

[54] **HYDRODESULFURIZATION OF HEAVY
PETROLEUM OIL AT HIGHER
TEMPERATURES AND SPACE VELOCITIES**
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[56] **References Cited**
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[57] **ABSTRACT**
Heavy hydrocarbon oils are desulfurized at high tem-
perature and high space velocity in the presence of a
catalyst comprising a Group VIII metal and a Group
VI metal or their compounds and also containing as an
agent for reducing the deactivation rate of the cata-
lyst, a small amount of a Group VII metal or com-
pound thereof.

13 Claims, No Drawings

HYDRODESULFURIZATION OF HEAVY PETROLEUM OIL AT HIGHER TEMPERATURES AND SPACE VELOCITIES

This invention relates to the desulfurization of petroleum fractions. More particularly, it is concerned with the catalytic hydrodesulfurization of heavy petroleum oils under conditions whereby the throughput and desulfurization of a unit may be increased and the hydrogen consumption in the desulfurization procedure may be reduced with prolonged catalyst life.

The catalytic desulfurization of petroleum hydrocarbons has been well known in the refining industry for many years. It has been discussed quite thoroughly in "Petroleum Processing" Nov. 1956, pages 116-138. The literature discloses reaction conditions, using a fixed bed of particulate catalyst, in the broad ranges of temperatures of from 400°-900°F., pressures of from 50-5000 psig, hydrogen rates of from 200-20,000 standard cubic feet per barrel (scfb) and space velocities of 0.1-20 volumes of oil per volume of catalyst per hour (v/v/hr.)

Experience has shown that in the commercial desulfurization of heavy oils such as vacuum gas oils and heavier stocks, that is, oils having an initial boiling point of about 500°F. or higher, using fixed beds and conventional desulfurization catalysts, the start-of-run temperature using fresh or freshly regenerated catalyst is preferably between about 625° and 650°F. and the end-of-run temperature about 750°F., a gradual increase in temperature being made to compensate for loss of activity of the catalyst throughout the onstream period. Pressures range generally between about 500 and 1,000 psig with hydrogen rates of about 500-2,000 scfb. Ordinarily in conventional commercial units the space velocity is controlled to obtain the desired amount of desulfurization with 85-90% desulfurization being considered as the most practical from an efficiency standpoint. For the most part, conventional commercial heavy oil desulfurization units are designed to operate at a space velocity of about 1.

It has been generally accepted in the industry that hydrogen consumption is a function of the amount of desulfurization and that as the percentage desulfurization increases so does the amount of hydrogen consumed. It is also a general belief in the industry that, other things being equal, a decrease in space velocity is required to obtain an increase in desulfurization. It has also been generally accepted that high temperatures result in shortened catalyst life due to loss of activity on the part of the catalyst through deposition of carbon and in the case of residue-containing charge stocks, metal-containing compounds on the surface of the catalyst particles.

For ecological reasons, it has become necessary to refine more and more petroleum fractions to reduce the sulfur content thereof thus making desulfurization costs enormous, not only in the amount of equipment that must be built but also in the costs of processing the various petroleum fractions such as the energy consumed in heating and pressurizing the petroleum fraction and in the cost of hydrogen consumed. It has been ascertained that process improvements leading to a reduction in hydrogen consumption of 100 scfb or an increase in desulfurization from 90-95% or a reduction in pour point of 40°F. would result in a great economic improvement over current operations. It would also be

a distinct improvement in the efficiency of a hydrodesulfurization unit if the catalyst deactivation rate could be reduced thereby prolonging the onstream periods and reducing the overall down-time for catalyst regeneration.

According to our invention, the efficiency of a desulfurization unit is improved by contacting a sulfurcontaining petroleum oil having an initial boiling point of at least about 500°F. with added hydrogen at a temperature between 750° and 850°F., a pressure between about 300 and 3000 psig and a space velocity between 3 and 10 preferably from 4 to 8 v/v/hr. in the presence of a hydrogenation catalyst comprising a Group VI metal and an iron group metal or compounds thereof supported on a refractory inorganic oxide and containing from about 0.1 to 5% by weight of a Group VI metal such as manganese or rhenium based on the catalyst composite.

Feeds which may be used in the process of our invention are heavy petroleum oil fractions having an initial boiling point of at least about 500°F. and preferably at least 625°F. Examples of feeds are gas oils such as vacuum gas oils, atmospheric residua, vacuum residua, heavy coker distillates, coal tar distillates and gas oils obtained from shale, tar sand and the like. Generally, they contain from 0.5 to 5.0 weight % sulfur.

The hydrogen used in our process may be obtained from any suitable source such as reformer by-product hydrogen, electrolytic hydrogen or hydrogen produced by the partial oxidation of carbonaceous or hydrocarbonaceous materials followed by shift conversion and CO₂ removal. The hydrogen should have a purity of at least 50% and preferably at least 65% by volume.

The catalyst used in the process of our invention comprises a Group VIII metal such as an iron group metal or compound thereof composited with a group VI metal or compound thereof on a refractory inorganic oxide support. Suitable Group VIII metals are particularly nickel and cobalt used in conjunction with tungsten or molybdenum. Preferably, the metals are in the form of the oxide or sulfide. Advantageously the iron group metal is present in an amount between about 1.0 and 10% and the Group VI metal is present in an amount between about 5 and 30% based by weight on the catalyst composite. Examples of refractory inorganic oxides useful as supports are alumina, magnesia, zirconia and the like or mixtures thereof. In a preferred embodiment the support is composed for the most part of alumina stabilized with a minor amount, e.g. up to about 5 wt. % silica.

The catalyst also contains as an agent for reducing the deactivation rate of the catalyst, a small amount e.g., 0.5-5.0 preferably from 0.2-2.0 percent of a Group VII metal e.g. rhenium or manganese based on the weight of the catalyst composite. These metals or their compounds are particularly effective in reducing the deactivation rate when the catalyst is used at high temperatures such as 800°-850°F. and high space velocities such as 4-8 v/v/hr.

Neither the catalyst nor its preparation form any part of our invention. The catalyst may be prepared by conventional means such as those disclosed in U.S. Pat. No. 2,437,533 issued Mar. 9, 1948. The catalyst may be prepared by forming the support which, as mentioned above, is, for example, alumina containing a small amount of silica. The support may then be impregnated with the desired metals by use of a solution

of a water-soluble compound of the metal. For example, water solutions of ammonium molybdate, cobalt nitrate, nickel nitrate, ammonium metatungstate, manganous nitrate or perhenic acid may be used for the impregnation. After the impregnation of the catalytic materials on the support, the composite is heated to dry and then calcined for several hours in air at high temperature e.g., 900°–1000°F. thereby converting the metals to the oxide.

The catalyst may be used as a slurry, a moving bed, a fixed bed or a fluidized bed. In a preferred embodiment, the catalyst is used as a fixed bed of particles which may be spheroids or cylindroids, the latter being preferred. When the catalyst is used as a fixed bed the oil flow may be either upward or downward with concurrent hydrogen flow or the flow of oil may be downward counter to upwardly flowing hydrogen. In a preferred embodiment the hydrogen and the oil both pass downwardly through the fixed bed of catalyst particles.

In commercial installations it is customary to separate the hydrogen from the desulfurization zone effluent and recycle the separated hydrogen to the desulfurization zone. To prevent the buildup of impurities such as low molecular weight gaseous hydrocarbons, hydrogen sulfide and ammonia, a portion of the recycled hydrogen may be bled from the system and replaced with fresh hydrogen. Hydrogen may also be added to the recycle stream to replace that consumed in the desulfurization process. The ammonia and hydrogen sulfide may also be removed from the hydrogen by scrubbing with a methanolamine-water solution.

The following examples are submitted for illustrative purposes only and it should not be construed that the invention is limited thereto.

EXAMPLE I

This example shows that the presence of rhenium in the catalyst reduces the deactivation rate of the catalyst. The composition of catalyst A is 3 wt. % cobalt, 12 wt. % molybdenum, 3 wt. % silica and the balance alumina. The cobalt and molybdenum are present as the oxides. The catalyst has a surface area of 290 m²/g, a pore volume of 0.63 cc/g and an average pore diameter of 82.5A. Catalyst B is the same as catalyst A except that it additionally contains 0.5 wt. % rhenium. The charge stock is a West Texas-New Mexico vacuum gas oil having an API Gravity of 22° and a sulfur content of 1.85 wt. %. In each run the charge is passed concurrently with hydrogen through a fixed bed of catalyst at the constant conditions of 800°F. 400 psig. 4 v/v/hr with 1,500 SCFB recycle hydrogen and 500 SCFB fresh hydrogen. The onstream period is reported in terms of barrels of feed per pound of catalyst.

TABLE 1

Charge	% Desulfurization	
	A	B
0.27	88.6	90.2
0.34	89.1	90.2
0.41	88.1	89.7
0.48	87.5	89.1
0.54	87.0	89.1
0.61	84.8	88.6
0.68	84.3	88.6
0.75	84.8	88.6
0.82	85.9	88.6
0.89	84.8	87.5
0.96	84.8	87.0
1.02	83.7	87.5
1.09	83.2	87.5

TABLE I-Continued

Charge	% Desulfurization	
	A	B
1.16	83.7	87.0
1.23	83.7	87.5
1.30	83.7	87.0
1.37	83.2	86.8
1.43	82.7	86.4
1.50	82.7	87.0

These data show that there is little difference in the initial desulfurization activity of the catalysts but that the rhenium-containing catalyst loses its activity at a much slower rate.

EXAMPLE II

Example I is repeated with catalyst C containing 3 wt. % nickel, 13.6 wt. % molybdenum and the balance alumina. Catalyst D is similar to catalyst C but in addition contains 1.0 wt. % rhenium. The reaction conditions are the same as those of Example I.

TABLE 2

Charge	% Desulfurization	
	C	D
0.20	89.1	91.3
0.28	88.7	90.8
0.35	88.5	90.8
0.42	88.1	89.6
0.49	88.3	90.3
0.56	86.9	90.0
0.63	85.7	89.5
0.70	84.5	89.5
0.77	84.8	89.3
0.84	85.2	89.3
0.91	84.6	89.2
0.98	83.7	89.0
1.05	83.2	89.2
1.12	83.5	88.9
1.19	83.5	88.9
1.26	83.6	88.4
1.33	83.1	88.6
1.40	82.7	88.5
1.47	82.5	88.5
1.54	82.6	88.4

These data show that the addition of rhenium to a nickel-molybdenum on alumina has substantially the same effect as its addition to a cobalt-molybdenum on silicastabilized alumina.

They also show that the presence of rhenium is effective in slowing the deactivation rate of the catalyst especially at a pressure below 500 psig under which conditions catalysts used for the desulfurization of heavy residuecontaining petroleum oils, that is, those having a Conradson Carbon Residue of at least 1.0 wt. %, are particularly susceptible to rapid deactivation.

EXAMPLE III

This is a substantial duplicate of Example II except that Catalyst E contains 1 wt. % manganese and the reaction conditions are 800°F., 350 psig, 6 v/v/hr. with a hydrogen circulation rate of 1,500 SCFB recycle hydrogen and 500 SCFB fresh hydrogen.

TABLE 3

Charge	% Desulfurization	
	C	E
0.27	89.7	90.7
0.34	89.1	89.8

TABLE 3-Continued

Charge	C	% Desulfurization E
0.41	88.7	89.2
0.48	88.4	89.4
0.54	88.2	89.0
0.61	87.4	89.1
0.68	87.0	89.0
0.75	86.5	88.9
0.82	85.2	88.5
0.89	84.4	88.6
0.96	83.6	88.4
1.02	83.0	88.2
1.09	82.3	88.3
1.16	82.7	88.1
1.23	82.0	87.9
1.50	80.4	86.6

These runs show that at a pressure of 350 psig, the deactivation rate of Catalyst C is higher than in Example II and also that the deactivation rate of Catalyst E is less than that of Catalyst C.

EXAMPLE IV

This example is similar to Example I with respect to charge stock and reaction conditions, the difference being that Catalyst F contains 2 wt. % rhenium. As in the other examples, the time on-stream is reported in terms of barrels of feed per pound of catalyst.

TABLE 4

Charge	% Desulfurization	Charge	% Desulfurization
0.27	90.3	0.82	88.8
0.34	90.3	0.89	88.9
0.41	90.1	0.96	88.5
0.48	89.8	1.02	88.0
0.54	89.4	1.09	88.1
0.61	89.0	1.16	87.9
0.68	89.1	1.30	87.6
0.75	88.7	1.50	87.6

A comparison of this example with catalyst A of Example I shows the effectiveness of the addition of 2 wt. % rhenium to the catalyst in reducing the deactivation rate of the catalyst at high temperature and low pressure specifically a temperature of 800°-850°F. and a pressure below 500 psig.

Obviously, various modifications of the invention as hereinbefore set forth may be made without departing

from the spirit and scope thereof, and therefore, only such limitations should be made as are indicated in the appended claims.

We claim:

- 5
1. A process for the hydrodesulfurization of a petroleum oil fraction having an initial boiling point of at least about 500°F. which comprises contacting said fraction in the presence of added hydrogen under hydrodesulfurization conditions with a catalyst comprising an iron group metal, oxide or sulfide thereof and a Group VI metal, oxide or sulfide thereof on a refractory inorganic oxide support selected from the group consisting of alumina, magnesia and zirconia and mixtures thereof and containing between 0 and 5 wt. % silica, said catalyst also containing from 0.1-5% by weight based on the catalyst composite of a Group VII metal or oxide thereof at a temperature between about 800° and 850°F. and a space velocity between about 4 and 8 v/v/hr.
- 10
2. The process of claim 1 in which the hydrodesulfurization pressure is below 500 psig.
- 15
3. The process of claim 1 in which the Group VIII metal is nickel.
- 20
4. The process of claim 1 in which the Group VIII metal is cobalt.
- 25
5. The process of claim 1 in which the Group VI metal is molybdenum.
- 30
6. The process of claim 1 in which the Group VI metal is tungsten.
- 35
7. The process of claim 1 in which the Group VII metal is rhenium.
- 40
8. The process of claim 1 in which the Group VII metal is manganese.
- 45
9. The process of claim 1 in which the petroleum oil fraction has an initial boiling point of at least 625°F.
- 50
10. The process of claim 1 in which the Group VII metal is present in an amount between 0.2 and 2.0 wt. %
- 55
11. The process of claim 1 in which the hydrodesulfurization pressure is above 300 and below 500 psig.
- 60
12. The process of claim 1 in which the support comprises alumina.
- 65
13. The process of claim 1 in which the catalyst support is composed of silica in an amount up to about 5 wt. % and the balance is alumina.

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