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3,420,642

PRODUCTION OF GASES CONTAINING METHANE FROM HYDROCARBONS

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9 Claims

ABSTRACT OF THE DISCLOSURE

This application relates to a process for the production of gases containing methane wherein a mixture of vaporized paraffinic hydrocarbons and steam, the hydrocarbons having an average of from 4–15 carbon atoms per molecule, is preheated to temperatures of at least 350° C. and then fed through a bed of nickel catalyst, the bed being maintained at temperatures between 400° C. and 550° C. The product of this reaction is then mixed with additional vaporized hydrocarbons and passed through a further bed of nickel catalyst, the bed being maintained at temperatures of from 400° C.–600° C. The ratio of the total weight of steam to hydrocarbons is greater than 1.6 to 1. This two-stage process prolongs the life of the catalyst.

This invention relates to the production of gases containing methane from hydrocarbons.

In British specification No. 820,257 there is described and claimed a process for the production of gases containing methane from mixtures of predominantly paraffinic hydrocarbons wherein the vapour of the hydrocarbons and steam are passed through a bed of a nickel catalyst under atmospheric or super-atmospheric pressure, and the hydrocarbon vapour and steam are passed into the catalyst bed at a temperature above 350° C. such that the bed is maintained by the reaction at a temperature within the range 400° C. to 550° C.

The pressure may be up to 50 atmospheres, but may be higher, if desired. Convenient pressures are within the range of 10 to 25 atmospheres.

The lower limit, 400° C., of the temperature range was chosen to minimise a tendency for loss of activity of the catalyst, while the upper limit, 550° C., was chosen to avoid carbon deposition on the catalyst. The proportion of steam relative to the hydrocarbons is greater than that which decomposes during the reaction and the excess of steam required depends on the average molecular weight of the hydrocarbons used and increases with an increase in molecular weight. However, the excess is not great, and 1.6 parts by weight of steam to 1 part by weight of hydrocarbon can be used with all mixtures of hydrocarbons containing an average of 4 to 10 carbon atoms per molecule. Since there is an excess of steam, the gases leaving the catalyst bed will always contain a proportion of water vapour, and, since the composition of the gases produced is controlled by chemical equilibria, the proportion of steam present in the product gas will remain unchanged provided that the working temperature, working pressure and ratio of reactants also remain unchanged.

The aforesaid specification also describes the subsequent treatment of the methane-containing gases so produced to reduce the concentration of methane to the required level.

It has been found that the aforesaid invention may be used with predominantly paraffinic hydrocarbons having an average of from 4 to 15 carbon atoms per molecule. It has also been found that in carrying out the hydrocarbon steam reaction in the manner described, the life of

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the catalyst is limited. The limitation in the life of the catalyst is more severe the higher the average molecular weight of the hydrocarbon used, and the lower the steam to hydrocarbon ratio employed. My copending patent application Ser. No. 349,752, filed Mar. 5, 1964, describes a method of prolonging the catalyst life by recirculating hot reaction gases containing water vapour through the catalyst bed mixed with the hydrocarbon vapour and steam being supplied.

The present invention is for an improvement in or modification of the invention described and claimed in British patent specification No. 820,257 and is based upon the observation that the life of the catalyst can be considerably increased by supplying the distillate feedstock to two or more consecutive stages of the catalyst bed, the whole of the steam being supplied to the first stage. The present invention accordingly provides a process for the production of gases containing methane in at least two stages from vaporised predominantly paraffinic hydrocarbons having an average of from 4 to 15 carbon atoms per molecule, wherein a first stage comprises passing a mixture of steam with part of the vaporised hydrocarbons which mixture is at a temperature of at least 350° C., through a bed of a nickel catalyst such that the catalyst is maintained by the reaction at temperatures of from 400° C. to 550° C., and at least one further stage comprising mixing with the gases resulting from the previous stage a further part of the vaporised hydrocarbons, and passing the mixture thus formed through a further bed of a nickel catalyst such that the catalyst is maintained by the reaction at temperatures of from 400° C. to 600° C., the ratio of the weight of the total supply of steam to that of the total supply of distillate to the catalyst beds being greater than 1.6.

When the whole of the steam is supplied to the first stage but only part of the distillate feedstock, the steam hydrocarbon ratio is high, thus prolonging the life of the catalyst in this stage. In a two-stage process the remainder of the feedstock is then mixed with the product gas and undecomposed steam from the first stage and this provides a means of increasing the proportion of water vapour in contact with the catalyst without increasing the overall proportion of steam with the feedstock. The life of the catalyst in the second stage is similarly prolonged by comparison with single stage operation.

The number of stages employed is preferably two; irrespective of this it is preferred that the proportion of the vaporised hydrocarbons admixed before each stage is in inverse ratio to the number of stages employed. The stages may be located in a single vessel or in separate vessels provided there is always thorough mixing of the vaporised hydrocarbons with the gases resulting from the previous stage.

In order to avoid deposition of carbon on the catalyst, it may be necessary in some cases to prevent the catalyst temperature from exceeding 575° C.

The ratio by weight of steam to vaporised hydrocarbons in the gases passing over the catalyst must not be less than 1.6 and preferably more than 2.0. The value of the ratio will rise as the vaporised hydrocarbons are decomposed, and will become infinite when this process is complete.

The gases entering a catalyst bed must be preheated to a temperature of at least 350° C. to ensure sufficient catalyst activity. The maximum preheat temperature is limited by the danger of thermal decomposition of the vaporised hydrocarbons and by the requirement that the catalyst be maintained by the reaction within a specified temperature range, and depends on the proportion of vaporised hydrocarbons present.

The present invention may also be used for raising the calorific value of gas produced by the gasification of dis-

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tillate with steam, since the addition of distillate at each stage progressively increases the concentration of methane in the product gas.

The effect of supplying the distillate in stages to the catalyst on the proportion of steam in contact with the catalyst is given in the following table.

TABLE I

Reactant (mols)	Single Stage	Two Stage	
		First	Second
Distillate.....	1.0	0.5	0.5
Steam.....	9.75	9.75	7.97
Steam/Distillate Ratio.....	9.75	19.50	15.94

The steam entering the second stage of the two-stage process, i.e., 7.97 mols., is the undecomposed portion of that supplied to the first stage. The values relate to a working temperature of 500° C. in the single stage process and 460° C. and 500° C. respectively in the first and second stages of the two-stage process. The ratio of steam to distillate is two by weight. The use of a greater number of stages enables higher proportions of steam to be maintained in contact with the catalyst and is particularly advantageous when high boiling distillates are gasified with the minimum of process steam.

In the specifications of U.S. application Ser. No. 351,190, filed Mar. 11, 1964, and British application Ser. No. 36,079/62, there are described improvements in or modifications to the processes which are described and claimed in British specification No. 820,257 which are designed to increase the life of the catalyst. The process of the present invention may be carried out, if desired, embodying the inventions described in those specifications.

Following is a description by way of example of two processes in accordance with the present invention;

EXAMPLE 1

A petroleum distillate having an average number of carbon atoms of 6.1, a boiling range of 26° to 140° C. and a specific gravity at 20° C. of 0.68 was used in both parts of this example. The petroleum distillate was freed from sulphur compounds to a level less than 0.2 part per million and, for comparison, mixed with steam in the proportion of 2 parts by weight of steam to 1 part by weight of distillate vapour. The mixture was preheated to 450° C. and, under a pressure of 350 lbs. per square inch gauge, passed downwardly through a bed of nickel alumina catalyst 12 inches deep. The catalyst bed was maintained at a temperature of 506° C. by the reaction. The mixture was passed through the bed at a space velocity of 44,000 vols./vol./hr. and a linear velocity of 1.65 ft./sec. until undecomposed distillate first appeared in the gases leaving the bed, this being regarded as the termination of the experiment.

In a second experiment identical distillate was mixed with steam in the proportion of 4 parts by weight of steam to 1 part by weight of distillate vapour. The mixture was preheated to 450° C. and, under a pressure of 350 lbs. per square inch gauge, passed downwardly through a bed of the same catalyst as that used in the first part of this example, 6 inches deep. The product gas and undecomposed steam left the bed at 460° C. and were mixed with the same weight of distillate vapour as that supplied to the first bed and passed into a second bed of nickel alumina catalyst 6 inches deep located below the first bed. The temperature of the catalyst in the second tube was maintained at a temperature of 502° C. by the further reaction. The mixtures were passed through the beds of catalyst at a linear velocity of 1.65 ft./sec. and at a combined space velocity of 44,000 vols./vol./hour until undecomposed distillate first appeared in the gases leaving the lower tube, this being regarded as the termination of the experiment.

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The results of the two experiments are compared in Table 2 below:

TABLE 2

Experiment	Time elapsing to appearance of undecomposed distillate
1.....	260 hours
2.....	1,520 hours

The composition of the gases produced in the two experiments was:

TABLE 3

	Experiment 1	Experiment 2	
		First stage	Second stage
CO ₂ , percent by vol.....	11.05	7.20	10.75
CO, percent by vol.....	0.45	0.15	0.40
H ₂ , percent by vol.....	8.50	6.80	8.25
CH ₄ , percent by vol.....	31.20	18.65	32.70
H ₂ O, percent by vol.....	48.80	67.20	47.90

EXAMPLE 2

A petroleum distillate having an average number of carbon atoms of 10.0, a boiling range of 112° C. to 245° C. and a specific gravity at 20° C. of 0.79 and freed from sulphur compounds to a level less than 0.2 part per million, was used in two comparative experiments. In the first the petroleum distillate was mixed with steam in the proportion of 2 parts by weight of steam to 1 part by weight of distillate vapour. The mixture was preheated to 530° C. and under a pressure of 350 lbs. per sq. in. gauge, passed downwardly through a bed of nickel-alumina catalyst 12 inches deep. The catalyst bed was maintained at a temperature of 535° C. by the reactions occurring. The mixture was passed through the bed at a space velocity of 11,000 vols./vol./hr. and a linear velocity of 0.44 ft./sec. until undecomposed distillate first appeared in the gases leaving the bed, this being regarded as the termination of the experiment.

In the second experiment, identical distillate was mixed with steam in the proportion of 4 parts by weight of steam to 1 part by weight of distillate vapour. The mixture was preheated to 530° C., and under a pressure of 350 lbs. per sq. inch gauge, passed downwardly through a bed of the same catalyst as that used in the first part of this example, 6 inches deep. The product gas and undecomposed steam left the bed at 500° C. and were mixed with the same weight of distillate vapour as that supplied to the tube and passed into a second bed of nickel alumina catalyst 6 inches deep located below the first bed. The temperature of the catalyst in the second bed was maintained at a temperature of 535° C. by the further reaction. The mixtures were passed through the beds of catalyst at a combined space velocity of 11,000 vols./vol./hr. and a linear velocity of 0.44 ft./sec. until undecomposed distillate first appeared in the gases leaving the lower bed, this being regarded as the termination of the experiment.

The results of the two experiments are compared in Table 4 below:

TABLE 4

Experiment	Time elapsing to appearance of undecomposed distillate
1.....	152 hours
2.....	602 hours

The compositions of the gases produced in the two experiments was:

TABLE 5

	Experiment 1	Experiment 2	
		First stage	Second stage
CO ₂ , percent by vol.....	12.3	8.35	12.15
CO, percent by vol.....	0.65	0.35	0.65
H ₂ , percent by vol.....	10.4	12.0	10.6
CH ₄ , percent by vol.....	30.9	15.4	31.1
H ₂ O, percent by vol.....	45.75	63.9	45.0

I claim:

1. A process for the production of gases containing methane in at least two stages from vaporised predominantly paraffinic hydrocarbons having an average of from 4 to 15 carbon atoms per molecule, wherein a first stage comprises passing a mixture of steam with part of the vaporised hydrocarbons which mixture is at a temperature of at least 350° C., through a bed of a nickel catalyst, said catalyst being maintained by the reaction at temperatures of from 400° C. to 550° C., and at least one further stage comprising mixing with the gaseous product of said first stage a further part of the vaporised hydrocarbons, and passing the mixture thus formed through a further bed of a nickel catalyst, said catalyst being maintained by the reaction at temperatures of from 400° C. to 600° C., the ratio of the total weight of steam to that of the total hydrocarbons being greater than 1.6 to 1.

2. A process as claimed in claim 1 wherein the number of stages employed is two.

3. A process as claimed in claim 1 wherein the fraction of the vaporised hydrocarbons admixed before each stage is in inverse ratio to the number of stages employed.

4. A process as claimed in claim 1, wherein in the second and any subsequent stage employed, the catalyst is maintained by the reaction at temperatures of from 400° C. to 575° C.

5. A process as claimed in claim 1 wherein the ratio by weight of steam to vaporised hydrocarbons in the gases passing over the catalyst is at least 1.6 throughout.

6. A process as claimed in claim 1 wherein the vaporised predominantly paraffinic hydrocarbons are formed by vaporising a light petroleum distillate.

7. A process as claimed in claim 1 wherein the pressure is from 1 to 50 atmospheres.

8. A process as claimed in claim 7 wherein the pressure is from 10 to 25 atmospheres.

9. A two-stage process for the production of gases containing methane by the reaction of vaporised light petroleum distillate with steam which process consists essentially in mixing about half the vaporised light petroleum distillate with steam and passing the mixture, preheated to a temperature of at least 350° C., and at a pressure of from 1 to 50 atmospheres, through a bed of a nickel catalyst, said catalyst being maintained by the reaction at temperatures of from 400° C. to 550° C., mixing the remainder of the vaporised light petroleum distillate with the gaseous product of said first stage and passing the mixture thus formed, at a temperature of at least 350° C. and a pressure of from 1 to 50 atmospheres, through another bed of a nickel catalyst such that the catalyst is maintained by the reaction at temperatures of from 400° C. to 575° C., the ratio by weight of steam to vaporised hydrocarbons in the gases passing over the catalyst being at least 2.0 to 1 throughout.

References Cited

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JOSEPH SCOVRONEK, *Primary Examiner*.

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