

EVALUATION OF REGENERATED NICKEL CATALYST *Part-IV*

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The soybean oil after hydrogenation by the local and the imported catalyst shows saturated fatty acids (32.8% and (34.4%) whereas unsaturated fatty acids (67.2%) and (65.6%) respectively. Secondly the clarity, bleachability, filtration time, iodine value and melting point of hydrogenated oil are the same either with the imported or the locally prepared nickel catalyst from the spent nickel catalyst.

Key words: Extended surface, Nickel catalyst, Spent nickel.

Introduction

The nickel can be claimed as one of the best metals for the creation of extended surface which attains active sites [1] possessing varying degree of unsaturation among the hydrogenation catalysts. In the heterogeneous system of nickel catalyst the adsorption [2,3] of hydrogen gas over unsaturated fatty acids in triglycerides is carried out in a complex form, then the step of desorption takes place to regenerate the catalyst with the formation of selected hydrogenated products.

The nickel catalyst prepared on the pilot plant Part-III has now been evaluated in the presented paper by comparative studies. The hydrogenation of soybean oil was carried out on an industrial scale [4] by the use of fresh locally prepared and of imported nickel catalyst in one of the batches under the same conditions such as the pressure of hydrogen, time for hydrogenation and filtration time. In another batch of hydrogenation of soybean oil, a mixture of fresh and used catalyst of locally prepared and of imported nickel catalyst was consumed under the same above mentioned conditions for comparative studies of local and imported nickel catalyst. In addition to it the gas liquid chromatography of latter samples was also accomplished to find out the percentage of unsaturated fatty acids of soybean oil before and after hydrogenation for comparative studies and eventually to determine the quality of the locally prepared nickel catalyst. The semi-solid plastic product names as Vanaspati ghee procured with locally prepared and imported nickel catalyst was also compared with standard specifications in order to visualize the quality of the locally prepared nickel catalyst.

Materials and Methods

1. *Hydrogenation of Oil by Locally prepared Nickel catalyst* [5]. The refined and bleached soybean oil (100 gm) was taken in a round bottom flask of capacity (500 ml) with an arrangement of stirrer, thermometer pocket, gas in let and outlet tube for hydrogen gas. The oil in the flask is heated on

an isomente to 120° and embedded nickel (0.5 gm) is added at this temperature with continuous stirring and then hydrogen gas is passed through at the temperature of 150°. The temperature is further increased to 180° which is kept constant for 3 hr, to complete the process of hydrogenation which is testified by the slip point of 37° of the material taken out of the batch. The heating process is stopped on achieving the slip point and the product is cooled to 100° to carry out filtration for the removal of the catalyst.

Saponification of Hydrogenated oil and methylation of fatty acids [6-7]. The hydrogenated oil (0.5g) was refluxed with 0.5 N ethanolic potassium hydroxide solution (8 ml) for three hr. The fatty acids were liberated on reacting with 2N sulphuric acid after the separation of unsaponifiable matter by diethyl ether. The fatty acids (400 mg) were converted into methyl esters (300 mg) by refluxing with dry methanol (6 ml) and 1% w/w sulphuric acid for 2 hr.

Thin Layer Chromatography [8]. The slurry of silica gel (30 gm) was prepared with distilled water (25 ml) to prepare thin layer chromatograms (20 cm x 20 cm) of thickness (0.25mm) for the purification of methylated acids (100 mg) after their activation by heating at 105°C for 60 min. The solvent system used for the development of these chromatograms was ether : hexane mixture (1:9 v/v). The non destructive locating reagent 2,7 dichlorofluorescein was used to have purple yellow coloured bands under an ultraviolet light at 254 μ m. The bands of purified methyl esters were scratched out and the material from silica gel was eluted by ether which was distilled to get pure methyl esters of the fatty acids. The silver nitrate (16.7%) impregnated thin layer chromatography was applied after the purification of methyl esters for the identification of saturated, mono and diunsaturated fatty acid as methyl esters which showed pink colouration with the same locating reagent and solvent system as used above.

Infrared spectrophotometry [9]. The purity of fatty acids before and after esterification was confirmed by infrared spectrophotometry. (Beckman IR model 5A). The

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adsorption was observed at 1350 cm^{-1} (CH_3 bend), 1460 cm^{-1} (CH_2 bend), 2860 cm^{-1} (CH_3 stretch), 2940 cm^{-1} (CH_2 stretch), 1700 cm^{-1} (stretch) and 1740 cm^{-1} ($\text{C}=\text{O}$ stretch).

Gas liquid chromatography [10]. The Instrument, Pye Unicam 204 Series having hydrogen flame ionization detector was used for the identification of methyl esters by the comparison of their retention times with the known methyl esters, using a column ($152.4\text{ cm} \times 0.95\text{ cm}$) on diatomite (80-100 mesh) at 200° with a flow rate of 40 ml per min. of nitrogen as a carrier gas. The percentage of each component of fatty acid was determined by triangulation.

Results and Discussion

The source of nickel in Pakistan is hardly available except the spent nickel catalyst or the imported nickel sulphate for the preparation of nickel catalyst. However, the production of nickel catalyst can be continued so far as the nickel catalyst for hydrogenation or nickel sulphate for electroplating is imported or the nickel metal has been explored in Pakistan. Keeping in view the availability of spent nickel catalyst in Pakistan, efforts have been made to utilize the spent nickel catalyst for the production of nickel catalyst to fulfil the demand of the country and save the foreign exchange spent on import of nickel catalyst. The parameters studied on laboratory scale for the recovery of fat by solvent, leaching of nickel as nickel sulphate and intermediate compounds etc. have been applied on pilot plant for the regeneration of nickel catalyst by wet method [11]. Efforts have been made for the designing and fabrication of most of the pilot units made of stainless steel to develop local technology leading to the production of nickel catalyst prior to its industrialization. The importance of technology can not be realized unless the product is evaluated upto the mark. However, the imported fresh and used nickel catalyst G-53 (W. Germany) and calcicate E-215-F (U.S.A.) have been compared with the locally prepared nickel catalyst (RGPSR), for hydrogenation of soybean oil under the same conditions (Table 1).

The colour, bleachability, FFA, Iodine value, melting point, hydrogenation period and filtration time before and after hydrogenation of soybean oil have been studied on industrial scale to have comparison of imported and locally prepared nickel catalyst just to have a clear picture about the quality of the locally prepared nickel catalyst. The fresh as well as used samples of three catalysts have been used under similar conditions to evaluate the locally prepared nickel catalyst (Table 2).

The (Table 2) reflects that the clarity, bleachability, filtration time, iodine value, melting point of soybean oil after hydrogenation either by the fresh or used imported nickel

TABLE-1 CONDITIONS FOR HYDROGENATION OF SOYBEAN OIL

S.No.	Description	Conditions
1.	Batch size	8.00 m.tons ($4' \times 1''$)
2.	Catalyst fed at	140°
3.	Gas pressure	1.5 Kg/cm ²
4.	Gas Injection temperature	150°
5.	Heating stopped at temperature	160°
6.	Filtration temperature	85°
7.	Maximum temperature attained	190°
8.	Melting point of catalyst G-53	59.5°
9.	Melting point of catalyst (Calcicate E-215 F)	61.0°
10.	Melting point of catalyst (REGPSR)	67.0°

TABLE-3 EVALUATION OF NICKEL CATALYSTS ON THE BASIS OF GAS LIQUID CHROMATOGRAPHY

Fatty Acids	Fatty Acids %age of soybean oil before hydrogenation	Fatty acids %age of soybean fat after hydrogenation PCSIR (REGPSR) Catalyst 21.0%	Imported (G-53) 23.0%
C _{14:0}	0.4	1.6	1.3
C _{16:0}	17.5	25.7	27.1
C _{18:0}	2.9	5.5	6.0
C _{18:1}	24.6	50.5	50.7
C _{18:2}	46.9	16.7	14.9
C _{18:3}	7.7	-	-

catalyst is almost the same as of locally prepared fresh or used nickel catalyst from the spent nickel catalyst. The percentage of free fatty acids of the hydrogenated soybean oil accomplished by fresh local catalyst is 0.13% and 0.7% higher than the imported catalysts (G-53) and (Calcicate-E-215-F) respectively. The comparative studies have also been carried out with used local catalyst which has shown 0.25% and 0.16% higher free fatty acids than the imported one (calcicate-E-215-F). It means that even the FFA of imported samples is not according to standard specification (0.25%). So the local sample as regards to this argument cannot be devalued. Similarly the hydrogenation period of fresh local sample is 9.52% and 16.25% higher than imported fresh samples of (G-53) and (Calcicate-E-215-F) respectively.

The hydrogenation period of used local sample is 10.0% and 4.76% higher than the used imported samples of (G-53) and (Calcicate-E-215-F) respectively. It can be visualised that the difference of hydrogenation period of the locally prepared nickel catalyst and (Calcicate-E-215-F) is not significant.

The little higher hydrogenation period and the percentage of free fatty acid of hydrogenated product can be interpreted due to the less percentage of nickel content (21.0%) of the locally prepared embedded nickel catalyst than the imported one having nickel content (23.0%) and secondly the nickel

TABLE 2. PHYSICO-CHEMICAL CHARACTERISTICS OF SOYBEAN OIL HYDROGENATED BY G-53 (W.GERMANY) AND CALCICATE E-215-F (USA) AND LOCALLY PREPARED (REGPSR) NICKEL CATALYST

No. Ni.Catalyst used Per 8 ton batch	Colour in 1" Cell		Bleach-		F. F. A. before hydro- gena- tion	F. F. A. after hydro- gena- tion %	Increase in F.F.A. %	Hydro- gena- tion time Hrs. Mnts	Filtration time Hrs. Mnts.	Iodine value before hydro- gena- tion.	Iodine value after hydro- gena- tion.	Melt- ing point C°	
	Before hydro- gena- tion Y R	After hydro- gena- tion Y R	ability %	ability %									
1. G-53 6.0kg fresh.	19.0	1.8	5.0	0.4	75.676	0.14	0.33	0.19	5-15	1-40	128	69.2	36.0
2. G-53 2.0Kg fresh + 12.0 Kg used.	17.0	1.3	4.0	0.3	76.667	0.08	0.33	0.25	5-00	1-45	128	69.8	36.0
3. Calcicate E-215-F 6.0Kg fresh +	16.0	1.7	4.0	0.4	75.757	0.11	0.39	0.28	5-20	1-50	128	68.9	36.0
4. Calcicate-E-215-F 2.0Kg fresh + 12.0 Kg. used.	17.0	1.3	4.0	0.3	76.667	0.14	0.42	0.28	5-15	2-00	126	69.5	36.0
5. Ni. REGPSR 6.0Kg fresh.	15.0	1.5	4.0	0.4	73.333	0.14	0.46	0.32	5-45	1-45	128	69.6	36.0
6. Ni.REGPSR 2.0Kg fresh + 12 Kg used.	16.0	1.3	4.0	0.3	75.862	0.14	0.58	0.44	5-30	2-00	128	68.8	36.0

catalyst had been prepared by the wet method and the imported one being prepared by dry method, may have some better characteristics. The imported nickel catalysts contain nickel content 23.0%. Activated fullers earth 12.0% fat 65.0% whereas locally prepared nickel catalyst has nickel content 21.0%, fullers earth 12.0% and fat 67.0%. Summing up the argument and by considering the merits and demerits of the locally prepared nickel catalyst in the light of (Table 2), it is concluded that the locally prepared nickel catalyst is as good as imported one.

The testing and evaluation of used nickel catalyst was accomplished not only on an industrial scale, but was also verified by carrying out gas liquid chromatography of hydrogenated samples by locally prepared nickel catalyst (REGPSR) and imported catalyst (G-53) as shown in (Table 3). The gas liquid chromatography was carried out after saponification of the oil, methylation, purification and infrared spectroscopy, photometry of methyl esters. This table shows that the soybean oil contains saturated fatty acids (20.80%) and unsaturated fatty acid (79.2%). The oil after hydrogenation by the local and imported catalyst shows saturated fatty acid content of 32.8% and 34.4% whereas unsaturated fatty acid content amounts to 67.2% and 65.6% respectively. So these results indicate the successful results of the locally prepared nickel catalyst. It is concluded that the selective hydrogenation by locally prepared nickel catalyst is as good as by the imported one.

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