FIG. 1

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FIG. 2.

Hydrogen sulfide sulfur

Non-mercaptan sulfur

Mercaptan sulfur

Space Time: Grams Catalyst-Hour/Grams of Liquid Feed

Composition: Moles per Mole of Sulfur Charged.

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Activity Ratio = 6.3

Co = 350 PPM Mercaptane Sulfur

Space Time: Grams Catalyst-
Hour/Grams of Liquid Feed

Conversion: Per Cent by Weight

Second Reactor

First Reactor

FIG. 3

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FIG. 4.

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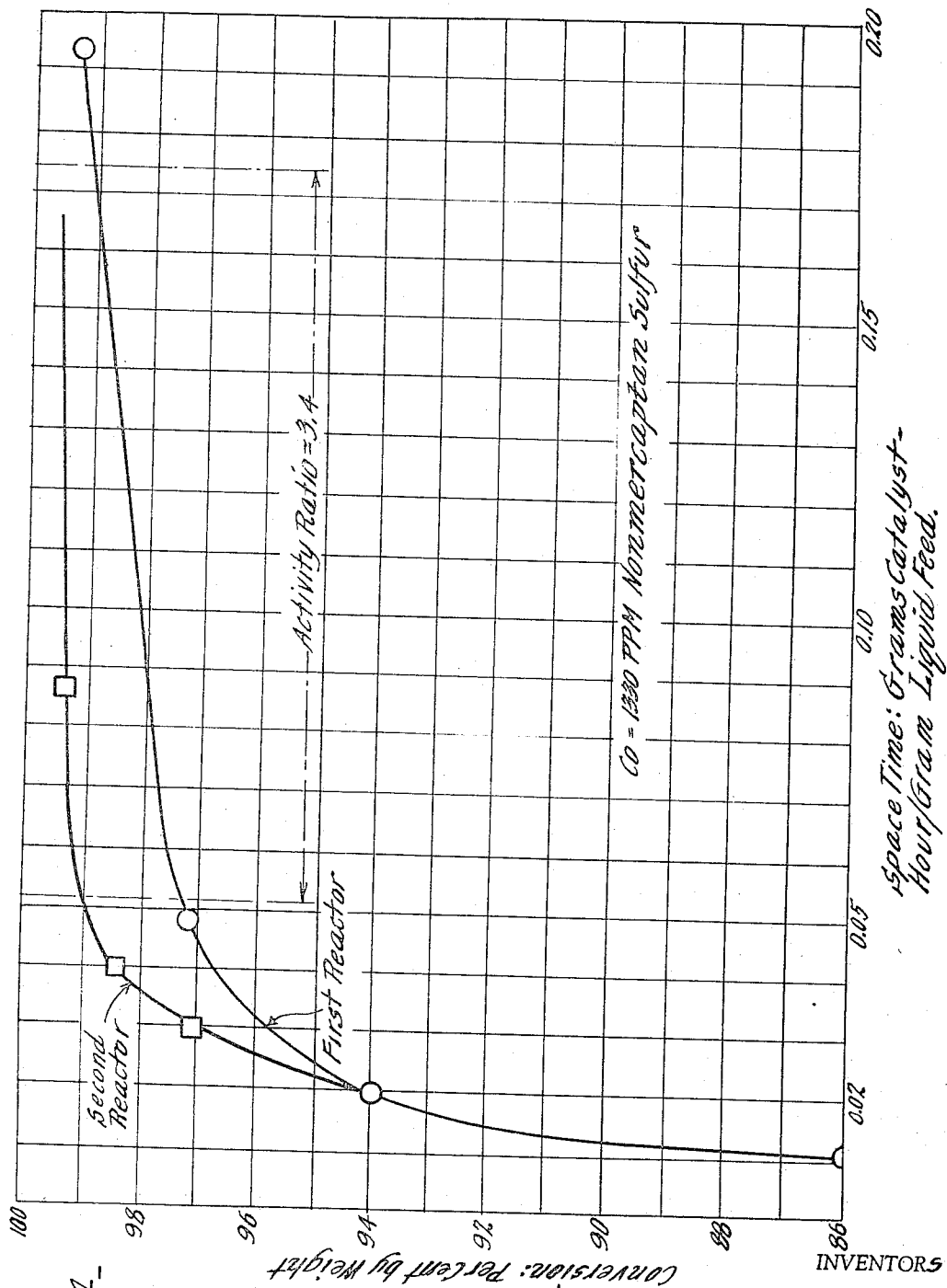Allen E. Somers.

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3,349,027
MULTI-STAGE HYDRODESULFURIZATION
PROCESS
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This invention relates to improved procedures for the catalytic hydrodesulfurization of light petroleum gases and distillate hydrocarbons boiling below about 650° F.

It has been known to remove sulfur compounds from petroleum hydrocarbons by contacting these petroleum hydrocarbons with hydrogen and hydrodesulfurization catalysts. This desulfurization of petroleum hydrocarbons bearing sulfur compounds is necessary to make market-able furnace oils and other fuels and to prevent deterioration of sulfur sensitive catalysts upon subsequent process-ing of the petroleum hydrocarbons.

Reaction conditions for catalytic hydrodesulfurization typical of those taught in the prior art are temperatures of from 300 to 800° F., pressures of from 100 to 1000 p.s.i., space velocities of from less than 1 to about 5 liquid hourly space velocity (LHSV), and hydrogen re-cycle rates of up to 2000 standard cubic feet of hydro-gen per barrel of hydrocarbon charge. The prior art teaches two-stage hydrodesulfurization with removal of sulfur compounds between the stages. However, the use of unusually high space velocities, in general, and use of unusually high space velocities in a multi-stage process with removal of sulfur compounds at a specific point be-tween stages is not taught in the prior art.

This invention has for its object the use of unusually high space velocities in a multi-stage catalytic hydrodesul-furization process, so that the judicious removal of gase-ous sulfur compounds (primarily H₂S) between the stages permits use of a much smaller catalyst bed as compared with catalyst beds necessary for the processes taught in the prior art.

Another more specific object of this invention is to ac-complish essentially complete removal of sulfur com-pounds from light petroleum gases, naphthas, and other distillate oils using a multi-stage catalytic hydrodesulfuri-zation process with unusually high space velocities.

The objects of our invention are accomplished by sub-jecting light petroleum gases or distillate hydrocarbons boiling below about 650° F. to a continuous, multi-stage catalytic hydrodesulfurization process. This continues hy-drodesulfurization process partially desulfurizes the hy-drocarbon in the first stage, then the hydrodesulfurization is interrupted before hydrogen sulfide can substantially inhibit further catalytic reaction and hydrogen sulfide is removed from the reaction product, then this partially hydrodesulfurized reaction product is again contacted with hydrogen and hydrodesulfurization catalyst under hydrodesulfurization conditions.

The charge stocks suitable for catalytic desulfurization by this invention are light petroleum gases and hydrocar-bon distillates boiling below 650° F. Natural gasoline,

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naphthas, furnace oils and natural gas are examples of suitable feed stocks. Feeds will ordinarily contain .05 to 1.0% sulfur.

Each of the hydrodesulfurization units of the multi-stage process operates at essentially the same conditions and with the same catalyst. However, it is within the scope of this invention to operate the successive units at differ-ing conditions, if necessary. Suitable operating ranges for our invention would be 400 to 750° F., 400 to 700 p.s.i.g., 30 to 200 LWHSV, 200 to 4000 s.c.f./bbl. of hydrogen, and a hydrogen purity of 50 to 100%. Preferred operating ranges are 500 to 600° F., 550 to 650 p.s.i.g., 50 to 100 LWHSV, 600 to 3000 s.c.f./bbl. of hydrogen and a hy-drogen purity greater than 75%.

The catalysts suitable for the hydrofining in this inven-tion may include the oxides and sulfides of Group VI and Group VIII (nonplatinum) metals alone or in ad-mixture with each other deposited upon a nonacidic sup-port or carrier such as activated alumina, bauxite, etc. Nickel-cobalt-molybdenum, cobalt molybdate or mixtures of cobalt oxide and molybdenum oxide on alumina are preferred and most often used because of their good ac-tivity, selectivity, long life, insensitiveness to poisons, strength and low cost.

The most important element of our invention, selection of the precise point of separation of sulfur impurities in the form of H₂S and mercaptans from the catalyst bed, was determined by extensive experimental work. It was found that the initial hydrodesulfurization reaction rates were extremely fast, resulting, for example, in a conver-sion of 95 to 99% at a LWHSV of 100. In addition, it was found that the presence of H₂S in the reacting mix-ture has a large deleterious effect on the desired conver-sion of sulfur compounds in the feed. By using a multi-stage process with unusually high space velocities, the H₂S can be removed from the catalyst bed before the deleterious effect of H₂S in the reacting mixture can pro-ceed to any appreciable extent.

In the following examples two sets of experimental runs were made. One set (Example 1) shows the adverse effect of the reverse reaction of H₂S and hydrocarbon upon the desired hydrodesulfurization reaction. The second set (Ex-ample 2) shows the improvement obtained by removing H₂S at a carefully selected point between stages.

Example 1

A study of conversion as a function of space-time, which is the reciprocal of space velocity, was made on a simulated naphtha charge having the sulfur content shown in the first column of Table I at 600° F., 650 p.s.i.g., 0.78 hydrogen ratio, and space velocities which varied between 5 and 400 LWHSV. The experimental re-sults are listed in Table I. The nonmercaptan sulfur con-centration decreased from 1330 p.p.m. to 10 p.p.m. as the space velocity decreased. However, the hydrogen sulfide content built up to a constant level of 360 to 390 p.p.m. In the accompanying drawings the nonmercaptan and mercaptan conversions were plotted versus space-time (the reciprocal of space velocity) to give the results shown in FIGURE 1. Note the extreme nonlinear be-havior for both nonmercaptan and mercaptan sulfur in-

dicating that a similar reaction mechanism is operative for both types of compounds. The complete composition

in a simulation of a first desulfurization stage (Run 1) to provide sufficient charge stock for a simulated second de-

TABLE I.—SPACE VELOCITY VERSUS SULFUR DISTRIBUTION IN HYDRODESULFURIZATION OF NAPHTHA

[Catalyst: 10-20 mesh NiCoMo on filtrol alumina; Feed: Naphtha]

	Feed	Run No.					
		1	2	3	4	5	6
Temperature, ° F	--------	602	602	602	601	600	602
Pressure, p.s.i.a	--------	665	665	665	665	665	665
H_2 Ratio, Mole/Mole	--------	0.77	0.78	0.77	0.77	0.77	0.80
Liquid Hourly Space Velocity, wt./wt./hr	--------	399	198	101	50	21	5
Total Sulfur in H_2 Stripped Liquid Product, p.p.m	--------	730	500	260	90	40	10
Mercaptan Sulfur in Liquid Product as Tested on H_2 Stripped Product, p.p.m	330	80	30	20	10	5	<0.5
Hydrogen Sulfide in Liquid Product, p.p.m	--------	228	--------	313	394	396	358
Nonmercaptan Sulfur in Liquid Product[a] (by difference), p.p.m	1,330	650	470	240	80	35	9.7
Conversion of Mercaptan Sulfur,[b] percent by wt	--------	75.6	90.8	93.9	96.9	98.4	99.9
Conversion of Nonmercaptan Sulfur, percent by wt	--------	51.1	64.7	82.0	94.0	97.2	99.3

[a] By difference between total sulfur and mercaptan in the stripped product.
[b] Conversion of mercaptan (originally present and/or formed from nonmercaptan).

profiles are plotted in FIGURE 2 as moles (or weight) of sulfur as the individual sulfur compounds per mole (or

sulfurization stage. After the hydrocarbon product from the first stage (Run 1) was stripped with hydrogen to

TABLE II.—EFFECT OF REMOVING H_2S AND LOW-BOILING MERCAPTANS IN HYDRODESULFURIZATION OF NAPHTHA

[Catalyst: 10-20 mesh NiCoMo on filtrol alumina; Feed: Naphtha]

	Feed	Run No.			
		1	2[a]	3[a]	4[a]
Temperature, ° F	--------	599	605	603	600
Pressure, p.s.i.a	--------	665	665	665	665
H_2 Ratio, Mole/Mole	--------	0.78	0.78	0.77	0.76
Liquid Hourly Space Velocity, wt./wt./hr	--------	50	101	51	15
Over-All Liquid Hourly Space Velocity, wt./wt./hr	--------	50	34	25	12
Mercaptan Sulfur in Liquid Product, p.p.m	330	10	0.9	0.9	<0.5 (0.3)
Total Sulfur in Liquid Product	1,660	90	39	22	9
Nonmercaptan Sulfur in Liquid Product (by difference), p.p.m	1,330	80	38	21	8.7
Conversion of Mercaptan Sulfur, percent by Weight	--------	97.0	99.7	99.7	99.9
Conversion of Nonmercaptan Sulfur, percent by Weight	--------	94.0	97.1	98.4	99.3

[a] The feed was the H_2-stripped product from Run 1.

weight) of sulfur charge versus space-time (defined as grams of catalyst-hour per gram of total liquid feed charged). These profiles show that the non-mercaptan and mercaptan reaction rates (slopes of the curves) are initially high and then decrease rapidly as the hydrogen sulfide builds up. A kinetic analysis shows that the partial pressure of hydrogen sulfide must inhibit the non-mercaptan and mercaptan hydrodesulfurization reaction rate constants.

Example 2

Another set of tests was made to show the advantage of using a two-stage hydrodesulfurization with removal of H_2S between stages. The charge stock was a simulated naphtha charge consisting of 7.8% coker naphtha, 5.9% visbreaker naphtha and 86.3% virgin naphtha. It contained 1660 p.p.m. total sulfur of which 330 p.p.m. were mercaptan sulfur and 1330 p.p.m. were nonmercaptan sulfur. The catalyst used was 10 to 20 mesh nickel-cobalt-molybdenum on Filtrol alumina consisting of an alumina base impregnated with 2.3% nickel, 1.2% cobalt and 11.0% of molybdenum.

The results from these tests are set forth in Table II. The charge naphtha was hydrodesulfurized at 599° F., 650 p.s.i.g., 50 LWHSV and 0.78 hydrogen ratio (mole/mole)

remove H_2S and ethyl mercaptan, it was rerun at essentially the same temperature, pressure and hydrogen ratio as in the first stage but at space velocities of about 100, 50 and 15 LWHSV to simulate a second desulfurization stage at three different space velocities. These data are set forth in Table II as Runs 2, 3 and 4 respectively.

The data from these runs were used to plot the points shown by squares labeled "Second Reactor" in FIGURES 3 and 4. FIGURE 3 concerns the conversion of mercaptan sulfur and FIGURE 4 the conversion of non-mercaptan sulfur compounds. In each graph, conversion is plotted against space-time. Those points shown by circles and called "First Reactor" are based on the data given in Runs 1, 4 and 5, Table I. Note that Run 1, Table II, is nearly identical to Run 4, Table I. Thus, the comparison in FIGURES 3 and 4 is permissible to show simulated first and second reactor runs. Run 1, Table II, was necessary only to produce sufficient charge stock for simulated second reactor runs.

The graphs show that the conversion of sulfur is rapid in the initial part of the reactor and only minor conversion results in the remaining portion. This is indicated by the leveling off of the curve. However, by removing H_2S between stages, in this instance at 0.02 spacetime, desulfur-

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ization in the second reactor increases sharply in FIGURE 3 from 97.0 to 99.6% in about 0.01 spacetime. This shows the judicious removal of H_2S at a precise point between the reactor units does have a very beneficial effect on the reaction. However, since this point cannot be found so precisely that no reverse reaction occurs, the mercaptans formed, if any, may be removed along with the H_2S at this point.

Another way to depict the advantage of interstage H_2S removal is by "Activity Ratio." For example, on FIGURE 3, choose the degree of mercaptan conversion as 99.6% by weight. To reach this desulfurization level with one reactor, a space-time of 0.163 is needed. However, with the high space velocity, multi-stage system, the space-time is only 0.026. Thus, the "Activity Ratio" is 0.163/0.026 or 6.3. From FIGURE 1 it will be evident that 0.01 to 0.07 space-time and preferably 0.02 to 0.05 space-time is an advantageous range in which to remove H_2S.

The closest direct experimental data comparison of a single reactor with a two-reactor system at similar operating conditions is Run 5 in Table I and Run 3 in Table II. These tests were made at essentially the same operating conditions except Run 5 was made at 21 LWHSV and Run 3 was at an overall space velocity of 25 LWHSV. Run 3 product, the two-stage operation with H_2S removal between stages, contained 0.9 p.p.m. mercaptan sulfur with 99.7% by weight over-all conversion of feed mercaptan sulfur. Run 5 product contained 5 p.p.m. mercaptan sulfur with 92.4% by weight conversion of feed mercaptans.

Thus, the data given in the tables and plotted on the graphs show that equivalent desulfurization and nearly complete desulfurization is possible using unusually high space velocities and much smaller reactors by removal of H_2S between the reactors.

The unusually high space velocity of this invention makes possible the use of much smaller reactors than those now in conventional use. For example, a cylindrical reactor for each unit of about 2 cubic feet would be sufficient for a 1000 barrel per day unit.

To adsorb the H_2S and mercaptans between stages, either of the following alternatives is satisfactory. Both methods use parallel multi-bed, preferably dual-bed units, containing materials which have an affinity for removing sulfur compounds, especially H_2S, from hydrocarbon streams. One of the alternative methods uses regenerable adsorbent, while the other uses a disposable adsorbent. The reactor effluent vapors including hydrogen are contacted with the adsorbents at about 500 to 600° F., about 550 to 650 p.s.i.g., and about 0.2 to 6.0 LHSV. The preferred adsorber temperatures and pressures are the same as those for the previous hydrodesulfurization unit to avoid the need for heat exchangers prior to or after the H_2S adsorber and also to avoid the need for compressors or pressure reducing equipment.

The preferred regenerable method is use of copper or copper oxide impregnated on a silicon carbide support as the adsorbent. Other possible regenerable adsorbents are nickel, iron, molybdenum, their oxides and compounds such as copper molybdate, cobalt molybdate or nickel molybdate supported on silica, silica-alumina, or alumina. These regenerable adsorbents are reactivated at given intervals. Regeneration is necessary only when the effluent from the adsorber shows sulfur content above that permissible. The sulfur content can be monitored by some automatic detecting unit such as a thermal conductivity cell to switch the reactor effluent from one of the parallel adsorbents to the other. For example, a mercaptan analyzer for process use has been developed by the Gulf Physical Sciences Division. This permits regeneration of one of

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the adsorbent beds while the hydrodesulfurization continues.

Regeneration should take place when 30 to 60% of the metallic content of the catalyst has been converted to the metal sulfide. Before regeneration the adsorbent bed is purged with an inert gas to recover hydrocarbons in the bed. Then an oxygen containing gas is admitted to the adsorbent bed. The oxygen content of this gas is controlled to maintain a temperature between about 1000 and 1300° F. at a pressure of atmospheric to about 500 p.s.i.g. The diluent inert gas to air ratio varies from none to about 20 volumes per volume. Another purge with inert gas is necessary to remove any oxygen from the bed prior to contact with reactor effluent. If the adsorbent is a metal or metal mixed with metal oxide, a reducing treatment is necessary to restore the metal to its original form.

The preferred nonregenerable adsorbent is zinc oxide or iron oxide. Operation of the parallel adsorbent bed would be the same as discussed above except that the spent adsorbent is replaced with fresh adsorbent rather than regenerated. The adsorbent beds to be used with a 2 cubic foot reactor would be about 170 cubic feet in volume.

Although we have at times mentioned removal of both hydrogen sulfide and mercaptans, this invention is not limited to removal of both. Any mercaptans or other sulfur impurities formed during hydrodesulfurization may be removed at the same time that H_2S is removed. Therefore, removal of sulfur compounds other than H_2S is not essential to this invention although it may advantageous in some cases.

What we claim is:

1. A continuous, multi-stage, catalytic process for the hydrodesulfurization of a hydrocarbon stream boiling below about 650° F. which comprises

treating said hydrocarbon stream with hydrogen in a first reactor in the presence of a hydrodesulfurization catalyst at hydrodesulfurization conditions of pressure and temperature and at a weight hourly space velocity of between about 21 and 200,

separating gaseous sulfur compounds from the hydrocarbon effluent stream from the first reactor, and

treating the hydrocarbon effluent stream with hydrogen in a second reactor in the presence of a hydrodesulfurization catalyst at hydrodesulfurization conditions of pressure and temperature and at a weight hourly space velocity of between about 21 and 200.

2. A process in accordance with claim 1 in which the weight hourly space velocity in said reactor is between about 30 and 100.

3. A process in accordance with claim 1 in which the weight hourly space velocity in said second reactor is between about 30 and 100.

4. A process in accordance with claim 3 in which the weight hourly space velocity in said reactor is between about 30 and 100.

5. A process in accordance with claim 1 in which hydrogen sulfide is removed from the hydrocarbon effluent stream from the first reactor.

References Cited

UNITED STATES PATENTS

3,155,608	11/1964	Hopper et al.	208—89
3,175,970	3/1965	Bercik et al.	208—89
3,228,993	1/1966	Kozlowski et al.	208—210
3,236,764	2/1966	Den Herder et al.	208—210
3,239,454	3/1966	Streed et al.	208—210

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,349,027   October 24, 1967

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 50, for "continues" read -- continuous --; column 5, line 29, for "92.4%" read -- 98.4% --; column 6, lines 48 and 54, for "said reactor", each occurrence, read -- said first reactor --.

Signed and sealed this 5th day of November 1968.

EAL)

ttest:

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