FORMCOKE PREPARATION IN CLEAN-COKE PROCESS

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The Clean-Coke Process being developed by U. S. Steel under contract with the U. S. Government (Energy Research and Development Administration) has been described previously.[1)*] Chemicals, fuels, and coke are the major products. However, an important phase of the Clean-Coke project is the ability to make an acceptable metallurgical coke from desulfurized char and heavy residual oils from the process. Of the various types of agglomeration (briquetting, pelletizing, nodulizing, or extrusion) considered, pelletizing appeared to have the best potential for more easily producing a superior product at the most reasonable cost by using char and binder derived from the process. The char as characterized in bench scale studies is low in density with a large percentage of cenospheres. Binder is available in large quantities. An advantage of producing coke by such a formcoke process is the reduction of pollution problems normally encountered in the conventional coke making process. The steps required for coke preparation will be carried out in a closed system with the off gases collected and returned to be processed through a common system. As a result, atmospheric pollution is practically non-existent.

Because the fluid-bed char-making unit was not yet constructed to produce desulfurized char at the time the coke-making phase of the process was initiated, char was produced in a

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* See References.

four-inch fluid-bed carbonizer using nitrogen as the fluidizing gas. Also, simulated binder was used because a binder was not available from the process in the quantity required for the coke-making studies. This paper presents the development of this method and shows some of the factors influencing the resultant coke properties.

Materials

Illinois No. 6 Seam coal, obtained from Franklin County, Illinois and washed at a 1.35 specific gravity, was charred in a fluid bed to a volatile matter content of 9 to 12 percent. This char was made by batch operation at a final bed temperature of 1150 F in an air-nitrogen fluidizing gas. Photomicrographs of the char are shown in Figure 1. The coal and char were nominally minus 10-mesh in size.

Various binders were used to determine how their properties would affect the resultant coke properties. The characteristics of these binders are listed in Table I. Some of the binders represent the type of binders available from the process whereas others represent binders from other sources having a wide range of properties.

Pelletization

A 24-inch pelletizing disc with a continuous-heated, (300 - 350 F) solids feeding system was used to study the pelletization of char fines with a heavy residual oil binder. The binder was heated in a surge tank and sprayed on the solids to form the pellets. Figure 2 shows the equipment installed for the present work.

Strong green pellets of the desired size (2- by 3/4-inch) were produced from all test binders by regulating the disc conditions, the temperature of the binder and the solids, and by changing the properties of the binder. Test conditions for typical runs are listed in Table II. The percentages of binder required increased as the fineness of the solid material was increased and generally made up about 30 percent of the mix except for the pellets made with fluxed coal extract. The reason for the need to use 38 percent of the fluxed-coal extract binder with the minus 28-mesh char is not known. The recycle material was reduced to about 10 percent in the later runs. The pellets are soft as they are discharged hot from the disc, but they can fall 3 to 6 feet without changing their shape. When they cool they become hard and have a nominal 350-pound crushing strength. A test in the ASTM shatter machine showed no degradation of cold green pellets at room temperature when dropped four times.

Studies were conducted with coke fines and coal tar pitch to determine factors affecting pelletizing rate. It was necessary to provide multiple sprays and solid feeders for feeding the disc. In short runs, 3.5 pounds per minute of plus 3/4-inch green pellets were produced. Test data indicate that about 12 to 15 tons per hour could be produced on a 20-foot disc.

Pretreatment and Carbonization of Pellets

With no pretreatment (curing) the green pellets agglomerated together during carbonization because the binder became soft and melted. In addition, any shearing action disintegrated the pellets to fines during the heating period while the pellets were soft. Preliminary studies showed that the pellets became soft at about 250 F and then hardened at about 900 F in the absence of oxygen. Tests also showed that pellets would harden permanently at 500 F in the presence of oxygen. Larger scale tests were then conducted in different types of equipment (such as a vertical retort, small test coke oven, and a stationary grate) to simulate the various methods that might be used for treating (curing) the pellets.

Pretreatment of the green pellets had to be initially conducted in shallow beds (two pellet depth) for long treating periods (3 to 5 hours). During these studies, it was found that mixing the pellets with an inert supporting medium reduced agglomeration, permitted deeper beds, and allowed faster heating rates to be used without cracking or destroying the pellets. Char fines or sized coke pellets (up to 3/4-inch top size) were used as media. The following methods were found effective in pretreating the green pellets:

1) Indirect heating in a Brennstoff Technik[2)] type coke oven which is relatively narrow (from 60 to 125 mm wide) and has walls made of iron, resulting in very fast heating rates. Pellets were heated from 900 to 1100 F in 1 and 3/4 hours. Agglomeration was prevented by mixing about 50 percent of 1/8 x 0 char as a supporting medium.

2) Direct heating in an intermittent vertical retort with 50 percent of a 1/2- by 1/4-inch supporting coke medium to 900 F in an inert atmosphere and to 500 F in an oxygen atmosphere for 1 and 3/4 hours (tested in bed depths up to 8-feet).

3) Direct heating on a grate with 50 percent of a 1/2- by 1/4-inch supporting coke medium to 900 F in an inert atmosphere and to 500 F in an oxygen atmosphere for 1-1/2 hours (tested in bed depths up to 18-inches).

Because shearing of the pellets is minimized in curing on a traveling grate, a grate using a 1/2- by 1/4-inch supporting coke medium and an oxygen atmosphere was selected as the most suitable equipment to use. A curing pot was installed for the present studies. Figure 3 is a diagram of the curing pot system.

When the pellets are cured or pretreated properly, they are sufficiently strong to withstand handling and will not soften upon further heating in the coking step. These treated pellets have been successfully coked in a continuous coking kiln by using inert gases to coke the pellets. The coked pellets have a good appearance (very few cracks and a metallic, smooth surface) with 97 to 100 percent of the pellets being recovered after coking to 1800 F. The normal yield obtained after driving off the volatiles of the green pellets in both the pretreatment and coking steps is about 70 percent. A method was also found to coke green pellets to 1800 F by using 50 percent 1/8-inch by 0 supporting char medium in a Brennstoff-Technik type coke oven for 5-1/2 hours. However, such a method would be expensive and it would be difficult to control pollution when discharging and quenching the coke and medium. Therefore, a continuous vertical coking kiln was built for the present studies. This kiln is shown in Figure 4.

Properties of Coke Pellets

The tests used to evaluate the quality of the coke pellets were tumbler strength, crushing strength (total force on whole pellet), compressive strength, and apparent specific gravity. Because of the large quantity of sample required for the ASTM tumbler test, the number of tests was minimized. However a good relationship was found between crushing strength and the hardness value (plus 1/4-in.) determined from the tumbler test, Figure 5. A discussion follows on some of the factors affecting the resultant coke properties.

Type of Binder

Table III shows some physical properties of formcokes produced from the various types of binders at similar conditions. The type of binder did have a significant effect on the properties of the resultant formcoke. It was possible to improve the effectiveness of some binders by using additives such as carbon black or coal or by air blowing. The strength of the formcokes generally increased as the carbon to hydrogen ratio and the Quinoline Insoluble content increased in the binder.

Size Consist of Char

The effect of grinding the char to finer sizes is shown in Table IV. As noted, the strength of the formcoke increased as the char was pulverized more finely. When the char containing large cenospheres and an open structure (see Fig. 1) is used in preparing the pellets, a weak formcoke is obtained. However, when these char particles are crushed to eliminate the cenospheres and puffy structure, the coke is improved considerably.

Type of Pretreatment and Carbonization

The type of pretreatment and carbonization did not appear to have a significant effect on the properties of the formcoke when the design conditions were used. A few typical results for the sample pellets treated in different ways are listed in Table V. From the data obtained to date, the final temperature within narrow ranges (1750 to 1950) had only a slight effect on coke properties.

Evaluation of Coke Pellets for Metallurgical Use

The method developed to produce a good quality coke pellet consisted of pelletizing finely ground char by spraying a heavy residual oil binder on a disc pelletizer. These green pellets are combined with 1/2 by 1/4 inch coke medium and then cured on a grate with an oxygen rich gas to 500 F in 1-1/2 to 2 hours. The cured pellets are then screened from the medium and coked to about 1800 F in a vertical coking kiln in 2-1/2 hours. A flow diagram of the coke preparation step is illustrated in Figure 6.

Using these conditions, several hundred pounds of formcoke pellets were produced; a sample of the pellets is shown in Figure 7. The physical and chemical properties of these formcoke pellets were tested for comparison with metallurgical coke and another type of formcoke that had been used successfully in a blast furnace test. The test results are listed in Table VI. From these test data, it can be concluded that these formcoke pellets will make a good blast furnace coke. The good quality of coke obtained in the Clean-Coke Process results from 1) the fine pulverization of the char to break it down to the denser wall sections, 2) the use of sufficient quantities of binder to wet the solid particles, and 3) the intimate distribution of char and binder to obtain maximum strength. The photomicrographs in Figure 8 show the good microstructure of the formcoke and the good distribution of the materials.

A unique method has been developed to process char and binder derived from the process into a good quality formcoke. Attaining a high grade product enhances the overall potential of the Clean-Coke Process. Currently, information from process-development units is being used in the design of a pilot plant capable of processing four tons of coal per hour.

References

1. K. A. Schowalter and N. S. Boodman, "The Clean-Coke Process for Metallurgical Coke," Chemical Engineering Progress, Vol. 70, No. 6, June, 1974, pp. 76-82.

2. D. C. Rhys Jones, "Briquetting," Chemistry of Coal Utilization, Sys. Vosl. H. H. Lowry Ed., John Wiley and Sons, 1963, pp. 675-753.

Table I

Selected Properties of Experimental Binders for Coke Pellets

	Asphalt AC 2000	Asphalt RC 800	Coal-tar Pitch	Coal-Digestion Pitch	Fluxed Coal Extract (De-ashed) Coal Blend)	Pipe Line Enamelling Pitch
Asphaltene Content, wt%	1.4	1.6	CNBD*	CNBD	CNBD	NA
Viscosity @ 60 C poise	1900	634	167	Non-Newtonian	310	NA
Softening Point, Ring and Ball, C	49.4	14.8	34.2	84.0	42.3	51.5
Coking Value, wt %	19.4	17.6	36.4	29.4	29.9	NA
Benzene Insoluble	0.1	0.1	13.9	22.3	19.2	10.5
Quinoline Insoluble	0.0	0.4	6.5	CNBD	0.4	3.5
Carbon/Hydrogen Ratio	0.67	0.66	1.60	1.38	1.37	NA

* Could not be determined.

NA = Not available on sample used.

Table II

Pelletizing Conditions to Produce Green Pellets

Solids, Size, 100% minus	Char					
	1/8 in.	28-mesh	100 mesh	28 mesh	28 mesh	100 mesh
% Char or Coke	60	60	60	60	53	57
% Pitch Coke	13	10	7	11	9	9
% Binder	27	30	33	29	38	34
Type Binder	Coal-Tar Pitch	Coal-Tar Pitch	Coal-Tar Pitch	Asphalt (AC2000)	Fluxed Coal Extract	Coal Digested Pitch
Temp of Binder	360	360	365	350	370	370
Disc Angle, degrees	41	40	38	42	40	38
Disc Speed, rpm	30	30	30	30	30	30
% Recycle (Minus 3/4-inch material)	NA	20	NA	10	12	4
Green Pellet App Sp Gr	1.05	1.18	1.25	0.91	NA	NA

NA = Not Available

Table III

Effect of Binder Type on Strength of Resultant Coke Pellet

Type of Binder	Coal-Tar Pitch		Asphalt RE800		Coal Digested Pitch		Fluxed Coal Extract	
Size of Char, 100% minus	28 mesh	100 mesh	28 mesh	100 mesh	28 mesh	100 mesh	28 mesh	100 mesh
Final Coke Temperature, F	1800	1800	1800	1800	1800	1800	1800	1800
Crushing Strength, lbs (Whole Pellet, 1-in.)	700	950+	210	475	475	915	470	820
Tumbler Strength, Hardness (Plus 1/4-in., 700 rev)	67	86	ND	ND	ND	ND	46	84
Apparent Specific Gravity	0.87	0.94	ND	0.75	0.86	1.10	0.76	ND

ND - Not determined.

Table IV

Effect of Char Size on Strength of Resultant Coke Pellet*

Char Pulverized to 98-100% minus	1/8-inch	28-mesh	65-mesh	100-mesh
Crushing Strength, lbs (whole pellet)	590	700	630	820
Tumbler Strength (1400 rev) Plus 1/4-inch Index	53	59	64	74
Apparent Specific Gravity	0.94	0.97	0.88	1.10

* Pellets made from Illinois No. 6 seam char and coal-tar pitch. Carbonized in pilot test coke oven to 1800 F.

Table V

Effect of Method of Pretreating and Carbonizing on Strength of Resultant Coke Pellet

Type of Pretreatment	Type of Carbonization	Crushing Strength, lb (whole pellet)	Tumbler Strength Hardness*	Apparent Specific Gravity
A. Pellet Produced from Minus 28-mesh char and Coal-tar Pitch				
1. Cured to 500 F (shallow bed at slow rate)	Pilot-Scale Coke Oven** (1800 F, no medium)	700	59	0.88
2. Preheated in Vertical Retort with Coke Medium to 900 F (Nitrogen Flow)	Pilot-Scale Coke Oven** (1800 F, no medium)	690	ND	0.81
3. None	Pilot-Scale Coke Oven** (with 1/8 in. x 0 coke fines, 1800 F)	750	59	ND
B. Pellets Produced from Minus 100-mesh char and Coal-tar Pitch				
1. Cured to 500 F (Shallow Bed and slow rate	Pilot-Scale Coke Oven** (1800 F, no medium)	835	74	1.13
2. Preheated in Vertical Retort with Coke Medium to 830 F	Pilot-Scale Coke Oven** (1800 F, no medium)	950	ND	1.10
3. None	Pilot Scale Coke Oven** (with 1/8 in. x 0 coke fines, 1800 F)	950	74	0.94
4. Preheated in Vertical Retort with Coke Medium to 830 F	Continuous Vertical Retort, 1800 F no medium	950	ND	1.10

* Plus 1/4-inch after 1400 rev.
** Brennstoff Technik type coke oven.

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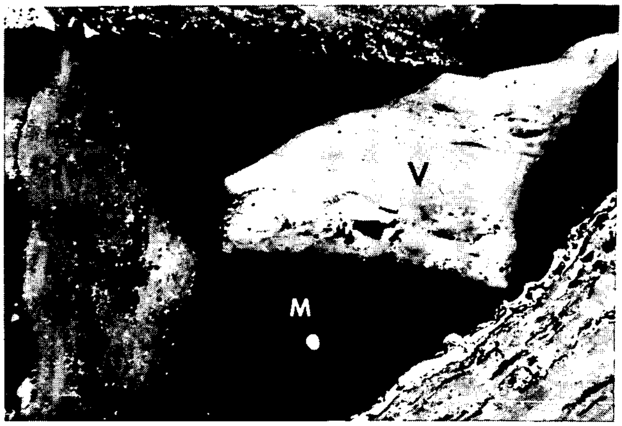
Table VI

Properties of Formcoke

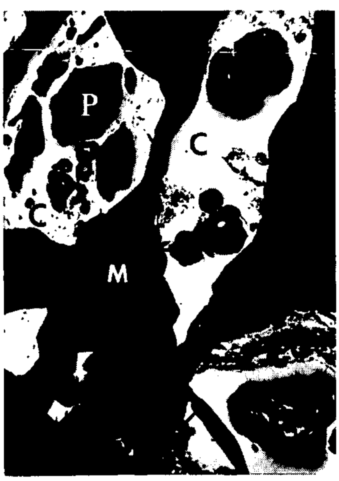
	Metallurgical Coke 1-1/4 x 3/4	Coke Pellet 1-1/4 x 3/4	FMC Corp. Formcoke 1-1/4 x 1
Tumbler Strength*			
Hardness, plus 1/4 inch	85	85	83
Crushing Strength, lbs	600	>1000	810
Compressive Strength, psi	2450	2150	3170
Bulk Density, lbs/ft^3	29	32	32
Apparent Density	0.94	1.0	0.90
True Density	1.90	1.93	1.69
Porosity	50-1/2	48	47
Chemical Analysis			
V.M.	0.8	1.0	6.2
Fixed Carbon	92.2	91.5	87.1
Ash	7.0	7.5	6.7
Sulfur	0.7	0.5	0.75

* 22 lb sample for 700 rev in ASTM Tumbler.

ILLINOIS COAL



CHAR



High-Volatile Char
Approximately 12% VM

Low-Volatile Char
Approximately 3% VM

Photomicrographs showing typical appearance of Illinois No. 6 coal and the char product from coal which is used to make Formcoke pellets. (V) Vitrinoid (principal coal entity), (C) Char, (M) Mounting media, (P) Pores. Reflected light. X200

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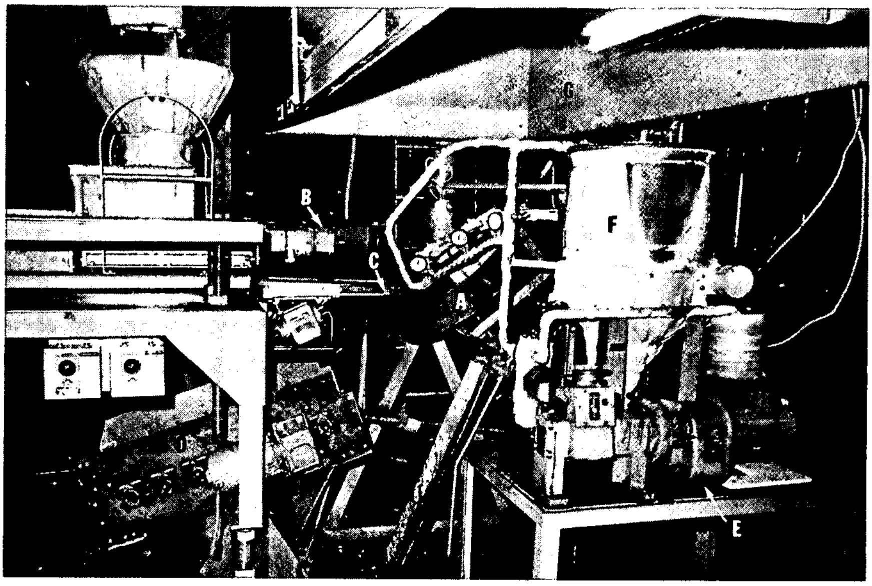
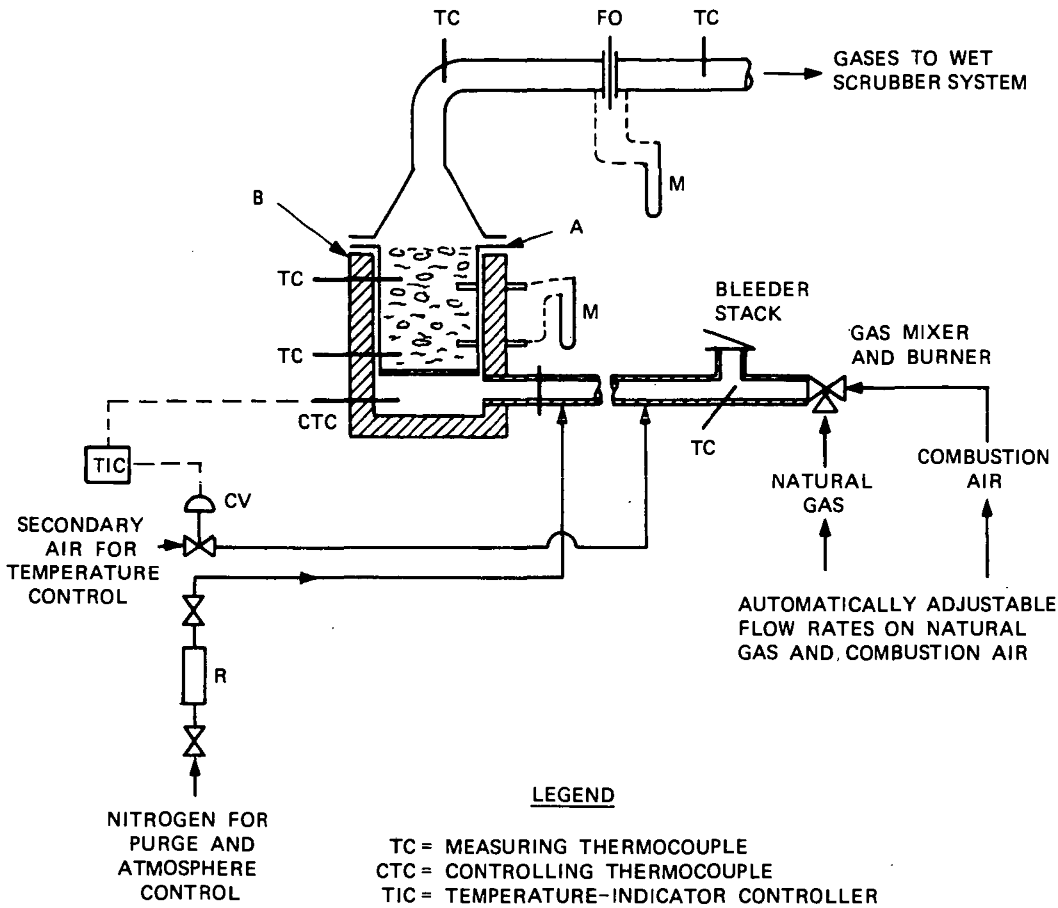
Figure 1



CHAR-PELLETIZING EQUIPMENT OF COKE-PREPARATION PROCESS-DEVELOPMENT UNIT

A Two-Foot Pelletizing Disc
B Char Screw Feeder
C Char Distributor
D Pellet Roller Screen
E Binder Pump No. 1
F Binder Surge Tank No. 1
G Exhaust System

Figure 2



LEGEND

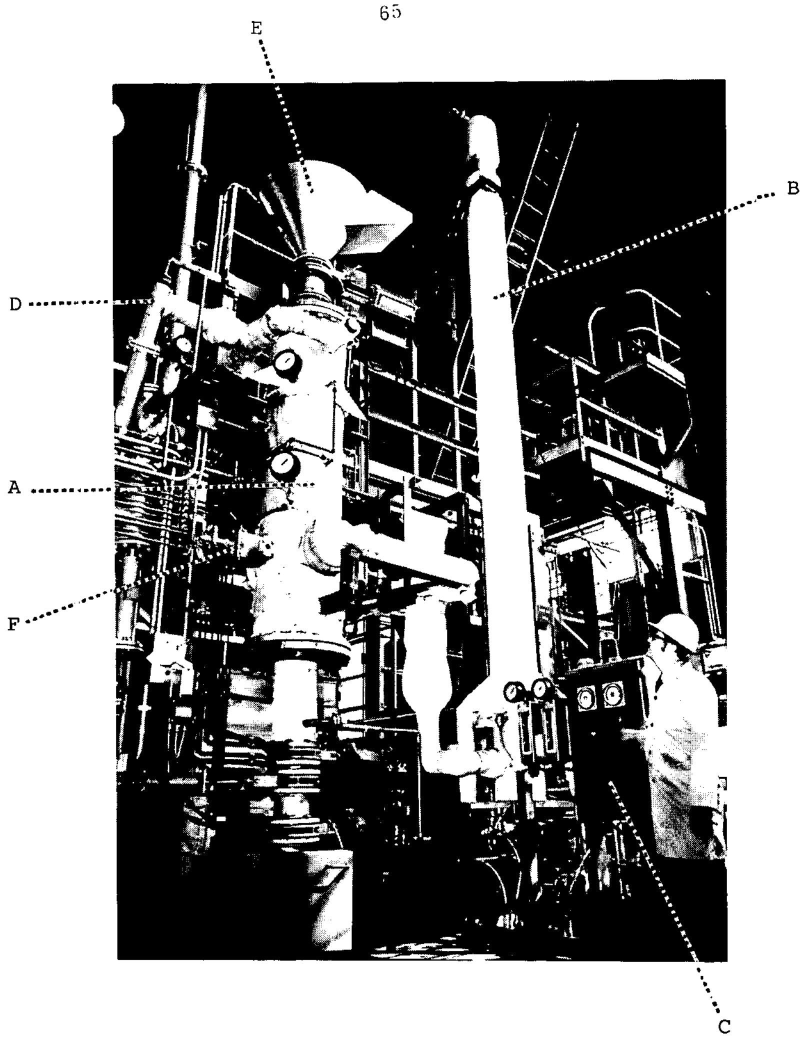
TC = MEASURING THERMOCOUPLE
CTC = CONTROLLING THERMOCOUPLE
TIC = TEMPERATURE-INDICATOR CONTROLLER
CV = CONTROL VALVE
FO = FLOW-MEASURING ORIFICE
M = MANOMETER
R = ROTAMETER

A - CURING BASKET WITH WIRE-MESH BOTTOM

B - REFRACTORY-LINED CURING POT

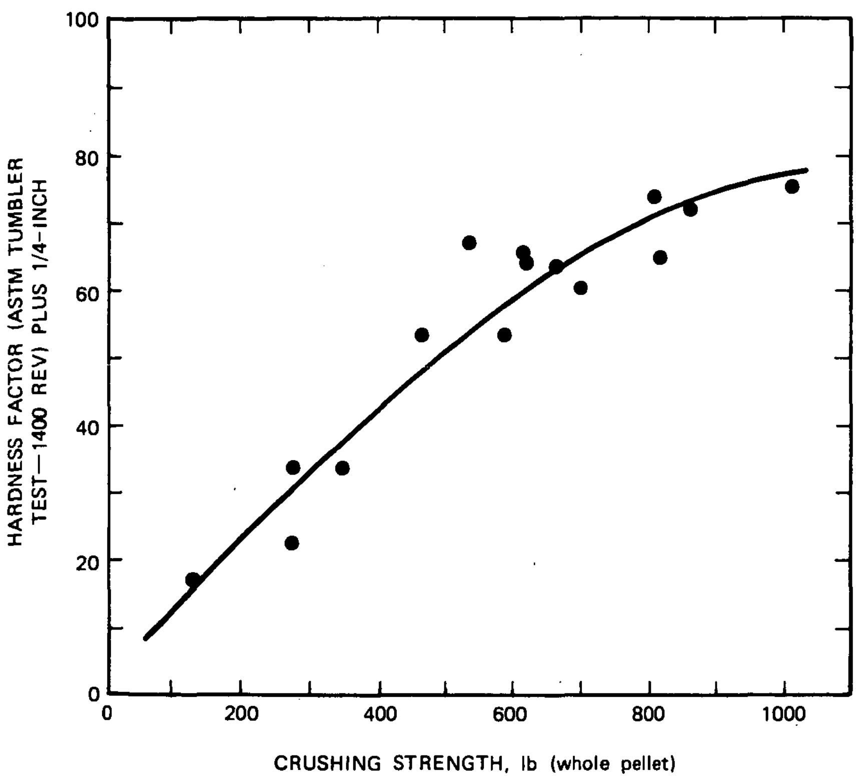
SCHEMATIC DIAGRAM OF CURING POT SYSTEM

Figure 3



Coking kiln and auxiliary equipment.

A. Coking Kiln
B. Kiln Gas Heater
C. Heater Control Panel
D. Kiln Gas Scrubber
E. Pellet Surge Hopper
F. Kiln Auxiliary Burner



RELATIONSHIP BETWEEN CRUSHING STRENGTH AND TUMBLER STRENGTH OF FORMCOKE PELLETS

Figure 5

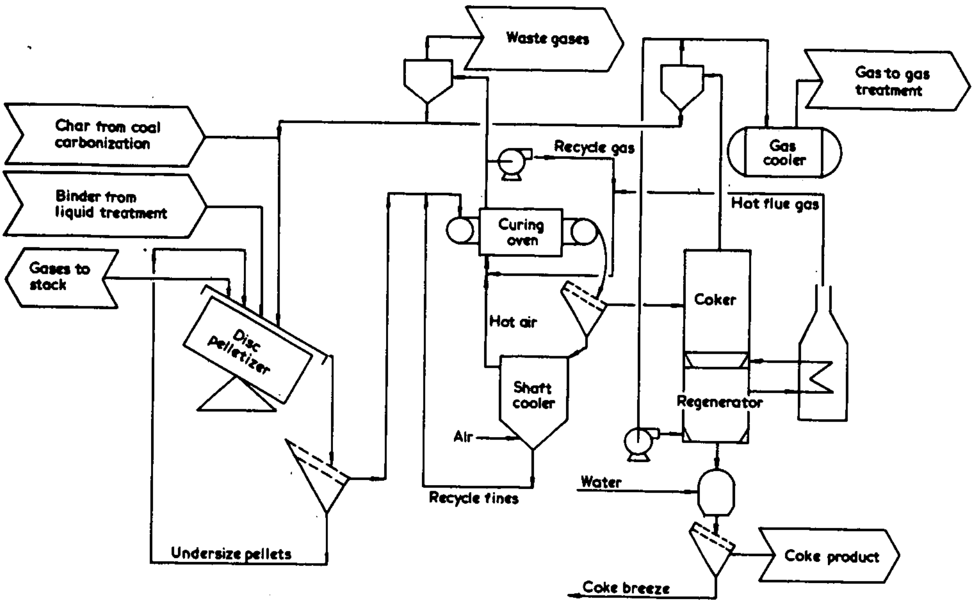
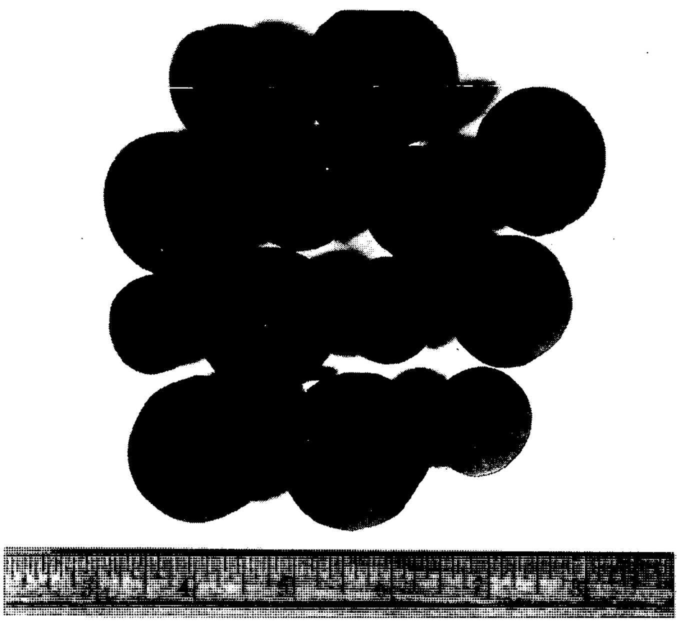


Fig 6. Illustration of equipment involved in the coke preparation during the Clean Coke Process

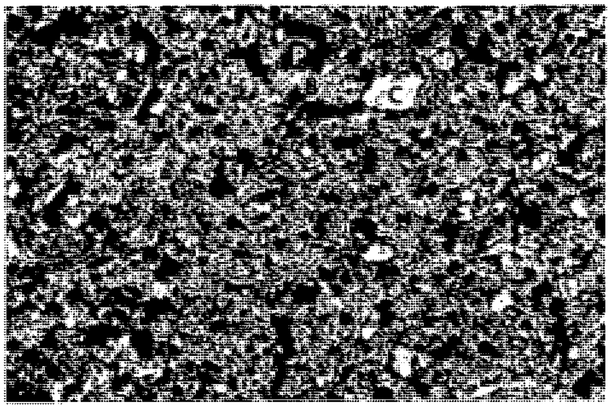
Broken Formcoke Pellets Showing
Fracture Surfaces. X1.25



Formcoke Pellet Product

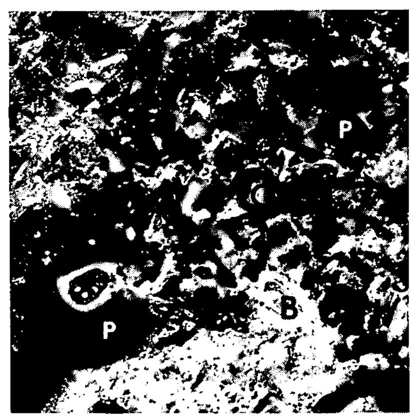
Photographs showing whole and broken of Formcoke pellets

75-H-424(008) Figure 7



Carbonized Formcoke Pellet Made From Minus 28-Mesh Char. X25

Good Mixing. X100



Poor Mixing. X100

Photomicrographs showing Formcoke pellet structure at low magnification and variation in microstructure due to mixing at high magnification. (C) Char, (B) Binder, (P) Pores. Reflected light.

Figure 8