage of naphtha fuel, delayed the plant's opening date beyond the life of the fuel cells. Faced with the need to replace the expensive cells, Con Ed instead demolished the plant.[61]

Increased adoption of computer information systems led users to demand more electricity and better system reliability. Power fluctuations and outages created expensive service interruptions in commercial and industrial operations. Generating power onsite, fuel cells reduced demand on electric grids and provided backup power during blackouts. Police in New York City's Central Park were at first unaware of a 2003 blackout when their sta-

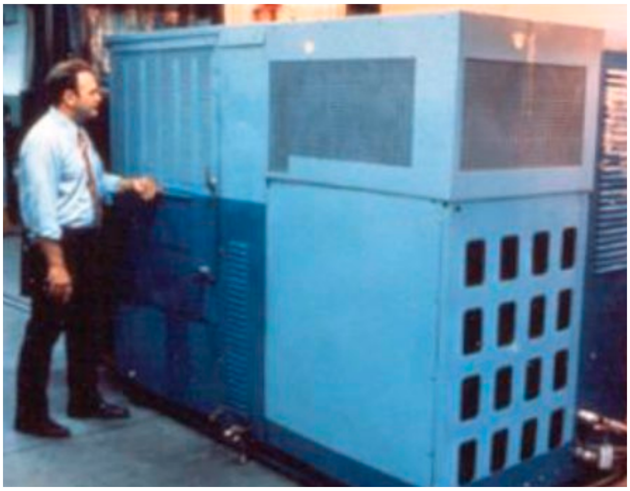

Figure 13. UTC 40 kW model PC-18 phosphoric acid fuel cell, 1979. Courtesy of the US Department of Energy.

Figure 14. Artist's rendering of the 4.8 MW Bedford–Stuyvesant fuel cell power plant. NMAH catalog no. 2008.0006.03. Smithsonian image.

tion's fuel cell kept lights and computers on. Seeking to tap the residential market, a company called Plug Power in 1998 demonstrated a stationary PEM unit in the Albany, New York house seen in figure 15. Promoted as the "first permanent home installation," the 5 kW power plant powered the home for about two years. The company partnered with GE and Detroit Edison with the goal of marketing a residential fuel cell by 2002.[62]

It seemed in the early 2000s that fuel cells might finally be finding a practical niche in stationary power, as several companies began selling commercial units. Advances in other technologies upset those plans, however. A substantial boost in natural gas supplies due to fracking led utilities to install more gas turbine power plants. Cost competitive wind turbines gave them yet another option to replace coal and nuclear plants. Breakthroughs in photovoltaics coupled with mass production dramatically cut the cost of solar cells. Utilities began installing solar farms for local use or to feed the grid. Many people installed solar panels to generate electricity for use or sale to local utilities during the day, while taking grid power in sunless times.

Manufacturers integrated small solar panels on equipment like road signs, replacing combustion generators and eliminating the need for either petroleum or hydrogen fuel.

AUTOMOTIVE CELLS

Like electric companies, car makers also needed to cut pollution and improve fuel efficiency. Unable to quickly adopt alternative fuels, they designed lighter cars with smaller engines, while pushing national governments to maintain oil supplies.[63] They also began to experiment, often under duress, with possible replacements for internal combustion engines. A compact fuel cell that emitted only water vapor held obvious attraction. Though high temperature and alkali cells would be ill-suited for cars, PEM cells looked promising. By 2002, major manufacturers were testing prototype fuel cell cars—and making grandiose promises, as Hultman and Nordlund noted.[64]

Figure 15. Plug Power house with PEM fuel cell in attached enclosure, 2001. Smithsonian image.

Transporting some form of hydrogen fuel constituted a major challenge. Few people would tolerate cars with exposed hydrogen tanks like Kordesch's Austin. One either needed a reformer to extract hydrogen from a fuel that existing stations could sell or to create a hydrogen distribution infrastructure. Either option would be difficult and expensive. Making, compressing, and storing hydrogen entailed high energy costs, cutting overall system efficiency.[65] Reforming fuel onboard the vehicle, as with a methanol fuel cell, provided one way to address the issue. However, byproducts of the reforming process poisoned cell catalysts, a familiar problem, and corrosion problems required use of an acid electrolyte.[66] The byproducts also belied claims of a non- polluting engine.[67]

Centralized refueling stations for urban trucks and buses, like the battery recharging stations of the early 1900s, seemed a reasonable first step. H-Power, Georgetown University, and the Energy Department adapted a 50 kW Fuji Electric phosphoric acid cell for transit buses and began test runs in 1994 (figure 16). Phosphoric acid cells require an extended warm-up period, making them better suited for commercial vehicles than for personal cars. Four years later, Georgetown, Nova BUS, and the US Transportation Department began tests of a bus powered by a 100 kW cell from a joint venture of Toshiba and United Technologies.[68]

Figure 16. H Power phosphoric acid fuel cell bus, 1996. Courtesy of the US Department of Energy.

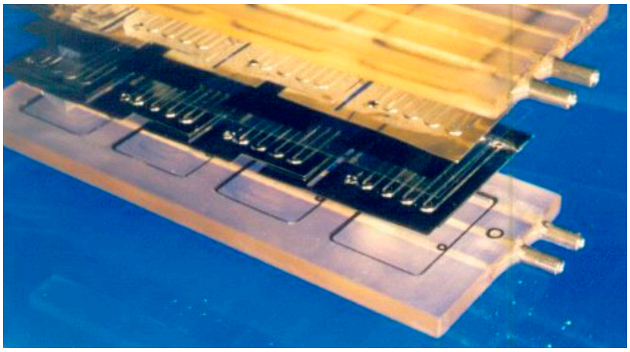

Figure 17. Micro-fuel cell by Fraunise ISE for mobile phone. Courtesy of Fuel Cells 2000.

During this time an unexpected cost hurdle emerged. One of the most expensive materials in many fuel cells, platinum, also proved critical for the catalytic converters that car makers needed to control engine emissions. Increased demand for platinum raised the price of the already expensive metal. Replacing an internal combustion engine with a fuel cell might eventually remove the need for catalytic converters and substitute one platinum containing product for another. But such a shift might take decades, and that pushed cost reductions too far out for most investors, reducing the attraction of automotive fuel cells.

Another option was to find a bridge technology that could work with the existing petroleum infrastructure. In 1997, major auto makers began to promote gas-electric hybrid vehicles that used a small gasoline motor in combination with an electrical generator to recharge batteries or power electric motors. They also invested at least as much in battery research as in fuel cells. The Tesla electric automobile in 2003 along with the company's massive battery factory in Nevada shows how sustained research and investment in both product and power source might lead to economies of scale.

Commercially available hybrids and battery powered cars began moving a market that might have supported mass production of fuel cells in a different direction.

Advances in battery technology also disrupted another potential market: portable electronics. Several companies experimented with micro fuel cells they hoped could replace rechargeable batteries in cell phones, laptop computers, and portable audio players (figure 17). Millions of small electronic devices created environmental concerns about the disposal of used batteries containing toxic materials like cadmium and mercury.[69] A Motorola engineer at a 2001 conference reported problems with water transport in cells for phones, but claimed progress on a cell for laptop computers.[70] Before commercial products could be introduced though, new nickel-metal hydride and then lithium-ion batteries changed the market. Despite the latter's thermal problems, batteries were easier to integrate into electronic devices than micro fuel cells.

One 2013 study found 109 firms in nine countries engaged in fuel cell research partnerships.[71] Despite all that effort and publicity, by the early 2010s fuel cells again fell out of favor. Plug Power demolished their test house in 2002 and shelved plans for residential PEM fuel cells. The Tennessee Valley Authority reactivated a closed nuclear facility instead of installing a regenerative fuel cell system. Auto makers, who promised affordable fuel cell vehicles in showrooms by 2004, quietly pulled back from all but a few high-priced models. US government funding for fuel cells was cut in 2008, with one official citing "four miracles" needed to bring the technology to market.[72] Even in spacecraft like the International Space Station, high efficiency solar panels rather than fuel cells provided power.

LESSONS OF NON-CYCLICAL HISTORY

Nearly two centuries after Grove's discovery, fuel cell researchers have made significant advances even while the basic concept remains unchanged. Thrice during that period fuel cells seemed on the verge of widespread adoption only to fade from view. History never repeats, despite the tired old adage. So how are we to take lessons from an account that seems to do just that? One key is to look for changes in the larger societal contexts within which technologies exist, especially economic and political changes, while remembering that human nature tends to persist. Understanding context helps explain historical differences. Understanding people helps explain historical similarities.

One lesson is to look beyond functional elegance to mundane economics. Since 1839 people have been captivated by the idea of combining hydrogen and oxygen to generate electricity and water. There simply must be a way to use that idea, so fuel cells have always been a solution in search of a problem. Yet technical elegance is neither necessary nor sufficient to produce a return on investment. Every time engineers found a seemingly realistic use for fuel cells, a competitor better met users' needs. Internal combustion engines, steam turbines, photovoltaics, and batteries all set technical and economic challenges for developers. But each of those power sources attracted additional investment that advanced their capabilities when a compatible application proved commercially successful. Advocates should pay close attention to alternate technologies and business models because there are no uncompetitive applications for fuel cells.

Nineteenth century researchers would recognize many difficulties their descendants struggle with. The need for expensive rare earths, especially platinum, is one; the need for readily available pure gases is another. Yet the technical environs within which those difficulties exist have changed. Inexpensive solar cells may enable efficient production of pure hydrogen. Recent experiments with aqueous fuels based on recyclable boron hydride may offer a sustainable fuel distribution infrastructure without the energy loss of compressing hydrogen.[73] Still, the basic material costs must be dramatically reduced for fuel cells to become commercially competitive.

Today's researchers do face hurdles many of their predecessors did not. For one, the need to design equipment that meets established standards. Whether those are electrical, manufacturing, or safety standards, once in place new devices must operate within those set parameters. Standards can advance quality and promote efficiency. Setting standards is an act of control that can eliminate some competitors and raise costs for others.[74] Standards internal to fuel cell technology have been crafted, but engineers must also account for external standards like building codes that affect other power sources as well.[75]

A related difference is the need for economic compatibility with associated system components. Fuel cells must work with power inverters and control equipment; ideally those should already exist in manufacturers' product catalogs. Special versions of those components can be made, but that introduces additional design, testing, fabrication, and certification costs that are counterproductive. Incompatible variations between fuel cell types exacerbates the problem.

Fuel cell researchers today enjoy advantages their predecessors could only dream of, such as computer-aided design and fabrication tools. The ability to model physical and chemical interactions before making experimental devices speeds research. Additive manufacturing may permit economical production of complex component designs. Researchers today also have the internet, a high-speed global communications system that permits far-flung collaborations. Access to searchable digital archives makes the results of ongoing and past research readily available. Changes in information technology shift the basic nature of scientific and engineering research in ways that should not be underestimated.

One of the most enduring human features of fuel cells is the feeling among advocates that solutions are close. In 1884, Edison gave himself five years to find an answer, and expected some "lucky" person would succeed.[76] In 1960, two GE engineers felt that use in "special applications...within the next five years" was "likely."[77] In 2010, a Penn State engineer commented on the "fickle" nature of US government support, giving another five-year estimate "to make hydrogen technologies consumer- ready."[78] In 2013, a policy analyst recognized that companies, "always believed things could be fixed with a little more time and a little more money;" and then proposed a major national research program "to uncover the secrets of the fuel cell."[79]

In part those feelings stem from technical naiveté conflating fuel cells that run on pure hydrogen with those that run on other fuels, a definitional difference that Eisler noted.[80] The economic and energy problems that made pure hydrogen a poor fuel choice have not been solved by research on reforming coal, gas, or petroleum fuels.

Technical advances provided a dose of positive reinforcement but failed to meet users' immediate needs as well as other technologies. A cold accounting for recurring optimism may indeed be "disheartening for young [engineers]," but it is also essential to avoid another round of wasted money and dashed hopes.[81] Practical fuel cells will not emerge from the lab unless they can be produced and operated sustainably in both environmental and economic terms.

Other similarities and differences exist, and we cannot predict how this story will unfold. Perhaps fuel cells are doomed to perpetual impracticality. Perhaps persistence will finally lead to mass adoption. Few people doubt the unsustainability of fossil fuels, only the timing of when they will run out or be abandoned to mitigate climate change. So demand for clean, low-cost power sources seems assured. Perhaps batteries and renewables will meet that demand. Perhaps a politically-driven shift away from combustion engines coupled with low-cost hydrogen generated using cheap solar power will radically alter energy costs in favor of fuel cells. We shall see.

In the meantime, we should approach with care the advice of Jons Jakob Berzelius as recalled by John Rhodin in 1926. "Let us patiently search Nature, she always gives an answer if we search long enough."[82] Sometimes patience indeed pays off. But as generations of fuel cell researchers can attest, sometimes nature refuses to cooperate and the answer is not what we want to hear.

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How the West was Won?
A History of Organic Photovoltaics

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Abstract. The history of organic photovoltaics has been characterised by the complex interplay between fundamental research, large scale manufacture and commercialization activities. In addition, the field is highly interdisciplinary; ranging across physics, chemistry and engineering. This environment has resulted in a frontier character to the field, with researchers constantly expanding into new areas and confronting new challenges as the area has developed. This article seeks to chart the developments in organic photovoltaic research, with emphasis on the last two decades, to provide some historical context to current status of the field.

Keywords. Photovoltaics, Conjugated Polymers, Renewable Energy, Flexible Electronics, Roll-to-Roll Printing, Bulk Heterojunction.

> *Come forth into the light of things,*
> *Let Nature be your Teacher.*
> —William Wordsworth
>
> *We have dominated and overruled nature, and from now on the earth is ours, a kitchen garden until we learn to make our own chlorophyll and float it out in the sun inside plastic membranes.*
> —Lewis Thomas

1. GO WEST YOUNG MAN
(SETTING THE SCENE)

The interaction of light with matter has framed existence since the Earth was first formed some 4.5 billion years ago, with the key step in abiogenesis being the synthesis of complex organic molecules occurring via photochemical processes. Ultimately, the creation of the biosphere via photosynthesis and the consequent development of our entire ecosystem has, of course, been driven by light-matter interactions. More recently, the expansion of human civilization has been enabled by the energy resources contained within fossil fuel sources; representing the historically stored effects of ancient photochemical processes.

The direct generation of electrical energy from light is a much more recent phenomenon. Photoelectrochemical effects were first reported in 1839, with the French physicist Alexandre Edmond Becquerel (1820–1891) observing the photovoltaic (PV) effect via an electrode in a conductive solution exposed to light.[1, 2] In 1876 William Grylls Adams (1836–1915) and his student, Richard Evans Day, observed the photovoltaic effect in solidified selenium, and published a paper; 'The action of light on selenium' in the Proceedings of the Royal Society.[3] In 1883 the American inventor Charles Fritts (1850–1903) developed the first selenium wafer based solar cells. These cells, which were typically around 2 x 2.5 inches in size, had a power conversion efficiency of around 1% and employed an extremely thin layer of gold as a transparent electrode.[4]

The history of the modern silicon solar cell (Figure 1) is much more recent. On April 25, 1954, Bell Labs announced the invention of the first practical silicon solar cell. Shortly afterwards, they were shown at the National Academy of Science Meeting. These cells had about 6% efficiency. The New York Times forecast that solar cells may eventually lead to "the beginning of a new era, leading eventually to the realization of one of mankind's most cherished dreams – the harnessing of the almost limitless energy of the sun for the uses of civilization."[5] Since then there has been an enormous development of silicon (and other inorganic) solar cell, technologies. Early work determined that the maximum theoretical efficiency of a single junction cell is 33.16%, the Shockley-Queisser limit[6], and maximum values of 27% have been reached for single junction crystalline Si cells[7], with four junction cell efficiencies of 39% achieved.[8]

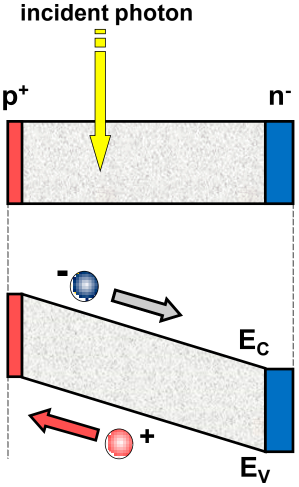

Figure 1. Schematic of modern silicon solar cell. Light absorbed in intrinsic region and creates free electron-hole pairs. The built-in electric field separates charges with holes migrating to the p-doped region and electrons migrating to the n-doped region; resulting in a tilting of the conduction (E_C) and valence (E_V) energy bands in the material.

Perhaps surprisingly, the history of photoelectrical processes in organic molecules is almost as long as that of inorganic materials. The photoconductivity of anthracene was first studied by the Italian physical chemist Alfredo Pochettino (1876–1953) at Sassari, Italy in 1906 [9] and later by Max Volmer (1885–1965) at Leipzig in 1913.[10] In 1958 the Nobel Laureate Melvin Calvin (1911–1997) and his student David Kearns worked with magnesium phthalocyanines (MgPc), measuring a photovoltage of 200 mV.[11] This early work suggested that a photovoltaic effect could be observed if a sandwich cell consisting of a low work function metal, an organic layer and a high work function metal (or conducting glass) is illuminated. Throughout the 1960s and onwards many organic dyes and biomolecules were discovered to exhibit photoconductivity and a photovoltaic effect, however it was not until the mid-1970's that this phenomenon would be utilized to generate electrical currents.

2. RIDING THE RANGE (THE FIRST DEVICES)

The first true organic photovoltaic (OPV) devices were developed in the 1970's and incorporated small organic molecules with porphyrins being a natural place to start given their fundamental role in photosynthesis. In 1975 Ching W. Tang (b. 1947) and Andreas C. Albrecht (1927–2002) at Cornell University showed that chlorophyll-a (Chl-a) from green spinach (Figure 2) could be sandwiched between metal electrodes and under optimal conditions (Cr/Chl-a/Al) had a power conversion efficiency (PCE) of 0.01%; orders of magnitude better than other organic devices at the time (which had efficiencies of around 10^{-6} %) and arguably the first working example of an organic solar cell.[12] In 1978 Larry R. Faulkner (b. 1944) and his student Fu-Ren OPVFan (b. 1946) demonstrated the generation of short circuit photocurrent in zinc and free base phthalocyanines (ZnPc and Pc, respectively) when sandwiched between an ohmic contact (Au) and a blocking contact (Al or In).[13] In 1979 Geoffrey Chamberlain and Peter Cooney of Shell Research Ltd observed similar effects in Al/CuPc/Au cells.[14]

In 1983 Chamberlain published "Organic Solar Cells: A Review" proclaiming that "remarkable progress

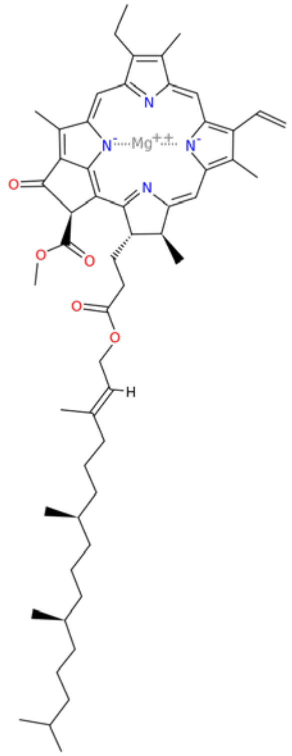

Figure 2. Structure of chlorophyll-a (Chl-a).

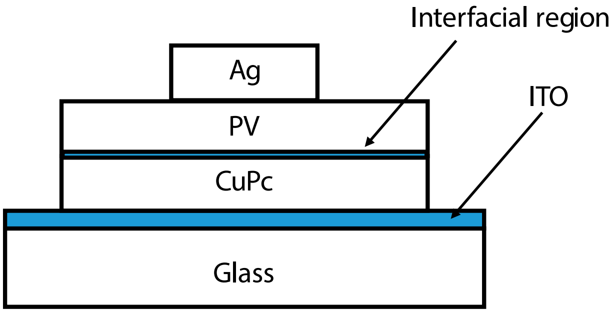

Figure 3. Schematic of Tang's bilayer device using copper phthalocyanine (CuPc) and a perylene tetracarboxylic derivative (PV).

has been made in recent years in improving the sunlight efficiency from about 0.001 % in the early 1970s to about 1% recently" and describing the range of porphyrin, phthalocyanines and other small molecules which had been been observed to produce photovoltaic effects.[15] Interestingly, even in these early days of organic photovoltaic research Chamberlain noted that "it is generally accepted, however, that cell efficiencies must be as high as possible and at least 5% to offset area-related costs arising from encapsulation materials, support structures etc."; beginning an efficiency-based bias which has haunted the OPV field ever since.

In 1986, Ching Tang was able to show (by fabricating a bilayer device with copper phthalocyanine and a perylene tetracarboxylic derivative) that the interfacial region was responsible for the generation of photocharges and therefore, for determining the devices photovoltaic properties. Exciton dissociation is known to be efficient at interfaces between materials with different electron affinities and ionization potentials, where the electron is accepted by the material with larger electron affinity and the hole by the material with lower ionization potential. A significant advantage of this device architecture over the prevalent single material devices was that charge generation was no longer dependent on the electric field but rather the work functions of the two layer materials. A PCE of ~1% was achieved.[16]

The process of photosynthesis (the conversion of solar energy into chemical energy) involves two protein complexes, photosystem I (PSI) and photosystem II (PSII), that drive photoinduced electron separation. Interestingly, and despite decades of research, by 2017 the best solid-state solar cell device based on photosystem I (PSI) still has a PCE of only 0.069%.[17] However, in 2018 Shengnan Duan fabricated devices by combining Chl-a as the PSI simulator (electron acceptor) with Chl-D as the PSII simulator (electron donor) in an indium tin oxide (ITO)/ZnO/Chl-a/(Chl-Ds)/MoO_3/Ag structure which mimicked the pathway of photoinduced electron transport from photosystem II (PSII) to photosystem I (PSI) in nature (Figure 4).[18] The optimized devices had a PCE of 1.30%, much higher than devices based on PSI alone.

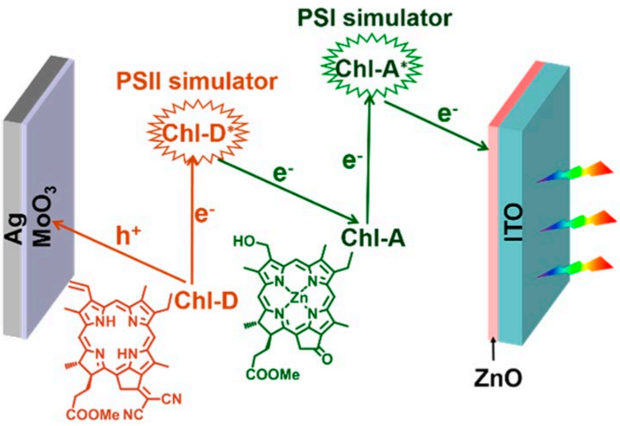

Figure 4. Schematic of indium tin oxide (ITO)/ZnO/Chl-a/(Chl-Ds)/MoO3/Ag devices mimicked the pathway of photoinduced electron transport from photosystem II (PSII) to photosystem I (PSI) in nature. Reprinted with permission from 18. Copyright (2018) American Chemical Society.

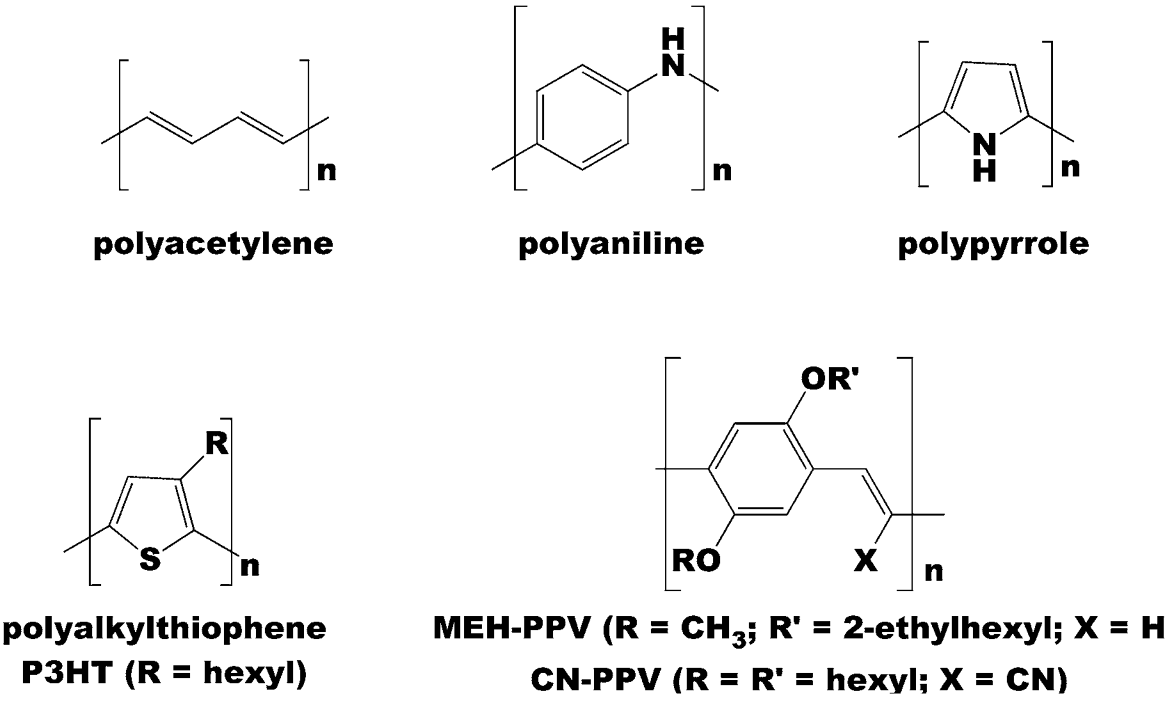

Figure 5. Chemical structures of some common conducting polymers.

By comparison, the history of conjugated and conducting polymers also dates back to the early 19th century.[19] Beginning in 1834, various forms of oxidized polyaniline were produced by Friedlieb Ferdinand Runge (1794 –1867) via the oxidation of aniline, although the structure of these materials was not determined until 1920.[20] In 1963 an important breakthrough in the field occurred when Donald Eric Weiss (1924–2008) and coworkers at CSIR, Australia identified iodine doped derivatives of polypyrrole (Figure 5) with resistivities down to 0.1 Ω.cm.[21-23] Until this time, other than conductive charge transfer complexes, organic molecules were still considered insulating materials. However, publishing in the Australian Journal of Chemistry, the initial results were not widely recognized or known. Nevertheless, a new class of compounds was born and gradually additional reports of conducting polymers encompassing new examples of oxidized polyacetylenes,[24] polyanilines, [25-28] and polypyrroles[29] surfaced. Finally, in 1977 Alan J. Heeger (b. 1936), Alan G. MacDiarmid (1927–2007) and Hideki Shirakawa (b. 1936) reported highly conductive, doped polyacetylene.[30] Following their award of the 2000 Nobel Prize in Chemistry for "the discovery and development of conductive polymers", this developing field became widely recognized and conducting polymer research exploded.

2.1 Single layer junctions – the earliest polymer OPVs

Interest in conjugated polymers as photovoltaic materials really commenced in 1994 when Heeger and co-authors fabricated photodiodes of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV; Figure 5) between indium tin oxide and calcium electrodes. The open circuit voltage (V_{OC}) and short circuit current (Isc) under 20 mW/cm^2 were 1.05 V and 1.1 μA/cm^2, respectively, and the sensitivity and the quantum yield at - 10 V were 5×10 mA/W and 1.4% el/ph (electrons per photon).[31]

Schottky cell devices fabricated from other conjugated polymers at the time (such as polyacetylene[32] and poly(alkylthiophenes)[33]) showed similar (low) efficiency photovoltaic behavior. In 1996 Lewis J. Rothberg (b. 1956) and coworkers, working on PPV diode devices[35,36], showed that a significant issue associated with simple single material organic diodes and solar cells is that exciton dissociation must occur at the dye/polymer electrode interface since the built in electric field imposed by the electrode materials is insufficient to drive charge separation. This limitation severely restricts the charge generation efficiency of the device and increases the likelihood of recombination of separated charges. In 1996 Richard Friend (b. 1953), Andrew Holmes (b. 1943) and co-workers produced bilayer MEH-PPV/C_{60} OPV

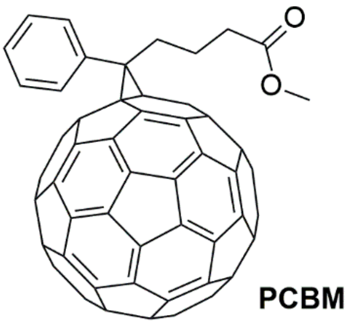

Figure 6a. Chemical structure of phenyl-C61-butyric acid methyl ester (PCBM).

devices. They showed that excitons generated in the MEH-PPV layer had a diffusion length of 7±1 nm and that photocurrent was only generated by excitons formed within this distance of the MEH-PPV-fullerene interface. Devices with a PCE of ~1.5% were achieved.[37]

2.2 Bulk heterojunctions – altering the paradigm of polymer OPVs

However, one of the most significant advances in polymer OPV research occurred in 1995 when Richard Friend, Andrew Holmes and co-workers applied the principles observed by Ching Tang in 1986 to produce highly efficient photodiodes from interpenetrating networks of MEH-PPV and poly(2,5,2′,5′-tetrahexyloxy-7,8′-dicyano-p-phenylene vinylene (CN-PPV; Figure 5). Phase separation of the two materials led to the spatially distributed interfaces necessary for efficient charge photogeneration, as well as the connected domains required to collect both the electrons and holes.[39]

Coincidentally, also in 1995, Fred Wudl (b. 1941) and co-workers overcame a major barrier to the use of fullerenes in OPV devices by reporting the synthesis of a range of soluble methanofullerene derivatives suitable for solution deposition of active layers.[40]

Previous work by Alan Heeger, Fred Wudl and co-workers in 1992 had demonstrated picosecond charge transfer from photo-excited conducting polymers (MEH-PPV) to fullerene (C_{60}).[38] Alan Heeger, Fred Wudl and co-workers then combined these ideas, taking advantage of the near perfect charge transfer between conducting polymers and fullerene by blending MEH-PPV with one of these methanofullerenes (phenyl-C61-butyric acid methyl ester or PCBM; Figure 6) together in an OPV device active layer with a 1:4 ratio. The resultant bicontinuous network (or bulk heterojunction; BHJ) resulted in devices with a PCE of 2.9%, more than two orders of magnitude higher than devices of MEH-PPV alone.[41]

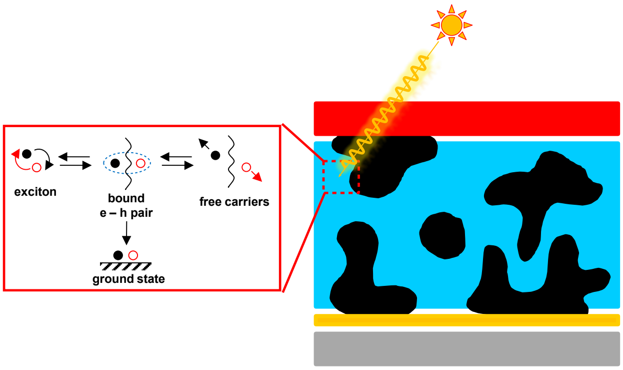

Figure 6b. Schematic of bulk heterojunction (BHJ) structure and charge generation process in OPV devices. An incident photon generates a coupled electron-hole pair (exciton) which diffuses to a donor (polymer) – acceptor (fullerene) interface to form a bound electron-hole pair. This bound state can then either recombine or separate into free charge carriers to generate a photocurrent.

Subsequently, N. Serdar Sariciftci (b. 1961), Jan C. Hummelen and coworkers showed that control of blend morphology in MDMO-PPV:PCBM devices was critical to optimized device performance.[42] Interestingly, the authors proposed that the PCE of 2.5 % achieved in these devices “approaches what is needed for the practical use of these devices for harvesting energy from sunlight”. Indeed, the BHJ active layer morphology has remained the basis for the majority of OPV devices to this day.

2.3 The Focus on Metrics – the millstone around the neck of OPVs

From the first days of OPV there has been an arguably disproportionate focus on PCE as the key metric for device performance. From 1993, Martin Green (b. 1948) has published regular (biannual) sets of solar cell and module efficiency tables summarizing the highest independently confirmed results for different technologies in *Progress in Photovoltaics*. As well as keeping researchers informed of the state-of-the-art in the field, a stated aim of these tables is “the encouragement of researchers to seek independent confirmation of research results and the further simulation of intercomparison of measurements between designated cell test centres”.[43]

Unfortunately, despite the importance of this topic and the clear necessity for rigorous characterization of devices in the field, independent confirmation of device performance (and in particular PCE) is still not commonplace. Whilst the highest performing devices are routinely tested by certified laboratories, such as the National Renewable Energy Laboratory (NREL), logistics and expense prohibit the vast majority of devices in published reports from being tested outside of the reporting laboratory.

This situation has led to some controversy in the field. In 2007 Rene Janssen (b. 1959) published a rebuttal of a paper by Wong et al. (July 2007 issue of *Nature Materials*) that presented a new platinum metallopolyyne donor polymer (P1) with a bandgap of 1.85 eV that provided a photovoltaic power-conversion efficiency, η, of up to 4.93% in combination with a C60 fullerene derivative (PCBM) as acceptor. This high efficiency represented an important step towards the development of more efficient plastic solar cells. Rene Janssen argued, however, that the optical properties of the new polymer presented in the paper were incompatible with the published high efficiency and that — based on the optical data — the efficiency was unlikely to exceed 2%.[44] In response, in 2008 the journal *Solar Energy Materials and Solar Cells* resorted to using an editorial to provide a guide on how efficiency data should be reported, especially whenever power conversion efficiencies require external quantum efficiencies (EQE) values above 50% over a large range of wavelengths or when reported power conversion efficiencies exceed 2.5%. In particular they stated that "extra care should be taken in submitted manuscripts to document the measurement's quality, relevance and independent verification".[45]

In 2011, the International Summit on OPV Stability (ISOS) published a series of generally agreed test conditions and practices to allow ready comparison between laboratories and to help improve the reliability of reported values.[46] In 2012 Henry Snaith (b. 1978) published "The perils of solar cell efficiency measurements", a critique on the use of PCE for characterising OPV devices." He pointed out that PCE as a performance metric has become so influential and has such a high level of perceived importance that it is now widely used as a key parameter for assessing the value or worth of an entire solar technology, particularly for new and emerging solar technologies, which must constantly justify their existence. Furthermore, in the specific field of OPV, ignorance and negligence are frequently causing solar cells to be mischaracterized, and invalid efficiency results have been reported in a number of journals.[47]

Unfortunately, little has changed since this time. Independent certification of "record" devices is now essentially mandatory for publication, but routine certification of published device performance is not commonplace. In light of the import which is placed upon OPV device efficiency by researchers and reviewers this oversight is a major problem and poses a significant barrier to the transfer of knowledge between practitioners.

3. THE TAMING OF THE OLD WEST (THE NEW MILLENNIUM AND THE MATURING OF THE FIELD)

In 2002, Pavel Schilinsky (b. 1974) reported the characterization of new poly(3-hexylthiophene):methanofullerene [6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM) solar cells, with a PCE of 2.8% and began a fascination with this material system which dominated the OPV research scene for a decade, and has continued to this day.[48] The appeal of the P3HT:PCBM system is not hard to see. Even the initial Schilinsky publication highlighted the excellent interpenetrating "bulk heterojunction" phase morphology, ideal for efficient photovoltaic performance.

Monochromatic (550 nm, the absorption maximum) external quantum efficiencies of up to 76% and internal quantum efficiencies of close to unity were reported and recombination of photoinduced carriers was negligible when operated in the photovoltaic mode. As a polymer, P3HT was easy to synthesize at large scale,[49-54] considerably more soluble and oxidatively stable than the PPV-based polymers which had been studied previously[55] and P3HT's semi-crystalline nature meant that thermal[56, 57] and solvent-annealing[58] of the blended active layer could be readily used to optimize donor and acceptor domain sizes and crystallinity.

Consequently, P3HT:PCBM solar cells became the "Best Seller in Polymer Photovoltaic Research" with Guillaume Wantz (b. 1977) and co-workers reviewing 579 papers published between 2002 and 2010 alone. The PCE of the P3HT:PCBM solar cells reported in these publications is moderate at best, with a wide range of reported values averaging around 3% and approaching 5% at best.[59] Nonetheless, P3HT remains a key model polymer for research in organic solar cells. However, as pointed out by Darren Lipomi (b. 1983) and co-workers, P3HT is structurally and morphologically very different from the majority of new generation polymers in OSC research. Consequently, the validity and value of transferring design and processing knowledge from the P3HT material system must be questioned.[60] Ultimately, however, the relatively poor overlap between the absorption of P3HT and the sun's irradiance spectrum prohibits significantly higher PCEs and this mismatch has driven the development of polymers with lower bandgaps which better match the suns irradiation.[61]

3.1 Lower Band gap materials

In polymer:fullerene solar cells the primary light absorbing component is the polymer, since most fullerenes do not absorb strongly in the visible and near-IR, where terrestrial solar intensity is at its greatest. Indeed, Paul Dastoor (b. 1968) and coworkers have shown that PCBM contributes only ~13% of the photocurrent in a P3HT: PCBM device under AM 1.5 illumination.[62] Consequently, over the last decade or so, attention has been focused at tuning and reducing the optical bandgap, *Eg*, of the polymer to increase device light absorption.[63]

The bandgap which determines light absorption in a conjugated polymer is a result of overlap and delocalization of π-orbitals along the polymer backbone. Increasing the planarity of this backbone maximizes the p-orbital overlap and extends the π-delocalization, lowering the bandgap.

A range of both structural and electronic methods have been employed to alter polymer planarity and/or π-delocalization.[64] Structurally, fused ring systems (either fully aromatic or using bridging atoms) and the use of steric peripheral groups on the backbone are both routinely used to enhance polymer planarity. Increasing the quinoidal nature of linked ring systems breaks aromaticity (and thus electron confinement to the ring), which allows more extensive delocalization. This last effect is particularly prevalent in polythiophene polymers, in part explaining their success in the OPV field.

Planarity of the polymer backbone is not the whole story however. P3HT itself can form ordered microcrystalline domains in which the polymer backbone is highly planar,[65] but has a wide bandgap of ~1.8 eV (which means it has a maximum solar photon absorption of ~ 46 %).[66]

The optical bandgap can be further reduced by alternating electron rich (donor, D) and electron poor (acceptor, A) subunits along the polymer backbone. The resulting molecular orbital mixing and intermolecular charge transfer between the D and A moieties produces a new set of hybrid molecular orbitals with a bandgap that can be lower than either of the subunits alone. In addition, it has been proposed that alternation of the donor and accepting components increases the double bond character between the units, which could enhance planarity and further decrease the bandgap.[67]

In 2006 Paul Blom (b. 1965) and co-workers presented model calculations for the potential for polymer: fullerene solar cells. They predicted that lowering the band gap of the polymer would result in devices exceeding 6% and that, ultimately, with optimized level tuning, band gap, and balanced mobilities polymeric: fullerene solar cells could reach power conversion efficiencies approaching 11%.[68] The first truly low bandgap polymer, poly(isothianaphthene) was reported by reported by Fred Wudl in 1984, with a bandgap of ~1.0 eV,[69] but initially the synthesis of suitable, soluble low band gap materials proved difficult.[70] However, in 2002 Christoph Brabec (b. 1966) et al. reported ~1% efficient devices from the recently synthesized poly(N-dodecyl-2,5,-bis(2'-thenyl)pyrrole-alt-2,1,3-benzeothiadiazole) (PTPTB) with PCBM. PTPTB consists of alternating electron-rich N-dodecyl-2,5,-bis(2'-thenyl)pyrrole (TPT) and electron deficient 2,1,3-benzeothiadiazole (B) units and is the first example of the use of a molecularly engineered lower bandgap material in OPV devices. The electrochemical bandgap of the polymer was determined to be 1.77 eV, placing just within the range of low bandgap materials as defined by the authors (*Eg* <1.8eV) but higher than the official definition as set in the Handbook of Conducting Polymers. (*Eg* <1.5eV).[71]

Since these humble beginnings, a wide range of donor-acceptor low band gap polymers have been synthesized from a growing catalogue of donor and acceptor building blocks.

In 2011 Mitsubishi Chemical announced the first certified single junction organic solar cell with a PCE of >10%.[72] The device was certified at NREL, but no detail information on either the active layer composition or the device structure was given.

The first device to reach the η > 10% milestone published in a full peer review journal, was a polymer tandem solar cell with a PCE of 10.6% reported by Yang Yang (b. 1958) and coworkers in 2013.[73] The D-A polymer used was poly[(5,5-bis(3,7- dimethyloctyl)-5H-dithieno[3,2-b:2',3'-d]pyran-2,7-diyl)-alt-(5,6-difluoro-2,1,3-benzothiadiazole-4,7-diyl)] (PDTP-DFBT) with a reported bandgap of 1.38 eV, in conjunction with PC71BM. A single-junction device was also reported with a spectral response that extended to 900 nm and which had a PCE of 7.9%. Since then, progress in OPV development has been rapid, especially in terms of electrode interfacial layers, new active layers (ternary systems), and the synthesis of new low bandgap polymers. The current certified efficiency record for a single junction organic solar cell lies at 11.2 ± 0.3% by Toshiba.[8, 74]

3.2 Understanding the Fundamental Physics

It was realized early on that the physical behavior of semiconducting polymers is dominated by their relatively low dielectric constant compared with that for inorganic semiconductors (ε_{P3HT}~3 vs ε_{Si}~11). Thus, there is much less screening in organic devices and so tightly bound

Frenkel excitons are formed upon light absorption rather than free electron-hole pairs. As a consequence, the energy levels in organic are localized and thus a band transport picture no longer holds. Instead exciton (and charge transport) occurs via a hopping mechanism. Finally, the picture for organic solar cells is further complicated by the fact that charge separation occurs via an intermediate charge-transfer state at the heterojunction.

The realization of these key differences has driven a re-evaluation of classical p-n junction theory and the development of new formalisms in understanding how organic solar cells work. Early work on different electrode materials suggested that V_{oc} depended on work function difference between electrodes.

However, work by Christoph Brabec on different acceptors in 2001 showed that changing the nature of the acceptor played a much bigger role than changing the work function. It was argued that Fermi level pinning through charged interface states between the nμative metal electrode and the fullerene reduction potential caused the insensitivity to work function.[80] Two possible origins for V_{oc} are either the HOMO-LUMO cross gap (V_{oc1}) or the electrode work function difference (V_{oc2}). In 2003, work by Blom's group showed that in the presence of non-ohmic contacts then Voc could depend strongly on work function difference.[81] A key driver for device design is to try to increase the V_{oc} to increase the power conversion efficiencies of OPVs. However, even when the HOMO-LUMO gap dominates we never observe V_{oc} equal to the calculated gap potential. In 2006, Scharber developed an empirical set of rules for determining the V_{oc} of a BHJ device with PCBM as the acceptor; arguing that there was always a general 0.3V loss in V_{oc}. For more than 26 different material combinations, no influence of the contact work function on the V_{oc} is observed. The 0.3V loss was postulated to be due to the dark current characteristics (~0.2V) and the field driven nature of the charge separation process (~0.1V) since the the open-circuit voltage depends on the slope of the field-driven current around the built-in voltage (V_{BI}).

In around 2008–2009 it was realized that electronic coupling at donor-acceptor interfaces, or in donor-acceptor blends, leads to the formation of an intermolecular charge-transfer complex that simultaneously influences the photogeneration of mobile charge carriers and the dark current due to thermal generation.[84-86] Later work (2010) argued that for bilayers, there are relatively "flat" donor-acceptor (D/A) and metal-organic (M/O) interfaces. There is a large distance between D/A and M/O interfaces and a large barrier resulting in a low electric field at the M/O interface and Fermi-level pinning. As such, unipolar transport dominates at interfaces and there is little effect of electrodes upon V_{oc}. For BHJ devices, however, intimate contact between D/A regions produces large field at M/O interface. In addition, it is possible to obtain an ambipolar carrier distribution at the electrodes. Both effects lower the barrier at the M/O interface and photogenerated carriers can no longer 'pin' electrode Fermi level.[82]

So, the question remains – does the HOMO-LUMO cross gap or the electrode work function determine V_{oc}. The answer is that both can affect the open circuit voltage. In the case of non-ohmic (blocking) contacts then we see that the V_{oc} is dominated by the electrode work function. However, for ohmic contacts we see that electrons can flow into the M/O interface producing accumulated charges and leading to band bending and Fermi-level pinning. The device structure also affects the V_{oc} since the distance of the D/A interface can affect the electric fields at the M/O interface. Large distances result in unipolar charge distributions at the M/O interface (and little dependency of V_{oc} on work function) whereas for ambipolar distributions the opposite is true.

In polymer-fullerene systems (and building from earlier work in organic light emitting diodes (OLEDs) and dye-sensitized solar cells), charge recombination was identified as a major loss mechanism; whether geminate (electron hole–pair recombines while still bound) and non-geminate (electron hole–pair recombines after charges have been separated). It is widely understood that non-geminate recombination in the blended bulk phase dominates in BHJ devices.[87-90]

4. OF RANCHERS, FENCES AND RANGE WARS (INITIAL ATTEMPTS TO UPSCALE AND COMMERCIALIZE)

Attempts to commercialise the technology has featured early in the history of organic photovoltaics with numerous start-up companies founded, growing, merging, being acquired or going bankrupt. Moreover, the commercialization space has encompassed companies focused on materials and devices. However, given the commercially sensitive nature of establishing start-up companies, publications in the area are few and piecing together the history of OPV commercialization is challenging.

4.1 The Early Promise

One of the earliest companies in this space was Quantum Solar Energy Linz (QSEL), founded in 1997 on the back of advances made at the Linz Institute for

Organic Solar Cells (LIOS) under the leadership of N. Serdar Sariciftci. In 2001, Konarka Technologies, Inc. was founded in 2001 as a spin-off from the University of Massachusetts, Lowell. Named after the Konark Sun Temple in India and co-founded by, amongst others, the Nobel laureate Alan Heeger, the company initially decided to work on both solid-state polymer-fullerene solar cells and liquid dye-sensitized solar cells (DSSCs). In 2003, Konarka acquired QSEL, in a move that was described at the time as designed to "make the company the worldwide leader in organic photovoltaics".

Meanwhile, again in the US, Plextronics was founded in 2002 in Pittsburgh as a spin-off company from Carnegie Mellon University primarily as a materials supply company based on the ability to synthesise regioregular P3HT developed by Richard McCullough (b. 1959). The business was aimed at supplying the anticipated market for conductive inks and process technologies with the advent of organic solar cells and organic light-emitting diode lighting. In the early days, Plextronics was extremely successful, highlighted as one of Pittsburgh's fastest growing companies in 2008 and raising over $40 M in equity capital.

On the west coast of the USA, Solarmer Energy was founded in California in 2006. The company licensed OPV technology developed by Yang Yang at the University of California, Los Angeles and new semiconducting material technology developed at the University of Chicago. Solarmer established a facility in El Monte, California and initially worked on developing OPV with a goal to demonstrate commercial grade devices and indeed its devices held the record for OPV efficiency in 2009 and 2010. However, it rapidly focused on supplying advanced organic materials to the research community.

A little later, in the UK, Ossila was founded in 2009 by David Lidzey (b. 1967) and James Kingsley at the University of Sheffield. The focus of the company was on the supply of materials and equipment for organic electronics research. Meanwhile, in Cambridge, the company Eight19 was founded in 2010 to commercialise organic solar cell technology developed by Richard Friend at the Cavendish Laboratory of the University of Cambridge. The company was named after the time taken for light to travel to the Earth from the Sun and raised over $7 million from the Carbon Trust and Rhodia to develop plastic organic solar cells.

4.2 The Crash

After nearly a decade of research and development, it became increasingly clear that the pathway to commercial scale OPV was challenging and unlikely to be realized in the short term. The inability to deliver on its initial promises resulted in a number of these initial start-up companies filing for bankruptcy and closing down. Probably the most dramatic was in May 2012, when Konarka filed for Chapter 7 bankruptcy protection and laid off its approximately 80-member staff. This event sent shockwaves through the OPV community and was the subject of much discussion at OPV conferences around the world. This event was followed by Plextronics filing for Chapter 11 bankruptcy in January 2014.

4.3 Rising from the Ashes

The assets and rights of Konarka's German operations (Konarka Technologies GmbH) were acquired by Belectric, a Germany-based solar developer, financier, and construction firm in late 2012, who established Belectric OPV GmbH with the aim of manufacturing bespoke OPV devices for the building integrated PV, automotive and consumer electronics markets. Their approach was to overcome the short lifetime of OPV's by creating thin plastic laminates that could be readily integrated into a range of products. Commencing with consumer products (such as OPV based garden ornaments) by 2016, Belectric OPV had already showcased installations such as the German Pavilion at the World Expo in Milan in 2015. In 2017, Belectric OPV was renamed OPVIUS developing a range of OPV products based on small OPV modules encased in polycarbonate laminates.

In March 2014, Solvay SA, an international chemical group headquartered in Brussels, completed the acquisition Plextronics Inc. to bolster its OLED electronic display technology and launch a new development platform with a strong Asian foothold.

In 2016, and after 6 years of technological partnership with the major names of the global chemical industry and an investment of €40 million, the French company ARMOR launched industrial production of a new generation of photovoltaic material, designed and manufactured in France. Called ASCA©, it is a OPV material based on combining the expertise of a number of different partners: CEA-INES France (devices and durability testing), CNRS-IMS France (materials and devices), CAMBRIOS Advanced Materials USA (silver nanowires), MERCK Germany (photoactive polymers and interface materials), LCPO France (organic polymers), AMCOR France (films and encapsulation), and ADHEX France (technical adhesives).

In May 2019, OPVIUS and ARMOR announced the decision to merge OPVIUS development, integration and marketing activities for flexible organic photovoltaic films with those of ARMOR. Their stated common

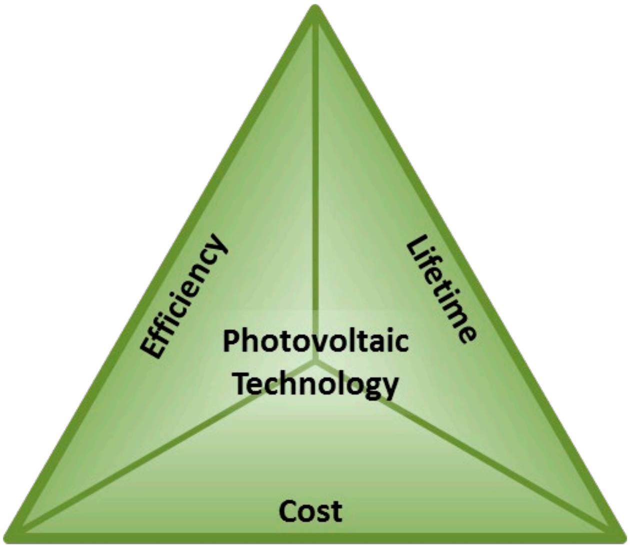

Figure 8. The three key parameters for successful photovoltaic technology: efficiency, lifetime, and cost.

objective was “to pool know-how in order to become the global benchmark company in flexible organic photovoltaic technology.”

In parallel with these commercialization activities there has been significant research effort undertaken in developing the scale-up technologies needed to mass manufacture OPV devices. Primarily based around roll-to-roll (R2R) printing[91], one of the earliest pioneers of large scale manufacturing was Frederik Krebs who was originally based at the Riso National Laboratory, Denmark and subsequently went on to found InfinityPV, with a focus on providing materials and tools to the research community.

5. HIGH NOON (THE VERDICT)

Devices with PCEs in excess of 15 % are now possible, far in excess of the 5 % efficiency threshold proposed by Chamberlain 1983, so why is OPV not a commercially viable technology? The last decade of research and commercialization attempts have highlighted that the successful commercialisation of OPVs is governed by three key parameters: device efficiency, lifetime and cost (Figure 7). As identified in this review, the OPV research community has primarily been focussed on improving device efficiency with device lifetime becoming increasingly recognised as an important research topic. However, reducing the cost of OPV materials has thus far had much less attention, yet is an equally important scientific challenge that is crucial to the future development of OPV. Indeed, it is the high cost of materials that is currently holding back scientific research at the large scale, and it is increasingly recognised that advances in the cost and scalability of organic photovoltaic (OPV) active materials are urgently required for the rapid industrial development of printed solar technologies.[92]

More recent work has highlighted the development of low cost materials for OPV manufacture[93] and the importance of understanding how the cost of materials and upscaling material manufacture impacts upon the viability of OPV as an energy generating technology[94]. However, one explanation for the fact that OPV has yet to become a viable commercial prodict is that R2R equipment is very costly to acquire, and as a consequence reports of large scale R2R processing are limited to very few research groups[95].

Looking to the future, it is clear that OPV is in the process of emerging from the classic “Valley of Death” commercialization phase with a number of restructured and consolidated companies developing large scale OPV products. Interestingly, those companies that have focused on supplying materials and tools to the research community appear to be those that have survived the “OPV crash” most successfully. Further development of the field requires the community to focus less on delivering ever higher efficiency OPV devices but rather to develop low cost efficient materials and architectures that can manufactured at scale to deliver on OPV’s promise for a low cost sustainable energy technology.

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