

LIQUEFACTION PATHWAYS OF U.S. COALS

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ABSTRACT

The solubility classes obtained from the thermal liquefaction of 69 high volatile bituminous U.S. coals using a single residence time and three reaction temperatures were combined into the following lumped parameters for examination of the data: (a) oils plus gases, (b) asphaltenes plus preasphaltenes, and (c) IOM (insoluble organic matter). The lumped parameters were plotted on a Wei-Prater diagram and the resulting graph suggested a common liquefaction pathway for these coals. The thermal pathway was verified using a single Western Kentucky #6 coal and a number of residence times and reaction temperatures. The utilization of a number of catalysts and solvents with different hydrogen donor abilities did not change the pathway observed thermally. The effect of coal rank was studied using a Wyodak subbituminous coal. The thermal pathway defined by the liquefaction of the Wyodak coal was substantially different from the pathway defined by the bituminous coals. Addition of a catalyst did not alter the observed pathway defined thermally for this coal.

INTRODUCTION

Historically, lumped parameter kinetic models have been used successfully to describe industrially significant complex processes such as catalytic cracking¹, catalytic reforming¹, addition polymerization², and condensation polymerization³. Not surprisingly, the same approach has been used in the description of the various liquefaction processes^{4,5}. A physically realistic and technically viable lumped parameter kinetic model for liquefaction would be of considerable value in the development of pathways, mechanisms and the scale-up of liquefaction processes.

In this work, the typical solubility classes obtained from the liquefaction products were lumped into the following parameters: (a) oils plus gases (O+G), (b) asphaltenes plus preasphaltenes (A+P), and (c) IOM (insoluble organic matter). The three lumped parameters were plotted on a Wei-Prater diagram (triangle graph) for interpretation. The resulting data suggested a common thermal liquefaction pathway. The effects of catalyst, solvent quality and coal rank are discussed.

EXPERIMENTAL

The description and range of values of the key coal properties of the 69 high volatile bituminous coals used in the initial work are given in Table 1. It should be noted that all of these coals have ≥ 80 vol. % vitrinite (dmmf) concentrations. The analyses of the three coals (W.Ky. #6, W.Ky. #9 and Wyodak) which were extensively studied are given in Table 2.

All of the liquefaction experiments were performed in 50 mL batch microautoclaves using a hydrogen atmosphere. Details of the liquefaction procedure and solubility class analysis of the products are given in detail elsewhere⁶.

The quantity of catalyst added to the 5g of dry coal were as follows: (a) Shell 324 (1g), (b) molybdenum naphthenate (1g), (c) Fe_2O_3 (.1g), (d) $\text{Fe}_2\text{O}_3 \cdot \text{SO}_4$ (.1g), (e) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (.25g), and (f) ZnCl_2 (.25g). All of the catalysts, with the exception of Shell 324, were sulfided in-situ by adding twice the stoichiometric amount of dimethyldisulfide required to sulfide the metal to the reactor. The Shell 324 catalyst was presulfided with dimethyldisulfide prior to the addition of coal and liquefaction solvent.

RESULTS AND DISCUSSION

The thermal liquefaction data obtained for the 69 high volatile bituminous coals using a 15 minute residence time and three reaction temperatures (385°C, 427°C, 445°C) are shown in Figure 1. The data suggest a common liquefaction pathway for these coals. A single bituminous coal (W.Ky. #6) was selected to verify the suggested pathway. Liquefaction conditions were selected to produce a series of conversion levels which would define the pathway of the coal from a minimum conversion level to a maximum conversion level. The results of these experiments are shown in Figure 2.

As can be seen in Figure 2, the thermal pathway of the Western Kentucky #6 coal over the entire range of conversions is identical to that suggested in Figure 1 for the diverse set of coals. In the initial stage of dissolution, the primary reaction is the conversion of coal (IOM) to the A+P intermediate. In this region of the pathway, the conversions show a positive linear correlation with the A+P yields. It is also observed in this region of the pathway that the O+G yields remain relatively constant. The pathway changes in the region of maximum conversion (and A+P yield). In this section of the pathway, the primary reaction taking place is in the conversion of the intermediate, A+P, to the final product O+G. During this stage of the liquefaction pathway, conversion remains relatively constant. At the highest reaction temperature (445°C) and long residence times (> 15 min.), the pathway appears to change. In this region, conversion, A+P and O+G yields concurrently decrease, indicating the possibility that retrograde reactions are predominant. The results of these experiments suggest that the high volatile bituminous coals studied in this work have a common thermal liquefaction pathway.

The liquefaction pathway defined by these coals indicates that a maximum in the intermediate yields (A+P) must be achieved prior to an increase in the O+G yields. It is desirable to alter the pathway in such a manner that the O+G yields increases with increase in coal conversion. A number of catalysts were studied to determine if the added catalyst effect the selectivity defined by these reactions and thus change the pathway. The catalytic pathway is compared to the thermal pathway using the Western Kentucky #6 coal and two iron based catalysts in Figure 3. As can be seen, the addition of these catalysts had no effect on the observed thermal pathway. Identical experiments employing a supported catalyst (Shell 324), an oil soluble catalyst precursor (molybdenum naphthenate) and two acid catalysts (ZnCl_2 and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) also produced the same pathway that was observed for the thermal experiments. Therefore, the effect of catalyst addition is to increase the rate of production of the intermediate, A+P. The addition of catalysts has no effect on the selectivity defined by the solubility classes.

The effectiveness of a catalyst may be influenced by the quality of the liquefaction solvent. To determine the effect of solvent quality, as measured by hydrogen donor ability, a series of experiments (catalytic and thermal) were conducted using a Western Kentucky #9 coal and a donor (tetralin) and a non-donor (1-methylnaphthalene). The results of these experiments are shown in Figure 4. As can be seen, these data show that no change was observed in the liquefaction pathway. Additional experiments which used a mixture of phenanthrene and hydrogenated phenanthrenes as the liquefaction solvent defined the same pathway described above.

The next task in this investigation was to determine if the catalytic and thermal pathways of low rank coals were the same as that defined by the high volatile bituminous coals. A Wyodak subbituminous coal was chosen for the initial thermal and catalytic (Fe_2O_3 , molybdenum naphthenate) experiments. The pathways obtained from the liquefaction of the Wyodak coal are shown in Figure 5. Clearly, the thermal and catalytic pathway are also identical for this coal. However, the pathway for the subbituminous coal is substantially different from the pathway defined by the bituminous coals. Similar to the pathway of the bituminous coal, there are two regions in the pathway of the subbituminous coal. During the initial coal dissolution stage, both the A+P and O+G yield increase with increasing coal conversion. The second region of this pathway is similar to that of the bituminous coal. Here the coal conversion increases minimally and the major reaction is the conversion of A+P to O+G. On the basis of these solubility class data, the subbituminous coal has an improved catalytic and thermal pathway when compared to that of the bituminous coals studied due to the concurrent increase in O+G yields with coal conversion.

CONCLUSIONS

The utilization of lumped solubility class parameters and the Wei-Prater diagram have shown that the bituminous coals studied have a common thermal liquefaction pathway. Attempts to change the observed pathway using a number of catalysts and liquefaction solvents were not successful. The role of the catalyst in this work is to increase the rates of the defined reactions. The catalyst provided no selectivity to the production of the final products, O+G.

The pathway defined by a subbituminous Wyodak coal was substantially different from the pathway of the bituminous coals. The major difference was the parallel increase in A+P and O+G yields with the increase in coal conversion. Similar to the bituminous coal data, addition of catalysts had no effect on the Wyodak thermally defined pathway.

ACKNOWLEDGMENT

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Table 1

Make-up of Sample Set and Range of Key Properties

A. Distribution of Samples by State:

Kentucky	36
Indiana	22
Ohio	10
West Virginia	1

B. Distribution by ASTM Rank Classification:

High volatile bituminous A, B, C

C. Ranges of Key Properties

	Wt.% V.M.(daf)	Wt.% C(daf)	Wt.% Total S.(daf)	Wt.% Org.S.(daf)	Wt.% Pyr.S.(daf)	Vol.% Vitrinite(dmmf)	R _o max
Minimum	34.27	76.04	.70	.55	.03	80.06	.388
Maximum	48.34	86.48	13.78	4.72	8.87	92.70	.984
Mean	43.15	80.67	4.15	2.25	1.70	86.78	.606

Table 2

Coal Analyses

	W.Ky. #6	W.Ky. #9	Wyodak
<u>Ultimate (wt.%, daf)</u>			
Carbon	82.87	76.80	71.02
Hydrogen	5.42	5.41	5.42
Nitrogen	1.72	1.90	1.37
Sulfur	5.15	8.41	1.00
Oxygen ¹	4.84	7.40	21.29
Reflectance (R _o max)	.77	.54	----

1 By difference

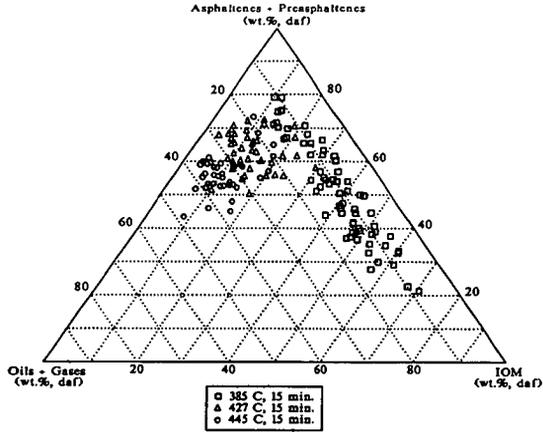


Figure 1. Solubility class distributions of 69 U.S. bituminous Coals

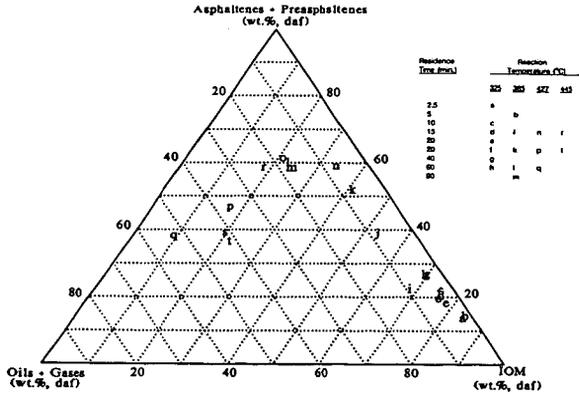


Figure 2. Thermal liquefaction pathway of a W.Ky.#6 bituminous coal.

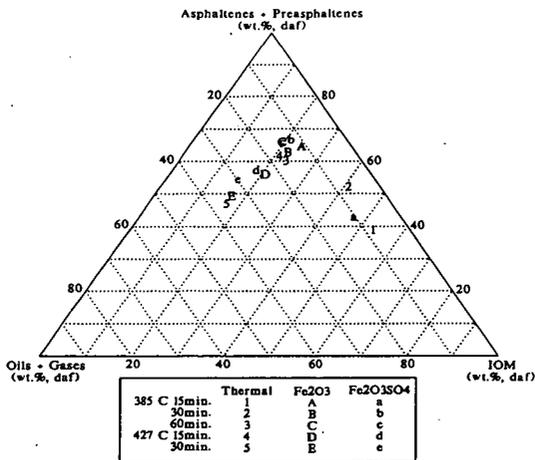


Figure 3. Catalytic pathway of a W.K.v. #6 bituminous coal.

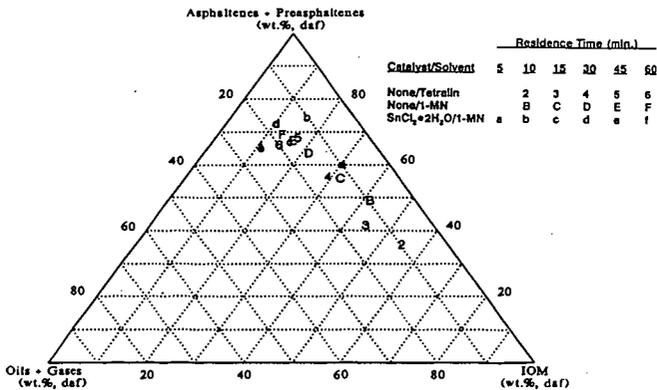


Figure 4. The effect of solvent quality on the pathway of a W.K.v. #9 coal.

