FACTORS AFFECTING THE RESULTS OF FISCHER ASSAY OF OIL SHALE

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ABSTRACT

A comprehensive comparison was made between four Fischer Assay procedures of oil shale, currently used in different countries.Based on the summary of comparison,a modified aluminum retort was recommended, and factors,especially the heating conditions, affecting the result of assay were examined in detail. As a result,a new modified Fischer Assay procedure was established, which has been approved by China Petrochemical Corporation as the new trade standard.

INTRODUCTION

In evaluating the economic value of oil shale resources and the oil recovery efficiency of a retorting furnace, the assay oil yield is one of the most important quality indexes. Generally, the method of determination is based on the low temperature carbonization in a small retort, strictly according to the specified procedure. Currently, there are four methods in use over the world, viz. (1) Fushun Method, based on ГОСТ 3168-53. (2) U.S.S.R. Standard ГОСТ 3168-66 (-81), "Method of Determination of the Yield of Semicarbonization Products for Brown Coals, Bituminous Coals, Oil Shales and Peats". (3) TOSCO Method, "Fischer Assay of Oil Shale-Procedures of the Oil Shale Corporation", Presented at the 7th Oil Shale Symposium,1974 and (4) ASTM D 3904-80 "Stan-

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dard Test Method for Oil from Oil Shale (Resource Evaluation by the USBM Fischer Assay Procedure)". These methods have their own respective features.

In our country,Fushun Method, which was based on U.S.S.R. Standard ГОСТ 3168-53, had been used up to 1986 since 1959. It has been found that the assay value and the repeatability are somewhat low. A new standard method of oil yield assay has established, which should produce higher oil yield, have better repeatability and be readily mastered by the analyst. A comprehensive comparison was made among the four methods mentioned above. A modified aluminum retort was recommended, and factors especially the heating conditions, affecting the result of assay were examined in detail. As a result, a new modified Fischer Assay procedure was established, which has been approved by China Petrochemical Corporation as the new Trade Standard ZBE 22001-86.

EXPERIMENTAL RESULTS AND DISCUSSION

A. Comparison among the 4 Fischer Assay Procedures

The principal parameters of the distillation retort of the 4 methods are summarized in Table 1,and the retorting conditions are shown in Table 2 and Fig.1. A sample of typical Fushun oil shale, having assay value around 7% (wt) is used, the properties of which are listed in Table 3. The results of assays are shown in Table 4.

From Table 4, we can see that there does exist some differences in the average values of several tests by these methods, and in the maximum differences between tests by each method,though these differences are all less than the allowable value. The reason may be that although there are many factors which will affect the assay results, some of these may be compensating. During the comparative tests,the difference in the wall temperature and the temperature at the center of the sample were measured at the different heating

stages.The data are also shown in Table 1.

Now we can say some words on these methods.

TOSCO Method A large quantity (100 g) and very small particle size (< 0.2mm) of test sample were used, but the average assay value was somewhat lower than that by ГOCT 3168-81 (50 g, < 1mm), and the maximum difference between tests was higher. Since there is an aluminum can within the stainless steel retort,which will affect heat conduction,the central temperature seriously lagged behind the wall temperature,and cracking of the distillation product near the wall may happen. Besides,the assay procedure is rather laborious.

ASTM 3904-81 The average assay value was higher than that of ГOCT 3168-81, but the maximum difference among the tests were also higher. The end temperature of retorting, 500°C, is rather low,so the holding time at the end temperature is prolonged to 40 min. The central temperature lag was much smaller than that of TOSCO Method.Furthermore,the control of rate of heating was not so easy as ГOCT 3168-81.

Fushun Method The weight of sample was the least (20g), the particle size the biggest (< 3mm), the rate of heating the lowest,while the assay value was the lowest (7.18 %) and the maximum difference among the tests was the highest (0.87 %).

ГOCT 3168-81 The weight of sample (50g),the particle size (<1mm), and the rate of heating were the medium among the four methods,while the central temperature lag was the least and the end temperature of the retorting was the highest.The average assay value (7.44 %) was lower than that of ASTM 3904-80, while the maximum difference between the tests was the smallest. The procedure can be readily mastered. As the holding time at end temperature was rather short (10 min), at the end of test there was some gas still evolving. For samples of higher oil yield, the effect may be significant.

B. Factors Affecting the Fischer Assay Results

Table 1.Principal parameters of the distillation retorts and temperature profile during retorting

Test method	Principal dimension				Heating surface area cm^2 /g shale
	Av.i.d. cm	Inside height cm	Inside surface area, cm^2	Effective volume cm^3	
ASTM3904-80	6.7	7.9	201	278	2.0
TOSCO Method	5.5	9.5	188	226	1.9
ГОСТ 3168-81	5.7	6.4	140	163	2.8
Fushun Method	4.65	6.3	109	107	5.5

Continued

Temperature profile during heating, °C

wall temperature								
200	250	300	350	400	450	500	510	520
central temperature								
120	160	202	255	327	400	443	---	---
15	15	20	20	30	90	110	---	---
175	205	260	320	380	432	472	---	510
140	195	280	328	378	428	478	488	---

Table 2. Principal operational parameters

Test method	ГОСТ 3168-81	ASTM 3904-80	TOSCO Method	Fushun Method
Retort	Al	Al	Stainless steel with Al inner can	Al
Wt. of sample, g	50	95 ± 10	100	20
Particle size, mm	< 1	< 2.36	< 0.2	< 3
End temperature, °C	520	500	500	510
Holding time, min	10	40	20	10
Total heating time, min	80	90	70	70-75
Coolant water	Flowing	0 ± 3°C	0°C	Ice water
Note		3 Al disks in sample	3 Al disks in sample	

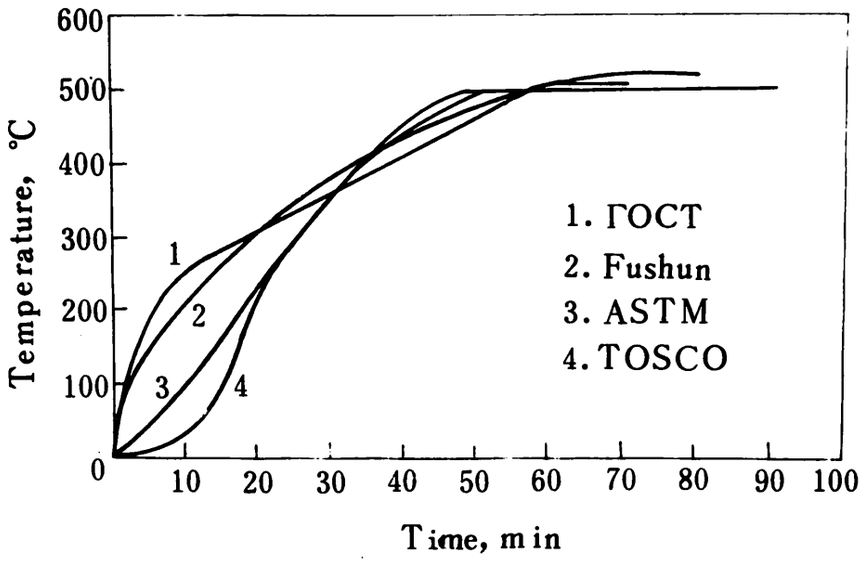

Fig.1. Temperature profiles of different Fischer Assay procedures

Table 3. Properties of a Fushun oil shale

Fischer Assay,%(wt)			Elemental Analysis,%(wt)			
Oil	Water	Spent Shale	C	H	N	S
7.18	4.82	85.81	11.14	1.95	0.47	0.42

Technical Analysis,%(wt)					
H_2O	Ash	Volatile	Mineral CO_2	Calorific Value,cal/g	
2.55	75.14	15.04	3.39	1,240	

Table 4. Fischer Assay of Fushun oil shale

Test NO.	ГОСТ 3168-81	ASTM3904-80	TOSCO Method	Fushun Method
1	7.39	7.85	7.34	7.67
2	7.66	7.93	7.33	7.50
3	7.30	7.84	7.78	6.88
4	7.52	7.94	7.37	7.15
5	7.42	7.74	7.24	6.80
6	7.34	7.48	7.61	7.18
7	----	7.62	7.14	7.05
Average	7.44	7.77	7.40	7.18
Max.difference among tests	0.36	0.46	0.64	0.87

Modification of the retort From the results of comprehensive comparison, it can be concluded that ГОСТ 3168-81 was the best among the four methods, but some modification may be desirable.The aluminum retort was somewhat modified: (1) the average inside diameter was reduced from 57 mm to 54 mm, and the internal height was increased from 64 mm to 75 mm. (2) the position of thermowell was moved to the opposite side to the outlet tube.

Particle size Tests were made according to new heating profile (average rate of heating 10°C/min,end temp. 520°C, holding time 20 min) for particle sizes from < 0.2 mm to 3-6 mm. It was found that very small difference in assay value existed between < 0.2 mm and < 3 mm, while the value was a little higher than 3-6 mm. So, sample of < 3mm, well-mixed, was utilized, so as to simplify the procedure of sample preparation and to save the time for preparation.

Cooling of distillation products and removal of water After comparative tests, ice water or flowing water at temperature below 15°C was used, and distillation with solvent was used to remove water. From toxic point of view solvent naphtha was applied instead of toluene.

Heating profile as the above factors being settled,the heating profile was examined in detail. An appropriate heating rate was favorable for decomposition of kerogen in oil shale in shorter time, and for leading out of the product to avoid unnecessary secondary cracking. Fig.2 shows five rather smooth profiles designed for study (the end temperature was at 520°C and the holding time was 20 min). From the data in Table 5, it can be seen that heating rate considerable affected the assay value, and a rate 10°C/min gave the highest value,7.75 %,which was equivalent to that of ASTM 3904-80,and higher than that of ГОСТ 3168-81.(7.44 %),while the total heating time can be shortened for twenty minutes.

The end temperature of retorting depends on the nature of different oil shales. For Fushun oil shale, tests were made in a rather wide range (fixed the heating rate at 10 °C/min and the holding time for 20 min). Data in Table 6 showed that an end temperature of 520°C was desirable (in this case the central temperature of sample was 510-513°C). This value was in agreement with the result of kinetics study[4]. Higher end temperature will cause the secondary cracking of the product vapor,leading to lower assay value.

The holding time at end temperature should be long enough to get minimum difference between wall temperature and the central temperature to obtain complete pyrolysis of kerogen. The data in Table 7 indicates that 20 min holding time was necessary and enough.

Adaptability of the new procedure As a result of the above studies,the principal points of the new procedure are as follows:

A modified aluminum retort, sample weight 50 g, average heating rate 10°C/min, end temperature 520°C, holding time 20 min, total heating time 70 min.

According to the new procedure, samples of China oil shales with different assay values were assayed,and compared with ГOCT 3168-81, ASTM 3904-80 and the Fushun Method (see Table 8). It can be seen that,for different China oil shales,the assay values by the new procedure are the highest. Compared to ГOCT 3168-81, for oil shale with medium assay value (around 7 %), the assay value was 0.2-0.3 % higher,and for oil shale with higher assay value (15-26 %), 0.6-0.7 % higher.

Repeatability of the new procedure The repeatability data of the new procedure,compared with other methods, are listed in Table 9. It can be seen that the standard deviation between parallel tests is lowest for the new procedure and is smaller than that of Fushun Method.

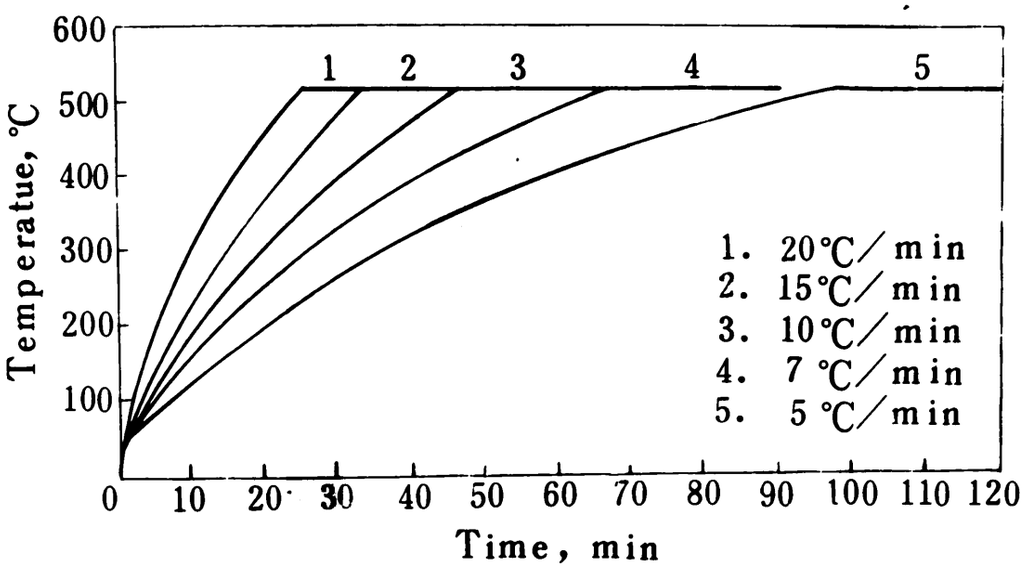

Fig.2 Test temperature profiles of Fischer Assay by new procedure

Table 5. Fischer Assay of Fushun oil shale at different heating rates

Av. heating rate, °C/min	20	15	10	7.0	5.0
	7.52	7.77	7.80	7.74	7.50
Oil yield %(wt)	7.66	7.66	7.72	7.60	7.62
	----	7.59	7.74	7.74	7.60
Average	7.59	7.67	7.75	7.69	7.57

Other conditions: End temperature 520 °C
Holding time 20 min

Table 6. Fischer Assay of Fushun oil shale at different end heating temperature

End heating temperature, °C	485	500	510	520	530	540	550
	6.92	7.18	7.58	7.80	7.56	7.67	7.68
Oil yield, %(wt)	7.40	7.47	7.68	7.72	7.73	7.72	7.40
	----	7.29	7.52	7.74	7.87	----	7.81
Average	7.16	7.31	7.59	7.75	7.72	7.70	7.63

Other conditions: Average rate of heating 10 °C/min
Holding time 20 min

Table 7. Fischer Assay of Fushun oil shale at different holding time at end temperature

Holding time at end temperature,min	0	10	20	30	50
Oil yield,% (wt)	7.72	7.37	7.60	7.62	7.44
	6.85	7.54	7.70	7.56	7.86
	6.15	7.55	7.54	7.62	7.42
Average	6.91	7.49	7.61	7.60	7.57

Other conditions: Average heating rate, 10°C/min
End temperature 520 °C

Table 8. Fischer Assay of different China oil shale

Test method	A*	Fushun	B*	Huadian	C*
Fushun Method	4.49	7.18	11.09	15.27	26.50
ГОСТ3168-81	----	7.44	----	15.51	27.75
ASTM3904-80	4.82	7.77	10.61	15.53	26.78
New procedure	4.85	7.83	11.72	16.20	28.30

* A: Fushun lean
  B: Maoming Rich
  C: Huang Xian

Table 9. Repeatability of different Fischer Assay procedures

Test method	$\bar{X}$	S
Fushun Method	7.18	0.32
ГОСТ 3168-81	7.44	0.15
ASTM 3904-80	7.77	0.17
New procedure	7.83	0.05

$\bar{X}$: Average assay value
S: Standard deviation

SUMMARY

1. Among the four current procedures of Fischer Assay of oil shale, ГОСТ 3168-81 has the advantage of appropriate weight of sample (50 g), readily mastered test procedure, and better repeatability.

2. A new assay procedure has been established with the following operating conditions:

Weight of sample	50 g
Particle size of sample	< 3 mm
Average heating rate	10 °C/min
End temperature of heating	520 °C
Holding time at end temperature	20 min

The distillation products were cooled with ice water or flowing water at temperature below 15 °C. Water in the products was removed by distillation with solvent naphtha.

3. The new assay procedure is applicable to China oil shales with assay value of 4-30 %, the difference between tests not exceeding the following value:

Max. deviation between parallel tests, %(wt)

Oil yield	Repeatability			Reproducibility		
% (wt)	Oil	Water	Spent Shale	Oil	Water	Spent Shale
< 10	0.4	0.4	1.0	0.8	0.8	1.5
10-20	0.8	0.4	1.0	1.2	0.8	1.5
20-30	1.5	0.4	1.0	2.0	0.8	1.5

4. The new assay procedure has been approved by China Petrochemical Corporation as Trade Standard ZBE 22001-86.

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