

garages are more tightly closed to conserve heat and less ventilation takes place. It is possible that considerably more carbon monoxide than that reported herein accumulates in similar garages in the coldest weather.

The tests reported were conducted in large garages wherein considerable volumes of carbon monoxide are required for the accumulation of dangerous concentrations. The data presented are in no way representative of the deadly conditions which arise in small garages when motors are operated within closed doors and windows and without ventilation, as is shown by the numerous accounts of deaths under such circumstances.

Acknowledgment

This investigation was undertaken at the request of G. S. Pope, chief engineer of the Government Fuel Yard. Joseph Burrows, superintendent of the garage, assisted in the investigation at Washington.

The recorder was installed in the garage at Pittsburgh and assistance therefore was given through H. J. Diemar, superintendent of service, Equitable Auto Company. The investigation was under the general direction of R. R. Sayers, chief surgeon, and A. C. Fieldner, chief chemist of the Bureau of Mines.

Destructive Distillation of Wood and Cellulose under Pressure¹

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UNTIL recently wood distillation has provided the sole supply of methanol for industry. During the last few years, however, the wood-distillation industry has been threatened with severe competition from the synthetic product, and hence the question has quite naturally arisen as to the possibility of increasing the yield of alcohol in the dry distillation of wood. In an effort to study this problem the present research was undertaken. Birch wood was distilled under pressure alone or in the presence of catalysts. In some cases hydrogen pressure was employed, and in others the autogenous pressure of the gases evolved in the distillation.

An increase in alcohol might result from one or more of the following causes: (1) vigorous reduction of the primary alcoholic groups in cellulose; (2) more complete conversion of the methoxyl in the wood to methanol; (3) combination of the gaseous products of distillation, carbon monoxide and hydrogen, particularly when in the nascent state; and (4) reduction of small amounts of formaldehyde usually formed in the distillation of wood. Of these four possibilities the first one would seem to offer most promise as far as quantity is concerned.

Cellulose in the form of sulfite pulp was used in similar experiments. This served to determine whether cellulose or lignin was the source of the increased yield observed with wood.

Previous Investigations

In his extensive studies of the destructive distillation of wood under atmospheric² and reduced³ pressures, Klason showed that a primary tar was first formed and that this decomposed exothermically at 275° C. The production of methanol was unaffected by reduction of the pressure. Klason was the first to show the production of small amounts of formaldehyde in the distillation. By distillation of cellulose he demonstrated that the alcohol in wood did not come from this component.

Palmer⁴ investigated the distillation of wood in the presence of phosphoric acid as a catalyst. Under atmospheric pressure an increase in the yield of methanol and acetic acid was found, but under autogenous pressure of 4 to 7 atmospheres a decrease

was observed. Hawley⁵ has been unable to confirm Palmer's results.

Hawley⁵ showed that lime, calcium carbonate, and sodium carbonate increased the yield of methanol. With maple wood sodium carbonate gave an increase of 40 per cent under favorable conditions. In these cases the increase in methanol approximately balanced the decrease in the methoxyl content of the tar and charcoal.

Bergius⁶ heated wood in the presence of water to about 340° C. under a pressure of 200 atmospheres and obtained a coal-like product. His yield of methanol was not recorded. This coal-like product was afterwards hydrogenated⁷ under hydrogen pressure of 100 atmospheres at 400° C., with the formation of an oily product. The production of methanol again was not investigated.

Bowen and Shatwell⁸ studied the reactions of hydrogen on cellulose under high pressures in the presence of copper hydroxide and nickel hydroxide as catalysts, and found that with nickel all, and with copper most, of the cellulose could be converted into liquid products. An examination of the products for methanol was not recorded. They also used a mixture of nickel and aluminum oxides and obtained similar results. Fierz-David and Hannig⁹ likewise investigated the action of hydrogen on cellulose and wood and observed the formation of oils. In the case of cellulose the production of methanol appears to have been less than 0.5 per cent. Fierz-David suggests that the action of the hydrogen and nickel may not be hydrogenation but rather the prevention of the coking of the tar formed.

Experimental Work

Birch wood which had been cut for about 12 months was used in the form of small cubes of approximately 1/4-inch (6-mm.) edge. When catalysts were employed, a known weight of hot, dry wood was placed in a solution of the required salt. Upon saturation the wood was again dried and weighed. Additional catalyst could be added by repeating the process, the total amount of catalyst introduced being estimated either by direct analysis or by difference in weight of the untreated and treated wood. Cellulose was used in the form of sulfite pulp dried at 120° C. before using in uncatalyzed runs. When catalysts were employed the moist pulp was placed directly in the salt solution and dried at 120° C.

A known weight of dry material, or material of which the moisture content was known, was placed in a chrome-vana-

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² *Z. angew. Chem.*, **25**, 1205 (1909); **27**, 1252 (1910); Hawley, "Wood Distillation," p. 52 (1923).

³ *J. prakt. Chem.*, [2] **90**, 413 (1914).

⁴ *Ind. Eng. Chem.*, **10**, 264 (1918).

⁵ *Ind. Eng. Chem.*, **14**, 43 (1922).

⁶ *Z. Elektrochem.*, **19**, 858 (1913).

⁷ Bergius, Friedländer's "Patentsammlung," XIV.

⁸ *Fuel Science Practice*, **5**, 138 (1926).

⁹ Fierz-David, *Chemistry & Industry*, **44**, 942-4 (1925); Fierz-David and Hannig, *Helv. Chim. Acta*, **8**, 900 (1925).

dium steel reactor of 5 cm. internal diameter and 45 cm. length, corresponding to a volume of 850 cc. The reactor was supplied with an electric heater and had a thermocouple well extending into its central part in order to permit representative temperature readings. The chamber was supplied with connections at both ends for introduction and removal of gases under pressure. Electrolytic hydrogen was supplied from a storage cylinder of 2 cubic feet (56 liters) capacity under a pressure of about 250 to 300 atmospheres.

In starting a run the heater was turned on and gas admitted to the chamber until the pressure was somewhat less than that at which the run was to be made. In order to secure uniform heating an hour was allowed for each rise of 100° C. By this procedure the exothermic reaction was hardly noticeable. When the temperature had reached 100° C. the exit valve was opened slightly to give the required gas flow, and the inlet valve was adjusted to keep the pressure in the chamber as nearly constant as possible. By employing a flow of gas throughout the run the products were continuously removed from the sphere of action, and it was hoped that by this means the greatest advantage might be obtained from the use of hydrogen, and that none of the methanol formed at low temperatures would be decomposed at higher temperatures. This dynamic method, therefore, represents an improvement on the enclosed, static systems employed by previous investi-

gators. According to Fierz-David⁹ the production of liquid products is really due to the prevention of the primary tar from coking. If this is true, the removal of the products as formed should favor the formation of liquids.

The liquid products were condensed under pressure and withdrawn from a receiver at intervals, while the exit gas, after passing a water scrubber, was collected in a holder in order to make possible analysis of a composite sample at the end of the experiment. On completion of the run the pressure was allowed to drop slowly, permitting any high-boiling liquids remaining in the chamber to distil over into the receiver. Depending upon the conditions studied, the duration of a run would be from 6 to 10 hours. When the apparatus had cooled, the liquid lines were blown out with gas in order to remove any product remaining in the system.

The gas was analyzed by the ordinary methods, while the liquid products, after topping in a distilling column, were subjected to careful fractionation in a micro-fractionating column developed in this laboratory for analytical purposes. The fractionation separated the products into (1) a constant-boiling mixture of methyl acetate, acetone, and methanol, and (2) pure methanol. Experiments with synthetic samples showed that the constant-boiling mixture contained approximately 15 per cent methanol. Hence, the yield of methanol could be found by adding 15 per cent of the low-boiling fraction to the alcohol fraction. The methyl acetate

was determined by saponification with standard caustic soda and the acetone estimated either by difference or, more accurately, by Messinger's method. In cases where a large amount of oil was formed, the methanol could not be determined very accurately by fractionation, and hence the methyl iodide method was used. The acetic acid was determined by titration with standard alkali.

Results

The results are summarized in Table I.

STANDARD RUN AT ATMOSPHERIC PRESSURE—Before commencing the experiments employing pressure and catalysts a preliminary distillation of wood was carried out under atmospheric pressure, to serve as a standard of comparison for later runs.

In the table yields are reported in grams per 100 grams of dry wood distilled. The figures for acetic acid and methanol include the potential methanol and acetic acid present in the form of ester. The results agree well with those found by other experimenters, as will be seen from the second horizontal column taken from Hawley's book.²

AUTOGENOUS RUNS—Runs 15, 3, and 16 were made under the pressure of the gases evolved in the reaction.

The low pressure in run 3 was caused by frequent tapping of the liquid products, allowing some of the gas to escape. In runs 15 and 16 the liquid was not withdrawn until the end of

the run. The yields of charcoal, acetic acid, and methanol showed a decrease with rise in final temperature. In runs 15 and 3 the alcohol yields were, respectively, 80 and 67 per cent above the standard run (1), but in run 16 the yields were negligible. This decrease indicates the decomposition of the products due to secondary reactions at temperatures above 375° C.

The residue showed lustrous particles resembling coal mixed with charcoal of the same type as in run 1. This is presumably due to the fact that the pressure prevents the volatilization of much of the tar, which therefore is decomposed giving a coke-like substance. In run 16, where the pressure and temperature were high, the quantity of tar in the liquid product was very small. Obviously, the high autogenous pressure in this run was a direct result of the decomposition of the tar into gaseous products. Analysis of the gases indicated the presence of large amounts of hydrocarbons. That hydrocarbons are evolved on heating tar above 400° C. has been shown by Bergström and Wesslen.¹⁰ It will be noticed that in these three runs, as in other pressure experiments, the carbon monoxide-carbon dioxide ratios in the gases were much lower than in runs at atmospheric pressure.

There seem to be several causes to which the observed increase in methanol might be attributed: (a) directly to

Wood and cellulose, either alone or impregnated with catalysts, have been distilled under pressure in an atmosphere of hydrogen, nitrogen, or of the gases evolved in the distillation.

Pressure alone favors the formation of methanol, as evidenced by a doubling of the methanol yield under a hydrogen pressure of 200 atmospheres. The autogenous pressure of the gases evolved in the distillation has a similar effect. With the catalysts studied the yield of methanol is usually decreased at atmospheric pressure and barely improved when higher pressure is employed. Check experiments on cellulose demonstrate that the increased methanol yield is derived from the methoxyl groups and not from the cellulose molecule. With nickel as a catalyst and hydrogen under 200 atmospheres, cellulose is almost completely converted into gaseous and liquid products, the latter consisting of phenols and saturated and unsaturated hydrocarbons. When nitrogen is substituted for hydrogen the cellulose is volatilized to practically the same extent.

Whether this process of decomposition of cellulose and wood to form phenols and hydrocarbons will meet with commercial success would seem to depend to a large extent on the development of suitable equipment for continuous operation.

¹⁰ "Om Träkolning," p. 180; Hawley, "Wood Distillation," p. 65 (1923).

the effect of pressure during the reaction, (b) the combination of carbon monoxide and hydrogen under the influence of pressure, and (c) the prevention of the decomposition of methanol under the influence of pressure.

RUN UNDER HYDROGEN PRESSURE, NO CATALYST—The conditions in run 4 should favor the methanol yield if (a), (b), or (c) above were important factors. Further possibilities of methanol formation were present in this case: (d) the direct hydrogenation of the primary alcoholic groups in cellulose, and (e) the reduction of formaldehyde and formic acid, although these reactions were not considered probable in the absence of the catalyst.

These results show that the methanol yield was about 105 per cent greater than that obtained in the standard run at atmospheric pressure (run 1). Less ester was produced than in the low-pressure autogenous experiment (run 15). The acetic acid yield was not altered by hydrogen pressure. The constancy of the total acetic acid in runs 1, 15, and 4 suggests that pressure does not alter the yield. The free acetic acid had diminished to 3.87 and 4.18 per cent in runs 15 and 4, but this decrease was balanced by an increase in ester. The stream of hydrogen in run 4 may have reduced the combination of acid and alcohol to ester by lessening their time of contact in the chamber. The charcoal in run 4 was similar in appearance to the autogenous residue. The quantity was somewhat less than in run 16, probably owing to the removal of the tar from the chamber before decomposition took place.

ZINC-CHROMIUM CATALYSTS—In the runs 2, 5, and 6 the wood was impregnated with a mixture of zinc and chromium

and hydrogen under high pressure also catalyze the reverse reaction when the pressure is reduced. In run 6 the temperature was kept at 340° C. for some time, since 300° to 400° C. is given as the optimum temperature range for the combination of carbon monoxide and hydrogen in the presence of the catalyst used.^{10,11} Nevertheless, the methanol yield was less than that obtained in the corresponding run (4) without catalyst, and there was a marked diminution in the acid formed. The charcoal in runs 5 and 6 showed more signs of destruction of the original form of the wood than in previous experiments. A rather large quantity of tar was formed and this tar was lighter than usual and slightly more oily, separating more readily from the aqueous layer.

COPPER-ZINC-ALUMINUM CATALYSTS—In run 8 a mixture of the nitrates was employed, but in run 10 this was altered to the equivalent mixture of the acetates. A very violent reaction near the beginning of run 8 caused the use of nitrates to be abandoned. This reaction may have been due to the nitration of cellulose with subsequent decomposition, or to reaction of the nitrates with hydrogen.

In run 8 a low-boiling oil obscured the fractionation curve. Most of this oil reacted with alkali, and a fractionation after hydrolysis showed that the methanol was greatly reduced. The yield of alcohol in run 10 was apparently very high. The acetic acid yield was large on account of hydrolysis of the acetate before decomposition. In later experiments using acetate as catalysts the acetic acid was therefore not estimated. It may be inferred that the high methanol yield is due to the simultaneous decomposition and reduction of

Table I—Distillation Data for Wood and Cellulose
(Basis 100 grams of dry wood or cellulose)

RUN	CATALYST	RATE OF GAS FLOW ^a Liters per hour	PRESSURE Atmos.	FINAL TEMPERATURE ° C.	ORGANIC RESIDUE Grams	RATIO CO:CO ₂	METHYL ACETATE Grams	ACETIC ACID Grams	METHANOL Grams
WOOD—STANDARD RUN AT ATMOSPHERIC PRESSURE									
1	None		1	372	42	0.5	0.125	5.68	1.52
Hawley	None		1	400	38.5	5.24	1.55
WOOD—AUTOGENOUS RUNS									
15	None		100	280	50	0.120	2.48	5.88	2.74
3	None		90	372	44	0.087	1.05	4.23	2.54
16	None		300	500	37	0.088	0.0	2.23	0.20
WOOD UNDER HYDROGEN PRESSURE									
4	None	30	200	483	33.6	0.13	1.84	5.67	3.11
2	Cr-Zn = 4b	30	1	378	42.5	0.47	Negl.	5.29	1.14
5	Cr-Zn = 1b	30	200	454	26.4	0.09	0.47	1.75	1.97
6	Cr-Zn = 0.5b	30	200	440	27.8	0.09	0.89	3.57	1.78
8	Cu-Zn-Alb	30	200	423	19	0.07	Negl.	..	0.5
10	Cu-Zn-Alb	30	200	450	26	0.064	3.8	11.2	4.77
11	Nickel acetate ^c	30	200	400	20	0.11	2.11	..	3.18
18	Nickel acetate ^c	30	200	500	8	0.11	1.61	..	2.06
7	None	40	10	364	..	0.52	0.20	7.15	1.33
19	Nickel acetate	40	10	500	25	0.18	1.66	..	2.13
13	Sodium carbonated ^d	50	200	525	42	0.20	Negl.	..	2.31
CELLULOSE UNDER HYDROGEN PRESSURE									
9	None	35	200	402	34	0.45	Negl.	..	Negl.
12	Zn-Cu-Al acetates ^e	35	200	520	10	0.10	Faint	..	Faint
14	Nickel acetate ^e	35	200	500	2.3	0.25

^a Normal temperature and pressure.
^b 3 to 5 grams, calculated as oxides.

^c 7.5 grams, calculated as oxide.
^d 33 grams.
^e About 5 grams.

nitrate before distillation. Mixtures of the oxides of zinc and chromium have been recommended repeatedly by Patart¹¹ and Badische Anilin und Soda Fabrik¹² as catalysts for the formation of methanol from carbon monoxide and hydrogen under pressure. The nitrates were chosen since they are readily soluble salts and give the oxides on heating. The proportion of the salts was varied in each experiment, the total amount of catalyst being 3 to 5 grams of metallic oxides per 100 grams of dry wood.

The results under atmospheric pressure (run 2) show a decrease in the yield of alcohol and a slight diminution of acetic acid. The methanol formation was expected to be reduced, since catalysts for the combination of carbon monoxide

acetic acid introduced with the catalyst. Results of other work in this laboratory would tend to exclude this possibility, however.

In both of these experiments there was a large yield of a light mobile tar and a small yield of charcoal. The structure of the wood was not retained by the charcoal. No doubt the wood had been partially converted into oils, a result which confirms the observation made by Bowen and Shatwell⁸ and by Fierz-David⁹ using copper oxide as a catalyst.

NICKEL CATALYSTS—Nickel acetate as a catalyst with 200 atmospheres of hydrogen was employed in runs 11 and 18. Nickel oxide has been shown by Ipatiew¹³ to be a very active hydrogenation catalyst under high pressures. On

¹¹ *Tech. Eng. News*, December, 1926.

¹² U. S. Patent 1,558,559 (October 27, 1925).

¹³ *Ber.*, 36, 1990, 2003, 2014, 2016 (1903).

this account it was thought that it might favor the reduction of the cellulose molecule and the formic acid and formaldehyde usually produced.

In run 11 the fractionation curve was obscured by a low-boiling oil. This experiment was then repeated in run 18, the product coming from the receiver below 350° C. being kept separate from the portion produced at higher temperatures. The fraction obtained from run 18 below 350° C. contained about 4 cc. of oil per 100 grams of dry wood; it was topped and fractionated in the usual way. The fractionation curve was fairly smooth and showed that this product contained most of the methanol. The high methanol content of run 11 as compared with run 18 is probably due to an error in fractionation introduced by the low-boiling oil, since no chemical check analysis was made. The amount of alcohol was not large compared with that obtained in the absence of catalyst in run 4.

Both of these runs gave nearly complete conversion of wood into liquid and gaseous products. Run 18 gave 92 per cent conversion, yielding 25 cc. of oil per 100 grams of dry wood. A portion of this oil was dried over sodium sulfate and subjected to a "micro-Engler" distillation. Of the liquid 40 per cent boiled within the range 60° to 225° C., 43 per cent of the distillate being soluble in 60 per cent caustic soda. After treatment with alkali, 26 per cent was dissolved in concentrated sulfuric acid. The remaining 31 per cent was insoluble and presumably consisted of saturated hydrocarbons. This portion had an odor resembling that of gasoline.

RUNS UNDER 10 ATMOSPHERES HYDROGEN PRESSURE—This pressure was of considerable interest since it might eventually be employed commercially.

The results of run 7 without catalyst showed a high acid production, but a poorer yield of methanol than under atmospheric pressure in run 1. In run 19 with nickel acetate as catalyst the methanol yield was about the same as in the corresponding high-pressure run 18. The ester formation was not so great as in run 18, showing the favorable influence of high pressure on ester formation. Messinger's method showed a slightly smaller quantity of acetone than in run 18, 0.221 per cent as against 0.284 per cent. Not much importance is attached to this apparent increase in acetone with increase in pressure, however, since the accuracy of the analysis is greatly affected by small amounts of unsaturated compounds. The CO:CO₂ ratio in run 7 was high, 0.52. This was reduced to 0.18 in run 19.

SODIUM CARBONATE AS CATALYST—Hawley² has shown that under atmospheric pressure sodium carbonate increases the methanol yield by about 40 per cent under favorable conditions.

The results of run 13 showed only a slight improvement on Hawley's figure for maple under atmospheric pressure in that a 52 per cent increase in methanol was realized. This yield, however, was not so great as that obtained when using hydrogen without a catalyst (run 4). There was little or no methyl acetate present in the liquid product, a result which would be expected in the presence of alkali.

CELLULOSE UNDER HYDROGEN PRESSURE—In order to throw further light on the source of alcohol increase, several experiments (runs 9, 12, and 14) were performed with cellulose (sulfite pulp). With catalysts very definite exothermic reactions were observed. They commenced at 230° to 240° C. and were accompanied by a rise in temperature to 300° C. or above. The corresponding pressure rise was negligible, indicating that there was little evolution of gas. There was practically no flat portion on the fractionation curve in any of these experiments on pulp. Hence it seems that little or none of the alcohol produced in the corresponding experi-

ments on wood (runs 4, 10, and 18) was obtained from cellulose. In runs 12 and 14 with catalysts large amounts of oil were produced, and accordingly the weight of the charcoal obtained was reduced. The use of nickel acetate favored the production of oils more than the mixture of copper, aluminum, and zinc acetates. This is in perfect agreement with the results of runs 10 and 18 on wood. Almost complete volatilization was obtained from nickel acetate, leaving a residue of only 2.3 grams organic residue per 100 grams of dry cellulose.

An experiment was also made with cellulose using zinc chloride as a catalyst. The results showed no indication of alcohol. A much lower temperature of decomposition was observed in agreement with the observations made by Schwalbe,¹⁴ who used a similar catalyst, magnesium chloride.

CELLULOSE UNDER NITROGEN PRESSURE—Fierz-David⁹ has suggested that the complete volatilization of cellulose in the presence of hydrogen and a catalyst is not due to hydrogenation. He believes that hydrogen merely acts as an inert gas improving the mechanics of the process. To test this theory cellulose impregnated with nickel acetate was distilled under 200 atmospheres of nitrogen. A considerable quantity of oil was formed, similar to the product of the first stages of the distillation in runs 12 and 14 with cellulose and hydrogen. The amount of charcoal was only slightly greater than in the corresponding run (12) with hydrogen. Thus a conversion of 86 per cent of the cellulose into volatile products was obtained. A small quantity of aqueous liquid was formed, boiling within the methanol range. This liquid was treated with phosphorus diiodide, but no traces of methyl iodide were obtained.

Summary

1—When wood is distilled in a closed system, the effect of autogenous pressure alone is to increase the yield of methanol by somewhere around 65 to 80 per cent depending upon the final temperature reached. These results were obtained with pressures slightly less than 100 atmospheres at temperatures ranging from 280° to 370° C. Further increase in temperature with a corresponding increase in pressure results in the decomposition of the initially formed products, and the methanol yield is poor.

2—Substituting hydrogen for the gases evolved by the destructive distillation of wood results in a somewhat higher increase in methanol yield. The figure 3.11 grams of methanol per 100 grams of dry birch wood, or 105 per cent above the yield at atmospheric pressure, apparently is the highest yield of methanol ever reported. Pressure does not affect the yield of acetic acid.

3—With the catalysts here studied the yield of methanol is usually decreased when atmospheric pressure is employed in the distillation. When combining the effect of catalysts with hydrogen under 200 atmospheres, the methanol yield is barely improved. Only in one case (run 10) was an increase of more than 200 per cent of methanol observed. Since the catalyst was used in the form of acetates, however, this figure should not be stressed, although as already mentioned, the possibility of obtaining methanol from the reduction of acetates seems rather remote.

4—Distilling the wood under a hydrogen pressure of 10 atmospheres results in a slight decrease of the methanol yield. At this pressure nickel does not materially alter the course of the reaction.

5—With nickel as a catalyst and hydrogen under 200 atmospheres more than 90 per cent of the original dry wood is converted into volatile products, resulting in a high yield of an oily product of which 40 per cent boils below 225° C.

¹⁴ *Papier-Fabr.*, **24**, 157 (1926).

This low-boiling fraction contains about 43 per cent phenolic compounds, 26 per cent unsaturated hydrocarbons, and 31 per cent saturated hydrocarbons. A catalyst containing copper gives a lower yield of oils. In no case is there an appreciable increase in methanol.

6—Experiments with cellulose demonstrate that the increases in methanol yield observed with wood are not due to the cellulose content. With nickel and hydrogen under 200 atmospheres practically all of the cellulose, or 98 per cent, is converted to volatile products, of which a large percentage are liquids of the general type mentioned above under 5.

7—In substituting nitrogen for hydrogen 86 per cent of the cellulose is converted to volatile products in the presence of nickel.

Conclusions

From these data it can be concluded that it is possible to convert the cellulose molecule into volatile products but that no success has been met with in controlling this reaction so as to obtain methanol. When reaction takes place the products are phenols and unsaturated and saturated hydrocarbons. Although high in some cases, there is no reason why the methanol yields observed should not have been derived from the methoxyl in the original wood, since according to Hawley only 70 per cent of this methoxyl is ordinarily recovered as useful products in wood distillation.

The results obtained when distilling cellulose under pressure in an atmosphere of nitrogen bring up the question as to the mechanism of hydrogenation in certain processes. Thus, it is claimed that in the berginization of coal the 5 per cent of hydrogen consumed in the process are converted into gaseous products and do not enter into the liquids.¹⁵

Whether the decomposition of cellulose and wood to form phenols and hydrocarbons will meet with any commercial success would seem to depend largely upon the development of suitable equipment for continuous operation. The fact that the reaction goes almost quantitatively makes the process compare favorably with the berginization of coal. The effect of the inert nitrogen pressure suggests as a possibility the substitution, for hydrogen, of the gases generated by the reaction itself. The catalyst field has barely been touched upon.

In continuing this investigation the mechanism of reaction will be studied for the dry distillation of cellulose and wood in atmospheres of hydrogen, carbon monoxide, and nitrogen, using different types of catalysts.

Acknowledgment

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¹⁵ Tropsch, Lecture delivered at the Institute of Chemistry, State College, Pa., July, 1927.

Effect of Temperature on the Rate of Decomposition of Nitrocellulose¹

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STABILITY tests for nitrocellulose fall into three classes: (1) the so-called "trace tests" in which the time taken to color a very sensitive reagent paper is noted; (2) tests in which the temperature of the nitrocellulose is raised to the point where decomposition is so rapid as to be detected by less sensitive reagents or by the observance of fumes; and (3), the tests which are dependent on the quantitative determination of the products of decomposition. Probably the best known examples of these methods are, respectively, the Abel KI test, the 135° C. or German test, and the Will test. All of these tests are open to criticism. Often the Abel KI test is a measure of the accumulation of nitrogen oxides over a period of time and is not a true indication of the keeping qualities of the nitrocellulose.² Furthermore, unless it is carried out under strictly defined conditions, results may be obtained which may lead to erroneous conclusions as the test paper is easily affected by traces of substances present in the atmosphere. The main objection to the German and Will tests is that they are conducted at

An improved method of studying the rate of evolution of nitrogen oxides from heated nitrocellulose at various temperatures has been developed.

It is shown that the logarithm of the rate of evolution of nitrogen plotted against temperature gives a straight line. The stability of the nitrocellulose sample examined is largely responsible for the slope of the resulting line. From the determination of the temperature coefficient of the decomposition rate, an idea of the stability of nitrocellulose at lower temperatures is obtained.

Additions of small amounts of various salts change the stability of nitrocellulose, as shown by the change in the temperature coefficient of the decomposition rate. This method is a valuable means of determining the effects various materials will have on stability.

an elevated temperature and results are not necessarily indications of stability at ordinary temperatures.

Frequently a sample of nitrocellulose may be considered stable by one test but unstable when subjected to another test. This is especially true when two tests, such as the Abel KI and German test, are applied to the sample. It was therefore deemed advisable to establish, if possible, a correlation between the various methods of judging stability. The

method described herein is the result of an extensive study on the subject and is offered as a better means of studying relative stabilities of uncolloided nitrocellulose.

This method of testing the stability of nitrocellulose is dependent on the determination of the rate of evolution of nitrogen oxides from heated nitrocellulose at two or more temperatures. The method of measuring the decomposition is a modification of that outlined by Philip,³ who measured the rate of decomposition of nitrocellulose heated in air at 135° C. by absorbing the nitrogen oxides formed in a potassium iodide solution. In order to adapt the method to lower temperatures the original apparatus and method of

¹ Received August 16, 1927.

² Robertson, *J. Soc. Chem. Ind.*, **29**, 133 (1910).

³ *Ingeniörs Vetenskaps Akademiens, Handlingar* **28**.