

[54] PROCESS FOR PRODUCING CARBON
BISULFIDE

[75] Inventors: James L. Manganaro, New York,
N.Y.; Morton Meadow, Trenton;
Sidney Berkowitz, Highland Park,
both of N.J.

[73] Assignee: FMC Corporation, New York, N.Y.

[22] Filed: Apr. 30, 1973

[21] Appl. No.: 355,992

[52] U.S. Cl. 423/443; 23/277 R

[51] Int. Cl. C01b 31/26

[58] Field of Search 423/443, 659; 23/277 R

[56] References Cited

UNITED STATES PATENTS

3,512,219	5/1970	Stern et al.	23/277 R
3,699,215	10/1972	Gerin et al.	423/443

Primary Examiner—O. R. Vertiz
Assistant Examiner—Michael L. Lewis

[57] ABSTRACT

Making carbon bisulfide by introducing a hydrocarbon stream co-currently with a stream of hot sulfur vapor converging thereon.

6 Claims, 3 Drawing Figures

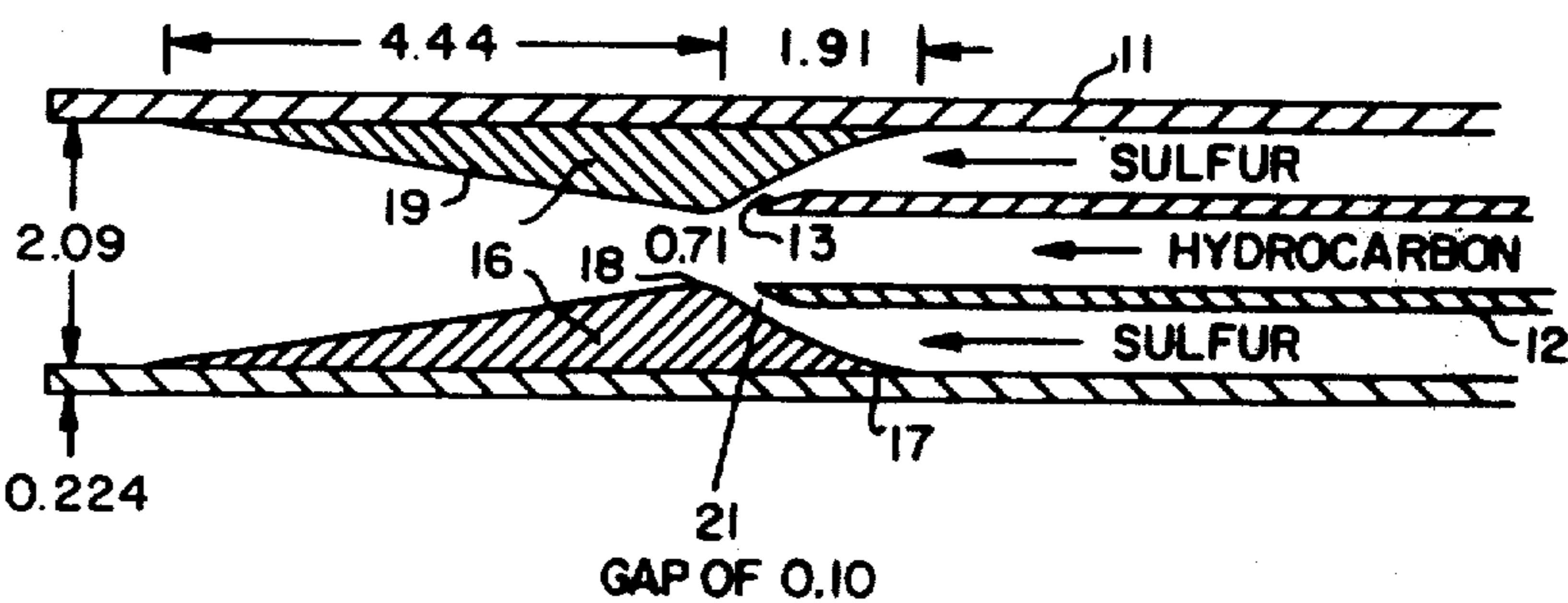


FIG. 1

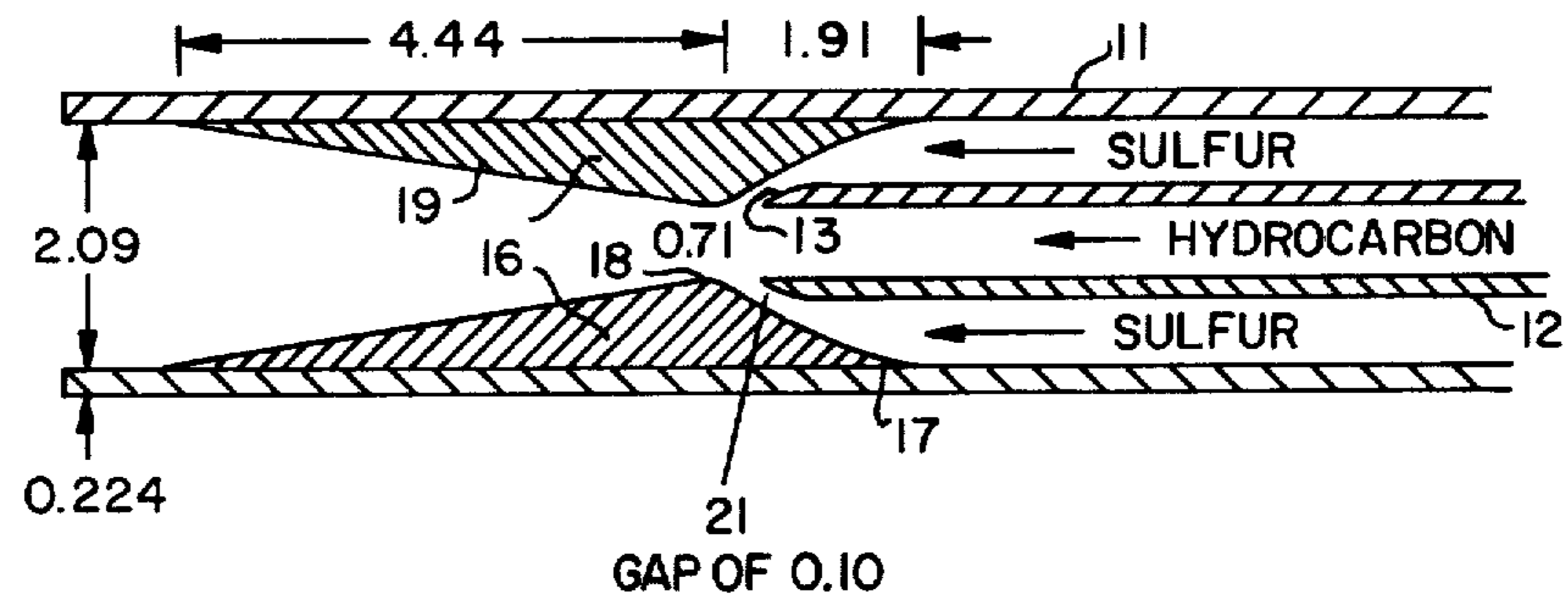
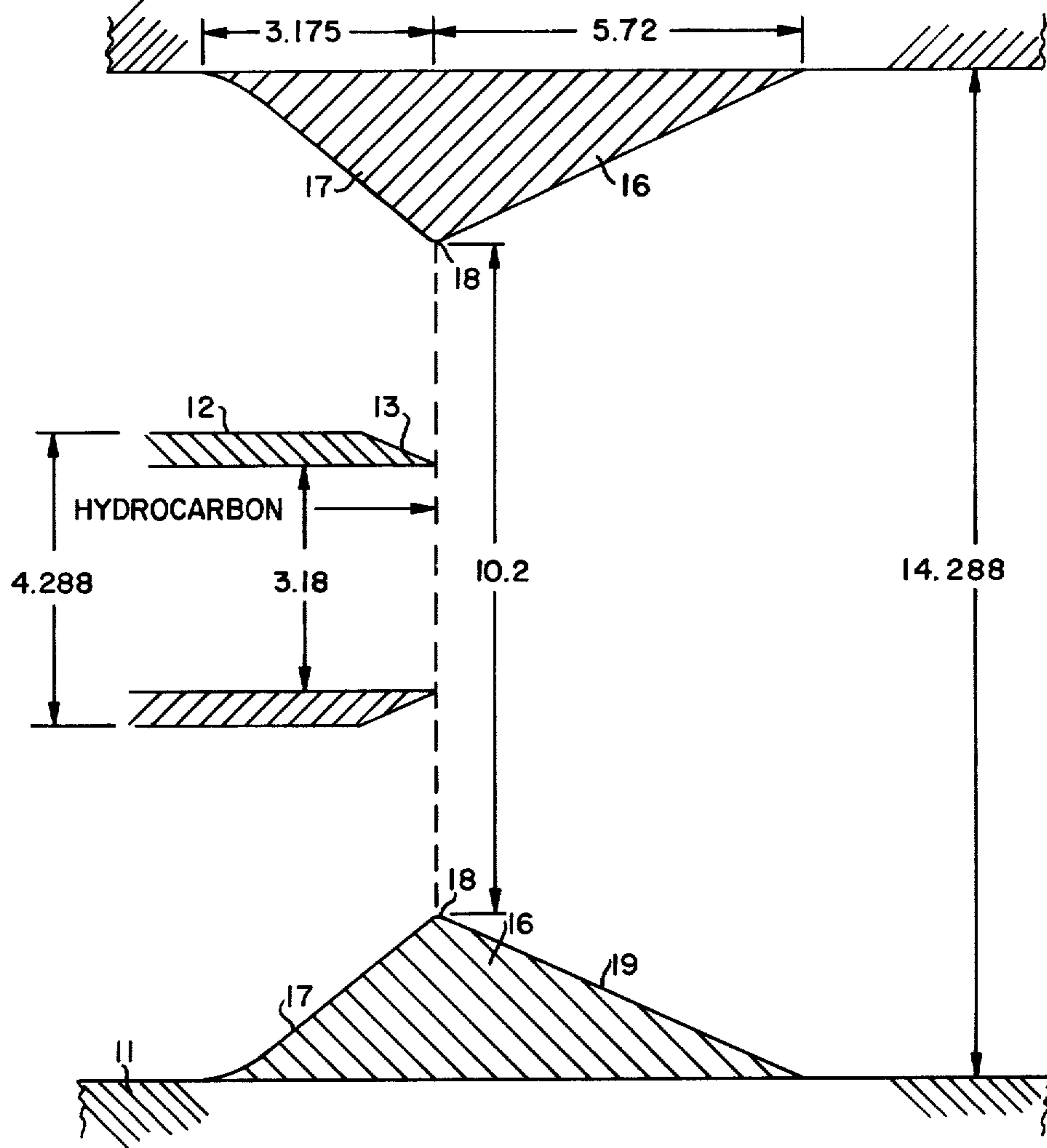
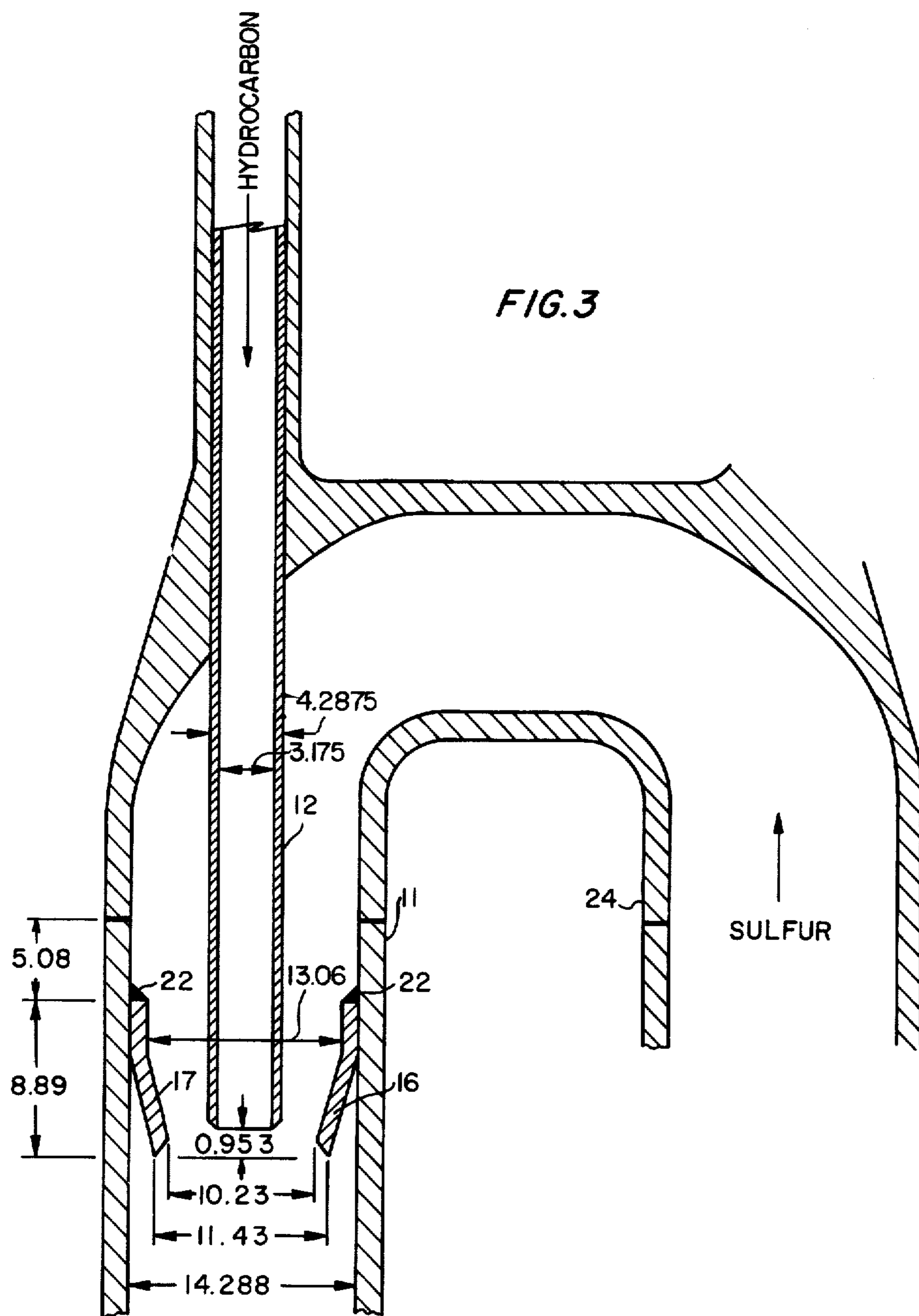


FIG. 2





PROCESS FOR PRODUCING CARBON BISULFIDE

This invention relates to a process and apparatus for carrying out the reaction of sulfur vapor and a hydrocarbon gas to produce carbon bisulfide continuously.

In accordance with one aspect of the invention a stream of hydrocarbon gas is fed co-current with a hot stream of sulfur vapor and the cross section of the sulfur vapor stream is decreased locally at the zone where it is brought into contact with the hydrocarbon stream so as to form a converging sulfur stream. Thus the sulfur vapor may be caused to travel the path of a converging cone whose apex lies along the centerline of the hydrocarbon stream. The resulting rapid convergence and impingement of the sulfur vapor upon the hydrocarbon stream produces an efficient and rapid mixing of the reactants, increasing the conversion to carbon disulfide, reducing the formation of undesirable by-products and reducing the probability of fouling of the reactor as a result of tar formation.

The invention is illustrated in the accompanying drawings in which FIGS. 1, 2 and 3 are cross-sections of various embodiments.

FIG. 1 shows an arrangement particularly suitable for use in a relatively small scale installation, in which the stream velocities (and Reynolds numbers) are not high.

FIGS. 2 and 3 show arrangements suitable for a large scale installation with high stream velocities. The arrangement shown in FIG. 2 (like that of FIG. 1) has a pressure recovery section, while that of FIG. 3 has no pressure recovery section.

The drawings are made to scale, with the dimensions indicated thereon.

In FIG. 1 the flow of the streams is from right to left. The heated sulfur vapor is introduced through a pipe 11 of circular cross section in an annular stream around a coaxial hydrocarbon feed tube 12. The latter is also of circular cross section; its inside diameter is 0.622 cm, its outside diameter is 0.953 cm, and its outlet end 13 is chamfered as shown. To form the sulfur vapor stream into a converging conical stream, there is a venturi insert 16 which fits securely within the otherwise uniform pipe 11 and which has an inwardly converging portion 17, a throat 18, and an outwardly converging (or pressure recovery) section 19. It will be seen that the sulfur vapor stream is forced through a narrow gap 21 thus greatly increasing in velocity (Bernoulli's principle) as it approaches and impinges upon the hydrocarbon stream. This increase in velocity increases the "force ratio" of the outer (sulfur) stream to the inner (hydrocarbon) stream and increases the interpenetration and mixing of the two streams. The force ratio is defined as $M_o V_o / M_i V_i$ where M_o and M_i are the mass rates of flow of the outer and inner streams respectively and V_o and V_i are the respective linear velocities of said streams. In the design shown in FIG. 1 this force ratio is in the neighborhood of 10, under the conditions specified in Example 1 below.

Downstream of the throat there is a gradually diverging section which, as is well known in nozzle design, serves as a pressure recovery section in which the velocity of the resulting mixed stream is reduced gradually and its pressure, which is lowest at the throat, increases correspondingly.

Corresponding parts of FIG. 2 are numbered identically to those of FIG. 1. In FIG. 2 the sulfur:hydrocarbon force ratio is about 2:1 for the following operating conditions: hydrocarbon (natural gas) feed tempera-

ture 100°C; sulfur feed temperature 680°C; feed pressures about 6.5 atmospheres (80 psig); excess sulfur (over that needed stoichiometrically for the reaction to form CS_2) 15% mass rate of flow of sulfur 6,580 kg per hour.

In FIG. 3 the parts are also numbered in the same way as FIG. 1. Here, as mentioned above, there is no gradually diverging pressure recovery section. The insert 16 is a tapered reducer circumferentially welded (as indicated at 22) to the inner walls of the pipe 11. Just downstream of its throat portion the insert 16 is chamfered at 45° as shown. Also illustrated in FIG. 3 is a portion of the sulfur-preheating section 24, through which the sulfur flows on its way to the mixing-reaction zone.

Reference is made here to the copending application of Meadow and Berkowitz entitled "Hydrocarbon Reactions" Ser. No. 355,991 filed on the same day as the present application, whose entire disclosure is incorporated by reference. That application describes the reaction between sulfur vapor and hydrocarbons in some detail and points out that the reaction between sulfur and higher hydrocarbons can take place very rapidly, specifying conditions for such reaction. In the practice of the present invention it is preferred to use the conditions set forth in said copending application. It is within the broader scope of this invention, however, to employ the process of this invention more generally. Thus it may be used beneficially under other conditions (such as lower mixing temperatures and lower pressures) than those set forth in that copending application. As noted in the copending application, after the initial mixing period, during which substantially all the higher hydrocarbon is reacted out of contact with the walls and in the absence of catalyst, the mixture may be led through further lengths of hot tubes around bends and into contact with various surfaces such as packings; during this further travel, substantially all the methane in the feed may be reacted with the sulfur under non-catalytic or catalytic conditions.

It will be understood that the hydrocarbon stream may contain substantial, even major, proportions of diluents, such as H_2S and/or CS_2 . The sulfur stream, too, may contain such diluents.

The following Examples are given to illustrate this invention further. In the Examples the volumes given represent, in accordance with standard practice, the volume calculated to standard conditions (STP) of a temperature of 0°C and an absolute pressure of 760 mm Hg. Residence times are given in seconds and are equal to 3600 divided by "space velocity" (S.V.) expressed in hours⁻¹; S.V. is the quotient of the total volume (in liters) of reactants at STP (with sulfur calculated as S_2) per hour, divided by the reactor volume (in liters).

EXAMPLE 1

Sulfur vapor preheated to 700°C and natural gas preheated to 400°C are brought together using the arrangement illustrated in FIG. 1, located in an electric furnace. Downstream of the venturi the mixture passes through the pipe 11 which takes the form of four two foot long side by side parallel sections (of the same three-fourths inch IPS, Schedule 40 stainless steel pipe) each of which is joined to its neighbor by a return elbow of the same stainless steel welded thereto so that the reaction mixture flows successively through the four sections in a sinuous path, all within the electric

furnace. The insert 16 is also made of stainless steel. After flowing through this tube (residence time 11 seconds) the reaction mixture is then immediately quenched, first in a vessel at 140°C (thereby condensing the sulfur in the reaction mixture). The non-condensed gases, including carbon bisulfide, then pass through a pressure-regulator, set to provide a back pressure of about 6.5 atmospheres (80 psig), from which the gases are passed to a condenser at 0°C and 74 psig to condense carbon bisulfide; non-condensed gases are vented at atmospheric pressure.

The hydrocarbon is a natural gas of the following molar composition: 89.7 percent methane, 4.18 percent ethane, 1.7 percent propane, 2.2 percent butanes, 2.04 percent nitrogen and 0.1 percent water. The sulfur is fed at a rate to provide an excess of 5 percent with respect to stoichiometry; specifically, the rates of supply of sulfur and hydrocarbon are 578 g per hour and 88.3 liters (at STP) per hour respectively. The temperature measured at the internal wall of the reactor pipe at point 15 cm downstream of the venturi throat inlet is about 700°C.

The conversion rate of the natural gas is quantitative and the carbon bisulfide has a purity of 99.99+ percent with less than 12 ppm benzene and thiophene as trace impurities. There is no evidence of tar formation in the recovered sulfur.

EXAMPLE 2

In this Example the apparatus is similar to that described in Example 1 but the arrangement of FIG. 3 is employed in a reactor pipe of 14.29 cm internal diameter. The hydrocarbon feed is natural gas having the following analysis (by mol percent): methane 96.35, ethane 2.32, propane 0.25, isobutane 0.02, butane 0.02, isopentane 0.01, n-pentane 0.01, hexane less than 0.01, other hydrocarbons 0.02, nitrogen 0.44, CO₂ 0.55, H₂ 0.02. The inlet pressure is about 6.3 atmospheres (about 78 psig), the sulfur is preheated to 664°C, the hydrocarbon feed is preheated to 115°C, the excess sulfur with respect to stoichiometry is 18 percent; the sulfur feed rate is 6,235 kg per hour and the hydrocarbon feed rate is 680 kg per hour. From the throat the mixture travels through a straight length of the pipe for about 9.1 meters, then around a bend and through more of the same type of pipe in the furnace, then (its temperature being about 630°-650°C) enters a packed reactor chamber containing silica gel particles, after which sulfur and carbon bisulfide are successively condensed from the mixture in conventional manner. Carbon bisulfide is produced in very high yield and at very high purity, having especially low benzene content.

In large scale operation, as in Example 2, the feed rates are such that the Reynolds numbers of the hydrocarbon stream and the sulfur stream (before it enters the reducing section) are often in the range of about 10⁵ to 10⁶. In Example 2, the force ratio, as previously defined, is above 2:1, specifically about 2.3:1, and can readily be calculated from the data given in that Example.

The linear speed of the stream of hydrocarbon is often very much greater than the linear speed of the

sulfur, before the sulfur stream starts to converge, e.g., well over 5 (such as about 10, 15, 20, 25 or more) times the linear speed of the sulfur. At the zone of impingement the sulfur has speeded up but is nevertheless often still moving at a lower linear speed than the hydrocarbon stream, but because of the greater mass rate of flow of the sulfur the force ratio is, preferably, well above 0.5:1.

It is understood that the foregoing detailed description is given merely by way of illustration and that variations may be made therein without departing from the spirit of the invention. The "Abstract" given above is merely for the convenience of technical searchers and is not to be given any weight with respect to the scope of the invention.

We claim:

1. Continuous process for producing carbon bisulfide by feeding a hydrocarbon gas stream co-current with and within a sulfur vapor stream to react therewith to form carbon bisulfide, wherein the improvement comprises decreasing the cross section of said sulfur vapor stream locally at the zone where it is brought into contact with said gas stream whereby to form a converging sulfur stream which converges onto said hydrocarbon gas stream, raise the velocity of said sulfur stream and increase the force ratio of said sulfur stream to said gas stream.

2. Process as in claim 1 in which said force ratio at the contact of said stream is about 0.5:1 to 10:1.

3. Process as in claim 1 in which said hydrocarbon gas stream has a substantially circular cross section and said sulfur vapor stream has a substantially circular annular cross section.

4. Process as in claim 1 in which the cross section of said sulfur vapor stream is decreased progressively and smoothly, said sulfur vapor stream impinging onto said gas stream at a zone having a throat through which said sulfur and hydrocarbon pass, the cross sectional area of said throat being at least as great as the cross sectional area of the hydrocarbon stream being fed into contact with the sulfur.

5. Process as in claim 1 and including the step of thereafter cooling the reaction mixture to recover the carbon disulfide produced by the reaction.

6. Process as in claim 5 and including the steps of feeding a hydrocarbon stream through a tube, said tube having an outlet, feeding co-current an annular sulfur vapor stream around said tube and toward said outlet at a linear velocity which is less than said linear velocity of the hydrocarbon stream passing through said outlet, and passing said sulfur stream through an annular zone of progressively decreasing cross section upstream of said outlet whereby to increase the velocity of the sulfur stream as it approaches said outlet and then impinging said sulfur stream of increased velocity onto the hydrocarbon stream emerging from said outlet, passing said sulfur and hydrocarbon through a throat adjacent to and downstream of said outlet and then increasing the cross section of the path of said the resulting reaction mixture.

* * * * *