In recent years the attention of investigators in the field of liquid phase oxidation of hydrocarbon materials has been concentrated on the development of continuous methods.

Most of the methods described are based on the use of the equipment - oxidation columns - now employed in plants producing synthetic fatty acids. Units for the continuous oxidation of hydrocarbons usually consist of several columns connected in series between which the material treated is transmitted by gravity [2], or by means of an air lift [1] or pumps [3]. These units have several drawbacks. Since the residence time of the material to be oxidized in the columns has remained unaltered, no gain in output has been obtained by changing over to the continuous process in the Synthetic Fatty Acid and Higher Alcohols Plant in Shebekino.

Upon checking the method proposed in paper [3] it was found that this author incorrectly determined the content of fatty acids in the oxidation product; the actual carbonyl numbers of the product were higher. This hampers an objective estimate of the suitability of the proposed continuous method.

Bearing in mind that the oxidation is a chain reaction, we may note that there is no justification for using a unit consisting of several reactors connected in series. When the material treated flows from one column to the next, the oxidation chain is broken, and the process is retarded, which will inevitably affect the total output.

In the units described [1, 3], fresh oxidation agent - air - is supplied to each of the four columns. In the last column the air reacts with paraffin that has been oxidized to a considerable extent, so that the probability of over-oxidation of the fatty acids to hydroxyacids and ketoacids increases.

By special experiments in our laboratory it was shown that reduction of the specific input of air and depression of the oxygen content at the reactor exit to 5% improves the quality of the oxidation products: the carbonyl number and the content of hydroxyacids in the fatty acids are lowered.

Hence, it follows that after a definite degree of oxidation has been attained the conditions in the reaction zone must be milder than those at the start: the temperature must be decreased and the oxygen concentration be low. These conditions may be fulfilled in a multisection apparatus designed for concurrent flow of the reacting components (hydrocarbon-gas).

The design of the apparatus proposed by us (see the figure) makes it possible to vary the temperature and the oxygen concentration in the various reaction zones, to introduce various admixtures during the reaction and to vary the catalyst concentration in the process stages. By varying the height of the zones, we may adjust the residence time of the paraffin in each zone. In a multisection apparatus the process can be controlled step-wise, so that the most favorable conditions are created in the various stages.

The apparatus consists of four sections divided by the perforated plates 12. The three lower sections are oxidation sections, and the fourth upper section serves as cooling condenser. All four sections are provided with cooling coils controlled by thermocouples and electronic regulators. A steam pipe for heating the liquid in the column to the required temperature during the starting-up period is connected to the coil of the lower oxidation section. The overflow of oxidation product is led through the connecting branch and the inspection cell 6 to the container 5. As the container gets filled, the oxidation product is pumped away by the centrifugal pump to be saponified. The
Multisection oxidation column with rising flows of liquid and gas: 1) cooled condenser; 2) temperature regulator; 3) thermocouple; 4) lower column part; 5) product receiver; 6) inspection cell; 7) coil; 8-10) oxidation sections; 11) gauge for measuring the liquid supply; 12) plate; 13) differential manometer; 14) gauge for measuring the liquid level; 15) pump.

The reaction rate. For this reason we used the following technological regime during operation in a four-section column of 40 mm diameter: a temperature of 140°C and a residence time of the paraffin equal to 33 min in the first section; a temperature of 130°C and a residence time of the paraffin equal to 2 h 55 min in the second and third sections (table, experiments 2, 3, 4); the temperature in the fourth section where the oxidation product was cooled and the volatile components were trapped was 65°C. The experiments in the multisection column showed that the problem of collecting the volatile products is very simply solved by incorporation of the fourth section—the cooling section. In this section the acids and hydrocarbons are completely trapped, forming the so-called oily condensate. The outgoing gases contain only water vapor and a small amount of water-soluble acids of low molecular weight. The velocity of the air calculated for an empty column equaled 0.2 m/sec.

The runs with Grozny and Novoufa paraffins under the above oxidation regime lasted one day. During oxidation of Grozny paraffin in 24 h the yield of oxidized paraffin amounted to 97.05%; the acid number equaled 65.6 mg KOH/g, the content of fatty acids 32%, the mean residence time of the paraffin in the column 4 h 12 min.

The starting material delivered by the "Twelfth Meeting of the Communist Party of the Soviet Union" plant in Ufa was thoroughly oxidized. At the mean residence time of 3 h 23 min the acid number reached the value of 73.7 mg KOH/g, and the content of fatty acids in the product equaled 32.4% (see the table).

As material to be treated in the multisection column we used Novoufa and Grozny paraffins. The Novoufa paraffin was delivered by the "Twelfth Meeting of the Communist Party of the Soviet Union" plant in Ufa as a mixture of fresh and recovered paraffins used there as starting material for the production of synthetic fatty acids. This mixture is characterized by an acid number of 0.63 mg KOH/g and a carbonyl number of 18.6 mg KOH/g. The Grozny paraffin melts at 51.6°C and contains 2.3% oil.

At normal pressure the paraffin is distilled as follows; 12.5% at 290-360°C, 80.0% at 360-430°C, 7.5% at 430-450°C. The acid number of the mixture of fresh and recovered Grozny paraffin equaled 0.58 mg KOH/g, and the carbonyl number was 2.3 mg KOH/g. The MnO₂ catalyst was added to the mixture of fresh and recovered paraffin at 120°C in the form of a suspension in water; after the water had evaporated, air was bubbled through the mixture of catalyst and paraffin at 130°C for 1 h, and the mixture was then kept in a thermostat at the same temperature for 2 h. By this treatment, 50% of the catalyst was dissolved, which raised the catalytic activity.

During preliminary experiments in a column with a single section it was found that keeping the paraffin during the start of the oxidation for a short time at 140°C does not impair the quality of the products, and considerably accelerates...