THE KINETICS OF FLASH HYDROGENATION
OF LIGNITE AND SUBBITUMINOUS COAL**MASTER**

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ABSTRACT

A reaction model, based on a single coal particle surrounded by H_2 gas, is developed for the hydrogenation of lignite and subbituminous coal. Conversion data from experiments conducted at various pressures, temperatures, particle residence times and gas residence times are correlated to calculate activation energies and to obtain one set of kinetic parameters. A single object function formulated from the weighted errors for the four dependent process variables, CH_4 , C_2H_6 , BTX, and Oil yields, was minimized using a program containing three independent iterative techniques. The results of the nonlinear regression analysis for lignite show that a first-order chemical reaction model with respect to C conversion, satisfactorily describes the dilute phase hydrogenation. The conversion data obtained from hydrogenation experiments using subbituminous coal is correlated using similar techniques. The results obtained from data analysis of the two types of coals are compared. The mechanism, the rate expressions, and the design curves developed can be used for scale-up and reactor design.

INTRODUCTION

Flash hydrogenation is a short residence time (1 to 10 sec) gas phase non-catalytic process in which pulverized coal is rapidly heated (20,000 - 30,000° c/sec) in a hydrogen atmosphere to obtain liquid and gaseous hydrocarbons directly. Experiments were conducted in a 2 lb/hr, 1" ID x 8 ft long

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downflow tubular reactor in the range of 500° to 900°C temperature and 500 to 3000 psi H₂ pressure for North Dakota Lignite and New Mexico Sub-bituminous coal. ⁽¹⁾ An on-line process gas chromatograph analyzed the gas stream for 10 chemical components every eight minutes from sample taps located at interval of two feet along the length of the reactor. ⁽²⁾ The heavier liquid hydrocarbons products ($\geq C_9$) were collected in liquid product condensers and were measured at the end of each experiment.

Modelling

The flash hydrogenation is assumed to take place via the following reaction steps:

The chemical reaction is assumed to be the rate controlling step. The reactions are considered to be first order with respect to fraction of C remaining in coal as well as converted to hydrocarbons and m^{th} order with respect to H₂ partial pressure. The details of the development of the model is reported elsewhere (3). The experimental data correlated was obtained from dilute phase operation in an excess of hydrogen atmosphere, so the partial pressure of hydrogen was considered to be approximately equal to the total system pressure and was assumed to be constant along the length of the reactor.

* non-reactive elemental carbon contained in the char product.

For isothermal conditions, the differential equations set up from the material balances of each component can be solved analytically to obtain the following relationships:

$$\begin{aligned}
 [CH_4] &= \frac{k_1}{u_{gs} k_{1234} - k_5} \left[e^{-k_5 P_{H_2}^m \frac{t_s}{u_{gs}}} - e^{-k_{1234} P_{H_2}^m t_s} \right] \\
 [C_2H_6] &= \frac{k_2}{u_{gs} k_{1234} - k_6} \left[e^{-k_6 P_{H_2}^m \frac{t_s}{u_{gs}}} - e^{-k_{1234} P_{H_2}^m t_s} \right] \\
 [BTX] &= \frac{k_3}{u_{gs} k_{1234} - k_7} \left[e^{-k_7 P_{H_2}^m \frac{t_s}{u_{gs}}} - e^{-k_{1234} P_{H_2}^m t_s} \right] \\
 [Oils] &= \frac{k_4}{u_{gs} k_{1234} - k_8} \left[e^{-k_8 P_{H_2}^m \frac{t_s}{u_{gs}}} - e^{-k_{1234} P_{H_2}^m t_s} \right]
 \end{aligned}$$

Arrhenius behavior of the rate constant with temperature was assumed as follows:

$$k_i = k_{i0} e^{-E_i / RT} \quad \text{for all } i$$

Regression Technique

A minimization program 'MINUIT' ⁽⁴⁾ was used on CDC 7600 to best fit the equations to the data and find the unknown parameters. Three

different minimization algorithms Monte Carlo, Simplex and Variable Metric, available in MINUIT, were used for the correlation.

A single object function was formulated for the four dependent variables - CH_4 , C_2H_6 , BTX and Oil yields.

$$F = W_1 \sum ([\text{CH}_4]_{\text{exp}} - [\text{CH}_4]_{\text{cal}})^2 + W_2 \sum ([\text{C}_2\text{H}_6]_{\text{exp}} - [\text{C}_2\text{H}_6]_{\text{cal}})^2 + \\ W_3 \sum ([\text{BTX}]_{\text{exp}} - [\text{BTX}]_{\text{cal}})^2 + W_4 \sum ([\text{Oils}]_{\text{exp}} - [\text{Oils}]_{\text{cal}})^2$$

Weighting factors inversely proportional to the variance of each dependent variable were used. ⁽⁵⁾ To take into account the variable number of data points available for each dependent variables, the weighting factors were taken proportional to the number of data points. The weighting factors can then be represented as follows:

$$W_i = \frac{N_i}{\sum (Y_i - \bar{Y}_i)^2} \quad \text{for } i = 1, 2, 3, 4.$$

Results of Regression Analysis

For simplification, it was assumed that all the activation energies for the initial formation of hydrocarbons from coal are the same, i.e. $E_1 = E_2 = E_3 = E_4$. A rationale for this is that during decomposition, coal is in equilibrium with the same transition complex regardless of the final products.

Data from 83 experimental runs, with H_2 /coal weight ratio of about 1, using North Dakota Lignite, were correlated. Details of the correlation for the lignite are reported elsewhere. ⁽³⁾ For New Mexico Sub-bituminous coal, data from 47 experimental runs, also with H_2 /coal weight

ratio of about 1, were correlated. For these runs, 166 data points, corresponding to different locations in the reactor, were available for CH_4 , C_2H_6 and BTX concentrations. Oil data, obtained from the total amount of oil collected in the condensers, were available for 17 runs.

The estimated values of various parameters for subbituminous coal is tabulated in Table 1 along with those found for lignite. The order of magnitude of the parameters is same for both the coals. The correlation coefficients and standard errors for the subbituminous coal are tabulated in Table 2. The standard error of 8% C conversion for CH_4 seems to be high but because of higher amounts and variation in the CH_4 data, a correlation coefficient of 0.92 is obtained which indicates excellent correlation. The correlation of the oil data is better compared to those of C_2H_6 and BTX data.

Using Student's t statistics, hypothesis: $\rho=0$ was tested. It was found that the hypothesis $\rho=0$ can be rejected at 0.005 significance level. It therefore appears almost certain that the %C conversions to CH_4 , C_2H_6 , BTX and Oils can be related to reaction temperature, H_2 partial pressure, particle residence time and gas residence time by the correlations.

Using Fisher's Z transformation, the 95% confidence limits for the overall correlation coefficient for the subbituminous coal were obtained.

$$0.70 < r < 0.84 \text{ at } 95\% \text{ confidence level.}$$

A sensitivity analysis was performed on the correlation. The kinetic parameters and correlation coefficients were estimated for $N = 166, 156, 146$ and 136 with $N_4 = 17, 16, 15$ and 14 respectively. The correlation

coefficients obtained are tabulated in Table 3. The correlation coefficients do not show any significant change (< 5% variation) indicating that the correlation is good.

Design curves were developed in the range of the experimental data from the kinetic parameters and rate expression, using Tektronix interactive graphic terminal connected with CDC 6600. Figures 1, 2 and 3 are plots of percent C conversion to CH_4 vs. reactor length, gas residence time and particle residence time, at various temperatures and pressures. For pressures of 1500 psi and 2500 psi, maxima in CH_4 yields are found within the range of experiments. CH_4 yield increases and it occurs at lesser residence times as the temperature increases. Figures 4, 5 and 6 are plots of percent C conversion to C_2H_6 , BTX and Oils, respectively vs. reactor length for various temperatures at 1500 psi. The maximum yields of these products decreases and it occurs at lesser residence times as the temperature increases.

Maximum yields of various products and the necessary operating conditions are tabulated in Table 4. Maximum yields from the subbituminous coal are found at 2500 psi which is the highest pressure used in the experiments for that coal. For comparison purpose, lignite yields are also tabulated for 2500 psi, even though some experiments were conducted at 3000 psi with the lignite, obtaining higher yields. For both coals, the CH_4 maximum is found at higher temperature and occurs at shorter residence times compared to C_2H_6 , BTX and Oils maxima. Higher maximum yields of CH_4 and BTX and slightly lower maximum yields of C_2H_6 and Oils were obtained for New Mexico Subbituminous coal compared to North Dakota

Lignite. Maximum %C conversion to CH_4 vs. pressure is plotted in Figure 7. The maximum CH_4 conversion shows a linear increase with increase in pressure for both coals. At all pressures, the maxima are found at 900°C and the subbituminous coal maximum yields to CH_4 are higher than those from the lignite.

Discussion of Results and Conclusions

The results of regression analysis show that a first order chemical reaction model with respect to fractional C conversion, with a production and a decomposition step for each of CH_4 , C_2H_6 , BTX and Oils, satisfactorily describes the dilute phase flash hydrogenation of both lignite and subbituminous coal.

The activation energies estimates were found to be $> 20,000$ cal/gmole. This justifies the assumption that chemical reaction is the rate controlling step. The activation energy for the initial formation of hydrocarbons was found to be $42,700$ cal/gmole for lignite and $43,200$ cal/gmole for subbituminous coal, with estimated errors of about $50\text{--}80$ cal/gmole, which are very small. This indicates that the error involved in the assumption, that all the activation energies for the initial formation of hydrocarbons from coal are the same ($E_1 = E_2 = E_3 = E_4$) is probably small. The values of these activation energies estimated are comparable to the mean activation energy of $48,700$ cal/gmole found by Anthony ⁽⁶⁾ for devolatilization of Montana Lignite and the activation energy of $48,900$ cal/gmole found by Bhatt ⁽⁵⁾ for hydropyrolysis of North Dakota Lignite. The kinetic parameters (k_{50} , k_{60} , k_{70} , E_5 , E_6 , E_7) corresponding to the decomposition steps for CH_4 , C_2H_6 and BTX are found to be almost the same for both lignite

and subbituminous coal, as to be expected. The pre-exponential factors for oils are different for the two coals probably due to some difference in nature of the oils produced. The pre-exponential factors (k_{10} , k_{20} , k_{30} , k_{40}) for initial decomposition of subbituminous coal are found to be different than that for lignite. At optimum conditions, subbituminous coal produces more CH_4 and BTX and slightly less C_2H_6 and Oils compared to lignite. The power of the hydrogen partial pressure, m , was found to be about +0.14 to +0.15. This indicates, in general, increase in %C conversion to hydrocarbons with increase in hydrogen partial pressure.

The correlation for subbituminous coal with overall correlation coefficient 0.78, having 95% confidence limits of 0.70 and 0.84, is considered good.

The mechanism, rate expressions and the design curves developed satisfactorily represent the experimental data and hence can be used for scale-up and reactor design.

The model developed might be applicable to other types of coal while the regression technique used is applicable to any experimental data for correlation.

Nomenclature

[BTX]	fraction of carbon converted to benzene, toluene and xylene
$\overline{[BTX]}_{\text{exp}}$	mean of $[BTX]_{\text{exp}}$
$[CH_4]$	fraction of carbon converted to methane
$[CH_4]_{\text{exp}}$	mean of $[CH_4]_{\text{exp}}$
$[C_2H_6]$	fraction of carbon converted to ethane
$\overline{[C_2H_6]}_{\text{exp}}$	mean of $[C_2H_6]_{\text{exp}}$
E, E _i	activation energy, cal/gmole
F	object function
k_i	rate constant, /sec
k_{io}	pre-exponential factor, /sec
k_{1234}	sum $k_1 + k_2 + k_3 + k_4$, /sec
m	order of reaction with respect to H ₂ gas
N, N _i	number of data points
[Oils]	fraction of carbon converted to Oils
$\overline{[Oils]}_{\text{exp}}$	mean of $[Oils]_{\text{exp}}$
P _{H2}	partial pressure of hydrogen, psi
r	sample correlation coefficient
R	gas constant, cal/gmole ^o K
t _s	solid residence time, sec
T	temperature (absolute), ^o K
u _g	gas velocity, ft/sec
u _s	solid velocity, ft/sec
u _{gs}	ratio u_g / u_s
W _i	weighting factors
Y, Y _i , Y _{ij}	dependent variable
$\overline{Y}, \overline{Y}_i$	mean of Y

Greek letter

ρ theoretical population coefficient of correlation

Subscripts

cal calculated value

exp experimental value

g gas

i ith component

s solid

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Table 1

Estimated Values of Various Parameters

	<u>North Dakota Lignite</u>	<u>New Mexico Subbituminous</u>
k_{10}, sec^{-1}	5.0×10^5	5.5×10^6
k_{20}, sec^{-1}	7.5×10^6	6.7×10^6
k_{30}, sec^{-1}	4.4×10^6	6.3×10^6
k_{40}, sec^{-1}	4.6×10^6	4.0×10^6
k_{50}, sec^{-1}	5.2×10^1	4.8×10^1
k_{60}, sec^{-1}	1.7×10^{10}	1.7×10^{10}
k_{70}, sec^{-1}	1.6×10^9	1.5×10^9
k_{80}, sec^{-1}	4.6×10^{16}	6.9×10^{16}
$E (E_1 \text{ thru } E_4), \text{cal/g mole}$	42,700	43,200
$E_5, \text{cal/g mole}$	20,100	20,900
$E_6, \text{cal/g mole}$	54,200	55,000
$E_7, \text{cal/g mole}$	50,300	51,100
$E_8, \text{cal/g mole}$	84,200	84,700
$m (\text{power of } P_{H_2})$	0.14	0.15

Table 2

Correlation Coefficients and Standard Errors
for the Subbituminous Coal Results

	<u>Correlation Coefficient</u>	<u>Standard Error, % C Conversion</u>
CH_4	0.92	8.0
C_2H_6	0.66	3.2
BTX	0.72	2.9
Oils	0.81	0.7
Overall	0.78	

Table 3

Results of the Sensitivity Analysis for the Subbituminous Coal Correlation

		<u>Correlation Coefficient</u>				
<u>N</u>	<u>N₄</u>	<u>CH₄</u>	<u>C₂H₆</u>	<u>BTX</u>	<u>Oils</u>	<u>Overall</u>
166	17	0.92	0.66	0.72	0.81	0.78
156	16	0.92	0.65	0.71	0.84	0.77
146	15	0.92	0.64	0.69	0.81	0.76
136	14	0.92	0.66	0.69	0.80	0.77

Table 4

Maximum Carbon Conversions to Various Products at 2500 psi

% C Conv. to	<u>Max. CH₄</u>		<u>Max. C₂H₆</u>		<u>Max. BTX</u>		<u>Max. Oils</u>	
	Lignite	Subbit.	Lignite	Subbit.	Lignite	Subbit.	Lignite	Subbit.
CH ₄	67	73	26	25	18	25	11	9
C ₂ H ₆	2	2	10	9	9	9	7	5
BTX	1	1	8	14	9	14	7	10
Oils	0	0	5	3	8	3	8	6
Total	70	76	49	51	44	51	33	30
Operating Conditions								
Pressure, psi	2500	2500	2500	2500	2500	2500	2500	2500
Temp., °C	900	900	750	750	725	750	700	700
Reactor Length, ft	3.5	4.5	8	8	8	8	8	8
Solid res. time, sec	3.9	5.0	8.8	8.8	8.8	8.8	8.8	8.8
Gas res. time, sec	16.6	21.4	38.0	38.0	38.0	38.0	38.0	38.0

FLASH HYDROGENATION OF SUBBITUMINOUS COAL

PRESSURE = 500 psi

H₂ FLOWRATE $\approx$ 1 lb./hr.

COAL FEED RATE $\approx$ 1 lb./hr.

Figure 1

Figure 2

FLASH HYDROGENATION OF SUBBITUMINOUS COAL

PRESSURE = 2500 psi

H₂ FLOWRATE $\approx$ 1 lb./hr.

COAL FEED RATE $\approx$ 1 lb./hr.

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7