Towards fuel antioxidants of new types

Leyla Veliyeva¹ · Arzu Sadiqova¹ · Zubeyda Israfilova² · Irada Rzaeva² · Malahat Kurbanova¹ · Vagif Farzaliyev² · Abel Maharramov¹ · Afsun Sujayev²

Received: 30 April 2021 / Accepted: 22 July 2021 / Published online: 13 August 2021
© The Author(s) 2021

Abstract
To find novel classes of potential fuel additives of multivalent activity, particularly antioxidants, a series of recently synthesized ethyl-6-amino-5-cyan-methyl-4-aryl-4H-pyran-3-carboxylates have been investigated using model oxidative reactions. The compounds studied appear to be prospective inhibitors of hydrocarbons oxidation. Some of them are antioxidants of combined action, breaking the chains of the oxidative reactions with cumene peroxide radicals and catalytically decomposing cumene hydroperoxide.

Keywords Multivalent · Inhibitor · Cumene peroxide · Radical · Antioxidant

Introduction
Resistance to oxidation is one of the most important performance characteristics of fuel and lubrication materials since many undesirable processes occurring in machines and mechanisms are associated with the formation of different oxidation products [1]. Therefore, the design of novel antioxidants of a higher efficiency represents an urgent challenge in the chemistry of additives.

The oxidation of hydrocarbons is known to be a radical-chain and degenerate-branched process, which simply can be represented as follows:

\[ R^\cdot + O_2 \rightarrow RO_2^\cdot \]

\[ RH + RO_2^\cdot \rightarrow R^\cdot + ROOH \]

\[ R^\cdot + ROOH \rightarrow RO_2^\cdot + RH \]

To inhibit this process, one should employ the compounds that would quickly react with the forming radicals (R’ or RO2’*) or destroy the hydroperoxide without generating other free radicals [2].

Since the antioxidant properties of additives are due to the presence of certain functional groups in their composition, the investigations into the synthesis and mechanism of the antioxidant action of organic compounds containing two or more functional groups in the molecule, which allow combining various types of antioxidants in one structure, is of undoubted research and practical interest [3].

On the basis of the foregoing, we conducted studies on the synthesis, study of the mechanism of action, as well as the relationship between the structure and the effectiveness of the antioxidant action of sulfur-containing polyfunctional antioxidants [4].

When choosing sulfur-containing polyfunctional antioxidants, we proceeded from combining the properties of two types of antioxidants in the molecule of the compound: an antioxidant that effectively breaks oxidation chains by reaction with peroxide radicals, and an antioxidant that decomposes hydroperoxides. As you know, the first type of antioxidants includes mainly phenols and aromatic amines, and the second type—sulfides. Therefore, they initially synthesized and investigated compounds containing a sulfide sulfur atom in a molecule in combination with phenolic fragments—phenolsulfides [5]:

\[ \text{OH} \quad \text{SR}^1 \]

\[ \text{R} \]

The mechanism of the antioxidant action of sulfur-containing antioxidants was studied using the well-known

---

¹ Organic Chemistry Department, Baku State University, Z. Khalilov 23, Baku, AZ 1148, Azerbaijan
² Laboratory of Fine Organic Chemistry, Institute of Chemistry of Additives, ANAS, 1029 Baku, Azerbaijan

Afsun Sujayev
sucayevafsun@gmail.com
kinetic method, the essence of which is to study the key reactions that determine the inhibitory effect of antioxidants: the termination of oxidation chains in the reaction with peroxide radicals and the decomposition of hydroperoxides. Isopropylbenzene (cumene) was used as a model hydrocarbon, the oxidation mechanism of which has been studied in detail [6, 7].

Studies have shown that the studied antioxidants inhibit the initiated oxidation of cumene by reacting with cumyl peroxide radicals. At the same time, these sulfur-containing antioxidants are at the level of known alkylphenol antioxidants in terms of the effectiveness of the termination of oxidation chains by reaction with peroxide radicals.

The presence of a sulfide fragment in the molecules of the synthesized antioxidants suggested their interaction with hydroperoxides. The very first studies of the reaction of phenolsulfides with cumyl hydroperoxide showed that their activity in the decomposition of hydroperoxides is incomparably higher than that of sulfides and other types of hydroperoxide breakers. It was found that phenolsulfides catalytically decompose hydroperoxides: one phenol sulfide molecule decomposes tens of thousands of hydroperoxide molecules.

Thus, the study of the antioxidant properties of phenolsulfides showed that they are antioxidants of combined action: they terminate oxidation chains by reaction with peroxide radicals and catalytically destroy hydroperoxides into molecular products.

Further, phenol sulfides were synthesized and investigated, in which a sulfur atom is combined with one phenolic fragment (monophenol sulfides) [8–11] and with two phenolic fragments (bisphenol sulfides) [12–16], which differ in the relative position of the sulfur atom and hydroxyl groups, the number substituents in the benzene ring of the phenol fragment and the nature of the substituent at the sulfur atom:

In addition, compounds were synthesized and investigated in which a sulfur atom is combined with an aniline fragment—aminosulfides [17]:

As well as compounds in which phenol sulfide and aminosulfide fragments are combined—aminophenol sulfides [18]:

![Chemical structures](image-url)
All of these compounds also turned out to be antioxidants with a combined effect.

In order to search for new antioxidants with a combined effect, a number of nitrogen-sulfur-containing compounds have been synthesized—thiourea derivatives [19–20] nitrogen-sulfur-containing heterocyclic compounds [21–22], which also turned out to be antioxidants with a combined effect.

In the present work, we have studied a series of recently synthesized, earlier unknown ethyl-6-amino-5-cyan-methyl-4-aryl-4H-pyran-3-carboxylates as potential polyfunctional multivalent fuel additives. Mechanism of their action was investigated and relationship between structure and efficiency of their antioxidant activity was estimated.

When selecting compounds for the study, it was assumed that the molecules should combine the properties of two types of antioxidants. The first one should effectively break the oxidation chains via the reaction with peroxide radicals, and the second one should decompose hydroperoxides. As is known, the first type of antioxidants includes mainly phenols and aromatic amines, and the second type consists of polyfunctional compounds.

Previously, antioxidants of combined action were found among thiourea derivatives and polyfunctional heterocycles.

### Results and discussion

#### Chemistry

Multicomponent domino reactions have become a useful method in the field of environmental and organic synthesis, which is due to their compliance with the requirements of green chemistry [22–26]. Polyfunctional substitute benzo-γ-pyrans synthesized by this method are important heterocyclic compounds. It has also been established that some 2-amino-4H-pyranes are important photoactive materials [27].

For the study, we have chosen eight representatives of the recently synthesized classes of ethyl-6-amino-5-cyan-methyl-4-aryl-4H-pyran-3-carboxylate compounds 1–8 as the antioxidant of combined action (Scheme 1).

All compounds are synthesized by original straightforward methods from available starting materials. When selecting the compounds for the study, we consider that if some of them would show promising performance characteristics, the synthetic procedures might be easily scaled up.

Given the important features of multifunctional 4H-pyran has, it is natural that there are many synthetic attempts to achieve the goal by applying simple reaction
strategies. Given the successful application of these compounds in a different field, the synthesis of their optical isomers on the basis of enantioselective synthesis is one of the most pressing issues (Table 1).

Given the successful application of 4H-pyran has in a different field, which contain different functional groups, we have synthesized them. Various aromatic aldehydes, acetic acid ether and malonitrile were used as the object of research. Optically active α-amino acid (L-glutamic acid) were used as chiral organic catalysts. The course of the reaction and the purity of the obtained substance were monitored by NTX chromatography. The scheme of the reaction is as follows (Scheme 2):

### Table 1

| Compound | Formula | Induction time of cumene autooxidation (T=110°C), τ, min | Reaction with RO₂⁻ (T=60°C) | Reaction with CHP (T=110°C) |
|----------|---------|-------------------------------------------------------|----------------------------|----------------------------|
|          |         | f          | kₕ₁·10⁻⁴ l/mol·s | Kₕ₁ l/mol·s | ν                  |
| 1        | ![Image](image1.png) | 250 | 2.6 | 3.6 | 15 | 12000 |
| 2        | ![Image](image2.png) | 220 | 2.2 | 3.2 | 13 | 10000 |
| 3        | ![Image](image3.png) | 130 | 1.59 | 1.92 | 8 | 6000 |
| 4        | ![Image](image4.png) | 210 | 1.81 | 2.88 | - | - |
| 5        | ![Image](image5.png) | 260 | 2.73 | 3.84 | 6 | 4500 |
| 6        | ![Image](image6.png) | 280 | 4.24 | 4.32 | 10 | 7000 |
| 7        | ![Image](image7.png) | 200 | 1.97 | 3.12 | 11 | 8000 |
| 8        | ![Image](image8.png) | 170 | 1.72 | 2.04 | - | - |
| Ionol    | ![Image](image9.png) | 150 | 2.10 | 2.00 | - | - |

**Antioxidant activity**

The study of cumene auto-oxidation in the presence of compounds 1–8 has shown that they effectively inhibit this process. The kinetic curves of auto-oxidation at 110 °C in the presence of compounds 1–8 are shown in Fig. 1, and the values of auto-oxidation induction period are given in Table. To establish the mechanism of the antioxidant action of the synthesized compounds, the kinetics of their reaction with cumene peroxide radicals and cumene hydroperoxide (CHP) has been investigated.

To evaluate the ability of the studied compounds 1–8 to break the oxidation chains via the reaction with cumene
peroxide radicals, the oxidation of cumene was initiated by azodiisobutyronitrile (AIBN) at 60 °C in the presence of these inhibitors. In all experiments, the concentration of the initiator was $2 \cdot 10^{-2}$ mol/l, and content of the inhibitor was $5 \cdot 10^{-4}$ mol/l. It was found that all studied compounds, to one degree or another, inhibited the initiated oxidation of cumene (Fig. 2):

Using the value of the induction time ($\tau$) of the initiated cumene oxidation, the stoichiometry coefficient $f$ was calculated. The latter is equal to the number of oxidation chains breaking under the action of one inhibitor molecule and products of its conversion:

$$f = \frac{\tau \cdot W_i}{[\text{InH}]_0}$$

where $\tau_{ind}$ is induction time, $W_i$ is initiation rate, $[\text{InH}]_0$ is initial concentration of the inhibitor.

To determine the value of the rate constant of the interaction of inhibitor with cumene peroxide radicals ($k_7$), the kinetic curves of the initiated oxidation of cumene were transformed from $\Delta[O_2] - \tau$ coordinates to $\Delta[O_2]^{-1} - \tau^{-1}$ coordinates. Using the slope of the straight line $tg \alpha = \frac{k_7[\text{InH}]_0}{k_2[RH]W_i}$

it was found that

$$k_7 = \frac{tgk_2[RH]W_i}{f[\text{InH}]_0}$$

where: $k_2 = 1,51 \text{ mol}^{-1} \cdot \text{s}^{-1}$, $[\text{RH}] = 7,17 \text{ mol}^{-1} \cdot \text{s}^{-1}$ [18].

The values of the kinetic parameters of the reaction of the synthesized compounds with cumene peroxide radicals are given in Table.

To evaluate the ability of the synthesized compounds 1–8 to decompose CHP, the reaction of cumene hydroperoxide with inhibitors has been implemented at 110 °C in chlorobenzene under nitrogen atmosphere (at this temperature, CHP is thermally stable). The studies have shown that the inhibitors, which contain a sulfur atom in the molecule, effectively decompose CHP (Fig. 3). Moreover, one molecule of the studied inhibitors is capable of decomposing several thousand CHP molecules, that is, the reaction has a catalytic character.
The number of CHP molecules ($v$), decomposed under the action of one molecule of the studied compounds, was calculated by the formula:

$$v = \frac{[CHP]_0 - [CHP]_\infty}{[InH]_0}$$

where $[CHP]_0$ and $[CHP]_\infty$ are the initial and final concentration of CHP, respectively, $[InH]_0$ is the initial concentration of the antioxidant.

It is found that for all compounds, the reaction with CHP is of the first order both in terms of antioxidant and CHP, and the initial reaction rate of the catalytic decomposition of CHP follows the equation:

$$w_0 = K[InH]_0 \cdot [CHP]$$

The values of the rate constant of CHP decomposition under the action of the studied compounds ($K$) and catalytic factor ($v$) are given in Table.

The Table also contains values of the induction time ($\tau$) of cumene autooxidation in the presence of the synthesized compounds, as well as the kinetic parameters of their reaction with cumene peroxide radicals and cumene hydroperoxide.

As shown from Table, all the studied compounds, except for compound 3, exhibit quite high antioxidant properties and surpass the well-known antioxidant like ionol (2,5-di-tert-butyl-4-methylphenol) in terms of antioxidant activity. Compounds 5, 6 and 1 possess the highest antioxidant activity. The latter is likely due to the fact that these compounds suppress peroxide radicals and very effectively break the oxidation chains. In addition, unlike ionol, they efficiently decompose hydroperoxides into molecular products. In the reaction with peroxide radicals, the stoichiometry coefficient ($f$) for these compounds is ~4, i.e. one molecule of these compounds breaks about four oxidation chains, while one molecule of ionol breaks only 2 oxidation chains. The reaction rate constant with peroxide radicals for these compounds is also higher than that for ionol.

**Conclusion**

In conclusion, a specially selected range of heterocyclic compounds (1–8), prospective multivalent fuel antioxidants of a new type, has been synthesized. The composition and structure of the compounds have been proved by modern physical–chemical methods.
It is established that these compounds are effective inhibitors of hydrocarbon oxidation. The mechanism of their antioxidant action involves the breaking of the oxidation chains via the reaction with peroxide radicals, and (for some compounds) catalytic decomposition of hydroperoxides into molecular products.

Materials and methods

Measurements

$^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ using a Bruker Avance 400 NMR spectrometer (400.13 and 100.6 MHz, respectively). The $^1$H chemical shifts (δ) were referenced to HMDS (0.05 ppm) in DMSO and the residual deuterated solvent, the $^{13}$C chemical shifts were expressed with respect to the deuterated solvent (77.10 ppm for DMSO). Coupling constants in hertz (Hz) were measured from one-dimensional spectra and multiplicities were abbreviated as following: br (broad), s (singlet), d (doublet), dd (doublet of doublets), m (multiplet). The chemical shifts were recorded in ppm, coupling constants (J) in Hz. IR spectra were obtained on a Varian 3100 IF-IR spectrometer (400–4000 cm$^{-1}$, KBr pellets or films). All spectra are given in Supporting Information (SI).

Experimental

Synthesis of ethyl-6-amino-5-cyano-methyl-4-aryl-4H-pyran-3-carboxylates (1–8)

The corresponding aldehyde (5 mmol), malonitrile (5.5 mmol), acetoacetic ether (5 mmol), 0.5 mmol optically active α-amino acid is taken as a catalyst in the flask. 8–10 ml of glycerin is used as a solvent. The reaction is carried out in a magnetic stirrer at room temperature. The resulting reaction product is filtered and recrystallized in ethanol.

Ethyl 6-amino-5-cyano-2-methyl-4-phenyl-4H-pyran-3-carboxylate (1)

IR (KBr): 3402.49 (NH$_2$), 3329.96 (NH$_2$), 2972.32 (C=H), 2190.34 (C≡N), 1692.10 (C=O), 1652.27, 1609.54, 1375.88, 1259.12, 1120.31, 1062.19 cm$^{-1}$. $^1$H-NMR (400 MHz, DMSO-d$_6$) δ = 1.21–1.30 (3H, CH$_3$, t), 2.50 (3H, CH$_3$, s), 3.81–4.05 (2H, CH$_2$, q), 4.60 (H, CH, s), 6.26 (2H, NH$_2$, s), 7.67–7.88 (5H, H-Ar, m) ppm. $^{13}$C-NMR (100 MHz, DMSO-d$_6$): δ = 12.53, 15.37, 55.53, 61.81, 108.85, 119.22, 125.51, 125.72, 127.53, 127.78, 142.85, 152.53, 154.37, 166.85 ppm.

Ethyl 6-amino-5-cyano-2-methyl-4-(p-tolyl)-4H-pyran-3-carboxylate (2)

$^1$H-NMR (400 MHz, DMSO-d$_6$) δ = 1.31–1.35 (3H, CH$_3$, t), 2.12 (3H, CH$_3$, s), 2.35 (CH$_3$, s), 3.93–4.05 (2H, CH$_2$, q), 4.44 (H, CH, s), 6.83 (2H, NH$_2$, s), 7.07–7.57 (4H, H-Ar, d, d) ppm. $^{13}$C-NMR (100 MHz, DMSO-d$_6$): δ = 14.59, 17.61, 21.43, 38.13, 58.36, 61.48, 107.31, 119.58, 128.36, 135.99, 141.51, 155.63, 159.87, 165.71 ppm.

Ethyl 6-amino-5-cyano-4-(4-methoxyphenyl)-2-methyl-4H-pyran-3-carboxylate (3)

$^1$H-NMR (400 MHz, DMSO-d$_6$) δ = 1.31–1.35 (3H, CH$_3$, t), 2.12 (3H, CH$_3$, s), 3.74 (CH$_3$, s), 3.93–3.4 (2H, CH$_2$, q), 4.44 (H, CH, s), 6.83 (2H, NH$_2$, s), 6.91–7.10 (4H, H-Ar, d, d) ppm. $^{13}$C-NMR (100 MHz, DMSO-d$_6$): δ = 14.59, 17.61, 38.45, 55.25, 56.48, 61.64, 108.25, 114.30, 119.58, 130.90, 136.73, 155.38, 158.75, 159.72, 165.25 ppm.

Ethyl 6-amino-5-cyano-4-(4-fluorophenyl)-2-methyl-4H-pyran-3-carboxylate (4)

$^1$H-NMR (400 MHz, DMSO-d$_6$) δ = 1.13–1.24 (3H, CH$_3$, t), 2.46 (3H, CH$_3$, s), 4.02–4.07 (2H, CH$_2$, q), 4.34 (H, CH, s), 6.91 (2H, NH$_2$, s), 7.12–7.43 (4H, H-Ar, d, d) ppm. $^{13}$C-NMR (100 MHz, DMSO-d$_6$): δ = 13.81, 17.61, 38.45, 56.81, 61.48, 107.31, 115.77, 119.14, 130.90, 139.45, 155.72, 159.12, 159.26, 165.14 ppm.

Ethyl 6-amino-4-(4-chlorophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (5)

IR (KBr): 3409.17 (NH$_2$), 3332.69 (NH$_2$), 2979.48 (C=H), 2193.69 (C≡N), 1693.41 (C≡O), 1650.55, 1609.34, 1489.39, 1335.42, 1266.26, 1174.09, 1120.47 cm$^{-1}$. $^1$H-NMR (400 MHz, DMSO-d$_6$) δ = 1.01–1.09 (3H, CH$_3$, t), 2.50 (3H, CH$_3$, s), 3.81–4.03 (2H, CH$_2$, q), 4.28 (H, CH, s), 6.26 (2H, NH$_2$, s), 7.29–7.52 (4H, H-Ar, d, d) ppm. $^{13}$C-NMR (100 MHz, DMSO-d$_6$): δ = 13.81, 17.61, 37.93, 58.53, 61.65, 108.75, 118.82, 128.54, 128.72, 130.53, 130.78, 131.51, 141.88, 155.55, 158.67, 165.85 ppm.

Ethyl 6-amino-4-(4-bromophenyl)-5-cyano-2-methyl-4H-pyran-3-carboxylate (6)

IR (KBr): 3408.10 (NH$_2$), 3330.18 (NH$_2$), 2979.27 (C=H), 2194.09 (C≡N), 1698.50 (C=O), 1654.77, 1608.19, 1483.62. 1374.06, 1262.54, 1180.44, 1068.31 cm$^{-1}$. $^1$H-NMR (400 MHz, DMSO-d$_6$) δ = 1.13–1.24 (3H, CH$_3$, t), 2.46 (3H, CH$_3$, s), 4.02–4.07 (2H, CH$_2$, q), 4.34 (H, CH, s), 6.26 (2H, NH$_2$, s), 7.29–7.52 (4H, H-Ar, d, d) ppm. $^{13}$C-NMR (100 MHz, DMSO-d$_6$): δ = 14.33, 17.37, 38.18, 58.53, 61.65, 107.85, 118.82, 128.54, 128.72, 130.53, 130.78, 131.51, 141.88, 155.55, 158.67, 165.85 ppm.
61.54, 107.84, 119.15, 131.25, 131.51, 143.58, 150.69, 155.74, 165.41 ppm.

Ethyl 6-amino-5-cyano-4-(4-hydroxyphenyl)-2-methyl-4H-pyran-3-carboxylate (7)

1H-NMR (400 MHz, DMSO-d6) δ = 0.84–0.89 (3H, CH3, t), 2.25 (3H, CH3, s), 3.77–3.87 (2H, CH2, q), 4.24 (H, CH2, s), 6.59 (2H, NH2, s), 6.71–6.90 (4H, H-Ar, d, d), 9.09 (OH, s) ppm. 13C-NMR (100 MHz, DMSO-d6): δ = 14.25, 17.00, 37.52, 58.29, 61.48, 107.87, 115.31, 119.15, 131.24, 136.61, 155.14, 156.77, 159.20, 164.92 ppm.

Ethyl 6-amino-5-cyano-4-(4-nitrophenyl)-4H-pyran-3-carboxylate (8)

1H-NMR (400 MHz, DMSO-d6) δ = 1.13–1.24 (3H, CH3, t), 2.40 (3H, CH3, s), 3.94–4.01 (2H, CH2, q), 4.28 (H, CH2, s), 6.88 (2H, NH2, s), 7.50–8.11 (4H, H-Ar, d, d) ppm. 13C-NMR (100 MHz, DMSO-d6): δ = 14.84, 17.61, 38.47, 58.05, 61.48, 107.91, 119.58, 124.03, 127.03, 143.58, 156.50, 159.74, 159.68, 165.58 ppm.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s13203-021-00278-8.

Declarations

Conflict of interest The authors declare that there are no conflicts of interest.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

1. Farzaliyev VM, Kuliev AM, Denisov ET, Aliev AS, Abdullaeva FA, Aliiev ShR, Akhundova MM (1976) Synthesis and study of the mechanism of antioxidant action of phenolsulfides. In: Study of the mechanism of action of additives. Reports of the II International Symposium on the Study of the Mechanism of Action of Additives, Halle/Saale-Germany, pp 269–274
2. Rubaij VL, Farzaliyev VM, Rusina IF, Sadikhova GK, Kyazimzade AK (1982) Investigation of the antioxidant activity of some bisphenol derivatives. Azerb Chem J 2:25–32
3. Kashkai AM, Kuliev FA, Kasaiikina OT, Gagarina AB (1982) Reactivity of amino phenol sulfides when interacting with peroxyl radicals and hydroperoxides. Neftekhimiya 22(3):423–427
4. Akhundova MM, Solyanikov VM, Denisov ET (1980) Amino-sulfide-catalyzed decomposition of cumyl hydroperoxide and inhibiting properties of aminosulfide conversion products // Izv. Acad Sci USSR Ser Chem 4:742–746
5. Farzaliyev VM, Aliev AS, Denisov ET, Abdullaeva FA (1975) The mechanism of the inhibitory action of phenolsulfides in the oxidation of cumene. Petrochemistry 15(6):890–895
6. Farzaliyev VM, Alkhalverdiev MA, Rzayeva IA (1998) The mechanism of antioxidant action of substituted 1,2-aminophenethiols in the oxidation of cumene. Petrochemistry 38(3):137–142
7. Farzaliyev VM, Alkhalverdiev MA, Magerramov AM, Bayramov NR, Rzayeva IA, Javadova ON (2008) Oxidizing properties of 2-propylphenol sulfides and their aminomethyl derivatives. J Appl Chem 81:78–81
8. Farzaliyev VM, Fernando WS, Scott G (1978) Mechanisms of antioxidant action. Auto synergistic behaviour of sulfur-containing phenols. Europ Polym J 14:785–788
9. Farzaliyev VM, Kuliev VA, Voronkov MG (1981) Kinetics and mechanism of reactions of inhibited oxidation of cumene by substituted 5-tert-butyl-2-hydroxyphenyl sulfides. Petrochemistry 21(4):607–612
10. Kuliev FA, Denisov ET, Farzaliyev VM, Voronkov MG (1981) Kinetics and mechanism of reactions of catalytic decomposition of cumyl hydroperoxide under the action of substituted 5-tert-butyl-2-hydroxyphenyl sulfides. Petrochemistry 21(6):898–905
11. Kuliev AM, Allahverdiev MA, Farzaliyev VM, Mamedov ChI (1982) Synthesis of some S-substituted derivatives of 4,6-di-tert-butyl-2-mercaptophenol. ZhORKh 52(9):2122–2126
12. Akhundova MM, Solyanikov VM, Farzaliyev VM, Denisov ET (1980) Investigation of the inhibitory ability of the reaction products of ethylene bis-(2-hydroxy-5-tert-butylyphenyl) sulfide with hydroperoxides. Izv. USSR academy of sciences. Ser Chem 12:2711–2714
13. Sudzhaev AR, Nadzhafova RA, Rzayeva IA, Safarov YuS, Allahverdiev MA (2011) Investigation of the antioxidant properties of thiocarbamide derivatives of some amino alcohols. J Appl Chem 84(8):1394–1397
14. Qashqai AM, Kuliev FA, Farzaliyev VM, Kasaiikina OT, Gagarina AB (1982) The effect of antioxidants such as polyphenol sulfides on the oxidation of hydrocarbons. Petrochemistry 22(1):86–92
15. Kashkai AM, Kasaiikina OT, Farzaliyev VM, Gagarina AB, Kuliev FA (1982) Inhibitory effect of sulfur-containing polyphenols and aminophenols in the process of hydrocarbon oxidation. Petrochemistry 22(4):497–500
16. Sattarzade RI, Rzayeva IA, Farzaliyev VM, Allahverdiev MA (2001) The mechanism of the antioxidant action of bis-(4-hydroxy-2,5-di-tert-butylyphenyl) sulfide in the oxidation of cumene. J Appl Chem 74(12):2023–2026
17. Akhundova MM, Solyanikov VM, Farzaliyev VM, Denisov ET (1980) Decomposition of cumyl hydroperoxide catalyzed by aminosulfides and inhibiting properties of products of conversion of aminosulfides. Izv. USSR Acad Sci Ser Chem 4:742–746
18. Qashqai AM, Kuliev FA, Farzaliyev VM, Kasaiikina OT, Gagarina AB (1982) Reactivity of amino phenol sulfides when interacting with peroxyl radicals and hydroperoxides. Petrochemistry 22(3):423–427
19. Allahverdiev MA, Abdinbekova RT, Farzaliyev VM, Magerramov AM, Rzayeva IA, Kurbanov MM (2005) Synthesis and antioxidant activity of some N-substituted thiocarbamides. J Chem Prob 1:12–14
20. Garibov EN, Rzayeva IA, Shikhaliyev NG, Kuliev AI, Farzaliyev VM, Allahverdiev MA (2009) Cyclic thiocarbamides as inhibitors of cumene oxidation. J Appl Chem 83(4):655–659
21. Allakhverdiev MA, Rzayeva IA, Sadigova SE, Farzaliev VM, Maharramov AM (2005) Synthesis and study of the antioxidant activity of 2-amino-4-phenyl-1,3-derivatives thiazole. Pet Chem 45(6):470–475

22. Magerramov AM, Kurbanova MM, Abdinbekova RT, Rzayeva IA, Farzaliev VM, Allakhverdiev MA (2006) Synthesis and antioxidant properties of some 3,4-dihydropyrimidin-2(1H)-one (thion)s. J Appl Chem 79(5):796–800

23. Domling A, Ugi I (2000) Multicomponent reaction with Isocyanides. Angewandte Chemie Int Ed Engl 39(18):3168–3210

24. Ganem B (2009) Strategies for innovation in multicomponent reaction design. Acc Chem Res 42(3):463–472

25. D’souza DM, Muller TJ. (2007) Multi-component syntheses of heterocycles by transition-metal catalysis. Chem Soc Rev 36:1095

26. Chao-Jun Li ChJ, Liang Ch (2006) Organic chemistry in water. Chem Soc Rev 35:68–82

27. Armesto D, Horspool WM, Martin N, Ramos A, Seoane C (1989) Synthesis of cyclobutenes by the novel photochemical ring contraction of 4-substituted 2-amino-3,5-dicyano-6-phenyl-4H-pyrans. J Org Chem 54(13):3069–3072