

Synthesis of Higher Carboxylic Acids from Indigenous Paraffin Wax - Part I

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ABSTRACT

Experiments at HDIP laboratory were conducted to collect some initial and useful laboratory data for synthesizing higher carboxylic acids at pilot plant level by the direct air oxidation of paraffin wax using different catalysts mentioned in literature which had not earlier been used in such reactions.

INTRODUCTION

Paraffin wax is found in many kinds of crude petroleum and is extracted from high boiling fractions during the refining process (Berridge, 1975). As they are by-product of petroleum refining, the prices of raw waxes usually are relatively low. Waxes derived from refining of lube oil have no saponification and acid values (Bennett, 1975), whereas waxes/fats and oils from vegetable and animal sources are esters of higher straight-chain carboxylic acids (Noller, 1966). For this reason and under normal economic conditions the fatty acids i.e. fats and oils of vegetable and animal origin are the most economical raw material for ordinary soap. We have serious shortage of the raw material (fatty acids) in the country for such and other purposes, partly due to low production of detergent based on propylene tetramer (dodecyl benzene) which necessitates the use of more fatty soaps (ordinary soaps).

The soap industries in Pakistan consume over two hundred thousand tonnes of non-edible fats. Pakistan is therefore compelled to import palm fatty acid and tallow from Malaysia and other countries at a considerable cost to meet the requirements of soap and other industries. The question arises how far this problem can be met by planning production of higher carboxylic acids/fatty acids from petroleum feed-stocks (mainly waxes).

Fortunately, in Pakistan today crude oils from Sind province have high wax content and after refining of crude oils raw waxes present a difficult problem of disposal except as cheap fuel. Realizing the strains on national economy and availability of raw waxes in the country, work has been started for production of synthetic fatty acids (F.A.). There are two methods for the production of F.A.: (1) an indirect

method of synthesizing F.A. from petroleum sources which involves reacting olefins with carbon monoxide and hydrogen at elevated temperature in presence of a catalyst, and (2) liquid phase catalytic oxidation of paraffin wax with air which is the direct and most widely used process and thousands of tonnes of synthetic fatty acids are being produced all over the world by this method (Schwartz & Perry, 1966).

Therefore, studies were conducted with a view to collect some initial and useful laboratory data on oxidation of paraffin wax using different catalysts listed in literature but not used earlier. The present paper reports results on synthesis of higher carboxylic acids from indigenous paraffin wax and forms Part I of a major study on utilization of locally available waxes.

EXPERIMENTAL

1. Oxidation Under Oxygen Pressure

A weighed quantity of paraffin wax sample was fed with oxygen at 100 psi for 10 hours at 100°C in a closed oxidation bomb. There was a slight decrease in the oxygen pressure after 10 hours indicating that a small quantity of oxygen was consumed by the sample. This decrease in oxygen pressure gives clue that oxidation of the wax has taken place. Analyses of the oxidized and unoxidized waxes have been carried out, results are at Table 1.

Table 1. Comparison of physical properties of wax before and after oxidation using catalyst.

	Un-oxidised wax	Oxidised wax
Melting point	56°C	54°C
Total Acid No.	Nil	1.7
Saponification No.	Nil	0.13

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2. Air Oxidation in Presence of Potassium Permanganate as Catalyst.

Another experiment for oxidation of wax was carried out using 0.3 % wt. potassium permanganate as catalyst. A 100-gram sample of paraffin wax was charged into an open small vessel made of aluminum. The catalysts consisting of 0.3 % KMnO_4 and 0.15 % Na_2CO_3 as promoter were added in the form of a concentrated aqueous solution. The temperature was raised to 150°C and air was blown into the vessel. The time for heating and blowing of air varied from 10 to 32 hours. The best result was obtained after 32 hours. The oxidized wax after 32 hours was washed with warm water to remove catalyst, salts and remaining lower acids. It was then saponified with 25 % NaOH solution. The resulting mixture was then treated with 10 % sulphuric acid to liberate fatty acids (Table 2; Assigner, 1968 and Schwartz and Perry, 1966).

3. Cobalt Naphthenate as Catalyst

A 100-gram sample of wax was treated with 0.3 % wt. cobalt naphthenate and air was blown into an open small aluminium reaction vessel. The operation was carried out at 150°C for 32 hours. Free fatty acids in the reaction mixture were liberated as mentioned in Experiment 2 (Results are given in Table 2).

	$\text{KMnO}_4(0.3\%) + \text{Na}_2\text{CO}_3(0.15\%)$	Cobalt naphthenate (0.3%)
Hours	32	32
Acid No.	13	15
Sap. No.	16	32
Melting point ($^\circ\text{C}$)	53	53

INFRA-RED SPECTRA OF CATALYTICALLY OXIDIZED WAXES

Infra-red (IR) analysis of the oxidized samples was conducted. Results of IR Spectra (Figures 1 and 2) are interpreted in Tables 3 and 4.

Table 3. Infra-red spectrum of potassium permanganate oxidized wax.

Peak position cm^{-1}	Possible functional group
2925 (s)	C-H (stretch of saturated hydrocarbon)
3375(w)	O-H from water, ROH
3605(w)	aromatics
1714(s)	carbonyl group of carboxylic acid
1615	impurity
1470(s)	
1413 small intensity (w)	C-H bending of CH_2 group
1379(s)	
1145(s)]	
728(s)]	C-C bond
623(w)]	

Table 4. Infra-red spectrum of cobalt naphthenate oxidized wax.

Peak position cm^{-1}	Possible functional group
2925(s)	C-H (stretch of saturated hydrocarbon)
3420(w)	OH-(moisture of alcohol)
1727(s)	may be -CO of carboxylic acid (1725 cm^{-1})
1463(s)	C-H bending vibrations
1414(w)	
1379(s)	
1175(w)	C-C bond
(s)	Strong and sharp band
(w)	Weak band

In the light of above interpretation it can be said that the wax has been oxidized to quite an extent. Besides, saponification and acid values also confirm that small amount of conversion of wax into fatty acids has occurred.

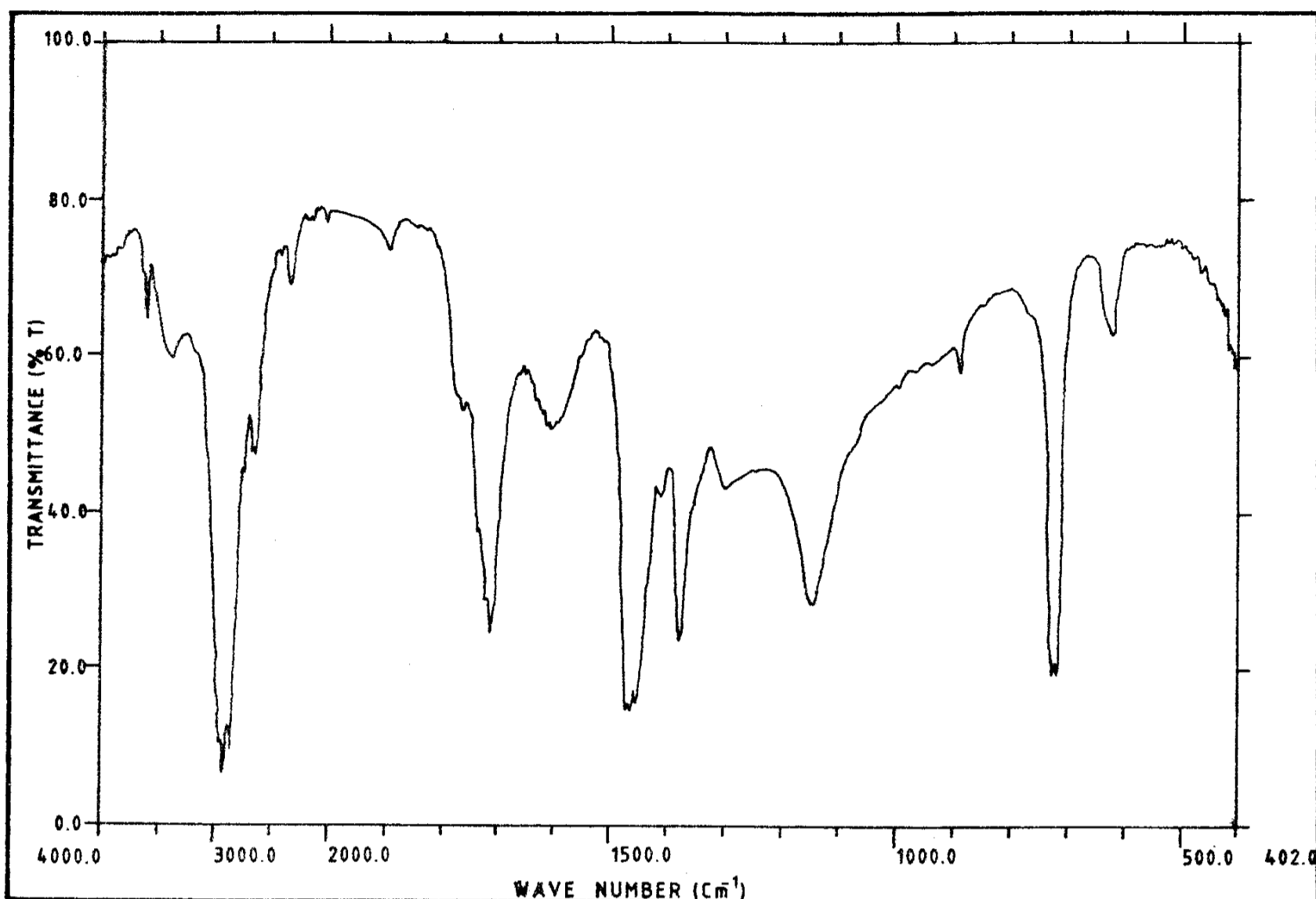


Figure 1— Infra-red spectrum of potassium permanganate oxidized wax.

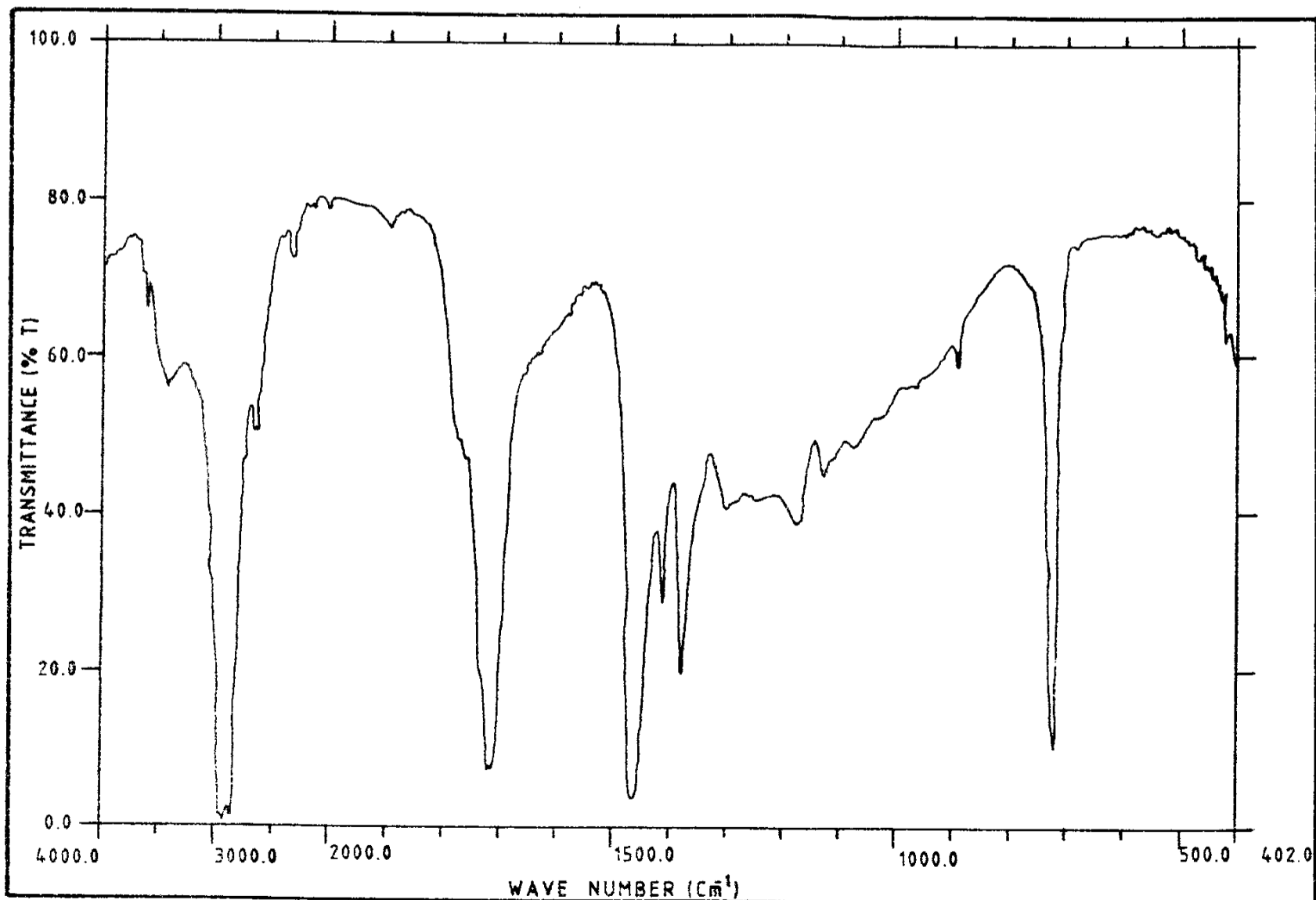


Figure 2— Infra-red spectrum of cobalt nephthenate oxidized wax.

DISCUSSION AND CONCLUSION

Very low acid and saponification values obtained in the first reaction indicate that oxidation reaction in a closed oxygen pressure bomb did not take place properly because of the absence of constant flow of oxygen which could distribute oxygen thoroughly during reaction.

Cobalt naphthenate which was not used earlier has produced comparatively better results (Experiment 3) than KMnO_4 plus Na_2CO_3 used as promoter (Experiment 2). Both experiments 2 and 3 suffered due to non-availability of specially fabricated reaction vessel having minute air dispersion arrangement. The fine distribution of air has great influence on the rate of oxidation specially when working at low temperature (Assinger, 1968). However, the results at laboratory scale are encouraging and pave the way for carrying out experiment at pilot plant level for the production of various carbon length (fraction) of fatty acids having different utilizations (Mozes, 1982).

Fatty Acid Fractions Utilization

C7-C9.— For esterification and subsequent hydrogenation to alcohols for plasticizers.

C10-C16.— For esterification and subsequent hydrogenation to fatty alcohols for detergents.

C12-C15.— For production of synthetic elastomers polymerization additives.

C16-C20.— For soap manufacturing.

C21-C23.— For lubricants and heavy metal soap production.

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