

Translation of Operating Results to Gasification on Commercial Scale

For the purpose of predicting oxygen and steam requirements as well as percent completion of gasification, yields of synthesis gas, etc., in the gasification of coal on commercial scale, it appeared desirable to translate the operating results to conditions expected to exist in large-scale plants. The most important among such conditions characteristic of large-scale operation are small or even negligible heat losses from the gas generator and the injection of superheated steam, which generally result in a reduced oxygen requirement and increased gasification of carbon. A procedure was therefore developed for the thermodynamic calculation of the operating results under zero heat-loss condition and for the assumed injection of steam superheated to various given temperatures.

The rather involved calculations and the underlying assumptions are similar to those used by H. Perry^{20/} and R. C. Corey,^{21/} although considerably simplified and extended to cover a broader field. Somewhat similar computations on a purely theoretical basis also have been made by H. R. Batchelder and J. C. Sternberg^{22/} in their thermodynamic studies of coal gasification, including the expression of heat effects by generalized equations.

The calculations and formulas developed are based on the assumptions (1) that the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) reaches equilibrium, but the reduction of carbon dioxide on carbon surface ($\text{CO}_2 + \text{C} = 2\text{CO}$) may not, and the latter reaction does not influence the former; (2) the CO_2

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^{22/} Ind. Eng. Chem., vol. 42, 1950, p. 877.

and H_2O do not dissociate to any appreciable extent; (3) the small amount of hydrocarbons, both saturated and unsaturated, in the synthesis gas are considered dissociated to elementary carbon and hydrogen at temperatures exceeding $1,800^\circ F.$; (4) all of the sulfur in the gas is in the form of H_2S ; and (5) the percent of carbon gasified would remain the same under zero heat loss condition.

Several of these assumptions have been confirmed by comparatively simple thermodynamic considerations and computations of the constants of effective equilibria from actually obtained experimental data. Calculation of the equilibrium composition from the known values of the equilibrium constant at various temperatures showed that, even at such comparatively low outlet-gas temperatures as $1,800^\circ F.$, negligible amounts of hydrocarbons remain undissociated.

For the fifth assumption above, there is little theoretical or practical justification. The assumption was made for convenience and expediency to simplify the lengthy procedure of computations. Actually, as shown by subsequent calculations, the elimination of heat losses should result in higher temperatures in the generator chamber which, in turn, should increase the velocity of the reduction of CO_2 on carbon surface to CO and cause an increase in carbon gasification. However, with heat losses already reduced to less than 5 percent when the generator is operated close to its maximum capacity (50 to 55 pounds of coal charged per hour), the increase in the percentage of carbon gasified under zero heat loss condition may be neglected.

The first step in the calculation of the temperature and composition of the exit gas under "no heat loss" condition for any given run consists in making an over-all material balance and heat balance, both based on 1 pound atom of carbon in the coal gasified under actual operating conditions. The actual heat loss (ΔH_1) thus determined and the corresponding measured exit-gas temperature (T_1 in degrees Rankine) are noted for the plotting of a curve later.

The next step consists in the stoichiometric calculation of the yield and composition of the output gas from the quantities and compositions of the input materials for an equilibrium condition corresponding to an assumed exit-gas temperature (T_2). Let the pound mols of CO_2 , CO , H_2O , H_2 , H_2S , and N_2 outputs in the synthesis gas, each per pound atom of carbon gasified, be designated by the letters a, b, c, d, f, and g, respectively. Let the symbols C, O, H, S, and N signify, respectively, pound atoms of carbon, oxygen, hydrogen, sulfur and nitrogen inputs per pound atom of carbon gasified. Knowing the percentage of carbon gasified in a given run, the values of O, H, S, and N are calculated from (1) the coal input (lb./hr.) and coal analysis, (2) oxygen input (cu. ft./hr.), and (3) steam introduced (lb./hr.). As, stoichiometrically,

$$C = a + b$$

$$O = 2a + b + c$$

$$H = 2c + 2d + 2f$$

$$N = 2g$$

$$S = f$$

Solving these five equations with six unknown quantities in terms of "a" (CO₂):

$$b = C - a$$

$$c = 0 - a - C$$

$$d = a - 0 + H/2 + C - S$$

$$f = S$$

$$g = N/2$$

But, as 1 pound atom of carbon was chosen as the basis:

$$a = \text{mols CO}_2$$

$$b = 1 - a = \text{mols CO}$$

$$c = 0 - a - 1 = \text{mols H}_2\text{O}$$

$$d = a - 0 + H/2 + 1 - S = \text{mols H}_2$$

$$f = S = \text{mols H}_2\text{S}$$

$$g = N/2 = \text{mols N}_2$$

Assume, now, the new exit-gas temperature (T₂), which for a zero heat loss condition must be higher than the actually measured exit gas temperature. Choosing, for example, 800° F. above T₁, the corresponding equilibrium constant (K_p) for the water-gas shift reaction (CO + H₂O = CO₂ + H₂) is obtained from prepared curves, showing values of K_p plotted on semi-log scale against $\frac{1}{T}$, where T is absolute temperature. Let the value of the equilibrium constant just found for the assumed temperature T₂ equal K. Then, by substitution into the equilibrium equation:

$$K = \frac{[a][d]}{[b][c]} = \frac{(a)(a - 0 + H/2 + 1 - S)}{(1 - a)(0 - a - 1)}$$

Solving this quadratic equation for "a", the single unknown quantity, by rearranging gives:

$$K = \frac{a^2 + Xa}{a^2 - 0a + 0 - 1}$$

where:

$$X = H/2 - O - S + 1$$

By further rearrangement:

$$a^2 + \frac{KO + X}{1 - K} a - \frac{KO - K}{1 - K} = \text{zero},$$

which is solved for "a" by the usual algebraic formula for quadratic equations. Knowing the value of "a", the values of b, c, and d are obtained from:

$$b = 1 - a$$

$$c = O - a - 1$$

$$d = a - O + H/2 + 1 - S$$

As now the input and output figures are known, a heat balance is made as the next step, in which the enthalpies of the output gases are calculated for the assumed temperature T_2 . From the heat balance, the heat-loss (ΔH_2), corresponding to the assumed exit-gas temperature (T_2 in degrees Rankine), is determined.

A graph is then prepared by plotting temperatures T_1 and T_2 (scale on the ordinate) against heat losses ΔH_1 and ΔH_2 (scale on the abscissa with negative values to the left and positive values to the right of a zero point). The two points thus plotted are connected by a straight line, and the temperature, T_0 , on the ordinate is read off at the level where a perpendicular raised at the zero heat-loss point on the abscissa intersects the straight line. The exit-gas temperature obtained for zero heat loss is then verified by looking up the corresponding equilibrium constant from the working chart and computing the values of a, b, c, and d by means of the quadratic equation derived above for the calculation of "a" and the three equations subsequently listed. If the heat balance made for exit-gas temperature T_0 by the use of these output figures, namely pound mols of CO_2 , CO, H_2O , H_2 , H_2S , and N_2 per pound atom of carbon gasified, gives a zero heat loss, the temperature T_0 graphically obtained above is considered the exit-gas temperature under zero heat loss condition, or "thermal balance temperature."

From the total number of mols of various gaseous components (CO_2 , CO, H_2 , H_2S , and N_2) per each atom of carbon gasified, obtained above, and from actual operating data pertaining to the run considered, such as feed-rate of the raw coal in pounds per hour and percent of carbon gasified, the output of dry synthesis gas in cubic feet per hour under zero heat loss condition is stoichiometrically calculated. By a similar computation, from the oxygen actually introduced in cubic feet per hour and the dry gas output in cubic feet per hour (calculated above), the oxygen requirement in cubic feet per MCF of synthesis gas made under the assumed zero heat loss condition is obtained. The oxygen requirement is also expressed on the usual basis of 1,000 cubic feet of CO + H_2 .

Other operating results, such as gas yield in cubic feet per ton of dry coal charged, and ratios of oxygen to coal and steam to coal charged, are

obtained for zero heat loss condition by similar simple stoichiometric calculations.

The composition of the wet and dry synthesis gas made under zero heat loss condition is computed from the number of mols of CO_2 , CO , H_2O , H_2 , H_2S , and N_2 per each atom of carbon in the coal gasified, all of which resulted from the calculations leading up to the computation of the exit-gas temperature under no heat loss condition. The composition of the exit gas is expressed on a percentage basis.

Up to this time, in the computation of the operating results for zero heat loss condition, no assumption has been made for the theoretical introduction of steam superheated to various given temperatures beyond that actually injected in the run or steam resulting from the vaporization of the moisture in the coal charged. In several runs, namely in those gasifying coals of high moisture and hydrogen content, and where the generator was operated considerably below its maximum capacity (about 55 pounds per hour), there has been no actual injection of steam. For such runs, in particular, and also because the gas-making unit has not been equipped for the superheating of steam to temperatures higher than 600° to 700° F., it seemed desirable to assume the introduction of highly superheated steam at rates comparable to operation on commercial scale (1 to 2 pounds of steam per pound of coal). The procedure developed for this set of thermodynamic calculations for the translation of the operating results to conditions assumed to exist on commercial scale, i.e. with negligible heat losses, is as follows:

A given input of steam, e.g. 1 pound per pound of dry, ash-free coal superheated to, say, $2,100^\circ$ F., is assumed. The objective, this time, is to calculate the percentage of carbon in the coal gasified, assuming a given exit-gas temperature, say, $1,800^\circ$ F. (Either one or the other of these two variables must be assumed to compute the operating results under zero heat-loss condition or for any other given heat loss.) All of the other assumptions, such as the water-gas shift reaction reaching an equilibrium, etc., on which all the previous computations have been based, are chosen again for the basis of the calculations.

The method of computation involves exactly the same steps discussed previously for the computation of the operating results under zero heat loss condition when no assumption was made for the theoretical introduction of steam as an additional reactant. The percent completion of the gasification of carbon under zero heat loss condition is calculated by assuming first a given value (e.g. 70 percent) for the percent C gasified. On this basis, as before, the number of mols of CO_2 , CO , H_2O , H_2 , H_2S , and N_2 in the output gas (corresponding to a water-gas shift equilibrium at the exit-gas temperature of $1,800^\circ$ F. assumed above) are calculated from the quantities and compositions of the input materials: coal, oxygen, and steam, including the theoretical addition of more steam at the assumed rate. Let the ratio of steam to dry, ash-free coal (e.g., 1 lb./1 lb.), to be assumed at the start, include the moisture in the coal, the steam actually injected, and the theoretical introduction of additional steam. From the input and output figures of a constructed material balance, a heat balance is made in which the temperature ($2,100^\circ$ F.) of the assumed additional steam is duly considered,

and the percent loss or gain of heat is determined. The value of heat loss (or heat gain) corresponding to the assumed percent C gasified is noted for later plotting.

A similar computation is made by assuming another value (e.g. 85 percent) for the percent C gasified, but using the same gas and steam temperatures, the same ratio of steam to coal, and otherwise identical operating conditions. The value of heat loss (or heat gain) obtained from the heat balance is, again, noted as a function of the assumed percent C gasified.

A graph is then prepared by plotting the percent carbon gasified (scale on the ordinate) versus the heat loss or heat gain (scale on the abscissa). The two points thus plotted are connected by a straight line, and the percent C gasified corresponding to zero heat loss is read at the level where a perpendicular raised at the zero point on the abscissa intersects the straight line. This is the percent completion of gasification corresponding to the assumed steam input, steam temperature and exit temperature of the make-gas under zero heat-loss condition. However, for the purpose of checking this result another material and heat balance is made, using the calculated percent C gasified and the corresponding assumed values as the basis of the computation. The heat balance should indicate no heat losses if there are no errors in the computation.

The value obtained for the percent C in the coal gasified is used to calculate the number of mols of CO_2 , CO , H_2O , H_2 , H_2S , and N_2 in the output gas corresponding to a water-gas shift equilibrium at the exit gas temperature of $1,800^\circ\text{F}$. assumed above. The computation follows the same pattern established at the start of the thermodynamic calculations described. From the molal quantities of the components of the output gas, the composition of the wet and dry synthesis gas made under zero heat-loss condition is calculated. The gas output, oxygen requirement, gas yield, and percent steam decomposition are then calculated stoichiometrically as previously.

The operating results obtained in the previously selected three typical runs, Nos. 33A, 46, and 49, translated to conditions expected to exist in operation on commercial scale, are shown in tables 11, 12, and 13. The first column of figures in these tables shows the actual results obtained in the respective runs, whereas the second and third columns show the calculated operating results in large plants where heat losses are assumed to be negligible. In the second column, it was assumed that the percent of carbon gasified would remain the same as that obtained in the actual run, the exit-gas temperature and all other operating results being calculated. For the third column, an exit-gas temperature of $1,800^\circ\text{F}$. was assumed, with a further assumption of 1 pound of steam (at $2,100^\circ\text{F}$.) injected per pound of dry, ash-free coal, and the percent of carbon gasified as well as all other operating results have been obtained by calculation. It should be noted that for the set of conditions shown in the second column, no addition of steam was assumed beyond the small amount shown in the first column for the actual run. It is hoped that the results predicted in these tables for the gasification of coal will be confirmed later by large-scale pilot-plant tests.

TABLE 11. - Translation of operating results to conditions in large-scale production - Run 33A

Operating conditions and results		Results calculated for operation on commercial scale	
Actual run. No assumptions made.	Assumed: Zero heat loss; same percent completion of gasification.	Assumed: Zero heat loss; exit gas temp. 1,800° F.; 1 lb. steam added per lb. of dry, ash-free coal, superheated to 2,100° F.	
Rate of coal feed, lb./hr. ^{1/}	15.9	15.9	15.9
Oxygen input, lb./lb. of dry coal.....	.684	.684	.684
Steam input, lb./lb. of dry coal.....	2/.047	2/.047	.994
Percent of carbon gasified.....	60.1	60.1	75.7
Heat losses, percent.....	12.9	nil	nil
Composition of synthesis gas, percent ^{3/} :			
CO ₂	17.1	7.6	21.5
H ₂	25.6	28.9	43.6
CO.....	51.4	62.0	33.9
Total HC.....	5.9	nil	nil
H ₂ S.....	nil	0.5	0.3
N ₂	nil	1.0	.7
Total.....	100.0	100.0	100.0
Exit gas temperature, °F.			
Oxygen requirement, cu. ft./MCF CO + H ₂ ...	4/1,970	3,800	1,800
Output of dry gas made, cu. ft./hr.	549	437	324
Output rate, cu. ft. CO + H ₂ /cu. ft. generator space per hr.	293	310	490
Yield of CO + H ₂ , cu. ft./ton of dry coal .	163.5	205.4	276.8
Yield of CO + H ₂ , cu. ft./lb. of dry ash-free coal	29,560	37,090	50,000
Ratio of H ₂ :CO in synthesis gas	15.6	19.5	26.3
Percent H ₂ O in raw synthesis gas50	.47	1.29
	14.4	18.1	32.1

1/ On as-charged (moist) basis.
 2/ Consists of steam originating from moisture in coal. No steam was added.
 3/ On dry, oxygen-free basis.
 4/ Calculated from the analysis of wet gas, assuming a water-gas shift equilibrium.

TABLE 12. - Translation of operating results to conditions in large-scale production - Run 46

Operating conditions and results	Results calculated for operation on commercial scale	
	Actual run. No assumptions made.	Assumed: Zero heat loss; same percent completion of gasification.
Rate of coal feed, lb./hr. ^{1/}	44.6	44.6
Oxygen input, lb./lb. of dry coal548	.548
Steam input, lb./lb. of dry coal	2/.020	2/.020
Percent of carbon gasified	54.9	61.7
Heat losses, percent	6.8	nil
Composition of synthesis gas, percent ^{3/} :		
CO ₂	7.1	2.7
H ₂	35.0	37.2
CO	55.4	57.5
Total HC	1.5	nil
H ₂ S	nil	1.6
N ₂	1.0	1.0
Total	100.0	100.0
Exit gas temperature, °F.	1,820	1,800
Oxygen requirement, cu. ft./MCF CO + H ₂ ...	354	281
Output of dry gas made, cu. ft./hr.	884	1,255
Output rate, cu. ft. CO + H ₂ /cu. ft. generator space per hr.	582.6	732.6
Yield of CO + H ₂ , cu. ft./ton of dry coal..	36,580	39,790
Yield of CO + H ₂ , cu. ft./lb. of dry ash-free coal	20.9	22.7
Ratio of H ₂ :CO in synthesis gas63	.65
Percent H ₂ O in raw synthesis gas	10.3	6.7
Assumed: Zero heat loss; exit gas temp. 1,800° F.; 1 lb. steam added per lb. of dry, ash-free coal, superheated to 2,100° F.		
Actual run.	44.6	44.6
No assumptions made.	.548	.548
	2/.020	2/.020
	54.9	61.7
	6.8	nil
	7.1	2.7
	35.0	37.2
	55.4	57.5
	1.5	nil
	nil	1.6
	1.0	1.0
	100.0	100.0
	1,820	1,800
	354	281
	884	1,255
	582.6	732.6
	36,580	39,790
	20.9	22.7
	.63	.65
	10.3	6.7

1/ On as charged (moist) basis.

2/ Consists of steam originating from moisture in coal. No steam was added.

3/ On dry, oxygen-free basis.

TABLE 13. - Translation of operating results to conditions in large-scale production - Run 49

Operating conditions and results	Results calculated for operation on commercial scale		
	Actual run. No assumptions made.	Assumed: Zero heat loss; same percent completion of gasification.	Assumed: Zero heat loss; exit gas temp. 1,800° F.; 1 lb. steam added per lb. of dry, ash free coal, superheated to 2,100° F.
Operating conditions and results			
Rate of coal feed, lb./hr. ^{1/}	37.5	37.5	37.5
Oxygen input, lb./lb. of dry coal654	.654	.654
Steam input, lb./lb. of dry coal	2/.020	2/.020	.898
Percent of carbon gasified	65.1	65.1	75.0
Heat losses, percent	12.0	nil	nil
Composition of synthesis gas, percent^{3/}:			
CO ₂	7.3	2.4	17.2
H ₂	28.7	32.9	45.6
CO	59.4	62.4	35.4
Total HC	3.6	nil	nil
H ₂ S	nil	1.5	1.1
N ₂	1.0	.8	.7
Total	100.0	100.0	100.0
Exit gas temperature, °F.			
Oxygen requirement, cu. ft./MCF CO + H ₂ ..	1,800	3,400	1,800
Output of dry gas made, cu. ft./hr.	425	350	291
Output rate, cu. ft. CO + H ₂ /cu. ft. generator space per hour	762	850	1,207
Yield of CO + H ₂ , cu. ft./ton of dry coal.	487.6	590.4	712.6
Yield of CO + H ₂ , cu. ft./lb. of dry ash-free coal	36,410	44,110	53,180
Ratio of H ₂ :CO in synthesis gas	20.8	25.1	30.3
Percent of H ₂ O in raw synthesis gas48	.527	1.290
1/ On as charged (moist) basis.	11.9	6.9	27.9
2/ Consists of steam originating from moisture in coal. No steam was added.			
3/ On dry, oxygen-free basis.			

CONCLUSIONS

As a result of the investigations carried out at the Morgantown Station of the U. S. Bureau of Mines during the past 2 years, a simple, easily controlled method has been developed for the continuous production of synthesis gas from powdered coals by entrainment in oxygen and steam. The laboratory-scale pilot unit built is well suited for testing various types of fuels for their relative value in synthesis-gas production and for much-needed fundamental research on the mechanism of powdered-fuel gasification.

A synthesis gas of high quality can be produced from raw coal. The quality of the synthesis gas made, expressed by the $\text{CO} + \text{H}_2$ content in percent and by the ratio of H_2 to CO , depends upon controllable operating variables, such as type and size of coal charged, coal feed rate, oxygen-to-coal and steam-to-coal ratios, and steam temperature. During the development of the process, which was described as divided into three stages, about 50 runs were carried out, in which two different types of bituminous coal were charged into the generator: a noncoking, low-ash, low-sulfur coal from Wyoming No. 9 seam and a strongly coking, high-ash, high-sulfur coal from the Sewickley seam in West Virginia. A synthesis gas of low CO_2 content (about 7 percent) can be made from both types of coal, pulverized sufficiently fine, either 70 percent or 90 percent minus 200-mesh, if the ratios of (1) oxygen to steam and (2) carbon to oxygen + steam chosen are high enough. For this purpose, an excess of carbon must be present with a deficiency of gasifying agents, which results in definite yields of carbonaceous residue, i.e., intentional "partial gasification." The synthesis gas made under these conditions is high in CO and low in H_2 content.

Plotting of the operating results against process variables did not produce conclusive trends in the curves obtained owing to an insufficient number of runs with all except one of the possible variables constant. With the apparatus developed to its present stage of precision (provided with the necessary automatic controls), runs may be carried out that should provide the missing data needed for further conclusions.

From both of the coals gasified, an extremely fine and fluffy carbonaceous residue resembling carbon black was obtained, which can be recycled back into the generator, alone or in admixture with raw powdered coal, and further gasified. There is a possibility that the residue obtained can be utilized for certain industrial purposes, burned in boiler furnaces, or briquetted for solid smokeless fuel.

The dry, ash-free coal gasified in a single pass ranged from 60 to 70 percent, with yields of $\text{CO} + \text{H}_2$ ranging from 15 to 22 standard cubic feet per pound of dry, ash-free coal charged, depending on the choice of values for the operating variables. The combined $\text{CO} + \text{H}_2$ in the synthesis gas produced ranged from 76 to 91 percent. With coal feed rates up to 45 pounds per hour, corresponding to hourly fuel throughput rates up to 33 pounds per cubic foot of generator volume, gas output rates as high as 600 standard cubic feet. $\text{CO} + \text{H}_2$ per cubic foot generator space per hour have been obtained. Indications are that even this unusually high gasification rate would be considerably exceeded when younger coals, such as

subbituminous coals and lignites, are gasified. Synthesis gas production rates as high as these per unit volume of generator space are important factors in reducing capital and production costs for the manufacture of gas on commercial scale.

Translation of the operating results to conditions existing in gasification on commercial scale, carried out by lengthy thermodynamic calculations, allowed interesting predictions. They should be confirmed by pilot-plant work on larger scale.