FATTY ACIDS FROM WAXES AVAILABLE IN PAKISTAN

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Locally available wax varieties-Chinese wax, Attock wax, 100 NHVI, 650 NMVI and BSHVI were subjected to liquid phase oxidation. The rate of formation of acidic components for Chinese wax and Attock wax was constant throughout the period observed (excluding the induction period) but dropped slowly to zero for 100 NHVI, 650 NMVI and BSHVI. Refining of the latter group of waxes resulted in enhancing this rate to varying degrees. The sweeting process gave the most encourageing results. The acidic components were esterified and resolved by liquid chromatography into various class compounds. The quantity of methyl esters and their carbon ranges were: Chinese wax, 47.06% and $C_{10}-C_{29}$; Attock wax, 48.50% and C_8-C_{31}; 100 NHVI-S, 27.08% and C_9-C_{28}; 100 NHVI-R, 36.41% and C_9-C_{28}; 650 NMVI-S, 23.42% and C_8-C_{29}; BSHVI-S, 32.41% and C_8-C_{30}.

INTRODUCTION

Fatty acids are important raw material for the manufacture of soaps, surfactants, fatty nitrogen compounds and surface coating compositions. They also find applications in the rubber, textile, plastic, cosmetics and food industries [1]. In recent times the demand for fatty acids has been increasing every year. The total disposition of this commodity, covering the period 1960-74 grew from 140000 to 578500 tons. The expected demand for 1985 is 7585000 tons[2].

For the production of synthetic fatty acids a number of potential and commercial processes which are based on oxidation of, carbonylation of, or addition of acid (or acid yielding moiety) to hydrocarbons have been described[3]. Liquid phase oxidation of hydrocarbons with air is the most widely used process and thousands of tons of synthetic fatty acids are produced by Russia, China, West Germany, Italy and USA by this method. Recent data regarding the production and disposition of these acids has also been reviewed in the literature[4,5].

The need for the production of synthetic fatty acids in Pakistan has been stressed previously[6]. The import of fatty acids in Pakistan during 1982-83 exceeded 4 crores of rupees[7]. The present work was, therefore, undertaken to explore the process conditions for the production of synthetic fatty acids using locally available petroleum waxes and to examine the nature of fatty acids obtained from these feed stocks.

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EXPERIMENTAL

Materials. Silica gel from Davison Chemicals, grade 62 was activated for 30 minutes in a microwave oven. Manganese stearate was obtained from K and K Laboratories, Caleveland Ohio. All the solvents were of analytical grade.

Chinese wax, which was procured from the local market in Lahore, had been imported from People's Republic of China. Attock wax was a product of the Attock Oil Company, Ltd., Rawalpindi which is processing Pakistani crude oil. The other three varieties — 100 NHVI, 650 NMVI, and BSHVI — were the products of the National Refinery Ltd. Karachi, which processed light Arabian Crude oil from Kuwait. The composition of all these waxes has already been described[8]. The preparation of wax derivatives 100 NHVI-S, 100 NHVI-R, 100 NHVI-U, 100 NHVI-A, 650 NMVI-S and BSHVI-S is either being described in the following sections or has been communicated earlier[8].

Apparatus for Oxidation of Waxes. The reactor consisted of a glass tube (1 cm dia and 14 cm in height), fitted with a ground joint at the top and a fritted disc at the lower end, which was joined to another glass tube (0.2 cm dia and 31 cm in height) to form a U shape. A claisen head was attached to the top of the reactor and glass sheath for the introduction of a thermocouple was lowered into the reactor through this head. A Dean and Stark tube and a condenser were attached to the other end of the Claisen head. The reactor was heated by immersing in a silicone oil bath maintained at 105-110°. The air supply

coming from a compressed air cylinder and passing through a pressure gauge and flowmeter was connected to the end of the narrow tube.

Procedure:

Sweating of Waxes. Ten grams of the wax were placed in a sintered funnel (pore size ASTM-C) and weighed exactly. The funnel was fitted to a filtration flask. The assembly was placed in an oven maintained at 32° for 36 hours. The quantity of wax retained on the funnel was: 100 NHVI, 3.82 g, 38.20%, 650 NMVI, 4.72g, 47.20% and SHVI, 100g 100%. The samples were designated by the addition of suffix "R"

Sulphuric Acid Treatment of 100 NHVI. One hundred grams of wax were placed in a beaker, melted by warming on a temperature controlled hot plate and stirred with a magnetic stirrer. Sulphuric acid (sp.gr. 1.84, 10ml) was added to the molten wax and this mixture was stirred for 3 hours. A tarry black lower layer was formed. Water was added (cautiously) and the mixture stirred well. After cooling the aqueous layer was drained off. The molten wax was repeatedly washed with water until a neutral wash water was obtained. The wax was dried on a filter paper. The product wax was lighter in colour than the starting material. The yield was 94.00g 94.0%. The sample was designated by the additon of sufficix "A".

Oxidation of Waxes. Seven grams of the particular wax were charged to the reactor, and the reactor was immersed in the heating bath, which was maintained at 70°C. A gentle flow of air at 1-2 PSIG was maintained through the reactor to avoid back flow of the molten wax. Seventy-eight milligrams of the catalyst (prepared by mixing together equimolar quantities of freshly prepared potassium stearate and manganese stearate and removing the water by desiccation over anhydrous calcium chloride) were added to the molten wax. The supply of air was then increased to 8.5 ml/min. After half an hour mixing a sample was drawn for zero hour value and the temperature was raised to 150° and maintained at this temperature for 25-30 minutes. The heat bath was removed if necessary to control the exothermic reaction. For the remaining period of oxidation, the temperature of the wax was maintained at 105-110°. The samples were drawn through top of the reactor at various intervals of time i.e., 0, 4, 10, 18, 20, 24, 28, 36, 43 and 48 hours. The acid numbers were determined by dissolving ca. 200 mg of the oxidate in neutral warm alcohol (15 ml) and titratring against 0.1N potassium hydroxide. The volatiles were condensed by circulating water through the condenser and collected in the Deans and Stark tube from which they were drained out and weighed. The yields were calculated on the basis of wax set in for oxidation.

Isolation of Acidic Components and Their Esterification. The oxidate (1-2g, depending upon its acid number) was dissolved in toluene (15 ml) and 0.5N ethanolic potassium hydroxide (10 ml) was added to it. This mixture was refluxed for 3 hours while being stirred and then diluted with distilled water. The soap solution was extracted twice with hexane and once with ether. The combined organic phases were washed to neutral, dried over anhydrous sodium sulphate and evaporated to give neutral or unsaponifiable matter. The alkaline solution was acidified with 2N sulphuric acid and the liberated acidic components were extracted with ether. Further work up of this extract gave the acidic components. The acidic components were dissolved in ether and diazomethane solution was added to them portionwise until the yellow colour persisted. The mixtures were left over-night in a hood.

Liquid Chromatography of the Esterified Acidic Components. Four hundred milligrams of the material were charged to a column of silica gel (16 g) packed in petroleum ether. The elution was monitored by thin layer chromatography. The hydrocarbons (farction 1) were eluted with petroleum ether; fraction 2, having an Rf typical of methyl esters was eluted with petroelum ether-ether (95:5); fraction 3,consisting of two components was eluted with petroleum ether-ether (80-20); fraction 4, having an Rf typical of lactones, was eluted with petroleum ether-ether (50:50); and the most strongly adsorbed material, fraction 5, was eluted by choloroform followed by methanol.

Gas Liquid Chromatography of Methyl Esters. The esters were analysed on a Hewlett Packard Model 5700A Gas Chromatograph equipped with a flame ionization detector. A Soltec Rikadenki Recorder B-281 for registration of signals and Hewlett Packard Integrator Model 3373 B for integration of peak areas were coupled with the gas chromatograph. The instrument conditions were maintained as: Injection port 250°, detector 350° Atn, 10 x 16 chart speed 15 cm/hour and the integrator at maximum. Helium (30 ml/min) was used as the carrier gas whereas the hydrogen (30ml/min) and air (240 ml/min) were used for the flame. The following two columns were used for the separations. Diethylene glycol succinate (DEGS) (Applied Science Laboratories) coated as 5% by weight on Gas chrom Q (Chromosorb 80-100 mesh) was packed in a stainless steel column (183 cm x 0.32 cm o.d.). The oven temperature was programmed at 100-180° with an increase of 4°/min and a hold at 180° until no more peaks appeared. The 3% SP 2300 (coated on supelcoport AWDMCS) packed

in a stainless steel column (183 cm x 0.32 cm o.d.) was programmed at 100-200° with an increase of 4°/min. and held at the final temperature until no more peaks appeared. Identification of the components was achieved by comparison of retention times, from the equivalent chain length formula[9] and co- injection of the standard samples. The results reported in Table 3 are those obtained on SP 2300 column.

RESULTS AND DISCUSSION

The following section is divided into three sub-sections (A) Rate of oxidation of waxes, (B) evaluation of the oxidates obtained from the waxes and their derivatives and (C) the quality of the fatty acids produced in commercially feasible samples.

A. Rate of Oxidation of Waxes. The first step in this study was to determine the rate of formation of acidic components during the oxidation of these waxes. The graphs of the acid number vs. time of oxidation are shown in Fig. 1. All the waxes showed an acid number of about 1 at zero time, which meant that the reaction proceeded during the time of homogenising the catalyst.

Chinese wax and Attock wax got oxidised at reasonable rate. Oxidation curves for both these waxes are nearly overlapping. The slack waxes showed an unusual behaviour. The acid number reached a maximum and then dropped slightly with the passage of time. This slight gradual decrease in the acid number of these three reaction mixtures might be due to esterification of acids with alcohols or thermal decarboxylation of certin fatty acids produced under the experimental conditions.

The retardation of oxidation reaction mentioned in previous paragraph may be due to the presence of nitrogen or sulphur containing compounds or unsaturated compounds. If sulphur compounds are responsible, the reaction should have longer induction period, but should proceed smoothly after the sulphur containing compounds have been oxidized[10]. The presence of unsaturation (olefinic or aromatic), does not hinder the initiation of the reaction, but slows it gradually which may be due to the addition of hydroperoxide to the unsaturated compounds[11].

In order to confirm the above mentioned inference the saturates from slack waxes i.e., 100 NHVI-S, 650-NMVI-S, and BSHVI-S were oxidised. The rates of oxidation were much faster than parent waxes and were comparable to those of Chinese Wax or Attock wax (see Fig. 1). This observation confirmed that the unsaturated compounds present in these waxes were responsible for retarding oxidation.
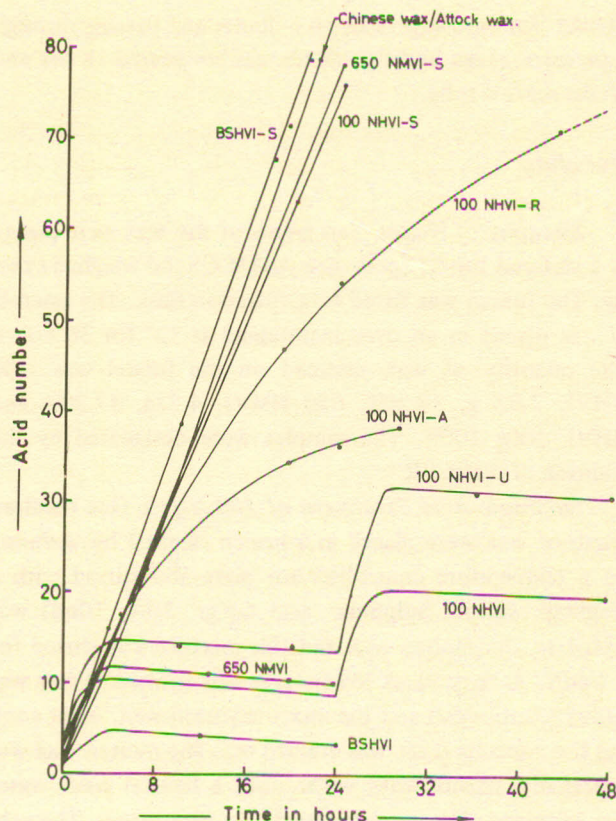

Fig. 1. Concentration of acidic components during oxidation of various wax varieties/derivatives.

On the basis of the chemicl composition [8], 100 NHVI seemed the most promising raw material among the slack waxes, and was, therefore, studied more thoroughly. It has been reported previously[6] that the oxidation reaction of this wax comes to a standstill after some time and it can be reinitiated by the addition of more catalyst. Similar results have been obtained in the present study (see Fig. 1). The acid number of the oxidate was not high enough to become commercially feasible. Moreover, the losses due to volatiles were noted to be high. This state of affairs emphasised the need for the refining of this wax variety.

The wax derivatives obtained by urea adduction or sulphuric acid treatment, or sweating were used as substrates. The development of acid number vs. time of oxidation for these wax derivatives is shown in Fig. 1. The rate of oxidation of the n-paraffin fraction obtained by urea adduction shows very slight improvement which is not of much practical use. The retardation of oxidation reaction in this case might have been caused by the unsaturated compounds which can also form adducts with urea[12].

The sulphuric acid treated sample 100 NHVI-A showed better response than 100 NHVI-U or parent wax. A part of the oxidation curve was comparable to the one for 100

NHVI-S. But its slope went on decreasing for the later period of oxidation. The extrapolated portion of this curve beyond 29 hours' time was practically flat. However, this state was reached after an acid number of 38.4 which is about 4 times the one for the parent wax. The higher yield of sulphuric acid treated sample (94.00%) than saturates (87.20%) indicates that some unsaturates which are present may cause retardation of oxidation reaction.

The wax derivative obtained from sweating experiments (100 NHVI-R) showed much better response to oxidation (Fig. 1). The oxidation rate declined in this sample as well but the acid number acquired in 43 hours was above 70 and the oxidate was fit for further work up on a larger scale. However, the yeidl of 100 NHVI-R was only 38.12% which is much lower than the saturates (87.20%) or the n-alkane content (48.14%). This low yield was due to the solubility of solid paraffins in liquid paraffinic (or other) hydrocarbons.

B. Evaluation of the Oxidates. The non-volatile oxidate in the reactor was of major interest. The acidic components were isolated by saponification. The results are given in Table 1. The yield of the acidic components was highest in Attock wax (42.45%) and lowest in BSHVI among the untreated waxes. The higher yield of acidic components in Attock wax than in Chinese wax (acid No. 78.7 and 78.4 respectively) indicated that comparatively higher molecular weight acids are present in Attock wax oxidate.

The acidic fractions were esterified with diazomethane as usual to give semi-solid products which on thin layer analysis revealed six class components with Rf values, .92, .84, .35, .29, .12 and an origin. The class components were resolved by liquid chromatography. Quantitative contribution of these class compounds is shown in Table 2. The possible chemical nature of each fraction is described separately.

Fraction 1 (Rf .92) was characterised (TLC and IR) as unreacted paraffin wax which remained emulsified in the alkaline layer during work up of the saponified mass. The content of this fraction ranged from 0.5 to 2.14%.

Fraction 2 (Rf .84) was found to be methyl esters of fatty acids (IR and TLC). This is the most desirable fraction and its content determines the quality of an oxidate. The methyl ester content was highest (48.50%) in Attock wax and lowest (23.42) in 650 NMVI-S. This content was comparatively higher in 100 NHVI-R than in 100 NHVI-S oxidate. These methyl esters were used for further evaluation of the quality of fatty acids produced in these oxidation experiments.

Fraction 3 was composed of two class components with Rf .35 and .29 and was designated as intermediates. The IR–spectrum of this fraction showed ester carbonyl 1735 cm^{-1} and ester C–O, 1160 cm^{-1}. The content of these intermediates was only 5.35% in the Cinese wax oxidate but was specially high in 100 NHV-S (27.60%) showing the latter as an inferior oxidate.

Fraction 4 (Rf .12) was designated as polars. The IR spectrum of these polars showed at least three functionalities, a hydroxyl, 3620 and 3510 cm^{-1}, lactone carbonyl,

Table 1. The acid number of oxidates and distribution of acidic and neutral compounds.

Substrate for oxidation	Time of oxidation in hours	Acid number of oxidates	Volatiles %	Saponifiable %	Unsaponifiable %	Loss %
Chinese wax	22	78.4	†	31.36	68.29	0.35
Attock wax	22	78.7	3.03	39.01	59.69	1.30
100 NHVI	48	19.8	†	15.4	81.80	2.80
100 NHVI-S	24	78.4	†	30.91	62.98	6.11
100 NHVI-R	43	71.3	†	38.88	56.45	4.65
100 NHVI-U	48	30.4	†	†	†	†
100 NHVI-A	29	38.4	1.15	†	†	†
650 NMVI	24	9.9	†	12.95	86.40	9.65
650 NMVI-S	24	76.0	1.78	49.12	50.42	0.46
BSHVI	24	2.9	†	7.29	90.83	1.88
BSHVI-S	21	79.9	2.0	43.97	54.23	1.80

† Not carried out.

1780 cm^{-1}; ester carbonyl 1735 cm^{-1} and ester C−O, 1170 cm^{-1}. The chemical constitutents of this fraction may be hydroxy esters, lactones, estolides, etc. These compounds may result from certain side reaction or over

Table 2. Distribution of class components (wt %) in acidic fractions of oxidates.

Source of oxidate	Hydrocarbons	Esters	Intermediates	Polars	Strongly adsorbed
Chinese wax	0.80	47.04	5.53	13.58	30.50
Attock wax	0.71	48.50	5.93	12.76	32.10
100 NHVI	1.50	30.06	8.85	13.38	46.21
100 NHVI-S	0.56	27.08	27.60	15.15	29.61
100 NHVI-R	2.14	36.41	8.36	16.22	36.65
650 NMVI	0.50	26.10	14.53	9.53	49.34
650 NMVI-S	1.00	23.42	17.10	18.25	42.10
BSHVI	2.14	19.06	19.89	11.95	46.96
BSHVI-S	0.61	32.02	13.02	13.73	39.82

Table 3. Distribution of individual normal fatty acids obtained from the oxidation of various substrates.

Acid chain length	Chinese wax	Attock wax	100 NMVI-S	100 NMVI-R	650 NMVI-S	BSHVI-S
C_8	†	0.79	0.19	1.26	1.51	0.69
C_9	†	1.81	1.46	3.10	3.08	2.05
C_{10}	1.31	2.93	4.34	4.94	4.49	3.71
C_{11}	4.0	3.90	6.95	6.15	5.38	4.88
C_{12}	6.51	4.52	8.56	6.81	5.96	5.54
C_{13}	8.00	5.32	8.17	7.26	5.09	5.08
C_{14}	8.76	5.03	8.47	7.11	5.25	5.27
C_{15}	8.48	5.11	7.71	7.10	4.52	4.82
C_{16}	8.48	5.58	9.23	8.69	6.20	6.32
C_{17}	7.93	4.96	6.47	6.61	4.00	4.51
C_{18}	7.56	4.60	7.50	8.16	5.72	6.01
C_{19}	6.81	4.87	4.77	5.96	3.50	4.21
C_{20}	6.59	4.87	4.07	5.60	3.44	4.79
C_{21}	5.99	5.07	2.48	5.23	4.24	4.90
C_{22}	5.28	4.94	1.91	3.43	3.99	4.87
C_{23}	4.61	4.98	1.30	2.72	4.43	4.94
C_{24}	3.19	5.06	0.93	2.13	4.37	2.98
C_{25}	1.72	5.03	0.49	1.42	3.59	2.67
C_{26}	1.12	3.04	0.34	0.96	1.09	2.38
C_{27}	0.66	2.41	0.15	0.55	0.79	1.91
C_{28}	0.33	1.82	0.06	0.27	0.48	1.49
C_{29}	0.07	1.20	†	†	0.31	1.07
C_{30}	†	0.67	†	†	†	0.63
C_{31}	†	0.18	†	†	†	†

† Not detected.

oxidation. They are usually found in paraffin wax oxidates but to varying concentrations. However, they can be converted to fatty acids by dehydration.

The last fraction 5 was strongly adsorbed on silica gel. The IR-spectrum of this fraction showed the keto carbonyl in addition to the functionalities described in the previous fraction. The presence of a keto group cannot cause so strong an adsorption on silica gel. However, the hydroxyl band was much stronger than the one in fraction 4 and this indicates the presence of polyhydroxy esters as possible class component in this fraction.

C. Quality of Fatty Acids. It is known from the literature[13] that the fatty acids obtained from an individual hydrocarbon are a mixture of various chain lengths, extending even to the parent hydrocarbon. However, the percentage of this particular acid is much smaller than the most predominant group of acids, indicating thereby the preferential attack on methylene rather than methyl groups. Accordingly, therefore, a broad range of fatty acids was expected from each wax variety. Because of this, therefore, the quality of fatty acids obtained from the oxidates was also examined. The oxidates with acid numbers of 70-80 only were compared due to their commercial feasibility. The methyl ester fractions were analysed by gas liquid chromatography on two different columns. Lower retention times were observed on SP 2300 column than on DEGS column. Qualitatively both the columns showed the same results. The total number of peaks observed were Chinese wax, 27; Attock wax, 42; 100 NHVI-S, 49; 100 NHVI-R, 42; 650 NMVI-S, 51; and BSHVI-S, 54. The retention times showed that the fatty acids ranged from C_8 to C_{31}. This indicates that some of the peaks, in all these chromatograms, do not correspond to the retention times of normal carboxylic acid esters. It is therefore, inferred that these esters are derived from non normal hydrocarbons present in wax samples.

For further examination of the quality of the fatty acids the percentage area under normal fatty acids was also compared. The quantitative results obtained on SP 2300 column are shown in Table 3. The normal fatty acid content was highest (97.47%) in methyl fraction from the Chinese wax. Furthermore the precentage of normal fatty acids produced from 100 NHVI-R is higher than that from 100 NHVI-S. This means that among all the purification procedures tried, the sweating of this wax was the most suitable process for the production of straight chain fatty acids whic are bio-degradable and hence create least pollution problems.

The fatty acids as stated earlier ranged from C_8 to C_{31}. The highest homologue produced in these experiments was about 8-10 carbon atoms smaller than the highest hydrocarbon in the parent wax. The distribution of the product acids is similar to the n-alkane distribution in the parent wax samples[8]. The acids produced from all these samples need fractionation to be fit for use in soap manufacture or lubircants or greases.

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