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QUANTUM-CHEMICAL CALCULATION OF DESTRUCTION OF OIL ASPHALTHEN STRUCTURE IN THE PROCESS OF ELECTROHYDROPULSE INFLUENCE

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At the last years interest to energetically influence on material for the reason change their characteristic remains stabiles high. With calculation of the individual particularities material and with using influence choices of the it is possible to change structure in necessary direction without observable external energy expenses. As such influence, for controlling structure of material used electrohydroimpulse influences on oil. Here with effects of increase of regulate nuclear structure reaches easy.

Keywords: electrohydroimpulse influences, destruction, quantum-chemical calculations, oil asphalthen structure.

The phenomena of pulse electric breakdown of liquids are of rising interest of experts due to rapid development of high-voltage pulse technics. High-voltage micro and nanosecond impulses are highly applied in experimental physical chemistry, electropulse technology, dielectrics physics, a radiolocation, a high-speed photo, etc.

In the process of influence on liquid of electric field discharge formation is preceded by course of electric current with effects accompanying it which make essential impact on ignition and discharge development. Research of current flowing in hydrocarbonic liquids allows to define key parameters of charge carriers and the nature of their occurrence, to study the mechanism of electronic emission in a liquid, to estimate electron multiplication capability in liquid volume, and also field distortions in an interval, caused by accumulation of volume charges.

While processing electrohydropulse (EHP) discharges of highly-tenacious oil some original phenomena occur, discharge self-isolation, contributing to increase in efficiency of the whole process. While passing EHP of the discharge through oil, liquid ions, being discharged on the growing streamer as on "a sliding" electrode, forms a thin gas film separating its issued trunk or a branch of streamer from the surrounding liquid on its occurred surface. Isolating film is formed by nuclear both molecular oxygen and hydrogen, gaseous peroxide of hydrogen, and also electrically neutral radicals H, OH, existing in water steams. The basic operating factor of chemical influence at a predischage stage of process of the discharge are the super-power electric fields, capable to stretch and transform into dipoles all unpolar molecules, and some of polar molecules even to break into ions. Here the natural conclusion can be done that if the magnetic field changes concentration of ions, and consequently, and free radicals in this or that volume of a cell of processing, thereby it has already been turning to obvious and active enough factor of chemical influence.

The purpose of research work is calculation of a geometrical configuration of the basic component of highly tenacious oil, oil asphalthen and calculation of a profile of a surface potential energy reactions of hydrogenation oil asphalthen in process of electrohydropulse influences by means of the quantum-chemical method. Oil asphalthen is the most highly condensed, highly-aromatized part of heavy oil. Average of aromatic cycles is 4 – 7, cycle paraffin ones is 1 – 2. Alkyl assistants are short and average C₁ – C₆. In oil asphalthen there are identified heterocycles of oxygen, sulfur, nitrogen, sulfides, ketonic, phenolic, spirit, carbon oxygen groups, porphyrinic and non-porphyrinic complexes, and also quinoid cycles and lactones [1].

Quantum-chemical calculations of the basic condition of asphalthen molecule are performed unempirically in the limited variant of a method of Hartry-Fock (OHF, English RHF) in basis 3-

21G (d) with geometry optimization in semi-empirical approximation PM3 (program complex Gaussian 03) [2,3].

The spatial asphaltene configuration includes aromatic, cyclic and heterocyclic rings. The asphaltene molecule has extremely difficult structure.

In Figure 1 the structural formula of the oil asphaltene molecule and mutual orientation of a part of the oil asphaltene molecule is presented.

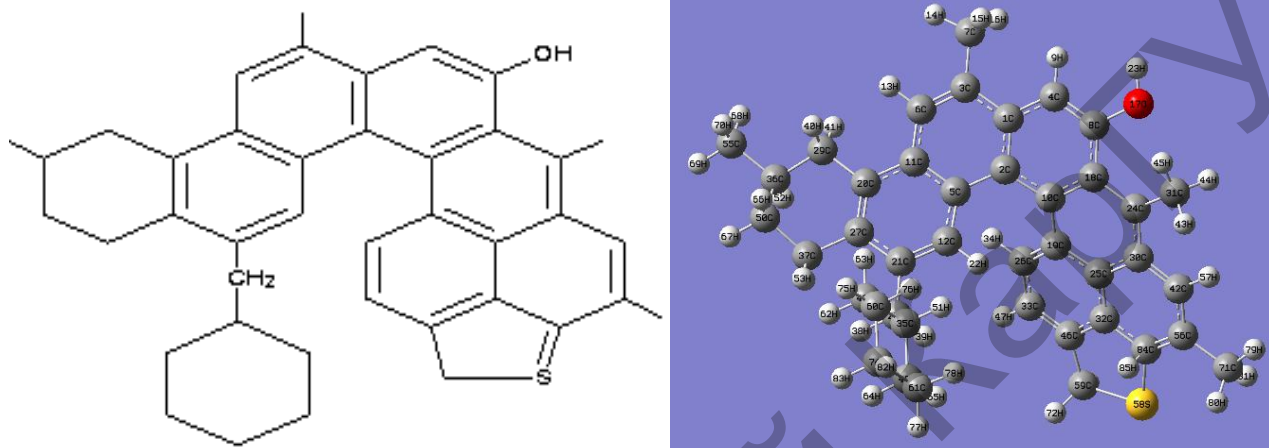


Fig. 1. The Structural formula of the oil asphaltene molecule and mutual orientation of a part of the oil asphaltene molecule

The spatial asphaltene configuration includes aromatic, cyclic and heterocyclic rings and, apparently from Figure 1 the right and left parts of the molecule are focused to each other at an angle $\sim 45-50^\circ$.

Numbering of atoms corresponds to the model for semi-empirical and non-empirical calculations.

The optimized PM3-structure is used for calculations in basis 3-21G (d) since presence of sulfur atom as a part of a molecule demands the account d-orbital that is possible within the limits of non-empirical calculations. Therefore the further discussion is spent by means of the data of calculation by method RHF/3-21G (d).

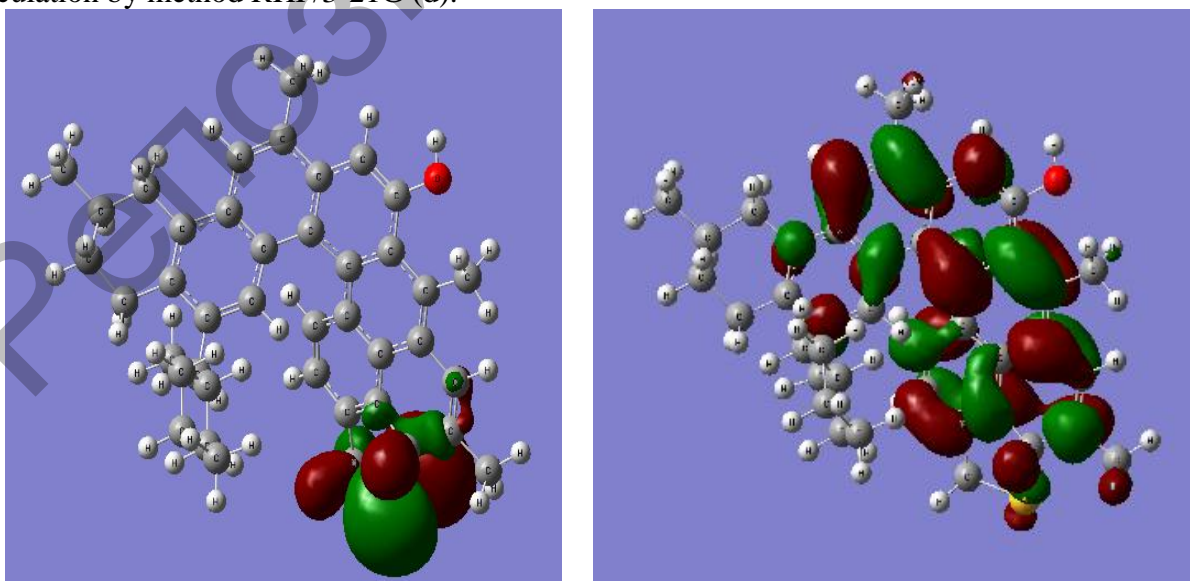


Fig. 2. Top and bottom occupied molecular asphaltene orbital

One of the further asphaltene transformations is molecule hydrogenation. As hydrogenation reaction is graduated, thus for preliminary studying we consider direct joining of a radical (atom) of hydrogen to asphaltene. Atom of hydrogen – is an electric reagent. Apparently, its joining to the considered molecule should occur to a nonsaturated aromatic asphaltene part. To define the direction of the attack we have applied approach boundary orbitals. In Figure 2 asphaltene TOMO (top occupied molecular orbitals) and BFMO (bottom free molecular orbitals) are resulted.

Orbital energy of a hydrogen radical makes - 0.11747 a.e. Energy asphaltene BFMO is equal 0.06663 a.e. The small energy difference allows to assume interaction of these orbitals. However owing to tiny energy intervals, nearby orbitals can also cooperate with attacking electrofil. Hence, the number of atoms – the attack centers can be more.

We have carried out the calculation of energy change of system while approaching of hydrogen atom to reactionary center C10 (it is chosen taking into account the great weight factors of molecular orbital) molecules with 0,5 and 0,1 Å pace.

The electronic configuration of asphaltene–hydrogen radical system contains 313 electrons, and, according to not empirical calculation, 157 electrons with spin alpha and 156 electrons with spin beta that corresponds 156 twice and one unitary filled molecular orbitals. Thanks to the choice of calculating method ROHF/3-21G (d) the problem of cleanliness of the spin condition didn't occur. Degree of cleanliness of the spin condition was estimated by size of a spin square which is equal 0,75 for a doublet.

In Figure 18 the profile of potential energy surface (PPES) of the reaction of hydrogenation oil asphaltene hydrogenation is resulted. In Figure 18 it is seen that energy raises at distance reduction between H and C10 to 1,4 Å, then energy falls and raises again. In the point 1,2 Å the minimum corresponding to formation of a new oil radical is observed.

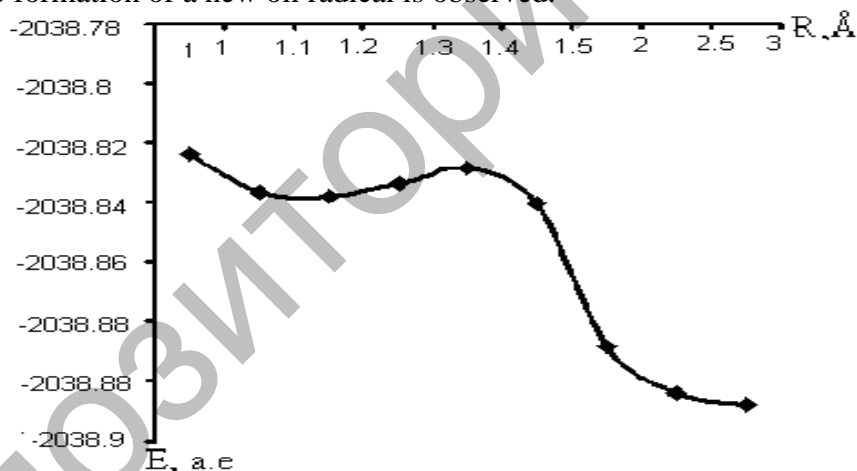


Fig. 3. The profile of potential energy surface of the hydrogenation oil asphaltene reaction

Thus, the recombination of oil asphaltene with the hydrogen atom, which is a free radical of 1st type, obviously, will occur in places of superfluous spin density. While attempting of quantum-chemical calculation of such system the geometry optimization will lead to heterocycle disclosing.

The quantum-chemical calculations resulted above confirm that reaction of oil asphaltene hydrogenation begins with attack by hydrogen atom (a free radical of the 1st type) polyaromatic heterocycle which contains atom of sulfur, nitrogen or oxygen.

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