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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in or relating to Processes for Producing Gaseous Mixtures containing Carbon Monoxide and Hydrogen suitable for Conversion into Hydrocarbons

We, LONDON TESTING LABORATORY LIMITED, a British Company, of 81, Cannon Street, London, E.C.4, and MICHAEL STEINSCHLAEGER, of no nationality, of the above Company's address, do hereby declare the nature of this invention to be as follows:—

This invention relates to the production of gaseous mixtures containing carbon monoxide and hydrogen and suitable for conversion into hydrocarbons.

It is known that mixtures of these two gases can be converted catalytically into mixtures of hydrocarbons which can be utilised as lubricants and as power fuels for internal combustion engines and the like. A number of methods are known for producing suitable mixtures of carbon monoxide and hydrogen from various industrial gases including coke oven gas and it is the chief object of the invention to evolve a process of increased efficiency making use of coal distillation gases such as coke oven gas as one of the starting materials.

According to the invention a gas, such as water gas, consisting principally of carbon monoxide and hydrogen is mixed with coal distillation gas, and the mixture is passed over a cobalt or nickel catalyst producing gases rich in methane these gases then being converted with steam in a decomposing plant yielding a gas consisting principally of a mixture of carbon monoxide and hydrogen. This gas can then be used in known manner for the catalytic production of hydrocarbons.

The proportion of carbon monoxide to hydrogen in the gas produced by the above process will generally be less than 1:2. In order to obtain the best yield of hydrocarbons, however, it is necessary that the relative proportions by volume of carbon monoxide and hydrogen in the gas should be between 1:1.8 and 1:2. According to a further feature of the invention, therefore, a suitable gas or gaseous mixture is added to the gases undergoing reaction or to the final gases. Thus water gas or the gas produced by the passage of water gas over a cobalt catalyst, being rich in carbon monoxide, can be added to the final gas after its conversion with steam in order to raise the relative proportion of carbon monoxide to the desired value. Also the gas after conversion with steam can be mixed with a further quantity of the mixture of water gas with coal distillation gas, the proportion of carbon monoxide in this mixture being adjusted if necessary to a suitable high value by modifying the quantity of coal distillation gas in the mixture.

Coal distillation gases contain a certain proportion of sulphur compounds which would poison the cobalt or nickel catalysts. It is, accordingly, necessary to remove these compounds practically completely from the mixture of gases before the latter reach the catalyst.

The invention will be more fully described with reference to two specific examples. 1,000,000 cubic metres of water gas produced from coke and containing 40% of carbon monoxide and 51% of hydrogen are mixed with 600,00 cubic metres of coke oven gas having the following composition:

Carbon monoxide, CO	-	6.0%
Methane, CH_4	-	26.0%
Hydrocarbons C_nH_m	-	2.0%
Hydrogen, H_2	-	58.0%

This produces a gas mixture containing 27.2% of carbon monoxide and 53.5% of hydrogen, these two reactive ingredients thus representing 80.7% of the total volume of gas.

These gases are then passed over a cobalt or nickel catalyst and with a 65% reduction in volume yield a gas having the following composition:

Carbon monoxide, CO	-	15.0%
Hydrogen, H_2	-	20.0%
Methane, CH_4	-	40.0%
Hydrocarbons, C_nH_m	-	2.0%
Nitrogen + carbon dioxide		23.0%

This gas is then submitted to the decomposition action of steam and on the basis of a 90% decomposition of methane and 100% decomposition of heavy hydrocarbons yield approximately 1,200,000 cubic metres of gas containing 25.2% of carbon monoxide and 62.4% of hydrogen. For the most efficient conversion into

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hydrocarbons oils suitable for use as lubricants or fuels, the relative proportions of carbon monoxide and hydrogen should be approximately 1:2. In order to achieve this 400,000 cubic metres of water gas are added whereby 1,600,000 cubic metres of gas containing 29.0% of carbon monoxide and 59.5% of hydrogen are obtained. This gas can then be mixed with 1,600,000 cubic metres of the original gas mixture which contains 27.2% of carbon monoxide and 53.5% of hydrogen, thus giving 3,200,000 cubic metres of gas containing 28.1% of carbon monoxide and 56.5% of hydrogen, this being suitable for the catalytic production of hydrocarbons.

According to a further example 1,140,000 cubic metres of coke water gas are mixed with 475,000 cubic metres of coke oven gas, giving 1,615,000 cubic metres of a mixture containing 53.1% of hydrogen and 30% of carbon monoxide. This mixture is passed over a cobalt catalyst with a 65% reduction in volume and the resultant gas is then decomposed as in the above example. The gases after this decomposition are mixed with the original mixture of water gas and coke oven gas giving a final gaseous mixture containing 28% of carbon monoxide and 56% of hydrogen which mixture is suitable for the catalytic production of hydrocarbons. If desired the composition of this gaseous mixture and the proportion of ingredients capable of reaction, i.e. carbon monoxide and hydrogen, can be adjusted by admixing a quantity of gases withdrawn from the system after the passage over the cobalt catalyst and before the decomposition.

This progress possesses a number of important advantages over those generally used heretofore. It will be seen that in the first example given above only 1,400,000 cubic metres of water gas and 600,000 cubic metres of coke oven gas were used, whereas in order to produce the same final quantity of mixed gases by the known process for the conversion of water gas alone it would have been necessary to use 2,880,000 cubic metres of water gas. Thus the plant used can be considerably reduced in size and, therefore, in cost.

Furthermore, comparatively small desulphurising apparatus can be used. The removal of sulphur compounds from gases on an industrial scale suffers from considerable difficulties and presents a problem which has not as yet been completely solved. It is possible by known methods to reduce the total content of sulphur compounds in the gas to about 0.2—0.6 grammes of sulphur per 100 cubic metres of gas. It is found, however, that even such a relatively low sulphur content poisons a cobalt or nickel catalyst to such an extent that after 2000 working hours there is a reduction in the catalyst efficiency of 40—50% as compared with a catalyst working on a gas completely free from sulphur. In the process of the present invention, however, a part of the gas mixture is substantially free from sulphur with the result that the sulphur content of the mixture as a whole is reduced and thus the life of the catalyst increased.

Dated this 17th day of February, 1938.

HASELTINE, LAKE & Co.,
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19—25, West 44th Street, New York,
U.S.A.,
Agents for the Applicants.

COMPLETE SPECIFICATION

Improvements in or relating to Processes for Producing Gaseous Mixtures containing Carbon Monoxide and Hydrogen suitable for Conversion into Hydrocarbons

We, London Testing Laboratory Limited, a British Company, of 81, Cannon Street, London, E.C.4, and Michael Steinschlaeger, of no nationality, of the aforesaid Company's address, 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:—

This invention relates to the production of gaseous mixtures containing carbon monoxide and hydrogen and suitable for conversion into hydrocarbons.

It is known that mixtures of these two gases can be converted catalytically into mixtures of hydrocarbons which can be utilised as lubricants and as power fuels for internal combustion engines and the like. A number of methods are known for producing suitable mixtures of carbon monoxide and hydrogen from various industrial gases including coke oven gas and it is the chief object of the invention to evolve a process of increased efficiency making use of coal distillation gases such as coke oven gas as one of the starting materials.

According to the invention a gas, such as water gas, consisting principally of carbon monoxide and hydrogen is mixed with coal distillation gas, and the mixture is passed over a catalyst producing gases rich in methane, these gases then being converted with steam at a temperature of 1400°—1450° C. in a decomposing plant lined with refractory bricks, yeilding a gas consisting principally of a mixture of carbon monoxide and hydrogen. The addition of steam amounts to 4 or 5 times the quantity theoretically necessary. This gas can then be used in known manner for the catalytic production of hydrocarbons. The temperature and pressure maintained in the catalytic stage are those commonly employed in the art for the production of gases rich in methane from gases containing carbon monoxide and hydrogen. In general, the temperature should be in the region of 180°—200° C. and the pressure should be atmospheric or slightly higher. The catalyst also is selected from those commonly used in the art, cobalt or nickel catalyst being particularly suitable. A particularly suitable catalyst is a cobalt-thorium-kieselguhr catalyst in the ratio 100:18:100.

The proportion of carbon monoxide to hydrogen in the gas produced by the above process will generally be less than 1:2. In order to obtain the best yeild of hydrocarbons, however, it is necessary that the relative proportions by volume of carbon monoxide and hydrogen in the gas should be between 1:1.8 and 1:2. According to a further preferred feature of the invention therefore, a suitable gas or gaseous mixture is added to the gases undergoing reaction or to the final gases. Thus water gas or the gas produced by the passage of water gas over a cobalt catalyst, being richer in carbon monoxide than in hydrogen, can be added to the final gas after its conversion with steam in order to raise the relative proportion of carbon monoxide to the desired value. In addition to or instead of the addition of gases rich in carbon monoxide the gas after conversion with steam can be mixed with a further quantity of the mixture of water gas with coal distillation gas, the proportion of carbon monoxide in this mixture being adjusted if necessary to a suitable high value by modifying the quantity of coal distillation gases in the mixture.

Coal distillation gases contain a certain proportion of sulphur compounds which would poison the cobalt or nickel catalysts. It is, accordingly, necessary to remove these compounds practically completely from the mixture of gases before the latter reach the catalyst.

The invention will be more fully described with reference to two specific examples. 1,000,000 cubic metres of water gas produced from coke and having the following composition:

Carbon monoxide CO	40.0%
Hydrogen H_2	51.0%
Methane CH_4	0.3%
Carbon dioxide + Nitrogen CO_2+N_2	8.7%

are mixed with 600,000 cubic metres of coke oven gas having the following composition:

Carbon monoxide, CO	6.0%
Methane, CH_4	26.0%
Hydrocarbons, C_nH_m	2.0%
Hydrogen, H_2	56.0%
Carbon dioxide + Nitrogen, CO_2+N_2	10.0%

This produces a gas mixture of the following composition:

Carbon monoxide, CO	27.2%
Hydrogen, H_2	52.8%
Methane, CH_4	10.0%
Hydrocarbons, C_nH_m	0.75%
Carbon dioxide + Nitrogen, CO_2+N_2	9.25%

The two reactive ingredients, carbon monoxide and hydrogen thus represent 80.0% of the total volume of gas.

These gases are then passed over a cobalt or nickel catalyst and with a 65% reduction in volume yield a gas having the following composition:

Carbon monoxide, CO	16.0%
Hydrogen, H_2	15.0%
Methane, CH_4	41.0%
Hydrocarbons, C_nH_m	2.0%
Nitrogen + carbon dioxide	26.0%

This gas is then submitted to the decomposition action of steam as hereinbefore described and on the basis of a 90% decomposition of methane and 100% decomposition of heavy hydrocarbons yields approximately 1,230,000 cubic metres of gas containing 25.2% of carbon monoxide and 62.4% of hydrogen. For the most efficient conversion into hydrocarbons oils suitable for use as lubricants or fuels, the relative proportions of carbon monoxide and hydrogen should be approximately 1:2. In order to achieve this 400,000 cubic metres of water gas are added whereby 1,630,000 cubic metres of gas containing 29.2% of carbon monoxide and 58.4% of hydrogen are obtained. This gas can be used in known manner for the catalytic production of hydrocarbons. If desired, it can be mixed with 1,600,000 cubic metres of the original gas mixture which contains 27.2% of carbon monoxide and 52.8% of hydrogen, thus giving 3,230,000 cubic metres of gas containing

28.2% of carbon monoxide and 55.6% of hydrogen, this also being suitable for the catalytic production of hydrocarbons.

According to a further example 1,140.000 cubic metres of coke water gas are mixed with 475,000 cubic metres of coke oven gas, giving 1,615,000 cubic metres of a mixture containing 53.1% of hydrogen and 30% of carbon monoxide. This mixture is passed over a cobalt catalyst with a 65% reduction in volume and the resultant gas is then decomposed as in the above example. The gases after this decomposition are mixed with the original mixture of water gas and coke oven gas giving a final gaseous mixture containing 28% of carbon monoxide and 56% of hydrogen which mixture is suitable for the catalytic production of hydrocarbons. If desired the composition of this gaseous mixture and the proportion of ingredients capable of reaction, i.e. carbon monoxide and hydrogen, can be adjusted by admixing a quantity of gases withdrawn from the system after the passage over the cobalt catalyst and before the decomposition.

This process possesses a number of important advantages over those generally used heretofore. It will be seen that in the first example given above only 1,400,000 cubic metres of water gas and 600,000 cubic metres of coke oven gas were used, whereas in order to produce the same final quantity (3,280,000 cubic metres) of mixed gases by the known process for the conversion of water gas alone it would have been necessary to use 2,880,000 cubic metres of water gas. Thus the plant used can be considerably reduced in size and, therefore, in cost.

Furthermore, comparatively small desulphurising apparatus can be used. The removal of sulphur compounds from gases on an industrial scale suffers from considerable difficulties and presents a problem which has not as yet been completely solved. It is possible by known methods to reduce the total content of sulphur compounds in the gas to about 0.2—0.6 grammes of sulphur per 100 cubic metres of gas. It is found however, that even such a relatively low sulphur content poisons a cobalt or nickel catalyst to such an extent that after 2000 working hours there is a reduction in the catalyst efficiency of 40—50% as compared with a catalyst working on a gas completely free from sulphur. In the process of the present invention, however, a part of the gas mixture is substantially free from sulphur with the result that the sulphur content of the mixture as a whole is reduced and thus the life of the catalyst increased.

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 gaseous mixtures containing carbon monoxide and hydrogen and suitable for conversion into hydrocarbons, in which a gas mixture consisting principally of carbon monoxide and hydrogen is mixed with coal distillation gases and the resulting mixture is passed over a catalyst producing gases rich in methane, these gases being then converted at 1400°—1450° C. with steam in a decomposing plant lined with refractory bricks, yielding a gas consisting principally of a mixture of carbon monoxide and hydrogen.

2. A process according to claim 1, in which water gas is mixed with coal distillation gases to form the primary gas mixture.

3. A process according to claim 1 or claim 2, in which in order to increase the proportion of carbon monoxide in the final mixture, a suitable gas or gaseous mixture is added to the gases undergoing reaction or to the final gases.

4. A process according to any of the preceding claims in which water gas or the gas produced by the passage of water gas over a cobalt catalyst is added to the gas mixture after conversion with steam.

5. A process according to any of the preceding claims, in which the gas mixture after conversion with steam is mixed with a further quantity of the mixture of water gas and coal distillation gases.

6. A process according to any of the preceding claims, in which a cobalt or nickel catalyst is used in the catalytic stage.

7. A process for the production of gaseous mixtures of carbon monoxide and hydrogen suitable for conversion into hydrocarbons susbstantially as hereinbefore described.

8. Gaseous mixtures of carbon monoxide and hydrogen when prepared by a process according to any of the preceding claims.

Dated this 17th day of February, 1939.

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