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ON THE SUBSTITUTION OF LIQUID, VAPORIZED AND GASEOUS HYDROCARBONS F ORSOLID FUEL IN BLAST-FURNACES.

BY CHARLES PLAGGE.

ACCORDING to Prof. H. Wurtz's analysis, the commercial crude petroleum may be considered as consisting of :

84 per cent carbon,
14 " " hydrogen,
2 " " oxygen,

100 lbs. petroleum.

Or, assuming the 2 oxygen to be combined with 0.25 H., it will contain :

84 per cent carbon,
13.75 " " hydrogen,
2.25 " " water.

Supposing the petroleum is but incompletely burned, in such a way that its carbon is only converted into carbonic oxide, its hydrogen into water, its siderurgic value will be as follows :

The 84 lbs. of carbon to be converted into carbonic oxide require $75 : 100 = 84 : x = 112$ lbs. oxygen, or 423 lbs. atmospheric air. The products of combustion will consist of :

196 lbs. carbonic oxide,
126 " water,
631.75 " nitrogen.

[NOTE.—In the following, CU°. will represent *caloric units centigrade.*]

84 lbs. carbon burned to carbonic oxide generate $84 \times 2{,}221 = 186{,}564$ CU°.
13.75 " hydrogen " " water " $13.75 \times 34{,}444 = 473{,}605$ "

Total heat generated by 100 lbs. petroleum = 660,169 "
Deducting the latent heat of the 126 lbs. of water, equal to 126×537 = 67,662 "
we obtain, as heat value of 100 lbs. of petroleum, incompletely burned = 592,507 "

The temperature obtained by the incomplete combustion of petroleum, we find by the equation $592{,}507 = [196 \times 0.288 + 126 \times 0.847 + 631 \times 0.275]\, x$,

$$\text{or, } x = \frac{592{,}507}{336} = 1763^\circ \text{ C.}$$

A very different result we obtain by the *complete* combustion of petroleum, by which its carbon is converted into carbonic acid, its hydrogen into water. In that case we find :

84 lbs. carbon burned to carbonic acid require 224 lbs. oxygen, or 861 lbs. of atmospheric air.
13.75 " hydrogen, as stated before, require 110 lbs. oxygen, or 423 lbs. of air.

The products of combustion are :

308 lbs. carbonic acid,
126 " water,
950 " nitrogen.

The heat generated by burning 84 lbs. carbon to carbonic acid is $84 \times 7900 =$ 663,600 CU°.
The heat generated by burning 13.75 lbs. hydrogen to water is (as before) 473,605 "

Total 1,137,205 "
Deducting, as before, the latent heat of the 126 lbs. of water 67,662 "
we obtain, as total available heat from the complete combustion of 100 lbs. petroleum = 1,069,543 "

The temperature thereby obtained is expressed by equation :

$$1{,}069{,}543 = [308 \times 0.212 + 126 \times 0.847 + 950 \times 0.275]\, x$$

$$x = \frac{1{,}069{,}543}{433} = 2470^\circ \text{ C.}$$

100 lbs. of petroleum, therefore, when burned to carbonic acid and water, produce not only 1,069.543—592,507=477,036 CU°. more heat, but also a temperature of $2470 - 1763 = 707^\circ$ C. higher than when burned merely to carbonic oxide and water.

While, therefore, petroleum, when incompletely burned, is scarcely serviceable for making pig-iron, it becomes very valuable for this purpose when we apply it in such a way that its carbon can be converted into carbonic acid, and its hydrogen into water.

The next point now to be considered will be, what amount of petroleum will be required for the making of 1 ton, of 2240 pounds, of pig-iron ? This amount naturally differs according to the ores used. In North-western Pennsylvania it takes, on an average, in cold-blast furnaces, 90 bushels of Connellsville coke, containing 3200 lbs. of carbon, to make 1 ton of pig-iron from magnetic oxide, or a mixture of protoxide and oxide of iron containing 853 lbs. of oxygen, in the amount of ore required to produce 1 ton of pig-iron, which, therefore, requires for its reduction 640 lbs. of carbon, if the latter is converted into carbonic oxide. Of the balance of the carbon used, amounting to $3200 - 640 = 2560$ lbs., 60 lbs. are required for the carbonization of the reduced metal, leaving 2500 lbs. of carbon to effect the dissociation of the oxygen from the iron, and to melt the reduced metal along with the slag materials, and to cover the loss of heat by radiation, waste heat of escaping gases, etc.

The amount of heat required for the dissociation of the oxygen in the iron ore, we can calculate as follows :

1 lb. of oxygen, burned with iron, generates 6212 CU°.

To dissociate, therefore, 853 lbs. of oxygen, combined with the ore producing 1 ton of pig-iron, will require $853 \times 6212 = 5{,}298{,}836$ CU° ; from this, however, has to be deducted the heat generated by the burning of the 853 lbs. oxygen, liberated from the ore, with 640 lbs. of carbon, to carbonic oxide, amounting to $640 \times 2221 = 1{,}321{,}440$ CU°. It therefore takes $5{,}298{,}836 - 1{,}321{,}440 = 3{,}977{,}396$ CU°, or $\frac{3{,}977{,}396}{2221} = 1790$ lbs. of carbon to dissociate 1 ton of pig-iron ; and $3200 - 640 + 60 + 1790 = 710$ lbs. of carbon, to cover loss of heat by radiation, for fusion, heat lost with waste gases, etc.

Substituting petroleum for carbon, and conducting the blast-furnace process in such a manner that the petroleum used is all converted into carbonic acid and water, we must consider, first, that of the 84 carbon contained in 100 lbs. petroleum, by being converted into carbonic acid, absorb from the ore 224 lbs. oxygen.
the 13.75 hydrogen, by being converted into water, absorb 110 " "

100 lbs. petroleum, therefore, take up 334 lbs. oxygen.
and to reduce 1 ton of pig-iron will require $334 : 853 = 100 : x$, and $x = 256$ lbs. of petroleum, which, burning to carbonic acid, with 853 lbs. oxygen set free by the reduction of the metal, will generate $\frac{256}{100} \times 10{,}695{,}543 = 2{,}738{,}030$ CU°. We shall, consequently, require for the dissociation of the iron from the oxygen 5298—8362,738,030 = 2,560,806 CU°, or $\frac{2{,}560{,}806}{1{,}069{,}543} = 239$ lbs of petroleum.

The 710 lbs. of carbon $= 710 \times 2221 = 1{,}576{,}910$ CU° required for smelting, loss by radiation, waste gases, etc., we can substitute by $\frac{1{,}576{,}910}{1{,}069{,}543} =$ 143 lbs. of patroleum.

The total consumption of petroleum, per 1 ton of pig-iron, will therefore be :

For reduction 256 lbs.
For dissociation of metal 239 "
For smelting, loss by waste gases, etc 148 "

Total 643 lbs. $= \frac{643}{6.69} = 96.4$ gallons.

Taking into consideration the much smaller size of furnace required by the substitution of hydrocarbons for solid fuel, the smaller amount of flux required, and more energetic action of the hydrocarbons, we may assume, especially when aided by hot-blast, that it will probably not require more than two barrels of petroleum per one ton of pig-iron ; the substitution of petroleum for solid fuel, therefore, would be very economical in many sections of this country. Still more economical, however, will be the substitution of natural gas for solid fuel, wherever the former is met with, as in many parts of North-western Pennsylvania, New-York, Ohio, Kentucky, West Virginia, etc.

According to the analysis of Prof. Wurtz, of the Bloomfield Gas Company (published in *American Gas-Light Journal*, March, 1870, p. 82), we find the value of the natural gas as follows. The gas contains

82.41 per cent marsh gas			64.81 carbon.
10.11 " carbonic acid			21.31 hydrogen.
4.31 " nitrogen	}	Equal to	0.26 water.
0.23 " oxygen			4.31 nitrogen.
2.94 " illuminating carbon			10.11 carbonic acid.

The 64.81 carbon burning to carbonic acid require 170.7 oxygen, contained in 652 lbs. of air ; the 21.31 hydrogen and 0.23 oxygen, burning to water, requires 171.48 oxygen, contained in 655 lbs. of air.

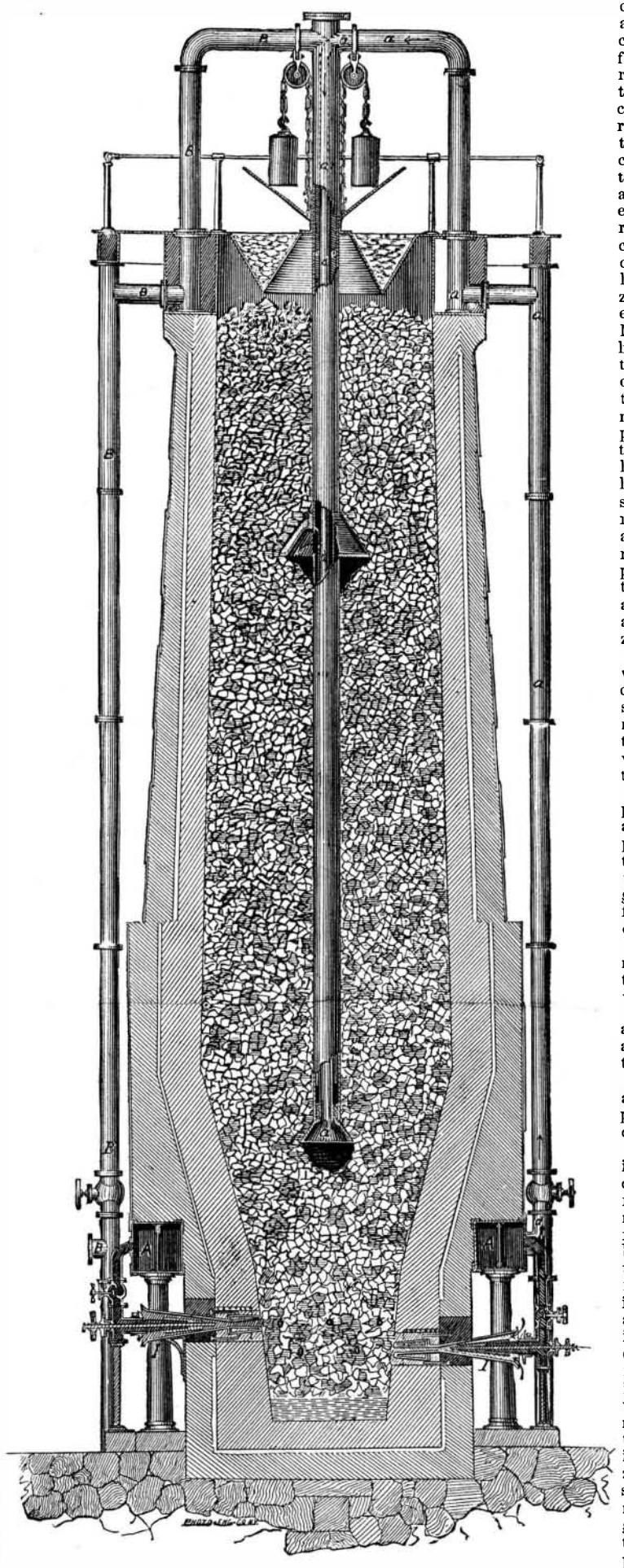
The products of combustion are

244.82 carbonic acid, 192.05 water, 970.16 nitrogen.

64.81 carbon, burning to carbonic acid, generate $64.81 \times 79.00 = 511999$ CU°.
21.34 hydrogen in water $21.34 \times 34444 = 735035$ "

Total 1247034 CU°.
Deducting the latent heat of 192.05 water 103120 "

We have heat value of 100 lbs. of natural gas 1143914 CU°.



The temperature of combustion is expressed by $1143914 = 244.8 \times 0.212 + 192 \times 0.847 + 970 \times 0.275$, or $x = \frac{1143914}{481} = 2378^\circ$C.

Incompletely burned to carbonic oxide and water, we obtain 64.81 carbon, burned, to carbonic oxide requires 85.35 oxygen contained in 328 lbs. air.

21.31 hydrogen, burned to water, requires 171.48 oxygen contained in 655 lbs. of air.

The products of incomplete combustion of 100 lbs. natural gas to carbonic oxide and water are :

149.36 carbonic oxide, 192.05 water, 741.50 nitrogen, 10.11 carbonic acid.
64.81 carbon, burning to carbonic oxide, generate $64.81 \times 2221 = 143943$ CU°.
21.34 hydrogen in water $21.34 \times 34444 = 735035$ "

Total 878978 CU°.
Deducting latent heat of water 103858 "

We find the heat value of 100 lbs. of gas, incompletely burned, 775858 CU°, and the temperature obtained thereby $\frac{775858}{411} = 1887^\circ$C.

These calculations show that liquid, vaporized, or gaseous hydrocarbons can be substituted successfully for solid fuel, only when we apply them in such a way that, by its combustion, it is entirely converted into carbonic acid and water.

Blunt Salisbury proposed the use of petroleum in blast-furnaces, by vaporizing the petroleum with superheated steam, and injecting it with the blast into the chamber of combustion of the furnace. Used in this way, the petroleum vapor must be but partially burned, converting its carbon into carbonic oxide, as the latter is necessary for the reduction of the metal. The temperature which, under these circumstances, can be obtained in the hearth is, as shown before, insufficient to work the furnace to advantage. To avoid these difficulties, instead of introducing the petroleum exclusively into the hearth, together with the blast, I divide the hydrocarbon to be used in such a way that into the zone of combustion only such a part of it is introduced as is wanted to produce the smelting of the reduced iron along with the slag materials, while the balance of the hydrocarbon required for the heating, roasting, reduction, and carbonization of the metal, is injected into the upper part of the furnace (the reducing zone). To introduce the hydrocarbon, and the blast required for the roasting process, I prefer to use a central tube, descending from the trundle down to such a point in the reducing zone as is judged best for working the furnace. To protect this tube (the hydrocarbon tube) against destructive heat, I surround it by an exterior tube of larger diameter, which leaves an annular space for the circulation of hot or cold blast, which latter enters said annular space at the top, circulating around the entire hydrocarbon tube, before it escapes by appropriate openings in the exterior tube into the interior of the furnace, at a certain depth below the upper surface of the charges, but above the level at which the hydrocarbons are admitted into the reducing zone. The outside (air) tube may be protected against destructive heat by a fire-proof lining ; also the outlet-openings for air and hydrocarbon be secured against shaking, and to facilitate their entrance into the interior of the furnace, by umbrella-shaped projections. By this or other equivalent arrangement, the blast introduced into the upper part of the furnace serves both as a protection of the hydrocarbon tube, and to burn all hydrocarbon vapors or gases which may not have been utilized in the reduction and smelting of the iron. The free oxygen admitted into the upper part of the furnace, above the reducing zone, oxidizes the deleterious admixtures of the ore, such as sulphur, phosphorus, etc., and the heat generated thereby assists to expel the carbonic acid and moisture of ore and flux, and to heat and prepare the ore for the reducing zone.

Into the combustion-chamber the liquid, vaporized or gaseous hydrocarbons are introduced with or without the aid of superheated steam, either mixed with the blast or separately from it, in which latter case I prefer to introduce the hydrocarbon at a level somewhat below the level where the blast enters.

The advantages which I claim for my process are : 1st. great saving in fuel (a) on account of the greater heat produced by the perfect combustion of the hydrocarbon with the least amount of blast ; (b) the complete utilization of the waste heat of the escaping gases for heating, roasting, and preparing for the zone of reduction the newly entering charges.

2d. Large increase in the daily output of metal by the great increase of the capacity of the furnace for ore, as no solid fuel is mixed with the ore.

3d. Superior quality of the metal produced, as most of the impurities of the ore and flux are eliminated by the roasting process before the charges enter the zone of reduction.

4th. The reduction of the metal is effected at such a low temperature that the least possible amount of impurities are reduced or can combine with the iron.

5th. The reduced and carbonized metal on its way toward the hearth, coming only into contact with neutral or slightly oxidizing or reducing gases (as the metal to be produced may require), can not absorb impurities from the slag material, as is the case in blast-furnaces as heretofore worked, where the reduced metal, on its way from the reducing zone toward the hearth, remains in constant contact with incandescent coal at a high and increasing temperature, and is, besides, exposed to a current of highly deoxidizing gases, which, after the complete reduction of the iron, act mainly upon he impurities of the ore and slag material, which are thereby reduced, and contaminate the reduced metal. In my process, the metal reduced at low temperature, on its way from the reducing to the smelting zone, can not be contaminated by injurious substances, as it comes only in contact with neutral, or slightly oxidizing, or reducing gases, and is subjected to the refining action of the carbonic acid, which acts as a powerful agent upon the removal of sulphur, silicon, or phosphorus, which may have been taken up by the reduced metal, converting them into sulphurous acid, silicic acid, and phosphoric acid.

If the ores contain much phosphorus, I prefer to moisten them with a strong solution of chloride of magnesia (the refuse or mother-liquor of salt-works) or with chloride of manganese. The chloride of magnesia heated to redness is decomposed ; its chlorine combines readily with the phosphorus of the iron, and escapes with the waste gases as perchloride of phosphorus. The chlorine of the chlorides likewise acts upon the carbon of the hydrocarbons, forming bichloride of carbon, which is highly volatile and a powerful resolvent for phosphorus. By using, in the described manner, the upper part of the furnace for heating and roasting the ores before they enter the reducing zone, the sulphur contained in the ore and flux is readily removed, as the steam formed by the combustion of the hydrocarbons decomposes the sulphide of iron as follows : $FeS_2 + H_2O = FeO + 2SH$, which latter, by the free oxygen of the blast introduced into the upper part of the furnace, is burned to SO_2 and H_2O.

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