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PRODUCTION OF GAS SUITABLE FOR USE AS TOWN GAS

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This invention relates to the production of gas suitable for use as town gas from hydrocarbon fractions of petroleum origin.

Traditionally, town gas has been obtained from the carbonisation of coal, but it has also been proposed to prepare it from petroleum fractions. When using petroleum fractions as starting materials, it is particularly advantageous economically if the process used produces one or more other valuable hydrocarbon products at the same time, and accordingly, the present invention has among its objects to provide a process in which both town gas and a normally-liquid product suitable for use in gasoline production or as a source of aromatics are produced.

According to the present invention, a fraction of petroleum origin consisting of or containing non-aromatic hydrocarbons and boiling within the gasoline or naphtha range is contacted at elevated temperature with a dehydrogenation and dehydrocyclisation catalyst under conditions such that a normally-liquid product with a higher aromatic content than the feedstock and a hydrogen-rich gas are produced, and the calorific value of the hydrogen-rich gas is reduced to a value appropriate to the use of the gas as a town gas by dilution with a gas of lower calorific value. The gas of lower calorific value may contain non-combustible gases for example carbon dioxide and nitrogen.

In a preferred form of the invention, the light hydrocarbon fraction is contacted with a fluidised or moving bed of catalyst which is continuously or intermittently withdrawn from the reaction zone, regenerated in a stream of gas consisting principally of oxygen and nitrogen, and returned to the reaction zone, the flue gas from the catalyst regeneration process being used to reduce the calorific value of the hydrogen-rich gas.

A particularly suitable process for producing a higher-aromatic content product and a make of hydrogen-rich gas from the said hydrocarbon fraction is one using a catalyst consisting essentially of chromium oxide supported on alumina carried out at a pressure of up to 50 p.s.i.g. (including atmospheric pressure or below) and without recycle of the hydrogen-rich gas produced or addition of extraneous hydrogen. The temperature range is from 450 to 580° C. and the space velocity from 0.1 to 1.0 v./v./hr. of liquid feedstock. The chromia on alumina catalyst may contain a minor proportion of one or more promoters for example a rare earth or mixture of rare earths, bismuth, boron, germanium or nickel, preferably in combination wiht an alkali metal, such as potassium. Another particularly effective promoter is a minor proportion of a spinel for example cobalt chromite, copper chromite, zinc titanate, or iron chromite, either as such or in the form of the naturally-occurring ore "chrome ironstone."

Preferably a substantial proportion of the feedstock boils below 100° C., particularly preferred feedstocks being a light straight-run distillate such as a light gasoline or a light relatively aromatic-free fraction of a catalytic reformate, for example a reformate obtained from a process using a platinum containing catalyst.

The normally-liquid product may be used in gasoline or as a source of aromatics, and the process conditions may be varied according to the use for which the product is intended. Increased severity increases the make of gas and the octane number of the liquid product but reduces the liquid yield. When carrying out the process for the production of towns gas and material for use in gasoline, the yields of gas and liquid and the octane number of the liquid product must be balanced against each other. On the other hand, when producing towns gas and a liquid product to be used as a source of aromatics, the decrease in overall liquid yield with increased severity may be advantageous rather than disadvantageous. This is because the yield of aromatics by weight of feed rises to a maximum with increased severity and thereafter stays substantially constant, although the overall liquid yield continues to decrease by conversion of olefins and paraffins to gas. Under the conditions of pressure and space velocity stated above, the maximum yield of aromatics occurs at about 525–570° C. It is preferred to operate at the upper end of this range since, without affecting the yield of aromatics, an increased quantity of hydrogen-rich gas can be produced for conversion to town gas.

The specification for an acceptable town gas is laid down by the gas boards, and may include a preferred range for calorific value, specific gravity, and hydrogen content. Since an important combustible constituent of the hydrogen-rich gas is the hydrogen itself, these three values are interdependent and dilution to reduce the calorific value decreases the hydrogen content and increases the specific gravity. Any of these values, which can be determined by standard tests, may therefore be used as a guide to determining the degree of dilution required.

The invention is illustrated by the following examples.

EXAMPLE 1

A light gasoline was contacted in the vapour phase with a fluidised bed of catalyst consisting of 10% chromia on alumina, promoted with 1% of cerium oxide and 1% of potassium oxide (the percentages being by weight of catalyst stable at 1020° F.) under conditions set out in Table 1 below. The vapours after having been freed from catalyst dust, were compressed in two stages to 70 p.s.i.g. and passed to a product recovery system in which a hydrogen-rich gas and a normally liquid fraction were separated by means of an absorber, a debutaniser and a re-run column. The hydrogen-rich gas was taken off overhead from the absorber, and the normally liquid fraction was taken off overhead from the re-run column.

The fluidised catalyst reactor was associated in conventional manner with a catalyst regenerator using air as the regenerating gas. The process conditions for the reactor and regenerator are set out in Table 1 below.

Table 1

Reactor:		
Temp	° C	549
	° F	1,020
Pressure—		
Top of bed	p.s.i.g.	8.0
Bottom of bed	p.s.i.g.	20.0
Space velocity	w./w./hr.	0.12
Catalyst/oil ratio		10:1
Regenerator:		
Temp	° C	704
	° F	1,300
Pressure—		
Top of bed	p.s.i.g.	25.0
Bottom of bed	p.s.i.g.	28.8

Inspection data on the light gasoline feed and the normally liquid fraction or product taken off overhead from the re-run column, are given in Table 2 below.

Table 2

Test	Feed	Product
ASTM Distillation, ° C.:		
IBP	44	41
10%	55	52
30%	61	62
50%	70	75
70%	79	89
90%	91	107
FBP	103	120
Specific gravity @ 60° F./60° F.	0.676	0.765
Octane number, research clear	57	98
Aromatics, percent vol.	2	48
Bromine No.	0.4	40
Sulphur, percent wt.	0.015	0.007

From Table 2 it will be seen that a high-volatility gasoline fraction of 98 research octane number (clear) is a product of the process. At the same time, products having the general characteristics of a town gas were obtained by diluting the hydrogen-rich gas taken off overhead from the absorber with cooled regenerator flue gas. For a town gas with a calorific value of 500 B.t.u./cu. ft., 100 volumes of dry absorber gas were mixed with 47.8 volumes of dry flue gas. Dry absorber gas and dry flue gas were also mixed in the required proportions to give a product having a specific gravity of 0.51.

Inspection data on the gases are set out in Table 3 below.

Table 3

	Absorber gas, percent vol.	Regenerator flue gas, percent vol.	Mixture to give 500 B.t.u. gas, percent vol.	Mixture to give gas with sp. gr. 0.51, percent vol.
CO_2	0.1	11.3	3.7	2.9
O_2	trace	1.1	0.3	0.3
Unsats	2.1		1.4	1.5
CO	0.1	6.3	2.1	1.6
H_2	71.2		48.2	53.7
C_1	12.2		8.3	9.2
C_2	6.5		4.4	4.9
C_3+	6.9		4.7	5.2
N_2	0.9	81.3	26.9	20.7
Total	100.0	100.0	100.0	100.0
Gross CV, B.t.u./cu. ft.	730	20.3	500	555
Sp. gr. (Air=1)	0.34	1.03	0.56	0.51

EXAMPLE 2

A light gasoline was contacted with a fixed bed of catalyst consisting of 10% of chromia on alumina promoted with 1% of cerium oxide and 1% of potassium oxide (the percentages being by weight of catalyst stable at 1020° F.) under the following conditions:

Temperature	560° C., 1040° F.
Pressure	Atmospheric.
Space velocity	0.2 v./v./hr.
Recycle gas	None.
Processing period	5 hours.

Details of the feed and the liquid product are set out in Table 4 below.

Table 4

Feed	Light gasoline 61.2 ON (Res.) Clear (C_5–112° C.)
Hydrocarbon Type Analysis:	
Aromatics, percent vol.	45.5
Olefins, do.	20
Saturates, do.	34.5
Aromatics, percent wt.	53
Yields on feedstock:	
Debutanised product, do.	54
Aromatics, do.	29
Benzene, do.	17
Toluene, do.	12
Aromatics in feed, do.	1
Aromatics gain, do.	28

The table shows a gain in aromatics of 28% by weight of feedstock. At the same time there was produced 2350 s.c.f. of gas per barrel of feed, or 320 lbs. per 1000 lbs. of feed. This gas contained 67% by volume of hydrogen. A further 60 lbs. of gas per 1000 lbs. of feed was taken off overhead from the stabiliser used to debutanise the liquid product. The two gases were combined to give a gas with a density of 0.520 g./l. at 0° C. and 760 mm. Hg (0.40 specific gravity) and a calorific value of 833 B.t.u./cu. ft. The combined gases were diluted with an inert gas consisting principally of nitrogen and having a specific gravity of approximately 1 in proportion to give a final gas with a density of 0.7 g./l. at 0° C. and 760 mm. Hg (0.54 specific gravity) and a calorific value of 620 B.t.u./cu. ft. The yield of this gas per 1000 lbs. of light gasoline feedstock was 12,400 cu. ft.

We claim:

1. A process for the production of town gas and an aromatic-enriched product comprising contacting a relatively aromatic-free petroleum fraction boiling within the range encompassed by the gasoline and naphtha range in a reaction zone with a dehydrogenation and dehydrocyclization catalyst consisting essentially of chromium oxide supported on alumina at a temperature of from 450° C. to 580° C., at a pressure not in excess of 50 p.s.i. ga., and in the absence of added hydrogen to the reaction zone to produce an aromatic-enriched product and a make of hydrogen-rich gas, recovering a normally liquid aromatic-enriched product and a hydrogen-rich gas, regenerating the spent dehydrogenation and dehydrocyclization catalyst in a regeneration zone by contacting same with a stream of oxygen-containing gas, recovering from the regeneration zone the regenerated catalyst for re-use in the contacting zone and a flue gas having a lower calorific value than said hydrogen-rich gas, and combining the recovered flue gas with the hydrogen-rich gas to reduce the calorific value of said hydrogen-rich gas to a value appropriate to the use of the formed blended gas as a town gas.

2. A process in accordance with claim 1 wherein the temperature in the contacting zone is from 525° C. to 570° C.

3. A process as claimed in claim 1 wherein a substantial proportion of the feedstock boils below 100° C.

4. A process as claimed in claim 3 wherein the feedstock is a straight-run, light gasoline.

5. A process as claimed in claim 3 wherein the feedstock is a light relatively aromatic-free fraction of a catalytic reformate.

6. The process of claim 1 wherein the catalyst in said contacting zone is in a fluidized bed, and catalyst is continuously withdrawn from the reaction zone; regenerated in said regeneration zone and returned to the contacting zone.

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