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Further Experiments on the Chemistry of Wood Smoke in Connection with the Fish Smoking Industry

By D. le B. Cooper

In the first paper of this series presented to the Board in 1925 by Mr. Dauphinee a concise, clear account for the need of research on the nature of wood smoke in connection with the fish smoking industry is set forth. Having determined that the acetic acid and formaldehyde content of a smoke played a large part in both the preserving qualities and the tensile strength of fish muscle the method of attack was this. Smoke was produced under varying conditions of air rate and the amount of formaldehyde and acid, expressed as acetic acid, determined at the same time noting the effect of the smoke as a whole on a piece of haddock muscle suspended therein. This method probably approaches to some extent the commercial method of smoking fish, but at the same time shows little on which it is possible to base a theory concerning the production of the important products during the partial combustion of sawdust. It was suggested that the temperature control be introduced in order to obtain some idea of the optimum temperature for the production of the important products, and assuming that some knowledge of the nature of the reactions proceeding at any time is available, to gain some idea of the particular fraction of the wood which under distillation or partial combustion gives rise to the important products. The work consists principally in the perfection of an apparatus designed to this end, which would serve for several sets of experiments, tests on the analytical methods, and the determination of the amounts of products produced under two sets of conditions.

EXPERIMENTS ON WOOD SMOKE

Apparatus.-

The object of the design of the apparatus was the controlled distillation of wood, and controlled partial burning with different amounts of air infusion. Provision was also made for the infusion of steam either along with, or without air.

Two types of apparatus were tried. In the first the control was attempted by using an oil bath containing an oil which could be heated to the proper temperature i.e. 350°-400°C. The design of the apparatus took the form of that shown in the accompanying diagram. The apparatus consisted of a long tube B, in which was charged the wood, surrounded with an oil bath A which could be heated to any desired temperature by means of bunsen burners.

The diameter of the inner tube was kept as small as possible consistent with enough yield for analysis (determined by experiment) and when fully charged held about 400 gms. of sawdust. The object in keeping the diameter of the tube as small as possible was to lessen the lag of heat transference between the outer oil bath and the middle of the charging chamber. The temperature lag with a tube of the size shown is approximately one hour.

The temperature of the oil bath and the interior of the sawdust tube was measured by high temperature mercury thermometers inserted in tube D and C. D is simply an open pipe and served also as an outlet for the oil bath. Tube C was a long iron tube sealed at the interior end and large enough to admit the introduction of a thermometer. In order to insure that the circulation in the oil bath was good, and that the temperature of the bath as shown by the single thermometer would approximate closely the temperature in all parts of the oil, the bath was heated by ten bunsen flames, four playing on each side near the base, and two directly underneath. The difference in temperature between the D and F was, in a trial case, very slight.

The difficulty with this type of apparatus lies in the securing of a proper oil. The oil should admit of the possibility of continued heating to 350°C in order to insure that all the products are driven off the wood. Several oils were tested with the results as shown in table I.

Table I

Oil Samples for Oil Bath *

Kind of Oil	Secured from	Lowest Flame	Temp. Reached
Cottonseed	Nat. Drug	310-300	355
Polarine Med.	Imp. Oil	200	240
Mobile B.	" "	275	310
Mobile BB	" "	280	320
Marvelube Sp.Hvy.	" "	240	300

Temperature in degrees Cent.

Tests made in the manner of open flash tests.

Test of Cotton Seed Oil Used in Bath

Highest temperature reached in final use of Oil 283°C. Higher temperature cause bumping and rapid distillation.

Temperature	Remarks
20	Black and Viscous.
100	Fluid. Gelatinous matter disappeared
190	Heavy Smoke Oil Dark.
230	Distinct signs of boiling.
260	Heavy flash.
280	Very heavy flash and rapid boiling.
248	Lowest point of flash.

Tests made after eight successive heatings to 300°C for periods of time ranging from one-half to three hours.

* Cl. Inter. Crit. Tables. P.66.

Whilst commercial cottonseed oil admits reaching the desired temperature, with the proper cautions described later, it was found that in actual use the oil would only serve for three successive distillations due to the change in the nature of the oil with the continued heating to high temperatures. This proved too expensive. Peanut oil was then tried in the hope that it would obviate this difficulty but was not successful. The apparatus was therefore discarded for this purpose, but has one advantage over the second apparatus, which is given later.

The second apparatus designed was one in which electricity was used as the heating element, and the control of the temperature was accomplished by means of a rheostat.

The apparatus consisted of two distinct sections, the furnace proper, and the charging tube. All metal work was of brass to eliminate hot spots in the furnace tube which would occur if iron were used, due to the presence of eddy currents or hysteresis in the iron. The charging tube was made of a piece of brass pipe with dimensions as shown in the diagram. It was similar to the inner tube of the oil furnace except that the seal at the end of a tube consisted of a brass flange in place of the simple cap. The flange could be made tight by the use of an asbestos gasket, and was much more convenient than the cap of the oil apparatus. The inner tube of the furnace proper, made of brass, was so fashioned that it admitted the charging chamber without any air space insuring good conduction of heat to the sawdust. The brass tube was wound with a thin sheet of asbestos paper for insulation. Over this was wound the resistance wire. Approximately 28 feet of 18 nichrome wire resistance .390 ohms per linear foot. The distance between each coil was approximately 3/4 inches near the center, but at each end the wire was bunched in order to insure equal temp. rise of the larger mass of metal at either end. The wire was then coated with an insulating cement to fix it firmly in place. At one end of the furnace at this place two holes 14 inches in length were made in the following manner to allow for admission of thermometers at the outer side of the charging tube. Two glass tubes about 16 inches in length were wound with a triple layer of ordinary newspaper and laid over the insulating cement. The tubes were then firmly sealed in by further application of cement till they had been entirely enclosed in a thick walled tube made of cement. When the temperature of the furnace had subsequently reached 500°C the paper surrounding the glass tubes was burnt away and the tubes could be withdrawn leaving two long tubes of a size sufficient for the admission of a thermometer just outside the outer part of the charging chamber. The temperature of the furnace could be noted at any time by means of thermometers or thermocouples inserted in these tubes. The whole of the cement layer was then firmly wrapped with asbestos wicking, outside of which was placed commercial pipe covering. The space between the pipe covering and the asbestos wicking was filled with ground asbestos. This was subsequently covered with a second pipe covering and the whole mounted on a wooden base. After prolonged working of the furnace between 250°-350°C the outside was sufficiently cool.

The complete range in temperature of the furnace was not tested, after an hours heating without the charging tube the furnace tube showed a dull red, which would indicate that the furnace was capable of maintaining a temperature in the vicinity of 800°C. Fully charged the temperature of the furnace could be raised to 350°C in one hour.

Comparison of Apparatus.-

The principal advantage of the electrical method of the control are mainly ones of convenience, comfort and expense. As mentioned above the oil bath was heated with ten bunsen burners which caused excessive temperatures in the laboratory. The oil bath required to be charged after every second experiment, and there was always present danger of fire through splashing oil in spite of the fact that the over heated oil was conducted through an air condenser outside the building. The electric furnace eliminated all these inconveniences and at the same time permitted of an equal degree of control of that temperature corresponding to the temperature of the outer oil bath. The main advantage of the oil heated apparatus over that heated by electricity was due to the large body of heat and the relatively sudden temperature changes to which the oil bath could be subjected. Thus, due to the infusion of air, the temperature of the sawdust chamber sometimes rose suddenly beyond the desired point. By the removal of flames the oil bath could be cooled very quickly and the excess heat produced in the sawdust absorbed when the amount of air infusion was small. Due to the insulation on the electric furnace very little control by this means was possible. However Dauphinee[1] has pointed out that a tube containing sawdust, the tube being unjacketed, could be made to burn with a sufficient air supply. Therefore it would seem that control of the inner temperature, using a tube of the size used above, by the method of cooling the walls of the side of the tube is more or less feasible, and in consequence the electrical method was continued throughout the

1. Dauphinee Loc. cir.

experiments, and by a different arrangement of the air supply this difficulty is obviated without making inapplicable or invalid any of the results obtained by this method.

The Collection Apparatus:-

The collection apparatus was for the most part a counterpart of the one used by Dauphinee in his experiments. The cooling with freezing mixture was omitted and an additional collection flask placed in the train in its stead. Dauphinee has pointed out that in the straight distillation most of the products could be collected, whilst during the distillation with air infusion much of the products must have been lost. It is recognised that inert gases passing through liquids containing liquids will evaporate both liquids and carry their vapors in its stream in the direct ratio of their partial vapor pressures and the amount of the inert gas. The more flasks in the train the more efficient the collection for this consideration alone. Dauphinee also points out that there is an undefined amount of the principal product lost, being carried on by the smoke, as distinct from the gases, due to the electrical nature of the smoke particles, and the energy exhibited by the extent of their surface. In one experiment in which five collecting flasks were used analysis of acetic acid and formaldehyde in the flasks in order of their position in the chain gives the following.

Air Rate	Flask Nos.				
	2	3	4	5	6
4.1 cu. ft. per hour	.21	.06	.05		
14.5 " " "	.37	.18	.10	.07	.06

The second column in which 5 receivers were used serves for comparison with column 1 in which only three receivers were used. Analysis shows therefore the expected results that the greater the air supply the more need for more collecting flasks. The figures are expressed as per cent. of formaldehyde on the dry weight of the wood. In comparison, it should be remembered that the total amount of formaldehyde differed with the two rates of air infusion. However, it seems reasonable to suppose that with water collection the addition of five collecting flasks to the main flask attached to the condenser by means of an adapter is sufficient to insure the collection of the major portion of the free formaldehyde.

The acetic acid results are on the whole much lower as the chain grows than those shown above for formaldehyde. Some idea of the amount of formaldehyde lost may be gained by the use of curves and the interpolation of values for an infinite number of flasks using as basis for calculation the area under the curve produced till it meets the axis. This was not taken into consideration in any of the results shown in the paper.

Notes on the Analysis for Formaldehyde;

In the case of the supposed uncalculated adsorption of the formaldehyde and the acetic acid by the charcoal in the smoke, or assuming that the smoke itself is finely divided charcoal, by the smoke itself; the following may be noted. In the first place charcoal produced at low temperatures has a much larger specific adsorptive power than the charcoal produced at higher temperatures. The method of producing smoke in this instance would therefore tend to produce a smoke of great specific absorptive power. The nature and the amount of the absorption depending as it does on the specific nature of the gas, and the partial pressure of the gas in a definite mixture; together with temperature, any data for gases and mixtures of gases given in the literature that might apply in the case of the gases produced by the partial combustion of wood must be regarded as merely indicative and of no definite value for quantitative calculation. However in the case of acetaldehyde and acetic acid two of the factors entering into the analysis performed in this set of experiments the following data are given.-

Volume of gas absorbed per volume of charcoal.

Temperature in centigrade degrees.

Pressure in millimeters of mercury.

(1) Gas	Vol.	Temp.	Press.
Acetic acid	85	159	624
Acetaldehyde	67	155	687

The presence of two vapors mutually soluble the one in the other also tends to increase the apparent absorption of each by the charcoal. Thus the presence of water

(1) Bancroft- Applied Colloidal Chem. P 4 (McGraw Hill)

vapour increases the apparent absorption of ammonia by charcoal, and a similar supposition might be made regarding formaldehyde and water vapour with some hope of being correct. Regarding the method of cooling the vapours from the partial combustion of wood the following might be said, the lower temperature of the absorbing material and the gases absorbed, the more the absorption. From purely theoretical stand point therefore it would seem wise to omit the ice salt coolers noted by Dauphinee in his paper, and use only water collector, which on the other hand may not be satisfactory for this reason. Bancroft quoting Engelder and Wild (Ber. 29: 1929(1896) makes the following statement:- "The presence of a film of air or vapour around a small particle is shown in a striking way by the fact that it is quite a simple matter to pass suspended phosphorus pentoxide through several wash bottles in spite of the tremendously hygroscopic nature." It should be still more difficult to remove smoke particles by this method, and until all the smoke particles have become precipitated little or no reliance may be placed on the results of analysis with varying amounts of air. At one rate of air it is quite evident that a certain number of smoke particles are produced, at another rate another number of smoke particles. The amount of formaldehyde or acetic acid produced in the actual combustion therefore may be more or less absorbed according to the amount of smoke produced.

In connection with the adsorption and absorption of smoke by washing in a solution containing ions of high charge the following experiment was performed. In Run 8B the fifth flask in the train was filled with a solution of magnesium sulphate. The presence of the ions prevents analysis but no change in the density of the smoke leaving the flask could be detected.

In connection with this it is suggested that the most probable way of precipitating the smoke particles is by use of the Cottrell method of electrical precipitation. After the precipitation of all the smoke particles the freeing of formaldehyde and acetic acid presents itself as another problem.

Another question naturally arises in this connection; does the actual smoke particle together with the absorbed material actually precipitate on the fish? or is the color of the fish, the surface, the taste etc. produced by the condensation of those materials carried along mechanically by the eddy currents and the particles of smoke?

The fact that the fish assume a better color after having been brined would seem to indicate that part of the function of the brine was to precipitate a portion of the actual smoke particles on the fish. The additional fact that the color is more quickly assumed, and a better color is produced by the use of sodium bicarbonate, would further substantiate this. As a purely technical problem the effect of various specific ions on the color without regard to the taste or odour of the fish might be tested. The ion having the greatest opposite charge to that of the smoke particle should produce the better color more quickly if it is the actual condensation of the smoke particles that cause the production of the color.

Methods of analysis:-

The methods of analysis were those of Dauphinee described in his report to the Board. An additional procedure was devised for convenience.

As mentioned by Dauphinee the presence of phenols obscure the end point of the reaction for the determination of formaldehyde to such an extent that in some cases the direct titration of the excess silver with KSCN was impossible. Dauphinee in all cases obviates this difficulty by distillation procedures described in his paper. In some cases it was found more convenient to precipitate the excess silver with a calculated excess of HCl and weigh the precipitate thus formed on a Gooch crucible. That this method of analysis is satisfactory was shown in two ways. The first an analysis of a smoke solution free enough from phenols that it could be analysed in the usual way and the results checked, and secondly the duplication of one run in which the precipitation method had been used, using in the duplication the distillation method described by Dauphinee.

One other curious result was noted in the case of the analysis for formaldehyde. During the analysis for formaldehyde in the solutions resulting from Run 4T it was discovered that the apparent formaldehyde content of the solutions increased the longer the KCN solution was allowed to remain in contact with it. Quantitative tests were made on this feature, and all the tests were checked with the help of Mr. Wyman. The method used was as follows:- the solutions were made up for analysis as described. One set was titrated immediately and the others allowed to stand for varying periods of time. The tests were made on an average smoke distillate obtained in the course of the experiments in the usual way. The results are expressed for greater clarity in terms of the number of ccs. of KSCN used in the titration. An equal aliquot of solution was used in each case.

Time	CC. KSCN
Immediate	1.50
	1.55
1 hr. 15 min.	3.75
	3.80
18 hours	7.57
	7.17
	7.40

The second test made with a solution of commercial formaldehyde in order to determine if there need be any definite length of time allowed to elapse before the formaldehyde content showed its true value. Following are the results:

Time	cc. KSCN
Immediate	2.75
	2.75
1 hour	2.75
	2.76

The distillate from the smoke was then collected in definite fractions. Using the fraction collected between 110°C and 260°C. the following results were obtained.

Fraction A Run T

Time	cc. KSCN
Immediate	2.75
	2.80
Over night	2.95
	2.94

Having determined that there was a definite if not regular change, an effort was made to determine the cause of the change. A rough experiment in which acetic acid was added in a more or less qualitative manner showed a slight increase in the KSCN value. This fact was in the case of strong solutions of acetic acid noticed by Dauphinee. Results were then tried with acetaldehyde.

1. More or less qualitative

Direct titration for formaldehyde		2.72	2.75
Two drops of acetaldehyde b.p. (app.)		13.75	3.53

2. Quantitative determination

Formaldehyde solution	5.66	5.68	5.66
Two cc. of acetaldehyde solution added, sol. .001629 gms. acetaldehyde per cc.	7.14	7.10	7.13

Calculation from the acetaldehyde content from the titration gives .001738 gms. of acetaldehyde per cc. solution. From the boiling point of the acetaldehyde Holleman[1] has shown that the probable content of the solution is at 41.6 C. (natural B.P.) 53.4 mols. per cent paraldehyde. From the data thus obtained it is suggested that the apparent increase of the formaldehyde content of the solution with the time is caused by the gradual reverse reaction,-

paraldehyde ⇌ acetaldehyde

caused by the union of the acetaldehyde in the solution to form a KCN acetaldehyde complex. This would also account for the difference in the weighed value and the determined value of the paraldehyde in the above determination. The author feels that much work needs to be done in this connection for it is quite evident with the figures given above that the results expressed as formaldehyde in the subsequent determinations also include all or part of the acetaldehyde content in the solution, and a probable part of its paraldehyde content according to the time the solution is allowed to remain standing in

1. Holleman Zeit fur Phy. Chem.- 43,129 (1903)

contact with the KCN. Allen's Commercial analysis page 330 says concerning this method- "Results by this method are said to be correct, even in the presence of acetaldehyde, if the liquid is titrated immediately after shaking." On page 114 of the same volume the following statements are made- "An aliquot containing about 0.04 grams acetaldehyde is then shaken in a closed flask containing 25 cc. of KCN solution." Follows a description of the Romijin method for formaldehyde and the following statement: " if the acetaldehyde is completely depolymerized, the cyanide method serves very well for its determination." These statements are contradictory, and the above experiment shows that the results of the Romijin method are not correct expressed in terms of formaldehyde when acetaldehyde is present at the same time.[1] This is the case in the solutions resulting from the distillation of wood. The analysis therefore really is at the best only a comparative one in which the time factor is a large function, and in order that some basis of comparison between the results of Mr. Dauphinee and the results in this paper might be made, correspondence with Mr. Dauphinee established his exact manipulation during the analysis and the following method was devised and followed. The minute manipulation is included because it has a bearing on the time, and in consequence must be an important consideration in the analysis.

Method for Formaldehyde:-

Arrange six beakers, previously cleaned with cleaning solution so that no grease or dirt adheres to the sides, in threes, called respectively Set. 1, Set. 2. In each of the beakers of Set 1 place 10 cc. of KCN solution. In each of the beakers of Set 2 place 10 cc. of silver nitrate and add 10 cc. of 40% nitric acid. Add to each of the beakers in Set 1 the amount of solution to be analysed and stir for one half minute. Add the solution of the silver nitrate at the end of the half minute and stir for one half minute. Filter immediately in the same order as the addition of the formaldehyde was made, washing the precipitate twice by decantation and once on the filter paper. Collect the filtrate in the beakers previously used for the silver nitrate solution and titrate immediately. The total time of the analysis is mainly dependent upon the rate of filtration, but with well cleaned funnels using a medium quantitative paper the total time of analysis after the addition of the silver nitrate solution should not require more than ten minutes.

1. Bunbury Dist. of Wood.

For future comparison two regular analyses were timed.

Analysis rate

	Time	Time	Aver.
Start	11.00½	10.05	4½
HNO_3	11.04½	10.09½	
Ready for filtration	11.07½	10.11¼	2¾
Smoke soln. added	11.08¼	10.13	
	11.09½	10.13½	
Solutions KCN-$AgNO_3$	11.10	10.14	
Mixed	11.11	10.15¼	1¼
Filtration completed	11.16	10.20	6
Titration completed	11.20½	10.25½	5¼

The method for the determination of acetic acid was that used by Dauphinee. A qualitative test for the presence of phenols was afforded without extra effort by the fact that the ferric chloride used as an indicator in the KSCN titration as stated by Haley(1) forms a good qualitative test for the presence of phenols.

The distillation of wood according to Bunbury (page 77 et seq.) proceeds in four distinct stages according to the temperature in the exterior of the retort. Bunbury says: "there is evidence of insipient decomposition at temperature a little above 100 in the cases of most of the woods investigated, but from 100 to 200 the reactions are slow and of no practical significance. From 200 up the decomposition is appreciable, and at about 275 there is a sudden and very rapid rise in the velocity of decomposition, considerable quantities of heat being evolved."

Full recognition of the above is necessary for the proper appreciation of the nature of the experiments carried out with regard to temperature control. Assuming that a certain definite fraction of the wood decomposes up to and including any definite temperature the effect of changing the receivers at any definite point in the reaction would be to include and separate those products resulting from a definite area of decomposition in the wood. The additional result of the air infusion should be peculiar

1. Haley Jol. Ind. Chem. 18, 1312 (1926)

to that portion of the wood undergoing distillation. A second factor entering into the discussion of the controlled distillation is the speed with which the reaction is allowed to proceed; thus a rise of as high as two per cent has been noticed in controlled distillation over a distillation that was not controlled.

In the succeeding results all per cents are on the dry weight of the wood used. The results for formaldehyde include also the acetaldehyde, and possibly other aldehydes present. The results expressed as acetic acid represent the total acidity of the wood.

Set I, Trial Runs:

The object of Set. I or trial runs was to determine the efficiency of the oil apparatus, the qualitative appearance of the smoke, and the specific effect of the air infusion. In no case was the combustion completed (Cf. Bunbury 894) so that the results may not be accurately compared with those following. The results therefore are omitted.

Set A. Run I

This run was made as a basic run for the comparison of all future results. For this purpose the distillation was strictly controlled and the proceedure during the course of distillation noted for future adherence. The receivers were changed at the usual places i.e. after the temperature had reached 270 and the distillation had ceased, and after the completion of the distillation at 300. Qualitative tests on the various fractions gives the following results.-

Fraction A. (1) No traces of phenols using the ferric chloride test.
(2) Shows presence of very little formaldehyde and practically no acid.

Fraction B. (1) Much tarry matter and phenols.
(2) Very little of either important products.

Fraction C. Showed the presence of much tarry matter, but less phenols.

Results:- Gms. Sawdust (dry weight) 352

Average air rate per hour in cubic feet. 0.0

The fractions are numbered A.B.C. The figures denote the position of a particular receiver in the chain, the one nearest the furnace being numbered 1.

FORMALDEHYDE

Receiver	Gms.	Tot. gms. in fraction	Per cent in fraction	Total per cent.
1A	.84			
2A	.10			
3A	.07	1.01	.286	
4A	.00			
1B	1.40			
2B	.12			.98
3B	.08	1.60	.455	
4B- C	.00			
1C	.65			
2C	.11			
3C	.09	.85	.241	

ACETIC ACID

Receiver	Gms.	Tot. gms. in fraction	Per cent in fraction	Total per cent.
1A	13.47			
2A	9.03	13.50	3.84	
3A	0.00			
1B	9.29			
2B	.05	9.34	2.65	6.85
3B	0.00			
1C	1.27			
2C	Trace	1.27	.37	
	0.00			

In the analysis for acid content receiver 4 was neglected for obvious reasons.

Run 2

Run 2 was an attempt to approach the conditions of Run 1 with the addition of air infusion. It was found impossible as heretofore noted to control the temperature sufficiently to collect the three distinct fractions as above. In this run as in all the runs of this series the following procedure was adhered to. The temperature on the outside of the reaction tube was raised quickly to 200°C and kept at that temperature till all the moisture had been driven off the wood, and the interior temperature showed 190°C. This insured uniform drying of the product, and also that at the start of each run the wood was in approximately the same condition, thereby eliminating any effect that distillation with moisture would cause. (cf. Bunbury)

In this run as in all the succeeding ones in which air was passed over the sawdust, the second and following receivers showed the presence of phenols in amounts varying with the position of the flask from the furnace. They also showed increased amounts of formaldehyde and acid varying as the amount of air and the amount of visible smoke produced.

Results Run 2:-

Gms. sawdust (dry weight) 303.
Average air rate per hour in cu. ft. 3.0.
Products of distillation and partial combustion were collected in one set of receivers only. The material in receiver one was analysed separately. The remainder of the chain made up to a definite volume and analysed as a whole.

FORMALDEHYDE

Receiver	Gms.	Tot. gms. in fraction	Per cent in fraction	Total per cent.
1, 2,3,4	5.42 ~~5.42~~ 1.18	6.60	2.18	2.16

ACETIC ACID

Receiver	Gms.	Tot. gms. in fraction	Per cent. in fraction	Total per cent.
1, 2,3,4	18.27 3.93	22.20	7.33	7.33

Run 3

Run 3 was an attempt to duplicate the results of Run 2 using the electric furnace in place of the oil furnace and a different method for the analysis for formaldehyde. The acid analysis shows good agreement. The results for the formaldehyde show considerable discrepancy, and since in the analysis by the Gooch method the solution was allowed to stand over night, the results in the light of further data are not comparable but are shown for the further indication of the effect of allowing the solutions to stand.

Results, Run 3:-

Gms. sawdust (dry weight) 315.
Average air rate per hour in cu. ft. 2.7.

FORMALDEHYDE

Receiver	Gms.	Tot. gms. in fraction	Per cent. in fraction	Total per cent.
1, 2,3,4	3.46 1.02	4.48	1.42	1.42

ACETIC ACID

Receiver	Gms.	Tot. gms. in fraction	Per cent in fraction	Total per cent.
1 2,3,4	17.99 4.59	22.58	7.17	7.17

Run 4

This run was carried out similarly to No. 2 with a greater amount of air infusion. The train was analysed in an effort to gain some idea of the amount of the important products being lost. In this run the effect of the air infusion on the temperature of the interior of the furnace tube became very noticeable, the temperature was taken therefore at three places along the temperature tube and is given below to show this effect.

P_1 is the temperature near the end of air inlet; P_2 about the centre of the temperature tube; P_3 at the end nearest the collection train. The temperatures at the outside of the reaction tube are given for comparison.

Time	Temperature			
	Inside			Outside
	P_1	P_2	P_3	
11.00		20		20
12.10		206		240 (Air commenced)
12.30	275	270	260	250
12.50	306	290	270	238
1.35	405	365	306	293
2.08	405	370	325	280

Results Run 4:-

Gms. sawdust (dry weight) 298.

Average air rate per hour in cu. ft. 4.1.

FORMALDEHYDE

Receiver	Gms.	Tot. gms. in fraction	Per cent in fraction	Total per cent.
1	3.04			
3	.62			
3	.19			
4	.14	3.99	1.34	1.34

ACETIC ACID

Receiver	Gms.	Tot. gms. in fraction	Per cent. in fraction	Total per cent.
1	14.48			
2	2.91			
3	1.15	19.26	6.46	6.46
4	.76			

Run 5

In this run the air rate was still further increased with a consequent increase in the difficulty of control. As in No. 4 the train was analysed in separate units, and some idea of the effect of air rate on the adsorption of the products may be gained by comparison of the results of the two runs.

Results Run 5:-

Gms. sawdust (dry weight) 311.
Average air rate per hour in cu. ft. 14.5.
In connection with the figure given for the average air rate this fact is to be noted. The meter used was a water meter the calibration of which was not guaranteed correct after the reverse pressure had passed 6 inches of water. In this run the pressure as indicated by a manometer in the train was considerably greater.

FORMALDEHYDE

Receiver	Gms.	Tot. gms. in fraction	Per cent. in fraction	Total per cent.
1	2.95			
2	1.15			
3	.55			
4	.32			
5	.21			
6	.12	5.30	1.71	1.71

ACETIC ACID

Receiver	Gms.	Tot. gms. in fraction	Per cent. in fraction	Total per cent.
1	10.13			
2	4.67			
3	1.96			
4	.93			
5	.60			
6	.45	18.74	6.03	6.03

It is heretofore mentioned that as the result of air infusion over the sawdust the temperature of the interior of the reaction tube could not be controlled. To obviate this difficulty air infusion at the collecting end of the apparatus was tried.

The additions to the apparatus are an electric air preheater, a mixing chamber, and an air chamber in which was set a sealed copper tube for the purpose of determining the temperature of the air at the time of infusion. The position and action of each of the new parts can readily be deduced from the diagrams.

Following are the specifications of furnace, which acted as the preheater. The furnace consisted of a brass tube 18 inches in length, reduced in diameter to a quarter inch at each end. A loose coil of resistance wire insulated from the sides of the brass tube by a layer of asbestos paper served as the heating unit. The unit consisted of 23 ft. No. 23 Nicrome Wire. The thermal insulation consisted of one layer asbestos wicking over which was wrapped a layer of asbestos paper also covered with one asbestos pipe cover. The rheostat for use with the furnace was of the electrolytic resistance type, constructed of an empty ether tin with an electrode which could be raised or lowered at will, the electrolyte consisting of 1½ gms. NaCl in 1570 cc. water, it enabled fairly accurate control of the temperature of the air at any rate.

It is pointed out before any results are given that this method of introducing the air presents several difficulties susceptible of control, which the first method did not show. Two controlling factors in the place of one are now present, the first the rate of air infusion, the second the temperature of the air at the time of infusion.

A change in either would cause a change in the relative amounts of the various products contained in the gases passing through the condenser. It was hoped however that by keeping the temperature of the air at the time of infusion the same as the internal temperature of the furnace or the mean between the outer and the inner temperature of the furnace that the sum total of those products analysed for, in the second method for any definite rate of air infusion, would agree with the results obtained from the former one.

The following experiments were performed.

Run 1, Series B.

The procedure of this run was exactly the same as that of Run 1 Series A. The analyses show fair agreement for the total amount.

Results:-

Gms. sawdust (dry weight) 311.
Average air rate per hour in cu. ft. 0.0.

Owing to the completeness of control to which the wood could be subjected using the electric furnace the exothermic reaction could apparently be retarded to such an extent that the temperature of the outer bath might be raised as high as 300°C. without causing vigorous action. This fact should cause a difference in the contents of the various fractions, and where it occurred a note is made.

Exothermic reaction retarded till the temperature had reached 325° i.e. in the third fraction.

FORMALDEHYDE

Receiver	Gms	Total gms. in fraction	Per cent. in fraction	Total . Per cent.
A1 A2	.20 .04	.24	.07	
B1 B2	.77 .01	.78	.24	
C1 C2	1.28 .86	2.10	.64	.97

ACETIC ACID

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total Per cent.
A1	13.20			
A2	.00	13.20	4.06	
B1	5.25			
B2	.00	5.25	1.62	
C1	4.45			
C2	.18	4.63	1.42	7.16

Run 2, Series B.

In this run in which the air was mixed with the distillation products, the apparatus for mixing consisted of a simple right angle three way elbow. The air was preheated to an undetermined temperature by means of bunsen burners. The temperature procedure in the distillation was the same as that used in the basic experiments. The products were collected in two fractions, instead of the usual three.

Results:-

Gms. sawdust (dry weight) 325.
Average air rate per hour in cu.ft. 7.8.

FORMALDEHYDE

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total Per cent.
A1	.54			
A2	.28	.82	.26	
B1	1.65			
B2	.85	2.50	.81	1.07

ACETIC ACID

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total Per Cent.
A1 A2	6.51 .98	7.50	2.41	
B1 B2	9.30 5.01	14.31	4.60	7.01

Fraction A showed no phenols present. Fraction B contained much phenols.

Run 3, Series B.

The object of the run was to determine the efficiency of a combustion chamber constructed with solder joints. The chamber failed before the run could be completed.

Run 4, Series B.

The object of this run was to determine the efficiency of the furnace preheater and a combustion chamber constructed of cast iron welded. The results were analysed and are given below. Here no provision was made for the taking of the temperature of the air at the time of infusion. It was found that the thermo-couple inserted in the tube set in the chamber for the purpose of taking the actual temperature of the combustion did not read correctly due probably to the thickness of the metal in the thermometer tube, and the heat leak from the chamber, which was not prevented by a heavy covering of asbestos.

Results: (Run 4):-

Gms. sawdust (dry weight) 325.
Average air rate per hour in cu. ft. 14.0.

FORMALDEHYDE

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total per cent.
A1 A2	1.71 .88	2.59	.80	.80

ACETIC ACID

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total Per cent.
A1 A2	19.33 3.16	22.49	6.93	6.93

Run 5, Series:-

In this run as in the succeeding ones the temperature of the air at the point of infusion was kept as nearly the mean temperature of the distillation as possible. A portion of haddock muscle was suspended in the second flask of the receiver. The effect of the various fractions of the flask was as follows:

Fraction A. Colour - Slight
Odour- Sour acid, which disappeared on standing.
Taste- Bitter, improved on standing.

Fraction B. Fish slightly coloured.
Taste - Bitter
Odour - Acid disappearing.

Results, Run 5, Series B:-

Gms. sawdust (dry weight) 325.
Average air rate per hour in cu.ft. 3.0.

FORMALDEHYDE

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total per cent.
A1 A2	.78 .43	1.28	.34	
B1 B2	.92 .57	1.49	.46	
C1 C2	2.71 .50	3.21	.99	1.79

ACETIC ACID

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total per cent.
A1	8.46			
A2	.04	8.50	2.62	
B1	5.90			
B2	.04	5.94	1.83	
C1	4.91			
C2	.15	5.06	1.56	6.01

Fraction C. Colour - Rich Brown
Taste - Bitter
Odour - Acid

Process of reaction.

From the rate of the reaction it was deduced that a partial exothermic reaction only occurred at points below 300°. On raising the furnace to 375° a vigorous exothermic reaction occurred. The smoke in the first two of the fractions was light, that in the third heavy.

Run 6, Series B.

As run 4 with a greater air rate per hour. In this run the reaction proceeded normally, and the air was strictly controlled at every point. This run was also characterized by the fact that the smoke was vigorous and heavy throughout. Unfortunately no fish was secured in time for a test. The observed nature of the smoke is, however, given below.

Fraction A:- At lower temperature smoke was acid and varied from light to none.

Fraction B:- Heavy smoke, dry and sweet smelling. Exothermic reaction commenced at 275°C. and showed signs of a secondary exotherm at 350°C.

Results, Run 6, Series B:-

Gms. sawdust, (dry weight) 325.
Average air rate per hour in cu. ft. 17.0.

FORMALDEHYDE

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total per cent.
A1 A2	1.24 .43	1.67	.51	
B1 B2	1.29 .66	1.95	.60	
C1 C2	.28 .23	.51	.16	1.27

ACETIC ACID

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total per cent.
A1 A2	12.00 .72	12.72	3.92	
B1 B2	5.79 3.08	8.87	2.73	
C1 C2	1.09 .59	1.68	.52	7.17

Run 7, Series B.

This run was also characterized by the fact that the exothermic reaction was postponed till the temperature had reached 325°C. The amount of distillate resulting from the run was a minimum. Fraction A contained about the usual amount owing to the effect of the water resulting from the drying of the wood. Fraction B contained only about 10 cc. of distillate. The effect of the various fractions on the fish was as follows:

Fraction A. Colour - light
Odour - acid
Taste - acid

Fraction B. Similar to A.

Fraction C. Colour - Darker
Odour - Slightly acid
Taste - Medium acid which disappeared as soon as the surface of the sample had dried.

Results:-

Gms. sawdust (dry weight) 325.
Average air rate per hour in cu. ft. 24.1.

FORMALDEHYDE

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total per cent.
A1	.22			
A2	.42	.64	.20	
B1	.17			
B2	.61	.78	.24	
C1	.47			
C2	.29	.76	.23	.67

ACETIC ACID

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total per cent.
A1	2.26			
A2	4.10	6.36	1.96	
B1	.32			
B2	2.38	2.70	.86	
C1	1.73			
C2	1.10	2.83	.87	3.69

Run 8, Series B.

In this run a large 2 litre Erlymeyer flask was substituted for the smaller vessel in which the fish was suspended in the hope that it would cause an improvement in the surface of the fish. In the former runs the fish was always wet when removed from the smoke; the larger flask made no improvements.

The fifth vessel in the chain of receivers was filled with a solution of magnesium sulphate. The smoke was not retarded.

The effect of the smoke on the fish was as follows:

Fraction A. Colour - very light
Odour - acid
Taste - bitter

Fraction B. Colour - light brown
Odour - acid
Taste - acid but not bitter

Fraction C. Colour - very light
Odour - sweet
Taste - very fair

Results:-

Gms. sawdust (dry weight) 325
Average air rate per hour in cu. ft. 30.5.

FORMALDEHYDE

Receiver	Gms.	Total gms. in fraction	Per cent in fraction	Total per cent.
A1	.61			
A2	.64	1.25	.38	
B1	.77			
B2	.83	1.60	.49	
C1	.18			
C2	.27	.45	.14	1.01

ACETIC ACID

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total per cent.
A1 A2	7.95 4.12	12.07	3.72	
B1 B2	2.62 5.45	8.07	2.49	
C1 C2	.61 2.16	2.77	.85	7.06

Run 9, No series.

It was suggested that the effect of a rapid distillation with the air entering the end of the furnace nearest the condenser, be tried. The procedure for Run 9 was as follows. The wood was dried in the usual manner. The furnace was turned on full till the temperature had reached 325°C. to cause as rapid distillation as possible. During the exothermic reaction the heat was shut off, to guard against explosions. After the exothermic reaction had ceased the furnace was again turned on full till the temperature had reached 400°C., and kept at this temperature till the distillation had ceased.

The fish showed the following characteristics:-

Colour - brown

Odour - medium acid

Taste - light acid.

Results;-

Gms. sawdust (dry weight) 325.
Average air rate per hour in cu. ft. 13.0.

FORMALDEHYDE

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total per cent.
A1 A2	.68 1.78	2.66	.82	.82

ACETIC ACID

Receiver	Gms.	Total gms. in fraction	Per cent. in fraction	Total per cent.
A1 A2	21.1 2.5	23.6	7.28	7.28

General discussion of results

The results of the first set of experiments, those runs classed as series A, check the results obtained by Mr. Dauphinee at this station in 1925. In addition some data on the results of the air infusion in connection with the possibility of temperature control are given.

The results of the second set, Series B. are not conclusive. The apparatus needs further perfection before duplicate runs can be made. Incorporation of the results in a curve with due consideration of the progress of each run gives a slight indication that the amount of formaldehyde gradually decreases with the air supply, the amount of acetic acid showing a very slight general increase. The error in the control of the apparatus is without doubt greater than that in the analysis.

Summary

1. Two types of apparatus for the temperature control of wood distillation and partial combustion are described.

2. Two sets of experiments are described, and the results given.

3. An error in the method for the analysis of formaldehyde has been corrected.

4. A short discussion of some of the factors influenceing the results prior to analysis is included.

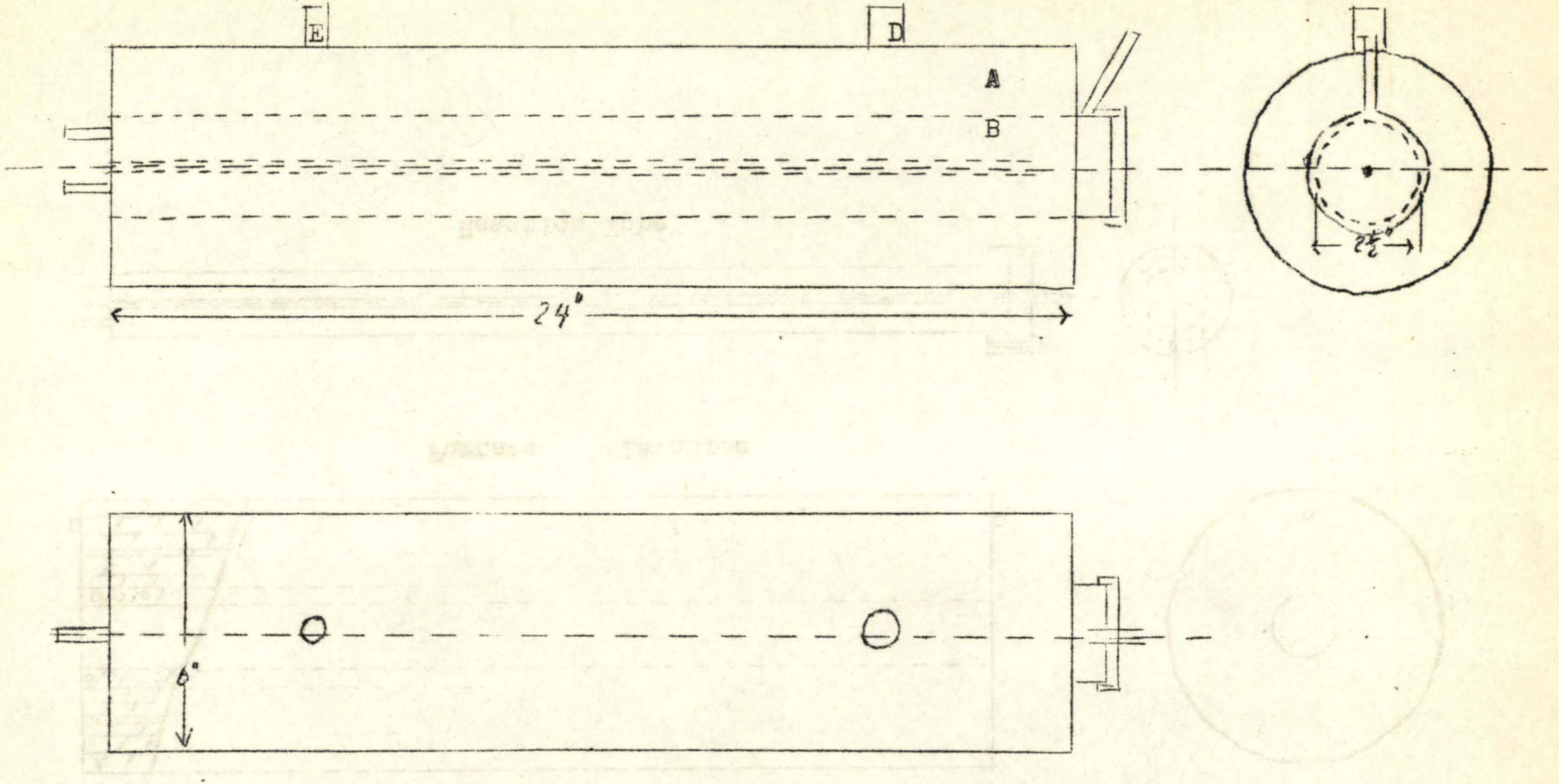
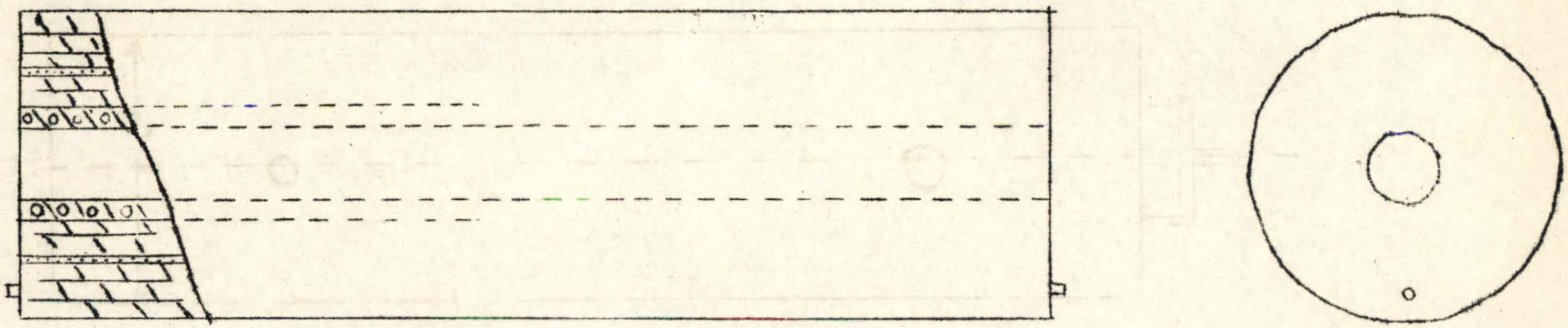
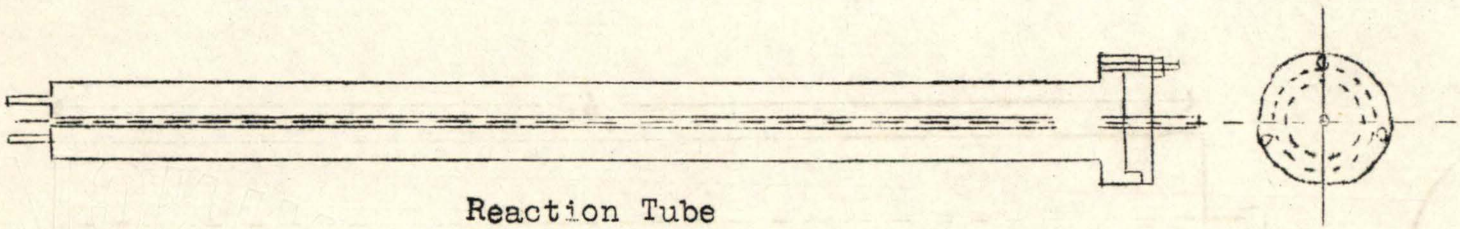


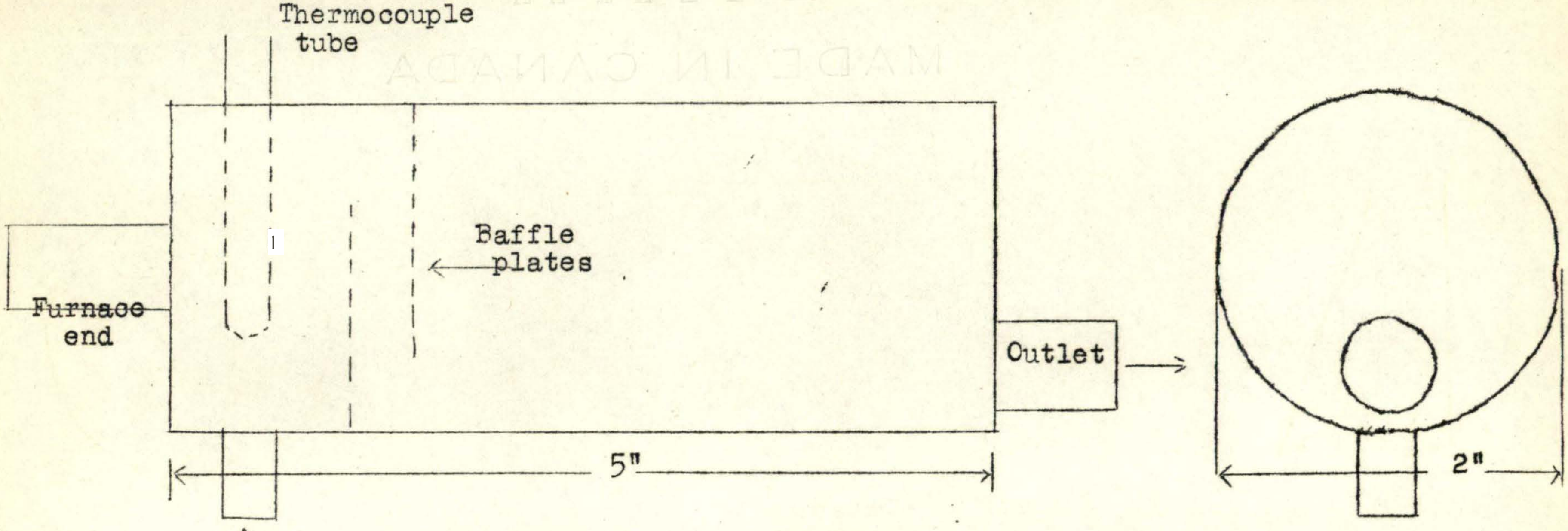
Diagram of Oil Furnace.



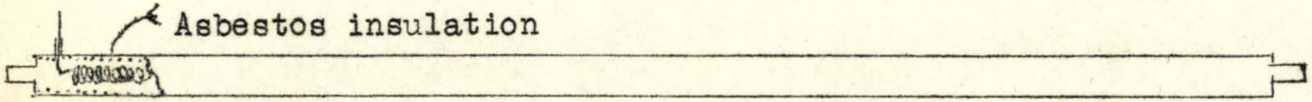
Furnace Elevation



Reaction Tube



Combustion Tube Elevation



Air Pre-heater -400 watts- 18" x 1/2"