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A Characterization and Evaluation of Coal Liquefaction Process Streams

**Quarterly Report
April 1 - June 30, 1997**

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ABSTRACT

This is the Technical Progress Report for the twelfth quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period April 1 through June 30, 1997. Described in this report are the following activities:

- Thirty-nine samples from four run conditions of HTI Run PB-07 were received. Appropriate samples were characterized by proton NMR spectroscopy, Fourier transform infrared spectroscopy, vacuum distillation, and solvent quality tests.
- The University of Delaware completed their subcontract this quarter. A meeting was held on April 30, 1997 at the University to close out the subcontract.
- Twelve sets of samples were chosen from the CONSOL sample bank for the study of the insoluble and presumed unreactive material from process stream samples. Each set consists of the whole process stream and the 454 °C⁺ (850 °F⁺) distillation resid derived from that process stream. Processing data for all samples were compiled. The samples represent four Wilsonville pilot plant runs and two HTI runs.

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Section 1

EXECUTIVE SUMMARY

CHARACTERIZATION OF SAMPLES FROM HTI RUN PB-07

In support of the Hydrocarbon Technologies, Inc. (HTI) bench unit program, CONSOL analyzed samples from four of the five run conditions of HTI's Run PB-07 (227-102). The five-condition run had a single objective, which was to determine the effect of different composition and levels of dispersed catalyst loadings on liquefaction of Illinois No. 6 coal processed in an ashy-recycle mode. Three catalysts (iron-containing GelCat™, phosphorous-containing GelCat™, and Molyvan A) were tested in a matrix of combinations. GelCat™ is HTI's proprietary catalyst. Samples were received from Condition 2 (Fe-GelCat™/P-GelCat™) several months after the other samples. Samples received and characterized were from Condition 1 (Fe-GelCat™), Condition 2 (Fe-GelCat™/P-GelCat™), Condition 3 (Fe-GelCat™/P-GelCat™/Mo), and Condition 5 (Mo). HTI reported operational problems in Condition 4 which tested a mixture of Mo and P-GelCat™. No samples were received from this condition. The characteristics of the process samples are essentially the same among the samples obtained from the same sampling location during different run conditions. There is no discernable effect on process sample characteristics of the use of the different dispersed catalysts.

RESID REACTIVITY

The University of Delaware completed all experimental resid reactivity work this quarter. The structure model was completed. The reaction model was completed for catalytic upgrading of coal resids and is undergoing refinement. Delivery of a final report and the computer models is expected next quarter. A review meeting was held on April 30, 1997.

A study of the insoluble portion of coal liquefaction process streams was initiated. The study includes isolation and examination of the insoluble materials from the whole process streams and the 454 °C⁺ (850 °F⁺) distillation resids derived from those process streams and evaluation of their impact on resid reactivity.

FUTURE WORK

Analyses will be completed for HTI Runs PB-01, PB-04, and PB-06.

The resid structure and reaction model will be completed by the University of Delaware. A topical report describing the University of Delaware subcontract findings will be compiled and issued. The computer model will be made available to the Department of Energy.

The study of isolated materials from process stream samples will be continued. Petrographic analyses of these materials are planned.

Section 2

INTRODUCTION

This is the Technical Progress Report for the twelfth quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period April 1 through June 30, 1997.

CONTRACT OVERVIEW

The objectives of this project are to support the DOE direct coal liquefaction process development program and to improve the useful application of analytical chemistry to direct coal liquefaction process development. This project builds on work performed in DOE Contract No. DE-AC22-89PC89883. Independent analyses by well-established methods are obtained of samples produced in direct coal liquefaction processes under evaluation by DOE. New analytical instruments and techniques to examine coal-derived samples are being evaluated. The data obtained from this study are used to guide process development and to develop an improved data base on coal and coal liquids properties. A sample bank, established and maintained for use in this project, is available for use by other researchers. The reactivity of the non-distillable resids toward hydrocracking at liquefaction conditions (i.e., resid reactivity) is being examined. From the literature and experimental data, a kinetic model of resid conversion is being constructed. Such a model will provide insights to improve process performance and the economics of direct coal liquefaction.

CONTRACT ACTIVITIES THIS PERIOD

- Thirty-nine samples from four run conditions of HTI Run PB-07 were received (Table 2). Appropriate samples were characterized by proton NMR spectroscopy, Fourier transform infrared spectroscopy, vacuum distillation, and solvent quality tests (Tables 3-8). The results are presented in the Results and Discussion section of this report.
- The University of Delaware completed all experimental resid reactivity work this quarter. The resid structure computer model was completed, and the resid reaction computer model is being completed. It will be ready by August 1, 1997, for delivery to CONSOL. A Topical Report inclusive of the University of Delaware's Final Report was planned. A meeting was held on April 30, 1997, at the University. Meeting handouts are appended to this report (Appendix 1).

- A study of the insoluble, and presumed unreactive material from process stream samples was initiated. Issues which are being addressed are: 1) The appropriateness of solubility to isolate unreactive material. 2) The influence of solvent (tetrahydrofuran or tetralin) on the nature of material isolated. 3) Enrichment of resids in this material by virtue of resid formation (i.e., as an artifact of high temperature vacuum distillation) 4) Ease of removal from process streams (instead of recycling) without throwing away convertible material. 5) Differences of these materials in quantity and quality from different coal sources, process streams, and from different liquefaction process conditions.

Twelve sets of samples were chosen from the CONSOL sample bank for this study. Each set consists of the whole process stream and the 454 °C⁺ (850°F⁺) distillation resid derived from that process stream. Processing data for all samples were compiled. The samples represent four Wilsonville pilot plant runs and two HTI runs.

ACTIVITIES IN PROGRESS

- Soxhlet extraction of the 24 resid and process stream samples was initiated to isolate insoluble materials.
- Characterization work on samples from HTI PB-04, PB-06, and PB-01 continues.

Section 3

RESULTS AND DISCUSSION

CHARACTERIZATION OF SAMPLES FROM HTI RUN PB-07

HTI Bench Run PB-07 was designed to determine the effects of different compositions and levels of dispersed catalyst loadings on direct liquefaction of Illinois No. 6 bituminous coal in an ashy-recycle mode. Run PB-07 (also known as Run 227-102) was made in HTI's bench unit 227 configured with two equal-volume back-mixed reactors with internal recirculation (Figure 1). An interstage vapor/liquid separator was employed. No pretreater/preheater was used during the run. The in-line fixed-bed hydrotreater was operated.

Process conditions were held constant throughout the five-condition test, except for the type and amount of dispersed catalyst used in each run condition (Table 1). Three catalysts (iron-containing GelCat™, phosphorous-containing GelCat™, and Molyvan A) were tested in a matrix of combinations. GelCat™ is HTI's proprietary catalyst. Samples received were from Condition 1 (Fe-GelCat™), Condition 3 (Fe-GelCat™/P-GelCat™/Mo), and Condition 5 (Fe-GelCat™). Samples were received from Condition 2 (Fe-GelCat™/P-GelCat™) several months after the samples generated in other conditions; analyses of Condition 2 samples were limited. HTI reported operational problems in Condition 4, which tested a mixture of Mo and P-GelCat™ 1, 1a. No samples were received from Condition 4.

HTI's preliminary conclusions from the data obtained in Run PB-07 are that the overall process performance was not significantly affected by the type or amount of catalyst used in Conditions 1, 2, 3, or 5.^{1, 1a} HTI's tentative conclusion is that at ca. 2500 ppm Fe-GelCat™ loading, the addition of ca. 100 ppm molybdenum or phosphorous has no significant impact on overall process performance (Table 2). Coal conversions and resid conversions are reported by HTI to be very high (96-97% and 87-89%, respectively). However, considering the high coal and resid conversions, the C₄-975 °F distillate yields are lower than expected (67-68% vs. 72-75% MAF). HTI reported that there was significant hydrocracking observed during the run. This is evident in the high gas yields (15-16%, MAF), high yields of light distillate, C₄-343 °C (50-55%, MAF), and low heavy vacuum gas oil (VGO) yields (2-3%, MAF). HTI tentatively concludes that this is possibly a consequence of the high (450 °C) reaction temperatures or the high Fe concentration (2500 ppm) used to liquefy Illinois No. 6 coal.

In support of HTI Run PB-07, CONSOL received 39 samples for analyses from four periods (2, 4, 10 and 16), representing four of the five run conditions (Table 3). Three of the samples were feed coals and six of the samples were the aqueous layer from the separator vessel. No analyses of the feed coal or the SOH water samples was performed.

Sample analyses were obtained for 30 process samples (Tables 4-9). With only several minor exceptions, there are no significant differences evident in the analyses of samples obtained from the four run conditions. Component distributions (distillate, resid, insoluble organic material (IOM), and ash content) are essentially unchanged for each sample type for the four conditions (Table 3).

Except for three samples, differences in the phenolic -OH content of samples obtained from the same sampling location are within the limits of repeatability for the method ($\pm 0.05\%$, abs.) (Table 5). The feed slurry for Condition 4 has a slightly elevated -OH content. The first-stage SOH oils obtained in Condition 5 are lower in -OH content than the other first-stage SOH oil samples examined, and the -OH content for the O-6 bottoms distillate fraction from Condition 3 is higher than the -OH content of the other two O-6 bottoms distillate samples. Because there are no other differences among these particular samples and their counterparts (component distributions are the same (Table 4), the proton NMR analyses are the same (Table 7), and the microautoclave solvent quality for the O-6 bottoms sample is the same (Table 6)), it is believed that these minor differences are not important.

The microautoclave test (Table 5) indicates that the solvent quality of the whole and distillate portions of the O-6 bottoms samples, the first-stage slurry samples, and the pressure filter liquid samples was unchanged as the catalyst was changed.

Whole samples from Condition 2 were analyzed only by ^1H - NMR spectroscopy. As can be seen in Table 6, these samples are very similar to others obtained from the same sampling locations during other run conditions. The proton NMR analyses of Condition 1, 3, and 5 whole process samples from each sampling location (Table 7), and the distillates (Table 8), and the resids (Table 9) from three locations vary slightly from sample to sample, but there are no consistent trends evident. These data confirm the unchanging nature of the samples produced with different catalysts.

The analytical methods applied to these samples have been shown to be sensitive to changes in process conditions in other bench-scale tests made at HTI. These changes include of reactor temperature, process unit configuration, space velocity/residence time, and feed properties. The lack of significant discernable differences in the samples from Run PB-07 indicates that by the time steady state was achieved in each process condition, there were no differences attributable to the catalysts. It thus can be concluded that the type and amount of catalysts used in these four test conditions did not affect process stream properties under the reaction conditions used throughout the run.

Section 4

EXPERIMENTAL

The experimental procedures used to produce results presented in this report were described previously.²⁻⁴

Section 5
CONCLUSIONS

Conclusions are provided in the Results and Discussions section of the report.

Section 6

REFERENCES

1. Personal communication with J. Hu, HTI, Inc, December 4, 1997.
- 1a. Comolli, A. G.; Zhou, P. Z.; Lee, T. L. K.; Hu, J.; Karolkiewicz, W. F.; Popper, G. "Direct Liquefaction Proof-of-Concept Program Topical Report Bench Run PB-07 (227-102)", DE-92148-TOP-09, December, 1997.
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3. Burke, F. P.; Winschel, R. A.; Robbins, G.A. "Recycle Slurry Oil Characterization, Final Report, October 1980 through March 31, 1985", DOE/PC 30027-61, March 1985.
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TABLE 1

HTI RUN PB-07 RUN CONDITIONS (a)

Condition	1	2	3	5
Period	1-4	5-7	8-10	14-16
Work-Up Period	4	7	10	16
Temperature, K-1, °C	446	446	446	446
Temperature, K-2, °C	456	458	457	451
Interstage Separator, °C	343	343	343	343
In-line Hydrotreater, °C	379	379	379	379
Space Velocity, kg feed/h/m ³	640	608	630	609
Recycle Solvent/Feed (b), kg/kg	0.92	0.93	0.91	0.89
Feed Coal	Illinois No. 6	Illinois No. 6	Illinois No. 6	Illinois No. 6
Catalysts, ppm				
Fe GelCat™	2500	2500	2500	2500
Molyvan-A	0	33	100	0
P GelCat™ (L-921)	250	100	100	0
Hydrotreater Catalyst	Criterion C-411 Trilobe	Criterion C-411 Trilobe	Criterion C-411 Trilobe	Criterion C-411 Trilobe

(a) HTI did not report conditions for Condition 4^{1a}

(b) Recycle consisted of a mixture of pressure filter liquids (PFL) and separator bottoms.

TABLE 2

HTI PRELIMINARY PROCESS PERFORMANCE RESULTS

Condition	1	2	3	4	5
Mass Balance Period	3	7/8	10	N/A	16
Material Recovery, %	99.3	98.8	94.9	N/A	104.7
Normalized Yields, % MF Coal					
C ₁ -C ₃	14.6	11.9	15.1		16.2
C ₄ -C ₇	7.0	8.0	5.9		12.3
IBP-177 °C	12.7	11.7	12.8		14.1
177-260 °C	16.1	12.2	13.5		12.6
260-343 °C	13.5	15.7	13.9		11.6
343-454 °C	10.2	13.4	11.2		8.3
454-524 °C	3.0	3.3	3.3		2.7
524 °C*	8.4	9.7	8.1		6.9
Unconverted Coal	3.3	3.0	3.2		3.2
H ₂ O	3.3	3.6	4.3		4.1
CO _x	1.1	1.3	1.5		1.7
NH ₃	1.3	1.4	1.4		1.4
H ₂ S	3.0	3.1	3.0		3.0
Process Performance, % MAF Coal					
Total Coinversion	96.3	97.0	96.3		96.4
Residuum Conversion	87.1	86.0	87.5		88.8
C ₄ -524 °C Yield	69.0	71.1	67.0		68.1
H ₂ Consumption	7.9	8.6	7.5		8.3
H ₂ Efficiency, kg dist/kg H ₂	8.7	8.3	8.9		8.2
C ₁ -C ₃ Gas Selectivity*	23.5	18.5	24.9		26.3

*Defined as a percentage of C₁-C₃ light gas yield relative to the C₄-524 °C distillate yield.

TABLE 3
SAMPLES RECEIVED
HTI RUN PB-07

Condition	1	2	3	4	5
Sample	Acquisition Period (a)				
Feed Coal	4A		10A		16A
Feed Slurry	4A		10A	11A	16A
Pressure Filter Liquid	4B	5B	10B		16B
Pressure Filter Solid	4B	7A	10B		16B
First Stage-Slurry	5A (b,e)		11A (b)		16B (c)
0-6 Bottoms	4B	5B,6A	10B		16B
First-Stage SOH (d) Oil	4B	6A	10B		16A, 16B
First-Stage SOH Water	4B		10B		16B
Second-Stage SOH Oil	4B	8A	10B		16B
Second-Stage SOH Water	4B		10B		16B

- (a) Periods are 24 h long. The designation A or B indicates which of the two 12 h shifts during the period the sample was obtained.
- (b) The first-stage slurry sample was taken following the end of the run condition. It represents the preceding run condition.
- (c) The first-stage slurry was taken at the end of Condition 5 and represents Condition 5.
- (d) SOH = separator overhead
- (e) Two individual first-stage slurry samples received from Period 5A.

TABLE 4
COMPONENT DISTRIBUTION
HTI RUN PB-07 SAMPLES

Sample	Component, %	Condition			
		1	3	4	5
Feed Slurry	Distillate (a)	ND	ND	ND	ND
	THFS (b)	53.5	51.5	49.7	54.3
	IOM	37.4	40.0	41.4	37.7
	Ash	9.1	8.5	8.9	8.0
First-Stage Slurry	Distillate (a)	28.8	31.5		27.7
	THFS Resid	50.3	47.1		54.8
	IOM	5.4	4.5		4.4
	Ash	14.7	15.3		12.6
O-6 Bottoms	Distillate (a)	41.2	42.1		41.4
	THFS Resid	39.9	39.7		41.3
	IOM	4.0	4.1		3.9
	Ash	13.1	12.7		11.8
Pressure Filter Liquid	Distillate (a)	48.9	44.4		47.0
	THFS Resid	49.1	52.7		51.3
	IOM	0.7	0.9		0.6
	Ash	<0.1	<0.1		<0.1
Pressure Filter Solid	Distillate (a)	ND	ND		ND
	THFS Resid	37.0	36.7		36.9
	IOM	15.0	14.2		14.6
	Ash	48.0	49.1		48.5

- (a) Distillation cut point 454°C
(b) THFS = Tetrahydrofuran Soluble

ND = none detected

TABLE 5

PHENOLIC -OH CONTENT OF HTI BENCH RUN PB-07 SAMPLES

Condition	1	3	4	5
Sample	Phenolic -OH, meq/g (peak location, cm ⁻¹)			
Whole Oils				
First-Stage SOH Oil	1.87 (3305)	1.89 (3308)		1.64 (3308), 1.75 (3307)
Second-Stage SOH Oil	ND	ND		ND
THF-Soluble Portion of Samples				
First-Stage Slurry 454°C ⁻ Distillate	1.18 (3302)	1.19 (3303)		1.16 (3303)
First-Stage Slurry 454°C ⁺ Resid	1.03 (3293)	1.07 (3294)		1.08 (3293)
0-6 Bottoms 454°C ⁻ Distillate	1.06 (3304)	1.16 (3304)		1.09 (3303)
0-6 Bottoms 454°C ⁺ Resid	0.90 (3295)	0.90 (3296)		0.89 (3294)
Feed Slurry	1.00 (3294)	0.95 (3293)	1.10 (3296)	0.93 (3292)
Pressure Filter Liquid (PFL) 454°C ⁻ Distillate	1.02 (3304)	1.05 (3303)		1.00 (3303)
Pressure Filter Liquid (PFL) 454°C ⁺ Resid	0.88 (3294)	0.89 (3295)		0.89 (3294)
Pressure Filter Solid (PFS)	0.92 (3296)	0.96 (3297)		0.96 (3296)

ND = none detected

TABLE 6
MICROAUTOCLAVE COAL CONVERSIONS
HTI RUN PB-07 SAMPLES

Sample		Condition		
		1	3	5
First-Stage Slurry	Distillate (a)	84.5	85.6	82.6
	Whole	62.0	63.5	63.8
O-6 Bottoms	Distillate (a)	87.3	86.7	85.7
	Whole	74.6	76.1	76.4
PFL	Distillate (a)	85.9	88.2	85.8
	Whole	73.3	76.2	70.1

Test Conditions: 398 °C, 30 min, 9 g sample, 6 g Old Ben Mine coal

(a) 454 °C- fraction of whole sample

TABLE 7
PROTON NMR OF WHOLE HTI RUN PB-07 SAMPLES

	Feed Slurry (a)				O-6 Bottoms (b)			
	Condition				Condition			
	1	3	4	5	1	2	3	5
Condensed Aromatic	23.9	23.9	26.2	24.6	25.6	22.0; 23.2	22.4	23.1
Uncondensed Aromatic	9.6	9.4	9.7	9.1	14.2	15.6; 15.6	16.4	15.6
Cyclic Alpha	17.1	17.1	19.4	15.4	17.3	14.3; 15.1	16.3	15.2
Alkyl Alpha	11.1	11.2	10.5	10.2	11.8	12.2; 12.2	12.1	12.5
Cyclic Beta	11.8	12.3	12.1	11.7	11.2	11.4; 11.2	11.8	11.4
Alkyl Beta	16.5	16.4	13.2	17.7	12.6	14.8; 13.8	12.4	13.3
Gamma	9.9	9.8	8.9	11.2	7.2	8.4; 7.8	8.6	9.0

	First-Stage SOH Oil (c)				Second-Stage SOH Oil (c)			
	Condition				Condition			
	1	2	3	5	1	2	3	5
Condensed Aromatic	8.6	8.1	7.5	7.1; 8.1	1.2	0.1	0.7	0.4
Uncondensed Aromatic	13.8	12.7	13.3	11.6; 12.0	3.4	4.8	4.9	3.0
Cyclic Alpha	10.8	10.7	11.6	9.8; 10.2	5.2	5.4	6.4	4.1
Alkyl Alpha	13.7	12.7	13.5	12.7; 13.1	5.5	6.0	6.4	5.2
Cyclic Beta	14.3	14.5	15.9	15.0; 13.8	25.2	21.6	23.3	22.1
Alkyl Beta	23.3	24.6	22.6	26.4; 26.1	33.0	34.8	33.6	34.7
Gamma	15.6	16.8	15.5	17.4; 16.7	26.4	26.8	24.8	30.6

- (a) Samples dissolved in 99.8% CDCl₃ (1% TMS), filtered prior to analysis.
(b) Samples dissolved in 99.96% d₅ pyridine, filtered prior to analysis.
(c) Samples dissolved in 99.8% CDCl₃ (1% TMS)

TABLE 7 (Continued)

PROTON NMR OF WHOLE HTI RUN PB-07 SAMPLES

	Pressure Filter Liquid (c)				Pressure Filter Solids (b)			
	Condition				Condition			
	1	2	3	5	1	2	3	5
Condensed Aromatic	25.0	25.6	23.3	24.3	32.7	26.6	30.4	31.0
Uncondensed Aromatic	15.3	13.4	13.6	14.2	8.2	4.2	6.4	8.5
Cyclic Alpha	16.1	16.1	16.5	16.3	17.7	15.9	17.3	17.2
Alkyl Alpha	11.7	11.6	12.2	11.9	11.2	10.0	11.1	11.3
Cyclic Beta	11.1	11.0	11.5	11.3	11.3	11.7	12.3	11.4
Alkyl Beta	12.6	13.8	12.0	14.0	11.3	21.0	12.6	12.5
Gamma	8.2	8.4	8.6	8.5	7.6	10.5	9.9	8.1

	First-Stage Slurry (a)			
	Condition			
	1	2 (d)	3	5
Condensed Aromatic	24.1	25.4	21.3	25.8
Uncondensed Aromatic	17.4	16.3	17.2	15.3
Cyclic Alpha	14.4	15.1	14.1	15.4
Alkyl Alpha	11.8	11.7	12.0	11.9
Cyclic Beta	10.8	10.7	12.0	10.8
Alkyl Beta	12.7	12.6	13.4	13.0
Gamma	8.8	8.3	10.0	7.9

- (a) Samples dissolved in 99.8% CDCl₃ (1% TMS), filtered prior to analysis.
 (b) Samples dissolved in 99.96% d₅ pyridine, filtered prior to analysis.
 (c) Samples dissolved in 99.8% CDCl₃ (1% TMS)
 (d) Average determination of duplicate samples

TABLE 8

PROTON NMR OF DISTILLATE HTI RUN PB-07 SAMPLES

	O-6 Bottoms			First-Stage Slurry			Pressure Filter Liquid		
	Condition			Condition			Condition		
	1	3	5	1	3	5	1	3	5
Condensed Aromatic	19.8	18.5	20.7	22.9	19.2	21.7	21.0	21.3	20.1
Uncondensed Aromatic	13.8	14.3	11.9	11.7	12.1	10.7	13.0	12.7	11.8
Cyclic Alpha	15.1	15.9	16.4	15.9	15.6	15.5	15.6	17.2	15.7
Alkyl Alpha	13.0	12.5	12.7	12.8	12.6	12.6	12.7	12.3	12.2
Cyclic Beta	12.1	13.1	12.2	12.6	12.9	12.2	12.1	12.3	12.1
Alkyl Beta	16.1	15.7	16.6	14.0	16.7	17.0	16.2	15.4	17.6
Gamma	10.1	9.9	9.6	10.0	10.9	10.3	9.4	8.9	10.6

Samples dissolved in 99.8 CDCl₃ (1% TMS).

TABLE 9
PROTON NMR OF RESID HTI RUN PB-07 SAMPLES

	O-6 Bottoms			First-Stage Slurry			Pressure Filter Liquid		
	Condition			Condition			Condition		
	1	3	5	1	3	5	1	3	5
Condensed Aromatic	39.0	38.2	41.4	41.1	35.6	39.0	41.7	39.7	36.0
Uncondensed Aromatic	9.2	9.5	7.2	6.3	8.9	8.5	7.3	7.5	11.3
Cyclic Alpha	18.2	17.9	18.9	19.1	18.2	18.4	18.5	18.9	17.2
Alkyl Alpha	10.3	9.7	9.7	9.9	10.3	10.2	10.0	9.8	10.3
Cyclic Beta	9.6	10.3	9.7	10.0	10.9	10.0	9.9	9.7	10.0
Alkyl Beta	7.9	8.5	7.9	8.2	9.5	8.5	7.9	9.0	8.6
Gamma	5.7	6.0	5.1	5.4	6.6	5.4	4.7	5.5	6.6

Samples dissolved in 99.96% d₅ pyridine, filtered prior to analysis.

Figure 1. Process Flow Diagram of Bench-Scale Liquefaction Unit (HTI Unit 227), as Configured for Run PB-07.

Appendix 1

Handouts

University of Delaware Subcontract Close-out Meeting April 30, 1997

KINETICS OF HYDROPROCESSING OF COAL-DERIVED VACUUM RESIDS

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Figure 1. Generalized Flowsheet of Closed-Coupled Integrated Two-Stage Liquefaction System (Wilsonville Facility).

KINETICS OF HYDROPROCESSING OF COAL-DERIVED VACUUM RESIDS

IMPORTANT QUESTIONS TO ANSWER

1. What are the optimum hydroconversion conditions?
2. How much of the high boiling product is hydrocracked to useful product in the recycling?
3. What is the effect of conditions of the original liquefaction process and the coal type on the convertibility of the resid?
4. What are the resid characteristics which affect resid reactivity?

KINETICS OF HYDROPROCESSING OF COAL-DERIVED VACUUM RESIDS

OBJECTIVES OF STUDY

1. To develop an empirical method for the evaluation of resid conversion and resid reactivity.
2. To develop simple kinetic parameters to define the resid reactivity based on experiments.
3. To correlate chemical and physical characteristics of resids with resid reactivity.
4. To develop a reaction model based on kinetics and structural information (to be presented at another time).

Reactor Apparatus for the Conversion of Coal-Derived Resid.

(Reference: Huang, H.; Calkins, W. H.; Klein, M. T. "A Novel Short Time Reactor System for Studying the Initial Stages of High Temperature and High Pressure Reactions" *ACS Fuel Chem Div. Preprints* 1993, 38 (3), 1080.)

A Typical Temperature-Time Profile of the SCTBR Reactor.

Analytical Data of Resids - 1

	W259V-131B Run # 13 Resid C	W260V-131B Run # 10 Resid H	W258V-131B Run # 1 Resid A	W261V-131B Run # 2 Resid D	W261V1067 Run # 3 Resid I	W261R 1235 Run # 4 Resid M	W262R 1235 Run # 5 Resid E
Elemental							
C, wt %	90.92	87.43	88.30	88.39	88.14	87.44	85.34
H, wt %	6.50	6.35	5.61	6.57	6.53	6.59	6.59
N, wt %	1.04	1.10	1.19	1.05	1.11	1.19	0.99
S, wt %	1.24	1.53	1.74	1.05	1.54	1.57	1.74
O, wt %	0.30	3.59	3.16	2.94	2.68	3.21	5.34
Phenolic -OH (meq/g)	0.69	0.69	0.80	0.78	0.92	0.77	0.82
Ash, wt %	8.42	11.69	13.71	9.32	14.74	12.76	11.94
Insoluble Organic Matter			13.3	5.9	9.3	8.8	15.0
Proton Distribution							
Condensed Aromatics	26.1	29.5	31.3	25.4	25.9	24.5	22.3
Uncondensed Aromatics	5.4	3.8	7.6	3.8	4.5	4.9	3.7
Cyclic Alpha	18.9	21.5	18.8	19.7	19.9	21.1	19.2
Alkyl Alpha	9.4	4.5	9.5	9.6	9.6	9.6	9.3
Cyclic Beta	14.8	14.3	12.9	15.3	14.7	15.2	14.6
Alkyl Beta	14.6	17.0	11.9	16.8	16.0	15.6	20.9
Gamma	10.8	9.3	8.1	9.3	9.3	9.2	10.0
SARA wt %							
Saturates	2.1	4.4	1.5	5.1	2.6	7.6	4.5
Aromatics	31.2	28.4	23.4	38.0	20.7	29.4	15.4
Resins	14.5	8.0	10.6	7.4	20.7	4.2	16.8
Asphaltenes	21.3	23.4	28.1	23.4	20.1	19.9	21.4
Pre-asphaltenes	7.8	6.1	5.0	7.2	7.4	8.5	7.1
THF Insolubles	18.4	29.3	31.3	16.2	27.8	27.3	31.1

Analytical Data of Resids - 2

	W262V-131B Run # 6 Resid G	W262V-1067 Run # 7 Resid F	W260V-1067 Run # 8 Resid L	W260R-1235 Run # 9 Resid K	W259V-1067 Run # 11 Resid J	W259R 1235 Run # 12 Resid B	W260V-1067 Run # 14 Resid H	W260V-1067 Run # 15 Resid C
Elemental								
C, wt %	85.84	86.03	86.77	86.61	90.10	89.99	90.34	89.06
H, wt %	6.77	6.75	6.25	5.89	6.38	6.18	8.55	8.36
N, wt %	0.93	0.93	1.10	1.09	1.05	1.15	0.66	0.31
S, wt %	1.73	1.94	1.95	1.82	1.49	1.50	0.34	0.21
O, wt %	4.73	4.35	3.93	4.59	0.98	1.18	0.10	2.06
Phenolic -OH (meq/g)	0.85	1.25	0.69	0.95	0.70	0.92		
Ash, wt %	12.23	13.29	14.25	13.13	10.07	8.61	0.40	4.09
Insoluble Organic Matter	13.9	14.2	13.9		6.3			
Proton Distribution								
Condensed Aromatics	22.2	20.4	27.2	20.3	27.8	30.7	14.7	14.5
Uncondensed Aromatics	3.7	3.9	6.8	4.3	3.8	2.6	5.9	4.3
Cyclic Alpha	18.1	18.6	18.3	17.2	21.2	20.9	16.3	14.5
Alkyl Alpha	9.4	9.0	8.8	9.4	9.6	10.2	9.6	8.0
Cyclic Beta	15.2	15.3	13.6	15.3	15.5	13.8	16.1	15.1
Alkyl Beta	21.3	21.9	16.6	21.2	13.4	13.4	24.2	30.0
Gamma	10.1	10.8	8.7	12.3	8.7	8.4	13.1	13.6
SARA wt %								
Saturates	6.1	6.9	2.9	6.1	6.1	1.8	16.4	25.2
Aromatics	20.8	21.9	20.4	26.3	22.7	26.5	53.1	50.3
Resins	11.7	9.1	19.9	7.9	11.0	11.2	23.0	11.3
Asphaltenes	23.5	19.4	19.3	17.9	30.3	25.7	4.9	4.1
Pre-asphaltenes	5.9	5.9	6.5	9.0	8.5	11.6	0.5	0.5
THF Insolubles	27.7	29.5	30.7	29.4	22.7	22.0	0.0	7.5

SELECTED PROPERTIES OF THE RESIDS

Resid	Feed Coal	No.	Stream (a)	f_a	VM wt %	FC wt %	Ash wt %	T _{peak} °C	Peak Height wt %/min (daf)
Resid L	Wyodak-Anderson	4	V1067	34.0	51.3	48.7	19.1	470.7	4.59
Resid K	Black Thunder	5	R1235	24.6	53.6	46.4	17.2	464.8	4.60
Resid H		6	V131B	33.3	57.1	42.9	15.2	475.3	4.67
Resid F		10	V1067	24.3	55.2	44.8	17.5	461.5	4.36
Resid E		11	R1235	26.0	53.4	46.6	15.6	454.4	4.24
Resid G		12	V131B	25.9	55.7	44.3	15.9	462.2	5.02
Resid I	Illinois No. 6	7	V1067	30.4	61.5	38.5	15.9	480.1	6.44
Resid M	Burning Star 2	8	R1235	29.4	59.7	40.3	13.7	481.8	6.16
Resid D		9	V131B	29.2	70.9	29.1	9.9	490.5	6.83
Resid J	Pittsburgh	1	V1067	31.6	57.6	42.4	10.2	490.1	7.20
Resid B	Ireland	2	R1235	33.3	61.1	38.9	8.7	493.6	7.43
Resid C		3	V131B	31.5	61.0	39.0	8.5	490.2	6.23
Resid A				38.9	51.8	48.2	17.0	472.1	4.75
Resid N				20.6			0.4		
Resid O				18.8			4.1		

(a) Stream

V1067 = interstage stream

R1235 = second-stage product stream

V131B = recycle stream

Scheme of the Reaction Product Work-Up Procedure

CONVERSION OF THERMAL HYDROPROCESSING OF RESID

Resid			Solid Residue		Liquid Residue			Conversion
Sample	Name	Ash	Ash	TSF	Tetralin	RSF	850 °F*	
Resid A	W258V-131B	17.0	50.1	79.7	88.2	11.8	9.6	15.0
Resid B	W259R-1235	8.7	33.5	81.0	88.0	12.0	9.6	15.9
Resid C	W259V-131B	8.5	35.0	82.7	86.2	13.8	10.8	17.7
Resid D	W261V-131B	9.9	45.8	87.1	87.9	12.1	9.7	17.1
Resid E	W262R-1235	15.6	43.5	76.0	88.4	11.6	8.6	19.6
Resid F	W262V-1067	17.5	47.8	76.9	87.4	12.6	9.7	17.7
Resid G	W262V-131B	15.9	46.5	78.3	88.7	11.3	8.7	18.2
Resid H	W260V-131B	15.2	46.6	79.5	87.7	12.3	9.0	21.3
Resid I	W261V-1067	15.9	50.8	81.8	88.9	11.1	8.5	19.4
Resid J	W259V-1067	10.2	38.7	82.0	86.4	13.6	11.5	12.9
Resid K	W260R-1235	17.2	49.0	78.4	86.9	13.1	9.8	19.7
Resid L	W260V-1067	19.1	51.3	77.6	89.2	10.8	8.3	17.8
Resid M	W261R-1235	13.7	45.6	81.1	90.1	9.9	7.9	16.0
Resid N	HTI POC-1, O-43	0.4	33.0	99.2	80.6	19.4	14.1	27.0
Resid O	HTI POC-2, O-43	4.1	38.0	93.1	70.6	29.4	22.4	22.1

Thermal: 420 °C; 30min; 1500 psig H₂
 Catalytic: 420 °C; 30min; 1500 psig H₂; 3 wt % Mo
 Control: 25 °C; 10 min; 1500 psig H₂

TSF: Tetralin Soluble Fraction, wt % (daf basis)
 RSF: Resid Soluble Fraction in tetralin, wt %
 850 °F*: Fraction Boiling above 850 °F

CONVERSION OF CATALYTIC HYDROPROCESSING OF RESID

Resid			Solid Residue		Liquid Residue			Conversion
Sample	Name	Ash	Ash	TSF	Tetralin	RSF	850 °F*	
Resid A	W258V-131B	17.0	51.5	80.7	82.5	17.5	9.9	35.0
Resid B	W259R-1235	8.7	40.0	85.6	79.8	20.2	11.2	38.1
Resid C	W259V-131B	8.5	41.4	86.8	81.4	18.6	11.5	33.1
Resid D	W261V-131B	9.9	54.9	91.0	77.9	22.1	14.1	32.9
Resid E	W262R-1235	15.6	44.2	76.6	80.6	19.4	11.3	32.1
Resid F	W262V-1067	17.5	49.4	78.3	79.6	20.4	10.7	37.4
Resid G	W262V-131B	15.9	48.3	79.8	79.2	20.8	11.5	35.8
Resid H	W260V-131B	15.2	50.9	82.7	75.6	24.4	11.3	44.6
Resid I	W261V-1067	15.9	56.6	85.5	76.2	23.8	11.9	42.7
Resid J	W259V-1067	10.2	43.8	85.4	76.5	23.5	11.9	42.1
Resid K	W260R-1235	17.2	52.1	80.8	78.1	21.9	12.4	35.2
Resid L	W260V-1067	19.1	53.5	79.5	79.1	20.9	11.7	35.0
Resid M	W261R-1235	13.7	53.7	86.3	80.2	19.8	11.7	35.3
Resid N	HTI POC-1, O-43	0.4	36.4	99.3	67.9	32.1	16.7	47.6
Resid O	HTI POC-2, O-43	4.1	48.3	95.4	70.2	29.8	19.1	34.3

Thermal: 420 °C; 30min; 1500 psig H₂
 Catalytic: 420 °C; 30min; 1500 psig H₂; 3 wt % Mo
 Control: 25 °C; 10 min; 1500 psig H₂

TSF: Tetralin Soluble Fraction, wt % (daf basis)
 RSF: Resid Soluble Fraction in tetralin, wt %
 850 °F*: Fraction Boiling above 850 °F

$$Conversion = \left(1 - \frac{Ash_0}{Ash}\right) \cdot \frac{1}{1 - Ash_0} \cdot \left(1 - \frac{850^\circ F^+}{RSF_{liquid}}\right)$$

Ash₀ determined by TGA: ± 0.005 (3%);

Ash determined by TGA: ± 0.005 (1%);

850 °F⁺ determined by SimDis TGA: ± 0.005 (5%);

RSF_{liquid} determined by GC: ± 0.02 (12%);

Conversion: ± 0.04 (12%).

Estimation of Experimental Error

Thermal and Catalyzed Hydroprocessing Conversions of the Resids vs Feed coal Type (Samples Taken for All Locations).

Thermal and Catalyzed Hydroprocessing Conversions vs f_a of the Resids.

Influence of the Catalyst Concentration on the Conversion of the Catalyzed Hydroprocessing of Resid C (420 °C; 30 min, 1500 psig H_2 ; Tetralin:Resid = 3:1 wt ratio).

Influence of the Hydrogen Pressure on the Conversion of the Catalyzed Hydroprocessing of Resid C (420 °C; 30 min, 1500 psig H₂; Tetralin:Resid = 3:1 wt ratio).

First-order Assumption:

$$\frac{dX}{dt} = k \cdot (1 - X)$$

$$\ln(1 - X) = -k \cdot t$$

Second-order Assumption:

$$\frac{dX}{dt} = k \cdot (1 - X)^2$$

$$\frac{X}{1 - X} = k \cdot t$$

Kinetics of Catalyzed Hydroprocessing of Resid

Conversion vs Time for the Catalyzed Hydroprocessing of Resid C
(420 °C; 30 min, 1500 psig H₂; 3 wt % Mo; Tetralin:Resid = 3:1 wt ratio).

Relative Reaction Rate Constant vs Time for the Catalyzed Hydroprocessing of Resid C
Using the First-Order Assumption (1500 psig H₂; 3 wt % Mo; Tetralin:Resid = 3:1 wt ratio).

Relative Reaction Rate Constant vs Time for the Catalyzed Hydroprocessing of Resid C
Using the Second-Order Assumption (1500 psig H_2 ; 3 wt % Mo; Tetralin:Resid = 3:1 wt ratio).

Conversion vs Time for the Catalyzed Hydroprocessing of Resid H
(1500 psig H_2 ; 3 wt % Mo; Tetralin:Resid = 3:1 wt ratio).

Relative Reaction Rate Constant vs Time for the Catalyzed Hydroprocessing of Resid H Using the First-Order Assumption (1500 psig H_2 ; 3 wt % Mo; Tetralin:Resid = 3:1 wt ratio).

Relative Reaction Rate Constant vs Time for the Catalyzed Hydroprocessing of Resid H Using the Second-Order Assumption (1500 psig H_2 ; 3 wt % Mo; Tetralin:Resid = 3:1 wt ratio).

Conversion vs Carbon Content (o:thermal; x:catalyzed)

Conversion vs H/C Atomic Ratio (o:thermal; x:catalyzed).

Conversion vs Uncondensed Aromatics (o:thermal; x:catalyzed).

Elemental Analysis of Solid Resid Residues

Sample Sample No.	Original C161-0	Cold Tetralin Washing C161-1	Tetralin Reflux C161-2	Hydroprocessing C161-3
Ultimate, day wt%				
C	82.16	65.01	52.87	44.34
H	5.93	3.21	1.83	1.56
N	0.90	1.21	1.01	0.69
S (total)	1.13	2.67	3.78	5.81
Ash	8.57	24.53	37.94	46.87
O (by diff)	1.31	3.37	2.57	0.82
H/C (atomic)	0.87	0.59	0.42	0.42

KINETICS OF HYDROPROCESSING OF COAL-DERIVED VACUUM RESIDS

SUMMARY AND CONCLUSIONS

1. Resids vary greatly in their reactivity toward hydroprocessing; however, a substantial amount is convertible to low-boiling fuels.
2. The reactivity is related to the type of coal used if the liquefaction is carried out thermally (without catalyst); however, if the liquefaction is done with 3 wt % added molybdenum catalyst, similar results were obtained with the three coals tested.
3. The reactivity appears to be related to the aromaticity (f_a) of the resid, i.e., the higher the aromaticity, the lower the conversion, if the hydroconversion is done thermally. If the hydroconversion is done with 3 wt % catalyst, there appears to be little if any correlation with aromaticity.
4. The resid must be soluble in the recycle solvent for hydroprocessing reactions to occur. There is approximately 10 to 15 wt % of a component in resids, which is not soluble in tetralin and is not convertible by hydroprocessing. This material will build up during recycling unless purged from the system and will reduce the productivity of the liquefaction process.
5. There is a strong dependence of hydroprocessing rate on catalyst concentration. There also is a strong dependence of hydroprocessing rate and conversion on the hydrogen pressure used.

PUBLICATIONS RESULTING FROM SUBCONTRACT DE-AC22-94PC93054

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2. H. Huang, K. Wang, M. T. Klein and W. H. Calkins "A Novel Method for the Determination of the Boiling Range of Liquid Fuels by Thermogravimetric Analysis", ACS Fuel Chem Div Preprints 40 (3) 485-491 (1995).
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4. K. Wang, S. Wang, H. Huang, M. T. Klein and W. H. Calkins "A Novel Smoothing Routine for the Data Processing in Thermogravimetric Analysis" ACS Fuel Chemistry Div Preprints 41 (1) 27-32 (1996).
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KINETICS OF HYDROPROCESSING OF COAL-DERIVED VACUUM RESIDS

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KINETICS OF HYDROPROCESSING OF COAL-DERIVED VACUUM RESIDS

POSSIBLE FUTURE PROGRAM

1. Expand kinetic studies to include the other (13) vacuum resid, which were only hydro-processed under one set of conditions.
2. Run a series of vacuum resid prepared under a range of liquefaction conditions to establish the relationship of resid reactivity and liquefaction.
3. Run hydroconversion of these (or other) coal-derived resid using Wilsonville recycle solvent instead of tetralin.
4. Devise method for determining the source and amount of the "unconvertible" portion of the resid stream, and consider methods of its elimination before recycle.
5. Perform more comprehensive multivariable analysis to detect relationships between resid reactivity and analytical data and process conditions.

Summary of All CONSOL Runs

A. Conditions of Consol Runs

Sample #	Resid(R)	Feed (ton)	T(c) (min)	Cataly	Sulf	(Ppsig)	Gas	Solvent(L)	R T Ratio
C001	A	Wyodak-Anderson Black Thunder	19	15		1500	112	Tetrafin	1:3
C002	A	Wyodak-Anderson Black Thunder	414	15		1500	N2	Tetrafin	1:3
C003	A	Wyodak-Anderson Black Thunder	408	15		1500	112	Tetrafin	1:3
C004	A	Wyodak-Anderson Black Thunder	410	7		1500	N2	Tetrafin	1:3
C005	A	Wyodak-Anderson Black Thunder	409	15		1500	N2	Tetrafin	1:3
C006	A	Wyodak-Anderson Black Thunder	411	15	y	1500	112	Tetrafin	1:3
C007	A	Wyodak-Anderson Black Thunder	408	15	y	1500	N2	Tetrafin	1:3
C008	A	Wyodak-Anderson Black Thunder	406	15	y	1500	N2	Tetrafin	1:3
C009	A	Wyodak-Anderson Black Thunder	408	15	y	1500	112	Tetrafin	1:3
C012	A	Wyodak-Anderson Black Thunder	400	15		1500	N2	Tetrafin	1:3
C013	A	Wyodak-Anderson Black Thunder	400	15		1500	N2	Tetrafin	1:3
C014	A	Wyodak-Anderson Black Thunder	392	15		1500	N2	Tetrafin	1:3
C015	A	Wyodak-Anderson Black Thunder	403	15		1500	112	Tetrafin	1:3
C016	A	Wyodak-Anderson Black Thunder	406	15		1500	N2	Tetrafin	1:3
C017	A	Wyodak-Anderson Black Thunder	409	0.06	y	1500	112	Tetrafin	1:3
C018	A	Wyodak-Anderson Black Thunder	408	1	y	1500	112	Tetrafin	1:3
C019	A	Wyodak-Anderson Black Thunder	412	3	y	1500	112	Tetrafin	1:3
C020	A	Wyodak-Anderson Black Thunder	410	5	y	1500	112	Tetrafin	1:3
C021	A	Wyodak-Anderson Black Thunder	411	10	y	1500	112	Tetrafin	1:3
C022	A	Wyodak-Anderson Black Thunder	408	30	y	1500	112	Tetrafin	1:3
C023	A	Wyodak-Anderson Black Thunder	422	40	y	1500	112	Tetrafin	1:3
C024	A	Wyodak-Anderson Black Thunder	408	60	y	1500	112	Tetrafin	1:3
C025	A	Wyodak-Anderson Black Thunder	419	0.06		1500	112	Tetrafin	1:2
C026	A	Wyodak-Anderson Black Thunder	420	1		1500	112	Tetrafin	1:2
C027	A	Wyodak-Anderson Black Thunder	410	3		1500	112	Tetrafin	1:2
C028	A	Wyodak-Anderson Black Thunder	409	5		1500	112	Tetrafin	1:2
C029	A	Wyodak-Anderson Black Thunder	410	10		1500	112	Tetrafin	1:4
C030	A	Wyodak-Anderson Black Thunder	400	15		1500	112	Tetrafin	1:2
C031	A	Wyodak-Anderson Black Thunder	405	15		1500	112	Tetrafin	1:3
C032	A	Wyodak-Anderson Black Thunder	405	15		1500	112	Tetrafin	1:4
C033	A	Wyodak-Anderson Black Thunder	412	60		1500	112	Tetrafin	1:4
C034	A	Wyodak-Anderson Black Thunder	405	30		1500	112	Tetrafin	1:4
C035	A	Wyodak-Anderson Black Thunder	20					Tetrafin	1:3
C036	A	Wyodak-Anderson Black Thunder	21					THF	1:3
C037	A	Wyodak-Anderson Black Thunder	20					Tetrafin	1:3
C038	A	Wyodak-Anderson Black Thunder	27	15		1500	112	Tetrafin	1:3
C039	A	Wyodak-Anderson Black Thunder	27	15		1500	112	Tetrafin	1:3

Summary of All CONSOL Runs

A. Conditions of Consol Runs										
Sample #	Resid(R)	Feed Coal	T(c) t(min)		Cataly	Sulf	P(psig)	Gas	Solvent(I)	R/T Ratio
C040	A	Wyodak-Anderson Black Thunder	27	15	MN(0.9%)	y	1500	H2	Tetralin	1:3
C041	A	Wyodak-Anderson Black Thunder	432	30	MN(0.9%)	y	1500	H2	Tetralin	1:3
C042	A	Wyodak-Anderson Black Thunder	436	60	MN(0.9%)	y	1500	H2	Tetralin	1:3
C043	I(am)		420	30	MN(0.9%)	y	1500	H2	Tetralin	1:3
C044	I(am)		423	60	MN(0.9%)	y	1500	H2	Tetralin	1:3
C045	I(am)+A		436	30	MN(0.9%)	y	1500	H2	Tetralin	1:3
C046	I(am)+A		435	60	MN(0.9%)	y	1500	H2	Tetralin	1:3
C047	A	Wyodak-Anderson Black Thunder	435	30	MN(0.9%)	y	1500	H2	Tetralin	1:3
C048	A	Wyodak-Anderson Black Thunder	435	30	MN(0.9%)	y	1500	H2	Tetralin	1:3
C049	A	Wyodak-Anderson Black Thunder	436	30	MN(0.9%)	y	1500	H2	Tetralin	1:3
C050	A	Wyodak-Anderson Black Thunder	436	30	MN(0.9%)	y	1500	H2	Tetralin	1:3
C051	A	Wyodak-Anderson Black Thunder	437	30	MN(0.9%)	y	1500	H2	Tetralin	1:3
C052	A	Wyodak-Anderson Black Thunder	437	30			1500	H2	Tetralin	1:3
C053	A	Wyodak-Anderson Black Thunder	436	30			1500	H2	Tetralin	1:3
C054	A	Wyodak-Anderson Black Thunder	436	30			1500	H2	Tetralin	1:3
C055	A	Wyodak-Anderson Black Thunder	437	30			1500	H2	Tetralin	1:3
C056	A	Wyodak-Anderson Black Thunder	436	30			1500	H2	Tetralin	1:3
C057	A	Wyodak-Anderson Black Thunder	400	0.167			1000	H2	Tetralin	1:8
C058	A	Wyodak-Anderson Black Thunder	400	0.33			1000	H2	Tetralin	1:8
C059	A	Wyodak-Anderson Black Thunder	402	0.5			1000	H2	Tetralin	1:8
C060	A	Wyodak-Anderson Black Thunder	406	1			1000	H2	Tetralin	1:8
C061	A	Wyodak-Anderson Black Thunder	410	2			1000	H2	Tetralin	1:8
C062	A	Wyodak-Anderson Black Thunder	414	5			1000	H2	Tetralin	1:8
C063	A	Wyodak-Anderson Black Thunder	394	10			1000	H2	Tetralin	1:8
C064	A	Wyodak-Anderson Black Thunder	407	20			1000	H2	Tetralin	1:8
C065	A	Wyodak-Anderson Black Thunder	390	30			1000	H2	Tetralin	1:8
C066	A	Wyodak-Anderson Black Thunder	393	45			1000	H2	Tetralin	1:8
C068	A	Wyodak-Anderson Black Thunder	418	30	MN(2%)	y	1500	H2	Tetralin	1:3
C069	A	Wyodak-Anderson Black Thunder	433	30	MN(3%)	y	1500	H2	Tetralin	1:3
C071	A	Wyodak-Anderson Black Thunder	407	30	MN(5%)	y	1500	H2	Tetralin	1:3
Sample #	Resid(R)	Feed Coal	T(c) t(min)		Cataly	Sulf.	P(psig)	Gas	Solvent(I)	R/T Ratio
C072	A	Wyodak-Anderson Black Thunder	421	30			1500	H2	Tetralin	1:3
C073	A	Wyodak-Anderson Black Thunder	422	30			1500	H2	Tetralin	1:3
C074	A	Wyodak-Anderson Black Thunder	419	30			1500	H2	Tetralin	1:3
C075	A	Wyodak-Anderson Black Thunder	427	30			1500	H2	Tetralin	1:3
C076	A	Wyodak-Anderson Black Thunder	419	30			1500	H2	Tetralin	1:3

Summary of All CONSOL Runs

Sample #	Resid(R)	A. Conditions of Consol Runs					Sulf. Pipsig)	Gas	Solvent(T)	R:T Ratio
		Feed Coal	T(c) t(min)	Cataly						
C077	A	Wyodak-Anderson Black Thunder	417 30				1500	112	Tetralin	1:3
C078	A	Wyodak-Anderson Black Thunder	415 30				1500	112	Tetralin	1:3
C079	A	Wyodak-Anderson Black Thunder	417 30				1500	112	Tetralin	1:3
C080	A	Wyodak-Anderson Black Thunder	415 30				1500	112	Tetralin	1:3
C081	A	Wyodak-Anderson Black Thunder	413 30	MN(3%)			1500	112	Tetralin	1:3
C082	A	Wyodak-Anderson Black Thunder	413 30	MN(3%)			1500	112	Tetralin	1:3
C083	A	Wyodak-Anderson Black Thunder	410 30	MN(3%)			1500	112	Tetralin	1:3
C084	A	Wyodak-Anderson Black Thunder	400 30				1500	112	Tetralin	1:3
C085	A	Wyodak-Anderson Black Thunder	407 30				1500	112	Tetralin	1:3
C086	A	Wyodak-Anderson Black Thunder	405 30	MN(4%)			1500	112	Tetralin	1:3
C087	A	Wyodak-Anderson Black Thunder	408 30	MN(4%)			1500	112	Tetralin	1:3
C088	A	Wyodak-Anderson Black Thunder	412 30	shell			1500	112	Tetralin	1:3
C089	A	Wyodak-Anderson Black Thunder	408 30	shell			1500	112	Tetralin	1:3
C090	I(Ag)	Wyodak-Anderson Black Thunder	411 30	shell			1500	112	Tetralin	1:3
C091	A	Illinois #6 coal from Algunc	21 30				1500	112	Tetralin	1:3
C092	A	Wyodak-Anderson Black Thunder	21 30	shell			1500	112	Tetralin	1:3
C093	A	Wyodak-Anderson Black Thunder	411 30	shell			1500	112	Tetralin	1:3
C094	A	Wyodak-Anderson Black Thunder	413 60				1500	112	Tetralin	1:3
C095	A	Wyodak-Anderson Black Thunder	412 60	MN(5%)			1500	112	Tetralin	1:3
C096	A	Wyodak-Anderson Black Thunder	425 30				1500	112	Tetralin	1:3
C097	B	Pittsburgh Ireland	421 30				1500	112	Tetralin	1:3
C098	C	Pittsburgh Ireland	422 30				1500	112	Tetralin	1:3
C099	D	Illinois #6 Burning Star #2	426 30				1500	112	Tetralin	1:3
C100	E	Wyodak-Anderson Black Thunder	420 30				1500	112	Tetralin	1:3
C101	F	Wyodak-Anderson Black Thunder	422 30				1500	112	Tetralin	1:3
C102	G	Wyodak-Anderson Black Thunder	422 30				1500	112	Tetralin	1:3
C103	H	Wyodak-Anderson Black Thunder	420 30				1500	112	Tetralin	1:3
C104	I	Illinois #6 Burning Star #2	420 30				1500	112	Tetralin	1:3
C105	J	Pittsburgh Ireland	421 30				1500	112	Tetralin	1:3
C106	K	Wyodak-Anderson Black Thunder	421 30				1500	112	Tetralin	1:3
C107	L	Wyodak-Anderson Black Thunder	418 30				1500	112	Tetralin	1:3
C108	M	Illinois #6 Burning Star #2	418 30				1500	112	Tetralin	1:3
C109	A	Wyodak-Anderson Black Thunder	422 30	MN(2%)			1500	112	Tetralin	1:3
C110	B	Pittsburgh Ireland	417 30	MN(2%)			1500	112	Tetralin	1:3
C111	B	Pittsburgh Ireland	31 10				1500	112	Tetralin	1:3
C112	C	Pittsburgh Ireland	30 10				1500	112	Tetralin	1:3
C113	D	Illinois #6 Burning Star #2	31 10				1500	112	Tetralin	1:3

Summary of All CONSOL Runs

Sample #	Resid(R)	Feed Coal	T(c) (min)	Cataly	Sulf.	P(psig)	Gas	Solvent (l)	R/T Ratio
C114	E	Wyodak-Anderson Black Thunder	22 10			1500	112	Tetralin	1:3
C115	F	Wyodak-Anderson Black Thunder	22 10			1500	112	Tetralin	1:3
C116	G	Wyodak-Anderson Black Thunder	22 10			1500	112	Tetralin	1:3
C117	H	Wyodak-Anderson Black Thunder	22 10			1500	112	Tetralin	1:3
C118	I	Illinois #6 Burning Star #2	22 10			1500	112	Tetralin	1:3
C119	J	Pittsburgh Ireland	22 10			1500	112	Tetralin	1:3
C120	K	Wyodak-Anderson Black Thunder	22 10			1500	112	Tetralin	1:3
C121	L	Wyodak-Anderson Black Thunder	24 10			1500	112	Tetralin	1:3
C122	M	Illinois #6 Burning Star #2	23 10			1500	112	Tetralin	1:3
C123	C	Pittsburgh Ireland	419 30	MN(3%)	y	1500	112	Tetralin	1:3
C124	D	Illinois #6 Burning Star #2	420 30	MN(3%)	y	1500	112	Tetralin	1:3
C125	E	Wyodak-Anderson Black Thunder	421 30	MN(3%)	y	1500	112	Tetralin	1:3
C126	F	Wyodak-Anderson Black Thunder	418 30	MN(3%)	y	1500	112	Tetralin	1:3
C127	G	Wyodak-Anderson Black Thunder	420 30	MN(3%)	y	1500	112	Tetralin	1:3
C128	H	Wyodak-Anderson Black Thunder	419 30	MN(3%)	y	1500	112	Tetralin	1:3
C129	I	Illinois #6 Burning Star #2	420 30	MN(3%)	y	1500	112	Tetralin	1:3
C130	J	Pittsburgh Ireland	420 30	MN(3%)	y	1500	112	Tetralin	1:3
C131	K	Wyodak-Anderson Black Thunder	419 30	MN(3%)	y	1500	112	Tetralin	1:3
C132	L	Wyodak-Anderson Black Thunder	421 30	MN(3%)	y	1500	112	Tetralin	1:3
C133	M	Illinois #6 Burning Star #2	418 30	MN(3%)	y	1500	112	Tetralin	1:3
C134	N	Wyodak-Anderson Black Thunder	423 30			1500		Tetralin	1:3
C135	O	Wyodak-Anderson Black Thunder	422 30			1500	112	Tetralin	1:3
C136	O	Wyodak-Anderson Black Thunder	423 30	MN(3%)	y	1500	112	Tetralin	1:3
C137	N	Wyodak-Anderson Black Thunder	421 30	MN(3%)	y	1500	112	Tetralin	1:3
C138	O	Wyodak-Anderson Black Thunder	21 10			1500	112	Tetralin	1:3
C139	N	Wyodak-Anderson Black Thunder	21 10			1500	112	Tetralin	1:3
C140	C	Pittsburgh Ireland	423 5	MN(3%)	y	1500	112	Tetralin	1:3
C141	C	Pittsburgh Ireland	422 10	MN(3%)	y	1500	112	Tetralin	1:3
C142	H	Wyodak-Anderson Black Thunder	420 5	MN(3%)	y	1500	112	Tetralin	1:3
C143	H	Wyodak-Anderson Black Thunder	421 10	MN(3%)	y	1500	112	Tetralin	1:3
C144	C	Pittsburgh Ireland	436 5	MN(3%)	y	1500	112	Tetralin	1:3
C145	C	Pittsburgh Ireland	435 10	MN(3%)	y	1500	112	Tetralin	1:3
C146	C	Pittsburgh Ireland	435 30	MN(3%)	y	1500	112	Tetralin	1:3
C147	H	Wyodak-Anderson Black Thunder	436 5	MN(3%)	y	1500	112	Tetralin	1:3
C148	H	Wyodak-Anderson Black Thunder	438 10	MN(3%)	y	1500	112	Tetralin	1:3
C149	H	Wyodak-Anderson Black Thunder	436 30	MN(3%)	y	1500	112	Tetralin	1:3
C150	C(p.s)	Pittsburgh Ireland	418 30	MN(3%)	y	1500	112	Tetralin	1:3

Summary of All CONSOL Runs

A. Conditions of Consol Runs										
Sample #	Resid(R)	Feed Coal	T(c)	t(min)	Cataly	Sulf.	P(psig)	Gas	Solvent(T)	R/T Ratio
C151	C(p.l)	Pittsburgh Ireland	421	30			1500	H2		
C152	C(p.l)	Pittsburgh Ireland	419	30	MN(3%)	y	1500	H2		
C153	C(p.l)	Pittsburgh Ireland	421	30	shell		1500	H2		
C154	C	Pittsburgh Ireland	20	30					Tetralin	1:3
C155	C	Pittsburgh Ireland	423	30	MN(1%)	y	1500	H2	Tetralin	1:3
C156	C	Pittsburgh Ireland	421	30	MN(3%)	y	1000	H2	Tetralin	1:3
C157	C	Pittsburgh Ireland	422	30	MN(3%)	y	2000	H2	Tetralin	1:3
C158	C	Pittsburgh Ireland	420	30	MN(2%)	y	1500	H2	Tetralin	1:3
C159	C	Pittsburgh Ireland	419	30	MN(5%)	y	1500	H2	Tetralin	1:3
C160	C	Pittsburgh Ireland	20						Tetralin	
C161	Processed C	Pittsburgh Ireland	418	30	MN(3%)	y	1500	H2	Tetralin	1:3
C162	I	Illinois #6 Burning Star #2	20						Tetralin	
C163	A	Wyodak-Anderson Black Thunder	20						Tetralin	
C164	D	Illinois #6 Burning Star #2	20						Tetralin	
C165	G	Wyodak-Anderson Black Thunder	20						Tetralin	
C166	A(p.s)		423	30	MN(3%)	y	1500	H2	Tetralin	1:3
C167	D(p.s)		422	30	MN(3%)	y	1500	H2	Tetralin	1:3
C168	G(p.s)		422	30	MN(3%)	y	1500	H2	Tetralin	1:3
C169	I(Am)+C		414	30	MN(3%)	y	1500	H2	Tetralin	1:3
C170	I(Am)+H		418	30	MN(3%)	y	1500	H2	Tetralin	1:3
C171	I(Am)+C		418	60	MN(3%)	y	1500	H2	Tetralin	1:3
C172	H	Wyodak-Anderson Black Thunder	20						Tetralin	

Note: Resid number

Resid name

A	258,V-131B
B	259,R-1235
C	259,V-131B
D	261,V-131B
E	262,R-1235
F	262,V-1067
G	262,V-131B
H	260,V-131B
I	261,V-1067
J	259,V-1067
K	260,R-1235
L	260,V-1067
M	261,R-1235
N	HRI,POC-01
O	HRI,POC-02
I(am)	Illinois #6 coal from Amoco
I(am)+A	Illinois #6 coal from Amoco+Resid A
Processed C:	Resid C, washed , extracted with Tetralin
C(p.s):	Solid Resid C,soaked with Tetralin
C(p.l):	Liquid Resid C,soaked with Tetralin
A(p.s):	Resid A,washed,extracted with Tetralin
D(p.s):	Resid D, washed , extracted with Tetralin
G(p.s):	Resid G, washed,extracted with Tetralin
MN:	Sulfided Mo Naphthenate
shell:	Shell 324-Ni/Mo on Al2O3, Amount equal to Resid

R/T Ratio: Resid : Solvent(Tetralin)

sulf.: Methyl disulfide

UD Molecular Modeling in Support of CONSOL's Coal Resid Program

Darin M. Campbell and Michael T. Klein

Analytical Data

- Elemental - C, H, S, N, O
- SARA (P) (I) and Molecular Weights (VPO) - Mole Fractions of Compound Types
- ^1H NMR - Aromatic, Condensed Aromatic, Alkyl Alpha, Cyclic Alpha, Alkyl Beta, Cyclic Beta, Gamma
- Phenolic Oxygen

Coal Resid Molecular Attributes

- Eleven Attributes
 - Paraffin Length
 - Number of Naphthenic Rings
 - Number of Sidechains
 - Length of Sidechains
 - Number of Aromatic Rings
 - Number of Naphthenic Rings on an Aromatic Core
 - Degree of Polymerization
 - Fraction of Heteroatom Cores
 - Fraction of Internal Naphthenics
 - Fraction of Cores with Phenolic Groups
 - Type of Intersheet Linkages

PDF Concept

- Flory (1936) - Modified gamma distribution to fit molecular size distribution of condensation polymers
- Whitson (1983) - Gamma distribution to fit molar and weight distributions of C_{7+} fraction of heavy components of crude
- Libanati (1992) - Log Normal distribution for molecular weight of products from a thermal degradation of an infinite polymer

Distribution	Name	Used to construct fractions:
Paraffin Length	npdis	Paraffins
# of Naphthenic Rings	nrdis	Naphthenics
Naphthenic # of Sidechains	nsdis	Naphthenics
Length of Naphthenic Sidechains	nsldis	Naphthenics
Resin # of Unit Sheets	rdpdis	Aromatics/Resins
Resin # of Aromatic Rings	rardis	Aromatics/Resins
Resin # of Naphthenic Rings	rnrdis	Aromatics/Resins
Resin # of Sidechains	rscdis	Aromatics/Resins
Resin Sidechain Length	rsldis	Aromatics/Resins
Asphaltene # of Unit Sheets	adpdis	Asphaltenes
Asphaltene # of Aromatic Rings	aardis	Asphaltenes
Asphaltene # of Naphthenic Rings	anrdis	Asphaltenes
Asphaltene # of Sidechains	ascdis	Asphaltenes
Asphaltene Sidechain Length	asldis	Asphaltenes
Preasphaltene # of Unit Sheets	pdpdis	Preasphaltenes
Preasphaltene # of Aromatic Rings	aardis	Asphaltenes
Preasphaltene # of Naphthenic Rings	anrdis	Asphaltenes
Preasphaltene # of Sidechains	ascdis	Asphaltenes
Preasphaltene Sidechain Length	asldis	Asphaltenes
Fraction of Aromatic Cores w/ 1 Ring	flrar	Resins, Asphaltenes, Preasphaltenes
Fraction of Aromatic Cores w/ Internal Naphthenics	flnrings	Resins, Asphaltenes, Preasphaltenes
# of Phenolic Oxygens per unit sheet	flrphh	Resins, Asphaltenes, Preasphaltenes
Intersheet Connections		
Fraction of Oxygen Connections	fiso	Resins, Asphaltenes, Preasphaltenes
Fraction of Sulfur Connections	fiss	Resins, Asphaltenes, Preasphaltenes
Fraction of Methylene Connections	fism	Resins, Asphaltenes, Preasphaltenes
Fraction of Biphenyl Connections	fisb	Resins, Asphaltenes, Preasphaltenes
Heteroatomic Rings		
Fraction of Oxygen Rings	frorings	Resins, Asphaltenes, Preasphaltenes
Fraction of Sulfur Rings	frsings	Resins, Asphaltenes, Preasphaltenes
Fraction of Nitrogen Rings (5 and 6 members in a 2 to 1 ratio)	frnrings	Resins, Asphaltenes, Preasphaltenes
Fraction of no Heteroatomic Rings	frhrings	Resins, Asphaltenes, Preasphaltenes

Attribute PDF's

- Attribute PDF's based on boiling point distribution

- Gamma and exponential distribution chosen for coal resid attribute pdf's

Stochastic Construction of a Naphthenic Molecule

Resultant Structure

Coal Resid Construction Algorithm

Conditional Probability

- Maximum number of rings per aromatic core
- Maximum number of unit sheets per molecule
- Only an aromatic core with at least three rings can have an internal naphthenic
- Naphthenic molecules with three or fewer rings have a minimum number of sidechains
- Resin/Aromatic molecules with only one unit sheet have a minimum number of rings

Optimization of the PDF Parameters

- Objective function

$$\chi^2 = \left(\frac{MW_{\text{exp}} - MW_{\text{pred}}}{0.1 * MW_{\text{exp}}} \right)^2 + \left(\frac{HWT_{\text{exp}} - HWT_{\text{pred}}}{0.16} \right)^2 + \left(\frac{CWT_{\text{exp}} - CWT_{\text{pred}}}{0.64} \right)^2 +$$
$$\left(\frac{SWT_{\text{exp}} - SWT_{\text{pred}}}{0.10} \right)^2 + \left(\frac{NWT_{\text{exp}} - NWT_{\text{pred}}}{0.11} \right)^2 + \left(\frac{OWT_{\text{exp}} - OWT_{\text{pred}}}{1.5} \right)^2 +$$
$$\sum_{i=1}^{n\text{fracs}} \left(\frac{1\text{HNMR}_{\text{exp}} - 1\text{HNMR}_{\text{pred}}}{0.02} \right)^2 + \sum_{i=1}^{n\text{fracs}} \left(\frac{SARA_{\text{exp}} - SARA_{\text{pred}}}{0.03} \right)^2$$

- Find global minimum by simulated annealing
- Other terms can be added if additional analytical information available

Optimal Sample Size

(Trauth, et al., 1993)

	Dist Type	Resid A	Resid B	Resid C
Saturates				
Paraffin Length (present)	2	25.0(2.0)	25.0(2.0)	25.0(2.0)
# of Nap. Rings	2	2.91(3.23)	3.23(2.69)	3.68(0.90)
# of Sidechains	1	5.83	0.89	5.16
Length of Sidechains	1	3.84	5.59	5.08
Resins/Aromatics				
Degree of Polymerization	2	4.37(3.24)	3.66(2.76)	4.11(1.11)
# of Ar. Rings (main 2-methyl)	1	6.29	7.57	7.01
# of Nap. Rings	1	0.92	0.83	0.41
# of Sidechains	1	0.82	1.21	0.80
Length of Sidechains	1	3.15	2.23	1.16
Asphaltenes				
Degree of Polymerization	2	6.71(1.13)	2.37(1.09)	3.21(1.19)
# of Ar. Rings	1	7.11	4.57	7.56
# of Nap. Rings	1	0.61	1.63	2.73
# of Sidechains	1	0.79	1.67	3.00
Length of Sidechains	1	1.35	1.69	1.98
Preasphaltenes				
Degree of Polymerization	2	3.04(3.08)	7.66(1.24)	2.39(3.77)
# of Ar. Rings	1	8.27	3.81	7.64
# of Nap. Rings	1	1.86	0.37	0.71
# of Sidechains	1	3.68	1.21	3.85
Length of Sidechains	1	2.79	4.08	4.01
InterSheet Linkages				
Fraction Oxygen		0.005	0.098	0.085
Fraction Sulfur		0.040	0.079	0.065
Fraction Methylene		0.043	0.171	0.010
Fraction Biphenyl		0.912	0.652	0.839
Heteroatom Cores				
Fraction Oxygen		0.315	0.061	0.029
Fraction Sulfur		0.105	0.056	0.031
Fraction Nitrogen		0.161	0.184	0.159
Fraction Aromatic Hydrocarbon		0.420	0.700	0.781
Fraction Internal Naphthenic		0.646	0.519	0.853
Fraction of Cores with Phenolic OH		0.154	0.213	0.150
Fraction of Cores with 1 aromatic ring		0.438	0.247	0.354
Fraction of Saturates that are paraffinic		0.1	0.1	0.1

* 2 - γ
 1 - α } distributions
 Page 1

	Dist Type	Resid D	Resid E	Resid F
Saturates				
Paraffin Length	2	25.0(2.0)	25.0(2.0)	25.0(2.0)
# of Nap. Rings	2	3.30(1.23)	3.16(0.62)	3.15(0.52)
# of Sidechains	1	1.25	4.51	4.36
Length of Sidechains	1	3.10	6.32	5.66
Resins/Aromatics				
Degree of Polymerization	2	1.40(1.41)	1.85(2.69)	2.78(2.20)
# of Ar. Rings	1	7.17	7.36	5.81
# of Nap. Rings	1	0.65	1.10	1.11
# of Sidechains	1	0.79	1.51	1.38
Length of Sidechains	1	3.57	3.47	2.19
Asphaltenes				
Degree of Polymerization	2	7.29(3.08)	7.27(3.26)	5.51(1.35)
# of Ar. Rings	1	6.17	7.01	7.04
# of Nap. Rings	1	1.52	1.13	0.61
# of Sidechains	1	2.00	0.71	0.64
Length of Sidechains	1	3.02	1.88	1.57
Preasphaltenes				
Degree of Polymerization	2	6.60(1.81)	5.57(3.32)	6.84(1.37)
# of Ar. Rings	1	8.91	6.72	8.25
# of Nap. Rings	1	1.18	1.32	1.14
# of Sidechains	1	0.33	4.19	1.08
Length of Sidechains	1	1.33	1.91	4.20
InterSheet Linkages				
Fraction Oxygen		0.010	0.115	0.188
Fraction Sulfur		0.154	0.039	0.396
Fraction Methylene		0.277	0.087	0.139
Fraction Biphenyl		0.560	0.759	0.276
Heteroatom Cores				
Fraction Oxygen		0.246	0.643	0.229
Fraction Sulfur		0.072	0.076	0.040
Fraction Nitrogen		0.168	0.184	0.161
Fraction Aromatic Hydrocarbon		0.514	0.097	0.569
Fraction Internal Naphthenic		0.957	0.897	0.904
Fraction of Cores with Phenolic OH		0.176	0.212	0.302
Fraction of Cores with 1 aromatic ring		0.385	0.251	0.432
Fraction of Saturates that are paraffinic		0.1	0.1	0.1

	Dist Type	Resid M
Saturates		
Paraffin Length	2	25.0(2.0)
# of Nap. Rings	2	3.07(0.58)
# of Sidechains	1	1.29
Length of Sidechains	1	3.75
Resins/Aromatics		
Degree of Polymerization	2	2.60(1.83)
# of Ar. Rings	1	7.29
# of Nap. Rings	1	1.11
# of Sidechains	1	0.45
Length of Sidechains	1	2.01
Asphaltenes		
Degree of Polymerization	2	4.56(3.97)
# of Ar. Rings	1	5.10
# of Nap. Rings	1	0.94
# of Sidechains	1	1.73
Length of Sidechains	1	2.11
Preasphaltenes		
Degree of Polymerization	2	8.70(2.76)
# of Ar. Rings	1	8.87
# of Nap. Rings	1	0.76
# of Sidechains	1	1.88
Length of Sidechains	1	3.61
InterSheet Linkages		
Fraction Oxygen		0.009
Fraction Sulfur		0.012
Fraction Methylene		0.043
Fraction Biphenyl		0.937
Heteroatom Cores		
Fraction Oxygen		0.283
Fraction Sulfur		0.106
Fraction Nitrogen		0.203
Fraction Aromatic Hydrocarbon		0.409
Fraction Internal Naphthenic		0.975
Fraction of Cores with Phenolic OH		0.206
Fraction of Cores with 1 aromatic ring		0.353
Fraction of Saturates that are paraffinic		0.1
		0.68397
		0.25533
		0.48918
		0.98654
		2.41502

	Resid A Exp.	Pred.	Chisq	Resid B Exp.	Pred.	Chisq	Resid C Exp.	Pred.	Chisq
Molecular Weight	488	549	1.61	543	587	0.63	474	543	2.12
Elemental Wt %									
Hydrogen	5.61	6.26	16.37	6.18	6.72	11.40	6.50	7.00	9.58
Carbon	88.30	86.76	5.79	90.00	88.45	5.86	90.92	89.26	6.73
Sulfur	1.74	1.76	0.06	1.50	1.53	0.07	1.24	1.18	0.41
Nitrogen	1.19	1.15	0.10	1.15	1.11	0.16	1.04	1.01	0.10
Oxygen	3.16	4.06	0.36	1.18	2.20	0.46	0.30	1.56	0.71
SARA Wt %									
Saturates	2.2	2.6	0.35	2.3	2.0	0.03	2.7	3.2	0.02
Resins	49.6	51.9		49.1	48.6		59.5	59.6	
Asphaltenes	41.0	38.3		33.5	34.2		27.7	27.9	
Preasphaltenes	7.3	7.1		15.1	15.2		10.1	9.4	
NMW Fractions									
Aromatic	7.6	8.6	0.24	2.6	3.8	0.39	5.4	7.0	0.61
Condensed Aromatic	31.3	35.8	5.17	30.7	34.9	4.37	26.1	31.6	7.50
Alkyl Alpha	9.5	8.7	0.16	10.2	12.4	1.17	9.4	11.0	0.63
Cyclic Alpha	18.8	17.4	0.47	20.9	18.1	1.91	18.9	17.9	0.27
Alkyl Beta	11.9	9.5	1.49	13.4	9.7	3.49	14.6	11.1	3.08
Cyclic Beta	12.9	13.5	0.09	13.8	14.1	0.02	14.8	12.5	1.31
Gamma	8.1	6.5	0.65	8.4	7.0	0.47	10.8	9.0	0.80
Phenolic OH (meq/g)	0.80	0.79	0.14	0.92	0.91	0.07	0.69	0.68	0.49
Objective Function			33.05			30.51			34.35

Sheet1

W201 V13B W202 R1235 W202 V1067

	Resid D Exp.	Pred.	Chlsq	Resid E Exp.	Pred.	Chlsq	Resid F Exp.	Pred.	Chlsq
Molecular Weight	394	471	3.86	612	617	0.01	453	504	1.31
Elemental Wt %									
Hydrogen	6.57	7.08	10.11	6.59	6.98	5.85	6.75	7.33	13.06
Carbon	88.39	87.30	2.91	85.34	84.89	0.50	86.03	84.81	3.65
Sulfur	1.05	1.09	0.12	1.74	1.75	0.01	1.94	1.92	0.06
Nitrogen	1.05	1.02	0.08	0.99	0.99	0.00	0.93	0.95	0.02
Oxygen	2.94	3.52	0.15	5.34	5.40	0.00	4.35	5.00	0.19
SARA Wt %									
Saturates	6.3	5.6	0.43	6.9	6.8	0.00	10.9	13.2	0.72
Resins	56.0	59.3		49.4	49.2		49.1	51.4	
Asphaltenes	28.8	28.0		32.8	32.9		30.7	26.9	
Preasphaltenes	8.9	7.1		10.9	11.2		9.3	8.5	
NMW Fractions									
Aromatic	3.8	5.2	0.48	3.7	1.9	0.77	3.9	5.7	0.81
Condensed Aromatic	25.4	30.1	5.44	22.3	25.9	3.28	20.4	24.5	4.21
Alkyl Alpha	9.6	8.3	0.45	9.3	9.7	0.04	9.0	7.8	0.36
Cyclic Alpha	19.7	18.2	0.54	19.2	17.5	0.76	18.6	16.8	0.84
Alkyl Beta	16.8	14.2	1.65	20.9	19.0	0.86	21.9	19.7	1.23
Cyclic Beta	15.3	15.4	0.00	14.6	15.7	0.30	15.3	15.8	0.05
Gamma	9.3	8.7	0.10	10.0	10.2	0.01	10.8	9.8	0.26
Phenolic OH (meq/g)	0.78	0.77	0.24	0.82	0.82	0.04	1.25	1.26	0.26
Objective Function			26.57			12.44			27.01

Sheet1

W202 V13B W202 R1235 W202 V1067

	Resid G Exp.	Pred.	Chlsq	Resid H Exp.	Pred.	Chlsq	Resid I Exp.	Pred.	Chlsq
Molecular Weight	543	575	0.35	515	536	0.17	478	557	2.73
Elemental Wt %									
Hydrogen	6.77	7.21	7.66	6.35	6.75	6.29	6.53	7.08	11.62
Carbon	85.84	85.18	1.07	87.43	86.75	1.12	88.14	87.24	1.97
Sulfur	1.73	1.69	0.16	1.53	1.55	0.06	1.54	1.44	0.99
Nitrogen	0.93	0.94	0.00	1.10	1.08	0.04	1.11	1.07	0.12
Oxygen	4.73	4.98	0.03	3.59	3.87	0.03	2.68	3.17	0.11
SARA Wt %									
Saturates	9.0	10.6	0.21	6.3	6.8	0.18	3.6	2.5	2.13
Resins	47.8	45.9		51.8	49.7		57.9	60.9	
Asphaltenes	34.6	35.4		33.3	34.8		28.2	21.5	
Preasphaltenes	8.7	8.2		8.7	8.6		10.3	15.0	
NMW Fractions									
Aromatic	3.7	4.3	0.08	3.8	4.8	0.23	4.5	5.1	0.08
Condensed Aromatic	22.2	24.9	1.81	29.5	32.0	1.60	25.9	28.9	2.24
Alkyl Alpha	9.4	8.9	0.06	4.5	4.6	0.00	9.6	9.6	0.00
Cyclic Alpha	18.1	16.4	0.72	21.5	20.1	0.49	19.9	18.7	0.39
Alkyl Beta	21.3	20.9	0.05	17.0	15.6	0.48	16.0	15.0	0.25
Cyclic Beta	15.2	14.6	0.08	14.3	15.2	0.18	14.7	14.8	0.00
Gamma	10.1	10.0	0.00	9.3	7.7	0.61	9.3	8.0	0.40
Phenolic OH (meq/g)	0.85	0.84	0.52	0.69	0.68	0.24	0.92	0.91	0.09
Objective Function			12.80			11.73			23.12

Sheet 1

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W 200 R1235

W 200 V1067

	Resid J Exp.	Pred.	Chisq	Resid K Exp.	Pred.	Chisq	Resid L Exp.	Pred.	Chisq
Molecular Weight	521	561	0.60	446	524	3.03	540	564	0.20
Elemental Wt %									
Hydrogen	6.38	7.03	16.38	5.89	6.73	27.33	6.25	6.64	5.80
Carbon	90.10	88.91	3.44	86.81	84.59	9.96	86.77	85.99	1.50
Sulfur	1.49	1.61	1.43	1.82	1.79	0.09	1.95	1.94	0.00
Nitrogen	1.05	1.10	0.19	1.09	1.13	0.14	1.10	1.12	0.04
Oxygen	0.98	1.35	0.06	4.59	5.76	0.61	3.93	4.31	0.07
SARA Wt %									
Saturates	7.8	7.1	0.79	9.1	8.5	0.35	4.2	4.0	0.10
Resins	42.8	47.3		50.9	51.6		58.4	57.9	
Asphaltenes	38.6	37.1		26.6	28.9		28.0	27.1	
Preasphaltenes	10.8	8.4		13.4	10.9		9.4	11.0	
NMW Fractions									
Aromatic	3.8	6.2	1.48	4.3	6.5	1.16	6.8	7.1	0.02
Condensed Aromatic	27.8	31.0	2.54	20.3	28.1	15.03	27.2	30.8	3.16
Alkyl Alpha	9.6	9.8	0.01	9.4	8.1	0.44	8.8	8.3	0.07
Cyclic Alpha	21.2	17.3	3.77	17.2	14.9	1.32	18.3	17.3	0.24
Alkyl Beta	13.4	12.0	0.49	21.2	16.8	4.80	16.6	15.0	0.64
Cyclic Beta	15.5	16.8	0.43	15.3	15.5	0.01	13.6	14.0	0.04
Gamma	8.7	6.9	0.81	12.3	10.2	1.12	8.7	7.6	0.33
Phenolic OH (meq/g)	0.70	0.69	0.28	0.95	0.95	0.02	0.69	0.70	0.46
Objective Function			32.71			65.41			12.65

W 200 R1235

	Resid M Exp.	Pred.	Chisq
Molecular Weight	445	490	1.05
Elemental Wt %			
Hydrogen	6.59	7.12	11.00
Carbon	87.44	86.78	1.05
Sulfur	1.57	1.51	0.36
Nitrogen	1.19	1.21	0.05
Oxygen	3.21	3.37	0.01
SARA Wt %			
Saturates	10.9	9.0	0.54
Resins	45.4	45.5	
Asphaltenes	31.5	29.7	
Preasphaltenes	12.2	15.7	
NMW Fractions			
Aromatic	4.9	4.3	0.10
Condensed Aromatic	24.5	27.8	2.70
Alkyl Alpha	9.6	8.3	0.39
Cyclic Alpha	21.1	18.5	1.75
Alkyl Beta	15.6	14.6	0.23
Cyclic Beta	15.2	17.6	1.48
Gamma	9.2	8.9	0.03
Phenolic OH (meq/g)	0.88	0.88	0.06
Objective Function			20.81

Results

- Hydrogen content is overpredicted
- Carbon content is underpredicted
- Condensed aromatic hydrogen is overpredicted
- Generally all other properties fall within one experimental standard deviation of the measured value

Discussion

- ^1H NMR data do not allow for such small hydrogen fractions
- ^1H NMR is on the THF soluble portion and elemental is on the complete resid (except ash)
- Only the THF soluble fraction is modeled (insoluble fraction is considered to be unreactive) - THF soluble fraction should exhibit a higher H/C ratio than the full resid

Structural Attribute Reaction Model

- React pdf attributes instead of individual molecules
 - An "N" dimensional model becomes "N" 1 dimensional kinetics model
 - CPU demands low
 - Monte Carlo structure building program provides molecular products

Structural Attribute Reaction Model

- Calculate concentrations from PDF's
 - paraffinic C₈ sidechains^(sc) on naphthenic:
 $y(C_8_SC) = \text{Naphthenic_mf} * \text{Number_SC} * \text{fraction_length8}$ *mf = mole fraction*
- React paraffins, sidechains, heteroatomic rings, internal naphthenics, and intersheet linkages

Current Reaction Rules

- Paraffins crack at middle of chain
- Sidechains can crack at ring, alpha to ring, beta to ring or at middle of chain
- Sulfur can be removed from bridges and rings to form H_2S
- Nitrogen can be removed from five membered rings to form NH_3
- Oxygen can be removed from bridges and rings to form H_2O
- Methane can be removed from internal naphthenics
- Methylene and biphenyl bridges can react

Rate Constants

- Paraffin rate constants related to carbon number
- Sidechain rate constants related to carbon number
- Reaction of intersheet linkages related to size of molecules (number of unit sheets)
- Reaction of heteroatom rings related to number of rings on the core
- Rate constants to be optimized on highest and
* lowest conversion feeds and an intermediate feed

Regenerate PDF's

- Calculate PDF's from concentration of reactive attributes
- Build a representative sample of molecules to obtain product distributions
- Use product distributions to obtain product properties

Status

- Model is coded
- Debugging and fine-tuning is underway
- Need to optimize rate constants to selected resids