

CHANGES IN WHISKY WHILE MATURING

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Bourbon and rye whiskies (108 barrels) were set aside periodically in lots of 5 during 1937 in warehouses in Pennsylvania, Indiana, and Kentucky. Samples were withdrawn at regular intervals from these barrels for 4 years, and significant characteristics determined. The data were treated statistically by punched card technique. The means and standard deviations of eleven major constituents of whisky were obtained for each storage period (or age) for all 108 barrels. The average maturing characteristics of American whisky are shown by charts and graphs. The eleven characteristics used as the basis for the maturing interpretation were proof, total acidity, fixed acidity, esters, aldehydes, furfural, fusel oil, solids, color, tannins, and pH. Because of the large sample size, accurate dispersion limits could be calculated. Limits of variation of "normal" whiskies are presented for different age levels of maturing from 0 to 4 years. The reliability of the results is indicated by showing that the data are approximately normally distributed and that averages from the 1938 set of barrels are not significantly different from those of the 1937 set. A table is presented as a set of empirical standards for American whisky, and the possibility of the use of the data as a basis for specifications for whisky is indicated. Further breakdown of the data in studies to follow is indicated in order to obtain standards for type, region of storage, cooperage, etc. Certain characteristics of maturing exhibit properties of regular curves, and preliminary mathematical treatment is presented.

THE quality of a beverage such as whisky is judged by the consumer on its properties affecting taste and odor. The development of the quality of whisky is dependent upon three fundamental production operations: fermentation, distillation, and maturing. This investigation is concerned solely with the last phase, maturing.

The maturing stage begins immediately after distillation, as the new colorless whisky is drawn into charred oak barrels. The barrels are placed in bonded warehouses (constructed of wood, brick, or concrete) and usually permitted to rest for four or more years under variably controlled conditions of temperature and humidity. The maturing stage ends with the withdrawal of the aged whisky from the barrels.

Three fundamental environmental factors are intimately related to the development of a whisky during maturing—temperature, humidity, and ventilation. The barrel, serving primarily as a container, also acts as a semipermeable membrane and permits the passage of alcohol and water vapors from the interior of the barrel to the outside. This phenomenon is an integral phase of maturing. In properly maintained warehouses, the barrel permits water vapor to escape at a faster rate than alcohol vapor; consequently, there is a gradual accumulation of alcohol at the expense of water inside the barrel. Thus the proof of the contents normally rises with age.

During this period, the maturing whisky undergoes definite and intended changes in aromatic and taste characteristics. These changes are caused by three major types of reactions occurring continually in the barrel:

1. Extraction of complex wood substances by the liquid.
2. Oxidation of the original organic substances and of the extracted wood material.
3. Reaction between the various organic substances present in the liquid to form new products.

The development of quality, therefore, consists of specific chemical and physical changes in the properties of the liquid, some of which are relatively simple to determine. These properties, or characteristics, are commonly used as a guide to and measure of quality. Experience and observation have shown that abnormalities arising in one or several of the physico-chemical characteristics will generally result in abnormalities of the taste characteristics of the liquid.

Due, in large measure, to the extended Prohibition period and to the empiricism of the pre-Prohibition industry, very little accurate information was available concerning the nature of maturing development. The two published investigations in this field originated in the laboratories of the Alcohol Tax Unit of the Treasury Department (3, 9). The techniques of sampling, analysis, and data presentation are almost identical in each case, although 28 years separate the two investigations.

The earlier work was based on thirty-one different barrels, all chosen from 3-month production in 1898. Most of these whiskies were distilled in types of stills now obsolete and stored in warehouses entirely different from those of today. The later work was based on twenty-two different barrels chosen from a 6-month production period of December, 1929, to May, 1930. Of the twenty-two barrels, three contained whiskies derived from such low-yield production as to indicate abnormal fermentation or distillation and thus result in atypical products.

These investigators worked under the handicap of being forced to rely on basic material and data furnished by producers not under their control, and on conditions not subject to their direct supervision. In both investigations, the average values for each characteristic were determined, and the minimum and maximum values (constituting the range) were used to indicate scatter. The exclusive use of the "range"

as a measure of dispersion must be treated with caution since it is subject to considerable individual variation. Indeed, Crampton and Tolman as well as Valaer and Frazier were forced either to indicate "next highest or lowest" values or to delete extreme values which were considered abnormal (4, 10). The subjective deletion of data, even when based on considerable experience, is a dangerous procedure. The limits of whisky characteristics set forth by both investigations (4, 10) are based on small sample sizes and one of the most inefficient measures of dispersion—the range.

HISTORY OF SAMPLES

The purpose of the present study is to examine the development of the maturing characteristics from data obtained from a large and varied sample which is characteristic of American type whisky. The dispersion of these data can then be determined, using the efficient function of standard deviation, and reliable limits of variation of normal whisky can be presented.

Straight whisky is defined by the Treasury Department (8) as "an alcoholic distillate from a fermented mash of grain distilled at not exceeding 160 proof . . . and aged for not less than 24 months in charred new oak containers." Bourbon whisky is usually produced from a mash containing 60-88 per cent corn; rye whisky generally comes from a mash containing 51 per cent rye. These two types make up the greater portion of American whisky.

The present work is based on 108 barrels of rye and bourbon whisky produced and set aside biweekly in lots of four to six barrels during the whole year of 1937. Table I shows the distribution of these barrels with respect to mash type, distillation characteristics, treatment, cooperage type, warehouse type, origin, and storage region. The 108 barrels afford an excellent cross section of the various methods of production used in manufacturing whisky.

One-pint samples were withdrawn from each barrel at the age of 0, 1, 3, 6, 12, 18, 24, 30, 36, 42, and 48 months, under the supervision of the plant chemist at each of the distilleries. These samples were forwarded to the research laboratory at New York immediately after withdrawal.

ANALYSES

Analyses were performed on all 1188 samples to determine the following characteristics: proof, total acidity, fixed acidity, esters, aldehydes, furfural, fusel oil, solids, color, tannins, and pH. The first eight characteristics were determined as outlined by the A. O. A. C. (2). All samples were brought to 25° C. before analysis.

PROOF. A National Bureau of Standards calibrated hydrometer, graduated in 0.2° C., was used for indicating proof. Temperature corrections were made with a Bureau of Standards calibrated thermometer.

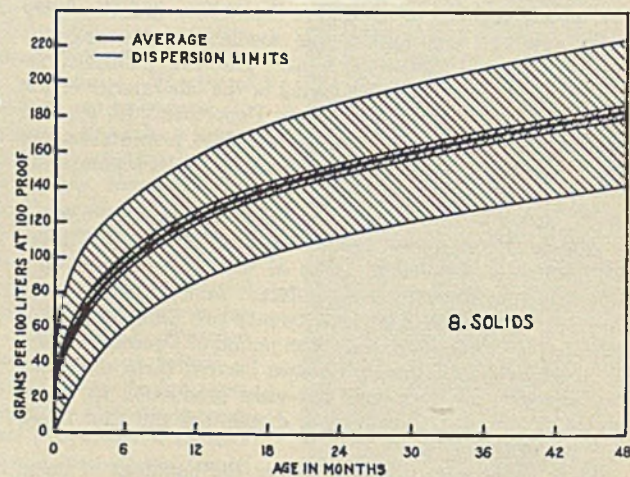
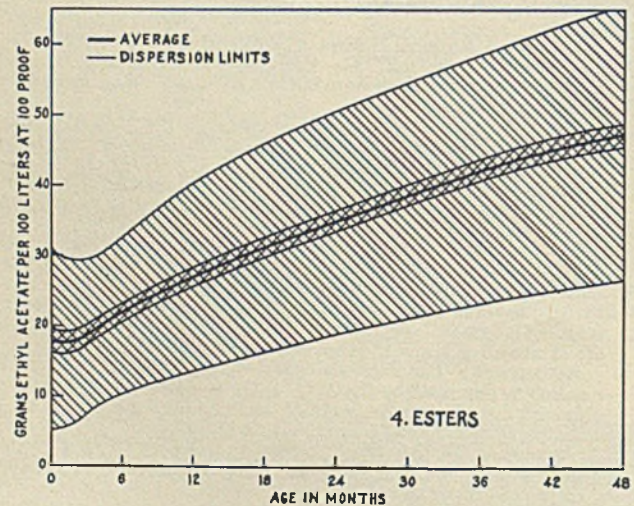
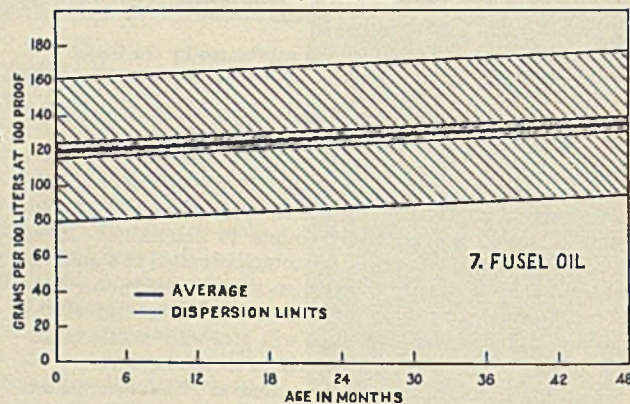
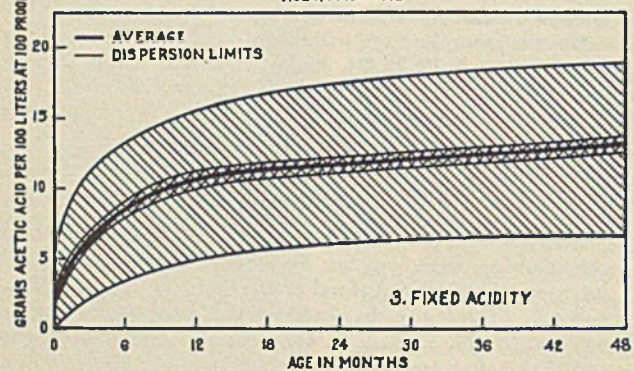
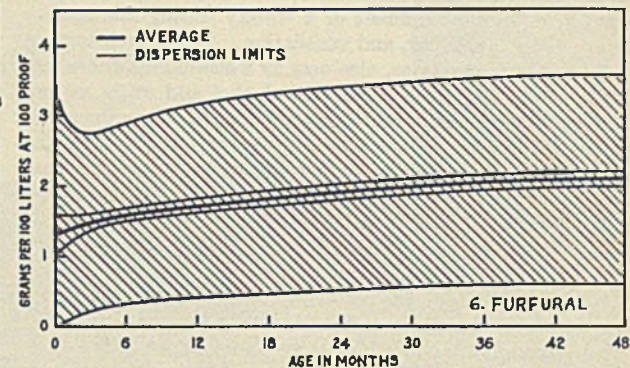
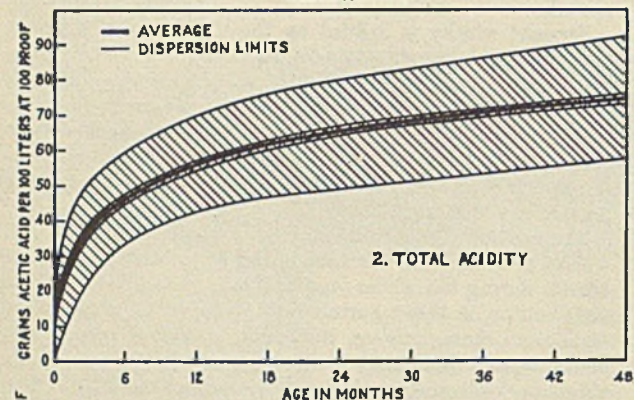
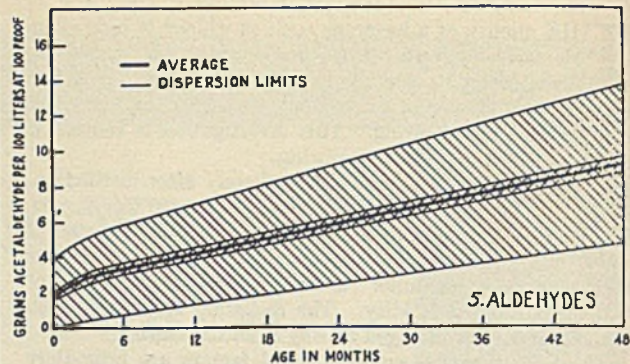
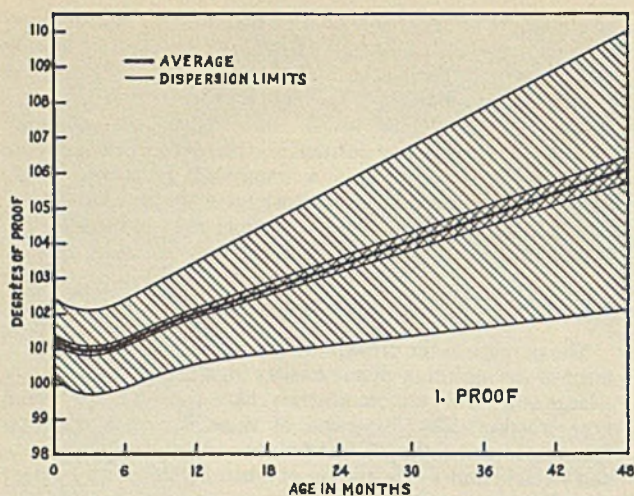
TOTAL ACIDITY. The method described by the A. O. A. C. was used without modification. The results are expressed as grams of acetic acid per 100 liters at 100 proof.

FIXED ACIDITY. The A. O. A. C. method was used without modification. The results are expressed as grams of acetic acid per 100 liters at 100 proof.

ESTERS. The distillate from a quantitative distillation through all-glass apparatus was saponified by permitting the sample to stand 24 hours at room temperature with excess sodium hydroxide. No blank was run. The excess sodium hydroxide was back-titrated with standard sulfuric acid. The results are expressed as grams of ethyl acetate per 100 liters at 100 proof.

ALDEHYDES. The titrimetric method, based on an iodometric reaction as described by the A. O. A. C., was used on the distillate obtained during ester determination. The results are expressed as grams of acetaldehyde per 100 liters at 100 proof.

FURFURAL. The A. O. A. C. method was used without modification. The results are expressed as grams of furfural per 100 liters at 100 proof.



Figures 1 to 8

Diagonally shaded areas = $\bar{X} \pm 2\sigma$; cross-shaded areas = $\bar{X} \pm 2\sigma_{\bar{x}}$.

FUSEL OIL. The Allen-Marquadt method as described by the A. O. A. C. was used. The carbon tetrachloride extractions and subsequent washings were done mechanically, and all distillations and reflux reactions performed in all-glass apparatus. The results are expressed as grams of amyl alcohol per 100 liters at 100 proof.

SOLIDS. The solids were determined by evaporation and weighing the residue in a tared aluminum dish, as described by the A. O. A. C. The results are expressed as grams per 100 liters at 100 proof.

COLOR. The color of the sample was determined on a null-type photoelectric colorimeter, designed by the Schenley Laboratories. A 100 W tungsten filament lamp was used as a source of light which passed through a matched pair of Corning daylight color glass filters before striking the photoelectric cells. The sample was reduced to 100 proof, brought to 25° C., and placed in a cell which presented one inch of path for the passage of light. The instrument was calibrated to read directly in per cent transmission (T) based on water as 100 per cent. The results are expressed in terms of color density ($d = \log 1/T$).

TANNINS. This determination is based on the Folin-Denis reagent which reacts specifically with compounds containing an oxyphenyl bond. This method was refined to conditions of optimum sensitivity (?) and used for tannin determination in whisky. The results are expressed as grams of tannic acid per 100 liters at 100 proof.

pH. The pH was determined on samples reduced to 100 proof at 25° C. with a glass-electrode electrometer (Coleman model 3C). The application and limitations of this determination were described in a previous publication (6).

The units for expressing all values in this study are grams per 100 liters calculated back to an alcoholic concentration of 100 proof (except color, pH, and proof itself). For color and pH, the standard 100 proof was obtained physically by reduction of the sample prior to determination.

The earlier investigators used the same system of units. In addition, however, they presented the data in a system of units based on a calculation back to original volume. This method of expressing the results was suggested by the fact that an actual loss in volume occurs during maturing by evaporation from the barrel.

The technique of expressing results in this latter fashion is merely of academic interest since it involves a wholly imaginary liquid. Nowhere during or following maturing does there exist a physical process which parallels this calculation.

in exceptional cases, as low as 80. A standard proof is necessary to correct for aqueous dilution following maturing, and the proof of 100 has been established as customary.

STATISTICAL TREATMENT OF DATA

The data were recorded on master cards and transferred to specially designed punched cards. The latter were sorted and tabulated mechanically. Two primary statistical functions were used to represent the mass of assembled data: The mean value as a measure of central tendency (\bar{X}) and the standard deviation as a measure of dispersion (σ). These two values were calculated for each characteristic at each age period for all 108 barrels; the summary is shown in Table II.

The rate of development of the mean value of each characteristic is charted in Figures 1 to 11, as well as the intervals of probable variation of single-barrel and 100-barrel lots.

The wide shaded region is obtained by laying off on either side of the mean for each age an interval of 2σ (Table II). This region defines the analytical normalcy of American whisky. Any barrel chosen at random will exhibit characteristics that lie within this region with a probability of 95 per cent.

The narrow cross-hatched region is obtained by laying off on either side of the mean for each age an interval of $2\sigma_{\bar{X}}$ (11). This region defines variation in analytical characteristics to be expected when 100-barrel lots are chosen at random. The 100-barrel lot is equivalent to a commercial batch unit and, therefore, serves as a basis for setting up specifications for the finished product.

The various types of whiskies studied are here reported without further breakdown into types and according to various definite techniques in production. The development of maturing characteristics as related to definite factors will be reported in later papers.

PROOF

The bonding proof (at zero age) is fixed by the distiller and is customarily set at 102 proof. The large variation of proof

TABLE I. HISTORY OF SAMPLES

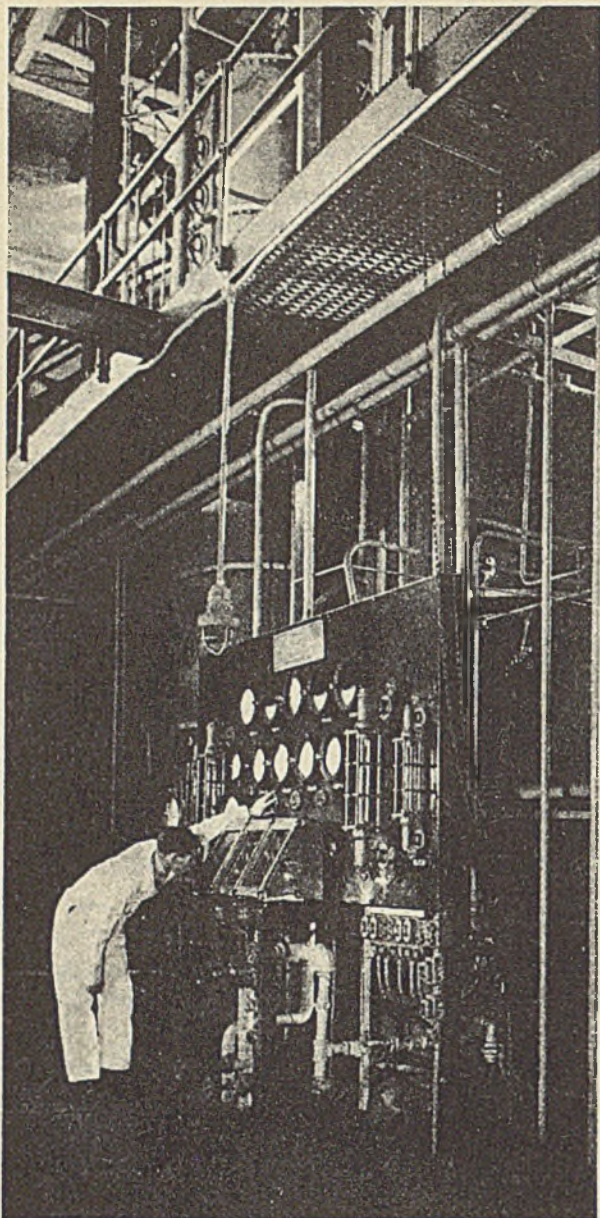
	Grain Formula		Distn. Proof		Treatment		Warehouse		Storage Region	
	Type	No. %	Proof	No. %	Type	No. %	Type	No. %	Location	No. %
Bourbon										
60% corn + 40% small grain	21	19	110-119	11 10	Untreated	52 48	Rack	40 37	Louisville, Ky.	19 18
			120-129	19 18	Oak chip	54 50	Concrete	68 63	Schenley, Pa.	28 26
80% corn + 20% small grain	2	2	130-139	60 55	Activated carbon	2 2			Lexington, Ky.	18 17
88% corn + 12% small grain	67	62	140-149	6 6	Total	108 100	Total	108 100	Lawrenceburg, Ind.	17 16
Rye									Frankfort, Ky.	26 23
61% rye + 49% other grains	18	17	150-159	12 11					Total	108 100
Total	108	100	Total	108 100						

Furthermore this method of expressing results may be misleading. In the investigation of Valer and Frazier, for example, the results calculated back to original volume in the case of aldehydes indicate a loss of aldehydes during maturing. The matured whisky, however, actually showed an increase in concentration of aldehyde, and it is this whisky which is the final product and the actual object of interest. It is immaterial whether the increase has occurred through loss in volume of solvent or by actual production of aldehyde through chemical reaction. The expression of the results in terms of 100 proof, however, is justified since the final product may be found in the barrel at a proof of 120 or higher, or may be adjusted for the purpose of bottling, sale, and consumption to a lower proof, usually ranging from 100 to 86 and,

values at zero age (Figure 1) is due chiefly to the fact that most samples were taken before, and a small portion was taken immediately after entry into barrels. The latter samples were invariably lower in alcoholic content by about 0.5 proof.

The most striking characteristic in proof development is the initial drop prior to the regular increase. This drop is caused by the residual moisture in the wood of the barrel.

The minimum average proof occurs at about 3 months of age. By the end of 6 months the whisky has regained its initial proof and then begins its linear increase. Neither of the previous investigators reported this phenomenon of initial drop, since the relatively large time period between successive samples in their studies did not permit observation



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of the initial lowering in proof. After stabilization of proof increase has occurred at 6-9 months, the rise in proof as indicated by the average line is uniform and equivalent to about 1.3° proof per year.

The scatter of the values about the average proof increases with age. This fact implies that those barrels which initially gain proof more or less rapidly continue to do so during the later maturing. This further indicates that the external conditions surrounding the barrels are probably the deciding factors in proof development.

The average increase in proof of whisky during 4 years of maturing is 4.7 proof.

TOTAL ACIDITY

The total acid development (Figure 2) is characterized by an extremely rapid increase during the early stages of maturing. Indeed, during the first 4 months the average acid content is

quadrupled. Between 6 and 15 months of age, the rate of increase of average acid content begins to fall off more rapidly and finally assumes a typical asymptotic approach to a maximum value which appears to be not greater than 80 grams per 100 liters at 100 proof.

This maximum average acid value is also of theoretical interest, since it is obviously related to the maximum amount of acid material extracted from the barrel by an alcoholic solution of 51 to 55 per cent alcohol by volume.

The characteristics of the curve emphasize the relatively greater importance of the first 6 to 12 months of maturing, since it is during this short period that the acid content increases to about two thirds its final value.

It is important to note that the region of scatter increases only during the first 6 to 9 months and then remains substantially constant. This type of scatter variation is characteristic of an "exhaustion" reaction; namely, there is only a limited amount of material to be extracted and, as this limit is reached, the region of scatter must necessarily remain constant.

Because of the nature of acid development, it can readily be seen that this characteristic is not a reliable indicator of age beyond the 2-year period. After 2 years the increase in acid content with time is negligible; it is considerably less than the amount of normal variation to be expected in the average value itself.

The total concentration of acid developed in the whisky is related to the quality of the whisky by influencing to a large extent the taste characteristics of the liquid. The average increase in total acid content of whisky during 4 years of maturing is 68 grams (calculated as acetic acid) per 100 liters at 100 proof.

FIXED ACIDITY

Normally, the fixed acid content of a new whisky is zero. Figure 3 indicates a fixed acid content at zero age of about 2 grams per 100 liters at 100 proof. This is a result of treating a portion of the whisky with oak chips prior to barreling. A part of the production was subjected to such treatment during the first few months of 1937.

The general features of this curve, indicating the development of the fixed acids during maturing, are similar to those for total acids. The rapid initial rise in acid content is considerably reduced in the case of fixed acids, and the limiting value is approached at the end of 12 months. The maximum average value appears to be not greater than 15 grams per 100 liters at 100 proof.

The difference between the average total and average fixed acids at 4 years (60.0 grams per 100 liters at 100 proof) is the volatile acid content. It appears difficult to believe that the major proportion of acid material extracted from the wood is volatile in nature. It is also improbable that this volatile acidity is obtained by simple oxidation of alcohols and aldehydes in the whisky since there would then be no limiting value to the total acid increase with time. The fact that the total acid content increases asymptotically points to a relation with a limited supply of extracted material.

It may be suggested at this point (experimentally unverified) that the volatile acids increase with age is indirectly dependent on extraction from the barrel. It appears likely that some of the extracted material is readily oxidized and that the original material is thus converted to acid material, volatile in nature. This possible mechanism of volatile acid formation is important from a quality consideration, since these volatile acids contribute to the aroma of the final product.

The average increase in fixed acid content of whisky during 4 years of maturing is 12.1 grams (calculated as acetic acid) per 100 liters at 100 proof.

ESTERS

The curve of average ester development during the maturing period has several interesting features (Figure 4). For the first time an initial drop in ester content is observed following the entry into the barrel. This lowering of ester content is not an apparent average drop but occurred in each of the barrels during the first three months. The two earlier studies by Crampton and Tolman, and Valaer and Frazier did not report this phenomenon because of the relatively large time period between sampling.

ALDEHYDES

The curve for average aldehyde development during maturing (Figure 5) indicates that after a slight irregular increase, the aldehyde concentration increases at a linear rate of about 1.7 grams per 100 liters at 100 proof per year.

This development of aldehydes is evidently obtained from the oxidation of the alcohols present in the liquid and by loss in volume of liquid by evaporation. Losses of aldehydes are also continually occurring as a result of evaporation from the barrel and conversion to acids by oxidation. The factors

TABLE II. CHARACTERISTICS OF WHISKY^a

Age, Mo.	Proof		Total Acidity		Fixed Acidity		Esters		Aldehydes		Furfural		Fusel Oil		Solids		Color		Tannins		pH	
	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ	\bar{X}	σ
0	101.4	0.53	6.8	4.0	2.0	1.4	18.2	6.3	1.7	1.1	1.2	1.1	118	21	11.4	8.5	0.048	0.050	1	2	4.76	0.18
1	101.0	0.60	21.6	7.2	3.9	2.1	17.2	6.0	2.2	1.0	1.3	0.8	120	20	50.2	16.8	0.178	0.052	14	7	4.60	0.16
3	100.9	0.54	38.2	7.1	6.5	2.9	18.9	5.3	3.1	1.2	1.5	0.6	123	22	74.4	18.8	0.234	0.056	25	8	4.45	0.09
6	101.2	0.63	45.6	6.2	8.4	2.2	22.1	5.3	3.3	1.4	1.6	0.7	122	24	96.2	17.5	0.273	0.058	31	10	4.37	0.19
12	102.1	0.67	56.9	7.0	10.8	3.3	26.8	6.9	4.0	1.4	1.7	0.7	124	21	123.1	18.0	0.305	0.050	37	8	4.29	0.07
18	102.6	0.88	60.4	7.9	11.1	3.5	31.4	7.4	4.9	1.5	1.8	0.9	127	19	139.1	16.9	0.335	0.049	40	6	4.27	0.09
24	103.4	1.17	66.1	7.3	11.5	3.2	35.3	8.0	6.0	1.8	1.9	0.7	126	18	151.6	18.3	0.361	0.045	43	7	4.26	0.10
30	103.9	1.43	68.6	8.6	11.8	2.8	38.7	9.1	7.1	2.1	2.0	0.7	128	20	162.6	18.3	0.380	0.046	46	9	4.24	0.10
36	104.5	1.55	70.6	8.2	12.2	2.7	41.6	8.8	7.8	1.9	2.0	0.8	136	21	167.5	21.2	0.395	0.046	50	7	4.23	0.10
42	105.4	1.61	71.7	8.8	12.6	3.0	45.4	8.2	8.0	2.4	2.1	0.6	135	19	175.2	19.7	0.407	0.045	56	8	4.21	0.10
48	106.1	1.97	75.1	8.6	14.1	2.8	46.2	10.1	9.2	2.3	2.1	0.7	138	22	185.3	21.3	0.419	0.045	59	7	4.19	0.10

^a All figures are expressed as grams per 100 liters at 100 proof, except proof (expressed as degrees proof), color (expressed as density), and pH.

$$\bar{X} = \frac{\sum X}{n} = \text{average value} \quad \sigma = \sqrt{\frac{\sum (X - \bar{X})^2}{n}} = \text{standard deviation}$$

The nature of the curve indicates that a condition exists initially which tends to lower the ester content; later this initial condition is overcome by one which favors the increase of ester content. During the first few months the acid content is low and there is little ester formation. The presence of a large surface of charred wood in the interior of the barrel, however, probably results in an adsorption of esters and thus lowers the ester concentration in the liquid. The rapid rise in acid content, however, soon drives the ester formation reaction forward, and the increase in ester concentration makes itself evident. Further work is planned on this phase of ester formation.

The rate of increase of average ester content after 6 months in the barrel is positive and regular, and shows signs of slackening only after the 4-year period. It is probable that the increase in ester content is asymptotic, since ester formation is dependent upon the acid concentration which, in itself, is represented by an asymptotic curve. It is evident that the region of slow ester development has not been reached at the 4-year period and that the ester content can therefore be used as an indicator of age in a more reliable manner than the acid content.

The region of scatter for individual barrels ($\bar{X} \pm 2\sigma$) increases slowly with age and at 4 years is relatively large. This extended range of scatter is probably the result of two factors: (a) the scatter from the acid content values, the magnitude of which creates the driving force for ester formation, and (b) the effect of temperature variation on the equilibrium constant of ester formation. Factor *b* probably predominates. The fluctuations of temperature throughout the year and in different parts of different warehouses are well known. At the present time this important variable is not under the positive control of the distiller.

The average increase in ester content of whisky during 4 years of maturing is 28 grams (calculated as ethyl acetate) per 100 liters at 100 proof.

favoring increase in aldehyde concentration exceed those favoring decrease by the amount given above.

The average increase in aldehyde content of whisky during 4 years of maturing is 7.5 grams (calculated as acetaldehyde) per 100 liters at 100 proof.

FURFURAL

This characteristic is of minor significance, primarily because of its very small variation with time. By custom it has usually been included in a complete analysis of whisky. The present data, as did those of the earlier investigators, indicate that its determination does not add to the evaluation of the product and, therefore, might be omitted from whisky analysis.

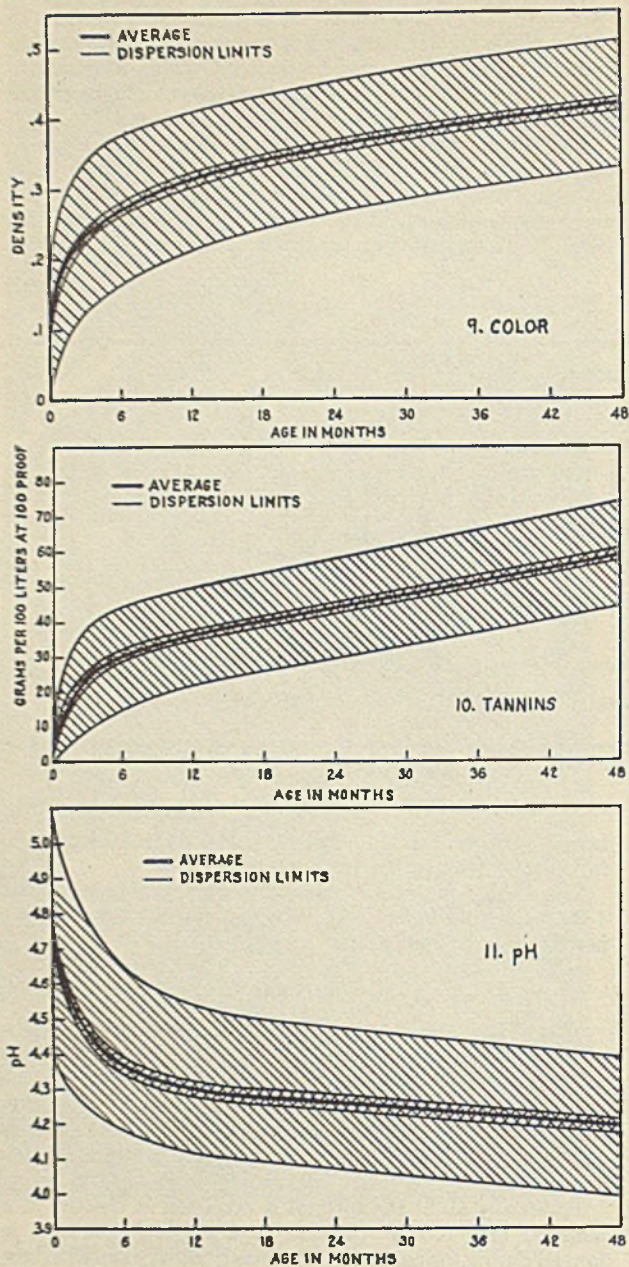
Practically all of the furfural is extracted at the end of 6 months, and further increase is negligible. Furfural is formed during the charring of the wood; whisky stored in new uncharred oak wood develops only traces of this substance.

During the first 6 months of maturing, there is an anomalous region of scatter. This occurrence is due to the fact that a small portion of the whisky received chip treatment prior to entry into the barrel. The large scatter at zero age reflects the variation in the chips, principally the degree of toasting. The rapid lowering of the scatter during the succeeding 3 months is due to the equalizing effect of the barrel, and as soon as the chip effect is overcome, the region of scatter remains constant.

The maximum average furfural content of whisky will not exceed 2.5 grams per 100 liters at 100 proof.

FUSEL OIL

The fusel oil content of a whisky is practically independent of maturing conditions. This characteristic is largely determined by the two factors of production preceding maturing, fermentation and distillation.



Figures 9, 10, and 11

Diagonally shaded areas = $\bar{X} \pm 2\sigma$; cross-shaded areas $\bar{X} \pm \sigma$.

The results (Figure 7) indicate that a slight increase in fusel oil concentration occurs during maturing. This increase is probably due to evaporation of solvent from the barrel, since the percentage increase in fusel oil concentration is approximately equal to the percentage loss in volume (12-15 per cent). The average increase in fusel oil concentration of whisky after 4 years of maturing is 20 grams (calculated as amyl alcohol) per 100 liters at 100 proof.

SOLIDS

The development of solids content during maturing is similar to that of the total acidity (Figure 8). The typical rapid initial increase of the average value and the increase in the region of scatter only during the first year are to be noted.

After 6 months of maturing the average solids content has increased to five times its original value. Thereafter the rate of increase drops off sharply and slowly approaches a limiting value.

The solids content, however, does not approach its asymptotic value as rapidly as does the total acidity. Even at the 4-year stage the increase in solids is appreciable. This characteristic of maturing cannot, therefore, be used as an indicator of the age of whisky. The maximum average value of the solids content cannot be reliably determined from the graph at this stage. It will probably not exceed 210 grams per 100 liters at 100 proof. The average increase in solids content of whisky during 4 years of maturing is 174 grams per 100 liters at 100 proof.

COLOR

The color of matured whisky is derived exclusively from the charred oak barrel and gradually shifts in hue (1) from colorless through yellow and amber to deep reddish brown.

The color development curve (Figure 9) is similar to those for total acidity and solids. The initial color of the zero age sample of 0.05 is again due to the chip treatment of a portion of the whisky prior to barreling. Within 2 months the color intensity has quadrupled. After 3 months the rate of color development begins to fall off and approaches a maximum average value which appears to be not greater than 0.45. The average increase in color intensity of whisky during 4-year maturing is 0.37.

TANNINS

The tannin content of a whisky is derived wholly from the barrel by extraction. The first portion of the tannin content-time curve (Figure 10) is similar to those of total acidity, solids, and color. A rapid increase in tannin concentration occurs during the first 6 months, followed by a decrease in rate. The curve, however, does not indicate an ever-decreasing rate to a maximum value, as might be expected from a study of the other extracted characteristics. Instead, after 12 months of maturing, the rate of increase of tannin concentration appears to become linear and increases indefinitely. Further data, beyond the 4-year period which are being gathered, will throw additional light on this phase of tannin development.

The observed indefinite increase in tannin concentration is probably apparent. The analytical determination for this characteristic is not specific, but includes the general group of organic compounds containing the oxy-phenyl bond. Although this grouping predominates in the tannin class, it is possible, as a result of the complexity of wood structure, that additional substances are extracted from the barrel which contain this grouping. The latter substances may cause the steady increase indicated by Figure 10. Eventually, however, even these substances will be exhausted, and the curve should flatten out to a typical asymptotic approach to a maximum value.

The average increase in tannin content of whisky during 4 years of maturing is 58 grams (calculated as tannic acid) per 100 liters at 100 proof.

pH

Due to the definition of pH, involving the reciprocal of hydrogen-ion concentration, the graph of pH development (Figure 11) is the mirror image of those for total acidity, solids, and color. Otherwise the features of this curve are similar to those mentioned.

Here again there is a rapid decrease of pH during the first 6 months of maturing, followed by a less rapid decrease during the next 6 months. The typical slow approach makes its

appearance after 1 year of maturing. The minimum average pH value appears to be not less than 4.15. The average decrease of pH of whisky during 4 years of maturing is 0.57.

MATHEMATICAL REPRESENTATION

It has been shown that the development of maturing characteristics of whisky by the extraction of a limited quantity

this equation is related to the maximum value that can be attained. The maximum value (y_{∞}) is equal to $1/b + y_0$.

In the case of total acidity the visual maximum value as obtained from the graph is approximately 80, and that calculated from the equation is 80. In the case of solids the comparison is approximately 210 and 201. In the case of color the comparison is approximately 0.49 and 0.44.

TABLE III. MATHEMATICAL REPRESENTATION OF MATURING CHARACTERISTICS

TOTAL ACIDITY				SOLIDS				COLOR			
$y = \frac{t}{0.069t + 0.0124t} + 6.8$				$y = \frac{t}{0.0367t + 0.00524t} + 11.4$				$y = \frac{t}{11.54 + 2.55t} + 0.05$			
t	$y_{\text{obed.}}$	$y_{\text{calcd.}}$	Difference	t	$y_{\text{obed.}}$	$y_{\text{calcd.}}$	Difference	t	$y_{\text{obed.}}$	$y_{\text{calcd.}}$	Difference
0	6.8	6.8	0.0	0	11.4	11.4	0.0	0	0.048	0.048	0.000
1	21.6	18.8	2.8	1	50.2	35.2	15.0	1	0.178	0.119	0.059
3	38.2	34.0	4.2	3	74.4	68.5	5.9	3	0.234	0.204	0.030
6	45.6	46.4	-0.8	6	96.2	99.2	-3.0	6	0.273	0.271	0.002
12	56.9	58.2	-1.3	12	123.1	131.5	-8.4	12	0.305	0.332	-0.027
18	60.4	63.9	-3.5	18	139.1	148.3	-9.2	18	0.335	0.361	0.026
24	65.1	67.2	-2.1	24	151.6	158.6	-7.0	24	0.361	0.377	-0.016
30	68.6	69.4	-0.8	30	162.6	165.6	-3.0	30	0.380	0.388	-0.008
36	70.6	71.0	-0.4	36	167.5	170.6	-3.1	36	0.395	0.396	-0.001
42	71.7	72.1	-0.4	42	175.2	174.3	0.9	42	0.407	0.402	0.005
48	75.1	73.0	2.1	48	185.3	177.3	8.0	48	0.419	0.406	0.013
∞	∞	80.0	∞	∞	∞	201.3	∞	∞	∞	0.440	∞

of wood material leads to an asymptotic approach to a maximum value. This type of growth, under certain conditions, can be expressed mathematically by an equation in the form of a hyperbola. Three of the characteristics, due to the regularity of their development, appeared to lend themselves to such treatment—total acidity, solids, and color.

The general family of hyperbolas,

$$y = \frac{t}{a + bt} + y_0$$

where t = age, months
 y = value of characteristic
 y_0 = value of characteristic at $t = 0$
 a, b = constants

was found to give a satisfactory representation of the observed data. By plotting $t/(y - y_0)$ against t , a straight line is obtained with b as the slope and a as the y -intercept. The equation of this line was obtained by the method of least squares.

TOTAL ACIDITY. For this characteristic the equation was found to be:

$$y = \frac{t}{0.069t + 0.0124t} + 6.8$$

Table III compares the observed values with those calculated from the equation; the agreement is good in this case.

SOLIDS. For this characteristic the equation was found to be

$$y = \frac{t}{0.0367t + 0.00524t} + 11.4$$

Table III compares the observed values with those calculated from the equation, and the agreement is fair. At the 1-month period, where the rate of increase is extremely great, the agreement is poor.

COLOR. For this characteristic the equation was found to be

$$y = \frac{t}{11.54 + 2.55t} + 0.05$$

The agreement between the observed values and those calculated from the equation (Table III) is fair.

These equations can be used with reliability for the interpolation between the periods of observation. Constant b in

RELIABILITY OF THE DATA

Two fundamental assumptions have been the basis of the foregoing discussion:

1. The 108 barrels are representative of normal whisky; i. e., these barrels constitute a large enough sample so as to be characteristic of the totality of whisky production.

If this is true, then the effect of additional samples will cause negligible changes in the averages (\bar{X}) and the standard deviations (σ). An additional 50 barrels randomly set aside in 1938 were carried through the same analyses and treatment. The averages (\bar{X}') and standard deviations (σ') were calculated for this set and tested for significant differences with the 1937 set. The differences between the two sets of data were found to be statistically insignificant for all characteristics. Assumption 1 can, therefore, be considered true.

2. The 108 barrels are normally distributed with respect to their analytical characteristics.

The chi-square test for goodness of fit (χ^2) was applied to several of the characteristics at several age levels. The test indicated that the observed distribution of the data did not differ significantly from a theoretically derived normal distribution. The data can, therefore, be considered as approximately normally distributed at least.

CONCLUSION

The results of observation of 108 barrels of whisky under normal maturing conditions have been chemically and statistically analyzed.

Each curve of average values shown in the figures, describing the rate of development of maturing characteristics, is surrounded by two regions of dispersion. The diagonally shaded region in each case determines an "area of variation" for normal individual barrels of whisky. Any normal barrel chosen at random will exhibit analytical characteristics that lie within these regions. Values falling outside these regions indicate abnormal maturing behavior. The limits of these regions have been determined from the inherent variation among whiskies caused by current methods of maturing.

Table IVA summarizes the analytical characteristics of normal whisky during 4 years of maturing, showing the average values (\bar{X}) and, the maximum and minimum normal

TABLE IV. ANALYTICAL CHARACTERISTICS OF WHISKY^a

Age, Years	Value ^b	Proof	Total Acidity	Fixed Acidity	Esters	Aldehydes	Furfural	Fusel Oil	Solids	Color	Tannins	pH
A. Individual Barrels												
0	<i>L_V</i>	102.5	14.8	4.8	30.9	3.9	3.1	160	28.3	0.148	6	5.12
	\bar{X}	101.4	6.8	2.0	18.2	1.7	1.2	118	11.4	0.048	1	4.76
	<i>L_L</i>	100.3	0.0	0.0	5.5	0.0	0.0	76	0.0	0.000	0	4.40
1	<i>L_V</i>	103.4	71.0	17.4	40.5	6.8	3.2	166	159.1	0.405	52	4.43
	\bar{X}	102.1	56.9	10.8	26.8	4.0	1.7	124	123.1	0.305	37	4.29
	<i>L_L</i>	100.8	42.8	4.2	13.1	1.2	0.2	82	87.1	0.205	22	4.15
2	<i>L_V</i>	105.7	80.6	17.5	51.4	9.6	3.3	162	188.2	0.451	57	4.46
	\bar{X}	103.4	66.1	11.5	35.3	6.0	1.9	126	151.6	0.361	43	4.26
	<i>L_L</i>	101.1	51.6	4.6	19.2	2.4	0.5	90	115.0	0.271	29	4.06
3	<i>L_V</i>	107.6	87.0	18.0	59.2	11.6	3.5	178	209.9	0.487	64	4.43
	\bar{X}	104.5	70.6	12.2	41.6	7.8	2.0	136	167.5	0.395	50	4.23
	<i>L_L</i>	101.4	54.2	6.5	24.0	4.0	0.5	94	125.1	0.303	34	4.03
4	<i>L_V</i>	110.0	92.4	19.0	66.3	13.8	3.6	182	227.9	0.509	73	4.39
	\bar{X}	106.1	75.1	14.1	46.2	9.2	2.1	138	185.3	0.419	59	4.19
	<i>L_L</i>	102.2	57.8	6.8	26.1	4.6	0.6	94	142.7	0.329	47	3.99
B. 100-Barrel Lots												
0	<i>L'_V</i>	101.5	7.8	2.7	19.7	2.0	1.3	122	13.5	0.061	2	4.80
	\bar{X}	101.4	6.8	2.0	18.2	1.7	1.2	118	11.4	0.048	1	4.76
	<i>L'_L</i>	101.3	5.8	1.3	16.7	1.4	1.1	114	9.3	0.035	0	4.72
1	<i>L'_V</i>	102.2	58.3	11.4	28.1	4.3	1.8	128	126.6	0.315	38	4.30
	\bar{X}	102.1	56.9	10.8	26.8	4.0	1.7	124	123.1	0.305	37	4.29
	<i>L'_L</i>	102.0	55.5	10.2	25.5	3.7	1.6	120	119.6	0.295	36	4.28
2	<i>L'_V</i>	103.6	67.5	12.1	36.8	6.3	2.0	130	155.1	0.370	44	4.28
	\bar{X}	103.4	66.1	11.5	35.3	6.0	1.9	126	151.6	0.361	43	4.26
	<i>L'_L</i>	103.2	64.7	10.9	33.8	5.7	1.8	122	148.1	0.352	42	4.24
3	<i>D'_V</i>	104.8	72.0	12.7	43.3	8.2	2.2	140	171.6	0.404	50	4.25
	\bar{X}	104.5	70.6	12.2	41.6	7.8	2.0	136	167.5	0.395	49	4.23
	<i>L'_L</i>	104.2	69.2	11.7	39.9	7.4	1.8	132	163.4	0.386	48	4.21
4	<i>L'_V</i>	106.5	76.8	14.6	48.2	9.7	2.2	142	189.5	0.428	61	4.21
	\bar{X}	106.1	75.1	14.1	46.2	9.2	2.1	138	185.3	0.419	60	4.19
	<i>L'_L</i>	105.7	73.4	13.6	44.2	8.7	2.0	134	181.1	0.410	59	4.17

^a All figures expressed as grams per 100 liters at 100 proof, except proof (expressed as degrees proof), color (expressed as density), and pH.

^b *L_V* = probable maximum = $\bar{X} + 2\sigma$; *L_L* = probable minimum = $\bar{X} - 2\sigma$; \bar{X} = average; *L'_V* = probable maximum = $\bar{X} + 2\sigma\bar{X}$; *L'_L* = probable minimum = $\bar{X} - 2\sigma\bar{X}$.

variation among individual barrels to be expected in each case (*L_V* and *L_L*).

The regions of dispersion discussed above are relatively large in many cases. This is a consequence of considering individual barrels, and of including within the region individuals which are normal and yet a considerable distance from the average value.

This effect is minimized to a great extent in industrial practice by the usual mixing of a large number of barrels to form a convenient operating unit. This unit frequently consists of 100 barrels. In this case the effect of a few individual barrels which exhibit characteristics away from the average value is practically eliminated. Therefore, the variation among these 100-barrel lots will be much smaller than among individual barrels.

The cross-hatched regions surrounding the average curves show quantitatively how much smaller the dispersion becomes for 100-barrel lots. Table IVB summarizes the analytical characteristics of normal whisky during 4 years of maturing, showing the same average values (\bar{X}) and the maximum and minimum variation among 100-barrel lots to be expected in each case (*L'_V* and *L'_L*).

Since these 100-barrel lots are the units of the finished product, Table V may be used as a basis for setting up specifications for the control of whisky quality.

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