Research on polar substance characterization and adsorption separation process of heavy oil

Longfei Fu¹*, Juan Wang¹, Qiangsuo Feng¹, Yongluo Liu¹, Tao Yan¹, Jinwei Tang¹ and Jialin Xie¹

¹Xi’an Thermal Power Research Institute Co., Ltd, Xi’an Shaanxi, 710032, China
*Corresponding author’s e-mail: fulongfei@tpri.com.cn

Abstract. The combustibility and fluidity is usually a major issue in heavy oil of power plant, which affects by asphaltene and insoluble matter due to the long-term storage. In this dissertation, the effects of asphaltene and insoluble matter characteristics on the heavy oil properties have been theoretically and experimentally studied using different methods. For the combustibility study, the asphaltene was precipitated and verified by X-ray diffraction energy and dispersive spectrum analysis. Also, the rotating disk electrode atomic emission spectrometry was carried out for fluidity study and then calorific value and ash content are calculated. The combustibility and fluidity of heavy oil were improved with the method of non-polar solvents and strong polar adsorption by removing asphaltene polar and insoluble substances. The experimental shows that calorific value is 9721Kcal/kg and viscosity is 14.7mm²/s.

1. Introduction
With the continuous price rise of crude oil, power plant based heavy oil tends to purchase lower price, so it faces the risk of the oil quality decline. Heavy oil is a dark black liquid, and its main composition is vacuum residue, cracking residue or a mixture of both[1,2]. The heavy oil is mainly used for ignition of heating units, and coal-fired units of power plants.
The combustibility and fluidity of heavy oil has a great influence on fuel supply and combustion for the power plant. It will increase the pressure of the fuel system, causing fuel supply failure when the viscosity is high. It is usually necessary to preheat the heavy oil before combustion to meet the requirements of injection for the reason of high viscosity under normal temperature and pressure. At the same time, high temperature will cause the nozzle temperature rise, the nozzle stability can’t guarantee during the combustion process [3-6].
The method of oil treatment can minimize the impact of oil products on the units[7]. Hu analyzed different requirements of heavy oil fuel in peak-regulating gas turbine power plant, the working principle and effect of the oil treatment unit are introduced and pointed out that optimizing the operation mode of the heavy oil treatment unit[8]. Micro porous molecular sieves are investigated as effective, environmentally safe and cost effective materials for purification of lubricants in late stages of oxidation. Molecular sieves have high selectivity to oxidation products and do not affect additives in oxidized oil, so that the purification degree can reach more than 90%. The effects of temperature, treatment time, solid content and oil type on the treatment effect were investigated[9]. Micro porous molecular sieve crystals with the character of micro porous structure and selectivity are used to
remove oxidation products in the fluid. The quality indexes of oil were kept in high standard with molecular sieve during the power plant operation[10].

Heavy oil has poor fluidity and difficulty combustion during storage and transportation as fuel oil. Therefore, the commonly adopted technology is based on the solvent effect of non-polar solvents when using heavy oil as fuel oil. Its fluidity and combustibility are seriously deteriorated, as molecular agglomeration of aldehydes, ketones and carboxylic acids for long-term storage[11-13]. The principle of polar adsorption to polymerize and separate polar substances such as aldehydes, ketones in this paper, and carboxylic acids change the viscosity and ignition point and improve combustion characteristics and fluidity performance.

2. Degradation mechanism and analysis

The experiment using heavy oil is residual fuel oil with high viscosity, density, impurities and metal content. It is easy to block the delivery pipeline, pump and fuel nozzle. Asphaltene is major component polar substance in heavy oil, and it is also the main factor of high viscosity and difficult to burn. Therefore, the content of asphaltene in oil firstly measured in the laboratory.

2.1. Influence mechanism and analysis of fluidity

Kinds of literature and experiments confirmed that these polar substances are mostly asphaltene, which physical and chemical properties and structure are closely related to the viscosity of heavy oil, and their existence can easily cause precipitation of heavy oil [14].

The difficulty lies in improving the fluidity and reducing the polar flame-retardant components. It is generally impossible to decompose the asphaltene under normal temperature and pressure because of the unique properties. Therefore, the simplest and most economical way is separating the asphaltene from heavy oil in industrial applications. The laboratory generally uses normal alkanes separate asphaltene from heavy oil.

The analysis of heavy oil showed that the viscosity at 100°C was 18.7mm²/s, which exceeded the limit of 14.9mm²/s specified in the standard by 25.6%. The result showing that its asphaltene content is high and the molecules are tightly aggregated.

2.2. Influence mechanism and analysis of combustibility

The combustion performance varies greatly due to the different element content of the oil. The main combustion indicators are calorific value, insoluble matter and ash, and the experiment carried out accordingly.

1) Rotating disk electrode atomic emission spectrometry was used to detect the content of heavy oil elements. The results are shown in Table 1.

| Elements Value (mg/kg) | Ag  | Al  | B   | Ba  | Ca  | Cd  | Cr  | Cu  | Fe  | K   | Li  | Mg  |
|-----------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Ag                    | 0   | 380.38 | 0.39 | 0.49 | 5084 | 1.64 | 0.52 | 0.16 | 30.82 | 9.67 | 0.14 | 41.58 |
| Mn                    | 0   | 5.09 | 98.15 | 0   | 2663 | 1.36 | 0   | 16.47 | 0   | 0.80 | 0.33 | 3.85 |

Table 1 shows that the aluminium content is 380.38 mg/kg, the calcium content is 5084 mg/kg. The iron content is 30.82 mg/kg, the magnesium content is 41.58 mg/kg, the sodium content is 98.15 mg/kg and the phosphorus content is 2663 mg/kg. The high content of metal elements such as aluminium, iron, magnesium, and sodium in the original heavy oil seriously affect the combustion performance of the heavy oil. These elements exist in various forms in heavy oil, including both organic and inorganic compounds. They will react with the anti-oxidation protective layer of the inner wall to form a certain amount of eutectic materials, when a part of metal elements are burned in the combustion chamber. The protective layer of the inner wall of the combustion chamber will be
dissolved and the corrosion of the inner wall will be accelerated, while the melting point is higher than the eutectic point. Other metals exist in the form of complexes in the heavy oil, and inorganic substances such as silicon and phosphorus exist in the heavy oil as heterocyclic compounds, which are polymerized with asphaltene and other components. These compounds cause difficulty and incomplete combustion of heavy oil.

2) After adding the heavy oil to diesel in proportion to dilute, the insoluble matter was tested by quantitative filter paper filtration method, and the insoluble matter accounted for 28.03%. The calorific value of heavy oil was 8712Kcal/kg using the calorific value test method of the cartridge, and the water content was 7% tested by the method rotary distillation. The insoluble matter was calcined in a horse boiling furnace at 400°C for 3 hours, the ash content in the insoluble matter was 84.42%, and the ash content in the heavy oil was calculated to be 23%. The composition was conducted by energy dispersive spectrum analysis method, shown in Figure 1 and Table 2.

![Figure 1: Energy dispersive energy spectrum analysis](image)

**Table 2. Energy dispersive energy spectrum test results**

|        | C     | O     | Al    | Si    | P     | S     | Ca    | Fe    | Ni    | La    | Total |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| spectrum 1 | 22.11 | 41.59 | 16.01 | 14.74 | 0.54  | 1.13  | 1.22  | 1.04  | 0.52  | 1.11  | 100.00|
| spectrum 2 | 28.84 | 56.85 | 5.84  | 5.05  | 0.09  | 1.95  | 0.58  | 0.78  |       |       | 100.00|
| spectrum 3 | 30.62 | 54.24 | 5.92  | 5.63  | 0.28  | 2.61  | 0.69  |       |       |       | 100.00|
| spectrum 4 | 15.21 | 38.68 | 19.32 | 19.04 | 0.72  | 1.41  | 1.77  | 1.81  | 0.52  | 1.53  | 100.00|
| spectrum 5 | 27.03 | 50.20 | 9.25  | 8.36  | 0.32  | 2.05  | 0.92  | 1.13  |       | 0.74  | 100.00|
| MAX      | 30.62 | 56.85 | 19.32 | 19.04 | 0.72  | 2.61  | 1.77  | 1.81  | 0.52  | 0.74  |       |
| MIN      | 15.21 | 38.68 | 5.84  | 5.05  | 0.09  | 1.13  | 0.58  | 0.78  | 0.52  | 0.74  |       |

The results show that the remaining materials are mainly metals and some incompletely burned inorganic substances. Heavy oil with high metal content has active electrochemical properties, which will greatly reduce the stability of oil. Ash from heavy oil combustion will also deposit on the pipe wall, boiler heating surface and other equipment, which will reduce the efficiency of heat exchanger. Aluminium and silicon usually remain in the residual oil as catalyst powder, and the oxides of aluminium and silicon are hard and easy to wear the combustion equipment.

After washing the heavy oil with petroleum ether, toluene and acetone, the purified product is obtained. Then, the crystalline structure was studied by X-ray diffraction; the result is shown in Figure 2.
By comparing the XRD results of heavy oil before and after purification, it can be seen that the characteristic peak representing asphaltene aromatic hydrocarbon appears at 25.7°. This peak represents the stacking structure of aromatic lamellae, which is consistent with the characteristic peaks reported about asphaltene, and the peak generally appears at 24~26°. The peak height of purified asphaltene is far lower than the original peak height, which indicates that the asphaltene content in heavy oil is obviously reduced.

It can be known by the above analysis, that heavy oil contains more insoluble matter, moisture and metal substances, which leads to a serious decrease of calorimetry and poor fluidity of heavy oil. The main reason for the deterioration is that the accumulation of polar substances in asphaltene and the agglomeration reaction occurs due to long-term storage causes in the oil[15]. In this experiment, diesel oil is chosen as the solvent to separate asphaltene.

3. Heavy oil recovery experiment and analysis

3.1. Non-polar solvent experiment

3.1.1. Experiment of non-polar solvents sorts. The non-polar components were diluted by adding n-heptane, petroleum ether and diesel oil in a 1:1 ratio. The viscosity of the mixture significantly reduced, and the flash point was also tested after dilution, the result shows in table 3.

| Solvents | N-heptane (mm²/s) | Petroleum ether | Diesel |
|----------|-------------------|----------------|--------|
| Viscosity | 8.1               | 6.7            | 11.2   |
| Flash point | 47               | 30             | 89     |

It can be seen from Table 3 that the viscosity of mixture has been greatly improved. The n-heptane can improve the viscosity and flash point in a certain extent and the petroleum ether can decrease the viscosity and flash point reduce to 30 °C enormously. The diesel appropriately improves the viscosity and flash point and the results meet the requirements of heavy oil operation standard.

3.1.2. Experiment of non-polar solvents amounts. The addition amount of diesel was further verified to ensure a higher flash point while reducing the viscosity, for determining the optimal addition amount of diesel. The experiment of diesel ratio was taken, the result is shown in table 4.
Table 4. The diesel ratio test results

| Ratio (heavy oil: diesel) | Viscosity (mm²/s) | Flash point (°C) |
|--------------------------|-------------------|-----------------|
| 9:1                      | 17.1              | 230             |
| 8:2                      | 16.0              | 180             |
| 7:3                      | 14.7              | 150             |
| 6:4                      | 13.2              | 106             |
| 5:5                      | 11.2              | 89              |

It can be seen from Table 4 that the viscosity and flash point are decreasing with the increasing ratio of diesel. The viscosity of heavy oil is improved and the flash point requirement can achieve the requirements under the ratio of 7:3.

3.1.3. Experiment of polar substances separates using strong polar adsorption. The molecular sieve is a carrier for the strong polar molecular adsorbent, ion exchange is carried out with rare earth metals, and sodium ions are substituted by multivalent ions, the molecular sieve's properties have been dramatically changed. The heavy oil that changes the height of the internal space and generates static electricity is composed of asphaltene polar compounds, which have a conductive dipole moment and are easily absorbed by strong polar molecular adsorbents[10].

In this paper, a strong polar adsorbent developed by ourselves is used to filter the diluted oil, which can remove the polar substances effectively, improve the storage and transportation stability. The experiment was taken for the recovery oil after filtering with a strong polar adsorbent. The insoluble matter is almost purification and the proportion is 0.83% which is about 3 percent in the recovery oil comparing 28.03% in the original oil. The calorific value is 9721Kcal/kg which increases 12 percent in the recovery oil comparing 8712Kcal/kg in the original oil. The moisture content has been largely removed and is only 0.004% and the viscosity has been greatly improved and is 10.3mm²/s of the recovery oil.

Rotating disk electrode atomic emission spectrometry was used to detect the content of recovery oil elements and the results are shown in Table 5.

Table 5. Recovery oil element content

| Elements | Ag (mg/kg) | Al | B | Ba | Ca | Cd | Cr | Cu | Fe | K | Li | Mg |
|----------|------------|----|---|----|----|----|----|----|----|---|----|----|
| Value    | 0.00       | 75.06 | 0.34 | 0.32 | 1056.00 | 0.67 | 0.15 | 0.01 | 6.09 | 1.36 | 0.13 | 6.67 |
|          |            |     |    |    |    |    |    |    |    |    |    |    |
| Elements | Mn | Mo | Na | Ni | P | Pb | Sb | Si | Sn | Ti | V | Zn |
| Value    | 0.00 | 2.19 | 6.64 | 0.00 | 973.40 | 1.61 | 0.00 | 6.77 | 0.00 | 0.00 | 0.16 | 1.24 |

From the above table, the aluminium content is 75.06 mg/kg which is about 20 percent in the recovery oil comparing 380.38 mg/kg in the original oil, and the iron, calcium, magnesium content is also reduced by 80 percent. The sodium content is 6.64 mg/kg in the recovery oil comparing 98.15 mg/kg in the original oil for the reason of the strong polar adsorption principle.

The substances remove effectively with the large specific surface area and high polarity of the strong polar adsorbent. The content of metal elements decreased significantly, the fluidity and combustibility of recovery oil have been greatly improved.

4. Conclusion

1) The polar substances causes heavy oil has high viscosity and spontaneous combustion point. The mechanical impurities and inorganic substances exist in polymerized with asphaltene and other components cause difficulty and incomplete combustion of heavy oil.
2) The diesel can improve fluidity and combustion performance in appropriate proportion. The strong polar adsorbent can eliminate the polar substances in the filtrate of heavy oil. The tendency of polar substances to accumulate and settle is avoided and the stability is improved with the polar material removal.

References
[1] Ghanavati M J, Ramazani A S A. (2013) Effects of asphaltene content and temperature on viscosity of Iranian heavy crude oil: Experimental and modelling study. J. Energy & Fuels, 12: 7217-7232.
[2] Doust A M, Rahimi M, Feyzi M. (2015) Effects of solvent addition and ultrasound waves on viscosity reduction of residue fuel oil. J. Chemical Engineering and Processing: Process Intensification, 95:353-361.
[3] Walter Knecht. (2008) Diesel engine development in view of reduced emission standards. J. Energy, 2: 264-271.
[4] Jana Moldanova, Erik Fridell, Olga Popovicheva, etc. (2009) Characters of particulate matter and gaseous emissions from a large ship diesel engine. J. Atmospheric Environment, 43: 2632-2641.
[5] WANG Xiaoyu, SONG Tianmin. (2009) Heavy Oil Viscosity Methods. J. Hebei Chemical Engineering and Industry, 11:2-3.
[6] Zhao Jie. (2019) Analysis of Viscosity Reduction Production and Gathering and Transportation Technology in Offshore Heavy Oil Field. J. Petrochemical Industry Technology, 10:1-6
[7] Miao Yong Chao. (2014) Study on the Physical and Chemical Properties of Heavy Oil with Dimethyl Ether and its Emission Characteristic. D. Ningbo University, 4:3-7
[8] Hu Yanli. (2011) Practice of Heavy Fuel Oil Treatment for Gas Turbine Power Plant. J. Power Equipment, 4: 268-270.
[9] Gerardo Majano, Svetlana Mintova. (2010) Mineral oil regeneration using selective molecular sieves as sorbents. J. Chemosphere, 5: 591-598.
[10] Jinwei Tang, Yefeng Li, Yonglou Liu, et al. (2016) Regeneration of used turbine oils using molecular sieves as sorbents. J. Petroleum Science and Technology, 10:1462-1467.
[11] Luo P, Gu Y. (2007) Effects of asphaltene content on the heavy oil viscosity at different temperatures. J. Fuel, 7:1069-1078.
[12] Fan H F, Li Z B, Liang T. (2007) Experimental study on using ionic liquids to upgrade heavy oil. J. Journal of Fuel Chemical & Technology, 1:32-35.
[13] Fan Z X, Wang T F, He Y H. (2009) Upgrading and viscosity reducing of heavy oils by BMIM AICl4 ionic liquid. J. Journal of Fuel chemical & Technology, 6: 690-693.
[14] Min Lingyuan. (2006) Potential hazards of oilfield development-asphaltene deposition. J. Science and Technology Information Development and Economics, 22:177-178.
[15] Ding Zhimin. (2009) Study on mixed phase separation behaviour of cracked heavy oil from residuum blending. China University of Petroleum, 6:1-14.