WEB OF SCIENTIST: INTERNATIONAL SCIENTIFIC RESEARCH JOURNAL
ISSN: 2776-0979, Volume 7, Issue 1, January- 2026

SYNTHESIS OF SYNTHETIC HIGHER FATTY ACIDS BY OXIDATION OF PARAFFINS

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Abstract
This article presents information on the processes of synthesizing synthetic higher fatty acids as a result of the oxidation of paraffins, the dependence of the number of acids, esters, and carbonyls in the reaction mixture on the duration of the process in the catalytic oxidation of paraffin, and the amount of carboxylic acid compounds in the product obtained by oxidizing paraffin.

Keywords: Paraffin, polyethylene, SFM, catalytic oxidation, carboxylic acids, fatty carboxylic acid.

INTRODUCTION

It is known that the practical importance of the oxidation process of paraffins and low molecular weight polyethylene in the organic and petrochemical synthesis industries is very difficult to assess.

Currently, three directions of paraffin oxidation processes are known:

- their oxidation in the gas phase to obtain lower alcohols and aldehydes;
- their thermal oxidation in the liquid phase in the presence of boric acid to synthesize higher secondary alcohols;
- their catalytic oxidation in the liquid phase to obtain carboxylic acids [1].

In the first direction, C10-C20 alcohols of normal structure are widely used as raw materials for the synthesis of surfactants (SFM). Oxidation of low molecular weight polyethylene and paraffin was carried out without the participation of a catalyst, and in the presence of 4.0-5.0% boric acid or potassium permanganate at a temperature of 165-170 oC in a bubbling apparatus using atmospheric oxygen (3.0-4.5% (Vol.) O2). It is known that these conditions facilitate the formation of alcohols, in which boric acid reacts with alcohols and converts them into esters, which prevent further oxidation:

$3ROH + H_3BO_3 \leftrightarrow B(OR)_3 + 3H_2O$

The resulting ester is separated and hydrolyzed with water, and then the boric acid formed as a result of hydrolysis is returned to the oxidation process [2].

If alcohols are not obtained due to the destruction of the carbon chain, then a mixture of mainly secondary alcohols, glycols and ketoalcohols is formed. In this regard, this fraction is considered a cheap raw material for obtaining SFM, this method of paraffin oxidation has not been widely used.

The third method is to obtain carboxylic acids by their catalytic oxidation in the liquid phase at temperatures from 105-120 oC to 170-200 oC [3].

This process proceeds in two ways:

- When C1-C8 lower paraffins are oxidized, they produce mainly acetic acid;
- When hard paraffins are oxidized, they produce synthetic organic acids (SYOK) with a carbon chain of C10-C20

, which are the raw materials for the synthesis of SFM.

It is known that due to the large length of the hydrocarbon chain, a very complex mixture of products is formed as a result of the synthesis. Due to the equal probability of attack at any secondary carbon atoms in the hydrocarbon molecule, chain breakage occurs at any carbon-carbon bond. As a result, incompletely oxidized products are obtained - ketones and alcohols of various structures [4].

When oxidizing hard C30 paraffin, 60% of acids from the C10-C20 fraction are formed, of which C1 - C4 acids, C5 - C9 and higher (with more than 20 carbon atoms) acids. The specific properties of higher carboxylic acids allow them to form oxyacids, lactones, ketoacids and dicarboxylic acids when oxidized. As a result of the formation of these mixtures, the quality of the main carboxylic acids deteriorates, and the degree of conversion of the initial paraffin decreases.

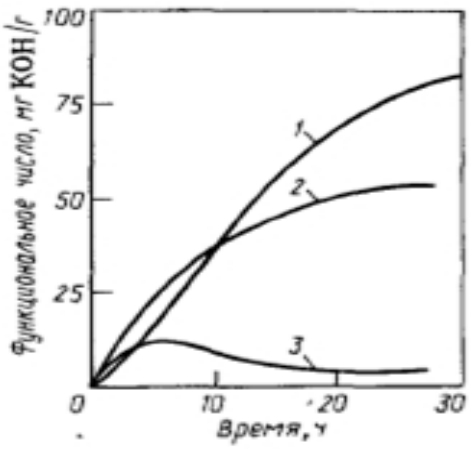

Figure 1. The dependence of the number of acid (1), ester (2) and carbonyl (3) groups in the reaction mixture on the duration of the process during the catalytic oxidation of paraffin.

The curves of the change in the number of acid, ester and carbonyl groups characterizing the corresponding carboxylic acid, ester and carbonyl compounds in the product synthesized by oxidation of paraffin were presented. It is clear that the concentration of ketones passes through a maximum, while that of esters at a lower conversion level of paraffin has not yet reached a maximum (Figure 1.) . The increase in the acid number slows down when 70-80 mg of KON is added per 1 g of product [4].

RESULT:

As a result of oxidation, the paraffin molecule was cleaved at different points, forming a mixture of fatty acids with different carbon atoms in its structure. Thus, when paraffin with 30 carbon atoms was oxidized, the yield of carboxylic acids was 80%. Two fractions C10-C16 and C17-C20 were used to obtain a surfactant. The acids of the first C10-C16 fraction approximately corresponded to those obtained from coconut oil. Toilet soap was obtained from it, and household soap from the acids of the C17- C20 fraction.

The composition (in%) of the resulting mixture of fatty carboxylic acids with different molecular weights is as follows (Table 1):

Table 1. The amount of carbonic acid compounds in the product obtained by oxidation of paraffin

Contents	Fatty acid content, % (mass)	Contents	Fatty acid content, % , (mass)
C_1—C_4	5,0-10	C_{10}—C_{16}	25,0-28,0
C_5—C_6	3,0-5,0	C_{17}—C_{20}	15,0-20,0
C_7—C_9	8,0-10	> C_{20}	20,0-25,0

Water-insoluble carboxylic acids C7-C9 are added to obtain the corresponding alcohols, plasticizers and lubricating oils are added to improve properties. The lower water-soluble acids C1-C4 are not currently available for use, as they are washed out by water.

Composition of the first fraction

Table 2 Fraction composition Fat carboxylic acid content, %.mass.

Fraction composition	Fat carboxylic acid content, %.mass.
Up to C_{10}	4,80–7,00
C_{10}–C_{11}	22,3–26,8
C_{12}–C_{13}	47,7–48,9
C_{14}–C_{16}	30,7–34,4
C16 high	17,0–20,4

Higher acids (>C20) were sometimes used to prepare household soap. The residue left after distillation was found to contain dicarboxylic acids used to obtain synthetic fibers. The fraction of carboxylic acids used in the preparation of SFM is given in Tables 1 and 2. Higher fatty alcohols formed as a result of the oxidation of paraffins are of great interest.

They can be isolated in the form of complex esters of boric acid (after the esters are saponified, the acids are extracted with an aqueous solution of alkali), the amount of these alcohols is 8.0-10.0% of the total mass of the initial paraffin.

Higher fatty alcohols contain from 8 to 26 carbon atoms in the molecule, of which 65.0-76.0% are primary normal alcohols. They can be successfully used in the synthesis of SFM of the alkyl sulfate type.

Composition of the second fraction

Table 3

Composition	Fat carboxylic acid content, %.mass.
Until C_{17}	27,0–41,8
C_{17}–C_{18}	22,7–24,7
C_{17}–C_{20}	43,9–49,7

As a result of oxidation of solid hydrocarbons at a temperature of 150-170 oC without a catalyst, low-quality carboxylic acids were obtained. The oxidation process was carried out in the presence of selected catalysts: an aqueous solution of potassium permanganate, some manganese salts, and manganese peroxide. These catalysts are insoluble in paraffin, therefore homogeneous catalysts (manganese salts of higher carboxylic acids) were selected, the temperature was maintained at 120-130 oC for 2 hours. It was observed that when sodium hydroxide (especially potassium hydroxide) or salts of carboxylic acids with these metals were introduced into the system, the catalyst activity increased significantly. The most favorable ratio was Mn2+: K+ = 1:1.Shuni takidlash lozimki, qattiq uglevodorod suyuq fazada oksidlanish tezligi ko`p omillarga – katalizator kontsentratsiyasi, Harorat, kislorod partsial bosimiga (havoni suyuq fazadan o`tish tezligiga) bog‘liq.

The technological scheme for obtaining synthetic detergent high-fatty acids by oxidizing hard paraffin is presented in Figure 1.

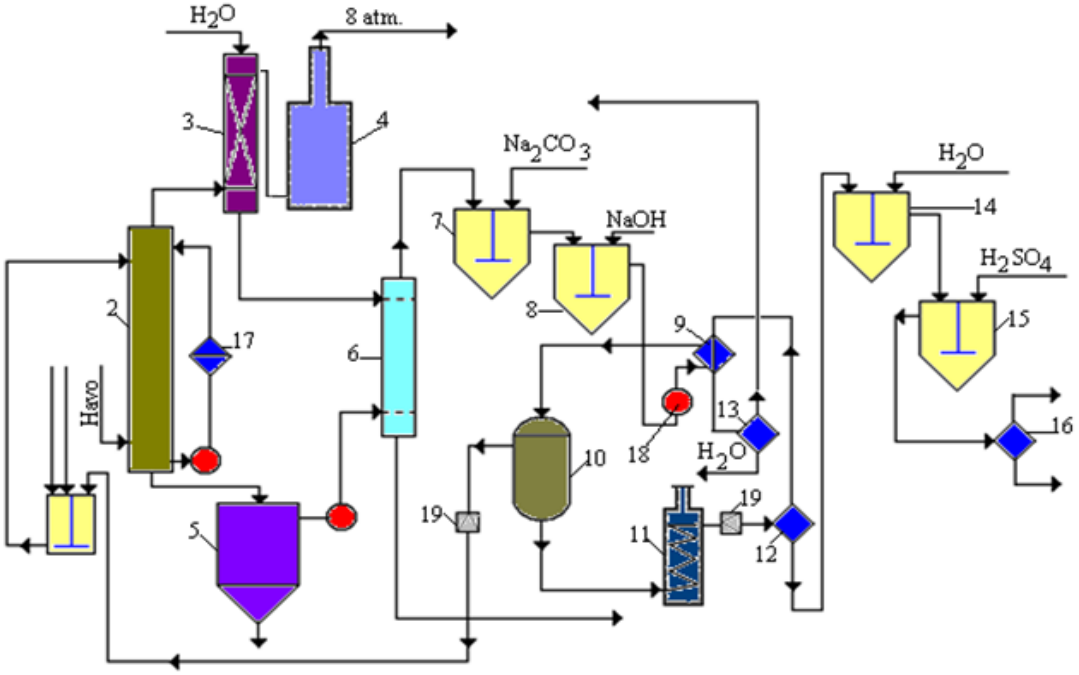

Figure 2. Technological scheme for obtaining synthetic detergent high-fatty acids by oxidizing hard paraffin.

1-mixer, 2-oxidation column, 3,6- washing columns, 4- incinerator, 5- clarifier, 7,8-saponification, 9- heat exchanger, 10- autoclave, 11- tube furnace, 12,13,16-separators, 14,15- mixer unit, 17-cooler, 18-pump, 19- reducing valve.

CONCLUSION:

In conclusion, it should be noted that higher acids (>C20) were sometimes used to prepare household soap, low-quality carboxylic acids were obtained by oxidizing solid hydrocarbons at 150-170 °C without a catalyst, and a technological scheme was developed to obtain synthetic detergent higher fatty acids by oxidizing hard paraffin.

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