

CORRELATION OF FLASH HYDROGENATION YIELDS  
WITH PETROGRAPHIC PROPERTIES

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INTRODUCTION

Recent studies (1,2) indicated that the rank (as measured by the carbon content) alone is not sufficient to predict the yield of volatiles from a coal during flash hydrogenation. The reason is that the rank provides only a gross means of chemical characterization. It is an average of different heterogeneous properties of coal, and does not adequately characterize the chemical structure.

As a consequence, two coals of the same rank may exhibit markedly different chemical properties, give different yields of volatiles and present different product distribution when subjected to flash hydrogenation (2).

On the other hand, a given maceral type occurring in different coals, has been reported to exhibit similar reactivity (3,4) in different processes.

Early work by the Bureau of Mines (5) established the clear dependence of the liquefaction behavior of a coal on its petrographic composition. Also, experimental results showed that vitrinites and exinites are the most readily liquefied (6), while fusinite is almost completely resistant to liquefaction (7).

After the new method of classification of maceral types by the reflected light was introduced (8), considerable information has been reported on the effect of petrographic composition on liquefaction (9-13).

The objective of the present paper is to show that it is possible to correlate flash hydrogenation yields with petrographic composition of the coal. The same type of correlation will be used to predict product distribution at fixed reaction conditions. Correlations based on the petrographic analysis of coal, can be used consequently, to build kinetic models of coal flash hydrogenation that would be applied to a large variety of coals.

EXPERIMENTAL

The experimental arrangements used in this study were similar to those described in previous papers (14). The analysis of products was performed by on-line mass spectrometry or by gas chromatography. Experiments were carried on at 100 atm. of hydrogen, a heating rate of 650°C/s., 10 s. of solids contact time, 0.6 s. of vapor residence time and temperatures from 600 to 1000°C.

A suite of eight U.S. coals from the Pennsylvania State University collection, from lignite to HVA, was used for this study. Their chemical properties and rank are tabulated in figure 1.

#### CORRELATION PROCEDURE

The fundamental assumption used for correlation purposes is that the total volatiles yield obtained during flash hydrogenation depends linearly on the maceral composition:

$$y = \sum_{i=1}^n r_i x_i \quad (1)$$

In a similar form, and since each one of the macerals can give a different product distribution, the yield of each one of the products can be assumed to depend linearly on the maceral composition:

$$y_j = \sum_{i=1}^n r_{ij} x_i \quad (2)$$

From equations (1) and (2) and in order to have a consistent set of definitions; we can deduce the following properties:

$$0 < \sum_{i=1}^n r_i \leq 1 ; 0 < r_i \leq 1 ; r_i = \sum_j r_{ij} \quad (3)$$

Also, the following correlation was used to transform the units of carbon conversion (% of original carbon) and weight loss (% of original dmmf. coal) (15):

$$y = 1.14w - 13.7 \quad (4)$$

A computer program on multiple linear regression was used to find the values of  $r_i$  in equation (1). After several tests with combinations of different macerals, it was found that the total yield was a function of the percentage of vitrinite and pseudo-vitrinite only. Consequently, the concentration of these two macerals were used as variables in all the correlations.

#### RESULTS

For comparison purposes, the data on total yields was correlated with the rank of the coal (carbon percent d.m.m.f.). The correlation was very poor, presenting a correlation coefficient  $\rho = 0.579$ .

When vitrinite and pseudo-vitrinite content are used as variables, the correlation improves considerably. The correlation coefficient of

the regression now is  $\rho = 0.99$ . Note that the number of free parameters in the new correlation is the same as in the rank case.

The correlation defined by equation (2) was applied to the yield of individual components during flash hydrogenation of different coals at fixed conditions. Figure 2 shows the results of the correlations.

#### DISCUSSION AND CONCLUSIONS

In view of the success of the attempts of correlating yields and products distribution with the petrographic composition of different coals, it is possible to conclude that the maceral content of a coal provides more information with respect to its reactivity (at least with respect to flash hydrogenation) than its rank. This conclusion, however, is based on a small group of different coals (8 coals only) and should be verified further with a larger sample of coals.

The fact that the yield of individual components can be correlated with the maceral composition, offers excellent possibilities for the use of maceral content-based correlations in the analysis of kinetic data from flash hydrogenation, and possibly for similar processes. It should be kept in mind that different macerals can present different selectivities towards individual components. Also, secondary reactions of the individual components (e.g., in the gas phase) could introduce deviations in the correlations.

As a final conclusion, correlations based on the petrographic composition of coals are a promising tool that could allow prediction of reactivities, total volatile yields and product distribution for any coal in flash hydrogenation given only its maceral content.

#### NOMENCLATURE

- $r_i$  : reactivity of the  $i^{\text{th}}$  maceral (dimensionless)
- $r_{ij}$  : reactivity of the  $i^{\text{th}}$  maceral to give the  $j^{\text{th}}$  product (dimensionless)
- $x_i$  : the maceral content of the coal (5) (weight % on dmmf coal)
- $y$  : total volatile yield (% of the initial carbon converted)
- $y_i$  : yield of  $i^{\text{th}}$  component (% of initial carbon converted)
- $\sigma$  : standard deviation of the regression defined from

$$\sigma^2 = \sum_{-i=1}^n \frac{(y_i, \text{experim.} - y_i, \text{calc})^2}{(n-2)}$$

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Sample No.	Rank	Province	Age	State	Moist	M.M. direct	C dmmf	O dmmf	S Dry	DAF
PSOC 326	HVA	Eastern	Carb.	PA	2.21	21.18	84.49	5.56	4.36	5.28
PSOC 270	HVA	Eastern	Carb.	AL	1.27	17.72	85.15	4.85	2.34	2.77
PSOC 284	HVA	Interior	Carb.	IL	3.11	25.08	83.71	7.12	5.23	6.70
PSOC 314	HVA	RockyM.	Cret.	UT	4.08	11.55	81.47	10.13	0.76	0.84
PSOC 280	HVC	Interior	Carb.	IN	11.32	18.31	81.58	9.51	3.78	4.50
PSOC 248	S.8it. A	RockyM.	Cret.	WY	19.17	3.34	75.44	17.04	0.64	0.66
PSOC 240	S.8it. B	Pacific	Tert.	WA	19.73	16.47	73.96	18.98	0.50	0.60
PSOC 246	Lignite	NorthGr. Plains	Tert.	ND	34.12	10.99	71.85	21.22	0.65	0.72

Figure 1. Selected coals for flash hydrogenation studies

<u>Component</u>	<u>Corr. variable</u>	<u>Corr. coefficient</u>	<u><math>\sigma</math></u>
Methane	$0.17V + 0.58(PV+E+R)$	0.9811	0.67%
Ethane	$0.08V + 0.05(PV+E+R)$	0.7661	0.52%
BTX	$0.08V + 0.127(PV+E+R)$	0.427	0.92%

Figure 2: Correlations applied to individual components