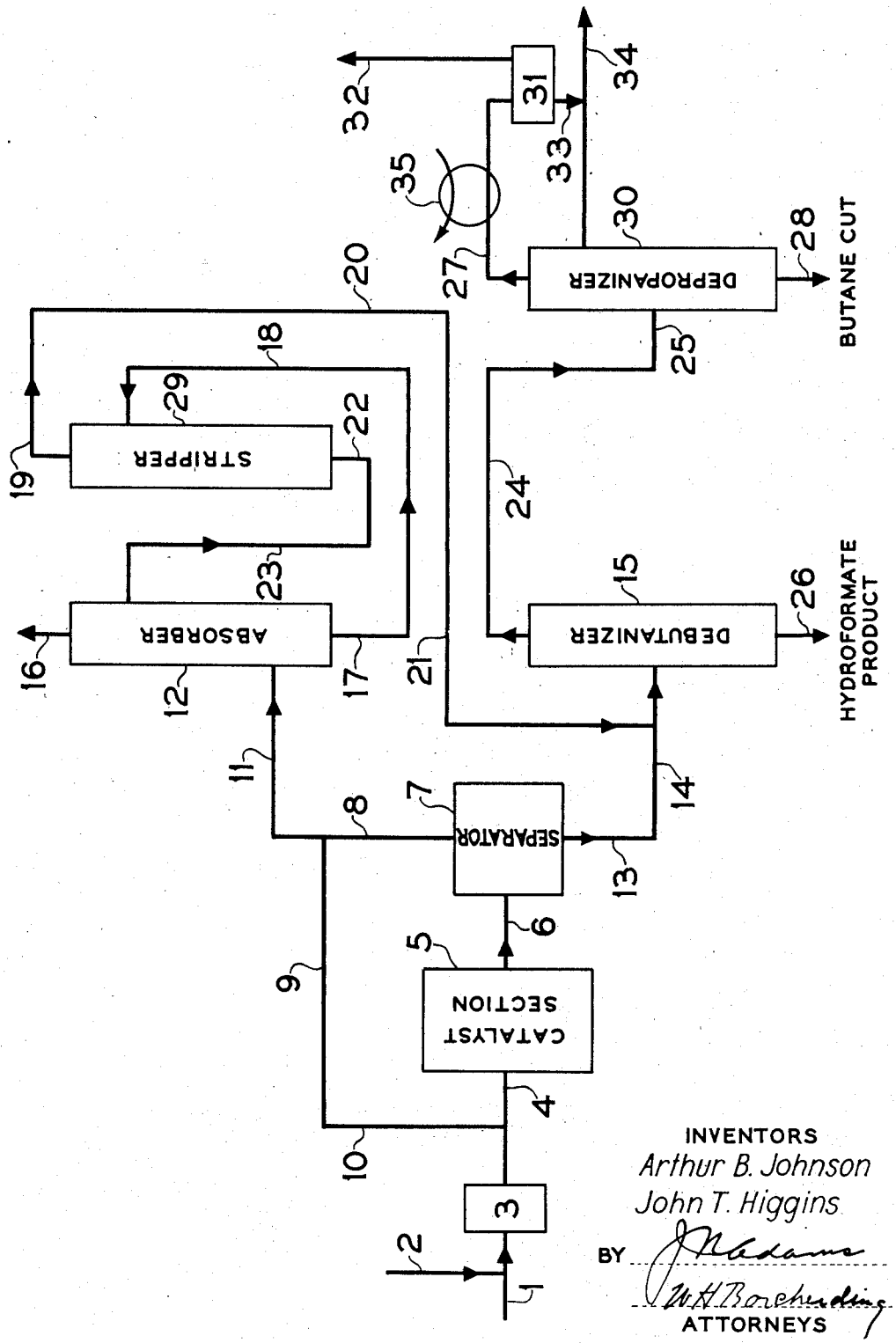
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PURIFICATION OF CARBONYL SULFIDE CONTAMINATED HYDROCARBON GASES

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PURIFICATION OF CARBONYL SULFIDE CONTAMINATED HYDROCARBON GASES

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This invention relates to the removal of carbonyl sulfide from petroleum gases.

Large quantities of liquefied petroleum gas are sold for use as industrial and automotive fuels. The basic materials for liquefied petroleum gas are C_3 and C_4 hydrocarbons produced in the various refining and cracking processes to which crude oil is subjected, and liquefied petroleum gases as now marketed usually contain both of these hydrocarbons. As obtained from these sources the petroleum gases contain appreciable quantities of sulfur compounds which are customarily removed in order to produce a liquefied petroleum gas of commercially acceptable quality. Among the sulfur compounds found in petroleum gases, especially as produced in thermal and catalytic cracking processes, is carbonyl sulfide. This compound is relatively unreactive, is present in very small amounts and is not effectively removed from the hydrocarbon gases by the conventional reagents employed in removing hydrogen sulfide, mercaptans and the like, and due to the closeness of its boiling point to that of propane it can not be satisfactorily separated therefrom by usual distillation procedures. This compound undergoes a slow reaction with water forming hydrogen sulfide and carbon dioxide. If hydrocarbon gases produced in cracking petroleum are desulfurized by conventional methods and immediately tested for corrosive sulfur, the test is ordinarily negative; however, if such gases are stored for a period of about ten days, positive tests for corrosive sulfur are obtained. This behavior is attributed to the failure of conventional methods to remove carbonyl sulfide and its subsequent reaction to form corrosive sulfur compounds. The usual object of the various desulfurization treatments applied to petroleum products by the industry is to reduce the sulfur content of the finished product below the point at which serious corrosion of the metal surfaces of burning equipment is observed. In the case of liquefied petroleum gas, the maximum allowable sulfur content is ordinarily much lower than on other petroleum products. Even a very low sulfur content in liquefied petroleum gases is found to cause the formation of sulfur or sulfide deposits which cause faulty operation of the equipment in which the gas is used. Such troublesome deposits are most commonly formed in the orifices of gas-air mixing equipment in industrial gas systems and in the carbureting units of automotive equipment. Thus, carbonyl sulfide, even though it is present in only very small quantities and is relatively unreactive in character, must be removed from liquefied petroleum gas and its economic removal constitutes a difficult and long-standing problem. Thus, it has constituted a serious obstacle to the profitable utilization of propane-propylene fractions derived from thermal cracking and similar thermal operations which inherently result in carbonyl sulfide contamination of this fraction.

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It has now been discovered that carbonyl sulfide may be effectively removed from such normally gaseous hydrocarbons by contacting the gases in the presence of added hydrogen with a hydroforming catalyst under conditions adapted to effect a hydroforming conversion of straight run naphtha with net production of hydrogen and preferably in conjunction and in integral combination with a conventional type of hydroforming operation.

"Hydroforming" is a term which has been generally adopted and well understood in the art to describe a process of converting low octane naphthas into a naphtha rich in aromatics and of high octane value by a procedure having as its salient features contacting the naphtha feed at elevated temperatures of the order of about 900–1050° F. in a catalytic reaction zone with a catalyst adapted to promote certain dehydrogenation types of reactions, under total pressures of the order of about 50–450 p. s. i. g. with a high partial pressure of hydrogen usually produced by recycling hydrogen rich gas produced in the process. Usual feed stocks to the hydroforming unit are low octane straight run naphthas. However, the process is likewise applied to the further conversion of a "second pass" operation over the catalyst of narrow boiling range cuts derived by fractional distillation of the hydroformate product from the hydroforming of naphtha fraction having a wide boiling range in a "first pass" operation, as, for instance, such cuts rich in toluene or xylenes where a fraction exceptionally rich in these individual aromatic compounds is desired.

Pursuant to the present invention, carbonyl sulfide is removed from normally gaseous hydrocarbons and other desirable results obtained by introducing these gases into the naphtha feed stream and passing them therewith through the catalyst section of a hydroforming unit. It has been ascertained that hydrocarbon gases, for example, in the amount of about 10,000 lb./hr. may be introduced into the feed stream of a hydroforming unit charging about 15,000 barrels per day of naphtha and that carbonyl sulfide is so effectively removed in this operation that its

content in the hydrocarbon gases recovered from the effluent from the hydroforming zone is below 0.04 part per million by weight calculated as sulfur. No change in the operation of the reformer other than in preheat requirement is noted and no significant loss in quality or quantity of the naphtha hydroformate is sustained. In addition to providing the desired carbonyl sulfide removal, the inclusion of the hydrocarbon gases in the feed stream is found to facilitate vaporization of the naphtha charge, the gases also act as a relatively inert heat carrier to the catalyst. When the hydrocarbon gases contain unsaturated compounds, a further advantage is obtained in the hydrogenation of these, for instance, the quantity of COS free propane recovered is increased by hydrogenation of propylene present in the added hydrocarbon gases.

The appended drawing is a simplified diagrammatic illustration of a hydroformer and gas recovery section suitable for the practice of the process of the invention. The naphtha charge is introduced through line 1, liquefied normally gaseous hydrocarbons are introduced into the naphtha feed stream via line 2, the combined charge is heated to reaction temperature in heating section 3 and introduced into the catalyst section 5 via line 4. The effluent from the catalyst section 5 is introduced into liquid-gas separator 7 via line 6. The separated gases, including the hydrogen produced by the hydroforming reaction, flow from separator 7 via line 8, a portion of the gas being recycled via lines 9, 10 and 4 and the remainder flowing to absorber 12 via line 11. Non-absorbed gas is taken for fuel via line 16 and the enriched or fat absorption medium is passed to stripper 29 via lines 17 and 18. The lean or stripped absorbent medium is returned to the absorber via lines 22 and 23 and the stripped gas is passed to debutanizer 15 via lines 19, 20, 21 and 14. The liquid from separator 7 is likewise passed to debutanizer 15 via lines 13 and 14. C_4 and lighter material is taken from debutanizer 15 to depropanizer 30 via lines 24 and 25. C_5 and heavier materials are taken from debutanizer 15 via line 26 constituting the desired hydroformate product. From depropanizer 30, C_4 and heavier materials are removed via line 28. A propane cut is removed via line 34 and lighter gases pass through line 27 and condenser 35 to reflux drum 31 from which depropanized gas is released via line 32 for fuel and propane flows into propane recovery stream 34 via line 33.

The practice of the invention and the advantages thereof are further illustrated by the following specific examples of its utilization on a commercial scale unit.

EXAMPLE I

The procedure differed from normal operation of the hydroformer in that, propane recovered from the thermal cracking of petroleum and containing 700 parts per million of carbonyl sulfide calculated as free sulfur was introduced through line 2 into the feed stream 1 of a commercial hydroformer. The propane recovered from this treatment via line 34 was found to contain less than 0.04 part per million by weight of carbonyl sulfide calculated as sulfur. The process was conducted as follows:

Normal operation of hydroformer

Straight run naphtha having an ASTM boiling range 200–330° F. is charged to the first pass operation of the reformer at the rate of 14,400 barrels per day at a space velocity of about 0.9 volume of liquid naphtha per volume of catalyst per hour. Temperature at the inlet to the catalyst section is about 1030° F. and a pressure of 190 p. s. i. g. is maintained. Hydrogen rich recycle gas is introduced into the catalyst section at a rate of about 4390 cubic feet per barrel. The catalyst is a coprecipitated molybdena-alumina catalyst prepared according to the method disclosed in the copending application of Claussen et al., Serial No. 545,734. Analysis of the significant streams from the recovery section is shown in the following Table I where Lean absorber gas refers to the gas taken from the absorber via line 16 in the drawing, Depropanized gas refers to the gas taken via line 32, Propane cut refers to material taken via line 34 and Butane cut refers to material taken via line 28.

TABLE I

Rates	Lean Absorber Gas	Depropanized Gas	Propane Cut	Butane Cut
SCF/hr.	373,000	3,235		
lb./hr.	6,490	306	1,425	3,185
BPOD.			193	381
Fractional Analysis	**Gas Volume, Per Cent**		**Liquid Volume, Per Cent**	
H_2	79.9	2.7		
CH_4	11.1	7.9		
C_2H_4				
C_2H_6	5.7	34.4	3.3	
C_3H_6		0.3	0.1	
C_3H_8	2.9	54.2	94.6	0.3
iC_4H_{10}	0.1	0.5		45.9
nC_4H_{10}	0.1		0.1	48.0
C_4H_8	0.2		1.9	2.5
iC_5H_{12}				3.0
nC_5H_{12}				0.2
C_5H_{10}				0.1
Average Molecular Wt.	6.6	35.9	42.9	57.1
Total C_3, Rates lb./hr.	1,255	205	1,347	8

It should be noted here that the depropanizer section of the particular hydroformer employed in the runs of this example was not designed to effect a high C_3 recovery via line 34. As indicated by the figures for total C_3 rates in the above table, the propane cut via line 34 amounted to only 47.8% of the total weight of C_3 hydrocarbons effluent from the recovery section.

Analysis of thermal propane

A propane cut produced in the thermal cracking of petroleum was separated for introduction into the hydroformer. It contained 700 parts per million by weight of carbonyl sulfide expressed as free sulfur after caustic washing to remove other sulfur compounds. Its further analysis expressed in liquid volume percentage is shown in the following Table II:

TABLE II

Compound	Liquid Volume, percent
CH_4	0.6
C_2H_4	0.6
C_2H_6	7.5
C_3H_6	29.5
C_3H_8	61.6
C_4H_{10}	0.1

Operation of hydroformer including thermal propane in charge

The normal operation of the hydroformer as given above was maintained the same with the exception that the naphtha feed rate increased slightly to 14,500 barrels per day. Thermal pro-

pane having the analyses shown above was introduced into the naphtha feed stream via line 2 of the drawing at the rate of 400 barrels per day. Analysis of the significant streams from the recovery section is shown in the following Table III.

TABLE III

Rates	Lean Absorber Gas	Depropanized Gas	Propane Cut	Butane Cut
SCF/hr	408,000	3,250		
lb./hr	8,630	298	2,740	3,250
BPOD			371	362
Fractional Analysis	**Gas Volume, Per Cent**		**Liquid Volume, Per Cent**	
H_2	75.9	4.4		
CH_4	12.1	11.5		
C_2H_4				
C_2H_6	6.3	29.9	0.2	
C_3H_6		0.3		
C_3H_8	4.8	53.3	90.5	
iC_4H_{10}	0.4	0.4	7.3	42.5
nC_4H_{10}	0.1	0.1	0.4	47.0
C_4H_8	0.2	0.1	0.7	2.5
iC_5H_{12}	0.2		0.2	7.0
nC_5H_{12}				0.6
C_5H_{10}			0.5	0.4
Average Molecular Wt.	8.0	34.8	45.4	59.1
Total C_3 Rates, lb./hr.	2,280	206	2,480	0

In normal operation of the hydroformer as shown in Table I, total C_3 hydrocarbon material is effluent from the recovery system in the several streams thereof at a rate of 2,815 lb./hr. The corresponding figure when operating with added thermal propane is seen from Table III to be 4,966 lb./hr. which represents an increase of 2,151 lb./hr. The C_3 content of the added thermal propane, as may be calculated from the data of Table II and the feed rate, amounted to 2,690 lb./hr., thus the increase of 2,151 lb./hr. in total C_3 hydrocarbons effluent from the recovery system indicates that 80% of the added C_3 hydrocarbons reappear in the recovery system streams.

The data of Table III indicates the almost complete absence of propylene from the recovery system streams while Table II indicates that 29.5% of the added thermal propane cut was propylene. From the data of Tables I, II, and III, it may be calculated that the gain in total propane effluent from the recovery system during operation with the added thermal propane cut amounts to more than 100% of the propane content of the added thermal propane cut. This data together with the fact that only 80% of the total C_3 hydrocarbons in the propane cut reappear in the recovery system streams indicates that a part of the propylene is hydrogenated and that the remainder of it is condensed probably by alkylation or polymerization to heavier material which is recovered in the liquid hydroformate.

The Propane Cut shown in Table III was caustic washed following its recovery and then stored for three weeks. At the end of this period it was tested for the presence of sulfur compounds and found to contain less than 0.04 part per million by weight of corrosive sulfur compounds calculated as free sulfur.

EXAMPLE II

Thermal propane was charged to the second pass operation of the catalytic hydroformer, first pass operation being the normal first pass operation as described in Example I. Temperature, pressure and catalyst were the same as in Example I but the naphtha charge was replaced by a narrow boiling cut rich in xylenes derived by the fractional distillation of the hydroformate product from line 26, and was introduced at the lower rate of 8036 barrels per day and hydrogen rich recycle gas was introduced at the higher ratio of 6790 cubic feet per barrel of naphtha. In normal second pass operation without the addition of thermal propane, the quantity of the liquid propane cut is essentially zero.

Thermal propane was introduced into the second pass operation at the rate of 400 barrels per day. The C_3 cut from the reformer product was caustic washed and analyzed for sulfur after three weeks storage. It contained less than 0.04 part per million of corrosive sulfur calculated as free sulfur. Analysis of the thermal propane charged and of significant streams from the reformer recovery section are shown below.

Analysis of thermal propane

The propane cut from the product of the thermal cracking of petroleum was separated for introduction into the hydroformer. It contained 700 parts per million by weight of carbonyl sulfide after caustic washing to remove other sulfur compounds. Its further analysis expressed in liquid volume percentage is shown in the following Table IV:

TABLE IV

Compound	Liquid volume, percent
CH_4	0.2
C_2H_4	0.4
C_2H_6	3.1
C_3H_6	24.2
C_3H_8	71.7
C_4H_{10}	0.1
C_4H_8	0.1
C_5H_{12}	0.1

The analysis of significant product streams from the recovery section during second pass operation charging thermal propane as described in Table IV above is shown in the following Table V:

TABLE V

Rates	Lean Absorber Gas	Depropanized Gas	Propane Cut	Butane Cut
SCF/hr	204,000	6,480		
lb./hr	5,500	673	1,187	1,985
BPOD			161	237
Fractional Analysis	**Gas Volume, Per Cent**		**Liquid Volume, Per Cent**	
H_2	61.7			
CH_4	21.6	4.8	0.1	
C_2H_4				
C_2H_6	10.0	23.3	8.0	0.1
C_3H_6	0.1	0.5	0.4	0.5
C_3H_8	6.3	71.2	90.7	0.2
iC_4H_{10}		0.2	0.6	26.6
nC_4H_{10}	0.2		0.2	36.2
C_4H_8	0.1			2.6
iC_5H_{12}				25.7
nC_5H_{12}				6.4
C_5H_{10}				1.7
Average Molecular Wt.	10.3	39.4	40.8	62.5
Total C_3 Rates, lb./hr.	1,520	540	1,083	12

From Table IV and the fact that thermal propane is charged at the rate of 400 barrels per day, it may be calculated that C_3 hydrocarbons are charged at the rate of 2830 lb./hr. Table V shows a C_3 recovery in the propane cut of 1083 lb./hr. or about 36% of the C_3 hydrocarbons charged. The remainder of the thermal pro-

pane charge leaves the recovery system in the lean absorber gas and depropanized gas streams and a part of its propylene content is converted to heavier hydrocarbon material and becomes part of the liquid product. Substantial increase in the recovered propane cut may be effected by increasing the efficiency of the recovery system with respect to propane segregation.

The above Examples I and II demonstrate that carbonyl sulfide may be effectively removed from hydrocarbon gases produced in petroleum cracking processes by the process of this invention. Such hydrocarbon gases ordinarily contain from 100 to 1000 parts per million of carbonyl sulfide calculated as free sulfur, gases from thermal cracking ordinarily containing larger amounts of carbonyl sulfide than those from catalytic cracking. Carbonyl sulfide is effectively removed by the process of the invention from the gases formed in either thermal or catalytic cracking. Carbonyl sulfide has not been found present in the gases formed in straight run separation of petroleum. The gases may be pretreated for the removal of sulfur compounds other than carbonyl sulfide and commonly receive such treatment as a finishing step in the cracking operation which produces them. Gases from petroleum cracking having an olefin content of about the same magnitude as those employed in the examples may be added to the naphtha charge in amount up to about 16 lbs. of gas per barrel of naphtha without altering the operation or the performance of the hydroformer unit. In the event that the gases have an appreciable nitrogen content, they are preferably washed with water or dilute acid, preferably sulfuric acid, to remove such compounds, since they act as catalyst poisons, particularly if an alumina-molybdena catalyst is used.

The conditions of operation necessary for carbonyl sulfide removal may be generally described as those conventionally employed or known to be suitable for the hydroforming of naphtha. If the process is conducted by adding the hydrocarbon gases to the naphtha charge to a normal naphtha hydroforming operation, the gas formed in the hydroforming of the naphtha will contain on the order of 70% hydrogen and will be formed in such quantity that recycle of a portion of this gas to the catalyst section will fully meet the hydrogen requirement. In first pass operation, 4000–4500 cubic feet of recycle gas per barrel of liquid charge are introduced into the catalyst section, while in second pass operation the ratio preferably will be on the order of 6500–7500 cubic feet per barrel. If the carbonyl sulfide removal is conducted, pursuant to a further possible modified embodiment of the process, by separately processing the hydrocarbon gases produced in cracking processes rather than by including them in the charge to a naphtha hydroforming process, it will be necessary to supply hydrogen from an outside source in quantity sufficient to maintain a ratio on the order of 3000 cubic feet of hydrogen per barrel of liquefied gas entering the catalyst section.

The preferred catalyst is the molybdena-alumina catalyst referred to in the examples; however, carbonyl sulfide removal is obtained with other conventional hydroforming catalysts and they are, therefore, considered to be within the scope of the invention.

The process of the invention achieves an efficient and complete removal of carbonyl sulfide as indicated in the data of the examples. Such removal of this refractory and unreactive sulfur compound makes possible the production of a commercial liquefied petroleum gas capable of long periods of use in burning equipment without development of sulfur caused operating difficulties due to corrosion and orifice stoppage. The tests for sulfur content of the product gases were conducted according to the method described by M. M. Holm in Industrial and Engineering Chemistry, analytical edition, July 15, 1936, at pages 299–300. The method is extremely sensitive in detecting corrosive sulfur and also in detecting carbonyl sulfide provided the gas to be tested is stored for a sufficient period to permit the slow reaction of carbonyl sulfide with water to occur. Three weeks storage have been found sufficient for this purpose.

The product gases issuing from the hydroformer are caustic washed immediately following their separation and then stored. If there is appreciable delay between the separation of the gases and the caustic washing step, the gases should be distilled to remove free sulfur which may be formed during the delay interval.

It is to be understood that the examples given above of the practice of the process are illustrative and various modifications thereof will be apparent to those skilled in the art, and that the invention is not to be limited otherwise than as prescribed in the appended claims.

We claim:

1. A process of treating carbonyl sulfide contaminated propane to effect separation of the carbonyl sulfide therefrom, which comprises commingling the mixture with a hydrocarbon fraction within the naphtha boiling range and added hydrogen, passing the commingled hydrocarbons and hydrogen over a hydroforming catalyst under conditions adapted to hydroform the naphtha, and recovering from the effluent of the catalytic zone carbonyl sulfide-free propane separately from the naphtha hydroformate.

2. A process of treating a carbonyl sulfide contaminated mixture of hydrocarbon gases to effect separation of the carbonyl sulfide therefrom, which comprises commingling the gas mixture with a hydrocarbon fraction within the naphtha boiling range and added hydrogen, passing the commingled hydrocarbons and hydrogen over a hydroforming catalyst under conditions adapted to hydroform the naphtha, and recovering from the effluent of the catalytic zone carbonyl sulfide-free hydrocarbon gases separately from the naphtha hydroformate.

3. A process of treating a carbonyl sulfide contaminated mixture of propane and propylene derived from a petroleum cracking operation to effect separation of the carbonyl sulfide therefrom, which comprises commingling the mixture with a hydrocarbon fraction within the naphtha boiling range and added hydrogen, passing the commingled hydrocarbons and hydrogen over a hydroforming catalyst under conditions adapted to hydroform the naphtha, and recovering from the effluent of the catalytic zone carbonyl sulfide-free propane separately from the naphtha hydroformate.

4. A process for treating carbonyl sulfide contaminated hydrocarbon gases to effect separation of the carbonyl sulfide therefrom, which comprises commingling said gases with added hydrogen, contacting the commingled hydrocarbon gases and hydrogen with a hydroforming catalyst under operating conditions suitable to hydroform

a petroleum naphtha, and recovering from the effluent of the catalytic zone carbonyl sulfide-free hydrocarbon gases.

5. A process for treating carbonyl sulfide contaminated hydrocarbon gases to effect separation of the carbonyl sulfide therefrom, which comprises washing said gases with dilute acid to remove acid soluble nitrogen compounds therefrom, commingling the washed gases with added hydrogen, contacting the mixture with a hydroforming catalyst under conditions suitable to hydroform a naphtha, recovering from the effluent of the catalyst zone carbonyl sulfide-free hydrocarbon gases, and washing the recovered gases with caustic soda.

6. A process for treating a carbonyl sulfide contaminated C_3—C_4 hydrocarbon fraction derived from a petroleum cracking operation, which comprises washing said fraction with dilute sulfuric acid to remove nitrogen compounds, commingling the washed fraction with petroleum hydrocarbons boiling within the naphtha boiling range and with added hydrogen, passing the commingled hydrocarbons and hydrogen over a hydroforming catalyst under conditions adapted to hydroform the naphtha, recovering from the effluent of the catalytic zone a carbonyl sulfide-free C_3—C_4 hydrocarbon fraction separately from the naphtha hydroformate, washing said fraction with caustic soda and then redistilling it to recover sulfur-free C_3—C_4 hydrocarbons.

7. The method of claim 2 wherein the hydroforming catalyst consists essentially of molybdena and alumina.

8. The method of claim 2 wherein the carbonyl sulfide content of the hydrocarbon gases is between about 100 and 1000 parts per million by weight calculated as free sulfur and wherein the hydroforming catalyst is a molybdena-alumina catalyst comprising a minor proportion of molybdena and a major proportion of alumina.

9. In a hydroforming process wherein naphtha and hydrogen are introduced into contact with a hydroforming catalyst in a reaction zone at a temperature between about 900° F. and 1050° F. under a pressure between about 50 p. s. i. g. and 450 p. s. i. g. to increase the octane value of said naphtha, the method of effecting the removal of carbonyl sulfide from carbonyl sulfide contaminated hydrocarbon gases concurrently with the hydroforming of the naphtha which comprises introducing the carbonyl sulfide contaminated hydrocarbon gases into contact with the hydroforming catalyst together with the naphtha and hydrogen under the aforesaid conditions and recovering hydrocarbon gases substantially free of carbonyl sulfide gases from the effluent from the reaction zone.

10. The method as defined in claim 9 wherein the carbonyl sulfide contaminated gases are produced during the cracking of sulfur containing petroleum oil.

11. The method as defined in claim 10 wherein the amount of carbonyl sulfide contaminated gas introduced into contact with the catalyst together with naphtha and hydrogen is so regulated that the ratio of hydrocarbon gas to naphtha contacted with the catalyst does not exceed about 16 pounds of hydrocarbon gas per barrel of naphtha.

12. In a process for the hydroforming of naphtha the method of effecting the removal of carbonyl sulfide from normally gaseous hydrocarbons containing carbonyl sulfide concurrently with the hydroforming of the naphtha, which comprises washing said gases to remove nitrogenous impurities, contacting the washed gases and naphtha with a molybdena-alumina catalyst in a reaction zone in the presence of hydrogen under conditions adapted to hydroform the naphtha, withdrawing a reaction product from the reaction zone and separating a normally gaseous fraction comprising carbonyl sulfide free hydrocarbon gases from the reaction product.

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