Main challenges in demulsifier research and application

Fusheng Zhang¹, Guoliang Liu, Junhan Ma, Jian Ouyang, Xiaoling Yi and Huimin Su
Research Institute of Petroleum Exploration and Development, PetroChina, Beijing, China
E-mail: zhfsh@petrochina.com.cn

Abstract. Main challenges in demulsifier research, such as demulsification of ASP flooding produced liquid, demulsification of heavy oil produced liquid, low temperature demulsification and fast demulsification, are summarized. Some importance technology routes to solve the challenges are proposed according to demulsification mechanisms and emulsion characteristics. The proposed routes include increasing aromaticity, molecular weight and branch degree of demulsifiers, and introducing double-function groups to demulsifiers for W/O and O/W emulsions, or groups with alkyl matching with alkyl carbon number of the crude oil into demulsifier molecule. The demulsification mechanisms of the above-mentioned research routes are described in detail.

1. Introduction
Main methods of demulsification and dehydration for the produced liquid include heat method, electrical method and heat chemical method. Demulsifiers with many structures have been developed according to different characteristics of the various produced liquids, and resolved preferably separation of oil and water. But new problems are continually arising along with the rapid development of petroleum industry, such as: (1) Water cut of the produced liquid from old fields in middle and later stages is higher than 90%. ASP flooding technology [1] has been extensively used and has made better effects on the increasing oil production and decreasing water cut, but the produced liquids are very stable and more difficult to demulsify and dehydrate; (2) With more attention being paid to the exploitation of heavy oil [2], sophisticated stimulation technologies including steam flooding, steam soaking, alkaline flooding and polymer flooding have enhanced oil recovery. However, the application of these technologies leads to the formation of more stable emulsions which makes demulsification or dehydration more difficult; (3) Heating or enhancing temperature of the produced liquid can improve the efficiency of oil-water separation [3]; but enormous energy is wasted. As saving energy is strengthening in oil fields now, many oil fields are in dire need of low temperature demulsification; (4) The production of offshore oil field arises greatly. Due to small oil-water separation tanks, oil and water must be separated in short time so as to meet the production demand. The offshore oil fields are in dire need of the demulsifiers for fast demulsification. Existing demulsifiers can hardly meet the demand of above-mentioned problems, so more severe requirements for demulsifiers are proposed and more application prospects are provided. Much research has been performed and some progresses have been made, although there are still many problems remained unresolved.
2. Demulsification of ASP flooding produced liquid

With the production of oil field being into middle and late stages, water cut in the produced liquid is increasing but production of crude oil is decreasing year by year. The application of chemical flooding technologies (including polymer flooding, surfactant flooding, binary combination flooding, ASP flooding) for enhanced oil recovery has gradually become one of the key technologies to sustainable development of oil fields. So far, polymer flooding technology has been applied in large-scale, pilot test of ASP (alkali/surfactant/polymer) flooding technologies has achieved good results on increasing-oil and decreasing-water, but the emulsion of produced liquid is very stable and difficult to demulsify.

The test of polymer flooding and ASP flooding in Daqing oilfield showed the following three problems: (1) Middle emulsion layer is thick in sedimentation tank; (2) Oil content in sewage is high (up to 3000mg/L) and cannot meet the requirement for the water reinjected; (3) The electric dehydrator is not stable and easily crushed. The above-mentioned problems will become increasingly prominent with the popularization and implementation of ASP flooding technology, and will be an important factor to restrict the application of chemical flooding technology.

2.1. Composition and emulsion state of produced liquid

There are big differences between composition and properties of produced fluid from early stage of oil field development (water flooding) and late stage (chemical flooding, such as polymer flooding and ASPA flooding): ① The produced fluids contain oil displacement agents such as alkali, polymers and surfactants; ② The content of heavy component (asphaltene and resin) from chemical flooding is higher than that from water flooding because chemical flooding can drive heavy oil (asphaltene and resin) firmly adsorbed on the rock surface; ③ Since the viscosity of produced liquid increases and the liquid carries solid particles (mechanical impurities, clay, fine sand and asphalt), content of the above-mentioned composition is higher.

The emulsion state of the produced liquid from water flooding compared with chemical flooding, has a qualitative change: emulsion state changes from W/O in early stage to O/W, W/O, and complex multiple emulsion (W/O/W, O/W/O) coexisting in the produced liquid at the same time, especially the produced fluid contains a large number of small O/W emulsion droplets which are very difficult to coalesce and separate.

2.2. Research routes

2.2.1. Study of demulsification mechanism. It is necessary to intensively study the mechanisms of complex emulsion formation and demulsification from produced liquid in ASP flooding to provide theoretical guidance for the design and synthesis of demulsifier. It is also necessary to study the influence of these changes on emulsion state, emulsion structure and emulsion stability because the composition of produced liquid between ASP flooding and water flooding is greatly changed.

2.2.2. Study of the dual-function demulsifiers. The emulsion structure of ASP flooding produced liquid in which O/W, W/O and multiple emulsion coexist, is very complex, so demulsifier of dual-function emulsion, which can meet demulsification of both O/W emulsion and W/O emulsion at the same time, could be designed and studied. There are two roles for these demulsifiers: ① Break W/O emulsion in produced liquid, resulting in water drops coalescence and water cut reduction in oil phase, ② Break the O/W emulsion in produced liquid, resulting in oil drops coalescence and oil cut reduction in water phase.

As we all know, polyether demulsifiers can meet the requirements of W/O demulsification and with coordination of electric dehydration technology, water cut in oil can meet the requirement of crude oil external transportation. Reverse demulsifiers [4] can break O/W emulsion, with coordination of filtration and sedimentation, oil cut in sewage meets the requirement of sewage discharge. The design and syntheses of dual-function demulsifiers which adapt to both W/O and O/W is an effective way to solve the problems of demulsification of the complex produced liquids.
2.2.3. **Increase of demulsifier molecule weight.** In the role of oil displacement agents and other natural emulsifiers and after the pore formation shear for a long time, produced liquid forms the tiny emulsion (W/O and O/W) that is more stable and difficult to break.

According to the demulsification mechanisms and the requirements of efficient demulsifiers, demulsifiers with high molecular weight and branched structure can solve above-mentioned problems. Above-mentioned demulsifiers are unique for the following reasons: ① it can be absorbed simultaneously on the surface of many emulsion droplets, so that the emulsion droplets have more opportunities of collision and coalescence; ② demulsifiers with high molecular weight are easy to form micelles, which can solubilize emulsifiers and lead to emulsion demulsification; ③ the interface film is not tight and low strength after demulsifiers with high molecular weight replace the emulsifiers on the water-oil interfaces.

3. **Demulsification of Heavy Crude**

Heavy oil produced liquid is very stable and difficult to demulsify because it has higher content of asphaltene and resin, higher density and viscosity.Produced liquid becomes more complex after the application of stimulation technology, such as steam soaking, polymer flooding, alkaline flooding and surfactant flooding.

World energy crisis is worsening nowadays. People are paying more attention to heavy crude oil because reserves of good quality oil explored easily are decreasing. Heavy oil production is for about 10% of total crude oil production in China [5], and the demulsification difficulty of produced liquid becomes prominent increasingly with the increase of heavy oil production, so research on special demulsifiers for heavy oil is much important.

3.1. **Composition and physical properties of heavy crude oil**

The nature of some paraffin crude and heavy crude are shown in following table.

| Crude Oil       | Zhongyuan Oilfield | Daqing Oilfield | Liaohe Heavy Oil | Shengli Heavy Oil |
|-----------------|--------------------|-----------------|------------------|-------------------|
| Saturated hydrocarbon /% | 69.5               | 73.2            | 21.4             | 17.7              |
| Aromatics /%      | 23.6               | 15.1            | 22.4             | 23.9              |
| Resin /%          | 6.8                | 10.1            | 51.8             | 54.5              |
| Asphaltene /%     | 0.1                | 1.6             | 4.0              | 3.9               |
| Density /g·cm⁻³   | 0.8509             | 0.8601          | 0.9016           | 0.9926            |
| Pour point /°C    | 33                 | 28              | 24               | 23                |
| Viscosity /mPa·s,50°C | 20                 | 30              | 20420            | 64160             |

Crude oil of Zhongyuan and Daqing is paraffin crude, whose saturated hydrocarbon content is greater than 50% with low density, viscosity and content of asphaltene and resin, and the ratio of asphaltene and saturated hydrocarbon is small. On the contrary, the crude oil of Liaohe and Shengli is asphaltene crude oil.

3.2. **Composition and structure of asphaltene and resin**

Structure and composition of asphaltene and resin have been studied deeply by various analytical methods. The basic structure of asphaltene and resin [6] is a core of fused aromatic ring which is surrounded with several cycloalkanes, aromatic hydrocarbons and heterocycles, and includes several alkane side chains on the ring and groups containing S, N, O (such as -OH, -NH₂, -COOH) and heavy metals complexed (such as Ni, V, Fe) in the molecules.

Because of the basic structure of asphaltene is a plane structure, the force (π-conjugated and the van der Waals force) among the molecule structure of aromatic plane is larger and hydrogen-bonds are easily formed between polar groups (-OH,-NH₂,-COOH). Under the two acting forces, it is easy to form asphaltene particles (3 to 5 fragrance tablets), and then asphaltene particles form micelles by the forces of inter-molecular hydrogen bonding and inter-particle dipole, and at last micelles are interconnected and greater associations are formed [5]. The asphaltenes are in the center of micelles,
and the dispersion media (resin and oil) are adsorbed into both interior and surface of micelles. Components of dispersion medium which have greater molecular weight, stronger aromaticity and stronger polarity are close to the center, while the lighter components are adsorbed around the micelles and transit to the oil phase gradually.

3.3. Influence of asphaltene and resin on the stability of heavy oil emulsion

The substances of heavy crude emulsion film are natural emulsifiers including asphaltene, resin, oil acid soap, wax crystals, carbonates and clay particles [7], among which asphaltene and resin have a greater effect on the stability of emulsion. The higher the content of asphaltene and resin, the more stable the crude oil emulsion is. Because heavy crude has a higher content of asphaltene and resin, its emulsion has higher stability. In addition, asphaltene and resin in heavy oil have strong polarity and adsorb easily impurities, the density contrast of oil and water is very smaller and multiple emulsion is easily formed, the above factors lead to very stable heavy oil emulsion.

The interfacial activity of asphaltene is not very strong with the oil-water interfacial tension of only 25 to 30 mN/m, but it has greater interfacial steric hindrance, so asphaltene has a greater effect on the stability of emulsion [8]. Interfacial film with certain viscoelasticity is formed after asphaltene is adsorbed at the oil-water interface, such interfacial films can withstand higher temperature, higher mechanical strength and higher pressure.

3.4. Research routes

3.4.1. Enhance aromaticity of demulsifiers. Process of demulsification emulsion includes demulsifier infiltrating into the interface, displacing natural emulsifiers in the interface and destroying the interfacial films, emulsified water droplets approaching and coalescing to each other, and water separation from the crude at last. Therefore, the performance of demulsifiers can be improved by enhancing the capability of diffusion in the emulsion, the capability of penetration into the interface film and the capability of replacing and solubilizing emulsifier according to demulsification mechanism.

The higher aromaticity results in demulsifiers having strong ability of diffusion and infiltration in heavy oil, main reasons are that ① heavy oil contains a large number of aromatic substances (such as resin, asphaltene), which resists diffusion of demulsifiers in heavy oil; ② asphaltene and resin are the main substances of heavy oil emulsion film, which has higher strength, and demulsifiers are not easy to penetrate. However, diffusion and infiltration of demulsifiers with higher aromaticity and similar structure with asphaltene and resin, is easier than the ones with non-aromaticity, so the capability of diffusion and infiltration can be improved by increasing the aromaticity of demulsifiers.

The higher the aromaticity degree of emulsifier, stronger it solubilizes interfacial film and reduces the film strength because the activity of film-forming substances (asphaltene and resin) depends on the its state in oil phase [9]. Asphaltene molecule has three state in crude oil: ① single asphaltene molecule is not able to stabilize emulsion; ② micelles can enhance the emulsion stability. The higher the concentration of micelle, the higher the emulsion stability; ③ existing in the form of condensation, asphaltene makes the greatest contribution to the emulsion stability. Therefore, the key of demulsification is to change the state of asphaltene in oil phase, and studies show that the balance of three existing states of asphaltene molecules in crude oil depends on the aromaticity of oil phase [10], oil phase with higher aromaticity has a stronger solubilizing ability to asphaltene by \( \pi \)-bond interactions between aromatic rings, so the film strength is reduced and the effect of demulsification can be improved.

Increasing the aromaticity of demulsifiers can be achieved by enhancing the aromaticity of the initiator of demulsifiers and modification of demulsifiers using aromatic compounds.
3.4.2. Enhance wettability of demulsifiers. The wettability of demulsifier is closely related to their molecular structure. Demulsifiers with a branch structure are not conducive to the association of molecules and the formation of micelles, but to the adsorption of molecules on solid surfaces which changes the wettability of surfaces[11,12]. Because of stronger carrying capability of heavy oil, the content of solid particles, such as asphaltene, paraffin, clay particles, metal salt and mechanical impurities, are high in the interface films of heavy oil emulsion, which increases the stability of emulsion. The enhanced wettability of demulsifiers can promote the demulsifier molecules diffusion to the emulsion droplet and penetrate through the protective layer on the solid particles and adsorb on the surface of the solid particles, because of the change of wettability of the particles surfaces and the decrease of surface energy which can drastically reduce the strength of interfacial films, the interfacial films rupture.

4. Low temperature demulsification
The treatment process of produced liquid commonly used in oilfields is demulsification and electric dehydration technology assisted with necessary heating. To improve demulsification efficiency, it is an effective way to reduce the viscosity of crude oil and enhance the temperature, but a lot of energy is wasted. A large amount of water is injected into the formation in late stage of oil field development, which results in the decline in temperature of produced liquid. To obtain good oil-water separation only by heating produced liquid to raise temperature, once the furnace is stopped, the middle emulsified layer of sedimentation tank will become thicken and the oil cut in sewage will be overproof. In order to save costs, it is generally hoped that the oil-water separation is able to meet the requirements without heating. Therefore, the study of low temperature demulsifier has practical and economic significance.

Methods of demulsifier complex and demulsifier modification are used in order to meet the requirements of low temperature demulsification [13]. For instance, the modification of demulsifiers using unsaturated acids has achieved good effect of demulsification at low temperature.

It is believed that the following technical routes are worth considering. Due to high viscosity of crude oil when temperature is very low, the diffusion rate of demulsifiers is affected. Based on carbon number distribution of crude saturated hydrocarbon and carbon chain length of substituted alkyl on the aromatic ring of asphaltene, adjusting the length of alkyl chain in the demulsifiers structure, can match the number of alkyl chain in demulsifiers with that of crude oil. Thus the hydrophilic and lipophilic keep a certain balance and the demulsifiers have faster diffusion rate in corresponding crude, improving the effect of low temperature demulsification.

5. Fast demulsification
The production of offshore oilfields increases in pace with the rapid development of offshore oil industry year by year. However, it is impossible to build large-capacity processing tanks in the small space of offshore platforms. Improving the efficiency of processing tanks requires fast demulsifiers.

A few reports about fast demulsifiers have been published, one of which is nano-demulsifier [14,15]. Nano-demulsifier is obtained by demulsifiers modification on the surfaces of nanoscale inorganic solid particle to improve its diffusion rate and permeation rate, thus the rate of demulsification is enhanced.

6. Conclusion and Suggest
- Compared with water flooding produced liquid, ASP flooding produced liquid and heavy oil produced liquid have a big difference in the emulsion structure and state and are very difficult to demulsify.
- Demulsification mechanisms of complex emulsion, which can provide fundamental knowledge for the development of new demulsifiers, needs further research.
References

[1] Cheng Jiecheng, Liao Guangzhi, Yang Zhenyu, et al. Pilot Test of ASP Flooding in Daqing Oilfield [J]. Petroleum Geology & Oilfield Development in Daqing, 2001, 20(2):46-49.

[2] Li Kui, Liu Zhaobin. Preparation and Application of Demulsifier for Quickly Breaking SuperHeavyoil [J]. Advances in Fine Petrochemicals, 2004, (7):34-37.

[3] Wu Zongfu, Huang Hongquan, Li Yongchang, et al. Development and Application of a New Emulsion Breaker of High Efficiency and Low Temperature [J]. Journal of Jianghan Petroleum Institute, 2003, 25(1):85-88.

[4] Liu Huiying, Song Nairen, Li Weifeng, et al. Studies and Application of Demulsifier CW-01 for Breaking-Down Reverse, O/W, Crude Oil Emulsions [J]. Design of Oilfield Construction, 1996, 41:39-42.

[5] Yu Liandong. Distribution of World Heavy Oil Reserves and Its Recovery Technologies and Future [J]. Special Oil and Gas Reservoirs, 2001, 8(2):98-103.

[6] Yang Xiaoli, Lu Wanzhen. Advances in Stabilization and Destabilization of Water-in-Crude Oil Emulsions [J]. Oilfield Chemistry, 1998, 15(1):87-96.

[7] Wang Biao. Recent Progress in Development of Demulsifiers for Crude Oils [J]. Oilfield Chemistry, 1994, 11(3):266-272.

[8] Li Ming-yuan, Zhen Peng, Wu Zhao-liang, et al. Investigation of Stability of Water-in-Crude Oil Emulsions: VI. Properties of Interfacial Film and Stability of Crude Oil Emulsions [J]. ActaPetroleiSinica (Petroleum Processing Section), 1995, 11(3):1-6.

[9] Yu Guo-xian, Chen Hui, Lu Shan-xiang, et al. Compound Formulation of Composite Demulsifier for Crude Oils [J]. Speciality Petro Chemicals, 2003, 10(5):1-4.

[10] Joseph D.M. Effects of asphaltenes solvency on stability of water-in-crude oil emulsion [J]. J Colloid & Interface Sci., 1997, 189:242-253.

[11] Gong Huijuan, Hu Gengyuan, Chen Guanxi. The Synthesis of CrosslinkedPolyethers and Their Application in Demulsifying Crude Oil [J]. Speciality Petro Chemicals, 2000, 7(4):1-4.

[12] Li Shuxian, Cui Jidong, Yao Yanfeng, et al. Preparation and Use of High-Molecular Amphipathic Demulsifier BC-068 for Dehydration of Heavy Crude Oils [J]. Oilfield Chemistry, 2004, 21(1):39-41.

[13] Fan Zhengzhong, Liu Qingwang, Wei Xiaoming. The Preparation and Appraisal of High Efficiency LTB Demulsifier for Heavy Crude at Low Temperature [J]. Oil Gasfield Surface Engineering, 2001, 20(1):29-30.

[14] Wu Tong, Wang Xingwang, Zhang Yunan, et al. Study on the Dehydration Process of Aging Oil by Demulsifier Modified With Nanometer-Silicon[J]. Contemporary Chemical Industry, 2013, 42 (11):1488-1490.

[15] Sun Zhenggui. Application of Polyether Demulsifier TA1031 Modified by Nano-Al2O3[J]. Journal of Petrochemical Universities, 2008, 21(3):9-12.