UDC 662.75

M.I.Baikenov, A.B.Tateyeva, A.Zh.Matayeva, D.A.Balabekova,
B.O.Yessebayev, A.B.Tleubergenova, R.S.Berzhanova

Ye.A.Buketov Karaganda State University
(E-mail: mataeva_aisha@mail.ru)

The impact of ultrasonic cavitation on the chemical transformations of model compounds

The effect of ultrasonic cavitation on various organic compounds in the presence of catalysts is investigated in order to identify the chemistry of reactions. In addition, practical applications of cavitation for cracking hydrocarbons in technological processes of oil-refining industry are considered and estimated. These findings indicate that the use of cavitation for destruction of organic compounds is effective for technological and economical aspects.

Key words: ultrasonic cavitation, destruction, isomerization of hydrocarbons, chemical transformation of model compounds.

Currently, due to the oil depletion and increase in prices of liquid fuel the interest in high-performance technology of oil is growing. At this point, the cavitational method is a great practical interest to processing of petroleum fuels. In general, cavitation can be defined as the phenomena of the formation, growth and subsequent collapse of microbubbles or cavities occurring in an extremely small interval of time (milliseconds) releasing large magnitudes of energy. The local effects of the cavitation phenomena can be given as generation of very high temperatures (of the order of 1000 to 5000 K) and pressures(100 to 5000 bar). The magnitudes of the pressures and temperatures are astrong function of the operating hydrodynamic and geometric constructional features of the reactor. Thus the resultant effects are really spectacular and such events simultaneously occur at millions of places in the reactor [1].

Many researchers, engaged in cavitation processing of different materials, have observed a number of physical and chemical transformations, especially in the ultrasonic cavitation. Approach to boosting the efficiency of cavitation is carried out by ultrasonic excitation in the presence of an electric field [2]. Electrostatic charge generated within the bubbles assists radical formation due to covalent bond breaking, which generate chain reactions in hydrocarbons with the end-result being low molecular-weight compounds and aromatics. The influence of the direct impact of cavitation on chemical reactions of alkanes is observed by cracking of hexadecane ($C_{16}H_{34}$) under the action of ultrasound. In this case, the gaseous products were H_2, CH_4, C_2H_4, C_2H_2 [3]. Only the first steps have been done in the learning of cavitation's effect on the physico-chemical transformations in liquids, because in many cases a clear explanation of the observed phenomena have not found yet [4].

Thus the aim of this study is to investigate the effect of cavitation on a variety of organic compounds in the presence of catalysts with the identification of the reactions' chemistry, as well as clarification of possible practical applications of cavitation for cracking hydrocarbons in oil refining.

The compounds of different nature, accordingly, different reactivity are selected as research objects for more detailed study about organic compounds' chemistry by cavitation processing. Linear alkanes — hexane, decane, and more stable against degradation of polyaromatic hydrocarbon- anthracene are used as initial organic substrates. These compounds are assumed to display different reactivity to cracking process allowing to make rigorous scientific basis for discussion about impact of cavitation on chemical conversion of model compounds.

Experimental part

Experimental studies were carried out in air atmosphere using the ultrasonic cavitation which allows to conduct the high-intensity processing of small volumes of liquid with a capacity about 600 watts. The intensity of the ultrasound processing — 250 W/cm^2, the operating frequency is ±22 kHz.

To study the influence of cavitational processing on model compounds chemically pure decane, decane–hexane, toluene–antracene–hexane were investigated in the presence of various catalysts. The catalysts were FeS_2, NiO and iron nanoparticles Fe_2O_3, prepared according to the procedure [5]. The processing time was 1 min 30 sec, the volume of processed samples — 50 ml, the ratio of compounds in the mixture were 1:1.

The qualitative and quantitative analysis of liquid organic compounds were done by gas chromatograph HP 5890/5972 MSD firm Agilent (USA). Conditions of chromatograph: column — DB — (5.30 m × × 0.25 mm × X 0.5 mkm), gaz — helium, 0.8 ml/min, thermostating 50 ºC — 4 min, 50–150 ºC — 10 ºC/min, 150–300 ºC — 20 ºC/min, 300 ºC — 4 min at vaporizer's temperature 250 ºC.

Identification of compounds were produced by the mass spectral database NIST 98.

Discussion of Results

The contents of compounds detected in the model liquids after the cavitational processing in the presence of catalysts are given in the Tables 1 and 2.

Table 1

The contents of compounds detected in the hexane after the cavitation processing

Without catalyst		In the presence of NiO		In the presense of nanoparticles Fe_2O_3	
Compounds	Mass conc., %	Compounds	Mass conc., %	Compounds	Mass conc., %
3-Ethyl-4-methyl-hexane	1.65	4-Methylpentene-2	0.03	3-Ethyl-4-methyl-hexane	0.01
3,5-Dimethyloctane	6.79	Decane	70.17	Nonane	1.04
Decane	50.16	3-Methyldecane	2.26	Decane	94.15
3-Methyldecane	0.62	Undecane	12.42	3-Methyldecane	0.02
6-Ethyl-2-methyl-decane	2.92	4,6-Dimethylundecane	11.28	Undecane	3.25
2,4,6- Triethyldecane	2.5	Dodecane	0.62	4,6-Dimethylundcane	0.19
Undecane	12.6	Tridecane	0.25	Dodecane	0.11
4,6-Dimethylundecane	15.11			Tridecane	0.05
Dodecane	0.56			Tetradecane	0.08
Tridecane	0.19			Hexadecane	0.3
Hexadecane	1.94				
Oxygen-containingcompounds					
2-Nonanone	0.05	2-Nonanone	0.48	2-Nonanone	0.27
2-Decanone	0.96	2-Decanone	0.9	2-Decanone	0.2
4-Decanone	0.9	4-Decanone	0.93	4-Decanone	0.16
3-Decanone	0.63	3-Decanone	0.66	3-Decanone	0.15
2-Methylheptanone-4	0.52				
Isooctane, (ethenyloxy)	1.9				

Analysis by gas chromatography-mass spectroscopy detects the contents of paraffin hydrocarbons from C_6 to C_{17} in the model compounds, both normal and isomers. The isomerization proceeds on freely radical mechanism. There are more isomers in case cavitational processing without catalysts. About 6.79 % of 3,5-dimethyloctane, 3-ethyl-4-methylhexane, also 12.6 % of undecane, 15,11 % of 4,6-dimethylundecane are formed in case cavitational processing without catalysts. In the presence of NiO the contents of undecane is 12.42 % and 4,6-dimethylundecane — 11.28 %. The 1.04 % of nonane and 3.25 % of undecane are formed in the presence of Fe_2O_3. Also oxygen-containing compounds are detected after cavitation processing and their contents depend on concentration of dissolved oxygen in the liquid. Such auto-oxidation processes are typical for heating of organic liquids, the cavitation is accompanied by heating.

Table 2

The contents of compounds detected in the mixture of decane and hexane after the cavitation processing

Without catalyst		In the presence of NiO		In the presense of nanoparticles Fe_2O_3	
Compounds	Mass conc., %	Compounds	Mass conc., %	Compounds	Mass conc., %
3,5-Dimethyloctane	22.55	Decane	82.77	2,2,3-Trimethylbutane	0.7
Decane	59.91	3-Methyldecane	0.39	2,3-Dimethylbutane	3.1
3-Methyldecane	0.4	2-Methyldecane	0.98	2,3-Dimethylpentane	42.98
Undecane	11.53	Undecane	12.69	Hexane	4.67
Dodecane	0.28	Dodecane	0.38	Decane	43.01
Tridecane	0.11	Tridecane	0.09	Undecane	1.85
				Dodecane	0.12
				Tridecane	0.23
Oxygen-containingcompounds					
2-Methyl-2-pentyl-oxirane	0.25	2-Nonanone	0.13	2-Methoxyoctene	0.12
2-Nonanone	0.23	3-Decanone	0.62	2-Nonanone	0.23
3-Decanone	0.57	5-Decanone	0.56	3-Decanone	0.09
5-Decanone	0.5	2,5,8-Trimethyl-nonanedione-4,6	0.58	5-Decanone	0.09
1,1'- Oxybisdecane	3.58			1,1'-Oxybisdecane	2.81
Hexanoic acid	0.09				

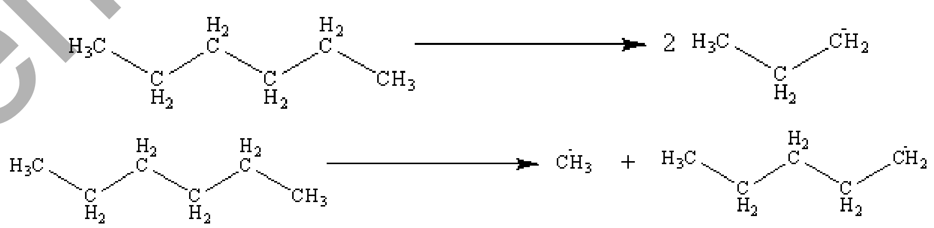
About 22.55 % of 3,5-dimethyloctane, 11.53 % of undecane are formed in case cavitational processing without catalysts. In the presence of NiO the contents of undecane is 12.69 %. The 42.98 % of 2,3-dimethylpentane and 3.1 % of 2,3-dimethylbutane, 1.85 % of undecane are formed in the presence of Fe_2O_3. The cavitation processing of model liquids consisting of decane and hexane is more effective in the presence of Fe_2O_3 and without catalyst.

The obtained findings allow to conclude that reactions of degradation are occurred intensively in the process of cavitation. As a result of these processes «activated» particles accumulate in the system [6].

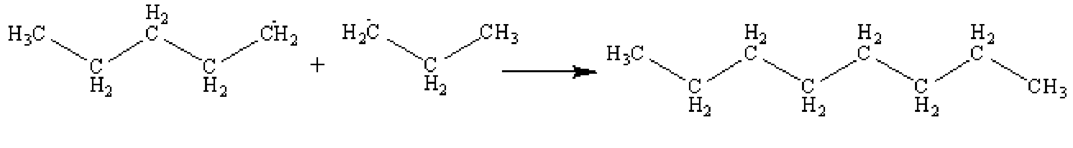
Usually lifetime of activated formation is short. However, some of these formations possess the determined stability and are capable to exist for definitive time. Process of radicals' disappearance takes place by two ways: as a result of disproportionation and recombination.

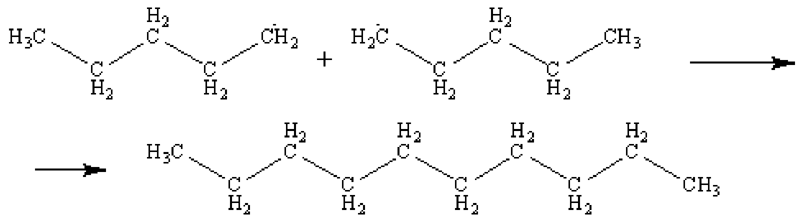
Describing the destruction of decane and hexane by ultrasonic cavitation it can be compared with the findings of research [7].

1. Originally, destruction of model compounds' proceeds on freely radical mechanism, initiated by the cavitation phenomenon. The bond breakage C–C occurs more intensively in the middle and at the first carbon atom of a molecule:



2. Lifetime of formed radicals extremely short, the break of a kinetic chain proceeds according to the following scheme:





As a result of repeating stages of growth and chain breakage the number of *n*-alkanes accumulates in the reaction system.

In the system of antracene–toluene-hexane about 3 % of 9,10-dihydroanthracene and 1 % of phenantrene are formed without catalyst. In the presence of the FeS_2 the content of 9,10-dihydroantracene is 3.61 %, fenantrene — 2.38 % and 1,2,3,4-tetrahydroanthracene — 0.75 %. It can be concluded that anthracene is hydrogenated in the presence of hexane which can be hydrogen donor. It is obvious that the obtained contents is not limiting and it is possible to increase it by selection of optimum conditions.

The obtained experimental findings show the positive impact of cavitation. Cavitational processing of liquid products can be used in technological processes of oil-refining industry, particular for receiving light fractions from heavy oil and increasing the octane number of oil fuel by an isomerization.

References

1 *Промтов М.А.* Кавитационная технология для улучшения качества топлива // Химическая и нефтехимическая технология. — 2008. — № 1–2. — С. 44.

2 *Бесов А.С., Колтунов К.У., Брулев С.О., Кириленко В.Н., Кузьменков С.И., Пальчиков Е.И.* Деструкция углеводородов в кавитационной области при активации электрическим полем // Письма в ПЖФ. — 2003. — № 5. — С. 71–76.

3 *Яковлев В.А., Заварухин С.Г., Кузавов В.Т. и др.* Химические превращения органических соединений при кавитационном воздействии. — 2010. — № 3. — С. 43–51.

4 *Параг Р., Анирудха Б.* Гидродинамический кавитатор. — 2001. — № 1. — С. 9–12.

5 *Синтай Су, Фэнгви Ма, Татеева А.Б.* Ожижение угля в присутствии катализаторов на основе железа // Вестн. Караганд. ун-та. Сер. Химия. — 2011. — № 4(64). — С. 60–64.

6 *Федоткин И.М., Немчин А.Ф.* Применение кавитации в технологических процессах. — Киев: Высш. шк., 1984. — С. 59.

7 *Дудкин Д., Кульков М.Г., Шестакова Е.Н.* Превращения углеводородов при механохимическом воздействии // Химия и технология топлив и масел. — 2012. — № 2. — С. 39–41.

М.И.Байкенов, А.Б.Татеева, А.Ж.Матаева, Д.А.Балабекова,
Б.О.Есебаев, А.Б.Тлеубергенова, Р.С.Бержанова

Ультрадыбыстық кавитацияның модельдік қосылыстардың химиялық айналымдарына әсері

Ультрадыбыстық кавитацияның әр түрлі органикалық қосылыстардың химиялық айналымдарына түрлі катализаторлардың қатысында әсері зерттелген. Сонымен қатар кавитацияның мұнай өңдеу саласында көмірсутектердің крекинг үрдісін жүргізуге мүмкіндігі бағаланған. Алынған мәліметтер бойынша, органикалық қосылыстардың деструкция үрдісінде кавитацияны қолдану технологиялық және экономикалық тұрғыдан тиімді.

М.И.Байкенов, А.Б.Татеева, А.Ж.Матаева, Д.А.Балабекова,
Б.О.Есебаев, А.Б.Тлеубергенова, Р.С.Бержанова

Воздействие ультразвуковой кавитации на химические превращения модельных соединений

Исследовано влияние ультразвуковой кавитации на различные органические соединения в присутствии катализаторов с выявлением химизма превращений, а также выяснение возможности практического применения кавитации для крекинга углеводородов в нефтепереработке. Полученные данные позволяют сделать вывод о том, что использование кавитации для деструкции органических соединений является технологически эффективным и экономически выгодным.

References

1 Promtov M.A. *Chemical and petroleum engineering*, 2008, 1–2, p. 44.

2 Besov A.S., Koltunov K.U., Brulev S.O., Kirilenko V.N., Kuzmenkov S.I., Palchikov E.I. *Letters to PZHF*, 2003, 5, p. 71–76.

3 Yakovlev V.A., Zavarukhin S.G., Kuzavov V.T. et al. *Chemical physics*, 2010, 3, p. 43–51.

4 Parag R., Aniruddha B. *Hydrodynamic cavitation reactors: a state of the art review*, 2001, 17, 1, p. 9–12.

5 Xintai Su, Fengyu Ma, Tateyeva A.B. *Bulletin of Karaganda State University, Chem. ser.*, 2011, 4(64), p. 60–64.

6 Fedotkin I.M., Nemchin A.F. *The use of cavitation on the technological processes*, Kiev: Vysshaya Shkola, 1984, p. 59.

7 Dudkin D., Kulkov M.G., Shestakova Ye.N. *Chemistry and technology of fuel and oil*, 2012, 2, p. 39–41.