SUMMARY

STUDIES ON RECLAMATION OF NICKEL FROM SPENT NICKEL CATALYST BY WET-REDUCTION METHODS

Spent nickel catalyst, a heavy metal waste of oil hydrogenation industry, is causing concern in its disposal because of environmental hazards besides loss of valuable nickel and associated fat. The pertinent information on reclamation of nickel from the spent catalyst is scanty in the available literature. Therefore, this research was undertaken with the objectives of quantitative recovery of nickel from the spent catalyst under modest conditions and reclamation of recovered nickel by wet-reduction technique to prepare catalyst of desirable hydrogenation activity.

Spent nickel catalyst containing av 1.7% moisture, 47.1% fat, 36.2% acid-insoluble ash, 9.6% nickel, 1.5% iron and 4.9% other impurities was extracted with 4-12 folds of n-hexanes (w/v) at 50°C under stirring for 30 min for recovery of its fat as such. This approach provided recoveries of fat which increased with increasing proportions of solvent to spent catalyst; a spent catalyst to n-hexanes proportions of 1:12 (w/v) provided 95% recovery of fat. However, difficulties were encountered in the
recovery of clear miscella by filtration through coarse as well as fine filter papers. Alternatively, the associated fat of the spent catalyst was recovered as mixed-fatty acids by its saponification with sodium hydroxide (10-18%, w/w) in 6 fold water under reflux conditions for 2 h followed by acidulation of soap solution with dilute sulphuric acid. This approach provided over 95% recovery of mixed-fatty acids on saponification of 100 parts of the spent catalyst with 16 or more parts of sodium hydroxide. The physico-chemical characteristics of recovered fat and mixed fatty acids, particularly the iodine values of 77.1 and 77.9 and slip points of 32.5° and 32.0°C, respectively, indicated that the spent nickel catalyst was perhaps a waste rejected from a two-stage counter-current hydrogenation process of oils.

The spent nickel catalyst in as such form was digested with 1-3 N HCl, HNO₃, H₂SO₄ and mixtures thereof in 1 to 3 stages of durations ranging from 1 to 3 h at 100°C using spent nickel catalyst to acid proportions of 1:3 to 1:8 (w/v) for recovery of its nickel. The results indicated that for the same hydrogen-ion concentration, the nickel recoveries with HCl and HNO₃ were greater than with H₂SO₄ which suggested some contribution of the counterions, besides hydrogen-ion concentration, in the recovery of nickel from the spent catalyst through inorganic acid
digestion under similar conditions. Besides, the recoveries of nickel from the spent catalyst were greater for a particular acid strength when mixtures of acids, particularly HCl and HNO₃ in 3:1 (v/v) proportion, were used which suggested some synergistic effect of the respective counterions of the acids on the extraction of nickel from the spent catalyst. Nickel recoveries of over 94% in iron-freed form were obtained when one part of the spent catalyst was digested for 3 h with six or more parts of 3 N mixture of HCl and HNO₃ (3:1 v/v).

Acid extracts of the spent nickel catalyst obtained using HCl, H₂SO₄ and mixtures thereof were treated with NaOCl to convert their content of iron from ferrous to ferric form; the acid extracts obtained using HNO₃, HNO₃ + HCl and HNO₃ + H₂SO₄ contained iron in ferric form and did not require this treatment. The iron from the acid extracts of nickel was precipitated out in the form of ferric hydroxide at pH 6.0 which provided maximum removal of iron (99.1%) with least losses of nickel (4.5%). Considering this loss of nickel during the removal of iron from the acid extract, the aforesaid digestion conditions could be expected to extract over 98.5% of the nickel originally present in the spent catalyst.

Nickel from the iron-freed acid extracts of the spent catalyst was recovered at pH 8.5 ± 0.5 as nickel
hydroxide or nickel carbonate. The wet precipitate of nickel hydroxide refluxed with formic acid (10%, v/v) in ~6% excess to stoichiometric requirements for 30 min provided nickel formate of high purity in quantitative yields. The dried nickel carbonate refluxed with oxalic acid (10%, w/v) and acetic acid (10%, v/v) in ~10% excess to stoichiometric requirements for 30 min provided nickel oxalate and nickel acetate, respectively, of high purity in quantitative yields. The dispersions of recovered nickel formate, nickel acetate and nickel oxalate prepared in refined peanut oil (50:50, w/w) were reduced at temperatures ranging from 230°C to upto 290°C for periods upto 1.5 h under a stream of hydrogen bubbling through the reaction mass at 50 ml/min. While the dispersions of nickel formate reduced easily, difficulties were encountered with dispersions of nickel acetate and nickel oxalate as the former produced a lumpy mass at its reduction temperature of 250°C and the latter could not be reduced in 1.5 h even at 290°C. Consequently, further experimental work was continued only with the nickel formate.

The dispersions of recovered nickel formate in refined peanut oil (50:50, w/w) were reduced to active catalyst under a stream of hydrogen at 230°C - 270°C for 0.25 - 1.50 h. The hydrogenation activity of the catalyst preparations, assessed by drop in iodine value of refined
peanut oil in hydrogenation for 15 min in a Parr pressure reactor employing 0.05% catalyst concentration (as metallic nickel by weight of the oil) at 175°C under 1.4 kg/cm² hydrogen pressure with agitation at 425 rpm, indicated the maximum reduction of nickel formate to active catalyst at 270°C in 1 h. Using this as a standard of complete reduction, the extents of reduction of nickel formate to active catalyst in other preparations were assessed as a function of time at 230°C - 270°C from the relative drops in iodine value of the oil effected by them in its hydrogenation. This in turn provided the residual proportion and quantum of nickel formate in the experimental dispersions as a function of reduction temperature and time that were required for kinetic studies of its wet-reduction to active catalyst. The wet-reduction of nickel formate in refined peanut oil was found to be a first order reaction with an activation energy of 141.0 KJ/mole.√

The dispersions of recovered nickel formate in refined peanut oil with support materials, viz. aluminium oxide, silica-gel, kieselguhr, activated carbon, or bleaching earth, in nickel formate : oil : support ratio of 50 : 45 : 5 (w/w), respectively, were reduced under a stream of hydrogen at 250°C for 2 h. The catalysts were assessed for hydrogenation activity while fresh as well as after storage for 6 months under ambient conditions by
determining iodine value, slip point, and fatty acid composition of the refined peanut oil hydrogenated for 1.5 h in aforesaid equipment and conditions. The results indicated higher activity, better selectivity and maximum stability of the catalyst supported on kieselguhr. Therefore, the parameters for wet-reduction of nickel formate with kieselguhr support were optimised in aspects of temperature and time of reduction as well as the proportion of this support material in the dispersions.

The reduction of the dispersion containing recovered nickel formate in refined peanut oil on kieselguhr support (50 : 45 : 5, w/w) at 230° - 270°C for 2 h in a stream of hydrogen under agitation and the assessment of hydrogenation activity of the catalyst preparations indicated that the optimum temperature of the reduction was 260°C. The reduction of the dispersions of the recovered nickel formate in refined peanut oil on this support (50 : 49 : 1 to 50 : 40 : 10, w/w) at 260°C for 2 h and the assessment of the hydrogenation activity of the catalyst preparations indicated that the optimum proportion of kieselguhr in the dispersion by weight was 7%. The reduction of the dispersion containing recovered nickel formate in refined peanut oil on kieselguhr support (50 : 43 : 7, w/w) at 260°C for 0.25 - 2.75 h and the
assessment of the hydrogenation activity of the catalyst preparations indicated that the optimum time for reduction at this temperature was 2.0 h.

The hydrogenation activity of the optimally reclaimed nickel catalyst was compared with that of the parent nickel catalyst. The hydrogenated peanut oil produced by the former catalyst exhibited iodine value of 58.6 and slip point of 39°C whereas that produced by the latter catalyst had iodine value of 72.2 and slip point of 34.5°C; thus, the reclaimed nickel catalyst established its superiority over the parent catalyst in hydrogenation of peanut oil for 1.5 h under the test conditions.

The results of this research suggest efficacy of digestion with 3 N mixture of HCl and HNO₃ (3:1, v/v) at 100°C for 3 h (spent catalyst : acid mixture :: 1 : 6, w/v) for recovery of nickel from the spent catalyst and also the efficacy of reduction of the recovered nickel formate in refined peanut oil with kieselguhr support (50 : 43 : 7, w/w) under a stream of hydrogen at 260°C for 2 h for obtaining the reclaimed catalyst of desirable hydrogenation activity.