The Effect of the Presence of Different Concentrations of Fusel Oil on the Determination of Alcohol by Picnometer and Hydrometer

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INTRODUCTION

During the course of operations in a commercial distillery it is frequently necessary to determine the ethyl alcohol content of samples from intermediate plates of the distillation columns which contain relatively large amounts of fusel oil and smaller quantities of other impurities. It is desirable to make this determination without resorting to time-consuming and complicated methods of analysis which are not regularly utilized in daily process control. Determination of the alcohol being removed from the column with the fusel-oil side stream, and establishing the relation between alcohol and fusel-oil compositions along the column are examples of this need.

The methods of analysis most commonly employed in distillery practice for the determination of alcohol are those of the picnometer, the refractometer, and the hydrometer. The last is by far the most used. The picnometer and hydrometer methods are based on the specific gravity of pure alcohol-water solutions at reference temperatures, while the refractometer method is based on the index of refraction of pure solutions, also at reference temperatures.

Obviously, the presence of substances other than alcohol and water will alter the physical properties of the solution, introducing errors in the results obtained with any of the above analytical methods. Fortunately, the quantities of impurities in the raw products of the first columns of the distillation unit, and especially in the finished product from the last column, are so low that the error introduced is usually negligible and falls well within the precision limits of the various analytical methods. In aged spirits and finished beverage products the effect of impurities is minimized by distilling the sample in the laboratory following established procedures before measuring its specific gravity or refractive index.

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When dealing with samples from intermediate plates of the rectifying column, in which the alcohol content is relatively low while the fusel-oil content could be 10 to 20 percent, and in some cases higher, a simple distillation of the sample would be ineffective. Even careful fractionation of the sample would not be satisfactory, since a substantial part of the fusel oil would pass into the overhead product if all of the ethyl alcohol present in the sample is to be recovered in the distillate. The difficulties encountered in the separation of fusel oil-alcohol-water by distillation have been discussed elsewhere (*1*).[2]

OBJECTIVE

This work was undertaken with the purpose of providing a method for correcting for the error introduced by the presence of different concentrations of fusel oil at different alcoholic strengths.

EXPERIMENTAL PROCEDURES

Solutions of known alcohol and fusel-oil contents were prepared and analyzed for apparent alcoholic content by means of the picnometer and hydrometer. Solutions containing 200, 500, 1,000, 2,000, 4,000, 7,000, 10,000, 20,000, and 30,000 mg. of fusel oil as amyl alcohol per 100 ml. of sample, at 10, 20, 30, 40, 50, 60, 70, 80, and 90 percent of alcohol by volume at 60° F. were prepared. The absolute alcohol used as source of ethanol was analysed in triplicate by the picnometer method and found to contain 99.25 percent of alcohol by volume at 60° F.

Commercial fusel oil from a Puerto Rican distillery was used as the source of fusel oil. The oil had been concentrated by extraction with water at its origin plant, and contained about 60 percent of fusel oil. It was further extracted twice, using one-half its own volume each time of water saturated with commercial table salt. After thorough mixing, the mixture was allowed to separate during several hours and the oily upper layer was decanted. The oil was then fractionally distilled at atmospheric pressure in a 1-inch glass column, 6 feet in height, packed with glass Raschig rings. Portions of 1,500 ml. were placed in a 2.5-l. flask and heat was supplied by a constant-temperature mineral-oil bath. The temperature of the oil bath was regulated to maintain an overhead rate of 30 ml. per hour at a reflux ratio of 10:1. The reflux ratio was automatically regulated by an electric timer and a magnetically operated flow-divider in the glass column head. The column was maintained at total reflux for a period of 2 hours before removal of the condensate began.

A first fraction of 150 ml., boiling between 83° and 87° C. was discarded to insure complete removal of any ethyl alcohol present. In doing so water and some of the lower homologues of the higher alcohols were also removed.

[2] Italic numbers in parentheses refer to Literature Cited, p. 145.

A second fraction of 1,150 ml., boiling between 87° and 132° C., was collected as purified fusel oil.

A third fraction, consisting of the residue remaining in the flask, was stored apart. After there was sufficient residue, 1,500 ml. were placed in the flask and fractionated as before, except that no first fraction was discarded. The residue was evaporated practically to dryness at 136° C. The product of this distillation was mixed with the fusel-oil fraction collected in the first fractionation. The oil mixture was analyzed in triplicate for specific gravity and fusel-oil content giving specific gravity values of $0.8212^{25°C.}_{25°C.}$ and 86,665 mg. of fusel oil as amyl alcohol per 100 ml. The apparent discrepancy of obtaining over 100 percent of fusel oil by weight occurred because the fusel-oil content is expressed as amyl alcohol while it actually consists of a mixture of alcohols containing appreciable portions of lower molecular-weight homologues. These figures are indicative of the high degree of purity of the fusel oil obtained.

The samples were prepared by pipetting previously calculated quantities of purified fusel oil and absolute alcohol into 250-ml. calibrated volumetric flasks and completing to volume with distilled water. Sixty-milliliter glass picnomeers provided with individual thermometer-caps were utilized. The calibration of the hydrometers used was checked with pure water-alcohol solutions of known composition.

RESULTS

The analytical results of this work are presented in table 1. It can be observed that numerous samples were discarded because of the presence of two liquid-phase layers.

The results show that the differences between apparent and true alcohol content obtained by the hydrometer and picnometer methods were almost identical throughout the range of alcoholic strength and fusel-oil content studied. This excellent agreement is to be expected since both methods are based on the specific gravity of the sample. The difference between apparent and true alcohol content by both methods varied with the alcoholic strength at any given fusel-oil concentration. At lower alcohol contents the error increased as the alcoholic strength increased, and after passing a maximum it decreased with further increase in alcohol content.

With the higher fusel-oil concentrations the maximum is not shown since partial solubility exists at the lower alcoholic strength and two liquid phases are formed. This variation is due to the combination of contraction and concentration effects. The error decreases as the alcohol-water content is such that its specific gravity approaches that of the fusel oil. If fusel oil with a specific gravity of $0.8212^{25°C.}_{25°C.}$ is added to an alcohol-water solution of that same specific gravity, which corresponds to an alcoholic strength of

approximately 185° proof, no error would be introduced in the determination of alcohol by the picnometer and hydrometer methods, should the con-

TABLE 1.—*Effect of fusel oil on the determination of alcohol by picnometer and hydrometer*[1]

Fusel oil, (mg. per 100 ml. of sample)	Analytical method	Actual alcohol content at which samples were prepared (degrees proof at 60° F.)								
		20° P.[2]	40° P.[2]	60° P.	80° P.	100° P.	120° P.	140° P.	160° P.	180° P.
200	Picnometer	20.4	40.1	59.8	79.9	100.1	119.9	140.0	160.1	180.2
	Hydrometer	20.2	40.0	59.2	80.0	99.0	120.0	140.1	160.4	180.4
500	Picnometer	20.7	40.6	60.8	80.8	100.8	120.9	140.8	160.4	180.8
	Hydrometer	20.6	40.4	60.2	80.6	100.4	120.8	140.8	160.9	180.4
1,000	Picnometer	21.5	41.7	62.0	82.2	102.2	122.1	142.1	162.2	182.1
	Hydrometer	21.8	41.6	61.8	82.4	102.4	122.3	142.4	162.6	182.6
2,000	Picnometer	23.3	43.8	64.4	84.5	104.6	124.4	144.4	164.1	184.0
	Hydrometer	23.6	43.8	64.9	84.1	104.8	124.6	144.3	164.4	184.2
4,000	Picnometer		48.4	(3)	89.8	109.6	128.9	148.7	168.5	188.0
	Hydrometer		47.8	(3)	89.2	109.4	129.1	149.0	168.7	188.4
7,000	Picnometer			77.4	97.2	116.2	135.7	155.2	174.6	—
	Hydrometer			77.2	97.0	115.9	135.3	155.7	174.4	—
10,000	Picnometer			85.4	104.5	123.3	142.4	161.5	181.0	—
	Hydrometer			84.8	104.1	123.1	142.4	161.7	181.5	—
15,000	Picnometer			97.7	115.9	134.3	153.3	172.1	190.6	—
	Hydrometer			97.2	115.3	134.3	153.8	172.2	190.8	—
20,000	Picnometer			109.0	126.5	144.8	163.1	181.7	—	—
	Hydrometer			108.6	126.4	144.8	163.2	182.0	—	—
30,000	Picnometer			129.7	146.7	164.3	182.6	—	—	—
	Hydrometer			129.6	146.9	164.6	182.7	—	—	—

[1] Analytical results in degrees proof at 60° F.
[2] Two liquid layers formed when blanks occur in this column.
[3] Sample discarded.

traction effects be negligible. Accordingly, at any given fusel-oil concentration the error would tend to decrease as the alcohol content is increased. However, the results obtained indicate that this effect is more than offset at the lower alcoholic content, probably by an expansion effect, and the error increases with increased alcohol content up to a maximum which de-

pends on the fusel-oil content. After this maximum the error decreases with increased alcoholic strength.

The experimental results obtained by the picnometer method have been plotted in figure 1. This graph allows rapid determination of the correction to be introduced if the fusel-oil content and the apparent proof of the sample are known. The results indicate that, at any true alcoholic strength, the error produced is directly proportional to the fusel-oil content. This fact

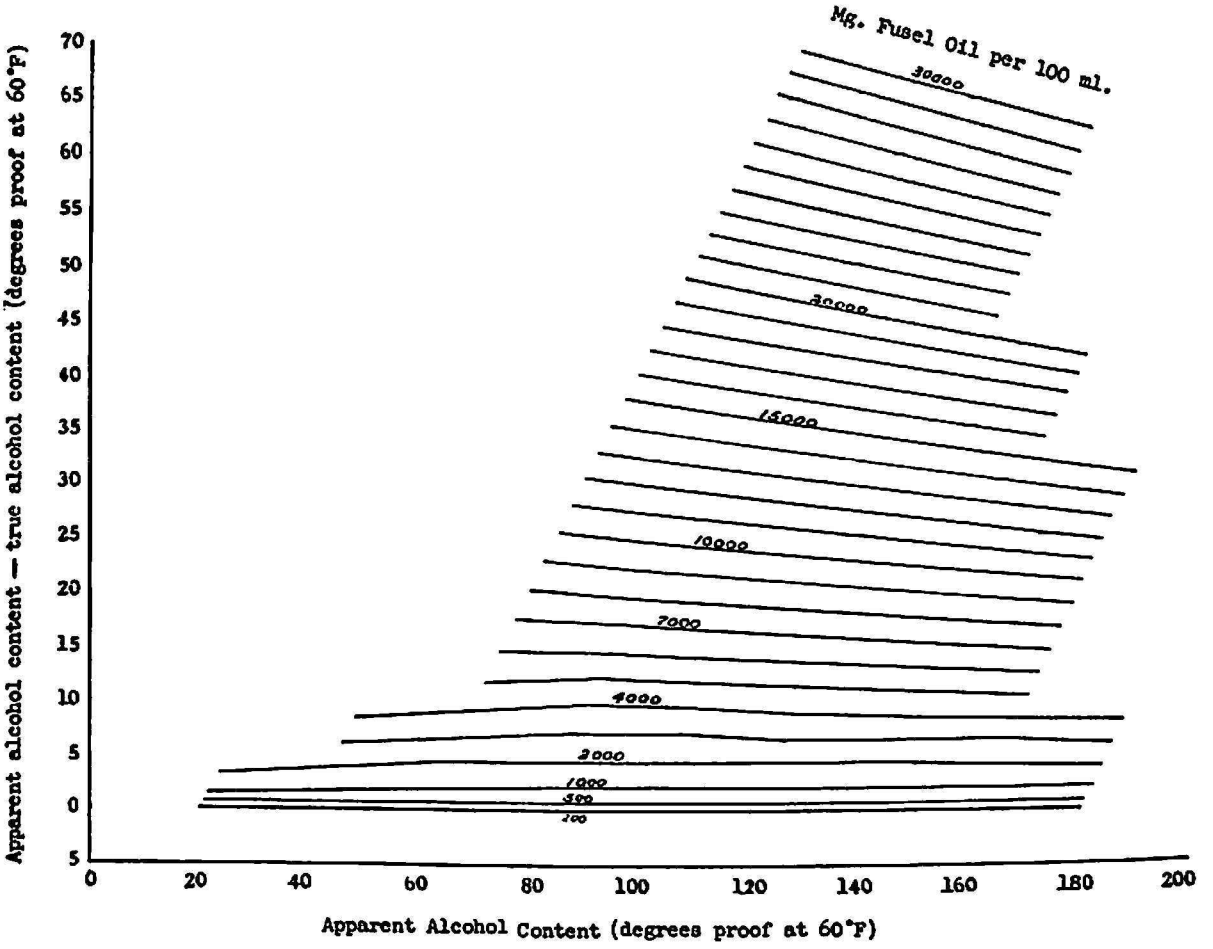

FIG. 1.—Effect of presence of fusel oil on the determination of alcohol by the picnometer and the hydrometer methods.

allows direct interpolation between the lines through experimental points of various fusel-oil concentrations. Since, in figure 1, apparent proof as abscissa has been plotted versus apparent proof-true proof as ordinate, the points of constant true alcohol content fall on a straight line the slope of which is 1 when equal scales are used in the abscissa and in the ordinate. In our case the ordinate scale is twice as large as the abscissa scale and, therefore, the family of lines of fixed true alcoholic content has a slope of 2. By interpolating along these lines between different fusel-oil contents, lines have been drawn in figure 1 at concentration intervals of 1,000 mg. of fusel oil as amyl alcohol per 100 ml. of sample.

The fusel-oil-content lines can be extrapolated, if necessary, to cover values of apparent alcohol outside the range covered by the experimental values plotted. It is believed that true alcoholic strengths can be determined with the aid of figure 1 within an accuracy of about 1-percent alcohol by volume at 60° F. A large-size plot would improve the accuracy. Figure 1 can be used for determining correction values for both the picnometer and the hydrometer methods since, as was stated previously, the experimental values obtained by both methods for the deviations caused by the presence of different concentrations of fusel oil are in excellent agreement.

Fusel-oil concentrations up to 200 mg. of fusel oil per 100 ml. of sample introduce negligible errors at any true alcoholic strength with the analytical methods studied.

SUMMARY

Based on experimental data, a graph has been prepared which allows rapid determination of the correction to be introduced in order to determine the true alcoholic content of a sample, if its fusel-oil content is known and the apparent alcoholic strength has been determined by the hydrometer or picnometer.

RESUMEN

Basado en datos experimentales, se ha desarrollado una gráfica de la cual puede obtenerse rápidamente la corrección que deberá usarse para obtener el contenido alcohólico verdadero de una muestra, si se conoce su contenido de aceite de fúsel y si su grado prueba aparente ha sido determinado por los métodos de alcoholómetro o picnómetro.

LITERATURE CITED

1. Robinson, C. S., and Gilliland, E. R., The Elements of Fractional Distillation, 3d. ed., pp. 71–80, McGraw Hill Book Co., Inc., New York, N. Y., 1939.