THE RECOVERY OF FUSEL OIL IN THE PHILIPPINES

By H. E. Foote

Chemist, Bureau of Science, Manila

THREE TEXT FIGURES

In investigating the possibilities of the profitable recovery of fusel oil in the distillation of alcohol, the Bureau of Science found that, up to June, 1923, no fusel oil had been recovered in the Philippines. Because the price of fusel oil in the United States was high and there were evidences of a rather serious shortage, it seemed a favorable time for the development of this branch of the alcohol industry in the Islands.

The following facts and results were obtained:

1. The average production of alcohol for the last five years in the Philippines has been 12,257,090 proof liters, or 3,242,616 proof gallons. Table 1 shows the yearly production for this period.

TABLE 1.—*Production of alcohol in the Philippines, 1919 to 1923.*[a]

	1919	1920	1921	1922	1923
Proof liters[b]	14,972,293	11,716,896	9,232,900	11,534,129	13,892,231
Proof gallons[b]	3,960,924	3,099,064	2,442,566	3,051,356	3,658,592

[a] Annual Reports of the Collector of Internal Revenue, Manila.
[b] One U. S. gallon is equivalent to 3.78 liters.

Table 2 shows the percentages of alcohol produced from various sources in 1923.

TABLE 2.—*Sources of alcohol produced in the Philippines in 1923.*[a]

Source.	Proof liters.	Per cent of total.
Nipa sap	3,809,108	27.30
Coco sap	654,903	4.70
Molasses	7,935,548	56.90
Cane sugar	1,539,064	11.00
Grain	83	
Other sources	3,075	.02
Total	13,941,771	99.92

[a] Annual Report of the Collector of Internal Revenue, Manila, 1923.

2. The quantity of fusel oil occurring in the crude alcohol before rectification is about 0.4 per cent. Practically all of the fusel oil formed in fermentation is found in the crude alcohol; that is, little or none is lost in the distillation of the fermented molasses.

3. About 0.2 to 0.23 per cent of fusel oil is actually obtainable on a commercial scale from the crude alcohol.

4. About 65 per cent of the total alcohol output in the Philippines is produced in distilleries large enough to warrant the recovery of fusel oil. The remaining 35 per cent is produced in plants whose capacities are so small that fusel-oil recovery would hardly be profitable. Hence, it is estimated that the potential production of fusel oil in the Philippines, that is, the amount that could probably be recovered profitably, is about 3,500 gallons annually.

5. Assuming a price in the United States of 4 dollars per gallon for the crude grade and 4.75 dollars for the refined grade, and transportation charges of 1 dollar per gallon, the approximate value of fusel oil in Manila on the basis of present prices would be as shown in Table 3.

TABLE 3.—*Approximate value of fusel oil in Manila.*

	Dollars per gallon.	Pesos per liter.	Pesos per pound.
United States price:			
Crude	4.00	2.12	1.16
Refined	4.75	2.51	1.42
Transportation	1.00	0.53	0.29
Manila price:			
Crude	3.00	1.59	0.87
Refined	3.75	1.98	1.13

Hence, the value of the fusel oil available in the Islands would be approximately 10,000 to 13,000 dollars, or 20,000 to 26,000 pesos, annually. Japan is also a market for fusel oil, and it has the advantage that transportation costs from the Philippines to Japan are lower than those from the Philippines to the United States.

Table 4 shows price fluctuations of fusel oil since 1871.

6. The methods of recovery of fusel oil are not difficult, involving only processes familiar to the distiller, and require little additional equipment.

TABLE 4.—*Price per gallon of fusel oil.*[a]

Year.	Refined.	Crude.
	Dollars.	*Dollars.*
1871	4.00	
1881	2.00	
1891	0.50	
1898	0.55 to 0.60	
1901	0.60 to 0.75	
1911	3.00 to 3.25	
1913	1.35 to 1.50	
1918	5.75 to 6.00	
1920	3.85 to 5.00	
1921	2.50 to 4.20	
1922	1.25 to 3.00	
1923	3.00 to 4.75	2.00 to 4.00
1924[b]	4.75 to (c)	4.00 to 4.30

[a] Oil, Paint, and Drug Reporter No. 14 101 (1922) 45 and 55, idem No. 14 103 (1923) 18 and 73; Drug and Chemical Markets 14 (1924) 283.

[b] January only.

[c] Nominal.

7. Although the quantities of fusel oil produced are small in relation to the quantities of alcohol, the costs of recovery are very low in comparison with its value.

8. One of the largest distilleries in the Islands, at Manila, is now successfully recovering all its fusel oil. Four others are making plans for its recovery as soon as possible. With the exception of one or two on the border line, these five distilleries constitute all of those in which the recovery of fusel oil would be clearly profitable.

Conclusion.—The work of the Bureau of Science has shown that fusel oil can be recovered profitably, and that small but paying quantities can be obtained at low cost and with little difficulty.

The fusel oil obtained from molasses consists mainly of two primary amyl alcohols, namely, the active $\begin{matrix}CH_3\\C_2H_5\end{matrix}\!\!>\!CH.\,CH_2OH$ (boiling point 131.5) and the inactive or isoamyl alcohol $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH.\,CH_2.\,CH_2OH$ (boiling point 129), while the fusel oil obtained from nipa contains, in addition, considerable amounts of intermediate products, chiefly propyl and butyl alcohols. The molasses oil distills almost completely between 127° and 132° C., while the nipa oil distills between 115° and 135° C.

The chief uses of fusel oil are (*a*) as a solvent for nitrocellulose, (*b*) in the manufacture of special paints, varnishes, and lacquers, (*c*) in pharmaceutical work, and (*d*) in the manufacture of artificial perfumes and flavors.

Experiments were carried out to determine the quantities of fusel oil occurring in the manufacture of alcohol, the points in the process where it occurs in greatest quantity, and the best methods of concentration and purification. In most distilleries in the Philippines, the fermented material containing 5 to 8 per cent of alcohol is distilled in a continuous still which produces crude alcohol of 100 to 140 proof, or 50 to 70 per cent strength. This is then rectified in a discontinuous or batch rectifier, the contents of a large boiler being distilled through the usual column, dephlegmator, and condenser giving a distillate which is divided into several fractions as follows: (*a*) "heads" or aldehyde, (*b*) high-grade alcohol, the main product, (*c*) "tails," and, in the case of nipa alcohol, (*d*) "amilico" or fusel oil. The fourth fraction is sometimes obtained in the rectification of molasses alcohol and consists of a fusel oil-alcohol-water mixture containing as a whole 5 to 25 per cent of fusel oil. The percentage of fusel oil occasionally runs much higher (even as high as 80 per cent) for short periods of time during the distillation.

Experiment showed that practically all of the fusel oil formed in the fermentation is carried over into the crude alcohol in the first distillation. No fusel oil was found in the spent wash or "lees," and none was found in the heads, or aldehyde fraction (except for occasional traces due to small quantities of fusel oil being left on the plates of the column from the preceding run).

TABLE 5.—*Values of coefficient k.*

Alcohol, per cent by volume in boiling liquid.	*k* for fermentation amyl alcohol, boiling point 132° C.	*k* for ethyl alcohol, boiling point 78° C.	Alcohol, per cent by volume in boiling liquid.	*k* for fermentation amyl alcohol, boiling point 132° C.	*k* for ethyl alcohol, boiling point 78° C.
95	0.23	1.0037	50	1.20	1.60
90	0.30	1.02	45	1.50	1.63
85	0.32	1.05	40	1.92	1.80
80	0.34	1.08	35	2.45	2.02
75	0.44	1.12	30	3.00	2.40
70	0.54	1.17	25	5.55	2.70
65	0.65	1.23	20	.....	3.30
60	0.80	1.30	15	.....	4.10
55	0.98	1.39	10	.....	5.10

This may be explained by reference to Table 5 and to fig. 1.[1] The figures under k for ethyl alcohol represent the ratio of the percentage of alcohol in the vapor to the percentage in the boiling liquid for various mixtures of alcohol and water; those under k for amyl alcohol represent the ratio of the percentage of fusel oil in the vapor to the percentage in the boiling liquid for mixtures of alcohol and water containing small amounts of fusel oil. Notwithstanding the considerably higher boiling point of the fusel oil, it is seen that this ratio at low alcohol concentration is higher for fusel oil than for alcohol itself.

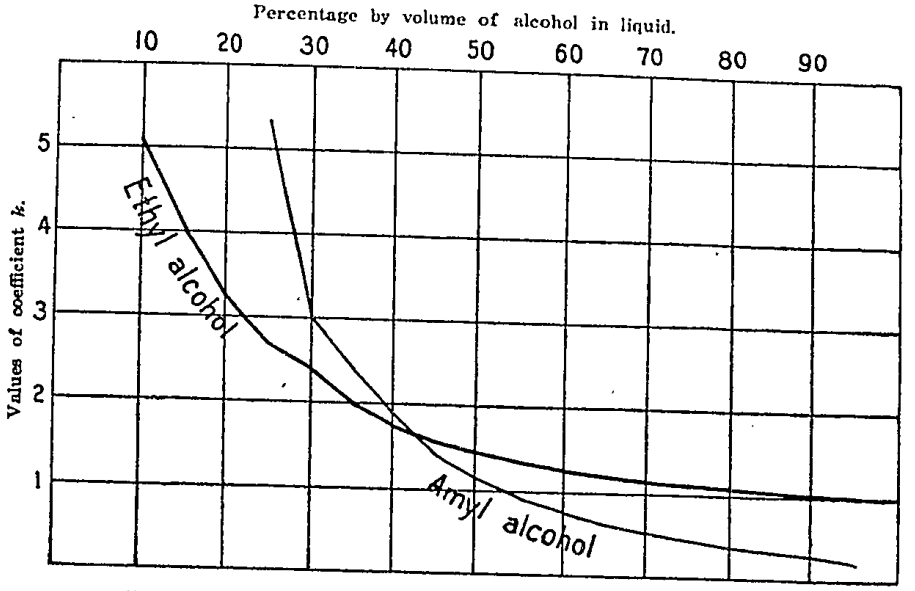

FIG. 1. Values of coefficient k for alcohol and secondary products.

Stated more simply, fusel oil is much more volatile with steam than with alcohol vapor. At concentrations of alcohol below about 43 per cent by volume—the point where the two curves cross—fusel oil is carried over completely; at 43 per cent the fusel oil-alcohol ratio is unchanged before and after distillation; and at higher concentrations of alcohol the fusel-oil content is reduced by fractionation. In the course of the experiments it was observed that at concentrations of alcohol in the distillate of about 90 per cent, or over, no fusel oil (less than 0.1 per cent) came over, whereas below this point as the grade fell off at the end of the rectification, fusel oil appeared in relatively large and increasing quantities (greater than 1 per cent).

[1] Monier-Williams, Power Alcohol. Frowde and Hodder & Stoughton, London (1921) 73, 74.

Therefore, the fusel oil is carried over into the distillate practically without loss in the distillaton of the low-grade fermented material. In the rectification, however, where the alcohol concentration in the column remains high until the "tail" fraction of the run is reached and the alcohol is becoming exhausted, the fusel oil remains behind in the boiler and in the lower part of the column. As the alcohol disappears, the fusel oil, having become concentrated in the water remaining in the boiler, gradually rises in the column until it appears in the distillate, at first in the 90 per cent alcohol, gradually increasing in strength as the alcoholic grade falls. Finally, at a grade of about 40 per cent alcohol or less, the distillate comes over in two immiscible layers, the fusel oil floating on the weak alcohol. The proportion of top layer increases to a maximum, sometimes reaching 100 per cent if large quantities of fusel oil were originally present, and then falls off as the fusel oil is exhausted.

In a few factories in the Philippines, the rectification is carried out in continuous stills. In this case the crude alcohol enters the rectifier at a concentration of 30 to 35 per cent. The fusel oil tends to collect at a point in the column where the alcohol concentration is 43 per cent, as explained above, and is accordingly tapped off from the rectifying column as near this point of maximum concentration as possible.

The above general considerations will make clear the following methods developed for the recovery of fusel oil:

The process of obtaining the fusel oil, when batch rectification is used, consists in selecting that portion of the third and fourth fractions described above (the "tails" and "fusel oil") which is richest in fusel oil and collecting it in a separate tank. This material—in quantity about 1.5 per cent of the total crude alcohol—contains 15 to 20 per cent of fusel oil. The point at which fusel oil begins to appear in worth-while quantities is recognized partly by the hydrometer reading (92° to 93° Gay-Lussac, uncorrected, temperature about 30° C.) and partly by the characteristic residual odor when a sample is rubbed on the hands and allowed to evaporate. The maximum fusel-oil content occurs at a grade of 50° to 60° Gay-Lussac, and the fraction is collected until the grade has fallen to 20° to 30° Gay-Lussac, or until the top layer has practically disappeared.

The fusel-oil content of the distillate at any moment, when the rate of distillation is uniform, plotted against the grade shown by the hydrometer shows a gradual and regular rise and fall as in fig. 2; but, since the grade falls off very slowly at first, then

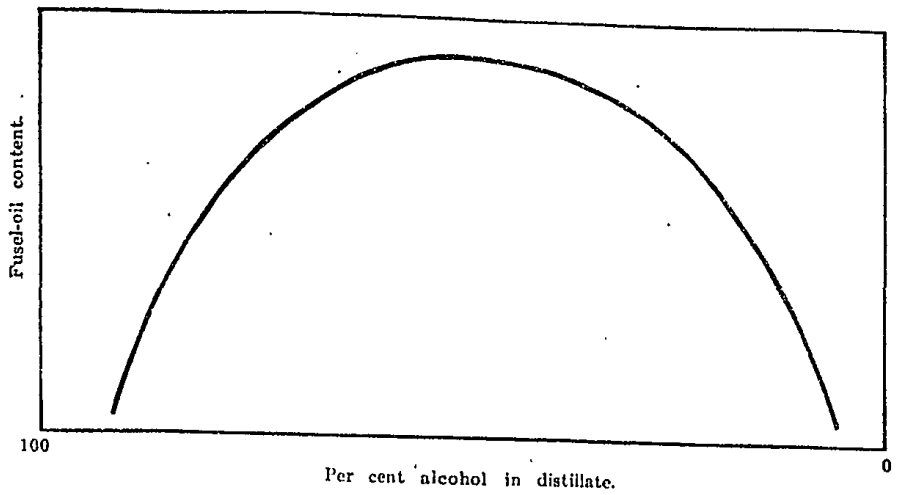

FIG. 2. Fusel-oil content against alcohol content.

with increasing rapidity down to the end, the fusel-oil content plotted against time shows a more gradual increase to a maximum and a rapid decrease at the end, as in fig. 3.

The 20 per cent fusel oil is stored until a sufficient quantity has accumulated and is then rectified in a small batch rectifier giving five fractions: (*a*) heads, (*b*) high-grade alcohol, (*c*) tails, (*d*) 20 per cent fusel oil as before, and (*e*) a fifth fraction in which fusel oil and water come over in two immiscible layers. The greater part of the fusel oil appears in the last fraction. The first fraction is small, the second rather large, the third and fourth are small, and the fifth is rather considerable in amount.

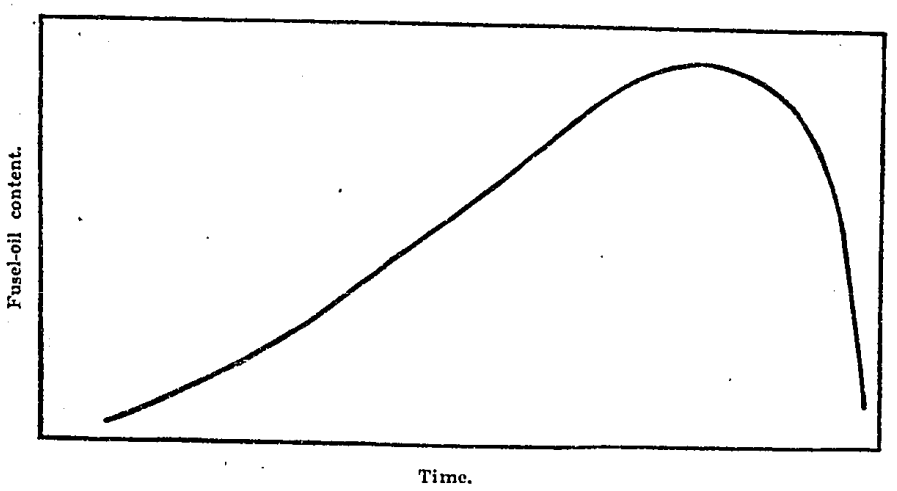

FIG. 3. Fusel-oil content against time.

The first four fractions are disposed of in the usual way exactly as in the large-scale rectification. The fifth is placed in a receiver by itself. The top layer is a fusel oil of from 70 to 90 per cent strength, and the bottom layer (about equal in quantity to the top layer) is water containing small amounts of alcohol and fusel oil.

If a crude fusel oil is desired as the finished product, the oil obtained as above is washed with water till it contains less than 10 per cent of alcohol. If a refined grade is required, the top layer, without washing, is rectified in the same rectifier and collected in three fractions: (1) alcohol containing fusel oil (this is placed in the 20 per cent fusel-oil receiver); (2) two-layer material consisting of (*a*) a top layer of crude 80 to 90 per cent fusel oil, about 70 per cent of the total, and (*b*) a bottom layer of water, about 30 per cent; and (3) refined fusel oil. The third fraction is usually 60 to 75 per cent of the total charge and boils, in the case of molasses alcohol, at 127° to 132° C. The distillation is carried as near to dryness as possible, using a gauge steam pressure of 50 to 150 pounds on the heating coil. In order to prevent excessive refluxing from the dephlegmator into the rectifying column, cooling water is not allowed to circulate after the two-layer fusel oil-water mixture is coming over; and when the dry fusel oil boiling above 127° is coming over, it is advisable to draw off the cooling water from the dephlegmator, leaving it dry.

If the rectification of alcohol in the plant is carried out continuously, the fusel oil will tend to collect on two or three plates where the alcohol concentration is approximately 43 per cent. The liquid on these plates is drawn off at such a rate and at such intervals that the fusel oil is prevented from accumulating on them in large quantities and is obtained at a maximum concentration. The fusel oil so obtained is partially freed from alcohol by washing and is further purified by rectification, as described.

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ILLUSTRATIONS

TEXT FIGURES