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FATTY ACIDS FROM HYDROCARBONS

Part I. Oxidation of Paraffin Wax from National Refinery (Ltd) Karachi

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Paraffin wax, from National Refinery Ltd., Karachi, has been oxidised with air and the fatty acids formed have been separated and analysed. GLC analysis shows the presence of both even and odd numbered fatty acids of carbon atoms from $C_{10} - C_{20}$.

INTRODUCTION

An acute shortage of edible and industrial oils and fats has existed in Pakistan since long. Pakistan has to face this situation in spite of the fact that it is basically an agricultural country and should be able to meet its requirements of various vegetable crops adequately. Unfortunately, so far as oils and fats are concerned, this expectation has not been realized mainly because of the low yield of oilseed crops.

The requirements of industrial fats and oils are predominantly in the soap, detergent and textile industries. In the absence of agricultural resources which could provide these fatty acids in Pakistan, the soap industry has exclusively been fed by imports. Forty thousand tons of industrial fats are imported every year [1]. Realizing the limitations of the agricultural sector and the strains on national economy, the PCSIR Laboratories, Lahore embarked upon the exploration of possibilities with regard to the production of industrial fatty acids both chemically and biologically.

Pakistan produces 20,000 tons of paraffin wax every year [2]. At the moment a major portion of this wax is not finding any useful application. It was, therefore, considered advisable to subject this wax to oxidation for obtaining fatty acids, in the first instance, for soap and allied industries.

The present studies were started with a view to establishing optimum conditions for the oxidation of wax to fatty acids and determining the composition of the acids thus formed. The data described here will form the basis of a pilot study which is at present in progress.

EXPERIMENTAL

Paraffin wax 100 NHVI from National Refinary Ltd. Karachi, was used for oxidation. This wax was refined and analyzed for its composition by GLC. It was known that it contained saturated hydrocarbons from $C_{18} - C_{36}$. The composition of the wax is shown in Fig. 1.

This Paraffin wax (500 g) was placed in an electrically heated column (5 x 90 cm) maintained at 130° to 135° and containing 10 g of manganese soap as catalyst. Dry and compressed air was passed through the melted mass of the wax from the bottom and it escaped at the other end through a condenser.

The extent of oxidation was followed by determining the acid value of the reaction mixture. After 60 hr an acid

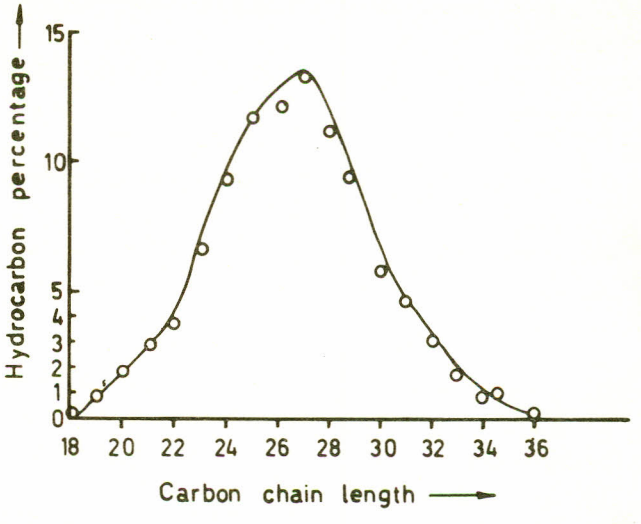

Fig. 1. A plot of hydrocarbon percentage versus carbon chain length of the paraffin wax of National Refineries, Karachi.

value of 70 mg KOH/g was reached when the oxidised mass had a melting point of 35 to 38°. The data are plotted in Fig. 2.

The reaction mixture was then washed with hot water (1000 ml x 3) and treated with 30% aquoeus sodium hydroxide while heating. This mixture was then extracted with hexane (500 ml x 3) to remove unoxidized wax and the aquoeus soap solutions were acidified with 4*N* sulphuric acid to liberate the fatty acids. The liberated fatty acids were extracted with diethyl ether (100 ml x 4) and then dried over anhydrous sodium sulphate and freed from the solvent under nitrogen to afford 30% fatty acids (150 g).

These acids (5 g) were converted to their methyl esters using the methyl alcohol and hydrochloric aicd method [3], and then subjected to GLC analysis using a DEGS column at 175° with nitrogen as the carrier gas. The composition of the respective fatty acids was determined by comparison with standard methyl esters of known fatty acids. Percentage of fatty acids *versus* their carbon chain length is given in Fig. 3.

DISCUSSION

The composition of the fatty acids, obtained by the catalytic oxidation of paraffin wax, (Fig. 3), shows the formation of both even and odd numbered fatty acids. It can be seen from Fig. 1 and 3 that the carbon chain cleaves approximately at the middle of the hydrocarbon chain length resulting in the formation of fatty acids of half chain length This observation is in conformity with the generally accepted mechanism of the oxidation of paraffin wax to fatty acids[4]. Although not shown here, the side products of the reaction are suggestive of the fact that the formation of hydroperoxides takes place as the first step of the reaction.

The composition of the fatty acids is further indicative of the fact that they can produce soap with good detergency. Studies carried out in these Laboratories on the soap formation and their properties support the above stated ideas.

Another interesting observation concerns the rate of change of wax into fatty acids. A plot between time and the extent of oxidation, as shown in Fig. 2, indicates that the optimum conversion into fatty acids is 30%; the unchanged paraffin wax under these conditions can be reused for further oxidation. However, under the conditions of the experiment, if the oxidation is allowed to proceed beyond 30%, formation of side products is accelerated. Further paraffin wax of chain length from $C_{18} - C_{36}$, was found to be most suitable as the starting material for the production of soap fatty acids.

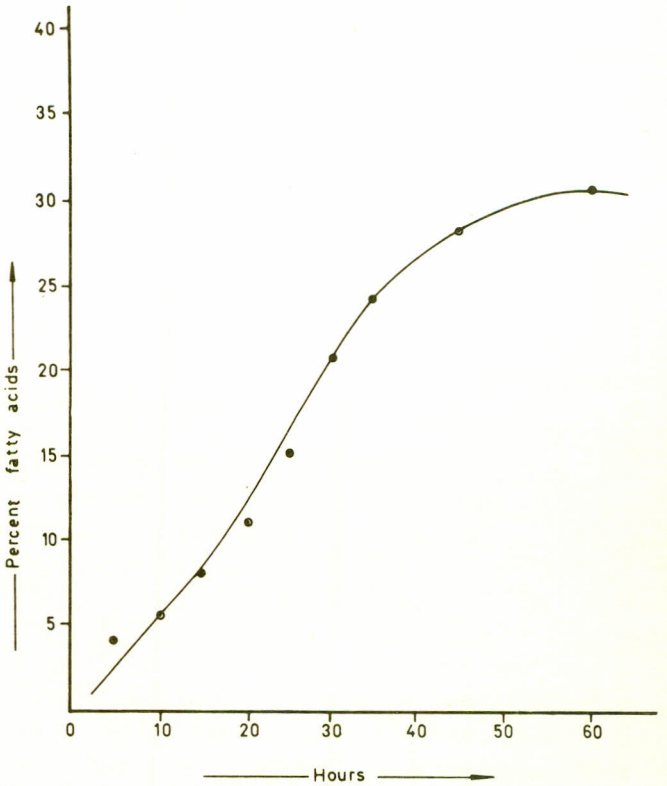

Fig. 2. Oxidation of paraffin wax into fatty acids.

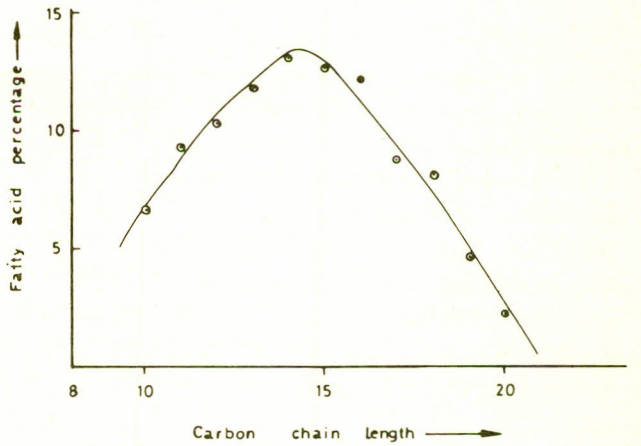

Fig. 3. A Plot of fatty acid percentage *versus* carbon chain length.

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REFERENCES

1. Regional Problems of Edible Oils and Fats Panel, Lahore, December 1975, CENTO Report No. 19.
2. N. Shakir, Private communication, National Refinery (Ltd.) Karachi and Attock Oil Co., Rawalpindi.
3. D. Glick, *Methods of Biochemical Analysis* (Interscience Publishers Inc., New York, 1954), Vol. III, p. 19.
4. F. Asinger, *Paraffins: Chemistry and Technology,* (Eng. Ed., Pergamon Press, 1968), p. 614.