PATENT SPECIFICATION

618,068

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3552

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COMPLETE SPECIFICATION

An Improved Synthesis of Hydrocarbons

(A Communication from STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organised and existing under the Laws of the State of Delaware, United States of America, having an office at Linden, New Jersey, United States of America).

I, CONRAD ARNOLD, a British Subject, of 29, Southampton Buildings, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to the synthesis of hydrocarbons including normally liquid hydrocarbons from carbon monoxide and hydrogen. Broadly speaking, this synthesis is a matter of record. There are, of course, two general methods for carrying out such a synthesis from the standpoint of equipment used and they are, first, the use of a stationary bed of catalyst and, second, the so-called fluid catalyst technique wherein the catalyst used in the process is suspended in the vapors during the reaction. The improvements relate to the latter type of operation, and in brief compass they involve maintaining a large ratio of catalyst to synthesis gases in the reaction zone. To support the catalyst to give the high loading required steam is employed as a diluent gas which is easily condensable and separable from the product.

When employing the stationary bed process it has been proposed to dilute the synthesis mixture of carbon monoxide and hydrogen with steam. It will be appreciated that in such a process the rate of flow of the synthesis mixture is in no way dependent on the amount of catalyst present, but may be varied at will depending on the requirements of the system.

As indicated previously, in certain processes involving the synthesis of higher hydrocarbons from carbon monoxide and hydrogen using the so-called "fluid catalyst" technique, high ratios of catalyst to synthesis gas charged to the reaction zone must be used. Difficulty is sometimes encountered in maintaining the large quantity of catalyst material required suspended and/or fully fluidized in the reaction gases. It has been proposed to increase the volume of the gas by the addition of non condensable inert gases which, while possible as a means of improving the suspension of the catalyst, is not desirable because of the increased amount of gas which must be handled in the system for recovering the liquid hydrocarbon products from unused synthesis gas and inert material.

As indicated, it has been found that these difficulties may be advantageously overcome and the equipment for carrying out the process considerably simplified by using the readily condensable gas, steam, to supplement the synthesis gas as an aid in maintaining the catalyst in suspension in the reaction zone. In ordinary practice the synthesis gas is produced at high temperatures, then is cooled and the water vapor content condensed and removed before charging the synthesis gases to the reaction zone.

The present invention accordingly comprises a process for the synthesis of hydrocarbons from a mixture of carbon monoxide and hydrogen by passing the mixture through a fluidized bed of Fischer synthesis catalyst under reaction conditions of temperature and pressure, wherein the said mixture is diluted with steam.

Broadly speaking, the improvements involve in the preparation of the synthesis gases the step of cooling the same after their formation (for example, by treating methane with steam), but in which the formed synthesis gas is cooled only to the temperature of the synthesis operation, say about 400 to 600° F. The cooling of the synthesis gases may be accomplished by direct introduction of a water spray into the hot synthesis gases thereby forming steam, which operation may be easily carried out by injection of the water into the transfer line connecting the synthesis gas generator and the synthesis reactor. If this means is employed the necessity of a separate piece of equipment to cool to atmospheric temperature is thereby eliminated and the amount of water necessary for cooling is reduced to a very low fraction of that formerly used.

In the accompanying drawing, a flow plan has been shown which will serve to illustrate a modification of this invention.

Referring in detail to the drawing, a mixture of methane, steam and carbon dioxide is introduced into the present system through line (1), thence heated in a fired coil (3) to a temperature of 1000° F., whereupon the materials are withdrawn through line (5) and charged into the synthesis gas forming reactor (10) containing a catalyst (C) which may be nickel on a support such as kaolin promoted by magnesia or the like. It is desired in this synthesis to form CO and hydrogen in substantially one to two volume ratio. To accomplish this result the proportion of methane, steam and CO_2 in line (1) should be about 1:1.6:0.7. The steam, methane and CO_2 are under a pressure of from atmospheric to 200 lbs. per square inch in the reaction zone and are resident therein for the period resulting from the treatment of from 50 to 400 volumes of methane (measured at standard conditions) per volume of catalyst per hour. The catalyst temperature is at about 1500° F.

The product is withdrawn through a foraminous support (G) for the catalyst and an exit line (12) at a temperature of about 1500° F. It is proposed to inject water via line (13) into line (12) to the extent that the gas is cooled to a temperature of between 400 and 600° F. whereupon the cooled gases are then discharged into a hydrocarbon synthesis reactor (15) containing a suitable catalyst (C_2), as follows: The catalyst which may be, for example, metallic cobalt together with a suitable support, such as kieselguhr, and promoter, such as thoria, in the form of a powder is withdrawn from supply hopper (17) through a standpipe (18) controlled by a flow valve (19) and discharged into line (12). The standpipe is provided with a plurality of taps (21) into which a slow current of steam may be injected for the purpose of causing the catalyst to flow smoothly through the standpipe (18). The catalyst of course forms a suspension in the synthesis gases in line (12) and is then conveyed into the synthesis reactor (15).

The catalyst, as stated, is in the form of a powder having a particle size of from 50 to 400 mesh, but preferably having a size of about 200 mesh for 90 per cent. or more of the same. The catalyst is maintained in "fluidized" state, i.e., in the form of a dense suspension by flowing the reactants upwardly through a grid (G_2) at a rate of from ½ to 5 ft. per second, preferably at a rate of 1½ to 3 ft. per second. The density of the suspension in the reactor from (G_2) to a point (L_2) is from 10 to 30 lbs. per cubic foot, and the mass of catalyst is in a highly turbulent, mobile state affording uniformity of temperature and thorough mixing throughout the entire mass. The amount of catalyst with respect to say CO, should be about 1 lb. of catalyst to 1 to 15 cubic feet of CO measured at 60° F. and 1 atmosphere pressure. Above (L_2) it will be noted that the reactor is expanded, which results in decreasing of the velocity of the gases passing into the expanded portion (E) sufficiently low so that the gas will not support the catalyst with the result that substantially all of the catalyst remains in the reactor at a point not higher than (L_2), the stream issuing from the reactor through (20) containing very little catalyst. This catalyst can be removed by any known procedure such as passage through one or more separators (S), such as centrifugal separators, electrical precipitators, so that the stream is substantially free of catalyst.

It will be unnecessary to describe the usual method for condensing out the desired normally liquid hydrocarbons and returning unreacted CO and hydrogen to reactor (15) for further processing, since these details have been disclosed and are known to others. The disclosure, therefore, will contain so much of the prior art as will make the present improvements understandable, for it is believed that this will serve to clarify and emphasize this invention.

In order to give more information regarding this invention, the following specific working example is set forth.

25,000,000 cubic feet per day of natural gas are charged to line (1) together with 2,000,000 lbs. of steam and 17,000,000 cubic feet of carbon dioxide. This charge mixture is treated in vessel (10) at 1500° F. and approximately 50 pounds gage pressure to form about 100,000,000 cubic feet per day of a synthesis gas composed mainly of hydrogen and carbon monoxide in a 2:1 H_2 to CO volume ratio. An amount of water sufficient to reduce the temperature of this stream to 400° is injected by means of line (13). To accomplish this about 2,000,000—2,500,000 lbs. of H_2O per day will be required, the exact amount depending on heat losses from the equipment, and the total steam in the stream thus cooled will amount to about 3,500,000 lbs. per day. It is desired to treat the hydrogen-carbon monoxide mixture and cause synthesis of hydrocarbon oils in reactor (15) at 400° F. and 50 lbs./sq. in., providing a catalyst bed of such volume that 100 volumes of the dry synthesis gas measured under standard conditions be conducted through the reactor each hour for each volume of catalyst; furthermore, it is desired to avoid actual superficial gas velocities based on inlet quantity lower than .75 feet per second (while this is not the lowest linear velocity at which satisfactory "fluidizing" of the catalyst bed will take place, some reduction in volume of the reactants takes place during conversion, so that higher than minimum linear velocity on inlet materials must be allowed for.) If this synthesis were to be carried out after removal of practically all of the steam from the synthesis gas, a vessel of about 27 feet diameter and 72 feet height would be required to meet the above conditions. The height of this vessel is excessive giving rise to numerous difficulties in design, construction and operation, and reduction in height is desirable. If the synthesis gas containing steam as described above is run directly to reactor (20), the required conditions can be met using a reactor only 40 feet high and having a diameter of 36 feet. The product from reactor (20) consists of about 3,000 barrels per day of normally liquid and solid hydrocarbons, together with some unreacted carbon monoxide and hydrogen, and steam. The outlet stream is run to a cooler in which practically all of the steam is condensed by means of cooling water, and a large portion of the synthetic hydrocarbons. The tail gas may then be scrubbed to recover additional liquid hydrocarbons, and may then be recycled in part to vessel (10) wherein it will replace an equivalent amount of fresh charge gas. The remaining tail gas may be burned to supply fuel requirements in the plant.

It is pointed out that the use of excess steam in synthesis gas preparation is in no way undesirable, the slight increase in carbon dioxide concentration in the synthesis gas resulting therefrom being easily counteracted by an increase in temperature of the reaction. By this means hot synthesis gas mixed with a volume of steam equal to from 25—100 per cent. the volume of H_2 plus CO produced is made available. The hot synthesis gas is cooled to synthesis reaction temperature by introduction of a water spray in the transfer line (13), thereby increasing the amount of steam.

As previously indicated, this invention consists in the means for maintaining a larger quantity of catalyst in contact with the reactants in the reaction zone than would otherwise be possible, the catalyst being in powdered form.

It is necessary to use additional quantities of gas to maintain the fluid-like suspension required, and this additional gas is supplied as added steam. The densable does not involve a serious steam, however, since it is readily con- problem in the purification and recovery of the desired product.

Having now particularly described and ascertained the nature of the said invention, and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A continuous process for the production of hydrocarbons, including normally liquid hydrocarbons, by forming a synthesis gas mixture of hydrogen and carbon monoxide, and subjecting this synthesis gas mixture to a synthesis reaction in the presence of a finely divided Fischer synthesis catalyst material maintained in fluidized form by the passage of the gas mixture therethrough, wherein a higher weight ratio of catalyst to reactant gas, than can be obtained with a reactant gas alone, is mainained by supplementing the reactant gas with a sufficient quantity of steam and separating the said steam from the product by condensation.

2. A process according to Claim 1 wherein the synthesis gas mixture issuing from the synthesis gas generator and comprising a mixture of hydrogen, carbon monoxide and steam is cooled to a temperature above the boiling point of water before passing to the synthesis stage, whereby the steam contained in the mixture is retained in the mixture and serves as part of the additional steam to maintain the catalyst in the fluidized form.

3. A process according to Claim 1 or 2, wherein water is fed into the stream of synthesis gas mixture leaving the generator before contacting the same with the synthesis catalyst, whereby the synthesis gas is cooled to the temperature of the synthesis reaction and the water is converted into the additional steam required to maintain the catalyst in the fluidized state.

4. A process according to Claim 3 wherein sufficient water is added to the synthesis gas issuing from the synthesis gas generator to cool the same to a temperature between 400° F. and 600° F.

before contacting with the synthesis catalyst.

5. A process according to any of the preceding claims, wherein the quantity of steam added amounts to from 25% to 100% of the volume of the synthesis gas mixture of carbon monoxide and hydrogen.

6. A process according to any of the preceding claims, wherein the reaction is carried out under pressure.

7. A process for the synthesis of hydrocarbons from a mixture of carbon monoxide and hydrogen by passing the mixture through a fluidized bed of Fischer synthesis catalyst in the synthesis zone under reaction conditions of temperature and pressure, wherein the said mixture is diluted with steam.

Dated this 29th day of July, 1946.

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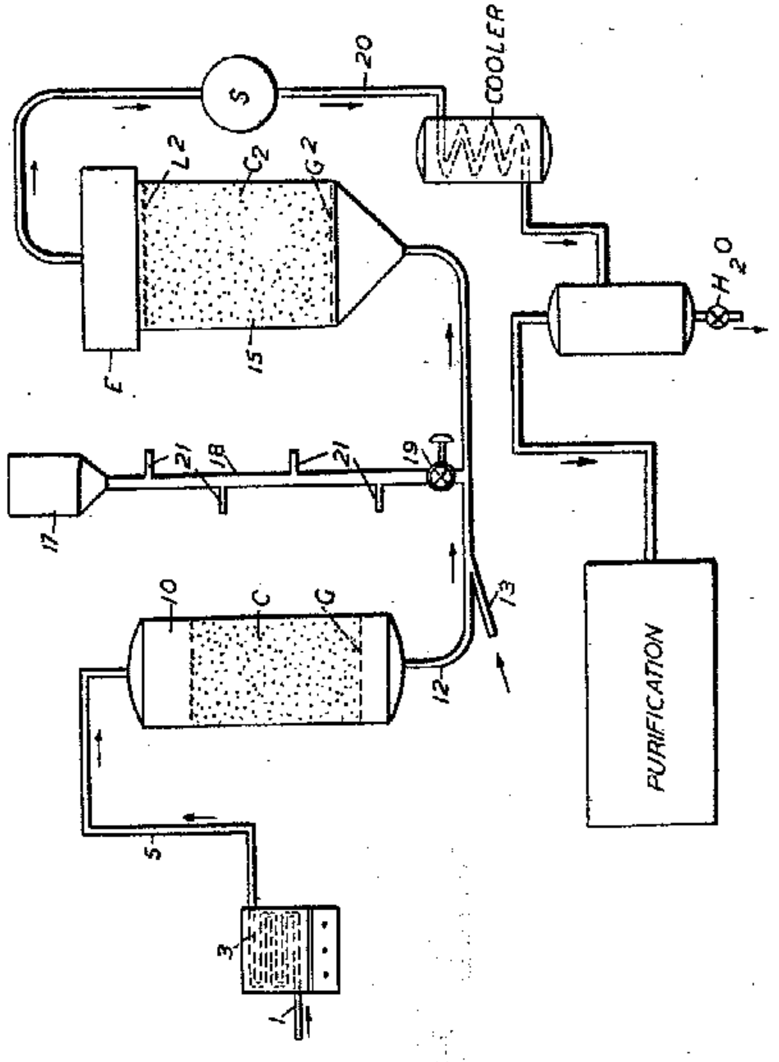
618,068 COMPLETE SPECIFICATION 1 SHEET

[This Drawing is a reproduction of the Original on a reduced scale]



H.M.S.O. (Ty.P.)