COLLOIDAL NATURES OF TWO TYPICAL CHINESES VACUUM RESIDUA I: COLLOIDAL STRUCTURES IN TERMS OF SFEF FRACTIONS

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ABSTRACT: The physical structures of vacuum residua are of industrial potentiality in applications such as prevention of heavy organics deposition in petroleum production and phase separation of coke precursors in petroleum refining. Disclosure of the physical structures of two representative Chinese vacuum residua, Daqing and Shengli vacuum residuum, and their SFEF (supercritical fluid extraction and fractionation) fractions on the colloidal scale by FFRTEM (Freezing Fracture Replication Transmission Electronic Microscopy) indicate that all of them assume colloidal structures with different structural details dependent heavily upon their compositions or origins.
KEYWORDS: colloidal structures, vacuum residua, SFEF fractions

INTRODUCTION

Although more and more information has been accumulated about the natures of the physical structures of VR(VR), very limited images of the physical structures of the original VR are now available with the exception of some apriori knowledge about the colloidal aspects of VR with the support of indirect experiments and field experiences[1,2]. It is currently recognized that the physical structures of VR assume locally ordered structures on the molecular scale and heterogeneous micell structures on the colloidal scale[1]. Presently, it seems that the core of all the left issues concerning the colloidal characters of VR is not only to ascertain, with direct evidences, their apparent colloidal features but also to uncover their building units (components or fractions) as well as formation mechanisms.

The authors have attempted with Freezing Fracture Replication Transmission Electronic Microscopy (FFRTEM) to disclose the physical structures of Daqing, Shengli and Gudao VR on the colloidal scale and to evaluate the contributions of the SARA pseudo-pure-components to the colloidal configurations[5]. Conclusions drawn state that VR are of sol structures; asphaltenes and heavy resins construct the dispersed phases and the other fractions form the dispersing media. Useful as the deductions from FFRTEM are, they need further confirmation as there leaves some room for improvement in sample separation and structure identification employed by the authors.

Firstly, the conventional separation procedure of SARA compositions of VR may incur breakdown or distortion of the real physical structures of original VR. With the supercritical fluid extraction and fractionation (SFEF) technique, however, the possible influences on the real physical structures of original VR could be controlled to the minimum for the solubility classes from the SFEF technique can best keep the continuity of both the compositional and the structural distributions of VR; and secondly, though the FFRTEM technique is able to display in a qualitative manner the colloidal nature of VR and the shape and size of the dispersed phases, it presents no information on the chemical compositions of both the dispersed and the dispersing phases without assistance from the sample separation technique. In fact, when solubility class compositions are employed to characterize the colloidal structures of VR, the validity and conciseness of the FFRTEM technique itself to determine the solubility class compositions of both the dispersed and the dispersing phases depend heavily on the fineness of the VR fractionation.

Still, the established FFRTEM technique was adopted in this study to unfold the colloidal structures of two typical Chinese VR and their SFEF fractions. In such a way, more valid and more direct evidences, instead of the apriori and indirect knowledge, could be accumulated to lend some support to the construction details of the colloidal VR.

MATERIALS AND METHODS

Separation of vacuum residua into SFEF fractions

A Supercritical Fluid Extraction and Fractionation (SFEF) technique[4], which was developed by the State Key Laboratory of Heavy Oil Processing, University of Petroleum, China, was utilized to separate nondestructively Daqing and Shengli VR into the proper number of subfractions. In the operation, n-pentane was used as the extractant with flow rate of 100mL /min; the initial pressure of 4.0MPa was set and the final pressure was controlled to be 12.0MPa with a linear pressure increase being kept at 1.0MPa/hr; the temperatures at the bottom of the extraction batch and at the top of the fractionation column were respectively 240℃ and 250℃.

With the technique, either narrow or wide fractions could be obtained by extracting varied quantity of lighter constituents out of VR. All the fractions left after extraction are the de-oil asphaltenes (DOA). The more the lighter constituents are extracted, the heavier the DOAs are. For example, in view of wider SFEF fractions adopted in this research, they become heavier and heavier from 30%DOA to 40%DOA to 50%DOA to 60%DOA. The original VR are the lightest as compared with their DOAs.

Elemental and SARA compositions of the studied vacuum residua and their SFEF fractions

Daqing vacuum residue (DVR) and Shengli vacuum residue (SVR), derived from two representative Chinese crude oils, were employed. Their main elements and SARA compositions were analyzed as listed in Table 1 and Table 2.

Table 1 Element and SARA compositions of Daqing vacuum residue and its SFEF fractions

	DVR	30%DOA	40%DOA	50%DOA	60%DOA
C, %	86.23	86.71	86.65	86.74	86.68
H, %	12.86	12.52	12.37	12.16	11.94
S, %	0.145	0.17	0.20	0.21	0.22
N, %	0.44	0.43	0.52	0.60	0.66
Saturates, %	41.9	22.3	19.2	14.1	9.15
Aromatics, %	32.7	38.0	38.5	39.3	39.3
Resins, %	25.4	39.6	42.5	46.6	51.2
Asphaltenes, %	0	0.15	0.19	0.20	0.28

Table 2 Element and SARA compositions of Shengli vacuum residue and its SFEF fractions

	SVR	30%DOA	40%DOA	50%DOA	60%DOA
C, %wt	85.88	85.29	85.42	85.30	84.82
H, %wt	11.34	10.99	10.62	10.39	10.04
S, %wt	3.01	3.88	4.05	4.44	4.32
N, %wt	0.95	1.18	1.26	1.37	1.44
Saturates, %wt	16.1	3.58	1.30	0.31	0.53
Aromatics, %wt	30.6	27.9	23.3	15.6	11.4
Resins, %wt	51.1	66.0	72.5	79.7	81.3
Asphaltenes, %wt	2.2	2.46	2.86	4.38	6.77

Microscopic technique for finer structure identification

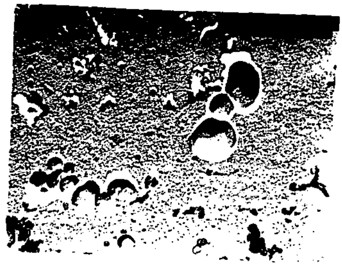
There are many direct or indirect approaches available to characterize colloidal dispersions and Transmission Electronic Microscopy (TEM) is among those direct viewing techniques most widely employed. Considering that TEM has peculiar requirements on the physical states (e.g. thickness) and properties (e.g. volatility) of the observed samples, the sample freezing and one-time replication technique was adopted in this study to prepare the TEM observed samples of VR and their SFEF fractions. Operational procedure of the freezing fracture replication TEM, abbreviated as FFRTEM, was detailed in Ref.[3].

RESULTS AND DISCUSSION

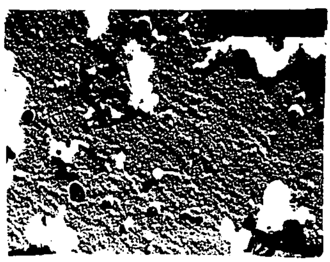
FFRTEM icons of vacuum residua and their SFEF fractions

In *Figures* 1 through 2 are displayed the FFRTEM photos of the two VR studied and their

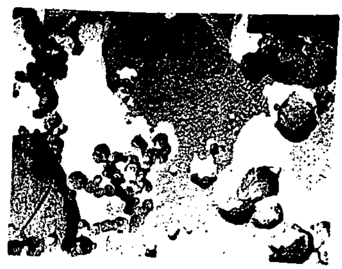
SFEF fractions. The fundamental colloidal attributes presented by these photos are clearly seen in terms of the size and size distribution and morphology of the dispersed phases, as well as the colloidal types of which they are.



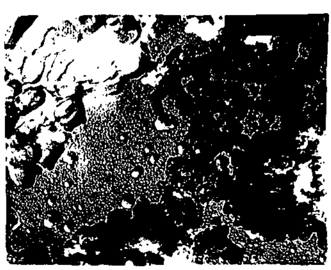
(a) original vacuum residue (61,000 times)



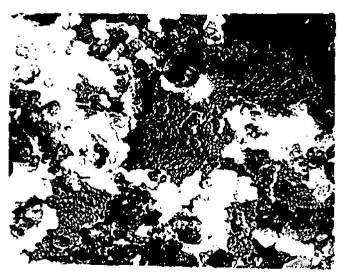
(b) 30% DOA (61,000 times)



(c) 40% DOA (61,000 times)

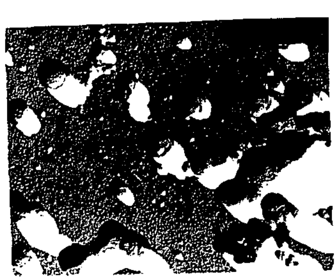


(d) 50% DOA (61,000 times)

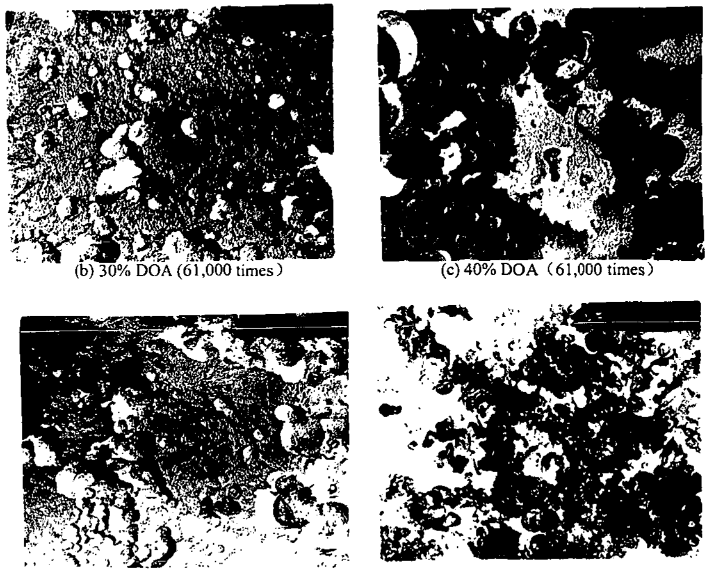


(e) 60% DOA (33,000 times)

Figure 1 FFRTEM icons of Daqing vacuum residue and its SFEF fractions



(a) original vacuum residue (61,000 times)



(b) 30% DOA (61,000 times)　(c) 40% DOA (61,000 times)

(d) 50% DOA (61,000 times)　(e) 60% DOA (24,000 times)

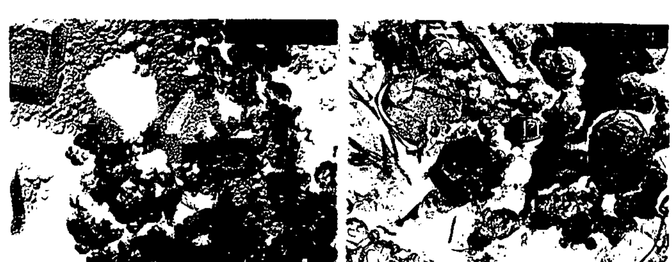
Figure 2 FFRTEM icons of Shengli vacuum residue and its SFEF fractions

Colloidal attributes of vacuum residua and their SFEF fractions

Conventionally, the so-called colloidal particles refer to the molecular aggregates with at least one dimension ranging between 1nm and 1 μ m, and considerable interfacial layers exist among the dispersed phases of the colloidal particles and the surrounding dispersing medium[5]. In the two VR and their SFEF fractions, though there occurs a wide size distribution of the dispersed particles, their dimensions are evidently in the spectrum of colloidal particles, and what is more, rather distinct interfaces can be viewed between the dispersed phases and their surrounding phase. It is therefore concluded that both Daqing and Shengli vacuum residue as well as their SFEF fractions are all colloidal dispersion systems.

Morphology of dispersed phases in vacuum residua and their SFEF fractions

The geometrical shapes of the colloidally dispersed phases are among the most distinguished parameters characterizing colloidal dispersing systems. It is evident from the FFRTEM photos in *Figures* 1 through 2 that the colloidal particles in the two VR and their SFEF fractions assume spherical and non-spherical shapes with the spherical or sphere-agglomerated dispersed particles in an overwhelming majority. On the other hand, the abundance of the spherical particles relative to the non-spherical particles exhibits rather differently in the original VR and their SFEF fractions. Concretely, almost all the dispersed particles in the two VR and their 30%DOA, 40%DOA and 50%DOA assume spheres or spherical stacking configurations; while in the 60%DOA of the two VR, there exist not only spherical dispersed particles but some tabulate dispersed phases of larger sizes as well. Such observations were further confirmed by the TEM photos displayed in *Figure* 3.



(a) (49,000 times)　(b) (12,000 times)

Figure 3 FFRTEM icons of 60%DOA of Daqing(a) and Shengli(b) vacuum residue

It is generally considered that, in the aggregated colloidal systems, the dispersed micell assume spherical shapes when the concentration of the surfactant remains low, e.g. not higher than CMC; when the surfactant is in such a high concentration that its content exceeds as ten times CMC as high or reaches more than 10%, the dispersed phases might as well adopt unsymmetrical configurations or layered stackings[5]. Since the asphaltenes and the resins in the VR and their SFEF are of the general characteristics of conventional surfactants both in structures and in behaviors, it is not so difficult to qualitatively clarify, in accordance with colloidal solution theories of surfactants, the variations of the geometrical shapes of the dispersed phases in the VR and their SFEF fractions as they become heavier and heavier.

Multidispersity of colloidal vacuum residua and their SFEF fractions

The multidispersion characteristics of the colloidal systems of the VR and their SFEF fractions are embodied in many aspects such as the morphology, average sizes and size distributions of the dispersed phases. Because of the non-homogeneity of the dispersed phases in size and geometrical shapes in the VR and their SFEF fractions, they are all multi-dispersing systems. On the other hand, as the SFEF fractions of the VR become heavier and heavier, the average size and quantity of the dispersed phases will undergo noticeable variations. Generally, more and more dispersed phases will come into being as the SFEF fractions of the VR go heavier.

Both the morphology and the multidispersity of the dispersed phases in the VR and their SFEF fractions imply that these dispersed phases are made from innumerable non-identical constituents or molecules of VR. Such a fact provides one more proof of the multidispersity of the colloidal VR and their SFEF fractions.

Colloidal types of vacuum residua and their solubility classes

Generally, the colloidal structures of the VR and their SFEF fractions become more advanced in the heavier fractions than in the lighter ones. In average, there appear more cross-linked dispersed phases in Shengli vacuum residue and its SFEF fractions than in those of its Daqing counterparts. In terms of the colloidal types, the original vacuum residua and their 30%DOA are more sol structures, while their 50%DOA and 60%DOA appear more gel structures. The structure of the 40%DOA goes in-between, that is, 40%DOA assumes sol-gel structures.

CONCLUSIONS

(1) The combinatorial SFEF-FFRTEM technique is among the most useful approaches to reveal the colloidal structures and attributes of VR and their SFEF fractions in a qualitative way.

(2) Both Daqing and Shengli vacuum residue as well as their SFEF are of colloidal structures with the basic colloidal attributes dependent upon their fractional compositions.

(3) The fact that the original VR and their SFEF fractions exhibit different colloidal structures and attributes implies that they may find different applications due to their unique physical structures and chemical compositions; or different thermodynamic or dynamic behaviors displayed by the original VR and their SFEF fractions may originate from the subtle differences of their physical and/or chemical structures.

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