- The possibility of diagnosing pipeline without coupling fluid;
- Insensitivity to the surface state;
- Special peculiarities for finding stress corrosion cracking;
- An ability to detect the state of the insulation coating.
- The main disadvantages of these pigs are:
- EMA converters require high power;
- The need for specific electronic equipment which is not widely available;
- The cost of these pigs is higher than the cost of conventional ultrasound and magnetic pigs.
- Here are some conclusions:

1. The pigs of the "British Gas Corporation are simpler but there is a possibility that the diagnostic results can be failed because of leakage of special chambers in the pipeline. If we use advanced high strength materials for chambers, it will reduce the weight and improve the design quality of diagnostics.

2. The pigs of the "Dacon" are less expensive than the others, but the cost and time spent for all manufacturing operations make them unprofitable.

3. Nowadays the pigs, which use electromagnetic acoustic transducers, are the most progressive in the field of in-line inspection of gas pipelines. The results of practice research show that the use of these pigs provide a more detailed and qualitative research. And their using reduces the risk of accidents. Analyzing the price we can honestly say that these pigs are the most expensive on the market. These pigs are not sensitive to the flaws on the surface which means that they can lead inspection of the pipeline without using the cleaning device.

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# UDC 665.76

# PHENOL ALKYLATION BY α-OLEFINS ON PURPOSE TO RECEIVE RAW MATERIALS FOR PRODUCTION OF MULTIPURPOSE ALKYLPHENOL ADDITIVES TO OILS

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The article describes mechanisms of phenol alkylation by  $\alpha$ -olefins and some modern and the most effective catalysts which are used for phenol alkylation on purpose to receive raw materials for production of multipurpose alkylphenol additives to oils

Usually in industry alkylphenols are received by phenols alkylation process on catalysts of acid type. As alkylation agents olefins are used most often, alcohols and alkyl halids are used less often. Preference is given to olefins, as they are available and cheap, also the mechanism of alcohols alkylation passes through the stage of the relevant alkenes formation and does not have any advantages in production organization and simplicity of receiving products.

Phenol and its homologs are easily alkylated by olefins in their liquid and gas phases in the presence of catalysts. The catalysts are usually mineral or organic acids, metal halogenides, cation-exchange resins, aluminosilicates and other compounds of acid nature.

Different quantities of isomeric mono- and dialkylphenols are formed during alkylation under the influence of catalysts. Low selectivity may be caused by secondary processes of isomerization. When comparing results of phenol alkylation on various catalysts it is difficult to give preference to any of them. It is possible to provide a high output of alkylphenols on any catalyst and to minimize by-products formation by selecting appropriate reaction conditions and a certain ratio of reacting components.

Replacement of hydrogen in an aromatic ring is related to reactions of electrophilic substitution. Strong acids are used as catalysts. Homogeneously and heterogeneously catalyzed reactions are usually distinguished.

The homogeneous catalysis of phenol alkylation reactions by olefins. The mechanism of phenol alkylation in the presence of sulfuric acid with formation of olefins sulfates is presented in figure 1.

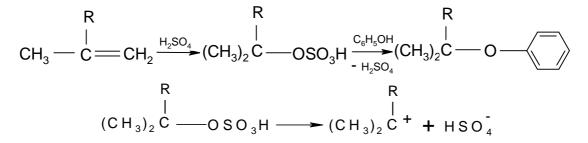


Fig. 1. Mechanism of phenol alkylation in the presence of sulfuric acid with formation of olefins sulfates

Also in the presence of sulfuric acid regrouping in molecules of alkylphenyl ether with alkylphenols formation may take place, the mechanism is presented in figure 2.

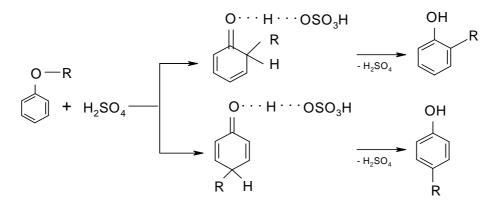


Fig. 2. Mechanism of the regrouping of alkylphenyl ether into alkylphenol through quinoid structure

Nowadays the use of the sulfuric acid is limited due to the advent of new types of catalysts and complexity of its separation from alkylation products. Also catalysis of adverse reactions such as destruction, polymerization of olefins, phenol sulfurization and sulphation should be considered as drawbacks of the sulfuric acid.

By-products formed reduce the general output of alkylphenols [1].

Heterogeneous catalysis of phenol alkylation by olefins. As heterogeneous catalysts aluminum oxide, aluminosilicates, zeolites, oxides of various metals can be used [2-5]. The mechanism of direct phenol alkylation on aluminium phenolate is presented in figure 3.

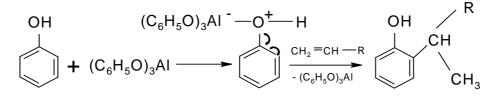


Fig. 3. Mechanism of direct phenol alkylation on aluminium phenolate

In the late sixties intensive studying of processes of phenol alkylation in the presence of sulphocationite began [6, 7].

In the alkylation process on cation the nature of homogeneous catalysis has been set. [8]. Reagents, first of all phenol, in the course of diffusion to active sulfonate groups are located, generally, inside of cationite granules and interact with its macromolecule forming solvate complexes and hydrogen bonds with aromatic cores of hydrocarbon framework. It causes swelling and loosening of structure of catalyst polymeric substance. In turgent cationite the chains of network polymer part and it becomes permeable for molecules of bigger size. So cationits give an opportunity to carry out interaction processes of wide range of olefins and phenols according to the unified flowing scheme in rather narrow criteria range.

Advantages of cation-exchange resins application for phenol alkylation by olefins in comparison to use of other catalysts [8]:

- higher output of monoalkylphenols;
- there are no processes of polymerization and depolymerization;
- a long service life and an easy regeneration;
- separation of alkylate from the catalyst by filtering;
- lack of sewage without the need for alkylate washing

Nowadays a huge choice of catalysts is offered for phenol alkylation for the purpose of receiving basic raw materials for production of multipurpose alkylphenolic additives. The main physical and chemical properties of the most effective catalysts, ion-exchange resins are presented in the table 1 [9].

| The catalyst                 | The producer    | Bulk density | Specific surface,<br>m <sup>3</sup> /g | Diameter<br>of pores, <u>Å</u> | General exchange<br>capacity,<br>equiv/kg | Maximum<br>operating<br>temperature, °C |
|------------------------------|-----------------|--------------|--|--------------------------------|---|---|
| Amberlyst<br>35 DRY<br>RESIN | DOW<br>(France) | 560          | 50                                     | 300                            | 5,0                                       | 150                                     |
| Amberlyst<br>36 DRY<br>RESIN | DOW<br>(France) | 770          | 33                                     | 240                            | 5,4                                       | 150                                     |

Table 1 – The main physical and chemical properties of catalysts

In the conditions as close as possible to industrial ones the analysis of products composition, which were received on catalysts Amberlyst 35 DRY RESIN and Amberlyst 36 DRY RESIN, has been carried out. The analysis of products of phenol alkylation by propylene tetramers has been carried out with application of modern tool methods of research (table 2).

Table 2 – Results of chromatographic analysis of alkylphenols at a molar ratio phenol: propylene tetramers of 2:1mol/mol, loading of the catalyst 20% (mass.) in relation to the mass of reactionary mix and reaction temperature of  $130 \,^{\circ}C$ 

| Type<br>of alkylphenol obtained                                      | Content<br>of propylene tetramers | Content of free phenol | Content<br>of mono-alkylphenol | Content<br>of di-alkylphenol |
|--|-----------------------------------|------------------------|--------------------------------|------------------------------|
| Alkylphenol on the<br>basis of Amberlyst 35<br>DRY<br>RESIN catalyst | 5,88                              | 8,21                   | 71,98                          | 13,93                        |
| Alkylphenol on the<br>basis of Amberlyst 36<br>DRY<br>RESIN catalyst | 6,01                              | 7,52                   | 73,01                          | 13,45                        |

It was shown that at alkylation temperature of 130-150 °C in general all catalysts are almost equally effective, but Amberlyst 36 DRY RESIN provides the greatest extent of propylene conversion, the highest output of monoalkylphenol (12% on raw materials).

#### Conclusion

1. In industry alkylphenols are usually received by phenols alkylation process on catalyst of acid type.

2. Different quantities of mono- and dialkylphenols are formed during the alkylation process under the influence of catalysts, low selectivity is caused by secondary processes of isomerization.

3. Nowadays the use of the sulfuric acid is limited due to the advent of new types of catalysts and complexity of its separation from alkylation products.

4. In the alkylation process on sulfocationites the nature of homogeneous catalysis has been set.

5. The choice of catalyst causes technological parameters of the process, final product output and its further use.

6. Today it is difficult to give preference to any catalyst.

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#### THE USAGE OF POLYMERIC PETROLIUM RESINS

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In this article the usage of polymeric petroleum resins is revealed. We understand polymeric petroleum resins as a special class of low molecular weight synthetic resins which are derived from petroleum feedstocks. Sometimes these resins are also called petroleum hydrocarbon resins.

The production of polymeric petroleum resins began to develop on the basis coke chemistry and is closely related to the production of coumarone-indene resins, the history of which dates approximately one hundred years back. Because of the lack of feedstock for production of coumarone-indene resins, used instead of natural producrs, polymeric petroleum resins were created on the basis of cheap and available materials. Development of ethylene-propylene production contributed greatly to the creation of polymeric petroleum resins, as it provides significant resources of liquid pyrolysis products [1].

The synthesis of polymeric petroleum resins is performed by polymerization of unsaturated hydrocarbons (monomers) which are contained in the feedstock. The formation of polymers from monomers occurs due to multiple bonds or rings opening and due to combination of original monomer molecules into the polymer macromolecules. For the synthesis of the polymeric petroleum resins ionic (catalytic) or radical polymerization of monomers is used. From the choice of existing methods of radical polymerization thermal and initiated polymerization are most commonly used.

For the production of light polymeric petroleum resins fractions of liquid pyrolisis products, boiling up below 200 degrees Celsius are used, and for the production of dark polymeric petroleum resins higher boiling fractions or heavy pyrolysis resins are used. These fractions of liquid pyrolysis products are separted by distillation [2].

Polymeric petroleum resins are used in different branches of industry. The particular practical interest is given to the usage of polymeric petroleum resins in oreder to reduce the consumption of expensive and difficult-to-obtain products of natural origin, for example, vegetable oils ( in paint materials), rosin (for papermaking), as well as wood-pyrogenic and indene-coumarone resins (in rubber mixes and for the manufacture of industrial rubber goods).

Paint and varnish industry consumes thousands of tons of edible vegetable oils, a large portion is used for production of dry oils and oil paints. Replacement of vegetable oils in paint and varnish materials for polymeric petroleum resins reduces the consumption of these valuable food products and makes it possible to use best farm lands for the production of other crops.

The intensive development of the petrochemical industry contributed to the emergence of a new group of synthetic binders for the production of paint materials, namely polymeric petroleum resins. The prospectivity of this group of synthetic binders is defined by cheap raw materials, the easiness in production, low investments and possibility of complex oil feedstock refining using non-waste technologies.

Pulp and paper industry is one of the major rosin consumers. In the process of paper manufacturing twenty-five per cent of all rosin produced in the world is used. Because of high development rate of such industries as pulp and paper, chemical, oil refining, petrochemical and others which are considered as major