

APPENDIX 5-A
Linear Regression Program

5-A.1 Abstract

The linear regression program is a generalized program for regression analysis or least squares curve fitting of functions which are linear in their coefficients. The program is written in FORTRAN IV in a way that the form of the equation being fitted may be modified by recompiling the input subroutine.

5-A.2 Description

The program is made up of a mainline program, a pivot subroutine, a regression subroutine, a t-test function subroutine and an input subroutine.

The input subroutine must be written such that there will be NP independent variables, and one dependent variable, NP + 1. The variables for one datum point are designated $X(I)$, with I going from 1 to NP + 1. (Note $X(NP + 1)$ will be the dependent variable.) A weight value must also be associated with each datum point. The weight is defined as WT. For an absolute fit, the weight value would be one for each point; for a relative fit the weight should be $(1/X(NP + 1))^2$. As a point of information, it should be noted that each variable may be a computed value such as $\sin X$, $\cos X$, e^X , $\ln X$, X^3 , or any computable value; the only restriction is that the equation being fitted is linear in the coefficients of the X's. These values may be computed within the subroutine. The input subroutine accepts input values, and returns control to the mainline program with values for $X(1) \dots X(NP + 1)$, where $X(1) \dots X(NP)$ are independent variables, and $X(NP + 1)$ is the dependent variable.

Card 1. (cont.)

PO = the significance level for taking a term out of regression.

The t values are the area under both tails of the curve (e.g., for PO = 0.05 with 5 degrees of freedom, t = 2.57). The t values are calculated by an approximation formula and are very inaccurate for 1 or 2 degrees of freedom. For 5 degrees of freedom, they are less than 1% in error.

Columns 21-51 contain NT(1) through NT(NP), where NP = number of coefficients. These variables control the way the program handles the correlating variables.

NT(J) = 0, X(J) is not considered in the regression analysis.

NT(1) = 1, X(J) is considered in the regression analysis.

NT(J) = 2, X(J) is forced into the correlation in a least squares fit.

Card 2.

NP, K
Format (2I4, 4OH)

NP = number of independent variables that are written into the input subroutine.

K = number of data points that will be used.

Columns (9-48) on this card may be used to print a message to identify the computation. The message in these columns will be printed.

Card 3.

Following Card 2, there must be K sets of cards containing the data to be correlated. The format of these cards is specified by the input subroutine, INLC5.

5-A.4 Output

First: values of NP and K and identifying message.

Next, a list of terms which are considered for regression and which are forced into the correlation by least squares.

Next (if specified by $NC(2) = 1$), the parameters which are currently in the correlation will be printed, along with their standard deviation, at each step of the regression. Following the list will be the standard deviation of the correlation at that step.

Next, each parameter that is in the correlation at the end of regression and the covariance array will be printed, along with its variance and standard deviation.

Next (if specified by $NC(3) = 1$), the complete array of correlation coefficients will be printed.

Next (if specified by $NC(4) = 1$), a table comparing each data point to the correlation will be printed. The columns are:

1. K = the point number
2. Y OBSERVED = the value of the dependent variable from the data
3. Y COMPUTED = the value of the dependent variable calculated from the correlation
4. DIFF = $Y - YC$
5. WEIGHTING FACTOR = the value of the weighting factor

The problem is completed at this point and the program will read the next control card unless the last card has directed it to CALL EXIT by $NC(6) = 1$.

5-A.5 Limits

The program will accept up to 30 independent variables, and up to 850 data points. If desired, the number of possible data points can be increased merely by changing the DEFINE FILE statement. The number of independent variables could be increased by increasing the size of arrays X, NT, SQRD, NV, COR, AP, and A. However, more independent variables may lead to truncation errors that will invalidate the correlation. The program tests for this by examining complementary terms in the matrix (Statement 9 in subroutine REGC5). These terms should be equal. If they differ by more than 10%, the regression will be stopped, and an error message printed, and the values of all parameters, etc., printed for diagnostic purposes.

5-A.6 Programs

Copies of the mainline, function and subroutines are attached. A sample input subroutine is also attached. This is for a correlation with a following form:

$$y = a_1x_1 + a_2x_2$$

where

$$x_1 = 1.0$$

$$x_2 = T$$

5-A.7 Execution of the Program

The main program LRMC5 and all the necessary subprograms are stored on the disk. The same program is stored in EXTENDED PRECISION as LREC5. To execute the program, SUBROUTINE INLC5 has to be compiled in a temporary mode and the program executed with one of the following control cards:

STANDARD PRECISION

//XEQ LRMC5

EXTENDED PRECISION

//XEQ LREC5

DATA SWITCH 14 is used in the program. If DATA SWITCH 14 is ON, the computer will abort calculations and branch to a new problem.

```

// JOB T
// FOR
*ONE WORD INTEGERS
* EXTENDED PRECISION
** INLC5 SUBROUTINE FOR DATA INPUT FOR LRMCS 10/13/67
    SUBROUTINE INLC5(X,WT)

C          *****
C.         DEFINE X ARRAY AND WEIGHT (WT)
C          SET X(NP+1) = DEPENDENT VARIABLE
C          *****

    DIMENSION X(31)
    IOUT = 5
    READ (2,100) Y,T
    WRITE (IOUT,900) Y,T
    X(1) = 1.0
    X(2) = T
    X(3)=Y
    WT=1.0
    RETURN
100 FORMAT (3F10.7)
900 FORMAT(3H Y=F6.1,4X,2HT=F5.1)
END
// DUP
*STORE      WS  UA  INLC5
// XEQ LRMCS

```

TEMP

2 7 SAMPLE PROBLEM W.T. MAY 1970

PI= 0.03000 PO= 0.05000
 Y= 2.0 T= 0.5
 Y= 5.0 T= 2.0
 Y= 7.0 T= 3.0
 Y= 9.0 T= 4.0
 Y= 11.0 T= 5.0
 Y= 13.0 T= 6.0
 Y= 15.0 T= 7.0

TERMS CONSIDERED 1 2
 TERMS FORCED IN 0

2 0.2197486E 01 0.4333E-01 0.5114E 00
 1 0.1000008E 01 0.4487E-02
 2 0.1999998E 01 0.1006E-02 0.5621E-02

I	A(I)	VARIANCE	STANDARD DEVIATION
1	0.1000E 01	0.2013E-04	0.4487E-02
2	0.1999E 01	0.1012E-05	0.1006E-02
		0.3159E-04	0.5621E-02

CORRELATION COEFF. ARRAY

1 1.000-0.880
 2-0.880 1.000

COVARIANCE ARRAY

1 0.201E-04-0.397E-05
 2-0.397E-05 0.101E-05

K	Y OBSERVED	Y COMPUTED	DIFF.	WEIGHTING FACTOR
1	0.2000E 01	0.2000E 01	-0.6675E-05	0.1000E 01
2	0.5000E 01	0.5000E 01	-0.2861E-05	0.1000E 01
3	0.7000E 01	0.7000E 01	-0.9536E-06	0.1000E 01
4	0.9000E 01	0.9000E 01	0.1907E-05	0.1000E 01
5	0.1100E 02	0.1099E 02	0.3814E-05	0.1000E 01
6	0.1300E 02	0.1299E 02	0.5722E-05	0.1000E 01
7	0.1500E 02	0.1499E 02	0.7629E-05	0.1000E 01

VAR. Y= 0.3255E-10


```

// FOR
*ONE WORD INTEGERS
*IDCS(CARD,DISK,1403 PRINTER)
*NAME LRMC5
**LINEAR REGRESSION MAINLINE (LRMC5), MAY 1970
   INTEGER STORA(30),STORB(30)
   DIMENSION X(32),NT(31),SQRD(32),NV(30),COR(30)
   COMMON A(31,31),N,K,NC(6)
   EQUIVALENCE (X(1),SQRD(1))
   DEFINE FILE 1(850,64,U,M),2(31,62,U,MM)
C  LEAST SQUARES ARRAY SET UP
   CALL DVCHK(NDIV)
   CALL OVERFL(NOV)
   IOUT = 5
   24 READ (2,600) NC,PI,PO,NT
   600 FORMAT(6I1,2F7.4,3I11)

C          *****
C  NC(1)=1 IN COL  1 TO READ NEW DATA DECK
C  NC(2)=1 IN COL  2 TO PRINT INTERMEDIATE RESULTS
C  NC(3)=1 IN COL  3 TO PRINT COV AND COR COEFF ARRAYS
C  NC(4)=1 IN COL  4 TO COMPARE DATA TO CORRELATION
C  NC(5)  NOT USED BY THE PROGRAM
C  NC(6)=1 IN COL  6 TO CALL EXIT AFTER THIS RUN
C  NT=0 FOR TERM NOT CONSIDERED IN REGRESSION
C  NT=1 FOR TERM CONSIDERED IN REGRESSION
C  NT=2 FOR TERM FORCED IN BY LEAST SQUARES

C  DATA SWITCH 14 ON, ABORT CALCULATION AND BRANCH TO A NEW PROBLEM
C          *****

   26 IF(NC(1))104,104,23
  104 WRITE (IOUT,900) PI,PO
      GO TO 4
C  NP IS THE NUMBER OF COEFF., K IS THE NUMBER OF POINTS
   23 READ(2,623) NP,K
   623 FORMAT(2I4,40H
      WRITE (IOUT,601)
   601 FORMAT (1H1)
      WRITE (IOUT,623) NP,K
      WRITE (IOUT,900) PI,PO
      N=NP+1
      NWT=N+1
      DO 1 I=1,N
      DO 1 J=1,N
1  A(I,J)=0.
      DO 2 KA=1,K
      CALL INLC5(X,WT)
      X(NWT)=WT
      CALL DVCHK(NDIV)
      GO TO (33,34),NDIV
   33 WRITE (IOUT,633) KA
   633 FORMAT (1H0,'ZERO DIVISION ON DATA INPUT',I4)
   34 CALL OVERFL(NOV)
      GO TO (35,36,35),NOV
   35 WRITE (IOUT,635) KA,NOV
   635 FORMAT (1H0,'OVERFLOW/UNDERFLOW ON DATA INPUT',I4,I5)

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36 WRITE (1'KA) (X(L),L=1,NWT)
   DO 3 I=1,N
   DO 3 J=I,N
   3 A(I,J)= A(I,J)+X(I)*X(J)*WT
   2 CONTINUE
   DO 32 I=1,N
32 WRITE (2'I) (A(I,L),L=1,N)
C  RESET ARRAY
   4 DO 5 I=1,N
   5 READ (2'I) (A(I,L),L=1,N)
   DO 49 I=2,N
   III=I-1
   DO 49 J=1,III
49 A(I,J)=A(J,I)
C  INITIALIZE NT ARRAY
   DO 6 I=1,N
   NT(I)=NT(I)-1
   IF(NT(I))6,6,8
C  WITH NT(I)=-1 ITH TERM WILL NOT BE PIVOTED
C  ON INPUT, SET I NEG. TO FORCE I-TH TERM INTO REGRESSION
   8 CALL PIVC5(I)
   NT(I)=2
   6 CONTINUE
   II=0
   JJ=0
   DO 11 I=1,N
   STORA(I)=0
11 STORB(I)=0
   WRITE (IOUT,602)
   DO 27 I=1,N
   IF(NT(I))27,28,29
28 II=1+II
   STORA(II)=I
   GO TO 27
29 JJ=1+JJ
   STORB(JJ)=I
27 CONTINUE
   WRITE (IOUT,628) (STORA(I),I=1,II)
628 FORMAT(17H TERMS CONSIDERED20I4/1H 10I4/)
   WRITE (IOUT,629) (STORB(I),I=1,JJ)
629 FORMAT(16H TERMS FORCED IN 20I4/1H 10I4/)
   WRITE (IOUT,602)
602 FORMAT (1H0//)
   CALL REGC5(NDF,PI,PO,NT)
C  READ NEW DATA CONTROL CARD WITH DATA SWITCH 14
   CALL DATSW(14,NSS)
   GO TO (24,47),NSS
47 CALL DVCHK(NDIV)
   GO TO (53,54),NDIV
53 WRITE (IOUT,653)
653 FORMAT (1H0,'ZERO DIVISION DURING REGRESSION')
54 CALL OVERFL(NOV)
   GO TO (55,56,55),NOV
55 WRITE (IOUT,655) NOV
655 FORMAT (1H0,'OVERFLOW/UNDERFLOW DURING REGRESSION',I5)
C  OUTPUT COEFF., VAR. OF COEFF., S.D. OF COEFF.

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56 WRITE (IOUT,603)
603 FORMAT(/1H0,3X1HI,3X4HA(I),9X8HVARIANCE,5X,18HSTANDARD DEVIATION/)
    VARY=A(N,N)/NDF
    DO 13 I=1,NP
    IF(NT(I))13,13,14
14 VAR= A(I,I)*VARY
    SD=SQRT (VAR)
    SQRD(I)=1./SD
    WRITE (IOUT,604) I,A(I,N),VAR,SD
13 CONTINUE
    SD=SQRT (VARY)
    WRITE (IOUT,605) VARY,SD
604 FORMAT (1H 14,3(2XE11.4))
605 FORMAT (1H ,17X,2(2XE11.4)//)
C OUTPUT COVAR., AND COR. COEFF. ARRAY
    IF(NC(3))7,7,9
    9 WRITE (IOUT,609)
609 FORMAT(25H CORRELATION COEFF. ARRAY)
    DO 15 I=1,NP
    IF(NT(I))15,15,16
16 II=1
    DO 18 J=1,NP
    IF(NT(J))18,18,17
17 COR(II)=A(I,J)*VARY*SQRD(I)*SQRD(J)
    NV(II)=J
    II=1+II
18 CONTINUE
    II=II-1
    WRITE (IOUT,618) I,(COR(L),L=1,II)
618 FORMAT(I3, 19F6.3 /(3X19F6.3))
15 CONTINUE
    WRITE (IOUT,660)
660 FORMAT(1H0 'COVARIANCE ARRAY')
    DO 60 I=1,NP
    IF(NT(I))60,60,61
61 J = 1
    DO 62 JA=1,NP
    IF(NT(JA))62,62,63
63 COR(J) = A(I,JA)*VARY
    J = J+1
62 CONTINUE
    WRITE (IOUT,661) I,(COR(JA),JA=1,II)
661 FORMAT(1H I2,11E10.3/(3X11E10.3))
60 CONTINUE
    7 IF(NC(4))10,10,19
19 WRITE (IOUT,619)
619 FORMAT(1H0,2X1HK,3X,10HY OBSERVED,3X,10HY COMPUTED,4X,5HDIFF.,
16X, 'WEIGHTING FACTOR')
    VARY=0.
    DO 20 KA=1,K
C READ NEW DATA CONTROL CARD WITH DATA SWITCH 14
    CALL DATSW(14,NSS)
    GO TO (24,48),NSS

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48 READ (1*KA) (X(J),J=1,NWT)
   F=0.
   DO 21 I=1,NP
   IF(NT(I))21,21,22
22 F=F+A(I,N)*X(I)
21 CONTINUE
   DIFF=X(N)-F
   VARY=VARY+DIFF**2*X(NWT)
20 WRITE (IOUT,620) KA,X(N),F,DIFF,X(NWT)
620 FORMAT (I4,5(2XE11.4))
   VARY=VARY/NDF
   WRITE (IOUT,612) VARY
612 FORMAT (8HOVAR. Y=E11.4)
10 IF(NC(6))30,30,31
30 CALL DVCHK(NDIV)
   GO TO (43,44),NDIV
43 WRITE (IOUT,643)
643 FORMAT (1H0,'ZERO DIVISION')
44 CALL OVERFL(NOV)
   GO TO(45,24,45),NOV
45 WRITE (IOUT,645) NOV
645 FORMAT (1H0,'OVERFLOW/UNDERFLOW',I5)
31 CALL EXIT
900 FORMAT(4H PI=F8.5,5X,3HPO=F8.5)
   END

```

** REGC5 SUBROUTINE FOR LINEAR REGRESSION APRIL 3,1970
 SUBROUTINE REGC5(NDF,PI,PO,NT)

C*****

C THE MAXIMUM NUMBER OF ITERATIONS THAT CAN OCCUR BEFORE REGRESSION *
 C IS STOPPED WAS FIXED AT 2*NUMBWR OF COEFFICIENTS *
 C MITER=2*NP *

C*****

DIMENSION NT(31)
 COMMON R(31,31),N,KA,NC(6)

IOUT = 5
 NP=N-1
 MITER=NP*2

ITER=1
 NDF=KA

DO 3 I=1, NP
 IF(NT(I))3,3,8

8 NDF=NDF-1
 3 CONTINUE

20 TS=0.
 K=0

TSR=1.E35
 KR=0

DO 10 I=1, NP
 TPA=R(I,N)*R(N,I)

IF(NT(I))10,2,1

C TERM IN REGRESSION
 1 IF(NT(I)-1)10,9,10

9 TPA=-TPA*NDF/R(I,I)/R(N,N)
 IF(ABS((R(I,N)+R(N,I))/R(I,N)) -0.10)101,101,102

102 WRITE(IOUT,903)
 903 FORMAT(' TERM IN REGRESSION')

105 WRITE(IOUT,902)
 WRITE(5,603)I,N ,R(I,N),R(N,I)

603 FORMAT(1H0,2I10,2E20.8)
 RETURN

101 CALL DVCHK(IDVCK)
 GO TO(40,41) ,IDVCK

40 WRITE(5,902)I,N,R(I,I),R(N,N)
 41 CONTINUE

IF(TSR-TPA)10,10,4
 4 TSR=TPA
 KR = I

GO TO 10

C TERM NOT IN REGRESSION
 2 TPA=TPA*(NDF-1)/(R(I,I)*R(N,N)-TPA)

CALL DVCHK(IDVCK)
 GO TO(51,52),IDVCK

51 WRITE(5,902)I,N,R(I,I),R(N,N)
 52 CONTINUE

6 IF(TS-TPA)5,10,10
 5 K=I
 TS=TPA

10 CONTINUE

C TS IS THE LARGEST T*T VALUE OF THOSE TERMS NOT IN REGRESSION
 C K IS THE INDEX OF THAT TERM

C TSR IS THE SMALLEST T*T VALUE OF THOSE TERMS IN REGRESSION
 C KR IS THE INDEX OF THIS TERM

PAGE 2 REGC5 SUBROUTINE FOR LINEAR REGRESSION

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    TT=TTTC5(P0,NDF)
    IF(TT -TSR)13,13,14
14  CALL PIVC5(KR)
    NT(KR)=0
    NDF=1+NDF
C  STOP REGRESSION WITH DATA SWITCH 14
    CALL DATSW(14,NSS)
    GO TO (12,16),NSS
16  IF(NC(2))20,20,15
15  VARY=R(N,N)/NDF
    DO 17 I=1,NP
    IF(NT(I))17,17,18
18  SDA=SQRT (R(I,I)*VARY)
    WRITE (IOUT,600) I,R(I,N),SDA
17  CONTINUE
    SDY=SQRT (VARY)
    WRITE (IOUT,601) SDY
    GO TO 20
13  TT=TTTC5(PI,NDF)
    IF(TT -TS)11,12,12
11  IF(ABS((R(I,N)-R(N,I))/R(I,N))-0.1)103,103,104
104  WRITE(IOUT,904)
    GO TO 105
904  FORMAT(' TERM TO BE PIVOTED IN')
103  CALL PIVC5(K)
    NT(K)=1
    NDF=NDF-1
    IF(ITER-MITER)30,31,31
30  ITER=ITER+1
    GO TO 16
31  WRITE(IOUT,900)ITER
12  RETURN
600  FORMAT (1H I3,3XE14.7,3XE10.4)
601  FORMAT (1H+,T41,E10.4//)
602  FORMAT (1H0,'REGRESSION STOPPED - TOO MANY TERMS - ACCURACY LOST')
900  FORMAT(//' REGRESSION STOPPED AFTER'15' ITERATIONS'/)
902  FORMAT(' DIVISION BY ZERO I='15,' N='15,2E15.5)
    END

```

```

** PIVC5 SUBROUTINE FOR LINEAR REGRESSION 5/13/67 .
C SUBROUTINE PERFORMS K-TH PIVOT OF GAUSS-JORDAN ELIMINATION
  SUBROUTINE PIVC5(K)
  COMMON A(31,31),N
  IF(A(K,K))24,25,24
25 WRITE(5,900)K,A(K,K)
24 CONTINUE
  PIV=1.0/A(K,K)
  DO 10 I=1,N
  IF (I-K)11,10,11
11 CPIV = -A(I,K)*PIV
  DO 20 J=1,N
  IF(J-K)21,20,21
21 A(I,J)=A(I,J)+CPIV*A(K,J)
20 CONTINUE
  A(I,K)=CPIV
10 CONTINUE
  DO 22 J=1,N
  IF(J-K)23,22,23
23 A(K,J)= A(K,J)*PIV
22 CONTINUE
  A(K,K)= PIV
  RETURN
900 FORMAT(' DIVISION BY ZERO IN PIVC5 FOR K='I5,3X,2HA=E15.7)
  END

```

```

** FUNCTION TTTC5 MAY 1970
  FUNCTION TTTC5(P,N)
  IOUT = 5
  IF(P-.0009)1,2,2
  1 WRITE (IOUT,601)
601 FORMAT (1H0,'PROBABILITY SPECIF.FOR T-TEST TOO LOW')
  CALL EXIT
  2 IF(P-.05)3,3,4
  3 TTTC5=.673-1.036*.434*ALOG(P-.0000597)+(1.209*P**(-.686)-3.166)/N
  1**(.84-.509*.434*ALOG(P))
  GO TO 5
  4 IF(P-.5)6,6,7
  7 WRITE(IOUT,602)
602 FORMAT(1H0,'PROBABILITY SPECIF. FOR T-TEST TOO HIGH')
  CALL EXIT
  6 TTTC5=.255-1.641*.434*ALOG(P+.0340)+(0.527*P**(-.872)-0.704)/N**(.
  199-.417*.434*ALOG(P))
  5.TTTC5=TTTC5*TTTC5
  RETURN
  END

```

APPENDIX 5-B

Solution of Simultaneous Equations
of Several Unknowns

5-B1

APPENDIX 5-B. Solution of Simultaneous Equations
of Several Unknowns

May 1970

5-B.1 General Description

Given M simultaneous non-linear equations in M unknowns,

$$F(1) = f_1(x_1, x_2, \dots, x_M; a_1, a_2, \dots, a_{M1}) = 0$$

$$F(2) = f_2(x_1, x_2, \dots, x_M; a_1, a_2, \dots, a_{M1}) = 0$$

...

$$F(M) = f_M(x_1, x_2, \dots, x_M; a_1, a_2, \dots, a_{M1}) = 0$$

where the a's are given and the x's are the unknowns, the program computes the correct values for the x's. The Newton-Raphson method is used in the computation of the x's.

The user must supply a subroutine subprogram (FXNC7) that computes the functions F(I). The initial guesses for the x's must also be given.

See attached program which solves

$$F(1) = a_1(x_1)^2 + \frac{x_2}{x_1} - a_3$$

$$F(2) = \frac{x_2}{(x_1)^2} - a_4$$


```

// JOB T
// FOR
*ONE WORD INTEGERS
*EXTENDED PRECISION
** SUBROUTINE FXNC7,USE WITH SEQC7 TO COMPUTE SIMULT. EQUATIONS
SUBROUTINE FXNC7
C *****
C DO NOT CHANGE ANY VARIABLES IN COMMON,EXCEPT F ARRAY
C FIRST EQUATION = F(1) = 0.0
C SECOND EQUATION = F(2) = 0.0
C M EQUATION = F(M) = 0.0
C *****
COMMON X(30),A(40),F(30)
F(1) = A(1)*(X(1)**2)+X(2)/X(1)-A(3)
F(2) = X(2)/X(1)**2 -A(4)
RETURN
END
// DUP
*STORE WS UA FXNC7
// XEQ SEQC7

```

TEST PROBLEM SOLUTION OF 2 SIMULT. EQS.
MAXIMUM NO. OF ITERATIONS = 15
NDR= 0
MAXIMUM RELATIVE CORRECTION ALLOWED= 0.000000
RELATIVE ERROR FOR X VALUES= 0.0000050
ABSOLUTE ERROR FOR F VALUES= 0.100E-04

INITIAL GUESSES
X(1)= 0.1200000E 01
X(2)= 0.2000000E 01
GIVEN CONSTANTS
A(1)= 0.1700000E 01
A(2)= -0.1900000E 01
A(3)= 0.1613333E 02
A(4)= 0.2777777E 00

ITERATION 1
X(1)=0.3642090E 01
X(2)=0.8515956E 01

ITERATION 2
X(1)=0.3072193E 01
X(2)=0.1027580E 01

ITERATION 3
X(1)=0.2999752E 01
X(2)=0.2573456E 01

ITERATION 4
X(1)=0.2999999E 01
X(2)=0.2500010E 01

ITERATION 5
X(1)=0.2999999E 01
X(2)=0.2499999E 01

FINAL RESULTS
X F
0.2999999E 01 0.1490116E-07
0.2499999E 01 -0.4656612E-09

```

// FOR
#ONE WORD INTEGERS
#EXTENDED PRECISION
#IOCS(CARD,1403 PRINTER,DISK)
#NAME SEQCT
** SOL. OF SIMULTANEOUS EQS. BY NEWTON-RAPHSON METHOD   MAY 1970
C   *****
C   PROB. BALANCED WHEN ABS(1-(X (I)ITER)/(X (I+1)ITER)) LESS THAN XERR
C   M=NUMBER OF ROWS
C   LAST IS THE NUMBER OF ITERATIONS BEFORE QUITTING
C   DLIMIT IS THE MAXIMUM RELATIVE CORRECTION ALLOWED
C   XERR = RELATIVE ERROR FOR X VALUES
C   FERR = ABSOLUTE ERROR FOR F VALUES
C   W.T. JUNE 4,1968
C   INTEGER OUT
C   DIMENSION F1(30),NAME(40)
C   COMMON X(30),A(40),F(30),W(30,31),M,M1,N
101 CALL OVERFL(IOVFL)
102 CALL DVCHK(IDVCK)
103 C = 1.002
104 OUT = 5
105 INPUT = 2
106 READ (INPUT,905) NAME
107 READ (INPUT,900) LAST,M,M1,LIST,NDIR,DLIMIT,XERR,FERR
C   LIST=1,PRINT INTERMEDIATE VALUES OF THE UNKNOWNNS
C   LIST=2,OMIT INTERMEDIATE PRINTOUT OF THE UNKNOWNNS
C   NDIR = 1, LIMIT CORRECTION BY DLIMIT
C   0, APPLY COMPLETE CORRECTION TO THE UNKNOWNNS
108 IF(LAST)500,500,101
109 IF(XERR) 105,104,105
110 XERR = 0.000005
111 IF(FERR) 107,106,107
112 FERR = 0.00001
113 CALL INPC7
114 WRITE (OUT,943) NAME
115 WRITE (OUT,944) LAST,NDIR,DLIMIT,XERR,FERR
116 WRITE (OUT,947) (JJ,X(JJ),JJ=1,M)
117 WRITE (OUT,948) (JJ,A(JJ),JJ=1,M1)
118 N=M+1
119 CI=1./C
120 CL=C-1.
121 DO 4 NIT=1, LAST
122 CALL FXNC7
123 DO 10 I=1,M
124 F1(I)=F(I)
125 DO 18 I=1,M
126 X(I)=X(I)*C
127 CALL FXNC7
128 X(I)=X(I)*CI
129 DO 16 J=1,M
130 W(J,I)=(F(J)-F1(J))/(X(I)*CL)
131 CONTINUE
132 DO 20 I=1,M
133 W(I,N)=-F1(I)
134 CALL INVC7
135 IT=1
136 IF(NDIR)30,30,29

```

PAGE 2 SOL. OF SIMULTANEOUS EQS. BY NEWTON-RAPHSON METHOD MAY 1970

```

29 DO 31 I=1,M
   IF(ABS(W(I,N)/X(I))-DLIMIT)31,31,32
32 POT=W(I,N)
   DO 33 J=1,M
   W(J,N)=W(J,N)*ABS(DLIMIT*X(I)/POT)
33 CONTINUE
31 CONTINUE
30 DO 22 I=1,M
   IF(ABS(W(I,N)/X(I))- .8)21,21,23
21 IF(ABS(1.0-X(I)/(X(I)+W(I,N)))-XERR)22,23,23
22 CONTINUE
   IT=2
23 DO 25 I=1,M
   X(I)=X(I)+W(I,N)
25 CONTINUE
   GO TO(27,28),LIST
27 WRITE (OUT,949) NIT,(I,X(I),I=1,M)
28 GO TO (4,26),IT
4 CONTINUE
   WRITE(OUT,605) LAST
26 CALL FXNC7
   DO 103 I=1,M
   IF(ABS(F(I))-1.0E-05)103,103,102
102 WRITE (OUT,902)
103 CONTINUE
   CALL OVERFL(IDVFL)
   GO TO(240,250,250),IDVFL
240 WRITE (OUT,928)
   GO TO 1
250 CALL DVCHK(IDVCK)
   GO TO(260,270),IDVCK
260 WRITE (OUT,929)
   GO TO 1
270 CALL OUTC7
   GO TO 1
500 CALL EXIT
C   FORMAT STATEMENTS
605 FORMAT(1X,15,29HITERATIONS WITHOUT CONVERSION)
900 FORMAT(5I5,3E15.7)
902 FORMAT(3H F(12,2H)=E12.5,4X,32H ERROR IN CALCULATION - CONTINUE/)
905 FORMAT(40A2)
906 FORMAT(15,E15.7)
928 FORMAT('OVERFLOW')
929 FORMAT('DIVISION BY ZERO')
943 FORMAT(1H1,40A2)
944 FORMAT(28H MAXIMUM NO. OF ITERATIONS = I4/ 6H NDIR=I2/38H MAXIMUM
   1RELATIVE CORRECTION ALLOWED= F10.6/30H RELATIVE ERROR FOR X VALUE
   2S= F10.7/30H ABSOLUTE ERROR FOR F VALUES= E10.3//)
947 FORMAT(' INITIAL GUESSES '/(3H X(12,2H)=E15.7 ))
948 FORMAT(' GIVEN CONSTANTS '/(3H A(12,2H)=E15.7 ))
949 FORMAT(/10H ITERATION 13/(16X,2HX(12,2H)=E13.7))
   END

```

```

** MATRIX INVERSION, PIVOT ON LARGEST ELEMENT IN COL.
SUBROUTINE INVC7
DIMENSION WW(30,31),L(30)
COMMON X(30),A(40),F(30),W(30,31),M,M1,N
DO 1 J=1,M
1 L(J) = 0
DO 203 K=1,M
I = 1
JP = 0
K1 = K-1
IF(K1)50,8,5
5 DO 7 J=1,K1
IF(L(J)-I)7,6,7
6 I = I+1
GO TO 5
7 CONTINUE
8 JR = I
IF(M-K)50,17,9
9 TEMP = W(I,K)
12 I= I+1
10 IF(K1)50,14,11
11 DO 13 J=1,K1
IF(L(J)-I )13,12,13
13 CONTINUE
14 IF(ABS(TEMP)-ABS(W(I ,K)))16,15,15
16 JR = I
TEMP = W(I ,K)
15 JP = JP+1
IF(M-K-JP)50,17,12
17 L(K) = JR
IF(ABS(W(JR,K))-1.0E-30)100,102,102
100 WRITE ( 5,900) JR,K,W(JR,K)
102 W(JR,K) = 1.0/W(JR,K)
DO 201 J=1,M
IF(JR-J)202,201,202
202 W(J,K) = -W(J,K)*W(JR,K)
201 CONTINUE
DO 203 I=1,M
IF(I-K)204,203,204
204 WPOT = W(JR,I)
W(JR,I) = WPOT*W(JR,K)
DO 203 J=1,M
IF(JR-J)205,203,205
205 W(J,I) = W(J,I)+WPOT*W(J,K)
203 CONTINUE
DO 20 J=1,M
I = L(J)
DO 20 K=1,N
20 WW(J,K) = W(I,K)
DO 22 J=1,M
I = L(J)
DO 21 K=1,M
21 W(K,I) = WW(K,J)
22 W(J,N) = WW(J,N)
RETURN
50 WRITE ( 5,901)
CALL EXIT
900 FORMAT(' IN MATRIX INVERSION ROUTINE A PIVOT TERM='2I3.E14.7)
901 FORMAT('LOGICAL ERROR IN MATRIX INVERSION ROUTINE')
END

```

```
SUBROUTINE INPC7
COMMON X(30),A(40),F(30),W(30,31),M,M1,N
READ (2,901) (A(I),I=1,M1)
READ (2,901) (X(I),I=1,M)
RETURN
900 FORMAT(2I5)
901 FORMAT(8F10.0)
END
```

```
SUBROUTINE OUTC7
INTEGER OUT
COMMON X(30),A(40),F(30),W(30,31),M,M1,N
OUT = 5
WRITE (OUT,900) (X(I),F(I),I=1,M)
RETURN
900 FORMAT(///14H FINAL RESULTS/8X,1HX,17X,1HF/(1H E15.7,3X,E15.7))
END
```


PART VI

COAL AND CHAR CHARACTERIZATION

- 6.0 Summary of Coal and Char Characterization
- 6a Petrography and Related Studies
- 6b Miscellaneous Support Studies
- 6c Calorimetry
- 6d Kinetics of Coal Gasification

6-1

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6.0. Summary of Coal and Char Characterization

The summaries of sub-parts in this category are presented under individual subheadings because of disparate content.

6.0.1. Petrography and Related Studies

Petrographic and related properties of coal were investigated at different stages in the hydrogasification process. Particles of caking bituminous coal inflate to round, hollow "cenospheres" when they are pretreated with air or diluted air, in a fluidized bed, and at elevated temperature, to destroy their tendency to agglomerate. The loss of the agglomeration tendency is attributed to a surface transformation, which forms a "skin" or "envelope" or "oxidized layer" of reacted coal that can be distinguished by its high reflectance. IGT believes this sheath remains rigid, and that this rigidity tends to limit further enlargement of particles during later, high-temperature stages of the HYGAS process. Both the pretreated particles and residue particles from hydrogasification vary greatly in structure and reflectance. The caking mechanism of pretreated low-volatile bituminous coal in the hydrogasification reactor was also investigated.

Petrographic study of the specified feed coals and some of their chars at different stages of processing has been fruitful in several ways. The detection of contaminating caking coal mixed with a nonagglomerating coal explained some anomalous hydrogasification processing results, although the examination was not early enough to avoid their occurrence. Agglomeration of pretreated high-rank bituminous coals was shown to result from the discharge of fluid material from the interior of pretreated particles as well as from the fluidity of the few particles that escaped pretreatment. Lack of anisotropy in the residue chars from lignite, subbituminous coal, and pretreated high-volatile C coal indicates that little or no fluidity developed in these coals; and accounts for the successful processing of lignite and subbituminous coal without pretreatment. Increasing amounts of anisotropy, indicating development of fluidity, were observed in chars from the higher rank bituminous coals. Increased anisotropy and a very different char particle structure were found when a high-volatile A bituminous coal was fed without pretreatment.

Differences in structure may become important if process development makes it possible to feed the coal without pretreatment. Because graphitization at higher temperature occurs only when the char has passed through a fluid stage with resulting anisotropy (Kipling and Shooter¹), the degree of anisotropy or lack of it may indicate differences in the electrical characteristics of the char; this may affect its behavior in the electrothermal gasification process for the production of hydrogen.

Correlating the petrographic properties of a coal and its suitability for hydrogasification, we find:

- Exinite is largely lost in pretreatment and, therefore, is of value only if the coal can be processed without pretreatment.
- Fusinite and semifusinite are expected to be less reactive than vitrinite but no quantitative data on this reactivity are yet available.

6.0.2. Miscellaneous Support Studies

Laboratory tests on the slurring of coal and char were performed prior to the pumping tests. Raw or pretreated Ireland Mine coal was easily wetted and formed into a slurry by stirring with water. Water removal from the slurry by centrifugation was investigated; pressuring the slurry substantially increased the amount of nonrecoverable water. Also investigated were slurring with benzene, the separation of benzene and water in the presence of coal fines, and the use of light oil rather than benzene as the slurry medium — the use of toluene proved to be a feasible alternative. In an investigation of fines formation from sudden heating of the pretreated coal slurry, only a small amount of fines was produced. The float-sink properties of chars were tested at different stages of hydrogasification; results indicate that the float-sink property depends greatly on the amount of noncondensable gas left in the pores of the residues after submersion.

Other support studies included the analyses of condensate water samples for phenol and hydrogen cyanide; analyses of the hydrocarbon liquids from two hydrogasification runs; and the analyses for ammonia in the water phase of the condensate from several runs, in which the results indicated that all or nearly all of the nitrogen was converted to ammonia. Use of the residues from electrogasification for removal of phenols from the water condensate was also investigated.

Minor components in the pilot plant hydrogasification reactor product gas were identified by gas chromatography and mass spectrometry.

The attrition resistance of the chars from hydrogasification and other sources was determined by a test developed for this purpose. The quantity of -200 mesh fines produced in the test was considered significant. Attrition resistance was constant or increased slightly with increase in conversion. This is characteristic of the residue as a whole, rather than of the coarse particles only.

6.0.3. Calorimetry

Calorimetry research was required to establish valid data on various heats of reactions upon which to base the design of an efficient coal hydrogasification plant. Data were required for:

- Raw coal in the coal pretreatment process,
- Pretreated coal in the low-temperature gasifier,
- Residue from the low-temperature gasifier after that residue has passed into the high-temperature gasifier, and
- Residue from the high-temperature gasifier.^{2, 3}

A thorough literature search revealed that no data had been reported on the heat of reaction of hydrogen and coal; therefore, two calorimeters were designed, constructed and operated by the Institute of Gas Technology to obtain the data required. One calorimeter was designed to measure the heat of reaction, and the other to measure heat capacity by the drop method. The heat-of-reaction calorimeter can be operated at temperatures up to 1500° F and at pressures up to 1500 psia. The drop calorimeter can be operated at atmospheric pressure and temperatures up to 1500° F. Results of the following investigations are reported in this section:

- 1) The heat of reaction of hydrogen with coals and coal chars after various degrees of gasification,
- 2) The heat of reaction of coal pretreatment, and
- 3) The heat capacity of various coals and coal chars

Ash balances were used to put these results on a common basis.

The majority of work involving the heats of reaction of hydrogen and coal was concentrated on the study of a high-volatile content bituminous coal from the Ireland Mine's Pittsburgh No. 8 seam. Samples involved raw coal in a size range of -20 to +325 mesh, pretreated coal, residue representative of that from the low-temperature stage of the hydrogasifier and residue representative of that from the high-temperature stage of the hydrogasifier. Some studies also were made on West Virginia Sewell coal (Sewell No. 1 Mine), West Virginia Block No. 5 coal (Kanawha Mine), Illinois No. 6 coal (Crown Mine), Colorado subbituminous coal and North Dakota lignite.

The average heat of reaction in raw coal gasification was about 1800 Btu/lb coal reacted; 52 weight percent of the organic carbon in the feed was gasified.

Examination of the temperature measurement, the pressure measurement, the temperature distribution in the calorimeter, the total mass balance and the calibration results obtained from the constant-heat-input method and the experimental runs on hydrogen and n-decane reactions indicate that the data reported should not have a deviation greater than 10%.

In determining the heat of reaction the coal sample was stored at 70° to 72° F in the neck of the calorimeter. When the calorimeter reached thermal equilibrium with the heater guard and the pressure was stabilized, the sample was lowered into the calorimeter body. In determining the heat of pretreatment, the coal was kept at 70° to 72° F while the air-filled calorimeter was stabilized at desired conditions. The coal was then dropped into the calorimeter after equilibrium condition had been reached; therefore, the measured heat of pretreatment included 1) the heat required to warm the coal from 70° F to the reaction temperature, and 2) the heat of pyrolysis.

During the tests, little devolatilization was noticed at 700°F, but the coal devolatilized rapidly at 800°F, as shown by the presence of tars. Thus, because a good portion of the coal weight loss at 800°F resulted from devolatilization and not from the oxidation reaction, the heat of reaction of the coal pretreatment was also calculated for 800°F, based on the data obtained at 700°F and the heat capacity information of both reactants and products. One should note that, although these experiments were carried out in a static-bed reactor, the IGT pilot plant pretreatment of coal is carried out in a fluidized-bed reactor. At 700°F, the rate of the devolatilization reaction apparently competes with that of the oxidation reaction. In the static reactor the poor gas-solids contacting favors devolatilization, while the intimate gas-solids contacting in the fluidized-bed reactor favors oxidation. For a fluidized pretreater, therefore, the calculated values of the heat of reaction at 800°F more nearly approach the actual values.

Based on the data obtained from this work and that available in the literature, the heat capacity of coal is believed to be a function of the volatile matter content and the temperature. The change of heat capacity with volatile matter content at a constant temperature is nearly constant for every temperature. The heat capacity and temperature are also nearly constant for every constant volatile matter content within the accuracy of the data.

Utilizing the two calorimeters developed by IGT, mean pyro-heat capacities of coal were determined. Results were obtained for temperatures that ranged to >1300°F for lignite, and to >1500°F for raw coal, pretreated coal, low-temperature residue and high-temperature residue. Plots of these data together with other data from the literature are presented.

Based on the data obtained from the work reported here, together with data available in the literature, a comparison chart was developed. Predicted values are plotted for comparison with the experimental data. The largest deviation between predicted and experimental data is about 10%, while the average deviation is about $\pm 5\%$.

It should be noted that the results obtained from this investigation are sufficient for a specific application only and should not be used for general analysis or correlation for all applications. To achieve a generalized correlation suitable for providing design information adaptable to any coal gasification process, further studies will be required.

6.0.4. Kinetics of Coal Gasification

A quantitative mathematical model to describe coal char gasification kinetics was developed based on experimental information obtained over a wide range of conditions. The model is intended for application to two reaction stages:

1. A "high-rate methane formation stage" corresponding to a limited period after a coal char containing reasonable volatile matter is initially exposed to a gasifying medium containing hydrogen. During this short-lived period, a coal char exhibits an exceptionally high, although transient, reactivity for methane formation.
2. A "low-rate gasification stage" corresponding to gasification of a char of relatively low reactivity, which results when reaction in the "rapid-rate" stage is completed.

The correlations corresponding to this model were evaluated on the basis of data obtained at constant environmental conditions with a thermobalance apparatus and a differential fluidized-bed system at 1500° to 1750°F and 1 to 70 atmospheres with a variety of gases and gas mixtures.

Consistencies between predictions of the correlations and results obtained from a variety of other experimental gasification systems employing integral gas-solids contacting are excellent.

6.0.5. References Cited

1. Kipling, J. J. and Shooter, P. V., "Factors Affecting the Graphitization of Carbon: Evidence From Polarized Light Microscopy," Carbon 4, 1-4 (1966) May.
2. Huebler, J., Schora, F. C., "Coal Hydrogasification," Chem. Eng. Progr. 62, 87 (1966).
3. Pyrcioch, E. J., Lee, B. S., Schora, F. C., "Hydrogasification of Pretreated Coal for Pipeline Gas Production," Amer. Chem. Soc. Div. Fuel Chem. Preprints 10, No. 4, 206 (1966) September.

PART 6a
Petrography and Related Studies

6a-1

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6a.0 Summary of Petrography and Related Studies

A summary of this work appears in section 6.0.

6a.1 Introduction

As part of its hydrogasification program, IGT has studied both petrographic and physical properties of the coals used and of the chars produced in various stages of the HYGAS Process. These data were required to supplement results from the usual chemical analyses (deemed inadequate for the purpose of determining events and their rates within coal particles), and to help identify those contributing factors that make coal gasification feasible and profitable for gasification.

6a.2 Objectives

Objectives of this study were:

1. To determine what happens to coal in various stages of the HYGAS Process, and
2. To develop a correlation between the petrographic properties of coals and their suitability for hydrogasification.

6a.3 Apparatus and Procedures

In a petrographic investigation of coal, specimen particles must be mounted in a resin or other medium. The mounted particles then are sectioned by grinding off some of the resin-coal briquette, the sectioned surface is polished, and the specimen is observed under an oil immersion microscope with vertical illumination at about 600X magnification. Observations include analysis for macerals by point counting, and determination of the reflectance of the vitrinite.

IGT chose a Zeiss Universal microscope for this work; it is equipped with both achromatic and Antiflex oil immersion objectives. The Antiflex objectives are designed to eliminate unwanted scattering and reflection of light from the illuminating beam into the image-forming beam. Most coal petrographers use the Leitz Ortholux microscope. Both the IGT investigators and the late Mr. J. A. Harrison of the Illinois State Geological Survey agreed that the Zeiss microscope showed better contrast between difficult-to-distinguish macerals and was not noticeably inferior to the Leitz instrument in any respect. In practice the Zeiss microscope with polarizing achromatic 40X, 0.85NA, oil immersion objective and prism reflector was found satisfactory for both maceral analysis and reflectance determination.

To determine reflectance, a 12.5X Kpl eyepiece mounted in the vertical tube of the microscope was fitted with an aperture that provided a 2.5 mm diameter field on the sample, and with Kodak Wratten filters Nos. 58 and 77 which give a pass-band in the green with peak at 548 nm. The intensity of the light beam was measured with a Photovolt 520M photomultiplier photometer.

Photometer signals were read on the 10 mV scale of a Varian G-14 recorder. The output circuit of the photometer was modified. A switch

and a 2000-ohm 10-turn potentiometer were added. The switch connects either the potentiometer or the photometer output meter to the cathodes of the reference and signal tubes in the cathode-follower circuits of the photometer. As a result, in one switch position, the photometer output meter was operative and the recorder signal could be taken in the original mode of the equipment. In a second switch position, the output meter was inoperative and the signal to the recorder was taken from the potentiometer.

A saturable reactor-type voltage stabilizer was initially used on the microscope lamp power supply. This proved unsatisfactory, especially with current supplied by the IGT total energy system, which has poor frequency regulation. The initial saturable regulator was replaced by a Wanless Model 60 hp-51C12 constant-voltage d-c power supply. The Wanless source performed satisfactorily after a starting resistance was inserted in the output circuit.

Six Bausch & Lomb high-index glasses, cut in the shape of 30-60-90° prisms and mounted in plastic, are customarily used as standards for photometer calibration. A set of these standards, covering the range from 0% to about 2% reflectance in oil, was supplied gratis by Bituminous Coal Research. To calibrate the photometer in the reflectance range of hydrogasification residues (2 to 7%), a substance with an index of refraction greater than optical glass was needed. A prism was cut from strontium titanate ($n_e = 2.435$) and polished. However, a satisfactory polish could not be obtained with available facilities. Instead, a brilliant-cut diamond measuring about 2 mm across its plateau was mounted in bakelite; the refractive index at 546 mm wavelength was calculated from the equation of Schrauf⁹ to be 2.42326. There is some variation among diamonds, presumably, and a precisely determined refractive index value would be preferable; however, the reflectance calculated from the Schrauf value correlated reasonably well with that of the glass standards, providing a very stable and convenient standard. A refractive index of 1.515 for oil was utilized in the calculation of the standard reflectances.

Other items of petrographic equipment were mostly as described by Cole and Berry³. However, the fragile, hollow particles of pretreated coal and hydrogasification residues were crushed and shattered when mounted in epoxy resin under hydraulic pressure, using the method of Cole and Berry. Alternative apparatus and procedure to vacuum-mount specimens were developed, and are described in Appendix 6a-A.

In order to check out petrographic procedures, several samples of test coals were analyzed for maceral content and reflectance at one or both of two outside laboratories (Pennsylvania State University and Bethlehem Steel Corporation). As shown in Table 6a-1, our maceral analyses agree reasonably well with those of the other laboratories. The variation that can be expected within a laboratory is indicated by individual results from three different operators at Penn State, and by the results of three replicate determinations by a single HYGAS operator. Our reflectance determinations (Table 6a-2) on high-volatile bituminous coals also agreed well with results from the other laboratories. For higher rank coal our values are higher by about 0.1%; the significance of this has not been established.

Table 6a-1. INTRA- AND INTERLABORATORY COMPARISON OF MACERAL ANALYSES ON IGT COALS

Laboratory	Operator or Run	Maceral Analysis (Mineral-Free Basis), vol							Total Inertinite
		Vitrinite	Exinite	Resinite	Semi-fusinite	Fusinite	Granular Micrinite	Massive Micrinite	
Ohio No. 6									
PSU*	Op. 1	79.3	5.4	--	3.0	5.4	3.5	2.9	14.8
PSU	Op. 2	77.2	7.7	--	2.7	3.1	7.0	2.3	15.1
PSU	Op. 3	76.1	6.2	--	1.4	6.0	6.9	3.4	17.7
PSU	Avg#	77.3	7.2	--	2.4	3.9	6.4	2.8	15.1
Bethlehem†	Avg	81.2	5.0	0.9	6.8	4.1	1.5	0.2	12.9
IGT	Run 1	81.7	5.2	0.1	3.6	1.9	5.8	1.7	13.0
IGT	Run 2	80.4	5.9	0.3	4.2	1.0	6.1	2.1	13.4
IGT	Run 3	76.2	6.9	0.1	5.2	3.9	4.9	2.8	16.8
IGT	Avg	79.4	6.0	0.2	4.3	2.3	5.6	2.2	14.4
Pittsburgh No. 8									
PSU	Avg	80.3	4.2	--	2.6	4.9	5.2	2.8	15.5
IGT	Avg	84.3	2.4	0.3	3.6	2.6	5.0	1.8	13.0
W. Va. No. 5 Block									
Bethlehem	Avg	71.4	6.9	1.7	9.9	4.9	5.1	0.1	20.0
IGT	Avg	68.2	10.4	0.1	5.7	3.5	8.8	3.3	21.3
Pocahontas No. 4									
PSU	Avg	67.0	0.3	--	9.0	10.3	6.8	6.7	32.9
Bethlehem	Avg	73.4	0.2	0.4	16.0	7.3	2.1	0.6	26.0
IGT	Avg	74.1	0.3	0.0	7.4	8.0	5.0	5.2	25.6

* Coal Research Laboratory of Pennsylvania State University.

† Homer Research Laboratory of Bethlehem Steel Corporation. Each analysis 500 counts/operator, three operators.

Including two additional analyses.

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Table 6a-2. INTERLABORATORY CHECK OF REFLECTANCE DETERMINATION

<u>Coal Sample</u>	<u>Institute of Gas Technology</u>	<u>Pennsylvania State University</u>	<u>Bethlehem Steel Corporation</u>
Illinois No. 6	0.45	0.45	--
Ohio No. 6	0.53	0.56	0.52
Pittsburgh No. 8	0.68	0.66	--
W. Va. No. 5 Block	0.81	--	0.81
Sewell (Fayette Co.)	1.45, 1.47	1.35	--
Pocahontas No. 4	1.78, 1.75	1.67	1.66

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To determine true density, the displacement of a fluid that will fill all the pores of the substance must be measured. Helium, water, methyl alcohol, and other fluids have been used for this purpose. Because the helium molecule is smaller than other molecules and thus can more easily penetrate pores, and because it has little tendency to be adsorbed, determination in helium generally is considered to provide true density¹¹. However, several investigators^{5,6,8} have shown that helium is adsorbed at room temperature by high-density carbons in amounts sufficient to cause appreciable error in density. The effect is related to the electrical conductivity of graphitized carbon, and is appreciable for carbons with densities of 1.9 g/cc and greater, but negligible for a number of carbons with densities less than 1.54 g/cc. Determination of density with helium at elevated temperature is recommended for high-density carbons. Little error should be encountered from adsorption in measurements at room temperature on hydrogasification feeds and residues, however, because these densities are not expected to be much greater than 1.60 g/cc. Helium densities of HYGAS samples were determined with a Beckman air-comparison pycnometer.

The apparent or particle density of 100-mesh and coarser particles can be determined by the displacement of mercury; the high surface tension of mercury prevents penetration of small pores. At atmospheric pressure, pores above about 14-micron diameter are penetrated. In addition, the same effect restricts the filling of small volumes formed about points of particle contact. For a given volume of solids, the number of these contact points increases rapidly as the average particle size decreases. Thus the pressure of mercury needed to decrease the sum of these contact volumes to a negligible amount increases as particle size decreases. According to Cartan and Curtis², pressures greater than atmospheric are required for particles smaller than 20 to 40 mesh, while with a pressure of 100 psi the density of 100-mesh particles (of alumina) has been measured with success.

At 100 psi, mercury penetrates pores of about 2-microns diameter. Little objection can be raised to determination of particle density for coal by this method. Pretreated coal and hydrogasification residues, however,

contain relatively large pores or vesicles, some of which may be open to entry. In addition, the fragility of these particles tends to exclude subjecting them to hydraulic pressure. For these reasons, IGT chose Ergun's gas flow method⁴ to determine particle density of pretreated coal and hydrogasification residue. The method was somewhat shortened by making measurements with only three rates of flow at each of two bed densities. The estimate of the standard deviation, based upon 21 duplicate determinations, was 7%.

Surface areas were determined by Numec Instruments and Control Corporation, using the Brunauer-Emmett-Teller (BET) method with carbon dioxide at 198 °K.

6a.4 Petrography of Feed Coals

The sources and ranks of the coals studied are shown in Table 6a-3, and petrographic analyses are reported in Table 6a-4. The important petrographic characteristics of the coal are the mean maximum reflectance of the vitrinite and the content of:

- Exinite, the group of macerals having the lowest reflectance and highest hydrogen content;
- Vitrinite, the component constituting the bulk of the coal and having an intermediate reflectance and hydrogen content; and
- Intertinite, a group of inert or semi-inert components having a high reflectance and low hydrogen content.

The reflectance of the vitrinite of a coal is an indicator of its rank. The reflectance of the eight bituminous coals tested in the IGT hydrogasification unit are shown in Figure 6a-1 plotted against volatile matter on a dry, ash-free basis. (The value of volatile matter taken here is the average of those reported on the feed of successful pretreatment runs.) A correlation and data points from a literature compilation are also shown.¹

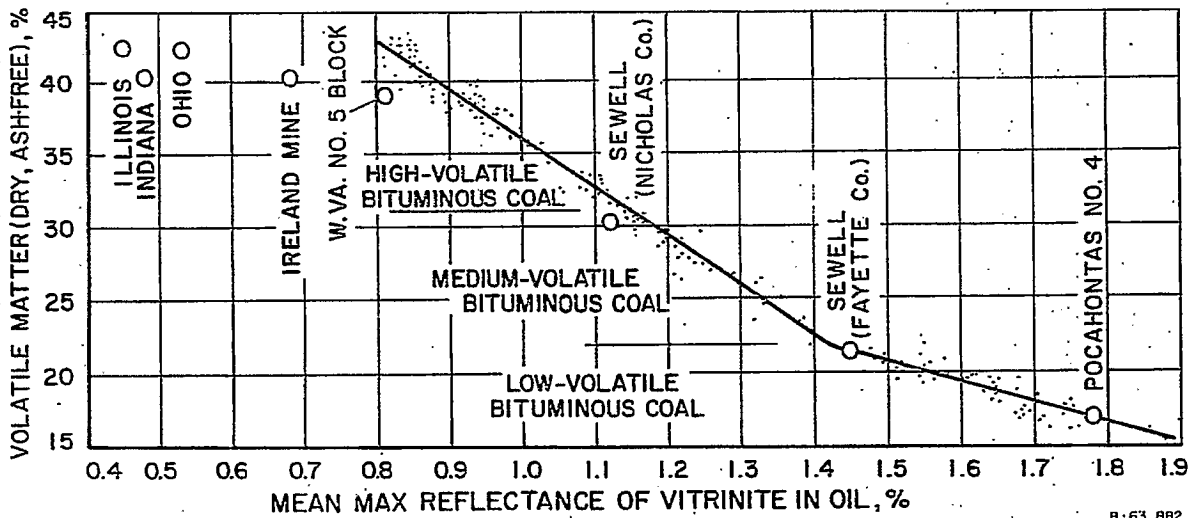


Figure 6a-1. VOLATILE MATTER AND VITRINITE REFLECTANCE OF TEST COALS

Table 6a-3. COAL SOURCES AND RANKS

Seam	Mine	County and State	Rank
Pocahontas No. 4	Stotesbury No. 10	McDowell County, West Virginia	Low-volatile bituminous
Sewell	Lochgelly No. 2	Fayette County, West Virginia	Low-volatile bituminous
Sewell	Sewell No. 1	Nicholas County, West Virginia	Medium-volatile bituminous
Pittsburgh No. 8	Ireland	Marshall County, West Virginia	High-volatile A bituminous
W. Va. No. 5 Block (Lower Kittanning)	Kanawha	Randolph County, West Virginia	High-volatile A bituminous
Ohio No. 6	Broken Aro	Coshocton County, Ohio	High-volatile B bituminous
Indiana No. 6	Minnehaha	Sullivan County, Indiana	High-volatile C bituminous
Illinois No. 6	Crown	Montgomery County, Illinois	High-volatile C bituminous
Colorado Subbituminous	Eagle	Weld County, Colorado	B subbituminous
N. Dakota Lignite	Glenharold	Mercer County, North Dakota	A lignite

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Table 6a-4. PETROGRAPHIC ANALYSIS OF COALS

Maceral Analysis; vol %	No. Dak. Lignite		Colo. Sub-bituminous	Illinois No. 6	Indiana No. 6	Ohio No. 6	Pittsburgh No. 8	W. Va. No. 5 Block	Sewell		Pocahontas No. 4
									Nicholas Co.	Fayette Co.	
Vitrinite	84.2		84.5	86.4	89.9	79.4	84.3	68.2	80.4	71.2	74.1
Exinite	5.0		1.7	2.7	4.3	6.0	2.4	10.4	3.8	1.8	0.3
Resinite	0.6		0.2	0.1	0.2	0.2	0.3	0.1	0.0	0.0	0.0
Semifusinite	4.9		6.7	3.8	2.2	4.3	3.6	5.7	1.8	13.1	7.4
Fusinite*	1.6		2.5	0.7	0.2	2.3	2.6	3.5	4.7	2.4	8.0
Granular micrinite	2.1		3.7	4.3	2.3	5.6	5.0	8.8	2.7	6.4	5.0
Massive micrinite	1.6		0.7	2.0	0.9	2.2	1.8	3.3	6.6	5.1	5.2
Total inertinite	10.2		13.6	10.8	5.6	14.4	13.0	21.3	15.8	27.0	25.8
Vitrinite Reflectance,											
0.10 to 0.19	2		--	--	--	--	--	--	--	--	--
0.20 to 0.29	35		1	--	--	--	--	--	--	--	--
0.30 to 0.39	51		9	9	5	--	--	--	--	--	--
0.40 to 0.49	12		28	76	54	31	--	--	--	--	--
0.50 to 0.59	--		40	14	36	59	1	--	--	--	--
0.60 to 0.69	--		19	1	5	7	58	8	--	--	--
0.70 to 0.79	--		3	--	--	3	40	38	--	--	--
0.80 to 0.89	--		--	--	--	--	1	39	--	--	--
0.90 to 0.99	--		--	--	--	--	--	13	--	--	--
1.00 to 1.09	--		--	--	--	--	--	2	--	--	--
1.10 to 1.19	--		--	--	--	--	--	--	--	--	--
1.20 to 1.29	--		--	--	--	--	--	--	--	--	--
1.30 to 1.39	--		--	--	--	--	--	--	--	17	--
1.40 to 1.49	--		--	--	--	--	--	--	--	28	--
1.50 to 1.59	--		--	--	--	--	--	--	--	11	--
1.60 to 1.69	--		--	--	--	--	--	--	--	32	--
1.70 to 1.79	--		--	--	--	--	--	--	--	4	10
1.80 to 1.89	--		--	--	--	--	--	--	--	6	55
1.90 to 1.99	--		--	--	--	--	--	--	--	1	24
2.00 to 2.09	--		--	--	--	--	--	--	--	1	8
No. of Readings	101		204	96	105	111	159	106	90	102	149
Avg Reflectance	0.31		0.52	0.45	0.48	0.53	0.68	0.81	1.12	1.45	1.78

* Reflectance greater than 2.2% Diameter less than 3

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6a. 5 Study of Pretreated High-Volatile Bituminous Coal and Hydrogasification Residues

In the HYGAS process development unit (PDU) operations discussed here, bituminous coal (only) was pretreated to destroy its tendency to agglomerate.

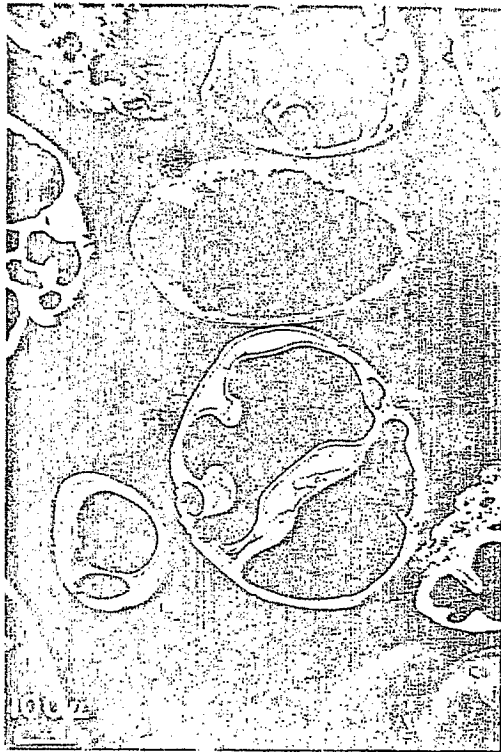
In the tests performed, crushed coal was treated with air (or, in early 10-inch-diameter PDU runs -- with nitrogen-diluted air) in a continuous, single-stage fluidized bed at between 700° and 800° F. The most striking feature of the coal particles (Figure 6a-2) is that many inflate to thin-walled hollow spheroidal forms during pretreatment. Variations in particle residence times that result from mixing in the fluidized bed cause the modification to vary greatly from particle to particle. A few particles exhibit reflectance as low as that of the original coal, appearing to be unchanged, and still having exinite in attrital areas.

The appearance of vesicles, the disappearance of exinite, and an increase in reflectance are characteristic of progress through the pretreatment process. In addition, micrinite becomes difficult to distinguish, and an outer zone of reflectance greater than that of the interior appears in most particles. The high reflectance of this outer zone, or sheath, is attributed to reaction with oxygen; increased reflectance in the mass of the particle apparently is caused only by carbonization. The sheath extends into cracks and is present in the interior of some vesicles, usually with reduced thickness.

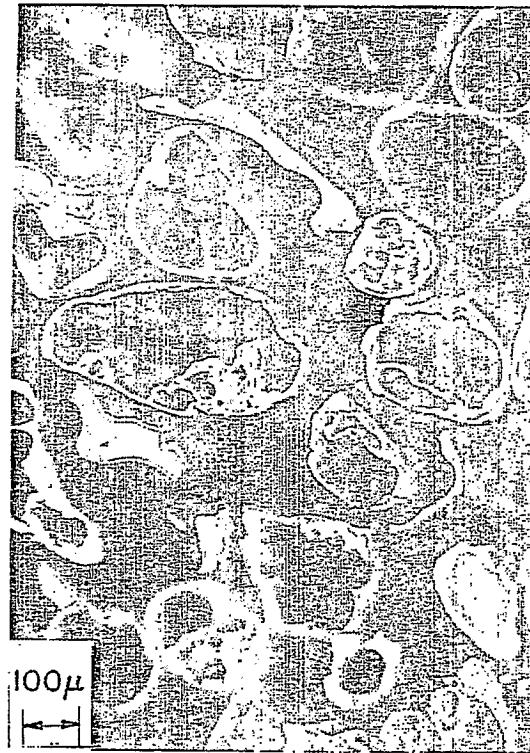
In the Ireland Mine (Pittsburgh No. 8) coal, reflectance of the pretreatment sheath ranges from about 2.0 to 2.6%; reflectance of the interior ranges from about 0.8% -- as observed on vitrinite of the original coal -- up to about 2.0%.

The pretreated coals from different seams appear to be quite consistent in particle structure following treatment, although quantitative determinations of cell wall thickness and vesicle size might disclose variations. A quantitative measure of swelling induced in Ireland Mine coal by pretreatment is provided in the average porosities of two sieve fractions; these are 66% for the -30+40 fraction, and 59% for the -60 +80 mesh fraction (Table 6a-5).

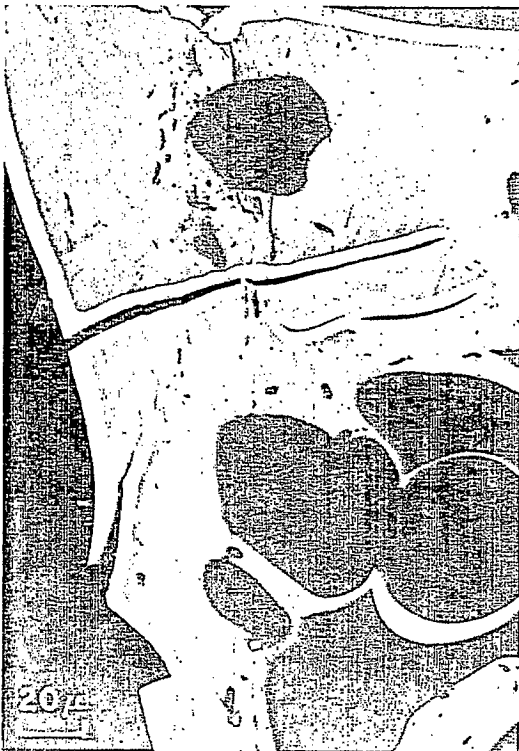
Residues from first and second-stage moving-bed hydrogasification runs utilizing Ireland Mine coal were chosen for intensive study. In the first-stage run (HT-70), the pretreated coal was reacted with a hydrogen-natural gas-steam mixture containing 30 mole percent steam, 43 mole percent hydrogen, and 27 mole percent hydrocarbon. The bed temperature averaged 1205° F, and the pressure was 1030 psig. About 21% of the pretreated coal (MAF) was gasified. In the second-stage run (HT-72) the residue from a first-stage run was reacted with a hydrogen-steam mixture containing 39 mole percent steam. The temperature averaged 1825° F and the pressure was 1023 psig. About 52% of the feed (MAF) was gasified, equivalent to 41% of the pretreated coal.



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Figure 6a-2. PRETREATED COAL

Table 6a-5. PARTICLE AND TRUE DENSITIES OF HYDROGASIFICATION FEED AND RESIDUES

Sample	Sieve Size,	Particle Density, g / cu cm	True Density, g / cu cm	Porosity, %	Ash Content (Moisture- Free), wt %
	USS				
Pretreated Coal	-30 40	0.51	1.52	66	13.7
	-60 80	0.63	1.53	59	15.6
Residue, 1st-Stage Hydrogasification	-30 40	0.48	1.80	73	17.3
	-60 80	0.54	1.77	70	19.1
Residue, 2nd-Stage Hydrogasification	-30 40	0.69	2.10	67	33.0
	-60 80	0.95	2.64	64	54.2
Residue, Free-Fall Hydrogasification	-30 40	0.26	2.13	88	--

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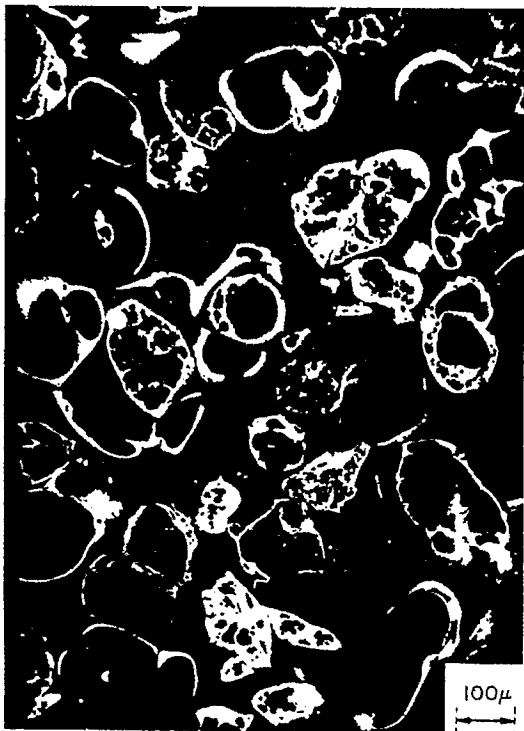
In a petrographic examination of the first-stage residue, no trace of the high-reflectance sheath that becomes conspicuous after coal pretreatment was present in any particle (Figure 6a-3). Occasional particles of the second-stage residue had a dark sheath (Figure 6a-4). Kinship of this dark sheath with the pretreatment sheath was evident from their similarity in form and in pattern of occurrence, particularly in cracks and around vesicles. While the contrast gives the sheath a dark appearance, photometric measurements showed that the reflectance of this "dark" sheath in particles of the second-stage residue was actually greater than that of the sheath of the pretreated coal. During the second stage of hydrogasification, the reflectance of the substrate evidently has increased more rapidly and become greater than that of the sheath.

Particles from both first- and second-stage runs varied greatly in both reflectance and structure. The structure of some particles appeared unchanged from that of pretreated coal. In others, additional vesicles — particularly small ones — were formed. In some of the particles, vesicle walls were extremely thin or partially destroyed, leaving a skeleton or foam structure. In these highly-inflated particles, the exterior wall frequently appeared to be more substantial than the interior vesicle walls; this may be a residual effect from the structure of the pretreatment sheath.

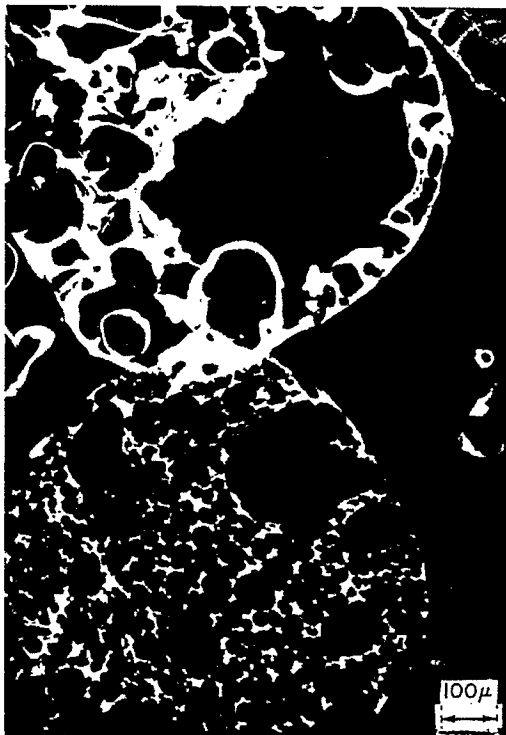
Particles from run HT-38, in which untreated coal was fed, were also examined. This coal was from the Pittsburgh No. 8 seam, but from a different mine (the Consolidation Coal Company's Montour 4). The hydrogasification reaction was conducted entirely in 18 feet of free fall. Severe caking of coal in both the feed tube and the reactor prohibited completion of the run; however, the structure of particles recovered from the base of the reactor is of interest (Figure 6a-5). These particles are much more uniform in appearance and reflectance than residues from runs with pretreated coal. Almost all of the particles have a foam structure, being filled with small vesicles, most of whose walls are perforated. The exterior walls sometimes appear thicker than interior walls, resembling to some extent the residue from pretreated coal. The free-fall particles, however, showed numerous exterior wall perforations that were absent in the residue that resulted when pretreated coal was used. Particle density and porosity (Table 6a-5) also show that, on the average, the particles swelled much more than residue from pretreated coal.

In addition, the free-fall residue had a grainy texture (Figure 6a-6), in marked contrast to the smooth appearance (excepting small voids) of most residue particles from pretreated coal (Figure 6a-7).

A few particles of residue from pretreated coal had a foam structure and a grainy texture; these probably evolved from feed particles that escaped pretreatment. This material occasionally appeared as a cement in agglomerated particles of the residue from pretreated coal; this and its foam structure indicate that it had passed through a fusion stage. Fusion of these particles is also indicated by their anisotropy, according to theories of coking and graphitization?



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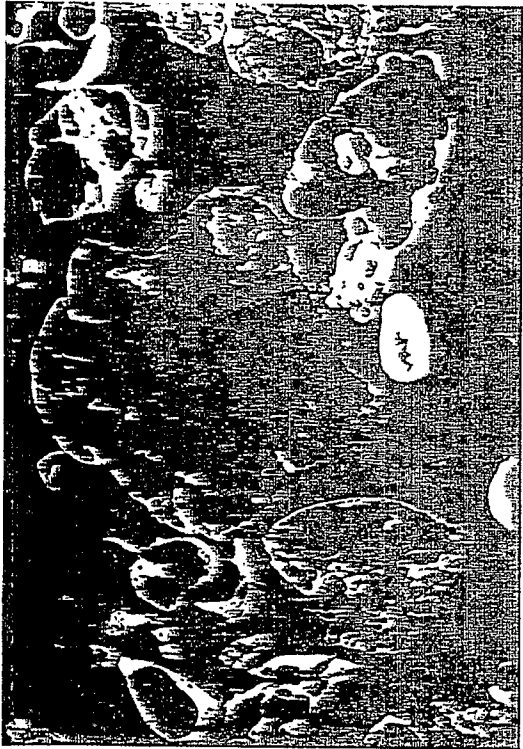


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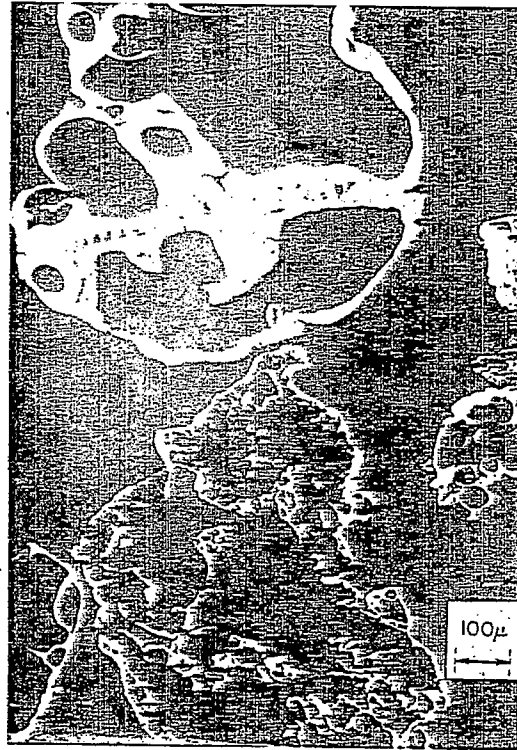


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Figure 6a-3. RESIDUE FROM FIRST-STAGE HYDROGASIFICATION



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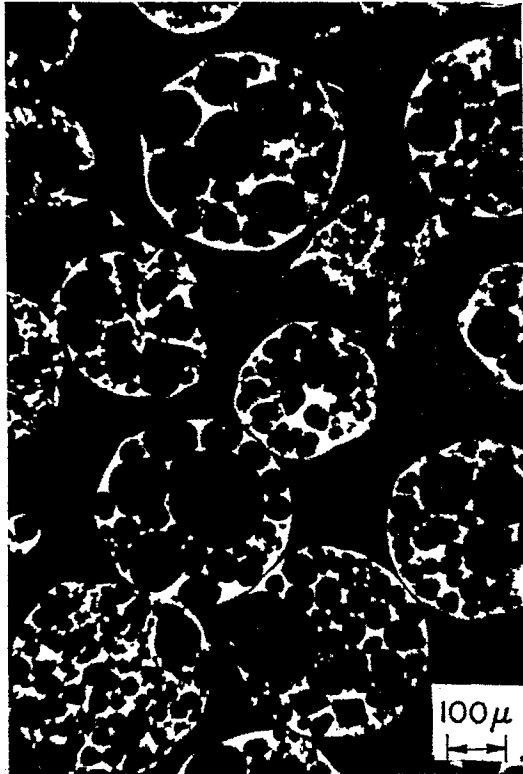


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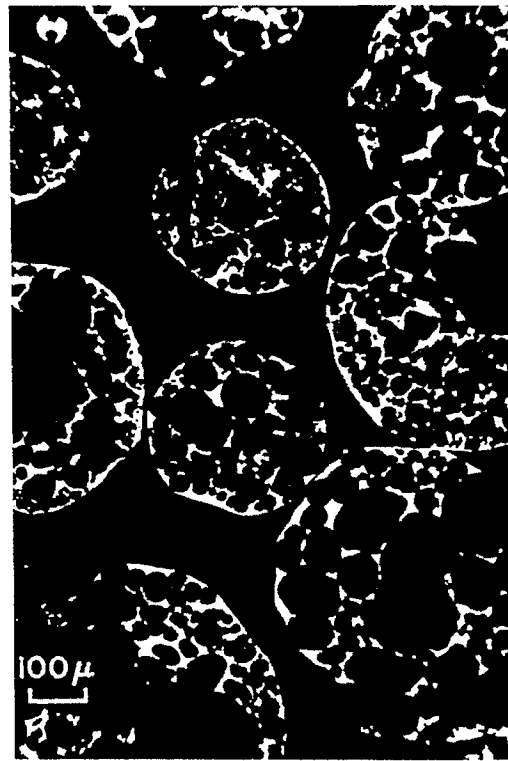


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Figure 6a-4. RESIDUE FROM SECOND-STAGE HYDROGASIFICATION



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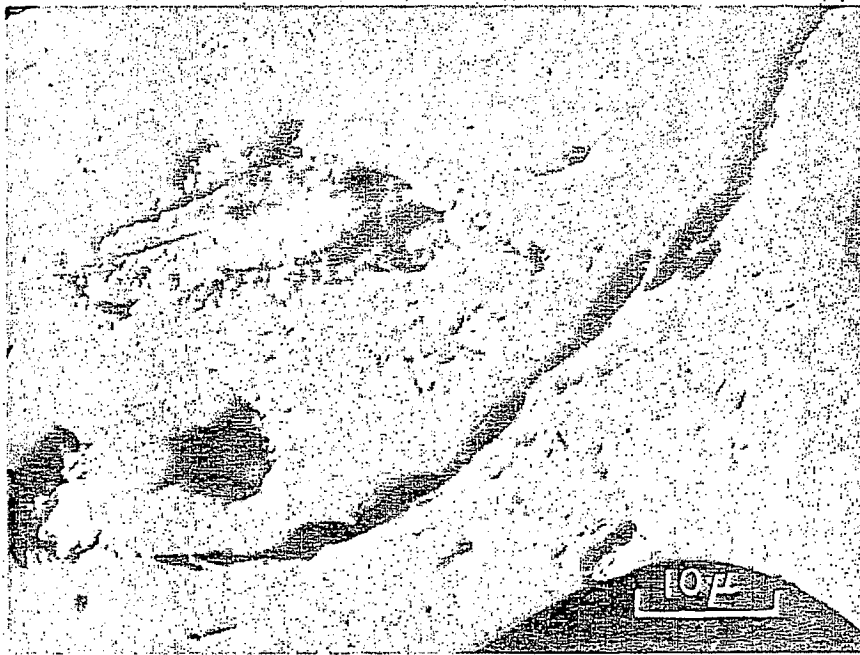
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Figure 6a-5. RESIDUE FROM FREE-FALL HYDROGASIFICATION



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Figure 6a-6. TEXTURE OF FREE-FALL RESIDUE FROM UNTREATED COAL



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Figure 6a-7. TEXTURE OF RESIDUE FROM PRETREATED COAL

The anisotropy is attributed to the formation of microscopic regions where the material is ordered in a pregraphitic layer structure. With a first-order red plate under high magnification, the graininess in the residue particles appeared as red rods, roughly $0.2 \times 10^4 \mu m$ in size, in a blue or yellow anisotropic matrix. Particles of residue from pretreated coal, when not grainy, show only occasional small areas of anisotropy around vesicles.

Generally, the particle-to-particle variation of the structure and reflectance of the hydrogasification residue is of interest because it may indicate variation in reactivity and conversion. The possibility has been considered that the subclass of vitrinite in the original coal may affect variation between particles. Such is the well-known differentiation between telenite and collinite in the Stopes-Heerleen system¹⁰, and other subclassifications have been proposed. Many of the IGT coal particles studied are not composed of a single subclass, however, while individual residue particles are rather uniform in both structure and reflectance (except for the particles that retain fusinite or semifusinite structure). It appears, then, that the history of the particle in the process is a more likely source of an observed variation than original structure, although the vitrinite subclass may have a minor role.

Structural variation can easily be explained on the basis of particle-to-particle variation in the amount of pretreatment; extended pretreatment of a particle results in greater loss both of volatile matter and of the potential for plasticity at higher temperatures. In the subsequent hydrogasification stage, such particles tend to develop less internal pressure, and are more resistant to the flow needed to develop additional vesicles.

The large variation in reflectance is more difficult to explain than are structural variants. The average reflectance of residue particles from the three hydrogasification runs that have been discussed are plotted against run temperature in Figure 6a-8. The standard deviations of the reflectance readings (one per particle) are also shown to indicate the particle-to-particle variation in reflectance. For comparison, the reflectance of pretreated coal heated for 40 minutes at temperatures in the same range is also shown in Figure 6a-8.

The residues from the two moving-bed hydrogasification runs show much greater variations than either the heated coal or the residue from the free-fall hydrogasification run. The bed temperature, as measured by an internal thermocouple, differed by less than 100°F from the average reactor-wall temperature throughout the bed of coal, during a 36-minute residence time. However, the temperature of the more reactive individual particles may rise substantially above the bed temperature because of the heat evolved in the reaction. This is especially true in the first stage, where the feed is highly reactive. IGT investigators believe the heat of reaction explains the origin of high reflectance particles found in first-stage residue.

The low reflectance of other particles — particularly in the second-stage residue — is not as easily explained as is high reflectance. To obtain more information on low reflectance, samples of pretreated coal and second-stage residue were heated in a laboratory tube furnace in hydrogen at atmospheric pressure. These data, reported in Table 6a-6, show a) that varied length of the heating period at 1850°F, from 10 minutes to 40 minutes, had little effect on the reflectance of the laboratory-heated samples of pretreated coal, and b) that the wide reflectance range of the second-stage hydrogasification residue was retained when it was heated to the same temperature. It may also be significant that the rise in reflectance with temperature is not substantial above 1300°F.

Table 6a-6. EFFECT OF HEATING PERIOD ON REFLECTANCE OF PRE-TREATED COAL AND CHAR HEATED IN HYDROGEN AT 1850°F

<u>Sample</u>	<u>Time of Heating, min.</u>	<u>Reflectance in Oil, %</u>	
		<u>Mean</u>	<u>Standard Deviation</u>
Pretreated Coal	10	6.90	0.38
	20	7.36	0.50
	40	7.17	0.47
	120	7.41	0.72
Residue, Second-Stage Hydrogasification	0	5.78	1.19
	20	6.83	1.32
	40	6.74	1.53

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Increase in surface area of the coal during processing is of interest in connection with the reflectance results. Determinations of area were made on the residue from Run HT-128. This run used pretreated Ireland Mine

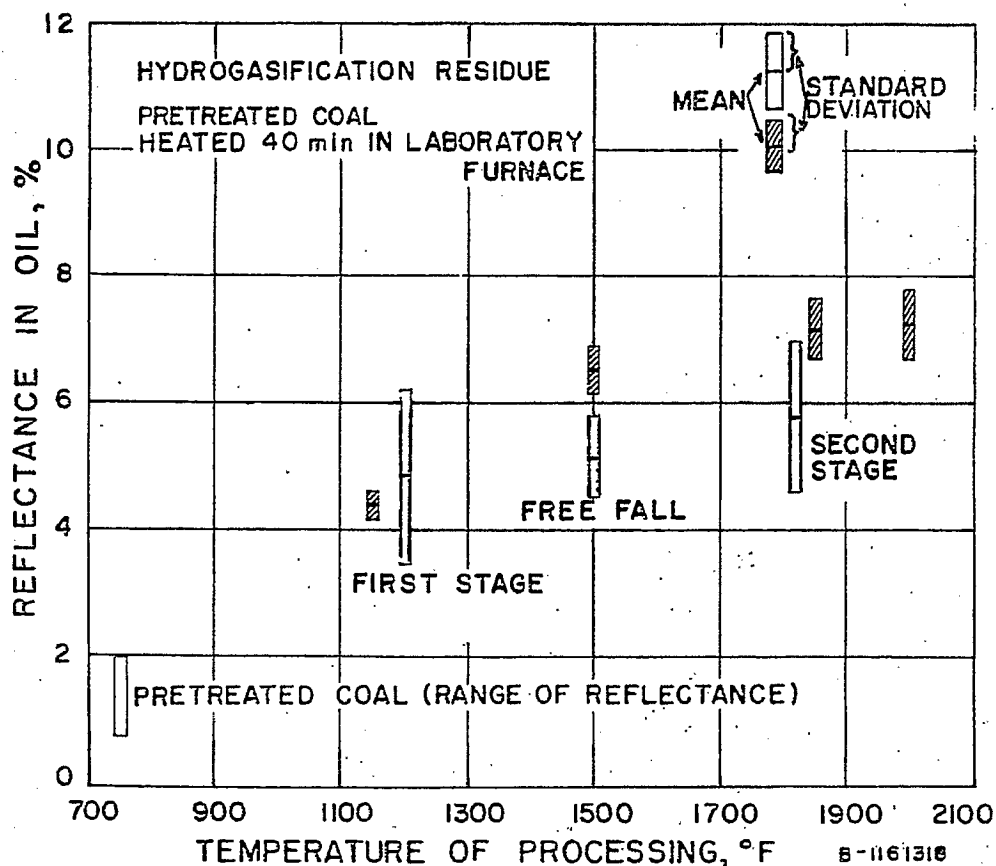


Figure 6a-8. REFLECTANCE OF HYDROGASIFICATION FEED AND RESIDUES

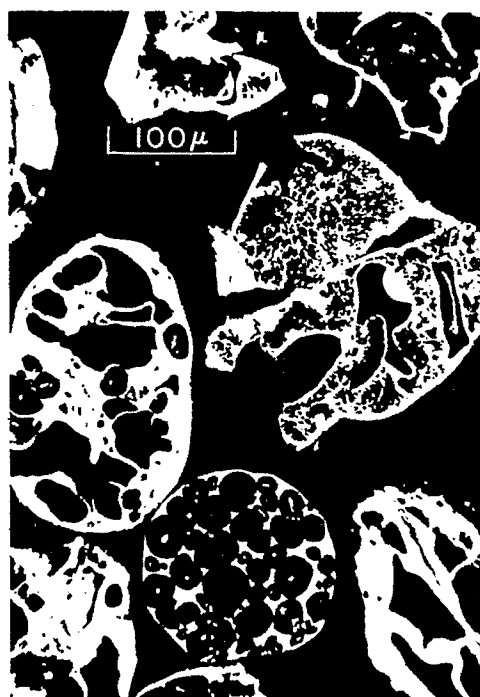
coal as feed, but utilized both free-fall and fluid-bed modes of operation. Carbon conversion in this run was 37.0%. The surface areas were:

Sample	Surface Area, sq m/g
Ireland Mine coal	131
Pretreated coal	148
Hydrogasification residue, Run HT-128	503

The total porosity, determined from true and particle density, includes both vesicles and small pores. Large microscopically visible pores (vesicles) did not affect the reflectance, because they were avoided in taking measurements. The surface area, on the other hand, provides an indication of the content of submicroscopic pores — those of diameter less than $0.1\mu\text{m}$. Increased porosity in this size range can be expected to cause decreased reflectance, which results from decreases in both the absorption index and the refractive index; the effect of porosity on the latter is governed by the Lorentz-Lorenz relation. Therefore, gasification in submicroscopic pores throughout the particle is very likely the cause of lower reflectance in residue particles than is obtained by carbonization at the same temperature. On the other hand, variation in reflectance between particles would be caused by differing reactivity that results from variation in effectiveness of pretreatment.

In later process studies on a variety of coals the two hydrogasification stages were combined in a single operation. The first stage was limited to a period of a few seconds while the pretreated coal dropped in free-fall through the rising gas in the upper 9 ft of the reactor tube. The second-stage hydrogasification occurred in a fluidized bed in the lower 3-4 ft of the reactor tube. With this processing regime it was not possible to obtain samples of char between the two stages. Most of the char residues investigated here were from runs in which the hydrogen fed was between 25 and 30% of the stoichiometric amount required for complete gasification, and the steam comprised 50% of the steam-hydrogen mixture.

Several different types of particle structure are found in the char residues after hydrogasification (Figure 6a-9).



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Figure 6a-9. TYPES OF CHAR STRUCTURE IN RESIDUE FROM WEST VIRGINIA NO. 5 BLOCK COAL

A fine-textured foam structure is prevalent in the residue from the highest rank, high volatile bituminous coal (West Virginia No. 5 Block) but becomes less frequent with decreasing rank until it is virtually absent in the residue from the Illinois No. 6 coal (Figure 6a-10). Otherwise, the residue particles from the different high-volatile bituminous coals appear quite similar in form. Also, there is little difference in reflectance; the mean reflectance of the residue from the lowest rank coal (Illinois No. 6) does not differ significantly from that of the Pittsburgh No. 8 (Table 6a-8).

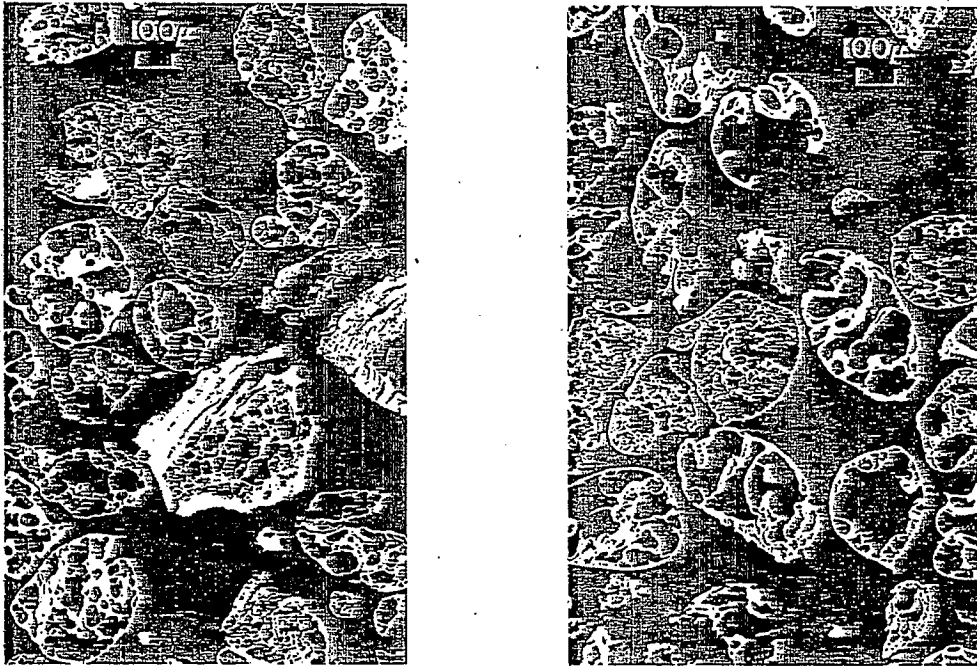


Figure 6a-10. RESIDUE CHARS FROM ILLINOIS NO. 6 COAL (left)
AND WEST VIRGINIA NO. 5 BLOCK COAL (right)

There is some difference in the anisotropy of the particles. The residue from the Illinois No. 6 coal exhibits very little anisotropy when observed with crossed polars. Less than half of the particles show any anisotropy, and these only in small areas. Anisotropy of the residue increases with coal rank. Thus, in the residue from the West Virginia No. 5 block coal most of the particles show at least a little anisotropy, while some, especially those with the foam structure, are predominantly anisotropic except for the pretreatment skin. The greater degree of anisotropy and the greater prevalence of foam structure in the residue from the higher rank coals indicates that a greater degree of fluidity is attained in the interior of these particles when the coal is rapidly heated in the hydro-gasification reactor.

6a.6 Low and Medium Volatile Bituminous Coals

The pretreated Pocahontas No. 4 coal showed the usual development of oxidized pretreatment skin, but very little or no vesicle formation (Figure 6a-11) and no significant loss of volatile matter. The pretreatment skin extends into many cracks. Many additional fine cracks were present in many particles. A high rate of attrition was observed in the pretreatment processing, which we attributed to the development of these cracks.

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Figure 6a-11. PRETREATED POCAHONTAS NO. 4 COAL

Pretreatment of the Fayette County Sewell seam coal, which is on the borderline between medium- and low-volatile rank, did result in vesicle formation (Figure 6a-12), although not to as great an extent as in the high-volatile coals. Fine cracks were also observed in the pretreated particles of this coal, and a high rate of attrition occurred in the pretreatment processing.

Figure 6a-12. PRETREATED SEWELL SEAM COAL
(Lochgelly No. 2 Mine)



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Hydrogasification of these two coals was difficult because the reactor plugged with agglomerated coal particles. To investigate this, agglomerated particles and residue from the Pocahontas coal were examined petrographically. Particles without skins, and the interiors of particles with skin were anisotropic and had a foam structure. Agglutination or cementing of particles was done by this foam material only. It was obvious (Figure 6a-13) that the foam material was supplied not only by the particles that had undergone little or no pretreatment, but also by particles with holes or breaks in the skin. It appears that the pretreatment skin can be broken and the contents discharged to the outside of the particle as a result of the simultaneous development of pressure and fluidity in the interior of the particles.

Only a small fraction of the residue from the Pocahontas coal — that from the pretreatment skin and probably that derived from inertinite — does not have a foam structure. The residue from the Sewell coal also has a large amount of foam structure, but has an appreciable, perhaps predominant, amount of material with vesicular structure similar to that of the residue from high-volatile bituminous coals. This can be attributed to the greater amount of devolatilization that occurred in the pretreatment of the Sewell coal. Some particles of the residue from the latter coal display the discharge of foam material from the inside of the particle that was observed in the residue from Pocahontas coal. The smaller proportion of foam structure in the Sewell residue, however, indicates that its agglomerating tendency should be appreciably less than that of the Pocahontas.

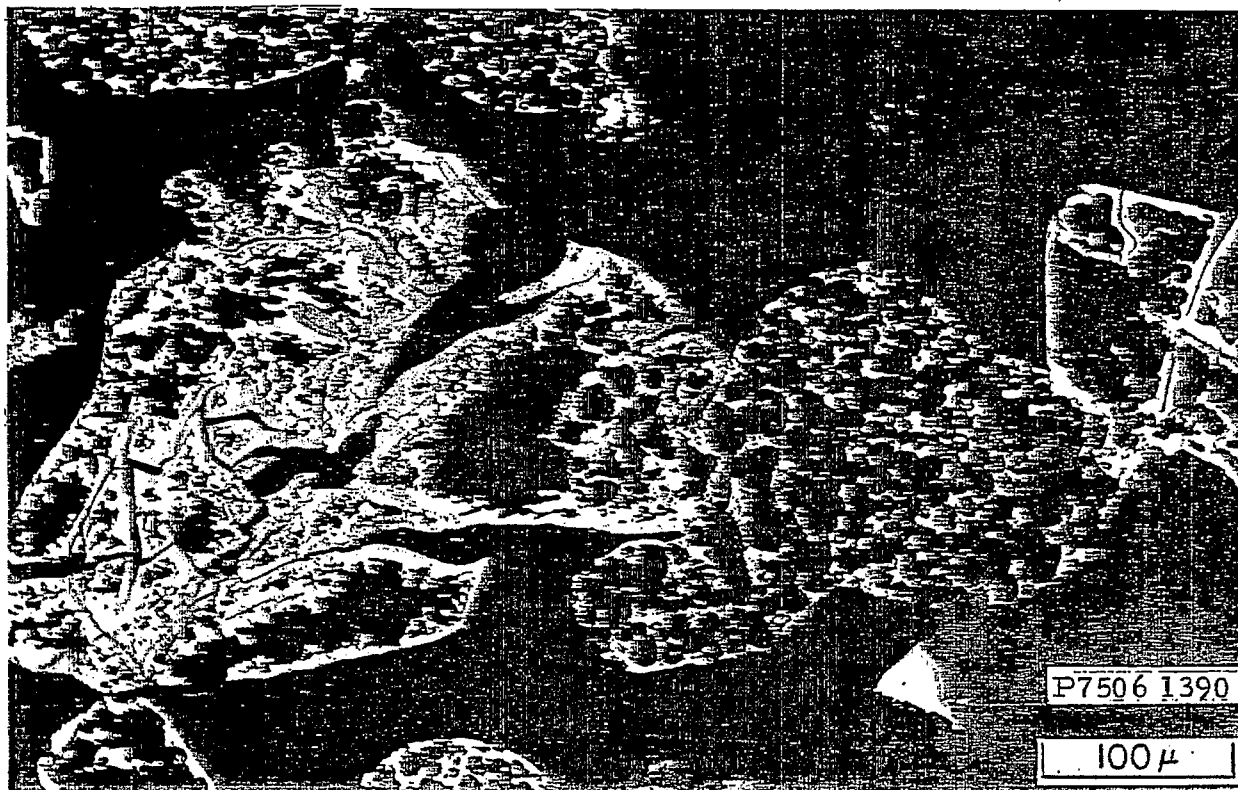


Figure 6a-13. RESIDUE CHAR FROM POCAHONTAS NO. 4 COAL OBSERVED WITH CROSSED POLARS

6a.7 Subbituminous Coal and Lignite

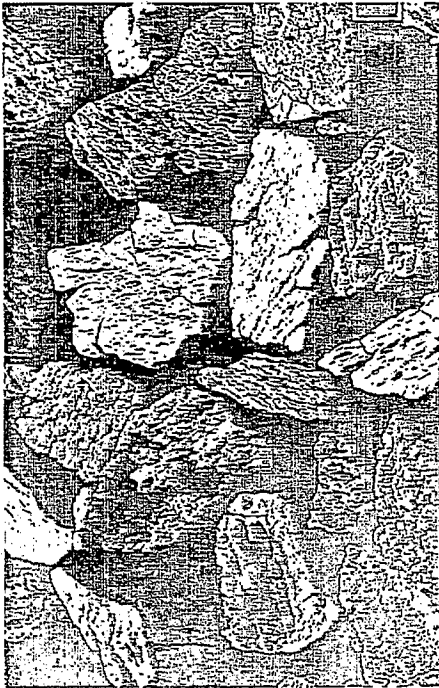
The residues from lignite and subbituminous coal hydrogasified without pretreatment have a different type of pore structure (Figures 6a-14 and 6a-15). The pores are typically lenticular in cross section rather than rounded, but rounding and expansion of the pores in some areas indicate the development of a degree of plasticity in some entire particles and in part of others. More of this pore expansion seems to have occurred in the lignite than in the subbituminous coal. This pore expansion may be caused by the greater fluidity conferred by the presence of exinite or resinite or both; these are somewhat more plentiful in the lignite than in the subbituminous sample.

Average reflectance of these residues is substantially less than that of residues from the bituminous coals (Table 6a-8), with that from lignite being least. In residues from both lignite and bituminous coal (Table 6a-8) the reflectance is appreciably less than that obtained when the same coal is heated at atmospheric pressure to the same temperature and for a comparable period of time (Table 6a-7). (Mean residence time in the hydrogasification fluidized bed is about 5 minutes.) The difference in reflectance probably is the result of the widening of submicroscopic pores by gasification reactions in the interior of the particles.

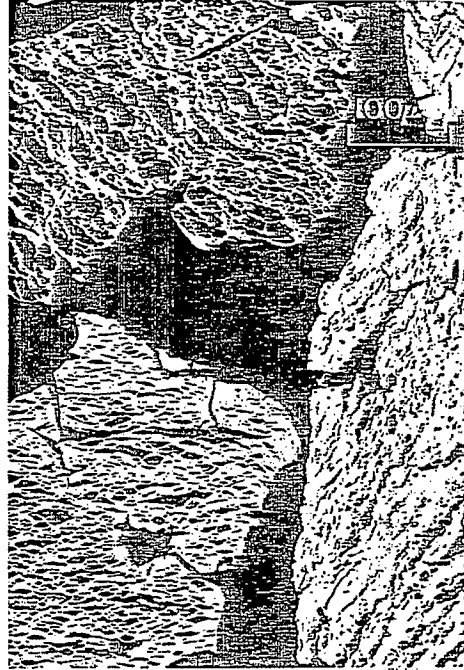
Appreciable amounts of Sewell seam coal were found in the Colorado subbituminous coal feed to PDU runs (Table 6a-7). The traces of foreign coal found in other coal feeds were attributed to small amounts of the previously processed coal having been left in inaccessible parts of the crushing and screening equipment. The amount of contamination in the Colorado feed is too large to be accounted for in this way. Laboratory agglomeration tests of the uncontaminated coal gave a free-flowing product. We believe that the contamination was responsible for the difficulties experienced in hydrogasifying the untreated coal.

Table 6a-7. REFLECTANCE OF COAL HEATED IN HYDROGEN

<u>Sample</u>	<u>Temp, °F</u>	<u>Time of Heating, min</u>	<u>Avg Reflec- tance in Oil, %</u>	<u>Std Dev, %</u>
Pretreated Pittsburgh No. 8	1660	3	5.66	0.92
Pretreated Pittsburgh No. 8	1660	6	5.60	0.89
Pretreated Pittsburgh No. 8	1660	20	6.11	0.56
North Dakota Lignite	1590	3	4.52	0.46
North Dakota Lignite	1590	6	5.10	0.43
North Dakota Lignite	1590	20	4.96	0.54



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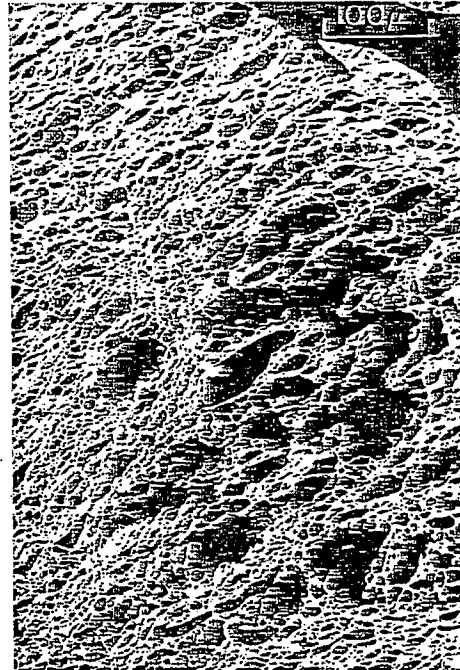


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Figure 6a-14. RESIDUE CHAR FROM NORTH DAKOTA LIGNITE



P7506 1393



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Figure 6a-15 RESIDUE CHAR FROM COLORADO SUBBITUMINOUS

Table 6a-8. REFLECTANCE OF HYDROGASIFICATION RESIDUES

<u>Coal</u>	<u>Pittsburgh</u>	<u>Illinois</u>	<u>Colorado</u>	<u>No. Dakota</u>
<u>Run. No</u>	<u>No. 8</u>	<u>No. 6</u>	<u>Subbituminous</u>	<u>Lignite</u>
	<u>HT-126</u>	<u>HT-155</u>	<u>HT-184</u>	<u>HT-139</u>
Reflectance in Oil, %	Distribution of Reflectance Readings, %			
0-0.9	--	--	--	6.3
1.0-1.9	--	0.4	2.6	19.8
2.0-2.9	2.2	1.3	22.6	17.8
3.0-3.9	22.7	17.1	59.1	20.7
4.0-4.9	48.4	62.8	12.2	1.5
5.0-5.9	22.9	16.2	3.5	0.9
6.0-6.9	3.0	1.3	--	--
7.0-7.9	0.8	0.8	--	--
8.0-8.9	--	0.4	--	--
No. of Readings	362	234	115	111
Avg Reflectance in Oil, %	4.49	4.45	3.56	3.44
Standard Deviation, %	0.80	0.71	0.70	0.90

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Table 6a-9. CONTAMINATION OF COLORADO SUBBITUMINOUS FEED WITH SEWELL SEAM COAL

<u>Sample</u>	<u>Sewell Coal, vol %</u>
Feed to HT-176	10.2
Feed to HT-177	9.4
Feed to HT-181	6.4
Feed to FP-122 (pretreated for Run HT-184)	9.0

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6a.8 Electrogasification Residue

Both feed and residue samples from electrogasification Run EG-19 were examined petrographically. The feed for this run was bituminous coal char from the FMC Corporation's Project COED. Both feed and residue (Figure 6a-16) were similar in appearance to residue obtained from the hydrogasification of Illinois No. 6 bituminous coal. There is no trace of pretreatment skin or of any anisotropy, however, and the amount of vesicle formation seems to be less in the FMC char. The lack of pretreatment skins and of anisotropy can be explained as the result of absence of oxygen and of a slower heat-up rate for the coal particles of the COED Process, compared to conditions in the HYGAS Process.

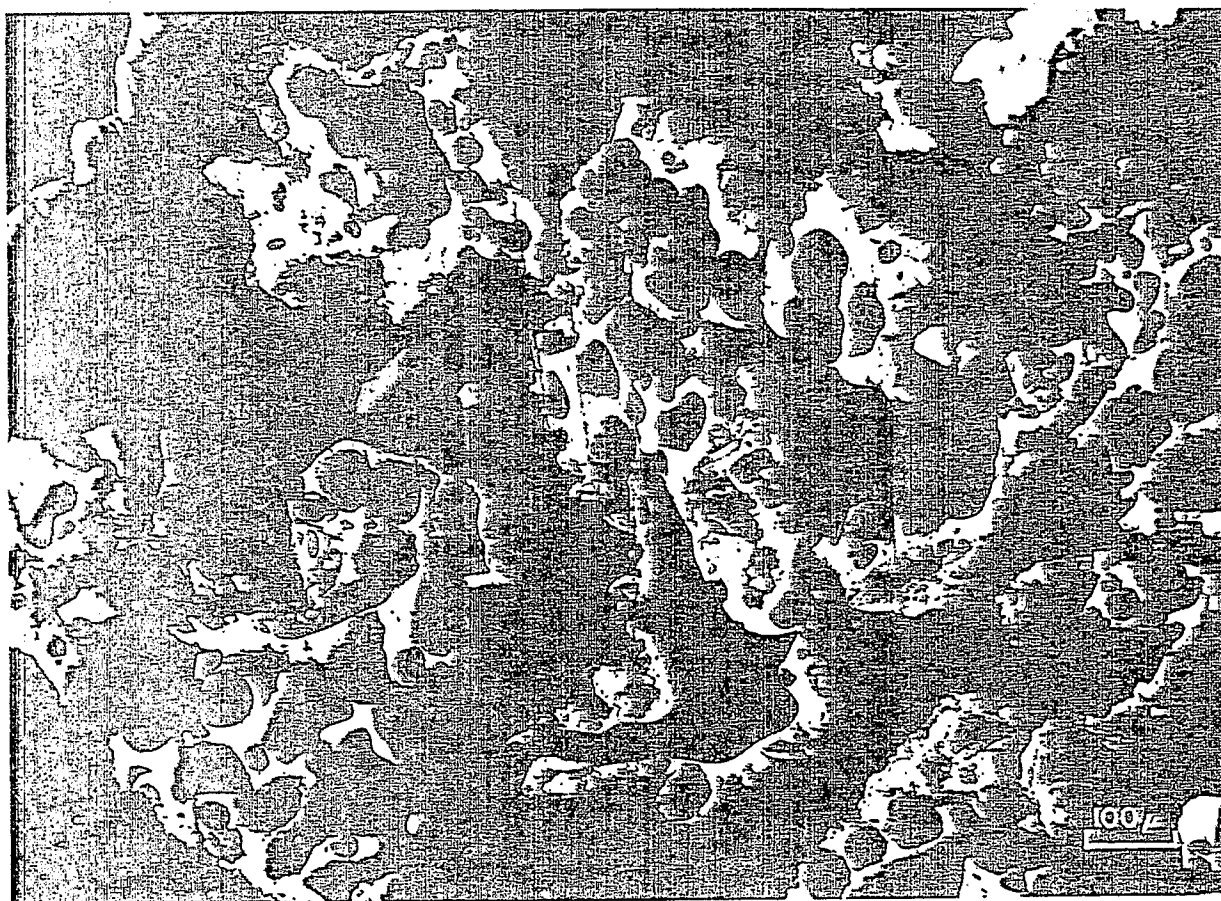


Figure 6a-16. FMC CHAR

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6a.9 Graphitization

Several residues from hydrogasification were examined quantitatively by X-ray. The study showed that only a minor amount of graphitization had occurred compared to the amount found in meta-anthracite. Samples investigated included raw coal, pretreated coal, residue from first-stage hydrogasification Run HT-70, residues from two second-stage runs — HT-72 (1825°F) and HT-73 (1950°F), and residues from free-fall Run HT-38.

Mineral matter had to be removed from the samples by treatment with both hydrochloric and hydrofluoric acid. An X-ray diffraction scan in the vicinity of the 3.35 A peak of graphite was obtained with a General Electric diffractometer. There was no evidence of graphitization in either raw or pretreated coal. In the residues, very broad diffraction peaks were observed, indicating ordering of pregraphitic layers. Total diffraction intensity and apparent crystallite size, calculated from the peak width, appear in Table 6a-10.

Table 6a-10. GRAPHITIZATION OF HYDROGASIFICATION RESIDUES

<u>Sample</u>	<u>Average Run Temp, °F</u>	<u>Average Crystallite Size, A</u>	<u>Diffraction Intensity Counts X 10⁻³</u>
Residue HT-70	1205	23	168
Residue HT-72	1825	21	170
Residue HT-73	1880	22	210
Residue HT-38	1500	22	336
Meta-anthracite	--	158	1215

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In spite of the moderate reaction temperature and short period of exposure to heat, the residue from the free-fall run showed more diffraction intensity at 3.35 A than any of the other residues. This high intensity probably resulted from greater fluidity during hydrogasification, probably because the coal had not been pretreated. The high rate of heating in the free-fall run, compared to a lower heating rate in a moving bed, may also play some role in diffraction intensity.

Similar X-ray measurements were made with a sample of Rhode Island meta-anthracite obtained from the Illinois State Geological Survey (hand specimen No. 766). These measurements are also reported in Table 6a-10. Both the amount of ordered material and the size of ordered clusters are clearly much less in hydrogasification residues than in meta-anthracite. Therefore, the low combustibility of meta-anthracite should not be characteristic of hydrogasification residue that results from processing bituminous coal particles, either pretreated or raw.

6a.10 Conclusions

Petrographic study of the specified feed coals and some of their chars at different stages of processing has been fruitful in several ways. The detection of contamination of a nonagglomerating coal by coking coal explained some anomalous hydrogasification processing results, although the examination was not early enough to avoid their occurrence. Agglomeration of pre-

treated high-rank bituminous coals was shown to result from the discharge of fluid material from the interior of pretreated particles as well as from the fluidity of the few particles that escaped pretreatment. Lack of anisotropy in the residue chars from lignite, subbituminous coal, and pretreated high-volatile C coal indicates that little or no fluidity developed in these coals, and accounts for the successful processing of lignite and subbituminous coal without pretreatment. Increasing amounts of anisotropy, indicating development of fluidity, were observed in chars from the higher rank bituminous coals. Increased anisotropy and a very different char particle structure were found when a high-volatile A bituminous coal was fed without pretreatment.

Differences in structure may become important if process development makes it possible to feed the coal without pretreatment. Because graphitization at higher temperature occurs only when the char has passed through a fluid stage with resulting anisotropy (Kipling and Shooter, 1966), the degree of anisotropy or lack of it may indicate differences in the electrical characteristics of the char; this may affect its behavior in the electrothermal gasification process for the production of hydrogen.

Correlating the petrographic properties of a coal and its suitability for hydrogasification, we find:

- Exinite is largely lost in pretreatment and, therefore, is of value only if the coal can be processed without pretreatment.

- Fusinite and semifusinite are expected to be less reactive than vitrinite but no quantitative data on this are available.

6a.11 References Cited

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APPENDIX 6a-A
Embedment of Fragile Particles

6a-A v

6a-A.1 Method

The apparatus and procedure were developed for mounting fragile, hollow, vesicular particles of treated coal without crushing or shattering them. A sectional view of the apparatus is shown in Figure 6a-A1. A mold holding the coal sample is evacuated to about 25-mm absolute pressure and is filled with epoxy resin while under vacuum. The bottom of the mold is maintained vacuum-tight so that upon readmission of the atmosphere the pressure helps to force resin around and into the coal.

These treated coal particles contain many closed pores that do not fill with resin in mounting. To obtain a scratch-free surface for reflectance determination it is necessary to fill the pores that are exposed by sectioning. To do this we reimpregnate the surface with resin after the next-to-last polishing step, which is done with 0.3-micron alumina.

6a-A.2 Mounting Procedure

To mount the particles, stopcock grease or another release agent is applied to the inside surfaces of the mold, including the base. Stopcock grease is applied to the outer part of the lapped surface of the mold base. The top part of the mold is then twisted onto the lapped surface of the mold base to form a vacuum seal as in a stopcock or ground joint. The mold is filled about 3 mm deep with the sample. To prevent the particles from floating on the resin, the sample is gently covered with No. 12 lead shot.

Epoxy resin (Armstrong C-4) is mixed with activator (Armstrong D). The apparatus, except for the glass tube, is then assembled as shown in Figure VI-A1, and resin is added to the cup up to about three-quarters of the ball diameter. The assembly of the apparatus is completed, and the apparatus is evacuated until the resin begins to foam. The apparatus is allowed to stand a few minutes until the foam subsides, then it is tipped until the ball rolls off the hole in the cup. When the resin has stopped running down, the atmosphere is let into the apparatus, the apparatus is disassembled, and the steel ball is cleaned before the resin hardens.

6a-A.3 Reimpregnation

To reimpregnate the briquette surface after the next-to-last stage of polishing, the bottom of a paper cup is covered with resin-activator mixture, and the dried briquette is placed face down into the resin in the cup. Then the cup is placed in the vacuum apparatus and evacuated until the mixture foams. The atmosphere is allowed to reenter. The briquette is then removed and placed face down on a thin smooth sheet of plastic (2-mil Mylar is satisfactory) on a smooth flat surface. A 1- to 2-lb weight is placed on the briquette to squeeze out excess resin. After the resin has hardened, the next-to-last polishing step is repeated to remove the film of resin left on the face.

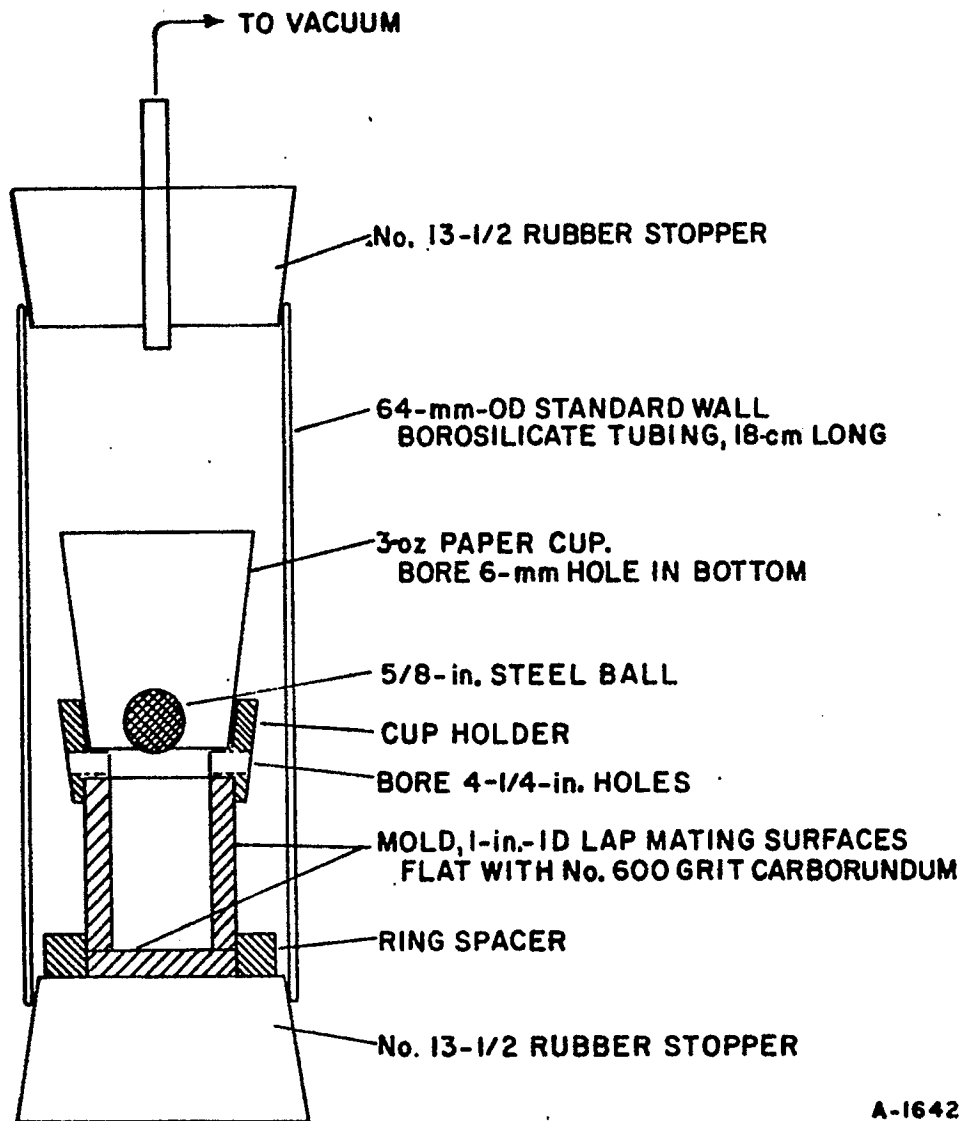


Figure 6a-A1. APPARATUS FOR EMBEDMENT WITH VACUUM

PART 6b
Miscellaneous Support Studies

6b-1

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6b.0 Summary of Miscellaneous Support Studies

A summary of this work appears in section 6.0.

6b.1 Introduction

Several studies to support the hydrogasification program were considered necessary. The investigations performed were: 1) The slurring of coal and char prior to pumping tests; 2) Analyses of condensate water samples for phenol and hydrogen cyanide, 3) Analyses of hydrocarbon liquids, 4) Analyses for ammonia in the water phase of condensate, 5) Removal of phenol from the condensate, 6) Analyses of the product gas from the PDU reactor for traces of higher hydrocarbons, and 7) Attrition resistance of hydrogasification residues.

Details of these studies are described herein.

6b.2 Slurry Properties

Some laboratory tests on slurring coal and char were undertaken preparatory to process studies. Results showed that the raw or pretreated Ireland Mine coal was easily wetted and formed into a slurry by stirring with water; if not stirred, the pretreated coal floated on the water without much wetting. About 1.3 grams of water per gram of coal was required to form a pumpable slurry when the pretreated coal and water were mixed at atmospheric pressure. However, a larger amount, about 1.6 grams per gram of coal, was required when the coal-water mixture was subjected to a pressure of 1000 psi, which no doubt forced water into the pores or vesicles of the pretreated coal.

The removal of water from the slurry by centrifugation was investigated; data are presented in Table 6b-1. Pressuring the slurry before centrifuging at 1000 revolutions per minute and 6-inch radius increased the amount of residual water from 0.13 grams per gram of coal to 0.75 grams per gram of coal.

Table 6b-1. REMOVAL OF WATER FROM COAL SLURRIES BY CENTRIFUGATION

Nominal Centrifuge Speed, rpm	Ireland Mine Coal	Pretreated Ireland Mine Coal	Hydrogasification Residue
	Water Retained, g/g coal *		
100	--	1.13	--
250	--	1.02	--
500	0.34	0.28 [†]	0.25
750	--	0.20	--
1000	0.07	0.13 [‡]	--

* Slurries prepared at atmospheric pressure; samples at a radius of 6 in. in centrifuge.

[†] Increased to 0.98 g/g of coal when slurry subjected to pressure of 1000 psi.

[‡] Increased to 0.75 g/g of coal when slurry subjected to pressure of 1000 psi.

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Slurrying with benzene instead of water was also investigated. About the same amount of benzene, 1.6 to 1.8 grams per gram of coal, was required to make a pumpable slurry when the mixture was subjected to a pressure of 1000 pounds per square inch. The separation of benzene and water in the presence of coal fines (-200 mesh) was investigated. Tentative conclusions are as follows:

1) The coal tends to be wetted preferentially by the benzene whether it is wetted first with water or with benzene.

2) The water and benzene rapidly separate (within 2 minutes) into a benzene layer and a water layer.

3) The benzene layer contains suspended coal that settles to the bottom of the layer.

4) The slurry has a tendency, especially on standing, to form a benzene-coal sludge that has about the same density as the water. This sludge may float on top or sink to the bottom of the water layer. After the coal is filtered out, the water and benzene quickly separate.

HYGAS researchers also investigated the use of a light oil rather than benzene as the slurry medium. This light oil is the IBP-160°C distillate

fraction of the tar recovered from hydrogasification Run HT-185 (Colorado subbituminous coal feed). The behavior of the light oil-water-coal mixtures was about the same as that of the benzene mixtures. The -200 mesh coal collected in the hydrocarbon layer, which separated quickly and completely from the water.

Fines formation from sudden heating of the pretreated coal slurry was also investigated. Explosive vaporization of benzene or light oil held in the vesicles of the coal may break particles. For this test, pretreated coal was mixed with benzene and subjected to 1000 pounds per square inch pressure to force the benzene into the vesicles. A sample of about 1 gram was dropped, a few particles at a time, into a flat-bottomed aluminum pot heated to 700°F. Although the accuracy of the test is not high due to the small size of the sample, the results presented in Table 6b-2, indicate that only a small amount of fines is produced.

Table 6b-2. TEST FOR FINES PRODUCED BY SHOCK HEATING OF COAL SLURRY

Sample	Sieve Analysis, wt %		
	+100	-100+200	-200
Pretreated Ireland Mine Coal			
After test, trial 1	95.8	3.5	0.6
After test, trial 2	97.6	2.2	0.7
Pretreated Illinois No. 6 Coal			
After test, trial 1	98.3	1.3	0.3
After test, trial 2	97.8	1.6	0.6

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There is a possibility that the benzene or light oil used for slurring may dissolve a portion of the coal, then deposit it on the outside of the particles when the liquid is evaporated. If a substantial amount is deposited, the agglomerating tendency of the coal is likely to increase.

The solubility of coal in benzene is greatly dependent on the extraction temperature. For example, Asbury¹ found that less than 0.1 weight percent of a Pittsburgh seam coal dissolved at 176°F, while 8.9 weight percent dissolved at 428°F in 1 hour.

To investigate this problem the coal-benzene mixtures were heated at temperatures from ambient to 500°F for a period of 1/2 hour; the benzene was then evaporated and an agglomeration test was run on the coal. Neither pretreated Illinois No. 6 nor pretreated Ireland Mine (Pittsburgh No. 8) coal showed an appreciable increase in agglomerating tendency when treated with benzene either at 300° or at 500°F. Dried lignite did show some agglomeration after treatment with benzene, but showed about the same behavior when tested before treatment with benzene. Subsequent petrographic examination of the lignite and of the residue from agglomeration tests indicated that the agglomeration was caused by the presence of a small amount of Sewell seam (Fayette Co.) coal. The latter was probably introduced in pilot plant grinding and drying operations.

The float-sink properties of chars were tested at different stages of hydrogasification. Because the chars are vesicular, they tend to float on water if it does not penetrate and fill the vesicles. This may cause difficulties in slurring the chars with water for removal from the hydrogasification and electrogasification reactors.

The following four samples were tested:

<u>Run No.</u>	<u>Sample</u>
F-OH-8	Pretreated Ireland Mine coal
R-OH-8	Hydrogasification residue from Ireland Mine coal
R-EG-47	Electrogasification residue from bituminous coal
R-HT-241	Hydrogasification residue from North Dakota lignite

The pretreated coal is not slurried with water in the HYGAS process, but was so tested to complete the picture.

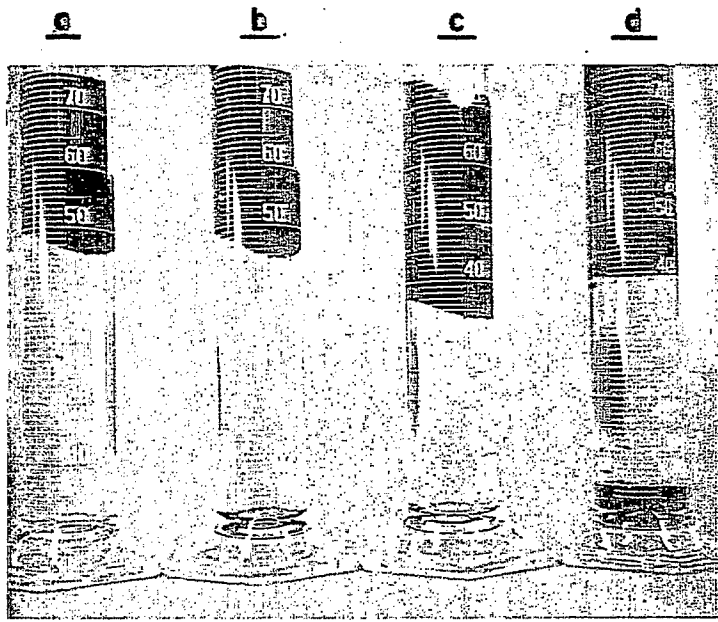
Results are reported for each sample tested under the following conditions:

- 1) 25 ml of the sample was poured into a graduated cylinder, containing 50 ml of water and allowed to stand for 1 hour.
- 2) The above samples were shaken.
- 3) 25 ml of the sample was boiled in water for 1/2 hour, then transferred to a graduated cylinder.
- 4) 25 ml of the sample was heated to 600°F or slightly higher, then quickly poured into 100 ml of water at room temperature.

The photographs in Figure 6b-1 show the results from the first three tests. In the first test no char sank except for a small amount of the lignite residue. After shaking, some char from each sample sank: The lignite char showed the greatest amount. In the third test, all of the chars sank after boiling, except for a small fraction of the pretreated coal.

Because of the steam generation, some of the char in the fourth test was thrown upward when it was poured into the water. Some of the char collected on the walls of the beaker; some fell back to the surface of the water and floated there. The amount on the walls and floating on the water was measured with the following results:

AFTER
STANDING
1 HOUR,
NO
SHAKING



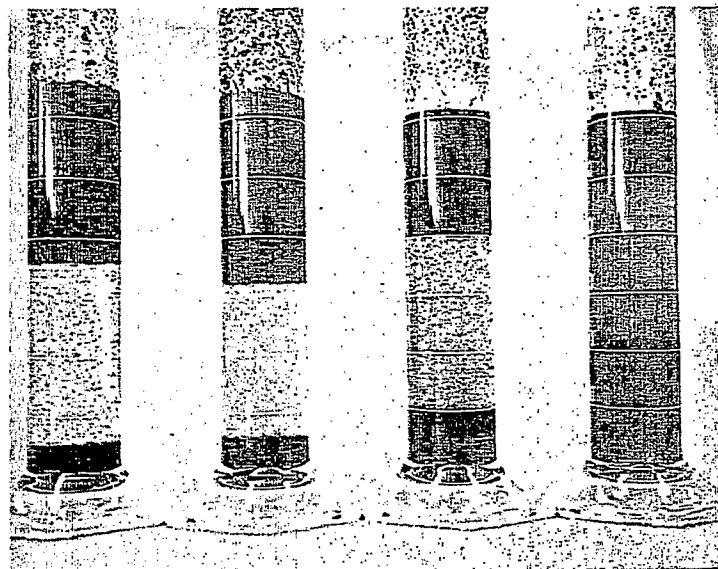
a: F-OH-8,
PRETREATED
IRELAND
MINE COAL

b: R-OH-8,
HYDROGASIFICATION
RESIDUE FROM
IRELAND MINE
COAL

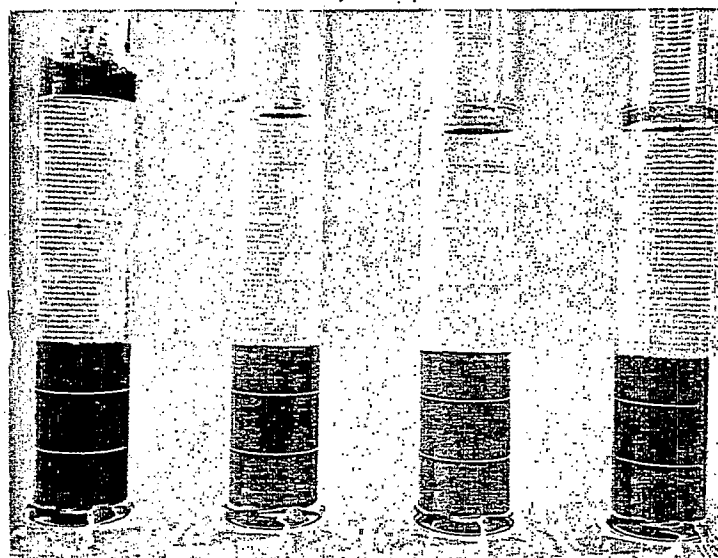
c: R-EG-47,
ELECTROGASIFICATION
RESIDUE FROM
BITUMINOUS COAL

d: R-HT-241,
HYDROGASIFICATION
RESIDUE FROM
NORTH DAKOTA
LIGNITE

AFTER
SHAKING



AFTER
BOILING



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Figure 6b-1. TEST RESULTS OF CHAR FLOAT-SINK PROPERTIES

<u>Sample</u>	<u>Amount Not Sinking, wt %</u>
Pretreated Coal From Ireland Mine	11
Hydrogasification Residue From Ireland Mine Coal	8
Electrogasification Residue From Bituminous Coal	4
Hydrogasification Residue From Lignite	4

HYGAS researchers believe that the float-sink property depends, to a large degree, on the amount of noncondensable gas left in the vesicles and other pores after submersion. Boiling expels these gases completely, while the vesicles of char heated to 600°F would theoretically be about 50% filled after cooling, if immersed in water at that temperature.

6b.3 Characterization of Product Streams From PDU

6b.3.1 Phenol and Hydrogen Cyanide

Condensate water samples from three hydrogasification runs were analysed at an outside laboratory for phenol and hydrogen cyanide:

<u>Run No.</u>	<u>Feed Coal</u>	<u>Phenol, mg/l</u>	<u>HCN, mg/l</u>
HT-EG-7	Ireland mine	5000	359
HT-248	Montana subbituminous	4500	4.6
IU4-OH7	Ireland mine	2040	536

No explanation is available for the small amount of cyanide in the second sample. A rerun of the analysis agreed with the first analysis.

6b.3.2 Hydrocarbon Liquids

The hydrocarbon liquids from two hydrogasification runs in the experimental unit were analyzed. Feed to these runs was lightly pretreated Ireland Mine coal. For results, see Table 6b-3.

Table 6b-3. ANALYSES OF HYDROCARBON LIQUIDS OBTAINED BY HYDROGASIFICATION WITH LIGHTLY PRE-TREATED IRELAND MINE COAL.

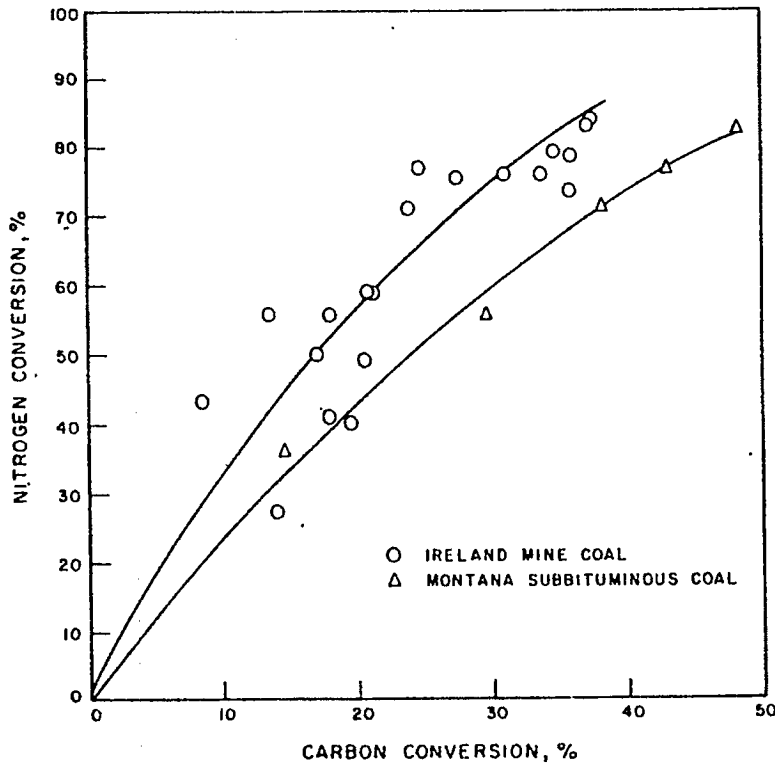
<u>Run No.</u>	<u>OH-7</u>		<u>OH-6</u>	
Date of Run	9-17-70		9-15-70	
Specific Gravity, 60:60	1.081		1.070	
Composition, wt %				
Carbon	87.5		87.3	
Hydrogen	6.50		6.61	
Distillation (500g) Fractions				
IBP °C	67		65	
IBP-160 °C, wt %	15.0		15.1	
160°-200 °C, wt %	6.0		5.9	
200°-300 °C, wt %	28.5		21.8	
300°-355 °C, wt %	19.0		20.9	
Residue, wt %	29.9		31.9	
Benzene in Total Sample, mol %	24.8		--	
Molecular Weight, estd	195		--	
IBP-160 °C Fraction				
Specific Gravity, 60:60	0.881		0.881	
Composition	<u>mol %</u>	<u>wt %</u>	<u>mol %</u>	<u>wt %</u>
Cyclopentadiene	0.1	0.1	0.1	0.1
Dicyclopentadiene	0.1	0.2	0.1	0.2
Benzene	68.3	64.0	66.7	62.4
Toluene	17.7	19.6	18.2	20.0
C ₈ Aromatics:				
Xylenes	5.1	6.5	6.8	8.6
Ethyl Benzene	3.1	4.0	2.0	2.5
C ₉ Aromatics	1.9	2.7	2.0	2.9
Styrene + Indene	0.1	0.1	0.6	0.7
Naphthalene	0.3	0.5	0.2	0.3
Unidentified	3.3	2.3	3.3	2.3

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6b. 3. 3 Ammonia

The fate of the nitrogen in the coal was investigated. Conversion to volatile products was calculated from the nitrogen content of the residue for all runs on Ireland mine pretreated coal from Run HT-94 to HT-169, and for Runs HT-211 to HT-216 on Montana subbituminous coal. Results are plotted in Figure 6b-2 against carbon conversion.

The water phase of the condensate from several runs was analyzed for ammonia, with the results shown in Table 6b-4. With the exception of one run (HT-252B) conversion to ammonia is close to the total conversion (Figure 6b-2), indicating that all or nearly all of the nitrogen is converted to ammonia.



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Figure 6b-2. CONVERSION OF COAL NITROGEN IN HYDROGASIFICATION

Table 6b-4. AMMONIA YIELD FROM HYDROGASIFICATION

Run No.	Coal	Carbon Conversion, wt %	Nitrogen in Coal, wt %	NH ₃ in Condensate Water, normality	Amount of Water Condensate lb/lb coal	Nitrogen Converted to NH ₃ , %	Yield of NH ₃ , lb/lb coal	Total N+ Converted %
HT-243*	Montana Subbituminous	30.0	0.93	1.45	0.503	51.9	11.7	60
HT-244	"	23.5	"	0.70	0.150	31.8	7.2	49
HT-248	"	27.4	"	1.34	0.326	64.0	14.5	56
HT-249	New Mexico Subbituminous	31.8	1.22	1.22	0.385	52.4	15.5	62
HT-252B	"	53.2	"	1.00	0.310	35.0	10.4	84
OH-7	Ireland Mine Bituminous	32.5	1.24	1.84	0.362	71.8	21.7	79

* At 500 psig; other runs at nominal 1000 psig.

† From graph, Fig. 6b-2

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6b.3.4 Phenol Removal

The filtering and adsorption properties of the residue from electrogasification were investigated. The objective was to remove the phenol from the condensate, obtained from the hydrogasifier effluent gas, by using the condensate to slurry the char from the electrogasification process. One test was run on the residue from Run EG-48. For later tests residues from Runs EG-34, EG-35, EG-37 and EG-46 were composited to provide a large sample from the processing of bituminous coal. Carbon conversions in the latter electrogasification runs ranged from 33 to 42%. Adsorption tests were made with pure phenol in water.

Water retention in the filter cake after filtration through a Buchner funnel was about 0.9 lb/lb of char. The following results were obtained:

<u>Sample</u>	<u>Initial Phenol Concn, ppm</u>	<u>Phenol Adsorbed, mg/g of char</u>	<u>Residual Phenol Concn, ppm</u>
EG-48 Residue	2590	7.6	17
Composite	4900	12.3	4.9, 6.8
Composite	52	0.13	0.014

The phenol concentration of 5000 ppm is about the maximum found in condensates from the experimental hydrogasification unit. The ratio of water to char in the tests, 2.5 by weight, exceeds the amount necessary for slurring the char to remove it from the electrogasification reactor.

In conclusion, it appears that the adsorptive capacity of the residue char varies, presumably with conversion. It will be possible to remove phenol from the condensate; however, it may be necessary to recycle the filtered condensate to slurring with another lot of char in order to reduce the phenol concentration below 5 ppb.

6b.4 Determination of Minor Components in PDU Reactor Product Gas

Using gas chromatography, with a flame ionization detector, a sample of product gas from the pilot plant hydrogasification reactor was analyzed for traces of higher hydrocarbons. Other components were determined by mass spectrometry. Combining the two analyses gave the analysis presented in Table 6b-5.

Table 6b-5. ANALYSIS OF REACTOR PRODUCTS AT 1530 HR,
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	<u>mol %</u>		<u>mol %</u>
Argon	0.2	Ethane	0.87
Carbon Dioxide	7.1	Propane	0.17
Carbon Monoxide	7.2	Isobutane	0.011
Helium	0.02	n-Butane	0.014
Hydrogen	49.5	Ethylene	0.043
Nitrogen	19.8	Propylene	0.17
Methane	14.6	Butenes	0.005

6b.5 Attrition Resistance of Hydrogasification Residues

A test for rating the attrition resistance of hydrogasification and other chars was developed. A microtumbler test correlated with Hardgrove grindability of coal was first investigated; the correlation of Terchick's² test results with the Hardgrove index is shown in Figure 6b-3. In this test 2 grams of a 20-30 mesh sieve fraction are placed in a 12-inch-long, 1-inch inside diameter cylinder with 12 steel balls; the cylinder is turned end-over-end for 800 turns at a specified rate. In the test used on coal, the amount passing a 100-mesh sieve is then determined. Results found on Ireland mine coal and on several chars are shown in Table 6b-6. The value found on Ireland mine coal agrees with those reported in the literature on Pittsburgh seam coal. Reproducibility is satisfactory, but so much of the char is ground in the test that its use for characterization of behavior in a fluidized bed is very questionable.

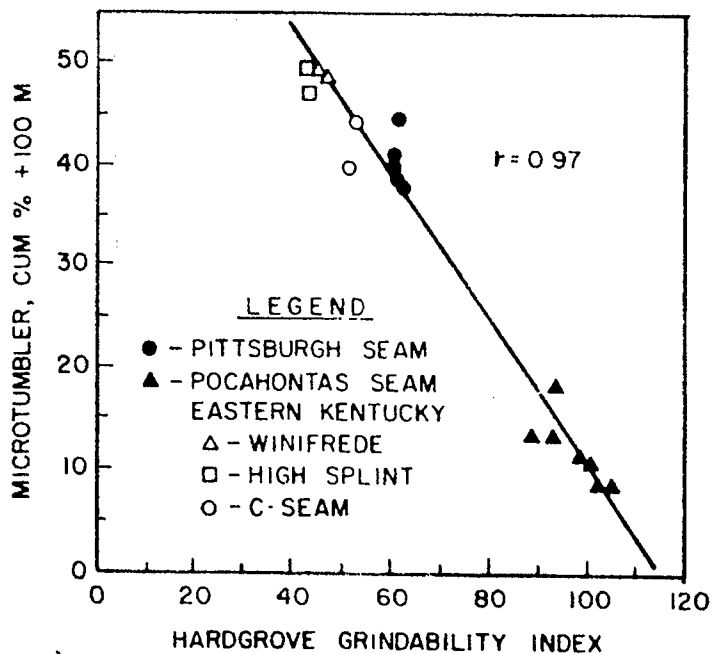
The test was modified by substituting twelve 5/16-inch polyethylene balls for the steel balls used in the original test. Tests were run on several sieve fractions from each sample (Table 6b-7).

The amount of -200-mesh fines produced in the test is considered to be the most significant test result. Residue from lignite shows the least attrition of the residues tested. FMC char and residues from bituminous coal show more attrition, with the bituminous coal residue having the most. Tests on residues of bituminous coal gasified to different conversions (Runs HT-154, HT-210, EG-34) again show slightly decreasing attrition with increasing conversion. Residue from bituminous coal shows a slight increase in attrition with decrease in particle size. However, it is possible that neither of these trends is statistically significant.

It is apparent that the constant or slight increase in attrition resistance with increase in conversion is characteristic of the residue as a whole rather than of the coarse particles only. Perhaps the decrease in strength expected because of the removal of material by gasification throughout the particle is compensated for by an increase in strength because of a coking type of reaction.

6b.6 References Cited

1. Asbury, R. S., "Action of Solvents on Coal. Extraction of Edenborn Coal by Benzene at Elevated Temperatures," Ind. Eng. Chem. 26, 1301-06 (1934).
2. Terchick, A. A., et al., "Mechanical and Related Properties of Some Eastern Coals," ACS Div. Fuel Chem Prepr. 7, 95-109 (1963).



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Figure 6b-3. RELATIONSHIP OF MICROTUMBLER STRENGTH AND HARDGROVE GRINDABILITY INDEX²

Table 6b-6. ATTRITION RESISTANCE TESTS WITH STEEL BALLS

Sample	Ash, wt %		Sieve Analysis of Tumbled Sample			
	Original Sample	-30+40 Sieve Fraction	USS 30	-30+100	-100+200	-200
Ireland Mine	--	--	0.8	37.9	24.7	36.6
			0.4	38.2	24.9	36.5
			0.6	38.2	23.7	37.5
Residue HT-210, Ireland Mine Coal	19.4	23.3	0.0	5.0	19.5	75.5
			0.1	3.4	19.2	77.3
			0.0	3.6	17.8	78.7
Residue HT-192, N. D. Lignite	14.6	12.5	0.0	16.9	17.7	65.5
			0.0	16.0	18.3	65.7
			0.0	8.3	19.9	71.7
			0.0	10.4	22.5	67.1
Residue EG-37	27.3	28.4	0.0	4.4	16.2	79.4
			0.2	3.6	14.9	81.3

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Table 6b-7. ATTRITION RESISTANCE TESTS WITH POLYETHYLENE BALLS

Sample	Carbon Conversion, wt %	Sieve Fraction, USS	Ash, wt %	Sieve Analysis of Tumbled Sample			
				On USS 30	USS -30+100	USS -100+200	USS -200
				wt %			
Ireland Mine Coal	--	-20+30	--	82.9	14.9	0.6	1.6
Residue, Ireland Mine Coal, Run HT-154	24.6	Unsieved	18.1	--	--	--	--
		-20+30	--	19.8	52.6	12.6	15.0
		-40+60	18.9	--	65.0	18.7	16.3
		-80+100	--	--	52.9	30.0	17.1
Residue, Ireland Mine Coal, Run HT-210	41.7	Unsieved	19.4	--	--	--	--
		-20+30	23.3	31.6	43.9	13.5	11.0
		-40+60	21.8	--	70.3	15.2	14.5
		-80+100	27.4	--	50.6	31.1	18.3
Residue From Electro-gasification, Run EG-34	37.2*	Unsieved	25.5	--	--	--	--
		-20+30	--	42.0	39.8	6.8	11.4
		-40+60	22.9	--	76.3	11.1	12.6
		-80+100	22.6	--	59.5	27.3	13.2
Residue From N.D. Lignite, Run HT-192	33.9	Unsieved	14.0	--	--	--	--
		-20+30	12.5	45.5	44.4	4.0	6.1
		-40+60	13.9	46.2	42.9	3.6	7.3
		-80+100	16.4	--	88.2	6.3	5.5
FMC Char, Feed to EG-26	--	Unsieved	15.8	--	--	--	--
		-20+30	--	69.5	20.8	4.9	4.8
		-40+60	16.7	--	84.1	7.6	8.3
		-60+80	17.2	--	78.2	12.5	9.3
Residue, Indiana No. 6 Coal, Run HT-161	31.9	Unsieved	16.0	--	--	--	--
		-40+60	--	28.3	48.3	8.1	15.3
		-40+60	--	27.6	53.5	9.7	9.2

* Electro-gasification only. Feed was residue from Indiana No. 6 coal.

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