

## THE FISCHER ASSAY, A STANDARD METHOD?

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### INTRODUCTION

The Fischer assay is not a standard analytical procedure. It does not produce quantitative values such as the weight percent nickel in a stainless steel or the ppm mercury in water. Rather, the Fischer assay is a performance test such as the octane number of motor fuels or the tensile strength of fibers. Because it is an assay -- a performance test -- the data obtained are quite dependent upon the test procedure. Variances in the test procedures, permitted in the widely accepted USBM Fischer assay method, do cause significant differences in the data obtained.

### HISTORY OF THE FISCHER ASSAY

The Fischer assay had its origins in the early low-temperature coal retorting research of Franz Fischer and Hans Schrader<sup>(1)</sup>. However, our present concern is with the USBM procedure as described in detail by Stanfield and Frost and Hubbard in Bureau of Mines Reports of Investigations 4477 and 6676 (2,3). The main details of the USBM procedure are shown in Figure 1. Many of the details are no longer followed by laboratories doing Fischer assays (some are no longer followed by the USBM (4)!).

The USBM Fischer assay presents many problems to analysts attempting to use this procedure. The suggested apparatus, particularly the cast-aluminum retort, is the major source of problems. The softening point of the aluminum alloy is quite close to the suggested retorting temperature and the seal of the plug and retort is not perfect. A diagram of the USBM apparatus is shown in Figure 2. We use these U.S.B.M. retorts in our laboratory. By carefully controlling the retort temperature through the use of continuous control and proportional heat (5), the problem of the retort melting has been lessened. Two retorts have been developed to obviate the softening and leakage problems. The TOSCO retort (6) shown in Figure 3, is constructed of steel. The head is fastened with four steel studs. Thermocouples are placed both in the retort and adjacent to the retort as shown. The overall configuration of the TOSCO retort is similar to the USBM retort. The Core Laboratories retort (7), shown in Figure 4, is also constructed of steel. The cap is threaded on. The Core retort represents a drastic change from the USBM system. Ten of these retorts are placed in an oven with a single temperature controller. The Core Laboratories retort systems require much less space than the TOSCO or USBM. Both modifications, TOSCO, and Core, are designed to duplicate data

obtained by the USBM procedure. Because of problems with the USBM apparatus, a standardized modification is clearly needed.

Fischer assay results, obtained from various laboratories, do indeed differ. This difference is illustrated in Table I. A sample of raw shale was carefully blended and riffle-split into 2 1/2 lb. packages for use as a standard in our laboratory. The mean results from ten replicates of this standard are shown. The four laboratories are not necessarily those mentioned previously. These data, I feel, show that the Fischer assay is not a standard method.

#### VARIANCE OF FISCHER ASSAY DATA

Without studying each laboratory's procedures in detail, it is impossible to determine the causes of variability shown in Table I. However, studies made in our laboratory show that modifications in the Fischer assay, many permitted in the USBM procedure, do have an effect on the data.

Mesh Size. The particle size of the sample has two different effects on the oil yield. First, it seems that oil shale richer in organics is more resistant to crushing than leaner shales. Thus, as shown in Table II, the oil yield tends to increase with increasing particle size (decreasing mesh size). Thus, neither lumps nor fines may be discarded. Careful splitting (without loss of dust) must always be used to obtain a valid sample. Grab samples, such as needed to obtain the 100.0 grams recommended in the USBM procedure, may not be representative.

The other effect that particle size has on oil yield as shown in Table III. Here the same original samples were reduced by grinding to smaller particle size. Again, the yield decreases with decreasing particle size. In this case, the cause is not clear. No apparent degradation, or partial retorting, seemed to occur with grinding.

In order to obviate effects of mesh size of Fischer assay data, the following are recommended:

- (1) Neither large pieces nor fine dust may be discarded.
- (2) Mass reduction should be by riffle splitting.
- (3) Samples should be ground to uniform, standard mesh size.

Temperature. In the USBM procedure, the temperatures of three components are defined. These components are the receiver, the condenser, and, of course, the retort.

Since temperature is the controlling factor of the Fischer assay in defining the gas-liquid split (the condensation of gaseous vapors into liquids) the temperature of the receiver has a pronounced effect on oil yields. This is shown in Table IV where the temperature of the receiver ranged from 20°F to 100°F. Changing from the prescribed 32°F to the permissible 100°F does affect the oil yield. An ice bath, recommended by Atwood (6) seems best suited for controlling the receiver temperature.

The temperature of the condenser is listed as 32 ± 9°F in the USBM procedure. Yet, the condenser has no effect on the oil yield data; any oil escaping the receiver and condensed in the condenser will not be measured. Because of the low pour point of crude shale oil, this material will remain on the condenser walls and not be weighed with the receiver and adapter. Studies in our laboratory have shown that removing the condenser from the

system has had no effect on the Fischer assay data. Perhaps the condenser can be eliminated.

The suggested time-temperature profile of the retort is shown in Figure 5. This is a strip-chart recording from our 12-position bench. Failure to reach the 932°F prescribed in the USBM procedure produced low results as shown in Table V. Increased time does not appear to increase the oil yield. The effect of increased temperature cannot be studied using the aluminum USEM retort. It has been suggested (8) that the location of the thermocouple well (beneath the spout) is poor. Truer readings and better control can be achieved if the thermocouple is located at the bottom center or rear of the retort. This position would be similar to that suggested by Atwood (6).

In order to obviate errors in Fischer assay data caused by various temperature fluctuations, the following are recommended:

- (1) The temperature of the receiver be controlled by an ice bath.
- (2) The condenser be eliminated.
- (3) The temperature of the retort be carefully controlled with the suggested relocation of the thermocouples to the rear of the retort.

#### FISCHER ASSAY ALTERNATES

With the uncertainties in the Fischer assay data, the capital costs in fabricating a Fischer assay bench, the larger laboratory space required, and the long time needed to complete the test, it is no wonder that several alternatives for the Fischer assay have been proposed in recent years. Some of these alternatives are listed in Table VI. Pulsed NMR (9) is used to measure the organic hydrogen content of shale. Direct organic carbon, by controlled combustion, eliminates effects of the inorganic carbonates (10). Thermal chromatography(11) and laser-chromatography (12) relate oil yields to the concentration of certain hydrocarbon released by heating. Although each of these alternatives has certain advantages, most suffer from the following disadvantages:

- (1) They offer little or no improvement in precision.
- (2) Instrument costs are similar to those of a Fischer bench.
- (3) Sample size are small. This requires additional sample preparation time and trouble.
- (4) They are used to measure only oil yields whereas the normal Fischer assay measures oil yield (gal/ton), water yield (gal/ton), gas + Loss (wt%), specific gravity of the oil, and coking tendency of the shale.

#### STANDARD FISCHER ASSAY

In spite of the differences in procedures and the variations in the data obtained, the Fischer assay seems destined to be the standard for the oil shale industry. No alternative procedure offered to date is completely satisfactory. With this in mind, the ASTM Committee D-2 on Petroleum Products and Lubricants has formed a subcommittee to solve the aforementioned inconsistencies and create a standard Fischer assay. In our laboratory, we await the results -- a standard Fischer assay test procedure!

ACKNOWLEDGEMENT

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# USBM FISHER ASSAY PROCEDURE

SAMPLE            100.0 GRAM -8 MESH

RETORT            CAST ALUMINUM WITH TAPERED PLUG

HEAT              AMBIENT TO 932°F IN 40 MINUTES  
                      HOLD AT 932°F FOR 20 MINUTES

COOLANT           ETHYLENE GLYCOL - WATER AT 32°F

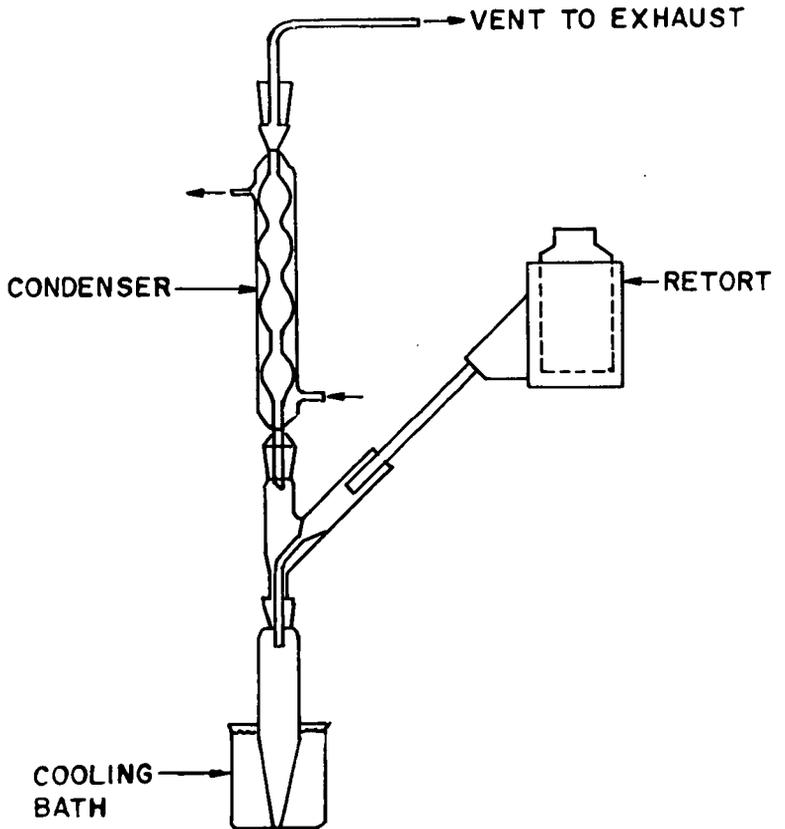
CONDENSERS       32 ± 9°F

RECEIVER          23 TO 100°F

Figure 1



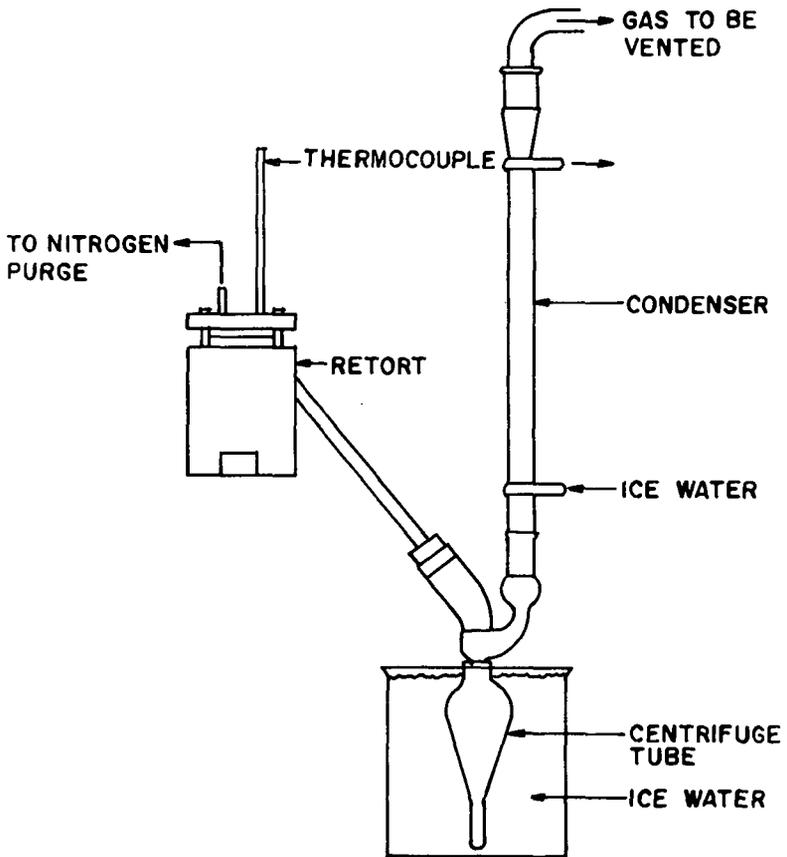
# USBM RETORT



USBM RI 6676 (1965)

Figure 2

# TOSCO RETORT



"ANALYTICAL CHEMISTRY PERTAINING TO OIL SHALE AND  
SHALE OIL " JUNE 24-25, 1974

Figure 3

**CL-7000 RETORT CUP  
120 GRAM CUP**

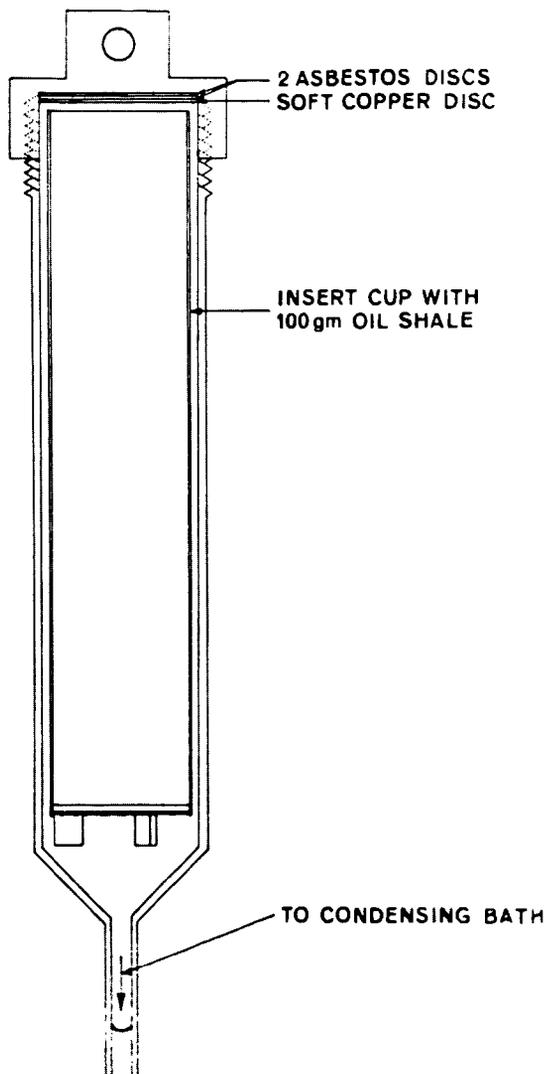


Figure 4

## FISHER ASSAY DATA

LABORATORY	A	B	C	D
OIL, GAL / TON	24.94 ± 0.17	25.35 ± 0.33	26.16 ± 0.71	24.07 ± 0.26
WATER, GAL / TON	3.28 ± 0.10	3.47 ± 0.16	3.86 ± 0.36	3.20 ± 0.11
OIL, SP. GR	0.9133 ± 0.0028	0.9014 ± 0.0020	0.8997 ± 0.0040	0.9162 ± 0.0012
GAS + LOSS WT. %	2.32 ± 0.24	1.98 ± 0.12	2.81 ± 0.21	2.37 ± 0.13

Figure 5

# SIZE DISTRIBUTION AND FISCHER ASSAY

MESH SIZE (MESH TO IN.)	DISTRIBUTION (WT %)	FISCHER ASSAY (OIL, GAL / TON)
+ 2 1/2	0.4	
-2 1/2 + 4	3.9	30.6
-4 + 6	8.3	31.7
-6 + 8	12.1	30.9
-8 + 14	31.5	29.8
-14 + 28	19.9	27.2
-28 + 48	10.9	25.6
-48 + 100	3.9	24.3
-100 + 200	2.1	22.1
-200	4.4	14.5

Figure 6

# FISHER ASSAY VS. GRINDING

	-8 MESH	-20 MESH	-65 MESH
XI-A	28.6	28.3	28.0
B	29.8		28.8
C	18.3		17.8
D	43.2		42.6
E	29.5		28.0

Figure 7

# FISHER ASSAY VS. RECEIVER TEMPERATURE

TEMPERATURE °F	OIL YIELD GAL / TON
19-24	28.8±0.7
32	29.1±0.5
35-45	28.1±1.1
65-100	27.5±0.8

Figure 8

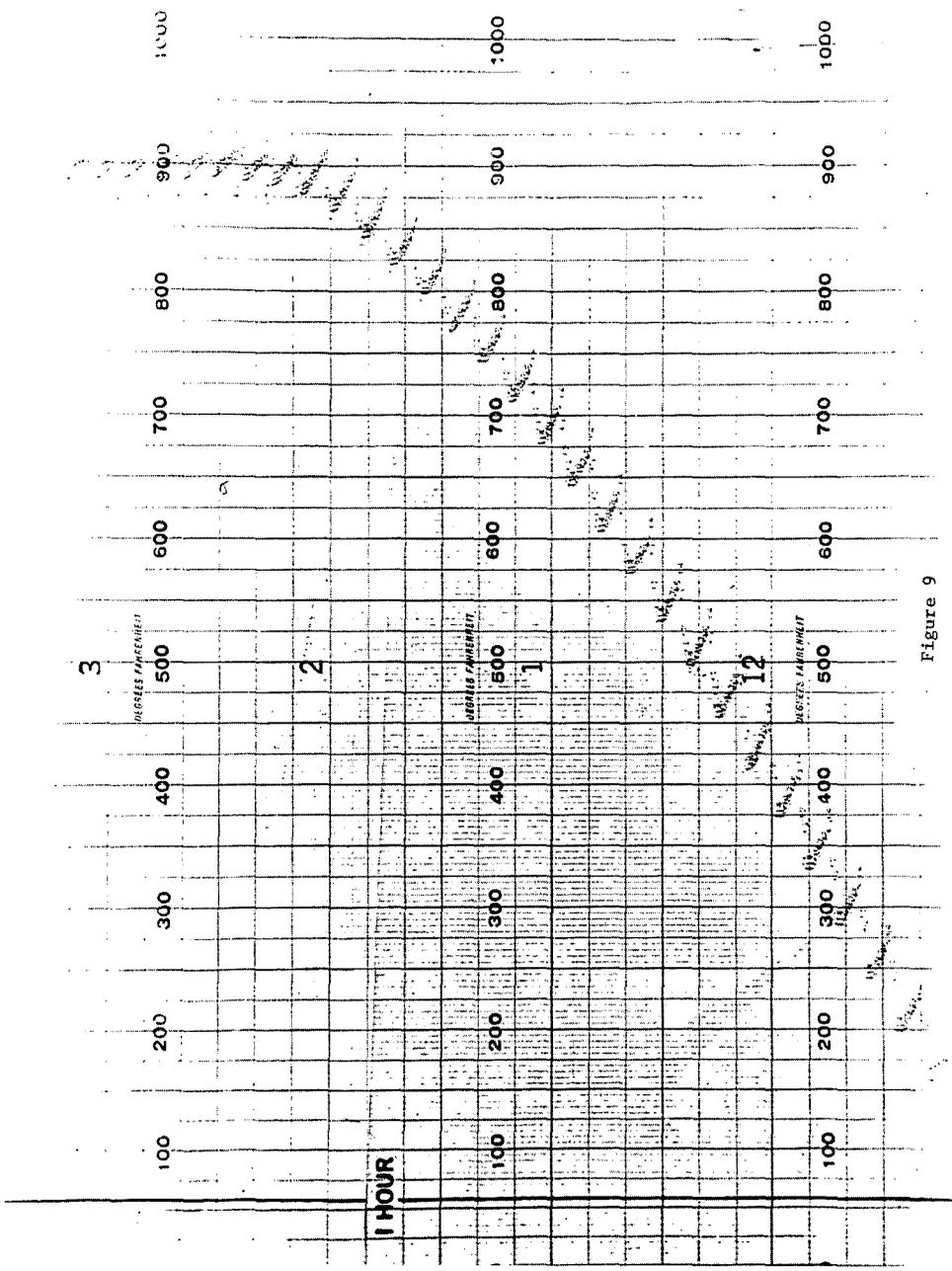


Figure 9

# FISHER ASSAY VS. RETORT HEATING

TIME (MIN)	TEMP (°F)	OIL YIELD (GAL / TON)
5	932	27.6 ± 1.0
20	932	29.1 ± 0.5
35	932	28.8 ± 0.7
20	825	27.8 ± 1.5
20	750	10.0 ± 4.1

Figure 10

# FISHER ASSAY ALTERNATIVES

THERMAL CHROMATOGRAPHY

ORGANIC CARBON

LASER - CHROMATOGRAPHY

PULSED NMR

Figure 11

