United States Patent [19]
Brunn et al.

[11] **3,859,200**
[45] **Jan. 7, 1975**

[54] **RESIDUAL OIL HYDRODESULFURIZATION PROCESS AT REDUCED HYDROGEN RATE WITH AMMONIA ADDITION**

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[73] Assignee: **Gulf Research & Development Company,** Pittsburgh, Pa.

[22] Filed: **Jan. 22, 1974**

[21] Appl. No.: **434,585**

[52] **U.S. Cl.** **208/216**
[51] **Int. Cl.** **C10g 23/02**
[58] **Field of Search** 208/216, 211, 209, 210

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Primary Examiner—Delbert E. Gantz
Assistant Examiner—G. J. Crasanakis

[57] **ABSTRACT**

A process for hydrodesulfurizing an asphaltic oil in the presence of a catalyst comprising Group VI and Group VIII metals on alumina together with hydrogen and added ammonia. The process is controlled at least in part by decreasing the hydrogen flow rate to compensate for catalyst aging, thereby increasing the concentration of ammonia in the reaction gaseous atmosphere.

12 Claims, 10 Drawing Figures

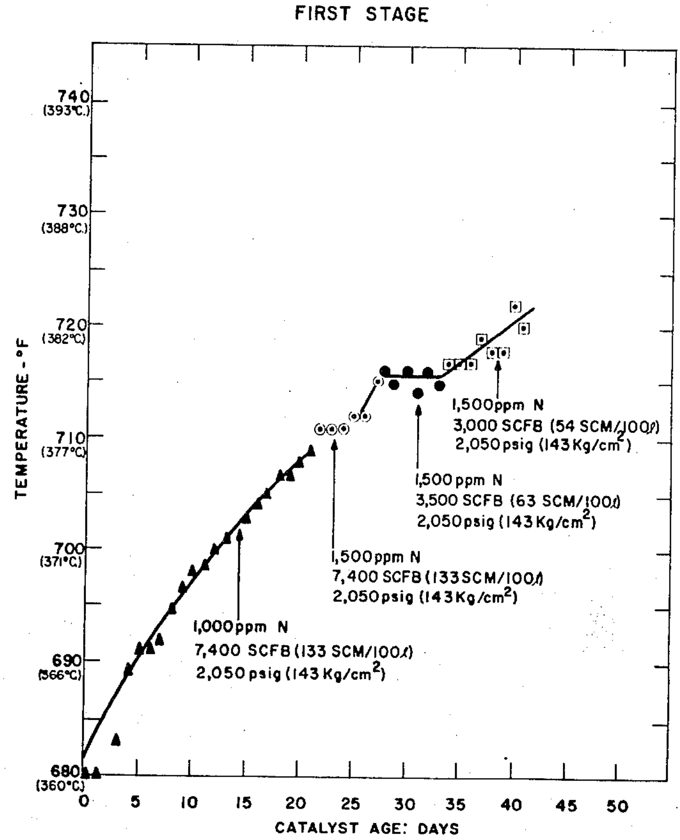


FIG. I

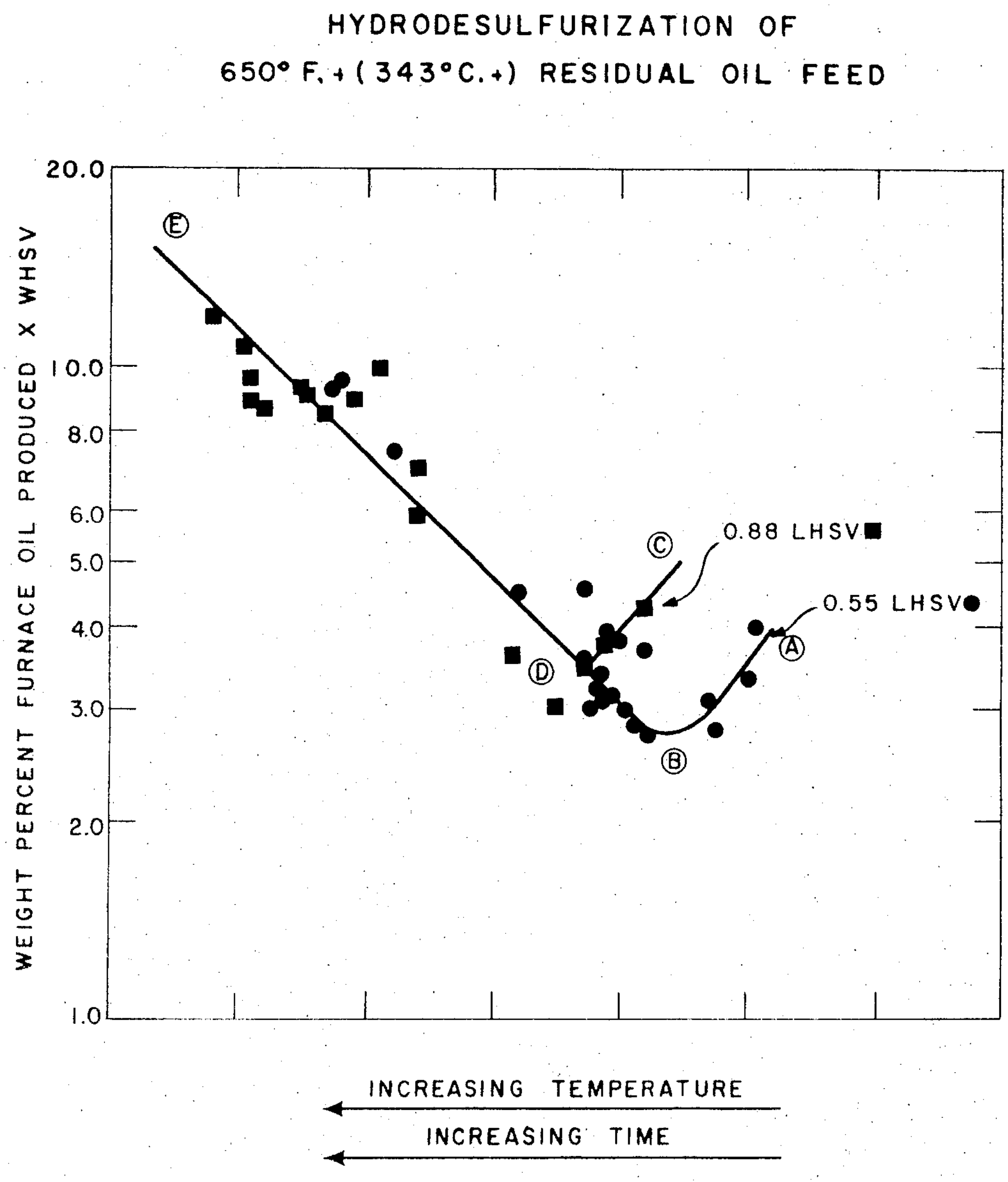

HYDRODESULFURIZATION OF
650° F.+(343°C.+) RESIDUAL OIL FEED
WEIGHT PERCENT FURNACE OIL PRODUCED X WHSV
20.0
10.0
8.0
6.0
5.0
4.0
3.0
2.0
1.0
Ⓔ
Ⓒ
Ⓓ
Ⓑ
Ⓐ
0.88 LHSV ■
0.55 LHSV ●
INCREASING TEMPERATURE
INCREASING TIME

FIG. 2

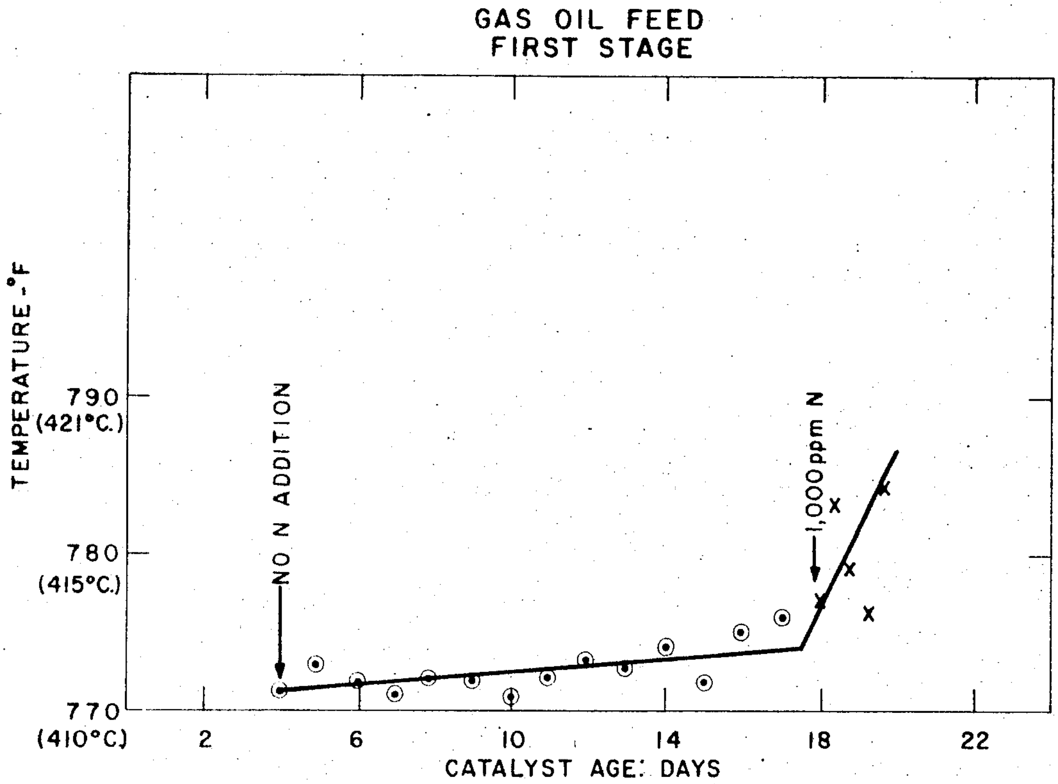

GAS OIL FEED
FIRST STAGE
TEMPERATURE - °F
790
(421°C.)
780
(415°C.)
770
(410°C.)
2
6
10
14
18
22
CATALYST AGE: DAYS
NO N ADDITION
1,000 ppm N

FIG. 3

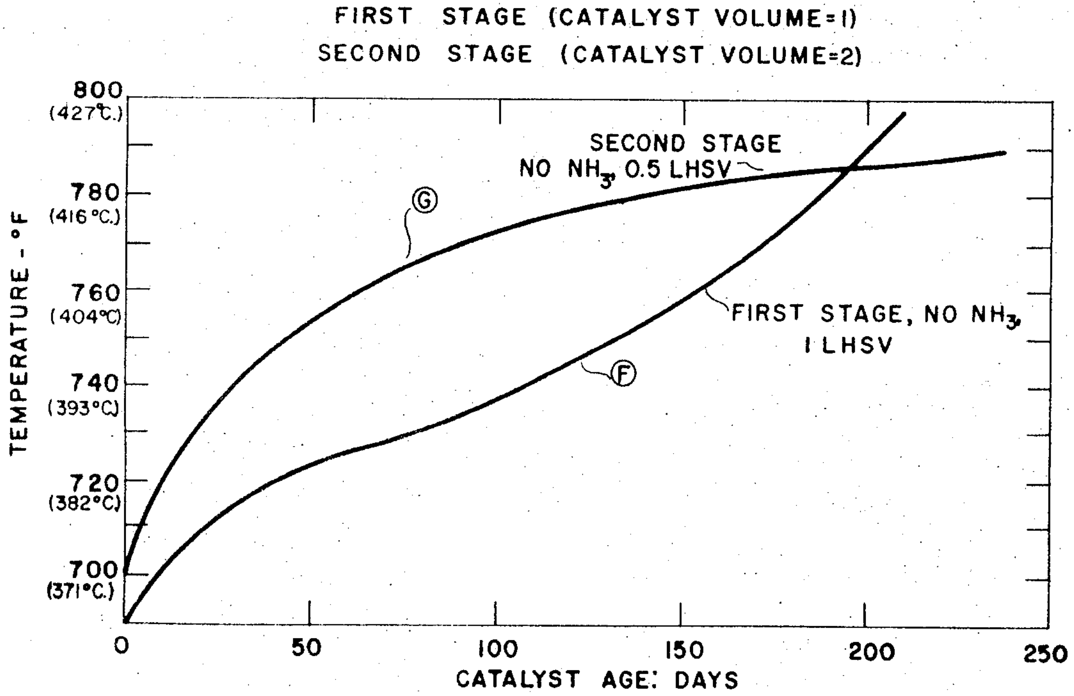

FIRST STAGE (CATALYST VOLUME=1)
SECOND STAGE (CATALYST VOLUME=2)
TEMPERATURE - °F
800
(427°C.)
780
(416°C.)
760
(404°C)
740
(393°C)
720
(382°C)
700
(371°C.)
0
50
100
150
200
250
CATALYST AGE: DAYS
SECOND STAGE
NO NH_3, 0.5 LHSV
G
FIRST STAGE, NO NH_3,
1 LHSV
F

FIG. 4

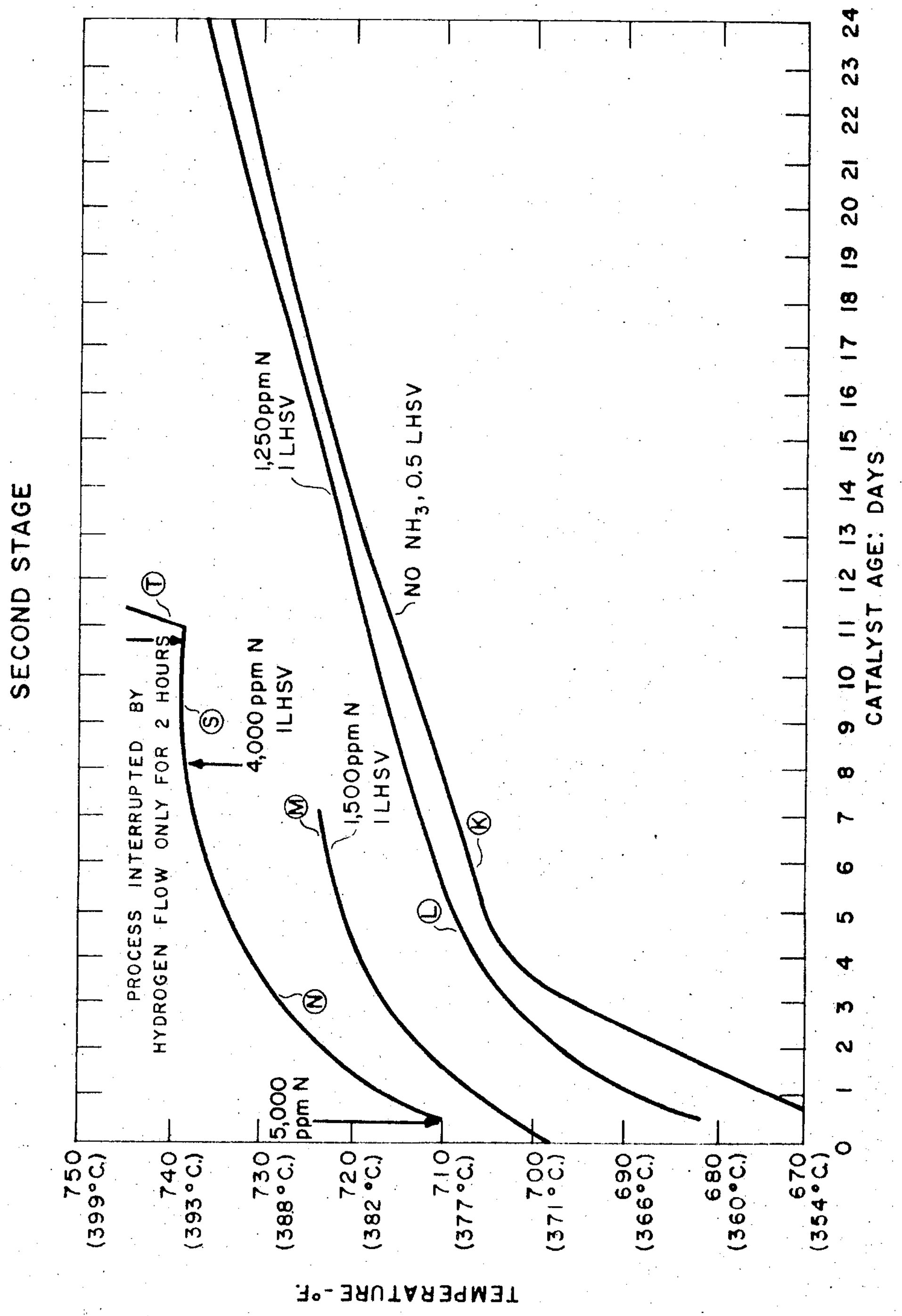

SECOND STAGE
TEMPERATURE-°F
750 (399°C.)
740 (393°C.)
730 (388°C.)
720 (382°C.)
710 (377°C.)
700 (371°C.)
690 (366°C.)
680 (360°C.)
670 (354°C.)
CATALYST AGE: DAYS
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
PROCESS INTERRUPTED BY HYDROGEN FLOW ONLY FOR 2 HOURS
Ⓣ
Ⓢ
4,000 ppm N 1 LHSV
Ⓜ
1,500 ppm N 1 LHSV
Ⓝ
5,000 ppm N
1,250 ppm N 1 LHSV
NO NH_3, 0.5 LHSV
Ⓛ
Ⓚ

FIG. 5

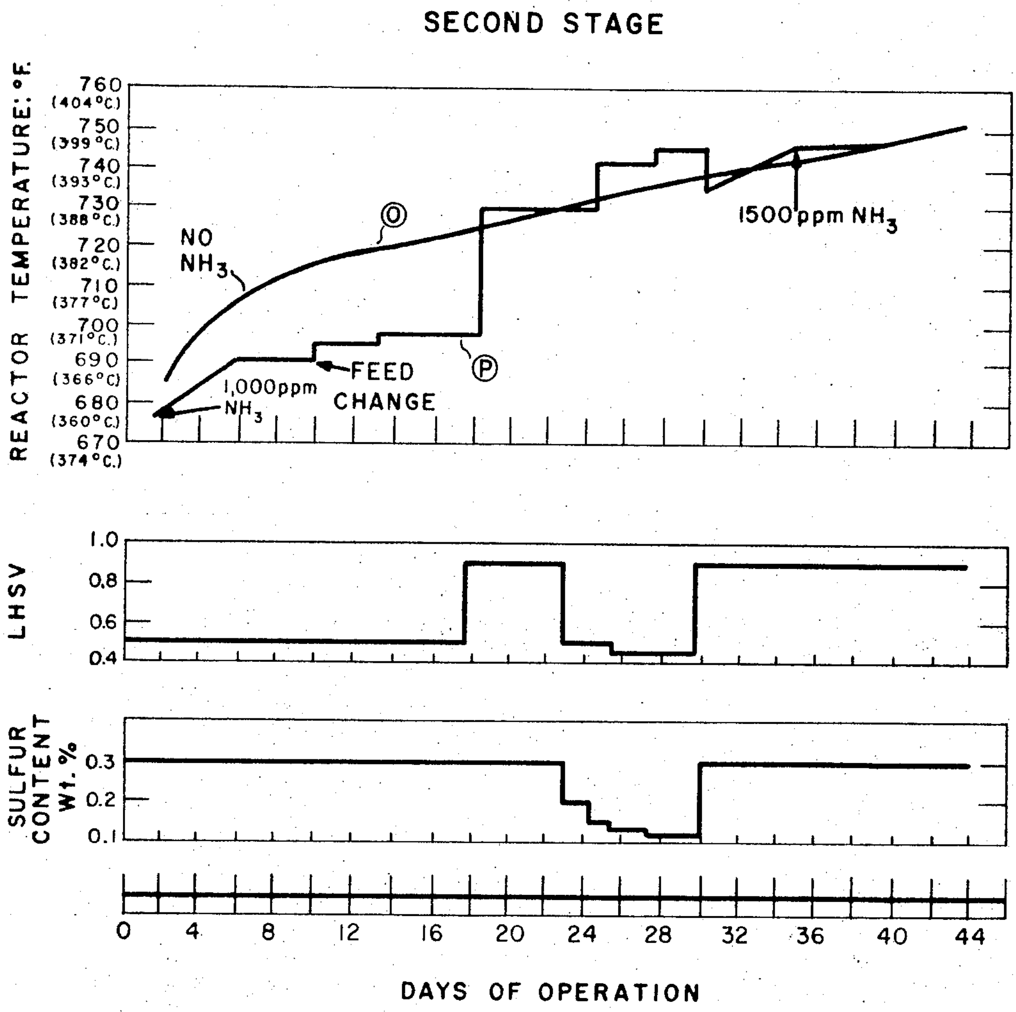

SECOND STAGE
REACTOR TEMPERATURE: °F.
760 (404°C.)
750 (399°C.)
740 (393°C.)
730 (388°C.)
720 (382°C.)
710 (377°C.)
700 (371°C.)
690 (366°C)
680 (360°C.)
670 (374°C.)
NO NH3
Ⓞ
Ⓟ
1,000 ppm NH3
FEED CHANGE
1500 ppm NH3
LHSV
1.0
0.8
0.6
0.4
SULFUR CONTENT Wt. %
0.3
0.2
0.1
0
4
8
12
16
20
24
28
32
36
40
44
DAYS OF OPERATION

FIG. 6

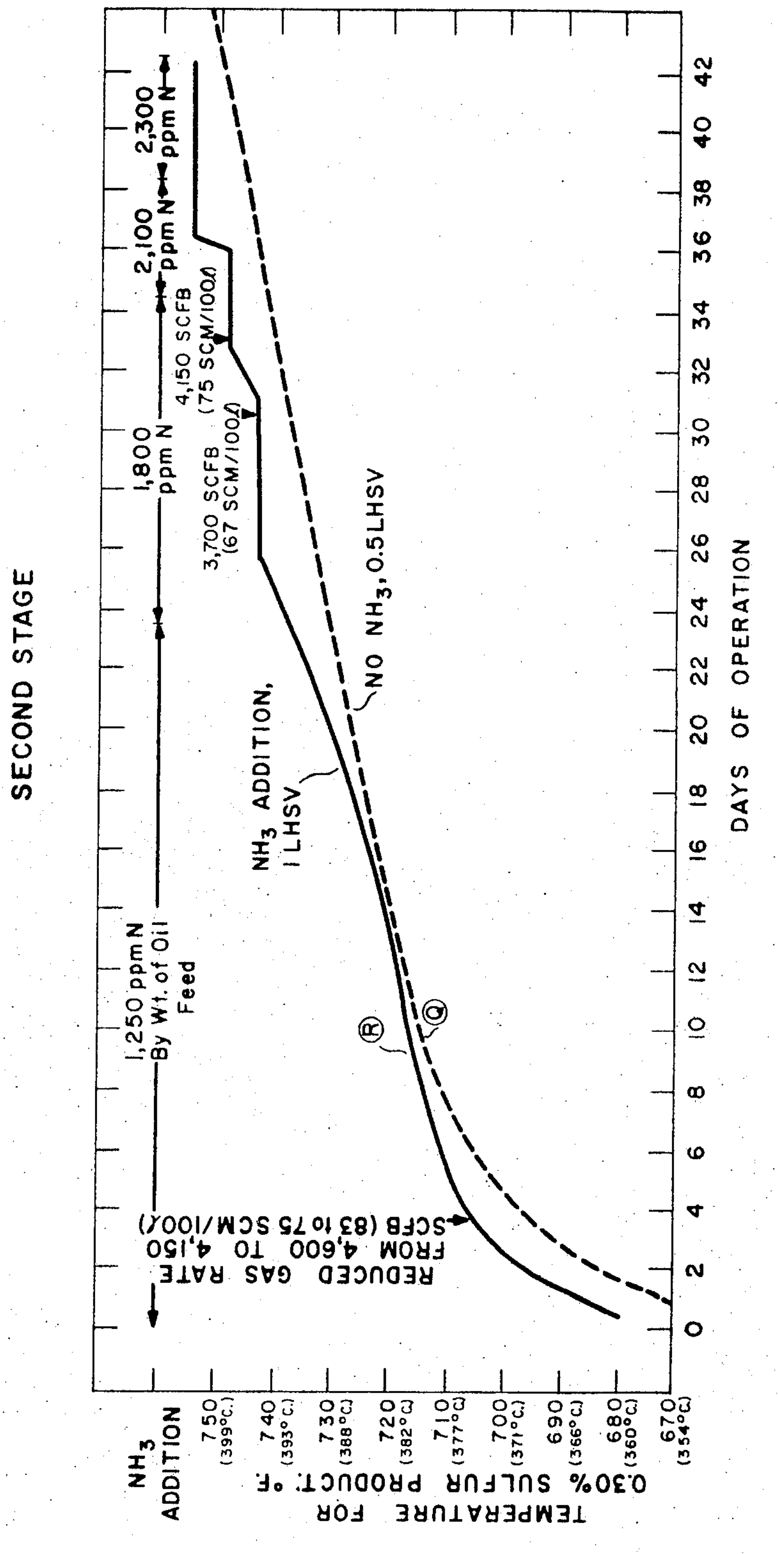

SECOND STAGE
1,250 ppm N By Wt. of Oil Feed
1,800 ppm N
2,100 ppm N
2,300 ppm N
REDUCED GAS RATE FROM 4,600 TO 4,150 SCFB (83 to 75 SCM/100ℓ)
3,700 SCFB (67 SCM/100ℓ)
4,150 SCFB (75 SCM/100ℓ)
NH3 ADDITION, 1 LHSV
NO NH3, 0.5LHSV
R
Q
NH3 ADDITION
TEMPERATURE FOR 0.30% SULFUR PRODUCT, °F
750 (399°C.)
740 (393°C.)
730 (388°C.)
720 (382°C.)
710 (377°C.)
700 (371°C.)
690 (366°C.)
680 (360°C.)
670 (354°C.)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
DAYS OF OPERATION

FIG. 7

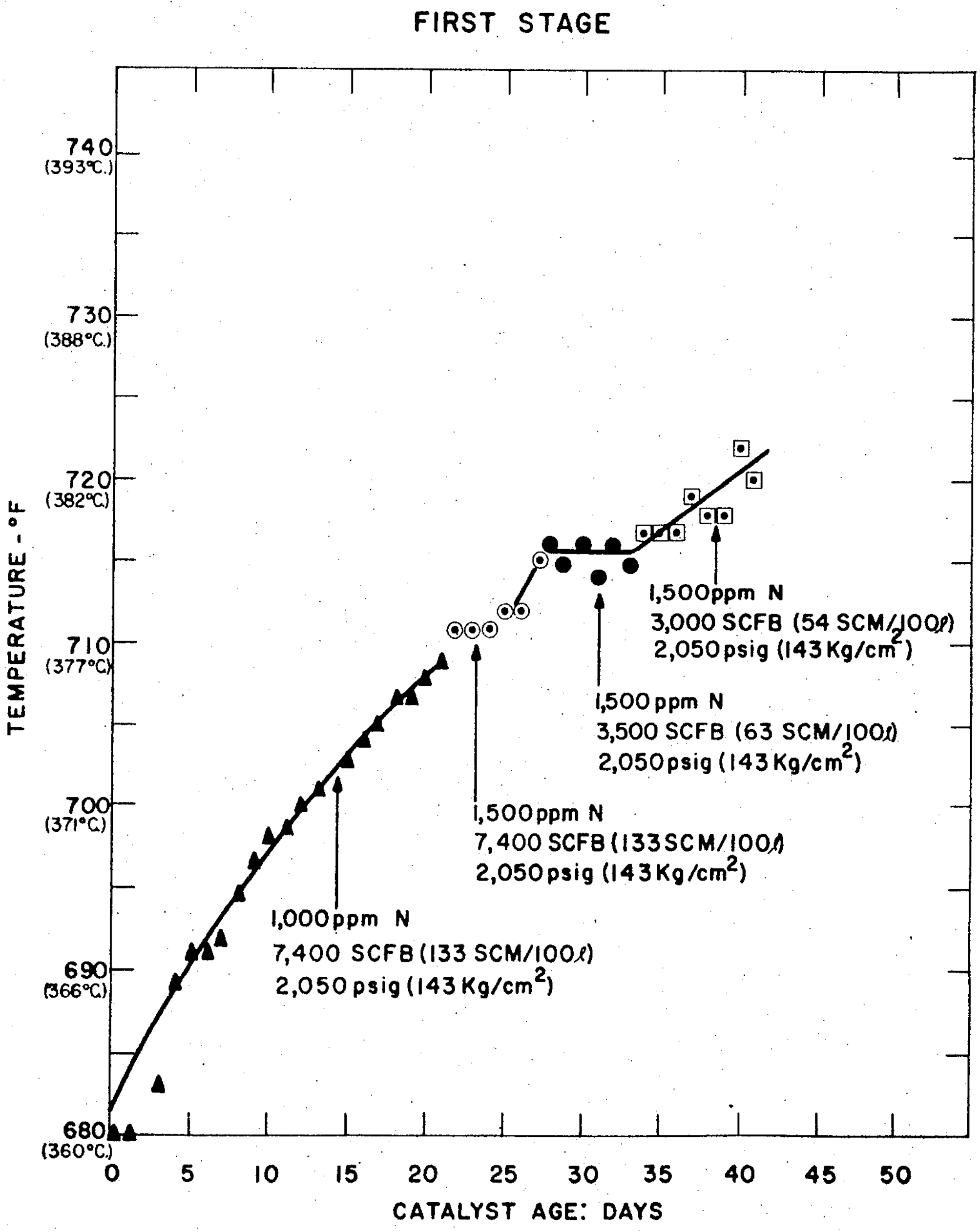

FIRST STAGE
TEMPERATURE - °F
740 (393°C.)
730 (388°C.)
720 (382°C.)
710 (377°C.)
700 (371°C.)
690 (366°C.)
680 (360°C.)
0
5
10
15
20
25
30
35
40
45
50
CATALYST AGE: DAYS
1,000 ppm N
7,400 SCFB (133 SCM/100 ℓ)
2,050 psig (143 Kg/cm^2)
1,500 ppm N
7,400 SCFB (133 SCM/100 ℓ)
2,050 psig (143 Kg/cm^2)
1,500 ppm N
3,500 SCFB (63 SCM/100 ℓ)
2,050 psig (143 Kg/cm^2)
1,500 ppm N
3,000 SCFB (54 SCM/100 ℓ)
2,050 psig (143 Kg/cm^2)

FIG. 8

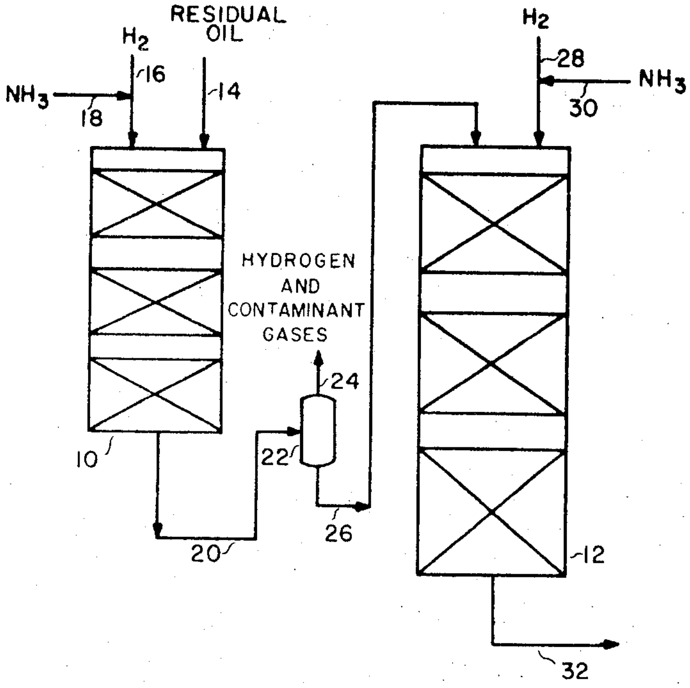

RESIDUAL OIL
H$_2$
16
14
NH$_3$
18
H$_2$
28
NH$_3$
30
HYDROGEN AND CONTAMINANT GASES
24
22
10
20
26
12
32

FIG. 9

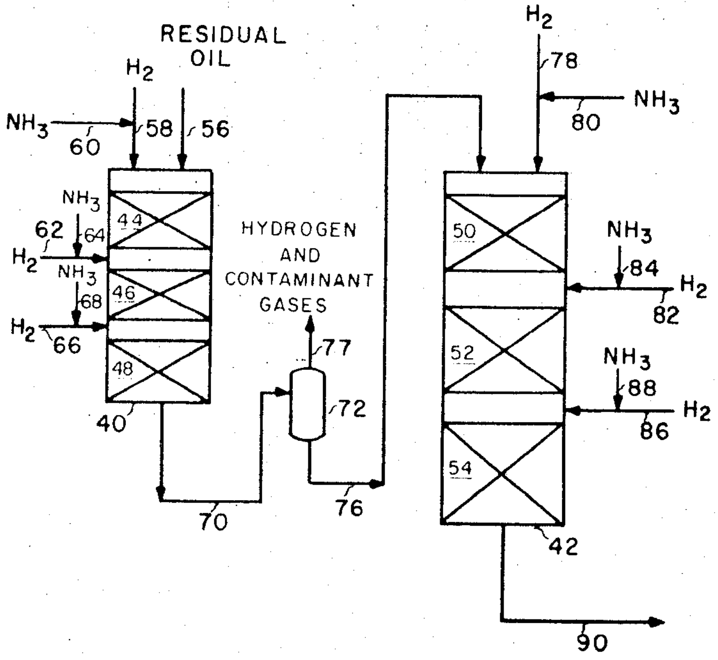
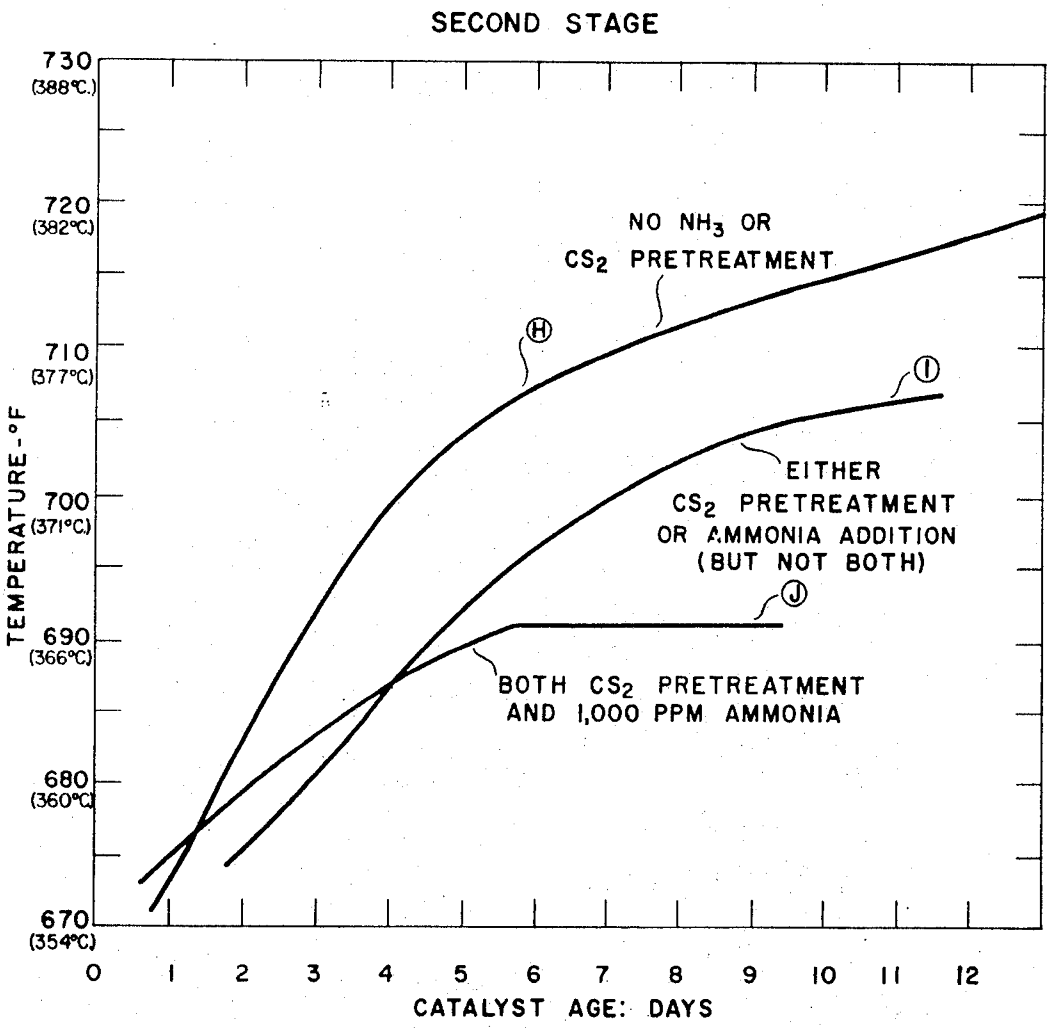

RESIDUAL OIL
H$_2$
58
56
NH$_3$
60
NH$_3$
64
62
H$_2$
44
NH$_3$
68
46
H$_2$
66
48
40
HYDROGEN AND CONTAMINANT GASES
77
72
70
76
H$_2$
78
NH$_3$
80
50
NH$_3$
84
H$_2$
82
52
NH$_3$
88
H$_2$
86
54
42
90

FIG. 10


SECOND STAGE
730 (388°C.)
720 (382°C)
710 (377°C)
700 (371°C)
690 (366°C)
680 (360°C)
670 (354°C)
TEMPERATURE - °F
0
1
2
3
4
5
6
7
8
9
10
11
12
CATALYST AGE: DAYS
NO NH3 OR CS2 PRETREATMENT
H
I
EITHER CS2 PRETREATMENT OR AMMONIA ADDITION (BUT NOT BOTH)
J
BOTH CS2 PRETREATMENT AND 1,000 PPM AMMONIA

RESIDUAL OIL HYDRODESULFURIZATION PROCESS AT REDUCED HYDROGEN RATE WITH AMMONIA ADDITION

This invention relates to a catalytic hydrodesulfurization process for removing sulfur from crude or residual petroleum oils, or from synthetic oils such as oils from tar sands, shale and coal, wherein ammonia or an ammonia precursor compound is injected into the reaction zone.

The present invention is particularly directed towards the hydrodesulfurization of a crude or asphaltic residual oil such as an atmospheric or vacuum reduced petroleum crude which contains the asphaltene fraction of the crude from which it is derived. The nickel, vanadium and sulfur content of the liquid charge can vary over a wide range. For example, for an atmospheric reduced crude nickel and vanadium can comprise 0.002 to 0.03 weight percent (20 to 300 parts per million) or more of the feed oil while sulfur can comprise about 2 to 6 weight percent of the oil. These are examples only and for some atmospheric and vacuum distilled crude residues the metals and sulfur levels can be higher. The feed oil generally contains nitrogen, a portion of which is converted to ammonia in situ. However, the injection of extraneous nitrogen over a fresh catalyst at start-of-run (SOR) in accordance with the present invention provides sufficient ammonia upstream in the catalyst bed to inhibit and moderate progressive coking of the catalyst bed with catalyst age, which coking otherwise would progressively proceed from the top downwardly through the catalyst bed. Normally, because of the low rate of nitrogen removal in residual oil hydrodesulfurization, sufficient ammonia is not present in the system to inhibit such coking.

The added ammonia precursor compound results in chemisorption of ammonia on the strong and weak acid sites of the catalyst, with greatest chemisorption occurring on the strong acid sites. It is an unexpected feature of this invention that ammonia chemisorption on the hydrodesulfurization catalyst inhibits hydrocracking activity and resulting coke formation without inhibiting desulfurization activity. Since hydrocracking activity and desulfurization activity are both dependent upon the acid sites on the catalyst support, it is unexpected that neutralizing these acid sites depresses one type of reaction utilizing these sites without depressing the other type of reaction also utilizing these sites.

A further unexpected feature of this invention is that controlled ammonia chemisorption causes the catalyst aging rate to be reduced or even stablized by reducing the hydrogen flow rate, within limits, as compared to a higher hydrogen flow rate. It is a highly unusual phenomenon of the present invention that process improvement can be achieved by reducing hydrogen flow rate when hydrotreating processes are almost universally improved by increased rather than decreased hydrogen flow rates. Another view of this unusual hydrogen flow rate phenomenon is that controlled levels of a relatively small amount of ammonia advantageously displace a relatively large amount of hydrogen, with the displacement advantage actually being lost if excessive hydrogen is present, which results in a low concentration of ammonia in the gas. A reason that hydrogen rate cannot be excessive is that the concentration of ammonia and hydrogen sulfide in the hydrogen are both important and reduction in hydrogen rate can advantageously increase ammonia concentration in the hydrogen gases.

The hydrodesulfurization process of this invention employs conventional residual oil hydrodesulfurization reaction conditions such as, for example, a hydrogen partial pressure of at least 750 or 1,000 pounds per square inch (52.5 or 70 kg/cm^2), generally, 1,000 to 5,000 pounds per square inch (70 to 350 kg/cm^2), preferably, and 1,000 to 3,000 pounds per square inch (70 to 210 kg/cm^2), more preferably. It is the partial pressure of hydrogen rather than total reactor pressure which determines hydrodesulfurization activity. Therefore, the hydrogen stream should be as free of other gases as possible and contaminated hydrogen gases are flashed from the first stage effluent followed by addition of fresh hydrogen to the flash residue when two hydrodesulfurization reactor stages are employed in series.

The gas circulation rate can be between about 2,000 or 3,000 and 20,000 standard cubic feet per barrel (36 or 54 to 360 SCM/100L), generally, preferably about 3,500 to 10,000 standard cubic feet per barrel (63 to 180 SCM/100L), or most preferably 3,500 to less than 7,400 standard cubic feet per barrel (63 to 133 SCM/100L) of gas preferably containing 85 percent or more of hydrogen. The mol ratio of hydrogen to oil can be between about 4:1 and 80:. Reactor temperatures can range between about 600° or 650° and 900°F. (316° or 343° and 482°C.), generally, and between about 690° and 800°F. (365° and 427°C.), preferably. The temperature should be low enough so that with a 650°F. + (343°C.+) feed oil, less than about 10, 15 or 20 percent of the feed oil which boils above 650°F. (343°C.) will be cracked to furnace oil or lighter, i.e. to materials boiling below 650°F. (343°C.). The liquid hourly space velocity in any reactor of this invention can be between about 0.2 and 10, generally, and between about 0.3 and 1 or 1.25 , preferably.

The catalyst employed in the process comprises sulfided Group VI and Group VIII metals on a non-cracking support such as alumina with the substantial absence of cracking components. Conventional Group VI and Group VIII metal combinations can be employed. Preferred catalysts are nickel-cobalt-molybdenum or cobalt-molybdenum or alumina. Examples of other metal combinations are nickel-tungsten and nickel-molybdenum. The support is a non-cracking alumina which is essentially free of silica, and which contains less than 1 weight percent silicon, generally, and preferably less than 0.5 or 0.1 weight percent of silicon.

Because of the non-cracking nature of the catalyst, the process conditions of the present invention provide a product oil (with or without ammonia addition) comprising more than 40 or 50 or more than 80, 85 or 90 percent by weight of material having a boiling point greater than the initial boiling point of the feed oil. Very little hydrocracking beyond what is required for desulfurization occurs in accordance with the present invention and therefore the hydrogen consumption will be generally in the range of only 150 to 1,500 and preferably in the range of 300 to 1,200 standard cubic feet per barrel of feed (2.7 to 27 and preferably 5.4 to 21.6 SCM/100L). The feed to the hydrodesulfurization reactor will generally have an initial boiling point of not less than 375°F. (191°C.) and will preferably have an initial boiling point of at least 620° or 650°F. (327° or 343°C.).

Thus, the amount of material obtained from the process whose boiling point is lower than the initial boiling point of the feed oil is less than 50 or 60 percent, generally, or preferably less than 10, 15 or 20 weight percent. A feed having an initial boiling point greater than 650°F. (343°C.) e.g. vacuum tower bottoms having an initial boiling point in the range of 750°F. to 900°F. (399° to 482°C.) or more may be employed in the process of the present invention. In that event, the amount of material obtained from the second hydrodesulfurization zone whose boiling point is below 650°F. (343°C.) will be less than 10 or 20 weight percent.

Tests were conducted to illustrate the ability of a nickel-cobalt-molybdenum or alumina catalyst of this invention to chemisorb ammonia. Tests were also conducted to illustrate the ammonia chemisorption ability of a similar catalyst after it had first been impregnated with sodium to reduce its acidity in advance of ammonia chemisorption. The characteristics of these catalysts are shown in the following table.

	Catalyst	
	NiCoMo on Alumina	Na Promoted NiCoMo on Alumina
Chemical analysis,Wt.%:		
Nickel	0.5	0.5
Cobalt	1.0	1.0
Molybdenum	8.0	8.0
Silicon	0.27	0.27
Sodium	0.09	0.09
Iron	0.02	0.02
Alumina	(1)	(1)
Physical inspections:		
Compacted Density, g/cc	0.69	0.72
Surface area, m²/g	194	181
Pore volume, cc/g	0.52	0.52
Pore size distribution, percent of P.V.:		
100–300 A radius	14	14
50–100 A radius	50	54
30–50 A radius	28	26
7–30 A radius	8	6
Surface acidity NH_3 adsorption, meq/g, °F.		
350 (177°C.)	0.62	0.44
400 (204°C.)	0.55	0.38
500 (260°C.)	0.43	0.285
600 (316°C.)	0.34	0.21
700 (371°C.)	0.27	0.16
800 (427°C.)	0.21	0.12
900 (482°C.)	0.16	0.09

(1) Difference

The above data show that an alumina supported catalyst of low acidity, even after its acidity is partially quenched by sodium impregnation, still retains sufficient acidity to chemisorb a significant quantity of ammonia. The data show that the quantity of ammonia adsorbed in both catalysts changes significantly with temperature increase, with the ammount of ammonia adsorbed on each catalyst being relatively great at low temperatures and descreasing with increasing temperrature. It is therefore an important feature of this invention that ammonia injection is employed in a process to produce a product of defined sulfur level requiring reaction temperature to progressively increase with catalyst age to compensate for catalyst deactivation. In this manner, the catalyst acid sites are provided with chemisorbed ammonia before temperatures for significant hydrocracking are reached at SOR so that both strong and weak acid sites, but primarily strong acid sites, are provided with chemisorbed ammonia. As catalyst aging progresses and reaction temperatures increase, an increasing quantity of ammonia is desorbed and this desorption occurs initially most easily from the weak acid sites and subsequently from stronger acid sites, providing progressively stronger catalyst sites for reaction purposes as catalyst age increases. Thereby, relatively weak catalyst sites are employed at start-of-run (SOR) and relatively strong catalyst sites are employed at end-of-run (EOR). Therefore, the stronger acid sites which are most apt to coke are not made available until the later stages of a catalyst cycle.

The advantage of ammonia injection in accordance with the present invention is due to interaction of ammonia with the alumina catalyst support but interaction of ammonia with the active hydrogenation metals on the alumina support to possibly form a metal ammonia complex is presumed to be detrimental to the hydrodesulfurization reaction and should be avoided entirely or to the greatest extent possible. Reaction of ammonia with the Group VI and Group VIII metals on the catalyst support will be avoided in part in accordance with this invention either by presulfiding these metals prior to process start-up or prior to ammonia addition. Presulfiding can occur in the presence of ammonia and hydrogen while maintaining a high hydrogen sulfide to ammonia ratio with a sulfur-containing gas oil or furnace oil sulfiding agent. Since presulfided Group VI and Group VIII metal sulfides tend to lose sulfur during a hydrotreating process if sufficient hydrogen sulfide is not present in the gas phase, it is also important that sufficient hydrogen sulfide is generated during the hydrodesulfurization process so that the average hydrogen sulfide concentration along the length of the reaction zone is equal to or greater than the average ammonia concentration along the length of the reaction zone. For example, if the hydrogen sulfide concentration at the inlet and outlet of a reaction zone is about 0 and 7,000 parts per million based on feed oil, respectively, the average ammonia concentration in the reaction zone must be less than about 3,500 parts per million. (At a second reaction zone inlet, it is usual for an amount such as 1,000 parts per million of hydrogen sulfide to be dissolved in the feed oil as the result of first stage desulfurization.) By maitaining a greater average concentration of hydrogen sulfide than ammonia in the reactor gases equilibrium is shifted towards the metal sulfide, which is active for desulfurization, instead of towards a metal ammonia complex. While the sulfide is the preferred active state of the catalyst metals, the reaction product of the catalytic metals and ammonia is considered to be relatively disadvantageous to the hydrodesulfurization reaction.

While it is relatively easy to maintain high hydrogen sulfide levels in a first hydrodesulfurization stage, particular caution is required to insure that hydrogen sulfide concentration is maintained above ammonia concentration in the second or third reactors of a series of hydrodesulfurization reactors, because these reactors hydrodesulfurize a previously desulfurized oil after flashing off gaseous reaction products and therefore treat a feed oil having a low concentration of sulfur, which sulfur is of a relatively refractory nature as compared to that processed in the first reactor of the series.

In the reactor system comprising a series of reactors, it is advantageous to remove by flashing the impure hydrogen from the first reactor effluent and charge fresh hydrogen to the second reactor in series in order to provide a high hydrogen partial pressure in the second reactor. If the hydrogen sulfide dissolved in the oil feed to the second reactor plus the hydrogen sulfide generated in the second reactor is insufficient to maintain the catalyst in the second reactor in a sulfided state and is insufficient to compete with the ammonia in the second reactor gaseous phase for reaction with the catalyst metals, it may be necessary to introduce hydrogen sulfide to the second reactor from an external source. Whether all of the hydrogen sulfide in the second reactor is generated in situ, or some very small amount of hydrogen sulfide is added to the second reactor from an external source, the average concentration of hydrogen sulfide in the second reactor must be above the average ammonia concentration in the second reactor.

Since the hydrogen sulfide concentration in a hydrodesulfurization reactor is lowest near the reactor inlet and highest near the reactor outlet, it is particularly advantageous to add only a portion of the total ammonia to the reactor inlet and to add the remaining portion of the total ammonia at one or more positions downstream in the reactor. Multiple ammonia addition tends to provide zones of increasing ammonia concentration corresponding to zones of increasing hydrogen sulfide cncentration and tends to avoid an excess in ammonia concentration relative to hydrogen sulfide concentration near the reactor inlet which would lower catalyst activity at the reactor inlet.

It is apparent from the above that the present invention is especially applicable to a hydrodesulfurization reaction because the presence of hydrogen sulfide generated in the process modulates the adverse effect of ammonia in the process. Therefore, in accordance with the present invention the amount of ammonia added is limited by the desired desulfurization reaction so that the concentration of ammonia in the reactor gases is less than the concentration of hydrogen sulfide in the reaction gases but is sufficiently high so that the average concentration of hydrogen sulfide in the reactor gases is increased by the improved desulfurization due to the addition of the ammonia.

FIG. 1 illustrates the acidic behavior of a fresh nickel-cobalt-molybdenum on alumina catalyst as reflected by change in measured production of 375° to 650°F. (191° to 343°C.) furnace oil during single stage hydrodesulfurization of an oil which boils above the furnace oil range. The oil is a 650°F.+ (343°C.+) atmospheric tower bottom of a Kuwait petroleum crude oil. The desulfurization reduced the sulfur content of the oil from 4 to 1 weight percent without ammonia injection. FIG. 1 shows that at start-of-run at each of the two space velocities tested a relatively elevated amount of by-product furnace oil is produced. As reaction time and temperature increase, the amount of furnace oil produced decreases (although not indicated the decrease occurs over a throughput of feed oil of about 1 or 2 barrels of oils per pound of catalyst) until a minimum quantity of furnace oil is produced. The decrease in furnace oil production is probably caused by a coating of acid sites of the catalyst with coke to irreparably destroy (absent combustion regeneration) the acidic nature of these sites. Thereupon, as reaction temperature continues to increase, furnace oil production steadily increases from its minimum value due to thermal (non-catalytic) cracking. FIG. 1 illustrates that an acid capacity existed in the fresh catalyst but, in the absence of ammonia injection, particularly in the absence of very early ammonia injection prior to passage of 1 or 2 barrels of oil per pound of catalyst, the acidic capacity is rapidly destroyed due to coke deposition and thereafter a further increase in temperature induces thermal (as contrasted to catalytic) cracking. This observation indicates that when employing the ammonia injection method of this invention in a hydrodesulfurization process utilizing progressive temperature increases to compensate for catalyst aging the best mode of reactor temperature control is to precede an incremental temperature increase with an incremental increase in added ammonia level to preclude coke formation due to the increase in temperature. Ammonia injection prior to coke formation induces only a temporary loss of catalyst acidity which is recovered in the same catalyst cycle upon a subsequent temperature increase to desorb ammonia from the catalyst surface, but coke formation prior to ammonia injection induces a loss in catalyst acidity which cannot be reversed by temperature increase and is apparently permanent for at least the same catalyst cycle. As the cycle proceeds and elevated temperatures are attained coke will no doubt block some of the acid sites present on the catalyst and therefore a lower ammonia level might be required because coke has substantially reduced the acidity in spite of the coke inhibiting effect of ammonia. At this point, a reduction in the level of ammonia addition may be required to permit sufficient activity of the active sites still available.

All data of FIG. 1 were taken in desulfurizing the feed oil from 4 to 1 weight percent. Since at point A more furnace oil was produced than at point B, the extent of curve segment AB indicates the extent of excess catalyst acidity in terms of excess furnace oil yield beyond that required to accomplish the desired degree of desulfurization. Similarly, the extent of the curve segment CD indicates the extent of excess catalyst acidity in terms of excess furnace oil yield beyond that required to accomplish the desired degree of desulfurization. Curves segments BE and DE indicate generally furnace oil produced by thermal rather than catalytic cracking activity.

In accordance with the present invention, ammonia is injected into the hydrodesulfurization process in an amount sufficient to quench excess initial catalyst acidity beyond that required to accomplish the desired degree of desulfurization, which excess catalyst activity tends to catalytically produce furnace oil and coke during initial hydrodesulfurization. Because the sulfur removed in a second series hydrodesulfurization stage is more refractory and is more deeply imbedded in asphaltene molecules than the sulfur removed in the first stage, this excess catalyst acidity tends to produce coke in a second series hydrodesulfurization catalyst stage. The amount of ammonia added should not be sufficient to depress catalyst acidity to an extent that the ability of the catalyst to accomplish desulfurization is overly inhibited. In general, the amount of ammonia injected, based on both feed oil and on the concentration of ammonia in the reactor hydrogen atmosphere, should be established so that a given degree of desulfurization can be accomplished with some process advantage, such as a greater total amount of sulfur removal within the temperature limits of the process or at a particular total throughput of feed oil per pound (gram) of catalyst, a lower temperature at a given catalyst age and product sulfur level, a higher space velocity, a smaller catalyst requirement to produce a product having a given sulfur level or a lower hydrogen partial pressure. Ammonia injection, by depressing coke formation at any given throughput of oil pound (gram) of catalyst, permits a lengthy cycle life in a second or subsequent series catalyst stage in which coke formation is considerably more serious than in a first catalyst stage. Therefore, ammonia injection can provide a second or subsequent series catalyst cycle life of 4 to 50, generally, or 10 to 40 barrels of feed oil per pound of catalyst (0.0014 to 0.017 or 0.0035 to 0.014 m^3/g). First stage cycle life is as great or greater than second stage cycle life.

The utility of ammonia injection is considerably greater in a second or a third hydrodesulfurization reactor than in a first reactor with which it is in series since a first hydrodesulfurization reactor is not deactivated as rapidly as a second or third reactor with which it is in series. coke deposition is considerably lower in a first reactor than in a second reactor. The life of the catalyst in a first reactor is more severely limited by metals deposition on the catalyst than by coke formation, while the life of the catalyst in a second or third series reactor is more severely limited by coke deposition than by metals deactivation. Since the coke laydown in second and subsequent series reactors is much greater than in the first reactor, the amount of catalyst of a similar composition required at a given space velocity is generally considerably greater (by a factor of 50 or 100 percent, or more) in a second series reactor than in a first reactor with which it is in series, even though the absolute amount of sulfur removed in the second reactor is less than in the first reactor.

One reason that the removal of sulfur is more difficult in a second series stage than in a first series stage is that the concentration of sulfur available for reaction is lower in the second stage feed (first stage effluent) than in the first stage feed. If a first hydrodesulfurization stage reduces oil sulfur level from 4 to 1 weight percent at one liquid hourly space velocity, the reaction rate constant at a given temperature is proportional to

$$(1/C_{SP} - 1/C_{SF})\ LHSV$$

where,

C_{SP} is the concentration of sulfur in the product oil, and

C_{SF} is the concentration of sulfur in the feed oil. The reaction rate constant in desulfurization of Kuwait atmospheric bottoms in a first reactor stage is given approximately as

$$(1/1 - 1/4)\ 1 = 0.75$$

Because the sulfur concentration is much smaller in the second stage oil stream than in the first stage oil stream, in order to expend the same amount of chemical work in the second stage to further reduce the sulfur concentration from a level of 1 to 0.3 weight percent, which is a much smaller absolute quantity of sulfur removal, about one-third the space velocity, or three times the quantity of catalyst at the same space velocity, should be employed in the second stage on the basis of second order kinetics to accomplish the same amount of chemical work which was expended in the first stage. This is illustrated in the following calculation:

$$(1/0.3 - 1/1)\ \text{LHSV} = 0.75$$

or,

$$\text{LHSV} = 0.33$$

Therefore, in this example either three times as much catalyst is required in the second stage as compared to the first stage or the second stage space velocity must be one-third the first stage space velocity when utilizing the same quantity of catalyst in two stages, or operation at a significantly higher catalyst average temperature is required.

A further reason that the chemical work or energy expended in a second residual oil hydrodesulfurization reactor stage is greater than in a first hydrodesulfurization reactor stage with which it is in series is that inherently the less refractory sulfur in the feed oil is removed in the first stage leaving the more refractory sulfur for removal in the second stage. The most refractory sulfur in residual oil is concentrated in asphaltene molecules. The first stage tends to remove sulfur close to the periphery of the asphaltene molecules, such as sulfur in alkyl groups projecting from the polycondensed aromatic ring nucleus of the asphaltene molecules so that minimum hydrocracking and, therefore, minimum coke formation is required to reach and remove these low refractory sulfur atoms. In contrast, second stage sulfur removal tends to penetrate to removal of sulfur imbedded within the polycondensed aromatic ring nucleus of asphaltene molecules so that more extensive hydrocracking and, therefore, more extensive coke formation is required to accomplish molecular penetration to these more refractory sulfur atoms.

The criticality of utilizing ammonia injection in a second stage of a residual oil hydrodesulfurization process which removes highly refractory sulfur, as compared to its use in a first stage with which it is in series in which less refractory sulfur is removed, is illustrated in the accompanying FIGURES. The criticality of utilizing ammonia injection in a residual oil hydrodesulfurization process as contrasted to a distillate oil hydrodesulfurization process is also shown in the FIGURES. Because of the relative absence of polycondensed aromatic ring molecules in distillate oils, the sulfur contained in distillate oils is much less refractory than the sulfur contained in asphaltene-containing residual oils. It is well known that catalyst cycle durations in distillate oil hydrodesulfurization processes are much less limited by coke formation than are catalyst cycle durations in residual oil hydrodesulfurization processes generally enabling lower hydrogen partial pressure operation for the relatively cleaner gas oil feedstocks.

FIG. 2 presents the aging curve in a process for 95 percent hydrodesulfurization of a 650° to 1,050°F. (343° to 565°C.) heavy gas oil containing 2.29 weight percent sulfur at 675 psig (40 kg/cm^2) with a nickel-cobalt-molybdenum on alumina hydrodesulfurization catalyst. The curve shows that catalyst aging is so slight that it was not a problem prior to ammonia injection. In direct contrast to the effect of ammonia in residual oil hydrodesulfurization catalyst aging, ammonia injection in the range employed in the residue process tests in distillate gas oil hydrodesulfurization triggered severe catalyst aging. This indicates that strong catalyst acid sites on the alumina catalyst support are apparently required in distillate oil hydrodesulfurization at the relatively low hydrogen partial pressure employed therein. Thus it appears that gas oil desulfurization cannot operate with the benefits observed in residue hydrodesulfurization if the ammonia levels are comparable. Thus, a significantly lower rate of ammonia injection, probably 100 parts per million, or less, based on fresh feed might be employed beneficially in distillate oil hydrodesulfurization.

FIG. **3** presents aging curves without ammonia addition for the first and second stages in series of a residual oil hydrodesulfurization process with an interstage flashing step to remove contaminant gases. Curve F represents the first stage aging characteristics of a nickel-cobalt-molybdenum on alumina catalyst in desulfurizing a 650°F.+ (343°C.+) Kuwait residual oil from 4 to 1 weight percent sulfur at 1 LKSV with a reactor metallurgy constraint temperature of 790°F. (421°C.). After flashing of hydrogen containing gaseous impurities and subsequent addition of fresh hydrogen, the flash residue of the first stage hydrodesulfurization step is hydrodesulfurized in a second stage to reduce its sulfur content from 1 to 0.3 weight percent. Curve G represents the second stage aging curve. The weight of catalyst employed in the second stage was twice that employed in the first stage reflecting the greater chemical work expended in the second stage due to the lower concentration of sulfur and the more refractory nature of the sulfur being removed. Even though a total of 3 weight percent sulfur was removed in the first stage and a total of only 0.7 weight percent sulfur was removed in the second stage and even though the second stage utilized twice as much catalyst as the first stage, FIG. **3** shows that throughout the catalyst aging cycle a considerably higher temperature was required in the second stage as compared to the first stage due to a much greater coke deposit on the second stage catalyst as compared to the first stage catalyst.

Because of the considerably more severe catalyst aging problem in the second stage as compared to the first stage due to greater coke deposition on the second stage catalyst, a considerably larger volume of catalyst is required in the second stage as compared to the first stage. Therefore, the method of this invention can be particularly directed to injection of ammonia into the second stage of a residual oil hydrodesulfurization process to reduce the catalyst volume requirement in the second stage and to thereby increase the space velocity capacity in the second stage to a level closer to that prevailing in the first stage, so that increased balance is imparted to a series multistage hydrodesulfurization reactor system.

Although it is usual for catalyst requirements to be greater in a second stage than in a first series stage, aside for ammonia injection and depending upon the relative desulfurization severities in the stages the catalyst requirement can be greater in the first stage than in the second stage. In this instance, ammonia injection into the first stage would tend to equalize the space velocity requirements in the two stages. For example, with a 53 percent Kuwait reduced crude whose sulfur content is reduced from 4 to 1 weight percent in a first stage at 1 LHSV, and whose sulfur content is further reduced to 0.1, 0.3, 0.5 and 0.8 weight percent, respectively, in a second stage with an interstage flashing step, the respective second stage space velocity requirements are as follows:

First Stage LHSV	Second Stage LHSV	Second Stage Product Sulfur
1.0	0.25	0.1
1.0	0.50	0.3
1.0	1.0	0.5
1.0	1.25	0.8

As a progressively deeper degree of sulfur removal occurs in the second stage, the sulfur becomes increasingly more difficult to remove. In a usual system, a space time of about 1.0 is required to remove 3 weight percent sulfur from feed oil in a first stage while a space time of about 2.0 is required to remove only 0.7 weight percent sulfur from the feed oil in a second stage. Therefore the efficiency of the catalyst utilization becomes lower with greater depth of sulfur removal. This efficiency may be referred to as Space Time Efficiency for residual oil hydrodesulfurization. Ammonia injection increases the efficiency of refractory sulfur removal. Catalyst efficiency for the two stages can be defined as follows:

$$\frac{\text{feed sulfur concentration}-\text{product sulfur concentration}}{\text{volume of catalyst/volume of oil/hour}}$$

In a three reactor series system, the respective space velocities required to reduce a feed oil having 4 percent sulfur to 1 percent sulfur in a first stage, to 0.3 percent sulfur in a second stage and finally to 0.1 percent sulfur in a third stage are:

First Stage: 1 volume catalyst/volume oil/hour to remove 3 percent of the sulfur
Second Stage: 2 volume catalyst/volume oil/hour to remove 0.7 percent of the sulfur
Third Stage: 2 volume catalyst/volume oil/hour to remove 0.2 percent of the sulfur

The efficiency as defined above for each stage is:

First Stage: 3/1 = 3
Second Stage: 0.7/2 = 0.35
Third Stage: 0.2/2 = 0.1

The overall efficiency for the three stages is 3.9/5 or 0.78.

The use of ammonia injection into the second and third stages to reduce catalyst requirements so that the same amount of catalyst is employed in each stage would provide a catalyst efficiency in each stage as follows:

First Stage: 3/1 = 3
Second Stage: 0.7/1.0 = 0.7
Third Stage: 0.2/1.0 = 0.2

The overall efficiency for the three reactor system employing ammonia injection is 3.9/3 or 1.3. It is therefore seen that the use of ammonia injection considerably increases catalyst efficiency in a residual oil hydrodesulfurization process.

FIG. **4** shows the results of tests made to illustrate the effect of ammonia injection rate in terms of ratio of ammonia to feed oil in the second series reactor of a residual oil hydrodesulfurization process employing a nickel-cobalt-molybdenum on alumina hydrodesulfurization catalyst. Curve K is the second stage catalyst aging curve in a test conducted without ammonia injection. Curve K has no indication of temperature stabilization, i.e., a relatively constant temperature with increasing catalyst age indicating catalyst coke level is stabilized. Curves L, M and N are catalyst aging curves for the second stage when injecting 1,250, 1,500 and 5,000 ppm of nitrogen as ammonia, respectively. FIG. **4** shows that as the ammonia addition rate increased, the required start-of-run reaction temperature to accomplish a fixed degree of desulfurization disadvantageously increased, so there was no start-of-run advantage in utilizing elevated levels of ammonia injection. These start-of-run data tend to indicate that ammonia injection is disadvantageous. However, after 7 or 8 days curve N has temperature stabilized, indicating that with advancing catalyst age an additional advantage appears due to ammonia injection. This temperature stabilization with advancing age disadvantageously occurs in curve N at an elevated temperature. Furthermore, curve N shows that ammonia injection at start-of-run inhibits desulfurization as compared to lower ammonia injection rates. On the other hand, although in curve M a trend is not yet sharply defined, curve M shows incipient stabilization at a lower temperature than in curve N. At the lower ammonia injection level of curve L there is no indication of temperature stabilization. It is apparent from FIG. **4** that to obtain a high level of advantage from ammonia injection, the ammonia to oil ratio and the catalyst age must be correlated. With the feed oil and test conditions of FIG. **4,** in order to obtain temperature stabilization with ammonia injection, more than 1,250 and preferably at least 1,500 but less than 4,000 or 5,000 parts per million of nitrogen based on feed oil are required. In addition, the catalyst must be aged somewhat depending upon the conditions employed in the run. The initial aging period prior to stabilization may be avoided by pretreatment of the catalyst with ammonia. For example, when the catalyst is presulfided with a sulfur-containing gas oil or furnace oil and hydrogen, ammonia can be added to the presulfiding step. Catalyst presulfiding occurs within the reactor and upon start-up of residual oil flow with hydrogen and ammonia more stable initial activity may be realized. FIG. **4** shows that when catalyst stability is achieved, the presence of ammonia permits the required product sulfur level to be achieved with smaller incremental temperature increases with catalyst age (a lower aging rate) than when the same process is operated without ammonia addition.

A highly important aspect of this invention is shown in FIG. **4**, at curve regions N, S and T. Curve region N shows that when 5,000 parts per million of nitrogen are added, the required reaction temperature at start-of-run is greater than the required start-of-run reaction temperature of curve M where 1,500 parts per million nitrogen as ammonia were added under otherwise the same conditions. The ammonia level of 5,000 parts per million exceeded the average concentration of hydrogen sulfide which was about 3,500 parts per million of sulfur as hydrogen sulfide, based on feed in the reaction zone. The significance of insufficient hydrogen sulfide in relation to ammonia is even more strongly illustrated by curve T. Curve T represents a period of an extremely rapid rate of catalyst aging. As indicated in FIG. **4**, the rapid aging rate of curve T was triggered by stopping oil flow and passing hydrogen only over the catalyst without either oil, hydrogen sulfide or ammonia. The flow of hydrogen over the catalyst apparently resulted in a severe loss of sulfur and ammonia from the catalyst, whereby catalyst metals were converted to metal hydrides. When feed oil was returned to the reaction system together with hydrogen and 4,000 parts per million of ammonia under conditions prevailing earlier, rapid aging curve T resulted. It appears that the hydrogen treatment resulted in a catalyst so devoid of sulfur and ammonia that the ammonia subsequently added successfully competed with the hydrogen sulfide generated in situ to react with the Group VI and Group VIII metals on the catalyst to render these metals substantially inactive for desulfurization, or possibly the ammonia was not as quickly adsorbed on the catalyst surface to prevent or inhibit coking as it had been doing during curve segment S, or some combination of these reasons.

If the catalyst is presulfided with gas oil and/or furnace oil with hydrogen, the presence of ammonia during the presulfiding step may tend to limit coking and reduce the SOR aging rate of the catalyst. The following comparative tests involving sulfiding with carbon disulfide at relatively low temperature and pressure, in one case with hydrogen and in another case with nitrogen in place of hydrogen, show a reduced coke content in the sulfided catalyst when employing nitrogen in place of hydrogen.

CS_2 Sulfiding of NiCoMo/
Al_2O_3 Catalyst

	Test 1	Test 2
CS_2 Pressure (atom)	0.26	0.26
Sulfiding Temp. °F	550 (288°C.)	550 (288°C.)
Sulfiding Time-Hour	1	1
Carbon on Catalyst, Wt. %	0.5	0.1
Gas Carrier	Hydrogen	Nitrogen

The stabilization feature of curve segment S indicates that even with a presulfided catalyst it is important for the average ammonia concentration in the reaction zone to be less than the average hydrogen sulfide concentration in the reaction zone so that throughout the catalyst cycle hydrogen sulfide can successfully compete with ammonia in reacting with catalyst metals. To further illustrate the importance of relatively high hydrogen sulfide concentrations relative to ammonia concentrations, curves N, M and L represent conditions wherein hydrogen sulfide concentrations are progressively relatively higher than the ammonia concentration resulting in a decrease in SOR temperatures and aging stabilization temperatures (where stabilization occurred). Therefore, the data of FIG. **4** show that the ammonia concentration should be sufficiently high to improve catalyst aging characteristics to an extent to permit either a reduction in catalyst requirements, a reduction in hydrogen requirements per barrel of feed oil, a reduction in hydrogen partial pressure, or so as to permit a greater amount of sulfur to be removed from the feed oil with a given weight of catalyst over a catalyst cycle, but the average ammonia concentration in the reactor should not be greater than the average hydrogen sulfide concentration.

FIG. **5** outlines further data taken to illustrate ammonia injection into a second series residual oil hydrodesulfurization stage. The catalyst employed in the tests was nickel-cobalt-molybdenum on alumina presulfided with carbon disulfide and the reactor reduced residue sulfur level from 1 to 0.3 weight percent, unless otherwise indicated in FIG. **5**. The reactor was operated at 0.5 LHSV, 2,120 psig (148 kg/cm^2), and 4,250 standard cubic feet per barrel of hydrogen (76.5 SCM/100L). Test conditions deviating from these conditions are indicated in FIG. **5**. Curve O indicates an aging run conducted without ammonia injection while curve P indicates an aging run conducted with 1,000 ppm of nitrogen injection as ammonia based on feed oil at start-of-run.

Referring to the ammonia injection aging run illustrated by curve P of FIG. **5**, it is seen that stable activity was attained after 5 days of operation at 0.5 LHSV with a temperature requirement of only 695°F. (366°C.) for a 0.3 weight percent sulfur product with 1,000 ppm of nitrogen injected. Curve O, also representing a test made at 0.5 LHSV to produce 0.3 weight percent sulfur product, shows that with no ammonia addition, the temperature requirement after five days is 706°F. (374°C.) and the aging rate does not stabilize but rather continues at about 1.5°F. (0.9°C.) per day.

Stable operation was also attained in curve P at 0.9 LHSV and 729°F. (387°C.) while producing 0.3 percent sulfur product with 1,000 ppm of nitrogen injected based on feed oil. Under more severe conditions, a 0.12 weight percent sulfur product was attained at conditions of 0.44 LHSV and 745°F. (396°C.). Under these conditions, the aging rate was moderate, i.e., about 0.6°F. (0.36°C.) per day.

Aging at a rate of about 3°F. (1.8°C.) per day was experienced in subsequent operation after 30 days as an apparent result of desorbing ammonia from the catalyst during an earlier higher temperature operation. However, the aging was arrested upon increasing the rate of ammonia addition from 1,000 ppm N to 1,500 ppm N.

FIG. **6** shows the results of second stage aging runs with a nickel-cobalt-molybdenum on alumina catalyst at 1.0 LHSV, 2,120 psig (148 kg/cm^2), and 4,600 standard cubic feet per barrel of hydrogen (83 SCM/100L), unless otherwise indicated in FIG. **6**. Curve Q shows the results of an aging run without ammonia injection while curve R shows the results of an aging run with ammonia injection. To take advantage of the improvement due to ammonia injection, an increased feed rate of 1.0 LHSV was employed in curve R as compared to a space velocity of 0.5 LHSV for curve Q. Initially, a 10°F. (5.5°C.) temperature elevation was required at the higher space velocity compared to the base test. After 13 days, the temperature elevation requirement was only about 2°F. (1.2°C.). However, activity failed to stabilize. Subsequent increases in ammonia addition from 1,250 ppm N to 1,800 ppm on the 24th day, 2,100 ppm N on the 35th day and 2,300 ppm N on the 38th day were required to moderate the aging rate. Each step-wise increase in ammonia addition resulted in temporarily stabilizing the activity, but at a higher temperature. However, the overall aging rate over this period was about 1°F. (0.6°C.) per day which is about the same as that obtained in the base test without ammonia at the lower space velocity.

A decrease in the reactor gas rate from 4,600 SCF/B (83 SCM/100L) to 4,150 standard cubic feet per barrel (75 SCM/100L) on the 4th day had no apparent effect on catalyst activity. A further decrease to 3,700 standard cubic feet per barrel (67 SCM/100L) on the 30th day, however, appeared to trigger aging at a rate of about 2°F. (1.2°C.) per day. Aging appeared to be arrested by restoring the gas rate to 4,150 standard cubic feet per barrel (75 SCM/100L). These observations indicate that the gas rate as well as the concentration of ammonia have an effect upon catalyst aging rate.

FIG. **7** contains data which further illustrate the effect of ammonia concentration in the hydrogen gas. FIG. **7** shows a first stage catalyst aging curve wherein ammonia injection is employed to reduce sulfur level in a Kuwait reduced crude residual oil from 4 weight percent to 1 weight percent in the presence of a nickel-cobalt-molybdenum on alumina catalyst at 0.88 LHSV, 2,050 psig (144 kg/cm^2) and 7,400 standard cubic feet per barrel of hydrogen (133 SCM/100L), unless otherwise indicated in FIG. **7**. As shown in FIG. **7**, aging was abruptly arrested after **28** days of operation when ammonia addition (as aniline) was held constant at 1,500 ppm N while the hydrogen gas rate was reduced from 7,400 to 3,500 standard cubic feet per barrel (133 to 63 SCM/100L). The effect of this change was to increase the ammonia concentration in the reactor gas, at a fixed ammonia injection rate based on feed oil, and also to increase hydrogen sulfide concentration. Subsequent reduction of the gas circulation rate to 3,000 standard cubic feet per barrel (54 SCM/100L), however, appears to trigger loss of aging stability, indicating that the advantage of optimum ammonia concentration cannot be achieved at the expense of an excessively reduced hydrogen rate so that the hydrogen gas rate should be greater than 3,000, **3,100** or 3,200 standard cubic feet per barrel (54, 56 or 58 SCM/100L).

FIG. **7** illustrates a highly unusual effect achieved by the ammonia injection method of this invention in that the catalyst aging rate is stabilized by a reduction in hydrogen feed rate. The reduction in hydrogen rate per se probably has an adverse effect on the process, but the adverse effect is apparently more than offset by the advantage achieved by the increase in ammonia concentration in the gas and by the increase in hydrogen sulfide concentration in the gas, since, as noted above, the hyydrogen sulfide concentration must be greater than the ammonia concentration. A process advantage ensuing on a reduction in hydrogen rate is highly unusual in the face of the almost universally observed phenomenon in hydrotreating processes that a decrease in hydrogen rate tends to inhibit the hydroprocessing reaction. The showing of FIG. **7** indicates that as hydrogen concentration in the reactor gases increases for any reason, e.g. due to addition to the reactor of a downstream hydrogen quench, it becomes advantageous to inject only a portion of the ammonia requirement at the reactor inlet and to inject additional ammonia downstream with the hydrogen quench in order to maintain optimum ammonia concentration in the reactor gases at every region of the reactor. Another important indication of the data of FIG. **7** is that the process can be controlled at least in part by reducing hydrogen throughput rate at a given ammonia injection rate thereby increasing ammonia concentration which in turn inhibits the catalyst aging rate independently of reaction temperature.

In accordance with this invention, ammonia precursors which are rapidly converted to ammonia under reaction conditions can be injected into a hydrodesulfurization reactor in place of ammonia itself. Examples of suitable ammonia precursors are aniline, pyridene, quinoline, pyrolle, amines, etc.

The process of this invention is illustrated schematically in FIG. **8**. As shown in FIG. **8**, reactors **10** and **12** each contain three spaced-apart fixed beds of Group VI and Group VIII metal on alumina catalyst particles. Crude or residual oil containing asphaltenes is charged through line **14** while hydrogen is charged through lined **16**. Ammonia or a compound which forms ammonia under reaction conditions is injected into hydrogen line **16** through line **18**. Hydrogen and feed oil are passed downwardly through the fixed catalyst beds under hydrodesulfurization conditions to remove the less refractory sulfur in the oil and reduce the sulfur content in the oil from 4 weight percent to 1 weight percent. Reactor **10** is smaller than reactor **12** and contains less catalyst, when reactors **10** and **12** contain the same catalyst, since it removes the less refractory sulfur from the feed oil and because the sulfur it removes is relatively high in concentration.

Effluent is removed from reactor **10** through line **20** and passed to flash chamber **22** wherein gases comprising hydrogen sulfide, ammonia, light hydrocarbons and hydrogen are flashed overhead through line **24**, leaving an oil residue which is removed through line **26** and passed downwardly through second series reactor **12** together with hydrogen entering through line **28**. Ammonia is charged to the hydrogen stream through line **30**. Refractory sulfur is removed in reactor **12** wherein the oil sulfur content is reduced from 1 to 0.3 weight percent, or lower. Product is removed from reactor **12** through line **32**.

A peferred embodiment of this process is illustrated schematically in FIG. **9**. As shown in FIG. **9**, hydrodesulfurization reactors **40** and **42** are disposed in series with each other. Reactor **40** would normally be smaller than reactor **42** for high level desulfurization of a high sulfur chargestock and contains less catalyst, when reactors **40** and **42** contain the same catalyst composition, since it removes the relatively less refractory sulfur from the feed oil and since the sulfur it removes is present in the feed oil at a relatively high concentration. The hydrodesulfurization catalyst employed in each reactor is comprised of Group VI and Group VIII metal on alumina. Reactor **40** contains spaced-apart fixed beds of catalyst **44, 46** and **48** while reactor **42** contains spaced-apart fixed beds of catalyst **50, 52** and **54.**

Crude or residual feed oil containing asphaltenes is charged to reactor **40** through line **56** while hydrogen is charged through line **58**. Ammonia or an ammonia precursor is charged to hydrogen line **58** through line **60**. Additional hydrogen for temperature quenching together with ammonia is added between the catalyst beds, first through lines **62** and **64** and then through lines **66** and **68**. Ammonia is added to the downstream quench hydrogen streams in order to regulate ammonia concentration in reactor gases as additional hydrogen is added without necessitating an unduly high ammonia concentration in the reactor inlet. The less refractory sulfur is removed in reactor **40** and the relatively high sulfur concentration in the oil is reduced from 4 to 1 weight percent.

Effluent is removed from reactor **40** through line **70** and passed to flash chamber **72** from which a gaseous stream comprising hydrogen sulfide, ammonia, light hydrocarbons and hydrogen is removed through line **77**. Oil residue is removed from flash chamber **72** through line **76** and passed to reactor **42** which is larger than and contains more catalyst than reactor **40.**

Hydrogen is charged to the top of reactor **42** through line **78** and ammonia or an ammonia precursor is injected into hydrogen line **78** through line **80**. Quench hydrogen and ammonia are charged to reactor **42** between catalyst beds through lines **82** and **84** and **86** and **88**. The amount of ammonia injected into the quench hydrogen streams regulates ammonia concentration in the reaction gases downstream in the reactor without necessitating an unduly high ammonia concentration in the hydrogen gases at the reactor inlet. Product is removed from reactor **42** through effluent line **90**.

The process of FIG. **9** is designed on the basis of the showing in FIG. **4** that an excessive ammonia concentration at the reactor inlet creates a need for an unduly high start-of-run reactor temperature prior to and after reaching temperature stabilization in the process and also in view of the showing in FIG. **7** that there is an optimum concentration of ammonia in the reactor gases. Therefore, the process of FIG. **9** permits optimization of ammonia concentration in the reactor gases at the reactor inlet, avoiding excessive ammonia concentration at the reactor inlet, and also prevents occurrence of insufficient ammonia concentration downstream in the reactor due to both addition of temperature quench hydrogen and to formation of hydrocarbon gases in the reactor.

Ammonia injection exhibits a synergistic advantage when employed in a hydrodesulfurization system wherein the catalyst has been presulfided with a low molecular weight organic sulfide, such as carbon disulfide, in the absence of hydrogen. In catalyst presulfiding tests under this procedure, carbon disulfide dissolved in furnace oil was fed over a bed of catalyst at a temperature of 400°F. (204°C.) and a pressure of 200 psig (14 kg/cm^2) in the absence of hydrogen in sufficient quantity and over a length of time to provide the equivalent of 0.10 pounds (45.4 grams) of sulfur per pound (454 grams) of catalyst.

When sulfiding a catalyst with higher molecular weight organic sulfides, the presence of hydrogen is required for extracting the sulfur from the organic molecule and for the catalyst sulfiding reaction to proceed. It is a feature of the low molecular weight organic sulfides contemplated herein that they sulfide the catalyst directly without the intervention of hydrogen. It is critical that hydrogen not be added during the carbon disulfide catalyst pretreatment because the hydrogen may react with the carbon disulfide or any other low molecular weight organic sulfide which is used to produce hydrogen sulfide and a hydrocarbon. The organic sulfide employed must be of sufficiently low molecular weight to sulfide the catalytic metals directly and in the absence of added hydrogen and hydrogen sulfide. The presence of hydrogen is conducive to the formation of metal hydrides on the catalyst in addition to metal sulfides. Metal hydrides can be detrimental since they are uncontrollably more active than metal sulfides and tend to hydrocrack excessively and build up coke. Excessive acidity in the catalyst opposes the catalyst acidity depressant effect of ammonia.

Suitable presulfiding conditions with low molecular weight organic sulfides include temperatures of 150° to 700°F. (66 to 371°C.) and pressures of from one atmosphere to 500 psig (35 kg/cm^2). Suitable low molecular weight organic compounds which can presulfide hydrodesulfurization catalysts without the addition of hydrogen include organic sulfides and mercaptans containing less than 4, 6 or 8 carbon atoms such as dimethyl sulfide, ethyl sulfide, diethyl sulfide, dipropyl sulfide, dibutyl sulfide, methylethyl sulfide and ethylpropyl sulfide.

For comparative purposes, one catalyst was presulfided with carbon disulfide without hydrogen and within the test conditions indicated above and a similar catalyst was sulfided conventionally by contact with a sulfur-containing gas oil and hydrogen at a temperature of 660°F. (349°C.) and a pressure of 2,120 psig (148 kg/cm^2). The conventional catalyst presulfiding method employs a sulfur containing gas oil and hydrogen, both of which materials are present in the hydrodesulfurization process itself so that the conventional presulfiding operation would inherently occur in situ in the course of the hydrodesulfurization process. In contrast, the low molecular weight organic sulfide presulfiding method would not inherently occur in situ in the hydrodesulfurization process since the low molecular weight organic sulfide is not present in feedstocks of the present process and since the hydrodesulfurization process always has hydrogen gas in the reactor atmosphere. The low molecular weight organic sulfide is not present in the hydrodesulfurization process because it boils below the initial boiling point of the hydrodesulfurization feed oil.

FIG. **10** shows the results of second stage residual oil hydrodesulfurization tests when charging the effluent from a first stage hydrodesulfurization reactor containing one weight percent sulfur to further reduce its sulfur content to a level of 0.3 weight percent utilizing progressively increasing temperatures with catalyst age and under reactor conditions including 2,120 psig (148 kg/cm^2), 0.5 LHSV and 4,250 standard cubic feet per barrel of hydrogen (77 SCM/100L). Curve H shows an aging run conducted without ammonia injection and without carbon disulfide catalyst pretreatment. The catalyst pretreatment utilized sulfur-containing gas oil and hydrogen. Curve I shows the aging results obtained when carbon disulfide pretreatment without ammonia injection was employed and when ammonia injection was employed without carbon disulfide catalyst pretreatment (but with gas oil and hydrogen presulfiding). Substantially the same aging curve was obtained in each case. Curve J is the aging curve obtained in a test employing both ammonia injection and carbon disulfide without hydrogen pretreatment of the catalyst.

Curve J indicates the occurrence of a synergism when both carbon disulfide pretreatment and ammonia injection are utilized together, as contrasted to the use of each by itself and without the other. FIG. **10** shows that at nine days of catalyst age, the use of each alone produced a 9°F. (5.4°C.) temperature advantage, while the use of both together produced a 22°F. (13°C.) temperature advantage, which is greater than the sum of the temperature advantage of each effect by itself. More importantly, the combination of carbon disulfide pretreatment and ammonia injection resulted in a stabilized catalyst aging rate after only 6 days, whereas when each effect was utilzed by itself, a stabilized catalyst aging rate had not occurred after 11 days, indicating that new coke is formed on the catalyst at a faster rate than it is removed.

The following table presents data illustrating the savings in nickel-cobalt-molybdenum catalyst requirement in a two-stage residual oil hydrodesulfurization process with an interstage flash of contaminant gases over a 6-month catalyst cycle wherein 650°F.+ (343°C.+) reduced Kuwait crude is reduced in sulfur content in a first stage from 4 to 1 weight percent sulfur and then further reduced after an interstage flash in a second stage to either a 0.3 weight percent or 0.1 weight percent sulfur level. The savings illustrated is achieved by CS_2 without hydrogen pretreatment of the catalyst and ammonia injection into the second stage only. The table shows that a considerable savings in hydrogen consumption accompanies CS_2 pretreatment and ammonia injection.

Product Sulfur Level,	0.3	0.3	0.1	0.1
CS_2 Pretreatment and Ammonia Injection	No	Yes	No	Yes
Overall Relative Catalyst Requirements	3.0	2.0	5.0	3.0
EOR H_2 Consumption, SCF/B (SCM/100L)	920 (16.6)	840 (15)	1140 (20.5)	980 (17.6)

The above data show that overall catalyst requirements in a two-stage residual oil hydrodesulfurization process are reduced at least one-third or even at least 40 percent, while overall hydrogen consumption at a given catalyst age to reduce feed sulfur level by a particular amount can be reduced 5 or 10 percent or more by carbon disulfide catalyst pretreatment and ammonia injection into the second reactor stage. Generally, in a two-stage process, the employment of carbon disulfide without hydrogen catalyst pretreatment and ammonia injection can reduce catalyst requirements at least 5 or 10 percent, and as much as 20 or 30 percent, or more. Hydrogen consumption can be reduced at least 1, 2 or 3 or at least 5, 10 or 15 percent, at a given sulfur removal level.

We claim:

1. A process for the hydrodesulfurization of an asphaltene-containing oil comprising passing said oil and hydrogen at a rate of 3,000 to 20,000 standard cubic feet of hydrogen per barrel of feed oil over a sulfided catalyst comprising Group VI and Group VIII metals on alumina at a temperature between 600° and 900°F., adding ammonia to said catalyst in an amount to increase hydrodesulfurization in said process as compared to the absence of said ammonia, the ammonia concentration in the reactor gases being lower than the average hydrogen sulfide concentration in said gases, and compensating for catalyst deactivation due to catalyst aging, at least in part, by decreasing hydrogen flow rate to said process within said range to increase ammonia and hydrogen sulfide concentration in the reactor gases.

2. The process of claim **1** wherein said hydrogen flow rate is decreased incrementally to compensate for progressive decrease in catalyst activity.

3. The process of claim **1** wherein said hydrogen flow rate is at least 3,500 standard cubic feet of hydrogen per barrel.

4. The process of claim **1** wherein ammonia is added to said catalyst prior to charging said oil within said temperature range.

5. The process of claim **1** wherein the ratio of said ammonia to said oil is changed during said process.

6. The process of claim **1** wherein said catalyst comprises cobalt and molybdenum.

7. The process of claim **1** wherein said catalyst comprises nickel, cobalt and molybdenum.

8. The process of claim **1** wherein the pressure is at least 750 psi.

9. The process of claim **1** wherein less than 20 percent of said oil is converted to material boiling below the initial boiling point of said oil.

10. The process of claim **1** wherein less than 10 percent of said oil is converted to material boiling below the initial boiling point of said oil.

11. The process of claim **1** wherein between 150 and 1,500 standard cubic feet of hydrogen per barrel of feed oil are consumed.

12. The process of claim **1** wherein at least 10 barrels of said oil are charged per pound of said catalyst.

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