Synthesis and research of fatty acids based on local secondary petroleum products

Kamoliddin Khujakulov, Babaxan Mavlanov, Sadriddin Fozilov, Rano Niyozova and Murodillo Komilov
Bukhara Engineering Technological Institute, Bukhara, Uzbekistan

E-mail: zehniddin2012@mail.ru

Abstract. The article analyzes the synthesis of higher fatty acids based on local secondary oil products of the Republic of Uzbekistan and the influence of various factors on their synthesis. The highest yield of fractional acids C10 - C17 during paraffin processing is observed as a result of paraffin oxidation with a boiling point of 260-350 °C. The fractional composition of the obtained fatty acids was analyzed by gas chromosome spectroscopy. The effect of the catalyst on the oxidation process on the duration of oxidation and the change in acid, ether and carbonyl numbers has been studied.

1. Introduction
By the end of 2020, the global oil sector is expected to suffer more than the global economy as a whole. Thus, according to the consensus forecast of a number of large energy agencies, consulting companies and investment banks, the world consumption of liquid hydrocarbons (LHC) in 2020 will decrease by 8-12%, and the world gross domestic product (GDP) - by 5-6%. By the end of 2021, global oil demand will, on average, be lower than the pre-crisis 2019. At the same time, the recovery growth of world GDP in 2021 will be higher than the indicators of 2019. The outstripping drop in the consumption of petroleum products is explained by the fact that the quarantine measures taken to contain the spread of the COVID-19 pandemic in the second quarter of 2020 implied stricter restrictions for the transport sector compared to restrictions for most other sectors of the economy.

Considering that the dynamics of consumption of certain types of petroleum products is determined, first of all, by the dynamics of economic activity in related sectors of the economy, one should see what impact the COVID-19 pandemic had on the key sectors-consumers of petroleum products: industry, air transportation, road and water transport. Taking into account the depth of the decline in the level of activity in the above sectors, the peculiarities of the lifting of quarantine restrictions in them, as well as changes in consumer behavior, it is possible to predict the expected paths of recovery in demand for the main types of petroleum products (motor gasoline, jet fuel, diesel fuel, etc.).

The dynamics of the restoration of demand for diesel fuel in the world, apparently, will go along the U-shaped curve (the industry drops slower, but also slowly restored). An additional impact on the trajectory of recovery demand will also have a reduction in the consumption of diesel fuel by reducing the attractiveness of passenger diesel cars in Europe. The risks of maintaining an economic recession in 2021 also negatively affect the forecasts for the restoration of consumer demand for diesel fuel. At the same time, a certain support for the consumption of diesel fuel will be an increase in the use of a diesel engine as bunkering fuel in the face of the beginning of the action of new environmental standards.
entered by the International Maritime Organization in 2020 [1].

Given the changes in the market of petroleum products, in order to exit the global economic crisis associated with the COVID-19 pandemic, the replacement of imports of raw materials, including synthetic products used for technical purposes instead of natural, is one of the actual directions in modern science.

For the first time, higher fatty acids were obtained by oxidizing solid paraffin, with paraffin in its composition containing hydrocarbons from C\textsubscript{18} to C\textsubscript{36}.

There is a method of producing fatty acids from oil and gas by continuous air oxidation of fresh and processed mixed aliphatic hydrocarbons. Another production method is the melting (oxidation) of branched-chain alcohols obtained by carbonylation and reduction of olefins [2].

In addition to the "oxo" of the syntheses considered for the production of products such as Laurinic acid, there is also a method of carboxylation of intermediate products of the ciegler obtained as a result of the polymerization of ethylene [3].

There is also a method of carboxylation of aliphatic hydrocarbons with a long chain for obtaining alcohols, acids or other acid-containing products, which consists in dehydrogenation of paraffins, carbonylation and separation of finite products with fractional distillation [4].

With continuous oxidation of paraffin in a multi-section column, the yield of fatty acids increases and the time of paraffin oxidation to the required depth decreases, but the molecular weight of fatty acids decreases [5].

A method is known for the oxidation method of liquid paraffins to acid oxygen acid at 130 °C in the dynamic system in the presence of manganese salts of synthetic fatty acids. In the case of using MnSFA salts of synthetic fatty acids (MnSFA), unwanted decarboxylation and decarbonyl processes of the desired products associated with auto oxidation are significantly reduced, and a high yield of fatty acids is achieved [6].

A method was developed for the production of branched carboxylic acids from branched olefins by means of a reaction with carbon monoxide and a solid acid catalyst, characterized in that the branched or its predecessor interacts in the reactor with continuous reverse stirring with continuously supplied carbon monoxide and water [7].

Known invention for the production of carboxylic acid in the gas phase, which is the production of carboxylic acid in the gas phase by hydroxycarbonylation of alkene in the presence of water using a heterogeneous metal catalyst based on sulfide [8].

The influence of the composition of raw materials on the yield and composition of acids was studied using the example of the oxidation of paraffins of paraffinic oils containing 91.2 and 73.4% of n-alkanes. The yield of technical mixed water-insoluble acids in terms of processed wax is 82.3 and 84.2% by weight, respectively. The corresponding yields of distilled acids C\textsubscript{5}-C\textsubscript{20} in relation to mixed technical acids are 68.3 and 64% by weight, and in relation to 100% acids 63 and 57.2% [9].

It is known that about 50% of the vegetable oils produced is spent on the production of technical products - soaps, enamels, varnishes, linoleum, marmot oils, rubber, etc. An increase in the production of vegetable oils leads to high capital costs and labor costs. For example, the production of 100,000 tons of fatty acids would require a 400,000 ha sunflower crop and at least four large oil extraction plants [10].

2. Methods and experiment

Based on the foregoing, the current level of consumer goods and technologies requires successful replacement of natural vegetable oils used in technical products, synthetic materials based on oil waste.

The main source of vegetable oil substitutes is synthetic fatty acids. They are much cheaper than natural ones, and their use can significantly save the national economy.

Synthetic fatty acids are obtained by oxidation of paraffins, which are by-products of oil, in the presence of catalase. Oxidized paraffin is embedded with an aqueous alkali solution and turns into acid and salts.

Refined white paraffin, separated from oil, is used as a raw material for the production of distilled
synthetic fatty acids. The composition of such paraffins is different, but it depends on the rate of oxidation and separation of non-mild products, the ratio of fatty acids with different molecular weights and structures, the quality of the acids, i.e., the yield depends on the composition of the paraffin, and technical and economic indicators of the plant. The content of solid purified paraffin of petroleum intended for the production of synthetic fatty acids should not exceed 2.20% according to GOST 23683-89, and the paraffin itself should be boiled under the limits [11].

Currently, the main part of oil refining in Uzbekistan falls on the Fergana refinery and the Bukhara refinery. The high-paraffinic oil fields in the country are listed in table 1.

**Table 1. Number of paraffin and other components in oil produced in Uzbekistan.**

| Place of Birth | Density, kg/m³ | Frozenation temperature °C | Number of individual components, % |
|---------------|----------------|-----------------------------|----------------------------------|
| Khangiz       | 894            | +20                         | 11.5 0.002 2.08 5.29 17.6        |
| Varik         | 869            | +10                         | 12.3 0.002 0.96 3.12 14.0        |
| Andijan       | 858            | +7.0                        | 13.4 0.260 1.50 4.37 8.60        |
| Mingbulok     | 857            | +8.0                        | 16.0 0.048 6.80 4.51 15.6        |
| South Almalyk | 849            | +5.0                        | 21.3 0.001 0.58 2.50 10.3        |

It can be seen that the extracted oils differ greatly in composition [12]. In terms of fractional composition, paraffin products often do not meet the requirements of GOST. When petroleum paraffins contain components that boil at high temperatures, (87.0-89.0) % of paraffin is released instead of the required 98.0% at a temperature of 460 °C. If there are components boiling at high temperatures that adversely affect the oxidation process, paraffin can be obtained mainly with a boiling point of at least +52 °C. When the extraction process of paraffin includes light fractions, boiling at temperatures below 400 °C, the use of paraffin fractions with a high boiling point (460-470 °C) adversely affects the quality and quantity of the resulting paraffin.

**Table 2. The number of paraffins derived from distillate fractions.**

| Indicators                  | Paraffins from distillate fractions |
|-----------------------------|------------------------------------|
| Boiling temperature, °C     | 300-400 °C 350-420 °C 420-500 °C   |
| Fractional composition:     |                                    |
| Beginning of boiling, °C    | 289.1 298.2 392.0                  |
| Boils away,% up to 400 °C   | 93.4 62.9 3.9                       |
| Boils away,% more than 450 °C| 95 98.2 64.3                      |
| End of boiling, °C          | 450.0 460.0 500.0                   |
| Exit,% on raw materials     | 14.7 31.0 56.2                     |

The quality and composition of fatty acids depend not only on the fractional composition of paraffin, which is its raw material, but also on the degree of purification and the presence of isostructural hydrocarbons in it.

The use of purified paraffin leads to the formation of additional oxidation products, which in turn not only adversely affect the processing, but also adversely affect the quality of the finished product. The speed of oxidation of crude paraffin is 20-30% less than that of purified. Un washing and autoclaving of soap is much slower, sometimes the process is completely absent, and together with soap, 2-3 times more non-soap products get into the oven. When treating refined paraffin, the ratio of the amount of non-soap deposited in the autoclave to the amount of non-soap stored in the soap is usually 1.0: 0.4-0.5, whereas when processing the crude paraffin, this ratio may increase. Up to 1: 1. This situation sharply reduces the productivity of the soap-making and non-soap shops at the stage of heat treatment.

The higher the amount of fat in the paraffin, the more additional products may be formed in the process of its oxidation, which reduces the absorption and removal of fatty acids.
Paraffin’s that have the same boiling point, but separated from different fractions, do not have the same chemical nature and form different products during the oxidation process. Thus, the boiling point of paraffin cannot determine its suitability for the oxidation process to obtain fatty acids, where the boiling limits of fractions and the presence of isoformed hydrocarbons in paraffin are more important.

The properties of some carboxylic acids synthesized from petroleum paraffins in the Republic of Uzbekistan are shown in Table 3.

Table 3. Results of oxidation of paraffin’s of different compositions.

| Indicators                          | Paraffins | Khangiz | Varik | Andijan | Mingbulok | South Almalyk |
|------------------------------------|-----------|---------|-------|---------|-----------|---------------|
| Temperature, °C                     |           |         |       |         |           |               |
| Beginning of boiling, °C            |           | 259     | 273   | 348     | 368       | 407           |
| The end of boiling, °C              |           | 348     | 389   | 469     | 472       | 489           |
| Melting, °C                        |           | 22.5    | 33.2  | 51.8    | 55.1      | 61.2          |
| Molecular weight                   |           | 268     | 273   | 395     | 437       | 448           |
| Average carbon atoms in the molecule: |         |         |       |         |           |               |
| Paraffin                           |           | 17.0    | 18.9  | 29.2    | 32.2      | 31.9          |
| Crude acids                        |           | 10.0    | 12.0  | 19.2    | 15.2      | 16.8          |
| The yield of acids, % on the starting paraffin | | | | | | |
| Acids in crude oil                 |           | 73.3    | 70.8  | 78.1    | 81.6      | 84.4          |
| Fractions C₃ – C₉                  |           | 16.2    | 16.9  | 12.2    | 11.0      | 9.1           |
| Fractions C₁₀ – C₁₇               |           | 35.2    | 31.2  | 26.3    | 23.9      | 17.2          |
| Fractions C₁₈ – C₂₀                |           | 11.1    | 13.7  | 24.2    | 31.3      | 32.2          |
| Vat residue, %                     |           | 9.2     | 7.7   | 12.9    | 16.2      | 23.2          |

The presence of isotropic hydrocarbons in the composition of paraffin’s depends mainly on the location of the oil field, as well as on the method of separating paraffin’s. Paraffin without isotropic hydrocarbons is necessary for the production of high-quality synthetic fatty acids, which are unbranched or contain their minimum quantity.

Comparing paraffins of different composition, it was found that the yield of raw fatty acids increases with an increase in the boiling point and the average molecular weight of the initial paraffin (Table 3). At the same time, the average amount of carbon atoms in a crude fatty acid molecule also increased. It is also observed an increase in the number of acids above the C₂₀ and the cubic residue. However, the number of Fractional acids C₅ - C₉ decreases.

The maximum yield of acids of fractions C₁₀ - C₂₀ corresponds to the average molecular weight of hydrocarbons 432. The presence (in %) of C₁₀ - C₁₇ acids in the C₁₀ - C₂₀ fraction is as follows:

- Paraffin Hankiza.................................................................62.8
- Paraffin Varik.........................................................................66.7
- Paraffin Andijan....................................................................49.4
- Paraffin Mingbulok.............................................................41.3
- Paraffin South Almalyk.......................................................33.2

Consequently, the higher the molecular weight of paraffin, the lower the output of the C₁₀-C₁₇ fractiononic acids. The largest output of the C₁₀-C₁₇ fractiononic acids during the processing of paraffin is observed in the processing of paraffin, which boils at a temperature of 260-350 °C.

Thus, the composition of the resulting mixture of synthetic fatty acids is primarily determined by the composition of its initial hydrocarbon mixture.

Therefore, when choosing a paraffin in the oxidation process, attention is paid to the required amount of synthetic fatty acids to be obtained.

Currently, fractional fatty acids C₇ - C₉ and C₁₀ - C₁₇ are of great importance for the national economy,
which are insufficient in nature, but they take place in the production of detergents, plasticizers and other products. To obtain such acids, it is advisable to use low molecular weight paraffins with a boiling point of up to 430 °C. Solid paraffins with boiling points above 430 °C are unsuitable for the production of fatty acids, since their processing produces large amounts of cubic residue and acids with a higher proportion than C_{20}, as well as isotopic acids, naphthenic and dicarboxylic acids.

The process of oxidation of paraffin hydrocarbons in the liquid phase of molecular oxygen consists of a complex complex of chemical reactions that develop in different ways and quickly and interact with each other.

The influence of external factors, such as temperature, catalyst, oxygen concentration, on the rate of a particular reaction has been studied. Thus, by changing the external effect, it is possible to create the most favorable conditions for the main reaction of the formation of fatty acids and to accelerate it several times.

The process of oxidation of paraffin to coal acids in the liquid phase is designed according to the following parameters: the oxidative conversion of paraffin does not exceed 30-35% (the number of acid acids per 1 g of the oxidant corresponds to ≈70 mg). At the beginning of the process, coalic acids begin to accumulate and maintain a temperature of 125-130 °C, then the temperature is lowered to 105-110 °C; The oxidation process is carried out at atmospheric pressure, the air enters the device through small pores (1-2 mm).

The reactor has a cylindrical shape with a diameter of 50 mm and a height of 250 mm; a mixer is installed inside. At the top of the reactor, a Dina and Stark holder with a refrigerator was installed. The process temperature was measured with a thermometer. The reactor itself was placed in an oil bath. Oxygen in the air was supplied with an air compressor, and the volume of air entering the reactor was monitored with a rheometer. 200 g of paraffin was added to the reactor, and after its dissolution, 1.5 g of KMnO_{4} was added in the form of a solution dissolved in 1.0 - 1.5 ml of distilled water. When the temperature in the reactor reached 180 °C, 1 kg of paraffin was supplied with air at a rate of 60 liters per hour, and this was controlled by a rheometer.

During the experiment, the reactor was maintained at a constant temperature and air flow rate, and the volume of water collected in the Dean and Stark holder was measured. The yield of the target product was 78-80% compared to the feedstock. When checking the acidity of the oxidizer with a special indicator paper, it was found that its pH value is 5. This indicates that the acidic environment of the product is low.

In the laboratory, the oxidation of the solid paraffin of the southern Almalyuk was carried out in the laboratory setting shown in figure 1.

![Figure 1](image-url)

**Figure 1.** Technological scheme for obtaining fatty acids by oxidation of paraffin’s: 1-reflux condenser, 2-Dina Stark, 3-mixer, 4-pin thermometer, 5-reactor, 6-oil bath, 7-electric oven, 8-dryer, 9-rheometer, 10-compressor V spectrum of the III version of the prototype.

During the oxidation of paraffin, atmospheric oxygen passes through the reactor and returns back to
the atmosphere through the refrigerant. The resulting water is collected in a trap, paraffin drops added to the volatile products of the oxidation process are condensed in the refrigerator and returned to the reactor. The easiest products of the process are thrown through the air. The oxidation process takes 4 hours. Selected the oxidant sample to determine the number of acids per hour.

3. Results and discussion

Synthesized higher fatty acids were analyzed in Gasochromatomas (GX-MS) spectrum Agilent 5975S Int MSD / 7890A GC (Agilent Technologies).

The separation of the mixture components was performed on a quartz capillary column Agilent HP-INNOWAX (30m×250μm×0.25μm) in the temperature mode: 60 °C (10 min) - 4 °C / min to 220 °C (10 min) - 1 °C / min to 240 °C (20 min). The volume of the influence of the sample 0.2 μl (hexane), the flow rate of the mobile phase is 1.1 ml / min (H2). The temperature of the injector 250 °C. EI-MS spectra were obtained in the range m/z 10-550 a.m.u. The components were identified based on the comparison of the characteristics of the mass spectra with the data of the electronic libraries W9N11.L, W8N05ST.L and NIST08 (figure 2).

![Figure 2. Chromatogram of synthesized fatty acids.](image)

In the process of oxidation, along with fatty acids, products are formed that react with alkalis only when heated, which are called esters. When pure paraffin is oxidized in a pilot plant with or without a catalyst, the amount of ethers begins to increase during the induction period, that is, when the acid number of the wax is 0, and the amount of ethers and acids is equal during oxidation, the process is complete (figure 3).
In production conditions, the number of ethers in oxide obtained in a catalytic process is less than the amount of acids, and is 60% of the number of acids. This can be explained by the formation of esters of acids and alcohols, since the concentration in oxidized paraffin is too small so that esterification can occur in the initial period. In addition, the rate of saponification of these substances is two times higher than in the hydrolysis of ethers, and the amount of alcohol and acids in the amount of soap products is much lower than required, taking into account the amount of ether oxides, the carbonyl number of oxides is very low (3-6 mg KOH per 1 g) and remains stable throughout the entire process, while the amount of ethers increases with an increase in the amount of acids at the beginning and increases only with the formation of free acids. At the second stage of the process (figure. 4).

The process of oxidation of paraffin can be carried out at a high speed at a temperature of 165-170 °C, but as a result, the finished product is painted in a dark yellow color, the accumulation of ether products occurs faster than the accumulation of acids (Figure. 5). Manufacturing sharply falls and the
quality of them is also low.

Scientific research in this area led to the conclusion that it is advisable to use manganese compounds as a catalyst in the oxidation of paraffin to fatty acids, mainly potassium permanganate.

When determining the role of potassium permanganate in the oxidation process, it was found that it not only affects the rate of oxidation and the composition of the resulting product, but also undergoes a number of changes. The interactions between potassium permanganate and oxidized paraffin are difficult to explain on the basis of results obtained using chemical reactions, due to the lack of a direct relationship between the amount of potassium permanganate used and the rate of oxidation [13–22].

There is an acceptable amount of potassium permanganate, providing a high oxidation rate. The catalyst is not the permanganate of potassium itself, but the products resulting from it in the process.

During the oxidation of paraffin, the catalyst gradually passes from a heterogeneous to a homogeneous state. Experiments in the study confirm that the potassium-manganese catalyst plays two roles in wax oxidation in the fatty acid production process. Initially, at the initial stage of oxidation, it initiates a chain reaction and speeds up the process. In the next step, oxidized paraffin-dissolved potassium permanganate complexes are played, providing rapid formation of fatty acids and minimal accumulation of additional products. The rate of formation of fatty acids during the oxidation of paraffin by molecular oxygen of the air largely depends on temperature. When oxidizing pure paraffin South Almalyk without a catalyst, the rate of increasing the number of acids in oxidized paraffin is reduced by 9-10 times with a decrease in temperature from 170 °C to 120 °C (figure 6).
With a subsequent decrease in temperature, the oxidation process slows down even more, but the proportion of oxidation products is practically not changed. In the method without a catalyst, the essential numbers are usually higher than acidic, and carbonyls are higher than the etheric numbers.

Temperature changes also affect the oxidation process in the presence of a catalyst. An increase in temperature has a negative effect on the quality of fatty acids obtained in the process in the presence of a catalyst.

When using potassium permanganate, the duration of the oxidation process of synthetic paraffin increased by 5 times when the temperature dropped from 125 °C to 80 °C until the amount of saponification reached 120-125 mg KOH per 1 g (figure. 7).

![Figure 7. The effect of temperature on the duration of oxidation of synthetic paraffin in the presence of 0.25% potassium permanganate.](image)

4. Conclusions
Research findings include the following:

- Higher fatty acids are synthesized by oxidation of petroleum paraffins of the Republic of Uzbekistan. In the oxidation process, the most optimal parameters were selected, and the product yield was 78-80% in relation to the weight of the raw material.
- Analyzed the fractional composition of the synthesized higher fatty acids in the spectrum of gas chromatography.
- Synthetic fatty acids are a technical product used in various sectors of the economy and can replace natural. Considering that synthetic fatty acids are richer and diverse natural in composition and properties, they can be used in all industries.
- From research it can be said that when using fatty acids from secondary petroleum products in the leather industry, positive results were obtained when studying the physical and mechanical properties of leather, especially porosity.

Acknowledgements
The authors are grateful to the Laboratory of the Institute of Plant Chemistry of the Academy of Sciences of the Republic of Uzbekistan for assistance in the analysis of synthesized higher fatty acids in the spectrum of gas chromatometry (GX-MS) brand Agilent 5975S inert MSD. / 7890A GC (Agilent Technologies).

References
[1] Alexey Gromov and Alexander Titov 2020 The long effect of the Pandemic COVID-19 National Industry Journal "Oil and Gas Vertical" 15 1-13
[2] Fineberg H 1979 Synthetic fatty acids. J Am Oil Chem Soc 56 805–9
[3] Sonntag N O 1969 New developments in synthetic fatty acids. J Am Oil Chem Soc 46 4-14
[4] Beard Lans A et al 2006 Process Of Producing Carboxylic Acids, Alcohols, Or Esters (Options) Pat. No RU 2268872
[5] Lebedeva N M et al 1971 Analysis of the operation of experimental equipment for the continuous oxidation of paraffin wax Chem Technol Fuels Oils 7 168–72
[6] Konoplyannik M M and Mitskevich N I 1965 Decarboxylation and decarbonylation in the autooxidation of liquid paraffins in the presence of various initiating additives Chem Technol Fuels Oils 1 698–702
[7] .Antonius Johannes, Maria Brida, Rene Johan Han, Jean-Paul Lange and Leonardus Petrus 2002 Pat. of Taiwan No TW513401B
[8] Barton David G 2019 Catalyst for the gas phase production of carboxylic acids No EP3207021B1

Scientific and Practical Conference "Fundamental and applied research in the modern world" (Boston: Bo Science Publisher) 96–9