

- (4) To explore ZSM-5 zeolite or MFI molecular sieves coating (on alumina, glass or metal support) catalyst to improve mass transfer characteristic and to maximize the reaction selectivity.

Task 4. Evaluation of Coal-based Fuel Oil Products

In this task, heavy fuel oils produced during the production of jet fuel will be analyzed, their atomization characteristics determined, and their combustion performance and emissions evaluated when fired in a natural gas/fuel oil designed watertube boiler. The objective of this task is to determine the effect co-processing on fuel oil emissions. The work will be performed in three subtasks.

Subtask 4.1 Fuel Analysis

In this subtask, the fuel oil produced by co-processing petroleum with coal will undergo a series of analysis. The analyses will be performed to: 1) ensure that the samples meet standardized fuel oil specifications; 2) determine the quantity of trace elements in the fuel oil; and 3) classify the fuel oil per established specifications. Testing will include evaluation of API gravity, viscosity, elemental composition, and heating value of the fuel. Results from the fuel oils will be compared to No. 6 fuel oil (Bunker C oil).

No work was performed in this subtask during this reporting period. The No. 6 comparison fuel oil will be analyzed during the next reporting period. In addition, test fuels will also be analyzed during the next reporting period.

Subtask 4.2 Fuel Atomization

In the subtask, the fuel oil will undergo atomization tests at the conditions (i.e., temperature and atomization pressures) they will be tested in the watertube boiler. A commercial heavy fuel oil will undergo similar atomization tests for comparison.

No work was performed in this subtask during this reporting period. Atomization tests will be performed using the No. 6 comparison fuel oil during the next reporting period. In addition, test fuels will also be analyzed during the next reporting period.

Subtask 4.3 Watertube Boiler Combustion Tests

In this subtask, combustion tests will be performed firing the commercial heavy fuel oil and test fuels in Penn States watertube boiler. During the tests, gaseous emissions (CO, SO₂, NO_x, CO₂, and O₂) will be monitored using a continuous emissions monitoring system per EPA protocol, soot formation will be measured using EPA Method 5 stack sampling, trace elements and mercury (both total and speciated) emissions will be measured using a combined EPA Method 29/Ontario-Hydro sampling method, boiler efficiencies will be determined, and flame structure and intensity will be recorded using an in-furnace camera.

Two activities were performed during this reporting period. The high-temperature in-furnace camera was procured and preliminary shakedown testing performed. The camera system, which consists of a portable camera with straight ahead and right-angle views, compressed air cooling system, remote control module, digital video recorder, monitor, and portable cart, is shown in **Figure 13**.



Figure 13. High-Temperature In-Furnace Camera System

The second activity involved preparing the research boiler for the testing. The boiler is used for a variety of testing and it has been reconfigured for the fuel oil testing. In addition, minor modifications/repairs are underway for the fuel oil testing. These will be completed during the next reporting period and testing of the No. 6 comparison fuel will be performed. Three to six tests will be performed to generate statistically representative emissions data. Tests will also be performed on the fuel oils when they become available.

Task 5. Pitch and Coke Material

Many items that we take for granted have some relation to carbon, including aluminum based products where anode carbon is used to reduce the aluminum ore, steel from arc-furnaces using graphite electrodes, and even electric contacts on the key-boards

(50). However, the carbon we use is increasingly dependent on the availability of petroleum-derived streams or other foreign sources (51). The decrease in domestic produced oil and the subsequent reliance on imported crude oil may have a serious impact on the future of carbon products and related materials in the US, since most carbon products are typically based on petroleum coke (52). Further, petroleum-derived carbon is also marred by increasing hetero-atom, especially sulfur, and heavy-metal content, and a paradigm shift in the petroleum industry of moving away from producing coke by increasing the use of hydro-cracking and hydro-treatment (53). Obviously, the introduction of coal-derived carbon precursors from co-coking, including carbon binders (pitch) and filler material (coke) can reduce the dependence of petroleum feedstocks for carbon materials.

Subtask 5.1: Sample Procurement and Preparation

Decant oil

A heavy petroleum stream, decant oil from United Refining, will be used for the co-coking experiments. Several drums of decant oil were obtained during this reporting period and shipped to PARC and Penn State.

Coal

During this report period an evaluation of coal mining/cleaning plant facilities in Pennsylvania was undertaken in an attempt to locate coals of high thermoplasticity, low ash yield (either natural or by advanced cleaning technology), low organic inert content and reasonably high production. Most raw coal has a fairly high ash yield and may be difficult to

clean even with advance cleaning technology. In previous investigations it was determined that further processing of the coal fraction subjected to froth flotation can lower ash yield and maintain thermoplasticity.

Coal sample procurement was conducted on January 21, 2004 at Mine No 84/Eighty Four Mining owned by CONSOL Energy Inc. in Washington Co., PA. Mine No. 84 is an underground mine producing about 4.2 million short tons annually of a high volatile Pittsburgh seam and is ranked number 56 in U.S. among coal producers. The plant is equipped with a state-of-the-art coal cleaning facility and was chosen due to the commercial potential of the different coal-cleaning streams for co-coking.

Arrangements were made for a three-member Penn State sampling team to collect a bulk coal sample and a sample from the froth flotation cells of the cleaning plant during a shift of operation that coal was being loaded for shipment on January 21, 2004. During our discussion with mine and cleaning plant personnel it was learned that a freeze-prevention agent was being applied to a portion of the coal. To avoid sampling coal containing this material we were directed to a belt drop area of 2 x 0 inch size coal coming from the cleaning plant and being placed on the belt containing coal with the additive applied. It was at this access point that cross-belt cuts of coal were collected over a three hour period to fill four 30-gallon steel drums (i.e., approximately 800 lbs). During this time two members of the team were sampling the two banks of four froth flotation cells. The froth effluent was collected across the full length of each cell and place in it own 10-gallon plastic drum. During the three hours of sampling eight drums

were filled from the froth cells, eventually to be combined into one froth flotation cell sample.

The stream of highest interest was the froth flotation fraction. There are several benefits using this fraction for co-coking, including:

- (i) no need for further grinding of coal prior to mixing with heavy oil residue;
- (ii) it is likely that the highly thermoplastic vitrinite macerals will be concentrated in the light fines from froth flotation thereby increasing the liquid yield during co-coking and improve the properties of the resulting coke; and
- (iii) greater possibility for further beneficiation of coal fines towards low ash co-coking coke.

The less than 2 inch clean coal fraction was procured as backup material.

Figure 14 shows the froth flotation setup of the plant and the corresponding ten samples taken. During the sampling operation the flotation cell was being operated with 96 cc/min of Freedom Industries, Inc. TF-944 froth agent (proprietary combination of alcohols and carboxylates) and 504 cc/min of diesel fuel as a collector agent. The froth generator to the left injected the froth into the middle of the left side of the froth cell. The froth was decanted off in eight chambers and one sample was taken from the entire side of each chambers using a quart size bucket. The samples were numbered 1 through 8 (Figure 1). An equal number of buckets was taken from each chamber and loaded into 20 gallons drums. Chamber 1 and 5, corresponding to Sample 1 and 5, contained the greatest amount of liquid while chamber 4 and 8 had the lowest amount of liquid and

virtually consisted of froth. Correspondingly, the volume of sample was decreasing according to the arrows in **Figure 14**. In addition, two composit samples were generated where Sample 9 contained about 14 buckets of each of the Sample 1 through 4 and Sample 10 about 14 buckets of Sample 5 through 8.

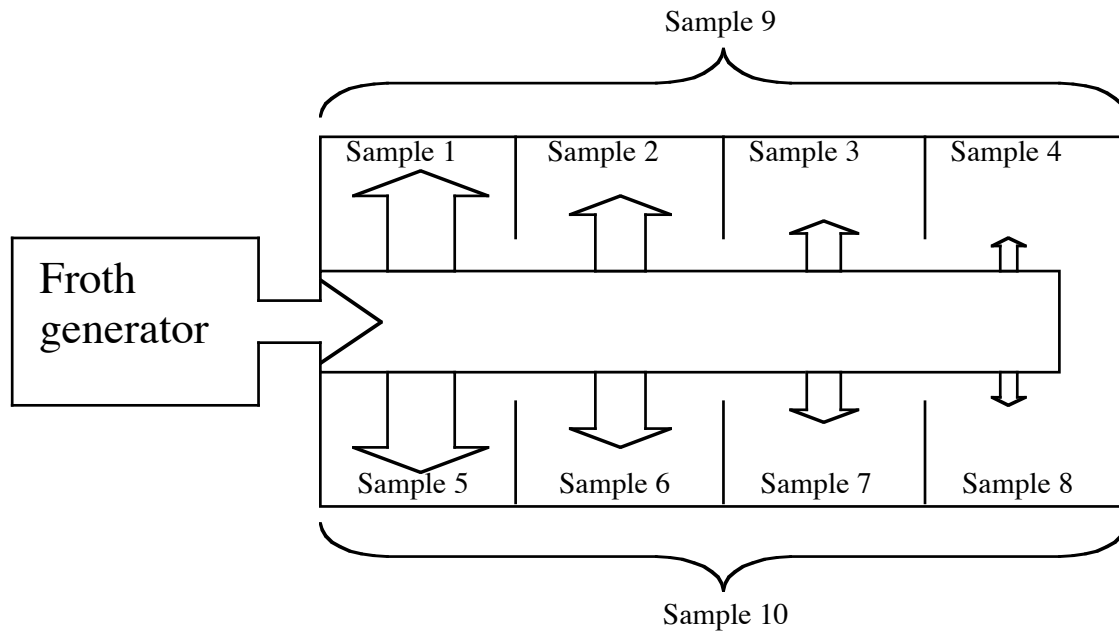
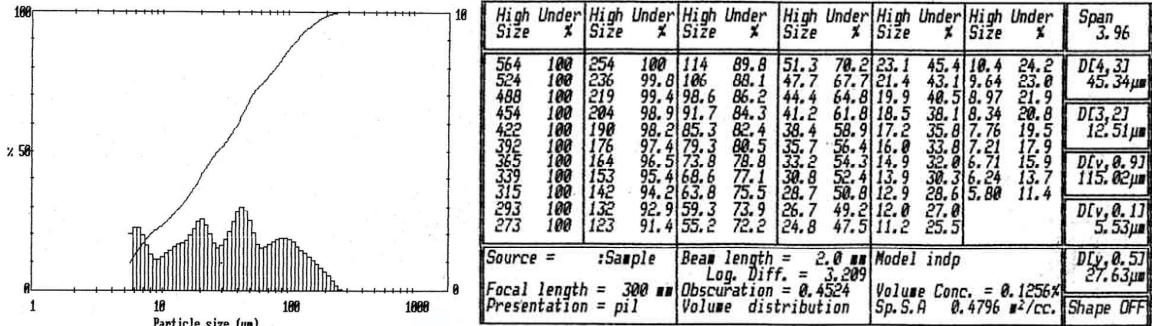


Figure 14. Froth flotation setup of the plant and the corresponding ten samples taken.

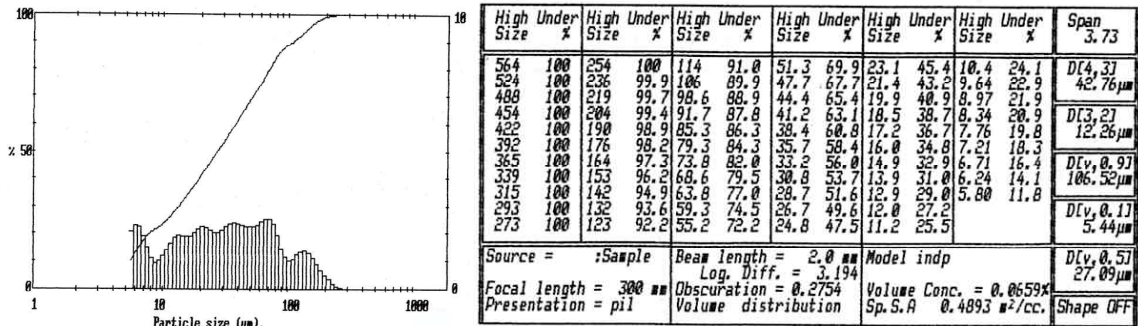
Small sub-samples of each drum have been removed for preliminary evaluation of solids content, proximate analysis, ultimate analysis, optical microscopy (**Table 12**) and particle size analysis.

Figures 15 through 24 compares the particle size distribution of Sample 1 through 10. Although there are some differences in the individual particle distributions between the different chambers, the overall particle size distribution seems to be similar for all the chambers. Indeed, this can be seen for Sample 9 and 10 (**Figures 22 and 23**,

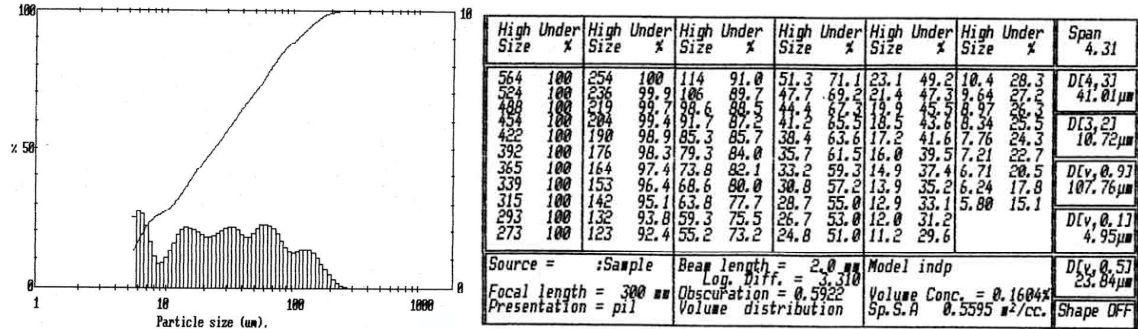
respectively) where nearly identical distributions are obtained from the two composite samples (see Figure 14).



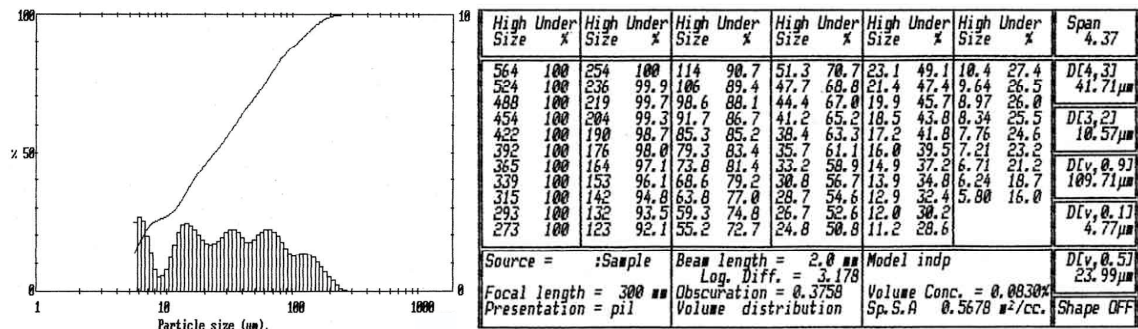
Figures 15. Particle size distribution of Sample 1.



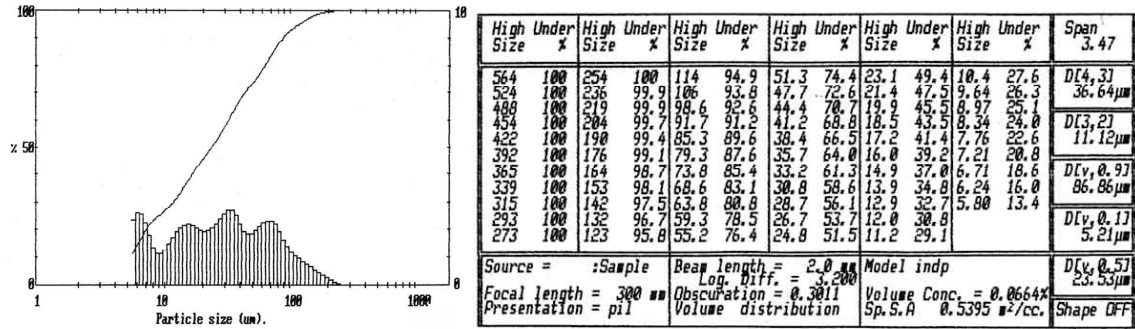
Figures 16. Particle size distribution of Sample 2.



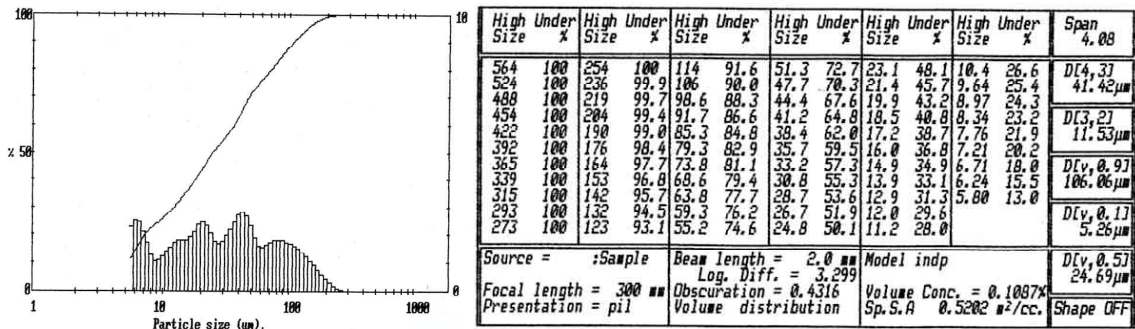
Figures 17. Particle size distribution of Sample 3.



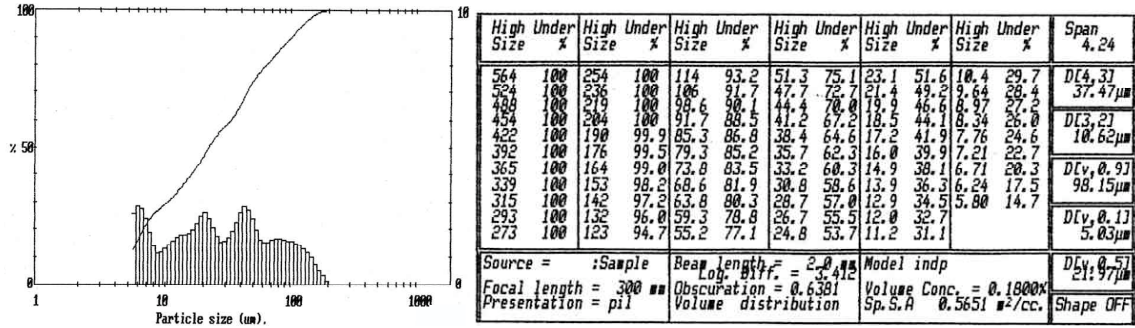
Figures 18. Particle size distribution of Sample 4.



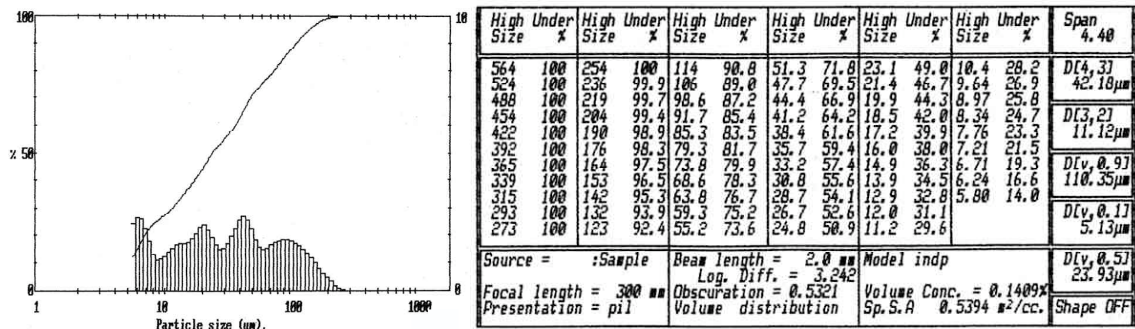
Figures 19. Particle size distribution of Sample 5.



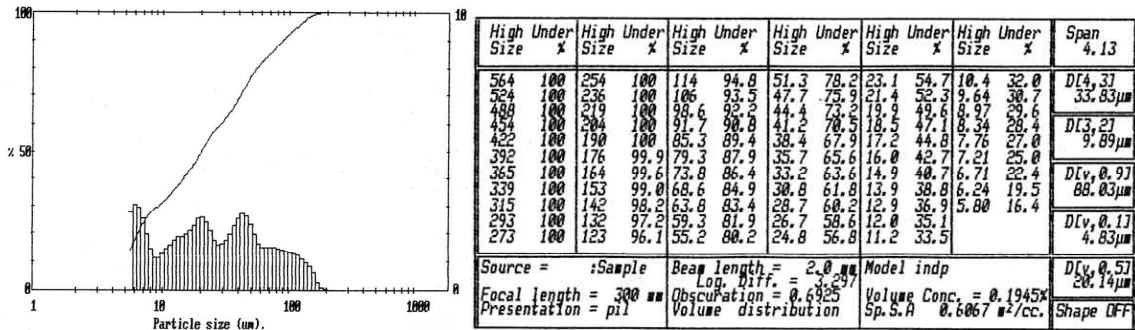
Figures 20. Particle size distribution of Sample 6.



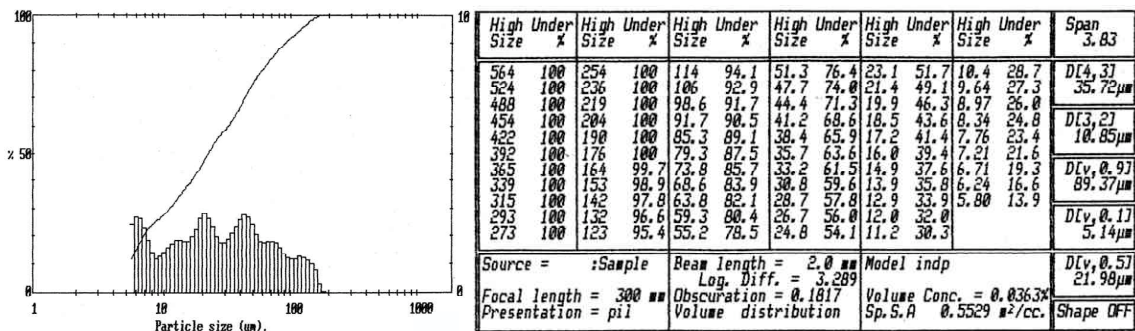
Figures 21. Particle size distribution of Sample 7.



Figures 22. Particle size distribution of Sample 8.



Figures 23. Particle size distribution of Sample 9.



Figures 24. Particle size distribution of Sample 10.

Figures 15 through 24 indicate that the froth section has no particle size higher than 250 mm, about 90% is below 110µm, 50% is below 70µm and 10% is below 25µm. This particle size distribution indicates that the fraction can be a good starting point for co-coking. As shown in Table 12, ash yield of the froth flotation samples are rather high (< 17%) which suggest that secondary cleaning procedures may be necessary.

Subtask 5.2: Examine the Resid from Fractionation of the Deeply-Hydrotreated RCO/LCO as a Pitch Material

Supplies and materials were purchased to start to examine the resid from fractionation of the deeply-hydrotreated RCO/LCO as a pitch material following activity in Subtask 5.3.

Subtask 5.3: Co-Coking of Coal and Heavy Petroleum Stream

Initial set-up for the co-coking of coal and heavy petroleum stream were checked and verified. Testes are scheduled to commence in next reporting period.

Subtask 5.4: Analysis of Co-Coking Coke

Analysis of co-coking coke will be performed following the work conducted in Subtask 5.3.

Subtask 5.5: Distillation And Analysis Of Co-Coking Binder Pitch

Supplies and materials were purchased to start distillation and analysis of co-coking binder pitch following activity in Subtask 5.3.

Subtask 5.6: Manufacture And Testing Of Carbon Artifacts

Laboratory setup and materials for manufacture and testing of carbon artifacts was prepared during the reporting period.

Sample Id.	Sample Type Location	Volume Collected (Liter)	% Solids (As Recd.)	% Moist. Sample (Dried)	% Ash (Dry) Coal	% V.M. (Dry)	% F. C. (Dry)	Carbon (Dry)	Hydrogen (Dry)	Nitrogen (Dry)	Sulfur (Dry)	Oxygen (Dry)
01	Froth Effluent 1	36.0	14.18 ± 0.19	0.89 ± 0.06	13.53 ± 0.06	30.83 ± 0.35	55.64	73.20 ± 0.07	4.68 ± 0.09	1.35 ± 0.02	1.87 ± 0.01	5.37
02	Froth Effluent 2	28.3	15.58 ± 0.28	0.91 ± 0.05	12.50 ± 0.01	30.88 ± 0.49	56.62	74.15 ± 0.29	4.69 ± 0.13	1.35 ± 0.05	1.90 ± 0.01	5.40
03	Froth Effluent 3	23.7	13.86 ± 0.08	0.90 ± 0.04	13.86 ± 0.18	30.93 ± 0.50	55.21	72.26 ± 0.10	4.50 ± 0.16	1.30 ± 0.00	2.12 ± 0.01	5.96
04	Froth Effluent 4	20.6	15.07 ± 0.09	0.81 ± 0.01	13.29 ± 0.09	30.60 ± 0.12	56.11	73.07 ± 0.14	4.19 ± 0.20	1.34 ± 0.02	2.26 ± 0.01	5.85
05	Froth Effluent 5	40.7	12.45 ± 0.10	0.82 ± 0.03	17.61 ± 0.04	29.48 ± 0.04	52.91	69.21 ± 0.05	4.09 ± 0.01	1.28 ± 0.01	1.96 ± 0.02	5.85
06	Froth Effluent 6	32.9	13.22 ± 0.08	0.88 ± 0.03	16.22 ± 0.24	29.99 ± 0.14	53.79	70.39 ± 0.06	4.31 ± 0.16	1.31 ± 0.00	1.98 ± 0.02	5.79
07	Froth Effluent 7	23.6	14.31 ± 0.11	1.06 ± 0.02	14.96 ± 0.02	30.64 ± 0.28	54.40	71.43 ± 0.16	3.92 ± 0.07	1.31 ± 0.01	2.03 ± 0.01	6.34
08	Froth Effluent 8	20.6	14.80 ± 0.14	0.83 ± 0.04	14.79 ± 0.20	29.94 ± 0.45	55.27	71.51 ± 0.16	3.95 ± 0.19	1.32 ± 0.03	2.11 ± 0.01	6.32
09	Froth Effluent Composite 1-4	26.7	15.82 ± 0.11	0.83 ± 0.05	15.02 ± 0.10	29.37 ± 0.01	55.61	71.66 ± 0.17	3.85 ± 0.15	1.35 ± 0.05	1.83 ± 0.02	6.29
10	Froth Effluent Composite 5-8	32.9	14.53 ± 0.00	0.93 ± 0.02	15.67 ± 0.04	29.52 ± 0.32	54.81	70.85 ± 0.11	3.79 ± 0.02	1.26 ± 0.02	1.85 ± 0.01	6.58

Table 12. Properties of Froth Effluent Samples

References

1. Schobert, H. H., Advanced Thermally Stable Coal-Based Jet Fuels, Annual Progress Report, AFOSR Grant F49620-99-1-0290, 2001-2002
2. Schobert, H. H., Advanced Thermally Stable Coal-Based Jet Fuels, Annual Progress Report, AFOSR Grant F49620-99-1-0290, 2000-2001
3. Schobert, H. H., Advanced Thermally Stable Coal-Based Jet Fuels, Annual Progress Report, AFOSR Grant F49620-99-1-0290, 1999-2000
4. Coleman, M. M., Fearnley, S. P., Kumar, S. and Sobkowiak, M., Fuel Stabilization, AFRL-PR-WP-TR-2000-2007, Final Report for 07/01/1995 – 12/31/1998, September 1999.
5. Song, C., Lai, W.-C., Schobert, H.H. Hydrogen-Transferring Pyrolysis of Long-Chain Alkanes and Thermal Stability Improvement of Jet Fuels by Hydrogen Donors. *Ind. Eng. Chem. Res.*, 1994, 33 (3), 548-557
6. Lai, W.-C and Song, C., 1996a Prepr. Pap.- Amer. Chem. Soc. Div. Fuel Chem. 41:524
7. Lai, W.-C and Song, C., 1996b *Fuel Processing Technology* 48:1

8. Selvaraj, L., Sobkowiak, M., Song, C., Stallman, J., Coleman, M. M. A Model System for the Study of Additives Designed to Enhance the Stability of Jet Fuels at Temperatures Above 400°C. *Energy & Fuels*, 1994, 8 (4), 839-845.
9. Yoon, E.M., Selvaraj, L., Song, C., Stallman, J., Coleman, M. M., High Temperature Stabilizers for Jet Fuels and Similar Hydrocarbon Mixtures. 1. Comparative Studies of Hydrogen Donors. *Energy & Fuels*, 1996a, 10 (3), 806-811.
10. Yoon, E.M., Selvaraj, L., Eser, S. and Coleman, M. M., High Temperature Stabilizers for Jet Fuels and Similar Hydrocarbon Mixtures. 2. Kinetic studies, *Energy & Fuels*, 1996a, 10 (3), 812-815.
11. Andrésen, J.M., Strohm, J.J., Boyer, M.L., Song, C, Schobert, H.H. and Butnark, S., *Am. Chem. Soc. Div. Petrol. Chem. Prepr.*, 2001a, 46(1), 208-209.
12. Andrésen, J.M., Strohm, J.J., Sun, L., Song, C. *Energy & Fuels*, 2001b, 15(3), 714-723.
13. Badger, M. W., Fickinger, A. E., Martin, S. C., Mitchell, G. D. and Schobert, H. H., 1998 Proc. 8th Austrian Coal Science Conference 245.

14. Badger, M. W., Fickinger, A. E., Mitchell, G. D., Adams, A. N. and Schobert, H. H., Proc. 205th International Technical Conference on Coal Utilization and Fuel Systems (in press).
15. Butnark, S., Badger, M.W. and Schobert, H.H., Amer. Chem. Soc., Div. Fuel Chem. Prepr., 1999, 44 (3), 662-665.
16. Butnark, S., Badger, M. W. and Schobert, H. H., 2000 Prepr. Pap.- Amer. Chem. Soc. Div. Petrol. Chem., 45:493.
17. Fickinger, A. E., 2000, M. S. Thesis, The Pennsylvania State University, University Park, PA.
18. Fickinger, A. E., Badger, M. W., Mitchell, G. D. and Schobert, H. H., 1999, Prepr. Pap.- Amer. Chem. Soc. Div. Fuel Chem 44:106.
19. Fickinger, A. E., Badger, M. W., Mitchell, G. D. and Schobert, H. H., 2000, Prepr. Pap.- Amer. Chem. Soc. Div. Fuel Chem 45:299.
20. Song, C., and Schobert, H. H., 2000, Prepr. Pap.- Amer. Chem. Soc. Div. Fuel Chem. 45:819.

21. Butnark, S., Badger, M. W. and Schobert, H. H., Determining the Desired Chemical Composition for Thermally Stable Jet Fuel, Amer. Chem. Soc., Div. Fuel Chem. Prepr., 2001, 46 (2), 492-494.
22. Butnark, S., Badger, M. W. and Schobert, H. H. and Wilson, G. R., Selection of Prototype Thermally Stable Jet Fuels 3. Jet Fuel Boiling Range and its Affect on Pyrolytic Stability, 2002 Prepr. Pap.- Amer. Chem. Soc. Div. Petrol. Chem., 47(3),:201..
23. Schobert, H. H., Badger, M. W. and Santoro, R. J., Progress Toward Coal-Based JP-900, 2002 Prepr. Pap.- Amer. Chem. Soc. Div. Petrol. Chem., 47:192.
24. Wilson, G. R.,project Report on AFOSR-Subcontract for Advanced Thermally Stable Coal-Based Jet Fuels for the Pennsylvania State University, PARC Technical Services Inc., Pittsburgh, PA. August 2002.
25. Hazlett, R.N., Thermal Oxidation Stability of Aviation Turbine Fuels, ASTM, Philadelphia, 1991.
26. C. Kwak, J. J. Lee, J. S. Bae and S. H. Moon, Appl. Catal. B 35 (2001) 59.
27. T. Kabe, Y. Aoyama, D. Wang, A. Ishihara, W. Qian, M. Hosoya, Q. Zhang, Appl. Catal. A 209 (2001) 237

28. S. T. Oyama, X. Wang, Y.-K. Lee, K. Bando, and F. G. Requejo, *J. Catal.* 210 (2002) 207
29. C. Stinner, R. Prins, and Th. Weber, *J. Catal.* 202 (2001) 187
30. S. T. Oyama, *J. Catal.* 216 (2003) 343.
31. S. T. Sie, *Fuel Proc. Tech.* 61 (1999) 149.
32. D. H. Broderick and B. C. Gates, *AIChE J.* 27 (1981) 663.
33. K. Sakanishi, T. Nagamatsu, I. Mochida and D. Whitehurst, *J. Mol. Catal. A* 155 (2000) 101.
34. J.H. Kim, X. Ma, C. Song, *J. Catal.*, in submission
35. J.H. Kim, X. Ma, C. Song, T. Oyama, Y.-K. Lee, *Am. Chem. Soc., Div. Fuel Chem.* 48(1) (2003) 40.
36. X. Ma, J. H. Kim, C. Song, *Prepr. Am. Chem. Soc., Div. Fuel Chem.* 48(2) (2003) 553.

37. Turaga, U. T., G. Wang, X. Ma, C. Song, and H. H. Schobert. *Am. Chem. Soc. Div. Petrol. Chem.* 47(1) 2002 89-92.
38. U.T. Turaga, G. Wang, X. Ma, C. Song, *Am. Chem. Soc., Div. Fuel Chem.*, 48 (2) (2003) 550.
39. U.T. Turaga, G. Wang, X. Ma, C. Song, *Catal. Today* 86 (2003) 265.
40. J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.*, 114(27) (1992) 10834-10843.
41. Stanislaus, A, and Cooper, B. H. 1994. Aromatic Hydrogenation Catalysis: A Review. *Catal. Rev. - Sci. Eng.*, 36, 75-123.
42. Cooper, B. H. and Donnis, B. B. L. 1996. Aromatic Saturation of Distillates: An Overview. *Appl. Catal. A.*, 137, 203-223.
43. Song, C., S. Eser, H. H. Schobert, and P. G. Hatcher. 1993. Pyrolytic Degradation Studies of a Coal-Derived and a Petroleum-Derived Aviation Jet Fuel. *Energy & Fuels*, 1993, 7 (2), 234-243.

44. Song, C. and W.-C. Lai. 1998. Chemistry for Thermal Degradation of Bicyclic Hydrocarbon Components of Jet Fuels in Pyrolytic Regime. Am. Chem. Soc. Div. Petrol. Chem. Prepr., 1998, 43 (3), 462-466.
45. Song, C. 2002c. Selective Conversion of Polycyclic Hydrocarbons to Specialty Chemicals over Zeolite Catalysts. *Cattech*, 2002, 6 (2), 64-77.
46. Schobert H.H. and C. Song. 2002. Chemicals and Materials from Coal in the 21st Century. *Fuel*, 2002, 81 (1), 15-32.
47. Shen, J.-P., C. Song and L. Sun. 2000. Preparation of High-Performance Catalyst for Shape-Selective Methylation of 2-Methyl naphthalene into 2,6-Dimethylnaphthalene. Paper presented at I&EC Symp on Green Chemistry, American Chemical Society Spring 2002 National Meeting, Orlando, FL, April 7-11, 2002.
48. Pu, S.-B. and Inui, T. 1996. Synthesis of 2,6-dimethylnaphthalene by methylation of methylnaphthalene on various medium and large-pore zeolite catalysts, *Appl. Catal. A: General*, 1996, 146, 305-316.
49. Fraenkel, D., Cherniavsky, M., Ittah, B. and Levy, M., 1986. Shape-selective alkylation of naphthalene and methylnaphthalene with methanol over H-ZSM-5 zeolite catalysts, *J. Catal.*, 1986, 101, 273-383.

50. Delhaes, P. Graphite and Precursors, Gordon and Breach Sci. Pub., Amsterdam, 2001
51. Farzin, Y.H. Resource and Energy Economics 2001, 23, 271-291.
52. Marsh, H. Introduction to Carbon Science Butterworth & Co Ltd., London, 1989.
53. Speight, J. G.; and Özüm, B. Petroleum refining processes Marcel Dekker, New York, 2002.

List of Acronyms and Abbreviations

1THQ	1,2,3,4-tetrahydroquinoline
5THQ	5,6,7,8-tetrahydroquinoline
AFOSR	Air Force Office of Scientific Research
API	American Petroleum Institute
BT	benzothiophene
CFR	Cooperative Fuels Research
DBT	dibenzothiophene
DDC	Detroit Diesel Corporation
DDS	direct desulfurization
DHQ	decahydroquinoline
DMBP	dimethyl biphenyl
DMDBT	dimethyldibenzothiophene
DMDCH	dimethyl dicyclohexyl
DMN	dimethyl naphthalene
EN	ethyl naphthalene
EPA	Environmental Protection Agency
FBP	final boiling point
FCC	fluid catalytic cracking
FID	flame ionization detector
FTIR	Fourier Transform Infrared
GCMS	gas chromatography-mass spectrometry
HDMDBT	hydrodimethyl dibenzothiophene
HDS	hydrodesulfurization
HDT	hydrotreated
HM	H-mordenite
HY	H Y-type zeolite
HYD	hydrogenation pathway
HZSM	H-synthetic zeolite material
IBP	initial boiling point
IC	internal combustion
IQT	ignition quality test
JP-900	jet fuel prototype stable to 900 F
LCO	light cycle oil
LHSV	liquid hourly space velocity
LTHDA	low temperature hydrotreating and dearomatization
MCHT	methyl cyclohexyl toluene
MCM	mesoporous catalytic material
MN	methyl naphthalene
NTP	normal temperature and pressure
PARC	Pennsylvania Applied Research Corporation
PB	propyl benzene
PCH	propyl cyclohexane
PCHE	propyl cyclohexene
RCO	refined chemical oil

SI	spark ignited
SpGr	specific gravity
SwRI	Southwest Research Institute
TLP	total liquid product
TOS	time on stream
WHSV	weight hourly space velocity