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# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

# Improvements in or relating to Hydrocarbon Synthesis

We, 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 Elizabeth, New Jersey, United States of America, 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 manufacture of valuable products by the catalytic conversion of carbon oxides with hydrogen. The invention is more particularly concerned with an improved method of utilizing tail gases from the synthesis of hydrocarbons and valuable oxygenated organic compounds by the catalytic conversion of carbon monoxide with hydrogen.

The catalytic synthesis of hydrocarbon oils and valuable chemicals from carbon monoxide and hydrogen has been assuming increasing importance in recent years as a source of fuels and raw materials supplementing and potentially replacing the steadily decreasing crude oil resources. The hydrocarbon synthesis may be operated on the basis of using either natural gas or carbonaceous solids such as coal, etc., for the production of synthesis gas containing carbon monoxide and hydrogen. Particularly, the process utilizing coal has not as yet advanced to a state of development at which the products of the synthesis would economically compete with similar products recoverable from natural mineral oils.

This situation has stimulated considerable research activity aiming at the improvement of the process as well as product yields and quality. Previous attempts in this direction have been concentrated largely on the valuable liquid or readily liquefiable synthesis products such as fuels, lubricants, oxygenated compounds, etc.

However, the hydrocarbon synthesis yields substantial amounts of a further by-product in the form of tail gas from which normally liquid synthesis products have been removed and which is rich in valuable constituents such as hydrogen, carbon monoxide, and hydrocarbon gases. This tail gas, which normally amounts to about 5,000—10,000 cu. ft. per barrel of liquid products formed, has the great advantage of being substantially sulfur-free but has been of limited value heretofore as a result of its usually low BTU value caused by relatively high dilution with $CO_2$ and/or nitrogen. While the gas may be scrubbed readily of $CO_2$, it is economically impractical to remove free nitrogen.

The nitrogen is introduced into the process by the coal or natural gas used as starting material for the synthesis gas and/or by air or $CO_2$ enriched air employed in the synthesis gas manufacture. This nitrogen content may interfere with the use of the tail gas as a fuel gas because it adversely affects the BTU value of the tail gas.

It has, therefore, been suggested, prior to the present invention, to convert synthesis tail gas in a conversion operation with an oxidizing gas such as steam, oxygen, or carbon dioxide to produce a gas having an $H_2$:CO ratio which will supplement the ratio obtained in the main reformer in which the bulk of synthesis gas is produced, for example, from natural gas. The combined gas from the two reformers is adjusted to an $H_2$:CO ratio of about 2:1 and used in the main synthesis reactor. However, this procedure requires substantial purging of tail gas in order to keep

[*Price* 2/-]

nitrogen from building up in the system. Nitrogen build-up is particularly disadvantageous because of the increased size of equipment required, the increased amount of heat transfer surface needed to heat and cool the recycled inert gas and the diluting effect of this gas on the reaction constituents. Up to about 50% of the tail gas must be vented to maintain the nitrogen content of the total process gas within permissible limits of, say, about 8—16%. The gas vented is unsuitable for the production of further synthetic products, since the high nitrogen content interferes seriously with the economical operation for the reasons given above.

It has also been proposed to convert synthesis tail gas from a first stage into secondary synthesis gas by reconverting the undesirable hydrocarbons into carbon monoxide and hydrogen by the use of steam and/or carbon dioxide at a high temperature, and then converting the gas mixture thus produced into hydrocarbons in the same or in a new contact stage. In a modified form of this proposal, additional liquid or gaseous hydrocarbons may be mixed with the synthesis tail gas from a first stage and the mixture converted at elevated temperatures with or without a catalyst to produce synthesis feed gas for a second and separate stage.

It has now been found that the use of free oxygen for the conversion of synthesis tail gas from a first stage into further synthesis feed gas and the employment of such further synthesis feed gas in a second and separate conversion stage permits more complete and economical utilization of synthesis tail gas. The nature of the invention and the manner in which it is carried out will be fully understood from the following description thereof read with reference to the accompanying drawing.

It is, therefore, the principal object of the invention to improve the economics of the catalytic synthesis of hydrocarbons and oxygenated products from CO and $H_2$ by a proper utilization of synthesis tail gas.

In accordance with the present invention, tail gas from a first synthesis stage, if desired, after suitable $CO_2$ removal, is converted by the use of free oxygen in a secondary synthesis gas generator to produce a secondary synthesis gas of any desired $H_2$:CO ratio and this secondary synthesis gas is converted to valuable synthesis products in a good synthesis stage. Tail gas from the second synthesis stage may either be again converted into synthesis gas and processed in a third synthesis stage or it may be used for fuel purposes in the process.

In this manner, by far the greater proportion of the tail gas of the first synthesis stage may be converted to additional amounts of normally liquid hydrocarbons and other valuable synthesis products while recycling of tail gas to the primary synthesis gas generator and the ensuing build-up of nitrogen in the system are avoided. This is of particular importance when viewed in the light of suitable processes of synthesis gas generation. The more economic gas generation processes involve the use of oxygen for the conversion of carbonaceous solids or natural gas. The production of oxygen of more than 95% purity is too expensive to be practical for a commercial synthesis operation. Oxygen of only 95% purity introduces substantial amounts of nitrogen into the system in addition to any nitrogen originating in the raw materials, such as coal or natural gas. The process of the present invention, by eliminating nitrogen build-up, permits the use of such low purity oxygen without adverse effects to the economics of the process.

The conditions employed in converting hydrocarbon gases of the type present in synthesis tail gas, such as methane, ethane, gaseous olefins, etc., into CO and $H_2$ will be determined mainly by the conditions, particularly the pressures, of the synthesis stages. When applying atmospheric or moderately increased pressures of, say, up to about 10 atmospheres which are conventional for cobalt type catalysts, oxidation with oxygen at similar pressures and temperatures of about 1400°—2000° F. may be employed to advantage. When operating the synthesis stages at the higher pressures of, say, about 15—50 atmospheres or higher, usually associated with the use of iron type catalysts, the oxidation process may be operated at the high pressures dictated by the synthesis stages without difficulties, as opposed to prior reformation processes using steam and/or $CO_2$ which require considerably low pressures for practical operation and would necessitate expansion and recompression of the process gases. The oxidation process of the invention is, therefore, more flexible.

Having set forth its general nature and objects, the invention will be best understood from the more detailed description hereinafter in which reference will be made to the accompanying drawing which shows the flow plan of a system suitable for carrying out the present invention.

Referring now to the drawing, the system illustrated therein essentially comprises two synthesis gas generation stages 10 and 30 and two synthesis stages 15 and 35 whose functions and cooperation will be forthwith explained using a carbonaceous solid such as coal or coke as an example for the basic raw material of the process. It will be understood by those skilled in the art, however, that the process of the invention may be practiced on the basis of other raw materials, such as natural gas, reduced crudes, asphalts, etc., in a substantially analogous manner to accomplish the objects and advantages of the invention.

In operation, coal is subjected in the gas generation stage 10 to a water gas reaction with steam, preferably in the form of a dense turbulent mass of finely divided solids fluidized by the upwardly flowing gaseous reactants and reaction products to resemble a boiling liquid. Heat required for the gasification reaction may be supplied by combustion of a portion of the coal either within the gas generator itself with oxygen of about 95% purity or in a separate combustion zone using air, from which highly heated solid combustion residue may be supplied to the gas generator, all in a manner known *per se*. The present invention lends itself specifically to a one vessel gasification system with combustion within the gasification zone because the nitrogen tolerance of the present process is considerably higher than that of conventional synthesis processes employing tail gas recycle to the synthesis gas generator. In order to save synthesis gas compression costs, the pressure of gas generation stage 10 preferably approaches that of synthesis stage 15 as closely as may be efficiently and economically accomplished and may range anywhere from atmospheric to about 50 atmospheres or higher. About 25,000—60,000 normal cu. ft. of a synthesis gas containing about 0.8—1.8 volumes of $H_2$ per volume of carbon monoxide and about 2—6% of nitrogen may be produced per tons of total bituminous type coal used for steam and synthesis gas production in systems of this type at gas generator temperatures of about 1500°—2000° F., depending on the type of heat supply and other reaction conditions in the gas generator.

A synthesis gas so produced which has undergone a desulfurization and, if desired, a $CO_2$ removal treatment may be supplied substantially at the pressure of the gasification zone of stage 10 or by further compression through line 12 to the first hydrocarbon synthesis stage 15. This stage is preferably operated using finely divided fluidized alkali-promoted iron catalyst at temperatures of about 500°—800° F. and pressures of 5—50 atmospheres. Upon conventional condensation and absorptive recovery of the normally liquid synthesis products, about 1—2 barrels of $C_3$+hydrocarbons and oxygenated compounds per ton of coal may be recovered through line 17. Hydrocarbons and oxygenated compounds may be separated in a conventional separation unit 19 into $C_3$+hydrocarbons and oxygenated compounds. These liquid products may be separately recovered through lines 21 and 23.

Depending on the quality of the coal used, synthesis tail gas which may amount to, say, about 7—18,000 cu. ft. per ton of total coal consumed in the process is withdrawn from stage 15 through line 25. The composition of this kind of tail gas which may have a heating value of about 300—650 BTU per cu. ft. is about as follows:—

| | | |
|---|---|---|
| $H_2$ | 10—30% | by vol. |
| $CO$ | 2—5 | ,, ,, |
| $CH_4$ | 15—35 | ,, ,, |
| $C_2H_6$ | 2—4 | ,, ,, |
| $C_2H_4$ | .5—1.5 | ,, ,, |
| $C_3H_6$ | .5—1.0 | ,, ,, |
| $C_3H_8$ | .5—1.0 | ,, ,, |
| $N_2$ | 5.0—15 | ,, ,, |
| $CO_2$ | 15—65.0 | ,, ,, |

This synthesis tail gas is preferably converted into synthesis feed gas without substantial pressure loss. For this purpose, oxidation of the tail gas with oxygen of about 95% purity is most suitable as outlined above. Since large amounts of $CO_2$ may interfere with the production of the desired $H_2$:CO ratio, it may be desirable to remove $CO_2$ from the tail gas in a conventional absorption system. About 1000—5000 normal cu. ft. of $CO_2$ per ton of total coal may thus be removed from the system through line 28 when using a synthesis gas having an $H_2$:CO ratio of the order of 1.7, in reactor 15.

The scrubbed tail gas is supplied through line 29 substantially at the pressure of stage 15 to the secondary gas producing stage 30. Some 2000—6000 normal cu. ft. of oxygen of about 95% purity is supplied, per ton of total coal, through line 32 and conversion takes place at temperatures of about 1800°—2500° F. and pressures similar to or only slightly lower than those applied in stage 15. About 10,000—20,000 cu. ft. (per total ton of coal) of a synthesis gas containing about 1.5—2.0 volumes of $H_2$ per volume of CO and about 4—10% of nitrogen is withdrawn from stage 30 through line 33 and passed to secondary synthesis stage 35 which may be operated at conditions substantially identical to those of stage 15.

Condensible synthesis products are withdrawn from stage 35 through line 37 and separated in unit 39 into $C_3+$ hydrocarbons and oxygenated products. These separate synthesis products may be recovered through lines 40 and 42, respectively, to be combined with the products in lines 21 and 23, respectively.

Some 3000—6000 normal cu. ft., per ton of total coal, of secondary tail gas is recovered from stage 35 and may be passed through line 44 to any desired use, such as heat generation, a waste gas turbine etc. The composition of this gas, which may have a heating value of about 200—350 BTU per cu. ft., may vary within the approximate ranges given below:

| | | |
|---|---|---|
| $H_2$ | 10—30% | by vol. |
| CO | 2—5 | ,, ,, |
| $CH_4$ | 5—10 | ,, ,, |
| $C_2H_6$ | 2—4 | ,, ,, |
| $C_2H_4$ | .5—1.5 | ,, ,, |
| $C_3H_6$ | .5—1.0 | ,, ,, |
| $C_3H_8$ | .5—1.0 | ,, ,, |
| $N_2$ | 15—45 | ,, ,, |
| $CO_2$ | 20—50 | ,, ,, |

It will be observed that the methane content of this gas is considerably lower and its nitrogen content considerably higher than that of the tail gas from synthesis stage 15. This is due to the fact that the methane introduced by the coal gasification in stage 10 has been largely removed in gas oxidation stage 30 and that additional amounts of nitrogen have been introduced with the oxygen from line 32, while the total amount of gas has been reduced.

The invention and its advantages over conventional tail gas recycle operation will be further illustrated by the following specific example.

### EXAMPLE.

Based on a primary synthesis gas generation stage producing from coal about 350,000,000 normal cu. ft. per day of $H_2+CO$ in the approximate ratio of 1.8:1 and containing about 2.5% $N_2$, yields obtainable in a system of the type illustrated in the drawing under the conditions specified above are about as follows:

FIRST SYNTHESIS STAGE:

| | |
|---|---|
| Gasoline, bbl./day | 10,250 |
| Gas oil ,, ,, | 930 |
| Alcohols ,, ,, | 945 |
| $CO+H_2$ produced from tail gas, normal cu. ft./day | 111,000,000 |

SECOND SYNTHESIS STAGE:

| | |
|---|---|
| Gasoline, bbl./day | 3,250 |
| Gas oil ,, ,, | 290 |
| Alcohols ,, ,, | 300 |

TOTAL PRODUCTION:

| | |
|---|---|
| Gasoline, bbl./day | 13,500 |
| Gas oil ,, ,, | 1,220 |
| Alcohols ,, ,, | 1,245 |

If about 50% of the first stage tail gas were vented and the remainder recycled to the first gasification stage, the total production under otherwise comparable conditions would be about as follows:

| | |
|---|---|
| Gasoline, bbl./day | 11,875 |
| Gas oil ,, ,, | 1,075 |
| Alcohols ,, ,, | 1,095 |

The increase in liquid yield obtainable by the process of the invention as compared with a conventional recycle process amounts to considerably more than 10% which is in addition to the above-mentioned procedural advantages and which is of considerable importance for the economies of the hydrocarbon synthesis.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of hydrocarbons and oxygenated products by the catalytic conversion of carbon monoxide with hydrogen which comprises converting carbonaceous materials in a gas generation zone into a gas mixture containing hydrogen and carbon monoxide in synthesis proportions, contacting said gas mixture with a synthesis catalyst at synthesis conditions in a synthesis zone to produce normally liquid reaction products and tail gas, separating said tail gas from said reaction products, converting said tail gas in a second gas generation zone with free oxygen into a second gas mixture containing hydrogen and carbon monoxide in synthesis proportions, contacting said second gas mixture in a second synthesis zone with a synthesis catalyst at synthesis conditions to produce additional normally liquid products and a second tail gas and separating said second tail gas from said additional products.

2. A process according to Claim 1, wherein said gaseous hydrocarbons are reacted at substantially the same pressure at which they are produced.

3. A process according to Claim 1 or 2, wherein carbon dioxide is removed

from said tail gas prior to reacting said gaseous hydrocarbons.

4. A process according to any one of Claims 1—3, wherein said carbonaceous material is a carbonaceous solid.

Dated this 19th day of May, 1948.
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