

Study on the Determination of Boiling Point Distribution of Heavy Oil by the New Method

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Abstract

A new Liquid Chromatography Distillation (LCD) method was applied to determine Boiling Point Distribution (BPD) of heavy oils, which refer to the residual oil of petroleum, coal asphalts and coal direction-liquid residue, etc. Through a series of studies, the LCD method was established by the Size Exchange Chromatography (SEC) of liquid chromatography and the BPD of some typical heavy oils were determined. It is also reported that this method could be applied in other processes related with heavy oil, such as making high-level road asphalt, modification of coal liquefaction residues, and hydrogenation of heavy oil. In this paper, some other distillation technologies including hydro-distillation, molecular distillation and membrane distillation are also reviewed systematically.

Keywords: Heavy oil product; Boiling point distribution; Liquid chromatography distillation method; Size exchange chromatography; Asphalts

Abbreviations

LCD: Liquid Chromatography Distillation; BPD: Boiling Point Distribution; SEC: Size Exchange Chromatography; Mo-D: Molecular Distillation; Me-D: Membrane Distillation; Bp: Boiling Point; Rt: Retention Time; Bp Av: Average Boiling Point; Hs: N-Heptanes Soluble Of Coal Liquefaction Residue; Ts: Toluene Soluble Of Coal Liquefaction Residue; Os.: Original Residue

Introduction

Distillation is one of the most common methods of separating mixtures, based on the differences of component volatility in a boiling liquid mixture. The components with lower boiling points are vaporized easier than those with higher boiling point.

The distillation technologies are indispensable for many fields, and can be classified into the new and traditional distillation technologies. The traditional distillation technology refers to single barrel-heating or tube type distillation. These technologies were mainly applied in the field of processing the products of coal and petroleum.

Distillation technologies also have the new developments and breakthroughs with the development of science and technology. Hydro-distillation is one of the new technologies. Since 1957, Holmes JC and Morrell FA firstly achieved the combination of gas chromatography with mass spectrometry, which is named as Hydro-distillation. Hydro-distillation technique is much better than ordinary distillation method, because the substances, which were separated difficultly in the traditional distillation technology, could be isolated and identified by the hydro-distillation technique [1].

Molecular distillation (Mo-D) technique or short-path distillation technique is another new distillation technology. At lower temperatures, the Mo-D of substances is based on the difference of free paths of molecular collisions [2]. Using Mo-D technique, when the distance between the surfaces of heated liquid and cold condensation is less or equal to the free path of substances molecular, the escaping substances molecular from liquid surface can reach the condensation surface and then be precipitated almost without collisions. Meanwhile, the heating time of substances is very short. For example, the Mo-D process only

needs 10 seconds, but the separation time of traditional method is 1 hour. The operating pressure of Mo-D is also very low (i.e., 0.001~1 mbar), while that of traditional distillation is 50 mbar. At the same time, Mo-D applications in many aspects have been reported, such as polymer [3] isocyanines, phenol resin, epoxy resin, acrylic paint and pharmaceuticals [4], etc.

Another new development of distillation technology is the membrane distillation (Me-D) technique. When using hydrophobic micro-porous membranes, the differences in vapor pressures of both sides of membrane will lead to the driving force of mass transfer and further separations. There are many unique applications of Me-D technique, such as the desalination of sea water [5], the removal of toxic arsenic in water [6,7], the concentrations of sucrose solution and fruit juice [8-10] and the concentrations of ginseng extract [11].

With the development of new distillation technologies, the traditional distillation technologies were also improved. For example, Ertan Alptekin [12] applied distillation methods to prepare bio-diesel instead of diesel fuel. In crude oil distillation industry, Motlaghi firstly proposed the model of neural networks and designed the optimal control of product quality [13].

New technologies including Hydro-distillation, Mo-D and Me-D all show new distillation characteristics, the most important one of which is the unique separation property. The greatest weakness of these technologies is that those methods could not instantly and vividly give boiling point distributions (BPD) of the sample. However, this is exactly the merit of traditional distillation. The determination of BPD is necessary in some areas, such as the utilization of heavy oil.

It's well known that heavy materials are difficult to use, but gas and light liquid from the processing of coal and petroleum, are easy and

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Received February 17, 2014; Accepted May 26, 2014; Published May 29, 2014

Citation: Zhang C, Huang Z, Zhang X, Yang L, Han YHX (2014) Study on the Determination of Boiling Point Distribution of Heavy Oil by the New Method. J Environ Anal Toxicol 4: 224. doi: [10.4172/2161-0525.1000224](https://doi.org/10.4172/2161-0525.1000224)

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important for using. In crude oil refining process, especially in thermal cracking and catalytic cracking of coal and petroleum, many residual oils, asphalts and heaviest “waste” residual are produced. The quantity of these heavy oils is often high. According to statistics, the quantity of heavy oils from the direct liquefaction of coal was as high as 20–35%, so it is important to develop the usage of heavy oil and establish a new method to determine BPD.

The traditional distillation can meet the above determination requirements at a certain extent, but its drawbacks are obvious. The distillation time is long, and the maximum distillation temperature is limited and then some substances of the high boiling point are not able to be steamed out [14,15]. In order to analysis of toxicology effectively and develop the utilization of heavy oils, we undertook the task to establish a new distillation method, which coordinates national project. The appearances of new technology give us great inspiration: trying to think, trying to make, and innovation would be occurred.

The principle of hydro-distillation is the separation of substances by the column layers of gas chromatography. Then can the liquid chromatography accomplish this distillation? The answer should be yes, because liquid chromatography has many branches, many types of columns. Currently, the Size Exchange Chromatography (SEC)-as is regarded as an important branch of liquid chromatography and the SEC is very effective to analyze heavy oil. In analysis, the elution of components follow the law that from larger molecular component to smaller molecular component. The molecule sizes are related to their corresponding boil point, so the establishment of LCD method will be feasible.

After a large number of experiments, a new LCD method was established. This method showed some good characteristics, such as small quantity of sample used, short distillation time and fine quantitative repeat, etc. Some typical heavy oils are determined by this method. This LCD method was also able to be used in some process developments [16,17], such as asphalt carbon fiber, the modification of coal liquefaction residues, and road asphalt. Additionally, LCD method also has other advantages including: High boiling point's detected, good repeats of qualitative and quantitative analysis, quick operation, less amount of sample used, and good working environment. Compared with conventional distillation method, these are advanced and noticeable.

Experimental

Instruments, Reagents and Samples

The instrument used is SHIMADZU LC-10A (Shimadzu, Japan) high performance liquid chromatograph, equipped with SPD-10AUP UV detector and RID-1 differential detector (concatenation). Column used is SHIMPACK GPC-801 (30 cm long, 0.8 cm id, polystyrene 6 μm) (Japan SHIMPACK companies). Tetrahydrofuran (THF) was as a mobile phase. The THF, produced by Tianjin Chemical Reagent Factory (Tianjin City, China), was analysis grade reagents. Aromatic reagents were provided from the Department of Shanghai Chemical Reagent Factory (Shanghai City, China).

Some heavy oils were chosen as typical representatives. Their BPD chromatograms and the average boiling points were studied. The name and source of these heavy oils were listed in Table 1.

The Establishment of Boiling Point Curve

Chromatographic conditions were determined as follows: UV detector (λ:254nm) and the differential detector (in series),

No	Name of sample	Source of sample
1	Coal tar pitch	Coking plants in Shanxi Province
3	Coal tar oil	Coking plants in Shanxi Province
5	Petroleum Asphalt	South Korea
6	Residue after heavy oil cracking	Oil refinery plant in Xinjiang Province
7	Ethylene product residue	Petroleum refinery plant in Xinjiang Province

Table 1: The Names and Sources of Typical Sample.

No	Component	Retention Time (Min)	Boil point (°C)
1	24 alkanes	5.766	391
2	22 alkanes	5.866	369
3	18 alkanes	6.05	317
4	Carbazole	6.986	354.8
5	Iso-30 alkanes	7.430	176
6	Decane	7.533	175
7	1,3-dimethyl cyclopentane	7.583	120
8	Biphenyl	7.601	254.3
9	2,7-dimethyl-naphthalene	7.666	262
10	1,3-dimethyl cyclopentane	7.683	129.5
11	Xylene	7.865	139
12	α-methyl naphthalene	7.886	242
13	2,2,4-trimethyl pentane	7.971	98.7
14	Naphthalene	7.989	217.9
15	Acenaphthylene	8.001	265
16	Toluene	8.016	110.6
17	Benzothiazole	8.050	231
18	Phenyl-p-cresol	8.070	199
19	Benzene	8.111	80

Table 2: Retention Times - Boiling Point Value.

tetrahydrofuran as the mobile phase, flow rate of 1.2 ml/min, column temperature at 19°C. Under these conditions, 19 pure reagents including carbazole, acenaphthylene, benzothiazole and naphthalene, etc were selected as the model compounds and were prepared as a solution of 0.01 - 0.04 g/100 ml to complete the chromatography trip. And then the relationship between boiling point (Bp, °C) and liquid chromatographic retention time (Rt, min) were obtained, and then the Rt-Bp equation would be established.

Results and Discussion

Curve Equation and Calculation Method

Curve Equation: 19 Pure aromatics reagents as statistics, their chromatographic retention time (Rt, min) and corresponding boiling points (Bp, °C) values are summarized in Table 2. And the corresponding mathematical relationship is as follows:

$$Y = 940.913 - 97.104 * X \quad (1)$$

Where Y represents boiling point (°C), X represents the retention time of chromatographic peaks (min). The equation (1) was derived from the data corresponding to the model compounds in Table 2.

Calculation Method:

(1) Boiling point distribution (BPD) chromatogram

When chromatography trip of sample was completed, the time (x coordinate) is converted to boiling point data by formula (1), and then the boiling point distribution chromatogram was obtained.

(2) The average boiling point (Bp_{av})

The chromatogram was divided into n portions (more than 100 per minute). The corresponding boiling point of each portion was got by formula 1, and then the average boiling point (Bp_{av}) will be attained according to following formula.

$$Bp_{av} = \frac{\sum[Bp_i * mv_i]}{\sum mv_i} \quad (2)$$

Where Bp_i represents the boiling point of each i region of samples and mv_i represents chromatographic response value of each i region.

(3) Calculation of Boiling point distribution (BPD): According to the formula (1), the chromatogram of sample can be divided into different range with certain boiling point range, such as the region of boiling point below 100°C, region of 100°C-200°C, 200°C-300°C, and so on. By the following formula (3) the percentage of every region of sample can be calculated out, respectively. And then the total boiling point distribution of sample can be obtained.

$$W_{a-b} \% = \frac{\sum mv_{(a-b)}}{\sum mv_{0-n}} \times 100\% \quad (3)$$

In formula (3), W_{a-b} % represents the weight percentage content of boiling point from a to b in samples. mv_(a-b) represents chromatographic response of boiling point range from a to b, and mv_(0-n) is chromatographic response of the entire sample.

Results of BPD

After heavy oil samples were analyzed, their chromatograms (boiling point - the time) were shown in Figure 1 and the corresponding BPD values were shown in Table 3. In order to compare the average boiling points, the error analysis results of its testing were listed in Table 4.

As high resolution separation column was used, heavy oils were well separated as shown in Figure 1 and different heavy oils showed the different BPD spectrum.

For traditional distillation methods with or without vacuum equipment, their most maximum values of boiling point, which could be determined, were 650°C and 550°C, respectively. However, for LCD method, the highest boiling point which would be detected in sample was higher than 800°C. Actually, as long as the compounds can be dissolved in tetrahydrofuran, substance of higher boiling point would be determined.

The other applications of LCD method

Coal - Oil Co-Refining for Making High-level Road Asphalt: China's energy resources are composed by limited amount of petroleum

oil and tremendous coal. And petroleum is oil-paraffin-based material which is not suitable for road asphalts. In order to reduce the amount of imports of crude oil and bitumen for long-term energy security, it is of the great importance to prepare oil from coal.

With modern process developments, the high-level road asphalt would be prepared by co-processing of coal-oil (coal-oil of refining) [17]. In order to prompt this research of coal-oil co-refining, the BPD of modulation pitch under aging treatment were determined under the following conditions. The asphalt dosage: 50 g; temperature: 163°C; aging time from 10 hr to 60 hr. The change of boiling point (bp) distribution of asphalt under aging treatment was shown in Figure 2.

The relationships of peak (high) values of corresponding boiling point 786.9°C and aging times were shown in Figure 3, and the equation 4 was setup, as follows.

$$Y = A + B_1X + B_2X^2 + B_3X^3 \quad (4)$$

in which X is aging time, Y is peak value. A: 0.23217, B₁: 0.05233, B₂: 6.52546E-4; B₃: -1.715E-5.

Determination of optimum aging time by LCD method is not negligible. It can save a lot of human and material resources for large-scale development, in particular, for batch test and batch production. From Figure 3, it can be seen that the peak value of boiling point (bp) 786.9°C increased with rising aging time. However, the increase only happens in the initial stage, and then the peak value showed

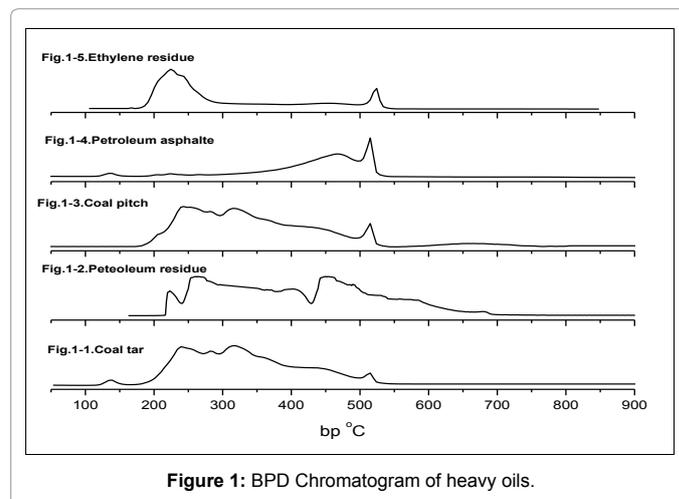


Figure 1: BPD Chromatogram of heavy oils.

Name of Samples	Average of Bp ₀ C	Figures	W%*					
			bp<200 °C	200-300 °C	300-400 °C	400-500 °C	500-600 °C	>600 °C
Coal tar	317.464	Fig.1-1	3.345	42.078	36.084	16.095	2.393	0.037
Residue petroleum cracking	394.966	Fig.1-2	9.029	26.424	13.978	27.151	16.696	6.722
Coal asphalt	340.554	Fig.1-3	3.691	33.218	37.843	16.585	3.712	4.951
Petroleum asphalt KP	839.409	Fig.1-4	0.967	8.701	19.999	55.119	14.967	0.245
"Ethylene" residue	306.257	Fig.1-5	6.366	57.291	13.118	13.363	9.441	0.421

Table 3: Determination Results of BPD.

Samples	Average of Bp (1)	Average of Bp (2)	Average 1,2	Difference 1,2	S.D%
Coal tar	317.464	317.445	317.464	0.019	0.006
Petroleum asphalt KP	419.702	419.707	419.705	0.002	0.001
Coal asphalt	340.506	340.602	340.554	0.048	0.014
Petroleum residue	397.227	392.705	394.966	2.261	0.572
Ethylene residue	306.420	306.094	306.257	0.163	0.053

Table 4: Standard Deviation (S.D.%).

the tendency of balance with the increasing aging time. Finally, the optimum time for aging the asphalt is determined to be 48 min. Under this aging time the treated asphalt contains the highest content of substance of 786.9°C.

The Development of Coal Liquefaction Residue: Direct coal liquefaction is one of main preparation method of oil from coal, in which coal is directly transformed into liquid oil under high temperature and high pressure of hydrogen [17]. Currently, in all direct coal liquefaction process, the content of liquefaction residue achieves 20-35%. The treatment method of liquefaction residues decides the economy of direct coal liquefaction, so these related researches are important and urgent topics.

In our studies, liquefaction residues were extracted by different solvents and the BPD of products was determined. The results of one typical coal liquefaction residue were given for explanation. When n-heptanes were used as extraction solvent, the n-heptanes soluble fraction of sample was named as Hs. After the n-heptanes insoluble matter was again extracted with toluene, the toluene soluble was named as Ts, and original residue was named as Os. Their BPD

characteristics and data results were shown in Figure 4 and Table 5, respectively. From results it is seen that different fractions exhibited different BPD characteristics. Comparing their Average Bp_{av} (average boil point), they were also different. The boiling point of Hs, Ts and Os are successively 466.52°C, 669.42°C and 583.15°C.

Hydrogenation of Heavy Oil: The hydro treating of liquefaction residue is another important treatment approach. It is beneficial to change the boiling point distribution and to increase the oil production rate. In this study, the following treatment condition is used. The volume of reactor is 25 ml. The temperature is 400°C. The hydrogen pressure is 7 MPa, and the heavy oil used is coal tar pitch. Through hydrogen treatment, the characteristics of sample were shown in

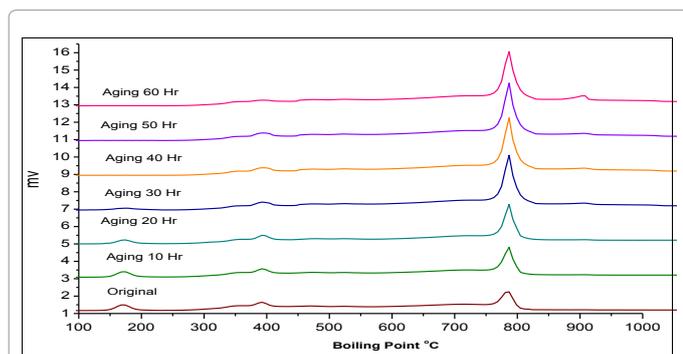


Figure 2: The change of BPD distributions at different aging time.

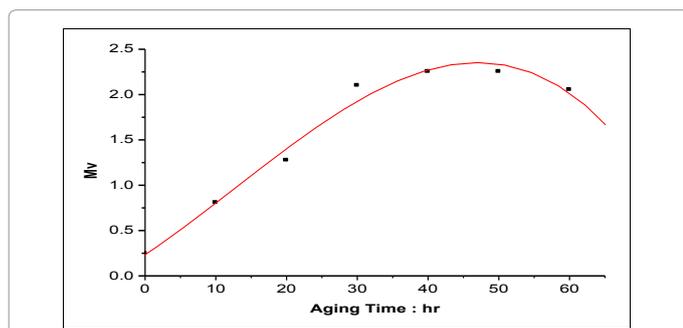


Figure 3: The change of peak value of 783.9°C at aging treatment.

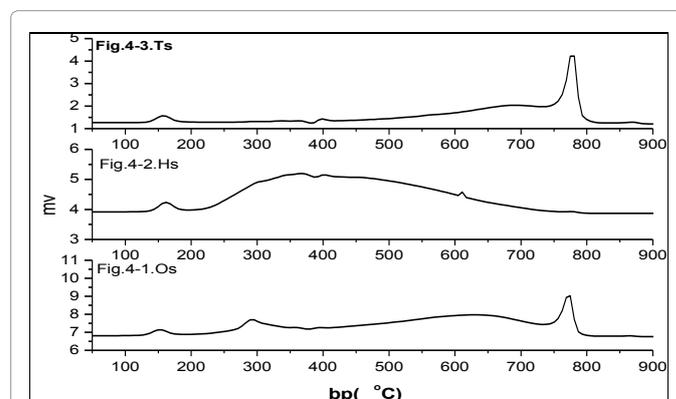


Figure 4: The BPD of coal liquefaction residue/Hs /Ts/ Os.

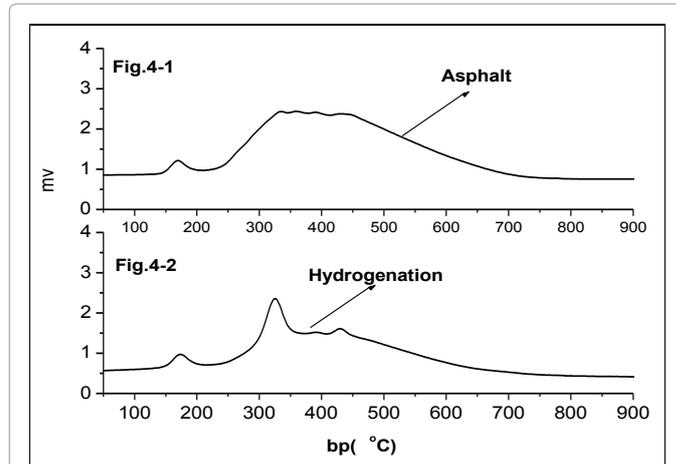


Figure 5: The BPD of asphalts before and after hydrogenation.

Sample W%	<25 °C	250-300 °C	300-400 °C	400-500 °C	500-550 °C	550-650 °C	650-750 °C	>750 °C	Bpav °C
Os	1.125	6.223	11.807	13.609	9.287	14.242	21.608	22.099	583.152
Hs	1.679	8.418	28.173	29.408	11.508	7.568	3.057	10.188	466.523
Ts	0.329	0.951	2.945	6.044	5.095	35.789	30.469	18.378	669.419

Table 5: BPD results of Os/Hs /Ts (W%).

W%	<250 °C	250-300 °C	300-400 °C	400-500 °C	500-550 °C	550-650 °C	>650 °C	Bpav °C
Hydrogenation	1.808	8.018	37.898	28.563	9.841	11.778	2.094	437.861
asphalt	0.118	3.477	19.423	16.464	5.183	43.686	11.649	572.556

Table 6: The BPD changes by hydrogenation.

Figure 5 and in Table 6.

The results showed that before and after hydrogenation of samples, the spectra were completely different, so hydro treating was beneficial to change the boiling point distribution. The average boiling point of the sample after hydrogenation became smaller than the original products.

Conclusion

The preliminary study on the liquid chromatography distillation (LCD) method has been performed. And a new method was established based on LCD to determine the boiling point distribution and average boiling points of heavy oils. Comparing to traditional distillation method, the new method has several advantages upon determining much higher boiling point of compounds. And only small amount of sample is required and analyses process is carried out more rapidly with good qualitative and quantitative repetitions at a better working environment, etc.

In this work, the boiling point distributions and average boiling points of some typical heavy oils were determined by this method. These heavy oils involve residue petroleum cracking, coal asphalt and petroleum asphalt KP, etc. Some processes developments such as making high-level road asphalt, the modification of coal liquefaction residues, and hydrogenation of heavy oil were cooperated and guided by this LCD method.

Acknowledgement

The authors gratefully acknowledge the financial support from the Natural Science Foundation of China (21177136), and the International Cooperation Project of Shanxi Province (2012081019).

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