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Authors:

Rue, D.M.

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Institute of Gas Technology
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Chicago, Illinois 60616

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CORRELATIONS DESCRIBING THE PRESSURIZED FLUIDIZED-BED HYDRORETORTING CARBON CONVERSIONS OF SIX EASTERN OIL SHALES

by

David M. Rue
Institute of Gas Technology
Chicago, IL 60616

A set of correlations has been developed to describe the pressurized fluidized-bed hydroretorting carbon conversions of six Eastern oil shales. Laboratory scale fluidized bed and thermogravimetric data were used to relate hydroretorting conditions and organic carbon conversions to oil, gas, and residue. Conversions have been found to depend on temperature, hydrogen pressure, and residence time over the ranges studied of 750 to 865 K, 0 to 7 MPa H₂, and 0 to 30 minutes, respectively. Gas yield increases with increasing temperature but is independent of changes in hydrogen pressure. Oil yield increases with increasing hydrogen pressure and has different relationships to temperature for the various shales. A single mechanism has been used to describe the carbon conversions of Alabama and Tennessee Chattanooga, Indiana and Kentucky New Albany, Michigan Antrim, and Ohio Cleveland shales under PFH conditions. The mechanism includes the simultaneous conversion of carbon to gas, oil, and an active carbon species which can form oil or remain as residue carbon. Yields are predicted over the temperature, hydrogen pressure, and residence time ranges used in PFH processing.

Introduction

The products of oil shale retorting include oil, hydrocarbon gases (C₁ to C₃), carbon oxides, hydrogen sulfide, water, ammonia, water soluble and insoluble gases in low concentrations, and residue shale. The conversion of organic carbon in the kerogen can be simplified to include only oil, hydrocarbon gases, and residue carbon as products. A mechanism describing organic carbon conversion must, however, accurately predict conversions based on the process operating conditions.

Mechanisms for carbon conversion usually describe parallel reactions to produce oil, gas, and char. Sequential reactions account for oil loss by coking and oil cracking¹. The development of mechanisms has focused on Green River^{2,3} and Australian⁴ oil shales.

Mechanisms describing carbon conversions from Western shale retorting can not be directly applied to the carbon conversions from Eastern shale hydroretorting. These mechanisms do not include the changes Eastern shale product yields realize in a

hydrogen atmosphere. Eastern oil shales have low hydrogen to carbon ratios, and retorting these shales in hydrogen produces increases in oil yield as a direct function of the hydrogen pressure.

A global mechanism for PFH hydroretorting carbon conversions of Eastern shales has been developed. Two oil product pathways are included. Oil can form directly from the kerogen as in several Western shale mechanisms, but significantly more oil can form depending on the hydrogen pressure.

Experimental

Six Eastern U.S. oil shales, representative of the total resource, were selected for study in laboratory-scale thermogravimetric and PFH reactors. Batches of each shale were crushed, riffled, and then stored under a nitrogen blanket in steel drums. Feed shale analyses and Fischer Assay (FA) oil yields are presented in Table 1. The two New Albany shales and the two Chattanooga shales have similar compositions and FA yields, but overall, there are substantial differences among the shales from different members. Geographic separation and

Table 1. Feed Shale Elemental Analyses and Fischer Assay Oil Yields

Shale Member	Alabama Chattanooga	Tennessee Chattanooga	Indiana New Albany	Kentucky New Albany	Michigan Antrim	Ohio Cleveland
Moisture, wt %	0.74	1.54	2.07	1.06	1.41	3.23
Ultimate, wt % dry						
Ash	73.12	77.99	78.16	76.35	82.52	81.20
Organic Carbon	16.38	11.40	14.67	14.21	7.39	10.85
Mineral Carbon	0.08	0.13	0.05	0.29	0.67	0.01
Hydrogen	1.69	1.23	1.66	1.59	0.95	1.36
Sulfur	8.93	7.08	3.07	5.37	3.05	2.25
Nitrogen	0.51	0.44	0.60	0.52	0.32	0.43
Fischer Assay, L/t	54	41	61	61	30	33

different periods of shale member deposition produced different shale and kerogen compositions. Large variations in organic carbon content, sulfur content, and FA oil yield are found among the shales. Organic hydrogen to carbon ratios are not related to the Fischer Assay oil yield which suggests the kerogen compositions of the shales are different. Differences in kerogen composition may influence shale reactivity and conversions during retorting.

The thermogravimetric testing was performed in a thermobalance which has been previously described⁵. The thermobalance allows constant recording of the weight of a 1 to 2 gram shale sample as it undergoes reaction at a specific temperature and hydrogen pressure. Weight loss versus time data is used to determine shale reactivities and rates of hydroretorting.

A description of the laboratory-scale PFH unit and its operation has also been published⁶. In the PFH unit a 175 to 200 gram sample of sized shale is charged to a fluidized sand bed maintained at a desired hydroretorting temperature and hydrogen pressure for a selected residence time. Product liquids and gases and residue shale analyses are used to determine material balances and oil yields.

Results and Discussion

Thermobalance tests were conducted with Indiana New Albany shale to determine the rate of weight loss at PFH conditions and to learn the effects of shale particle size on conversion and rate of weight loss. Weight loss versus time data for tests with size consists between -40+60 and -200+270 mesh are shown in Figure 1. The overall weight loss after 30 minutes is the same for all sizes, but the rate of weight loss increases with decreasing particle size. The rate of weight loss after 3 minutes is the same

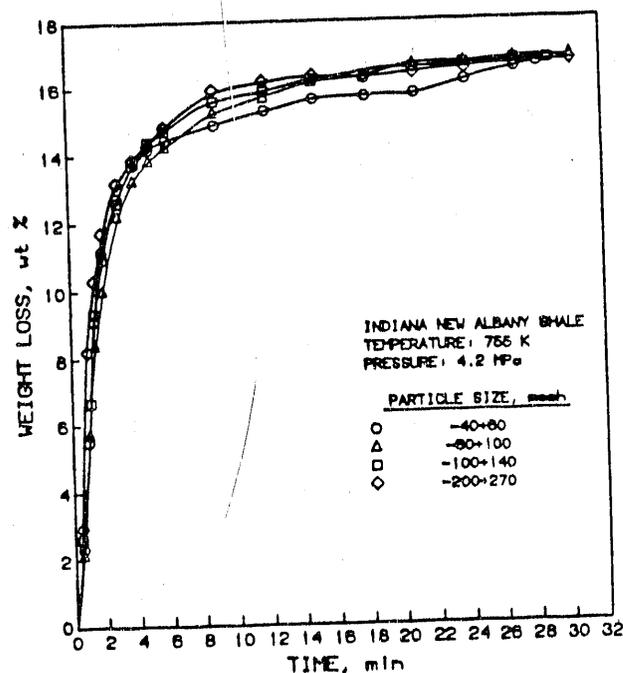


Figure 1. Effect of Particle Size on Indiana New Albany Shale Weight Loss in the Thermobalance

for all particles smaller than 60 mesh (250 μ m). Weight loss is rapid at 755 K and 4.2 MPa H₂. More than 75 percent of weight loss is achieved in 3 minutes, and greater than 92 percent is obtained in 12 minutes.

Thermobalance weight loss at PFH conditions is well described as the sum of two simultaneous, first order reaction paths. The 'fast' and 'slow' reaction path weight losses are

approximately proportional to the carbon conversion to oil and gas, respectively.

$$W = W_g \exp(-k_g t) + W_o \exp(-k_o t) \quad (1)$$

where

$$k_g = A_g \exp(-E_g/RT) \quad (2)$$

$$k_o = A_o \exp(-E_o/RT) \quad (3)$$

Values of the pre-exponential factors and activation energies describing the rates of Indiana shale carbon conversion to oil and gas are presented in Table 2. No kinetic parameters were determined for the other five shales.

Batch PFH tests were conducted with all six shales. All feed shales were sized to -60+100 mesh to eliminate mass transfer effects on conversions. Residence times of 20 minutes were used to insure all reactions were complete. PFH organic carbon conversions to oil and gas were obtained in a number of batch tests with each shale. These conversions have been used to develop correlations describing organic carbon conversions for each shale in relation to temperature and hydrogen pressure.

Relationships exist between hydroretorting product yields and both the hydrogen pressure and the temperature. Over the hydrogen pressure range studied (2.8 to 7.0 MPa), changes in pressure have no effect on the gas yield for all six shales. Oil yield, however, increases with increasing hydrogen pressure. This result suggests oil and gas come from different types of carbon in the shale. When PFH temperature is increased in the range of 750 to 865 K, gas yield increases for all six shales. Oil yield increases with increasing temperature for some shales but decreases with increasing temperature for other shales.

A single mechanism is proposed to describe the carbon conversion to products for all six shales. This mechanism is composed of a set of carbon conversion correlations which describe product yields. The PFH products containing carbon include hydrocarbon gas (C_{Gas}), oil from two paths (C_{Oil1} and C_{Oil2}), and residue from two paths (C_{Res1} and C_{Res2}). Two intermediate, active carbon species (C^* and C^{**}) which can form oil and residue are also included. Constants for each shale have been determined empirically.

Several conclusions from the batch PFH tests have been used to develop the proposed carbon conversion mechanism shown in Figure 2. Shale organic carbon can form product gas, the first oil product (Oil1), or an active carbon species (C^*). Product gas appears to not be affected by oil yield. Oil and gas are proposed to form from different fractions of the shale carbon with the fraction forming gas increasing with temperature. The first oil product, C_{Oil1} , is equivalent to the oil formed with no hydrogen present and has been set equal to the Fischer Assay oil yield.

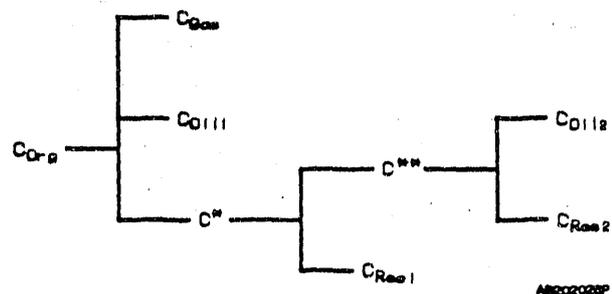


Figure 2. Proposed Mechanism for PFH Organic Carbon Conversion

When no hydrogen is present the active carbon species C^* remains with the shale as residue carbon (C_{Res1}). The presence of hydrogen, however, enables a portion of the C^* carbon to form a second active carbon species C^{**} which can form additional oil. The increase in the oil precursor species C^{**} with increasing hydrogen pressure is reasonable since Eastern shales are hydrogen deficient and need added hydrogen to produce higher oil yields.

The oil precursor C^{**} can form either the second oil product, C_{Oil2} , or additional residue carbon, C_{Res2} . The paths leading to C_{Oil2} and C_{Res2} are parallel and temperature dependent. The rates of the paths are different for each shale and can lead to either an increase in C_{Oil2} or an increase in C_{Res2} with increasing temperature.

The set of equations describing organic carbon conversion by the proposed mechanism is listed below. The rate expressions for gas production, C_{Gas} , and oil production, C^{**} , are described by the slow and fast reaction paths observed in the thermobalance tests. Batch PFH residence time tests with Indiana shale have shown the production of oil is faster than hydrocarbon gas

production.

$$-\frac{dC_{Gas}}{dt} = k_{Gas} \cdot C_{Gas} \quad (4)$$

$$-\frac{dC^{**}}{dt} = k_{Oil} \cdot C^{**} \quad (5)$$

Integrating these equations and performing material balances provides all of the needed carbon conversion correlations for the proposed hydroretorting mechanism.

$$C_{Gas} = C^*_{Gas} \cdot (1 - \exp(-k_{Gas}t)) \quad (6)$$

$$C^* = 1 - C_{Gas} - C_{Oil} \quad (7)$$

$$C^{**} = k_p \cdot C^* \cdot (1 - \exp(-k_{Oil}t)) \quad (8)$$

$$C_{Oil} = C_{Oil1} + C_{Oil2} = C^*_{Oil1} + C^*_{Oil2} \cdot C^{**} \quad (9)$$

$$C_{Res} = C_{Res1} + C_{Res2} = C^* - C_{Oil2} \quad (10)$$

Parameters used in the carbon conversion correlations are defined as follows with temperature in degrees K, hydrogen pressure in MPa, and time in seconds.

$$k_{Gas} = A_{G1} \exp(-E_{G1}/RT) \quad (11)$$

$$C^*_{Gas} = A_{G2} \exp(-E_{G2}/RT) \quad (12)$$

$$k_p = 1 - \exp(-a \cdot P_{H_2}^b) \quad (13)$$

$$k_{Oil} = A_{O1} \exp(-E_{O1}/RT) \quad (14)$$

$$C^*_{Oil2} = k_{Oil2} / (1 + k_{Oil2}) \quad (15)$$

$$k_{Oil2} = A_{O2} \exp(-E_{O2}/RT) \quad (16)$$

Carbon conversion correlation constants for all six shales are listed in Table 2. Values of A_{G1} , E_{G1} , A_{O1} , and E_{O1} have only been determined for Indiana New Albany shale based on thermobalance test results. Values of all other correlation constants, including k_p , are based on the results of batch PFH tests.

Carbon conversions for the shales have been calculated over the temperature range (750 to 865 K) and hydrogen pressure range (0 to 7 MPa) for which the correlations are defined. Comparisons of the experimental and calculated organic carbon conversions to oil and gas are presented in Figures 3, 4, 5, 7, 8, and 9. Carbon conversions are shown as

Table 2. Organic Carbon Correlation Constants

Shale Member	Alabama Chattanooga	Tennessee Chattanooga	Indiana New Albany	Kentucky New Albany	Michigan Antrim	Ohio Cleveland
A_{G1}	12.25	3.56	5.25	1.74	3.56	13.12
E_{G1} , cal/g mole	6945	4569	5442	3780	4569	6818
A_{O1} , s ⁻¹	ND	ND	0.108	ND	ND	ND
E_{O1} , cal/g mole	ND	ND	5500	ND	ND	ND
C^*_{Oil1}	0.285	0.315	0.35	0.35	0.31	0.26
a	0.287	0.102	0.123	0.296	0.925	0.281
b	0.73	1.5	1.35	1.2	0.45	0.8
A_{G2}	3.5×10^4	7.0×10^7	1.2×10^4	2.0×10^6	2.5×10^7	9.0×10^7
E_{G2} , cal/g mole	-16,450	-25,400	11,050	18,850	25,400	-25,400
A_{O2} , cal/g mole	ND	ND	14,000	ND	ND	ND
A_{O1} , s ⁻¹	ND	ND	21,100	ND	ND	ND
E_{O2} , cal/g mole	ND	ND				

ND - Not Determined

functions of both temperature and hydrogen pressure. Figure 6 shows the effects of pressure on the experimental and calculated Indiana shale carbon conversion to oil.

For all six shales the fit of the calculated carbon conversions to oil to the best nonlinear least squares fit lines through the experimental data is within 2 percent of the feed carbon. For the gas, all calculated conversions are within 1 percent of the feed carbon compared to the best fit of the experimental conversions. Scatter among the actual data produces somewhat greater standard deviations between the calculated carbon conversions and the experimental points.

Conclusions

PFH weight loss and organic carbon conversion have been described by two reaction paths. The fast carbon conversion path produces oil and is complete in 5 to 10 minutes at hydroretorting temperatures of 750 to 865 K. The slow reaction path produces hydrocarbon gases and requires more than 20 minutes to complete at PFH conditions.

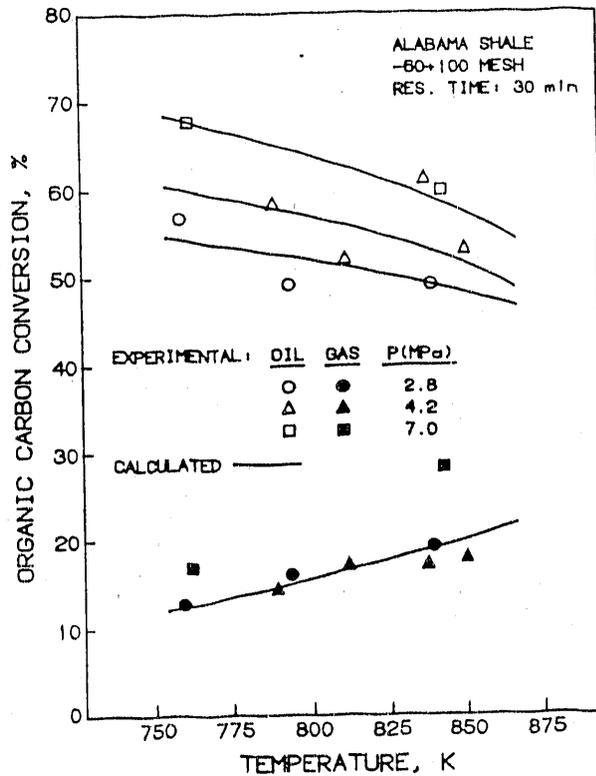


Figure 3. Comparison of Experimental and Calculated Alabama Shale Carbon Conversions

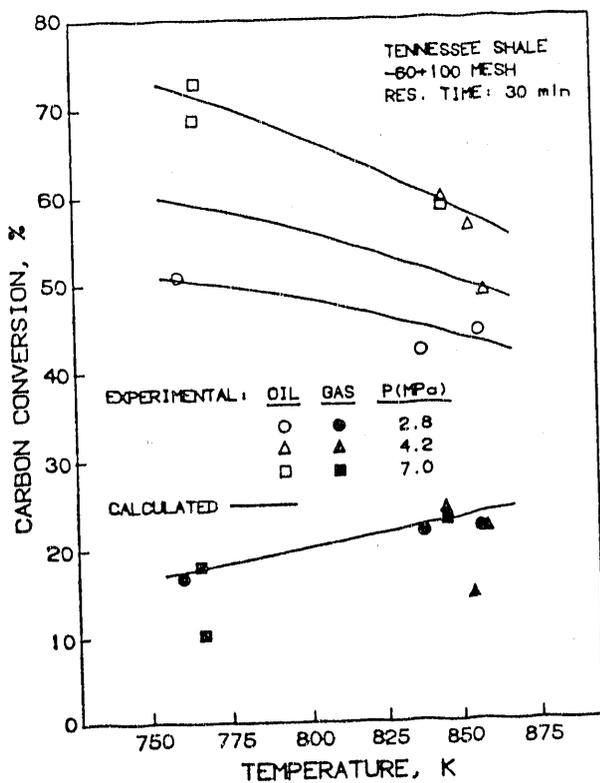


Figure 4. Comparison of Experimental and Calculated Tennessee Shale Carbon Conversions

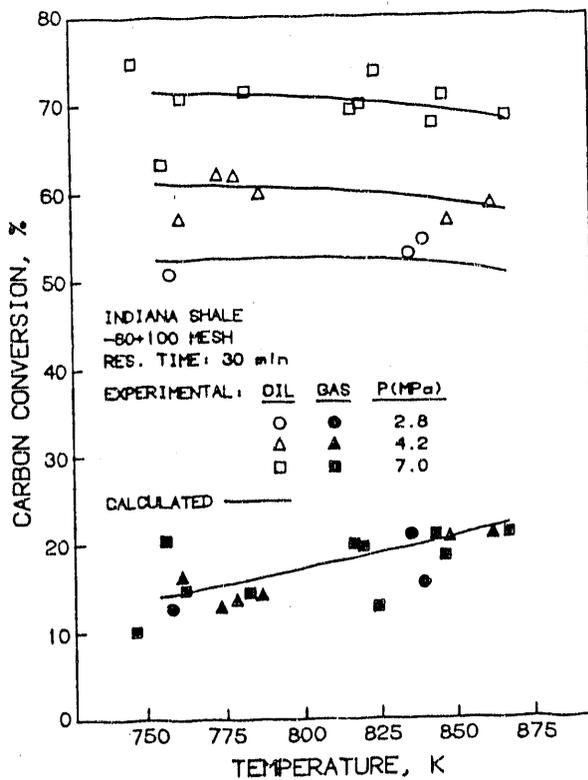


Figure 5. Comparison of Experimental and Calculated Indiana Shale Carbon Conversions

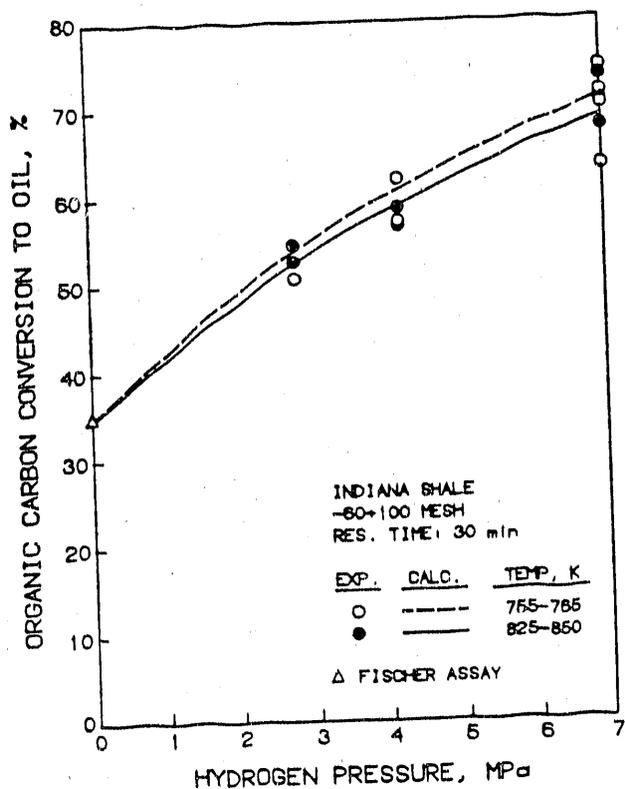


Figure 6. Indiana Shale Carbon Conversion to Oil

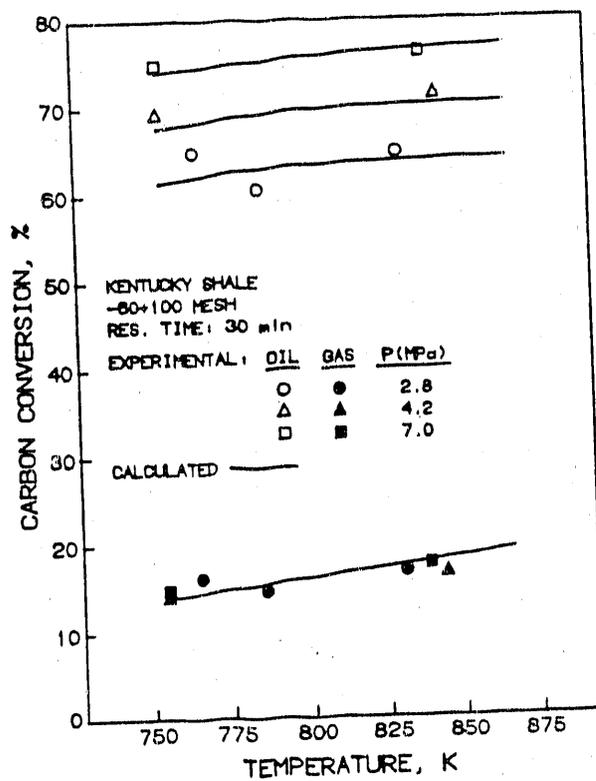


Figure 7. Comparison of Experimental and Calculated Kentucky Shale Carbon Conversions

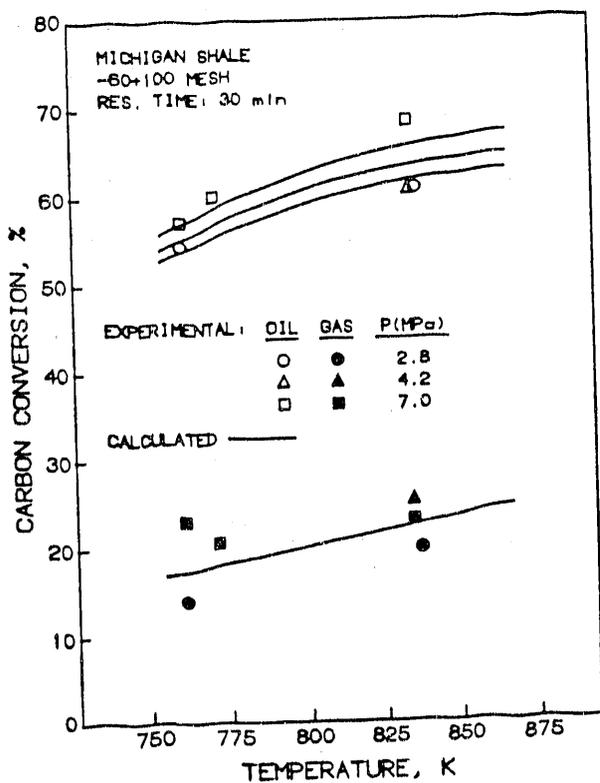


Figure 8. Comparison of Experimental and Calculated Michigan Shale Carbon Conversions

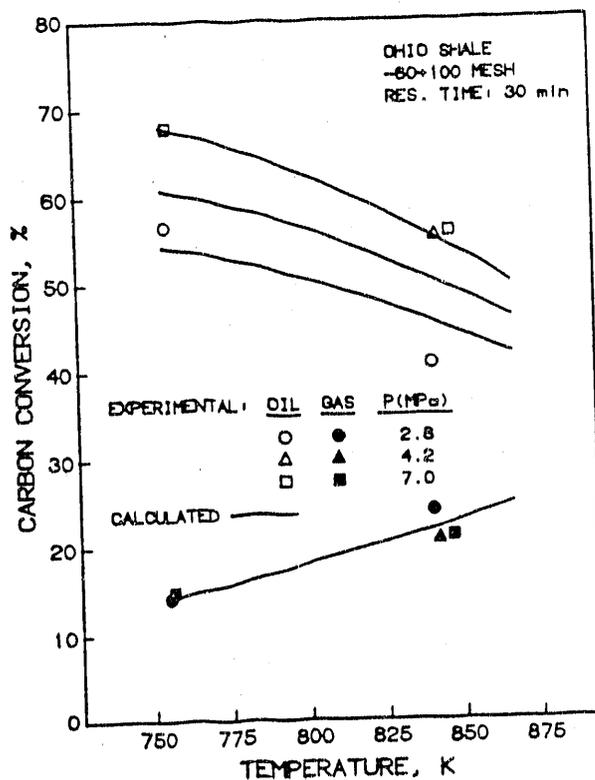


Figure 9. Comparison of Experimental and Calculated Ohio Shale Carbon Conversions

Carbon conversion products consist of gas, oil, and residue. The product gas yield for all six shales studied increases with increasing temperature and is unaffected by changes in hydrogen pressure. Product oil is the sum of the oil generated with no hydrogen present and the oil generated in a hydrogen atmosphere. The oil generated without hydrogen is equivalent to the Fischer Assay oil yield. With hydrogen present the fraction of active carbon capable of forming oil increases with increasing hydrogen pressure. This active carbon species can either form oil or remain as residue carbon. The rates of oil and residue carbon formation from the active carbon are different for the various shales studied. Oil and residue formation from these competing reactions explains why some shales show an increase in oil yield with increasing temperature and other shale oil yields are unaffected or decline with increasing temperature.

The proposed mechanism describing the PFH organic carbon conversions for Eastern shales has been based on laboratory scale data. The predictions of yields in relation to temperature, hydrogen pressure, and residence time will be used to guide the selection of operating conditions for larger bench scale PFH tests with Eastern shales. When data become available from larger bench scale PFH tests, the mechanism will be modified to reflect the effects of larger scale operations on yields.

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