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Research Progress of Intensified Vacuum Distillation for Crude Oil

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***Abstract*—With the increasing tendency of heavy and inferior crude oil and the maturity of high viscosity and high density crude oil recovery technology, the proportion of refined heavy crude oil will be larger and larger. Adding a certain amount of intensifier in crude oil to improve crude processing conditions, enhance the degree of crude distillation, and improve the total extraction rate of crude oil is a very important research topic in the world oil refining industry. It is an important foundation for developing deep processing technology and technology of crude oil and making full use of limited oil resources.**

Keywords—crude oil; distillation; intensified agents; application

I. INTRODUCTION

With the gradual reduction of petroleum resources in China, in order to make up for the decline of the output of old oilfields, the major oilfields are exploiting heavy heavy oil in succession, so it is particularly important for the entire oil refining industry to make full use of the limited petroleum resources reasonably. At present, refineries are facing a series of problems, such as shortage of crude oil, increasing proportion of heavy oil and increasing demand for light oil. These problems have become the bottleneck restricting the survival and development of refineries in China. How to improve the yield of light oil has become a common concern of refineries[1]. In order to solve this contradiction, it is necessary to adopt economical and effective methods to improve the yield of light oil on the premise of guaranteeing the quality of oil. After adding intensifier into heavy oil, the system state can be changed, the intermolecular interaction in the heavy oil dispersion system can be adjusted, and the low molecular hydrocarbons in the solvent shell can be released into the distillate oil to improve the yield of light oil. The traditional refining process is based on the theory that petroleum is a molecular solution. It is assumed that the macrophase and composition of raw materials are only related to the properties of the solution, and only the relative volatility is considered, while the heterogeneity of petroleum is ignored. In order to improve the yield of distilled products, it can only be achieved by increasing distillation efficiency. Under the influence of this theory, people mainly devote themselves to improving the internal components of the unit, optimizing the operating conditions, improving the vacuum system and adopting advanced control systems to improve the distillation efficiency and crude oil distillation extraction rate, but all of these require large capital investment, and because these technologies are increasingly perfect and developed. The potential of using these means to increase the extraction rate is gradually decreasing[2]. Therefore, people began to shift the focus of research to try to find a material that can activate the crude oil system, through the activation of crude oil to achieve the purpose of increasing the extraction rate, based on this idea enhanced distillation technology has been developed. In the process of crude distillation, complex structural units are formed in the system, whose nuclei are associative colloids or bubbles, and their proportions depend on the properties and proportions of high and low molecular compounds in heavy oil. The natural surfactant in the material forms a solvation layer, which makes the dispersed phase and the dispersed medium in a relatively balanced state. The purpose of adding a fortifier when distilling crude oil is to change this equilibrium. Generally speaking, the composition of components in the system will not be in the best state (i. E. activation state), that is, will not be in the state of the highest gas phase yield of distillation, additive enhanced crude distillation has great potential. From the point of view that petroleum is a colloid dispersion system, it is a convenient and economical method to increase the yield of light oil by adding intensifier and intensifying crude distillation in the process of petroleum processing. Intensified distillation with intensifier can improve the extraction rate, mainly because the intensifier changes the characteristics of residue dispersion system, so that the "complex structure unit" of associating colloid is in the extreme state with the smallest nuclear radius, shielding the effect of the adsorption force field of associating colloid.

II. STRENGTHENING MECHANISM

The new technology of intensifying crude distillation and improving light oil distillation with activator was developed on the basis of "adjustable phase transition theory". The mechanism of action of distillation intensifier can be divided into colloid structure mechanism, surface tension mechanism and polymerization inhibition mechanism[3]. In practice, it can be used to optimize or prepare activator with reasonable structure and good performance, and to control the size and physicochemical properties of "complex structural unit" to improve the yield of light oil. The mechanism of colloidal structure was developed on the basis of the theoretical basis put forward by the former Soviet Union researchers, and was quoted by many researchers at home and abroad[4]. However, there are still some problems in the strengthening mechanism: (1) The strengthening mechanism of heavy oil distillation process is unclear, and the results obtained from different raw materials are different, which brings great difficulties to the screening of strengthening additives. (2) domestic experimental research mostly adopts gradual gasification device, such as en's distillation and real boiling point distillation. This is very

different from the continuous gasification in industry, so the results and conclusions are difficult to be applied in industry, and can not be compared under the same temperature and vacuum conditions. (3) the error of domestic experimental results is large, and the reliability of the results is questionable. (4) In the past, petroleum by-products were used as intensifying additives in intensified crude oil distillation at home and abroad. The large amount of oil by-products (a few percent of the raw materials) increased the load of processing units, and brought about problems such as transportation and storage, and reduced unit capacity. In view of the above problems, it is necessary to study the strengthening mechanism of crude distillation process more deeply, so as to guide the selection of strengthening additives[5].

III. Composition Design of Distillation Intensifier

According to the mechanism of enhanced crude distillation, the intensifier can be designed to be composed of the following components and their complexes: surface tension reduction component, colloid structure modification component, free radical inhibition component and solubility adjustment component. The design principles of strengthening agents can be summarized as follows: (1) taking into account the surface activity and dispersion of strengthening agents; (2) increasing the interfacial tension of colloidal structure and reducing the surface tension of bubbles; (3) solving the compatibility of components; (4) not affecting the performance of subsequent processing and final products. Theoretically, the optimum composition and molecular structure of intensified distillation additives can be designed by determining the chemical composition, physical composition or various physical and chemical macroscopic properties of distillation raw materials and conducting molecular or colloid thermodynamic calculations. Up to now, the main types of distillation intensifiers have been used as follows: (1) aromatic hydrocarbon concentrates, such as lube base oil refining extracts, cracking tars, catalytic cracking and refining oils, slurries, furfural extracts and other components rich in aromatic hydrocarbons; (2) surface active substances, such as C12-C14 and C16-C20 higher fatty alcohols, synthetic fats, etc. Fatty acids, etc. (3) Composite activator, such as aromatic hydrocarbon concentrate with trace phenol or polymer and silicone oil mixture; 4) Synthesis of polymer. The addition of distillation intensifier in crude oil can counteract the excess surface tension and release low molecular hydrocarbons from the system, which is activated. However, the amount of reinforcement is limited, and the excessive addition will lead to the association of the reinforcement molecules and reduce the extraction rate of crude oil. Because there are many factors affecting the activation state of petroleum dispersion system, the most basic method to determine the activation state is still in the determined state, using experimental methods to determine the amount of reinforcement and process parameters. At present, there are several commonly used methods to determine the activation state of petroleum dispersions: (1) stability coefficient method; (2) resistance drop method; (3) viscosity measurement method; (4) particle diameter method.

IV. Application of Intensified Distillation Intensifier

Overseas research has developed from the use of a single aromatic-rich activator to the use of higher fatty alcohols and other surfactants, from laboratory research to industrial applications. Among them, intensified atmospheric and vacuum distillation and nhanced catalytic cracking have been carried out in industrial experiments. A commercial test was carried out in Xinwufa Refinery of the former Soviet Union, in which heavy aromatics accounted for 32.6% of the total aromatics and 74.9% of the total aromatics were mixed with heavy oil in front of the vacuum furnace. The process parameters were stable and no different from conventional distillation. The extraction rate of vacuum distillation increases by 7.7% (relative feed) or 4.3% (relative crude oil) When the extraction oil is added to 2.5% (feed), the drawing rate of wax oil will increase by 3.6% (for waxy oil)[8]. Generally speaking, in order to improve the yield of light fraction oil, 5-6.0% activator is added, and the extraction rate can be increased by 2-17% without affecting the properties and quality of the oil. The earliest research on intensified distillation in China was carried out in Guangdong Petrochemical College, followed by Daqing Petroleum Institute, East China University of Technology, Petroleum University, Zhejiang University, Liaoyang Petrochemical College and the Refining Research Institute of Luoyang Petrochemical Engineering Company, as well as the major domestic refineries. Several types of intensified distillation activators have been developed, such as composite activators, small molecule aliphatic alcohols, fatty acids and synthetic polymers. In 1987, Guangdong Petrochemical College added 2% VF4 to Daqing crude oil and Daqing atmospheric residue whose boiling point was higher than 30 C for intensified distillation. The results showed that the total extraction rate of crude oil increased by 4.7% (to crude oil) and the total extraction rate of atmospheric heavy oil increased by 4.5% (to crude oil). The results also show that the increased fractions of crude oil and atmospheric heavy oil after intensified distillation are light fractions latent in crude oil or atmospheric heavy oil, and the properties of the fractions remain unchanged[9]. The East China University of Science and Technology, in cooperation with the Research Institute of Qilu Petrochemical Company, carried out two industrial tests of intensified distillation in the first atmospheric and vacuum distillation unit of Shengli Refinery of Qilu Petrochemical Company from April to May and November 1996. The activator is a surfactant containing c, H and O. The activator contains no metal ions and is called acid-base neutral and chemical. Inertia is only 50ppm. The results show that the yield of vacuum distillate can be increased by 1% and 2.4%, and the color of vacuum distillate can be lightened and the quality can be improved[10]. The intensified distillation of Xinjiang crude oil was studied in Zhejiang University using high molecular polymer as activator. The results showed that adding a small amount of polymer active additives could increase the yield of Distillate by 3 percentage points[11]. The intensified distillation experiments of Daqing crude oil with up to 10 activators were carried out in Petroleum University. The results show that the total extraction rate of the intensified Daqing crude oil can be increased by 1-2 percentage points under the condition that the operation conditions and production quality of the production unit are basically

unchanged[12]. The research results at home and abroad show that the activator is not only beneficial to atmospheric and vacuum distillation units, but also has a positive impact on the followup production. If activator is used in catalytic cracking, coke yield and selectivity can be reduced. In addition, it is also possible to be used in other fields, such as reducing the thermal decomposition temperature, changing the decomposition rate constant, reducing the coking of delayed coke oven tubes and improving the lube oil refining yield. Deep drawing of crude oil and atmospheric residue also reduces the processing load of oxidized asphalt and delayed coking, and is beneficial to improving the quality of asphalt and needle coke.

V. Existing Problems and Development Trend

The development trend of intensified distillation of crude oil is as follows: (1) Laboratory research on intensified distillation has made great achievements, but there are still many problems in its industrial application. In the future, we should continue to deepen the study of its activation mechanism, and at the same time, strengthen the study and discussion of chemical engineering in the process of industrialization. (2) The research and development of intensified distillation activator has changed from blindly screening stage in laboratory to exploring its intrinsic activation mechanism and guiding the development of new activator. (3) As the intensified distillation activator has a positive effect on atmospheric and vacuum distillation and its subsequent processing, the intensified distillation technology will develop from intensifying atmospheric and vacuum distillation only to intensifying atmospheric and vacuum distillation, catalytic cracking, delayed coking and other processes simultaneously. (4) Selecting more effective experimental equipment and methods, using excellent computer simulation software to simulate the operation of the unit before and after dosing, strengthening the prediction and evaluation of light oil potential content in crude oil or residue, further clarifying the application potential of intensified distillation with activator, and improving the evaluation of intensification effect. The accuracy will provide reliable guidance for industrial application. (5) On the basis of the study of strengthening mechanism, more attention should be paid to non-aromatic hydrocarbon-rich activators, especially those with strong interaction with crude oil or residue components, high activity and good stability.

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