Selectivity of Sample Preparation by Micro Carbon Residue Method with Heat Transfer Fluids

Jianhua Yang¹, Jingmiao Li², Dong Jin³ and Linyuan Guo^{1*}

¹China Special Equipment Inspection and Research Institute, Beijing

²China Special Equipment Inspection and Research Institute, Beijing

³China Special Equipment Inspection and Research Institute, Beijing

Abstract. In heat transfer fluids, the carbon residue value is an indicator that provides its relative coking tendency. The micro carbon residue method is widely used because of the simple and convenient operation procedures and low pollution. However, when the carbon residue value is less than 0.1%, the sample needs to be prepared and then tested in the furnace. Therefore, this article aims at the measurement of carbon residue by the heat transfer fluids micro method. The heat transfer fluids is classified according to the product type and the maximum allowed temperature. The sample is prepared by pretreatment. In the method for determining micro carbon residue, whether the sample prepared by pretreatment is selective.

1 Introduction

Heat transfer fluids is a general term for organic materials that can be used as an indirect heat transfer medium including heat transfer fluids, hot oils, organic heat transfer carriers, heating media, etc.[1]. According to the state of use, it can be divided into unused heat transfer fluids and in-use heat transfer fluids. According to the product type, the unused heat transfer fluids can be divided into refined heat transfer fluids, ordinary synthetic heat transfer fluids and synthetic heat transfer fluids with special high thermal stability. Among them, the general synthetic type and the synthetic type with special high thermal stability are divided according to the maximum permitted bulk temperature, and the two are collectively called the synthetic type. The synthetic type is different from the mineral type. The former is produced by a chemical synthesis process, and the latter is a distillate obtained by distillation and refining of petroleum.

At present, heat transfer fluids can be widely used in many fields such as petrochemicals, wood processing, automobiles, and clothing manufacturing. They are inseparable from the advantages of continuous use under low pressure and high temperature, but cracking and degradation will also occur during this process, making the heat transfer fluids deteriorates and forms coking in the pipeline to form carbon residue[2].

The carbon residue value is used to estimate the general tendency of various petroleum products to form carbonaceous sediments after evaporation and thermal cracking under high temperature conditions to provide a relative tendency of petroleum products to generate coke[3]. The main components that easily form carbon residue are mostly colloids, asphaltenes, polycyclic

aromatic hydrocarbons, and non-volatile additives in the sample[4-6].

The determination methods of carbon residue in petroleum products include conradson method, LAN's method, electric furnace method and micro method, and they are all widely used. For heat transfer fluids, conradson method (GB/T 268-1987 "Petroleum products- Determination of carbon residue- Conradson method"), electric furnace method (SH/T 0170-1992 (2000) "Petroleum products- Determination of carbon residue- Electric furnace method") and micro method (GB/T 17144-1997 "Petroleum products- Determination of carbon residue- Micro method") to detect the carbon residue value. The conradson method is the arbitration method for the determination of carbon residue in heat transfer fluids. However, the sample is directly heated on an open flame, manual operation is required throughout the whole process, which not only causes greater environmental pollution, but also greater harm to the human body of the experimental personnel, and will also cause certain artificial error. Therefore, the electric furnace method and the micro method are generally used to determine the carbon residue in the heat transfer fluids. However, compared with the electric furnace method, which needs to ignite the sample steam after the sample was heated, the micro method has the advantages of high degree of automation and low pollution.

Although the micro method does not require the person to manually ignite to observe the flame and the state of the sample, it avoids manual errors in this regard and reduces environmental pollution. However, the direct measurement of the sample into the furnace test requires a measurement range of 0.10%(m/m) ~ 30.0%(m/m), and the measurement result is equivalent to conradson residual carbon. For samples with a carbon residue value of less

*Corresponding author's e-mail: hxfzx2017@126.com

than 0.10% (m/m), the samples need to be prepared before they can be tested in the furnace. As for the unused heat transfer fluids, according to the requirements in Table 2 of GB 23971-2009 "Heat transfer fluids", the carbon residue (mass fraction) is not more than 0.05%. It can be seen that all the unused heat transfer fluids need to prepare samples when using micro method to detect the carbon residue. But it not only consumes time and energy, but also consumes too many samples. Therefore, in this paper, 10%(V/V) distillation residue was prepared according to sample pretreatment, and further experimental comparison is made on the detection of distillation residue and untreated samples, so as to analyze whether the sample pretreatment was selectable in micro method measurement of carbon residue.

Common unused heat transfer fluids can be divided into 280°C, 300°C, 310°C, 320°C, 330°C, 340°C, 350°C and 400°C, according to the maximum permitted bulk temperature, of which the mineral type heat transfer fluids involves 280°C, 300°C, 310°C and 320°C, the synthetic type heat transfer fluids involves 300°C, 310°C, 320°C, 330 °C , 340 °C , 350 °C and 400 °C . Therefore, the experimental data can be classified as the comparison of the carbon residue value between the synthetic heat transfer fluids and the mineral heat transfer fluids.

2 Experiment

2.1. Material

Nitrogen, purity 99.999%; Clean brown glass bottle (20ml).

2.2. Instruments

Shanghai Tanaka ACR-M3 automatic micro carbon residue tester, equipped with sample tube, sample rack, waste liquid bottle, tweezers etc.; Optidist automatic atmospheric distillation analyzer, equipped with flask, measuring cylinder, heating plate, cork etc.; Mettler Toledo analytical balance, measuring range 220g, sensitivity 0.1mg.

2.3. Sample Preparation

Assuming that the carbon residue value of the test sample is lower than 0.10%(m/m), according to the GB/T 17144-1997 "Petroleum products- Determination of carbon residue- Micro method", sample pretreatment is required. The specific pretreatment process is as follows:

2.3.1. Accurately measure 100mL sample into 125mL or 200mL distillation flask, remove the temperature line and replace it with another cover, fix it on the instrument, and select 50mm or 38mm heating plate;

2.3.2. Before using the automatic atmospheric distillation apparatus, it is necessary to set the

temperature of the heating plate (the instrument's limit heating temperature -10°C) and the heating stop volume (89mL);

2.3.3. When the heating stops, observe the volume of liquid in the receiving measuring cylinder. When it reaches 90mL, change a clean and dry 20ml brown glass bottle to collect the remaining reflux liquid, and fully mix it with the remaining samples in the flask to obtain 10%(V/V) distillation residue.

2.4. Weighing and recording quality m_1

In order to reduce the weighing error, the clean sample tube matching with the micro carbon residue tester with a capacity of 4mL is clamps with tweezers, and the mass m_1 of the empty tube was recorded, accurate to 0.1mg.

2.5. Weighing and recording quality m_2

3.00g±0.50g of the sample prepared in 2.3.3 was taken and loaded into the weighed empty tube to avoid hanging the sample wall. The mass m_2 of the empty tube and the sample was recorded to an accurate level of 0.1mg.

2.6. The weighed sample is put into the micro carbon residue tester along with the sample rack for carbon residue detection:

The partial pressure of the nitrogen bottle is controlled at 2.5MPa ± 0.1MPa, and the pressure regulator on the instrument controls the pressure at 147KPa. The nitrogen flow rate was 150mL/min before the start of the test. When the test started, the flow rate was purged at 600mL/min for 10min. At this time, the test temperature rose to 100°C; after that, the nitrogen flow rate was reduced to 150mL/min and heated in stages. After 47 minutes, the furnace temperature reached 500°C; finally purged with the current nitrogen flow, the furnace temperature was stabilized at 500°C±2°C for 15 minutes; after the end, the purge and cooling were continued with a nitrogen flow of 600mL/min, and the instrument temperature program was closed after 95 minutes.

2.7. Weighing and recording quality m_3

Until the temperature drops below 250°C, take out the sample rack and put it into a desiccator to cool to room temperature. Weigh the mass of the sample tube after the test and record the mass m_3 to the nearest 0.1mg. If the sample splashes and blisters, this test is invalid and needs to be repeated.

2.8. According to formula (1), the carbon residue value of 10%(V/V) distillation residue can be calculated, %(m/m)[7] :

$$X = \frac{m_3 - m_1}{m_2 - m_1} \times 100 \quad (1)$$

Then convert to the original sample carbon residue value according to formula (2) X' :

$$X' = \frac{X}{10} \quad (2)$$

Then calculate the repeatability r according to formula (3) to ensure the credibility of the data [7]:

$$r = 0.0770 X'^{(2/3)} \quad (3)$$

The final total carbon residue is the sum of the ash content or nonvolatile additive content in the sample and the carbon residue value.

3 Comparison of experimental results

3.1. Synthetic heat transfer fluids with special high thermal stability

The maximum permitted bulk temperature of the samples at 330°C, 340°C, 350°C and 400°C, can be prepared according to experiment 2.3 10%(V/V) distillation residue,

Table1. Carbon residue values of synthetic heat transfer fluids and mineral heat transfer fluids

product type	sample number	thermal stability test temperature/°C	carbon residue value of original sample/%		
			parallel measured value		mean
synthetic type	1	300	0.0013	0.0013	0.0013
	2		0.0057	0.0057	0.0057
	3		0.0450	0.0442	0.0446
	4		0.0013	0.0013	0.0013
	5	310	0.0013	0.0013	0.0013
	6		0.0040	0.0033	0.0036
	7		0.0013	0.0013	0.0013
	8	320	0.0013	0.0013	0.0013
	9		0.0023	0.0020	0.0022
	10		0.0013	0.0013	0.0013
	11	330	0.0013	0.0013	0.0013
	12		0.0030	0.0030	0.0030
	13		0.0013	0.0013	0.0013
	14	340	0.0024	0.0018	0.0021
	15		0.0040	0.0043	0.0042

and the calculated carbon residue value is less than 0.01%, as shown in Table 1.

3.2. Ordinary synthetic heat transfer fluids

The samples with the maximum permitted bulk temperatures of 310°C and 320°C can also be prepared with 10%(V/V) distillation residue according to experiment 2.3, and the calculated carbon residue value is lower than 0.01%, as shown in Table 1.

The maximum permitted bulk temperature is 300°C. Some samples can prepare 10%(V/V) distillation residue according to experiment 2.3, and the calculated carbon residue value is lower than 0.05%, as shown in Table 1.

3.3. Refined mineral heat transfer fluids

The samples with the maximum permitted bulk temperature of 280 °C and 300 °C, two thirds of the samples can prepare 10%(V/V) distillation residue according to experiment 2.3, and the calculated carbon residue value is mostly lower than 0.01%, all lower than 0.05%, as shown in Table 1.

The samples with the maximum permitted bulk temperatures of 310°C and 320°C, three quarters of the samples can prepare 10%(V/V) distillation residue according to experiment 2.3, and the calculated carbon residue value is mostly less than 0.01%, all less than 0.05%, as shown in Table 1.

mineral type	16		0.0013	0.0013	0.0013
	17	350	0.0033	0.0037	0.0035
	18		0.0050	0.0037	0.0044
	19		0.0013	0.0013	0.0013
	20	400	0.0013	0.0013	0.0013
	21		0.0013	0.0013	0.0013
	22		0.0013	0.0013	0.0013
	23	280	0.0057	0.0055	0.0056
	24		0.0107	0.0110	0.0108
	25		0.0013	0.0013	0.0013
	26	300	0.0070	0.0074	0.0072
	27		0.0325	0.0331	0.0328
	28		0.0013	0.0013	0.0013
	29	310	0.0013	0.0013	0.0013
	30		0.0013	0.0013	0.0013
	31		0.0013	0.0013	0.0013
	32	320	0.0017	0.0017	0.0017
	33		0.0459	0.0443	0.0451

3.4. Comparison before and after sample processing

In addition, carbon residue test was conducted between

samples prepared and those without sample preparation but with increased amount of sample injection. The specific carbon residue data are shown in Table 2. See Table 3 for the comparison of test data of whether the sample has been pre-processed.

Table2. Sample weighing and carbon residue value

sample number	sample status	m ₁ /g	m ₂ /g	m ₃ /g	carbon residue value/%	original carbon residue value/%
34	sample preparation	12.9874	15.9724	12.9971	0.3250	0.0325
		12.2998	15.2874	12.3097	0.3314	0.0331
	no sample preparation	12.2823	18.2883	12.2840	/	0.0283
		14.3189	20.3193	14.3209	/	0.0333
35	sample preparation	14.3804	17.3824	14.3939	0.4497	0.0450
		14.4176	17.4061	14.4308	0.4417	0.0442
	no sample preparation	14.3393	17.3395	14.3406	/	0.0433
		14.3925	17.3985	14.3938	/	0.0432
36	sample preparation	14.5019	17.5080	14.5157	0.4591	0.0459
		14.5824	17.5863	14.5957	0.4428	0.0443

no sample	14.5010	17.4948	14.5023	/	0.0434
preparation	14.4850	17.4863	14.4861	/	0.0367

Table3. Difference between sample preparation and no sample preparation carbon residue

sample number	sample status	carbon residue, difference and repeatability of original samples/%			
		mean	difference	repeatability	repeatability between the two
34	sample preparation	0.0328	0.0006	0.0079	0.0077
	no sample preparation	0.0308	0.0050	0.0076	
35	sample preparation	0.0446	0.0008	0.0097	0.0096
	no sample preparation	0.0432	0.0001	0.0095	
36	sample preparation	0.0451	0.0016	0.0098	0.0094
	no sample preparation	0.0400	0.0067	0.0090	

4 Analysis of experimental results

4.1. It can be seen from Table 1 that the samples with synthetic heat transfer fluids and the maximum permitted bulk temperature between 310 °C and 400 °C can effectively prepare 10% (V/V) distillation residue, and the carbon residue value obtained is not more than 0.05%. The main components of the samples are mostly hydrogenated terphenyls, diphenyl, diphenyl and diphenyl ether, etc.

4.2. The synthetic heat transfer fluids and the maximum permitted bulk temperature at 300 °C can be normally prepared except for some samples that cannot be effectively prepared. The carbon residue value obtained is not more than 0.05%, and the main components of the samples are mostly alkyl benzene and alkane. The maximum permitted bulk temperature at 280 °C synthetic heat transfer fluids rarely appeared and was not included in the experimental comparison.

4.3. Most of the refined mineral heat transfer fluids can effectively prepare 10%(V/V) distillation residue, and the carbon residue value obtained is not more than 0.05%, and the main components of the samples are mostly hydrocarbon and alkyl benzene. A few hydrocarbon and alkyl benzene cannot be prepared.

4.4. Through pretreatment experiments, it was found that in the process of preparing 10%(V/V) distillation residue, some samples could not be distilled at the limit temperature of the atmospheric distillation apparatus, so they could not be prepared normally.

The current conradson carbon residue method and micro carbon residue method are based on ISO 6615-1983 and ISO 10370:1993, respectively. The current reference methods are updated to ISO 6615-1993 (Conradson carbon residue method) and ISO 10370-2014 (Micro

carbon residue method), respectively, but these methods also do not specify what should be done when samples cannot be prepared. Electric furnace process is a reference to the former Soviet union countries standard ГОСТ 8852-74, the current reference of this method has not been updated, this method has not clearly pointed out that when the sample could not be should be how to deal with.

Although the three standard methods for the determination of heat transfer fluids carbon residue all involve the preparation of 10%(V/V) distillation residue, it is indicated in part II of the ISO 6615-1993 method summary that for light products with more than 90%(V/V) distilled below 370 °C, subsequent experiments can be conducted on the residue after 90%(V/V) distillation[8]. It can be seen that there is no problem that samples cannot be prepared by conradson method, instead, it is the electric furnace method and the micro method. No matter what the sample composition is, the sample preparation is involved without the use of heat transfer fluids. In the case that the sample cannot be prepared, the conradson method can only be used for the test.

However, through experimental comparison, for samples that cannot be prepared, refer to ASTM:D4530-15 (micro carbon residual method) 6.2: appropriately increase the sample size and enter into furnace heating test directly. But at present, the determination results of this method cannot be verified to be equivalent to conradson carbon residual method[9]. The samples that can be prepared effectively and have a large carbon residue value are selected for comparison test by directly adding normal sample quantity or twice sample quantity. The values obtained are within the range of repeatability.

5 Conclusion

The heat transfer fluids can be selectively prepared when it is used to prepare the samples: it mainly prepares the samples with the maximum permitted bulk temperature of 280 °C and 300 °C for the ordinary synthetic heat transfer fluids, and the refined mineral heat transfer fluids. Ordinary synthetic heat transfer fluids with the maximum

permitted bulk temperature of 310°C and 320°C, and the synthetic heat transfer fluids with special high thermal stability can be used without pretreatment or according to the actual situation.

Some samples cannot be prepared because of many heavy components. The normal sample amount or increase the sample amount can be used directly test or choose to use the conradson carbon residue method for experiment.

References

1. GB 23971-2009 Heat transfer fluids. S.
2. Li Y., (2017) Discussion on Determination Method of Acid Value of Heat transfer fluids. J. Guangzhou Chemical Industry, 45: 18-19/41.
3. WEN P., SUN Z.H., LI S.F., MU B.Q., LI C., (2014) Teaching Reformation of Determination Experiment of Carbon Residue in Petroleum Products. J. Contemporary Chemical Industry, 43: 509-511.
4. Wang H., Wen P., (2011) Determination method of carbon residue in petroleum products. J. Modern Instruments, 17: 73-75.
5. Luo Y.D., Guo Y.C., (2007) Research on Carbon Residue in the Petroleum by Micro Determination. J. Guangdong Chemical Industry, 34: 110-114.
6. Ren F., (2006) Determination of Carbon Residue in Petroleum Products. J. Guangdong Chemical Industry, 33: 63-64/54.
7. GB/T 17144-1997 Petroleum products-Determination of carbon residue- Micro method. S.
8. ISO 5516-1993 Petroleum products-Determination of carbon residue-Conradson meth. S.
9. ASTM:D4530-15 Standard Test Method for Determination of Carbon Residue(Micro Method). S.