

Destructive Distillation of Agricultural Wastes

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LARGE quantities of cellulosic agricultural wastes are produced annually, for which little economic use now exists. Farm income might be increased if economically profitable means of disposal or utilization of these materials could be found. To be of real effect on this farm problem, any utilization process should be capable of absorbing large tonnages of material, and the derived products should find markets without serious disturbance to existing industries. Therefore the application of the destructive distillation process to such materials was studied, with the expectation that it would meet the required conditions.

On the farm the disposal of cellulosic farm wastes involves labor or expense, although some utilitarian return is sometimes securable. Considerable accumulations of certain of these wastes, such as corncobs, oat hulls, fruit pits, nutshells, etc., also occur annually at industrial plants where agricultural crops are processed into food products, a disposal expense frequently being incurred as a charge against the manufacturing operation. In either case, the securing of a profit instead of a loss by use of the materials as a source of chemical products would be desirable. Processing plants might be able to pay higher prices for crop materials, or farm income might be increased indirectly.

Since the collection costs of the waste materials from the farm itself are comparatively high, the waste accumulations at processing factories seemingly constitute a more logical basis for a destructive distillation industry founded on farm waste materials; in these instances the collection costs have been partially or completely absorbed in the process cost of the main product.

From a commercial standpoint the process of destructive distillation has been of diminishing importance in recent years. Destructive distillation is a drastic chemical process, tending to bring about complete decomposition into gas and coke, with no by-product recovery. Even if properly controlled, the net yields of usable products are usually comparatively low, and the liquid organic products recovered are complex mixtures frequently difficult to purify. Originally the process was a basic industry, and hardwood served as the principal raw material; but the production of methanol, acetic acid, and recently of acetone by synthetic processes, the substitution of coke iron processes for former charcoal iron, and a tendency toward higher wood costs have combined gradually to restrict the wood distillation business. It has receded from its former prominent position and exists today largely as a by-product industry in connection with blast furnace or lumber operations (13). Since the products from the distillation of farm wastes resemble and will compete with those of hardwood distillation, the effect of the wood distilling industry yet remaining, which would follow from the use of

The history of the development of the continuous-feed destructive distillation process, as applied to farm waste materials, is shown. Process yields are given for different types of retorts and for many different farm waste materials. Methods of operation of continuous feed retorts and suggestions as to future design are stated. The composition and adaptability of the products for commercial use are discussed.

farm products in this field, must be considered. Since farm wastes may be inferior to wood as raw materials, from a net cost standpoint, improvements in the process operations or better means for their control must be accomplished in order that these agricultural materials may compete on an equal cost basis. However, such developments may also favorably affect the wood chemical industry.

The wood distillation industry in the United States may be classified into two divisions: The hardwood distillers operate about thirty plants, mostly in Michigan, Pennsylvania, New York, West Virginia, and Tennessee, which are frequently by-product operations of other industries; the softwood (or pine tar) operators operate about five plants in Florida, North Carolina, Mississippi, Georgia, and Louisiana, whose main products are pine tar, pine oil and pine creosote, destructively distilled turpentine, and by-product charcoal (9). The softwood plants operate on dead resinous stumpwood, but the hardwood plants usually employ cordwood or wood waste, and must season any green cut raw material for about a year before use unless predrying is resorted to. Since the usual products of the hardwood operations are acetic acid, acetate of lime, denaturing-grade methanol, and charcoal (the hardwood tar being practically unsalable in usual raw form), and the softwood industry usually does not recover methanol and acetic acid because of the small amounts yielded by softwood materials, there is little competition between the two groups except perhaps on charcoal. However, the basic retort equipment and general plant assembly for the two industries are similar although differently operated. In both industries the older plants generally operate under the so-called discontinuous oven retort process where the wood raw material is distilled in horizontal iron retorts which are exterior-fired and sealed to prevent access of air, the volatile products from these oven retorts being condensed for subsequent refining (?). For convenience in handling, the wood is usually loaded in steel "buggies" which run on a track extending through the retort, and the charcoal remaining in the buggies after the distillation is completed passes through successive airtight coolers for conditioning. Such oven plants are rated as to their capacity in cords of wood per day, a standard buggy usually holding 1 to 2 cords of wood and the retort ovens usually accommodating 2 to 4 buggies per 24-hour cycle.

A more recent trend has been toward the distillation of comminuted wood or sawdust by a continuous-flow principle,

whereby a considerable saving in retort investment and plant space may be achieved. Although the main products from these continuous retorts are practically identical with the former oven products, a somewhat different technique of distillation is required.

Owing to the physical nature of the materials, the application of existing discontinuous retort practice to farm wastes is not economically feasible. Since the per-day capacity of the ordinary discontinuous retort is limited by the time consumed in charging, preheating, distilling, and discharging, the operation time and cost for a given unit would be out of proportion to the yield of products secured in the case of lighter bulky materials occupying relatively large space for a given weight in comparison with wood, and a much larger distillation unit would be required for equivalent production. In addition, heat transfer through such bulky raw materials is poorer, and the smaller quantity of condensable products evolved per time and charge unit would probably be seriously overheated or "cracked" by the temperatures required to initiate and maintain the distillation. Capital charges on such products would be high. The continuous process and equipment is obviously much more applicable to farm waste materials since fruit pits, nutshells, and grain hulls are in a physically divided form comparable to sawdust, suitable for mechanical handling, and other wastes can be easily reduced to similar form. Because of the considerable commercial development of continuous retorts for the distillation of sawdust, the experimentation on farm waste as described here has largely followed the development lines usual to sawdust utilization. Since the various granular farm wastes differ from sawdust and from one another in the matter of hardness, density, oil content, occluded air space, moisture retention, etc., a separate study of each variety of waste is necessary.

Historical

Doubtless many investigators have experimented with the destructive distillation of various farm wastes in laboratory equipment, using the ordinary discontinuous process, but commercially considered, the results were probably not promising so that infrequent publication of findings was made. More interest attaches to the development and application of the continuous-feed type of retort apparatus to these materials.

About 1916 McLaurin experimented at Saskatchewan University with the destructive distillation of wheat straw in discontinuous retorts (15). As an outgrowth of this work a

commercial company was formed some years later by G. H. Harrison and associates, at St. Paul Park, Minn., for the purpose of destructively distilling straw and marketing the products. This group evolved and operated a continuous-feed retort (Figure 1), which, as finally designed, consisted of eight iron tubes, about 8 inches in diameter and 12 feet in length, which were placed horizontally in a brick firebox. Each tube was equipped at the front end with plungers actuated by eccentrically driven mechanisms, by means of which chopped straw was thrust continuously through the tubes; the distillation vapors and resultant carbon were discharged into an airtight steel box at the opposite end. The vapors passed upward to a tar collection and condensing system, and the carbon was passed from the bottom of the box by a water-jacketed screw conveyor through a ball mill to storage. The noncondensable gas was returned to the firebox and used as retort fuel to supplement a fuel oil burner. Owing to the design and the high temperatures employed, the yields of utilizable liquid products were low, and the volatile, lower boiling products ordinarily recoverable were largely burned to tar and coke owing to passage through the hot area of the tube. Difficulty was experienced with stoppage of the tubes by coking; the result was burning and warping of the metal, as well as leakage of products. Difficulty was also experienced with subsequent spontaneous ignition of the carbon in storage. The plant was closed about 1927. Harrison and associates subsequently erected a modified retort at Merrill, Wis., which resembled the previous design but incorporated certain improvements. The distilling tubes were slanted downward toward the discharge end, in contrast to the previously horizontal position; the evolved vapors were recovered from the feed end, to avoid passage through the hot area, and the plunger feed mechanism was simplified and improved. By these changes it is understood that the yield of desired distillation products was increased. The continued use of relatively high temperatures probably destroyed a portion of the evolved acetic acid. As in the previous St. Paul operation the watery pyrolygneous acid was not considered worth recovering and was discarded; no apparatus for recovering methanol or acetic acid was installed in either plant, and the main commercial products were carbon, tar, tar oil, and gas. This plant operated for several years but was later dismantled. In both of these commercial operations the resulting raw products (tar and carbon) were not sold as such but were incorporated into paints, fly sprays, roofing, and similar specialties which ordinarily might command sufficiently high prices to offset the low returns securable from straw.

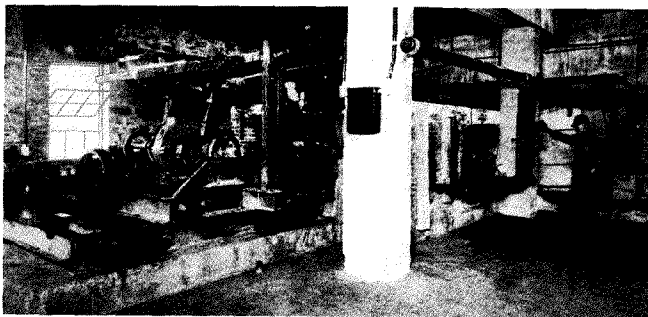


FIGURE 1. ORIGINAL HARRISON RETORT AT ST. PAUL PARK, MINN.

During the World War the Seaman (18) and Stafford (19) continuous-feed distillation retorts were evolved and operated commercially by the hardwood distillation industry, with sawdust as a raw material for the production of acetic acid, methanol, and charcoal. The owners of these processes tried destructive distillation of several farm waste materials and tested certain obvious materials to ascertain the gross yields securable in their respective equipment. The results were apparently never published and were perhaps chemically in-

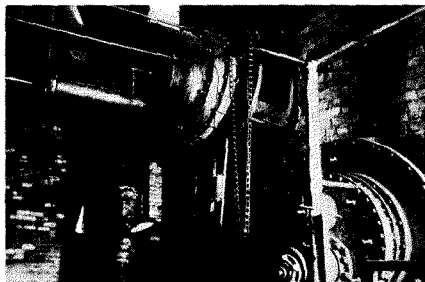


FIGURE 2. CHARGING AND DISCHARGING ENDS OF NEW RETORTS AT ST. PAUL PARK, MINN.

complete. Since the yields from farm wastes were not then economically attractive in comparison with sawdust, further tests probably were not made. (As early as 1917, the Arthur D. Little Company filed a special report with the owners of the Seaman patents on the distillation of wood and straw in a Seaman apparatus located at Gauley Mills, W. Va.)

In August, 1930, the author conducted several experiments for the Bureau of Chemistry and Soils, United States Department of Agriculture, on the continuous distillation of rice hulls, cottonseed hulls, and corn stalks. For these tests the use of Seaman retorts then located at the wood distillation plant of the Thomas Berry Company, Manistique, Mich., was secured for one week through the courtesy of the company. At about this same time the Quaker Oats Company conducted a similar test on furfural (oat hull) residues in the Seaman retorts of the James Manufacturing Company, Kane, Penna. Later in 1930 the author was assigned by the bureau to supervise the rebuilding of the old Harrison plant at St. Paul Park, Minn., which had been taken over by new capital, and to conduct experimental process studies. At this plant a new continuous-flow retort (Figure 2) of the inclined tubular, rotating, screw-feed type was designed and installed in 1931, and experimentation was made with a variety of materials over a period of several years by the author and associates.

About 1930 Cline and co-workers developed a special continuous-flow retort type designed to utilize pine and other wood chips at the plant of the Florida Wood Products Company in Jacksonville, Fla. At about the same time a retort utilizing the exothermic heat principle was placed in commercial operation on (block) resinous pine wood at New Augusta, Miss., at the plant of the American Pine Chemical Company. As a result of experiments in a Colorado pilot plant, Dwyer also patented a retort (4) consisting of a series of horizontal cones, which never reached commercial stage, however, as far as present information indicates.

Late in 1931 the Bureau of Chemistry and Soils established a field station, later known as the Agricultural By-Products

Laboratory, at Ames, Iowa, in cooperation with the Iowa State College, for the large-scale study of farm waste utilization problems under the direction of the author. The studies on destructive distillation were continued at this laboratory. A large continuous-feed retort of the Cline design was secured and erected after preliminary study of the existing continuous-retort types available. The use of this retort was through the courtesy of the patentee for experimental and noncommercial purposes only; the patentee furnished continued advisory assistance without cost but retained commercial rights. Pilot-scale operation studies were conducted, supplemented by essential laboratory studies.

The Edison Institute of Technology also made experiments on farm waste distillations at Dearborn, Mich. (about 1930-33) in a discontinuous retort of about one-ton capacity. Commercial distillation plants utilizing peach and apricot pits, walnut shells, etc., have recently (1934-36) been operated in California, particularly at San Jose. Some earlier attempts had been made to utilize rice hulls in Louisiana for the production of activated carbon. A discontinuous retort, consisting of narrow vertical tubes about 12 inches in diameter and run by exothermic heat, has been operated at Stege, Calif., on fruit pits as raw material. The tubes are filled with a charge from the top and then connected to a condenser, and the charge is ignited at the bottom, which is then closed to exclude air. The combustion zone ascends through the charge, driving the distillation vapors upward and in turn bringing the upper cold material to the exothermic point.

At Los Angeles several small plants have operated on walnut shells for the production of charcoal only, no attempt being made to recover by-products. In one plant the shells are charged into small, loosely capped cylinders which are placed in the tubes of a special furnace for "firing off". In another plant an attempt has been made to carbonize shells continuously by passage through a brick firebox in an open trough with a conveyor screw. Other retort installations have been proposed from time to time; as far as can be ascertained, none have reached commercial production.

Retorts and Processes

The application of continuous destructive distillation methods to cellulosic materials has somewhat paralleled the development of the equipment, design, and processing procedure of the continuous low-temperature distillation of coal. Many patents have been granted on apparatus suitable for use in either field, since the problems and essential requirements are somewhat similar. Continuous retort designs must provide adequate stirring of the raw material during distillation, prompt removal of evolved vapors from the heated zone, adequate control of temperature, constant rate and ease of charging and discharging without admission of air, prevention of coking, ease of cleaning delivery pipes, economical use of noncondensable gases evolved, low power and fuel consumption, etc. Present continuous-feed retort designs have evolved from the discontinuous or batch process, through intermediate forms, in which small batches were intermittently charged, distilled, and discharged, to the present types in which a continuous flow of materials through the retort is maintained by use of appropriate devices. The principal difficulties occur in establishing and maintaining an equilibrium through unvarying and adequate feed flow, the proper agitation and even heating of the mass, and a constant rate of passage and discharge without clogging the apparatus or admitting air at either the charging or discharging end. Many designs have been patented which attempt to control these factors adequately, so as to set up and maintain continuous controlled decomposition and distillation.

In the discontinuous process of destructive distillation, the composition of the products evolved from a single charge of raw material continually changes as the distillation proceeds, the progressive decomposition being effected by gradually increasing retort temperatures until the evolution of condensable products ceases entirely; carbon dioxide and hydrogen are evolved from the coke residue (10). In a continuous process the temperature, rate of feed, and other factors must be adjusted in a fixed balance to establish a distillation equilibrium; during its maintenance there is a continuous and comparatively uniform evolution of chemical products in fairly constant percentages, and the equilibrium continues effective until upset by slight variation in any factor of the operation. Such equilibrium might be established and maintained at any arbitrary decomposition temperature within a reasonable range, with corresponding change in the chemical constitution and percentage of evolved products for such different temperatures. There is, however, a tendency for a given unit and material to reach equilibrium at a usual operating temperature. As will be shown, the yields of specific substances evolved in a continuous distillation may vary with the operating factors used, and a commercial operation must necessarily select such operating factors as will give the highest economic yields of the desired products from the existing installation.

Contemporary commercially successful designs of continuous-feed retorts suitable for lignocelluloses, as at present available, are limited to a few types, and are principally the Seaman, the Stafford, the Cline, and the Freeman retorts.

The Seaman retort (18) usually consists of an iron cylinder, 30 feet long and 3 feet in diameter, mounted at a 3 per cent inclination in a firebox and rotating around its long axis by means of steel tires mounted at each end which rest on rollers; the retort is driven by a ring cog mechanism at a usual speed of about 8 r. p. m. The turning motion is synchronized to a feed (plunger) mechanism and to a barrel (compartment type) carbon discharge, by means of which a stream of raw material is introduced into, and distillation vapors and carbon are continuously removed from, the retort while air is excluded. Packed glands permit the retort to turn against the fixed feed and discharge devices. Volatile products are removed at the upper or feed end of the retort, and it is usually advisable to install a dust collector preceding the vapor condensing system. The noncondensable gas is returned to the firebox as fuel, and coal, gas, or oil serves as the main fuel supply. Internal

pressures during distillation usually do not exceed 0.5 inch of water. Seaman installations have been operated at Cherry River, W. Va., Manistique and Iron Mountain, Mich., San Jose, Calif., and Philadelphia and Kane, Penna.

The retorts erected at St. Paul Park, Minn. (Figure 3), are of an inclined, rolling, tubular design. The retort is suspended in a brick firebox by external mountings, is rotated by means of flexibly mounted steel tires, and rides on roller bearings. The complete rolling mechanism is so designed as to be entirely shielded from firebox temperatures and to compensate for expansion of the retort. Sprocket chains serve as drives, and a variable and reversible independent screw feed mechanism is used instead of plunger feed to obviate jamming. To conserve space and secure heat economy, two stages of retorts are used, which are placed parallel to each other but at different levels and slanted in opposite directions in the same firebox. The first retort tube has a cone-shaped section, this is possible because of the progressive shrinkage of bulk in the decomposition of light farm wastes. Air exclusion is secured by the use of packed ring glands at each end of the retort, and the open ends of the tube are enclosed in special airtight compartments from which vapors are drawn. The material is passed from the first to the second retort by a crossover screw. The retorts are heated by oil burners, and waste noncondensable distillation gases are also used as fuel.

The Stafford retort (9) utilizes gravitation instead of moving mechanisms to secure movement of material, which is fed continuously through a barrel-shaped (air-excluding) valve at the top of the retort. The retort is an insulated, stationary steel cylinder, through which the material descends by gravity and is progressively heated by conductivity from the uprising vapors until an exothermic zone is reached near the retort bottom where distillation is completed. The residual carbon is then discharged from the retort bottom by a barrel (compartment) mechanism.

The retort is first filled and externally heated from below until decomposition of the material at the bottom begins, and the bulk shrinkage at that point allows a flow of material to be then started. No external heat is applied to the retort after the exothermic reaction has been initiated, the descending preheated raw material being continuously brought to the exothermic point by the ascending distillation vapors, which are finally removed at the top. This type of retort therefore utilizes the lowest possible operating temperatures. Power requirements are said to be low, and the evolved vapors are relatively free from dust, because of the absence of mechanical movement.

A Stafford installation is located at Iron Mountain, Mich., and operates on wood chips and sawdust. A former Stafford installation in Tennessee is understood to have ceased operation.

The Cline retort (Figures 4 and 5), as erected at Ames (3), consists of a stack of superimposed and stationary hollow, circular, flat-top, cast-iron distillation tables joined in vertical series and resting on a stationary base. All internal joints are flanged and sealed so as to be gastight. These tables are internally heated by a fan circulation of hot gases from an auxiliary combustion chamber. Each heating element or table has an angular open segment of 36 inches, and the complete stack of elements is enclosed in a rotating shell which, with its adjuncts, is the only moving part of the retort proper. Exclusion of air from this shell is accomplished by the use of water seals at top and bottom. Material is charged

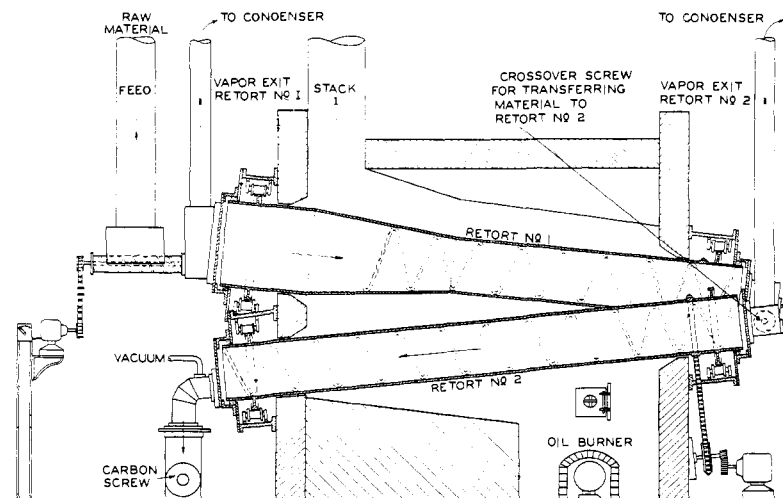


FIGURE 3. CROSS SECTION OF ST. PAUL RETORT

by means of synchronized plunger feed onto the flat-top surface of the upper distillation table. It is carried around as a thin layer, with constant stirring, by ring-shaped scrapers, one for each table, which rest on the table tops and are flexibly attached to and dragged by the rotating shell. When the material has been carried completely around and reaches the open segment of the top table, it falls through to the next table, where it is again carried around; the open segment of each lower table is located 36 inches by rotation from the previous one. The total number of turns thus accomplished by the material depends on the number of heating tables used (ten in present installation). The shell speed is variable through use of a speed-changing mechanism, and therefore a selective period of retention can be secured. Vapors from the distillation pass upward through the open segments of the apparatus through a dust collector dome into a condenser. Carbon passes from the bottom of the machine through a compartment-type discharge which excludes air, and which is synchronized to the movement of the shell as well as to the movement of the feed plunger. By preheating of material or by adjustment of retort temperatures, the effect of an exothermic zone can be secured at various sections of the apparatus.

The auxiliary combustion chamber consists of a tubular iron shell, lined with a layer of insulating brick and an inner layer of firebrick, which is attached to the retort base by a narrowed neck. This chamber is mounted on rollers so as to move freely under expansion. At the rear end of the chamber an oil burner is mounted. The hot combustion-chamber gases enter the retort base, pass upward through and inside of the heating tables, and at the top are capped into a central return flue and pulled downward by action of an external blower mechanism. Therefore these heating gases are always sealed off from the distillation vapors rising from the material undergoing decomposition.

Temperatures can be controlled by reducing the combustion chamber temperature (decreasing the oil burner flame), by varying the rate of circulation of heating gases inside the hollow heating elements, or by recirculating optional amounts of spent heating gas through the elements along with the incoming combustion-chamber gases by means of the multi-speed auxiliary blower fan located beside the combustion

chamber. Use of water seals in place of packed glands reduces the power requirements extensively and avoids gland leakage, but introduces the unavoidable factor of diluting slightly the resulting products by internal evaporation of water from the seals. (Subsequent changes in the design have recently been made.) A duplicate of the Ames installation, located at Jacksonville, Fla., has been used principally for experimentation on the distillation of pine wood chips.

The Freeman retort (6) in England is a vertical shell arrangement and has some similarity to the Cline; the design principle is reversed, however, in that the center moves and the exterior remains stationary. The center consists of flat tables mounted on a central vertical shaft. Fixed scrapers, attached to the outer stationary shell, move the material.

Many other retort types could be mentioned. The number of devices which have been patented is large, and the published designs seem to cover every conceivable means of meeting the requirements or accomplishing the ends outlined above. To the best of our information, most of them have received no commercial tryout.

Products

There is great similarity in the general composition of the products secured from various lignocellulosic raw materials by destructive distillation. The lignocelluloses constituting farm wastes have essentially the same general constitution as wood, because of the presence of certain recurring, but differing percentages of lignin, cellulose, hemicelluloses, extractives (gums and sugars), and ash; the composition of a single plant even varies between its several parts. But since each of the several organic plant constituents probably has a different decomposition temperature and may evolve basically different percentages of end products, the percentage composition of the products evolved from vegetation will reflect the variations in raw material components. Temperature of distillation will also affect the product.

The process of destructive distillation is chemically complex. When heated in the absence of air, lignocelluloses begin to evolve water and carbon dioxide at comparatively low temperatures. At a point varying between 225° and 275° C., the evolution of gas increases, carbon and methane also

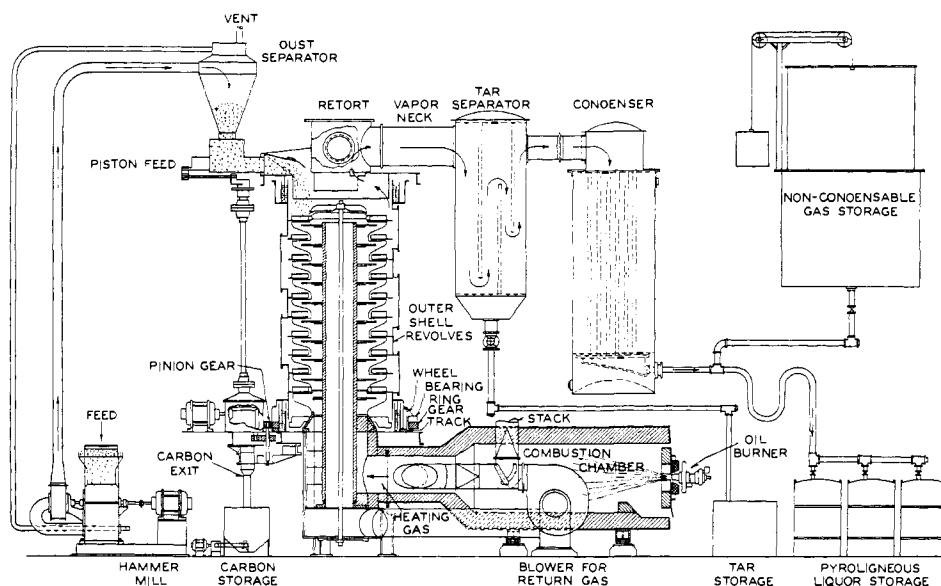


FIGURE 4. CROSS SECTION OF CLINE RETORT

appear, and the decomposition proceeds rapidly, the reaction changing from endothermic to exothermic. Noncondensable gases containing illuminants, methane, carbon monoxide, carbon dioxide, and hydrogen are evolved, besides many condensable aliphatic-chain compounds (formic, acetic, and propionic acids, methyl alcohol, acetone, etc.) and also various aromatic compounds such as phenols. Under high-temperature conditions these products may interact, polymerize, or decompose in the retort to form higher phenols, acetals, lactones, etc., and tar results as a further product. Such tar may be "soluble" or "insoluble" in the products of the distillation, depending on its constitution which is a factor of temperature of formation, time of exposure in the apparatus, thermodecomposition, etc. At higher temperatures greater quantities of noncondensable gas are evolved, and relatively smaller yields of condensable products are obtained (14). The residual charcoal contains varying amounts of hydrogen and chemically unsaturated matter in decreasing amounts as the temperature is raised (14).

The physical state of the material being distilled may influence the yield of product. Wet material reduces the internal retort temperature and also prolongs the time required for decomposition; dense material breaks down slowly, decomposition of the exterior of the mass preceding that of the interior, while light material decomposes easily, with release of relatively greater amounts of gases. Composition of evolved gases may be affected, under retort conditions, by relative concentration, dilution, or vapor velocity per area of heated iron with which the products come in contact.

The end products from such thermal decomposition of vegetable material in the absence of oxygen are therefore the result of the interaction of a great many factors, many of which are beyond control. Because of this complexity it is difficult to arrive at definite conclusions on the basis of a few tests only.

In reference to the various end products, Kurth and Ritter (12) believe that carbohydrates are the source of acetic acid. Hurd (8) states in general that lignin yields the greater percentages of methanol and acetic acid (from the acetyl or methoxyl groups present). Cellulose yields little methanol but considerable acetic acid. Pentosans give acetic acid and considerable furfural, besides the usual gas and tar by-products. Starches or hexoses which may be present in dried plant material or even pure cellulose may yield levoglucosan (or similar compounds) under vacuum distillation. Allyl alcohol is generally found in the product, and ammonia compounds, amines, and pyridine also occur. Cellulose tars seem to yield principally phenol, higher phenolic homologs probably coming from the lignin.

Many of the reports of previous investigations are incomplete as to the conditions of the experiment, and the data may be open to interpretations other than the conclusions given. Tar formation may be a factor of the retort temperature or amount of interaction or "cracking" (polymerization) of the vapors inside the retort, as well as of the original chemical constitution of the material, amount of resin, pentosan, water-soluble extractives, protein, etc. Resins from interaction of furfural and phenol are often present. Crude pyroligneous liquors almost invariably contain small percentages of nitrogen compounds, and frequently nitrogen occurs in the noncondensable gases in amounts in excess of the computed nitrogen-oxygen ratio which might result from air leakage. Liquors from wastes high in nitrogen (tobacco stems, for example) will contain higher percentages of evolved nitrogenous compounds. The products secured from the distillation of highly nitrogenous noncellulosic materials, such as leather, feathers, etc., are different from those secured from cellulosic materials.

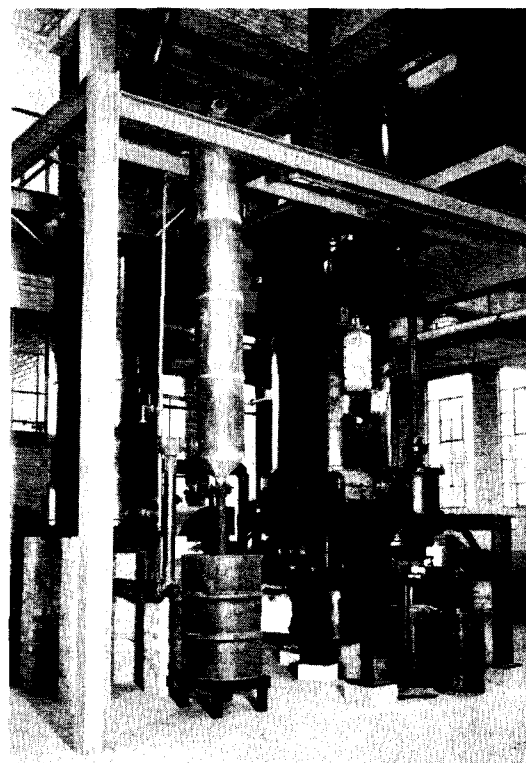
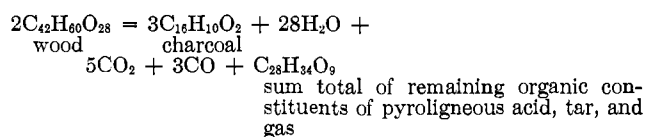


FIGURE 5. CLINE RETORT, ERECTED IN AGRICULTURAL BY-PRODUCTS LABORATORY BUILDING, AMES, IOWA

Klar (10), Klason (11), and others have attempted to chart the progressive stages of the decomposition reaction which might basically be considered according to Klar's formula (10) to be:



Essentially the reaction expresses the reversion of carbohydrate to water and carbon, in successive stages, including the oxidation of some of the carbon to carbon dioxide when oxygen is present. The degree of completeness of the reversion is a matter of control and of periodical removal and recovery of intermediate products. In the successive stages of decomposition, water and carbon dioxide gas are first evolved (endothermic stage), followed by release of illuminants, methane, and aliphatic chain compounds (exothermic stage) and (especially in commercial practice) a third stage in which the incompletely reverted carbon (charcoal) and polymerized products (tar) are further broken down to secure additional quantities of by-products or to accomplish other purposes.

In the case of a continuous feed of raw material into a continuous-flow retort, all these successive phases are occurring simultaneously in different retort zones. The product from the retort at any given moment is the resultant average of the several decomposition reactions which occurred at an indeterminable previous period, the actual time lag being difficult to establish. In continuous-feed operation, even with fixed exterior heat application, minor changes in rate of feed may depress or elevate the internal retort temperature at the several zones.

With excess heat the unsaturated organic vapors present in the retort will tend to combine or to polymerize, releasing water or noncondensable gas. Further exposure to higher heat may again "crack" the polymer bodies to form gas, residual coke, and intermediate products, usually again of unsaturated nature. The tar in solution in the pyroligneous acid (so-called soluble tar) may change into heavier or settled tar (i. e., relatively insoluble in the reaction products at ordinary temperatures), and lastly, the composition of the noncondensable gas may be affected at high temperatures by the driving off of unsaturated bodies from the residual charcoal (lowering the volatile-matter content of the charcoal), or from the tar.

It is evident, therefore, that the experimenter is confronted with an extremely complex condition; an exact chemical study of all the phases of the complicated series of reactions and interactions is practically impossible since the interaction is largely uncontrollable and unpredictable in extent, owing to the unknown time, temperature, catalytic, and other conditions momentarily created, changed, or destroyed within the apparatus.

Because means of absolute scientific control are lacking and the existing hardwood distillation industry presents a somewhat definite economic standard of valuation, the relative competing value of the products securable from various farm wastes must be measured against the costs of the same products derived from wood or from waste wood or sawdust; the latter, along with the synthetic chemical industry, sets the present economic standard. The following retort tests were therefore directed to measurement of net commercial products obtainable under such exact distillation conditions as could be achieved. In some instances successive batches of a given material were distilled in the same apparatus under conditions that would give a net effect of low-, medium-, or high-temperature treatment. The large-scale tests made in the Cline retort were frequently designed to secure results comparable with those obtained with laboratory units of various types. An attempt was made to secure data on maximum yields from large-scale operations through extended laboratory work.

Other tests on the Cline unit sometimes duplicated the conditions and material used in earlier tests in commercial retorts of different design; or conversely, the operating conditions of the same material in the same retort were varied in order to determine differences in yields. Extended chemical examination was made of the gases and other products (tar, pyroligneous liquor, oils, carbon, etc.) resulting from all these large- and small-scale distillations. Comparison studies were also made between nitrogenous and cellulosic materials, and a large number of individual materials (available only in relatively small quantities) were tested to determine the probable yields to be expected under commercial operating conditions.

Experimental Work on Continuous Retorts

The following data were secured under somewhat limiting conditions. Earlier work at Manistique, Mich., was done on commercial retorts, in advance of any theoretical or laboratory study. Under the conditions accurate temperature control or adequate equilibrium maintenance was impossible, and all laboratory facilities for immediate control were lacking. Retort runs were therefore made on the trial materials under such arbitrary conditions as seemed logical, samples of products being taken for subsequent analysis. Such data became

available only after completion of the tests. At St. Paul, the available laboratory facilities were inadequate for research work, since they were barely suitable for over-all control of the commercial operation of the retorts in the production of sale products. Experimentation with widely varied retort conditions was impossible. Mechanical difficulties had to be met repeatedly and changes in design accomplished between runs. An exact comparison of the earlier results with the later data is therefore difficult because of the progressive nature of the experimentation. At Ames also, frequent changes in the assembly of the Cline retort pilot plant had to be made, and again some of the earlier data are inadequate in so far as complete measurement and control of all the factors are concerned. Owing to the exigencies of operating the apparatus in a college building, the quantities of materials used and operation procedures usually had to be limited. Supplies of some materials were limited, so that some of the test runs were too short to yield reliable performance data after the establishment of definite equilibrium. Further changes in the installation are contemplated, and plans for future work embrace the measurement of factors not fully considered in the earlier work. This paper must be considered, therefore, as a tentative or progress report, since further work may lead to conclusions differing somewhat from statements presented here. The data as assembled are arranged in a sequence which ignores the actual accomplishment dates, to secure a more adequate presentation.

Manistique Operation

It was necessary to use the retort installation as it stood to make the desired tests during a temporary shutdown of the regular sawdust distillation operation. Since no laboratory facilities were available, operations were based purely on judgment, with the collection of samples which were sent to Washington for later analysis. Firebox temperatures could be ascertained only approximately, and no actual retort temperatures or gas measurements were securable. Therefore, quoted figures must be considered as merely approximate, and yields may be far from optimum. However, the feasibility of handling farm wastes in this type of apparatus was conclusively shown. Several tests were made on rice hulls at various temperatures; they passed through the apparatus without mechanical difficulty, and the conclusion was reached that large quantities could be distilled per day in moderate-size equipment. The temperatures of distillation

TABLE I. DESTRUCTIVE DISTILLATION RESULTS AT MANISTIQUE^a

Material	Total Charge (as Received) Lb.	Rate of Feed Lb./hr.	From Raw Material				
			Liquor %	Charcoal %	Acetic acid %	Methanol %	Acetone %
Rice hulls	11,150	1392	40.9	38.44	2.99	2.07	0.41
Low-temp.	980	980	43.2	39.80	3.58	1.30	0.62
High-temp.	980	980	41.2	37.10	3.17	1.30	0.81
Cottonseed hulls	6,277	1770	40.2	20.62	3.75	1.31	0.64
Hard wood planer cuttings (as control)	12,400	3300	67.0	18.70	6.67	1.52	...
Cornstalks (baled)	23,410	(24 hr. in discontinuous oven)	4.0	27.35	...	1.85 ^b	0.65 ^b

^a Retort turning at 6 r. p. m.; plunger, 22 strokes per minute.

^b Per cent of pyroligneous liquor.

for rice hulls could be reduced considerably below those previously required for sawdust, or the comparative rate of feed could be increased. In the case of cottonseed hulls the comparative rate of feed had to be reduced and the temperatures raised. There seemed to be residual oil present in the cottonseed charcoal, and difficulty was experienced with continued burning and loss of this charcoal which issued from

the retort glowing, in spite of the use of a water-cooled conveyor. All weights had to be made on burning material. The rice hull charcoal issued from the retort conveyor cold but also burned upon absorbing oxygen from the atmosphere.

A carload of cornstalks was shipped to Manistique for trial. This material was purchased "crushed and baled", and could not be passed into the feed mechanism of the continuous-type retort even after the material was reduced to small size in a cornstalk shredder. The remaining baled material was therefore loaded on the steel cars of a standard, four-car, rectangular, oven-type wood distillation retort which happened to be available, and an attempt was made to distill the charge. At the outset a tremendous amount of gas was evolved which necessitated slow firing of the charge. Little liquor was recovered, and the attempt at distillation was finally abandoned for fear of damaging the retort by overheating. Operation data on tests are given in Table I.

St. Paul Operation

The new company desired to arrive at a commercial production basis quickly without a preliminary laboratory stage. The obvious procedure was to build a retort of arbitrary design based on such data as were available, which would probably function with some degree of success, so that commercial production could proceed during experimentation. The rolling-tube design was selected as offering fewer mechanical difficulties and the greatest likelihood of effective carbonization of reasonably large quantities of chopped straw under the proposed conditions. The necessity of fitting the equipment into the existing space and of minimizing construction and operating expenses until the design was experimentally proved was encountered. It was necessary to tear out practically all existing equipment from the old plant, and repair and reinstall the usable portions of the apparatus. The retorts were constructed by a local foundry company, the driving mechanism from the old Harrison retort being partly retained. Changes in firebox design, feed mechanism, dust collectors, vapor piping, etc., were made from time to time during the experimental period.

No plant or operation costs can be given.¹ The experimentation resulted in increased knowledge of the problems of operation of continuous retorts and disclosed several inherent operating weaknesses of the rolling-tube design, principally as to sagging of the tubes at the center under heat, and gland friction and leakage of air into or vapor from the retort under varied pressure conditions. The difficulty of distilling fibrous materials in comparison with granular materials was amply demonstrated, and certain information as to the use of ham-

TABLE II. DESTRUCTIVE DISTILLATION RESULTS AT ST. PAUL (1931)^a

Run No.	Material	Amount of Material Lb.	Charcoal Yield %	Pyro-ligneous Liquor %	Total Acid on Material as Received %	Retort Conditions
1-6	Wheat straw	4,125 ^b	25.50 ^c	35.3 ^c	2.2	Various, trial
7-9		2,900 ^b	24.00 ^c	35.3 ^c	2.5	Various, trial
12-14		3,063 ^b	25.50 ^c	38.1 ^c	2.6	Wide temp. ranges
20		1,600	24.00	42.6	2.8	Rapid feed
18	Straw chaff	883	34.00	53.0	4.2	Rapid feed
17	Oat hulls	1,280	21.20	41.5	3.6	Changing temp.
19	Rice hulls	1,500	33.60	53.8	3.3	Changing temp.
11	Cornstalks	730	22.30	46.5	2.1	Changing temp.
10	Sawdust (35% H ₂ O)	1,224	15.10	61.4	3.2	Control
15-16		3,120	18.80 ^c	62.0 ^c	4.5	Control
21-22		2,350	30.30 ^c	80.0 ^c	4.0	Rapid feed
23-43 ^d	Oat hulls	37,405	32.30 ^c	39.3 ^c	3.74	Various conditions

^a Frequent revamping of equipment took place between trial runs.

^b Total.

^c Average.

^d Results after run 22 were secured in 1932 by B. M. Becker. During the interim the fire boxes were rebuilt.

mer mills for reducing fibrous materials to a finely divided state for processing was secured. This is possible with grain straws and perhaps cornstalks, but is impracticable with flax straw or other fibrous materials. The results of the tests are given in Table II.

Ames Experimentation

The Cline retort secured through the courtesy of the patent owners² was first erected in the Chemical Engineering Building of the college, where grinding machinery, research laboratories, and other facilities were available. The destructive distillation experiments were continued during 1932-35 by the staff of the Agricultural By-Products Laboratory under the author's direction.

The results obtained in the Ames experimentation on the Cline retort are presented in Table III. At the conclusion of this group of runs the retort was moved from the chemical engineering building and re-erected in the new building of the Agricultural By-Products Laboratory (Figure 5).

Figure 6 is a typical study of a Cline operation, although it does not show special conditions occasionally encountered. Retort temperatures were established by readings from pyrometers inserted in the shell at top, middle, and bottom (averaged as the "av. internal temp.") and in the base, to record the temperature of the heating gases from the combustion chamber as these gases entered the bottom heating element of the series, the temperatures varying with the control of the oil burner. The readings through the shell indicate temperatures outside the heating elements and are assumed to be the temperatures of the stream of vapor from the distillation passing that point. This internal temperature curve is therefore

¹ Rebuilding of plant and the erection and initial successful operation of the new retorts were completed by February, 1931. The first active experimentation ceased in May, 1931. Subsequently several members of the Ames staff were assigned to the plant during 1932 to conduct some follow-up experimentation which was, however, restricted by the depressed commercial situation then obtaining.

² In 1932, after some preliminary experimentation with the Cline retort at Ames, the author conducted a test run on pine wood chips on the similar Cline unit at the plant of the Wood Chemical Products Company, Jacksonville, Fla., through the courtesy of the owners. The experimental procedure used at Ames was followed as far as possible, so as to secure check operation data. The results were as follows:

Wood used (after hogging), 11½ measured cords, 5874 lb. (dry basis)
Resin content of wood, 26.3%
Wood charged, 1366 lb./hr.

Yields

Charcoal, 861 lb. or 14.65% (dry basis)
Liquor, 512 gal. (4416 lb.) or 75.18% (dry basis), consisting of
Pyro-ligneous acid, 279 gal. or 54.5% by vol.
Tar, 233 gal. or 45.5% by vol.
Total acid in pyro-ligneous liquor, 4.22% as acetic (equivalent to 34.7 lb. acid/ton of dry wood, and the liquor contained 0.14% acetone and 0.64% methanol).
Tar, 79 gal./dry ton (sp. gr., 1.043 at 26° C.)
Fuel oil used, 109 gal. at 2.5 cents
Redistillation of tar gave 5.5% light oil, 35.0% tar oil, 33.0% rosin oil, and 27.5% pitch and loss

The object of this run was to investigate further the operating characteristics of the retort: the actual yields securable from wood were of secondary importance. In fact, wood was used merely because it was the only raw material immediately available. Both the Ames and the Jacksonville units were considered by the inventor as pilot-plant trial installations for development of an improved design rather than as completed units for general commercial use.

TABLE III. SUMMARY OF DESTRUCTIVE DISTILLATION RUNS IN THE CLINE RETORT (AMES)

ANALYTICAL DATA OF CONDENSABLE DISTILLATES IN THE CANE RUNS (TUNES)																			
Run No.	Material	Total Charge (as Received)	Rate of Feed	Moisture in Material	Yields ^a			Analysis of Liquor					Volatile Matter in Carbon	Yield of Noncondensable Gas	Internal Temp.		Retort Speed	Conditions of Run	
					Liquor	Carbon	Settled tar	Total acid on dry raw material	Formic acid	Methoxyl (as methanol)	Variation in acidity	High point			Low point				
		Lb.	Lb./hr.	%	%	%	%	%	%	%	%	%	%	Cu. ft./ton	° C.	° C.	R. p. m.		
A-2	Corncoobs	1,139	720	23.15	53.60	19.96	...	3.08	5.02	0.75	0.86	0.96	5-7.5-10	First measured run	
A-11		1,916	852	20.00	57.82	21.19	...	5.42	5.78	0.77	0.70	1.09	11.7-6.0	12.4	425	210	5-7.5-5-2	Descending heat and speed	
A-16		3,133	450	26.40	65.01	20.17	4.82	4.95	7.12	0.66	0.69	1.07	11.7-4.3	...	420	290	5-8-10	First long run	
A-39		2,000	500	5.95	49.00	24.65	6.00	5.63	5.43	0.79	0.81	0.38	11.5-9.5	8.56-16.8	327	293	8c	Very even operation	
A-50		2,952	738	20.0	56.70	20.00	2.65	3.25	5.10	0.55	0.69	0.91	10.1-7.4	...	349	288	5-6-8	Rate of feed uneven, heat low due to oil burner trouble	
A-51		2,605	651	18.65	52.00	20.61	4.06	4.42	6.36	Not analyzed	10.5-6.5		404	293	1-3-5	Rate of feed very uneven, with uneven heat line	
A-52		3,544	430	18.65	60.30	22.00	1.61	5.62	5.83		9.4-8.6		388	371	6c	Even temp. and feed slowly decreasing, condenser plugged with tar	
A-53		3,400	680	18.73	58.30	20.42	4.15	5.85	5.64		10.0-6.7		399	354	6-8	Fairly even temp. speed and feed, higher temp. than previous runs	
A-54		3,425	473	17.00	60.50	21.90	3.91	5.20	5.54		9.3-6.6		410	387	6c	Fluctuating feed and even heat. Plugged condenser	
A-55		3,600	900	14.50	55.10	21.20	4.97	6.17	5.70		10.1-8.9		3700	338	327	8c	Fluctuating feed and very even heat
A-56		2,150	950	7.21	58.00	23.70	8.70	5.15	5.57	371	...	5-10-8	Operation periodically interrupted by power failing	
A-57		9,267	883	8.36	53.93	22.70	8.08	4.85	5.90	0.75	0.63	..	11.0-7.5	...	4680	371	310	7c	Very even heat line, a long run
A-35	Pecan shells	2,120	300/430 ^b	4.13	40.00	28.82	8.01	2.04	4.14	0.31	0.51	1.13	11.1-3.0	10.9-5.0	..	421	254	2-7	Down and up and down, very slow
A-36		3,253	1029/723 ^b	4.13	44.57	34.37	5.62	3.12	5.02	0.35	0.48	0.77	12.1-8.5	14.3-27.0	...	388	254	5-7-3	Descending curve
A-61		10,184	1018	9.60	46.90	26.80	10.72	3.58	5.20	0.40	0.23	0.63	10.38-9.61	23.4	4160	393	329	6-5-6	Fairly even temp., uneven feed
A-62		6,244	892	9.60	48.30	26.80	10.78	3.07	5.26	0.46	0.23	0.82	10.38-9.61	23.4	4300	399	335	6c	Feed very erratic, interrupted run
A-63		7,950	994	9.60	48.00	26.50	10.78	3.07	5.32	0.40	0.43	0.89	11.50-10.7	23.4	3926	399	388	6c	Steady operation
A-64		5,975	996	9.60	47.20	28.00	10.62	3.75	5.40	0.41	0.46	0.71	11.4-10.6	23.4	4120	416	349	6c	Steady operation
A-5	Oat hulls	500	660	5.94	36.60	35.00	...	3.34	3.31	0.72	0.58	1.26	304	222	10c	Descending curve
A-10		1,433	660	5.50	52.13	29.38	...	5.20	4.24	0.24	0.89	1.23	9.7-5.8	15.0	...	480	310	2-3-8-10	...
A-19		2,882	576	5.94	52.74	23.90	6.90	4.02	3.90	0.42	0.70	0.95	8.2-4.0	8.3-10.2	...	400	340	5-10	Ascending heat curve
A-60		2,464	189/15 min.	11.00	48.40	23.45	9.80	4.09	4.50	0.40	0.53	0.63	9.9-6.42	...	4560	Intermittent feed
A-24	Peanut shells	1,753	584	9.97	49.80	26.60	5.49	2.34	2.55	0.06	0.54	1.52	6.1-2.6	13.0	...	440	346	5-7.5-8	Dipped, ascending heat curve
A-38		1,791	566	6.72	50.00	29.73	11.60	3.11	3.70	0.14	0.72	0.44	7.8-2.2	9.7-13.7	...	388	327	5-8-10	Very even heat line, increasing speed
A-37	Tobacco stems	1,828	914	8.77	42.10	29.81	8.50	1.80	1.29	0.14	0.65	0.05	3.4-1.9	10.5-16.5	...	421	338	6-5	Fairly even operation
A-40		1,390	1110	8.77	40.40	33.40	6.90	1.77	1.66	0.20	0.79	0.06	4.4-2.9	44.4-20.2	...	288	204	8-3	Decreasing speed, increasing temp.
A-66		3,312	824	18.00	36.80	32.65	3.26	2.06	1.35	0.22	0.80	1.03	3.6-2.7	29.7-19.35	4316	253	245	5c	Decreasing feed
dry tar																			
A-3	Cornstalks	235	235	9.63	55.00	22.50	...	2.66	3.00	0.36	0.47	1.88	262	218	7.5c	Ascending heat curve
A-13		808	180	10.50	58.50	26.10	3.88	3.16	3.98	0.59	0.43	1.08	8.6-2.5	25.1-12.5	...	415	240	1-5-8	Descending heat curve
A-4	Barley straw	500	120/180 ^b	7.94	44.00	27.60	...	1.74	2.14	0.32	0.69	1.38	380	327	5-10	...
A-12		874	175	11.80	60.33	24.37	...	2.51	2.54	0.28	0.54	1.12	5.6-2.5	390	310	5-10	Run divided, high- and low-temp. sections
A-17	Elevator screenings	1,078	430	8.40	66.10	23.75	7.37	4.97	1.98	0.21	0.50	0.36	3.7-2.7	12.7	...	410	350	5c	Decreasing feed
A-20	Neutralized furfural residue	3,816	996	23.80	47.22	29.43	5.30	2.48	1.04	0.19	0.51	0.81	2.9-1.2	9.4-18.0	...	380	270	5-7-5	Uneven descending heat curve, dusty run
A-21	Unneutralized furfural residue	3,480	1098	24.24	53.27	28.83	4.24	4.08	1.52	0.24	0.47	0.54	3.6-1.9	9.4	...	330	270	5-7	More even heat line
A-22	Cottonseed hull bran	1,700	850	11.32	52.64	26.18	4.20	2.65	4.32	0.24	0.67	1.04	8.1-4.0	6.5-12.0	...	380	335	5c	...
A-25	Pyrethrum flowers (ext.)	1,850	822	7.05	43.50	27.80	10.80	4.15	1.87	0.05	0.50	1.77	5.3-2.5	10.8	...	450	350	10-8	Descending curve
A-65	Pyrethrum flowers (ext.)	2,154	905	7.50	37.60	29.20	9.99	3.53	3.08	0.39	0.65	0.28	7.89-7.31	8.50-14.10	5272	344	297	6c	Uneven, decreasing feed, lower temp.
A-67	Walnut shells	3,850	1110	6.70	46.30	28.75	9.30	4.20	6.68	0.20	0.64	..	14.67-13.1	...	3914	366	249	5-6-5	Uneven feed, descending curve

^a Computed on material as received, unless otherwise indicated.^b Variation in rate of feed.^c Constant ratio.

assumed to be the index of the actual heat conditions of the test, the retort base temperatures merely indicating the application of make-up heat to maintain the distillation at the proper rate.

About one hour was required for the retort to reach an equilibrium after the flow of material was started, although the cold retort received about a 2-hour preliminary heating before material was introduced. As equilibrium is established, it is usually necessary to reduce the input of heat from the combustion chamber to compensate for the exothermic heat evolved. The amount of such control followed the trend of the shell internal temperatures, which were read every 15 minutes. The first material charged into the retort seems to build up at the start and to affect the amounts of further material pushed into the retort by the feed mechanism for a subsequent short period. The motion of the retort shell and flow of input material may be gradually increased to the desired speed after an equilibrium is almost established, by continuous balancing of factors.

Gas pressure and evolution of noncondensable gas were determined at two separate points. The internal retort pressure was measured by a U-tube manometer at the vapor exit neck, but

the actual evolution of gas was measured by inserting a standard orifice plate and manometer in the exit line after the gas had passed through a baffle-plate, water-scrubber tower. During the test operation, serially numbered samples of carbon and of pyroligneous products were taken at the same time as the temperature and pressure readings, and these samples were subsequently analyzed. Exit carbon was caught in drums and weighed, and the pyroligneous liquid was either caught and weighed in drums or else measured continuously in a receiving tank or scale tank. After settling, this liquor was decanted from the settled tar, the tar weights being obtained in most instances. The data thus assembled enable the conditions of any run to be duplicated in subsequent runs with reasonable accuracy.

Despite the fact that the plunger-type feed was synchronized to the shell movement, so that larger amounts of material entered the retort per time period, with faster shell rotation it was found that, even for a fixed shell speed, there was considerable variation in the weight of material delivered by the plunger in a definite time interval. This plunger operated under a mechanical system; as the plunger retracted, raw material fell by gravity into the plunger trough space from a hopper situated directly above, and the top of the piston trough then closed by a sliding plate in advance of the forward thrust of the piston. In many of the earlier test runs it had been assumed that the net feed through this mechanism was relatively constant, and no account was taken of the effect of this unknown fluctuation. In the case of later runs weighed amounts of feed were placed in the hopper so as to establish the actual amounts handled by the piston for the test periods.

Thus far no successful runs have been possible in the Cline unit on relatively fibrous materials such as cornstalks, straw (wheat, barley, flax, etc.), and cottonseed hulls (whole, with linters attached). Materials such as ordinary straw or cornstalks must be reduced to small pieces by hammer milling, and even then difficulty with piston feeding is encountered. Flax straw forms a mass of tow and will not pass through the machine, nor can cottonseed hulls be forced through. Each of these tests resulted in breakage and damage to the equipment. A rolling-tube retort type is required for such materials.

The time of retention of material in the Cline retort, for various speeds, was as follows:

Speed	Time of One Revolution, Sec.	% of Max. Speed	Speed	Time of One Revolution, Sec.	% of Max. Speed
1	380	15.7	6	134	44.8
2	310	19.3	7	110	54.7
3	250	23.6	8	95	63.1
4	200	30.0	9	70	85.7
5	160	37.6	10	60	100.0

Since the retort contained ten elements above the base, the actual passage time was considered as being eleven times the revolution period for the speed used.

Certain conclusions concerning the normal operation of retorts of the rolling-tube type can be arrived at from the tests at Manistique and St. Paul. The speed of rotation of tubes should be slow, since too fast a movement stirs up dust which is carried out with the distillation vapors and causes plugging of condensing and refining equipment. The slant of the retort

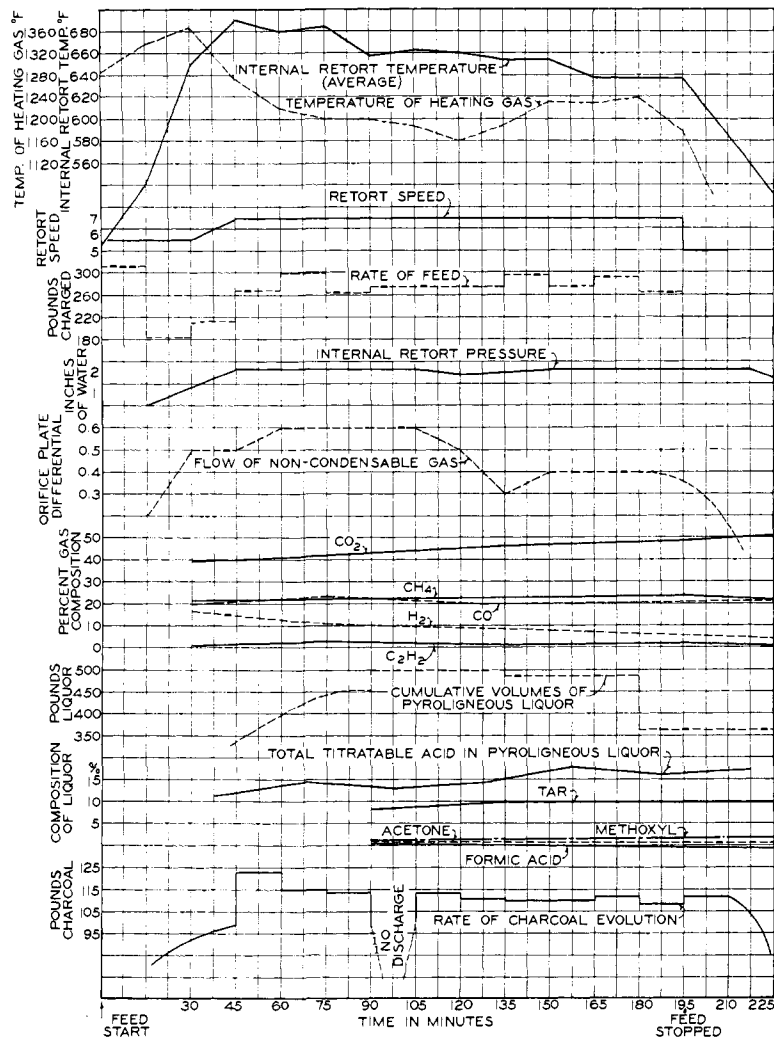


FIGURE 6. TYPICAL CLINE RETORT OPERATION (BLACK WALNUT SHELLS)

has probably as much effect on the forward motion of the mass as the tube rotation has. (The St. Paul retorts were equipped with an inner spiral band, welded to the tubes, with the object of retarding the forward movement of the mass.) Some of the distillation vapors emerging at the feed end of the retort condense upon and are absorbed by the entering cold raw material. Before decomposition the wetted material is then carried downward into a relatively hotter zone than would be the case with dry material. Decomposition of such entrained condensate probably occurs also. Preheating of material is suggested. Tube design must provide for expansion both on long axis and in diameter. Such expansion must not tend to bind the gland packing, and this packing must also be protected from intrusion of vapor, as well as from heat sufficient to burn the packing or grease. Tubes must be constructed to withstand sagging under heat conditions, and too great a length of tube invites trouble. Tubes should be kept in rotation during heating and cooling.

Plunger-feed mechanisms have a tendency to jam with certain materials. A screw-feed mechanism (preferably reversible in direction) may give less mechanical trouble. The feed mechanism works better on hot (preheated) dry materials, and this preheating can be achieved by use of waste retort heat.

It seems to be impracticable to secure in a single tube the required gradations from preliminary heat, through de-

composition, to high-temperature "finishing" of the charcoal (removal of unsaturated bodies liable to cause spontaneous combustion when the charcoal is subsequently exposed to the air). Such "finishing" should be done with some admission of oxygen and is best accomplished in a subsequent independent apparatus.

Where the use of a variety of raw materials is contemplated, particle sizes for the various materials should be so selected as to allow adherence to normal retort operation procedures to the greatest possible degree in order to secure uniformity.

In the operation of retorts of the Cline type, the gravity flow and positive forward movement of the materials over the distillation tables resulting from the use of scraper rings avoids some of the operation difficulties of the rolling-tube types. Gland leakage and retardation of retort turning by gland friction are eliminated, but other difficulties may be encountered. A rolling-tube retort can handle a sudden internal gas pressure, or fluctuation of pressure, within the limits of the seals on the condensing apparatus, which can be made reasonably large. Outward leakage of vapor through the glands would be of short duration only, and the gland will continue to exclude air. The Cline unit, as erected at Ames, is limited to gas pressures less than the equivalent height of the top or bottom shell water seals (usually less than 6 inches of water). Once these seals are blown, vapor may leak outward or air may penetrate to the inside of the shell until the seals are restored. The seal wells collect tar and acid water, and should be more amply protected. Evaporation of water from the seals continuously dilutes the condensate from the retort.

The entire series of superimposed heating elements in the Ames unit were originally so designed (subsequently re-designed) that the bottom element, which received the greatest heat, supported the weight of all the elements above it. Any sagging or collapse of a bottom heating element threw all the upper ones out of alignment, jammed the scraper rings, and stopped the turning of the retort shell. Any interference with, or breakage of, scraper rings may have the same effect. A shear pin must therefore be installed in the drive mechanism so as to automatically cut off the power if the turning motion is impeded, and an automatic cutoff of heat from the combustion chamber should also be provided.

Feed, rotation, and charcoal discharge of a continuous retort should always be in synchronism. An independent feed may choke the top of the retort if operated too rapidly. Because of the tendency of distillation vapors to escape through the mass of incoming material, a plunger feed mechanism is usually designed so as to maintain a coned plug of densely pressed material ahead of the plunger at the point of entrance to the retort. With soft materials (such as ground corncobs) the plug may mash together sufficiently to stop retort vapor from escaping, but noncrushable materials (such as walnut shells) may allow vapors to pass outward through the plug interstices. Increasing the length of the plug puts more back pressure on the feed piston; and in the case of wetting of the plug by condensation of escaping watery or tarry vapors, a further strain on the feed piston may be encountered. Here lies the advantage of a screw feed; the effect of a long plug is secured, but the plug is continually in motion and stoppages can usually be cleared by double reversal of direction. It is, however, more difficult to synchronize a screw feed mechanism to a retort operation.

Utilization of Products

In order to accomplish an economic program of utilization of agricultural wastes by the destructive distillation process, it is essential that market outlets for the products be obtainable. These products are mainly acetic acid, crude methanol, char-

coal, tars, tar oils, creosotic derivatives from the tars, and gas.

As Table III shows, the methanol yield is usually relatively low and therefore the methanol-acetone fraction can be considered as representing merely a small and relatively unimportant by-product. The refining methods which would necessarily have to be applied to the products from farm wastes are identical with those commonly used in the wood distillation process, particularly as to the water-soluble products. The amount of acetic acid recoverable from certain wastes, such as corncobs or walnut shells, approximates closely the usual yields from hardwood, while the percentage of formic acid in some instances may be higher than from hardwood; methanol and acetone, however, are relatively low.

The tars from the destructive distillation of farm wastes, as in the case of the similar hardwood tars, are very complex materials (1, 16, 17). It is believed that the soluble tars differ somewhat in chemical constitution from the usual wood distillation tar; this statement cannot be chemically substantiated, however, since it is predicated on the relatively higher original pentosan and extractive content and lower cellulose and lignin percentages in these farm waste raw materials. Comparison reactions applied to wood tar and farm waste tar in parallel experiments seemed to yield products of somewhat different character. However, the complexity of these products makes a definite analysis almost impossible.

The tar may be refined to secure certain derived products by washing with warm water to remove acetic acid and cooling to re-separate the tar from the water, after which the tar is distilled in a fire-driven iron still, with optional passage of live steam through the tar. This distillation often presents difficulties since the presence of much water is likely to cause foaming and since certain tars seem to decompose partially upon heating, with release of gas. Vacuum distillation may constitute an important method of handling. When the diminution of distillate flow gives warning of an approaching coking stage of the residue in the still, distillation must be stopped. The remaining tar pitch, which is now asphaltic in consistency, must be removed from the still immediately before it solidifies into solid pitch. On a dry basis about 25 per cent of crude tar oil may be obtained from an average tar by ordinary distillation. A typical analysis of corncob tar is given in Table IV.

TABLE IV. CORNCOB "SETTLED" TAR^a

	%	Lb.
Tar produced from raw material	4.65	93 ^b
Water in tar	12.00	20.46
Net tar	..	72.56
Crude oil recovered from tar	25.00	23.28 ^c
Pitch residual from oil recovery	75.00	49.26 ^c
Crude oil fractions		
Up to 170° C.	16.92	3.94 ^d
From 170-230° C.	48.20	11.20
Above 230° C.	34.88	8.14
Total oil	..	23.28
Acid water loss on distn.	..	2.40
Phenols in crude oil fractions (sol. in 10% NaOH)		
In light fraction (up to 170° C.)	4.00	0.157
In middle fraction (170-230° C.)	55.00	6.17
In heavy fraction (above 230° C.)	54.00	4.39
Amount of fraction sol. in 10% H ₂ SO ₄		
Light	2.19	0.0865
Middle	1.75	0.196
Heavy	1.02	0.083
Residual neutral oil		
In light fraction	41.10	1.626
In middle fraction	40.16	4.504
In heavy fraction	44.98	3.667
Amount of neutral oil fraction sol. in concd. H ₂ SO ₄		
Light	60.0	0.973
Middle	80.0	3.60
Heavy	80.0	2.93

^a Settled tar represents about half the total tar, produced in runs A-50 to A-57 (averages).

^b Pounds per ton, wet basis.

^c Dry tar basis.

^d Including acids and phenols.

TABLE V. COMPOSITION OF NONCONDENSABLE GASES OBTAINED BY DESTRUCTIVE DISTILLATION^a

Material	Temp. ° C.	Run	CO ₂ %	Illuminants %	H ₂ %	CO %	CH ₄ %	O ₂ %	N (by difference) %
Tobacco stems	373	Continuous	59.1	3.3	11.8	9.8	16.0	0.0	0.0
Pecan shells	280	Continuous	44.2	4.2	7.2	7.6	36.1	0.7	0.0
Cottonseed hull bran	350	Continuous	46.3	2.0	12.1	2.4	33.8	0.4	3.0
Cottonseed hulls	408	Continuous	36.6	1.6	16.6	1.9	42.4	0.9	0.0
Oat hulls	...	Batch	42.6	2.7	7.9	7.9	38.0	0.9	0.0
Furfural residues (oat hulls)	330	Continuous	31.2	3.6	14.0	4.6	39.7	0.4	6.5
Pyrethrum flowers (extd. residue)	370	Continuous	58.4	3.6	6.2	1.8	27.7	1.2	1.1
Cornstalk (pressboard)	...	Batch	47.2	4.4	4.0	13.5	29.7	0.0	1.2
Corn cobs	414	Continuous	39.8	2.5	13.3	19.7	22.2	0.6	1.9
Peanut shells	397	Continuous	45.8	2.8	9.0	1.4	31.2	1.0	8.8
Corn, grain (dry)	...	Batch	13.7	0.9	15.5	2.4	13.2	1.6	52.7
Leather (Schwing scrap)	...	Batch	44.4	3.6	7.9	1.3	38.5	1.0	3.3
Chicken feathers	...	Batch	63.2	5.1	4.2	2.2	24.0	1.3	(Sulfur)
Peat moss	...	Batch	45.2	1.6	20.3	2.0	17.5	0.8	12.6

^a The relative volume percentages of constituents shown are incidental to the particular temperature and other factors of the distillation, and may vary widely.

The crude tar oil contains amino bodies, pyridine, allyl compounds, higher aliphatic alcohols and ketones, and many unsaturated bodies, as well as aromatic compounds. It is comparatively easy to separate the cresols and related bodies from the raw oil by treatment with alkali, with subsequent regeneration of the mixed phenols from the alkaline solution by acidification with sulfuric acid. The presence of an alkali-soluble oil fraction necessitates its removal by steam distillation at this point previous to complete neutralization of the alkali.

This alkali treatment tends to make the residual oil more stable because of the breaking up of esters and polymerization of unsaturated bodies which occur in the original oil during the treatment; but although chemical analysis of the treated oil presents fewer difficulties, the constitution shown by such analysis no longer resembles that of the original raw oil. Attempts at analysis of the raw oil are hindered by a condition of continual breaking down of the unsaturated compounds present, under any method of treatment. A large quantity of oil might be analyzed by a succession of different methods so as to determine the percentages of definite constituents; many investigators have attempted this (16, 17), but even in this case overlapping compounds will confuse the actual situation. In these reports data as to the conditions of formation of such tars are often lacking, as well as analyses of the material from which the tar was produced, and such reports therefore represent only generalized information as to the probable constituents of the average tar.

The residual oil (or neutral oil) unabsorbed by the alkali treatment is distilled and roughly divided into three fractions designated as light, middle, and heavy. The light fraction has been used experimentally as an insecticide, and experiments by the Bureau of Entomology and Plant Quarantine have indicated an effect somewhat similar and comparable to commercial tobacco extract when used against the stick-tight flea, the poultry tick, and the bott fly (*Gasterophilus intestinalis*). Direct application of the material to the skin of the animal seems to be possible without discomfort or ill effects and the oil seems to be sufficiently powerful to destroy both larvae and eggs.

Thus far no commercial use has been found for the heavier fractions of the neutral oil. Experimentation on hydrogenation, esterification with both organic acids and alkalies, hydrolysis, halogenation, and treatment with ferric or aluminum chloride have been made on the various oil fractions, both for the purpose of removing or changing the powerful odor of the oil and for the formation of new compounds, but with little success. Owing to the general similarity of the raw oil to the usual wood distillation oil, there seems to be a definite possibility in the use of this product as a denaturant in certain industrial alcohol formulas.

In so far as uses for the raw tar are concerned, the probab-

ity is that a certain amount of purification would be required for any use. In St. Paul the heavy boiled tar was used for roofing. Tars from various materials have characteristic odors; straw tar has a particularly penetrating, sharp, naphthenic odor, for example, and corn cob tar has a sweet creosotic odor. Soluble tar usually has a sweeter, more creosotic odor than settled tar. On distillation, soluble tars give a waxy distillate at higher temperatures.

The charcoal recovered from the retort is somewhat unsuitable for ordinary charcoal uses because of its physical division into small pieces and hence must be further processed in order to find an outlet in most of the ordinary charcoal trade channels. Sawdust charcoal is now sold in briquetted form by the industry; therefore experimental briquettes were made with farm waste charcoals using starch, molasses, tar, pitch, and similar compounds as binders.

With certain of the more dense charcoals it was believed that an activation process might be economically applied. Considerable experimental work on steam activation was carried out, particularly with pecan shell charcoal, and the final activated product was commercially tried in the treatment of municipal water supplies. Samples were made in the laboratory which were apparently equal to commercial activated carbons. Some attention was paid to the use of charcoal as an ingredient of chicken or stock feeds.

The waste gases from the retort may be water-scrubbed to remove small quantities of water-soluble compounds and tar fog. The scrubbed gas may be used as fuel, despite the high carbon dioxide content, or the carbon dioxide may be recovered in the usual manner. The remaining gases can be used as a source of organic compounds by high pressure-high temperature catalysis.

A large number of analyses have been made of the non-condensable gases evolved during runs of various materials, particularly in the Cline retort. Since the gas samples from a continuous retort, as taken, merely represent the gas passing the orifice at a given time and reflect the momentary conditions in the retort a few minutes preceding the time of sampling, a great deal of unexplainable fluctuation is encountered, with occasional relatively large percentages of nitrogen. A few analyses of gases from various materials are presented in Table V, but it must be understood that the composition will vary both with the retort conditions and with the material.

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EVAPORATIVE INDEX

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A simplification of the Maxwell-Stefan equation is given, for the rate of evaporation at a definite point on a liquid surface:

$$E = K(D_1Mp_{A1})$$

This equation can be extended to cover the rate of evaporation over a finite liquid surface and can be used as a comparison of evaporating rates of liquids. The term "evaporative index" is suggested for the group D_1Mp_{A1} . By comparison of experimental and calculated values of the evaporative index, both for the author's data and for results reported in the literature, the practical utility of D_1Mp_{A1} is demonstrated.

Vapor pressure curves, covering the range from room temperature to the boiling point, are given for several liquids.

IN RECENT years some confusion has arisen, particularly in the patent literature, with reference to the interpretation of evaporation phenomena. Much of this confusion seems to be due to the fact that there is no convenient physical constant which can be used as a measure of the relative evaporation rates of liquids.

In earlier patents the favorite method of specification of evaporation rate was the boiling point or boiling range. At present vapor pressure is used to a large extent for the same purpose. That these two methods of expression are essen-

tially the same was pointed out by Cox (2), Calingaert and Davis (1), and Davis (3).

In 1913 de Heen (9) suggested the use of the product of molecular weight and vapor pressure of a liquid as a measure of its evaporation rate. This is a useful empirical constant and has been applied more recently by Hofmann (10) in evaporation work.

The object of the present study is to develop a constant which will serve as a reliable expression of the relative evaporation rates of liquids under identical experimental conditions, and which is simple enough to be of practical service in industry.

Mechanism of Evaporation

The concept of a diffusional resistance on the surface of a liquid, due to the presence of a stationary or relatively slow-moving film of air, has been useful in the understanding of evaporative processes and is retained here. (The term "air" is used throughout this discussion in place of the more general term "gas" for simplicity.) This "stagnant" film is usually conceived to be of such thickness that it will offer the same resistance to the transfer of molecules of vapor into the air stream as does the actual region of slow-moving air on the surface of the liquid (the effective film thickness).

For the case of vapor diffusing through such a film of air, the Maxwell-Stefan equation (13) leads to the following expression for the rate of evaporation, at a definite point on the liquid surface:

$$N_A = \frac{DP}{RTx} \ln \frac{p_{B2}}{p_{B1}} \quad (1)$$

Substituting D_1/P for D , this equation becomes: