ACID TREATMENT OF IRAQI PARAFFIN WAX

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ABSTRACT

Iraqi paraffin wax, with 4.4 wt% oil content, was treated with sulfuric acid for reduction of aromatics content to value that suitable for food and medicinal uses. Acid treatment was done using sulfuric acid with 90 –110 wt% concentrations, acid to wax ratio from 0 up to 10%, temperature range 75 to 95o C and 0 to 2 hours treatment time.

A relation between wax loss due to acid treatment and operating conditions was obtained by using 2nd order polynomial equation to fit data of Box-Wilson experimental design.

The acid treatment results indicate that the wax loss did not affect by treatment temperature. Minimum acid concentration that constraining wax to react is about 100 wt%, long treatment time (>1.5 hours) and acid to wax ratio greater than 5 wt% cause a "burned" product with dark color. This dark color product did not show any improvement in color when it was bleached with 20% clay to wax ratio at 90o C and for 1.5 hours.

INTRODUCTION

The purity of waxes is an important aspect in their grading. The required extent of purity, obviously, depends on the type of the field of application.[1]

Waxes applied in food conservation and packing must be an odorless and free from compound damaging the human organism, above all polycyclic aromatics substances. Similar, but even stricter specifications are applied for paraffin products to be used for medical purposes. Purity criteria, including whiteness and color stability, calls for refinement of paraffin products.[1]

De-oiling in addition to improving the mechanical properties of paraffin waxes, is also a refining process [2], since to meet the above-mentioned purity requirements, a correspondingly low oil content is essentially. The wax properties like white colors, oxidation stability, are became satisfied when its aromatic contents are low or nil. The complete purification of macro- and microcrystalline waxes and paraffin liquid at ambient temperature is hence equivalent to the removal of impurities. Usually present in small concentrations, like unsaturated compounds, mono-, bi-, and polycyclic aromatics, hydrocarbon derivatives containing sulfur, nitrogen and oxygen atoms, hetero-cyclic compounds, while n-alkane, branched alkane and naphthene compounds should as far as possible remain intact.[1]

At present, both traditional and modern processes are being applied on a worldwide basis. These can be classified essentially into three groups purification process based on: treatment with chemicals, adsorption and hydrogenation.[1,3] Among the chemical refining agents, sulfuric acid has long hat the most general application. It was first employed of refining animal and vegetable oils, and since the beginning of the petroleum industry (about 150 years ago), sulfuric acid has been successfully applied to the purification of practically all petroleum products.[3]

The sequences in the application of reagents to an oil is important and usually follows a fixed routine; after treatment with acid an oil is neutralized with alkalis or adsorbents. Adsorbents are usually applied as the final operation rather than as the first operation. They should be used to remove only the impurities that the cheaper acid can not remove.[3]

In purification with sulfuric acid, only those alkanes that contain tertiary carbon atoms will react and naphthenes also are reluctant to react with sulfuric acid. On the other hand, aromatics will be sulfonated, unsaturated hydrocarbons yield polymerized products and neutral esters and resinous components are converted via polymerization and oxidation reactions into asphaltenes. Microcrystalline wax, owing to their composition, react much more readily than paraffin wax.[1]

Oleum is also suitable for purifying paraffin waxes; however, operating temperature must be very carefully chosen.[1]

In sulfuric acid purification of macrocrystalline paraffin waxes it is usually satisfactory to treat the initial product with 5wt% sulfuric acid in one stage, and subsequently with 5wt% bleaching earth. For microcrystalline waxes, multistage acid and clarification operations are frequently needed. The yield in the purification of paraffin waxes is around 90 to 95wt% while the value of microcrystalline waxes may be as low as 50wt%.[1]

Hobson [2] pointed that the sulfuric acid treatment is impossible for microcrystalline waxes because the acid tar formed can not be separated from microcrystalline wax.

Experimental work by Ismaylov et.al.[4] is the nearest study to wax purification. They studied sulfuric acid purification of liquid paraffin oil with a boiling range of 270-370°C obtained from diesel fuel. The aromatic content, initially 0.4wt%, could reduced, by treatment of two acid concentrations, 98.6 and 102wt% at acid to oil ratio 3-4% and treatment temperature of 45-60 °C for one hour (60 min) reaction time, to particularly zero.

EXPERMANTAL WORK

Purification process by acid treatment was used to remove aromatic hydrocarbons from paraffin wax that cause a refused property, especially for medicinal and food grade, when its concentration greater than 0.1 wt%.[5,6]

Raw materials

Paraffin wax

Paraffin wax was purchased from Daura refinery. The chemical and physical properties are shown in table 1.

Table 1. Chemical and physical properties of paraffin wax.

Property		Property	
Melting point,°C	66	Color, ASTM D1500	0.5-
Congealing point,°C	63	Ash, wt%	0.17
Oil content, wt%	4.4	Aromatics, wt% (UV)	0.99
Penetration, mm	21	Aromatics, wt% (LSC)	0.96

2.1.2 Fuming Sulfuric acid (Oleum)

Oleum was obtained from the Sigma Company. The chemical and physical properties of Oleum are shown in table 2.

Table 2. Chemical and physical properties of Oleum.

Free SO_3, %	80
Concentration as H_2SO_4 ,wt%	110
Chemical formula	H2SO4.(4.9) SO3
Specific gravity (16°C / 4°C)	1.984-5

Wax purification process

Purification process is used to remove aromatic hydrocarbons, which are defined as cancer producing materials.

Purification process was done in laboratory unit. This unit consists 500 ml 2 neck Pyrex flask. A mixer with stainless steel cross shape impeller was used for agitation. Mercury thermometer with a suitable range of temperature (0-260o C) was used to measure the temperature inside the flask.

Heat was supplied to this apparatus by heating mantel, which was connected to a voltage regulator in order to adjust the heating temperature.

The ranges of operating conditions, for wax purification process, are shown in table 3.

Table 3. Operating conditions of wax purification process.

Temperature, o C	75-95
Time, h	0 - 2
Acid to wax ratio, wt %	0 – 10
Acid concentration, wt%	90 – 110
Mixing speed, rpm	1000

The treated wax was washed with water two times, then the washed wax was separated.

RESULTS AND DISCUSSION

Purification of paraffin wax was done by sulfuric acid treatment. Acid treatment was chosen as purification process for following reasons:

The product of this process can be reached to very low aromatic concentration, which is suitable for food and medicinal uses.

Relatively high oil content of raw paraffin wax (4.4 wt%). All purification processes except acid treatment process required de-oiled waxes as raw materials.(7,8)

Loss of paraffin wax due to treatment with sulfuric acid was predicted by Box-Wilson experimental design.(9)

A second order polynomial mathematical equation employed in the range of the independent variables (Temperature (x1), acid to wax ratio (x2), treatment time (x3) and acid concentration (x4)). The general form of second order polynomial for four variables is represented by the following equation.

$$Y=\begin{Bmatrix} a0+a1x1+a2x2+a3x3+a4x4+ \\ a5x12+a6x22+a7x32+a8x42+ \\ a9x1x2+a10x1x3+a11x1x4\,a12x \\ 2x3+a13x2x4+a14x3x4 \end{Bmatrix} \quad (1)$$

Table 4 shows the experiments, which are conducted, according to Box-Wilson method and the experimental response represented by loss weight percent of paraffin wax. For postulating the best form of the above equation, the coded data of table 4 is first fitted to equation 1 so that the analysis of variance of central composite design could be applied. By this analysis each effect of the fitted polynomial equation could be tested for its significance.

The analysis of variance (F-test) is used for testing the significance of each effect in equation (1). Using the coded data of central composite design given in table 4, the coefficients in equation 1 can be calculated simply by using least squares method.

After the coefficient values of equation 1 calculation, it is possible to compute estimated values of the paraffin wax weight loss percent (Yi) and the corresponding residual e.i =Y-Y.i. An estimate of the experimental error variance Sr2 is obtained by dividing the residual sum of squares $\sum e.i2$ by γ (number of degree of freedom).

Where:
γ =number of experiments -number of coefficients in the equation 1

So: $\gamma = 28 - 15 = 13$ (2)

And $Sr2 = \sum e.i2 / \gamma$ (3)

The estimated variance of coefficients Sa2 are then calculated by equation 4:

$$Sa2 = Sr2 \ / \sum \ x2 \quad (4)$$

The effect of treatment temperature on paraffin wax loss

Results in table 6 shows that there is no effect of temperature on paraffin wax loss in the range 75 to 95 °C. This observation is a good agreement with the results of Morrell and Egloff for acid treatment of cracked gasoline [3,10].

Experiment of paraffin wax treating at temperature higher than 105 °C, with sulfuric acid of 100 wt% concentration and acid to wax ratio of about 3wt %, gives discolored dark product and this dark color can not be improved by bleaching clay (earth). This dark color is a result of naphthene reaction with acid at high temperature [11] and reaction of olefins to form tar that is partly cause of the discolorization [3].

For treatment temperature about 110 to 115o C, the product formed a stable emulsion when it was washed with water. This phenomenon may be due to sulfonic acid ($R\text{-}O\text{-}SO_2\text{-}OH$) formation by direct sulfonation and sulfo-oxidation reaction of higher alkanes [1].

Effect of acid concentration and acid to wax ratio on paraffin wax loss

Purification process of paraffin wax was done using sulfuric acid of concentration 90 to 110 wt% and acid to wax ratio from 0 to 10wt %. The paraffin wax loss is increasing rapidly with acid concentration and acid to wax ratio as shown in figures 1 to 4. Morrell and Egloff[10]. Observe this behavior for acid treatment of cracked gasoline.

As acid concentration increases, the ability of acid to react with different type of hydrocarbons increasing[3]. Saturated and unsaturated high molecular weight hydrocarbons reacted with acid. Part of the hydrocarbons- acid products is dissolved by un-reacted acid as an acid sludge [12]. When acid to wax ratio increase the amount of reacted saturated and unsaturated high molecular weight hydrocarbons is increased and the products dissolved in the remaining un-reacted acid causes increasing of loss as acid sludge.

High acid to wax ratio ($\geq$ 5wt %) cause a "burn" discolorized product as results of dissolving reacted naphthenic hydrocarbons and polymerization reaction of olefins (tar-forming) in the acid sludge. No color improvement observed when this dark product was bleached with clay. Thus treatment of paraffin wax should be done at acid to wax ratio less than 5 wt% to obtain a light color purified wax and it can be easily to color improve by bleaching. Hobson [2] referred to use "trace" amount of acid in wax purification process.

It can easily noticed from figures 1 to 4 that the minimum acid concentration required for wax to react is about 97.5 wt% for acid to wax ratio 2.5 wt% and decrease to about 95 wt% for acid to wax ratio 10 wt%.

For lubricant stocks, acid of 93 wt% concentration, or even weaker, is sufficient for purification [3].

Thus, the minimum acid concentration required increases with molecular weight and complexity of chemical structures.

The effect of time on paraffin wax loss

The time of contact of acid and wax is greatly important. It can be notice that the paraffin wax loss affected linearly by time of treatment as shown in figures 5 to 9.

For acid concentration less than 100 wt%, no significant loss for time less than 1 hour and acid to wax ratio less than 5 wt% is observed. For time more than 1.5 hour and acid concentration higher than 105 wt%, the possibility of production "burned" product is increasing with acid to wax ratio. This is due to long contact time that causes formation of tar-forming substance and sulfonic acid and then produces dark color product.

Acid treatment of microcrystalline wax, gives stable dark emulsion, when washed with water. This observation is agreement with Hobson [2].

CONCLUSIONS

Conclusions that would be drawn out from the present study are:

1. Acid treatment for paraffin wax can be done at 75 to 95 °C, using sulfuric acid concentration 90-110 wt%, acid to wax ratio between 1 to 5 % and treatment time up to 2 h.
2. Loss of paraffin wax due to purifying step is unaffected by temperature in the range 75 to 95 °C.

3-Temperature greater than 100o C, acid to wax ratio higher than 5 % and/or long time (about 2 h) gives a stable dark color wax with high wax loss.

Table 4. Coded, real value and the response of the experiments to be conducted according to Box-Wilson.

Run No.	Coded variables				Real variables				Wax loss wt%
	X1	X2	X3	X4	X1 (Temperature, °C)	X2 (Acid to wax ratio, %)	X3 (Treatment time, h)	X4 (Acid concentration, wt%)	
1	1	1	1	1	90	7.5	1.5	105	12.06
2	-1	1	1	1	80	7.5	1.5	105	4.67
3	1	-1	1	1	90	2.5	1.5	105	1.63
4	1	1	-1	1	90	7.5	0.5	105	3.93
5	1	1	1	-1	90	7.5	1.5	95	0.50
6	-1	-1	1	1	80	2.5	1.5	105	0.81
7	-1	1	-1	1	80	7.5	0.5	105	2.47
8	-1	1	1	-1	80	7.5	1.5	95	0.23
9	1	-1	-1	1	90	2.5	0.5	105	0.69
10	1	-1	1	-1	90	2.5	1.5	95	0.14
11	1	1	-1	-1	90	7.5	0.5	95	0.19
12	-1	-1	-1	1	80	2.5	0.5	105	0.39
13	-1	-1	1	-1	80	2.5	1.5	95	0.08
14	-1	1	-1	-1	80	7.5	0.5	95	0.10
15	1	-1	-1	-1	90	2.5	0.5	95	0.06
16	-1	-1	-1	-1	80	2.5	0.5	95	0.03
17	2	0	0	0	95	5	1	100	0.921
18	0	2	0	0	85	10	1	100	2.54
19	0	0	2	0	85	5	2	100	2.20
20	0	0	0	2	85	5	1	110	11.20
21	-2	0	0	0	75	5	1	100	0.55
22	0	-2	0	0	85	0	1	100	0
23	0	0	-2	0	85	5	0	100	0
24	0	0	0	-2	85	5	1	90	0.1
25	0	0	0	0	85	5	1	100	0.52
26	0	0	0	0	85	5	1	100	0.51
27	0	0	0	0	85	5	1	100	0.60
28	0	0	0	0	85	5	1	100	0.54

Table 5. Values, variance and significantly for coefficients in equation 1

Coefficient no.	Effect of	Value(a)	S_a^2	a^2/S_a^2	Significantly*
0	-	0.544	-	-	-
1	x_1	0.400	0.202	3.92	Non significant
2	x_2	0.951	0.202	22.16	Significant
3	x_3	0.621	0.202	9.45	Significant
4	x_4	1.956	0.202	93.76	Significant
5	x_1^2	0.003	0.202	0.0002	Non significant
6	x_2^2	0.145	0.202	0.515	Non significant
7	x_3^2	0.089	0.202	0.194	Non significant
8	x_4^2	1.226	0.202	36.84	Significant
9	x_1x_2	0.399	0.248	2.59	Non significant
10	x_1x_3	0.375	0.248	2.29	Non significant
11	x_1x_4	0.060	0.248	0.06	Non significant
12	x_2x_3	0.431	0.248	3.02	Non significant
13	x_2x_4	1.069	0.248	18.85	Significant
14	x_3x_4	0.647	0.248	6.81	Significant

Correlation coefficient R= 0.970
Variance =0.941
$^*F_{1,13}$= 4.67

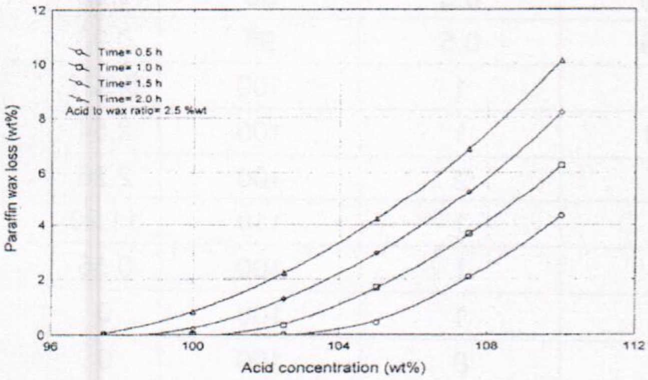

Fig. 1. Effect of acid concentration on paraffin wax loss at different treatment time.

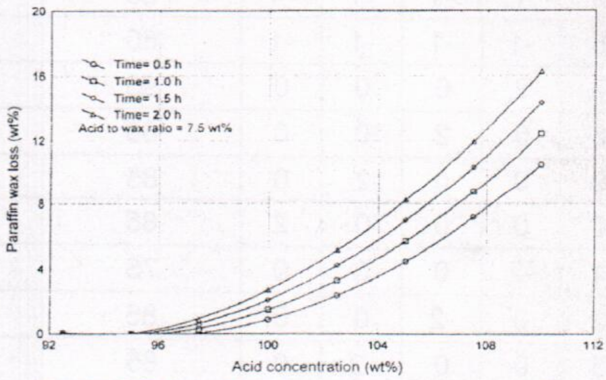

Fig. 3. Effect of acid concentration on paraffin wax loss at different treatment time.

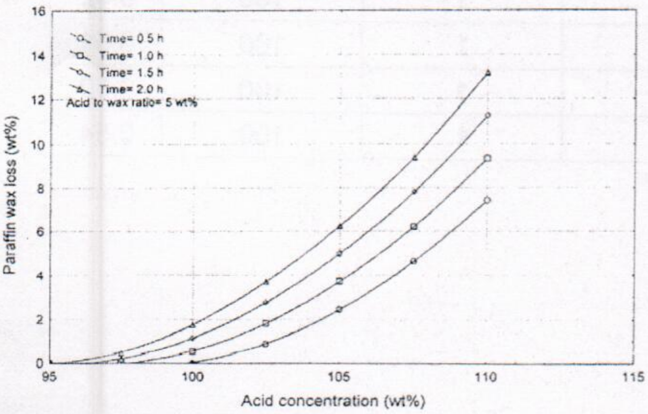

Fig. 2. Effect of acid concentration on paraffin wax loss at different treatment time.

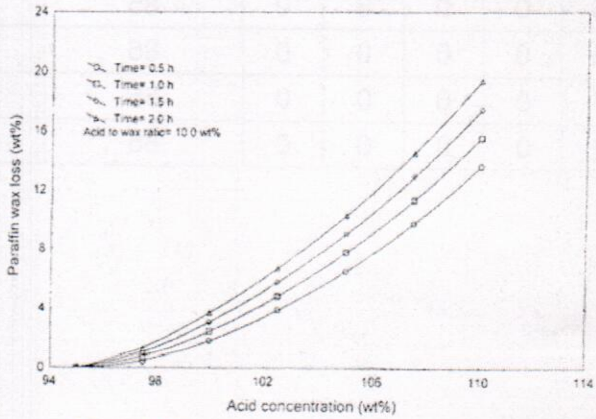

Fig. 4. Effect of acid concentration on paraffin wax loss at different treatment time.

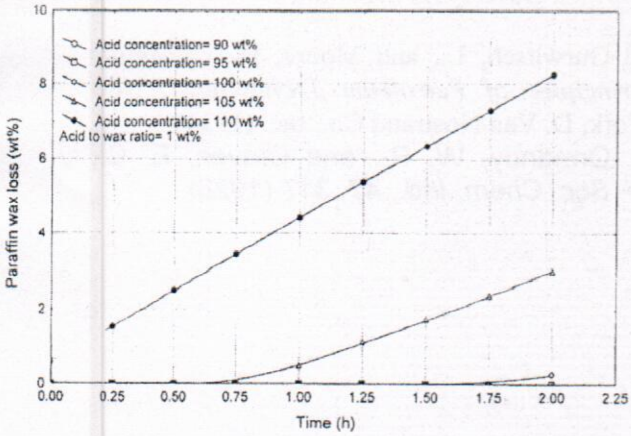

Fig. 5. Effect of treatment time on paraffin wax loss at different acid concentration.

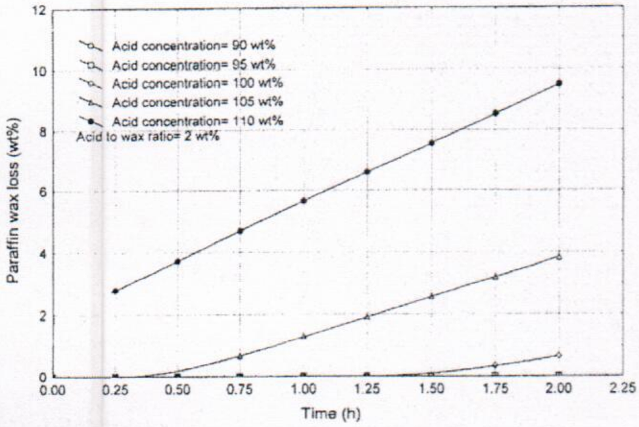

Fig. 6. Effect of treatment time on paraffin wax loss at different acid concentration.

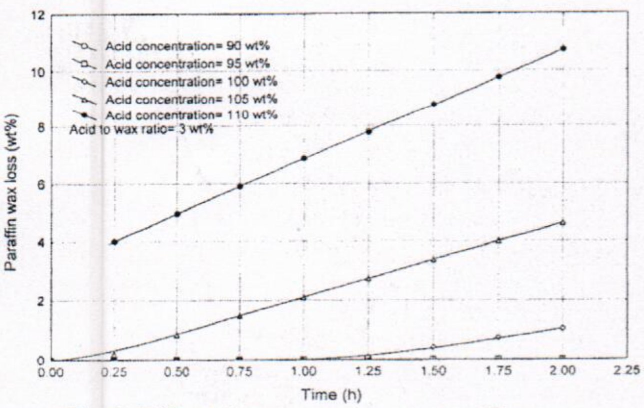

Fig. 7. Effect of treatment time on paraffin wax loss at different acid concentration.

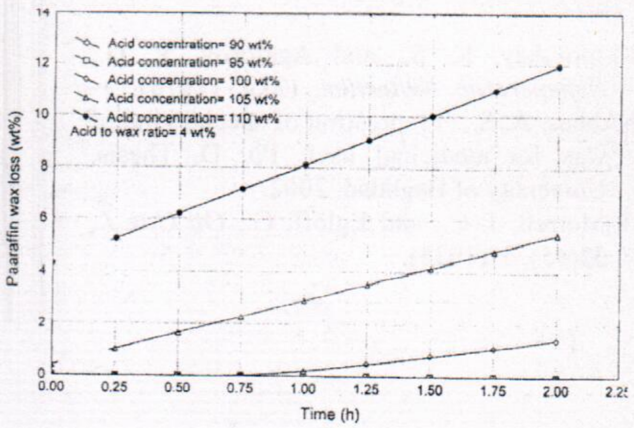

Fig. 8. Effect of treatment time on paraffin wax loss at different acid concentration.

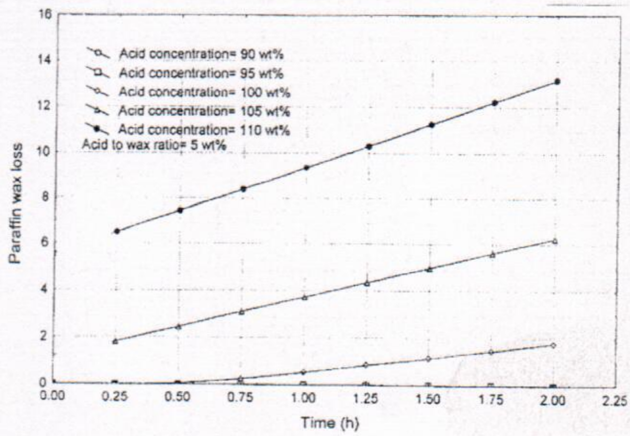

Fig. 9. Effect of treatment time on paraffin wax loss at different acid concentration.

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