

# LIQUEFACTION PATHWAYS OF SUBBITUMINOUS AND BITUMINOUS COALS

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## INTRODUCTION

Lumped parameter kinetic models have successfully been used to describe industrially significant and complex chemical processes such as catalytic cracking (e.g. 1), catalytic reforming (e.g. 2) and addition polymerization (e.g. 3). The complexity of the liquefaction process has necessitated the use of this approach in studying the thermal and catalytic pathways of this process. In this work, the lumped parameters used are the standard solubility class: a) oil plus gases (O+G), b) asphaltenes and preasphaltenes (A+P) and, c) coal insoluble organic matter (IOM). The lumped solubility classes produced from the thermal liquefaction of a large number of U.S. bituminous coals were plotted on a ternary plot. The resulting data suggested a common pathway for all of the bituminous coals. A Wyodak coal was also studied to determine the pathway of a subbituminous coal for comparison.

## EXPERIMENTAL

The description and the range of values of some of the key coal properties of the 69 high volatile bituminous coals used in the initial study are given in Table 1. The properties of the three coals (W. Ky. #9, W. Ky. #6 and Wyodak) used in the more extensive studies are given in Table 2.

All of the liquefaction experiments were done in 50 mL batch microautoclaves using a hydrogen atmosphere. Details of the liquefaction procedure and solubility class determinations are given elsewhere (4). In this work, oils are defined a pentane solubles, asphaltenes are benzene soluble and pentane insoluble, preasphaltene are pyridine soluble and benzene insoluble and IOM are pyridine insoluble. In the catalytic experiments, all catalysts, with the exception of Shell 324, were sulfided *in-situ* by adding twice the stoichiometric amount of dimethyldisulfide required to sulfide the metal of the catalyst. The Shell 324 catalyst was presulfided prior to the additions of coal and liquefaction solvent to the reactor.

## RESULTS AND DISCUSSION

The lumped parameters obtained from the thermal liquefaction of the initial 69 coals at a 15 min. residence time and three reactions temperatures (385°C, 427°C, 445°C) were plotted in a ternary graph (Figure 1). These data suggest a common liquefaction pathway for all of the coals. A Western Kentucky #6 and #9 were selected to verify the apparent pathway. Reaction conditions were selected to cover a maximum range of conversions.

The thermal liquefaction pathway of the W. Ky. #6 coal is shown in Figure 2. As can be seen in Figure 2, the thermal pathway over a large range of conversions is identical to the pathway suggested in Figure 1 for the diverse set of coals. There appears to be two distinct stages in the liquefaction of these coals. In the initial stage, the primary reaction is the conversion of the coal to asphaltenes plus preasphaltenes. This reaction continues until the A+P and coal conversion reaches a maximum yield. During this stage, the oil plus gas yield remains relatively constant. In the second stage of the thermal pathway, the primary reaction is the conversion of A+P to O+G. The coal conversion increases very little in this stage of the pathway. At the higher temperature and long residence times, the pathway appears to change again. Both the O+G and A+P yields decrease suggesting the possibility of retrograde reactions are taking place. These results suggest that these bituminous coals have a common thermal liquefaction pathway.

The pathway defined for the bituminous coals indicates that a maximum in the A+P yields is achieved before there is a substantial increase in the O+G yield. It is desirable to change the pathway in such a manner as to achieve increases in the O+G yield as coal conversion increases. A supported catalyst (Shell 324) and an oil-soluble catalyst precursor (molybdenum naphthenate) were utilized in an attempt to favorably alter the liquefaction pathway to increase the O+G yields as coal conversion increases. The same W. Ky. #6 sample was used in the catalytic studies. The results of these experiments are shown in Figure 3. The pathway defined using both catalysts are similar to

the defined thermal pathway for this coal. The major effect of catalyst addition on the pathway is to increase the rate of production of the intermediate, A+P, and has no major effect on the selectivity defined by the solubility classes. Therefore, the observed data for the thermal and catalytic processes of the bituminous coals are consistent for the following series of reactions:



A subbituminous Wyodak coal was studied next to determine if the lower rank coal has the same thermal and catalytic pathway as those defined for the bituminous coals. The results of similar experiments performed for the Wyodak coal are shown in Figure 4. Both the thermal and catalytic pathways defined for the Wyodak coal are significantly different from the pathways defined for the bituminous coals. For the subbituminous coals, as conversion increases, there is a parallel increase in both the O+G and A+P yields. These yields continue to increase until a maximum in coal conversion is achieved. The major reaction taking place after these maxima have been achieved is the conversion of A+P to O+G with little additional coal conversion taking place. This stage is similar to the second stage of the bituminous coal pathway. The addition of a catalyst does not alter the subbituminous coal pathway (Figure 4). As was observed with the bituminous coals, the addition of a catalyst only increases the rate of production of the intermediates and does not alter the selectivity defined by the thermal pathway.

## CONCLUSIONS

The utilization of a lumped solubility class parameters plotted on a ternary plot show that the bituminous coals studied have a common liquefaction pathway. Attempts to change thermal pathway by catalyst addition were unsuccessful. The addition of a catalyst only increased the rates of production of products. The addition of a catalyst had no effect on the selectivity defined by the pathway.

The pathway defined for a subbituminous coal was significantly different than that defined for the bituminous coals. For the subbituminous coal, as conversion increases in the first stage, both the O+G and A+P yield increase. In the first stage for the bituminous coal only the A+P yield show a substantial increase in yield with conversion and the O+G yields remain fairly constant. The second stage of the pathway for the subbituminous coal, the primary reaction in the conversion of A+P to O+G which is similar to the second stage of the bituminous coal pathway. The addition of a catalyst to the subbituminous coal had no effect on the selectivity of the pathway.

## ACKNOWLEDGMENT

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## REFERENCES

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A. Distribution of Samples by State:		B. Distribution by ASTM Rank Classification:					
Kentucky	36	High volatile bituminous A, B, C					
Indiana	22						
Ohio	10						
West Virginia	1						
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 <sub>o</sub> 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			
Ultimate (wt.%, daf)	Wyodak	W. KY. #6	W. Ky. #9
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 <sup>1</sup>	4.84	7.40	21.29
Reflectance (R <sub>o,max</sub> )	.77	.54	---

1. By difference.

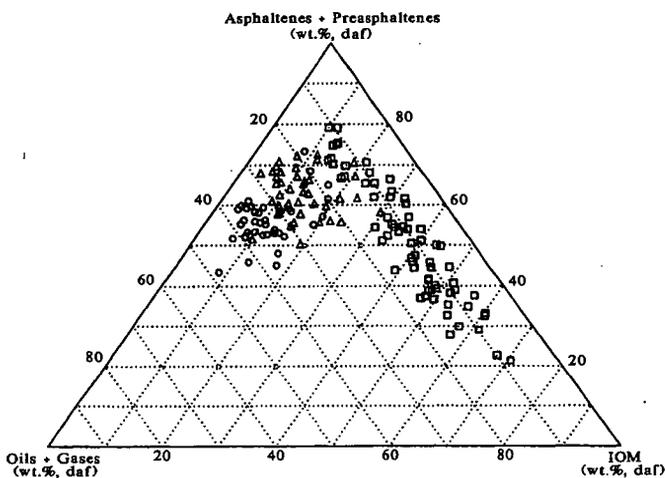


Figure 1. Solubility class distribution of the liquefaction products obtained from the thermal dissolution of bituminous coals using a 15 min. residence time, 3 reactions temperatures (385°C, □; 427°C, △, 445°C, ▲, ○) and a H<sub>2</sub> atmosphere (ca. 2000 psig @ 445°C).

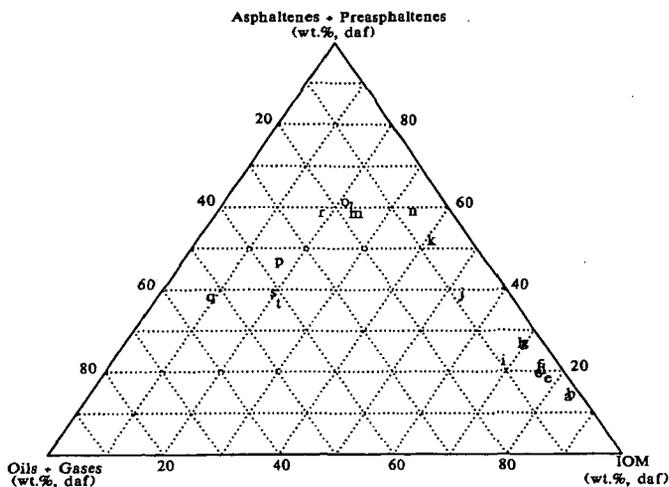


Figure 2. The thermal liquefaction pathway of a W.Ky. #6 bituminous coal using a  $H_2$  atmosphere (ca. 2000 psig @ 445°C) using various reactor temperatures and residence times (325°C and 2.5 min., l; 5 min., b; 10 min., c; 15 min., d; 20 min., e; 30 min., f; 40 min., g; 60 min., h; 385°C and 5 min., i; 15 min., j; 30 min., k; 60 min., l; 90 min., m; 427°C and 5 min., n; 15 min., o; 30 min., p; 60 min., q; 445°C and 5 min., r; 15 min., s; 30 min., t).

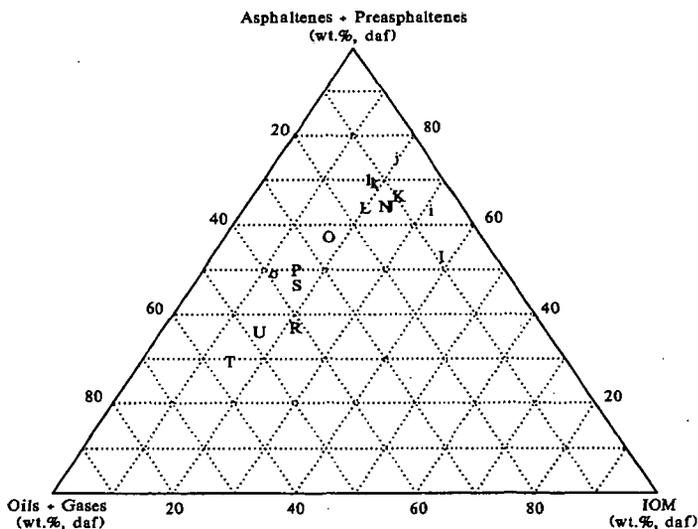


Figure 3. The catalytic liquefaction pathway of a W.Ky. #6 bituminous coal using a  $H_2$  atmosphere (ca. 2000 psig @ 445°C) and a Shell 324 catalyst (385°C and 5 min., I; 15 min., J; 30 min., K; 60 min., L; 427°C and 5 min., N; 15 min., O; 30 min., P; 445°C and 5 min., R; 15 min., S; 30 min., T; 60 min., U) and a molybdenum naphthenate catalyst (385°C and 5 min., i; 15 min., j; 30 min., k; 40 min., l; 427°C and 15 min., o).

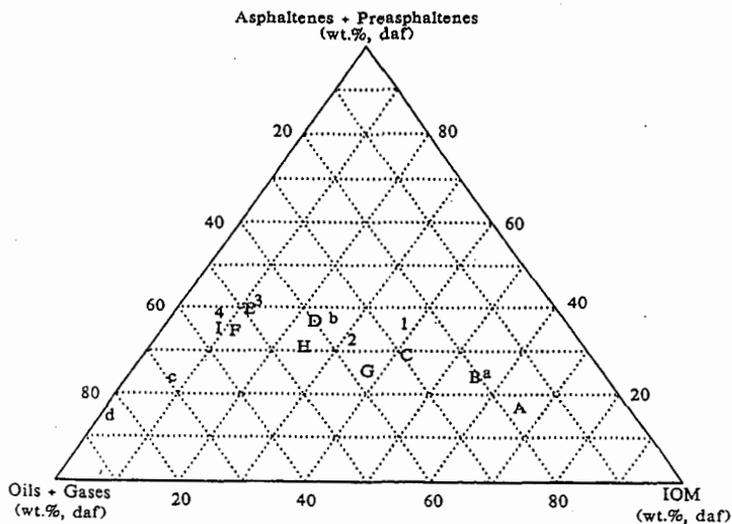


Figure 4. Thermal and catalytic liquefaction pathway for a Wyodak coal using a  $H_2$  atmosphere (ca. 2000 psig @ 445°C) and a number of different reactor temperature and residence times (No catalyst: 385°C and 5 min., A; 15 min., B; 30 min., ; 427°C and 15 min., D; 30 min., E; 60 min., F; 445°C and 5 min., G; 15 min., H; 30 min., I; ultrafine  $Fe_2O_3$ : 385°C and 15 min., 1; 30 min., 2; 427°C and 15 min., 3; 30 min., 4; No naphthenate: 385°C and 5 min., a; 15 min., b; 427°C and 30 min., c; 60 min., d).