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QUANTUM - CHEMICAL CALCULATION OF DESTRUCTION AND HYDROGENATION OF THE OIL ASPHALTEN UNDER INFLUENCE OF SHORT PULSE DISCHARGES

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Last years the interest to energetically influence on material for the reason change their characteristic remains stabiles high. The calculation of the oil material's individual particularities show it is possible to change structure in necessary direction using shock influence without observable external energy expenses. As such influence, for controlling structure of material used electro-hydro-impulse influence on the oil. It is can be reached easy to increase of regulate nuclear structure using this effect. Results of properties study of the heavy oil from the Karazhanbas field, which was subjected to electro-hydro-pulse discharge for the purpose of demetallization, are presented.

Keywords: oil asphalten, polycyclic systems, quantum-chemical calculations, semi-empirical approximation PM3, electro-hydro-pulse processing.

Introduction

Oil asphalt is the most highly condensed, highly aromatized part of heavy oil. The average number of aromatic cycles is 4–7, cycloparaffinic 1–2. Alkyl substituents are short and medium C_1 – C_6. Identified heterocycles of oxygen, sulfur, nitrogen, sulfides, ketone, phenolic, alcohol, carboxylic acid groups, porphyrin and non-porphyrin complexes, as well as quinoid cycles and lactones are present in oil asphaltene. In [1], it was shown that polycyclic systems provide stabilization of unpaired electrons, the source of formation of which are broken bonds in the boundary atoms of condensed carbon. The concentration of paramagnetic centers in high viscosity oil (HVO) was previously determined in [1], the concentration of free radicals is 1.1×10^{17} spin/g, the EPR line width (ΔH = 0.43 Er). However, the EPR showed us only the total amount of free radicals in the HVO and did not allow us to identify them.

1. Statement of the problem

Quantum-chemical calculations of the ground state of the asphaltene molecule were carried out non-empirically in the limited version of the Hartree-Fock method (RHF method) in the 3-21G (d) basis with geometry optimization in the semi-empirical approximation PM3 (Gaussian 03 software package) [2]. The asphaltene molecule has an extremely complex structure. Figure 1 shows the structural formula of the petroleum asphaltene molecule.

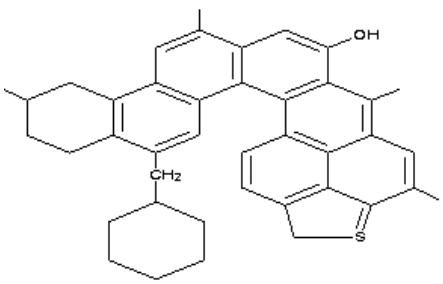

Fig. 1. The structural formula of the oil asphaltene molecule [1]

The spatial configuration of asphaltene includes aromatic, cyclic and heterocyclic rings and, as can be seen from Figure 2, the right and left parts of the molecule are oriented relative to each other at an angle of ~ 45-50 °. The numbering of atoms corresponds to the model for semi-empirical and non-empirical calculations. The optimized PM3 structure was used for calculations in the basis of 3-21G (d), because the presence of a sulfur atom in the molecule requires d-orbitals to be taken into account, which is possible in the framework of non-empirical calculations. Therefore, further discussion is carried out using the calculation data by the RHF/3-21G (d) method.

One of the further transformations of asphaltene is the hydrogenation of a molecule. Since the hydrogenation reaction is stepwise, for a preliminary study we considered the direct addition of a hydrogen radical (atom) to asphaltene. The hydrogen atom is an electrophilic reagent. Its attachment to the studied molecule should occur, apparently, to the unsaturated aromatic part of asphaltene.

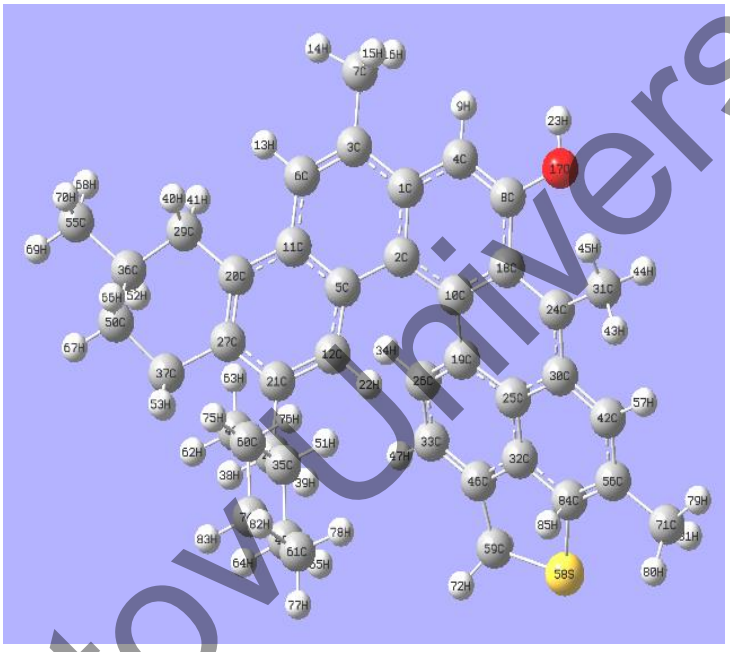

Fig.2. Mutual orientation of a part of a petroleum asphaltene molecule

To determine the direction of attack, the approximation of boundary orbitals was used. Figures 3 and 4 show the HOMO (upper occupied molecular orbital) and LUMO (lower unoccupied molecular orbital) asphaltene, respectively.

The orbital energy of the hydrogen radical is 0.11747 a.u. The LUMO energy of asphaltene is equal to 0.06663 a.u. A small difference in energies suggests the interaction of these orbitals. However, due to the smallness of the energy intervals, nearby orbitals can also interact with the attacking electrophile. Consequently, the number of atoms - centers of attack may be greater.

2. Discussion of experimental studies results.

We calculated the change in the energy of the system as the hydrogen atom approaches the C10 reaction center (selected taking into account the large weight coefficients of the molecular orbital) of the molecule with a step of 0.5 and 0.1 Å. The electronic configuration of the asphaltene - hydrogen radical system contains 313 electrons, of which, according to a non-empirical calculation, 157 electrons with alpha spin and 156 electrons with beta spin, which corresponds to 156 double and one once filled molecular orbitals, are shown in Figure 5.

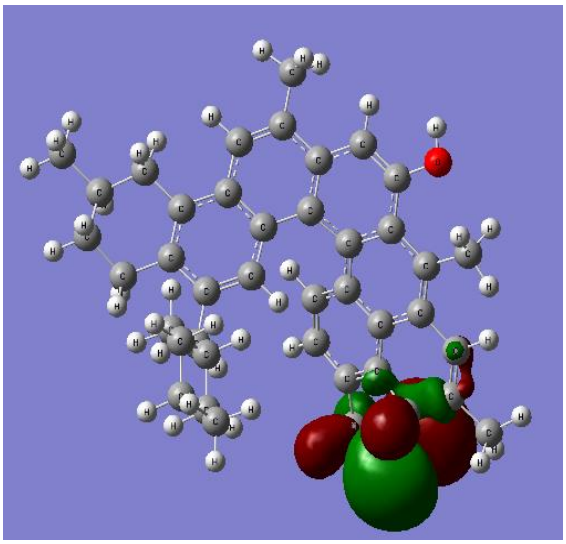

Fig.3. HOMO level of asphaltene

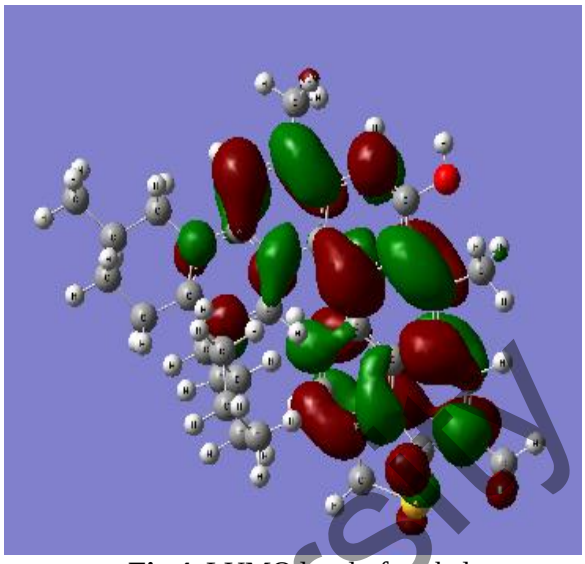

Fig.4. LUMO level of asphaltene

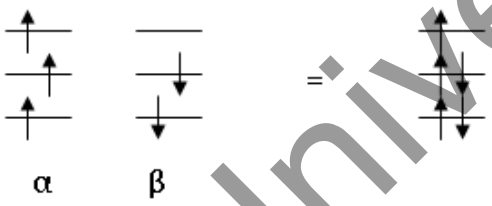

Fig.5. Schematically presented mechanism of filling with molecular orbitals in the calculations according to the ROHF method.

Due to the choice of the ROHF / 3-21G (d) calculation method, the problem of the purity of the spin state did not arise. The degree of purity of the spin state was estimated by the value of the square of the spin, which is 0.75 for the doublet. Figure 6 shows the surface profile of the potential energy E of the petroleum asphaltene hydrogenation reaction. From Figure 6 it is seen that the energy rises with a decrease in the distance between H and C10 to 1.4 Å, then drops and rises again. At 1.2 Å, a minimum is observed corresponding to the formation of a new oil radical.

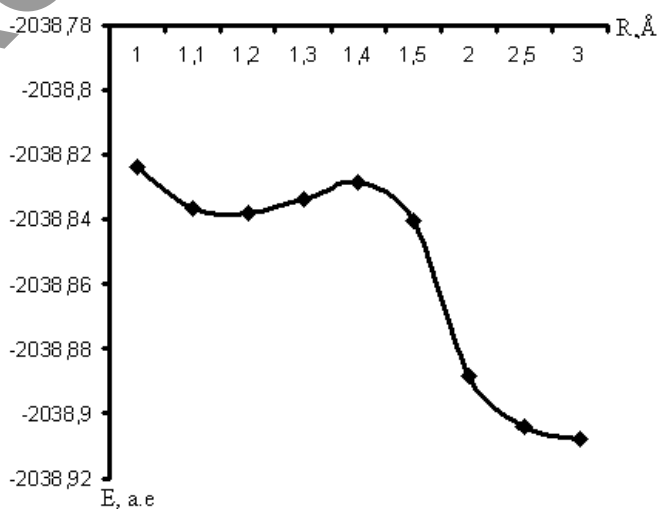

Fig.6. Surface profile of potential energy of petroleum asphaltene hydrogenation reaction.

Thus, the recombination of petroleum asphaltene with a hydrogen atom, which is a type 1 free radical, will obviously occur in places of excess spin density. When trying to quantum-chemical calculation of such a system, optimization of the geometry will lead to the opening of the heterocycle. Heavy oils, bitumen, oil residues differ from ordinary oils and oil products in the increased content of heavy metals (vanadium, nickel, iron, copper, molybdenum), sulfur, nitrogen, asphaltenes and resins [3]. Heavy metals (vanadium V, nickel Ni) adversely affect the quality of the target product and make it difficult to process, therefore demetallization of heavy oil residues and HVO is an important stage before their further processing [4]. The results of experiments with heavy oil from the Karazhanbas field, which was subjected to electrohydropulse discharge for the purpose of demetallization, are presented in Table 1.

Table 1. High viscosity oil demetallization of the Karazhanbas field, heavy oil is pre-processed using electrohydropulse discharge

Raw materials, products processed by high viscosity oil	Ni, g/t	V, g/t	The degree of demetallization of high viscosity oil, %		The degree of enrichment of the solid residue, %	
			Ni	V	Ni	V
HVO of Karazhanbas field	65-70	320				
Fraction of HVO under $T_{boiling}$> 300 ^{0}C	30	60	73	65		
Solid residue	480	650			4.3	3.8

Conclusion

The results of the HVO demetallization and the HVO fraction above 300° C (Table 1), are showed that the degree of demetallization for vanadium is 65%, for nickel 73%, the enrichment of the solid residue for vanadium increased by 3.8%, and for nickel 4.3%, respectively. The accumulation of heavy metals by a substance in the solid phase can occur due to complexation with chemical active groups (OH, COOH, SO_3, NH_2, etc.). Nickel and vanadium metals in the BBH of the Karazhanbas deposit are contained in porphyrin and non-porphyrin complexes, which form the basis of oil asphaltenes [5]. The above quantum chemical calculations confirm that the hydrogenation reaction of petroleum asphaltene and the demetallization process begin with an attack by a hydrogen atom (type 1 free radical) of a polyaromatic heterocycle that contains a sulfur, nitrogen or oxygen atom.

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