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Modified Byproduct of Coke Phenols as Effective and Prospective Inhibitors for Petrochemical Industry

Alexey Fedorovich Gogotov

Additional information is available at the end of the chapter

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Abstract

Experimental author results on the use of technogenic phenols as inhibitors are presented to undesirable polymerization in petrochemical manufactures. The basic ways of increase inhibiting properties of coke-chemical phenols are shown, such as rectification for separation of two-nuclear derivatives or some examples of their chemical modification, allowing to increase the inhibiting efficiency of phenolic mixes, for example, by novolak phenol-formaldehyde condensation or oxidative coupling reactions. The received derivatives of phenols are recommended both for processing pyrocondensates and for rectification of styrene.

Keywords: pyrocondensates, styrene, phenolic inhibitors, sterically hindered phenols, technological phenols, phenols from wood, coke-chemical phenols, increase inhibiting properties, rectification, chemical modification, phenol formaldehyde condensation, oxidizing coupling

1. Introduction

Petrochemical industry can be represented in general as two main branches, and they are (a) pyrolysis industry and (b) manufacture of individual monomers, for example, butadiene, styrene, and so on. Both of them have one strong problem that is undesirable polymerization of olefinic monomers during distillation and purification. Thermal impacts during fractioning process are usually accompanied with the formation of active alkyl radicals to be prone to polymerize, which results in decreasing of yields of main products, contamination of equipment with polymer residues, and impairment in the control of distillation process. Such ever-present phenomenon during distillation process could be removed by several methods, and

the most reasonable one is the use of special additives, the so-called inhibitors. Inhibitors are chemicals, which stabilize reactive monomers, they could react fast with free radicals, and so the latter are withdrawn and could not activate polymerization, notably, inhibitors stop spontaneous polymerization. Inhibitors cut off every chain reaction until they are spent.

2. The basic classes of inhibitors

The following substances of different chemical classes can be used as inhibitors, for example:

- (1) quinones
- (2) nitro- and nitroso compounds;
- (3) amines and hydroxyl amines and their derivatives;
- (4) stable nitroxyl radicals;
- (5) different phenolic compounds;
- (6) salts of aliovalent metals;
- (7) sulfur- and phosphor-containing compounds, as well as
- (8) high-molecular-weight inhibitors on the basis of the above classes.

Every compound class has its specific action on monomer stabilizations, and so its own intrinsic advantages and disadvantages. The most common among them are the representatives of four and five groups.

It should be noted that phenol inhibitors demonstrate some technological advantages, than others (**Figure 1**).

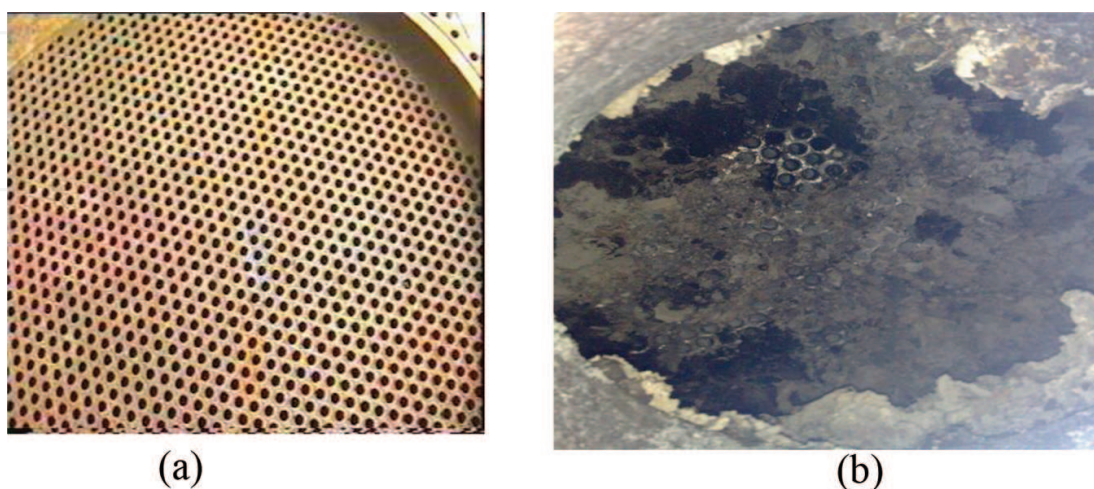


Figure 1. Surface appearances of heat exchangers T-58 EP-300 utility after application of phenol inhibitors (a) and nitroxyl radicals (b).

3. Phenolic inhibitors

Among the phenol inhibitors, two main series are differentiated:

- (1) Sterically hindered phenols (SHPs)
- (2) Technogenical phenols.

The latter are multicomponent phenol mixtures produced during thermal treatment of organic raw materials—wood and coal. These mixtures are different in their compositions and properties.

Unlike the other inhibitor classes, the phenolic compounds advantageously combine their antioxidant properties together with the capacities to trap radicals [1].

Practical applications reveal the monoatomic SHP—Ar-OH and their derivatives to be the most effective.

Diatomic phenols Ar(OH)₂ (e.g., hydroquinone, pyrocatechol, pyrogallol, trimethylhydroquinone, 1,6-naphthalene diol, etc.) are more effective as radical process inhibitors in anoxic environment when compared with others. Three and more atomic phenols show their best antioxidant properties.

Phenol inhibitors can be divided into small number of classes depending on their properties and structures, according to the following characteristics:

- (1) The number of aromatic fragment Ar: they are true phenols or naphthols—the oxy derivatives of condensed aromatic hydrocarbons;
- (2) The number of hydroxyl groups in one aromatic circle (nuclei): they are mono- and polyphenols;
- (3) The number of Ar(OH)_n fragments in one molecule of antioxidant: they are mononuclear and polynuclear phenols (*bis*-phenols, *tris*-phenols, etc.); and
- (4) The so-called shielded SHP phenols, where both *o*-substituents of OH-group in the aromatic circle are *tert*-alkyl groups, usually they are *tert*-butyl ones.

Sterically hindered phenols dramatically differ from other phenols. They are often used as industrial antioxidants, stabilizers, and anti-polymerizers, and many of them possess very high inhibiting activities.

At present, the most common in use are SHP having *tert*-butyl substituents, and the most well-known among them are as follows:

Ionol (2,6-di-*tert*-butyl-*p*-cresol, butyloxytoluene, BOT, alkophen, BP, topanol-O, DBC, topanol-OC, topanol-OF, 4M26B, CAO, Agidol-1, etc.), ***tert*-butyl pyrocatechine** (TBPC), and di-*tert*-butylhydroquinone.

4. The mechanism of phenol action as inhibitors

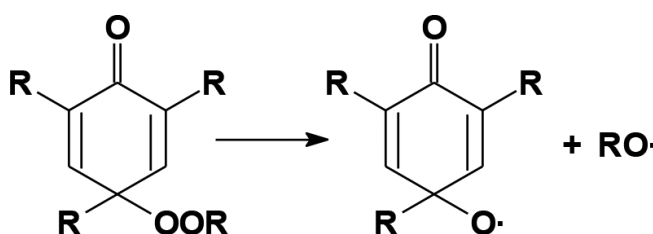
Involving phenols in radical reactions results in detachment of hydrogen atom from hydroxyl group on the first stage of the process with the formation of phenoxyl radical:



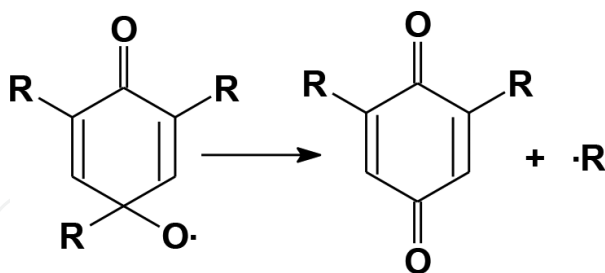
The formation of phenoxyl radicals was confirmed by electron paramagnetic resonance (EPR) method, which was supported with kinetic isotopic effect, when hydrogen atom is changed for deuterium.

Phenoxylic radicals are formed in the reaction of phenols with peroxide radicals: alkoxy, alkyl, carboxyl radicals, as well as with molecular oxygen. The subsequent behaviors of phenols in radical reactions depend on properties of the phenoxyl radicals formed.

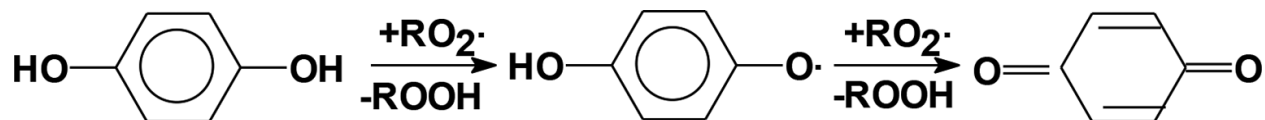
The reaction of peroxide and phenolic radicals leads to the formation of quinolide peroxides. Another active radicals add to PhO^* similarly. The quinolide peroxides so formed could be decomposed at O-O bond to give active radicals even at moderate temperatures:



The alkoxy radical could be subsequently dissociated to give quinone:



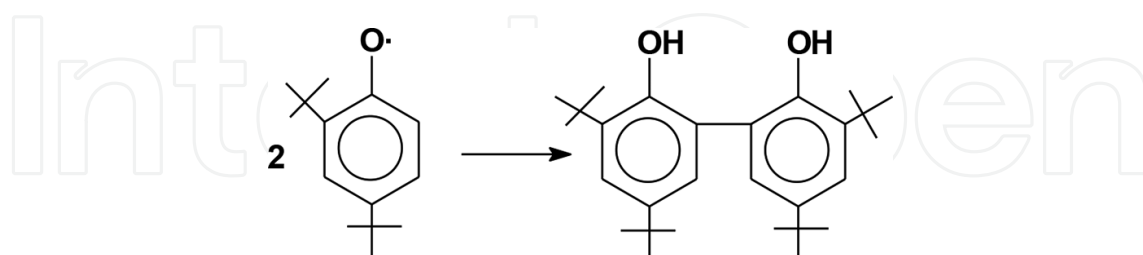
Hydroquinone, when reacting step by step with two peroxide radicals, transforms into quinone:



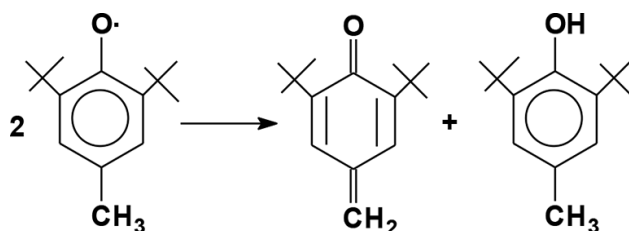
Together with the interaction of phenoxyl and peroxide radicals, the competitive reaction bimolecular loss of phenoxyl radicals takes place:



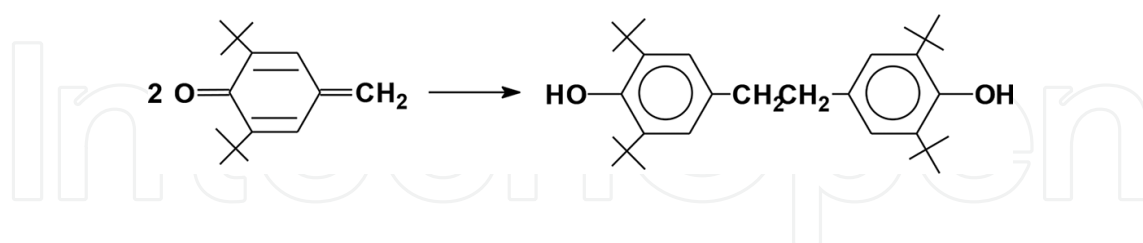
The reaction direction depends on a structure of phenoxyl radical. Some radicals having at least one non-substituted "active" position are typically recombined into dimeric phenol compounds, for example:



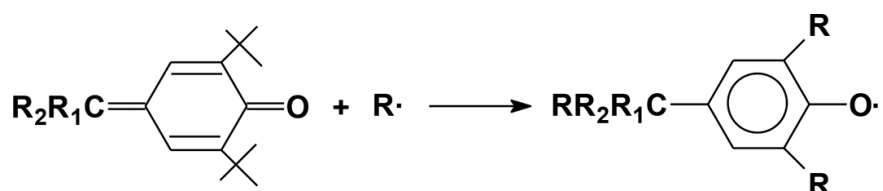
2,4,6-Trisubstituted phenoxyls do not form stable dimers as a rule. If the radical has *n*-, or *sec*-alkyl substituents, the reaction of disproportionation is possible to obtain methylene quinone and to recover the initial phenol:



Methylene quinones are capable of dimerization with the formation of polynuclear phenols:

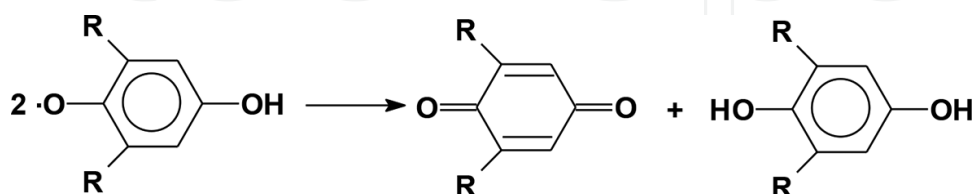


Methylene quinones could react with radicals to be added to unsaturated double methylene bond, generating phenoxyl radicals:

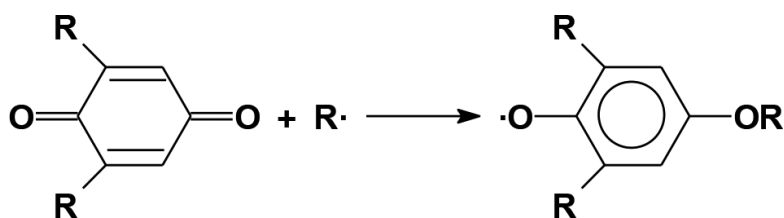


The activities of methylene quinones are almost equal to the same for the most reactive alkenes (diene, vinyl aromatic compounds), as well as sterically hindered quinones, but unlike the latter, they are very active to peroxides.

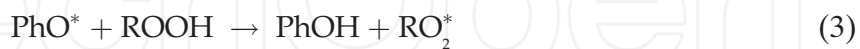
The disproportionations involving H-atoms of OH-groups are rather typical for phenol radicals, which have two hydroxyl groups in the circle, the so-called diatomic phenols—pyrocatechol and hydroquinone. The stabilization of phenoxyl radicals formed is possible owing to *ortho*- and *para*-quinones' generation. The disproportionation products in this case are quinoid compound and initial phenol:



The quinones obtained when compared with the starting ones are effective acceptors of alkyl radicals, which add the radicals according to the scheme. So, the products of phenol inhibitor oxidation turn to be the generator of secondary inhibitors.



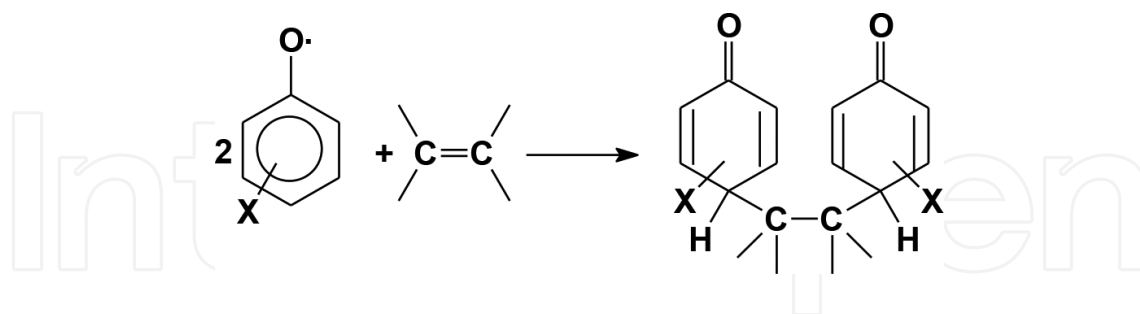
Phenoxyl radicals could react with some molecules. The most important reactions are as follows:



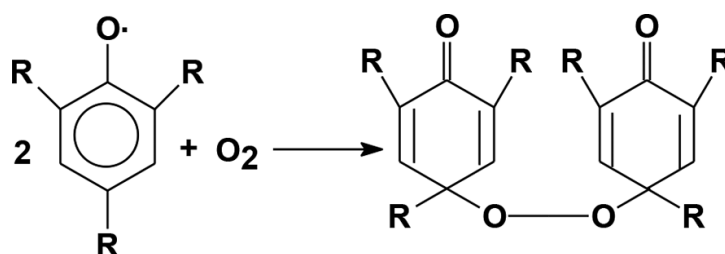
The inhibitor becomes ineffective, if the equilibrium of the phenoxyl radical and peroxide reaction is shifted to the formation of RO_2^* .

The reaction, where phenoxyl radical attacks C-H bond of hydrocarbon, is the most unwelcome for inhibition process. This reaction results in the formation of active alkyl radical and regeneration of a chain.

The processes of addition of phenoxy radicals to unsaturated compounds lead to the formations of dimeric cyclohexadienones:



As the result of the reaction of phenoxy radicals with molecular oxygen, the symmetric quinolide peroxides are formed:



Some reactions of phenoxy radical dissociation with emissions of active radicals are realizable.

As it is demonstrated on the schemes shown earlier, the application of phenol compounds allows to increase the inhibiting effect due to partial regeneration in the system "phenol-quinone" [1].

The stability of forming phenoxy radicals depends fundamentally on substituents in *ortho*-position to hydroxyl group, and it increases with the increasing branches and bulks of the substituents [2]. The properties of SHP become apparent, if the substituent is *tert*-alkyl at least. For the phenols having methyl substituents or having no substituents in *ortho*-position of hydroxyl group, the inhibiting effects are considerably low, and often it occurs to be missing or even having a negative value. That is why monoatomic phenols unsubstituted in *ortho*-position to hydroxyl group are practically unknown as inhibitors.

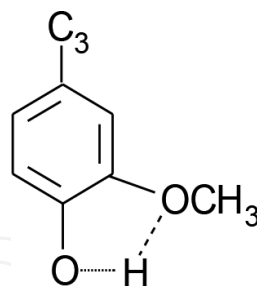
Diatomic phenols of resorcin series reveal their inhibiting activity as compounds with CH-activity, that is, according to another mechanism [3]. The distinctive features of the resorcin series compounds are their extreme manifestations of inhibiting activity, but in a very narrow concentration interval and in considerable less (1–2 order of magnitude) concentrations, than for other diatomic phenols.

During pyrolysis of plant raw materials besides monoatomic phenols, cresols and xylenols (32.8%) and insufficient amounts of pyrocatechine and methylpyrocatechine (7.1%), the derivatives of guaiacol (20.1%) and syringol (31.3%) are dominated (**Table 1**).

Component	Component composition, %
Phenol	3.5
Crezols	13.9
Xylenols	15.4
Guaiacol	7.1
4-Methylguaiacol	5.3
4-Ethylguaiacol	4.2
4-Propylguaiacol	2.1
Eugenol	1.4
Pyrocatechine	5.7
Methylpyrocatechine	1.6
1,3-Dimethyl ether of 5-methylpyrogallol	12.7
1,3-Dimethyl ether of 5-ethylpyrogallol	10.3
1,3-Dimethyl ether of 5-propylpyrogallol	6.5

Table 1. Composition of phenols for pyrolysis of wood.

It is found that guaiacol and syringol derivatives in non-polar media do not reveal their inhibiting activities, so the hydrogen atom of phenol hydroxyl group forms the hydrogen binding with oxygen atom of neighboring (in *ortho*-position) methoxyl group, which prevents the phenoxy radical formation:



5. Coke-chemical phenols

During thermal processing of coals, the main components of coke-chemical phenol (CCP) mixtures are different mono- and diatomic phenols, where compositions are dependent on coalfield (**Table 2**).

Table 2 demonstrates the essential differentiations in mono- and diatomic phenol proportions in different storage reservoirs. These proportions play very important role to produce effective inhibitors from CCP. It is experimentally established that the optimal proportion is <2:1.

As an example, the composition of phenols from storage reservoir No. 2 is given in **Table 3**.

According to **Table 3**, diatomic phenols are predominantly presented with pyrocatechine and his gemologists, as well as with insignificant amount of resorcin and its derivatives and with minor amount of methyl and dimethyl hydroquinone.

That is why the first alternative to increase the inhibiting activity of CCP is the fractionating of the phenol mixture for the purpose of isolating diatomic phenols from monoatomic ones. During fractionating, the distillate of diatomic phenols, the so-called "pyrocatechine fraction"

Reservoir No	Monoatomic phenols, %mass	Diatomic phenols, % mass	Nonphenolic admixtures, % mass	Proportions of mono- and diatomic phenols
1	72.3	25.9	1.8	2.79
2	51.7	39.9	8.4	1.30
3	68.3	25.3	6.3	2.70
4—Overall (Summary) mixture (res.1: res.2: res.3 = 1.2:1.7:1.5)	62.4	32.5	5.1	1.92

Table 2. Comparative composition of CCP from different storage reservoirs.

Monoatomic phenols		51.67
They include:		
Phenol	3.30	2-Ethyl-4-methyl phenol 0.16
2-Methyl phenol	10.14	4-Ethyl-3-methyl phenol 0.69
4-Methyl phenol	13.32	3-Ethyl-5-methyl phenol 0.20
2,6-Dimethyl phenol	4.34	2,3,5-Trimethyl phenol 0.27
2-Ethyl phenol	1.03	4-Propyl phenol 0.15
2,4-Dimethyl phenol	11.57	2-Methyl-5-(1-methylethyl phenol 0.32
4-Ethyl phenol	3.74	2,3,6-Trimethyl phenol 0.10
3,5-Dimethyl phenol	0.75	4-(1-methylpropyl)phenol 0.10
2,4,6-Trimethyl phenol	0.42	2-Butyl phenol 0.13
2-Propyl phenol	0.15	4-Ethyl-2-methoxyphenol 0.09
2-Ethyl-6-methyl phenol	0.66	2-Naphthol 0.04
Diatomic phenols		39.90
They include:		
Pyrocatechine	17.16	4-Ethyl resorcin 2.21
3-Methyl pyrocatechine	9.67	4,5-Dimethyl resorcin 0.29
4-Methyl pyrocatechine	4.96	Methyl hydroquinone 0.17
Resorcin	1.69	2,3-Dimethyl hydroquinone 2.17
2-Methyl resorcin	1.51	3,4-Methylene dioxyanisole 0.07

Table 3. Component composition of phenol mixture in storage reservoir No. 2.

(PCF), has been isolated. The fraction is analyzed and tested as polymerization inhibitor of industrial condensates for EP-300 utility of Angarsk Polymer Plant (APP) of "ROSNEFT" Joint-Stock Company, Irkutsk region, Russia [4]. Inhibiting activities of PCF and other inhibitors have been tested in accordance with the standard protocol of 8489-85 RU State Standard. The industrial samples of liquid pyrolysis products (pyrocondensates) of straight-run distillation of gasoline and hydrocarbon gases have been used as investigation objects.

The estimation of their inhibiting activities has been modeled under very closed conditions, or even under more hard conditions, than that for real-system "column-boiler" at the rectification process of pyrolysis semi-products, where the example is chosen from pyrocondensate of typical utility of "Ethylene/propylene-300" of APP, where production is benzene produced by hydrodealkylation.

Laboratory experiment on modeling polymer formation has included the following:

- (1) Initiation of polymer formation in pyrocondensate by temperature impact with the addition of investigated inhibitor.

For this purpose, pyrocondensate of 100 cm³ was loaded into a metal autoclave, and the inhibitor was added (or not added in blank experiment); the autoclave was sealed hermetically and placed into a preliminary heated thermostat at 130°C for 1 h.

- (2) The amounts of the polymer formed products were detected by RU State Standard 8489-85 by the equipment "POS-77M."

Effectiveness of inhibiting was estimated in accordance with the formula:

$$\text{Effectiveness} = \frac{C_{\text{blank}} - C_{\text{inhib}}}{C_{\text{blank}}} 100\% \quad (6)$$

where C_{inhib} and C_{blank} are the amounts of experimental resins in pyrocondensates in inhibit and blank experiments, correspondingly.

6. Increase inhibiting properties of phenols by rectification

During the rectification process of total coke-chemical phenols (TCCPs), the isomers of diatomic phenols were concentrated in the distillation residue after monoatomic phenol separation (DRAMPS). Some samples of the DRAMPS product were taken from the operating "FCh-16" phenol inhibitor production utility of JSC "Angarsk Petrochemical Company" (APCC), and then pyrocatechine fractions were distilled (up to 300°C) from them. Their inhibiting properties were tested. The laboratory results served as a basis for the design of technical requirements for the prototype production of the inhibitor, and then technical regulations for the production were developed. The pilot butches of PCF inhibitor were produced on the plant utility. The composition of the laboratory and pilot plant samples was proved by chromato-mass spectrometry method, and they are presented in **Table 4**, and their quality factors in accordance with the State Standard demands are presented in **Table 5**.

Components	DRAMPS	PCF samples	
		Laboratory	Plant
Phenol	4.7	2.5	1.4
Methylphenol	3.9	1.9	1.2
Dimethyl and ethylphenols	6.8	3.3	2.3
Trimethyl and propylphenols	5.1	3.7	3.0
<i>Tert</i> -butyl phenol	1.5	1.6	1.2
<i>Tert</i> -butylmetylphenol	1.0	–	0.9
Sum of monatomic phenols	23.0	13.0	10.0
Pyrocatechine*	14.3	15.2	18.2
Methyl pyrocatechine	26.8	37.8	37.9
Dimethyl- and ethyl pyrocatechines	11.4	20.8	14.2
Trimethyl- and propyl pyrocatechines	1.1	1.4	1.6
<i>Tert</i> -butyl pyrocatechine (TBPC)	2.0	0.9	1.6
<i>Tert</i> -butyl- and methyl pyrocatechines	2.7	0	1.6
<i>Tert</i> -butyl-dimethyl pyrocatechine	0.7	0	1.5
Sum of diatomic phenols	59.0	76.1	76.6
Nonidentified (resins)	18.0	10.9	13.4

*minor amounts of resorcin and its derivatives were identified by GLC-method together with pyrocatechine

Table 4. Compositions of DRAMPS and PCF, % mass.

Factors	Standard with State regulations. 38.40154-90	Experimental results
Appearance	Liquid of light yellow up to brown color	
Density at 20°C, g/sm ³ sup>	Not more than 1.2	1.1
Fraction composition, % vol.:		
Boiled-off before 240°C	Not more than 10	7.5
Boiled-off before 285°Cs	Not more than 96	96.2
Water content, % mass	Not more than 0.5	0.5

Table 5. Quality factors of the “PCF” pilot batch.

The results of the laboratory investigations of different phenol samples are presented in **Table 6**.

Thus, it is shown that fine fractionating phenol mixtures to remove inactive monoatomic phenols allow to obtain special preparation of diatomic phenols "PCF," having its inhibiting activity close to the well-known individual and expensive preparation such as *tert*-butyl pyrocatechine (TBPC), belonged to sterically hindered phenols (SHPs).

No.	Inhibitors	Practical yields of resins, mg/100 sm ³	Effect of inhibiting, %
1	Blank experiment	233	—
2	Initial overall CCP	177	24
3	PCF fraction	77.6	66.7
4	PFR on the basis of CCP	76.4	67.2
5	CCP, modified with oxidized coupling	64.8	72.2
6	5-Methyl resorcin (from resorcin fraction)—0.009%	78.8	66.2
7	Ionol	139.8	40.0
8	TBPC	75.0	67.8

Table 6. Effectiveness of inhibiting polymer formations for EP-300 pyrocondensates at the inhibitor consumption of 0.025 %.

The obtained PCF preparation was introduced into EP-300 production unit of Angarsk Polymer Plant of Petrochemical Company "ROSNEFT" and was employed for 2 years up to its run-out in the company stocks.

The problem of utilization of CCP without the stage of power cost-based phenol vacuum fractionating has been arisen. But the problem is not unequivocal: its main disadvantages, for example, good water solubility and unpleasant organoleptic properties are not removed by this way of utilization, and in addition to that, the major part of overall (summarized) phenols (more than 2/3 of total amount) is not found in any application.

7. Increase inhibiting properties of phenols by chemical modification

That is why new methods of utilization of summarized CCP (SCCP) have been elaborated to avoid the stage of preliminary power cost-based fractionating.

Analysis of literary sources reveals some ways to decrease water solubility of phenols, they are as follows:

- (1) Phenol formaldehyde condensation (PFC) under acid catalysis (by novolak method)
- (2) Phenol alkylation
- (3) Oxidative cross-linking of phenols

8. Phenols modification by phenol formaldehyde condensation

During the process of novolak polycondensation, the phenols become insoluble in water, but phenol formaldehyde resins (PFRs) have a good solubility in organic solvents, for example, in alcohols. The first step of phenol transformation is the chemical modification of SCCP without their preliminary fractionating to synthesize FFR with the view of obtaining inhibitor having the highest activity.

Indeed, the standard novolak PFR from monoatomic phenols has demonstrated inhibiting effect of 30%, when it is tested as phenol inhibitor at 0.03% mass consumption. Novolak polycondensate, obtained from summarized coke-chemical phenols (SCCP, No. 4., **Table 2**), demonstrates ~67% effect at the same consumption [5]. Unmodified SCCPs show 24% effect at the consumption of 0.03% mass (**Figure 2**).

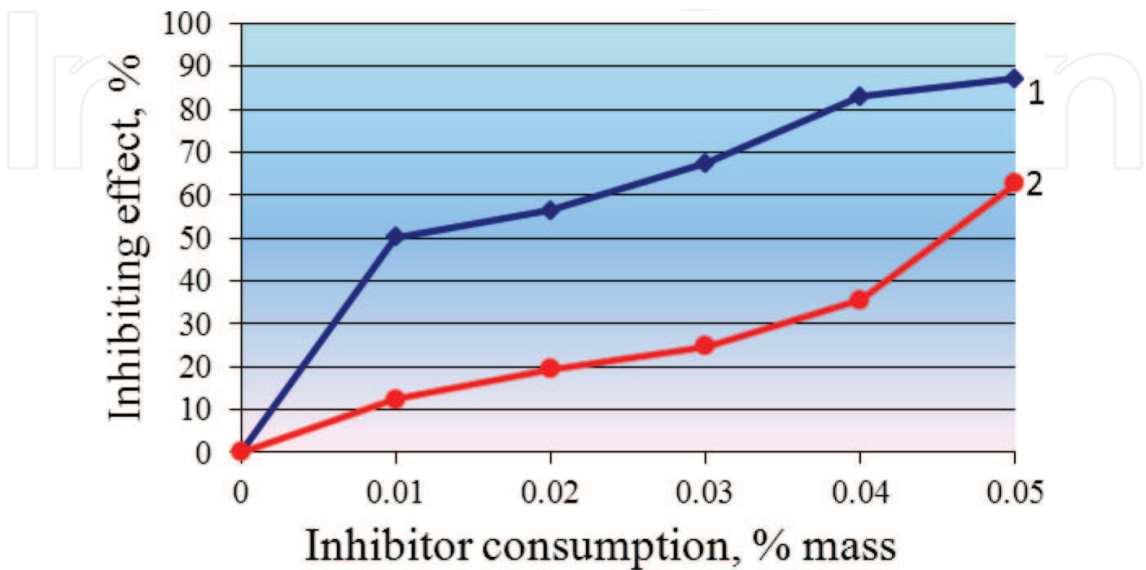


Figure 2. Dependency of inhibit effect on the consumption of PFR (1) and SCCP(2).

It must be accentuated that PFR, synthesized from separate fractions of monoatomic phenols obtained from summarized phenols, or diatomic phenols are worse than for PFR, produced from non-fractionated phenols, where inhibiting effects are 30–35%, at the same as above consumption of 0.03% mass. This fact is the witness of synergism of the mixtures of monoatomic and diatomic phenols after their phenol formaldehyde polycondensation. The effect is found by us early [6] during inhibiting the thermo-polymerization process of styrene with ionol and TBPC inhibitors. The inhibiting factors of the resins obtained from phenols of different stock reservoirs are quite different (**Table 7**).

Reservoir	No. 1	No. 2	No. 3	Summarized
Effectiveness, %	33.2	74.7	38.5	67.2

Table 7. Comparative effect of PFR produced from phenols of different stock reservoirs at the consumption of 0.03% mass.

The results of **Table 7** support the considerable inhibiting effect of synthesized novolak resins that depends on the ratios of mono- and diatomic phenols in the initial mixtures. Indeed, the increase of monoatomic phenol amounts leads to the decrease in inhibiting effect, and just the reverse, it leads to increasing this effect at the increasing diatomic phenol amounts (reservoir No. 2).

However, it should be noted that inhibiting activity of synthesized PFR from SCCP is fundamentally dependent on molecular mass (viscosity) of the resin taken.

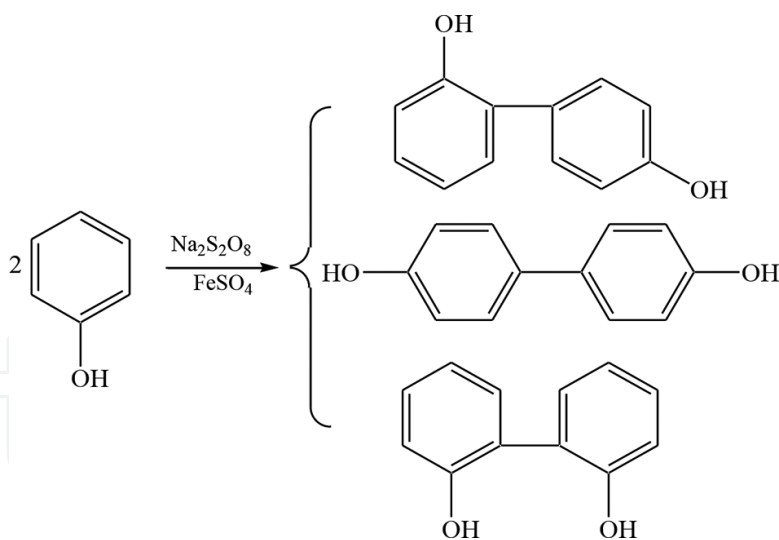
Dependency of the inhibiting effectiveness from viscosity of PFR at the consumption of 0.03 % mass is as follows:

Viscosity of resins, sec.	70	135	240	540	720
effectiveness, %	56.3	74.7	43.9	8.1	0

According to these dates, the resins having viscosity in the rage of 135 s (Viscosimeter VZ-4) are the most effective. There is dependence between amounts of residual phenols in synthetic tar-water and viscosity of the resin. For example, in the best point (74.7%) the amount of non-reacted phenols on water phase reached almost 5% of their load, and all the phenols are presented by monoatomic isomers.

9. Phenol modification by oxidizing coupling

That is why it is necessary to find conditions for the perfect binding of phenols. It appears to be the method of oxidative cross-linking of phenols by their treatment with persulfates of alkali metals. The mechanism of the modification includes dimerization of phenols to form C-C bond involving unsubstituted (free) *ortho*- and *para*-positions of hydroxyl group, the mechanism is accompanied by a series of different reactions. The method of oxidative cross-linking is presented by a scheme:



And it was employed as the method of modification of SCCP to obtain the inhibitor of thermopolymerization for processing semi-products of pyrolysis [5]. As far as dimeric phenols practically are non-water soluble, it is supposed that oxidative dimerization of phenols allows to remove one of the main disadvantages of coke-chemical phenols—their high water solubility.

During the first stage of the reaction of the oxidizer and phenol, the generation of phenoxyl radical occurs (for monoatomic phenols) and then its mesomerization with the transfer of radical

center from oxygen atoms to carbon atoms of aromatic circle and subsequent recombination of the formed radicals takes place [7]. During oxidation of di- and polyatomic phenols, the mechanism is more complicated, and the possibility of the generation of quinoid compounds is not excluded, as well as some other secondary inhibitors. During the oxidation reaction, quinone methides, polymers, and subsequent oxidative products of primary formed binuclear compounds could be formed. It is evident, the yields of individual product at so diversity of the products obtained in the oxidation are not high. The secondary reactions between oxidized substrates and the starting phenols are not precluded. That is why the summary effect of oxidized phenol mixture essentially depends on the structures of initial phenols and amounts of the oxidizer used (**Figure 3**). As it was stated above during the one-step cross-linking modification of phenols under action of persulfates of alkali metals, the dimers of phenols are formed, which are not soluble in water, but well soluble in alcohols and alkyl acetates.

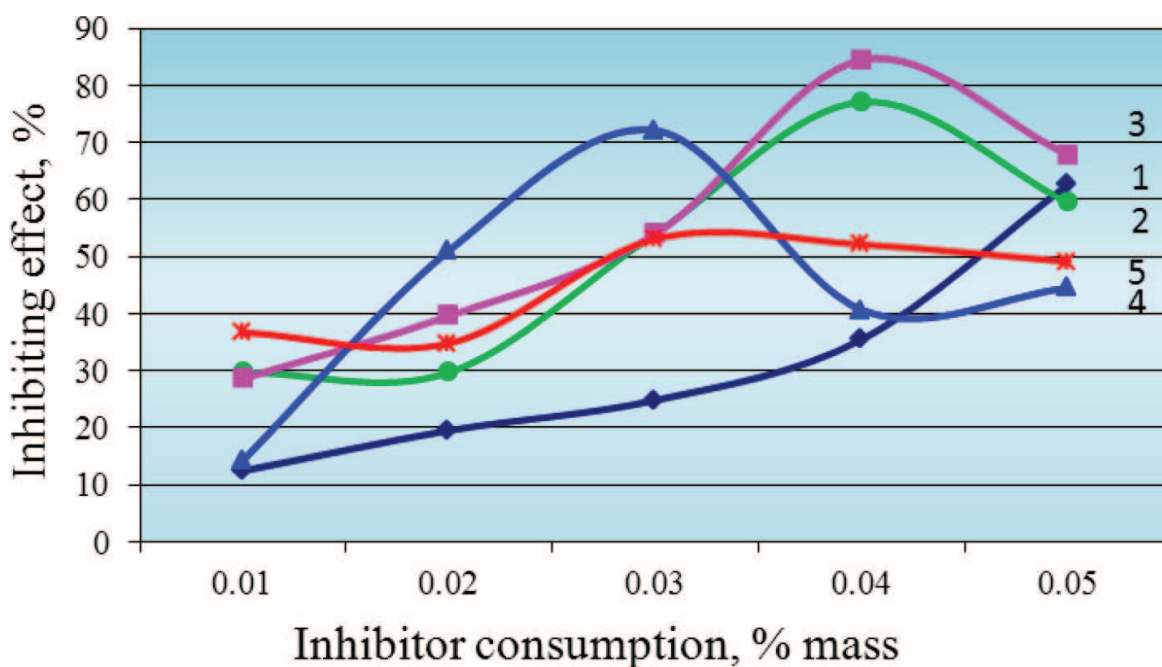


Figure 3. Inhibiting activity of SCCP after treatment with sodium persulfate; oxidizer consumption: 1—0%, 2—10%, 3—25%, 4—50%, 5—75% mass.

According to the data of chromato-mass-spectrometry and nuclear magnetic resonance (NMR)-spectroscopy ^1H and ^{13}C for the products obtained by the oxidation of monoatomic phenol with sodium persulfate, the expected dimeric products of "ortho-ortho," "para-para," and "ortho-para" cross-linking are obtained in a combination of 9:50:19%, respectively.

The analysis of inhibiting activity of oxidative cross-linking SCCP mixtures demonstrates that the maximal effectiveness of 72–84% is manifested for oxidized mixtures with the consumption of oxidizer of 25% mol relatively to the overall phenol mass and with the inhibitor consumption of 0.03–0.04% mass.

Thus, we have developed single stage and rather simple methods of chemical modifications of CCP, which make it possible to obtain high-performance phenol inhibitors for the processing of pyrolysis liquid products of petrochemical industry.

10. Application of CCP in inhibitors synthesis for styrene produce

The approaches to inhibiting process for pyrocondensates and individual monomers are rather different. For example, as a rule for the inhibiting of thermo-polymerization of liquid products of pyrolysis, it is necessary to apply individual compounds as inhibitors, for example, TBPC or ionol, whereas for the prevention of undesirable polymerization of individual monomers, such as styrene, for example, it is advisable to use more effective so-called "inhibiting compositions."

It is known [8] that the phenol oligomer, obtained by phenol formaldehyde condensation, manifests rather low effectiveness as inhibitor in the production process of styrene, so it means that all production processes of phenol modifications for obtaining inhibitors are considerably different. For example, a method of acid-oxidative condensation of CCP to obtain effective co-inhibitor for the process of styrene distillation has been developed by us [9]. Chemical modification of CCP to give "modified phenol co-inhibitor" (MPC) is the synthesis one-pot reaction by the subsequent treatment of the substrate with catalytic amounts of concentrated sulfuric acid at heating up to 95°C for 1 h, then the hot acidic phenol solution is treated with hydrogen peroxide in the presence of catalyst that is iron (II) sulfate for 1 h, and thereafter the oxidate is cooled and neutralized with sodium nitrite at room temperature. The phenol oxidate is extracted with alkyl acetate, and the solution obtained is employed for the inhibiting of styrene thermo-polymerization. The estimation of the efficiency is made by thermal processing of pure styrene in the standard conditions at heating to $120 \pm 1.5^\circ\text{C}$, with the blowing of nitrogen under stirring for 2.5 h. The amount of the polymer formed is detected by sedimentation of the styrene probe (2 sm^3) from autoclave and its dilution with ethyl alcohol (8 sm^3) and then centrifugation and separation of the sediment, the latter's drying and weighting according to the State Standard RU 10003-90.

The results of the experiments with different inhibiting compositions of styrene thermo-polymerizations are presented in **Table 8**.

It is clear from **Table 8** that neither itself MPC nor itself MB (Mannich Base - 2,6-di-*tert*-butyl-4-dimethyl-aminometyl phenol, N,N'-dimethyl(3,5-di-*tert*-butyl-4-oxybenzyl)amine) (entry 2) possess satisfactory inhibiting properties, but their compositions "MCP + MB" in different combinations are rather competitive in comparison with the best known inhibitors, and they could be recommended as inhibitors for the styrene production.

Accordingly, the task-oriented chemical modification of coke phenols could solve the very complicated ecological problem the utilization of toxic technogeneous phenols transforming them into competitive reagents for petrochemical industry, namely high effective phenolic inhibitors of polymerization.

Chemical modification of phenols in this line could be realized by other methods, for example, by the reaction of SHP with bulky bi- and tricyclic substituents, for example,

diisobornylphenols [2] and diadamantylphenols [9], or by the generation of the so-called inhibiting systems employing phenols, solvent, and turpentine [10]. That is another subject for investigations.

The system applied for the styrene mass, %	Time, min			
	60	90	120	150
	Formation of the polymer, mass %			
1. MB (0.03) + MPC (0.045)	0.08	0.12	0.23	0.35
2. MB (0.03)	0.88	1.51	3.68	8.81
3. MPC (0.045)	0.21	0.68	1.93	4.61
4. MB (0.025) + MPC (0.05)	0.10	0.19	0.32	0.44
5. AHM-700 (0.017)	0	0.10	0.23	0.55
6. "Nalco EC 3264A" 0.0200%	0.14	0.17	0.25	0.36
7. Kawakami (98BH+99BH), with 0.025% each	0	0.39	0.42	0.45
8. IPON* 0.025%	0.10	0.18	0.33	0.48
9. DOQ**(0.006)+0,2[MB (0.025) + PNP (0.0125)] + 0.8(MB +PNP)-1 h	0.33	0.66	1.35	1.91

*IPON - Russian analog Nalco inhibitor on base nitroxilic radicals **DOQ - Quinone-dioxime; PNP - p-nitro-phenol;
 AHM - isobutyl-2,4-dinitro-phenol

Table 8. Comparative effect of PFR produced from phenols of different stock reservoirs at the consumption of 0.03% mass.

11. Conclusions

- (1) The possibility of the task-oriented utilization of anthropogenic phenols without their preliminary fractionating to produce the inhibitors of undesirable polymerization, which are demanded products for different branches of petrochemical industry: high-effective and competitive on qualitative and cost-oriented properties has been demonstrated and the effectiveness has been proved experimentally.
- (2) It is shown that multicomponent mixtures of diverse mono- and diatomic coke-chemical phenols could be purposefully transformed by known single-staged methods into high-effective phenol inhibitors of thermo-polymerization applicable to the processing liquid pyrolysis products of petrochemical hydrocarbons, and the inhibitors designed are able to become the competitors of the known expensive inhibitors that are pure-isolated sterically hindered phenols.
- (3) The new one-pot tree-stage method of coke-chemical phenols' processing into "modified phenol co-inhibitor" that is the component of highly effective compositions of styrene distillation has been offered.

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