Chemistry, Technology and Application of Substances

Vol. 2, No. 2, 2019

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CREATING THE BASIS OF NON-EXHAUSTIVE TECHNOLOGY OF CYCLOHEXAN OXIDATION

https://doi.org/10.23939/ctas2019.02.091

The bases for complex processing and creation of non-waste technology of oxidation process of cyclohexane are proposed. The methods of using by-products of the oxidation process of cyclohexane – alcohol fraction and acid mixture are considered. The method of using the alcohol fraction as an effective additive to diesel fuels is studied. It was investigated that alcoholic additive improves the technological and operational properties of diesel fuels. The method of using a mixture of acids obtained in the process of oxidation of cyclohexane for the esterification of them with butyl alcohol and the preparation of a valuable ester, dibutyl adipinate, was studied.

Key words: oxidation, cyclohexane, alcohol fraction, adipic acid, esterification, ester, diesel fuel.

Introduction

As for today one of the most important issue of the Ukrainian industry is complex processing of by-products and waste-free technologies that reduce material consumption of the product, its cost, and that significantly reduce the level of pollution of air, water, soil.

The main disadvantage of industrial oxidation processes of hydrocarbons is a free radical mechanism that requires complex conditions (temperature and pressure) and causes low selectivity during deeper oxidation. Among industrial processes oxidation of cyclohexane (CH) – intermediate product in the production of polyamide fibers – plays a significant role [3]. The peculiarity of the process is the formation of a large number of by-products, most important of which are alcohol fraction and acids, mainly adipic acid, that do not find a qualified use due to the complications of their obtaining and purification. These products are mostly burned, that leads to an increase in production cost factors. In addition, low conversion rates of raw materials lead to high energy consumption in the production, which is due to the recycling of unreacted raw materials.

Taking all of mentioned into account, it is therefore important to focus research on the finding of new improvements of the known methods of use of the by-products. The use of the alcohol fraction as an effective additive to fuels [10–12] and a mixture of acids as raw materials for their esterification with alcohol are perspective.

It is known [1] that one of the directions of disposal of alcohol waste can be to add them to the fuel of the carburetor engines. It was investigated that the addition of alcohol waste to gasoline, facilitates their fractional composition, which leads to improved engine performance in various regimes; with the temperature of the beginning of boiling rises, which prevents premature evaporation of fuel in the fuel system of the engine. It also improves the character of combustion of fuels, increases detonation resistance of fuels, improves their operational properties.

One of the methods of use of acids is to obtain acid esters by their esterification with alcohol [2, 4, 5–9, 13]. Subsequently, the esters obtained can be used as plasticizers for polymers. In the case of esterification with lower alcohols, the esters obtained can be separated at boiling point and used as raw material for the allocation of individual acids.

The aim of the study

Study of methods for the use of by-products of the oxidation process of cyclohexane – alcohol fraction and acid mixture, for a comprehensive recycling and creation of zero waste technologies of this process.

Materials and methods of the research

To study the method of use of the alcohol fraction, the taken alcohol fraction (AF) was – the waste of the oxidation process of the production of adipic acid from PJSC "Rivne Azot" and the direct fission fraction of diesel fuel after atmospheric distillation. We have prepared mixtures of diesel fuel samples with AF additives in the following bulk proportions:

1. diesel (100 %) + AF (0 %),
2. diesel (95 %) + AF (5 %),
3. diesel (92 %) + AF (8 %),
4. diesel (90 %) + AF (10 %),
5. diesel (89 %) + AF (11 %),
6. diesel (88 %) + AF (12 %),
7. diesel (87 %) + AF (13 %)
8. diesel (86 %) + AF (14 %),
9. diesel (85 %) + AF (15 %)
10. diesel (82 %) + AF (18 %),
11. diesel (80 %) + AF (20 %).

For the created mixtures density was found by ρ^{15} pycnometric method, kinematic viscosity ν by capillary viscometer. After that, the distillation of diesel fuel and prepared mixtures was performed, during which their fractional composition was determined, namely: the temperature of the beginning of boiling, the boiling point of 10 %, and 50 % of the points. The fractional formulations obtained were analyzed and cetane indices were determined for the analyzed samples.

For diesel fuels, the main parameters that characterize the period of ignition delay from compression of the fuel-air mixture are the cetane number and the cetane index (CI) – an indicator used in European standards.

The determination of the CI was carried out according to CT CEB 5871-87 method of determining the density of diesel fuel at 15 °C and the average boiling point of the 50 % (by volume) of its amount. The cetane index was calculated by the formula:

$$CI = 454.74 – 1641.416 \cdot \rho + 774.74 \cdot \rho 2 – –0.554 \cdot t + 97.803 \cdot (lgt)2,$$

where ρ^{15} – density of diesel at 15 °C, g/sm^3; t – boiling temperature of 50 % (volume) analyzed mixture, °C.

To study the method of use of a mixture of acids, mainly adipic acid, was used oxidate obtained by oxidation of CH in the presence of a catalytic system [NC-CEE] (NC: CEE = 1: 1). The composition of oxidation products containing this oxidate is given below (Table 1).

The obtained acids from the mixture of the remaining products were separated by washing with water. The resulting aqueous solution of organic acids was concentrated by evaporation of water. The composition of the resulting acid solution is given in Table. 2.

Table 1

Composition of products obtained by oxidation of cyclohexane (CH) in the presence of binary catalytic system NC-CEE. k, % – 11,96

C(HPCH), mol/l	C(AC), mol/l	C(DCA), mol/l	C(COL), mol/l	C(CON), mol/l
0.026	0.433	0.090	0.177	0.225
S(HPCH), %	S(AC), %	S(DCA), %	S(COL), %	S(CON), %
0.24	39.15	8.09	15.98	20.37

Table 2

Composition of water solution of acids

C(AC), mol/l	C(HPCH), mol/l	C(DCA), mol/l	C(COL), mol/l	C(CON), mol/l
0.476	0.001	0.023	0.009	0.014

Results and discussion

The results of experimental data and calculations for pure diesel fuel and its mixtures with additives of alcohol fraction (AF) are shown in Table 3.

According to the data of the table, the graphs of the dependence of CI, kinematic viscosity, boiling start temperatures and boiling of 10 % and 50 % of the points from the concentration of alcohol fraction

in diesel fuel were constructed. To evaluate the operational properties of the prepared fuel mixtures, their fractional composition was analyzed.

According to the results of the analysis, the following conclusions can be drawn. Additives of alcohol fraction increase the cetane index of diesel fuel in a definite interval, which is observed at a concentration of SF from 10 % to 13 %, which is visible on the curve of Fig. 1.

This positively affects the characteristics of self-combustion, because faster is the pre-oxidation of fuel in the combustion chamber, and the faster the mixture lights up and the engine starts. AF additives above 15 % lower the cetane index of diesel fuel.

With the addition of the alcohol fraction, the temperature of the boiling start decreases, which characterizes the starting properties of the fuel (Fig. 2). With the decrease of this temperature, the amount of easily evaporating substances increases, which makes it easier and at lower ambient temperature to start the engine.

Similarly, with addition of alcohol fraction, the boiling temperature of 10 % of fuel is lowered, which also improves engine start-up properties. Especially this dependence is manifested when the concentration of SF is reached – 10 % (Fig. 3).

Table 3

Results of research for the diesel and its mixture with AF

Dies. %v	AF, % vol	ν 20, сСт	ρ_4^{15}, kg/м^3	T_{boil}, °C	t_{10}, °C	t_{50}, °C
100	-	4.07	835.75	174	214	278
95	5	4.01	833.47	140	202	273
92	8	3.74	833.31	136	170	273
90	10	3.72	832.95	134	152	272
89	11	3.70	830.24	134	151	271
82	12	3.68	825.50	134	150	271
87	13	3.65	828.34	135	150	268
86	14	3.78	830.74	133	152	263
85	15	3.91	831.40	132	150	262
82	18	3.96	831.91	130	148	255
80	20	4.01	832.34	128	148	250

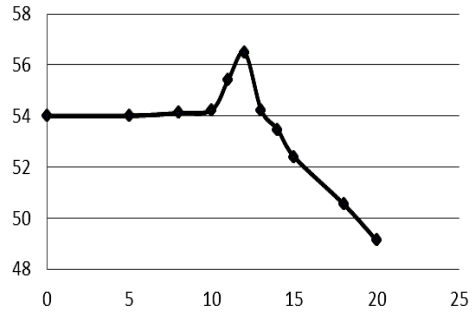

Fig. 1. Dependence of CI from concentration of AF (%) in diesel

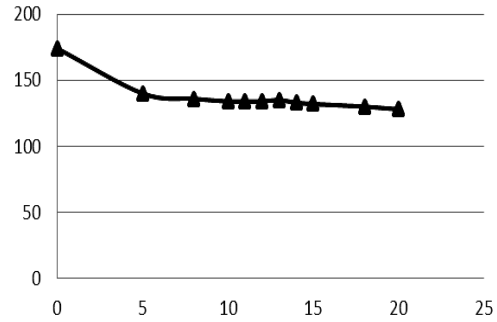

Fig. 2. Dependence of T_{boil}. Of mixture from concentration of AF (%) in diesel

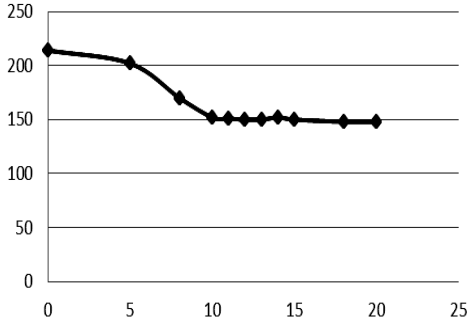

Fig. 3. Dependence of T_{boil}. 10 % mixture from concentration of AF (%) in diesel

From Fig. 4 it is evident that with the addition of alcohol fraction the temperature of boiling up to 50 % of the amount of fuel decreases, and until the concentration of AF = 12 % is reached, this dependence is manifested by a smooth decrease, and even higher concentration of alcohol fraction of 12 % begins a sharp decrease of T_{50}. This has a positive effect on diesel engine, because it facilitates its evaporation and thus provides the possibility of smoother and more stable engine operation, significantly improves its maneuverability, as well as significantly reduces fuel consumption.

The viscosity of diesel fuel largely determines the operation of diesel equipment diesel engine. Figure 5 shows the effect of SF additives on the viscosity of the fuel mixture. Additives of alcohol fraction reduce the viscosity of diesel fuel in a definite interval, which is observed at a concentration of AF from 5 % to 18 % with a minimum of 12–13 %. Reducing the viscosity of the fuel leads to easier fuel spraying, which ensures the most complete and rapid evaporation of it. The fineness of the sawing is estimated by the size of the droplets, which provide the most complete and fast evaporation and should be within the limits of 5–40 microns. The less viscous fuel is better ignited and burned, which leads to a reduction in its cost and exhaust smoke. It is also positive that the viscosity of the mixtures analyzed does not decrease less than 3 cSt, because low-fueled fuel during operation increases the wear of parts of the fuel pump.

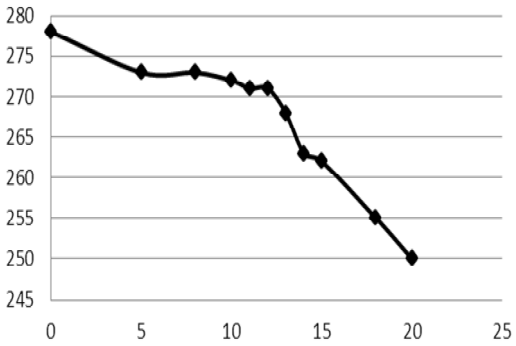

Fig. 4. Dependence of T_{boil}. 50 % mixture from concentration of AF (%) in diesel

Addition of a withdrawal of the process of oxidation of cyclohexane – alcohol fraction – to diesel fuels positively affects their fractional composition, which leads to improvement of engine operation in various regimes; improves its starting properties, improves engine maneuverability, facilitates spraying and reduces fuel consumption and its propensity to form steam-air cocks in the engine power supply. Additives of alcohol fraction increase the cetane index – a characteristic that is used in European standards. The optimum concentration of the alcohol fraction additive is in the range of 10 to 13 % by volume.

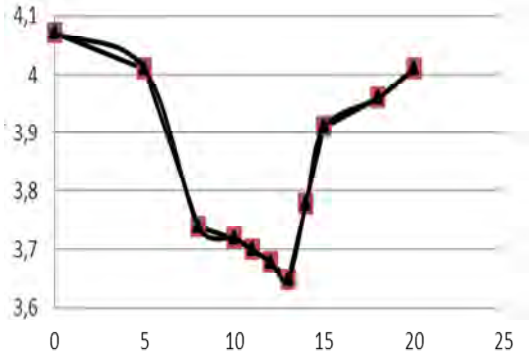

Fig. 5. Dependence of viscosity from concentration of AF (%) in diesel

The resulting aqueous solution of organic acids – the waste of the process of oxidation of CG was subjected to esterification with alcohol. The esterification of the aqueous layer of acids in the excess of n-butanol in the presence of an ion exchange resin KU-2 was carried out at boiling point of the azeotropic water-n-butanol azeotrope T = 365 K.

After the esterification process, distillation of water and unreacted n-butanol was performed. The mass of the resulting mixture of esters is m (sums) = = 4.467 g. An analysis of the composition of the resulting mixture of products was carried out, which is shown in the table (Table 4). The yield of esters is n = 57.6 %.

For an approximate comparative estimation of the efficiency of using this complex method of oxidation products, we will convert the amount of products obtained into 1000 kg of the reacted CH and compare them with similar data obtained in the presence of individual NC, provided that the acids are neutralized and the adipates obtained are burned (Table 5, 6).

Thus, in the oxidation of 1t cyclohexane in the application of an industrial catalyst – NC, m (COL, CON, AA) was obtained = 863 kg of a mixture of COL, CON and adipic acid, which was neutralized

by the m (NaOH) = 228 kg of sodium hydroxide (tab. 5). In the case of oxidation of CH in the presence of a binary catalytic system NC-CEE (1: 1) m = 860 kg of the mixture of COL and CON, dibutyl adipinate m = 727 kg and m = 69 kg of adipates were obtained (Table 6). Comparing the obtained data, we can see that the amount of the resulting mixture of COL and CON in both cases is practically equal, however, in the presence of NC-CEE, we received more acids, which were used as raw material for obtaining additional amount of target products, namely dibutyl adipinate.

Table 4

Composition of received cube of esterification of adipic acid and n-butanole at T=365 K

C(AC), mol/l	C(HPCH), mol/l	C(DBA), mol/l	C(COL), mol/l	C(CON), mol/l
0.090	0.000	0.668	0.000	0.000

Table 5

Amount of obtained aim products from 1 ton of reacted cyclohexane in the presence of NC

Compound	Used, kg	Recieved, kg
Cyclohexane	1000	–
n-butanole	–	–
Sodium hydroxide	228	–
COL + CON	–	863
Adipates	–	462
Dibutyl adipate	–	–
Sum of the aim prod.	–	863

Table 6

Amount of obtained aim products from 1 ton of reacted cyclohexane in the presence of catalytic system NC–CEE

Compound	Used, kg	Recieved, kg
Cyclohexane	1000	–
n-butanole	417	–
Sodium hydroxide	31	–
COL + CON	–	860
Adipates	–	69
Dibutyl adipate	–	727
Sum of the aim products *	–	1587

** Mixture COL, CON and dibutyl adipate.*

Conclusion

The obtained results testify to the possibility of creating a non-waste technology for oxidation of cyclohexane by complex processing of by-products of the process – alcohol fraction and acid mixtures. The method of using the alcohol fraction as an effective additive to diesel fuels was studied. The method of using a mixture of acids obtained in the process of oxidation of cyclohexane for the esterification of them with butyl alcohol and the preparation of a valuable ester, dibutyl adipinate was studied.

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СТВОРЕННЯ ОСНОВ БЕЗВІДХОДНОЇ ТЕХНОЛОГІЇ ОКИСНЕННЯ ЦИКЛОГЕКСАНУ

Запропоновано основи комплексної переробки і створення безвідходної технології процесу окиснення циклогексану. Розглянуто методи використання побічних продуктів процесу окиснення циклогексану – спиртової фракції та суміші кислот. Вивчено метод використання спиртової фракції як ефективної добавки до дизельних палив. Досліджено, що добавки спиртової фракції покращують технологічні та експлуатаційні властивості дизельних палив. Вивчено метод використання суміші кислот, що одержують в процесі окиснення циклогексану, для естерифікації їх із бутиловим спиртом та одержання цінного естеру – дибутиладипінату.

Ключові слова: окиснення, циклогексан, спиртова фракція, адипінова кислота, етерифікація, естер, дизельне паливо.