Oil relations between China and Russia- Electrochemical Behavior of organic sulfur compounds

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Abstract. The main purpose of this paper is that the demonstration fuel electrochemical hydrogenation desulfurization method is feasible. First, many sulfur compounds in fuels are summarized as thiophene, which is a typical representative of materials. Then, analyze and judge the reaction mechanism of thiophene electrochemical hydrogenation desulfurization. Furthermore, typical of this oil in the thiophene sulfur compounds the reaction mechanism, by analogy, that the electrochemical hydrogenation of oil desulfurization method is feasible.

1. Sulfur compounds in coal and petroleum products
Sulphur exists widely in coal and oil, but the sulfur content in different coal and oil varies greatly due to different producing areas and mining periods. The difference varies from hundreds of ppm to tens of thousands of ppm. The distribution of sulfur in coal and petroleum is not uniform. In petroleum, for example, the content of sulfur increases with the increase of boiling range. The highest sulfur content is vacuum residue, 70% of the sulfur in the oil concentrated in vacuum residue, and the lowest sulfur content is gasoline fraction.

Thiophene, mercaptan, disulfide and thioether are the main sulfur-containing compounds in coal and petroleum, in addition to a small number of sulfones and sulfoxides containing both sulfur and oxygen.

The performance of oil is affected by the sulfur compounds contained in the oil, which is harmful in many aspects. For example, in the process of raw oil transportation, storage and production, metal equipment will be corroded by sulfur compounds; sulfur dioxide as the tail gas of fuel combustion into the atmosphere, will cause environmental hazards such as acid rain, increase environmental costs; sulfur compounds as impurities, is likely to poison the catalyst used in the production reaction.

In addition, high temperature and high pressure are often used in coal and petroleum processing, the thermal stability of sulfur compounds in the process of processing is a major factor affecting the product, so it is necessary to consider its content in coal and petroleum. It is known that the thermal stability of sulfur compounds in coal and petroleum varies greatly due to their different molecular structures and chemical properties. Among them, thiophene has the highest decomposition temperature, up to 800 ~ 900 °C, followed by sulfides, up to 400 °C, and the lowest sulfur compounds, which can be decomposed at about 200 °C. Because the bond energy of C-C bond is much larger than that of C-S bond, the C-S bond breaks more easily under heating than that of C-C bond.
Taking mercaptan as an example, it is easy to decompose into olefin and H2S under heating conditions. Moreover, the greater the molecular weight, the lower the thermal stability of thiols. The thermal stability of mercaptan with different structure is different because of the shielding of SH group in the molecule. The thermal stability of mercaptan with tertiary mercaptan is higher than secondary mercaptan and tertiary mercaptan is higher than primary mercaptan.

Sulfides can be classified into aryl sulfides, cyclic sulfides and alkyl sulfides according to their structural differences in coal and petroleum. Most of them are prone to thermal decomposition reaction, and their products are mainly unsaturated hydrocarbons and H2S.

Thiophene ring is an aromatic conjugated system, so its thermal stability is very high, in general, the ring itself is not easy to break, containing thiophene derivatives in heavier fractions, and mostly belong to benzothiophene, dibenzothiophene and naphthalene thiophene, but also with substituents.

2. Low temperature coal tar low temperature electrolysis hydrogenation

2.1. Properties of coal tar at low temperature
The liquid products obtained from coal carbonization at 500~700 °C are called low temperature coal tar. The difference between low temperature coal tar and high temperature coal tar lies in the fact that there are more saturated hydrocarbons and olefins and less non-substituted low-grade aromatic hydrocarbons. Moreover, there are many kinds of compounds in low temperature coal tar, but the content of each substance is not high. The presence of high boiling phenols and other compounds has increased the proportion of acidic substances in low temperature coal tar. The preparation of fuel oil from low temperature coal tar is simple, mainly through separate distillation. However, because there are many kinds of compounds in low-temperature coal tar, unsaturated compounds will be oxidized by oxygen in the air after long-term exposure to air, resulting in quality changes. Moreover, as a fuel oil, low-temperature coal tar contains a large number of sulfur compounds which will cause serious corrosion to pipeline equipment.

Therefore, it is necessary to hydrogenate low-temperature coal tar to increase - H content and remove heteroatoms by reduction to improve the quality of oil.

2.2. Traditional method of low temperature coal tar upgrading by hydrogenation
Traditionally, hydrocracking and catalytic hydrocracking processes are used for low temperature coal tar upgrading. The advantages of hydrocracking and catalytic hydrocracking technology are mature technology, good effect, can greatly reduce the sulfur content, oil product quality is good. But the shortcomings are also obvious, the reaction process conditions are more harsh, the requirements of high temperature, high pressure environment, high requirements for reaction equipment and operating costs. Sometimes catalysts are needed to provide catalysis for the reaction, or hydrogen is provided as a hydrogen source, increasing the cost of production.

2.3. Electrochemical method for low temperature coal tar upgrading by hydrogenation
Because the traditional low temperature coal tar hydrogenation upgrading conditions are demanding. Therefore, the electrochemical electrolysis hydrogenation technology can only be carried out under mild conditions, with obvious advantages. The electrochemical method consumes less substances, produces more easily controlled side reactions, requires less equipment, simplifies the mixing separation process of raw materials and products, and reduces pollution. Electrolytic hydrogenation technology can make the hydrogenation of organic matter proceed under mild conditions. The reaction can be controlled and the selectivity of the reaction can be improved by changing the electrode potential. At present, in the production of many special chemical products and fine chemical products, electrolytic hydrogenation technology has been successfully applied [1.2].
2.4. Experimental analysis of electrochemical method for low temperature coal tar upgrading by hydrogenation.

The suitable system for electrolytic hydrogenation of tar is DMF as solvent, ethanol as cosolvent, water as H+, Bu4NBr as supporting electrolyte and Pb as cathode.

The reason for choosing Pb as electrode material is that when Pb is used as cathode, dihydro and tetrahydro compounds are formed in Tar by hydrogenation, and olefin components are completely hydrogenated saturated. However, 87% of phenanthrene and anthracene were converted into dihydro compounds, and the decrease of fluorene oxide and methylphenanthrene was significant, which indicated that Pb electrode had excellent hydrogenation ability as cathode.

Experiments show that tetrabutylammonium bromide (Bu4NBr) can be used as a good supporting electrolyte in the electrolytic hydrogenation system. Bu4NBr has good surface activity and is a good phase transfer catalyst. The electrolyte in the system is homogeneous.

When N, N-dimethylformamide (DMF) was used as solvent, the hydrogenation reaction of tar was more remarkable, and the electrolytic potential of tar was higher than that of SCE.

Fig 1. and Fig 2. show current-potential curves using N, N-dimethylformamide (DMF) and acetonitrile as solvents, respectively.

![Fig. 1 current potential curves of tar electrolysis in acetonitrile system](image)

![Fig. 2 current potential curves of tar electrolysis in DMF system.](image)

The cosolvent and proton donor in the system are ethanol and water [3~5] respectively.

An important characteristic of the system is water as a proton donor. Under the influence of water concentration, when the water concentration is too low, the system lacks enough H+, and excessive oxygen brought in by the water concentration is too high will inhibit the reduction hydrogenation reaction.

Fig. 3 is a curve showing the effect of water concentration on the conversion of tar to electrolysis.
3. Conclusion.

As a supporting electrolyte, the concentration of Bu4NBr will affect the properties of the double layer structure on the electrode surface and the conductivity of the electrolytic system, thus, it will also affect the hydrogenation process of tar components. When the concentration of Bu4NBr is too high, the supporting electrolyte covers the electrode surface, which reduces the contact opportunity between the electrode and tar, thus affecting the tar hydrogenation reaction and reducing the hydrogenation conversion.

The reaction temperature also has an effect on the electrolysis effect, which is mainly reflected in the influence on the electrode surface double layer structure, mass transfer and electrolysis reaction. The reaction temperature should not be too high or too low. Too high, there are surplus polymerization products. So, the reaction temperature of the electrolysis system should be between 30 and 33 degrees C. then the reaction of tar hydrogenation will be the best.

Therefore, electrolysis hydrogenation provides a low temperature and atmospheric pressure way for tar processing. The content of fatty hydrogen and H/C atomic ratio of tar can be increased by choosing suitable electrolytic system and optimum reaction process.

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