Substantia
An International Journal of the History of Chemistry

Firenze University Press
www.fupress.com/substantia

Citation: S. C. Rasmussen (2019) From Aqua Vitae to E85: The History of Ethanol as a Fuel. *Substantia* 3(2) Suppl. 1: 43-55. doi: 10.13128/Substantia-270

Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

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

Seth C. Rasmussen

Department of Chemistry and Biochemistry, North Dakota State University, NDSU Dept. 2735, P.O. Box 6050, Fargo, ND 58108-6050, USA
E-mail: seth.rasmussen@ndsu.edu

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

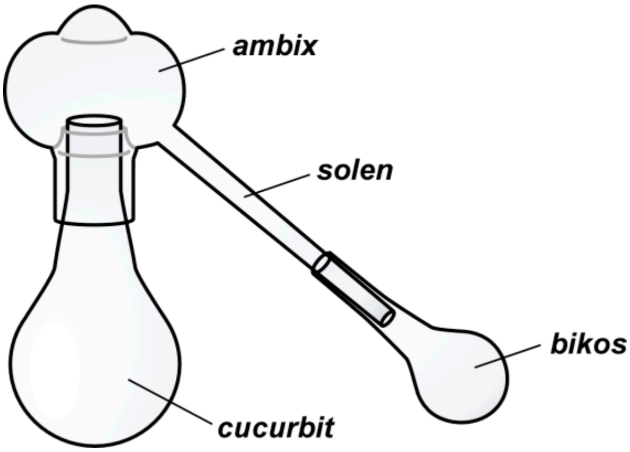

Figure 1. Basic components of the early still [*reprinted from reference 22 with permission from Springer Nature*].

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

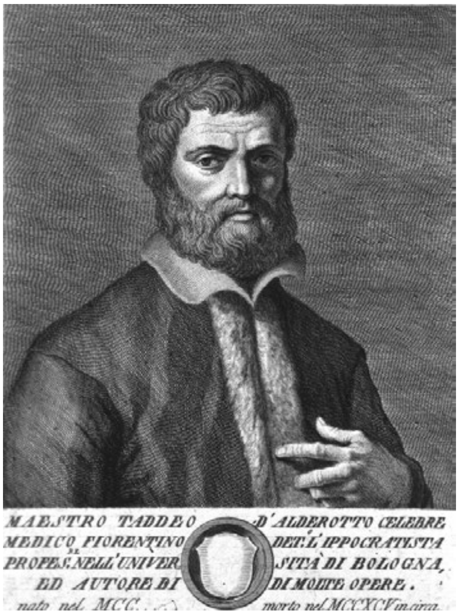

Figure 2. Engraving of Taddeo Alderotti of Florence (ca. 1210-1295) [*The National Library of Medicine*].

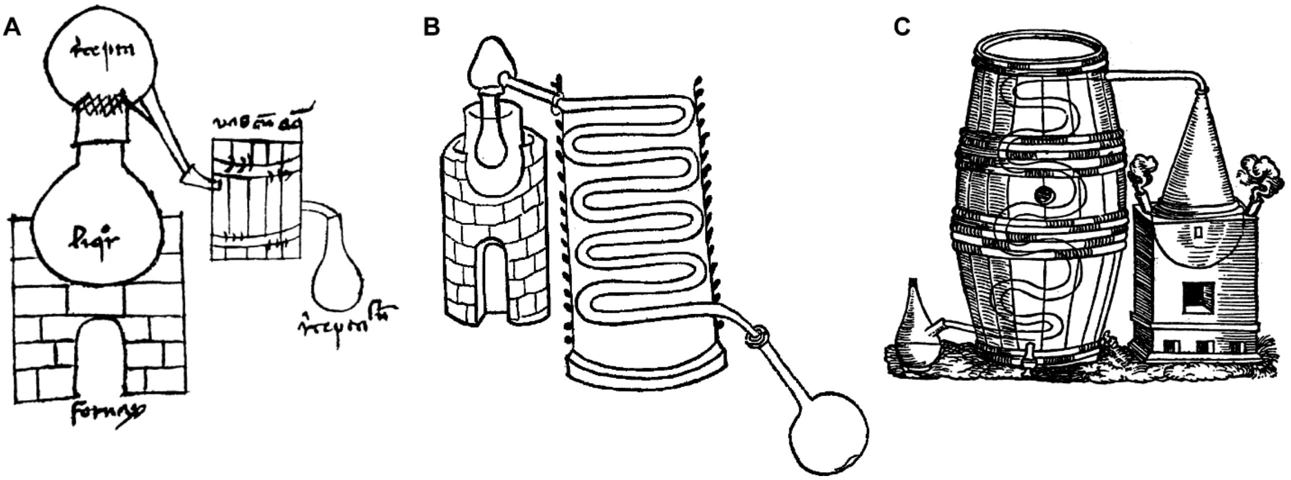

Figure 3. External cooling trough as depicted in the treatise of Johann Wenod (A) and illustrations of the worm-like nature of the "worm-cooler" cooling coil from: (a) Philipp Ulstadt's *Coelum Philosophorum seu De Secretis Naturae Liber,* 1525 (B) and Walter Ryff's *Neu Gross Destillierbuch*, 1556 (C).

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]

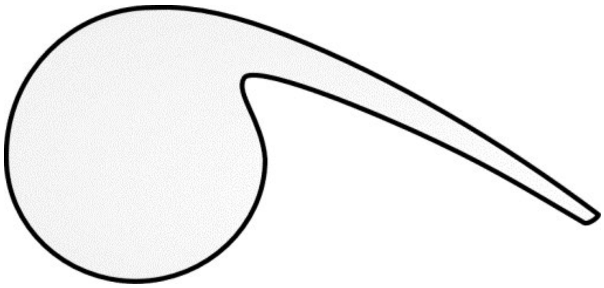

Figure 4. Illustration of a basic early retort.

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.

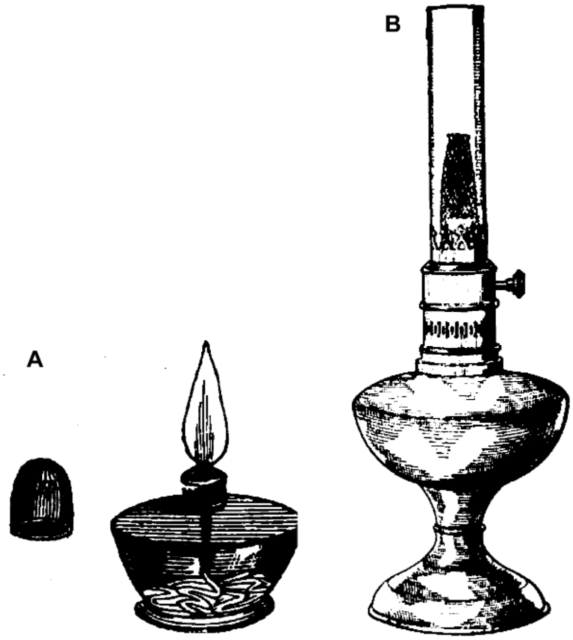

Figure 7. A simple spirit lamp, circa 1830 (A) and an incandescent alcohol lamp, circa 1900 (B).[63,64]

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.

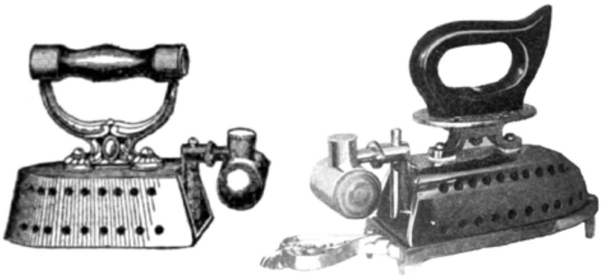

Figure 8. Alcohol-fueled flatirons, circa 1900.[67,68]

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

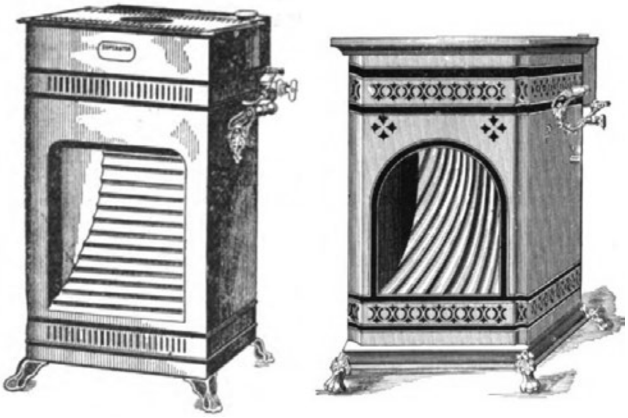

Figure 9. Alcohol-fueled space heating stoves, circa 1900.[67,68]

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.

REFERENCES

1. S. C. Rasmussen, *The Quest for Aqua Vitae. The History and Chemistry of Alcohol from Antiquity to the Middle Ages*, SpringerBriefs in Molecular Science: History of Chemistry, Springer, Heidelberg, **2014**, pp. 1-12.
2. S. C. Rasmussen in *Chemical Technology in Antiquity* (Ed.: S. C. Rasmussen), ACS Symposium Series 1211, American Chemical Society, Washington, D.C., **2015**, Chapter 10, pp. 89-138.
3. L. Gwei-Djen, J. Needham, D. Needham, *Ambix* **1972**, *19*, 69.

4. G. Broughton, J. E. Janis, C. E. Attinger, *Plast. Reconstr. Surg.* **2006**, *117* (Suppl.), 6S.
5. J. M. Stillman, *The Story of Early Chemistry*, D. Appleton and Co., New York, **1924**, pp 184-192.
6. R. J. Forbes, *A Short History of the Art of Distillation*, E. J. Brill, Leiden, **1970**, pp 76-98.
7. H. M. Leicester, *The Historical Background of Chemistry*, Dover Publications, Inc., New York, **1971**, pp 76-77.
8. A. J. Liebmann, *J. Chem. Educ.* **1956**, *33*, 166.
9. E. O. von Lippmann, *Chem. Ztg.* **1920**, *44*, 625.
10. B. L. Vallee, *Sci. Am.* **1998**, *279*(6), 80.
11. J. B. Lambert, *Traces of the Past. Unraveling the Secrets of Archaeology through Chemistry*, Addison-Wesley, Reading, MA, **1997**, pp 134-136.
12. I. S. Hornsey, *A History of Beer and Brewing*, The Royal Society of Chemistry, Cambrige, **2003**, pp. 9-20.
13. P. E. McGovern, U. Hartung, V. R. Badler, D. L. Glusker, L. J. Exner, *Expedition* **1997**, *39*, 3.
14. F. S. Talyor, *Ambix* **1937**, *1*, 30.
15. F. S. Taylor, *Ann. Sci.* **1945**, *5*, 185.
16. S. C. Rasmussen, *How Glass changed the World. The History and Chemistry of Glass from Antiquity to the 13th Century*, SpringerBriefs in Molecular Science: History of Chemistry, Springer, Heidelberg, **2012**, pp 51-65.
17. R. J. Forbes, *A Short History of the Art of Distillation*, E. J. Brill, Leiden, **1970**, pp 17-24.
18. E. J. Holmyard, *Alchemy*, Dover Publications, New York, **1990**, pp 47-54.
19. F. S. Talyor, *The Alchemists*, Barnes & Noble, New York, **1992**, pp. 39-46.
20. E. J. Holmyard in *A History of Technology*, Vol. 2 (Ed.: C. Singer), Clarendon Press, Oxford, **1956**.
21. J. M. Stillman, *The Story of Early Chemistry*, D. Appleton and Co., New York, **1924**, p 151.
22. S. C. Rasmussen, *The Quest for Aqua Vitae. The History and Chemistry of Alcohol from Antiquity to the Middle Ages*, SpringerBriefs in Molecular Science: History of Chemistry, Springer, Heidelberg, **2014**, pp. 79-94.
23. S. C. Rasmussen, *Bull. Hist. Chem.* **2008**, *33*, 28.
24. R. J. Forbes, *A Short History of the Art of Distillation*, E. J. Brill, Leiden, **1970**, pp 55-65.
25. F. Gies, J. Gies, Cathedral, *Forge, and Waterwheel. Technology and Invention in the Middle Ages,* HarperCollins Publishers, New York, **1994**, p. 163.
26. F. Roger, A. Beard, *5,000 Years of Glass,* J. B. Lippincott Co., New York, **1948**, p. 233.
27. S. C. Rasmussen, *How Glass changed the World. The History and Chemistry of Glass from Antiquity to the 13th Century*, SpringerBriefs in Molecular Science: History of Chemistry, Springer, Heidelberg, **2012**, pp 21-36.
28. S. C. Rasmussen in *Chemical Technology in Antiquity* (Ed.: S. C. Rasmussen), ACS Symposium Series 1211, American Chemical Society, Washington, D.C., **2015**, Chapter 10, pp. 267-313.
29. J. B. Lambert, *Bull. Hist. Chem.* **2005**, *30*, 1.
30. W. E. S. Turner, *J. Soc. Glass Technol.* **1956**, *40*, 39T.
31. W. E. S. Turner, *J. Soc. Glass Technol.* **1956**, *40*, 277T.
32. C. J. Philips, *Glass: The Miracle Maker,* Pitman Publishing Corporation, New York, **1941**, pp 43-44.
33. V. Dimbleby, W. E. S. Turner, *J. Soc. Glass Technol.* **1926**, *10*, 304.
34. S. English, W. E. S. Turner, *J. Am. Ceram. Soc.* **1927**, *10*, 551.
35. R. J. Forbes, *A Short History of the Art of Distillation*, E. J. Brill, Leiden, **1970**, p 114.
36. K. Cummings, *A History of Glassforming*, A & C Black, London, **2002**, pp. 102-133.
37. G. Sarton, *Introduction to the History of Science,* Vol. III, Part I. The William & Wilkins Co., Baltimore, **1947**, pp. 170-173.
38. D. Jacoby, *J. Glass Studies* **1993**, *35*, 65.
39. S. C. Rasmussen, *How Glass changed the World. The History and Chemistry of Glass from Antiquity to the 13th Century*, SpringerBriefs in Molecular Science: History of Chemistry, Springer, Heidelberg, **2012**, pp. 37-50.
40. E. O. von Lippmann, *Arch. Gesch. Med.* **1914**, *7*, 379.
41. K. Sudhoff, *Arch. Gesch. Naturw. Techn.* **1914**, *5*, 282.
42. J. R. Partington, *A History of Chemistry*, Martino Publishing, Mansfield Centre, CT, **1998**, Vol. 2, p. 266.
43. K. Sudhoff, *Arch. Gesch. Med.* **1914**, *7*, 396.
44. R. J. Forbes, *A Short History of the Art of Distillation*, E. J. Brill, Leiden, **1970**, pp. 108-112.
45. A. J. Inde, *The Development of Modern Chemistry,* Harper & Row, New York, **1964**, pp. 13-18.
46. R. J. Forbes, *A Short History of the Art of Distillation,* E. J. Brill, Leiden, **1970**, p. 217.
47. R. S. Tubbs, A. N. Bosmia, M. M. Mortazavi, M. Loukas, M. Shoja, A. A. C. Gadol, *Childs Nerv. Syst.* **2012**, *28*, 629.
48. R. J. Forbes, *A Short History of the Art of Distillation*, E. J. Brill, Leiden, **1970**, pp. 120-124,175-177.
49. M. P. Crosland, *Historical Studies in the Language of Chemistry*, Dover Publications, Inc., New York, **1978**, pp. 285–286.
50. A. Fleming, *Alcohol, the Delightful Poison*, Delacorte Press, New York, **1975**, p. 12.
51. D. J. S. Thonpson, *Alchemy and Alchemists,* Dover Publications, Inc., New York, **2002**, pp. 79–83.

52. J. F. Benton, *Viator* **1982**, *13*, 245.
53. C. C. Pines, *Am. J. Police Sci.* **1931**, *2*, 500.
54. M. P. Crosland, *Historical Studies in the Language of Chemistry,* Dover Publications, Inc., New York, **1978**, pp. 107-108.
55. J. R. Partington, *A History of Chemistry*, Martino Publishing, Mansfield Centre, CT, **1998**, Vol. 2, p. 316.
56. E. O. von Lippmann, *Angew. Chem.* **1912**, *40*, 2061.
57. R. J. Forbes, *A Short History of the Art of Distillation*, E. J. Brill, Leiden, **1970**, pp. 47,107.
58. J. R. Partington, *A History of Chemistry*, Martino Publishing, Mansfield Centre, CT, **1998**, Vol. 4, p. 353.
59. A. J. Inde, *The Development of Modern Chemistry*, Harper & Row, New York, **1964**, p. 189.
60. H. A. Mount, *Sci. Am.* **1921**, *125*(10), 164.
61. S. C. Rasmussen, *The Quest for Aqua Vitae. The History and Chemistry of Alcohol from Antiquity to the Middle Ages*, SpringerBriefs in Molecular Science: History of Chemistry, Springer, Heidelberg, **2014**, pp. 95-105.
62. H. W. Wiley, *Industrial Alcohol: Sources and Manufacture*, Farmer's Bulletin No. 268., U.S. Department of Agriculture, Washington, **1906**.
63. J. J. Griffin, *A Compendium of Experimental Chemistry*, *Part First, Comprising Chemical Manipulation and Analysis by the Blowpipe*, 8th ed. Richard Griffin and Co., Glasgow, **1838**, pp. 17-21.
64. R. F. Herrick, *Denatured or Industrial Alcohol,* John Wiley & Sons, New York, **1907**, pp. 207-238
65. H. Bernton, W. Kovarik, S. Sklar, *The Forbidden Fuel. A History of Power Alcohol*, University of Nebraska Press, Lincoln, **2010**, pp. 8-13.
66. R. Adunka, M. V. Orna, *Carl Auer von Welsbach: Chemist, Inventor, Entrepreneur,* SpringerBriefs in Molecular Science: History of Chemistry, Springer, Heidelberg, **2018**, pp. 62-73.
67. J. K. Brachvogel, *Industrial Alcohol. Its Manufacture and Uses,* Munn & Company, New York, **1907**, pp. 373-398.
68. W. L. C., *Iron Age* **1906**, *78*, 1273.
69. R. F. Herrick, *Denatured or Industrial Alcohol*, John Wiley & Sons, New York, **1907**, pp. 1-16
70. M. S. Carolan, *Soc. Stud. Sci.* **2009**, *39*, 421.
71. J. K. Brachvogel, *Industrial Alcohol. Its Manufacture and Uses,* Munn & Company, New York, **1907**, pp. 12-14.
72. S. Morey, *Am. J. Sci. Arts* **1826**, *1*, 104.
73. R. F. Herrick, *Denatured or Industrial Alcohol,* John Wiley & Sons, New York, **1907**, pp. 277-328.
74. P. Acharya, *J. Indian Leather Technol. Assoc.* **2012**, *62*, 997.
75. J. DiPardo, *Outlook for Biomass Ethanol Production and Demand,* United States Department of Energy, **2000**.
76. R. G. Skerrett, *Sci. Am.* **1920**, *123*(12), 274.
77. H. Bernton, W. Kovarik, S. Sklar, *The Forbidden Fuel. A History of Power Alcohol*, University of Nebraska Press, Lincoln, **2010**, pp. 35-37.
78. H. Bernton, W. Kovarik, S. Sklar, *The Forbidden Fuel. A History of Power Alcohol,* University of Nebraska Press, Lincoln, **2010**, pp. 59-70.
79. Available online (accessed July 17, 2019).
80. Available online (accessed May 27, 2019).