

A COMPARISON OF LIQUIDS PRODUCED FROM COAL BY RAPID
AND SLOW HEATING PYROLYSIS EXPERIMENTS¹

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It is well-known that the quality and yield of pyrolysis liquids depend strongly on the conditions at which coal is devolatilized. However, quantifications in pyrolysis yield and quality and the trade-off relations in them are not well-known and are currently being developed under the mild gasification program. In this study, selected Argonne coal samples were devolatilized in fixed-bed and entrained-flow reactors. The liquid products were characterized by a number of techniques including field ionization mass spectroscopy (FIMS), Fourier transform infrared spectroscopy (FTIR), elemental analysis and nuclear magnetic resonance spectroscopy (NMR). The quality and yield trade-off relationships as well as the characteristics of the liquids generated in the diverse processing conditions are presented.

INTRODUCTION

Mild gasification is defined as the devolatilization of coal at relatively "mild" conditions of temperature and pressure aimed at producing a high-quality (as defined by relatively high H/C ratio) liquid product which can be used with little or no upgrading (1). One approach that has been taken is to allow the tars to undergo some secondary reactions while percolating through a packed bed (2). Relatively few studies have addressed in a systematic way how this process influences the composition and quality of tar produced, and we are aware of only a few previous studies (2-4) where a comparison has been made to rapid heating rate tars produced from the same coal.

¹ A portion of the work described in this study was performed at Morgantown Energy Technology Center.

In the present study, we compared tars which were produced at the US DOE in a slow heating, fixed bed system with those produced at Advanced Fuel Research, Inc. (AFR) in rapid heating, entrained flow reactor system. Tars produced from these coals by slow heating in vacuum in the inlet of the SRI Field Ionization Mass Spectrum (FIMS) provide an additional point for comparing the effect of reaction severity on the nature of the evolved tars. The tars were subsequently analyzed by a variety of techniques. The study was done on tar samples produced primarily from the Argonne Premium Coal Samples.

EXPERIMENTAL

Tar Preparation - Bulk samples of the Argonne coals were obtained from Karl Vorres and sieved to produce +200, 200X325 and -325 mesh size fractions. The -325 mesh size fraction was sent to METC and pyrolysis experiments were done in the Slow Heating Rate Organic Devolatilization Reactor (SHRODR) described previously (2,4). A thick bed (3.8 cm) of coal was heated at 12.5 °C/min to a final temperature of 650°C and held for 60 min. However, tar evolution from the reactor was essentially complete during non-isothermal heating and 5-10 min of the initial heat-treatment. The tars were taken off overhead using a water cooled condenser. The experiments were done without sweep gas. Samples of the 200 X 325 mesh size fraction of each coal were subjected to pyrolysis in AFR's entrained flow reactor system, described elsewhere (6). The experiments were done with a maximum reactor temperature of 700°C. The heating rate has been estimated to be 5000 - 10000°C/s while the time at final temperature is approximately 0.5 s (7). The entire effluent from the reactor system is collected in a polyethylene bag which is secured on a plexiglass manifold covered with aluminum foil. The tars form an aerosol and collect on the walls of the bag and the foil liner. The tars used in the present study were scraped from the foil liner.

Tar Analysis - The tars were analyzed by FT-IR at AFR using a KBr pellet method. A quantitative analysis technique has been developed at AFR using a Nicolet 7199 FT-IR. The techniques, which are described in previous publications (8,9) have been used to determine quantitative concentrations of the hydroxyl, aliphatic and aromatic hydrogen, and aliphatic and aromatic carbon for a wide number of coals, lignins, chars, tars, coal liquefaction products, oil shales, coal extracts and jet fuels. Qualitative information is also obtained concerning the types of ether linkages (oxygen linked to an aliphatic or aromatic carbon), carbonyl contents, the distribution of aromatic hydrogen (whether 1,2 or more adjacent hydrogens on a ring) and the forms of aliphatic hydrogen (methyl or methylene).

The tars were analyzed by Field Ionization Mass Spectrometry (FIMS) at SRI International. FIMS has proven to be an invaluable technique for the analysis of complex mixtures, particularly fossil fuels (9). The technique of field ionization consists of passing the vaporized material of interest through a very high electric field, typically about 1 MV/cm. Field ionization is unique in its ability to produce unfragmented molecular ions from almost all classes of compounds. The sample is vaporized by gradually heating the samples while continuously collecting mass spectral data. The pyrolysis tars studied evolved below 200°C (under vacuum) and presumably did not undergo any thermal reaction during FIMS analysis. If desired, the samples can be heated to temperatures as high as 500°C and the coals themselves were pyrolyzed in the inlet by heating them at 3°/min to 500°C. Mass analysis was performed by a medium resolution 60' magnetic sector analyzer, which has a maximum range up to 2000 daltons. The tars were also characterized by elemental analysis at METC and by NMR performed at the University of North Dakota Mineral and Energy

Research Laboratory. The NMR spectra were analyzed by a technique used by Clutter et al (12) to identify the key structural parameters of the tars.

RESULTS AND DISCUSSION

FIMS Analysis - A summary of the FIMS results is given in Table 1. In general, the tars produced from the slow-heating fixed bed reactor has low average molecular weights and narrow molecular weight distributions. A comparison is made of FIMS spectra from the three experiments for three of the coals in Figs 1-3. The overall MW profiles of the tars formed by in-situ pyrolysis in the FIMS and the entrained-flow reactor are similar to each other. In both cases, the tars represent primary products of pyrolysis with little secondary reactions. Consistent with the lower N content of the SHRODR tars, FI-mass spectra of these liquids show a lower abundance of odd-mass peaks. In-situ pyrolysis tars appear to have relatively greater amounts of low molecular weight materials than the EFR tars. This difference is perhaps due to differences in the sampling efficiency. It is interesting to note that both SHRODR and FIMS tars are richer in simple phenols like cresols and catechols than the EFR tars which contained larger amounts of poly-phenols. In the case of in-situ FIMS of coals, these peaks evolved only at higher temperatures (>350°C) and represent thermal fragments from a large matrix. Again, differences in the methods for collecting tars in the various experiments may be partly responsible.

FT-IR Analysis - A comparison of the results from FT-IR analysis of the EFR and SHRODR tars is given in Table 2 (data provided in relative units). These analyses were done with the KBr pellet method. Because of the high volatility of the SHRODR liquids, the results on the fixed bed samples are not as reliable as for the EFR tars. The SHRODR liquids will be repeated using a liquid cell for verification. The FT-IR analysis of the tars from slow heating and rapid heating indicates that the former liquids were more aliphatic (less aromatic), lower in oxygen content, lower in heteroatom content, and the aromatic rings are less substituted. These indicators are consistent with the concept behind mild gasification, which stresses the fact that higher quality liquids can be produced from fixed-bed or moving-bed systems, although in lower yields (1,2).

Elemental Analysis - A comparison of the H/C (atomic) ratios of the pyrolysis liquids generated in the fixed-bed and entrained-flow reactors for several coals are shown in Fig. 4. The H/C (atomic) ratio of the parent coals are also shown in this figure. For all coals, the H/C of the fixed-bed liquids were significantly higher than the corresponding tar generated in the entrained-flow reactor(s). The Arkwright coal sample utilized in previous studies showed similar differences. The Arkwright (Pittsburgh seam) coal was also pyrolyzed at METC's entrained-flow reactor (also known as Advanced Gasification Facility, AGF; performed at 650 °C, nominal residence time 2 sec, 100 psig He). The H/C of the tar generated in the AGF is remarkably similar to that produced at BNL, as reported previously (4). Detailed elemental analyses are continuing.

NMR Results - A comparison of the NMR results (Fig. 5) obtained in two reactors demonstrate that the fixed-bed liquids are significantly less aromatic (as defined by carbon or proton aromaticity) than the tars generated in the entrained flow reactor. Furthermore, the fixed-bed reactor produces liquids with more mono- and di-aromatics while the tar formed in the entrained flow reactor are enriched in tri-aromatics and other larger molecules.

Results of this study confirm that rapid heating rate processes increase the yield of tar (Table 3) at the expense of tar quality (Fig. 1-4). Similar trade-off between tar yield and tar quality was reported by Khan (2,4) when comparing results from SHRODR experiments on Pittsburgh No. 8 coal with fluidized bed experiments by Tyler (10). A comparison was also made between the SHRODR tars and tars produced in an entrained flow reactor at Brookhaven National Lab (BNL) where differences similar to those found in the present study were reported (2).

The results of this study are consistent with the limited data reported by Peters and Bertling (3) who compared tars generated in a rapid- and slowly heated reactors. The tar yield in the fluid-bed was higher than the liquid generated in the fixed bed reactor. However, no elemental, NMR or FT-IR analyses of tars were provided. They proposed that in the slow heating process, the longer residence time of the tar leads to condensation and decomposition of the pitch to yield primarily coke, with some formation of light gases and light oils. Majumder et al (13), in contrast, attributed lower tar yield in a fixed bed reactor to the polymerization reactions alone and argued that "cracking" of tars is not significant. One can propose that the differences in the yield and composition of tar between the two experiments are a result of both cracking processes (which remove high molecular weight products as light oils), and repolymerization processes (which deliver high molecular weight products as coke). The relative importance of these two processes depends on the coal type, bed geometry, particle size, and heating rate in a complex way which is currently not well understood. Serio (11) investigated homogeneous cracking reactions of tars produced at low temperature and low residence time in a gas-swept fixed-bed reactor. The changes in the molecular weight distribution between the rapidly heated and slowly heated tars are consistent with a thermal cracking process which would produce primarily lower molecular weight material.

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REFERENCES

1. Khan, M. R., and Kurata, T. "The Feasibility of Mild Gasification of Coal: Research Needs," DOE/METC-85/4019, DE85013625, 1985, pg. 80.
2. Khan, M. R. *Fuel Sci. & Tech. Intl*, 5 (2), pp 185-231. Also, Khan, M.R., Proc. of the Seventh Annual Gasification and Gas Stream Cleanup Systems Contractors review meeting, DOE/METC-87/6079, vol. 1, p. 170, (1987).
3. Peters, W., and Bertling, H., *Fuel*, 44, 317, (1965).
4. Khan, M.R., Proc. 1987 Int. Conf. on Coal Science, J.A. Moulijn et al., editors, Elsevier, Amsterdam, pp. 647-651.
5. Solomon, P.R., Hamblen, D.G., Carangelo, R.M., Krause, J.L., Ninetheenth Symposium (International) on Combustion; The Combustion Institute, Pittsburgh, PA, p. 1139, (1982).
6. Serio, M.A., Hamblen, D.G., Markham, J.R., Solomon, P.R., *Energy Fuels*, 1, 138, (1987).
7. Solomon, P.R., Coal Structure, *Advances in Chemistry Series*, 192, 95, (1981).
8. Solomon, P.R., Hamblen, D.G., and Carangelo, R.M., *ACS Symposium Series*, 205, Coal and Coal Products: Analytical Characterization Techniques, American Chemical Society, Washington, DC (1982), Pg. 77.
9. St. John, G.A., Butrill, S.E., Jr., and Anbar, M., "Field Ionization and Field Desorption Mass Spectroscopy Applied to Coal Research", in Organic

- Chemistry of Coal, (Ed. J. Larsen), ACS Symposium Series, 71, 1978, p.223.
10. Tyler, R.J., *Fuel*, 50 (4), 218, (1980).
 11. Serio, M.A., Ph.D. Thesis, Dept. of Chemical Eng., Massachusetts Institute of Technology, Cambridge, MA, (1984).
 12. Clutter, D.R., Petrakis, L. Strenger, R.L., Jr., and Jensen, R.K., *Anal. Chem.*, 44, 1395 (1972).
 13. Majumder et al, *Fuel*, 52, 11 (1973).

TABLE 1 - RESULTS FROM FIMS ANALYSIS OF TARS

COAL	SHRODR		IN-SITU FIMS		EPR	
	Wt. Av. MW	MW Range	Wt. Av. MW	MW Range	Wt. Av. MW	MW Range
Pocahontas	-	-	426	100 - 700	566	200 - 900
Upper Freeport	324	100 - 500	526	100 - 900	536	100 - 900
Pitts. No. 8	326	100 - 500	497	100 - 900	484	150 - 800
Lewiston-Stockton	-	-	546	100 - 900	478	150 - 750
Utah Blind Canyon	331	120 - 600	524	100 - 900	493	130 - 850
Wyodak	-	-	527	100 - 850	504	100 - 800

TABLE 2 - SOME RESULTS FROM FR-IR ANALYSIS OF TARS FROM THE TWO REACTORS

COAL	SHRODR			EFR		
	H _{ar} /H _{tot}	H _{ch}	C=O	H _{ar} /H _{tot}	H _{ch}	C=O
Pocahontas	.41	.27	(32.3)	.43	.13	6.7
Upper Freeport	.25	.18	8.6	.40	.23	9.3
Pitts. No. 8	.24	.18	5.7	.37	.29	9.1
Lewiston-Stockton	.23	.14	9.8	.37	.33	12.7
Utah Blind Canyon	.13	.19	5.7	.28	.32	13.0
Wyodak	.15	.19	14.5	.30	.35	20.3

TABLE 3 - COMPARISON OF TAR YIELDS FROM VARIOUS REACTORS

(Yield on dry-ash-free-basis)

COAL	SHRODR	EFR
Pocahontas	8	10
Upper Freeport	14	22
Pitts. No. 8	19	30
Lewiston-Stockton	13	17
Utah Blind Canyon	20	26
Wyodak	12	13

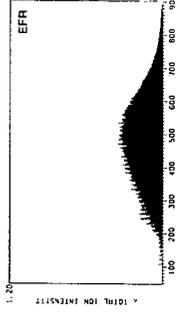
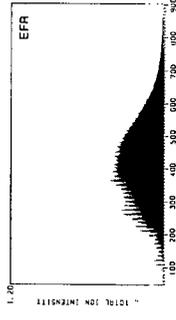
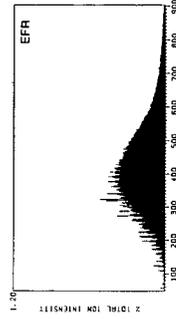
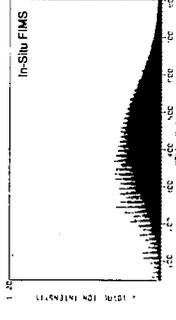
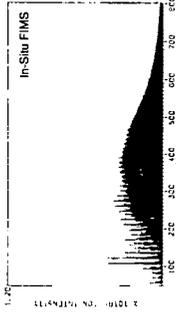
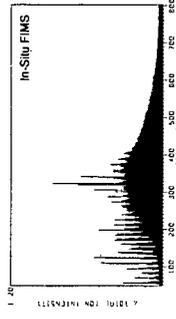
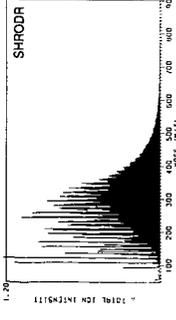
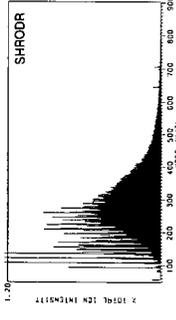
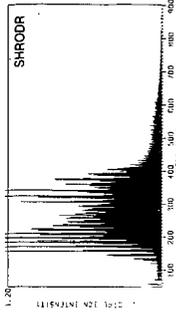
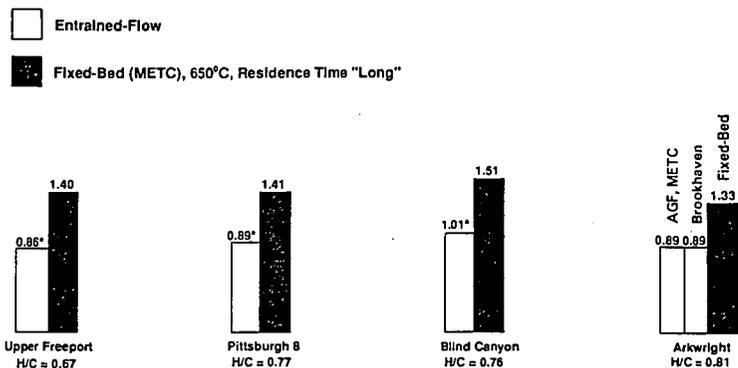


Fig. 3 - FIMS Spectra from Utah Blind Canyon Coal

Fig. 2 - FIMS Spectra from Pittsburgh No. 8 Coal

Fig. 1 - FIMS Spectra from Upper Freeport Coal

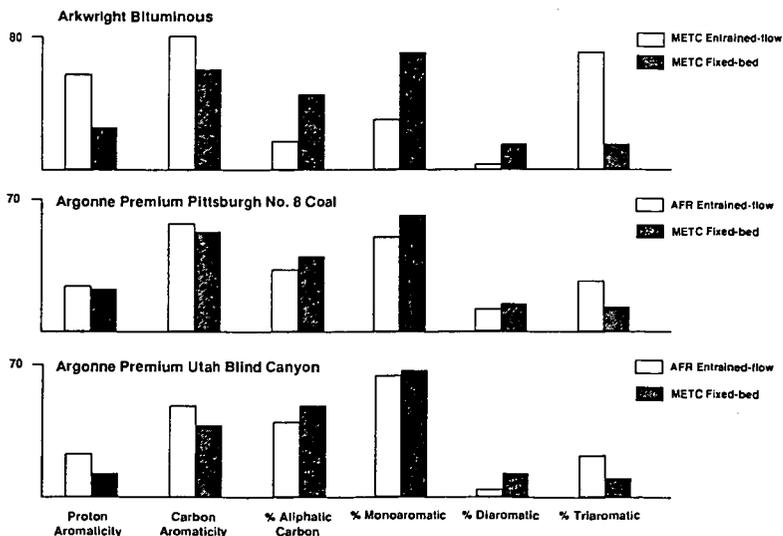
Fig. 4 - Comparison of H/C of Coal Pyrolysis Liquids Generated in Fixed-Bed and Entrained-Flow Reactors



* Data from Entrained Flow Reactor Unit of Advanced Fuel Research

C89-991-3 AA5

Fig. 5 - Influence of Processing Conditions on the characteristics of Pyrolysis Liquids (average structural properties)



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