Reclamation of Nickel from Spent Nickel Catalyst[1]

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Spent nickel catalyst containing an average 9.6% nickel was obtained locally from an oil hydrogenation industry. It was digested with 1-3N HCl, HNO_3, H_2SO_4 and mixtures thereof in one to three stages of durations ranging from one to three hr at 100°C using spent nickel catalyst to acid proportions of 1:3 to 1:8 (w/v). Nickel recoveries of over 94% were obtained when one part of spent catalyst was digested for three hr with six or more parts of 3N mixture of HCl and HNO_3 (3:1, v/v). Acid extracts of spent nickel catalyst obtained using HCl, H_2SO_4 and mixtures thereof were treated with NaOCl to convert their content of iron in the ferric form. The iron from the nickel extract was precipitated out in the form of ferric hydroxide at pH 6.0. Nickel from the iron-freed acid extracts was recovered at pH 8.5 ± 0.5 as nickel hydroxide. Nickel formate was prepared by refluxing nickel hydroxide with 10% formic acid in about 6% excess to stoichiometric requirements for 30 min. The dried nickel formate was reduced in peanut oil at 230°C to 270°C for 0.25 to 2.75 hr. The reduction at 260°C on kieselguhr support, employing nickel formate:oil:support in ratio of 50:43:7, for two hr provided catalyst of maximum activity. The hydrogenation activity of the reclaimed catalyst, assessed by standard AOCS procedure, was greater than that of the parent catalyst.

Hydrogenation of triacylglycerols, particularly oils, involves addition of hydrogen across the double bonds or ethylenic linkages of its unsaturated fatty acids. It is a means of modifying their physicochemical properties as it converts liquid oils into semisolid plastic fats. The hydrogenation reaction in commerce is commonly catalyzed by metallic nickel. The Vanaspati industry in India hydrogenates nearly one million tons of edible oil annually and consumes over 1,200 tons of nickel catalyst containing an average 20% metallic nickel (1). However, there being no reserves of nickel in the country, India imports nickel to meet its requirements.

The catalyst rejected from use in the oil hydrogenation industry varies widely in its composition, which depends largely upon the proportion of support material used for nickel and the filter aids used for facilitating removal of catalyst from the hydrogenated oil. While fat and acid-insolubles are the major constituents of spent nickel catalyst, as these together account for up to 93.8%, its content of metallic nickel varies from 3.5 to 18.1% (2,3). Because the latter is associated with siliceous and metallic impurities like iron and aluminum and catalyst poisons such as phosphorus and sulfur, the spent nickel catalyst is largely discarded as a waste. At present, there is considerable concern about disposal of this heavy metal waste because of environmental hazards and the loss of valuable nickel.

Several scientific studies conducted in the past for recovery of nickel from spent catalyst in that or the defatted form considered its digestion with organic as well as inorganic acids. The organic acids used were formic acid (3-6) and acetic acid (3,6). The inorganic acids used were hydrochloric acid (2,3,6,7), nitric acid (2,3,6,8-11), sulfuric acid (2,3,6,12-15) and combinations of the latter with nitric acid (2,16) or sulfonic acid (17,18). However, the techniques are generally unattractive to the industry for techno-economic reasons. These include sub-optimal recoveries of nickel with organic acids; excessive bulk and the requirement of longer durations or multiple stages of digestion with dilute solutions of inorganic acids, and substantial impurities, severe corrosion and handling problems in digestion of spent catalyst with concentrated solutions of inorganic acids.

The technical literature on reclamation of recovered nickel from spent catalyst is scanty though the fresh inorganic and organic nickel salts are normally dry- and wet-reduced, respectively, to prepare active nickel catalysts suitable for oil hydrogenation purposes (19). Furthermore, the pertinent information on techno-economically feasible process(es) of recovery and reclamation of nickel from spent catalyst in nickel-importing countries is an industrial secret of big businesses. Therefore, this study was undertaken to generate relevant information for quantitative recovery of nickel from spent catalyst under modest conditions, and its reclamation by the wet-reduction technique to prepare catalyst of an activity comparable to the parent catalyst.

EXPERIMENTAL PROCEDURES

Materials. Samples of spent nickel catalyst along with its parent catalyst were obtained from M/s Hindustan Vegetable Oil Corp., Kanpur, India.

Refined peanut oil (i.v. 101.7 and 99.4) used for the experiments was obtained from M/s Hindustan Lever Ltd., Bombay.

Support materials, viz. aluminium oxide, LR grade (Sarabhai Merk, Baroda); silica-gel without binder, LR grade (BDH India Pvt. Ltd., Bombay); kieselguhr, LR grade (S.D. Fine Chemicals Ltd., Boisar, Maharastra); activated carbon, and bleaching earth of commercial grade, were used for reclamation of recovered nickel from the spent catalyst.

Methods. Analysis. Using AOCS procedures (20), the spent nickel catalyst was analyzed for its moisture content by weight loss from a five-g sample dried at 101 ± 1°C for two hr, for its fat by extracting a five-g sample with petroleum ether (b.p. 60°-80°C) for three hr in a Soxhlet apparatus, for ash by incinerating a two-g sample at 600 ± 15°C for two hr., and for acid-insoluble ash by treating the ash with five ml conc HCl followed by washing with water. The iron content of spent catalyst was estimated by the thiocyanate method (21). A gravimetric method based on dimethyl glyoxime was used to determine the nickel contents of spent and parent catalysts (22).

The iodine value, slip point and *trans*-isomers of the oil samples were determined by AOCS procedures (20)

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(Cd 1-25, Cc 3-25, and Cd 14-61, respectively). Fatty acid composition of the oil samples was determined by gas liquid chromatography (GLC) of their methyl esters.

Recovery of nickel from spent catalyst. Spent nickel catalyst in 25 g quantities was digested with 1-3N HCl, HNO_3, H_2SO_4 and mixtures thereof in one to three stages for durations ranging from one to three hr at 100°C using various proportions of spent catalyst to acid ranging from 1:3 to 1:8 (w/v). The acid digest was filtered hot (at ~ 50°C) under reduced pressure and the residue on Whatman No. 1 filter paper was washed with 20-ml aliquots of hot water (~ 50°C) twice, admixing the washings with the filtrate (acid extract).

The acid extracts obtained using HCl, H_2SO_4 and mixtures thereof were treated with NaOCl and boiled for two min to convert iron from ferrous to ferric form. The acid extracts obtained using HNO_3, HNO_3 + HCl, and HNO_3 + H_2SO_4 contained iron in ferric form and hence did not require this treatment.

In order to ensure maximum removal of iron from acid extract as ferric hydroxide without an appreciable loss of nickel, optimization experiments were carried out in which the acid extract was adjusted to different pH's ranging from 4.5 to 7.0 with 10% sodium hydroxide solution. The precipitate so obtained was heated to boiling for about five min and removed by filtration under reduced pressure. The precipitate so removed was analyzed for its nickel content, and the filtrate containing extracted nickel was analyzed for its iron content. From these experiments, it was found that pH of 6.0 was optimum for the removal of iron from the acid extract. Therefore, the bulk of the acid extract was adjusted to pH 6.0 with sodium hydroxide solution for the removal of iron.

The iron-freed acid extract was adjusted to pH 8.5 ± 0.5 with 50% (w/v) NaOH solution and heated to 70°C. The precipitate of nickel hydroxide was washed twice with water and recovered by filtration under reduced pressure. Assuming quantitative recoveries of nickel, the nickel hydroxide precipitate was converted into nickel formate by refluxing for 30 min with stoichiometric amounts of formic acid (10%, w/v) which actually amounted to about 6% excess addition on the basis of actual recovery of nickel from the spent catalyst. The reaction mixture was evaporated to dryness on a boiling water bath to crystallize nickel formate as $HCOO)_2Ni \cdot 2H_2O$. The percent recovery of nickel by the experimental process was calculated from the nickel content of resultant nickel formate and that of the spent nickel catalyst.

Reclamation of recovered nickel. Experimental dispersions of recovered nickel formate in commercial samples of refined peanut oil were prepared without any support material (50:50, w/w) and with support materials, viz. aluminum oxide, silica gel, kieselguhr, activated carbon, or bleaching earth, in a nickel formate:oil:support ratio of 50:45:5 (w/w/w), respectively. These dispersions were reduced under a stream of hydrogen bubbling through the reaction mass at 50 ml/min at 250°C for two hr while stirring in a glass assembly. After cooling to 150°C in an atmosphere of hydrogen, the catalyst was flaked by pouring on a chilled glass surface. The reclaimed nickel catalyst was assessed for its hydrogenation activity by determining the iodine value and slip point of the refined peanut oil hydrogenated for 1.5 hr in a Parr pressure reactor (Model 4522M, Parr Instruments Co.). The hydrogenation reaction was carried out using 0.05% catalyst concentration (as metallic nickel by weight of oil) at 175°C under 20 psig (1.4 Kg/cm^2) hydrogen pressure and agitation at 425 rpm. The hydrogenation activity of experimental samples of reclaimed catalyst was assessed in the same manner after its storage for six mo in sealed polyethylene bags under ambient conditions. The storage studies revealed that the catalyst support on kieselguhr was the most stable; therefore, subsequent studies were carried out on kieselguhr-supported catalyst.

The temperature for reduction of nickel formate to active nickel catalyst was optimized by dispersing the recovered nickel formate in refined peanut oil on kieselguhr support (50:45:5, w/w/w) and reducing it in a stream of hydrogen for two hr at 230-270°C under agitation. The optimum temperature of reduction was found to be 260°C.

The proportion of kieselguhr for reclamation of nickel was optimized by reducing dispersions of recovered nickel formate in refined peanut oil on this support (50:49:1 to 50:40:10 w/w/w) at 260°C for two hr. The hydrogenation activity of the catalyst preparations was assessed by the procedure described above. The studies revealed that the dispersion in the proportion of 50:43:7 (w/w/w) of nickel formate:oil:kieselguhr provided the catalyst of maximum activity.

The optimum time for reclamation of nickel in refined peanut oil on kieselguhr support (50:43:7 w/w/w) was assessed by reducing recovered nickel formate at 260°C for 0.25 to 2.75 hr and assessing the hydrogenation activity of the catalyst. The hydrogenation activity of the parent nickel catalyst was assessed in the same manner as that used for hydrogenation activity of the reclaimed catalyst.

RESULTS AND DISCUSSION

Composition. The composition of the spent nickel catalyst used in this study (Table 1) revealed its nickel content of 9.6% to be slightly less than half of that commonly encountered in commercial samples of fresh nickel catalyst (20-23%) used for hydrogenation of edible oils (19). The appreciable proportion of 1.5% iron impurity in the spent catalyst was perhaps a consequence of the use of mild steel hydrogenation vessels by the Indian industry. The nickel content of the parent catalyst was 21.0%.

TABLE 1

Composition of Spent Nickel Catalyst[a]

Constituent	Content (%, as is)	
Moisture	1.7	
Fat	47.1	
Ash	51.2	
Acid-insoluble ash		36.2
Nickel		9.6
Iron		1.5
Other impurities (by difference)		4.9

[a] Average of two determinations.

TABLE 2

Efficacy of Inorganic Acids and Mixtures Thereof in Recovery of Nickel From Spent Catalyst[a]

		Recovery of nickel[b] as a function of acid strength and stages of digestion[c] (% nickel present in spent catalyst)							
		1N			2N			3N	
	Proportions	Stages			Stages			Stages	
Acids	(v/v)	1	2	3	1	2	3	1	2
HCl	–	36.1	61.2	75.0	51.9	67.2	75.3	68.0	73.9
HNO_3	–	39.4	63.7	77.6	51.8	68.0	78.0	67.0	74.0
H_2SO_4	–	27.8	52.1	65.7	36.6	56.4	69.6	45.1	57.0
$HCl+HNO_3$	3:1	45.3	78.9	84.0	63.6	83.4	90.0	77.5	85.5
$HCl+HNO_3$	1:1	44.0	78.5	84.0	63.0	83.5	89.6	75.6	84.7
$HCl+HNO_3$	1:3	41.8	76.1	81.0	61.7	81.2	88.8	72.8	82.0
$HCl+H_2SO_4$	3:1	37.0	73.3	78.9	56.4	78.8	88.1	68.4	80.2
$HCl+H_2SO_4$	1:1	36.3	72.0	78.5	55.5	78.3	88.1	66.9	79.4
$HCl+H_2SO_4$	1:3	36.0	70.7	77.1	54.4	77.5	87.4	66.2	78.8
$HNO_3+H_2SO_4$	3:1	40.0	74.5	80.5	58.8	79.1	88.9	69.2	82.4
$HNO_3+H_2SO_4$	1:1	39.8	74.3	80.1	57.1	78.3	87.8	68.4	81.0
$HNO_3+H_2SO_4$	1:3	38.7	73.7	79.8	56.6	78.1	87.3	67.7	80.0

[a] Spent catalyst to acid proportion of 1:3 (w/v) in each stage of digestion.
[b] Average of two determinations with variations up to ± 0.5%.
[c] Digestion for one hr at 100°C in each stage.

Recovery of nickel from spent catalyst. The details of recovery of nickel from spent catalyst through digestion with 1-3N HCl, HNO_3, H_2SO_4 and mixtures thereof in one to three stages of one-hr duration each at 100°C using spent catalyst to acid ratio of 1:3 are given in Table 2. It is apparent that for the same hydrogen ion concentration, the nickel recoveries with HCl and HNO_3 were greater than with H_2SO_4, suggesting some contribution of the counter ions, besides hydrogen ion, in the recovery of nickel from the spent catalyst through inorganic acid digestion. The recoveries of nickel from spent catalyst for any particular acid strength and/or stage(s) of digestion were comparatively greater when mixtures of acids were used. The mixture of HCl and HNO_3, particularly at 3:1, had an edge over the other acid mixtures. These results suggest some synergistic effect of the respective counter ions of the acids on the extraction of nickel from the spent catalyst.

Although the total recovery of nickel for any particular acid strength increased with an increase in the number of stages of digestion, the recovery of nickel was maximum in the first stage and minimum in the third stage of three-stage digestion. Furthermore, the recovery of nickel in the first stage of digestion of spent catalyst increased with an increase in strength of the acid used. However, the higher acid strength resulted in concurrent decreases in recovery of nickel in the second and the third stages of digestion.

The above results suggested consideration of a single stage digestion for recovery of nickel from the spent catalyst with the possibility of improving its recoveries by increasing the acid strength and/or effecting changes in the other operating conditions during digestion. Consequently, further experiments were planned for obtaining maximum recovery of nickel in a one-stage process of digestion of spent catalyst.

The recoveries of nickel from spent catalyst through single-stage digestion with a 1-3N mixture of HCl and HNO_3, in 3:1 (v/v) proportion for one to three hr at 100°C using spent catalyst to acid proportions of 1:3 to 1:8, given in Table 3. As expected, the nickel recoveries improved as both the digestion time and the spent catalyst to acid proportion increased. It is also apparent that nickel recoveries of 94% or greater were obtained on digesting one part of spent catalyst with six or more parts of the aforesaid acid mixture of higher concentration (3N) for three hr.

The results of the experiments carried out for optimization of pH for the removal of iron from the acid extract of spent catalyst are depicted in Figure 1. These results indicated that as the pH of the extract was adjusted to higher levels, the extent of iron removal through precipitation increased simultaneously. On the other hand, when the pH of the extract was adjusted above 6.0, the loss of nickel by simultaneous precipitation as nickel hydroxide with ferric hydroxide increased sharply. Therefore, in order to achieve maximum removal of iron with the least losses of nickel, a pH of 6.0 was found optimum wherein 99.1% iron could be removed for a loss of 4.5% nickel.

Considering the above loss of nickel during the removal of iron from the acid extract, the digestion conditions mentioned above could be expected to extract over 98.5% of the nickel originally present in the spent catalyst.

Reclamation of recovered nickel. The effect of support material, used in reduction of recovered nickel formate, on hydrogenation activity of reclaimed catalyst is shown in Table 4. It is apparent that catalyst preparations without support and those supported on

TABLE 3

Recovery of Nickel From Spent Catalyst Through Single Stage Digestion at 100°C with $HCl+HNO_3$ (3:1, v/v)

Acid strength	Digestion time (hr)	Recovery of nickel[a] as a function of spent catalyst to acid proportions (% nickel present in spent catalyst) 1:3	1:4	1:5	1:6	1:7	1:8
1N	1	45.3	60.4	71.0	75.1	76.9	78.9
	2	54.7	66.4	75.8	78.4	80.3	82.1
	3	60.8	71.0	78.1	80.7	83.1	85.4
2N	1	63.6	72.6	76.3	80.2	82.7	85.1
	2	67.8	75.7	79.9	84.0	86.8	88.4
	3	71.3	78.4	83.1	87.5	90.1	91.7
3N	1	77.5	81.9	84.3	86.9	89.1	90.9
	2	82.2	85.8	88.4	90.1	91.9	93.3
	3	86.3	89.6	92.8	94.2	94.3	94.4

[a] Average of two determinations with variations up to ± 0.5%.

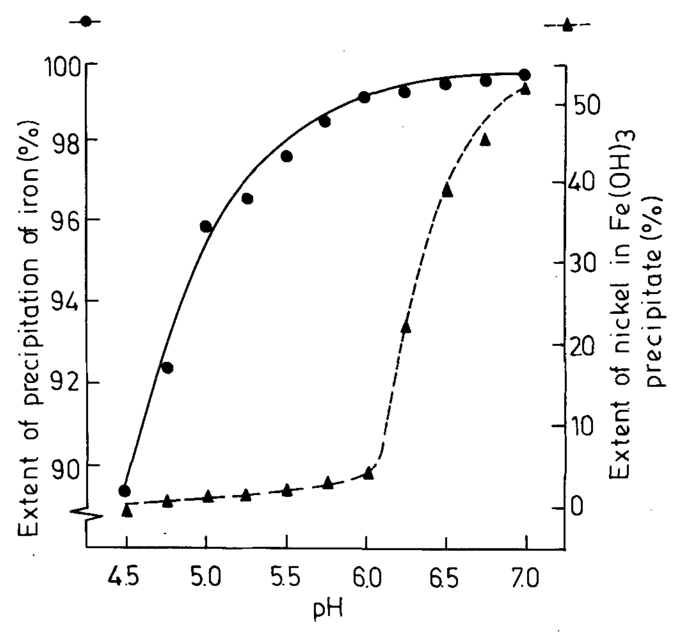

FIG. 1. Effect of pH on removal of iron from acid extract of spent nickel catalyst and loss of nickel in ferric hydroxide precipitate. (Values based on iron and nickel contents of the spent catalyst.)

bleaching earth were relatively less effective than catalyst preparations on other support materials, viz. aluminum oxide, silica gel, kieselguhr and activated carbon. The catalyst preparations on the latter supports exhibited noticeable differences with respect to their activity as well as selectivity. The catalyst supported on aluminum oxide removed comparatively less linoleic acid from the peanut oil. It also effected a greater rise in the saturated fatty acid content of the oil. The catalyst supported on silica gel produced more *trans*-isomers. The activity of the catalyst supported on activated carbon was relatively low. The catalyst supported on kieselguhr effected lesser production of *trans*-isomers with a greater drop in linoleic acid and iodine value of the oil, which indicated the higher activity and selectivity of this catalyst.

These results indicate the importance of using a support material for improving the activity of the catalyst, which depends upon its crystal lattice structure, porosity and other related factors. In the present experiments, it is apparent that use of kieselguhr as a support material in the reduction mix probably contributed to the improved catalyst structure and surface heterogeneity which influence the activity of hydrogenation catalyst (19).

The details of studies carried out on the activity of the reclaimed catalyst after its storage for six mo are given in Table 5. The studies indicated that the catalyst preparations on alumina support were highly unstable and that those on silica gel and activated carbon supports were not satisfactory. Considering the hydrogenation activity of fresh and stored catalyst, the performance of catalyst supported on kieselguhr was adjudged to be the most satisfactory.

The effect of temperature of reduction of recovered nickel formate with kieselguhr support in refined peanut oil on hydrogenation activity of reclaimed catalyst is shown in Table 6. It is apparent that a reduction temperature of 260°C provides reclaimed catalyst of higher activity. These results also suggest that the reclamation behavior of the recovered nickel formate in its wet-reduction parallels that of the fresh nickel formate (19). The catalyst obtained by reduction at 270°C was found to have poor activity and selectivity, which indicated a reduction temperature above 260°C had a damaging effect on the catalyst; the above damaging effect of reduction at high temperatures has also been reported by Patterson (23).

The effect of the proportion of kieselguhr support in the reduction mix on hydrogenation activity of reclaimed catalyst is shown in Table 7. The hydrogenation activity of the catalyst improved with increasing proportion of kieselguhr, up to 5%, in the reduction mix. The

TABLE 4

Effect of Support Material on Hydrogenation Activity of Reclaimed Nickel Catalyst Reduced at 250°C for Two Hours (I. Freshly Reduced Catalyst)

Catalyst support[a]	Nickel content of catalyst (%)		Hydrogenation activity of catalyst[b]		Changes in content of fatty acids[b] (% wt)			
			I.V.	Slip point (°C)	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	*trans*-isomers
		Original peanut oil	101.7	-	3.5	42.4	37.7	Nil
Catalyst without support	21.9		70.8	34.0	10.8	64.0	8.8	13.2
Aluminum oxide	22.3		59.8	39.5	18.3	61.5	3.8	21.1
Silica-gel	22.1		61.9	38.0	13.5	68.7	1.4	22.6
Kieselguhr	22.2		59.6	38.5	15.7	66.7	1.2	19.7
Activated carbon	22.1		62.7	37.5	12.7	69.2	1.7	20.8
Bleaching earth	22.1		69.2	31.0	7.7	72.0	3.9	16.1

[a] 5% level in dispersion used for reduction (nickel formate:peanut oil:support, 50:45:5, w/w/w).

[b] Average of two determinations for hydrogenation period of 1.5 hr (with I.V. variation up to 0.6 and slip point variations up to 0.5°C).

TABLE 5

Effect of Support Material on Hydrogenation Activity of Reclaimed Nickel Catalyst Reduced at 250°C for Two Hours (II. Catalyst Stored for Six Months)

Catalyst support[a]	Nickel content of catalyst (%)		Hydrogenation activity of catalyst[b]		Changes in content of fatty acids[b] (% wt)			
			I.V.	Slip point (°C)	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	*trans*-isomers
		Original peanut oil	99.4	-	3.6	43.8	35.9	Nil
Catalyst without support	21.9		69.6	34.5	11.0	63.9	8.4	14.2
Aluminum oxide	22.3		92.4	14.0	4.0	51.1	28.2	4.8
Silica-gel	22.1		77.5	27.0	6.0	65.1	12.2	12.2
Kieselguhr	22.2		59.7	38.5	15.4	66.6	1.3	20.4
Activated carbon	22.1		70.3	30.5	10.0	65.5	7.8	10.1
Bleaching earth	22.1		69.9	29.5	6.7	72.5	4.1	15.4

[a] 5% level in dispersion used for reduction (nickel formate:peanut oil:support, 50:45:5, w/w/w).

[b] Average of two determinations for hydrogenation period of 1.5 hr (with I.V. variation up to 0.6 and slip point variations up to 0.5°C).

activities of catalyst preparations on this support at 5% and 7% levels in the reduction mix were comparable. Because the hydrogenation activity of the latter catalyst preparation had an edge over that of the preparation on kieselguhr support at 10% level in the reduction mix, the proportion of this support at 7% was adjusted optimum in the reduction mix.

The effect of time of reduction of recovered nickel formate with kieselguhr support in refined peanut oil on hydrogenation activity of reclaimed catalyst is shown in Table 8. The results show that as the time of reduction at 260°C is increased to two hr, the catalyst activity increases to attain a maximum. The activity in reclaimed catalyst decreases with reduction time exceed-

TABLE 6

Effect of Temperature of Reduction on Hydrogenation Activity of Reclaimed Nickel Catalyst[a]

Temperature of reduction (°C)	Nickel content of catalyst (%)		Hydrogenation activity of reclaimed nickel catalyst[b]		Changes in content of fatty acids[b] (% wt)			
			I.V.	Slip point (°C)	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	*trans*-isomers
		Original peanut oil	99.4	-	3.6	43.8	35.9	Nil
230	21.5		84.0	23.5	7.8	53.1	22.4	5.8
240	21.6		71.6	31.0	10.3	63.4	9.6	12.8
250	21.3		59.5	38.5	15.5	66.7	1.1	20.1
260	21.7		58.6	39.0	15.9	66.8	0.6	20.4
270	21.7		68.0	34.0	10.3	67.2	5.8	14.1

[a] Prepared by 2 hr reduction of dispersion containing nickel formate in peanut oil on kieselguhr support (50:45:5, w/w/w).

[b] Average of two determinations for hydrogenation period of 1.5 hr (with I.V. variations up to 0.6 and slip point variations up to 0.5°C).

TABLE 7

Effect of Proportion of Kieselguhr Support on Hydrogenation Activity of Reclaimed Nickel Catalyst[a]

Composition of reduction mixture (weight %)			Nickel content of catalyst (%)		Hydrogenation activity of catalyst[b]		Changes in content of fatty acids (% wt)			
Nickel formate	Peanut oil	Kieselguhr			I.V.	Slip point (°C)	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	*trans*-isomers
				Original peanut oil	99.4	-	3.6	43.8	35.9	Nil
50	50	-	23.6		64.3	36.5	12.7	66.9	3.7	18.3
50	49	1	23.5		63.0	37.0	13.3	67.0	3.0	19.1
50	47	3	22.4		60.9	38.0	14.6	66.8	1.9	19.7
50	45	5	21.7		58.6	39.0	15.9	66.8	0.6	20.4
50	43	7	22.2		58.6	39.0	16.2	66.7	0.4	19.8
50	40	10	22.4		58.8	39.0	16.7	65.2	1.4	19.1

[a] Prepared by reduction of dispersion at 260°C for 2 hr.

[b] Average of two determinations for hydrogenation period of 1.5 hr (with I.V. variations up to 0.6 and slip point variations up to 0.5°C).

ing two hr, perhaps because of damage to the catalyst structure which becomes pronounced beyond 2.5 hr of reduction. However, on the contrary, it was observed that the *trans*-isomer formation increased with the catalyst reduced for 2.25 and 2.50 hr.

The hydrogenation activity of the reclaimed catalyst prepared by reducing the recovered nickel formate in refined peanut oil with kieselguhr support (50:43:7) at 260°C for two hr was compared with that of the parent catalyst (Table 9). The former was observed to have an edge over the latter in this regard, as the former produced hydrogenated peanut oil of 58.6 I.V. with a slip point of 39°C in comparison to the latter producing oil of only 72.2 I.V. with a slip point of 34.5°C in its hydrogenation for 1.5 hr under the test conditions.

The results of this study suggest an efficacy of digestion

TABLE 8

Effect of Time of Reduction on Hydrogenation Activity of Reclaimed Nickel Catalyst[a]

Time of reduction (hr)	Nickel content of catalyst (%)		Hydrogenation activity of catalyst[b]		Changes in content of fatty acids[b] (% wt)			
			I.V.	Slip point (°C)	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	*trans*-isomers
		Original peanut oil	99.4	-	3.6	43.8	35.9	Nil
0.25	21.5		86.8	19.0	5.4	55.4	22.5	4.2
0.50	21.5		80.0	24.5	7.6	59.0	16.7	6.8
0.75	21.5		75.6	28.0	8.9	61.3	13.1	9.8
1.00	21.6		71.8	30.5	10.4	62.8	10.1	11.5
1.25	21.5		68.4	32.5	12.0	63.3	8.0	13.9
1.50	21.5		65.1	35.0	13.3	64.3	5.7	16.6
1.75	21.5		62.3	37.5	14.5	65.6	3.2	18.1
2.00	22.2		58.6	39.0	16.2	66.7	0.4	19.8
2.25	22.2		61.4	37.5	13.5	68.6	1.2	21.6
2.50	22.2		63.2	35.5	12.2	69.5	1.6	25.5
2.75	22.2		71.8	30.0	9.2	65.5	8.6	12.6

[a] Prepared by reduction of dispersion containing nickel formate:peanut oil:kieselguhr, 50:43:7, w/w/w at 260°C.

[b] Average of two determinations for hydrogenation period of 1.5 hr (with I.V. variations up to 0.6 and slip point variations up to 0.5°C).

TABLE 9

Comparison of Hydrogenation Activity of the Reclaimed Nickel Catalyst[a] With That of Parent Nickel Catalyst

Catalyst	Nickel content of catalyst (%)		Hydrogenation activity[b]		Changes in content of fatty acids[b]			
			I.V.	Slip point (°C)	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	*trans*-isomers
		Original peanut oil	99.4	-	3.6	43.8	35.9	Nil
Reclaimed catalyst	22.2		58.6	39.0	16.2	66.7	0.4	19.8
Parent catalyst	21.0		72.2	34.5	7.9	66.8	8.6	15.6

[a] Prepared by reduction of dispersion containing nickel formate:peanut oil:kieselguhr, 50:43:7, w/w/w.

[b] Average of two determinations for hydrogenation period of 1.5 hr (with I.V. variation up to 0.6 and slip point variation up to 0.5°C).

with 3N mixture of HCl and HNO_3 (3:1, v/v) at 100°C for three hr (spent catalyst:acid mixture, 1:6) for recovery of nickel from the spent catalyst and also the efficacy of reduction of recovered nickel formate with kieselguhr support in peanut oil at 260°C for obtaining the reclaimed catalyst of desirable hydrogenation activity.

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