for use in fractional distillation are 1.083[2] and 1.023, respectively. The former system was found to deviate appreciably from an ideal solution. From the information now available, systems of sufficient ideality to permit valid use of the relation $\alpha = P_A/P_B$ are limited to close-boiling mixtures of the same hydrocarbon class—i. e. paraffin-paraffin, naphthene-naphthene, and aromatic-aromatic compounds.

Analytical error in vapor-liquid equilibrium determinations becomes pronounced at extremes of concentration, and consistent errors which may be due to slight impurities are most pronounced at the low-boiling end of the curve. Such errors do not of themselves justify rejection of data on intermediate concentrations.

The fractional distillation method is proposed as the most reliable to date for verification of vapor-liquid equilibrium data and determination of α for close-boiling hydrocarbon systems in which it is essentially constant.

Acknowledgment

The Bureau of Industrial Chemistry of the University of Texas loaned the fractionation equipment. The relative volatility of *n*-heptane–isooctane was determined by E. E. Ludwig.

[2] The multiplier to convert theoretical plates from the basis of $\alpha = 1.07$ is 0.85, and the corresponding HETP multiplier is 1.176.

Literature Cited

(1) Beatty and Calingaert, Ind. Eng. Chem., 26, 504, 905 (1934).
(2) Bromiley and Quiggle, *Ibid.*, 25, 1136 (1933).
(3) Brooks, Howard, and Crafton, *J. Research Natl. Bur. Standards*, 24, 33 (1940).
(4) Bruun, J. H., Ind. Eng. Chem., Anal. Ed., 8, 224 (1936).
(5) Edgeworth-Johnstone, *J. Inst. Petroleum Tech.*, 25, 558 (1939).
(6) Fenske, M. R., Ind. Eng. Chem., 24, 482 (1932).
(7) Fenske, Tongberg, and Quiggle, *Ibid.*, 26, 1169 (1934).
(8) Griswold and Ludwig, *Ibid.*, 34, 117 (1942).
(9) Kelso and Felsing, *Ibid.*, 34, 161 (1942).
(10) Lewis and Luke, *Ibid.*, 25, 725 (1933).
(11) Podbielniak, W. J., Ind. Eng. Chem., Anal. Ed., 13, 644, Fig. 8 (1941).
(12) Smith, E. R., *J. Research Natl. Bur. Standards*, 24, 299 (1940).
(13) Smoker, E. H., *Trans. Am. Inst. Chem. Engrs.*, 34, 165 (1938).
(14) Timmermans, Jean, in International Critical Tables, Vol. III, p. 244, New York, McGraw-Hill Book Co., 1928.
(15) Tongberg, Quiggle, and Fenske, Ind. Eng. Chem., 26, 1213 (1934).
(16) Walker, Lewis, McAdams, and Gilliland, "Principles of Chemical Engineering", 3rd ed., p. 521, New York, McGraw-Hill Book Co., 1937.

Activated Carbon Treatment of Raw Whisky

G. C. WILLIAMS AND E. A. FALLIN[1]
University of Louisville, Louisville, Ky.

The chemical changes and changes in taste characteristics that take place when a distillate from an alcohol fermentation process is treated with each of several activated carbons are reported. The effect of one carbon was investigated over a temperature range from 20° to 80° C.

Tables of results are included, and figures illustrate the percentage change effected by the treatment.

At room temperature it was noted that the change in acids, esters, aldehydes, and fusel oil was slight but not consistently in one direction. Permanganate time was increased in all treatments and to approximately the same extent. However, the treatment at elevated temperatures definitely produced an increase in acids and permanganate time, while it indicated decreases in ester, aldehydes, and fusel oil.

IN DISTILLATION industries, adsorption methods are often used to remove impurities, particularly those present at relatively low concentrations. These methods are used although very little is known of the actual chemical changes effected by the treatment. In a liquid mixture or solution, some constituents are preferentially attracted to the surface of different adsorbents to the almost complete exclusion of others.

The program described in this paper was to determine some of the more important chemical changes brought about in the raw whisky by different kinds of activated carbons, and to determine the effect of temperature on one of the carbon treatments. Taste preference was utilized to show a correlation with the extent of these chemical changes. Such a relation would substantiate the effects of the various treatments.

The chemical changes involved are many and complex. Different amplitudes are affected by the kinds of material used as containers during storage, as shown by laboratory investigations of Valaer and Frazier of the Bureau of Internal Revenue (*6*). They found upon storing raw whisky for four years in charred white oak barrels that the most rapid changes of acids, esters, solids, and color took place in the first six months. During the four years acids increased from 24.9 to 56 mg. per 100 ml. while esters increased from 7.4 to 21.3 mg. per 100 ml. Fusel oil content, however, dropped from 69 to 58.4 mg. per 100 ml.

It was also found that raw whisky changes while standing

[1] Present address, M. F. A. Milling Company, Springfield, Mo.

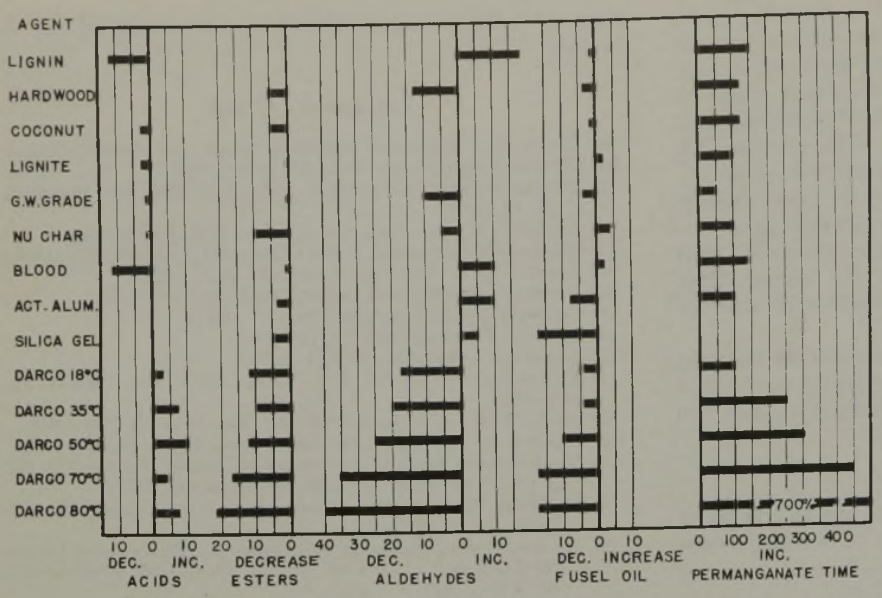

FIGURE 1. EFFECT OF VARIOUS TYPES OF ACTIVATED CARBON ON RAW RYE WHISKY

in glass. The acids, aldehydes, and furfural contents decrease while the esters and color increase. It was nearly four years before the whisky had lost the major portion of its green or slop taste and odor.

The practice of some distilleries has been to treat raw whisky with charcoal to remove undesirable green characteristics. In 1908 Dudley (*3*) found that fatty oils and other insolubles could be removed from raw whisky distillates by filtration through a sugar maple wood charcoal. He also asserted that soluble constituents are removed partly by adsorption but principally by diffusion into the charcoal, where particles of higher molecular weight are held longer while the lighter materials pass more rapidly.

Thomas and Hochwalt (*5*) patented a process for making an improved beverage substantially free of usual green characteristics by subjecting the liquor to a hydrogenation treatment in the presence of a catalyst of finely divided platinum, nickel, and cobalt. By this method, it is maintained, the odor and taste characteristics are permanently improved.

Chabot (*1*) found that beer worts treated by activated carbon were greatly improved in taste and foam retention properties, and that protein turbidity was removed.

Fritzweiler and Dietrich (*4*) purified absolute alcohol by percolation through carbon. Wuoorinen and Lawren (*7*) reported that birchwood charcoal removes a large number of aldehydes from alcoholic solutions, formaldehyde being an exception. In some cases they found that the removal was more easily accomplished in lower proof alcohols.

Chaney (*2*) stated, from a study of the properties of activated carbon in industrial application, that the adsorption power for particles of colloidial dimensions is a mathematical function of the ratio of its activity to its apparent density, fineness being constant. The adsorption is most effective if the carbon carries an opposite electric charge.

Zahariz, Angelescu, and Motoc (*8*) stated that animal charcoal removes, in varying amounts, the different impurities in commercial alcohols when the adsorption is performed under conditions precluding oxidation.

As a general review on effects that may be expected from treating an alcohol solution with activated carbon, it is worthwhile to consider many different viewpoints.

The treatment of a solution with an adsorbent such as activated carbon results in the phenomenon of the adhesion of molecules of a gas or dissolved substances to the surfaces of the solid bodies. This results in a relatively high concentration of the gas or solution at the place of contact, while the carrier solution is freed of these substances.

Activated carbon has a large surface area per unit volume which is increased with a reduction in particle size. Some kinds of activated carbons, too, are more porous than others and have a larger surface area per unit volume. This surface area is capable of holding the adherent molecules. The amount adsorbed increases with the length of time allowed for the treatment until equilibrium is reached. Agitation of the solution will accelerate the contact with the adsorbent and thus reduce the time required for reaching this equilibrium.

An increased temperature will decrease the viscosity of the alcoholic solution. This results in an increasing number of *usable* pores of the activated carbon and an increase in the *usable* surface area, and thus varies the amount adsorbed. A temperature change will also alter the rate of circulation and diffusion.

The removal of the adsorbed substances from the solution will disturb the chemical equilibrium, and additional chemical changes will take place. Any variation in temperature or pressure will affect both the rate of chemical change and the solubility factors. The chemical and mechanical changes will be accelerated as the temperature and pressure are increased.

The presence of air in the pores of an adsorbent will oxidize some solutions. The raw whiskies treated in the following experiments contain alcohol, acids, esters, and aldehydes which may be oxidized by the air present, but these substances will also be adsorbed by the carbon. Either oxidation or adsorption may predominate according to the kind of activated carbon used and the temperature and pressure maintained during the treatment.

Whiskies and Carbons Used

The distillate from an alcohol fermentation process of 51 per cent rye, 39 per cent corn, and 10 per cent small grain mash was stored in one-gallon glass bottles. This whisky was clear, 100-proof alcohol and had no visible colloidal suspended materials. A 100-proof, raw bourbon whisky from a grain mash of 51 per cent corn and 49 per cent small grain was also used. This, too, was clear and had no colloidal suspension perceptible to the naked eye.

For treating raw whiskies, several different kinds of activated carbon of various particle sizes were used, as well as activated alumina and silica gel as adsorptive agents.

All the samples were tested for proof before and after treating. A special test was used as an indication of the amount of reducing compounds present in the alcohol, which was considered to give an indication of various impurities. This test was called "permanganate time", as it consists in bringing a 50-ml. sample to 18° C. in a Nessler tube and adding 1 ml. of standard potassium permanganate solution. The time which elapses from the adding of the permanganate until the solution turns from pink to yellow is the permanganate time.

The alcohol solutions were treated with various carbons. For each test 0.4 gram of activated carbon was made into a thin paste and gradually diluted with a portion of the one-liter sample of alcohol to be treated. The remaining part of the liter was quickly added and the solution placed in a one-gallon, glass-stoppered bottle. The bottle was shaken for 30 minutes, and the carbon filtered out through ashless double-acid-washed filter paper. It was filtered the second time to make certain that all traces of carbon were removed. This procedure was carried out on each treatment with the several difierent kinds of activated carbons, activated alumina, and silica gel. Only Darco carbon was used for further experiments at elevated temperatures.

At the higher temperatures the entire shaking mechanism was placed inside an oven where the treatments were carried out at constant temperatures of 35°, 50°, 70°, and 80° C. Chemical analyses were run for acids, esters, fusel oil, aldehydes, and permanganate time. These tests were made on the samples both before and after treatment with the various adsorptive agents (Table I).

Since it was desired to determine the effects of activated carbon on the residual nitrogen content of whisky, a one-liter sample of bourbon was treated in the usual manner and an analysis made for residual nitrogen, before and after treatment:

Bourbon Whisky	Untreated, Mg./Liter	Treated with Darco, Mg./Liter	Per Cent Change
I	0.464	0.3712	20.0
II	0.476	0.2784	20.5

Samples of treated and untreated bourbon and rye whiskies were submitted to a taste-preference laboratory with the following results:

Whisky Sample	% Preference	Probable Error
Untreated bourbon	35.0	1.35
Bourbon, Darco-treated at 18° C.	65.0	
Untreated rye	21.6	1.25
Rye, Darco-treated at 35° C.	34.2	2.5
Rye, Darco-treated at 80° C.	44.2	

The various chemical analyses were carried out principally by A. O. A. C. methods. Aldehydes were calculated as acetaldehyde from the colorimetric determination. Acids were determined by titration of 0.05 *N* sodium hydroxide and calculated as acetic acid. Esters were calculated as ethyl acetate. The esters were determined by back-titrating with sulfuric acid the sample used for the acid determination, which had been made alkaline and allowed to stand overnight. This is in accord with standard procedure.

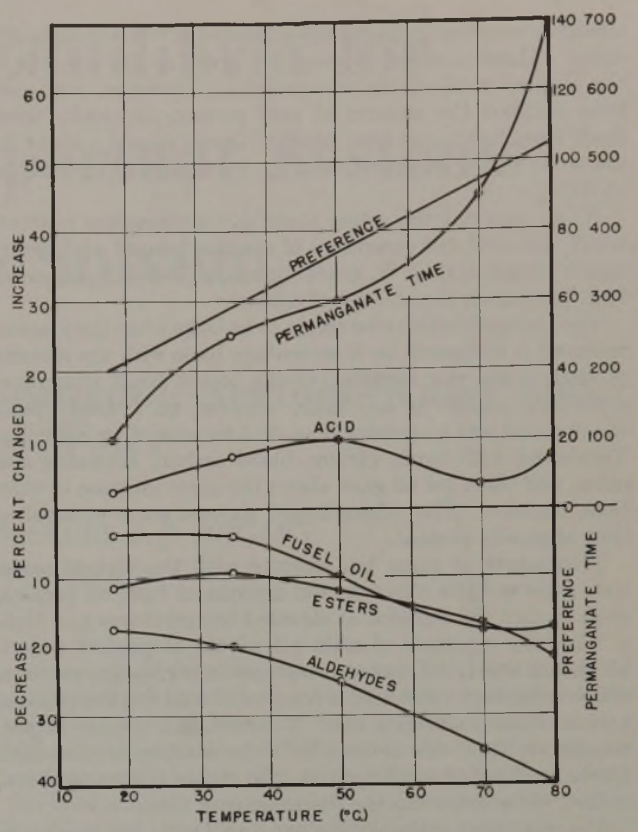

FIGURE 2. ACTION OF DARCO G-60 ACTIVATED CARBON AT ELEVATED TEMPERATURES ON RAW RYE WHISKY

Chemical Changes Due to Carbons

The data show that the amounts of various impurities present in the ethyl alcohol of raw rye whisky are materially changed by treatment with activated carbon, silica gel, or activated alumina. A much greater change is shown, however, in the treatments conducted at elevated temperatures.

Figure 1 gives the percentage of chemical changes that take place during treatment. Figure 2 indicates the chemical

TABLE I. EFFECT OF VARIOUS CARBONS ON WHISKY SAMPLES

Sample No.	Adsorptive Agent	Chemical Analysis, Mg./100 Ml.				Permanganate Time, Sec.	Proof	Per Cent Change by Carbon Treatment				
		Acids	Esters	Aldehydes	Fusel oil			Acid	Esters	Aldehyde	Fusel oil	Permanganate time
R-1	None	3.9	10.50	1.15	270	30	100.4					
R-2	None	4.0	10.50	1.15	270	30	99.1					
R-3	None	3.9	10.50	1.10	260	..	100.0					
R-4	None	4.0	10.50	1.00	260	30	99.7					
R-5	None	...	...	1.00	255	..	99.5					
R-1	Lignin carbon	3.45	10.50	1.35	265	75	99.2	11.50	0	17.40	− 1.85	150
R-2	Hardwood carbon	4.00	9.95	1.00	260	65	98.8	0	− 5.25	−13.05	− 3.70	117
R-2	Coconut carbon	3.90	10.05	1.15	265	65	99.1	−2.50	− 4.28	0	− 1.85	117
R-2	Lignite carbon	3.90	10.40	1.15	275	60	99.8	−2.50	− 0.95	0	1.85	100
R-3	G.W. grade carbon	3.85	10.40	1.00	250	45	99.5	−1.30	− 0.95	− 9.10	− 3.85	50
R-3	NuChar	3.85	9.45	1.05	270	60	99.2	−1.30	−10.00	− 4.55	3.85	100
R-4	Blood carbon	3.55	10.40	1.10	265	70	97.9	11.25	− 0.95	10.00	1.93	133
R-4	Activated alumina	4.00	10.15	1.10	240	60	99.6	0	− 3.33	10.00	− 7.70	100
R-4	Silica gel	4.00	10.05	1.05	215	30	98.9	0	− 4.28	5.00	−17.30	0
R-1	Darco[a], 18° C.	4.00	9.30	0.95	260	60	99.0	2.50	−11.42	−17.40	− 3.70	100
R-5	Darco[a], 35° C.	4.30	9.55	0.80	245	105	97.2	7.50	− 9.05	−20.00	− 3.92	250
R-5	Darco[a], 50° C.	4.40	9.25	0.75	230	120	96.6	10.00	−11.90	−25.00	− 9.80	300
R-5	Darco[a], 70° C.	4.15	8.75	0.65	210	165	96.7	3.75	−16.65	−35.00	−17.60	450
R-5	Darco[a], 80° C.	4.30	8.25	0.60	215	240	96.6	7.50	−21.42	−40.00	−17.30	700

[a] Grade G-60.

changes occurring in the samples treated at various temperatures. These chemical changes are given as the per cent of the original value of the raw samples. However, most carbons reduced the amount of acid present, especially those made from lignin and from blood. Darco caused a slight increase at higher temperatures, the maximum being reached at 50° C.

In no case did the esters show any increase due to treatment, and, with the exceptions of samples treated with lignin, lignite, blood, and G. W. grade carbon, all showed a considerable decrease in the amount of esters.

The change in aldehydes seems to be large when the amount removed is compared on a percentage basis with the amount present in the raw sample. Owing to the small amount of aldehydes present at any time, however, on a weight basis the removal was no greater than that for any other impurity. Treatment with lignin carbon, blood carbon, activated alumina, and silica gel all gave about the same increase in aldehyde content. The others tested showed some removal of that originally present.

Treatments at room temperature with the various materials showed little effect on the amount of fusel oil present, even though the removal at elevated temperatures was high.

With the exception of silica gel, all the absorptive materials caused nearly 100 per cent increase in permanganate time, which indicates a considerable removal of reducing compounds, such as sulfur, nitrogen, etc. A tremendous change in permanganate time was noticed for those samples treated with Darco at elevated temperatures; the higher the temperature, in fact, the greater was the permanganate time.

The activated carbons NuChar and Darco are similar in effect. The change Darco produced was magnified at higher temperatures. The activated carbons from lignin and blood also resemble each other in the effect produced but are different from NuChar and Darco in that they increase the aldehydes and lower the acids. This latter reaction may be attributed to the presence of alkalies in these carbons.

The residual nitrogen determinations show that the untreated raw bourbon samples contained an average of 0.470 mg. per liter. The treatment of the sample with Darco at room temperature removed 20 per cent of the nitrogen in the sample.

The taste preference indicates strongly that the treatments remove undesirable taste characteristics. As far as the treatment of the bourbon is concerned, the difference is statistically significant, as indicated by the probable error of 1.35. This means that in approximately 85 chances out of 100, the trend toward improvement is duplicable.

In a similar manner the various samples of rye whisky are well differentiated from one another in terms of preference. The 30° C. treatment is significantly superior to the control, while the 80° C. treatment is reproducible to the extent of 100 per cent with respect to the control.

The adsorptive powers of the various activated carbons at room temperature, regardless of particle size, were only slightly different in effect on whiskies in comparison to those at elevated temperatures.

It appears that certain of the adsorptive agents were effective in causing oxidation of the ethyl alcohol to acids and aldehydes in excess of the amount adsorbed by the carbon itself. Other agents either failed to cause oxidation or, if oxidation did take place, were sufficiently adsorptive to remove the new substances thus produced as well as a portion of those impurities already present, so that to all appearances oxidation might never have occurred.

It is probable that only a small amount of oxidation did occur during these treatments, since small quantities of carbon were first made into a thin paste, diluted several times, and then added to the whisky sample. As Figures 1 and 2 show, considerable activity took place at elevated temperatures. Acids were increased but only at 70° C. However, there was a decided and uniform decrease of aldehydes and esters as the temperature was increased.

An even more outstanding change is noticeable in the permanganate time. A 700 per cent increase was obtained for treatment at 80° C., which would indicate a high removal of reducing compounds such as those made up of sulfur, nitrogen, etc., that were carried over in the distillation from the fermentation process. The determination showing a removal of 20 per cent residual nitrogen also supported this conclusion.

The tests for taste preference showed that treatment with activated carbons removed from the raw whisky impurities that are undesirable to human taste.

Conclusions

These tests gave definite evidence that the treatments carried on at elevated temperatures were superior to those at room temperature for removing the impurities from the distillate of an alcohol fermentation process.

Taste preferences and the desirable effects of aging on whiskies are not completely understood. Some theories hold for low fusel oil, aldehyde, and acid values; some consider a high ester value necessary; and a third group considers the relative amounts of all materials more important than the absolute values of each. On this basis it may be of interest to consider the action of activated carbon as a substitute for some aging time in the whisky industry, as well as a possible procedure for the reduction of impurities in the manufacture of industrial alcohol.

Literature Cited

(1) Chabot, G., *Petit J. brasseur*, **47**, No. 2022, 351–4 (1939).
(2) Chaney, N. K., J. Ind. Eng. Chem., **13**, 1043 (1921).
(3) Dudley, William, *J. Am. Chem. Soc.*, **30**, 1784–9 (1908).
(4) Fritzweiler and Dietrich, German Patent 529,381 (1928); *Z. Spiritusind.*, **54**, 209–10 (1931).
(5) Thomas and Hochwalt, U. S. Patent 2,138,435 (1938).
(6) Valaer and Frazier, Ind. Eng. Chem., **28**, 92 (1936).
(7) Wuoorinen and Lawren, *Ann. Acad. Sci. Fennicae*, **A24**, 2, 3–10 (1924).
(8) Zahariz, Angelescu, and Motoc, *Chimie & industrie*, **Spec. No.**, 989–95 (April, 1934).