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COMPLETE SPECIFICATION

Improvements in or relating to Changing the Composition of Coke Oven Gas

We, KOPPERS COMPANY INC., a Corporation organized under the laws of the State of Delaware, one of the United States of America, of Koppers Building, City of Pittsburgh, State of Pennsylvania, United States of America; Assignees of GILBERT VINCENT McGURL, a Citizen of the United States of America, of 140, Roseville Avenue, City of Newark, State of 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:—

This invention relates to gas diffusion for rearranging the composition of fuel gases. More particularly the invention relates to the revision of the composition of coke oven gas by diffusion when using producer gas as a sweep gas and thereby revising both the coke oven gas and the producer gas.

The carbonization of coal in byproduct coke ovens produces a comparatively uniform quality of gas which, when the aromatic hydrocarbons are removed, has a heating value of 530 to 580 B.Th.u. and a comparatively low specific gravity. This gas is being widely used in cities for heating purposes. The construction of a coke oven battery requires that all of the ovens be operated simultaneously so that the total or average output of gas is quite uniform and cannot be conveniently and economically varied to follow the daily or seasonal demand cycle.

To take care of this variation in gas demand, it is customary to supplement the coke oven battery with water gas generators and then to mix the water gas with the coke oven gas to meet the demand. Some mixes of coke oven gas and water gas are not satisfactory because the B.Th.u. values may vary considerably and the gravity of the gas will also vary quite widely. The gas burning appliances do not operate satisfactorily with these variable types of gas so that it is important to deliver a comparatively uniform quality of gas for city distribution. It has been found that when the specific gravity of the domestic gas is quite uniform, then the appliances will properly burn such gas.

The most desirable method of changing the composition of coke oven gas is to vary the hydrogen content. When hydrogen is removed from the gas, the specific gravity and the B.Th.u. value are increased therefore coke oven gas may be revised to obtain the desired heating value and specific gravity more advantageously by diffusion to rearrange the constituents particularly the hydrogen content rather than attempting to obtain the desired gas by blending two or more different types of gases.

The primay object of the present invention is to provide a method of changing the composition of coke oven gas by selective separation of the hydrogen therefrom.

Another object of the invention is to provide a method of separating hydrogen from coke oven gas by diffusion. In the diffusion method of hydrogen separation from coke oven gas, the hydrogen passes through a porous boundary as the gas flows in a continuous stream across one face of the boundary. The diffusion is substantially aided if another gas commonly termed "a sweep gas" is moved across the face of the boundary opposite the face across which the coke oven gas is flowing. The sweep gas is used to control the pressure distribution of the two gases on opposite sides of the boundary. The sweep gas has a flow through the boundary into the feed gas and also acts to sweep from the face of the boundary the hydrogen and other gases that have penetrated through the boundary from the feed gas side by diffusion.

The "pressure distribution" of the feed and sweep gases on opposite sides of a boundary involves several factors:—

First, the size of the pores which determine the porosity of the boundary or diaphragm. For the revising of fuel gas, the boundary should have a pore size which is many times larger than the mean free path of the gas molecules. This mean free path of the molecules is the average distance which a molecule travels before colliding with another or an adjacent molecule. Depending upon the length and the desired resistance to flow of the gas through the pore, the width or diameter of the pore may be from 1 to 10000 times and preferably from 1 to 100 times the mean free path of the molecule.

Second, the pressure of the gas streams at opposite sides of the boundary or the average pressure differential across the pores of the boundary, or across the boundary.

Third, the area of the boundary, which takes into consideration the pressure differentials at the inlets or outlets of the boundary, or the average pressure differential over the entire area of the boundary. When the feed and sweep gas streams flow concurretnly or in the same direction across the opposite faces of the boundary, the pressure differential at the entrance end is dependent on the pressure differential of the two inlet gas streams, and there will be a gradual decrease or increase of the pressure differential as the streams advance across the boundary area, depending upon whether the pressure drop due to flow resistance in the sweep stream is more or less than the pressure drop in the feed stream. If the feed and sweep gas streams flow in counter-current direction along the faces of the boundary, then the pressure differential across the boundary at the entrance end of the sweep gas is at its maximum because the resistance to flow and the diffusion of the feed gas through the boundary has altered and lowered the pressure of the feed gas while the pressure of the sweep gas is at its maximum. Therefore, with counter-current flow the diffusion rate will be the highest at the entrance end of the sweep gas, and lowest at the entrance end of the feed gas.

Fourth, the hydrodynamic flow of the sweep gas through the pores of the boundary. This hydrodynamic flow is the free flow of sweep gas through the boundary pores not due to diffusion but due to the pressure differential across the boundary.

We have found that a low B.Th.u. producer or blast furnace gas which has a radically different composition than the composition of coke oven gas is an exellent sweep gas for facilitating the separation or redistribution of hydrogen in coke oven gas. Producer and blast furnaces gases have comparatively high specific gravities so that there is relatively small amount of diffusion of these gases through the boundary into the coke oven gas. On the other hand, the low specific gravity hydrogen readily passes through the boundary and is swept away from the boundary by the high specific gravity gas. If hydrogen is passed through the boundary from coke oven gas into producer or blast furnace gas, the addition of hydrogen to these gases is very advantageous in that it lowers the specific gravity of the gases and substantially increases the B.Th.u. heat values.

Accordingly, a further object of the invention is to utilize producer or blast furnace gas as a sweep gas in the diffusion separation of hydrogen from coke oven gas.

In accordance with the relative volumes of sweep gas and feed gas being revised, it is desirable to maintain a fixed differental pressure on opposite sides of the boundary, this differential pressure across the boundary being high if the boundary is quite porous. The temperature of the gases flowing across the boundary should be maintained above the dew points of any constituents in the gases and the velocity of the sweep gas should be such that it will sweep away from the face of the boundary the consituents diffusing through the boundary.

The pressure distibution of the sweep and feed gases with reference to the porous boundary of a diffusion apparatus depends upon the specific gravity of the gases, the pressure differential across the boundary, the velocity of movement of the gases across the face of the boundary and the area of the boundary. It is possible by the control of these various features to obtain a selective separation of hydrogen from coke oven gas.

Typical compositions of coke oven, producer and blast furnace gases are shown in the following Table.

TABLE 1.

Property	Producer Gas	Coke Oven Gas	Blast Furnace Gas
Specific Gravity	0.9	0.4	0.9
B.Th.u./Cu.Ft.	130	586	85
Analysis			
Carbon dioxide	3.5	1.8	11.5
Illuminants	—	3.7	—
Oxygen	0.5	0.2	—
Carbon monoxide	30.0	6.3	27.5
Hydrogen	10.0	53.0	1.0
Nitrogen	54.5	3.4	60.0
Methane	1.5	31.6	—

My tests have shown that at the same time that the coke oven gas is being revised, the sweep gas may also be revised so that alarge number of different types of gas may be produced. The revised producer or blast furnace gas which is enriched with the hydrogen and hydrocarbons of the coke oven gas is a good heating gas for coke ovens. Further, the revision of the sweep gas may be controlled to distribute the hydrogen and carbon monoxide in the ratio of molecular volumes of 1:1 or 2:1 to provide an excellent synthesis gas for the hydrogenation of carbon monoxide in the Fischer-Tropsch reaction.

A still further object of the invention is to provide a method of changing the composition of coke oven gas with a producer sweep gas to simultaneously upgrade the producer gas into a predetermined type of gas.

With these and other objects in view, the invention consists in the method of changing the composition of coke oven gas comprising feeding the coke oven gas as a stream along one side of a porous boundary passing a high specific gravity fuel gas, such as producer gas in a stream to sweep the other side of the boundary and controlling the pressure distribution of the gases on opposite sides of the boundary to control the movement of constituents through the boundary from one stream to the other.

The various features of the invention are illustrated in the accompanying drawing which is a diagrammatic flow sheet of an apparatus in which the preferred method of revising coke oven gas by diffusion may be carried out.

Coke oven and producer gases are generally maintained at a comparatively low pressure (6 to 12 inches of water pressure). Accordingly the diffusion process for revising coke oven gas is carried out at substantially atmospheric pressure, that is, these gases will have a sufficient pressure to control their flow through the diffusion apparatus.

Referring to the drawing, the diffusion revision of coke oven gas may be carried out as follows:—

Coke oven gas is introduced through a line 10 and flow regulator 12 into a meter 14 to establish a definite flow rate. The gas passes through a heater 16 which is preferably heated by steam to a temperature above the condensation temperature or dew point of any of the constituents in the gas at the boundary. From the heater 16 the gas passes through a line 18 into a chamber 20 of a diffusion apparatus. This gas is then distributed throughout the area of the chamber 20 and passes through tubes 22 which connect with porous diffusion boundaries 24 that form a continuation of the tubes 22. The streams of coke oven gas pass through the diffusion boundary tubes, then through tubes 26 into a chamber 28 and thence flow through a line 30 into a cooler 32. The coiler 32 is preferably cooled by water or other cooling medium in order to standardize the temperature of the gas so that it may flow through a line 34 through a meter 36 to measure its volume.

The producer sweep gas is introduced into the apparatus through a line 38 and flow regulator 40 to establish a definite predetermined flow rate of producer gas. The producer gas then passes through a meter 42 into a heater 44 where it is heated by steam to raise it to substantially the same temperature as the coke oven gas as maintained by the heater 16. This preheated gas then passes through a line 46 to a line 48 or a line 50 in accordance with the manner in which the sweep gas is circulated through the diffusion apparatus. If the sweep gas is to pass through the diffusion apparatus in a parallel concurrent stream with the feed gas then the sweep gas will enter a chamber 52 of the diffusion apparatus through the line 48. The sweep gas will then be distributed throughout the chamber 52 and pass upwardly through the tubes 54 around the porous boundary tubes 24. After passing across the porous boundaries, the sweep gas enters a chamber 56 and then flows out through a line

58 through a cooler 60 to be conditioned for passing through a line 62 into a meter 64. If the sweep gas is to pass across the porous boundaries in a stream parallel to the coke oven gas stream but counter-current to the flow of the coke oven gas, then the sweep gas will pass through the line 50 to the line 58, thence into the chamber 56, then down across the porous boundary tubes 24 into the chamber 52, and out through the line 48. From the line 48 the gas will pass through the line 66 to the line 58 and thence through the cooler 60 and meter 64. To assists in obtaining a good temperature condition for diffusion, the tubes 54 are surrounded by a heating jacket 68 into which steam is introduced through an inlet 70 and water of condensation taken out through a line 72.

The pressure distribution across the porous boundary tubes 24 is maintained by means of a regulating valve 74 in the sweep gas line 58 and a regulating valve 76 in the feed gas line 30. The flow regulators 12 and 40 in the coke oven and producer gas lines respectively control the flow rate of coke oven gas and producer gas. The pressure of the gas flowing across the opposite sides of the porous barrier of the diffusion tubes is controlled by the valves 74 and 76. The valve 74 is controlled to maintain a pressure of the sweep gas on the outside of the tubes 24 slightly higher than the pressure of the feed gas within the tubes 24. This pressure differential then controls the hydrodynamic flow of sweep gas through the porous tubes and the diffusion of constituents from one gas stream into the other gas stream. The pressure differential is small but is sufficient to maintain a hydrodynamic flow and definite diffusion through the diaphragm.

From Table I it will be seen that the hydrogen content of coke oven gas is much higher than the hydrogen content of producer gas or blast furnace gas. Hydrogen has a very much lower specific gravity than carbon dioxide, carbon monoxide, nitrogen or the hydrocarbons in coke oven gas. Since the rate of diffusion through a porous diaphragm is roughly inversely proportional to the square root of the molecular weights of the gases, the hydrogen will have the highest velocity of any of the constituents in the feed and sweep gases. Therefore, the revision of coke oven gas when using producer gas as a sweep gas will consist principally in the redistribution of hydrogen by diffusion through the porous boundary. By maintaining a higher pressure on the sweep gas side of the boundary, than on the feed gas side of the boundary, the free flow will be from the sweep gas into the feed gas. On the other hand, the coke oven gas constituents tend to set up a counter-diffusion through the boundary which is opposed by the free flow and diffusion of the constituents of the producer gas through the porous boundary. The net result is an exchange of constituents passing through the boundary from each stream into the other. However, the higher diffusion velocities of the lighter constituents in the coke oven gas, partcularly hydrogen, will result in a net addition of hydrogen to the producer gas from the coke oven gas and a small redistribution of other constituents between the two gas streams.

By controlling the boundary area and the volume ratio of the gases on opposite sides of the boundary a decrease of the specific gravity of the producer gas in the range of 12 to 20% may be obtained. Simultaneously, while decreasing the specific gravity of the producer gas 12 to 20%, the specific gravity of the coke oven gas may be increased in the range of 42 to 50%.

In Tables II to VII inclusive are shown data of the revision of a coke oven gas, of substantially the composition cited above, through a porous boundary in which tubes are used which have a porosity of 6400 openings per square inch, the openings being substantially square with a dimension of 0.0035 inches on each side. These boundary tubes are made of a copper screen coated with corrosion resistant nickel. The data of Tables II to VII was obtained by using seven porous boundary tubes 1½ inches inside diameter with an effective length of 24 inches. In all cases the gas was corrected to 30 inches of mercury pressure and 60° F. for the meter readings.

TABLE II

Feed (Coke Oven Gas) in=643 C. F. H.
(Coke Oven Gas) out=708 C. F. H.
Sweep (Producer Gas) in=520 C. F. H.
out=455 C. F. H.

	Sweep		Feed	
	In	Out	In	Out
	%	%	%	%
H_2 as determined by Conductivity Cell	10.5	29.5	51.7	39.0
Orsat Analysis				
CO_2	4.9	3.2	1.6	2.3
Illuminants	0.9	0.6	3.0	2.2
O_2	0.5	0.2	0.6	0.5
H_2	10.8	29.5	55.6	40.1
CO	28.5	21.9	5.6	12.5
CH_4	1.2	5.7	29.0	21.8
C_2H_6	—	—	—	—
N_2 (By difference)	53.2	38.9	4.6	20.6
Specific Gravity	0.870	0.697	0.370	0.538

TABLE III

Feed (Coke Oven Gas) in=643 C. F. H.
(Coke Oven Gas) out=816 C. F. H.
Sweep (Producer Gas) in=530 C. F. H.
out=357 C. F. H.

	Sweep		Feed	
	In	Out	In	Out
	%	%	%	%
H_2 as determined by Conductivity Cell	10.5	28.3	51.7	39.2
Orsat Analysis				
CO_2	4.9	3.7	1.6	2.6
Illuminants	0.9	0.7	3.0	2.2
O_2	0.5	1.0	0.6	1.7
H_2	10.8	30.1	55.6	39.8
CO	28.5	21.1	5.6	12.8
CH_4	1.2	4.5	29.0	13.4
N_2 (By difference)	53.2	38.9	4.6	27.5
Specific Gravity	0.870	0.699	0.370	0.576

TABLE IV

Feed (Coke Oven Gas) in=187 C. F. H.
(Coke Oven Gas) out=307 C. F. H.
Sweep (Producer Gas) in=476 C. F. H.
out=356 C. F. H.

	Sweep		Feed	
	In	Out	In	Out
	%	%	%	%
H_2 as determined by Conductivity Cell	10.5	23.1	54.3	31.8
Orsat Analysis				
CO_2	4.0	3.8	1.7	2.8
Illuminants	0.0	0.0	2.8	2.2
O_2	0.8	1.0	1.5	1.3
H_2	11.8	22.1	53.9	31.6
CO	28.7	24.6	6.7	15.8
CH_4	0.0	2.0	17.2	16.1
C_2H_6	1.5	1.8	2.9	0.0
N_2 (By difference)	53.2	44.7	13.3	30.2
Specific Gravity	0.874	0.783	0.431	0.637

TABLE V

Feed (Coke Oven Gas) in=390 C. F. H.
(Coke Oven Gas) out=516 C. F. H.
Sweep (Producer Gas) in=482 C. F. H.
out=356 C. F. H.

	Sweep		Feed	
	In %	Out %	In %	Out %
H_2 as determined by Conductivity Cell	11.6	23.8	54.3	39.2
Orsat Analysis				
CO_2	4.9	4.0	1.7	2.7
Illuminants	0.0	0.0	2.6	1.9
O_2	0.2	0.1	0.7	0.7
H_2	12.4	24.0	54.9	39.7
CO	28.5	23.7	6.3	13.1
CH_4	1.4	0.1	24.6	17.4
C_2H_6	1.2	1.9	0.6	1.2
N_2 (By difference)	51.4	46.2	8.6	23.3
Specific Gravity	0.889	0.782	0.394	0.560

TABLE VI

Feed (Coke Oven Gas) in=586 C. F. H.
(Coke Oven Gas) out=533 C. F. H.
Sweep (Producer Gas) in=241 C. F. H.
out=294 C. F. H.

	Sweep		Feed	
	In %	Out %	In %	Out %
H_2 as determined by Conductivity Cell	11.9	34.7	55.7	48.1
Orsat Analysis				
CO_2	4.9	3.8	1.7	2.3
Illuminants	0.0	0.8	2.6	2.5
O_2	0.2	0.5	0.7	0.8
H_2	12.4	34.9	54.9	48.9
CO	28.5	18.4	6.3	8.8
CH_4	1.4	8.3	24.6	23.0
C_2H_6	1.2	0.4	0.6	0.6
N_2 (By difference)	51.4	32.9	8.6	13.1
Specific Gravity	0.889	0.642	0.394	0.453

TABLE VII

Feed (Coke Oven Gas) in=584 C. F. H.
(Coke Oven Gas) out=484 C. F. H.
Sweep (Producer Gas) in=400 C. F. H.
out=500 C. F. H.

	Sweep		Feed	
	In %	Out %	In %	Out %
H_2 as determined by Conductivity Cell	11.9	32.2	55.7	45.8
Orsat Analysis				
CO_2	4.9	4.2	1.7	2.6
Illuminants	0.0	0.8	2.6	2.4
O_2	0.2	0.2	0.7	0.8
H_2	12.4	32.3	54.9	47.7
CO	28.5	18.6	6.3	8.7
CH_4	1.4	6.7	24.6	22.8
C_2H_6	1.2	0.8	0.6	1.1
N_2 (By difference)	51.4	36.4	8.6	13.9
Specific Gravity	0.889	0.769	0.394	0.466

The data of Tables II, II, IV and V were taken at a time when the sweep gas was passed through the diffusion apparatus as illustrated in the drawings in a path concurrent with the flow of feed gas.

The data of Tables VI and VII were taken when the sweep gas flowed in a counter-current path to the feed gas.

From this data it will be seen that the composition of the coke oven gas has been quite widely changed, particularly with reference to its hydrogen. and carbon monoxide contents. The specific gravity of the revised gases shown in the Tables is very acceptable for domestic purposes. Further the B.Th.u. value of the producer gas has been increased approximately 10%. It will be seen also that the ratio of carbon monoxide to hydrogen in the reformed sweep gas may be quite widely varied. In accordance with the data of Tables IV and V the molecular ratios of hydrogen to carbon monoxide in the revised producer gas are approximately 1:1, while in accordance with the data of Tables VI and VII the molecular ratios of hydrogen to carbon monoxide in the revised producer gas are substantially 2:1. Such gases are well suited as synthesis gases for the Fischer-Tropsch process. Although nitrogen is present in these gases, it has been found that a high percentage of nitrogen it not detrimental to the catalytic hydrogenation of carbon monoxide with a catalyst in the Fischer-Tropsch reaction.

In the apparatus illustrated in the drawing, seven porous boundary tubes have been used. It is apparent, however, that the apparatus may be designed to use any desired number of tubes and the porous area may be varied in accordance with the gases being treated in order to get the desired diffusion separation of products. In the diffusion operation there is always an exchange of gas from one side of the boundary into the gas at the other side of the boundary but the rates of diffusion of the gaseous constituents may be controlled and modified in order to get a comparatively selective separation of the desired components.

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 method of changing the composition of coke oven gas comprising feeding the coke oven gas as a stream along one side of a porous boudary passing a high specific gravity fuel gas, such as producer gas in a stream to sweep the other side of the boundary and controlling the pressure distribution of the gases on opposite sides of the boundary to control the movement of constituents through the boundary from one stream to the other.

2. Method according to Claim 1, which comprises controlling the movement of hydrogen through the boundary from the coke oven gas to the producer gas.

3. Method according to Claim 1 in which the control of the boundary area and the volume ratio of the gases on opposite sides of the boundary are such as to increase the hydrogen content of the producer gas and the carbon monoxide and nitrogen content of the coke oven gas while decreasing the specific gravity of the producer gas in the range of 12 to 20%.

4. The method according to Claim 1 in which the boundary area and the volume ratio of gases on opposite sides of the boundary cause a movement of hydrogen through the boundary to the producer gas and nitrogen and carbon monoxide to the coke oven gas to such an extent that the specific gravity of the coke oven gas will be increased in the range of 42 to 50%.

5. Method according to any of the preceding Claims, which comprises passing producer gas in concurrent flow to the coke oven gas.

6. Method according to any of the preceding Claims, which comprises passing producer gas in counter-current flow to the coke oven gas.

7. Method according to any of the preceding Claims, in which the pore size of the boundary is from 1 to 100 times larger than the mean free path of the coke oven gas molecules.

8. Method of changing the composition of coke oven gas substantially as described with reference to the accompanying drawings.

Dated the 21st day of April, 1947.
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