

## CATALYTIC OXIDATION OF PETROLEUM WAXY DISTILLATES

Hassan A. Farag\*, Nadia Ali Ghanem\*\* and Aida Mohamed El-Kayar\*\*\*

\*Chemical Engineering Department, Qatar University, Doha, Qatar.

\*\*APRCO, Alexandria, Egypt.

\*\*\*Chemical Engineering Dept., Alexandria University  
Alexandria, Egypt.

### ABSTRACT

The catalytic oxidation of petroleum waxy distillate (boiling range 400 - 440°C at 760 mm Hg) using  $\text{KMnO}_4$  catalyst and air was studied in a batch reactor. The effect of reaction temperature (100-160°C), air flow rate (0.5-1.5 L/min per 100 g wax) and catalyst weight (0.4-0.6 % by wt. of wax) on the acid number of the reaction mixture was studied. Monobasic acids with an average number of carbon atoms/molecule of  $\text{C}_{15}$ - $\text{C}_{16}$  could be obtained. The surface active properties of the soap solutions made from the obtained fatty acids (after separation from the reaction mixture, followed by purification) confirm that this soap can be successfully used as household soap. This will help to reduce the consumption of edible oils for soap making.

### INTRODUCTION

The catalytic oxidation of petroleum waxy distillate (boiling range 400-440°C at 760mm Hg) using  $\text{KMnO}_4$  catalyst and air was studied in a batch reactor. The effect of reaction temperature (100-160°C), air flow rate (0.5-1.5 L/min. per 100 g wax) and catalyst weight (0.4-0.6% by wt. of wax) on the acid number of the reaction mixture was studied. Monobasic acids with an average number of carbon atoms/ molecule of  $\text{C}_{15}$ - $\text{C}_{16}$  were obtained. The surface active properties of the soap solutions made of the obtained fatty acids (after separation from the reaction mixture, followed by purification) confirm that this soap can be successfully used as house-hold soap. This will help to reduce the consumption of edible oils for soap making.

In recent years there has been a considerable interest in synthetic fatty acids. Fatty acids have several uses in industry. They are used to manufacture many products including soap, detergents, chemicals, resins and plastics, rubber goods products, lubricating oils and greases, paints, and varnishes and cosmetics.

Most fatty acids produced in the world are made by hydrolysis of natural fats and oils. The total net production cost of one pound of fatty acids from the oxidation of paraffin is far much less than that from natural fats and oils (2).

The aim of this paper is to study the catalytic liquid phase oxidation of non-aromatic hydrocarbons using air to produce monobasic fatty acids. Also the technical properties of soaps made from these fatty acids related to their deterative characteristics are evaluated.

## BACKGROUND

Commercial use of the oxidation of wax to fatty acids began more than a century ago (2). The complete oxidation of waxes leads to formation of carbon dioxide ( $\text{CO}_2$ ) and water ( $\text{H}_2\text{O}$ ). Under mild oxidizing conditions peroxides, alcohols, ketones, and organic acids may form the major portion of the reaction products, leading to a complex reaction mixture of oxygen containing products.

The important factors determining the rate and direction of liquid phase oxidation of paraffins with air to fatty acids are temperature, air flow rate, catalyst and composition of the paraffin mixture being oxidized. In general, higher temperatures increase the paraffin conversion but also enhance the oxidation of higher oxygenated products to lower acids. (2,4) The optimum temperature for the oxidation of paraffins with air to give a suitable yield of fatty acids lies in the range 115-125°C (5,6).

Early attempts to oxidize paraffins in the liquid phase with air in the absence of catalysts succeeded only at relatively high temperatures and after a long induction period giving colored products. Catalysts increase the oxidation rate by reducing the time required to initiate the reaction; the reaction is self-catalyzing once it is initiated (2). The use of catalysts brought good yields of fatty acids (7, 8). A number of metal oxides were found to accelerate this reaction (9). The most popular catalysts are the manganese salts, e.g.  $\text{KMnO}_4$ , the consumption of which does not exceed 0.3% based on the weight of the wax (10, 11, 12, 13). The presence of  $\text{KMnO}_4$  not only accelerates the oxidation reaction, but also results in the destruction of inhibitors interfering with autoxidation (2).

The production of synthetic fatty acids by oxidation of paraffin wax is organized on industrial scale to give in the first place fatty acids containing 10 - 20 carbon atoms in its molecule and having wide technical applications. Composition of the mixture of hydrocarbons used for oxidation, in the form of various types of technical paraffin wax, is very diverse with respect to molecular

weight and lies in the range of  $C_{16} - C_{36}$  (4).

Air is used exclusively to oxidize paraffins to monobasic acids in commercial operations. The rate of oxidation of paraffins with air is affected by flow rate of air through the paraffins. Best results were obtained when the rate of air flow was such that foam is produced. Oxidation in the foam phase will give higher reaction rates, particularly at high temperatures, where the diffusion of oxygen into the paraffin may be the controlling step in the reaction (2).

## EXPERIMENTAL

### Raw Material

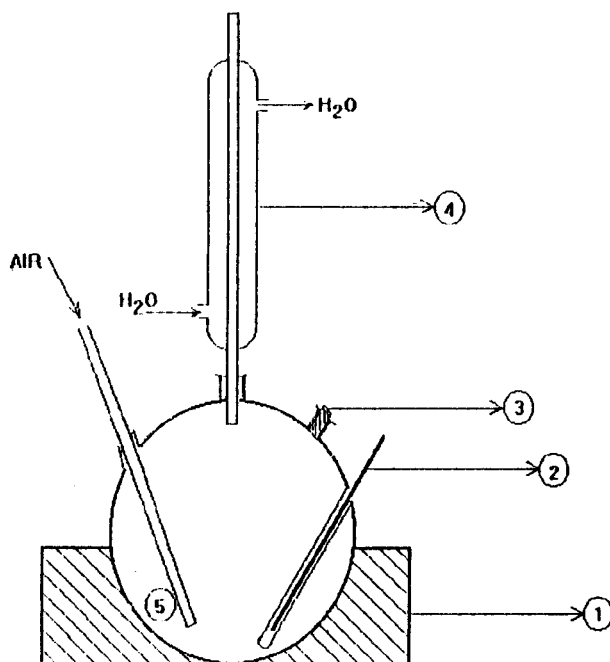
The feed to the oxidation process was paraffin wax separated from the waxy distillate (boiling range 400 - 440°C at 760mm hg) obtained by vacuum distillation from El-Alamein Egyptian crude. The paraffin was separated from the waxy distillate by solvent dewaxing using MEK: Benzol: Toluene mixture of the ratio 40: 30: 30 (by volume). The paraffin wax was then deoiled by melting through a column packed with activated aluminium silicate (14). Wax aromatic content was determined by the n-d-M method (15). Table 1 shows the characteristics of the raw material obtained after the dewaxing and deoiling steps.

**Table 1: Characteristics of Paraffin Wax Separated from the Waxy Distillate**

Characteristic	Value
Boiling Range at 3 mm Hg Initial, °C Final, °C	217 250
Oil content, Wt. %	1
Average Molecular weight	400
Acid Number, mg KOH/g	0.001
Saponification Number, mg KOH/g	0.04
Bromine Number, g Br <sub>2</sub> /100g	0.083
Melting Range, °C	55 - 59
Total sulfur, wt. %	Nil
Refractive Index at 70°C	1.4411
Density at 70°C, g/ml	0.7950

## Wax Oxidation

Figure 1 shows the experimental apparatus used for the oxidation step. One hundred grams of the wax were put in the round bottom flask with the required amount of the catalyst. The mixture was heated to the required temperature, then air was bubbled into the wax - catalyst mixture. The acid number of the mixture was monitored by withdrawing a sample every 3 hours. The maximum acid number reached was 60; after which heating and air bubbling were stopped.



1. Electrical Heater, 2. Thermometer, 3. Charging and sampling,  
4. Condenser, 5. Sintered Glass

**Fig. 1: Apparatus for oxidation of paraffin wax with air**

## Extraction of the Fatty Acids

Two hundred and fifty ml. of hot distilled water were added to the resulting oxidation mixture to extract water - soluble acids. The lower (water) layer was then separated by a separating funnel. Two hundred ml. of 8N NaOH solution were added to the residual upper (organic) layer, which contained the high molecular weight fatty acids and unoxidised organic matter. The resulting mixture was then refluxed with stirring in a round - bottom flask for 8 hours. After

cooling the mixture, it was treated with 400ml. of petroleum ether (40 - 60°C) added in 20 ml portions till a clear aqueous solution was obtained. This aqueous solution was separated by a separating funnel, cooled to room temperature, and then acidified with 600 ml conc. HCl. The liberated fatty acids were extracted with 400 ml of petroleum ether (40-60°C). The petroleum ether was then distilled off on a water bath to obtain the free fatty acids.

### **Fractionation of the Free Fatty Acids Produced**

The ethyl esters of the free fatty acids were prepared by refluxing 60 g of the free fatty acids with 124 g of absolute ethyl alcohol for 24 hours. The mixture was left to cool, then washed with 20 ml of saturated NaCl solution and dried over anhydrous sodium sulfate. The mixture was fractionated under vacuum (5mm Hg residual pressure) and two fractions were collected: 177 - 182°C (I) and 182 - 187°C (II).

Forty gram of the ethyl ester were refluxed with 80 ml of 8N NaOH solution for 2 hours until the odour of the ester could no longer be detected. One hundred ml of the refluxed mixture were distilled and collected. The alcohol layer was separated by a separating funnel and the residual organic layer was acidified with 120 ml of conc. HCl and the liberated free fatty acids were extracted with petroleum ether (40 - 60°C).

### **Preparation of Soap from the Produced Fatty Acids**

Five g of the fatty acids were refluxed with 3 g of NaOH (98%) for 30 minutes until no oil globules were present. After cooling, 5 ml of saturated NaCl solution were added to salt out the sodium salt of the fatty acids. The sodium salt was then filtered and then left to dry in air.

Soap solutions of conc. : 0.01, 0.02, 0.03 and 0.04 g-mole/L water were prepared. These solution were used to determine the surface active properties of the soap as surface tension, interfacial tension, wetting power, foaming and detergency power.

### **Determination of Surface Active Properties of the Prepared Soap Solution**

#### **Surface and interfacial tension:**

The DU - NOUY tensiometer, based on the ring method was used. The method consists of measuring the force required to pull a platinum ring of known

diameter away from the surface of the liquid.

**Wetting power (Drave's method):**

A five g skein of gray cotton yarn is submerged in the test solution and the time for the air in the yarn to be replaced by penetration of the solution is recorded. The end point is observed as that moment when the skein sinks.

**Foaming:**

The static test developed by Ross and Mills was used. The apparatus used is a jacketed cylinder in which a portion of the test solution is placed. The foam is generated by pouring the second portion of the solution from a specified height through a standard orifice into cylinder. The foam height against time is recorded.

**Detergency:**

The launder-Ometer and reflectometer (16) were used.

## RESULTS AND DISCUSSIONS

Figure 2 shows the effect of reaction temperature on the rate of wax oxidation as presented by the change in the acid number with time. As expected, the

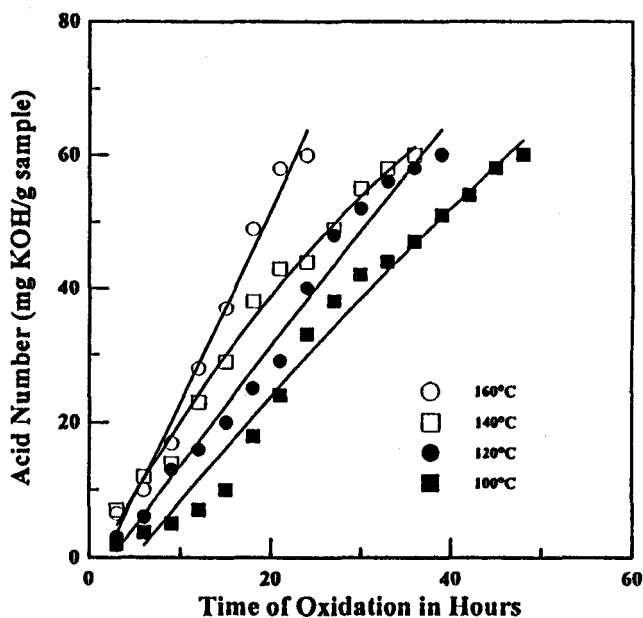


Fig. 2: Effect of reaction temperature on the rate of oxidation

oxidation rate increases with temperature, specially at 140° and 160°C. This result conforms with the published data of many researchers (2,4).

Figure 3 shows the effect air flow rate (expressed in L/min per 100 g wax) on the rate of oxidation of the waxy distillate as manifested by the change of the acid number with time. As expected increasing the air flow rate increases the rate of oxidation.

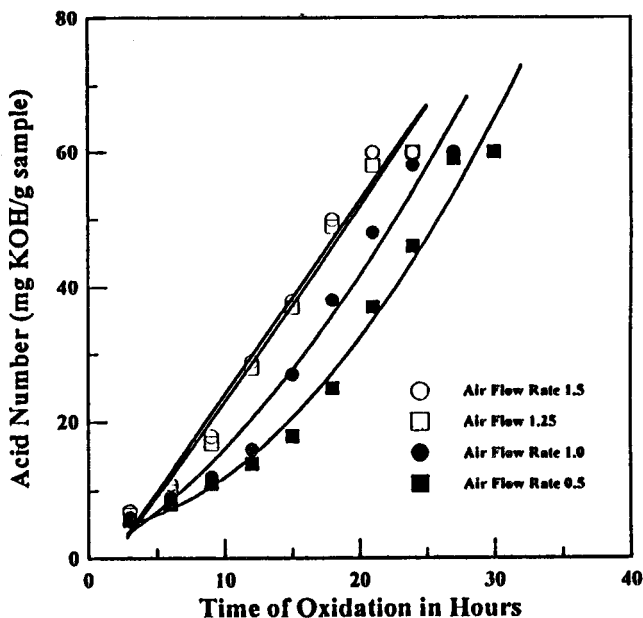


Fig. 3: Effect of air flow rate on the rate of oxidation

Low air flow rates (0.5 l/min per 100 g wax) gave low oxidation rates due to poor mixing of the reaction mixture. On the other hand increasing air flow rate up to 1.25 l/min 100 g wax led to foam formation. Oxidation in the foam phase increases the turbulence in the reaction mixture and contact area between the oxygen gas and the waxy distillate. Consequently, the controlling step in the oxidation reaction, the diffusion of oxygen gas into the reaction mass is thus enhanced (2) and therefore the oxidation rate increases. Moreover increasing air flow rate prevents accumulation of neutral oxygen - containing compounds at the surface film and the waxy distillate (2,4). Air flow rates higher than 1.5/ L/min per 100 g wax could not be used as at this value splashing of reaction mixture took place.

Figure 4 shows the effect of catalyst mass (as % of weight of wax) on the rate of wax oxidation. It is clear from this figure that increasing catalyst mass beyond 0.5% (of wax mass) leads to a marked increase in the rate of wax oxidation. This increase is more manifested at longer reaction times (18 and 24 hours). The increase of catalyst amount might promote reaction initiation and reduce the induction period prior to start of reaction (4).

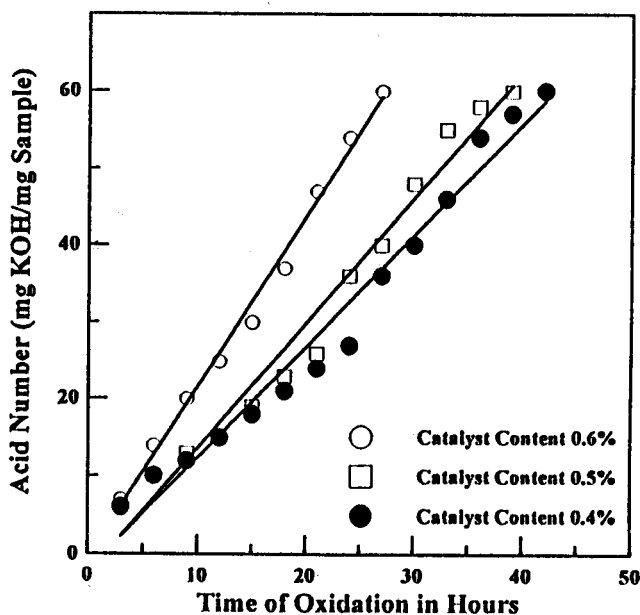


Fig. 4: Effect of catalyst content on the rate of oxidation

Figure 5 shows the effect of soap concentration in its solution in water on the surface tension of these solutions. It is clear from this figure that the first amount of soap added (0.1 g-mole/L) led to a sharp decrease in the surface tension (almost 50% of the value of pure water). Further additions of the soap had a less marked effect on the solution surface tension. This result points out the economic advantage of this soap as the low concentration gave enough reduction in the surface tension, which is an essential feature for any soap to act successfully.

Figure 6 shows the effect of soap concentration in its solutions in water on the interfacial tension. There is a linear decrease in interfacial tension with the increase of soap concentration. A four fold increase in soap concentration lead to a 40% decrease in the interfacial tension. According to Perry (17) aqueous



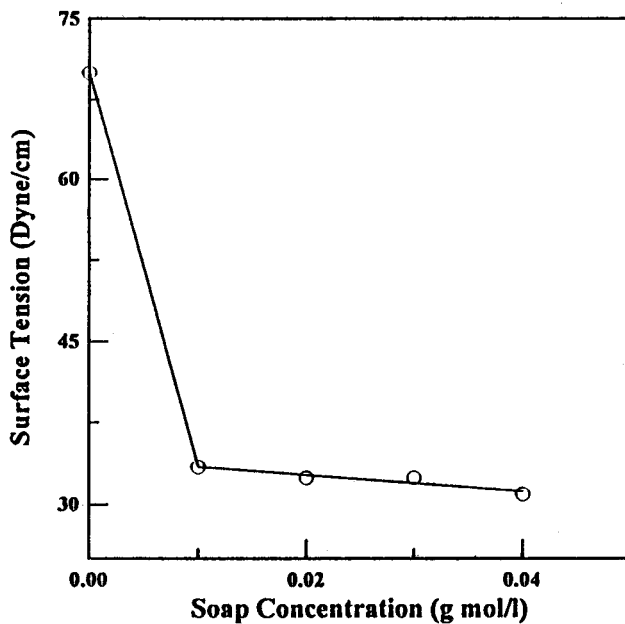


Fig. 5: Effect of soap concentration on the surface tension

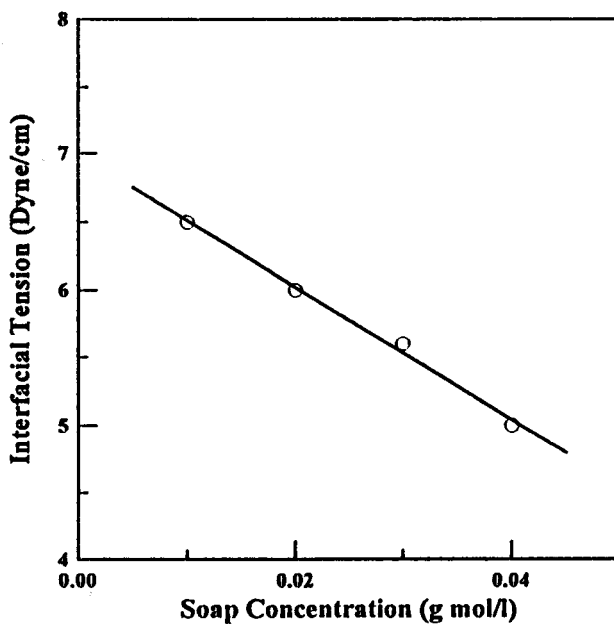


Fig. 6: Effect of soap concentration on the interfacial tension

solutions of surface active agents generally give surface tension in the range 29-54 dyne/cm and interfacial tension below 10 dyne/cm. Consequently the produced soap gave quite promising results in this respect.

Figure 7 shows the effect of soap concentration in its solution in water on the wetting time (in seconds). There is a sharp decrease in this time (almost by 30% of its original value) on increasing the soap concentration beyond 0.03 g mole/L. Decreasing the wetting time means a better surface active agent (16), since it means better penetration of the soap solution through the mass of cotton fibers or other porous structures, in which capillarity comes strongly in to play. The driving force which helps a liquid to penetrate a capillary space in a solid material

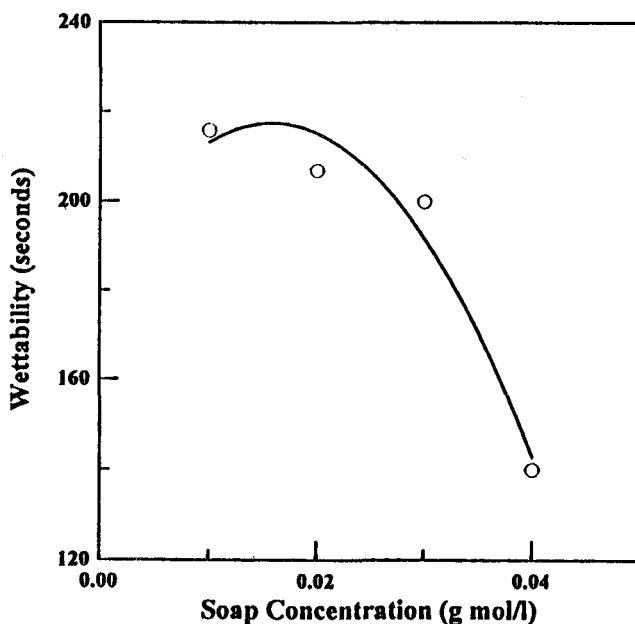


Fig. 7: Effect of soap concentration on the wetting time

increases by the decrease of the contact angle of the liquid against the solid. Powney (16) has pointed out that the entry of a liquid into very small interstices will be followed by a local impoverishment of its content of surface active molecules due to the adsorption of a relatively great amount of the latter on the solid surfaces. In the later stages of penetration, therefore, the rate at which diffusion can take place to replenish this impoverishment is important.

Figure 8 shows that a stable foam is obtained at any soap concentration in water (in the range 0.01-0.04M). A low surface tension leads to foam stability. Adam (16), discussing the stability of foams, has emphasized the necessity of a stable film being able to vary easily and quickly in surface tension, both in order to meet permanent differences of stress in its different parts and to absorb local mechanical shocks. In this connection it is significant that most solutions of foam-inducing substances (particularly those of low or medium molecular weight) should exhibit their maximum foam producing capacities, not at concentrations, at which surface tension minimum, but at rather lower concentrations, where variation in concentration has a marked effect on surface tension.

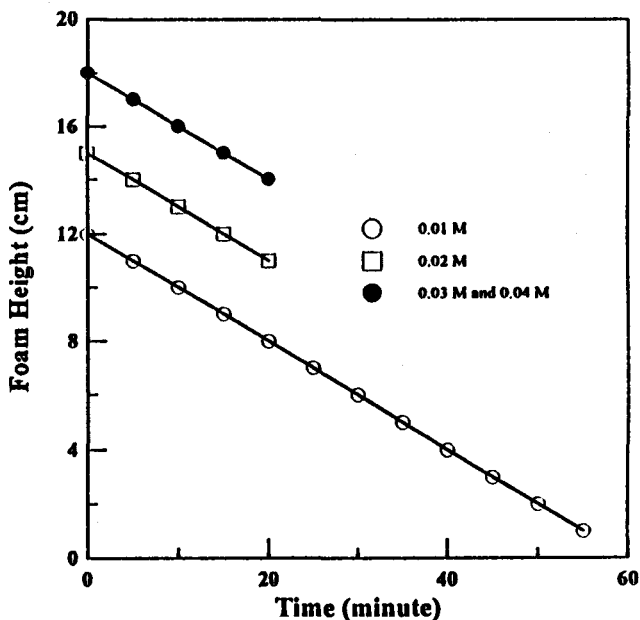


Fig. 8: Foam stability for soap solutions

Figure 9 and 10 show the results of cleaning tests of prepared soap solutions (0.01-0.04M) at 35° and 50°C. Both first and second washings gave good results. Preston (16) has pointed out that, in the washing of fabrics, the detergency of a given sodium soap rises to a maximum at a relatively low concentration of the soap; after which the detergency is slightly increased or not at all by further addition of soap into the solution.

Bailey (16) has stated that the range of a good cleaning agent as sodium myristate at 71°C is between 4 and 40 at different concentrations. Hence the fatty acids produced soap can be considered a good cleaning agent at 35° and 50°C.

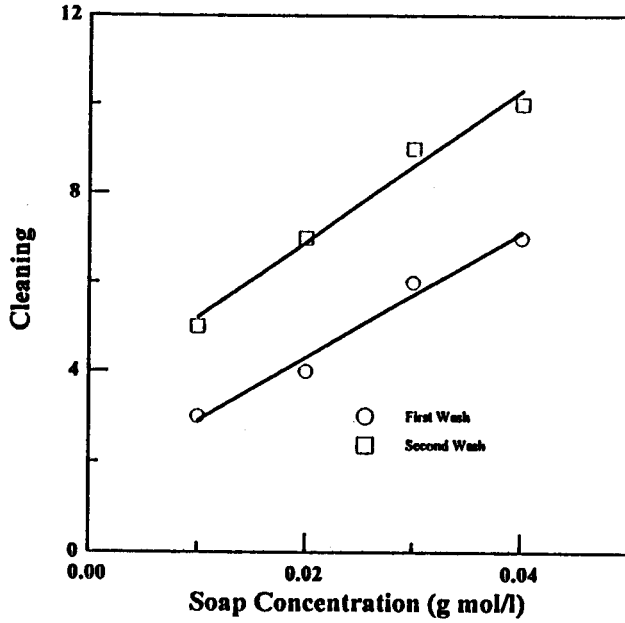


Fig. 9: Cleaning results at 35°C

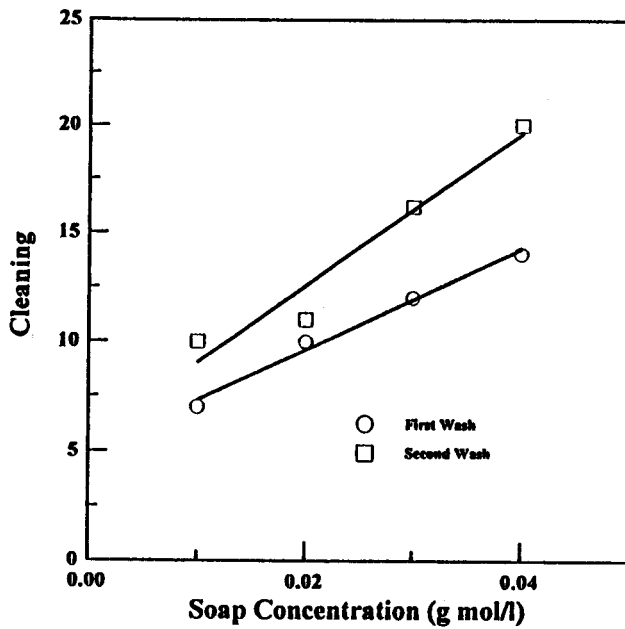


Fig. 10: Cleaning results at 50°C

## CONCLUSIONS

1. The catalytic oxidation of paraffins separated from a waxy distillate (boiling range 400-440°C at 760 mm Hg) by solvent dewaxing, using air and  $\text{KMnO}_4$  was studied.
2. The rate of oxidation of the paraffins increases with the increase in reaction temperature (100-160°C), air flow rate (0.5 -1.5 L/min per 100 g wax) and amount of catalyst (0.4 - 0.6% of mass of paraffins).
3. A concentration of only 0.01 g mole/L of soap in water reduced drastically the surface tension (by more that 50%).
4. Interfacial tension of soap solutions decreased gradually with the increase in soap concentration.
5. Wettability and foam height increased with the increase of soap concentration.
6. Detersive power increased with soap concentration and temperature (wash experiments).
7. Good quality soap could be prepared from the separated free fatty acids.

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