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# Useful Additives for Jet Fuel Based on Decarboxylation of Petroleum Acids

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**Abstract**

The novel power consuming and high-density additives to fuels based on mixture of mono-, bi- and polycyclic naphthenic hydrocarbons received by catalytic decarboxylation of petroleum acids have been proposed. The physico-chemical indices and thermoability of this additives have been determined.

***Keywords:*** *petroleum acids, additives to fuels, thermoability, naphthenic acids, naphthenic hydrocarbons*

## 1. Introduction

It is known that, because of cyclic hydrocarbons have high density and thermoability , they attract great attention as additives to fuels. The investigations of last years literature showed, the potential of application of cyclic hydrocarbons and its derivatives as fuels or additives to fuels. So, in work [1] the nature sesquiterpenes – valencene, premnospirodiene and cariofillene have been isomerized in the presence of heterogeneous catalyst Nafion SAC-13 with further hydrogenation of obtained product. It is shown that, in the case of cariofillene, the main product of isomerization was tricyclic hydrocarbon, but in the case of valencene and premnospirodiene, dominant product was δ-selinene. In both case, the density of fuel increase by 6 % and its thermoability by 13 %.

In other work [2], cycloalkane hydrocarbons were received by aldol condensation of cyclopentadiene and butanal with futher hydrodeoxygenation of obtained product. It is shown that, among used solid-base catalysts , hydrotalcite of magnesium-aluminium showed the better activity.

It is marked that, bicycloalkanes with high density may be used as additives to diesel and jet fuels and obtained from cycloolefins by two-step process with high yield (nearly 80 %) [3]. The dimerization of cycloolefins of $C_5$-$C_8$ series was carried out in the presence of iron (3) salts and hydrogenation of intermediate in the presence of metallic catalysts.

In analogical works [4,5], the process for receiving of power consuming fuels and additives to them with high density based on selective dimerization of α-pinen, camphen, limonene and turpendine in the presence of heterogeneous catalysts, such as montmorrilonit K-10 have been proposed. The yield of dimmers of terpenes consist 90 %.

Renewable highly density additives to aviation fuels were synthesized with high yield (95,6 %) by Gilbert reaction based on cyclopentanone which may be separated from lignocelluloses with futher hydrodeoxygenation [6,7]. This reaction carried out without solvents and in the presence of catalysts – solid bases and Raney metals. The better activity is shown by hydrotalcite of magnesium – aluminium and nickel Raney. The final products of this reaction were bicyclopentane and tricyclopentane which have high density of 86 g/ml and 0,91 g/ml, respectively.

The result of this investigations showed that, bi- and polycyclic hydrocarbons are more optimum additives to diesel and jet fuels. However, in described investigations of authors, very laborious initial compounds as raw material are used and this method can not be applied for the synthesis of cyclic derivatives. Therefore, investigating new methods of synthesis of cyclic compounds is also actual in the modern stage.

One of the efficient method of receiving of mono-, bi- and polycyclic hydrocarbons was catalytic decarboxylation of useful initial product (such as petroleum acids separated from crude oils) which have been proposed in our papers [8-10].

## 2. Experiment

The product of decarboxylation of petroleum acids (PA) and also fractions received after vacuum distillation (pressure 15 mm Hg) were used as analyzed compounds (Table 1).

Table 1. Physico-chemical properties of initial PA and fractions received from it.

| Fraction PA | T, $^{0}C$ | Acid number, mg KOH/g | $n_D^{20}$ | $d_4^{20}$ |
|---|---|---|---|---|
| Initial | ------ | 212 | 1,4690 | 0,9643 |
| I fraction | 158-201 | 250 | 1,4650 | 0,9608 |
| II fraction | 202-207 | 201 | 1,4680 | 0,9543 |
| III fraction | 211-224 | 216 | 1,4700 | 0,9489 |

The catalytic decarboxylation of PA have been carried out by following method [8]. Stationary reactor is filled with catalysts and heated to determined temperature. After that, calculated amount of PA was passed by dosator with determined volume rate through reactor. After cooling, reaction product was collected and its physico-chemical properties such as density, $n_D^{20}$ and acid number were investigated.

Nano-sized magnesium oxide received by method [9] was taken as catalyst of decarboxylation of PA. The structure of nano-magnesium oxide was studied by microscope C3MY-5 in semicontact phase. It was found that, medium size of particles of magnesium oxide is 100 nm.

## 3. Result and Discussion

It is known that , petroleum acids consist of mono-, bi-, tri-, tetra- and polycyclic acids which have small branched alkyl radicals. The composition of PA components is shown in Table 2 [10].

Table 2. Components of PA

| Components | Content, % |
|---|---|
| Aliphatic acids | 16,06 |
| Monocyclic acids | 18,91 |
| Bicyclic acids | 17,44 |
| Tricyclic acids | 13,32 |
| Tetracyclic acids | 10,40 |
| Pentacyclic acids | 10,56 |
| Hexacyclic and aromatic acids | 13,31 |

The final product of decarboxylation of PA was mixture of mono-, bi- and polycyclic hydrocarbons which have high melting point and density. That is why, we carried out investigation for determination of thermoability of received product. Thermoability of received product is determined by known method GOST 21261-92.

The results of these investigations are presented in Table 3.

Table 3. Thermoability of decarboxylation product of initial compound and received fraction of PA (total number of initial PA was 212 mg KOH/g)

| PA fractions | T, $^0$C | Acid number, мg KOH/g | $n_D^{20}$ | $d_{20}^4$ | Thermo ability, MDj/кg |
|---|---|---|---|---|---|
| Initial | 250 | 124,7 | 1,5020 | 0,9625 | 38.210 |
| I fraction | 250 | 115,6 | 1,5030 | 0,9641 | 39.600 |
| II fraction | 250 | 117,7 | 1,4990 | 0,9750 | 38.575 |
| III fraction | 250 | 116,3 | 1,5000 | 0,9711 | 38.412 |
| Initial | 300 | 64,7 | 1,4990 | 0,9630 | 38.610 |
| I fraction | 300 | 52,8 | 1,5010 | 0,9581 | 39.725 |
| II fraction | 300 | 50,7 | 1,5000 | 0,9692 | 38.915 |
| III fraction | 300 | 47,6 | 1,5010 | 0,9710 | 39.024 |
| Initial | 350 | 2,7 | 1,5040 | 0,9683 | 39.215 |
| I fraction | 350 | 2,9 | 1,5010 | 0,9711 | 41.470 |
| II fraction | 350 | 1,5 | 1,5020 | 0,9692 | 41.737 |
| III fraction | 350 | 1,7 | 1,4990 | 0,9732 | 41.831 |

As it is seen from Table 3, the decarboxylation product of PA has high thermoability (nearly 42000 MDj/kg) and also low acid number (1,5-1,7 mg KOH/g) and high density (0,96-0,98 g/мl). The best results are obtained at $350^0$C temperature in the presence of nano-sized magnesium oxide.

## 4. Conclusions

Summarizing all, it is determined that, the novel power consuming and high-density additives to fuels based on mixture of mono-, bi- and polycyclic naphthenic hydrocarbons received by catalytic decarboxylation of petroleum acids. Based on described results, synthesized decarboxylation product of PA was proposed as additive to fuels [9].

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