



Use and regeneration of nickel oxide for desulfurization of fuel oil
by Paul A Haas

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering at Montana State College
Montana State University
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Abstract:

The use of nickel oxide in the presence of hydrogen for the desulfurization of a fuel oil and the regeneration of spent nickel catalyst was investigated. The effects of temperature, space velocity, physical condition of catalyst, recycle, and hydrogen rate were studied. Spent catalyst was treated by various methods and the materials produced tested for activity as desulfurization catalyst.

The desulfurization unit consisted of an adjustable rate oil feed pump, a combination preheater and reactor, a condenser system, an exhaust system, and an arrangement for collecting and recycling the oil. A fluid regenerator for the oxidation of spent catalyst with air was also constructed. The nickel oxide acted as a chemical reagent to combine with the sulfur in the oil to produce nickel sulfide. Temperature proved not to be an important variable for this process. Less than 50 per cent of the nickel oxide present in any of the catalyst tested was converted to nickel sulfide before the desulfurization reaction ceased. This cessation of activity was not due to mechanical blocking of the catalyst pores as the conversion to nickel sulfide was no greater for powdered nickel oxide than for nickel oxide pellets. The amount of desulfurization depended on the contact time and seemed to be independent of whether this contact time was obtained by one pass at a low space velocity or several recycles at a higher space velocity. The hydrogen rate was not an important variable although high hydrogen rates reduced the amount of desulfurization.

The hydrogen reduced some of the nickel oxide to free nickel.

Free nickel is an active desulfurization agent under the conditions used and may have been the desulfurization agent for this process. The oxidation of nickel sulfide with air produced nickel sulfate which had no activity as a desulfurization agent. Nickel oxide prepared by decomposition of nickel hydroxide and nickel carbonate precipitated from solutions could not be activated with air or hydrogen to produce an active desulfurization catalyst.

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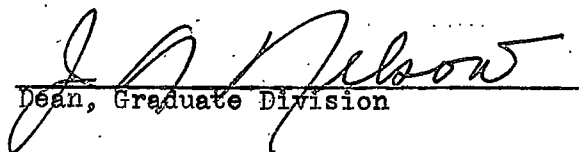
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ABSTRACT

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Introduction

The presence of sulfur in fuel oil is objectionable and the amount of sulfur may have an important effect on the value of the oil. A high sulfur oil tends to be corrosive to the equipment in which it is handled and used; and when the oil is burned, the sulfur dioxide produced may form sulfurous acid with the water of combustion. The sulfurous acid may be further oxidized to sulfuric acid.

Increasing demand for oil has led to the increased production and use of high sulfur crudes such as those produced in the West Texas, Rocky Mountain, and California areas. A fuel oil produced from these crudes may be of very good quality except for its sulfur content. An economical method of reducing the amount of sulfur in such oil without adversely affecting the other qualities would be valuable.

The sulfur in oil may be present as free sulfur, hydrogen sulfide, mercaptans, thioethers, disulfides, thiophanes, or thiophenes. The free sulfur or hydrogen sulfide can be removed by distillation or washing^s. The exact nature of the other sulfur compounds present in any given sample of oil is usually hard to determine. Mabery (7) carried out some of the earliest investigations in this field. When a crude is fractionated, the sulfur generally appears in greater concentration in the higher boiling fractions. Thus, a straight run fuel oil or gas oil will contain a higher percentage of sulfur than a straight run gasoline or naphtha from the same crude. Also, the sulfur compounds in the higher boiling fractions are generally more stable

and harder to remove. The largest part of the sulfur in the fractions boiling above the gasoline range from a high sulfur crude seems to be present in cyclic compounds. McKittrick (8) found that the sulfur in a naphtha from a cracked California Midway crude was mostly thiophenic.

There are many processes for removing sulfur from gasoline. Variations of acid or alkali washing and various catalytic desulfurization processes are the most commonly used. However, most of these processes are not satisfactory for removing sulfur from fuel oil. The use of sulfuric acid for removing sulfur from fuel oil obtained from a high sulfur crude is impractical because of high acid consumption and high oil loss. The processes involving caustic washing are effective on mercaptans, but have little effect on cyclic sulfur compounds. Destructive hydrogenation is effective in removing the sulfur compounds, but is an expensive process. Catalytic desulfurization would seem to be the most promising process for commercial use. Catalytic methods usually remove the sulfur by converting it to hydrogen sulfide. The addition of hydrogen may make a catalytic desulfurization process more effective and may reduce the amount of unsaturation of the product.

Nickel compounds or free nickel are active catalysts for many reactions. M. H. Gwynn (3) (4) has patents on the preparation and use of catalysts for the hydrofining of oils. These concern the use of black oxides, particularly nickel oxide, with hydrogen for the desulfurization of hydrocarbon distillates. The nickel or nickel compounds may be catalysts acting to remove the sulfur as hydrogen sulfide, or may be reagents according to the following reaction:



Hereafter, the desulfurization agents containing nickel will be referred to as catalyst without the implication that they do not change chemically during the process, i.e., the term "nickel catalyst" will refer to a material which may act as a true catalyst or as a chemical reagent.

This investigation was concerned with the use and regeneration of nickel catalysts. The effects of temperature, space velocity, physical condition of the catalyst, recycle, and hydrogen rate were investigated. Further investigation of a variable was discontinued when it was felt the results indicated that untested values of the variable would not give better desulfurization.

Nickel compounds are not cheap and the desulfurization of a fuel oil with nickel catalyst would be practical only if the weight of oil desulfurized per weight of catalyst were high. As part of this investigation, spent catalyst was treated by various methods and the products tested to determine their activity as desulfurization catalysts.

The Comparison Unit

Figure 1 is a drawing of the apparatus called the Comparison Unit. The comparison unit was designed so that various catalysts could be tested under specified conditions of temperature, space velocity, hydrogen rate, and quantity of oil. The oil was recycled and samples could be taken when desired.

The reactor body was a piece of 25 mm glass tubing with the female section of a 29/42 ground glass taper joint on the top and the male section of a 35/25 ball joint on the bottom. The total length including joints was about 17 inches. A glass thermowell stuck up into the reactor with its opening about $1\frac{1}{2}$ inches above the bottom joint. An iron-constantan thermocouple was used with a Leeds and Northrup potentiometer calibrated directly in degrees Centigrade. The reactor body was mounted in an 11 inch length of $1\frac{1}{2}$ inch standard steel pipe. The pipe was wrapped with asbestos tape and then with a heating coil that had a maximum output of 750 watts at 130 volts. A Variac was used to control the voltage input to the coil and thus control the temperature of the reactor. The unit was insulated with another layer of asbestos tape and asbestos mud. With the method of assembly used, the glass reactor could be replaced when damaged without disturbing the heating coil.

The male section of a 29/42 glass taper joint was necked down for the hydrogen feed line and provided with a side arm inlet for the oil feed. The hydrogen supply was a cylinder provided with a pressure

regulator and needle valve. The hydrogen rate was measured with a calibrated glass orifice and manometer.

The lower joint of the reactor was clamped to a glass water cooled condenser about 15 inches long. This condenser was connected to an ice cooled finger condenser by means of a ball joint. A stopcock was provided to take off samples or to remove water that condensed with the oil. The condensed oil flowed out a side arm through another stopcock into a graduated 500 ml separatory funnel used as an oil reservoir. A tube with its lower end near the bottom of the separatory funnel was provided for blowing in air for mixing the oil. The bottom of the oil reservoir was connected to the oil pump through a three-way stopcock used to take samples. A Merkle-Korff type bel- lows pump was used. Stainless steel tubing of 1/8 inch outside diameter was used for the oil feed line.

The uncondensed gases passed through the ice cooled condenser to the exhaust line. A cadmium chloride bubbler was used for some runs to trap the H_2S given off. A wet test gas meter was used in the exhaust line. A small separatory funnel, not shown in Figure 1, was put in the exhaust line to trap entrained liquids not removed by the ice cooled condenser. The material collected was returned to the oil reservoir through a line connected from the bottom of the separatory funnel.

The Fluid Reactor System

A unit was constructed to investigate the possibility of regenerating the nickel catalyst by oxidation with air in a fluid regenerator. Two glass fluid reactors were obtained and one of them set up in the system shown in Figure 2. When the glass reactor failed from thermal strains, a metal reactor was constructed from standard pipe nipples and reducing couplings and used with the same air preheater and catalyst feed systems.

The fluid reactors were constructed according to designs modified from plans obtained from the Phillips Petroleum Company. The reactors had cylindrical upper sections 12 to 15 inches long and $2\frac{1}{2}$ to 3 inches in diameter. The center sections were 20 to 25 inches long and tapered to the cylindrical lower sections which were 6 inches long and less than one inch in diameter. The reactors were wound in turn with asbestos tape, the heating coils, and a second layer of asbestos tape. A coil with a resistance of 22 ohms and a maximum output of 750 watts at 130 volts was used for heating the glass reactor. The metal reactor used a similar heating coil on the tapered part of the reactor and a 110 ohm, 230 volt, 600 watt coil on the upper part of the unit. These heating coils were used with Variacs to control the heat input to the reactor. Single thermowells extending into the middle of the reactor with their openings near the tops of the reactors were used. The glass reactor was insulated with pipe insulation; the metal reactor with magnesia slabs and asbestos mud. The exit at the top of the fluid reactor was con-

nected to an exhaust line.

The feeding of catalyst into the reactor was done in batches by an air injector. The catalyst hopper was a piece of 1 inch standard pipe connected to the side arm of a small tee with a reducing coupling. Air, controlled by a needle valve, flowed straight through the tee into the reactor. The catalyst hopper was capped to prevent the loss of air and provided with a bypass to equalize the air pressure above and below the catalyst.

The bottom of the reactor was connected to a tee with the combustion air line connected to one arm of the tee and a thermowell installed in the other. The air line was wrapped with asbestos tape and a 22 ohm, 750 watt, 130 volt heating coil, and then covered with asbestos mud insulation. The air rate was controlled with a needle valve and measured with a calibrated glass orifice and manometer. The metal to glass connections were made with glycerin and litharge joints wherever the temperatures were too high for rubber hose.

The air preheater was an old reactor filled with steel scrap and ball bearings. The reactor body was a 24 inch length of 3 inch standard pipe with a cap welded on the lower end and half of a flange fitting on the upper end. The other half of the flange fitting had a nipple and a cap tapped for the air inlet. The cap welded on the lower end was tapped for the exit line. The reactor was wound with asbestos tape and heating coils, and covered with magnesia slab and asbestos mud insulation. Two 750 watt, 130 volt, 22 ohm heating coils

and one 110 ohm, 600 watt, 260 volt heating coil were used with Variacs to control the heat input to the air preheater. Thermowells of 1/4 inch standard pipe were welded in the reactor at positions 4, 8, and 12 inches from the bottom.

Iron and constantan thermocouples were used with a Leeds and Northrup potentiometer to measure temperatures. The potentiometer was calibrated directly in degrees Centigrade.

Procedure for Comparison Unit

A. General Procedure for Runs

The stainless steel screen used as a packing support in the reactor was inserted in the reactor from the bottom. A two inch layer of 1/8 inch diameter fish spines was used in the reactor below the catalyst. Twenty grams of catalyst were used for each run. The space above the catalyst to the top joint was filled with fish spines. The reactor system was assembled as shown in Figure 1, the glass joints lubricated with stopcock grease and clamped, and the Variac turned on. The desired amount of oil was weighed out and put in the oil reservoir. The pump was set at approximately the desired rate and primed by pumping the bellows by hand. The water to the condenser was turned on and the finger condenser filled with ice. After the reactor had reached the operating temperature, the oil pump and a stop watch were started. The hydrogen pressure regulator and needle valve were set to give the manometer reading corresponding to the desired hydrogen rate.

The temperature and hydrogen rate were checked frequently during runs and kept at the desired values. The finger condenser was kept full of ice and excess liquid water siphoned out. The oil was kept mixed by bubbling air through a tube extending into the oil reservoir. Samples were taken from the three-way stopcock in the line between the oil reservoir and the pump. The weights of the samples were recorded along with the temperatures and volumes indicated by the gas meter for runs where the gas meter was used.

At the end of a run, the oil was drained through the three-way stopcock and weighed. After the reactor had cooled, it was disassembled from the system and emptied. The catalyst was separated from the packing material, weighed, and stored in a sample bottle. The space velocity was determined by weighing the amount of oil pumped in a measured length of time by the pump at the setting used for the run.

B. Details of Procedures for Individual Runs

The reactor was prepared for Run 3 by pouring the powdered catalyst over 1/8 inch diameter fish spines filling half of the reactor. A plug of glass wool was used in the bottom of the reactor. The pressure drop was too large using this arrangement and repeatedly blew loose the ground glass taper joint at the top of the reactor. The charge for Run 4 was prepared by wetting 40 grams of 1/16 inch diameter fish spines with oil and mixing them with 20 grams of powdered catalyst. This method of catalyst support was successful and was used for the other runs with powdered catalyst.

The high hydrogen rate used in Run 6 blew part of the catalyst into the condenser. Run 7 was attempted using a plug of glass wool to prevent the loss of catalyst, but the pressure drop through the reactor was too great. Run 8 was successfully made at the conditions of Run 7, using glass helices in place of the glass wool plug.

Procedure for Fluid Regeneration

Fluidization was studied in the unjacketed glass reactor at room temperature. Particles larger than 60 mesh did not fluidize well while catalyst losses in the exhaust gases became serious with catalyst passing a 200 mesh screen. A wide range of air velocities gave good fluidization without large losses with 60 to 100 mesh catalyst particles.

Before starting a run, the feed was put in the catalyst feed hopper. The air to the preheater was turned on and adjusted to the desired rate. The Variacs were turned on and adjusted until the fluid reactor and the air entering the fluid reactor were at the operating temperature. The catalyst was fed into the reactor with air. The air rate and temperature were kept at constant values for the duration of the run. Then the air and Variacs were shut off. After the fluid reactor had cooled, the bottom connection was loosened and the product of the run removed. The feed hopper was checked to insure that all the catalyst had been fed into the reactor at the start of the run.

Analytical Methods

The sulfur contents of the samples of oil were determined by the lamp sulfur method as described in the ASTM manual of standards. (2) Four sets of apparatus were used with water aspirators to provide suction for air for combustion. The air supply was obtained from outdoors to prevent errors from NH_3 , HCl , H_2S , or other gases which might be present in the laboratory air. Approximately two milliequivalents of sodium carbonate solution were used for each determination. Modified methyl orange indicator was used. All of the samples for the lamp sulfur determinations were dried with calcium chloride and filtered.

Standard quantitative methods were used for analyses of the catalysts. Nickel was determined by the volumetric cyanide method. The sulfates were determined by the standard gravimetric precipitation as barium sulfate. The volumetric benzidine method for sulfate was found to be satisfactory for the soluble sulfate extracted with a water leach. Sulfides were oxidized to sulfates and determined gravimetrically.

The ASTM distillation procedure for light hydrocarbon fractions (1) was applied to samples of oil to obtain the distillation data tabulated in Table V. The specific gravities of these samples were determined with a Westphal balance.

Procedure for Chemical Regeneration

The chemical regeneration of nickel catalyst was carried out by two similar methods. One method involved the production of nickel hydroxide and the other involved nickel carbonate.

The initial step was the dissolving of spent nickel catalyst in acid. When nitric acid was used, foaming was bad and brown oxides of nitrogen were given off. Hydrochloric acid gave a more moderate reaction with less fuming. Part of the catalyst was ground up, but it was found that this was not necessary for solution. The solutions of nickel chloride and nickel nitrate were filtered to remove carbon silica and other insoluble material.

A solution of nickel nitrate and nickel chloride was made alkaline with sodium hydroxide to precipitate nickel hydroxide. A solution of nickel nitrate was made alkaline with potassium carbonate to precipitate nickel carbonate. Both precipitates were voluminous and seemed to contain large percentages of water. The precipitates were filtered and washed with water. The filter cakes were mixed with water to form uniform slurries which were allowed to stand 12 hours. These slurries were filtered and the filter cakes washed with water. The nickel hydroxide was dried 24 hours in an oven at 140-160°C. The dried material was partly black and partly green. The hydroxide was formed into 1/8 inch diameter pellets by the Harshaw Chemical Company. The nickel carbonate was dried 24 hours at 105-110°C. The nickel

hydroxide pellets and the dried nickel carbonate filter cake were activated and tested in the comparison unit as described in Table II.

Materials

The oil used for all the desulfurization runs was a straight run fuel oil which was refined from a Wyoming crude at the Husky Oil Company refinery in Cody, Wyoming. Inspection data for this oil are included in Table V. The oil was light colored with a sulfur content of slightly over two percent and an average molecular weight of about 200. Work done at the Husky Oil Company laboratories indicated that the sulfur in this oil was nearly all in the form of the homologues of thiophene and thiophane. Removal of 30 per cent of the oil by extraction with sulfur dioxide removed 75 per cent of the sulfur. About 0.7 per cent sulfur seemed to be the minimum obtainable by this method.

Reagent grade chemicals were used for the analytical work and for the chemical regeneration of the nickel catalyst. Hydrogen was obtained in cylinders from the National Cylinder Gas Company.

Most of the fresh catalyst was manufactured by the Harshaw Chemical Company. Some samples were prepared by M. H. Gwynn (3) (4). Spent catalyst and some samples of regenerated catalyst were obtained from the Husky Oil Company. All of the catalyst was in the form of 1/8 inch diameter pellets when received.

Methods for Calculations

The catalyst and oil losses were calculated on the basis of the inputs to the runs. A negative catalyst loss indicated an increase in weight by the catalyst. The hydrogen rates are given in standard cubic feet per hour. The volumes indicated by the wet test meter during calibrations were corrected for pressure, temperature, and the vapor pressure of water. The amounts of catalyst and oil were measured by weight. All space velocities were therefore expressed as grams of oil per gram of catalyst per hour.

Sulfur balances were made for the runs on the comparison unit to correct for the effects of losses and for the oil removed for samples. The oil losses were distributed as equally as possible over the time intervals for a run. A corrected weight of oil for the end of each time interval was obtained by subtracting the weight of the sample and the distributed loss. The difference between the weights of sulfur at the beginning and the end of a time interval (based on the same weight of oil) was considered to be the amount of sulfur removed during that interval. The total amount of sulfur removed during a run was tabulated in Table III as grams of sulfur removed per gram of catalyst.

The quantitative calculations were of the type ordinarily used for the methods of analysis employed. The calculations for the lamp sulfur determinations were of the following form:

$$\begin{aligned}(\text{ml of Na}_2\text{CO}_3)(\text{N of Na}_2\text{CO}_3) &= (\text{meq. of Na}_2\text{CO}_3) \\(\text{ml of HCl})(\text{N of HCl}) &= \frac{(\text{meq. of HCl})}{} \\ \text{Difference} &= (\text{meq. of S}) \\ \frac{(\text{meq. of S})(1.60)}{\text{Wt. of oil burned}} &= \text{Percent S in oil}\end{aligned}$$

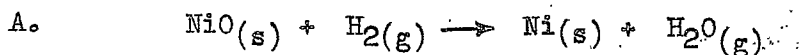
"N" stands for normality, "ml" for milliliters, and "meq." for milliequivalents.

Thermodynamic Calculations

The data in Table I were collected and used to make thermodynamic calculations for various reactions involving nickel compounds. Most of the values of ΔH are from Lange (6). Many of the values of S are from Hougen and Watson (5). The Bureau of Mines Bulletin No. 434 (9) was used for some values, particularly for the values for nickel compounds. The values of ΔH and ΔS for the reactions listed were calculated. The calculations were made to see whether these reactions were thermodynamically possible at various temperatures. The accuracy desired did not require calculations to compensate for variations in S and ΔH with temperature. The values for ΔS at 298°K and ΔH at 291°K were used in the formulas:

$$\Delta F = \Delta H - T\Delta S$$

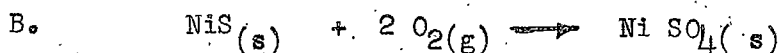
$$T_{NE} = \frac{\Delta H}{\Delta S}$$



ΔH_F	-58.4	0	0	-57.8	$\Delta H =$	0.6
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S	9.20	31.23	7.12	45.13	$\Delta S =$	11.82
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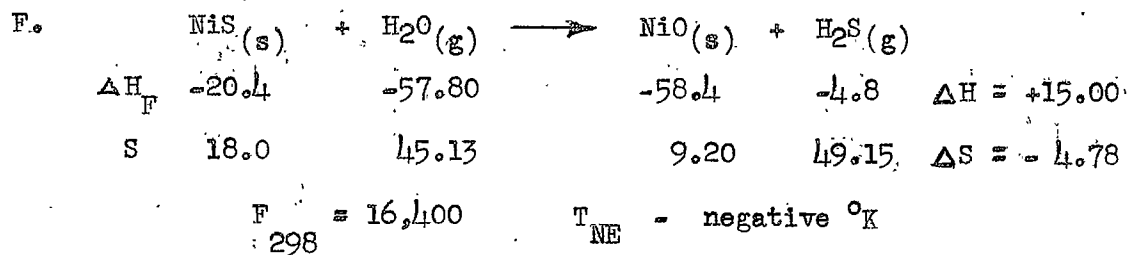
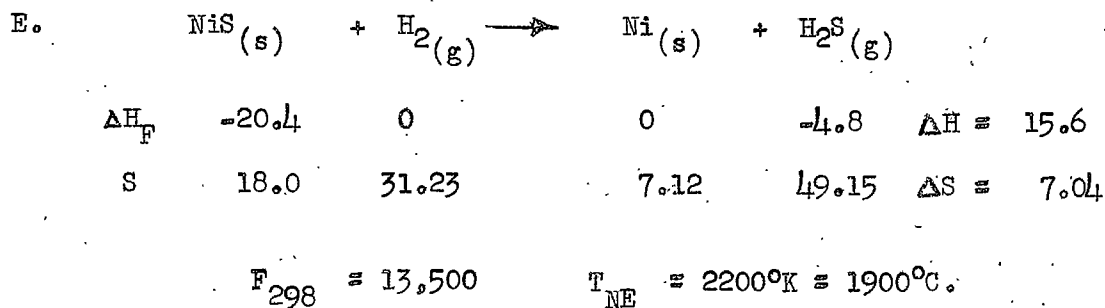
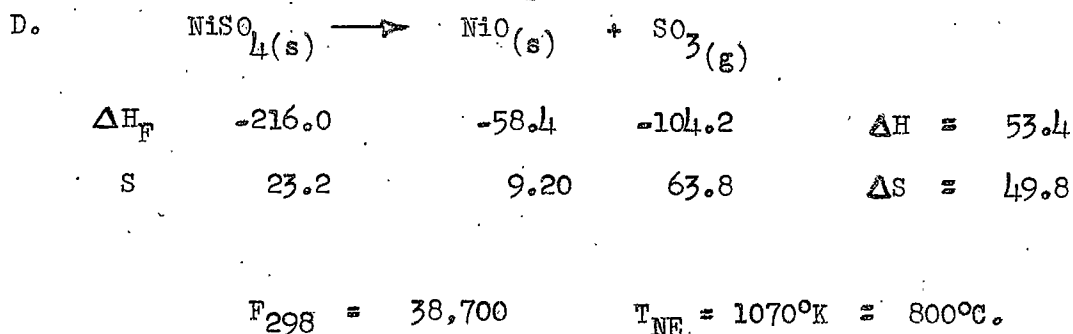
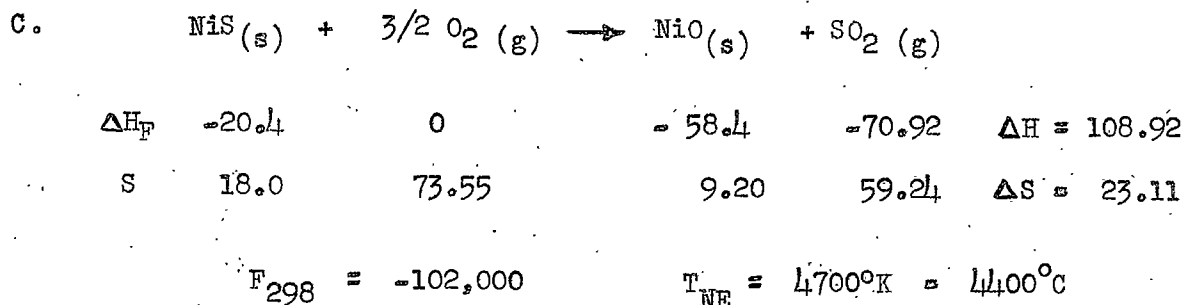
$F_{298} =$	-2,900	$T_{NE} =$	51°K	$=$	-220°C
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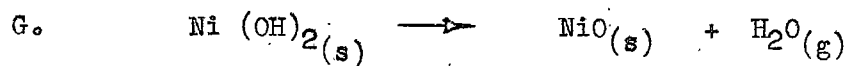


ΔH_F	-20.4	0	-216.0	$\Delta H =$	195.6
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S	18.0	98.06	23.2	$\Delta S =$	92.86
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$F_{298} =$	-168,000	$T_{NE} =$	2100°K	$=$	1800°C
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ΔH_{F} -129.8 -58.4 -57.80 $\Delta H = 13.6$

S 15 9.20 45.13 $\Delta S = 39.33$

$F_{298} = 1,900$ $T_{\text{NE}} = 346^{\circ}\text{K} = 70^{\circ}\text{C}$

Results

For the first runs, charges of 420 grams of oil and 20 grams of catalyst were selected. This amount of oil was approximately the capacity of the oil reservoir and contained approximately the amount of sulfur that would be required for complete conversion of 20 grams of nickel oxide to nickel sulfide by a quantitative reaction. With the space velocity of 20.9, the oil was cycled over the catalyst about once per hour.

The effects of temperature were investigated by Runs 1 and 2. The temperature of 675°F used for Run 2 was close to the maximum that could be used without excessive cracking. White fumes due to cracking were observed at 625°F for Runs 10, 11, and 18. The ASTM distillation for Run 10 (see Table V) did not show the low first drop temperature that would indicate the presence of lights from cracking. The desulfurization seemed to be independent of temperature at 625°F and above. Since the process does not take place at room temperature, there is some temperature range below 625°F where the desulfurization does depend on temperature. A temperature of 625°F was selected for the operating temperature for the investigation of other variables.

Effective desulfurization seemed to have almost ceased at about 1.53 per cent sulfur in the oil at the end of six hours for Runs 1 and 2. Runs 5 and 6, made with smaller amounts of oil, showed that the nickel catalyst could lower the sulfur content of the oil below this

value. Personnel at the Husky Oil Company laboratories were able to obtain oil with as low as 0.1 per cent sulfur from large quantities of nickel catalyst and the fuel oil used for this investigation. The use of a cadmium chloride bubbler in the exhaust line showed that very little of the sulfur removed from the oil was given off as hydrogen sulfide. Examination of the spent catalyst from runs showed that the nickel oxide was converted to nickel sulfide. The nickel oxide was a chemical reagent reacting almost quantitatively with the sulfur compounds in the oil. As a chemical reagent, one gram of nickel oxide would require $(32)/(58.69+16)$ or 0.43 grams of sulfur for complete conversion to nickel sulfide. On Runs 1 and 2, made with pelleted pure nickel oxide, the catalyst removed less than 30 percent of this theoretical amount of sulfur before effective desulfurization stopped. The catalyst used in Run 17 was approximately 70 per cent nickel oxide. It removed sulfur equivalent to 45 per cent conversion of the nickel oxide present to nickel sulfide before the run was ended.

Nickel sulfide has a larger molecular volume than nickel oxide. It might have been possible for the nickel sulfide mechanically to block the pores of the catalyst and thus prevent the nickel oxide in the center of the pellets from coming in contact with the oil. This was checked in Runs 3 and 4 by using 60 to 200 mesh catalyst. This material was prepared by grinding pure nickel oxide pellets with a mortar and pestle. The final results were almost identical for pelleted and powdered catalyst. The powdered catalyst exposed no more

active material to the oil than the pellets.

Run 9 was made with a space velocity of approximately half of the value used for previous runs. The results indicated that the actual total contact time determined the amount of desulfurization. For Runs 5 and 9, approximately the same results were obtained by putting the oil through once at one space velocity or by putting it through twice in the same length of time at double the space velocity. The maximum space velocity that could be investigated was limited by the preheater section of the reactor. The minimum amount of heating and cooling would be required if a space velocity low enough to give the desired desulfurization in one pass were used. The space velocity of 20.9 used for the first runs was also used for Run 10 and thereafter, so the runs would have the same basis for comparison. With this space velocity, the oil was cycled over the catalyst at least once per hour. At the Husky Oil Company laboratories, a space velocity of 0.2 was used with the feed oil used for this investigation to obtain nine volumes of oil per volume of catalyst with the sulfur content of the oil below 0.5 per cent. This amount of desulfurization corresponds to the removal of less than 0.1 gram of sulfur per gram of catalyst.

The air bubbler used to mix the oil in the oil reservoir was not installed until Run 3. Therefore, when the samples were taken for Runs 1 and 2, they may not have been truly representative of the oil. Samples taken without mixing might have had higher sulfur contents

than the true averages because the desulfurized oil from the reactor tended to form layers on top of the oil already in the reservoir. The largest amounts of sulfur were removed during the first two time periods for all runs. Part of the sulfur in the oil was easy to remove and it would be removed first. The activity of the nickel catalyst dropped off as it was partially converted to nickel sulfide. The combination of high catalyst activity and easy to remove sulfur compounds caused the high initial rates of desulfurization. The grams of sulfur removed per gram of catalyst was lower for runs made with smaller amounts of oil as shown by comparison of Runs 5 through 9, with Runs 1, 2, and 4. Apparently part of the catalyst was active enough to desulfurize some of the sulfur compounds, but could not remove the sulfur from the more refractory compounds left after partial desulfurization. It would seem that a scheme of counter-current desulfurization using partially spent catalyst on fresh oil and fresh catalyst on partially desulfurized oil would have advantages.

The high hydrogen rates used in Runs 6 and 8 seemed to reduce the amount of desulfurization. Since the nickel oxides are not active unless they are treated with hydrogen, there should be an optimum rate between no hydrogen and the high rate used for Runs 6 and 8. The disadvantage of the high hydrogen rate was probably that it carried the oil through faster and reduced the actual contact time. The hydrogen rate of about 2.5 SCF of hydrogen per hour used for most of

the runs was 10 to 15 times the quantitative amount of hydrogen that would be required for complete desulfurization according to the following reaction:



It was noticed that catalyst removed from a cold reactor after a run became hot when first exposed to air. It was also noticed that all used catalyst was attracted by a magnet. None of the fresh catalysts had this property. Further investigations showed that a magnet attracted fresh catalyst heated with hydrogen, but had no effect on fresh catalyst heated in air. The strength of this attraction decreased after the catalyst had been out of the reactor for a few days. These observations led to the conclusion that some of the nickel oxide was reduced to free nickel by the hydrogen. Such a reaction is thermodynamically possible. (See thermodynamic calculations). Run 12, made with UOP Hydrogenation Catalyst, indicated that free nickel was an active desulfurization agent under the conditions used. Hydrogen alone was not effective in removing sulfur under the same conditions. The nickel catalyst was not an active desulfurization agent until it had been treated with hydrogen. The removal of 0.10 gram of sulfur per gram of catalyst by the UOP Hydrogenation catalyst compares favorably with the 0.112 and 0.113 grams of sulfur per gram of catalyst removed by the pure nickel oxide in Runs 1 and 2. From this, it would seem that free nickel produced by the reducing action of hydrogen may be the active desulfurization agent when nickel oxide

catalyst is used.

Thermodynamic calculations were made for various reactions which might be used to convert nickel sulfide to nickel oxide or free nickel. The treatment of nickel sulfide with hydrogen or steam to produce hydrogen sulfide and free nickel or nickel oxide are both thermodynamically unfavorable. Calculations also show that the oxidation of nickel sulfide with oxygen could produce either nickel sulfate or sulfur dioxide and nickel oxide. The nickel sulfate is stable after it is formed and could not be decomposed by heat except at temperatures that would sinter the catalyst. Runs 15, 16, 19, 20, and 21 showed that nickel sulfate had no activity as a desulfurization catalyst. Runs 16, 19, 20 and 21 are essentially duplicates of Run 15. In the catalysts tested, the nickel sulfide had been converted to nickel sulfate by oxidation with oxygen diluted with nitrogen, steam, and/or sulfur dioxide. Some active material should have been left in the spent catalyst before oxidation, but the regenerated pellets showed no signs of activity for removing sulfur.

Nickel oxide can be prepared by thermal decomposition of nickel hydroxide, nickel carbonate, or nickel nitrate. Both nickel hydroxide and nickel carbonate are insoluble in water. Nickel sulfide can be put into solution by digestion with acids or by oxidation to nickel sulfate which is water soluble. As part of this investigation, spent catalyst was put in solution with hydrochloric and nitric acids. Nickel hydroxide and nickel carbonate were precipitated from these

solutions, filtered, washed, and dried. The precipitates were decomposed to nickel oxide by heat. Activation was carried out at high and low temperatures in streams of air or hydrogen. None of the materials produced were active desulfurization catalysts.

A run was made in the fluid regenerator at 340°C for one hour with air as the fluidizing gas. The feed was 60 to 100 mesh spent catalyst. No odor of sulfur dioxide was noticeable in the exit gas. When samples of the product were dissolved in hydrochloric acid, the odor of hydrogen sulfide could be detected, but the amount given off was small. The sulfate extracted from the product with a hot water leach was called soluble sulfate and the sulfate requiring digestion with acid for solution was called insoluble sulfate. The product of the run was 7.20 per cent soluble sulfate and 7.83 per cent insoluble sulfate. This would correspond to 24.2 per cent nickel sulfate if all the sulfate were in the form of nickel sulfate. The total sulfate content of the spent catalyst used as feed was under one per cent. The product of the run on the fluid regenerator was 53.4 per cent nickel and 19.4 per cent material insoluble in 1-1 hydrochloric acid.

Summary

There is a considerable range of temperature, 600 to 675°F, where the desulfurization is independent of temperature. The maximum temperature that can be used is limited by cracking.

The nickel oxide desulfurizes by acting as a chemical reagent combining with the sulfur in the oil to produce nickel sulfide. All of the samples of catalyst tested became inactive when less than 50 per cent of the nickel oxide present was converted to nickel sulfide. This cessation of activity was not due to mechanical blocking of the catalyst pores, but must have been due to part of the nickel oxide being in an inactive form. The existence of inactive forms of nickel oxide was demonstrated when nickel oxide prepared by chemical methods was found ineffective as a desulfurization catalyst.

The desulfurization depends directly on the total contact time and seems to be independent of whether this contact time was obtained by one pass at a given space velocity or several recycles at a higher space velocity. The combination of high initial catalyst activity and easy to remove sulfur compounds caused a high rate of desulfurization at the start of a run which rapidly dropped off until the remaining nickel oxide was ineffective in removing the refractory sulfur compounds which were left in the oil.

The hydrogen rate did not seem to be a critical factor except that high hydrogen rates carried the oil through faster and thus reduced the

contact time. The hydrogen reacted with nickel oxide to produce some free nickel. Free nickel was an active desulfurization agent under the conditions used and may have been the active desulfurization agent for this process.

The oxidation of nickel sulfide with air produced nickel sulfate which had no activity as a desulfurization agent. Nickel oxide prepared by decomposition of nickel hydroxide and nickel carbonate precipitated from solutions could not be activated with air or hydrogen to produce active desulfurization catalyst.

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Literature Cited.

- (1) ASTM STANDARDS, Part 5 (1949) D 86-46
- (2) ASTM STANDARDS ON PETROLEUM PRODUCTS AND LUBRICANTS, 272,
D 90-41-T (1941)
- (3) Gwynn, M. H. U. S. Patent 2,073,578 - March 9, 1937.
- (4) Gwynn, M. H. U.S. Patent 2,174,510 - October 3, 1939.
- (5) Hougen, O. A. and Watson, K. M. CHEMICAL PROCESS
PRINCIPLES Vol. II, John Wiley & Sons, Inc.
New York, N. Y. 1947
- (6) Lange, N. A. HANDBOOK OF CHEMISTRY, Sixth Edition,
Handbook Publishers, Inc. Sandusky, Ohio, 1946
- (7) Mabery, C. F. Am. Chem. J. 13 232 (1891)
- (8) McKittrick, D. S. Ind. Engr. Chem. 21 585-592 (1929)
- (9) United States Bureau of Mines Bulletin No. 434 (1941)

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