

# FUEL

**the science and technology of Fuel and Energy**



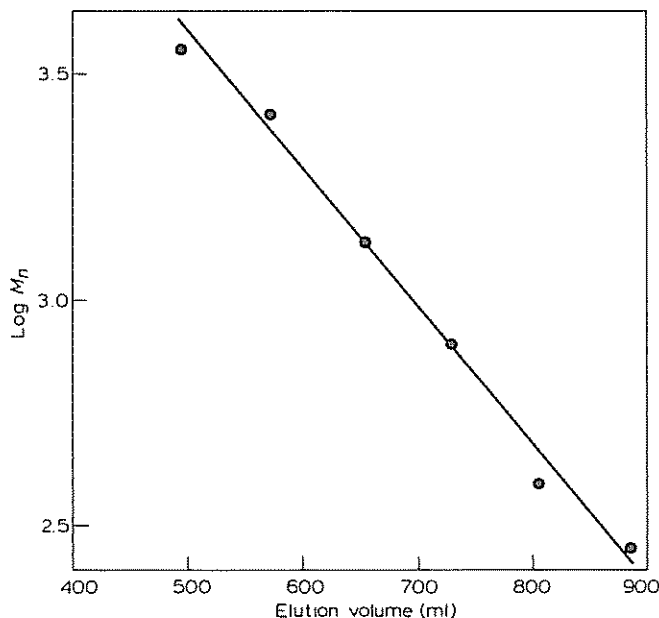


Figure 1 Logarithm of molecular weight  $\log M_{ni}$  versus elution volume  $EV_j$

emphasized that the analytical data (Table 1) do not show any significant accumulation of heteroatoms in certain fractions<sup>†</sup>.

The number-average molecular weight  $\bar{M}_n$ <sup>15</sup> of the collected material can be calculated from the yields  $m_i$  and the molecular weights  $M_{ni}$  of the individual fractions:

$$\bar{M}_n = \frac{\sum_i m_i}{\sum_i \frac{m_i}{M_{ni}}} = 614 \text{ g mol}^{-1}$$

and corresponds reasonably well to the number-average molecular weight,  $\bar{M}_n = 725 \text{ g mol}^{-1}$ , measured by osmometry in the starting pyridine-soluble material. This is demonstrating the consistency of the applied technique. The weight-average molecular weight  $\bar{M}_w$ <sup>15</sup> approximates to:

$$\bar{M}_w \approx \frac{\sum_i m_i M_{ni}}{\sum_i m_i} = 1008 \text{ g mol}^{-1}$$

assuming that the distribution of the individual fractions is narrow and thus the approximation  $M_{ni} \approx M_{wi}$  is valid. A polydispersity index  $\bar{M}_w/\bar{M}_n \approx 1.64$ <sup>15</sup> is obtained. For the coal extract studied the molecular weight distribution ranges from 280 to 3600 amu and is remarkably asymmetric increasing steeply to the most frequent mass around 400 but decreasing gradually to higher molecular weights (Figure 2 and 3). Correspondingly, the most frequent molecular weight differs from  $\bar{M}_n$  and  $\bar{M}_w$  by  $\approx 200$  and 400 amu, respectively.

According to empirical formulae calculated from the

† G.p.c. studies of asphaltenes and crude oil residues showed V-shaped curves with distinct minima in the medium ranges when plotting heteroatom contents or C/H ratios versus molecular weight of elution volume. This is apparently due to adsorption effects (see Reference 1, page 136 and references cited therein)

analytical compositions of the g.p.c. fractions (Table 1) the H/C ratio decreases with increasing molecular weight<sup>†</sup>. From <sup>1</sup>H-n.m.r. spectra (60 MHz, D<sub>5</sub> pyridine) one can conclude that the decreasing H/C ratio is mainly due to decreasing benzylic and aliphatic hydrogen contents. On moving to higher molecular weight fractions the u.v. spectra (in pyridine) show increasing specific extinction coefficients of the structureless long-wavelength absorption (350–700 nm) apparently indicating that the higher fractions contain more extended polycyclic aromatic chromophores. This striking dependence between molecular weight and composition is currently being investigated in more detail on other coal-derived products.

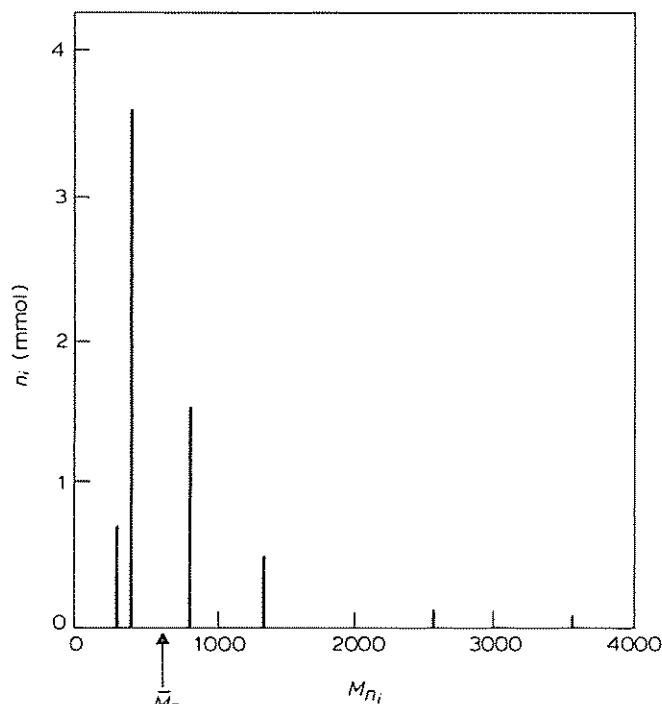


Figure 2 Molecular weight distribution of the coal extract

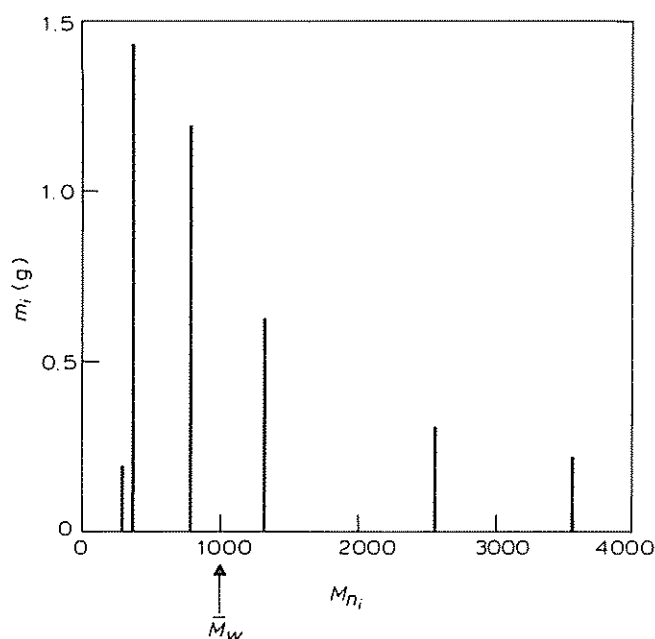


Figure 3 Molecular weight distribution of the coal extract

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## Effect of surfaces on the yield of volatiles from coal

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The ASTM proximate analysis includes a detailed procedure for determining the 'volatile matter' of coals<sup>1</sup>. If the procedure is followed precisely with respect to sample weight (1 g), crucible specifications (platinum, 10–20 ml capacity) and temperature–time history ( $950 \pm 20^\circ\text{C}$ , 7 min), the results are consistent and reproducible. If aspects of the procedure are varied, however, it is well-known that the yield of volatiles, expressed as wt% dry coal, will deviate from the ASTM value.

Previous data have shown a considerable reduction in volatile yield when pyrolysis is performed in the presence of surfaces, either inherent in the bed of coal or as an additive mixed with the coal<sup>2</sup>. This Letter demonstrates that, depending on the nature of the introduced surface, the yield of volatiles can be significantly enhanced. This is consistent with the hypothesis of Essenhigh<sup>3</sup> that the ASTM volatile matter yield, and indeed most measured values, are substantially lower than the 'true' volatile yield from coals.

In fixed bed pyrolysis experiments, data indicating a sample weight effect on the yield of volatiles have been interpreted more strictly as a bed depth effect<sup>2,4,5</sup>. A reduction in the yield of volatiles accompanies an increase in the bed depth. In essence, the coal particles forming the bed act as a trap for primary volatiles, in particular the tars, and provide surface at which secondary char-forming reactions can occur.

Extrapolation of this argument provided the basis for explaining data obtained from disperse phase pyrolysis experiments. These experiments, usually performed in entrained-flow furnaces, produced yields of volatiles considerably in excess of the ASTM value<sup>2,6–8</sup>. The observed enhancements have been shown to be associated with the dilute-phase operation of the furnace rather than with the commonly associated rapid heating rates<sup>2</sup>. In the disperse phase, contact between primary volatiles and coal or char particles is minimized.

If Saran char, petroleum coke or activated carbon is mixed with coal prior to devolatilization in fixed or fluidized beds, the yields of both tars and total volatiles are reduced<sup>2,9</sup>. This has been attributed to secondary char

formation on the exterior surface of the additive particles<sup>2</sup>. The absence of any increase in the yields of low-molecular-weight hydrocarbons was interpreted as indicating that the reduction in tar yield was due, not to cracking reactions, but to polymerization or condensation reactions occurring within the coke bed<sup>9</sup>. Cracking of simple hydrocarbons can produce carbon and hydrogen and in the limit condensation and polymerization reactions can produce a graphitic deposit<sup>10</sup>.

In recent experiments, mixtures of  $\gamma\text{-Al}_2\text{O}_3$ , typical of the alumina used as a porous support for metal catalysts, and a Texas lignite were pyrolysed in ASTM volatile matter crucibles. Runs were also performed with mixtures of the lignite and the same support loaded with Co and Mo oxides.\* Typically, metal loadings of  $\approx 10$  wt% are used for hydrodesulphurization applications<sup>11</sup>. Various amounts of the additives, in the form of 1 mm diameter cylindrical pellets, were mixed thoroughly with 0.2 g of the 70  $\times$  100 mesh fractions (US Standard Sieve) of the Texas lignite prior to devolatilization. Analyses for the lignite, which gave a yield of volatiles of 46.9 wt% dry coal on pyrolysis of 0.2 g, were given previously<sup>2</sup>.

The test results are shown in *Figure 1*, as a plot of the fractional yield of volatiles (compared to the yield from 0.2 g of lignite) as a function of additive/coal ratio. The curves have been corrected for weight loss from the additives. Similar curves were also generated for the same additives and a high-volatile A bituminous coal. Addition of  $\text{Al}_2\text{O}_3$  pellets to the lignite gave results similar to those previously observed for the addition of Saran char, petroleum coke and activated carbon, i.e. the total yield of volatiles was reduced. Blackening of the  $\text{Al}_2\text{O}_3$  pellets during the pyrolysis and subsequent regeneration by burning off in air were consistent with the formation of carbonaceous deposits.

Addition of the Co–Mo– $\text{Al}_2\text{O}_3$  pellets, however, resulted in a significant enhancement of the yield of volatiles. Some blackening of the pellets confirmed the

\* The  $\text{Al}_2\text{O}_3$  and Co–Mo– $\text{Al}_2\text{O}_3$  samples were kindly supplied by Gulf Research and Development Company

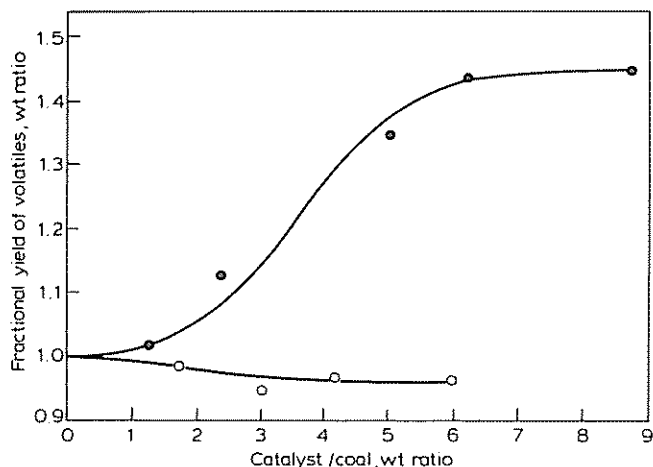


Figure 1 Variation in yield of volatiles, relative to that from 0.2 g of lignite, as a function of catalyst/coal ratio for 70 x 100 mesh Texas lignite. ●, Co-Mo-Al<sub>2</sub>O<sub>3</sub>; ○, Al<sub>2</sub>O<sub>3</sub>

continued occurrence of some secondary char formation. Addition of an equal weight of Co-Mo-Al<sub>2</sub>O<sub>3</sub> to lignite produced little measurable increase in yield, but a dramatic rise occurred at about a 2:1 catalyst/coal ratio. For the experimental conditions, the yield enhancement became independent of the catalyst/coal ratio above approximately 6:1, and represented a fractional yield increase > 1.4. This corresponds to 66 wt% of the dry lignite. The ability to achieve such enhancements in the yield of volatiles has considerable implications for the design of coal utilization systems. In most gasification systems, for example, it is advantageous to maximize the yield of volatiles.

It is known that cobalt catalyses the gasification reaction,  $C + 2H_2 \rightarrow CH_4$ , and pyrolysis gases from lignites have been shown to contain significant quantities of hydrogen<sup>12</sup>. TGA runs in H<sub>2</sub> for 7 min at 950°C on mixtures of the lignite chars and Co-Mo-Al<sub>2</sub>O<sub>3</sub> indicated

that the carbon/hydrogen reaction may account for a yield increase of only  $\approx 1.04$ . It is postulated, therefore, that at significantly high catalyst/coal ratios the primary volatiles, particularly the tars, react at the catalyst surface in such a way as to minimize polymerization or condensation reactions. Of principal importance is the ability of the catalyst to dissociate molecular hydrogen present in the volatiles to atomic hydrogen, which in turn can react with hydrocarbon free radicals as they are produced. This contention is supported by the, as yet, qualitative observation that the tars change in nature from black and viscous to clear and fluid in the presence of the Co-Mo-Al<sub>2</sub>O<sub>3</sub>.

While it has been recognized for many years that secondary reactions can alter the distribution of pyrolysis products<sup>10</sup>, the present work demonstrates that such reactions can significantly alter the total yield of volatiles.

## REFERENCES

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# Calendar

2-7 August 1981

**Advanced Coal Preparation**

*New England College, Henniker, New Hampshire, USA*

Engineering Foundation, 345 East 47th Street, New York, NY 10017, USA

4-6 August 1981

**COGLAC: coal gasification, liquefaction and conversion to electricity**

*Pittsburgh, Pennsylvania, USA*

A. J. Brainard, Dept. Chem. Petrol. Eng., 1234 Benedum Hall, University of Pittsburgh, Pittsburgh, PA 15361, USA

23-28 August 1981

**182nd National Meeting of the American Chemical Society**

*New York, USA*

A. T. Winstead, 1155 16th Street NW, DC 20036, USA

7-9 September 1981

**International Conference on Coal Science**

*Dusseldorf, FRG*

z. Hd. Herrn Dr Ingo Romey, Bergbau-Forschung GmbH, Postfach 13 01 40, D-4300 Essen 13, West Germany; or Dr I. Wender, Office of Advanced Research and Technology, MS C-156, US Dept. of Energy, DC 20545, USA

8-11 September 1981

**Underground Coal Conversion: 7th annual symposium**

*Fallen Leaf Lake, Lake Tahoe, California, USA*

Dr D. Stephens, Lawrence Livermore National Laboratory, PO Box 808, L-367, Livermore, CA 94550, USA

14-16 September 1981

**Microscopy of Coals, Cokes, Carbon and Graphite**

*York University, York, UK*

Administrater, Royal Microscopical Society, 37/38 St Clements, Oxford OX4 1AJ, UK

20-22 September 1981

**33rd Canadian Conference on Coal**

*Regina, Saskatchewan, Canada*

Coal Association of Canada, 210, 909 5th Avenue SW, Calgary, Alberta T2P 0N8, Canada

28 September-1 October 1981

**2nd International Gas Research Conference**

*Bonaventure Hotel, Los Angeles, California, USA*

G. Eowan, Gas Research Insitute, 10 West 35th Street, Chicago, IL 60616, USA

5-6 October 1981

**Outlook for Synfuels**

*Washington DC, USA*

R. Hildwine, Pasha Publications, Suite 713, 1730 K Street NW, DC 20006, USA

6-8 October 1981

**Analytical Chemistry in Energy Technology: 25th conference**

*Gatlinberg, Tennessee, USA*

W. S. Lyon, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

13-15 October 1981

**Materials for Coal Conversion and Utilization: 6th annual conference**

*Gaithersburg, Maryland, USA*

S. J. Schneider, B-308 Materials Building, National Bureau Standards, DC 20234, USA

28-30 September 1981

**28th Canadian Spectroscopy Symposium**

*Government Conference Centre, Ottawa, Canada*

Dr J. W. McLaren, Division of Chemistry, National Research Council of Canada, Montreal Road, Ottawa, Canada, K1A 0R9

27-29 October 1981

**Polynuclear Aromatic Hydrocarbons: 6th international symposium**

*Battelle's Columbus Laboratories, Columbus, Ohio, USA*

R. A. Gibson, Battelle's Columbus Laboratories, 505 King Avenue, Columbus, OH 43201, USA

1-3 December 1981

**Peat as an Energy Alternative: symposium**

*Sheraton National Hotel, Arlington, Virginia, USA*

K. Fisher, Institute of Gas Technology, IIT Center, 3424 South State Street, Chicago, IL 60616, USA

9 December 1981

**Alternative Fuels and Future Fuels Specifications for Stationary Gas Turbine Applications: symposium**

*Phoenix, Arizona, USA*

J. S. Clark, Mail Stop 500-122, NASA Lewis Research Center, 2100 Brookpark Road, Cleveland, OH 44135, USA

14-16 December 1981

**Alternative Energy Sources: 4th Miami international conference**

*Miami Beach, Florida, USA*

Dr N. T. Veziroglu, Clean Energy Research Institute, University of Miami, PO Box 248294, Coral Gables, FL 33124, USA

February 1982

**Chem-Coal: a chemical feedstock — international symposium**

*Johannesburg, South Africa*

F. L. D. Cloete, SA Institute of Chemical Engineers, CERG-CSJ PO Box 395, Pretoria 0001, South Africa