

Correlation of Coal Quality to Coal Liquefaction

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Introduction

A large-scale direct coal liquefaction plant will consume substantial quantities of coal as a feedstock material. Due to the nature of the coal mining industry this supply will be acquired from several mines operating in different coal reserves. Procurement of coal from multiple sources, over time will undoubtedly lead to variations in the characteristics of the plant feed. Physical and chemical coal properties are known to vary within a reserve due to the mechanisms of seam formation and subsequent geologic metamorphism. In addition, mining methods and physical beneficiation affect the organic and inorganic constituents in the mine product. Furthermore, the specification of a single seam, for example Ky #9 or Ill. #6 as the source for potential feed-coals, is insufficient since it has been shown that substantial variations in coal properties can exist within a single seam.

Although it is clear that variations in feed coal properties can affect plant operations and yields, few quantitative relationships have been developed. The difficulty in understanding the importance of coal characteristics is in part related to the complex nature of coal, and problems in the selection, characterization and testing of representative feedstock samples. The driving force for developing this understanding is directly related to the selection and procurement of the essential raw material for liquefaction processing. A scientifically based understanding of how to select coal sources from within a mining region and how to compensate for variations from an individual mine will improve the operability and economics of any direct liquefaction plant.

This study has investigated the degree to which coal properties change within a supply region and how these variations impact on yields and economics of an SRC-I type process. Statistical data analysis has isolated critical coal properties influencing liquefaction reactivity and quantitative prediction equations have been developed.

General Coal Characteristics Influencing Reactivity

Research work to identify the suitability of U.S. Coals for direct liquefaction were begun by the U.S. Bureau of Mines station at Bruceton, PA in the early 1940's^{1,2}. These efforts investigated coals of varying petrographic composition and rank, concluding that these characteristics significantly affected the ease by which a coal could be liquefied. More recently, work has been completed by a number of investigators which confirms that the total reactive maceral content of the coal is related directly to its overall conversion to extractable products^{3,4,5}.

Although coal rank is recognized as a derived property related directly to a coal's composite organic chemical structure, its impact on liquefaction reactivity is not clearly understood. Most researchers are in agreement that coals higher in rank than high volatile A bituminous are poor candidates for liquefaction feedstocks due to low reactivity. This limitation presents little problem for the development of a coal liquefaction industry since these high rank coals represent only ten percent of the country's production. The

more abundant lower rank coals have displayed divergent reactivities depending upon the experimental conditions and method of investigation. Neavel⁷ has shown that the coal conversion to benzene solubles plus gases is inversely proportional to the rank of the coal for residence times from 2.5 to 30 minutes. These results are generally in agreement with those of Whitehurst⁸ and Yarzab⁹ for long residence times. However, Whitehurst⁸ has shown that in short residence time coal liquefaction, low rank coals are substantially less reactive than high volatile bituminous coals of similar petrographic composition. In processing coals under SRC-II conditions using disposable iron catalysts, Wright¹⁰ has found that lignites and subbituminous coals have higher conversions and greater yields of distillate than high volatile bituminous Pittsburgh Seam coals. Thus, providing that reaction conditions are chosen correctly, the coal is prepared properly prior to liquefaction and sufficient catalyst is present, lower rank coals would appear to have higher reactivity than high volatile bituminous coals.

One coal characteristic not explained by measures of rank and petrographic composition is the nature of inherent mineral matter. Many authors have shown that mineral matter in coal can act as an inherent catalyst for improving liquefaction yields. The consensus of this work has been that iron sulfides, particularly pyrite,⁹ are the most effective catalysts present in the inherent coal mineral matter.¹⁰ Although some differences in pyrite catalysis activity have been reported,¹⁰ most work has shown that the very high levels (up to 10% pyrite on coal) must be added to affect a significant change in the yield structure of Eastern Bituminous Coals.^{11,12} Low iron subbituminous coals can be made more reactive with somewhat lower levels of pyrite addition.¹³

Experimental Investigation of Coal Reactivity

The International Coal Refining Company (ICRC) Research Group has been heavily involved with developing experimental data to support the SRC-I Demonstration Plant Project. A portion of this effort was to determine the effects of feed coal variation on plant performance. Although the majority of potential feed coals for this plant would come from a restricted area (Illinois Basin), it became clear in this program that three major technical areas would need investigation as follows:

- o Coal variation from an individual mine,
- o Coal variation within the reserve area, and
- o Effects of these variations on liquefaction yields.

Due to design and operation considerations, a decision was made early in the demonstration plant program to consider only use of washed coals. This constraint significantly limited the number of mine operations which could be considered as suppliers.

An experimental program was established with the Institute of Mining and Minerals Research, University of Kentucky, to sample mining operations in a pattern to provide geographic and stratigraphic diversity. The sample locations, in relation to the mining regions are shown in Figure 1. Samples were collected from the run-of-mine coal as well as the washed coal. Several mining operations were studied for both long- and short-term variation in coal properties.

In the short term coal variability study, samples were collected from the operation daily and analyzed for changes in composition. Figure 2 shows the daily shifts in sulfur and ash content for a mine in the KY #9 seam. These results demonstrate that the coal cleaning plant is necessary not only to

reduce the amount of mineral matter in the coal, but also to buffer variations in composition due to mining. An additional benefit from coal preparation is an increase of approximately three percent in the total reactive maceral content of the clean coal, enhancing the liquefaction potential.

Based upon the results from the short term study, a five day period was selected as the time in which to composite a sample to define a plant's average output. Thus, once a month a five day period was sampled and composited for each of six months. These results (Figure 3) show that some long term shifts in clean coal composition can occur. The variations may result from changing characteristics of an individual coal reserve or changes in mine operations. A liquefaction processing plant will need the flexibility to deal with these changes if they would significantly affect operations.

The second portion of this project was to define the regional variation in coal composition. Table 1 shows the range in several clean coal properties across the region compared to the variation which might be expected from an individual plant. These results illustrate that the variation across the region is generally two to four times that which might be expected from an individual plant. Furthermore, the absolute ranges in variables, such as vitrinite reflectance, pyritic sulfur and total reactive macerals, are such that they will affect substantially coal liquefaction results. Therefore, despite the contention that coal supply from an individual mine will shift with time, there are probable advantages to selecting and blending coals from mines whose average composition is in the high reactivity range.

The third portion of this program was to test the set of clean coals to determine the effects of variations in properties on coal liquefaction. In this program the coals were liquefied in a 100 pound per day continuous bench scale process development unit (CPDU) under standard conditions as follows:

- o Reaction Temperature 840°F
- o Reaction Time 30 min
- o Total Pressure 2000 psig
- o H₂ Flow Rate 28,000 SCF/Ton Coal
- o Coal Concentration 40 wt.% in Wilsonville Recycle Solvent

These are essentially the SRC-I standard process conditions with the exception of the shorter (30 min) residence time. All samples from the process unit were analyzed by a standard workup procedure to determine the yields of products on a dry ash-free coal basis and hydrogen consumption.

Figure 4 shows the range in reactivity demonstrated by these coals as related to oils yield and hydrogen consumption. These two factors are useful for assessing coal reactivity since they are among the most sensitive economic parameters in a liquefaction plant. The results show a group of high reactivity coals (>25% oils yield), a group of average coals (15-25% oils yield), and one very low activity sample.

Ranges in coal reactivity of this magnitude impact both on plant operations and on revenue economics. Improvements to plant operation may include: improved solvent balance, less loss of preasphaltenes to the gasifier residue, and the flexibility to operate at lower severity. The advantages of operation at a decreased severity are lower duty on the fired preheater and better reaction stability. Of course, to operate with a high reactivity coal at high severity would require some additional hydrogen capacity and this element does impact on operations and economics.

Table 2 shows a yield and economic comparison of operating a hypothetical single-stage SRC-I type plant in a maximum heavy fuel oil mode. This analysis assumes that all the middle oil produced will be blended with the solid SRC and sold as heavy oil. The comparisons are shown on an identical plant case, operating with an average and, alternatively, a high activity coal. Although this assessment has been simplified and contains several assumptions, it is clear that using the high activity coal, including the hydrogen penalty, results in a significant (11%) improvement in revenues. Since these coals are sold currently on a fuel basis (cents/mm btu) there can be compelling economic incentives for choosing high activity coals.

The advantages in operations and economics for a simple thermal process (i.e. SRC-I) also appear to be present for more complex catalytic systems. Figure 5 shows the results of processing a low activity and a high activity coal, with and without a slurry phase catalyst. In this comparison, it is evident that the catalyst acts to provide an incremental improvement in oil yield over the baseline non-catalyst case. Rather than seeing the yield structures converge due to catalytic processing, they maintain approximately the same differential as the original coal reactivity. Although these results demonstrate that initial coal activity dominates in one stage thermal and catalytic processes, it is not clear what impact it has on integrated two-stage processing.

Analysis of Liquefaction Data

In order to realize an advantage due to coal reactivity in either operations or economics, it is necessary to understand methods of selecting high activity coals. One objective of this research program was to develop correlations between coal characteristics and liquefaction product yields. In order to develop these types of correlations it is necessary to have a homogeneous data set which provides a sufficiently broad, and normally distributed, pattern of variables. Although the current dataset is probably too small (13 coals) to develop highly correlated relationships, it is useful for determining trends in the data.

The coal characteristics and liquefaction yield data sets were both analyzed to detect and minimize strong statistical intercorrelations. This analysis resulted in the selection of four independent coal variables and five relatively independent liquefaction variables which were correlated against each other (Table 3). Based on the relationships detected from Table 3 the following empirical prediction models were calculated.

$$\text{Total Conversion} = (14.1 \text{ (Pyritic Sulfur)} + 4.1 \text{ (Vitrinite reflectance)} + 77.2) \times \text{Total Reactive Macerals}/100 \quad \text{Eq. 1}$$

$$R^2 = 0.82$$

$$\text{Oil Yield} = 16.2 \text{ (Pyritic Sulfur)} - 1.2 \text{ (Volatile Matter)} + 13.6 \text{ (Vitrinite Reflectance)} + 52.9 \quad \text{Eq. 2}$$

$$R^2 = 0.47$$

The multiple R-squared for equation #1 (0.82) is relatively good for complex multivariate relationships such as those existing in coal research. The constant term in this equation (77.2) is relatively large in comparison to

the values of the predicted variable and attempts to generate a strong relationship would work to reduce this value. The parity plot in Figure 6 of the observed conversion versus the predicted conversion shows there are no significant outliers (or large residuals) in this data set and that predictive relationship is reliable. Unfortunately, the R-squared for equation #2 is not as good (0.47). Figure 7 is the parity plot of oil yield observed versus oil yield predicted for this equation; it indicates that there are no single or patterned outliers. This suggests that an additional characterization factor is probably necessary to improve the prediction of oil yield.

This analysis of the data set resulted in the selecting of many of the same variables as those determined by the Pittsburg & Midway Coal Mining Co. for the prediction of SRC-II yield structures. The relationship between pyritic sulfur in the clean coal and the conversion of total reactive macerals detected in the statistical analysis (correlation coefficient equals 0.902) is shown in Figure 8. This relationship shows that as pyritic sulfur drops below 1.10 wt. percent, the coal conversion reactivity decreases significantly. However, in another portion of the research program, experiments on the importance of coal preparation showed that levels of pyritic sulfur had little effect on liquefaction yields. The results from one of these experiments are shown in Figure 9. Despite coal samples which range in ash and pyritic sulfur in excess of those detected in the data analysis, the liquefaction yields are rather consistent.

The reconciliation of these seemingly diametrically opposed results appears to reside in the activity of the pyrite present in cleaned coals versus that in the run-of-mine and partially cleaned samples. A series of coals all cleaned to approximately the same ash level would be expected to contain approximately the same amount of pyrite, if it were distributed in the same manner in all the samples. The cleaned coals in the data analysis set (similar in preparation and ash content) ranged in pyritic sulfur from 1.42 to 0.65 percent, indicating that some of the samples probably contained pyrite which was finely dispersed in the organic matrix and was not removed by cleaning. Generally, these coals were those which had high activity for liquefaction. The pyrite that would be present in the level 1 and level 2 cleaning shown in Figure 9 would be comprised substantially of coarse material from seam partings and pyrite nodules. The experimental data on these samples indicate that this type of pyrite has little catalytic effect in the SRC-I liquefaction system. The majority of the catalytic activity appears to be provided by the finely dispersed pyrite retained in certain cleaned coals.

The importance of pyrite dispersion is also in general agreement with results determined in the disposable catalyst programs.^{11,12,15} These workers found that additions of particulate pyrite at levels approaching 5 weight percent pyritic sulfur on coal were necessary to show much catalytic activity. However, when iron was added to the coal in a dispersed system, much lower levels resulted in high catalytic activity.¹⁶ Hence, not only the amount, but more importantly the form of the pyrite in the coal appears to be the most important factor in controlling its contribution to the coal activity.

One can conclude also from the data analysis that the level of geochemical maturity, or rank of the coal as measured by vitrinite reflectance, is of significance to liquefaction yields. Although the range of rank in these samples is not as large as might be necessary to fully identify this effect, increases in rank correlate negatively with both oil yield and conversion. The subtle differences in the ranks of the coals in this sample suite do reflect changes in the structural chemistry of the coal macerals. In this range of geochemical maturity, coals lose oxygen and are believed to undergo

rearrangement and ring condensation. These reactions may tend to result in a more refractory organic phase to dissolution and liquefaction. A negative correlation of liquid yield and conversion with coal rank parameters was also reported by the P&M workers.

Summary

It is clear from the preceding discussion that variations in coal properties do affect liquefaction results. The observed differences between coals can be as large as those between Western Subbituminous compared to Eastern Bituminous, or as small as changes in coal within a single seam or individual mine. These variations in properties do affect liquefaction yields, plant operations and economics. Selection of coals, even from a restricted region, can be advantageous since critical properties vary more from source to source than from an individual mining operation.

Research at ICRC and elsewhere has shown that quantitative relationships can be developed between coal characteristics and yields. These efforts have shown that the amount of dispersed pyrite in the coal, the geochemical maturity and the petrographic composition are important coal parameters. Clean coals from this region with less than 1.10 wt. percent pyritic sulfur were found to have significantly reduced liquefaction reactivity. Unfortunately, the prediction of oil yield from coal properties has proven difficult and will probably require the addition of more fundamental parameters of coal chemistry to improve its precision.

An improved understanding of the relationship of coal properties to liquefaction results would be useful from a scientific point of view as well as a processing standpoint. The advantages of selecting and manipulating coals for improved processing results are self evident. The impact of pyrite dispersion in the organic matrix may indicate that initial dissolution reaction and associated hydrogen rearrangement, promoted by an in-situ catalyst, are instrumental in defining the final product distribution. The ability to better understand the mechanisms of coal dissolution from a fundamental point of view may lead to new improved processing concepts, as well as a better understanding of the U.S. coal resource.

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TABLE 1
COAL CHARACTERISTICS VARIATION IN SUPPLY REGION

	MEAN	VARIABILITY*	COEFFICIENT OF VARIATION	MAXIMUM COEFFICIENT OF VARIATION OF A SINGLE PLANT
ASH	9.2	±4.7	0.25	0.11
HEATING VALUE	12283	±1100	0.09	0.04
TOTAL SULFUR	3.1	±1.3	0.21	0.12
PYRITIC SULFUR	1.4	±1.0	0.36	0.23
T. R. MACERALS	93.3	±3.1	0.02	0.01
VIT REFLECTANCE	0.57	±0.18	0.16	0.04

* ± 2 STANDARD DEVIATION

TABLE 2
YIELD AND ECONOMIC COMPARISON

PRODUCTS	AVERAGE ACTIVITY COAL	HIGH ACTIVITY COAL
	YIELD*	YIELD*
FUEL GAS	4.5	7.4
LIGHT OILS	8.0	12.8
MIDDLE OILS	0.0	0.0
HEAVY OILS	17.5	29.1
SOLID SRC	44.8	27.1
TOTAL PRODUCTS	74.8	76.4
TOTAL REVENUE**	\$ 8.90	\$ 9.88

*LBS OF PRODUCT/100 LBS DAF FEED COAL

**DOLLARS OF REVENUE/100 LBS DAF FEED COAL (1990 PRICES IN 1981 DOLLARS)

TABLE 3
CORRELATION OF INDEPENDENT COAL CHARACTERISTICS AND LIQUEFACTION YIELD DATA

	HYDROGEN CONSUMPTION	HYDROCARBON GASES	TOTAL OILS	CONVERSION OF TRM	ASPHALTENES/PREASPHALTENES
DAF HYDROGEN	0.176	0.156	0.022	0.103	-0.191
DRY PYRITIC SULFUR	0.661	0.131	0.527	0.902	0.214
DAF VOLATILE MATTER	—	0.283	-0.243	0.121	-0.311
VITRINITE REFLECTANCE	-0.153	-0.289	-0.159	-0.360	-0.120

Figure 7
PARITY PLOT - PERCENT OIL YIELD OBSERVED VS.
PERCENT OIL YIELD PREDICTED

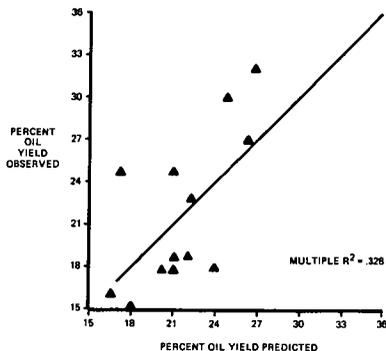


Figure 8
RELATIONSHIP OF PYRITIC SULFUR CONTENT
TO COAL REACTIVITY

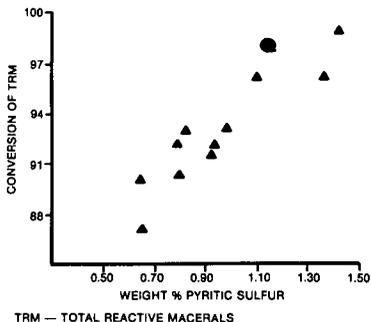


Figure 9
EFFECTS OF COAL CLEANING ON
SRG-I LIQUEFACTION

