

THE UTILIZATION OF SPENT NICKEL CATALYST

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Spent nickel catalyst can be utilized for the recovery of fat (58.0%), nickel (8.0%), filter aids (30.0%), iron as an impurity (4.0%). The fatty acid composition of fat as determined by GLC is $C_{12:0}$ (2.2%), $C_{14:0}$ (1.8%), $C_{16:0}$ (37.4%), $C_{18:0}$ (10.7%), $C_{18:1}$ (42.6%), $C_{18:2}$ (5.3%). The reactivated filter aids showed bleachability (64.5% when reactivated at 350°).

Key words: Filter acid, Bleachability, Leaching.

Introduction

Industrially vegetable oils are converted into fat known as Vanaspati Ghee in the presence of hydrogen gas and by use of 0.1–0.4% nickel/oil as catalyst [1–4]. Currently nickel catalyst worth 20 million rupees is imported for this purpose. However, the nickel catalyst is deactivated in due course of time and becomes a waste material. The spent nickel catalyst contains fat (58.0%), nickel (8.0%), filter aids (30.0%), iron as an impurity (4.0%). The filter aids separated by filtration is reactivated for bleaching of oils. Encouraging results have been obtained. The fatty acid composition was determined by thin layer and gas liquid chromatography.

Experimental

Recovery of fat. Fat in the spent nickel catalyst (100 gm) was extracted in hexane (1000 cm³) using soxhlet technique for 3 hrs. Miscella thus obtained was heated on a water bath and hence was distilled off under reduced pressure leaving fat (58.0 gm).

Liberation and methylation of fatty acids. The fat (500 mg) was refluxed with a mixture (40 cm³) of methanol, benzene and acetyl chloride (20:4:1) for 1½ hrs. Diethyl ether and saturated sodium chloride solution was used for washing. The ether layer containing methyl esters was separated by a funnel and dried over anhydrous sodium sulphate and filtered. Distillation of ether gave methyl esters.

Application of thin layer and gas liquid chromatography. The methyl esters (80 mg) were purified by thin layer chromatography using hexane: ether (9:1) solvent prior to using liquid chromatography to identify fatty acids. The non-destructive locating reagent 2,7 dichlorofluorescein was used to obtain purple yellow coloured bands under an ultraviolet light 366 nm. A column (152.4 cm x 0.95 cm) was prepared by coating polyethylene glycol succinate (10.0%) on diatomite "C" (80–100 mesh). After conditioning the column was operated at 200° to separate pure methyl esters into fatty acids using gas liquid chromatography (Pye Unicam 204 Series).

Leaching of nickel as nickel sulphate and its purification.

Fat free material from experiment No. 1 was treated with hexane to remove fat (58 gm) and the remainder was heated with dilute sulphuric acid for 1 hr. to leach out nickel as nickel sulphate. It was filtered to separate filter aids (30 gm). The filtrate was purified by treating with conc. nitric acid (3.5 gm) at 100° for 1½ hrs. and then neutralized with saturated sodium carbonate solution till pH 4.5. Later on cooled to room temperature and filtered to remove iron as an impurity (4 gm) before the determination of nickel content (8 gm).

Estimation of nickel. A portion (100 cm³) of the purified nickel sulphate solution (1500 cm³) was treated with citric acid (5 gm), neutralized with dilute aq. ammonia solution and then acidified with dilute HCl while warming at 60–80° for ½ hr. a slight excess of 1.0% alcoholic solution of dimethyl glyoxime was added and dilute ammonia solution added dropwise until the liquid was slightly ammoniacal. After standing for 1 hr., the mixture was filtered and the precipitate was washed with cold water to remove chloride. The product was dried at 120° until it attained constant weight. The percentage of nickel was calculated as given below:

i. wt. of Ni. (C ₄ H ₇ O ₂ N ₂) ₂ precipitate	=2.66 gm
ii. Mol.wt. of Ni. (C ₄ H ₇ O ₂ N ₂) ₂	=288.71 gm/mole
iii. 288.71 gm of compound contains nickel	=58.71 gm

$$\text{Hence 2.66 gm of compound contains nickel} = \frac{58.71 \times 2.66}{288.71} = 0.54$$

iv. 100 ml of the solution contains nickel	= 0.54 gm.
v. 1500 ml of the solution contains nickel	= $\frac{0.54 \times 1500}{100} = 8.0$

iv As the 100 gm of nickel waste was taken,
 hence the percentage of nickel was found to be 8.0%.

Reactivation of filter aids. 100 gm of filter aids was dried and powdered to 200 mesh, then heated in 4N sulphuric acid (250 cm³) for 4 hrs. on a sand bath. After filtering it was washed until pH 5 was reached. To ensure complete removal of moisture, it was placed in an electric furnace at 250° for 4 hrs. before grinding to 200 mesh for use in bleachability studies.

Bleachability test. Crude cottonseed oil (50 gm) and reactivated filter aid (0.5 gm) was stirred over an oil bath at 115-120x for 5 minutes and rapidly filtered. The colour of the mother liquor was compared with natural cottonseed oil by taking 15 ml each of crude and bleached oil in 1" cell of lovibond Tintometer.

In the case of colour index for natural cottonseed oil 10 yellow is considered equivalent to one red upto the limit of 3.5 of red. So the reading for natural cottonseed oil and treated sample is as given below:

- (i) Colour Index of natural oil = $2^R \cdot 8$ 20.4
 = $2.8 \times 10 + 20.4$
 = 48.4
- (ii) Colour Index of treated sample = 0.8 9.2
 = $0.8 \times 10 + 9.2$
 = 17.2
- (iii) Bleaching efficiency = $\frac{\text{Reduction in index} \times 100}{\text{Initial colour index}}$
 = $\frac{31.2 \times 100}{48.4}$
 = 64.5%

Results and Discussion

An attempt is made for the utilization of waste material [5-9] which contains inactive nickel metal as oxide, filter aids and fat. Firstly the fat from the waste material is dissolved in hexane[10-12]. It has been observed that if the fresh waste material is processed a white fat is recovered otherwise light yellow coloured fat is obtained due to its oxidation. However, in the first case the quality of fat is such that it can be utilized for edible purposes whereas coloured fat can be used for the production of soap. For industrial implementation, fat recovery should be maximised for a given quantity of solvent. Experiments were performed by varying weight/volume ratio of waste and solvent. The results are shown in (Table 1). It can

TABLE 1. THE RECOVERY OF FAT OUT OF 100 g OF WASTE MATERIAL WITH DIFFERENT VALUES OF HEXANE

S.No.	Hexane (cm ³)	Material: Hexane	Yield (%)
1	250	1:2.5	25
2	500	1:5	35
3	750	1:7.5	40
4	1000	1:10	45
5	1100	1:11	45
6	1250	1:12.5	45

be seen that extraction is most efficient at a weight: volume ratio of 1:10. The fatty acids as methyl esters [13] are identified after their purification[14-21]. The fatty acid composition shows saturation (52.1%) and unsaturation (47.9%) (Table 2). This composition may be modified by the addition of saturated fatty acids or by the hydrogenation of unsaturated fatty acids to make it fit for the preparation of quality soap. Usually

TABLE 2. THE FATTY ACID PERCENTAGE COMPOSITION OF RECOVERED FAT

S.No.	Fatty Acids	Percentage
1	Lauric	2.2
2	Myristic	1.8
3	Palmitic	37.4
4	Stearic	10.7
5	Oleic	42.6
6	Linoleic	5.3

a mixture of fatty acids such as lauric, myristic, palmitic, stearic, oleic and minor proportion of other fatty acids is recommended for the preparation of soap.

The fat free material (42 Kg) was heated with steam and stirring in the presence of dilute sulphuric acid in a glass lined 500 litres vessel (Fig. 1) to leach out nickel as nickel sulphate[22- 25]. The risk for the contamination of iron is avoided by the use of glass lined vessel. The nickel sulphate solution is filtered in a 50 litres glass lined filtration unit (Fig. 2) operated at a pressure of 20 Lbs./inch² to accelerate the process. The grey precipitate of filter aids after proper treatment[26] as described in the experimental section shows (64.5%) bleaching efficiency. The reactivated filter aid is evaluated[27] as regards to bleachability, oil retention, mois-

TABLE 3. COMPARATIVE STUDIES OF TREATED FILTER AID WITH IMPORTED SAMPLES

S. Samples No.	Bleach-ability (%)	Oil Reten-tion (%)	Moisture (%)	pH	Bulk Density (gm/ml)
1 Tarana Tonsil (Germany)	68.0	34.8	6.0	4.2	0.7528
2 Tarana Optimum (Germany)	71.0	35.7	6.6	5.5	0.6488
3 New Wales (England)	63.5	33.1	8.9	3.6	0.6934
4 South Korea	68.6	30.1	5.1	3.1	0.7479
5 Treated Filter aid	64.5	36.2	6.4	5.0	0.6769

ture, pH and bulk density. These properties of the reactivated filter aids and of imported samples are compared in (Table 3). The differences in bleaching efficiency and other properties may be due to the earth from different resources and secondly due to the application of different techniques for the activation. The reactivation of filter aids from the spent nickel catalyst is carried out on a laboratory scale. The same process may be applied on a pilot plant scale to study further economic feasibility.

The nickel sulphate as filtrate is purified by removing iron[28] as an impurity (4.0%). The iron in ferrous state is converted into ferric under the process of oxidation and then precipitated as ferric hydroxide at specific pH 4.5. The percentage of nickel (8.0%) in the nickel sulphate is deter-

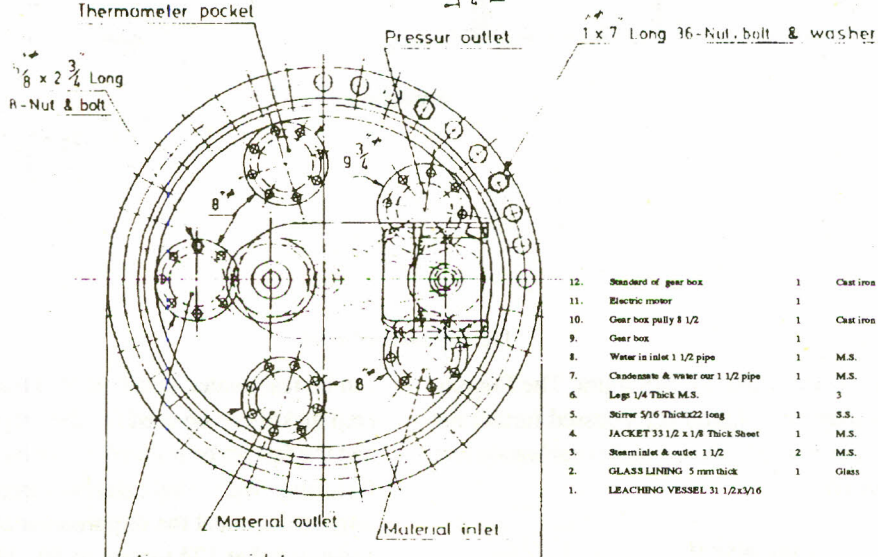
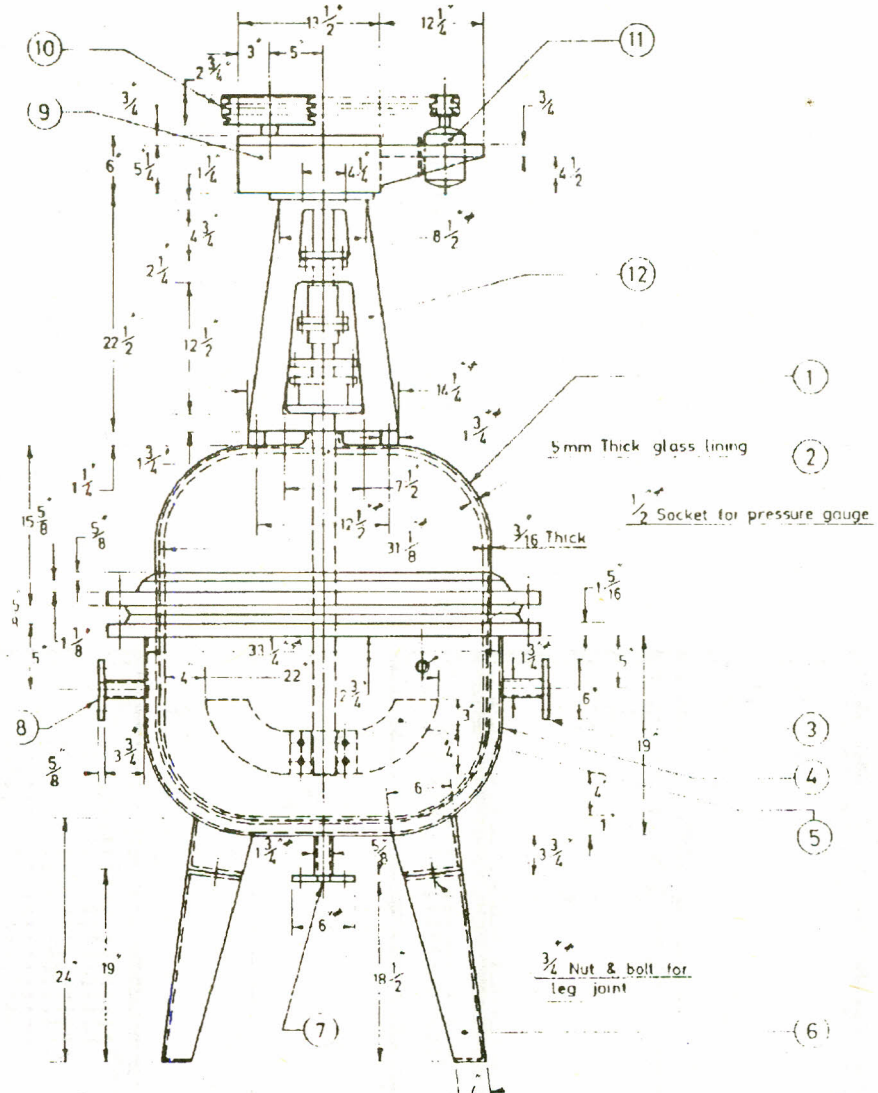


Fig 1. Leaching tank

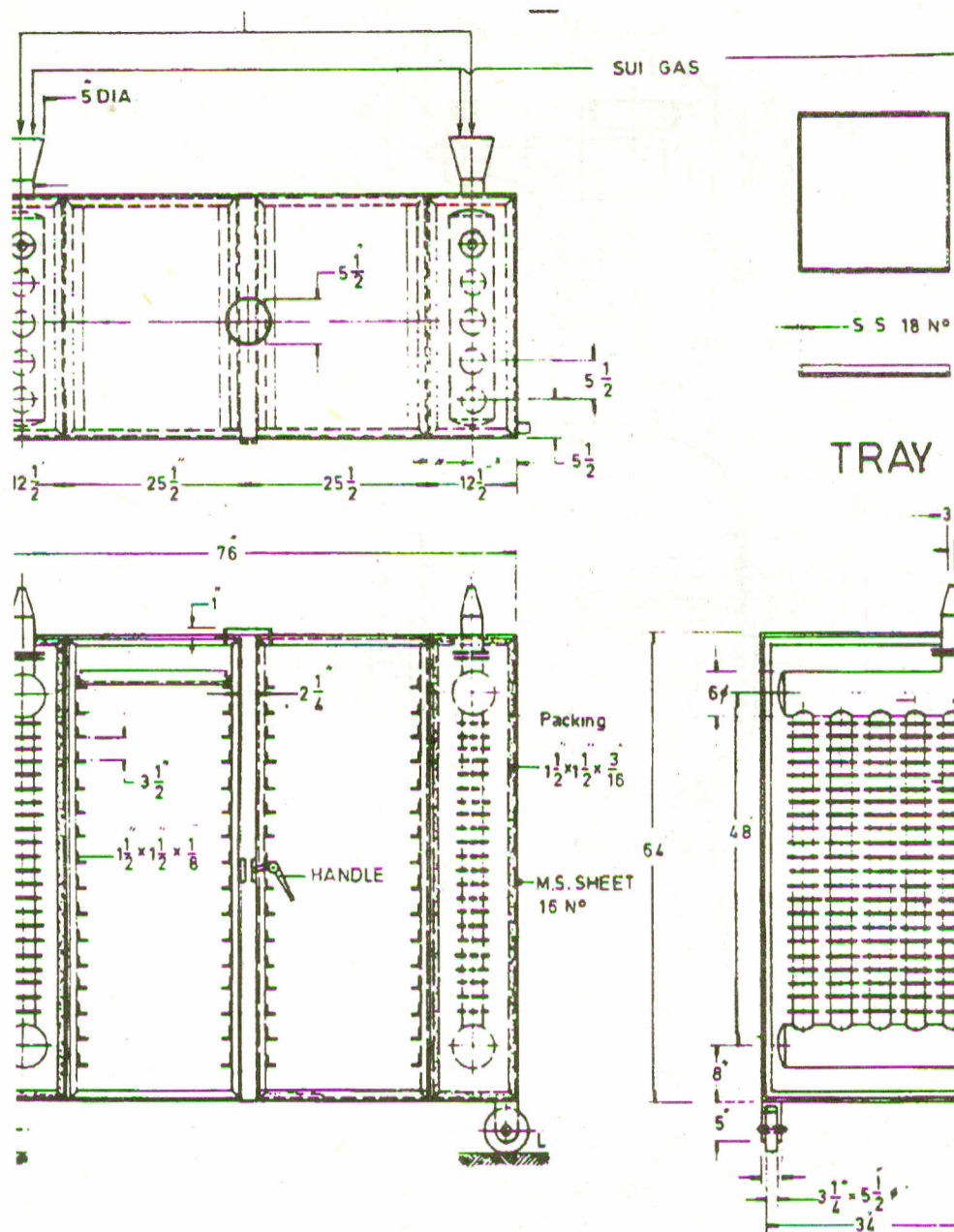


Fig. 2. Glass lined vessel

collected from Suraj Ghee Mills, Sheikhpura, The Punjab. The purified nickel sulphate solution is processed further for the preparation of intermediate salts of nickel carbonate and nickel formate (Part II).

Conclusion

The above work demonstrates that the spent nickel catalyst can be treated to recover fat, nickel and filter aids. The latter

can be reactivated nearly to its bleaching power. The recovered nickel can be used for the preparation of nickel catalyst and the fat can be utilized either for edible or for soap manufacturing. The nickel catalyst approx. 300 tonnes per year is imported to meet the requirement of the country. It has been estimated that 174 tonnes of fat, 24 tonnes of nickel and 90 tonnes of filter aids can be recovered from 300 tonnes of spent nickel catalyst worth Rs. 13.26 million.

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