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THE CHEMICAL ENGINEERING OF THE HARDWOOD DISTILLATION INDUSTRY

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It would require more time than we have at our disposal to go into the details of the chemical engineering of the hardwood distillation industry. They will be apparent to a certain extent in the accompanying lantern slides, though many interesting points must not even be mentioned. General features will be pointed out sufficiently to give a broad survey of the problems involved in plant operation.

The industrial demand which the hardwood distillation industry meets is sufficiently indicated by the mere mention of acetic acid, methyl alcohol, acetone, chloroform, and formaldehyde, without burdening you with statistics of their production, consumption, exportation and importation. The number of industries and objectives in the arts which benefit by the availability of these substances is surprisingly great, though not all of them are exclusively the products of this industry.

DEVELOPMENT

The development of the industry appears to have been very simple. From the earliest times charcoal appears to have been used in the arts and especially in metallurgy. That liquid products could be formed, during the charcoal production, was very early observed. Uses were gradually found for these products and in course of time a demand was created for them with the result that wood carbonization was largely changed in method, so as to improve the yield of the desired by-products. The historical development of this industry is one of the most interesting in the annals of Industrial Chemistry, because it illustrates so well the battledore and shuttlecock fortune of so many of these industries. So often the by-product of to-day becomes the main product of to-morrow; and the new industry, which appears the worst competitive enemy of one industry, becomes the greatest blessing of the old industry in the next decade. The liquid products accompanying charcoal production are said to have been recovered by the ancient Egyptians and utilized by them in embalming the dead. Pliny mentions their recovery in Syria and Theophrastus in Macedonia. As chemical knowledge in those days appears to have been very limited and engineering skill as much so, the recovery of liquid products must have been trifling and it was many centuries before chemical knowledge made possible and the arts demanded intelligent development. Notwithstanding the later development of the engineering as well as chemical side of the industry, the essential features of primitive wood carbonization have come down practically unaltered to the present day. This primitive charcoal burning is still practiced wherever wood is plentiful in Russia, Scandinavia, Austria-Hungary, Germany (Westphalia and the Harz), New Jersey, Maryland, etc.

In spite of various uses to which they were put in early times no real appreciation of the value of the liquid substances known to be formed during carbonization of wood came until the dawn of modern chemical investigation. Lack of sufficient fundamental chemical knowledge was largely responsible for this. For instance as early as 1658 Glauber identified the so-called "burnt-wood acid" with acetic acid, yet not until 1802 was it identified with the acetic acid of fermentation, by Thenard. In 1661 Robert Boyle discovered wood-spirit in wood distillate, yet not until 1812 did Taylor notice its analogy to grain alcohol. The true character of this "spirit" was established only after a series of investigations by Colin, Dobereiner, Gmelin, Liebig, Sweitzer and especially Dumas and Péligot, ending about 1835.

As a result of these investigations together with those on the composition of the wood-tar and wood gas, there came an increased effort to recover such of these by-products as were suitable for use in the arts in general, as well as in the organic chemical industries that were at this time struggling for a footing upon the investigations of the great masters of our science. The first step in this revolution was the use of by-product kilns and retorts, in place of the old sod covered pits or heaps, for carbonization. It would seem that from this point, at least, the development of the industry should have been consistent and perhaps rapid but this was not the case.

Apparently the first product to have been systematically recovered was the wood-gas. This was first used in England for illuminating purposes somewhat prior to the chemical developments just mentioned. The honor, however, for the exhaustive investigation of the illuminating, heating and power value of this gas, belongs to the Frenchman, Phillip Lebon.

The weakly illuminating wood gas was soon outclassed, however, by the development of coal gas production and the whole hardwood distillation industry had a precarious existence during a large part of the last century even in spite of the fact that a satisfactory method of purifying the crude acetic acid had been devised as early as 1824 by Mollerat and Jasmeyer. The products of the destructive distillation of coal, such as coke, illuminating gas, tar and tar-distillates were sharp competitors of the wood products. Yet when the wood industry seemed about to be relegated to the primitive woods, the sudden development of the coal-tar color industry started a demand for acetic acid, methyl alcohol and acetone which has since been augmented by the demand for the same products in the production of celluloid and smokeless powder as well as many synthetic organic substances used in pharmacy and the arts. The demand for methyl alcohol within a few years after Perkins' discovery of aniline dyes became so great that the price was enormous. It is not surprising, therefore, that at that time in England wood was distilled with the sole object of getting wood alcohol. A like situation is said to have arisen at one time in benzol manufacture, coal having been for a while distilled with the sole object of obtaining benzol for aniline production.

These general statements regarding the development of the industry bring us to the present situation where we recover mainly the primary products wood gas, raw liquor (pyroligneous acid), tars and oils, and charcoal. It should be noticed in passing that while most engineering skill is a matter of quite recent development and chemical engineering is perhaps the most recently developed phase of engineering, yet it has been able reasonably to keep pace with chemical development in this industry at least, and this may be due largely to the fact that the development of engineering methods and the understanding and fabrication of engineering materials of construction developed along with the science of chemistry and are somewhat dependent upon it.

THE PROBLEM OF THE INDUSTRY

Broadly speaking, the problem of the hardwood distillation industry is the complete utilization of the weight of the original wood as far as this is possible by economical chemical engineering manipulation, for the production of the products which it will yield of main industrial use or value, *i. e.*, charcoal, acetic acid and methyl alcohol.

Economical chemical engineering involves the use and sequence of such operations as will give the maximum financial return, per unit of raw material consumed, consistent with a proper balance between low cost of operation, low initial cost of plant and highest speed of turn over (processing raw material).

When wood is heated sufficiently in the atmosphere it tends to burn of course to residual ash, steam and carbon dioxide, for the most part. If the air is partially excluded we obtain residual charcoal and volatile products varying widely in composition, depending upon the extent of air exclusion, from the condition of almost complete combustion of volatile products, to practically entire elimination of combustion or atmospheric oxidation when air is excluded as completely as possible. The problem of the industry may be met therefore by heating the wood sufficiently to carbonize it and in such a way as to eliminate as far as possible any atmospheric oxidation of the volatile products, and at the same time handle the distillates in such a way as to minimize refining or purification difficulties.

Modern chemical engineering skill has met the conditions of reasonably efficient solution of the problem with fair success as is shown by the extent of the industry¹ and without doubt it will advance still further.

Every problem, however large, is merely a series of smaller sub-problems and each of these in turn is often resolvable into still other problems. In studying the problem of any chemical industry it is natural to divide it as far as possible into:

- 1—The nature of the demand or market for the products, or objectives of the industry;
- 2—The chemistry involved;
- 3—The operations or engineering involved.

The chemistry of the hardwood distillation industry finds its basis in the phenomena attending destructive distillation. Much more should be known about destructive distillation than is known. Our concern at this time, however, is with the engineering problems involved in the utilization of this chemistry. Suffice it to say in the matter of the chemistry involved, that the products of heating the wood, as is usually the case in destructive distillation, are gaseous, liquid (condensate) and solid (residual charcoal). The gas as a whole is combustible. The liquid is acid and in two (or three) nearly non-miscible phases—tar (and oil) and dilute alcoholic acetic acid, with dissolved tar and other substances.

CHEMICAL ENGINEERING OPERATIONS

The engineering operations of the industry group themselves mainly into four divisions as follows:

- I—Preliminary handling of raw material.
- II—Destructive distillation proper or so-called primary distillation.
- III—Treatment of the liquid distillate or secondary distillation.
- IV—Refining operations and derived product production.

The latter is not generally connected with what is known as the Crude Hardwood Industry and will, therefore, be indicated with great brevity.

The engineering operations themselves are as follows:

I—PRELIMINARY HANDLING OF WOOD

- 1—Harvesting the timber { Cutting
Splitting
- 2—Seasoning, transportation and storage

II—PRIMARY DISTILLATION (Destructive distillation, proper)

- 1—Loading oven cars
- 2—Charging and sealing ovens
- 3—Firing ovens (Distillation)
- 4—Condensation and fuel gas recovery
- 5—Pulling ovens (Discharging hot charcoal cars)
- 6—Cooling charcoal
- 7—Pulling charcoal coolers
- 8—Ageing charcoal
- 9—Screening charcoal

Final Product: CHARCOAL FOR THE MARKET

III—SECONDARY DISTILLATION (of condensate obtained in II, 4)

- 1—Settling "Raw Liquor" (condensate II, 4)
- 2—Separation of tar (and oil) from "Raw Liquor" (continuous decantation)
- 3—Redistillation of settled tar (for further recovery of "Raw Liquor") from copper or wooden stills.

¹ THIS JOURNAL, 7 (1915), 47.

- 4—Condensation of acid distillate [Oil added to "Boiled Tar," water added to original "Raw Liquor" (condensate II, 4)]
 - 5—Redistillation of settled "Raw Liquor" (for further tarry bodies elimination) from continuous copper stills
 - 6—Condensation of "boiled liquor"
 - 7—"Mixing" "boiled liquor" with lime (Neutralization)
 - 8—Distillation of neutralized "boiled liquor" in lime-lee still (iron)
 - 9—Condensation of weak alcohol-acetone
 - 10—Settling or filtering lime-lee still residue (aqueous calcium acetate)
 - 11—Evaporation and crystallization of lime-lee residues
 - 12—Drying (sacking, weighing, analysis) crystallized acetate of lime
- Product: GRAY ACETATE OF LIME (80 PER CENT) FOR THE MARKET
- 13—Redistillation of weak alcohol-acetone for oil separation and concentration (Burcey pans, fractionation)
 - 14—Condensation of alcohol-acetone in fractions
- Product: CRUDE 82 PER CENT ALCOHOL-ACETONE FOR MARKET OR REFINERY

IV—REFINING AND DERIVED PRODUCT MANUFACTURE

(a) Alcohol:

- 1—Chemical treatment of crude alcohol (NaOH or H₂SO₄)
- 2—Distillation and condensation for elimination of chemicals, etc.
- 3—Fractional distillation in column still
- 4—Condensation with "heads and tails" elimination

Product: REFINED METHYL ALCOHOL AND ACETONE-ALCOHOL FOR MARKET

(b) Gray Acetate:

- 1—Distillation with sulfuric acid (or HCl)
- 2—Dust elimination from vapors
- 3—Condensation of acetic acid (Commercial)
- 4—Refining by redistillation and fractionation after chemical or electrical treatment

Product: REFINED AND CONCENTRATED ACETIC ACID FOR MARKET

(c) Gray Acetate:

- 1—Destructive distillation
- 2—Dust elimination from vapors
- 3—Condensation of crude acetone and oils
- 4—Separation of oils from acetone
- 5—Chemical treatment for acid elimination
- 6—Redistillation for "white oil" elimination
- 7—Fractional distillation of acetone
- 8—Condensation

Product: ACETONE FOR THE MARKET

Each and every one of these operations calls for its own special form of apparatus or construction and modifies to a varying extent the design and operation of the plant. They are the essential operations or chemical engineering proper which must be carried out to secure the results obtained in first-class practice. There has been indicated also, in a limited way, how some of these operations must be carried out. Sufficient preliminary discussion of the development of the industry has been given to illustrate the connection which appears to have existed between the development of both chemical knowledge and engineering skill, and the growth and development of this industry.

In concluding I must express my indebtedness to Mr. Edward H. French, to whom I owe my first opportunity (a number of years ago) of working upon the problems of this industry, upon which he was himself engaged, and who has been of much assistance in securing plant photographs from which slides have been prepared.

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WHAT CHEMISTRY HAS DONE TO AID THE UTILIZATION OF WOOD

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An attempt to discuss fully the influence of chemistry on the utilization of waste wood leads so deeply into practically all fields of chemistry that a paper of this kind must necessarily be limited to a small number of topics. Attention is given, therefore, to those phases of this subject which are of most importance commercially and which seem to show greatest promise for the future. The number of eminent chemists who have contributed to the few subjects to be discussed is so large that it is impossible to treat their individual researches as they deserve. Such being the case, a brief mention here and there of a few investigations by the Forest Service, with which the writer