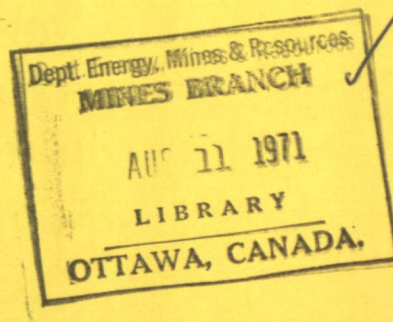




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PRELIMINARY EVALUATION OF PROPOSED METHODS OF
PROCESSING PETROLEUM FLUID COKE AS A REINFORCING
ADDITIVE FOR THE PRODUCTION OF METALLURGICAL COKE AND
FOR THE MANUFACTURE OF HIGH-PURITY CARBON BLACK



W. A. O. HERRMANN AND K. W. BOWLES

FUELS RESEARCH CENTRE

FEBRUARY 1971

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PRELIMINARY EVALUATION OF PROPOSED METHODS OF PROCESSING
PETROLEUM FLUID COKE AS A REINFORCING ADDITIVE
FOR THE PRODUCTION OF METALLURGICAL COKE AND FOR
THE MANUFACTURE OF HIGH-PURITY CARBON BLACK

by

W. A. O. Herrmann* and K. W. Bowles**

SYNOPSIS

This report attempts to evaluate by standard but approximate methods the economic feasibility of three conceptual processes for the desulphurization of high-sulphur-content petroleum fluid coke, in which the heat necessary to operate the process is supplied: (a) by electricity; (b) by combustion of a part of the finished petroleum coke with oxygen or air; and (c) by converting the entire production of petroleum coke to carbon monoxide in one operation with the fluid coking, followed by the decomposition of the carbon monoxide to pure carbon black.

It was found that the desulphurized fluid coke produced by electric heating will cost about \$38.26 per ton** after applying the credits, while with oxygen combustion the cost will amount to \$33.85 per ton. Even if it were possible to release 0.47 ton per hour of sulphurous gases into the atmosphere, the latter cost would not be reduced beyond \$25.55 per ton. The third method is not comparable with the first two, since the quality and also the quantity of the product by comparison are quite different. The cost per ton of carbon black would be about \$58.59 or \$32.76 after applying the credits.

In the first two methods the consumption of considerable amounts of energy and hydrogen in the course of the formation of undesired methane

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***Throughout this report the metric ton will be used, which equals 2,205 lb.

had to be disregarded entirely because too many unknown factors were involved. Methane formation from the elements, however, cannot be suppressed at the operating temperature of 1520°C (2768°F). The use of argon instead of hydrogen as a vehicle, to eliminate this undesirable reaction, as in the laboratory tests, would impose prohibitive costs.

The third process investigated here makes use of the ease with which gases can be purified, especially if they are at elevated pressures. The decomposition of the purified carbon monoxide produces a completely sulphur- and ash-free carbon black, the characteristics of which would be adjusted by recycling it. As a by-product a gas containing 77 vol % of hydrogen is produced, which can be used to improve the operation of the fluid coker or other hydrofining operations. Furthermore, the production of technically pure carbon dioxide could easily be integrated with this process.

Since the selling price of metallurgical coke is about \$35.00 per ton, it is very difficult to achieve an economical operation by direct thermal desulphurization of petroleum coke by the first two methods. Producing chemically pure carbon black, which sells at about \$137.80 to \$143.40 per ton (6.25 to 6.50 cents per lb), improves the economics of the desulphurization of petroleum coke quite considerably, in spite of the increased manufacturing cost above that of the desulphurizing process by combustion heating without by-product sulphur recovery.

If one gallon of naphtha at a conventional carbon-black plant costs 17.6 cents and yields about 72 wt %, i.e. 5.8 lb, of carbon black, then the raw material costs alone are 3.0 cents per lb of carbon black and the sale price of the carbon black has to be 6.35 cents per lb, or \$140.00 per ton, in order to achieve a turnover ratio of 0.98 on the investment capital of \$144.00 per annual ton of carbon black. By comparison the cost of the petroleum fluid coke is 0.26 cent per lb of carbon black. In addition to the much cheaper raw material cost, the production cost for the carbon-black process including credits is only 1.5 cents per pound of carbon black. Consequently the carbon monoxide route is promising, provided that the assumptions with respect to the rate of the decomposition reaction and the heat transfer rates can be confirmed in laboratory and pilot-plant tests, and that the quality of the carbon black so produced is satisfactory.

Direction des mines
Rapport de recherches R 219

L'EVALUATION PRELIMINAIRE DE METHODES PROPOSEE DU TRAITEMENT
DU COKE FLUIDE DE PÉTROLE COMME ADDITIF RENFORÇANT
POUR LA PRODUCTION DE COKE MÉTALLURGIQUE
ET DE NOIR DE CARBONE DE GRANDE PURETÉ

par

W. A. O. Herrmann* et K. W. Bowles**

RÉSUMÉ

Ce rapport vise à évaluer, par des méthodes courantes mais approximatives, la rentabilité de trois procédés conceptuels pour la désulfuration du coke fluide de pétrole à forte teneur en soufre, dans lesquels la chaleur nécessaire aux opérations est fournie: a) par l'électricité; b) en brûlant une partie du coke de pétrole fini avec de l'oxygène; et c) en transformant tout le coke de pétrole en oxyde de carbone en une seule opération avec le cokage fluide, suivie par la décomposition de l'oxyde de carbone en noir de carbone pur.

On a établi que la désulfuration du coke fluide en le chauffant électriquement coûte environ \$38.26*** la tonne, alors que la combustion à l'oxygène coûte \$33.85 la tonne. Même s'il était possible de rejeter 0.47 tonne par heure de gaz sulfureux dans l'atmosphère, ce coût ne pourrait être abaissé en dessous de \$25.55 la tonne. La troisième méthode n'est pas entièrement comparable aux deux premières, car la qualité ainsi que la

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***On utilise tout au long de ce rapport la tonne métrique, qui équivaut à 2205 livres.

quantité du produit obtenu sont très différentes. Le coût du noir de carbone serait d'environ \$58.59 la tonne, ou \$32.76 après avoir appliqué les crédits pour les sous-produits.

Dans les deux premières méthodes, on n'a pas tenu compte des quantités considérables d'énergie et d'hydrogène consommées au cours de la formation de méthane indésirable, en raison du trop grand nombre de facteurs inconnus. Il est cependant impossible de prévenir la formation de méthane à partir des éléments en présence, aux températures employées (1520°C ou 2768°F). L'emploi de l'argon comme moyen d'éliminer cette réaction indésirable serait d'un coût prohibitif.

Le troisième procédé étudié dans ce rapport met à profit la facilité avec laquelle les gaz peuvent être purifiés, surtout à des pressions élevées. La décomposition de l'oxyde de carbone purifié produit un noir de carbone entièrement débarrassé de soufre et de cendres, dont les caractéristiques peuvent être stabilisées par recyclage. On obtient comme sous-produit un gaz dont 77 p. 100 du volume est formé d'hydrogène, et qui peut servir à améliorer le fonctionnement du four à coke fluide ou toute autre opération d'hydrofinissage. La production de bioxyde de carbone techniquement pur pourrait aisément être intégrée à ce procédé.

Étant donné que le prix de vente du coke métallurgique est d'environ \$35.00 la tonne, il est très difficile d'obtenir une opération rentable par la désulfuration thermique directe du coke de pétrole au moyen des deux premières méthodes. La production de noir de carbone chimique pur, qui se vend à un prix entre \$137.80 et \$143.40 la tonne (6.25 à 6.50 cents la livre) améliore sensiblement le rendement de la désulfuration du coke de pétrole en dépit de coûts de production accrus en plus de celui du procédé de désulfuration en chauffant par combustion sans récupération de sous-produit de soufre.

Si un gallon de naphte coûte, à la raffinerie, 17.6 cents et donne environ 72 p. 100 de son poids (5.8 livres) en noir de carbone, la matière première coûte à elle seule 3.0 cents la livre de noir de carbone et le noir de carbone doit se vendre 6.35 cents la livre, ou \$140.00 la tonne, afin d'obtenir un remboursement de 98 p. 100 des capitaux engagés de \$144.00 par tonne de noir de carbone par année. Le coût comparatif du coke de pétrole fluide est de 0.26 cent par livre de noir de carbone produit. En plus du coût de la matière première, moins coûteuse de beaucoup, le prix de fabrique pour le procédé du noir de carbone y compris les crédits est seulement 1.5 cents la livre du noir de carbone. Il semble donc que la méthode à l'oxyde de carbone est prometteuse, à condition que les données relatives au taux de décomposition et de transfert de la chaleur puissent être confirmées par des essais en laboratoire et en usine pilote, et que la qualité du noir de carbone ainsi produit soit satisfaisante.

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INTRODUCTION

Fluid coke is a high-sulphur refinery terminal product commanding a restricted market. There is a shortage of low and medium volatile coking coals used for blending with a high volatile coal to produce firm cokes of acceptable quality for blast furnaces. This report examines the economics of two process routes for the production of coking coal additives from fluid petroleum coke as a substitute for low volatile coal.

In the present production of metallurgical coke of the required grade, Sydney coal must be blended with imported U. S. coal in order to raise the stability factor from about 30 to approximately 60. This investigation was undertaken to determine the feasibility of using the less expensive petroleum fluid coke as a reinforcing blending agent to produce specification-grade metallurgical coke. Since petroleum coke has a sulphur content of about 4.5%, it is necessary to desulphurize it to the specification requirement of less than 1%. This is done by heat treatment in a fluidized bed for about 24 hours at an average reaction temperature of 1520°C. It is assumed that the quantity of this heat-treated fluid coke so produced shall be sufficient, when admixed with coal and carbonized, to amount to 10 wt % of the annual coke production, which is about 455,000 metric tons (500,000 short tons) of metallurgical-grade coke per year.

Two methods of introducing the required heat into the desulphurization reaction vessel will be considered in this report: (a) by direct electrical resistance heating with graphite electrodes, and (b) by combustion of the gases evolved during the process and of a substantial amount (about 7%) of the coke charge. The feasibility of these two processes will then be compared on the basis of their respective costs.

Contrary to the low economic value of fluid coke, carbon black enjoys a stable and a high-price market demand. Therefore, an alternative economically attractive conceptual process for the conversion of fluid coke to carbon black via gasification is examined in greater detail. This process could easily be

adapted for the use of coal as a substitute for fluid coke.

This proposed process employs elevated pressure and a unique design of the gasifier and the carbon monoxide decomposer to ensure the maximum use of the process heat and the lowest possible operating cost. However, the operating pressure is low enough to permit the use of conventional equipment.

The entire production of fluid coke is gasified, at elevated pressure by oxygen and recycled excess carbon dioxide, to carbon monoxide. The gaseous impurities and recycle CO_2 , can easily be removed by scrubbing with water under pressure. After purification the carbon monoxide is decomposed in two steps, at 850° and 470°C , in order to (1) accelerate the reaction and (2) to provide the heat for the fluid coking operation by making possible the exchange of the heat liberated from the decomposition reaction with the various gas recycle streams and the feed for the fluid coker.

In order to carry out the required calculations of this report, the values for the specific gravities, specific heats and heats of combustion of the materials involved in the process, as well as the coefficients of heat transfer, were taken from recognized sources of technical information (1) (2). The figures for the costs of processing equipment, construction, contingencies, labour, utilities, as well as other factors contributing to the cost of production, were taken from Aries and Newton, "Chemical Engineering Cost Estimation" (3), and from C. Chilton, "Cost Engineering in the Process Industries" (4). The data and methods of calculation of the required quantity of fluidization gases were taken from M. Leva, "Fluidization" (5).

1. EVALUATION OF THE PROCESS OF DESULPHURIZING PETROLEUM
FLUID COKE BY ELECTRICAL HEATING

Description of the Process

The desulphurizing process, as shown diagrammatically in Figure 1, consists of heating petroleum fluid coke in a fluidized bed in a vertical cylindrical reactor by electrical resistance heating to about 1520°C. The petroleum coke contains sufficient hydrogen to extract the sulphur as hydrogen sulphide. The fluidization of the coke passing down through the reactor is effected by blowing recycle gas upward through the coke-cooling zone at the bottom of the reactor. The gas then passes through slots into the reaction space proper, and through another layer of slots into the coke preheater zone at the top of the reaction vessel. From here the mixture of recycle gas and reaction gas passes through a dust precipitator and then through two heat exchangers (condensers) in which they are cooled in heat exchange with the ingoing recycle gas. A standard water or air cooler lowers the temperature of the gas mixture to the point where the sulphurous components can be scrubbed out with water or solvent. The sulphur-free gas mixture serves as the recycle gas. The excess sulphur-free gas may be used as a fuel gas. The sulphurous gases released from the depressurized water or solvent are burned in a Claus oven to obtain elemental sulphur, which is recovered and sold along with the tar recovered from the condensers.

Basis of the Calculations

For the desulphurization of the fluid coke the calculations were based on the following processing data:

- (1) It is anticipated, on the basis of the volatile content of the coking coal, that a total coke yield of 71.5% may be obtained from the coal-fluid coke mixture. Of this coke, approximately 83.4% would be available in sizes larger than 40 mm. Of this product it is assumed that the stability factor will be about 60%.
- (2) The sulphur in the crude petroleum coke can be reduced by heating it in a vessel at atmospheric pressure in the fluidized state—either electrically or by oxygen combustion of the gases, tar,

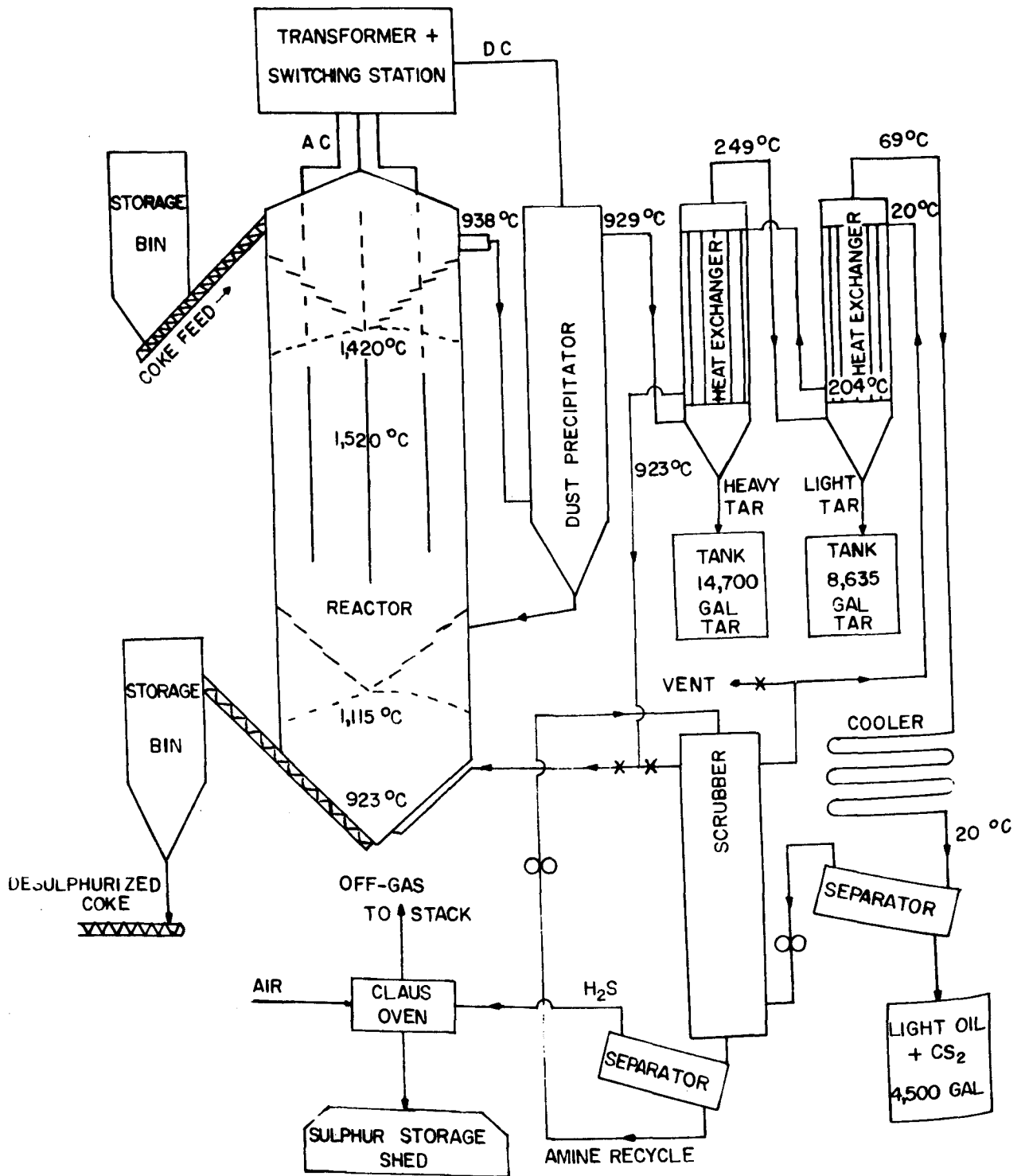


FIGURE I - FLOW DIAGRAM FOR DESULPHURIZATION OF FLUID PETROLEUM COKE BY ELECTRICAL HEATING

sulphur, and some of the coke—to reduce the sulphur content from 4.5 to 0.5 wt %. The kinetics of this process are described in a report of E. Barrillon ⁽⁶⁾. In that report it is stated that petroleum coke having a grain size of about 96% between 0.074 and 0.833 mm can be desulphurized at a temperature of 1400°C in a stream of pure argon from 2.8 wt % to 0.5 wt % sulphur in about 48 hours. Figure 4 in his report shows, however, that the greatest specific surface and reactivity are obtained if the coke is treated at 1500°C. It may be assumed that, at 1500°C reaction temperature in a fluidized bed, in which higher gas velocities contribute to a faster removal of the sulphur-containing gases, the reaction time can be shortened to 24 hours.

- (3) In addition to the removal of the sulphur, about 1.5 wt % tar and 1.6 wt % gas (containing 75 vol % H₂ and 25 vol % CH₄ and having a density of 0.241 kg/Nm^{3*}) are removed from the petroleum coke. Furthermore, about 0.9 wt % is considered as processing losses, mainly dust and gas, leaving 0.920 ton/ton coke product.

Calculation of the Quantities of Process Materials

In order to produce 455,000 metric tons per annum of metallurgical-grade coke, the feed to the coke ovens will be

$$\frac{455,000}{(0.715)(0.834)} = 762,000 \text{ tons/year coking coal,}$$

including the 10 wt % low-sulphur petroleum coke, which will amount to

$$(762,000)(0.1) = 76,200 \text{ tons/year or } \frac{76,200}{8,000} = 9.52 \text{ tons/hr.}$$

Considering the losses (sulphur, tar, gas and dust), the quantity of petroleum coke to be charged to the process is

$$\frac{76,200}{1 - 0.04 - 0.015 - 0.016 - 0.009} = 82,800 \text{ tons/year,}$$

* Nm³ throughout this report means normal cubic metre (at 0°C and 760 mm Hg).

$$\text{or } \frac{82,800}{8,000} = 10.35 \text{ tons/hr dry crude petroleum coke.}$$

Since the crude petroleum coke contains 0.45 wt % moisture, 10.82 tons per hour are required to produce 10.35 tons per hour of dry fluid coke.

If, as mentioned previously, the crude petroleum coke during its heating develops 1.5 wt % tar, 4.0 wt % S and 1.6 wt % gas containing 75 vol % H₂ and 25 vol % CH₄, then the following gas volumes are liberated:

$$\text{Vol of H}_2\text{S (calculated as S)} = \frac{(10,350 \text{ kg/hr}) (0.04) (22.4)}{32} = 289.8 \text{ Nm}^3/\text{hr}$$

$$\text{Vol of H}_2 + \text{CH}_4 = \frac{(10,350 \text{ kg/hr}) (0.016) (22.4)}{5.5} = 674.0 \text{ Nm}^3/\text{hr}$$

The latter mixture of the reaction gases consists of 505.5 Nm³/hr H₂ and 168.5 Nm³/hr CH₄. Since 289.8 Nm³/hr H₂ are consumed to form 289.8 Nm³/hr H₂S, there remains:

$$289.8 \text{ Nm}^3/\text{hr H}_2\text{S} + 215.7 \text{ Nm}^3/\text{hr H}_2 + 168.5 \text{ Nm}^3/\text{hr CH}_4 = 674 \text{ Nm}^3/\text{hr}$$

corresponding to a composition of:

$$43.0 \text{ vol } \% \text{ H}_2\text{S}, 32.0 \text{ vol } \% \text{ H}_2, \text{ and } 25.0 \text{ vol } \% \text{ CH}_4.$$

As calculated later in this report*, about 20,111 Nm³/hr gas are recycled to the system after removing the H₂S by scrubbing. This gas contains 56.15 vol % H₂ and 43.85 vol % CH₄. Since the reaction gas is developed during the reaction, it is assumed that the recycle gas in the reaction vessel is mixed on the average with half of the reaction gas. The resulting average fluidizing gas for electrical heating is composed of 20,111 Nm³/hr recirculation gas and half of the above-mentioned 674 Nm³/hr of reaction gas, making a total of 20,448 Nm³/hr. Therefore, this gas mixture contains:

$$(289.8) (0.5) = 144.9 \text{ Nm}^3/\text{hr H}_2\text{S},$$

$$\text{corresponding to } \frac{(144.9) (100)}{20,111 + 337} = 0.709 \text{ vol } \%$$

$$\text{and by difference the H}_2 \text{ content} = \frac{(56.15) (99.29)}{100} = 55.75 \text{ vol } \%$$

* See page 13.

and the CH_4 content = $\frac{(43.85)(99.29)}{100} = 43.54$ vol %.

Consequently the density of the gas = 0.3724 kg/Nm^3

or $(0.3724)(1.205) \frac{293}{1793} = 0.07327 \text{ kg/Nm}^3$ or 0.00458 lb/ft^3

at reaction temperature (1520°C) and pressure (1.205 atmospheres).

In the coke preheater zone, the residence time of the crude petroleum coke is three hours, during which it is heated by the off-gases from ambient temperature to 1420°C . In the coke-cooler zone the finished coke is cooled by direct contact with the H_2S -free recycle gas in 4.6 hours from 1520° to 905°C .

Ordinarily it would be sufficient to have one reactor with its accompanying equipment. But it is considered more economical in the long run to have two reaction systems in case of a temporary shut-down of one due to some minor cause. Then at least 50% production can be maintained continuously.

If, under favourable conditions, the residence time in the reaction vessel can be shortened from 48 to 24 hours, the true density of the coke is 1.39 kg/l or 86.79 lb/ft^3 and the void space in the coke preheater and the fluidized coke bed is 85% and in the coke cooler is 80%, then the volume required for each system is as follows:

$$\begin{aligned} \text{coke preheater, } V_p &= \frac{(10.82 \text{ tons/hr})(0.5)(3 \text{ hr})}{(1.39)(1-0.85)} \\ &= 77.8 \text{ m}^3, \end{aligned}$$

$$\begin{aligned} \text{reaction vessel, } V_r &= \frac{(10.35 \text{ tons/hr})(0.5)(24 \text{ hr}) + 0.61}{(1.39)(1-0.85)} \\ &= 598.6 \text{ m}^3, \end{aligned}$$

$$\begin{aligned} \text{coke cooler, } V_c &= \frac{(9.52 \text{ tons/hr})(0.5)(4.6 \text{ hr})}{(1.39)(1-0.80)} \\ &= 77.8 \text{ m}^3. \end{aligned}$$

The reaction vessels accommodate these volumes in such a way as to permit the crude petroleum coke to flow downward in a fluidized state from the preheaters through the reactors and coke coolers counter-currently to the

fluidizing gas, which enters the bottom cones through slots and passes upward through the coke coolers and from there again through slots into the reaction zones, where heat is generated electrically. From the reaction zones the gas mixture passes through slots to the coke preheater zones and discharges into the heat exchanger (condenser) trains.

Calculation of the Heat Losses

The two reaction systems include two reactors, one of which is shown diagrammatically in Figure 2. Each reactor has a cylindrical body of 8.0 m ID and 17.28 m inside height, a bottom cone of 45° angle, and a top cone of 26.5° inclination. The top cone, the cylindrical body and the bottom cone constitute the preheater zone, the reaction zone and the coke-cooling zone, respectively. If these reactors are lined with one layer of mullite brick 10 cm (4 in.) thick, one layer of schamotte brick 10 cm thick, and, at the outer wall, one layer of magnesia-asbestos brick also 10 cm thick, the cylindrical part will have an inner surface area of 434.3 m² and an outer surface area of 476.3 m²; the logarithmic mean of these areas is then 451.4 m². The heat loss*, assuming an average reaction temperature of 1470°C and an ambient temperature of 20°C, is as follows:

$$Q = A (t_e - t_a) \frac{1}{S_1/L_1 + S_2/L_2 + S_3/L_3}$$

where Q = heat loss, kcal/hr;

A = area, m²;

t_e = temperature inside reaction chamber, °C;

t_a = ambient temperature, °C;

S₁, S₂, S₃ = thickness of individual layers, m; and

L₁, L₂, L₃ = specific heat-transfer rates of the layers,
kcal/(°C) (hr) (m²) (m⁻¹);

$$\text{then } Q = (451.4) (1450^\circ\text{C}) \frac{1}{0.1/2.0 + 0.1/0.4 + 0.1/0.055}$$

$$= (451.4) (1450) (0.471)$$

$$= 308,284 \text{ kcal/hr for each cylindrical part}$$

or 616,568 kcal/hr for both.

*Due to the heat transfer from the gas to the coke particles, the effect of any boundary layer adjacent to the interior wall is insignificant. Because of the efficiency of the insulation, the temperature drop is 1433°C and therefore the remaining temperature drop of 0.9°C through the inside boundary layer and of 16.6°C through the exterior boundary layer is negligible.

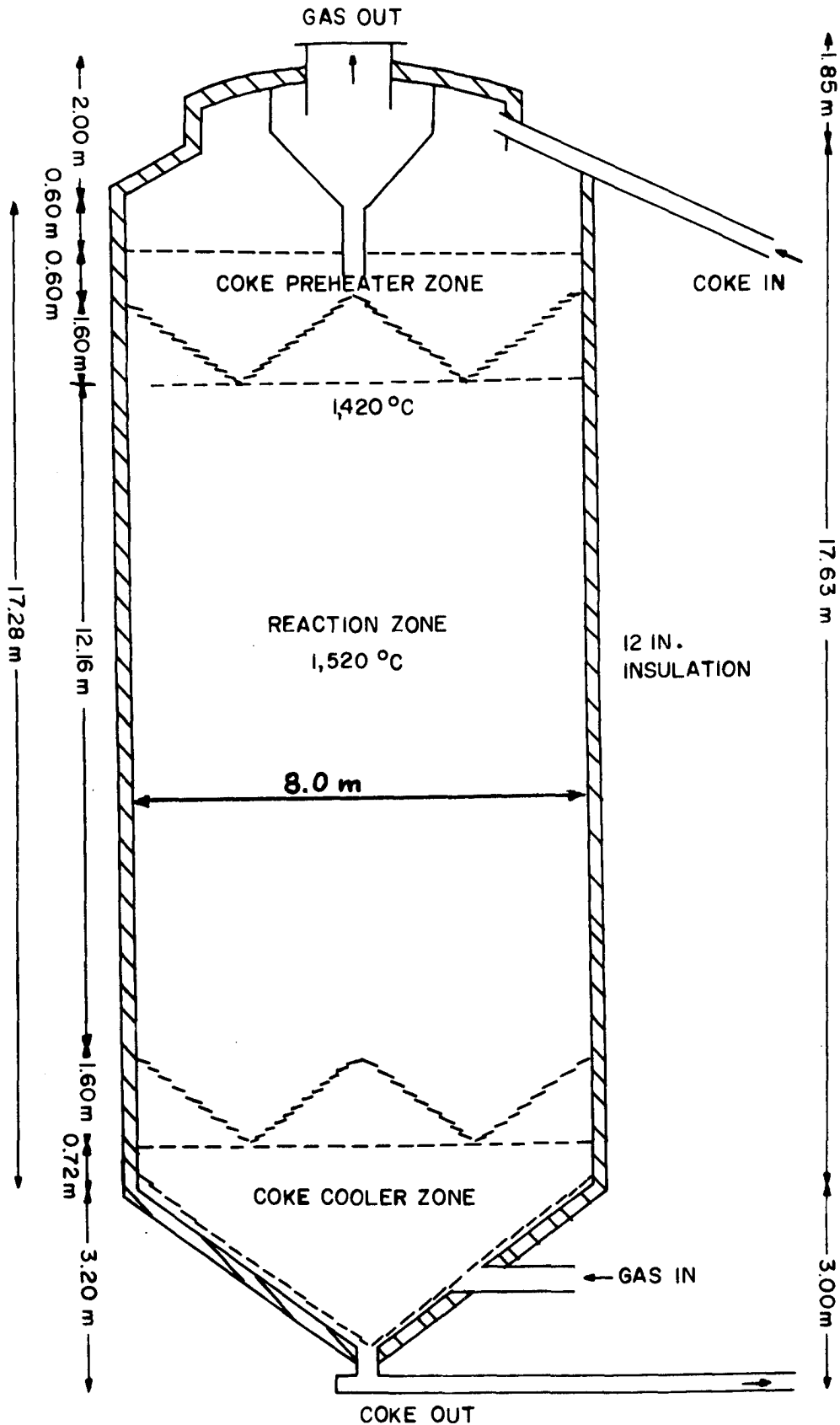


FIGURE 2 - COKE DESULPHURIZATION REACTOR

Since the bottom and top cones are contacted by gas only, having temperatures less than 1420°C, the heat losses are lower. The log mean area of the top cone is

$$\frac{64.86 - 56.20}{\ln (64.86/56.20)} = 59.78 \text{ m}^2$$

and of the bottom cone is

$$\frac{82.14 - 71.08}{\ln (82.14/ 71.08)} = 76.29 \text{ m}^2.$$

The heat losses per °C for both top cones are therefore

$$(2) (59.78 \text{ m}^2) (0.471) = 56.313 \text{ kcal/hr}^\circ\text{C},$$

and for both bottom cones, if the insulation is the same as in the reaction zone, the heat losses are

$$(2) (76.29) (0.471) = 71.87 \text{ kcal/hr}^\circ\text{C}.$$

In the above calculations, for mullite a heat conductivity of 2.0 kcal/°C hr m² m⁻¹ and a permissible temperature of 1700°C and higher; for schamotte, of 0.4 kcal/°C hr m² m⁻¹ and 1450°C; and for magnesia-asbestos, of 0.055 kcal/°C hr m² m⁻¹ and 1250°C, have been used.

Calculation of the Gas Rate Required for the Fluidization

For the calculation of the required fluidization gas quantity, the following assumptions were made:

- (1) The petroleum coke shall have an average particle size of 0.018 in. (20 to 200 mesh) or 0.0015 ft and a true density of 1.39 kg/l or 86.79 lb/ft³.
- (2) The fluidizing gas shall have the same density as the gas developed by the reaction on heating, except that from the recycle gas the H₂S is removed by scrubbing.

The curve ℓ in figure 2-6 of Leva's "Fluidization"⁽⁷⁾ gives the void space in a coke bed at incipient fluidization as 60% for a particle diameter of 0.018 in. But for a more complete fluidization the voidage will be increased, as shown in figure 4-3⁽⁸⁾, to about 85%, at which point the laminar gas flow changes to turbulent flow. Since the expression

$(1 - E) / E^{3*}$ is inversely proportional to the mass velocity of the fluidizing medium ⁽⁸⁾, the ratio of the complete fluidizing gas flow to the incipient fluidizing gas flow may be calculated as follows:

$$\frac{(1 - 0.6)}{(0.6)^3} \bigg/ \frac{(1 - 0.85)}{(0.85)^3} = 8/1.$$

By rearranging Leva's equation 2-2⁽⁹⁾, the bed height can be found as:

$$L_{mf} = \frac{W}{(1 - E_{mf}) (dS - dF) (A)},$$

where L_{mf} = bed height at minimum fluidization, ft;

W = weight of coke bed, lb;

E_{mf} = voidage fraction at minimum fluidization;

dS^* = solid density, lb/ft³;

dF = fluid density, lb/ft³; and

A = cross-sectional area, ft².

Since each of the reactors contains only one half of the coke to be processed, the bed height at complete fluidization for the case of electrical heating becomes:

$$\frac{(0.5) (10.35 \text{ ton/hr}) (24 \text{ hr})}{(50.27 \text{ m}^2) (1 - 0.85) (1.39 \text{ ton/m}^3 - 0.00007 \text{ ton/m}^3)} = 12.26 \text{ m.}$$

In the practically atmospheric pressure vessels of 8.00 m inner diameter, the fluidizing gas has to overcome only the pressure head imposed by the height of the coke bed according to equation 2-1 of Leva's "Fluidization" ⁽¹⁰⁾:

$$\Delta P = L_{mf} (1 - E_{mf}) (dS - dF),$$

in which ΔP = pressure drop and the other designations are the same as in equation 2-2. Then

$$\begin{aligned} \Delta P &= (12.3 \text{ m}) (1 - 0.85) (1.39 - 0.00007 \text{ ton/m}^3) \\ &= 2.48 \text{ ton/m}^2 = 0.248 \text{ kg/cm}^2. \end{aligned}$$

To this pressure drop the head loss in the preheater coke bed must be added. With a retention time of 3 hours, the bed height is:

$$\frac{(0.05) (10.35 \text{ ton/hr}) (3 \text{ hr})}{\left(\frac{50.27 \text{ m}^2}{3}\right) (1 - 0.85) (1.39 \text{ ton/m}^3 - 0.00007 \text{ ton/m}^3)} = 4.21 \text{ m,}$$

* In this report, $E = \epsilon$, the voidage fraction in figure 4-3 of Leva's "Fluidization", and $d = \rho$ in Leva's equation 2-2.

and the pressure drop is:

$$\Delta P = (4.21 \text{ m}) (1 - 0.85) (1.39 - 0.00007 \text{ ton/m}^3) = 0.806 \text{ ton/m}^2 = 0.0806 \text{ kg/cm}^2.$$

The total pressure at the bottom of the reaction zone is, therefore,

$$1.000 + 0.248 + 0.081 = 1.329 \text{ kg/cm}^2$$

and the average pressure is

$$(0.5) (1.329 + 1.081) = 1.205 \text{ kg/cm}^2 = 17.11 \text{ psi.}$$

The reduced pressures, which are the ratios of actual pressure to critical pressure ($P_{red} = P_{act} / P_{crit}$), the reduced temperatures ($T_{red} = T_{act} / T_{crit}$), and the viscosities under operating conditions (1520°C and 1.205 kg/cm²) of the gases involved in the process, are listed below:

| Gas | Reduced pressure (kg/cm ²) | Reduced temperature (°K) | Viscosity (cP) |
|------------------|---|-----------------------------|-------------------|
| H ₂ | 1.205/13.24 = 0.0910 | 1793/33.3 = 53.8 | 0.029 |
| CH ₄ | 1.205/47.4 = 0.0254 | 1793/190.7 = 9.41 | 0.044 |
| CO | 1.205/36.2 = 0.0333 | 1793/134.0 = 13.37 | 0.059 |
| H ₂ S | 1.205/91.2 = 0.0132 | 1793/373.4 = 4.80 | 0.068 |

The low values for reduced pressures and temperatures result in a viscosity ratio, according to figure A-3 of Leva's book on fluidization (11), of 1.0, i.e. no change in viscosity with increased pressure or temperature. Therefore, the viscosities given above were used to calculate the viscosity of the fluidization gas mixture as follows:

For electric heating the viscosity of the average fluidization gas, consisting of 0.71 vol % H₂S, 55.75 vol % H₂ and 43.54 vol % CH₄, will be:

$$(0.0071) (0.068) + (0.5575) (0.029) + (0.4354) (0.044) = 0.03581 \text{ g/m sec} = 2.408 \cdot 10^{-5} \text{ lb/ft sec.}$$

The required mass velocity of the fluidizing medium can then be computed from equation 3-23 of Leva's book on fluidization (12):

$$G_{mf} = \left[\frac{0.005}{(0.278) (10^3)} \right] \left(\frac{D_p^2}{\mu} \right) (g_c) (dF) (dS - dF) \left[\frac{(\phi_s)^2 (E_{mf})^3}{(1 - E_{mf})} \right],$$

where

G_{mf} = mass velocity of fluid for minimum fluidization, lb/ft² hr⁻¹;
 D_p = particle diameter, ft;
 μ = fluid viscosity, lb/ft sec;
 g_c = gravitational conversion factor;
 dF = fluid density, lb/ft³;
 dS = solid density, lb/ft³;
 ϕ_s = particle shape factor;
 E_{mf} = voidage at incipient fluidization.

The value of 0.09 for the expression $\frac{(\phi_s^2) (E_{mf}^3)}{(1 - E_{mf})}$ can be taken from figure 3-13⁽¹³⁾

for the assumed particle diameter of 0.018 in.

Therefore, Leva's equation 3-23 becomes

$$G_{mf} = \frac{5 \times 10^{-3}}{0.278 \times 10^{-3}} (0.09) (32.2) \frac{(1.5 \times 10^{-3})^2}{2.408 \times 10^{-5}} \left[(0.00458) (86.79 - 0.00458) \right]$$

= 1.936 lb/ft²hr = 9.45 kg/m²hr or 475.0 kg/hr for the area of the reactor
 = 1,278 Nm³/hr at incipient fluidization.

At about 8 times the value for incipient fluidization, the gas rate to be used will be 10,224 Nm³/hr, or 20,448 Nm³/hr for both reactors, for electrical heating.

Since the reaction gas develops during the reaction, the fluidizing gas mixture will not contain any sulphur-containing reaction gas at the bottom entrance of the reactor; but the full amount of 674 Nm³/hr will be mixed with the recycle gas at the top outlet. The average fluidizing gas will therefore contain (0.5) (674) = 337 Nm³/hr reaction gas and requires consequently 20,448-337 = 20,111 Nm³/hr recycle gas.

The average vertical velocity of the fluidizing gas is, for the case of electrical heating:

$$\frac{1.936 \text{ lb/ft}^2 \text{ hr}}{(0.00458 \text{ lb/ft}^3) (3600)} = 0.117 \text{ ft/sec. at incipient fluidization or } 0.936 \text{ ft/sec at operating conditions.}$$

According to diagram 2-5 of Leva's book on fluidization ⁽¹⁴⁾, the fluidizing velocity for sand of a density of 2.56 kg/l, but with a smaller particle size of 0.01 inch, is 1.2 ft/sec for incipient fluidization. This diagram indicates, also, that this velocity has to be increased for proper fluidization. For preliminary estimation it can be assumed that, at about 8 times the value for incipient fluidization, the gas flow will be uniform over the whole cross-section of the vessel, resulting in satisfactory fluidization. In this case the voidage increases from 0.6 to 0.855, i.e. the same as calculated formerly for fine coke particles.

Calculation of the Transfer Areas of the Heat Exchangers (Condensers)

The composition of the reactor outlet gas is calculated for the case of electrical heating from the volume and composition of the recycle gas (20,111 Nm³/hr consisting of 56.15 vol % H₂ and 43.85 vol % CH₄) and the reaction gas (674.0 Nm³/hr consisting of 43.0 vol % H₂S, 32.0 vol % H₂ and 25.0 vol % CH₄). Thus the total reactor outlet gas amounts to 20,785 Nm³/hr and consists of:

$$\frac{(20,111) (56.15) + (674.0) (32.0)}{20,111 + 674} = 55.33 \text{ vol \% H}_2,$$

$$\frac{(20,111) (43.85) + (674.0) (25.0)}{20,111 + 674} = 43.21 \text{ vol \% CH}_4,$$

$$\text{and } \frac{(674.0) (43.0)}{20,111 + 674} = 1.46 \text{ vol \% H}_2\text{S}.$$

In the temperature range of 1420°C, at which the reactor outlet gas leaves the reaction zone, to about 900°C at which it leaves the coke preheater zone, the average specific heat of the gas is calculated from the percentages and specific heats of the components as follows:

$$(0.5533) (0.320) + (0.4321) (0.886) + (0.0146) (0.0592) \\ = 0.5666 \text{ kcal/Nm}^3 \text{ }^\circ\text{C}.$$

If in the preheater 10.35 ton/hr times 388 kcal/ton°C have to be heated from 20° to 1420°C, then 5,622,120 kcal/hr plus 51,600 kcal/hr of heat losses have to be taken from the heat of the gas leaving the reaction zone.

Since this reactor gas gives off

$$(20,785 \text{ Nm}^3/\text{hr}) (0.5666 \text{ kcal/Nm}^3\text{°C}) = 11,777 \text{ kcal/hr °C},$$

it is cooled from 1420°C in the coke preheater by

$$\frac{5,622,120 + 51,600}{11,777} = 482\text{°C}$$

to the preheater outlet temperature of 938°C.

From the reactor the gases pass on to the electric precipitator (see flow diagram, Figure 1) in order to prevent fouling of the heat-transferring surfaces in the condensers by mixtures of coke dust and thick tar. In this precipitator they may lose about double as much heat as in the cones of the reaction vessels, i.e. 102,800 kcal/hr, or, since the heat capacity is about 11,777 kcal/hr°C, they are cooled by 8.8° to 929°C. This temperature drop should be kept low to prevent premature precipitation of tar which would cause difficulties in the dust removal system.

From the dust precipitator the reactor gases pass on to the "hot" condenser, which is a vertical-tube, floating-head heat exchanger having a cone at its bottom end to collect the tar. The gases flow inside the tubes upward so that the lighter tar precipitates at the upper end of the tubes, washing down the heavier tar from the lower end into the cone receiver. Eventually hot tar has to be recycled back to the head of the heat exchanger, in which the gases are cooled 680°C from 929° to 249°C. In this temperature range the specific heat of the reactor gas, as calculated from the composition and specific heat of the components, is the following:

$$(0.5533) (0.313) + (0.4321) (0.713) + (0.0146) (0.475) = 0.4882 \text{ kcal/Nm}^3\text{°C}.$$

The amount of heat from this gas, exchanged in this "hot" condenser, is therefore:

$$(20,785 \text{ Nm}^3/\text{hr}) (680\text{°C}) (0.4882 \text{ kcal/Nm}^3\text{°C}) = 6,908,621 \text{ kcal/hr}.$$

To this must be added the heat of condensation of the tar (latent heat plus sensible heat), as follows:

$$\text{amount of tar} = 1.5\% \text{ of } 10,350 = 155 \text{ kg/hr}$$

$$\begin{aligned} \text{amount of heat} &= (155) (63.1 \text{ kcal/kg}) + (155) (0.45 \text{ kcal/kg°C}) (660\text{°C}) \\ &= 9,781 + 46,035 = 55,816 \text{ kcal/hr}. \end{aligned}$$

The total amount of heat exchanged is, therefore,

$$6,908,621 + 55,816 = 6,964,437 \text{ kcal/hr.}$$

Of this amount, 65,100 kcal/hr is lost by radiation.

The 20,111 Nm³/hr recycle gas, to which the above heat is transferred, has a specific heat of:

$$(0.5615) (0.313) + (0.4385) (0.686) = 0.4766 \text{ kcal/Nm}^3 \text{ } ^\circ\text{C.}$$

Since this gas receives the following amount of heat:

$$(20,111) (0.4766) = 9,584.9 \text{ kcal/hr } ^\circ\text{C,}$$

it will therefore be heated from 204°C in the "hot" condenser by

$$\frac{6,964,437 - 65,100}{9,584.9} = 719^\circ\text{C}$$

to the "hot" condenser outlet temperature of 923°C.

Since the heat transfer rate for an oil film is 150 Btu/ft² hr °F and that for a gas film, if a fouling factor of 2.7 is applied, is 44 Btu/ft² hr °F, the overall film heat-transfer rate is:

$$\frac{1}{(1/150) + (1/44)} = 34 \text{ Btu/ft}^2 \text{ hr } ^\circ\text{F} = 165.9 \text{ kcal/m}^2 \text{ hr } ^\circ\text{C.}$$

The log mean temperature difference is 16.4 °C. The required heat transfer area in the "hot" condenser will therefore be:

$$\frac{6,964,437 \text{ kcal/hr}}{(16.4^\circ\text{C}) (165.9 \text{ kcal/m}^2 \text{ hr } ^\circ\text{C})} = 2,560 \text{ m}^2, \text{ or } 27,520 \text{ ft}^2.$$

In the "cold" condenser the reactor outlet gas will be cooled from 249°C to 69°C, a decrease of 180°C. The average specific heat in this temperature range is:

$$(0.5533) (0.309) + (0.4321) (0.450) + (0.0146) (0.381) = 0.371 \text{ kcal/Nm}^3 \text{ } ^\circ\text{C.}$$

The amount of heat given off is therefore:

$$(20,785 \text{ Nm}^3/\text{hr}) (0.371 \text{ kcal/Nm}^3 \text{ } ^\circ\text{C}) (180^\circ\text{C}) = 1,388,022 \text{ kcal/hr.}$$

Of this amount, 11,400 kcal/hr are lost through radiation.

The counter-current recycle gas has an average specific heat of:

$$(0.5615) (0.309) + (0.4385) (0.450) = 0.372 \text{ kcal/Nm}^3 \text{ } ^\circ\text{C}$$

and the amount of heat extracted is therefore:

$$(20,111 \text{ Nm}^3/\text{hr}) (0.372) = 7481 \text{ kcal/hr } ^\circ\text{C}.$$

Therefore the recycle gas will be heated from 20°C by:

$$\frac{(1,388,022 - 11,400) \text{ kcal/hr}}{7481 \text{ kcal/hr } ^\circ\text{C}} = 184^\circ\text{C}$$

to the temperature of 204°C, at which it leaves the "cold" condenser. The log mean temperature difference in the "cold" condenser is 47°C.

Assuming the overall film heat transfer rate for the "cold" condenser is the same as for the "hot" condenser, i.e., 165.9 kcal/m²hr °C, the heat transfer area for the "cold" condenser becomes:

$$\frac{1,388,022 \text{ kcal/hr}}{(47^\circ\text{C}) (165.9 \text{ kcal/m}^2\text{hr } ^\circ\text{C})} = 178 \text{ m}^2 = 1915 \text{ ft}^2.$$

In the jacketed cooler, the 20,785 Nm³/hr reactor outlet gas must be cooled from 69°C to about 20°C in order to extract the H₂S. The average specific heat of the outlet gas in this temperature range is:

$$(0.5533) (0.308) + (0.4321) (0.373) + (0.0146) (0.380) = 0.3371 \text{ kcal/Nm}^3\text{ } ^\circ\text{C}$$

and the amount of heat extracted is:

$$(20,785 \text{ Nm}^2/\text{hr}) (0.3371 \text{ kcal/Nm}^3\text{ } ^\circ\text{C}) (49^\circ\text{C}) = 343,325 \text{ kcal/hr}.$$

This corresponds to a water consumption, if it is heated from 18°C to 30°C, of:

$$\frac{343,325 \text{ kcal/hr}}{12 \text{ kcal/kg}} = 28,650 \text{ kg/hr, or } 105 \text{ Imp gal/min}.$$

Calculation of Heat Requirement for the Reaction

In the coke cooler the coke from the reactor is cooled by the recycle gas from 1520°C to 923°C; the latter is the temperature of the recycle gas entering the coke cooler. The heat given off is therefore:

$$(9.52 \text{ ton/hr}) (388 \text{ kcal/ton}^\circ\text{C}) (1520 - 923^\circ\text{C}) \\ = 2,205,175 \text{ kcal/hr}.$$

Heat losses from the walls of 65,100 kcal/hr* have to be deducted from this amount, leaving 2,140,075 kcal/hr. The average specific heat of the recycle gas in the range of 900 to 1100°C is:

$$(0.5615) (0.317) + (0.4385) (0.858) = 0.5542 \text{ kcal/Nm}^3\text{ } ^\circ\text{C}.$$

The temperature of the 20,111 Nm³ recycle gas will therefore be raised from 923°C by

*See page 10. (71.87 kcal/hr °C) (923° - 20°C approx.).

$$\frac{2,140,075 \text{ kcal/hr}}{(0.5542 \text{ kcal/Nm}^3\text{°C}) (20,111 \text{ Nm}^3/\text{hr})} = 192\text{°C}$$

to 1,115°C, the temperature at which the recycle gas leaves the coke cooler and enters the reaction zone.

In order to supply the heat necessary to raise the temperature of the recycle gas from 1115°C and of the coke from 1420°C, both to the reaction temperature of 1520°C, and also to cover the radiation heat losses of the cylindrical part of the two reactors, electric power is used. The average specific heat of the recycle gas entering the reaction zone is calculated as follows:

$$(0.5615) (0.323) + (0.4385) (0.972) = 0.6076 \text{ kcal/Nm}^3\text{°C}.$$

The amount of heat required by the recycle gas is therefore:

$$(20,111 \text{ Nm}^3/\text{hr}) (0.6076) (405\text{°C}) = 4,948,875 \text{ kcal/hr}.$$

Taking the specific heat of coke as 388 kcal/ton°C in this temperature range, the amount of heat required by the coke is as follows:

$$(10.35 \text{ ton/hr}) (388) (100\text{°C}) = 401,580 \text{ kcal/hr}.$$

The heat required to cover the radiation losses in the cylindrical portion of both reactors is 616,568 kcal/hr as calculated previously*. The total heat input is therefore:

$$4,948,875 + 401,580 + 616,568 = 5,967,023 \text{ kcal/hr}$$

and this is supplied by 6,937.3 kW.

Calculation of Process Costs

From the figures arrived at in the above calculations of the material and heat balances, the required equipment and its costs can now be estimated. The results are compiled in Table 1. The physical plant costs and fixed investment are shown in Table 2.

*See page 8.

TABLE 1

List of the Equipment Size and Costs
for the Desulphurization of Fluid Coke by Electrical Heating

| No. Req'd | Designation of Equipment | Equipment Size | Purchased Cost |
|-----------------------------|--|----------------------------|----------------|
| <u>Two Reaction Systems</u> | | | |
| 2 | Storage bin for crude and desulphurized coke | 1,800,000 gal | \$ 40,000 |
| 2 | Reaction vessel, ceramic lined, 1,140 m ³ | 251,000 gal | 288,000 |
| 4 | Screw conveyor | 70' x 16" ID | 112,000 |
| 2 | Electric precipitator | 5,760 ft ³ /min | 26,000 |
| 2 | Hot condenser, 13.9 x 10 ⁶ Btu/hr | 13,760 ft ² | 85,000 |
| 2 | Cold condenser, 2.65 Btu/hr | 960 ft ² | 35,000 |
| 2 | Jacketed cooler | 53 gal/min | 6,000 |
| 2 | Separator receiver, 8 psi | 440 gal | 2,000 |
| 2 | Scrubber | 50' x 200" ID | 160,000 |
| 2 | Separator receiver, 8 psi | 440 gal | 2,000 |
| 2 | Claus oven | 455 lb/hr | 10,000 |
| 2 | Blower, 100 kW | 5,850 ft ³ /min | 32,000 |
| 2 | Liquid recycle pump | 20 gal/min | 500 |
| 2 | Complete reaction systems | | 798,500 |
| <u>Auxiliary Equipment</u> | | | |
| 1 | Transformer and switching station | 120,000 kW | 96,000 |
| 1 | Tank for heavy tar | 14,700 gal | 5,000 |
| 1 | Tank for light tar | 8,635 gal | 4,000 |
| 1 | Tank for scrubbing solvent | 4,500 gal | 3,000 |
| 1 | Storage shed for 8,200 ft ³ sulphur | 2,000 ft ² | 30,000 |
| 1 | Flare | 18,000 ft ³ /hr | 4,000 |
| 1 | Inert gas generator | 75,000 ft ³ /hr | 18,000 |
| 1 | Inert gas holder | 75,000 ft ³ | 60,000 |
| | Auxiliary equipment | | 220,000 |
| | Total purchased equipment cost (1955) | | \$1,018,500 |

The above computed purchased equipment costs for the year 1955 have to be multiplied by a factor of 1.042^{13} to arrive at the probable costs for 1968: $(\$1,018,500) (1.663) = \$1,693,766$.

TABLE 2

Calculation of the Physical Plant Cost and Fixed Investment for the Desulphurization of Fluid Coke by Electrical Heating

| | | |
|---|----------------------------|-------------|
| Purchased equipment cost (1968) | | \$1,693,766 |
| Equipment installation | 43% of purchased cost | 728,319 |
| Piping, valves, supports, etc. | 36% of purchased cost | 609,756 |
| Instrumentation | 5% of purchased cost | 84,688 |
| Insulation | 10% of purchased cost | 169,377 |
| Electrical | 15% of purchased cost | 254,065 |
| Buildings and foundations | 50% of purchased cost | 846,883 |
| Land and yard improvement | 12% of purchased cost | 203,252 |
| Utilities | 25% of purchased cost | 423,442 |
| Physical plant cost | | 5,013,548 |
| Engineering and construction | 30% of physical plant cost | 1,504,064 |
| Contractors' fees | 7% of physical plant cost | 350,948 |
| Direct plant cost | | 6,868,560 |
| 10% contingency on direct plant cost | | 686,856 |
| Fixed capital investment | | 7,555,416 |
| Cost of land for site, 10 acres at \$5,000 (which need not be depreciated) | | 50,000 |

If the life of the plant is assumed to be 17 years, according to Aries and Newton ⁽¹⁵⁾, then, at an interest rate of 8%, the amount to be depreciated per year, according to the "Koppers Handbuch der Brennstofftechnik" ⁽¹⁶⁾, is 3%.

The total of the depreciation plus interest per year is, then,
 $(7,555,416) (0.03) + (7,605,416) (0.08) = 226,662 + 608,433 = 835,095$.

The labour requirements, according to Aries and Newton ⁽¹⁷⁾, and based on a production capacity of 230 tons/day, are 0.25 man hour per step per ton for the coke desulphurizing operation and 2.4 man hours per step per ton for the recovery and handling of the by-products. The coke desulphurizing operation involves three steps:

- (1) Unloading the crude petroleum coke,
- (2) loading the desulphurized coke, and
- (3) operation of the reaction systems.

The by-product recovery involves also three steps:

- (1) Handling the solvents,
- (2) operating the equipment, and
- (3) loading the sulphur and tar.

Thus, for the coke desulphurizing operation the labour requirements are:

$$3(230 \text{ tons/day}) (0.25 \text{ man hr/ton}) = 172.5 \text{ man hours per day,}$$

while for the by-product recovery a lesser amount is needed, as follows:

$$3(13.7 \text{ tons/day}) (2.4 \text{ man hr/ton}) = 98.6 \text{ man hours per day.}$$

The whole operation, if the figures are increased by 16.7% for sickness and holidays, would require 316.4 man hours per day.

The manufacturing costs are compiled in Table 3.

TABLE 3

Manufacturing Costs for the Desulphurization of
Fluid Coke by Electrical Heating

| | | Cost per year | Cost per ton |
|--|--|------------------|-----------------|
| Labour | (316.4 man hr/day) (365 days) at \$3.50/man hr | \$ 404,201 | \$ 5.304 |
| Supervision | 25% of labour | 101,050 | 1.326 |
| Maintenance | 7% of physical plant cost | 350,948 | 4.606 |
| Plant supplies | 15% of maintenance | 52,642 | 0.691 |
| Utilities | Electricity (10,000 kW) (8,760 hr) (0.25¢/kWh) | 218,750 | 2.871 |
| | Water (15,000 gal/hr) (8,760 hr) (\$0.15/1000 gal) | 19,688 | 0.258 |
| Direct manufacturing cost | | 1,147,279 | 15.056 |
| Payroll overhead | 17% of labour cost | 68,714 | 0.902 |
| Laboratory | 15% of labour cost | 60,630 | 0.796 |
| Plant overhead | 100% of labour cost | 404,201 | 5.304 |
| Shipping costs | 76,176 tons coke + 4,554 tons by-products at \$1.20/ton | 104,949 | 1.377 |
| Indirect manufacturing cost | | 638,494 | 8.379 |
| Depreciation (3%) and interest (8%) (= 11% per year) | | 835,095 | 10.959 |
| Property taxes | 1.5% of physical plant cost | 75,203 | 0.987 |
| Insurances | 1.0% of physical plant cost | 50,135 | 0.658 |
| Fixed manufacturing cost | | 960,433 | 12.604 |
| Total manufacturing cost | | 2,746,206 | 36.039 |

The cost of the finished product is composed of the price of the raw material, the manufacturing costs, and the credits for the by-products, as shown below in Table 4.

TABLE 4

Cost of Production of Low-Sulphur
Fluid Coke by Electrical Heating

| | <u>Per Year</u> | <u>Per Ton</u> |
|--|------------------|----------------|
| Total manufacturing costs | \$2,746,206 | \$36.039 |
| Crude petroleum coke (10.35 tons/hr) (8,000 hr/year) at \$4.00/ton | 331,200 | 4.346 |
| Total expenditures | 3,077,406 | 40.385 |
| Credit for sulphur (3,312 tons/year) (\$32/ton) | 105,984 | 1.391 |
| Credit for tar (1,242 tons/year) (\$8/ton) | 9,936 | 0.130 |
| Credit for heating value of gas (384.2 Nm ³ /hr) (8000 hr) (5,193 kcal/Nm ³) | 46,285 | 0.607 |
| Cost of finished product | 2,915,201 | 38.257 |

Although the desulphurized coke will be admixed in a ratio of only 10 wt % with the coking coal, the resulting price of the metallurgical coke will increase. If the cost of mixing is neglected, the extent of this increase can be calculated from the coke yield and the stability factor as follows:

$$\frac{(\$38.26) (0.1)}{(0.715) (0.834)} = \$6.42/\text{ton.}$$

2. EVALUATION OF THE PROCESS OF DESULPHURIZING PETROLEUM FLUID COKE BY PARTIAL COMBUSTION WITH OXYGEN

The alternative heating method considered in this report, the generation of the required heat by the combustion of a part of the finished coke-carbon, requires somewhat less equipment and therefore less capital cost, as will be shown later.

If the system is heated by burning the gases and carbon with oxygen, but under reducing conditions, the sulphur is only temporarily burned to SO_2 . The SO_2 then reacts under reducing conditions very quickly with H_2 to form H_2S or with CO to form COS . Likewise, water-vapour reacts with carbon to give $\text{H}_2 + \text{CO}$. Methane, as well as the tar, is also converted to CO and H_2 . Since the heat from the conversion of sulphur, tar and gases is not enough to heat the crude petroleum coke to reaction temperature and to compensate for heat losses in the reactors and heat exchangers, a certain amount of finished petroleum coke has to be burned with oxygen to carbon monoxide. The quantity of coke to be burned and the volume and composition of the gas thereby developed are determined by the heat required to raise the temperature of the crude petroleum coke to reaction temperature and by the heat losses through the reactor walls. Since the heat losses are determined by the dimensions of the reactor and its insulation, these have to be calculated.

A flow diagram of this process is given in Figure 3. The equipment required for this process is similar to that of the electric heating process, with the exception that only one heat exchanger (condenser) instead of two are necessary and the gas recycle pump is smaller.

Calculation of the Gas Composition and Gas Rates

In the following calculations of the products and heats of reaction, one metric ton of crude petroleum coke will be considered as the basis. When 4 wt % of sulphur is eliminated from one ton of coke, 40 kg of sulphur are produced, which are converted to 42.5 kg H_2S , occupying 28 Nm^3 and giving up 150.5 kcal/kg S of exothermic heat. This corresponds to 6,020 kcal/ton of coke and a consumption of 2.5 kg or 28.0 Nm^3 of hydrogen.

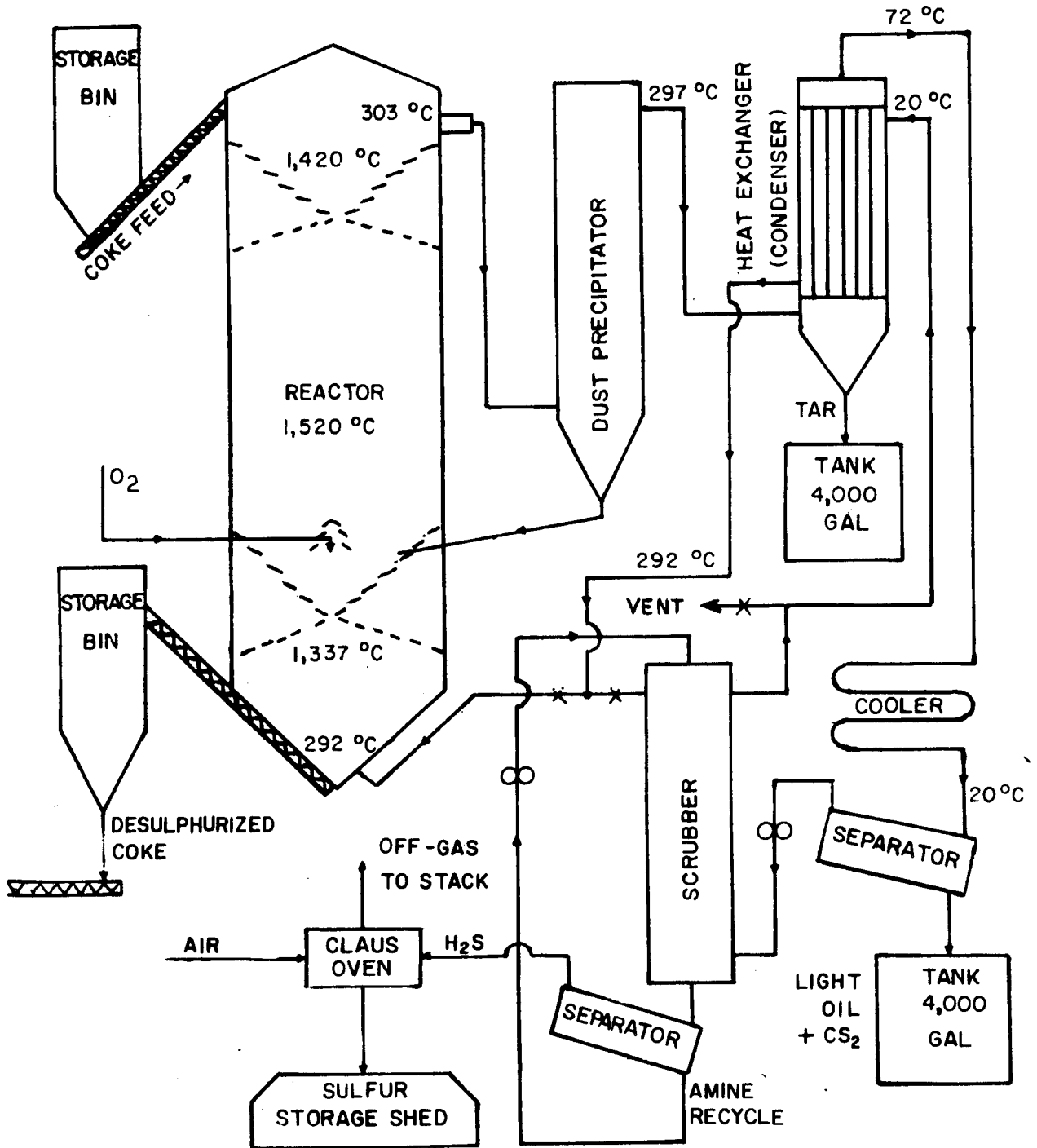


FIGURE 3 - FLOW DIAGRAM FOR DESULPHURIZATION OF FLUID PETROLEUM COKE BY COMBUSTION HEATING

The gas developed from the petroleum coke is 1.6 wt % or 16 kg/ton, consisting of:

$$\frac{(0.25) (16) (16\text{kg})}{(0.25) (16) + (0.75)(2)} = 11.64 \text{ kg CH}_4 \text{ and } \frac{(0.75) (2) (16\text{kg})}{(0.25) (16) + (0.75)(2)} = 4.36 \text{ kg H}_2.$$

The CH₄ contains 8.73 kg C, which is oxidized by 11.64 kg O₂ to 20.37 kg or 16.3 Nm³ CO. Since 2.5 kg H₂ are consumed to form H₂S, the remaining H₂ amounts to:

$$11.64 - 8.73 + 4.36 - 2.5 = 4.77 \text{ kg H}_2 \text{ or } 53.4 \text{ Nm}^3.$$

The amount of heat per ton of coke developed from the partial oxidation of the CH₄ is:

$$(16.3 \text{ Nm}^3 \text{ CH}_4) (375 \text{ kcal/Nm}) = 6,113 \text{ kcal.}$$

The tar content of the coke feed is 1.5 wt % or 15 kg/ton, which will be converted to:

$$\frac{(15) (0.943) (28)}{(12)} = 33.0 \text{ kg, or } 26.4 \text{ Nm}^3, \text{ of CO per ton of coke,}$$

$$\text{consuming: } \frac{(33) (16)}{(28)} = 18.85 \text{ kg O}_2$$

and liberating: 15 (1 - 0.943) = 0.855 kg, or 9.5 Nm³, of H₂ per ton of coke.

This reaction yields 278 kcal/kg tar or 4,170 kcal/ton of coke.

To summarize the above, the total quantity of gaseous products and heat developed on heating one ton of fluid petroleum coke is:

| | |
|------------------|--------------------------------------|
| H ₂ S | 28.0 Nm ³ |
| CO | 16.3 + 26.4 = 42.7 Nm ³ |
| H ₂ | 53.4 + 9.5 = 62.9 Nm ³ |
| Heat | 6,020 + 6,113 + 4,170 = 16,303 kcal. |

Raising the temperature of one ton of petroleum coke from 1420 to 1520 °C requires (100°C) (388 kcal/ton °C) = 38,800 kcal/ton.

But since only 16,303 kcal/ton are available from the above reactions, 22,497 kcal/ton have to be supplied by the combustion to CO of some of the petroleum coke produced, liberating 2,220 kcal/kg carbon. In addition, heat from the partial combustion of the fluid coke must also be supplied to cover the same heat losses as calculated for electrical heating and to raise the temperature of the recycle gas up to reaction temperature. The total heat thus required is as follows:

| | | | |
|--|---|--|----------------|
| Additional heat to raise temperature of petroleum coke | = | 22,497 kcal/ton | |
| Heat losses | = | $\frac{616,568 \text{ kcal/hr}}{11.179 \text{ tons/hr}}$ | = 55,154 " |
| Heat to raise temperature recycle gas | = | $\frac{824,745 \text{ kcal/hr}}{11.179 \text{ tons/hr}}$ | = 73,776 " |
| Total heat | | | <u>151,427</u> |

This amount of heat is supplied by the partial combustion of

$$\frac{151,427 \text{ kcal/ton}}{2,220 \text{ kcal/kg}} = 68.21 \text{ kg/ton of fluid coke}$$

to produce 159.25 kg/ton, or 127.5 Nm³/ton, of carbon monoxide.

It was shown in the electric heating process that, with a feed rate of 10.35 ton/hr of crude petroleum coke, 9.52 tons/hr of desulphurized coke was obtained. This corresponds to a production of 920 kg of desulphurized coke per ton of crude petroleum coke. Therefore, to make up for the consumption of 68.21 kg/ton of desulphurized coke in the partial combustion process, the crude coke feed must be increased to

$$10.35 \left(\frac{920}{920 - 68.21} \right) = 11.178 \text{ ton/hr.}$$

This represents an increase of 0.828 ton/hr.

The oxygen required for the partial oxidation of the petroleum coke, CH₄, and tar respectively amounts to:

$$90.96 + 11.64 + 18.85 = 121.45 \text{ kg O}_2 \text{ per ton of crude petroleum coke, corresponding to 1,357.6 tons per hour or 950.6 Nm}^3 \text{ pure O}_2 \text{ per hour.}$$

From the quantities of gases produced in the reaction zone, the composition of the gas before and after scrubbing is calculated as follows:

| | | Product gas leaving reactor before scrubbing | | Recycle gas entering reactor after scrubbing | |
|------------------|--------------------------------|--|-------------------------------|--|--------------|
| H ₂ S | 28.0 Nm ³ /ton coke | x 11.179 ton/hr | = 313.0 Nm ³ /hr | = 10.82 vol % | - |
| H ₂ | 62.9 " | x 11.179 " | = 703.1 Nm ³ /hr | = 24.30 vol % | 27.28 vol % |
| CO | 170.2 " | x 11.179 " | = 1,902.7 Nm ³ /hr | = 64.88 vol % | 72.72 vol % |
| | 261.1 " | x 11.179 " | = 2,918.8 Nm ³ /hr | = 100.00 vol % | 100.00 vol % |

The water scrubber extracts the H₂S which contains also some COS.

The average fluidizing gas in the reaction zone is composed, as calculated below, of 13,153.4 Nm³/hr recycle gas of the above composition and a density of 0.912 kg/Nm³, plus half of the above computed volume of product gas, i.e., 1,459.4 Nm³/hr. Since the product gas develops during the reaction, its mixture with the 13,153.4 Nm³/hr recycle gas consists of:

$$\begin{array}{l} \text{H}_2\text{S} \quad \frac{(1,459.4) (10.82)}{13,153.4 + 1,459.4} = 1.069 \text{ vol } \% \\ \text{H}_2 \quad \frac{(13,153.4) (27.28) + (1,459.4) (24.30)}{13,153.4 + 1,459.4} = 26.99 \text{ vol } \% \\ \text{CO} \quad \frac{(13,153.4) (72.72) + (1,459.4) (64.88)}{13,153.4 + 1,459.4} = 71.94 \text{ vol } \% \end{array}$$

This gas has a density of 0.938 kg/Nm³, corresponding to 0.185 kg/m³ (0.01153 lb/ft³) at reaction conditions.

Since each of the reactors contains only one-half of the coke to be processed, the bed height for complete fluidization in the case of combustion heating becomes approximately:

$$\frac{(0.5) (10.35 \text{ ton/hr}) (24 \text{ hr}) + (0.81 \text{ ton})}{(50.27 \text{ m}^2) [(1 - 0.855) (1.39 \text{ ton/m}^3 - 0.000185 \text{ ton/m}^3)]} = 12.50 \text{ m.}$$

The above figures show that the 0.81 ton/hr coke burned in the partial combustion add only 24 cm to the height of the bed used in the electric heating process* and therefore the same reaction system can be used for both processes.

As was shown in the case of the electric heating process**, the viscosity of the average fluidization gas for combustion heating will not be affected by the increased pressure. Therefore the value of the viscosity may be calculated from the above volume percentages and the viscosities of the components as follows:

$$\begin{aligned} & (0.01069) (0.068) + (0.2699) (0.029) + (0.7194) (0.059) \\ & = 0.05104 \text{ g/m sec} = 3.362 \times 10^{-5} \text{ lb/ft sec.} \end{aligned}$$

* See page 11.

** See page 12.

This compares with $2,408 \times 10^{-5}$ lb/ft sec for the electric heating process.

Using the same method of calculation as was done for the electric heating process, the gas rate for incipient fluidization, G_{mf} , is:

$$\left[\frac{(5) (10^{-3})}{(0.278) (10^{-3})} \right] (0.09) (32.2) \frac{(1.5 \times 10^{-3})^2}{(3.362 \times 10^{-5})} \left[0.01153 (86.79 - 0.01153) \right]$$

$$= 3.4924 \text{ lb/ft}^2\text{hr} = 17.0429 \text{ kg/m}^2\text{hr}.$$

Multiplying by the cross-sectional area of the reactor, the gas rate becomes:

$$(17.0429) (50.27) = 856.7 \text{ kg/hr}.$$

Dividing by the density of the gas, the volumetric gas rate is:

$$\frac{856.7}{0.938} = 913.3 \text{ Nm}^3/\text{hr}.$$

For complete fluidization at about 8 times the incipient fluidization rate (14), the gas rate then becomes:

$$(913.3) (8) = 7,306.4 \text{ Nm}^3/\text{hr}.$$

This rate applies to one reactor. Therefore, for two reactors the gas rate will be twice this value which is $14,612.8 \text{ Nm}^3/\text{hr}$. From this amount, half the gas volume developed during the reaction, i.e. $1,459.4 \text{ Nm}^3/\text{hr}$, must be deducted to obtain the required recycle gas volume:

$$14,612.8 - 1,459.4 = 13,153.4 \text{ Nm}^3/\text{hr}.$$

Calculation of Heat Transfer in Coke Preheater Zone

The gas leaving the reaction zone consists of $2,918.8 \text{ Nm}^3/\text{hr}$ of Product gas plus $13,153.4 \text{ Nm}^3/\text{hr}$ of recycle gas, making a total of $16,072.2 \text{ Nm}^3/\text{hr}$. This reaction gas heats the coke entering the preheating zone from 20°C to 1420°C by giving off the following amount of heat:

$$(11.178 \text{ ton/hr}) (383 \text{ kcal/ton}^\circ\text{C}) (1400^\circ\text{C}) = 5,993,644 \text{ kcal/hr}.$$

The heat losses in the coke preheater zone will be only $20,000 \text{ kcal/hr}$.

The gas leaving the reaction zone has a composition of:

| | | |
|----------------------|---|---------------|
| H_2S | $\frac{(2,918.8) (10.82)}{16,072.2}$ | = 1.965 vol % |
| H_2 | $\frac{(13,153.4) (27.28) + (2,918.8) (24.30)}{16,072.2}$ | = 26.74 vol % |
| CO | $\frac{(13,153.4) (72.72) + (2,918.8) (64.88)}{16,072.2}$ | = 71.30 vol % |

In the range of 1420° to 300°C the average specific heat is:

$$(0.0197) (0.532) + (0.2674) (0.320) + (0.7130) (0.335) = 0.3349 \text{ kcal/Nm}^3\text{°C.}$$

Multiplying by the gas flow rate, the heat flow rate is

$$(0.3349) \text{ kcal/Nm}^3\text{°C} (16,072.2 \text{ Nm}^3/\text{hr}) = 5,382.6 \text{ kcal/hr°C.}$$

This gas will be cooled by the coke feed from 1420°C by

$$\frac{(5,993,644 + 20,000) \text{ kcal/hr}}{5,382.6 \text{ kcal/hr°C}} = 1117\text{°C}$$

to a preheating zone outlet temperature of 303°C.

Since the tar in the presence of oxygen has been converted to CO and H₂, no condensation of tar will occur. Even if there were some condensation it would be precipitated on the coke feed and carried back into the reaction zone for final conversion. In the dust precipitator the gas will be cooled from 303° by

$$\frac{(112.6 \text{ kcal/hr°C}) (303-20\text{°C})}{5,382.6 \text{ kcal/hr°C}} = 5.9\text{°C}$$

to an outlet temperature of 297°C.

Calculation of the Heat Transfer in the Heat Exchanger (Condenser)

One heat exchanger is sufficient to further cool the reactor outlet gas from 297°C by 225°C to 72°C. The average specific heat of the reactor outlet gas in this temperature range is:

$$(0.0197) (0.417) + (0.2674) (0.311) + (0.7130) (0.315) = 0.316 \text{ kcal/Nm}^3\text{°C.}$$

Multiplying by the gas flow rate, the heat flow rate is:

$$(0.316 \text{ kcal/Nm}^3\text{°C}) (16,072.2 \text{ Nm}^3/\text{hr}) = 5,078.8 \text{ kcal/hr°C.}$$

The decrease in heat content is:

$$(5,078.8 \text{ kcal/hr°C}) (225\text{°C}) = 1,142,730 \text{ kcal/hr,}$$

of which 23,400 kcal/hr are lost through radiation, leaving 1,119,330 kcal/hr

to heat the recycle gas. In the range of 0° to 300°C the recycle gas (H₂ and CO), entering the heat exchanger at 20°C, has an average specific heat of:

$$(0.2728) (0.310) + (0.7272) (0.313) = 0.3122 \text{ kcal/Nm}^3\text{°C.}$$

Multiplying by the gas flow rate, the heat flow rate is:

$$(0.3122 \text{ kcal/Nm}^3\text{°C}) (13,153.4 \text{ Nm}^3/\text{hr}) = 4,106.5 \text{ kcal/hr°C.}$$

This gas will be heated by the reactor outlet gas from 20°C by:

$$\frac{1,119,330 \text{ kcal/hr}}{4,106.5 \text{ kcal/hr°C}} = 272\text{°C}$$

to the outlet temperature of the heat exchanger of 292°C.

Since the average log temperature difference between the two sides of the heat exchanger is 20.2°C and the film heat transfer coefficient is:

$$\frac{1}{(1/44 + 1/44)} = 22.0 \text{ Btu/ft}^2\text{hr°F} = 107.3 \text{ kcal/m}^2\text{hr°C,}$$

the required heat transfer area for the heat exchanger is then:

$$\frac{1,119,330 \text{ kcal/hr}}{(107.3 \text{ kcal/m}^2\text{hr°C}) (20.2\text{°C})} = 516.4 \text{ m}^2 = 5550 \text{ ft}^2.$$

The reactor outlet gas leaving the heat exchanger must be cooled from 72°C to about 20°C in an air or water cooler before the sulphur compounds can be extracted by scrubbing with water or other suitable solvent.

In the jacketed water-cooler, the 16,072.2 Nm³/hr reactor outlet gas must be cooled from 72°C to about 20°C for the scrubbing operation. The average specific heat in this temperature range is:

$$(0.0197) (0.380) + (0.2674) (0.308) + (0.7130) (0.313) \\ = 0.313 \text{ kcal/Nm}^3\text{°C.}$$

With a gas flow rate of 16,072.2 Nm³/hr, the amount of heat extracted by the cooling water is:

$$(16,072.2 \text{ Nm}^3/\text{hr}) (0.313 \text{ kcal/Nm}^3\text{°C}) (72\text{°} - 20\text{°C}) = 261,591 \text{ kcal/hr.}$$

This corresponds to a water consumption rate of:

$$\frac{261,591 \text{ kcal/hr}}{30\text{°} - 18\text{°C}} = 21,799 \text{ litres/hr or } 80 \text{ gal/min}$$

The coke-cooling zone reduces the temperature of 9.52 tons/hr of coke product from 1520° to 292°C, i.e., by 1228°C. At a specific heat of 388 kcal/ton°C, the heat flow rate is:

$$(9.52 \text{ tons/hr}) (388 \text{ kcal/ton°C}) = 3,694 \text{ kcal/hr°C.}$$

This heat is transferred to the recycle gas. In the range of 300° to 1300°C, the average specific heat of the recycle gas is:

$$(0.2728) (0.319) + (0.7272) (0.332) = 0.3285 \text{ kcal/Nm}^3\text{°C.}$$

Multiplying by the gas flow rate, the heat flow rate is:

$$(0.3285 \text{ kcal/Nm}^3\text{°C}) (13,153.4 \text{ Nm}^3/\text{hr}) = 4,320.9 \text{ kcal/hr°C.}$$

The heat from the coke, amounting to

$$(3,694 \text{ kcal/hr}^\circ\text{C}) (1228^\circ\text{C}) = 4,536,232 \text{ kcal/hr,}$$

less the heat lost by radiation of 22,700 kcal/hr, leaves 4,513,532 kcal/hr to heat the recycle gas from 292°C by

$$\frac{4,513,532 \text{ kcal/hr}}{4,320.9 \text{ kcal/hr}^\circ\text{C}} = 1045^\circ\text{C}$$

to an outlet temperature from the coke cooling zone of 1337°C. As the temperature in the reaction zone is 1520°C, the recycle gas must be heated further to make up the 183°C difference.

The product of the gas flow rate and the specific heat for the recycle gas in the temperature range of 1300° - 1500°C is:

$$(13,153.4 \text{ Nm}^3/\text{hr}) \left[(0.2728) (0.325) + (0.7272) (0.349) \text{ kcal/Nm}^3/\text{hr}^\circ\text{C} \right] \\ = 4,506.82 \text{ kcal/hr}^\circ\text{C}.$$

The amount of heat required to heat the recycle gas from 1337° to 1520°C is:

$$(4,506.82 \text{ kcal/hr}^\circ\text{C}) (183^\circ\text{C}) = 824,748 \text{ kcal/hr.}$$

In addition to this heat, 616,568 kcal/hr is needed for radiation heat losses and 433,745 kcal/hr for heating the 11.178 tons/hr of crude fluid petroleum coke from 1420°C to 1520°C. But (11.178 tons/hr) (16,303 kcal/ton) = 182,224 kcal/hr is liberated from the conversion of the gases. Therefore, the total amount of heat that is required to be introduced into the reaction zone to maintain the reaction temperature of 1520°C is as follows:

$$824,748 + 616,568 + 433,745 - 182,224 = 1,692,837 \text{ kcal/hr.}$$

This amount of heat is supplied by the combustion of

$$\frac{1,692,837}{2220} = 762.5 \text{ kg/hr of desulphurized coke}$$

to 1,779.2 kg/hr or 1,424 Nm³/hr carbon monoxide.

Therefore the feed rate of crude fluid petroleum coke to the reactor must be greater than the 10.35 tons/hr required in the electric heating process, by the additional amount of the quantity of desulphurized coke burned divided by the yield of desulphurized coke from the crude fluid coke, as follows:

$$10.35 + \frac{0.7625}{0.92} = 11.178 \text{ tons/hr.}$$

This amount is in exact agreement with the value of 11.178 tons/hr calculated previously*.

Calculation of Process Costs

From the results of the above calculations of the material and heat balances, the required equipment and its costs can now be estimated. The results are given in Table 5.

This table shows the computed purchased equipment costs for 1955. They have to be multiplied by a factor of 1.042^{13} , or 1.663, in order to arrive at the probable costs if purchased in 1968, i.e. $(869,500) (1.663) = \$1,445,979$.

The fixed capital investment is shown in Table 6. If the life of the plant is assumed to be 17 years, according Aries and Newton⁽¹⁵⁾, then at an interest rate of 8 per cent the amount to be depreciated per year, according to "Koppers Handbuch der Brennstofftechnik"⁽¹⁶⁾, is 3%.

The total of the depreciation plus interest per year is then:

$$(6,450,107) (0.03) + (6,500,107) (0.08) = 193,503 + 520,009 = \$713,512.$$

The labour requirements, according to Aries and Newton⁽¹⁷⁾, and based on a production capacity of 230 ton/day, are 0.25 man hour per step per ton for the coke desulphurizing operation and 2.4 man hours per ton per step for the recovery and handling of the by-products. The coke desulphurizing operation involves 3 steps, the same as with electrical heating. The by-product recovery, if operated, involves also 3 steps as formerly. The operation of the oxygen facilities is not very different, with respect to labour costs, from the operation of a transformer and switching station, if oxygen is purchased from outside facilities. Therefore the labour requirements for the coke desulphurizing operation are:

* See page 27.

TABLE 5

List of the Equipment Size and Costs
for the Desulphurization of Fluid Coke by Combustion Heating

| No. Req'd | Designation of Equipment | Equipment Size | Purchased Cost |
|-----------|--|----------------------------|----------------|
| | <u>Two Reaction Systems</u> | | |
| 2 | Storage bin for crude and desulphurized coke | 1,900,000 gal | \$ 42,000 |
| 2 | Reactor, ceramic-lined, 1,140m ³ | 251,000 gal | 288,000 |
| 4 | Screw conveyor, | 70' x 16" ID | 112,000 |
| 2 | Electric precipitator | 4,610 ft ³ /min | 20,000 |
| 2 | Heat exchanger, 1.143 x 10 ⁶ kcal/hr | 2,775 ft ² | 48,000 |
| 2 | Blower, 80 kW | 4,610 ft ³ /min | 28,000 |
| 2 | Complete reaction system | | 538,000 |
| | <u>Auxiliary equipment</u> | | |
| 1 | Transformer and switching station | 10,000 kW | 15,000 |
| 1 | Flare | 6,600 lb/hr | 18,000 |
| 1 | Inert gas generator | 75,000 ft ³ /hr | 18,000 |
| 1 | Inert gas holder | 75,000 ft ³ | 60,000 |
| | Auxiliary equipment | | 111,000 |
| | <u>Desulphurizing Equipment</u> | | |
| 2 | Cooler, jacketed, 95 ft ² | 108 gal/min | 10,000 |
| 2 | Scrubber | 50' x 200" ID | 160,000 |
| 2 | Separator receiver, 8 psi | 440 gal | 2,000 |
| 2 | Liquid recycle pump | 20 gal/min | 500 |
| 2 | Claus oven | 455 lb/hr | 10,000 |
| 1 | Tank for scrubbing solvent | 4,500 gal | 3,000 |
| 1 | Tank for COS at 8 psi | 10,000 gal | 5,000 |
| 1 | Storage shed for 8,200 ft ³ sulphur | 2,000 ft ² | 30,000 |
| | Desulphurizing equipment | | 220,500 |
| | Total purchased equipment cost with scrubbing (1955) | | 869,500 |

(3) (230 tons/day) (0.25 man hr/ton) = 172.5 man hours per day

and for the by-product operation are:

(3) (10.6 tons/day) (2.4 man hr/ton) = 76.3 man hours per day.

If these figures are increased by 16.7% to compensate for sickness and holidays, the total will be 201.4 man hours per day for the coking operation only, and 290.3 man hours per day for both the coking and by-product recovery operations.

TABLE 6

Calculation of the Physical Plant Cost and Fixed Investment
for the Desulphurization of Fluid Coke by Combustion Heating

| | | |
|---|----------------------------|------------------|
| Purchased equipment cost (1968) | | \$1,445,979 |
| Equipment installation | 43% of purchased cost | 621,771 |
| Piping, valves, supports, etc. | 36% of purchased cost | 520,552 |
| Instrumentation | 5% of purchased cost | 72,299 |
| Insulation | 10% of purchased cost | 144,598 |
| Electrical | 15% of purchased cost | 216,897 |
| Buildings and foundations | 50% of purchased cost | 722,990 |
| Land and yard improvements | 12% of purchased cost | 173,517 |
| Utilities | 25% of purchased cost | 361,495 |
| Physical plant cost | | 4,280,098 |
| Engineering and construction | 30% of physical plant cost | 1,284,029 |
| Contractor's fees | 7% of physical plant cost | 299,607 |
| Direct plant cost | | 5,863,734 |
| 10% contingency on direct plant cost | | 586,373 |
| Fixed capital investment | | 6,450,107 |
| Cost of land for site, 10 acres at \$5,000 (which need not be depreciated) | | 50,000 |

The manufacturing costs are compiled in Table 7 below:

TABLE 7

Manufacturing Costs for the Desulphurization of
Fluid Coke by Combustion Heating

| | Cost per year | Cost per ton |
|--|------------------|-----------------|
| Labour (290.3 man hr/day) (365 days) at \$3.50/man hr | \$ 370,858 | \$ 4.867 |
| Supervision 25% of labour | 92,715 | 1.217 |
| Maintenance 7% of physical plant cost | 281,344 | 3.692 |
| Plant supplies 15% of maintenance | 42,202 | 0.554 |
| Utilities Electric power (2,996 kW) (8,760 hr) (0.25¢/kWh) | 65,625 | 0.861 |
| Water (14,000 gal/hr) (8,760 hr) (\$0.15/10 ³ gal) | 18,396 | 0.241 |
| Direct manufacturing cost | 871,140 | 11.432 |
| Payroll overhead 17% of labour cost | 63,046 | 0.827 |
| Laboratory 15% of labour cost | 55,629 | 0.730 |
| Plant overhead 100% of labour cost | 370,858 | 4.867 |
| Shipping costs 76,176 tons coke + 3,577 tons sulphur at \$1.20/ton | 95,704 | 1.200 |
| Indirect manufacturing cost | 585,237 | 7.624 |
| Depreciation (3%) + interest (8%) (= 11% per year) | 713,512 | 9.364 |
| Property taxes 1.5% of physical plant cost | 64,201 | 0.843 |
| Insurances 1.0% of physical plant cost | 42,801 | 0.562 |
| Fixed manufacturing cost | 820,514 | 10.769 |
| Total manufacturing cost | 2,276,891 | 29.825 |

The cost of the finished product is composed of the price of the raw material (which, in the case of heating by combustion with oxygen, is the cost of the crude coke plus the cost of oxygen), the manufacturing costs, and the credits for the by-products, as shown in Table 8.

TABLE 8

Cost of Production of Low-Sulphur
Fluid Coke by Combustion Heating

| | <u>Per Year</u> | <u>Per Ton</u> |
|--|------------------|----------------|
| Total manufacturing cost | \$2,276,891 | \$29.825 |
| Crude petroleum coke, (11.18 tons/hr) (8,000 hr/year) at \$4.00/ton | 357,696 | 4.694 |
| Oxygen, (1.358 ton/hr) (8,000 hr/year) at \$15.00/ton | 162,960 | 2.139 |
| Total expenditures | 2,797,547 | 36.658 |
| Credit for sulphur, (3,577 ton/year) at \$32.00/ton | 114,464 | 1.502 |
| Credit for heating value of gas, (2605.8 Nm ³ /hr) (1649.2 kcal/Nm ³) (8,000 hr) at (\$2.90/10 ⁶ kcal) | 99,660 | 1.308 |
| Cost of finished product | 2,583,423 | 33.848 |

The desulphurized coke is admixed in a ratio of 10 wt % with the coking coal. If the cost of mixing is neglected, the resulting price of the metallurgical coke will increase as calculated from the price of the desulphurized coke, the coke yield and the stability factor as follows:

$$\frac{(33.85) (0.1)}{(0.715) (0.834)} = \$5.68/\text{ton}.$$

As shown above, the corresponding increase for the electric heating process amounted to \$6.42/ton. Therefore the method of heating by oxygen combustion is able to lower the cost of the metallurgical coke by \$0.74 per ton.

In the following a variant of the combustion heating method will be considered in which scrubbing of the gas and the by-product sulphur recovery is

omitted. This assumes that about 894 kg/hr or 313 Nm³/hr SO₂ from the combustion of the excess gas can be released into the air. In this process, air is used instead of pure oxygen. Therefore a much larger amount of excess gas is released into the open air without scrubbing, namely:

$$(950.6 \text{ Nm}^3/\text{hr}) \frac{100}{20.8} = 4,570.2 \text{ Nm}^3/\text{hr air, containing } 3,619.6 \text{ Nm}^3/\text{hr N}_2,$$

which enters the process and replaces a corresponding volume of recycle gas. Consequently, 3,619.6 Nm³/hr more of the excess gas + 2,918.8 Nm³/hr of the reaction gas, i.e., 6,538.4 Nm³/hr, have to be withdrawn from this process. This excess gas has a concentration of H₂S of only:

$$\left(1.965 \text{ vol } \%\right) \left(\frac{2918.8}{6538.4}\right) = 0.877 \text{ vol } \%$$

and the recycle gas has consequently a H₂S concentration of only:

$$\left(0.877\right) \left(\frac{13,153.4 - 4,570.2}{13,153.4}\right) = 0.572 \text{ vol } \%.$$

With such a low sulphur concentration in the recycle gas, it is considered that it is still possible to extract the required 4.0% of sulphur from the coke without scrubbing the recycle gas. This must be confirmed by experimental work.

A flow scheme of this process is presented in Figure 4. Table 9 gives the fixed capital investment for this type of process.

Assuming as before that the depreciation is 3% and the interest rate is 8%, then the total of the depreciation plus interest per year is:

$$(4,814,398) (0.03) + (4,864,398) (0.08) = \$144,432 + \$389,152 \\ = \$533,584.$$

The labour requirements are lower, since only the coking operation is involved. The manufacturing costs are compiled in Table 10.

The cost of the low-sulphur fluid coke is given in Table 11. The cost figures in this table shows that without the recovery of by-products the price of the metallurgical coke would increase by the following amount:

$$\frac{(25.55) (0.1)}{(0.715) (0.834)} = \$4.29/\text{ton}.$$

Therefore, compared with the electric heating process, the cost increase of the metallurgical coke with this process is \$2.13 less per ton.

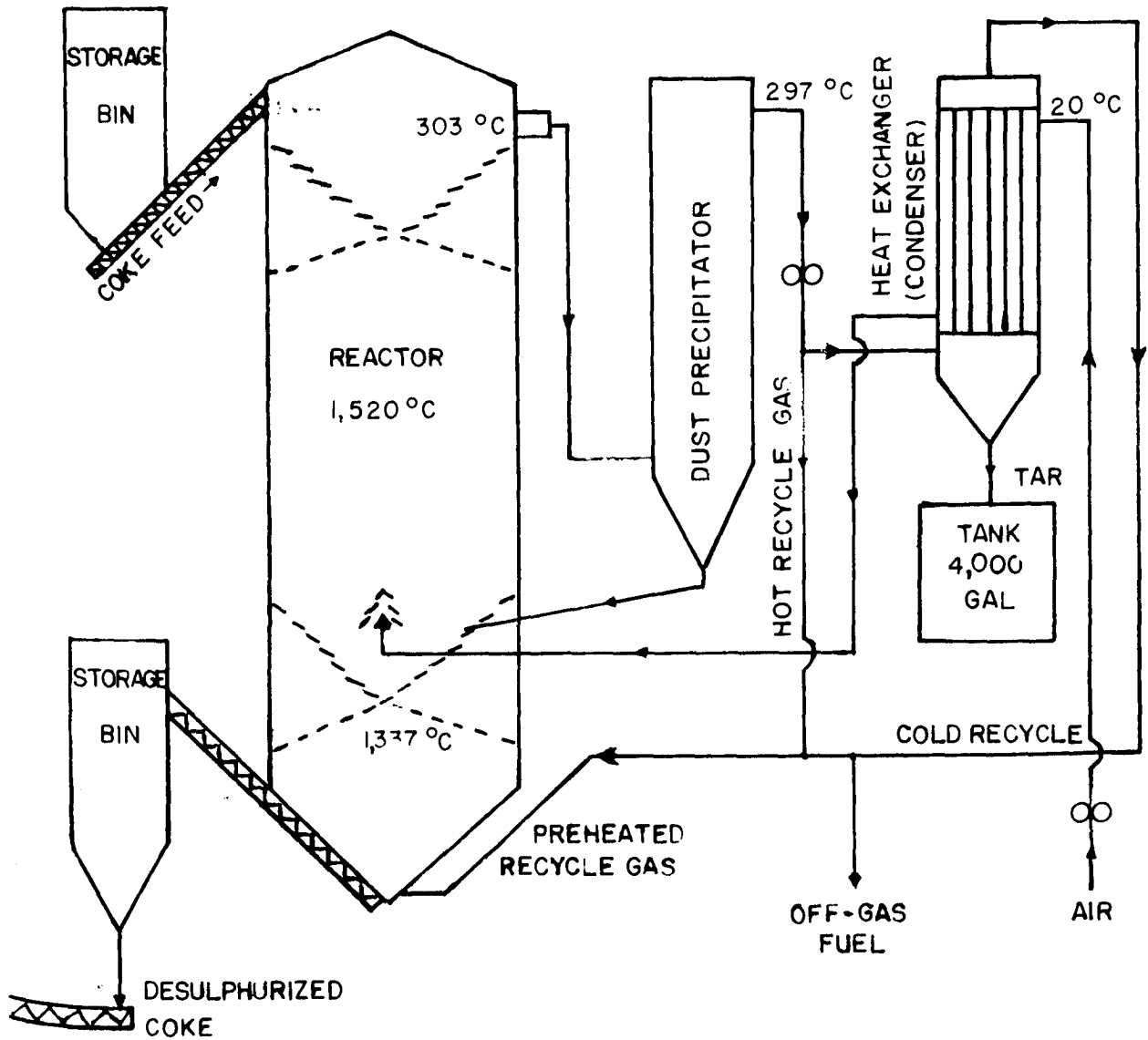


FIGURE 4 - FLOW DIAGRAM FOR DESULPHURIZATION OF FLUID PETROLEUM COKE BY COMBUSTION HEATING WITHOUT SULPHUR RECOVERY

TABLE 9

Fixed Investment for the Desulphurization of Fluid Coke by
Combustion Heating Without By-Product Sulphur Recovery

| | <u>Purchased Cost</u> |
|--|---------------------------|
| Two complete reaction systems | \$ 538,000 |
| Auxiliary equipment | 111,000 |
| Total purchased equipment cost in 1955 | 649,000 |
| Total purchased equipment cost in 1968, (649,000)(1.663) A | 1,079,287 |
| Physical plant cost, A + 196% A, (1,079,287 + 2,115,403) B | 3,194,690 |
| Direct plant cost, B + 37% B, (3,194,690 + 1,182,035) C | 4,376,725 |
| 10% contingency on direct plant costs | 437,673 |
| Fixed capital investment | 4,814,398 |
| Cost of site as before | 50,000 |

In order to achieve a further saving in the production cost for the low-sulphur fluid petroleum coke, the desulphurization should be combined with the fluid coking operation. In the so-called 'burner' in this process, however, coke is heated only to a maximum of 690°C and is steadily mixed with fresh, high-sulphur coke coming from the fluid coker. Therefore this type of operation does not lend itself to a combined operation with the desulphurization, which requires a much higher temperature--of at least 1400°C. Furthermore, the diffusion of the sulphur atoms in the solid coke particles is so slow at such low temperatures that the resulting retention times would require prohibitively large reaction vessels.

TABLE 10

Manufacturing Costs for the Desulphurization of Fluid Coke by
Combustion Heating Without By-Product Sulphur Recovery

| | | <u>Cost per year</u> | <u>Cost per ton</u> |
|--|--|--------------------------|-------------------------|
| Labour | (201.4 man hr) (365 days) at \$3.50/man hr | \$ 257,289 | \$ 3.376 |
| Supervision | 25% of labour | 64,322 | 0.844 |
| Maintenance | 7% of physical plant cost | 222,250 | 2.917 |
| Plant supplies | 15% of maintenance | 33,338 | 0.438 |
| Utilities | Electric power (2500 kW) (8,760 hr) (0.25¢/kWh) | 54,750 | 0.719 |
| | Water (10,000 gal/hr) (8,760 hr) (\$0.15/10 ³ gal) | 13,140 | 0.172 |
| <hr/> Direct manufacturing cost | | <hr/> 645,089 | <hr/> 8.466 |
| Payroll overhead | 17% of labour cost | 43,739 | 0.574 |
| Laboratory | 15% of labour cost | 38,593 | 0.506 |
| Plant overhead | 100% of labour cost | 257,289 | 3.376 |
| Shipping costs | 76,176 tons coke at \$1.20/ton | 91,411 | 1.200 |
| <hr/> Indirect manufacturing costs | | <hr/> 431,032 | <hr/> 5.656 |
| Depreciation (3%) + interest (8%) (= 11% per year) | | 533,584 | 7.002 |
| Property taxes | 1.5% of physical plant cost | 47,625 | 0.625 |
| Insurances | 1.0% of physical plant cost | 31,750 | 0.417 |
| <hr/> Fixed manufacturing cost | | <hr/> 612,959 | <hr/> 8.044 |
| <hr/> Total manufacturing cost | | <hr/> 1,689,080 | <hr/> 22.166 |

TABLE 11

Cost of Production of Low-Sulphur Fluid Coke by
Combustion Heating Without By-Product Sulphur Recovery

| | <u>Per year</u> | <u>Per ton</u> |
|---------------------------------|-----------------|----------------|
| Total manufacturing cost | \$1,689,080 | 22.166 |
| Crude petroleum coke | 357,696 | 4.694 |
| <hr/> | | |
| Total expenditures | 2,046,776 | 26.860 |
| <hr/> | | |
| Credit for heating value of gas | 99,660 | 1.308 |
| <hr/> | | |
| Cost of finished product | 1,947,116 | 25.552 |
| <hr/> | | |

3. EVALUATION OF A PROCESS FOR THE PRODUCTION OF SULPHUR- AND ASH-FREE CARBON BLACK FROM REFINERY VACUUM RESIDUUM

Introduction

The difficulties of achieving an economic desulphurization of fluid petroleum coke by combining it with the operation of a fluid coker in one step—and the long retention times of 24 hours or more even at the required temperature of the blast furnace, approximately 1500°C—led to a method of eliminating the sulphur in the gaseous state, in which the slow diffusion of the sulphur atoms in solids, the high temperatures, the solvents (argon or hydrogen), as well as construction materials, present no great problems. Furthermore, a more valuable product is obtained. The principle of this process consists of gasifying the entire intermediate product of fluid petroleum coke to carbon monoxide, purifying the latter, and decomposing the purified carbon monoxide to pure carbon black and carbon dioxide, part of which is recycled to the gasifier to economize on carbon. The heat released by this decomposition is then used to operate the fluid coker.

Description of the Process

Figure 5 represents a flow scheme of this process, showing the temperatures and pressures. The process equipment consists of a fluid coker, with its accompanying burner exchanged for a combined coke heater, heat exchanger and fluid gasifier. In this gasifier the entire net fluid coke production is gasified at about 1050°C. In the heat exchanger the raw gas from the gasifier preheats the carbon dioxide-oxygen mixture to about 1022°C and at the same time is thereby cooled to about 830°C. It is joined then with about 3.4 times its volume of raw gas recycled from the coke heater, dust precipitator and the first decomposer. Decomposer No. 1 acts also as a heat exchanger: the purified raw gas inside the tubes is decomposed to carbon and carbon dioxide, and the heat of this reaction heats the raw gas outside the tubes from about 500°C to about 830°C. This raw gas then heats the fluid coke, recycling between the coke heater and the fluid coker, thus transferring

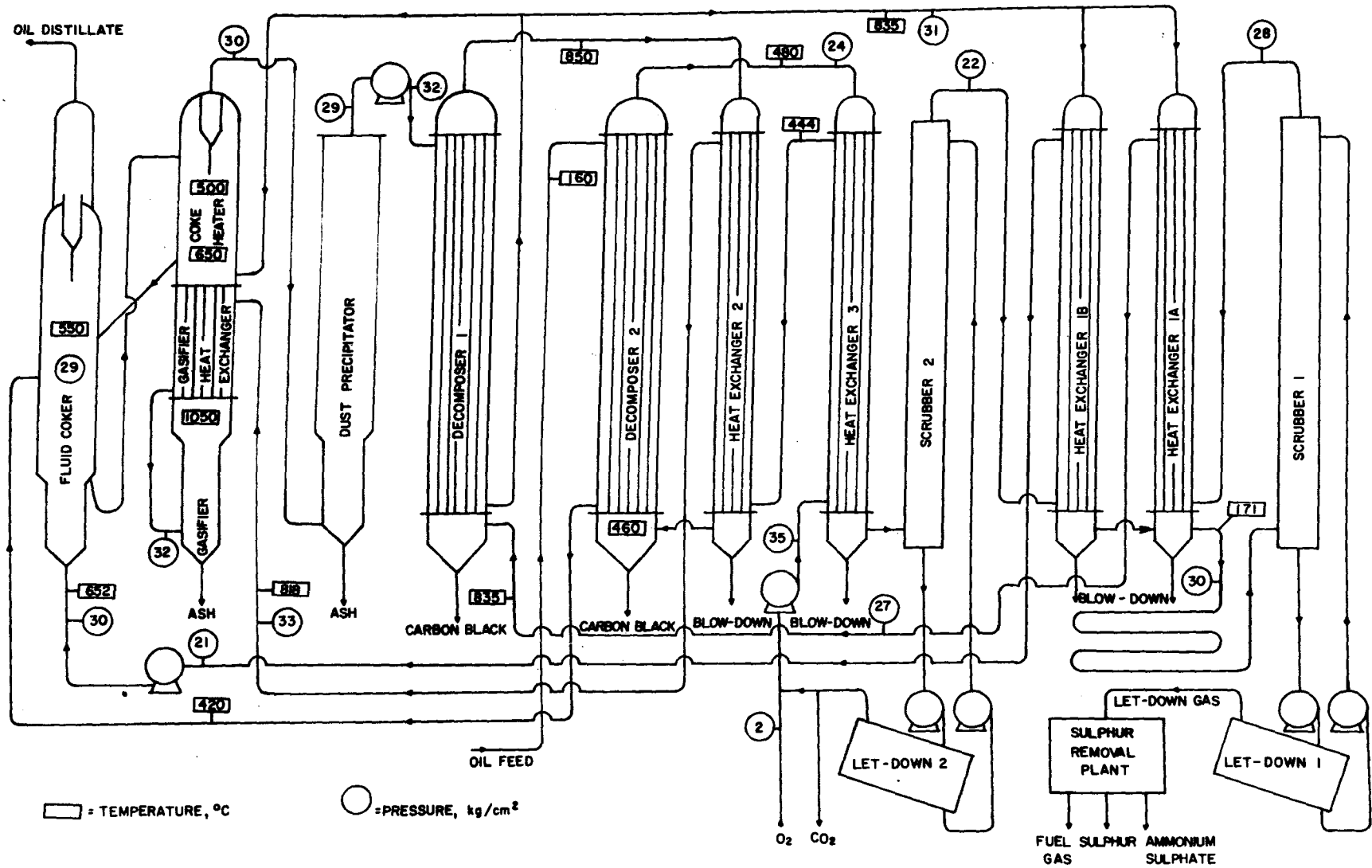


FIGURE 5- FLOW DIAGRAM FOR THE PRODUCTION OF CARBON BLACK FROM REFINERY VACUUM RESIDUUM

the heat from the decomposition reaction to the fluid coker. The excess raw gas produced is cooled in heat exchangers 1A and 1B in parallel, and thereafter in a cooler to 20°C, to be scrubbed with water in order to take out the carbon dioxide together with the sulphur and nitrogen compounds, and also some carbon monoxide. After the extraction of sulphur and nitrogen compounds from the let-down gas, it can be used as fuel gas. The purified gas, containing over 90 vol % of carbon monoxide, is re-heated in the heat exchanger 1A and then decomposed in the first decomposer at about 845°C to enable the heat of reaction to be transferred to the fluid coker. Then, after heat exchange with the oxygen-carbon dioxide mixture in the heat exchanger No. 2, the decomposition is completed at about 475°C in the second decomposer. The off-gas from the second decomposer is cooled in the heat exchanger No. 3 before scrubbing out the carbon dioxide and leaving the hydrogen, which may be used in the fluid coker. Since the carbon dioxide from the second scrubber is pure, part of it is recycled, together with the required volume of 95% pure oxygen, through the third and second heat exchangers to the gasifier. Since the reaction $2\text{CO} = \text{C} + \text{CO}_2$ ⁽¹⁸⁾ is shifted to the right side at elevated pressure, the whole operation will be carried out at about 30 kg/cm^2 (426 psi), which simultaneously facilitates the heat transfer and the scrubbing of the gases with water to eliminate the sulphur and other impurities. An additional advantage is gained by the reduction of the heat losses through the decrease of the surface area of all vessels containing gases at elevated pressure. Since the entire operation is carried out at 30 kg/cm^2 , the surface of the vessels is reduced in the ratio of about $1/30^{2/3} = 0.10356$. These vessels would have approximately the same weight and should not cost more than the corresponding atmospheric pressure vessels.

The reaction, which produces the carbon from carbon monoxide in the first decomposer at about 845°C, also releases about 62% of the heat to be transferred to the coke preheater for the fluid coker. Similarly, about 38% of the reaction heat is transferred to the oil feed for the fluid coker from the decomposition at about 475°C in the second decomposer. The

decomposition reaction proceeds inside of the bundles of 2-inch-wide tubes, cooled from the outside like Fisher-Tropsch reactors. An electrically insulated ionizing wire in the centre prevents precipitation of carbon on the tube walls and thus maintains a good heat transfer rate.

Preliminary Considerations

In this third feasibility study it is assumed that a refinery treats 80,000 bbl/d of 32° API (0.866 kg/l) crude, i.e. 10,998,893 metric tons per year, producing about 10 wt % or 45.829 tons/hr vacuum residuum of 3.2° API (1.048 kg/l). If this residue is treated in a standard fluid coker in such a manner that all the resulting condensate, boiling above 523°C at atmospheric pressure, i. e., 28 vol % or 26 wt % of the vacuum residue feed, is recycled, the quantities of the various products are as given in Table 12 (19).

TABLE 12

Yields and Latent Heats on Fluid Coking of 45.829 kg/hr Vacuum Residuum With 26 wt % Recycle

| | Material | | Latent Heat | |
|-------------------------------|----------|--------|-----------------|-------------|
| | wt % | kg/hr | kcal/kg | kcal/hr |
| Fresh feed | 74.0 | 45,829 | 9,040 | 414,294,160 |
| Recycle | 26.0 | 16,102 | - | - |
| Total input | 100.0 | 61,931 | 9,040 | 414,294,160 |
| Propane | 10.5 | 4,812 | 11,070 | 53,268,840 |
| Butanes | 1.9 | 871 | 10,920 | 9,511,320 |
| Gasoline, up to 220°C | 15.5 | 7,103 | 10,300 | 73,160,900 |
| Distillate, 221 to 523°C | 42.3 | 19,386 | 9,790 | 189,788,940 |
| Net coke | 23.8 | 10,907 | 7,814 | 85,227,298 |
| Coke burned | 6.0 | 2,750 | 7,814 | 21,488,500 |
| Total output | 100.0 | 45,829 | (Average 9,436) | 432,445,798 |
| Difference (heat of reaction) | | | 396 | 18,151,638 |

The difference in the heats of combustion of the products entering and leaving the reactions would theoretically give the heat of reaction, but would be too high an estimate as no account would be taken of the heat losses. A better way to arrive at the heat required for the coking operation is as outlined below:

Since the fluid coke comes directly from the fluid coker it contains: no moisture, 5.4 wt % total volatiles, and 0.6 wt % ash.

The analysis of the maf coke is as follows:

| | |
|----------|------------|
| Carbon | 88.04 wt % |
| Hydrogen | 2.01 |
| Sulphur | 6.44 |
| Nitrogen | 1.60 |
| Oxygen | 1.91 |

The sieve analysis (Tyler) is:

| | |
|-------------|----|
| + 30 sieve | 2% |
| - 30 + 50 | 28 |
| - 50 + 80 | 44 |
| - 80 + 100 | 6 |
| - 100 + 200 | 16 |
| - 200 | 4 |

The fluid coke leaves the coke preheater at about 690°C and enters it at about 500°C. The oxygen consumption is calculated below for 1 kg of maf coke:

$$\frac{704.4 \text{ g C}}{12} = 58.70 \text{ mol C, consuming } 58.70 \text{ mol O}_2 \text{ for CO}_2$$

$$\frac{176.0 \text{ g C}}{12} = 14.67 \text{ mol C, consuming } 7.33 \text{ mol O}_2 \text{ for CO}$$

$$\frac{20.1 \text{ g H}}{2} = 10.05 \text{ mol H}_2, \text{ consuming } 5.03 \text{ mol O}_2 \text{ for H}_2\text{O}$$

$$\frac{64.4 \text{ g S}}{32} = 2.01 \text{ mol S, consuming } 2.01 \text{ mol O}_2 \text{ for SO}_2$$

$$\frac{16.0 \text{ g N}}{28} = 0.57 \text{ mol N}$$

$$\frac{19.1 \text{ g O}}{32} = 0.60 \text{ mol O}_2, \text{ saving } 0.60 \text{ mol O}_2$$

1,000.0 g total consume 72.47 mol O₂

As air contains 20.8 vol % O₂ and the flue gas contains 4.4 vol % O₂, the air consumption for 1 kg maf coke will be:

$(72.47 \text{ mol O}_2) (22.415) [100/(20.8 - 4.4)] = 9.905 \text{ Nm}^3$, or 9.865 Nm^3 per kg of fluid coke. Of the latter amount, 0.4341 Nm^3 is unused O₂ and 7.813 Nm^3 is N₂ and Ar.

The composition and specific heat of the flue gas resulting from the burning of 1 kg maf coke is shown below:

| Constituent | mol | Nm ³ | vol % | kcal/Nm ³ °C | kcal/kg maf coke °C |
|-----------------------|---------------|-----------------|---------------|-------------------------|---------------------|
| CO ₂ | 58.70 | 1.3158 | 12.94 | 0.492 | 0.6367 |
| CO | 14.67 | 0.3288 | 3.24 | 0.324 | 0.1051 |
| H ₂ O | 10.05 | 0.2242 | 2.20 | 0.383 | 0.0842 |
| SO ₂ | 2.01 | 0.0451 | 0.44 | 0.515 | 0.0227 |
| N ₂ total | 371.94 | 7.8258 | 76.91 | 0.321 | 2.4688 |
| O ₂ unused | 20.63 | 0.4341 | 4.27 | 0.338 | 0.1445 |
| Total | 478.00 | 10.1738 | 100.00 | 0.3403(Average) | 3.4620 |

The heat content in fresh flue gas from 690 to 500°C, produced from 2750 kg/hr coke burned, would be only:

$$(2750 \text{ kg/hr}) (3.462 \text{ kcal/kg}^\circ\text{C}) (690 - 500^\circ\text{C}) = 1,809,006 \text{ kcal/hr.}$$

The combustion of the coke is not quite complete, but as seen from the flue gas analysis, only 80% CO₂ is produced along with 20% CO⁽²⁰⁾. Consequently the net heating value of the coke is reduced as follows:

$$(7,814 \text{ kcal/kg coke}) \frac{(0.8) (94.05) + (0.2) (26.42)}{94.05} = 6,697 \text{ kcal/kg coke}$$

and the total heat of combustion of 2,750 kg/hr coke is:

$$(2,750 \text{ kg/hr}) (6,697 \text{ kcal/kg}) = 18,416,750 \text{ kcal/hr.}$$

This heat of combustion is about ten times as high as the heat in the corresponding amount of fresh flue gas. Since, however, at temperatures higher than about 650°C the formation of CO would be too high, leading to an excessive fuel consumption, flue gas must be recycled, which simultaneously facilitates the fluidization of the fluid coke.

The volume of flue gas discharged into the open corresponds to the fresh flue gas. By heating the combustion air to 324°C it is cooled from 500 to 217°C and gives off:

$$(2,750 \text{ kg/hr}) (3,381 \text{ kcal/kg}^\circ\text{C}) (500 - 217^\circ\text{C}) = 2,631,334 \text{ kcal/hr.}$$

This amount of heat preheats the combustion air by:

$$\frac{2,631,334 \text{ kcal/hr}}{(2,750 \text{ kg/hr}) (9,905 \text{ Nm}^3/\text{kg}) (0.318 \text{ kcal/Nm}^3^\circ\text{C})} = 304^\circ\text{C}$$

The heat lost with the flue gas discharged is then:

$$(2,750 \text{ kg/hr}) (3,340 \text{ kcal/kg}^\circ\text{C}) (217 - 20^\circ\text{C}) = 1,809,445 \text{ kcal/hr.}$$

In addition to this, the 10,907 kg/hr net coke produced are discharged at 690°C and consequently cause a loss of:

$$(10,907 \text{ kg/hr}) (0.390 \text{ kcal/kg}^\circ\text{C}) (690 - 500^\circ\text{C}) = 808,209 \text{ kcal/hr.}$$

If additionally about 200,000 kcal/hr are lost through radiation, then the overall heat balance in the standard fluid coker is about as follows:

| | | |
|---|-------------------|---|
| Radiation losses | 200,000 kcal/hr | |
| Preheating the combustion air | 2,631,334 | " |
| Lost in flue gas | 1,809,445 | " |
| Lost in net coke produced | 808,209 | " |
| Heat transferred by the recycle coke to the fluid coke proper (by difference) | 12,967,762 | " |
| Total heat from combustion of 2,750 kg/hr coke | <u>18,416,750</u> | " |

In the process for the production of carbon black from vacuum residuum, the same amount of heat (12,967,762 kcal/hr) is required to heat the recycle coke for transfer to the fluid coker. Of this amount,

$$(61,931 \text{ kg/hr}) (0.818 \text{ kcal/kg } ^\circ\text{C}) (520-420^\circ\text{C})$$

$$= 5,065,135 \text{ kcal/hr}$$

are used to preheat the feed oil and recycle oil from 420°C to 520°C, and in addition

$$(48,274 \text{ kg/hr}) (57 \text{ kcal/kg}) = 2,751,618 \text{ kcal/hr}$$

are needed to vaporize the recycle oil and the 70.2 wt % volatiles in the feed. Deducting these quantities of heat, plus about 200,000 kcal/hr for losses from the heat introduced, the heat of reaction is found to be 4,951,009 kcal/hr or 108 kcal/kg feed. This figure is in agreement with actual plant experience and will therefore be used in later computations.

Calculations of the Composition and Flow Rate of the Raw Gas From the Gasifier

In the following calculations the same assumptions are made as for the above calculations of the heat of reaction, namely, an oil feed of 45.829 ton/hr refinery vacuum residue of 3.2° API to be treated in a fluid coker with 26 wt % recycle oil boiling above 523°C at atmospheric pressure.

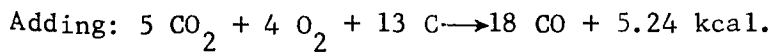
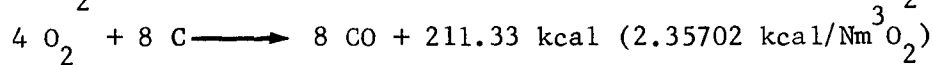
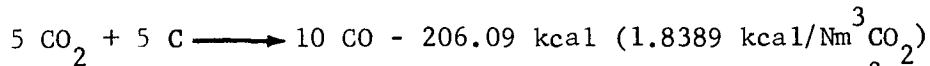
In this process not only the "coke burned" but also the excess net coke produced in the fluid coker will be converted to carbon monoxide in the gasifier as shown in Table 13 ⁽²⁰⁾ and the following calculations:

TABLE 13

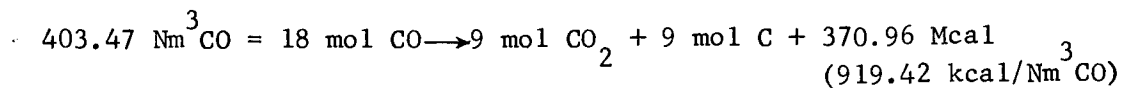
Material Balance for the Gasification of Fluid Coke, kg/ton of Coke

| | Coke | Ash | Tar | CH ₄ | H ₂ | H ₂ S | NH ₃ | CO + CO ₂ |
|----------|---------|-----|------|-----------------|----------------|------------------|-----------------|----------------------|
| Carbon | 875.1 | 0.8 | 12.0 | 3.0 | - | - | - | 859.3 |
| Hydrogen | 20.0 | - | 1.0 | 1.0 | 12.0 | 1.4 | 1.1 | 3.5 |
| Nitrogen | 15.9 | - | 0.6 | - | - | - | 5.3 | 10.0 |
| Sulphur | 64.1 | - | 0.2 | - | - | 21.6 | - | 42.3 |
| Oxygen | 19.0 | - | 1.2 | - | - | - | - | 17.8 |
| Ash | 5.9 | 5.9 | - | - | - | - | - | - |
| Total | 1,000.0 | 6.7 | 15.0 | 4.0 | 12.0 | 23.0 | 6.4 | 932.9 |

The reaction in the gasifier proceeds approximately according to the following equations:



The decomposition of the carbon monoxide proceeds according to the following equation:



There is an excess of 4 mol CO₂ to be vented. Since the equilibrium concentration of CO₂ in the gasifier raw gas at 30 kg/cm² and 1050°C is about 10.5 vol %, approximately 2.08 mol CO₂ have to be charged, in addition to the 5 mol for the reaction, in order to shift the equilibrium so that 89.5% CO is in the mixture of CO and CO₂ in the raw gas. Since the gases are under pressure in the entire system, it is easy to scrub the excess CO₂ together with the other impurities from the gases before they enter the decomposers. The analysis of the gasifier raw gas is calculated from the composition of the coke and the results are given in Table 14, together with the required carbon dioxide and oxygen consumption.

TABLE 14

Composition and Specific Heat of the Gasifier Raw Gas and
Consumption of Oxygen and Carbon Dioxide

| Constituent | (1) Coke Feed | Gas Feed | | Raw Gas Product | | | Specific Heat | Product of sp ht and vol % |
|------------------|------------------------|------------------------|-------------------------------------|--------------------|---------------------------------|---------|--|-------------------------------|
| | kg per ton coke (2) | kg gas per ton coke | Nm ³ gas per ton coke | kg per ton coke | Nm ³ per ton coke | vol % | kcal/Nm ³ °C 1050-830 °C | |
| O ₂ | 17.8 | 687.267 | 480.959 | - | - | - | 0.422 | - |
| C | 859.3 | - | - | - | - | - | - | - |
| CO ₂ | - | 1,855.015 | 938.393 | 643.182 | 327.578 | 11.739 | 0.603 | 0.0708 |
| CO | - | 0.482 | 0.342 | 2,739.703 | 2,192.409 | 78.571 | 0.358 | 0.2813 |
| H ₂ | 15.5 | 0.381 | 4.329 | 15.881 | 176.559 | 6.328 | 0.333 | 0.0211 |
| CH ₄ | 4.0 | 0.558 | 0.778 | 4.558 | 6.369 | 0.228 | 1.180 | 0.0027 |
| N ₂ | 10.0 | 32.959 ⁽⁵⁾ | 26.357 | 42.959 | 34.370 | 1.232 | 0.357 | 0.0044 |
| NH ₃ | 6.4 | - | - | 6.400 | 8.423 | 0.302 | 0.722 | 0.0022 |
| H ₂ S | 23.0 | - | - | 23.000 | 15.127 | 0.542 | 0.532 | 0.0029 |
| COS | 42.2 ⁽³⁾ | - | - | 79.125 | 29.525 | 1.058 | 0.680 | 0.0072 |
| TOTAL | 978.2 ⁽⁴⁾ | 2,576.662 | 1,451.068 | 3,554.808 | 2,790.360 | 100.000 | | 0.3926 |

(1) In gasifier at temperature of 1050°C. (2) Containing mineral matter. (3) S in COS.

(4) Excluding mineral matter. (5) Composed of 32.092 kg N₂ from the CO₂ recycle plus 0.867 kg N₂ impurity in the oxygen (95%).

The calculation of the specific heat of the raw gas product is also shown. The purity of the oxygen was assumed to be of 95 vol %. These calculations are based on one ton of coke feed. With a feed of 13.657 ton/hr of coke, the yield of raw gas product and its CO and CO₂ contents are as follows:

13.657 ton/hr total fluid coke produces
 (13.657) (2,790.360) = 38,107.947 Nm³/hr raw gas,

of which

(13.657) (2192.409) = 29,941.74 Nm³/hr are CO

and

(13.657) (327.578) = 4,473.733 Nm³/hr are CO₂.

After scrubbing out the CO₂ and the other gases, the remaining 28,775.324 Nm³/hr CO are decomposed to 14,387.662 Nm³/hr CO₂ and 7.705 ton/hr of a high-purity carbon black corresponding to a production of about 62,000 tons per year. To shift the equilibrium composition of the raw gas towards the production of practically 100% carbon monoxide from the carbon available, 11,945.9 Nm³/hr CO₂ are recycled to the gasifier. This is necessitated by the operation of the gasifier at elevated pressure. The residual gas from the scrubber No. 2 consists of 2,965.5 Nm³/hr of 76.7 vol % H₂ and is used to augment and beneficiate the fluidizing gas for the fluid coker or other refinery operations. A corresponding gas volume must be vented from the condenser train of the fluid coker to be used as fuel gas in combination with the 5,040.4 Nm³/hr CO₂-CO mixture discharged from the desulphurization of the waste gas from scrubber No. 1.

Heat Balance

The reaction heat released by the decomposition of the CO amounts to:

$$(28,775.246 \text{ Nm}^3/\text{hr}) \left(\frac{370.96 \text{ Mcal}}{403.47 \text{ Nm}^3} \right) = 26,456,648.2 \text{ kcal/hr.}$$

Of this amount of heat, 16,540,463 kcal/hr (62.5%) are released in the first decomposer at about 845°C and are used to heat the recycle raw gas (for preheating the coke for the fluid coker) from 500 to about 830°C, and the remaining 9,916,186 kcal/hr (37.5%) are used to preheat the oil feed for the coker

from 160°C to 420°C in the second decomposer. The heat balance is regulated for the entire system by adjusting the ratio of CO₂ to O₂, flowing to the gasifier, thus adjusting the temperature of the exit gas and with this the temperatures in the heat exchangers.

The heat of formation of 6,572.7 Nm³/hr carbon dioxide from carbon in the combined gasification and decomposition reactions, corresponding to 28,459,791 kcal/hr, represents the total heat input of the entire operation including the fluid coking. This compares with only 1,459,902 kcal/hr of heat input for the direct desulphurization of coke (if it works), which does not, however, include the heat of 18,416,750 kcal/hr required for the operation of the fluid coker. Therefore, including the fluid coker, the total heat input for the direct desulphurization amounts to 19,876,652 kcal/hr. The difference between this amount and 28,459,791 kcal/hr, amounting to 8,583,139 kcal/hr, represents the additional heat input required for the carbon-black process. On the other hand, lower temperatures are sufficient, a scrubber gas is produced having a total heating value of 11,973,631 kcal/hr, and a superior product is obtained in the form of a completely sulphur- and ash-free carbon black.

Pressure Gasification and Gas Purification

At the required pressure of 30 kg/cm², the gasification of the coke in the fluidized state is efficient enough to gasify between 9.66 and 25.6 kg/hr per litre reaction volume at temperatures from 752°C to 1050°C⁽²¹⁾. At atmospheric pressure and these temperatures the CO₂ concentration would be very low. But at the required operating pressure the highest temperature of the range, 1050°C, is necessary in order to reduce the CO₂ content of the raw gas from the gasifier to the lowest obtainable value of 10.5 vol % of the sum of the CO and the CO₂. By comparison, at atmospheric pressure the CO₂ concentration would be only 0.4 vol %. On the other hand, it is easy to eliminate the CO₂ from the raw gas prior to the decomposition reaction by scrubbing it with water, as this operation is facilitated by the higher pressure. Furthermore, the compression costs are lowered by the use of the elevated pressure. This CO₂ is then part of the CO₂ that must be vented in any case. Since the scrubber off-gas has a certain CO content, it can be used as fuel elsewhere.

The retention time in the gasifier, in comparison to the direct desulphurization of fluid petroleum coke at 1520°C, is shortened from 24 hours to about 6 minutes ⁽²¹⁾. Thus, the reaction volume required is only 0.00416 times the one needed for the direct desulphurization of the coke. Furthermore, since the temperature is 1050°C instead of 1520°C, the heat loss through the walls will be greatly reduced.

The 38,107,947 Nm³/hr raw gas leaving the gasifier have to preheat the carbon dioxide-oxygen mixture entering the gasifier heat exchanger from 818°C to 1022°C and simultaneously the coke to be gasified from 833°C to 1022°C. The 13,657 kg/hr coke to be gasified are fed from the coke heater, above the heat exchanger, down through special pipes of the heat exchanger to the gasifier. In the coke heater the coke is preheated in the fluidized state from about 500° to 650°C. About 133,123 Nm³/hr raw gas are recycled through the first decomposer, where they are heated from 500°C to 835°C. This recycle raw gas enters the coke heater and mixes with the gasifier gas leaving the heat exchanger at 827°C, so that the resultant temperature is 833°C. This gas mixture preheats about 276.9 ton/hr fluid coke, which is recirculated between the fluid coker and the coke heater, where it takes up about:

$$(276,900 \text{ kg/hr}) (0.390 \text{ kcal/kg}^\circ\text{C}) (150^\circ\text{C}) = 16,198,650 \text{ kcal/hr.}$$

Processing the Raw Gas

Part of the cooling gas (raw gas) from the first decomposer passes through the two heat exchangers, in parallel, 1A and 1B; the larger, 1A, for reheating the scrubbed raw gas from 20 to 835°C, and the smaller, 1B, for heating the H₂-rich scrubber No. 2 off-gas from 20 to 652°C. The raw gas on the inside of the tubes is cooled from 835 to 171°C, and then in an air or water cooler to 20°C, before being scrubbed by 56 litres of water per Nm³ to eliminate CO₂, NH₃, H₂S, and COS from the raw gas. From this scrubber gas, released in the letdown vessel, the NH₃ is recovered as (NH₄)₂SO₄ and sulphurous constituents are recovered by scrubbing with dimethylantraquinone-sulphonate-sodium vanadate solutions to recover the elemental sulphur.

The reheated, purified process gas (carbon monoxide) is decomposed only to about 62.5%, which can be done at 845°C. This offers the possibility of transferring the 62.5% of the heat of reaction by recirculating about 133,000 Nm³/hr dust-free raw gas between the first decomposer and the fluid coke heater.

The partly decomposed process gas from the first decomposer passes through the second heat exchanger where it is cooled from 850°C to 470°C inside the tubes. It heats countercurrently the CO₂-O₂ mixture to the gasifier from 444° to 818°C.

Fine carbon-black particles carried over from the first converter do not disturb the system since the flow velocities in the heat exchanger-tubes and outside the tubes of the decomposers are four times as much as inside the tubes of the decomposers and any dust entrained serves here as a catalytic surface on which new carbon is deposited. The ionizing wires prevent the carbon from depositing on the heat-transfer surfaces and contribute to its precipitation in the centre of the tubes, where it is carried down with the gas flow and discharged from the bottom cone. Before scrubbing the gas from the second decomposer it is freed from the last traces of carbon black in filter bags. Part of this carbon is recycled into the fresh process gas to the first decomposer, to serve as a catalytic surface for the deposition of carbon to enlarge the particle size to the desired diameter, thus regulating the quality of the product.

In the second decomposer the decomposition of the CO is completed from 62.5 to 99.6% and the volume of the residual gas decreases from 31,653 Nm³ to 17,351 Nm³. From here the gas passes through precipitators and then through the third heat exchanger. Here it is cooled from 480°C to 26°C, heating counter-currently the CO₂-O₂ mixture from 20°C to 444°C. The cool residual gas is freed from the rest of the entrained carbon black in filter bags. After that, still under pressure, it is scrubbed with 50 litres of water per Nm³ gas. From 17,351 Nm³ of this residual gas, 82.9 vol % is dissolved, consisting of 99.4 vol % CO₂, part of which is recycled to the gasifier. The rest is vented or can be compressed in cylinders and sold.

The 2,966 Nm³/hr of undissolved, residual gas contains 76.7 vol % H₂ and is sent to the fluid coker or other refining operations under pressure.

Calculation of the Transfer Area of the Heat Exchangers and Decomposers

As a basis for the calculations of the heat transfer area, the equations given in "Koppers Handbuch der Brennstofftechnik" (22), and data given in Nelson's "Petroleum Refinery Engineering" (23) were used. The specific heats were taken from nomograms in Perry's "Chemical Engineers' Handbook" (24) (see also Figure 7). The film heat-transfer rates were taken from curves given in Nelson's "Petroleum Refinery Engineering" (25) (see also Figures 8 and 9). The transfer factors for radiation were taken from "Koppers Handbuch der Brennstofftechnik" (26). Since the temperatures in the heat exchangers are relatively high, the heat transfer by radiation plays an important role and, since the raw gas and purified gas have to be kept separate, heat transfer by means of intermittent, direct contact with heat-transferring materials is not feasible. For the calculations of the quantity of water needed for scrubbing the gases, the solubility coefficients for the corresponding gases, given in "Chemiker Kalender 1936", were used (27). The lower, or net, fuel value of the gas released from scrubber No. 1 after eliminating the sulphur and ammonia is 581.4 kcal/Nm³.

The heat transfer on both sides of the tubes was calculated separately for conduction, including fouling factors, as well as for radiation. The improvement due to elevated pressure has, however, not been considered. The fouling factor assumed for a 3-mm(1/8 inch)-thick layer of lamp black, is 3.8 (28). But for safety reasons, fouling factors 30% higher for inside the tubes and 60% higher for outside the tubes were used to compensate for an eventual deposition of carbon black. The increased values were 5 and 6, respectively. The configurations of the heat exchanger tubes, as well as of the corresponding cross-section and transfer areas, are described in Figure 6. The calculation of the heat exchangers and decomposers is based on a rhomboid arrangement of the tubes. The OD of the heat-exchanger tubes is 1.000 in., the ID 0.875 in. and the distance from centre to centre is 1.25 in.; while

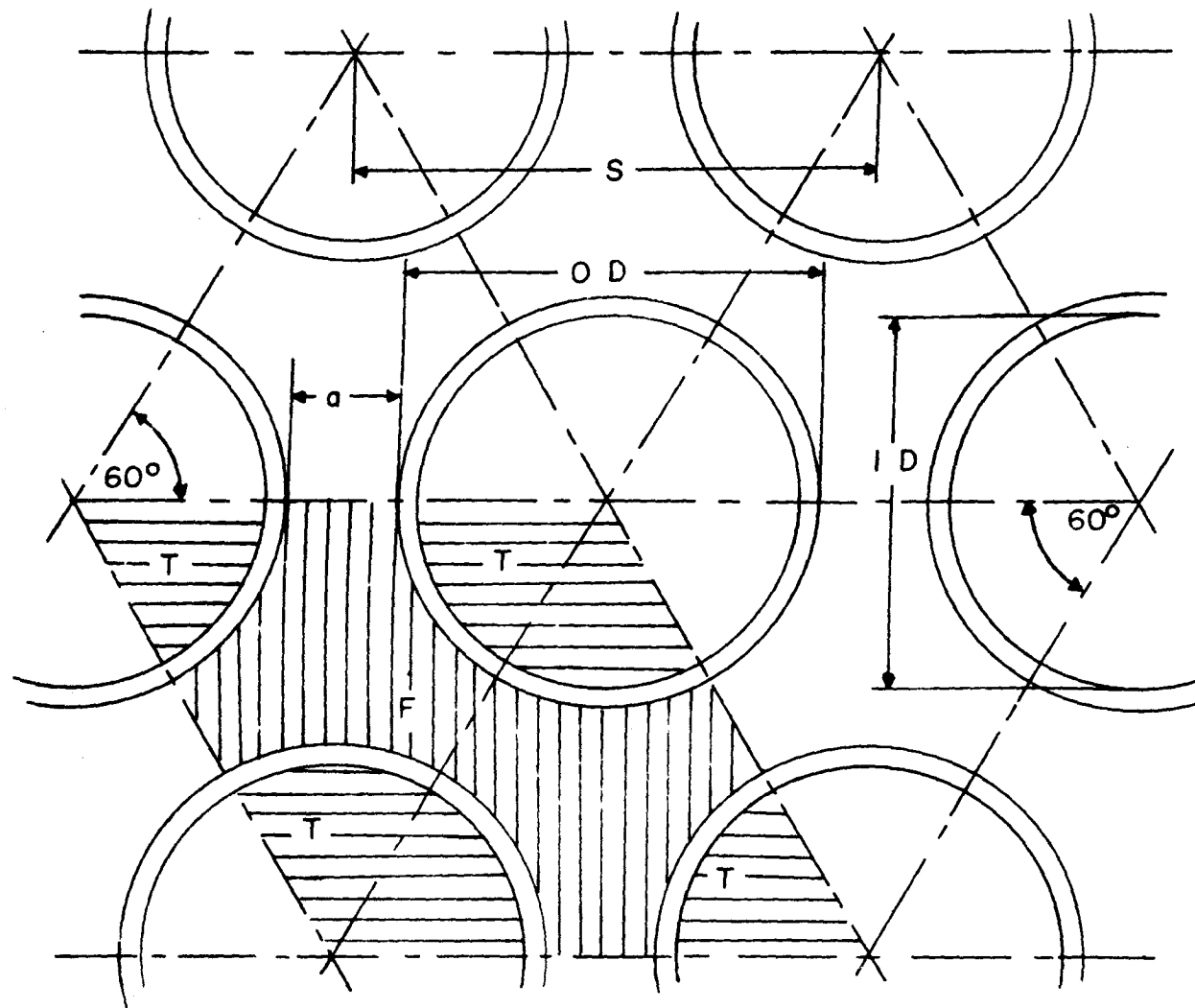


FIGURE 6 - TUBE SPACING IN HEAT EXCHANGERS AND DECOMPOSERS
 (SEE TABLE 15 FOR EXPLANATION OF SYMBOLS.)

the OD of the tubes for the decomposers is 2.000 in., the ID 1.875 inch, and the distance from centre to centre is 2.375 in. This geometric arrangement and these tube dimensions result in the values for the transfer areas per unit cross-section as given in Table 15.

From the analysis of the inlet raw gas to scrubber No. 1, the amount of scrubbing water and the composition of the scrubbed gas and let-down gas were calculated as shown in Table 16. The average specific heats of the component gases at various temperature ranges, as shown in Table 17, were calculated from the specific heat-temperature curves shown in Figure 7. These curves were drawn from data obtained from Perry's "Handbook of Chemical Engineering" (24). The average specific heats of the gases passing through heat exchanger No. 1 and decomposer No. 1 were calculated from their compositions and the specific heats of the components in that temperature range, and are shown in Table 18. The average specific heats of the gases passing through heat exchangers Nos. 2 and 3 and decomposers No. 2 were calculated in a similar manner, as shown in Tables 19 and 20. From the analysis of the gas from decomposer No. 2, the amount of scrubbing water and the composition of the scrubbed gas to the fluid coker and of the let-down gas (CO_2 for the CO_2 - O_2 mixture to the gasifier) were calculated as shown in Table 21. As before, the average specific heats of the CO_2 - O_2 mixture were calculated from its composition as it pertains to its passage through heat exchangers No. 3 and No. 2, and the gasifier heat exchanger. The results are shown in Table 22. The fuel value of the purified let-down gas from scrubber No. 1 was calculated from the composition and net fuel value of the components; the results are shown in Table 23.

The heat rates, in kcal/hr, for the heat transfer by conduction and radiation in the heat exchangers and decomposers were calculated from the mass flow rates in kg/hr and the specific heats in the relevant temperature range. The results are given in Table 24. The film transfer rates for the heat transfer by conduction in the heat exchangers and decomposers were calculated from the mass velocities in $\text{kg/m}^2 \text{ sec}$, using the curves in Figures 8 and 9 (25). These film transfer rates were corrected by applying a

. TABLE 15

Heat Transfer Area per Unit Cross-section with Dimensions of
Heat Exchanger Tubes and Tube Sheet

| | Gasifier Heat Exchanger | All Other Heat Exchangers | Decomposers |
|--|-------------------------------|---------------------------------|-------------|
| Inside diameter of tubes, in. | 0.875 | 0.875 | 1.875 |
| " " " " cm | 2.223 | 2.223 | 4.763 |
| Outside diameter of tubes, in. | 1.000 | 1.000 | 2.000 |
| " " " " cm | 2.54 | 2.54 | 5.08 |
| Space between tubes, (a), in. | 0.250 | 0.250 | 0.375 |
| " " " " cm | 0.635 | 0.635 | 0.9525 |
| Length of one side of rhombus, (s), cm | 3.175 | 3.175 | 6.0325 |
| Total area of rhombus, cm ² | 8.73014 | 8.73014 | 31.4896 |
| Area of one tube, cm ² | 5.06709 | 5.06709 | 20.2683 |
| Free area outside of tube, (F), cm ² | 3.66305 | 3.66305 | 11.2213 |
| Free area inside of tube, (T), cm ² | 3.8795 | 3.8795 | 17.7953 |
| Average free area, cm ² | 3.7713 | 3.7713 | 14.5083 |
| Length of tubes, ft | 23.0 | 33.0 | 24.0 |
| " " " cm | 701.5 | 1,006.5 | 732.0 |
| Median circumference of tubes, cm | 7.481 | 7.481 | 15.4567 |
| Transfer area per one tube, cm ² | 5,266.6 | 7,529.6 | 11,314.3 |
| Total transfer area per cm ² of actual cross-section of heat exchanger or decomposer, cm ² | 1,396.49 | 1,996.55 | 779.85 |

TABLE 16

Calculation of the Composition of the Scrubber No. 1 Gases

| Component | Inlet Raw Gas | | Solubility at 20°C, 760 mm Hg, <i>l/l</i> H ₂ O | Dissolved Gas, <i>l/l</i> H ₂ O | Required vol H ₂ O, <i>l</i> per Nm ³ of Raw Gas | <i>l</i> Gas Dissolved in 56 <i>l</i> H ₂ O * | Scrubber let-down gas, vol % | Scrubbed Gas | | |
|------------------|---------------|--|--|--|---|--|---------------------------------------|---|--------|--------------------------------|
| | Vol % | Partial Pressure, kg/cm ² | | | | | | <i>l</i> /Nm ³ of Raw Gas | vol % | Density, kg/Nm ³ |
| CO ₂ | 11.739 | 3.522 | 0.7430 | 2.617 | 44.9 | 117.39 | 69.298 | - | - | - |
| CO | 78.571 | 23.571 | 0.02319 | 0.7466 | 1,436.5 | 30.61 | 18.070 | 755.10 | 90.910 | 1.1370 |
| H ₂ | 6.328 | 1.898 | 0.01819 | 0.0345 | 1,834.0 | 1.932 | 1.141 | 61.35 | 7.386 | 0.0066 |
| CH ₄ | 0.228 | 0.068 | 0.03308 | 0.00225 | 1,013.0 | 0.126 | 0.074 | 2.174 | 0.259 | 0.0018 |
| N ₂ | 1.232 | 0.370 | 0.01545 | 0.00572 | 2,156.0 | 0.320 | 0.189 | 11.998 | 1.445 | 0.0018 |
| NH ₃ | 0.302 | 0.091 | 682.998 | 62.153 | 0.0485 | 3.02 | 1.783 | - | - | - |
| H ₂ S | 0.542 | 0.163 | 2.582 | 0.4209 | 12.87 | 5.42 | 3.199 | - | - | - |
| COS | 1.058 | 0.317 | 0.962 | 0.3050 | 34.68 | 10.58 | 6.246 | - | - | - |
| | 100.000 | 30.000 | | | 56.0 | 169.398 | 100.000 | 830.602** | | 1.1635 |

* The amount of scrubbing water required is found by dividing the vol/Nm³ of the determining component (CO₂) in the inlet raw gas by the volume dissolved per litre of H₂O. In this case the calculation is $\frac{(11.739)(10)}{2.617} = 44.9$ *l* per Nm³ of raw gas. In order to ensure that all the COS is dissolved, a surplus of 56 *l* is used.

** Volume remaining after scrubbing 1.00 Nm³ raw gas. Consequently, 38,107.947 Nm³/hr raw gas yield 31,652.537 Nm³/hr scrubbed gas and 6,455.410 Nm³/hr let-down gas.

TABLE 17

Specific Heats in kcal/kg °C and kcal/Nm³ °C of the Gases in the Process

| Gas | Unit of Sp Ht | Temperature Range, °C | | | | | | | | | |
|------------------|-------------------------|-----------------------|---------|---------|---------|---------|---------|---------|--------|--------|--------|
| | | 1050-830 | 850-830 | 850-508 | 840-500 | 840-460 | 508-480 | 830-126 | 830-20 | 480-30 | 460-20 |
| O ₂ | kcal/kg °C | 0.295 | 0.285 | 0.276 | 0.275 | 0.273 | 0.256 | 0.254 | 0.250 | 0.236 | 0.235 |
| | kcal/Nm ³ °C | 0.422 | 0.408 | 0.395 | 0.393 | 0.390 | 0.366 | 0.363 | 0.357 | 0.337 | 0.336 |
| CO ₂ | kcal/kg °C | 0.305 | 0.299 | 0.291 | 0.290 | 0.288 | 0.280 | 0.279 | 0.276 | 0.266 | 0.265 |
| | kcal/Nm ³ °C | 0.603 | 0.591 | 0.575 | 0.573 | 0.569 | 0.554 | 0.552 | 0.545 | 0.526 | 0.524 |
| CO | kcal/kg °C | 0.287 | 0.282 | 0.276 | 0.275 | 0.274 | 0.268 | 0.267 | 0.265 | 0.258 | 0.257 |
| | kcal/Nm ³ °C | 0.358 | 0.352 | 0.344 | 0.343 | 0.341 | 0.334 | 0.333 | 0.331 | 0.332 | 0.320 |
| H ₂ | kcal/kg °C | 3.710 | 3.660 | 3.600 | 3.595 | 3.585 | 3.530 | 3.525 | 3.500 | 3.430 | 3.425 |
| | kcal/Nm ³ °C | 0.333 | 0.329 | 0.324 | 0.323 | 0.322 | 0.317 | 0.316 | 0.314 | 0.308 | 0.307 |
| CH ₄ | kcal/kg °C | 1.180 | 1.130 | 1.062 | 1.060 | 1.058 | 0.970 | 0.962 | 0.938 | 0.868 | 0.860 |
| | kcal/Nm ³ °C | 0.846 | 0.810 | 0.761 | 0.760 | 0.758 | 0.696 | 0.690 | 0.674 | 0.623 | 0.617 |
| N ₂ | kcal/kg °C | 0.286 | 0.281 | 0.275 | 0.274 | 0.272 | 0.267 | 0.266 | 0.264 | 0.257 | 0.256 |
| | kcal/Nm ³ °C | 0.357 | 0.351 | 0.343 | 0.342 | 0.340 | 0.333 | 0.332 | 0.330 | 0.321 | 0.320 |
| NH ₃ | kcal/kg °C | 0.936 | 0.870 | 0.783 | 0.778 | 0.770 | 0.697 | 0.685 | 0.660 | 0.589 | 0.583 |
| | kcal/Nm ³ °C | 0.722 | 0.671 | 0.604 | 0.600 | 0.594 | 0.538 | 0.528 | 0.509 | 0.455 | 0.450 |
| H ₂ S | kcal/kg °C | 0.346 | 0.334 | 0.317 | 0.316 | 0.314 | 0.299 | 0.297 | 0.293 | 0.277 | 0.275 |
| | kcal/Nm ³ °C | 0.532 | 0.514 | 0.487 | 0.486 | 0.483 | 0.460 | 0.456 | 0.450 | 0.426 | 0.423 |
| COS | kcal/kg °C | 0.250 | 0.248 | 0.246 | 0.246 | 0.245 | 0.243 | 0.243 | 0.242 | 0.240 | 0.240 |
| | kcal/Nm ³ °C | 0.680 | 0.684 | 0.668 | 0.668 | 0.666 | 0.660 | 0.660 | 0.658 | 0.652 | 0.652 |

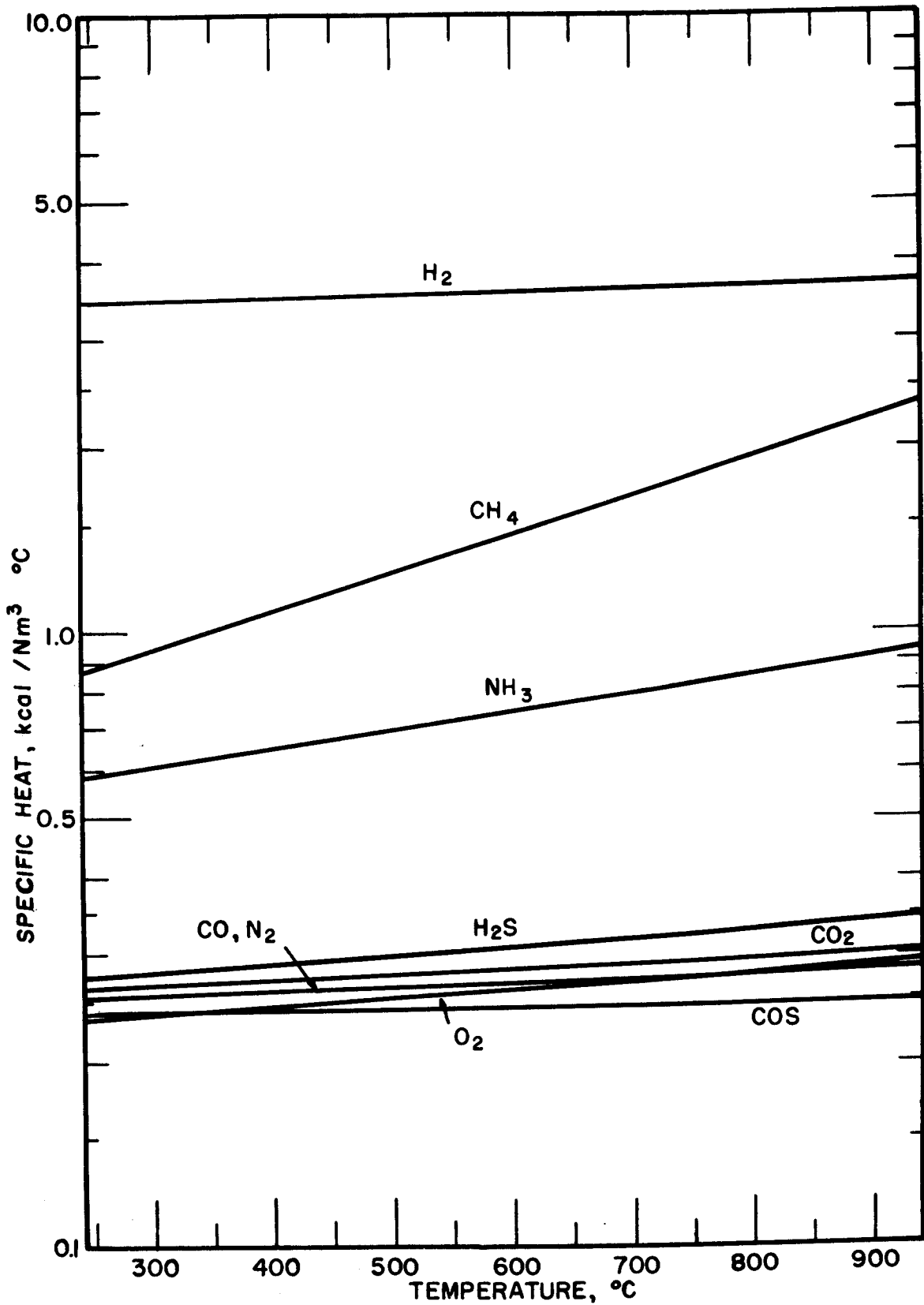


FIGURE 7 - SPECIFIC HEAT OF GASES VS TEMPERATURE

TABLE 18

Calculation of the Average Specific Heats of the Gases in Heat Exchanger No. 1
and Decomposer No. 1 from their Composition

| Component | Inlet Raw Gas in Heat Exchanger No. 1 (A&B) | | | Scrubbed Raw Gas in Heat Exchanger No. 1A. | | | Scrubbed Raw Gas in Decomposer No. 1. | |
|------------------|--|---|--|---|--|--|---|--|
| | vol % | Sp Ht, 830-126°C, kcal/Nm ³ °C | Product of vol % and Sp Ht, kcal/°C | vol % | Sp Ht, 20-830°C, kcal/Nm ³ °C | Product of vol % and Sp Ht, kcal/°C | Sp Ht, 830-850°C, kcal/Nm ³ °C | Product of vol % and Sp Ht, kcal/°C |
| CO ₂ | 11.739 | 0.552 | 0.0648 | - | - | - | - | - |
| CO | 78.571 | 0.333 | 0.2616 | 90.910 | 0.331 | 0.3009 | 0.352 | 0.3200 |
| H ₂ | 6.328 | 0.316 | 0.0200 | 7.386 | 0.314 | 0.0232 | 0.329 | 0.0243 |
| CH ₄ | 0.228 | 0.690 | 0.0016 | 0.259 | 0.674 | 0.0017 | 0.810 | 0.0021 |
| N ₂ | 1.232 | 0.332 | 0.0041 | 1.445 | 0.330 | 0.0048 | 0.351 | 0.0051 |
| NH ₃ | 0.302 | 0.528 | 0.0016 | - | - | - | - | - |
| H ₂ S | 0.542 | 0.456 | 0.0025 | - | - | - | - | - |
| COS | 1.058 | 0.660 | 0.0070 | - | - | - | - | - |
| | Average specific heat = 0.3632 | | | Average specific heat = 0.3306 | | | Av specific heat = 0.3515 | |

TABLE 19

Calculation of the Average Specific Heats of the Gases in Heat Exchanger No. 2 and Decomposer No. 2
from their Composition

| Component | CO ₂ -O ₂ Mixture to Gasifier-Heat Exchanger | | | Gas from Decomposer No. 1 | | Gas from Decomposer No. 1 in Heat Exchanger No. 2 | | Gas from Decomposer No. 1 in Decomposer No. 2 | |
|--------------------------------|--|---|---|---|--------|---|---|---|---|
| | vol % | Sp Ht, 460-830°C, kcal/Nm ³ °C | Product of vol % and Sp Ht, kcal/Nm ³ °C | Volume, Nm ³ per 100 Nm ³ raw gas | vol % | Sp Ht, 850-508°C, kcal/Nm ³ °C | Product of vol % and Sp Ht, kcal/Nm ³ °C | Sp Ht, 460-480°C, kcal/Nm ³ °C | Product of vol % and Sp Ht, kcal/Nm ³ °C |
| O ₂ | 33.145 | 0.390 | 0.1293 | - | - | - | - | - | - |
| CO ₂ | 64.669 | 0.569 | 0.3680 | 22.729 | 37.673 | 0.575 | 0.2166 | 0.554 | 0.2087 |
| CO | 0.024 | 0.341 | 0.0001 | 30.053 | 47.813 | 0.344 | 0.1714 | 0.334 | 0.1664 |
| H ₂ | 0.292 | 0.322 | 0.0009 | 6.135 | 10.169 | 0.324 | 0.0329 | 0.317 | 0.0322 |
| CH ₄ | 0.054 | 0.758 | 0.0004 | 0.215 | 0.356 | 0.761 | 0.0027 | 0.696 | 0.0025 |
| N ₂ | 1.816 | 0.340 | 0.0062 | 1.200 | 1.989 | 0.343 | 0.0068 | 0.333 | 0.0066 |
| Average Specific Heat = 0.5049 | | | | 60.332 | | Av Sp Ht = 0.4304 | | Av Sp Ht = 0.4614 | |

TABLE 20

Calculation of the Average Specific Heats of the Gases in Heat Exchanger No. 3 from their Composition

| Component | Gas from Decomposer No. 2 | | | | CO ₂ -O ₂ Mixture to Heat Exchanger No. 2 | | |
|-----------------|---|--------|--|--|---|--|--|
| | Volume, Nm ³ /100Nm ³ Raw Gas | vol % | Sp Ht, 480-30°C, kcal/Nm ³ °C | Product of vol % and Sp Ht, kcal/Nm ³ °C | vol % | Sp Ht, 20-460°C, kcal/Nm ³ °C | Product of vol % and Sp Ht, kcal/Nm ³ °C |
| O ₂ | - | | - | - | 33.145 | 0.336 | 0.1114 |
| CO ₂ | 37.529 | 82.422 | 0.526 | 0.4335 | 64.669 | 0.524 | 0.3389 |
| CO | 0.453 | 0.995 | 0.322 | 0.0032 | 0.024 | 0.320 | 0.0001 |
| H ₂ | 6.135 | 13.475 | 0.308 | 0.0415 | 0.292 | 0.307 | 0.0009 |
| CH ₄ | 0.215 | 0.472 | 0.623 | 0.0029 | 0.054 | 0.617 | 0.0003 |
| N ₂ | 1.200 | 2.636 | 0.321 | 0.0085 | 1.816 | 0.320 | 0.0058 |
| | 45.532 | | Average Specific Heat = 0.4896 | | Average Specific Heat = 0.4574 | | |

TABLE 21

Calculation of the Composition of the Scrubber No. 2 Gases

| Component | Solubility at 20°C and 760 Torr | Inlet Gas from Decomposer No. 2 | | Volume of Gas Dissolved | | Scrubber Let-down Gas vol % | Scrubbed Gas to Fluid Coker | |
|-----------------|---------------------------------------|------------------------------------|--|-------------------------------|---------------------------------|--|--------------------------------|--------|
| | | vol % | Partial pressure, kg/cm ² | l/l H ₂ O | l in 50 l H ₂ O * | | l/Nm ³ | vol % |
| CO ₂ | 0.74300 | 82.422 | 24.727 | 18.372 | 824.220 | 99.412 | - | - |
| CO | 0.02319 | 0.995 | 0.299 | 0.00693 | 0.347 | 0.042 | 9.53 | 5.619 |
| H ₂ | 0.01819 | 13.475 | 4.043 | 0.07354 | 3.677 | 0.443 | 130.32 | 76.691 |
| CH ₄ | 0.03308 | 0.472 | 0.142 | 0.00470 | 0.235 | 0.028 | 4.44 | 2.624 |
| N ₂ | 0.01545 | 2.636 | 0.791 | 0.01222 | 0.611 | 0.074 | 25.62 | 15.066 |
| | | 100.0 | 30.002 | | 829.090 | 100.0 | 170.910 | 100.0 |

* The amount of scrubbing water required is found by dividing the vol/Nm³ of the determining component (CO₂) in the inlet gas by the volume dissolved per litre of H₂O. In this case the calculation is $\frac{(82.422)(10)}{18.372} = 50$ l per Nm³ of inlet gas.

TABLE 22

Calculation of the Average Specific Heats of the CO₂-O₂ Mixture to the Gasifier From Its Composition

| Component | CO ₂ -O ₂ Mixture to Gasifier | | CO ₂ -O ₂ Mixture in Heat Exchanger No. 3 | | CO ₂ -O ₂ Mixture in Heat Exchanger No. 2 | | CO ₂ -O ₂ Mixture in Gasifier Heat Exchanger | |
|-----------------|---|--------|---|---|---|---|--|---|
| | Nm ³ /hr | vol % | Sp Ht, 20-460°C, kcal/Nm ³ °C | Product of vol % and Sp Ht, kcal/Nm ³ °C | Sp Ht, 460-840°C, kcal/Nm ³ °C | Product of vol % and Sp Ht, kcal/Nm ³ °C | Sp Ht, 833-1050°C, kcal/Nm ³ °C | Product of vol % and Sp Ht, kcal/Nm ³ °C |
| O ₂ | 480.359 | 33.145 | 0.336 | 0.1114 | 0.390 | 0.1293 | 0.422 | 0.1399 |
| CO ₂ | 938.393 | 64.669 | 0.524 | 0.3389 | 0.569 | 0.3680 | 0.603 | 0.3900 |
| CO | 0.442 | 0.024 | 0.320 | 0.0001 | 0.341 | 0.0001 | 0.358 | 0.0001 |
| H ₂ | 4.329 | 0.292 | 0.307 | 0.0009 | 0.322 | 0.0009 | 0.333 | 0.0010 |
| CH ₄ | 0.778 | 0.054 | 0.617 | 0.0003 | 0.758 | 0.0004 | 0.846 | 0.0005 |
| N ₂ | 26.357 | 1.816 | 0.320 | 0.0058 | 0.340 | 0.0062 | 0.357 | 0.0065 |
| | 1,451.068 | 100.0 | Av Sp Ht = | 0.4574 | Av Sp Ht = | 0.9049 | Av Sp Ht = | 0.5380 |

TABLE 23

Fuel Value of Purified Scrubber No. 1 Let-down Gas

| Component | vol % | Net Fuel Value, kcal/Nm ³ | Product of vol % and Net Fuel Value, kcal/Nm ³ |
|----------------------------------|--------|---|---|
| CO | 18.070 | 3020 | 545.70 |
| H ₂ | 1.141 | 2570 | 29.32 |
| CH ₄ | 0.074 | 8550 | 6.33 |
| Total fuel value of purified gas | | | = 581.35 kcal/Nm ³ |

fouling factor given by Nelson⁽²⁸⁾. The results of these calculations are given in Table 25. The heat density, in kcal/m² hr, was obtained by multiplying the combined film transfer rate by the average log temperature difference and these heat densities are also given in Table 25. The radiation heat transfer rates, given in Table 26 were obtained from the following formula⁽²⁶⁾:

TABLE 24

Calculation of the Heat Rates for Heat Transfer by Conduction and Radiation in Heat Exchangers and Decomposers

| | Heat Exchanger in Gasifier | Heat Exchanger No. 1A | Heat Exchanger No. 1B | Heat Exchanger No. 2 | Heat Exchanger No. 3 | Decomposer No. 1 | Decomposer No. 2 |
|--|--|--------------------------|--------------------------|--|--|---------------------|---------------------|
| INSIDE | | | | | | | |
| Heat source - gas | Raw Gas | Raw Gas | Raw Gas | Process Gas | Process Gas | Process Gas | Process Gas |
| Volume rate, Nm ³ /hr | 38,107.947 | 35,456.396 | 2,651.551 | 22,991.287 | 17,351.310 | 31,652.537 | 22,991.287 |
| Density, kg/Nm ³ | 1.275 | 1.275 | 1.275 | 1.487 | 1.691 | 1.164 | 1.487 |
| Mass rate, kg/hr | 48,587.636 | 45,206.905 | 3,380.728 | 34,257.018 | 29,341.065 | 36,843.553 | 34,257.018 |
| Specific heat, kcal/Nm ³ °C | 0.3926 | 0.3632 | 0.3632 | 0.4304 | 0.4896 | 0.3515 | 0.4164 |
| Temperature range, °C | 1,050-827 | 835-171 | 835-171 | 850-470 | 480-26 | 835-850 | 470-480 |
| Heat rate, kcal/hr | 3,333,497 | 8,550,848 | 639,447 | 3,760,271 | 3,856,821 | -166,888 | -95,736 |
| Heat source - chemical reaction | | | | | | Reaction Heat | Reaction Heat |
| Heat rate, kcal/hr | | | | | | 16,476,962 | 10,893,385 |
| TOTAL heat rate, kcal/hr | 3,333,497 | 8,550,848 | 639,447 | 3,760,271 | 3,856,821 | 16,310,074 | 10,797,649 |
| OUTSIDE | | | | | | | |
| Heat source - gas | CO ₂ - O ₂ Mixture | Process Gas | Hydrogen Gas | CO ₂ - O ₂ Mixture | CO ₂ - O ₂ Mixture | Recycle Gas | |
| Volume rate, Nm ³ /hr | 19,817.236 | 31,652.537 | 2,965.512 | 19,817.236 | 19,817.236 | 133,123.263 | |
| Density, kg/Nm ³ | 1.791 | 1.164 | 0.346 | 1.791 | 1.791 | 1.275 | |
| Mass rate, kg/hr | 35,492.670 | 36,843.553 | 1,026.067 | 35,492.670 | 35,492.670 | 170,397.773 | |
| Specific heat, kcal/Nm ³ °C | 0.5380 | 0.3306 | 0.3400 | 0.5049 | 0.4574 | 0.3632 | |
| Temperature range, °C | 818-1022 | 20-835 | 20-652 | 444-818 | 20-444 | 500-835 | |
| Heat rate, kcal/hr | 2,174,981 | 8,528,428 | 637,767 | 3,739,571 | 3,847,511 | 16,284,654 | |
| Heat source - solid or liquid | Fluid Coke | | | | | | Liquid Coker Feed |
| Density, kg/litre | | | | | | | 1.048 |
| Mass rate, kg/hr | 13,657.0 | | | | | | 61,931 |
| Specific heat, kcal/kg°C | 0.441 | | | | | | 0.6700 |
| Temperature range, °C | 833-1022 | | | | | | 160-420 |
| Heat rate, kcal/hr | 1,135,888 | | | | | | 10,787,361 |
| TOTAL heat rate, kcal/hr | 3,310,869 | 8,528,428 | 637,767 | 3,739,571 | 3,847,511 | 16,284,654 | 10,787,361 |
| Heat losses through shell wall, by diff., kcal/hr | 22,628 | 22,420 | 1,680 | 20,700 | 9,310 | 25,420 | 10,288 |

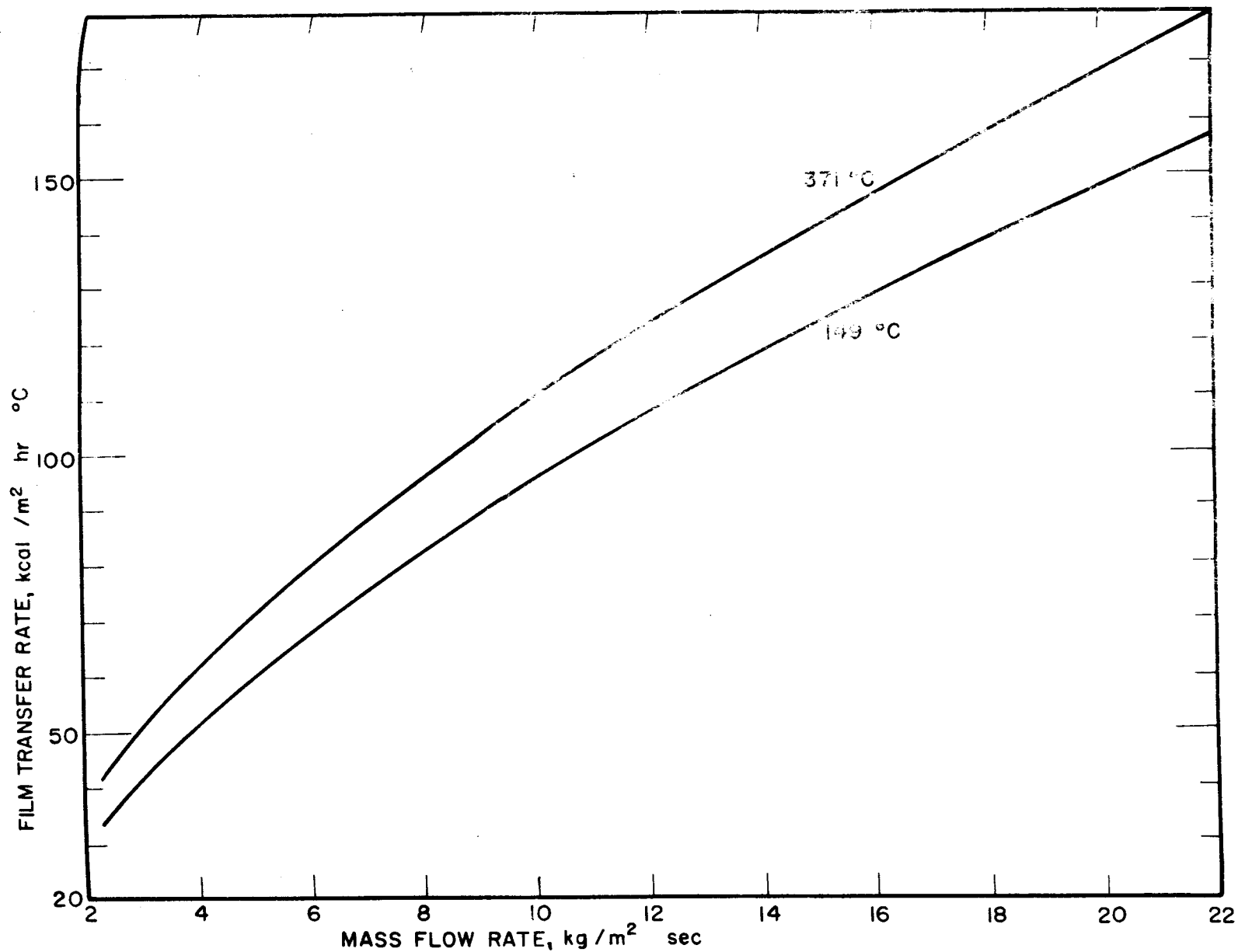


FIGURE 8 - FILM TRANSFER RATE VS MASS FLOW RATE OF GASES
IN THE RANGE FROM 20 TO 180 kcal/m² hr °C

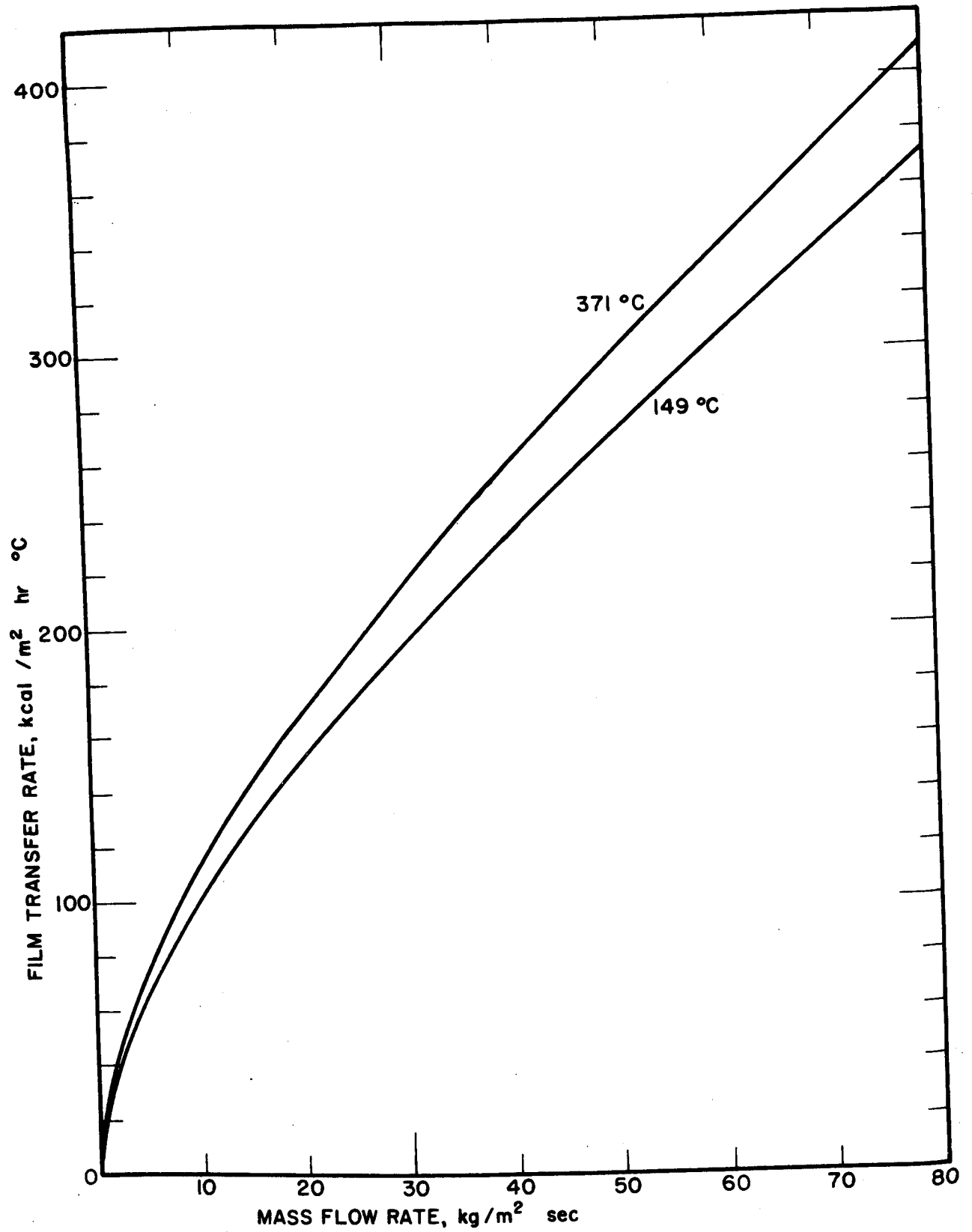


FIGURE 9- FILM TRANSFER RATE VS MASS FLOW RATE IN THE RANGE FROM 0 TO 400 k cal/ m² hr °C

TABLE 25

Calculation of the Film Transfer Rates for Heat Transfer by Conduction in Heat Exchangers and Decomposers

| | Heat Exchanger in Gasifier | Heat Exchanger No. 1A | Heat Exchanger No. 1B | Heat Exchanger No. 2 | Heat Exchanger No. 3 | Decomposer No. 1 | Decomposer No. 2 |
|--|-------------------------------|--------------------------|--------------------------|-------------------------|-------------------------|---------------------|---------------------|
| INSIDE | | | | | | | |
| Pressure, kg/cm ² | 30.5 | 30.0 | 31.5 | 26.5 | 32.5 | 27.3 | 25.8 |
| Mass rate, kg/hr | 48,587.636 | 36,843.553 | 1,026.067 | 34,257.018 | 29,341.065 | 36,843.553 | 34,257.018 |
| Cross - section, m ² | 2.41 | 2.56 | 0.173 | 1.252 | 1.805 | 1.495 | 1.480 |
| Mass velocity, kg/m ² sec | 5.60 | 4.12 | 4.76 | 7.60 | 4.51 | 7.03 | 6.43 |
| Film transfer rate, kcal/m ² hr °C | 64.0 | 51.6 | 57.0 | 79.0 | 55.0 | 75.0 | 70.8 |
| Fouling factor | 5 | 4 | 4 | 4 | 4 | 5 | 5 |
| Corrected film transfer rate, kcal/m ² hr °C | 48.4 | 43.9 | 46.4 | 58.5 | 45.0 | 54.5 | 52.3 |
| OUTSIDE | | | | | | | |
| Pressure, kg/cm ² | 31.5 | 28.0 | 28.0 | 31.5 | 25.0 | 29.3 | 32.0 |
| Mass rate, kg/hr | 35,492.670 | 45,206.905 | 3,380.728 | 35,492.670 | 35,492.670 | 170,397.773 | 45,892.000 |
| Cross - section, m ² | 2.27 | 2.56 | 0.173 | 1.252 | 1.805 | 1.495 | 1.485 |
| Mass velocity, kg/m ² sec | 4.35 | 4.925 | 5.59 | 7.88 | 5.46 | 31.7 | 8.60 |
| Film transfer rate, kcal/m ² hr °C | 54.0 | 59.0 | 64.0 | 81.0 | 63.0 | 199.4 | 8.60 |
| Fouling factor | 3 | 4 | 4 | 4 | 4 | 6 | 4 |
| Corrected film transfer rate, kcal/m ² hr °C | 46.4 | 47.7 | 50.9 | 59.4 | 50.3 | 90.9 | 64.3 |
| COMBINED INSIDE AND OUTSIDE | | | | | | | |
| Combined film transfer rate, kcal/m ² hr °C | 23.73 | 22.87 | 24.3 | 30.35 | 23.80 | 34.04 | 28.80 |
| Av log temperature difference, °C | 15.9 | 30.0 | 165.7 | 31.3 | 17.2 | 103.0 | 93.3 |
| Heat density, kcal/m ² hr | 377.31 | 686.10 | 4,026.51 | 949.96 | 409.36 | 3,506.12 | 2,687.04 |

TABLE 26

Calculation of the Heat Transfer Rates by Radiation in Heat Exchangers and Decomposers

| | Heat Exchanger in Gasifier | Heat Exchanger No. 1A | Heat Exchanger No. 1B | Heat Exchanger No. 2 | Heat Exchanger No. 3 | Decomposer No. 1 | Decomposer No. 2 |
|--|-------------------------------|--------------------------|--------------------------|-------------------------|-------------------------|---------------------|---------------------|
| To, °C | 924 | 503 | 503 | 629 | 232 | 668 | 296 |
| To/100, °K/100 | 11.97 | 7.76 | 7.76 | 9.02 | 5.05 | 9.41 | 5.69 |
| Ti, °C | 943 | 428 | 336 | 660 | 253 | 843 | 675 |
| Ti/100, °K/100 | 12.16 | 7.01 | 6.09 | 9.33 | 5.26 | 11.16 | 9.48 |
| Tm/100, °K/100 | 12.065 | 7.385 | 6.925 | 9.175 | 5.155 | 10.285 | 7.585 |
| log To/100 | 1.07809 | 0.88986 | 0.88986 | 0.95521 | 0.70329 | 0.97359 | 0.75511 |
| log Ti/100 | 1.08493 | 0.84572 | 0.78462 | 0.96988 | 0.72099 | 1.04766 | 0.97681 |
| log Tm/100 | 1.08153 | 0.86835 | 0.84042 | 0.96261 | 0.71223 | 1.01221 | 0.88010 |
| log (To/100) ⁴ | 4.31236 | 3.55944 | 3.55944 | 3.82084 | 2.81316 | 3.89436 | 3.02044 |
| log (Ti/100) ⁴ | 4.33972 | 3.38288 | 3.13848 | 3.87952 | 2.88396 | 4.19064 | 3.90724 |
| log (Tm/100) ⁴ | 4.32612 | 3.47340 | 3.36168 | 3.85044 | 2.84892 | 4.04884 | 3.52040 |
| (To/100) ⁴ | 20,538.0 | 3,626.1 | 3,626.1 | 6,619.7 | 650.37 | 7,841.8 | 1,048.2 |
| (Ti/100) ⁴ | 21,864.0 | 2,414.8 | 1,375.6 | 7,577.4 | 765.52 | 15,511.0 | 8,076.8 |
| (Tm/100) ⁴ | 21,189.0 | 2,974.4 | 2,299.7 | 7,086.7 | 706.18 | 11,190.0 | 3,314.4 |
| Qo = (To ⁴ - Tm ⁴) (10 ⁻⁸) (3.8) kcal/m ² hr | 2,473.8 | 2,476.5 | 5,040.3 | 1,774.6 | 1,220.8 | 12,723.2 | 8,611.6 |
| Qi = (Ti ⁴ - Tm ⁴) (10 ⁻⁸) (3.8) kcal/m ² hr | 2,565.0 | 2,126.5 | 3,511.6 | 1,864.7 | 2,254.9 | 16,419.8 | 18,097.1 |
| Combined heat transfer rate, kcal/m ² hr | 1,260.0 | 1,145.0 | 2,069.0 | 908.0 | 792.0 | 7,170.0 | 4,594.0 |

Note: To - average temperature outside tube bundle; Ti - average temperature inside tube bundle; Tm - average of To and Ti; Qo - heat transfer rate outside; Qi - heat transfer rate inside.

$$Q = C \left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4$$

where Q = heat transfer rate, kcal/m² hr,
 C = radiation factor, kcal/m² hr °K⁴ ,
 T_1 = higher temperature, °K,
 T_2 = lower temperature, °K.

The combined heat transfer rate for radiation was obtained from Kirchhoff's law as follows:

$$Q_c = \frac{1}{\frac{1}{Q_o} + \frac{1}{Q_i}}$$

where Q_c = combined heat transfer rate, kcal/m² hr,
 Q_o = heat transfer rate outside tube bundle,
 Q_i = heat transfer rate inside tube bundle.

The heat density for conduction and the heat transfer rate for radiation were added to obtain the combined heat transfer rate for conduction and radiation, in kcal/m²/hr. Then by dividing the heat rate by the combined heat transfer rate, the heat transfer area was found. The results of these calculations are shown in Table 27. From these areas and the data in Table 15, the dimensions of the heat exchangers and decomposers and the heat losses were obtained. The results of these calculations are also given in Table 27.

Gas Recirculators and Compressor

The power requirement of the gas recirculators and the compressor was calculated from the gas volume per hour, the operating pressures, and the kappa factor, according to the equation given in "Koppers Handbuch der Brennstofftechnik"⁽²⁹⁾. This equation is as follows:

TABLE 27

Calculation of the Size of Heat Exchangers and Decomposers

| | Heat Exchanger in Gasifier | Heat Exchanger No. 1A | Heat Exchanger No. 1B | Heat Exchanger No. 2 | Heat Exchanger No. 3 | Decomposer No. 1 | Decomposer No. 2 |
|---|-------------------------------|--------------------------|--------------------------|-------------------------|-------------------------|---------------------|---------------------|
| Heat rate, conduction and radiation, kcal/hr | 3,333,497 | 8,550,848 | 639,447 | 3,760,271 | 3,856,821 | 16,310,074 | 10,797,649 |
| Heat density, conduction, kcal/m ² hr | 377.31 | 686.10 | 4,026.51 | 949.96 | 409.36 | 3,506.12 | 2,687.04 |
| Heat transfer rate, radiation, kcal/m ² hr | 1,260.0 | 1,145.0 | 2,069.0 | 908.0 | 792.0 | 7,170.0 | 4,594.0 |
| Combined heat transfer rate, conduction and radiation, kcal/m ² hr | 1,637.31 | 1,831.10 | 6,095.51 | 1,857.96 | 1,201.36 | 10,676.12 | 7,281.04 |
| Heat transfer area required, m ² | 2,035.96 | 4,669.79 | 104.05 | 2,023.87 | 3,210.38 | 1,527.72 | 1,482.98 |
| Heat transfer area required, ft ² | 21,915.07 | 50,265.62 | 1,119.99 | 21,784.94 | 34,556.53 | 16,444.38 | 15,962.80 |
| Interior cross-section of shell, m ² | 5.43 | 5.74 | 0.1116 | 2.60 | 4.12 | 3.63 | 3.65 |
| Inside diameter of shell, m | 2.63 | 2.70 | 0.376 | 1.82 | 2.29 | 2.15 | 2.16 |
| Outside diameter of shell, m | 3.31 | 3.30 | 0.976 | 2.42 | 2.89 | 2.75 | 2.76 |
| Height of shell, m | 7.04 | 10.065 | 10.065 | 10.065 | 10.065 | 10.065 | 10.065 |
| Exterior surface area of shell, m ² | 65.6 | 94.7 | 7.83 | 70.3 | 85.1 | 80.7 | 80.9 |
| Av temperature drop across shell wall, °C | 924 | 503 | 503 | 629 | 232 | 668 | 270 |
| Overall heat transfer coefficient through shell wall, kcal/m ² /hr °C | 0.471 | 0.471 | 0.471 | 0.471 | 0.471 | 0.471 | 0.471 |
| Heat losses through shell wall, calculated, kcal/hr | 25,900 | 22,450 | 1,090 | 20,700 | 9,310 | 25,420 | 10,300 |
| Heat losses through shell wall, by diff (from Table 24), kcal/hr | 22,628 | 22,420 | 1,680 | 20,700 | 9,310 | 25,420 | 10,288 |

$$L_{\text{adiab.}}, \text{ in hp} = (n) (10,000) \frac{\kappa}{\kappa-1} (P_1) \left[\left(\frac{P_2}{P_1} \right)^{\frac{\kappa-1}{n\kappa}} - 1 \right] \frac{Q}{(3,600) (75) (0.72)}$$

$$= (0.0508) (n) \frac{\kappa}{\kappa-1} (P_1) \left[\left(\frac{P_2}{P_1} \right)^{\frac{\kappa-1}{n\kappa}} - 1 \right] Q$$

where L = theoretical work in hp per m³/hr gas,
n = number of stages,
κ = Kappa factor = C_p/C_v,
P₁ = suction pressure, atmospheres absolute,
P₂ = delivery pressure, atmospheres absolute,
Q = gas volume, m³/hr.

The results of these calculations are presented in Table 28.

The recirculator for the 171,231.21 Nm³/hr of raw gas recycle requires a driving turbine or electric motor of about 2,280 hp. The recirculator for the 2,965.512 Nm³/hr of coker fluidizing gas requires only a 52-hp electric motor. However, the compression of the 19,817.24 Nm³/hr CO₂-O₂ mixture from 1.3 (5 psi over-pressure) to 35 kg/cm² requires 4,430 hp with an efficiency factor of 67%. The expansion of the let-down streams from the two scrubbers yields only 2,165 hp with the same efficiency. Since the requirement for the compression step of the expansion turbines is 4,883 hp, then the difference of 2,718 hp must be delivered by a steam turbine (which also serves to pressurize the whole system for start-up).

Pressure Gasifier

The estimation of the required volume of the pressure gasifier (excluding the coke heater but including the heat exchanger) and the required quantity of steel is based on figures given in "Fluidisation in the Development of Gas-Making Processes" by Horsler and Thompson (21). A cross-sectional view of the gasifier is given in Figure 10.

TABLE 28

Power Requirements and Cost of Gas Recirculators and Compressor

| | Recirculator for raw gas recycle | Recirculator for coker fluidizing gas | Compressor for CO ₂ -O ₂ mixture |
|--|-------------------------------------|--|---|
| Gas volume, Nm ³ /hr | 133,123.263 (1) | 2,965.512 (3) | 12,888.821 (CO ₂) |
| " " " | <u>38,107.947</u> (2) | - | <u>6,928.415</u> (O ₂) |
| Total gas volume, Q, Nm ³ /hr | 171,231.210 | 2,965.512 | 19,817.236 |
| Volume at operating conditions, m ³ /hr | 16,718.673 | 129.909 | 21,269.047 |
| Suction temperature, °C | 500 | 20 | 20 |
| Suction pressure, P ₁ , kg/cm ² | 29.0 | 21.0 | 1.3 |
| Discharge pressure, P ₂ , kg/cm ² | 32.0 | 30.0 | 35.0 |
| Number of stages, n | 1 | 1 | 3 |
| $\frac{\kappa}{\kappa-1}$ | 3.70 | 3.46 | 4.08 |
| $\frac{\kappa-1}{n\kappa}$ | 0.270 | 0.290 | 0.0817 |
| Power requirement, hp | 2,278.7 | 51.8 | 4,430.4 |
| " " , kW | 1,677 | 38.1 | 3,260.8 |
| Cost of equipment, including driver, installed, at (\$210/hp) ^{0.87} . | \$174,299.00 | \$6,810.00 | \$317,351.00 |

(1) Raw gas from decomposer No. 1.

(2) Raw gas from gasifier.

(3) Scrubbed gas to fluid coker.

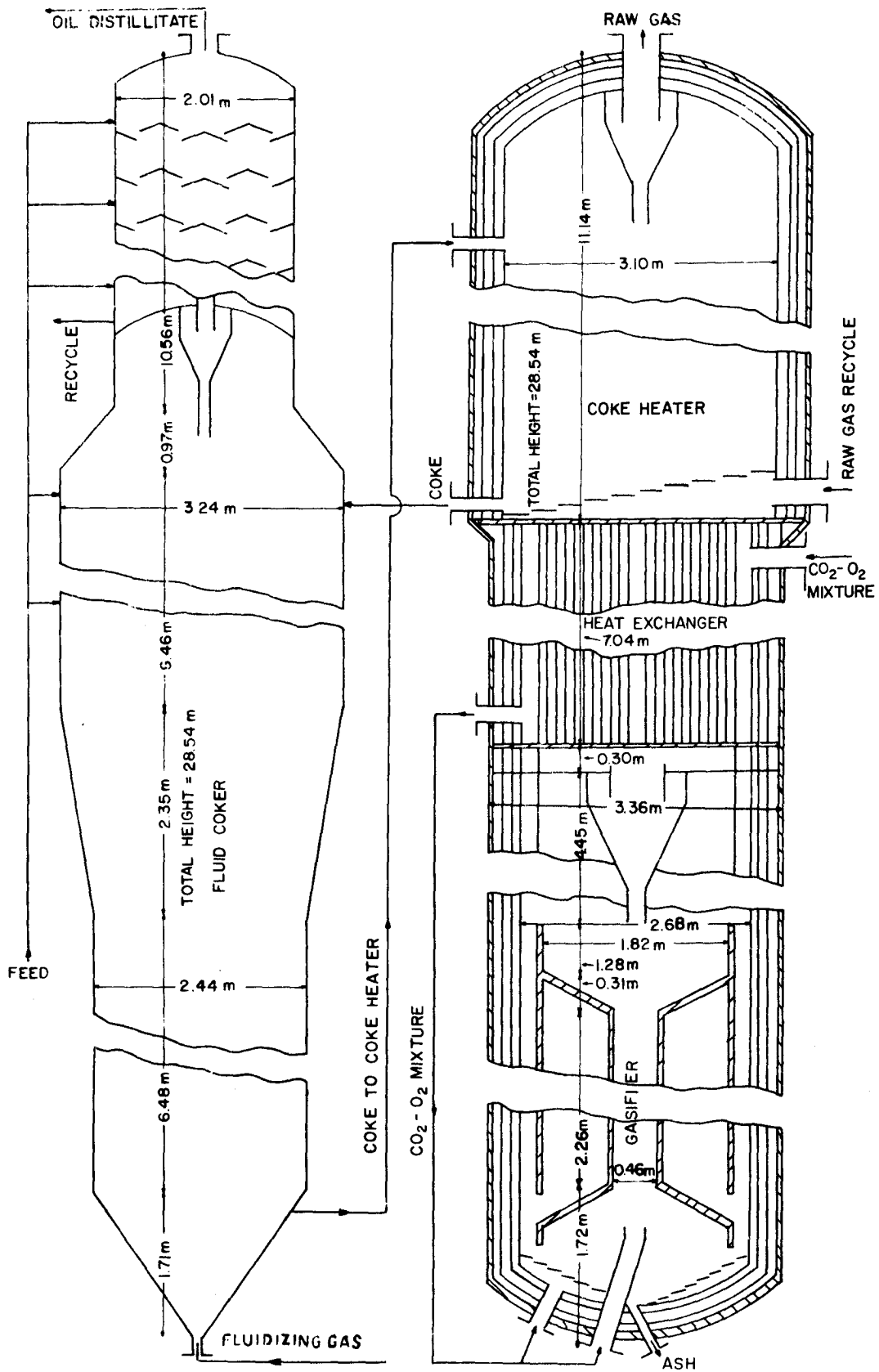


FIGURE 10 - FLUID COKER WITH COMBINED COKE HEATER - HEAT EXCHANGER - GASIFIER

The corresponding calculations are presented as follows:

Volume of gas processed at operating conditions

$$= \frac{(38,107.947 \text{ Nm}^3/\text{hr raw gas}) (1050 + 273)}{(29.05) (273)}$$
$$= 6,357.211 \text{ m}^3/\text{hr} = 1.7659 \text{ m}^3/\text{sec}.$$

Reaction volume required at 14.25 seconds of retention time

$$= (1.7659) (14.25) = 25.1641 \text{ m}^3.$$

At a main bed (gas) velocity of 1.03 ft/sec or 0.313 m/sec, the required cross-section is

$$\frac{1.7659}{0.313} = 5.64 \text{ m}^2,$$

which corresponds to a shaft diameter of 2.68 m.

From the required reaction volume and the cross-section, the height of the main bed shaft is:

$$\frac{25.1641}{5.64 \text{ m}^2} = 4.45 \text{ m}.$$

Since the gas velocity in the riser is 35 ft/sec or 10.68 m/sec, the cross-section of the riser is:

$$\frac{1.7659}{10.68} = 0.1653 \text{ m}^2$$

and a riser diameter of 0.458 m (18.0 inch) is required.

If 9.05 lb of coke particles per ft³ of gas, or 145.4 kg/m³, are in the riser and

$$\frac{(13,657 \text{ kg/hr}) (14.25 \text{ sec})}{3,600 \text{ sec/hr}} = 54.06 \text{ kg of coke}$$

must be processed (gasified) in 14.25 seconds, the gas volume required in the riser for the fluidization and the gasification of the coke particles is:

$$\frac{54.06 \text{ kg/hr}}{145.4 \text{ kg/m}^3} = 0.372 \text{ m}^3.$$

From the cross-section and volume the height of the riser is found to be:

$$\frac{0.372 \text{ m}^3}{0.1653 \text{ m}^2} = 2.26 \text{ m}.$$

The steel required for the pressure gasifier, including the heat

gasifier are concerned. The cost of the dust precipitator is found from its capacity, and the cost of the compressor, gas recirculators and pumps from their power consumption and pressure rating. All the above costs, with the exception of that for the gasifier, were found from graphs in Chilton's "Cost Engineering in the Process Industries"⁽⁴⁾. Table 29 gives a compilation of the costs of all the equipment required. In this table the cost figures are given for the year 1968. These were calculated from cost figures of previous years, obtained from various sources, by multiplying by a factor of 1.05 per year. The cost of \$85,000 for the transformer, switching-station, flare and safety equipment (excluding inert gas generator) was obtained by reducing the \$93,000 used for the desulphurization of fluid coke by combustion heating by \$8,000, since CO₂ is available directly from the process and nitrogen from the oxygen plant. As the cost of the fluid coker, including the coke heater, already includes the cost of this equipment, it is considered that the portion required solely for the carbon black plant can be reduced to 25% of this value.

The calculation of the approximate cost of the pressure gasifier, including the heat exchanger, is as follows:

| | |
|---|--------------|
| Total mild steel, shaped and welded, | |
| 70.600 tons, \$1,825/ton | \$128,845.00 |
| Total Sicromal steel, shaped and welded, | |
| 22.630 tons, \$5,475/ton | 123,899.00 |
| Insulating bricks, in place, | |
| 32.732 tons, \$247/ton | 8,085.00 |
| Insulating bricks, high temperature, in place, | |
| 9.957 tons, \$988/ton | 9,838.00 |
| Total cost, including 25% for contingencies | \$270,667.00 |

From the total purchased cost of equipment the physical plant cost and fixed investment were found by multiplication with factors also given in Chilton's "Cost Engineering in the Process Industries"⁽⁴⁾. The results are given in Table 30.

TABLE 29

List of Equipment, Size, and Purchased Costs for the Production of Carbon Black

| No. | Type of Equipment | Size, Capacity | Purchased Cost |
|--|--|------------------------|----------------|
| 1 | Fluid gasifier | 328 tons coke/day | \$ 270,667 |
| 1 | Heat exchanger, Sicromal bundle, \$7.95/ft ² | 21,915 ft ² | 174,224 |
| 1 | Gas recirculator with 15 hp driver, 30.5 to 31.5 kg/cm ² | 100 scfm | 3,260 |
| 1 | Cyclone dust separator, \$0.285/cfm | 9,840 cfm | 2,791 |
| 1 | Electrostatic precipitator, \$0.85/cfm | 9,840 cfm | 8,364 |
| 1 | Heat exchanger, floating head, insulated shell, 450 psi, 316 SS bundle, \$7.95/ft ² | 50,266 ft ² | 399,615 |
| 1 | Heat exchanger, same as before, \$12.26 ft ² | 1,120 ft ² | 13,731 |
| 1 | Heat exchanger, same as before, \$7.95/ft ² | 21,784 ft ² | 173,183 |
| 1 | Heat exchanger, same as before, \$7.95/ft ² | 34,512 ft ² | 274,370 |
| 1 | Cascade cooler, \$8.57/ft ² | 1,467 ft ² | 12,572 |
| 2 | Decomposers, 316 SS bundle, 2-inch Δ-grid, insulated shell, 450 psi, ionizing wires, \$12.26/ft ² | 16,444 ft ² | 403,207 |
| 2 | Scrubbing towers, 3 ft ID, 60 ft high, 450 psi | 424 ft ³ | 61,337 |
| 1 | Gas recirculator, ΔP = 42.6 psi, 450 psi, 500°C | 2,279 hp | 174,299 |
| 1 | Gas recirculator, ΔP = 128 psi, with driver | 51.8 hp | 7,371 |
| 1 | Gas compressor, ΔP = 497 psi, with driver | 4,430 hp | 345,588 |
| 1 | Scrubber water pump + expansion turbine + 2,750 kW motor (or turbine) | 7,800 gpm | 53,525 |
| 1 | Scrubber water pump + expansion turbine + 1,230 kW motor (or turbine) | 3,175 gpm | 26,649 |
| 1 | Receiver-separator-suction tank, H ₂ O | 2,000 gal | 4,536 |
| 1 | Suction tank for DMASV | 1,000 gal | 1,701 |
| 1 | Scrubber tower, 2 ft ID, 15 ft high, for S removal | 47.2 ft ³ | 1,446 |
| 1 | Scrubber tower, 2 ft ID, 15 ft high, for aeration | 47.2 ft ³ | 1,446 |
| 1 | Sulphur filter | 5 m ² | 7,938 |
| 1 | Solution recycle pump, 316 SS + motor | 15 hp | 8,215 |
| 1 | H ₂ SO ₄ settler-scrubber, for NH ₃ removal | 2,000 gal | 18,144 |
| 1 | Sulphur storage shed + equipment, \$30/ft ² | 2,000 ft ² | 60,000 |
| 1 | Ammonium sulphate storage shed + equipment, \$20/ft ² | 10,000 ft ² | 200,000 |
| | Portion of transformer, switching-station, flare and safety equipment, 25% of \$85,000 | | 21,250 |
| Total purchased cost less oxygen plant and less fluid coker* | | | \$2,729,778 |
| 1 | Oxygen plant complete, 95% O ₂ at 5 psi | 235.8 ton/day | 3,775,080 |
| Total purchased cost including oxygen plant, but less fluid coker* | | | \$6,504,858 |
| 1 | Fluid coker*, complete with site utilities, offsite facilities, etc. | 65,982 bbl/day | \$9,461,300 |

* Including coke heater.

TABLE 30

Compilation of the Physical Plant Cost and Fixed Investment
for the Production of Carbon Black

| | | | |
|--|-------|-------------------|--------------|
| Purchased cost of equipment in 1968 | | | \$ 2,729,778 |
| Engineering + installation | 25% | of purchased cost | 682,445 |
| Piping, valves, supports, etc. | 25% | " | 682,445 |
| Instrumentation, service facilities | 22.7% | " | 619,660 |
| Electrical installations | 9.1% | " | 248,410 |
| Buildings, foundations, including services | 18.2% | " | 496,820 |
| Land and yard improvements | 4.5% | " | 122,840 |
| Insulation | 5.7% | " | 155,597 |
| Utilities and other costs | 47.7% | " | 1,302,104 |
| ----- | | | |
| Physical plant cost not including oxygen plant and fluid coker | | | 7,040,099 |
| ----- | | | |
| Oxygen plant complete | | | 3,775,080 |
| ----- | | | |
| Total physical plant cost | | | 10,815,179 |
| Cost of additional land (10 acres at \$5,000.00) | | | 50,000 |
| ----- | | | |

The physical plant cost, including oxygen facilities, would be approximately \$10,815,000 where the oxygen plant is considered a separate entity. Since, however, the latter will be integrated in one plant together with the fluid coker, gas generation, purification, and carbon black production, the equipment as well as operating costs⁽⁴⁾ could eventually be reduced. The investment cost for a standard furnace carbon black (from naphtha) plant is \$145.42 per annual ton in 1960⁽⁴⁾. In 1968 this cost would probably have to be increased by a factor of 1.05⁸, giving \$217.84. This means that a plant for the production of 62,000 annual tons of carbon black from naphtha would have cost in 1968 about \$13,506,000, which is about \$2,691,000, or 24.9%, more than the additions to a fluid coker described in this report.

Since the carbon black plant with the oxygen plant is operated in conjunction with a fluid coker and both can be fully automatized, the operating labour is almost nil. The labour is assumed to be required for maintenance, safety, cleaning, and for shipping the products and by-products.

Table 31 represents a compilation of the manufacturing cost, and Table 32 shows the cost per year and per ton of carbon black product after applying the credits for the by-products.

Conclusions

Table 32 shows that the cost of producing carbon black from refinery residuum is \$32.76 per ton of carbon black, or 1.5 cents per pound. At the present market price for carbon black of about 6.35 cents per lb, or \$140.00 per metric ton, there seems to be an attractive profit margin for the process described in this report, provided the assumptions made with respect to heat transfer rates and the speeds of reaction can be validated.

If one gallon of naphtha costs at the refinery 17.6 cents and yields 5.8 lb of carbon black, then, for one metric ton of carbon black, the cost of this raw material alone (380 gal) will be \$66.80. Even without the credits for by-products including gases, the total cost for the production of carbon black from refinery vacuum residuum of \$58.59 per ton of carbon black is lower than the above cost by 12.3%.

TABLE 31

Manufacturing Costs for the Production of Carbon Black

| | Cost per year | Cost per ton |
|---|------------------|-----------------|
| Labour a) for carbon black, (0.2 man-hours per ton) (184.9 tons/day)(365 days) at \$3.50/man-hr | \$ 48,618 | \$ 0.7841 |
| b) for by-products, (0.5 man-hours per ton) (23.2 tons/day)(365 days) at \$3.50/man-hr | 14,697 | 0.2370 |
| Supervision, 20% of labour | 12,663 | 0.2042 |
| Maintenance, 1.5% of physical plant cost | 105,601 | 1.7032 |
| Plant supplies, 15% of maintenance | 15,840 | 0.2555 |
| Utilities, (6,219 kW) (8,760 hr) at 0.25¢/kWh (14,000 gal/hr water) (8,760 hr) at 15¢/1,000 gal | 136,196 | 2.1967 |
| | 18,396 | 0.2967 |
| Direct Manufacturing Cost | 352,011 | 5.6774 |
| Payroll overhead, 17% of labour | 12,933 | 0.2085 |
| Laboratory, 15% of labour | 11,412 | 0.1841 |
| Plant overhead, 100% of labour | 48,618 | 0.7841 |
| Shipping costs, 0.8¢/lb or \$17.60/ton | 1,091,200 | 17.6000 |
| Indirect Manufacturing Cost | 1,164,163 | 18.7767 |
| Property taxes, 1.5% of physical plant cost | 105,601 | 1.7032 |
| Insurance, 1.0% of physical plant cost | 70,401 | 1.1355 |
| Depreciation, 3% and interest, 8% | 774,411 | 12.4905 |
| Fixed Manufacturing Cost | 950,413 | 15.3292 |
| Cost of oxygen at 12% profit, 235.8 tons/day at \$10.32/ton and 335 days/year including capital costs, maintenance, labour, and utilities | 815,208 | 13.1485 |
| Total Manufacturing Cost | 3,281,795 | 52.9318 |

TABLE 32

Cost of Production of Carbon Black

| | Per year | Per ton |
|--|------------------|----------------|
| Total manufacturing cost | \$3,281,795 | \$52.9318 |
| Crude petroleum coke (10,907 ton/hr)(8,040 hr/yr) at \$4.00/ton | 350,769 | 5.6576 |
| Total Expenditures | 3,632,564 | 58.5894 |
| Credits for | | |
| a) Sulphur, (0.8713 ton/hr)(8,040 hr/yr) at \$32.00/ton | 224,168 | 3.6156 |
| b) Ammonia, (0.0874 ton/hr)(8,040 hr/yr) at \$85.00/ton | 59,729 | 0.9634 |
| c) Fuel gas, (3.79305 x 10 ⁶ kcal/hr)(8,040 hr/yr) at \$37.20/10 ⁶ kcal (in eastern locations) | 1,134,456 | 18.2977 |
| d) H ₂ enriched gas (calculated as 100% H ₂), (2,274.3/Nm ³ /hr)(8,040 hr/yr) at \$0.01/Nm ³ | 182,854 | 2.9493 |
| Total Credits | 1,601,207 | 25.8260 |
| Total Cost of Carbon Black | 2,031,357 | 32.7634 |

It is, of course, also possible to convert cheap lignite coal in a pressure gas producer — like the Lurgi or Totzek gas generators — to carbon monoxide and produce technically pure carbon black with otherwise the same equipment. The financial aspects would be about the same as with refinery residuum, since the price per ton of starting material is approximately the same.

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