

# QUANTUM-CHEMICAL MODELING OF THE ELECTRONIC STRUCTURE OF AROMATIC HYDROCARBONS OF CATALYTIC CRACKING OF VACUUM DISTILLATE

V.I. Stebeneva, G.Y. Nazarova

Scientific Supervisor – DSc, Professor, E.N. Ivashkina

Linguistic Advisor – PhD, Assistant, Engineer, N.S. Belinskaya

National Research Tomsk Polytechnic University

634050, Russia, Tomsk, st. Lenina, 30, [stebeneva\\_valeriya@mail.ru](mailto:stebeneva_valeriya@mail.ru)

The catalytic cracking of crude oil is one of the advanced cracking processes (over 80%). Solving the problem of production optimizing using mathematical and kinetic-thermodynamic modeling allows to obtain products that satisfy to international environmental, economic and operational requirements.

The work objective is definition of thermodynamic parameters to developing mathematical model of catalytic cracking reactions, involving aromatic hydrocarbons of vacuum distillate.

Aromatic compounds have a significant influence on the yield and composition of the catalytic cracking products. In order to determine the most probable chemical reactions of aromatic hydrocarbons of catalytic cracking of vacuum distillate was performed the thermodynamic analysis of reactions with using the methods of quantum chemistry (DFT/B3LYP, 6-31G).

Initially, the aromatic content of the feedstock

of gas chromatography-mass spectrometry results performed by the method of internal normalization without consideration of correction factors for each component.

Modeling of aromatic hydrocarbons and calculation of thermodynamic parameters were performed at  $T=848\text{ K}$ ,  $P=1.08\text{ Mpa}$  (temperature of reaction start) for the following reaction [1]:

- 1) benzene dealkylation to form an olefin;
- 2) cracking of iso-alkyl substituent on the middle of the molecule to form a iso-alkyl-substituted aromatics and olefin;
- 3) cracking of alkyl substituent in the beta-position relative to the positively charged carbon atom of the benzene ring

Results of the thermodynamic parameters calculation are shown in Table 1.

Table 1 shows that reaction №3 characterized by most probable thermodynamic of chemical reactions, due to formation of a stable tertiary carbo-

**Table 1.** The values of thermodynamic parameters for various reactions involving aromatics hydrocarbons

№	Reaction type	$\Delta G$ , KJ/mole	$\Delta H$ , KJ/mole
1	1-butylonylbenzene $\leftrightarrow$ benzene+tridecene-7	-82.54	64.38
2	1-butylonylbenzene $\leftrightarrow$ 1-octanebenzene+pentene-2	-88.07	59.11
3	1-butylonylbenzene $\leftrightarrow$ 1-pentylbenzene+octene-2	-97.43	55.33
1	1-methyldodecylbenzene $\leftrightarrow$ benzene+tridecene-2	-67.54	82.37
2	1-methyldodecylbenzene $\leftrightarrow$ 1-methylpentylbenzene+hexene-2	8.00	82.31
3	1-methyldodecylbenzene $\leftrightarrow$ 1-ethylbenzene+dodecene-2	-76.11	74.49
1	1-pentiloktilbenzol $\leftrightarrow$ benzene+tridecene-6	-82.69	64.35
2	1-pentiloktilbenzol $\leftrightarrow$ 1-benzenonane+butene	-81.13	55.13
3	1-pentiloktilbenzol $\leftrightarrow$ 1-hexylbenzene+heptene-2	-94.04	56.24

for catalytic cracking has been established experimentally using the liquid-adsorption chromatographic fractionation. The concentration of aromatic hydrocarbons was 35.57 wt%. The hydrocarbon structures were determined using gas chromatography-mass spectrometer Hewlett Packard Gas Chromatograph System 6890 with 5973 Mass Selective Detector and GC Chemstation software. Processing

**Table 2.** The dependence of thermodynamic parameters from the number of carbon atoms in the alkyl substituent

Hydrocarbon	$\Delta G$ , KJ/mole	$\Delta H$ , KJ/mole
1-ethylonylbenzene	-88.54	55.00
1-ethyldecylbenzene	-91.93	54.94
1-ethylundecylbenzene	-92.16	54.94
1-ethyldodecylbenzene	-98.15	54.78

cation of benzene type. Then, the dependence of the thermodynamic parameters from the number of carbon atoms in the alkyl substituent of the benzene ring was determined for selected type of reactions.

The results of Table 2 show that with increasing

the number of carbon atoms in the alkyl substituent also increases the thermodynamic probability of cracking reactions, due to the weakening of internal communication links in the alkyl substituent.

### Reference

1. Tilicheev M.D. *Chemistry of cracking.* – M.: *Book-on-Demand*, 2013. – P.269.

## ELECTROCHEMICAL OXIDATION OF NITROPHENOLS

E.V. Sukhoroslova, E.V. Zangieva, A.B. ladykina  
 Scientific supervisor – PhD, Associate Professor, O.S. Kukurina  
 Linguistic advisor – PhD, Associate Professor, O.S. Kukurina

*National Research Tomsk Polytechnic University  
 634050, Russia, Tomsk, Lenina Avenue, 30, annaanna.borisovna@mail.ru, kukurina@tpu.ru*

Phenol and substituted phenolic compounds, especially nitro-derivatives are extremely toxic and namely nonbiodegradable pollutants. They are discharged in the effluent from the chemical process industries which are either manufacturing or using them. Thus the various techniques of phenolic pollutants destruction are still burning issues nowadays. And chemical oxidation is considered to be the most universal method.

The process of destructive pesticides oxidation is carried out in a laboratory installation, the basic unit of which is the electrochemical cell [1].

To increase the rate of oxidation of toxic organic substances and prevent stagnant zones in the reactor used continuous stirring. The oxidation process is carried out in the kinetic region [2].

The process of oxidative degradation was investigated on nitrophenol. The substance to be subjected to oxidative degradation, dissolved in 80 ml of sulfuric acid and transfer into the apparatus. The concentration of the electrolyte may vary from 10 to 96 wt.%. A voltage is applied to the electrodes

ates and final products by means of UV spectrophotometry, gas chromatography with mass selective detector and high performance liquid chromatography.

During the experiment were obtained following data. This data show the presence of absorption bands at 210 nm – oxygenated compounds; 270 nm – phenol derivatives; 350 nm – nitrophenol.

According to the chromatography data at 0 minute is the largest peak, with the peak decreases over time, this means that the nitrophenol concentration in the solution decreases. Delay time 8.53 minutes carboxylic acids. That is, the oxidation passes through their formation. Phenol delay time – 14, 76 minutes at peak chromatograms of phenol was not detected. As the peak of hydroquinone – 24.85 minutes.

Thus the organic component of molecules is oxidized through intermediate products formation (such as acids, alcohols and aldehydes) up to simple compounds. At the same time some of these groups are destroyed on the cathode by reduction [4].



Fig. 1.

of the adjustable constant current source. During oxidation in reactor temperature can be increased up to the boiling point of the solution, in this case necessary to provide heat removal. At certain time intervals samples were taken for analysis [3].

We carried out the identification of intermedi-

Thus, according to UV-spectroscopy the nitrophenol oxidation intermediates are phenol and carboxylic acids, and gas chromatograph with mass spectroscopy determines the carboxylic acids without phenol.