

## STUDIES IN THE PROCESSING AND UTILIZATION OF GREASE-LIKE WASTE PRODUCT FROM THE EPHEDRINE PLANT OF MARKER ALKALOIDS, QUETTA

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A grease-like tacky product of greenish black colour is obtained as a by-product in considerable quantities (1500–2000 lb per month) at the Ephedrine Processing Plant of Marker Alkaloids, Quetta. The greasy nature and high acetyl number led to the processing of this material with a view to get products of industrial utilization in wax-based compositions. Methods of processing and the characteristics of the resulting products have been described in detail. Possible uses of such products have also been suggested in this paper.

### Introduction

A grease-like tacky product of greenish black colour is obtained as a by-product in considerable quantities (1500–2000 lb per month) at the Ephedrine Processing Plant of Marker Alkaloids, Quetta. The physical and chemical constants of the raw grease are as follows: Moisture 8%; inorganic matter (dust) 2%; acid number 20–21; saponification number, 135–140; iodine number 100–104; unsaponifiable matter 40–45%; acetyl number 77–80; and m.p. 40°–45°C.

Previous work reported by Siddiqui and Hahn<sup>1</sup> was limited to the extraction and characterisation of saponifiable and unsaponifiable matter of the grease. The present investigations were undertaken to study the possible industrial utilisation of the grease employing the methods of recrystallisation, sulfonation, decolourisation with subsequent recrystallisation, distillation with or without vacuum, and deodourisation.

### Processes

**Recrystallisation.**—When the grease was recrystallised thrice with hot alcohol, a resin-free, a pale green colour solid was obtained in a yield of 20%. The product melted at 63–65°C. The recrystallisation reduces iodine number, unsaponifiable content and the acidity but improves colour and hardness of the product. Acid value 13.8; saponification value 131–133; iodine value 56–58; unsaponifiable content 25–30%.

**Sulphonation.**—The unsaponifiable fraction of the grease is known to contain nearly 12% alcoholic substance, named Ephedra Alcohol.<sup>1</sup> Sulphonation of grease and of the unsaponifiable matter was undertaken but the resultant products did not show any significant detergent properties.

**Decolourisation.**—The raw grease was decolourised by using bleaching materials like fuller's earth and activated charcoal. Varying percentages of decolourising substances were used. 10% solutions of grease in mineral turpentine were found suitable to avoid great losses in the process of bleaching. Even with 200% decolourising material the greenish black colour of the original grease changed to dark brown. With repeated recrystallisations (usually three) with hot alcohol or acetone this dark brown product yielded almost a colourless solid substance but the yield was low (10% on the weight of the raw grease). No change was observed in the characteristics of the refined product when compared with the recrystallised material.

**Distillation under Vacuum.**—When subjected to a temperature of 300–350°C under a reduced pressure of 5–10 mm Hg, it yielded a butter-like brown product m.p. 40–45°C. Nearly 75% of the grease could be distilled under these conditions. Fractional distillation under high vacuum at different temperatures gave soft waxy products with an objectionable odour. Recrystallisation (twice) of these products with hot alcohol or acetone yielded fairly white substances. The physical and chemical constants of these fractions have been listed in Table 1.

Further quantities of waxy products were obtained from the respective mother liquors. Insoluble residues obtained during hot alcoholic recrystallisation of these distillation products were resinous and had low acid and saponification numbers.

**Distillation without Vacuum.**—Distillation of the grease at high temperatures (300° and above) without vacuum gave dark brown-coloured odoriferous oily liquids (Table 2)

Odour in raw grease caused by the presence of essential oils was removed by steam distillation. The essential oils thus obtained were employed as perfumes in toilet soap formulations. The typical smell of these products was not found pleasant and durable.

### Results and Discussion

Recrystallisation of raw grease with hot alcohol reduces iodine number, unsaponifiable content and the acidity. The lowering of iodine number, acidity and unsaponifiable content in the process of recrystallisation of raw grease with hot alcohol shows the partial removal of unsaturated material, free fatty acids and the compounds present in the nonsaponifiable portion, namely alcohol and hydrocarbon, whose occurrence has been reported by previous researchers. The improvement in hardness of the recrystallised product (melting point rose from 45–50°C to 63–65°) is a further indication of the loss of unsaturated substances. The reduction in colour in the process of recrystallisation indicates the removal of the chloroplast pigments (chlorophyll, xanthophyll and carotene) whose presence in a considerable quantity has been mentioned by Siddiqui and Hahn.<sup>1</sup> Attempts are being made to isolate the green pigment (chlorophyll) from the alcoholic extracts of raw grease.

The waxy nature of the recrystallised grease could possibly be exploited for its use in wax-based polishes and cream composition. Decolourisation of grease by physical methods does not appear to be suitable as large amounts of fuller's earth and activated charcoal are required. Chemical bleaching could possibly be employed to overcome great losses of material during this operation.

Distillation under vacuum and without vacuum provides a good means to obtain products of interesting characteristics after recrystallisation with hot alcohol (Tables 1 and 2). Among the three fractions the first one collected in the process of distillation under vacuum appears to be quite useful having properties close to those of bees-wax and could probably be utilized as its substitute in polish compositions. Moreover, high acetyl value (64) of this material makes it very suitable to impart some properties of hard waxes like carnauba. The other two fractions collected in the above process do appear to have properties of waxy materials (Table 1) but their higher values for saponification and unsaturation make them inferior in grade and moreover their yield is comparatively low.

Further yield of these substances extracted from the respective mother liquors was discarded due to their dark brown colour and high free fatty acid content. The insoluble residues resulting from the hot alcoholic recrystallisation of the above mentioned three fractions do not seem to have much fatty matter as indicated by their low acid and saponification numbers.

The fractions collected in the process of high temperature distillation of grease without vacuum show a remarkable decrease in the saponification and iodine numbers and an increase in the yield. This could possibly be attributed to the distillation of unsaturated fatty matter from grease in the early stages of the process leaving behind more unsaponifiable portions. Low values for the acetylation of these fractions obtained through distillation do not justify their use in waxy compositions.

TABLE 1

Fraction No.	Temp.	Yield %	M. p.	A.V.	S.V.	I.V.	Acet. V.	Unsap. %
1	300–310°	5.3	62–70°	49.7	30–32	11–13	64.0	60–63
2	310–325°	3.3	56–57°	38.4	53–55	44–45	—	—
3	325–345°	2.6	58–60°	58.2	50–52	28–29	—	—

TABLE 2

Fraction No.	Temperature	Yield %	A.V.	S.V.	I.V.
1	300–310°	3.5	38.5	80–83	139–140
2	310–315°	9.5	82.4	79–82	124–125
3	315–330°	4.75	73.5	83–84	90–92
4	330–345°	13.25	57.1	61–63	95–97
5	345–375°	22.0	6.8	25–27	74–75

The first fraction with a high percentage of unsaturated fatty matter could be further investigated to find its usefulness. The lower amounts of fatty substances as shown by its number for saponification discard the possibility of its use in paint and varnish industry alongwith other unsaturated fatty oils.

### Conclusion

The results indicated in the paper show no immediate utilization of the waste product. However, trials carried out for the utilization of raw grease in the emulsion form for the waterproofing of hard board and chip board showed positive results. This material, however, can only be

employed for such purposes where colour is no consideration.

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### Reference

1. N. Siddiqui and G. Hahn, Pakistan J. Sci. Ind. Res., **2**, 245 (1959).

contained in Perspex tubes of sizes from 2.4 in to 2.5 in internal diameter with an inlet for the fluid. A cotton disc was placed at the top of the conical base so that the cross section remained constant. The apparatus is shown in Fig. 1. In these experiments, air, hydrogen and the sulphur gas (consisting of 95% methane) were utilized.

The fluidizing gases were supplied both by compressor and gas cylinders, depending on the rate of gas required for each series of experiments. The gases were admitted at the base of the column through the cotton disc, resting on wire-gauze of 300 mesh B.S.S., and their rates were measured with rotameters and also with wet and dry displacement meters.

In each experiment a known weight of sample which was already dried at 100 ± 2°C. was placed in the Perspex tube and the gas was passed with such an increasing rate that fluidizing conditions were obtained. For each run the difference between the gas pressure above the bed and at a point 0.2 in above the base of the bed was measured. All the coal samples were crushed and screened to have the sizes as shown in Table 1.

The specific gravities of each size fraction of each coal were measured and are shown in Table 2, and the densities and viscosities of the gases used are shown in Table 3.

### Results and Observations

With gradual increase in the gas velocity from zero there was a progressive change of pressure as shown in Figs. 2, 3 and 4 for 30+72 mesh Malakwal coal.

The increase in pressure drop was in a linear manner with increasing rate of gas velocity up to the point A without any obvious movement of the coal particles. With slight increase in the

Introduction

In connection with studies of Pakistan coals, it was considered necessary to examine the effect of different gases on coal in a fluidized condition instead of a static bed condition. In spite of certain disadvantages the fluidized bed technique for reaction between solid particles and gases, seems to offer several advantages over static bed methods which include high heat and mass transfer rates, ability to treat coal fines, ease of solids handling, high output per unit of reaction space and saving in capital. This is an important consideration in connection with the economic utilization of the indigenous coal and resources of the country on industrial scale. It was assumed that fluidized fuel beds used on large scale would be at least 6 ft in depth and at high temperature. The fluidizing gas would be air or steam passing upwards at a velocity of approximately 1 ft per sec at the reaction temperature. Lower velocities would give too low rates of gasification.

The coals were available as irregular particles of all sizes up to 3/16 inches but could be crushed to smaller sizes. This paper describes the experiments which were carried out with the object of examining the separate effects of a number of variables.

The principal variables could be the particle size, size distribution, density and shape factor, the velocity, density and viscosity of the gas, and the diameter and depth of the bed. Some of these were examined in the present work, including size range rather than size distribution.

### Experimental

Four different indigenous coal samples from Malakwal, Dighar, Sharg and Sar Kangar areas in West Pakistan, having specific gravities between 1.2 and 1.6, were used. The coal particles were