



## Project Summary

# Analysis of Volatile Products from the Slow Pyrolysis of Coal

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The evolution of volatile matter was studied for a subbituminous coal pyrolyzed in a bench-scale fixed-bed reactor, and for both a lignite and subbituminous coal pyrolyzed in a bench-scale fluidized-bed reactor. The pyrolyses were carried out under inert gas atmospheres, at a pressure of 135 kPa (5 psig), temperatures ranging from 400 to 1000°C, and heating rates ranging from 1.45 to 6.0°C/s. The pyrolysis products—tar, water, char, and gases—were separated and analyzed. Primary gas, aliphatic hydrocarbon, aromatic hydrocarbon, and sulfur gas species were quantified by gas chromatography. The effects of equilibrium temperature, heating rate, coal rank, and reactor design on asymptotic weight loss, elemental volatilization, gas species production and product composition, and tar/gas production ratios were examined.

Plots of asymptotic (long-time) weight loss vs. temperature for the slow pyrolysis (<45°C/s) of the coals pyrolyzed in this study and three other coals ranging in rank from lignite to bituminous fall very close to a single curve over a temperature range of 400-1000°C. Similar plots based on published data for the rapid pyrolysis ( $10^3$ - $10^5$  °C/s) of three coals covering the same range in rank also fall close to a single curve, which lies below the slow pyrolysis curve and approaches it at temperatures of about 900°C.

Equilibrium weight loss and release of elemental oxygen, carbon, and hydrogen increased with temperature. In the fixed-bed pyrolysis of subbituminous coal, the volatilization of sulfur and yields of hydrogen, carbon oxides, methane, benzene, thiophene, and carbon disulfide increased with temper-

ature, while yields of toluene, xylene, C2-C4 aliphatic hydrocarbons, hydrogen sulfide, carbonyl sulfide, and methyl mercaptan exhibited maxima at temperatures between 700 and 900°C.

In the fluidized-bed pyrolysis of both lignite and subbituminous coal, yields of hydrogen, carbon monoxide, methane, ethylene, benzene, toluene, xylene, and thiophene increased with temperature, while volatilization of sulfur and yields of carbon dioxide, pyrolytic water, ethane, C3-C4 aliphatic hydrocarbons, hydrogen sulfide, carbonyl sulfide, and methyl and ethyl mercaptans were maximized at temperatures between 700 and 900°C. The data on sulfur release suggest that the devolatilization of this element is affected at high temperatures by decreases in internal surface area and porosity of the coal particles.

Carbon disulfide was produced from the pyrolysis of subbituminous coal in both the fluidized- and fixed-bed reactors at temperatures above 800°C. It was not produced in the fluidized-bed pyrolysis of lignite. Conversely, ethyl mercaptan was produced in the fluidized-bed pyrolysis of lignite, but did not appear in the products of either the fixed- or fluidized-bed pyrolysis of subbituminous coal. Yields of ethyl mercaptan were lower than yields of methyl mercaptan.

For all systems studied, tar-to-gas production ratios dropped with increasing temperature. For slow pyrolysis over the temperature range of 400 to 900°C, tar production and tar-to-gas ratios were lower and weight losses greater than for rapid pyrolysis. As noted above, coal rank had no significant effect on asymptotic devolatilization. Tar yield increased and carbon

monoxide, carbon dioxide, and pyrolytic water yields decreased with increasing coal rank. The yields of the individual aliphatic hydrocarbons in the fluidized bed were greater for subbituminous coal than for lignite.

*This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## Introduction

The principal obstacle to using coal as an energy source is environmental. Large quantities of potentially hazardous organic and inorganic species are formed during coal conversion, and must be captured and removed somewhere between the point of formation and the point of release of effluents to the environment. If coal conversion is to be designed to be environmentally sound, the chemistry—thermodynamics and kinetics—of the formation of pollutants must be understood.

The first step in any coal conversion process—combustion, gasification, or liquefaction—is pyrolysis. The coal fed to the process is brought to a high temperature, leading to the formation and release of volatile species, including hydrocarbon, sulfur, and nitrogen gases, tars, and volatile trace metals. While much attention has been given in the literature to the principal reactions of pyrolysis, little has been done regarding the formation of minor but potentially hazardous species.

In the present study, several coals were pyrolyzed in laboratory-scale fixed- and fluidized-bed reactors, and the volatile products were quantitatively analyzed. The extents of total devolatilization, elemental release, and individual product species formation were correlated with the pyrolysis temperature, the heating rate, and the rank of the feed coal. This report describes the experimental systems used, gives the results obtained, and discusses the implications with respect to coal conversion processes. Information and results beyond those given in the report are available.

## Experimental

Research was performed using bench-scale, batch fixed- and fluidized-bed reactors. The coal feed to both reactors was set at 5 g, which provided adequate

samples of the pyrolysis products for analysis. The fluidized-bed reactor was found to provide more consistent and reproducible results, and was therefore used for most of the study.

The fluidized-bed reactor consists of a stainless steel tube, 5/8-in. (1.59 cm) I.D., with top and bottom stainless steel frits. A Lindberg Model 55035 furnace is used as a preheater, heating the sweep gas from room temperature to 300°C. The reactor is contained in a Lindberg Model 54032 single-zone tube furnace with a 1 ft (30.48 cm) long heating zone. The reactor temperature can be varied between 200 and 1200°C, with heating rates ranging from 2.22°C/sec at 400°C to 2.38°C/sec at 1000°C. Helium and argon have been used as sweep gases. Results have not shown any noticeable dependence on which gas was used.

Water and tar in the reactor effluent are captured in a packed ice-water-cooled trap downstream from the reactor. The tubing from the fluidized bed to the cold trap is heat-traced to avoid condensation prior to the trap. The noncondensing volatiles are collected in an evacuated 1-liter stainless steel bomb, or in a glass bomb coated internally with hexamethyldisilazane to reduce the adsorption of trace sulfur and hydrocarbon species.

Pyrolysis experiments were performed on samples of 40x100 mesh New Mexico Navajo Mine (NMNM) subbituminous coal, and on samples of 40x100 mesh Montana lignite. Ultimate and proximate analyses of these coals are given in Tables 1-4.

Two replications were performed per temperature per reactor. The tar, water, gases, and char were physically separated, collected, and analyzed. The condensed species were analyzed for carbon and hydrogen using a standard ASTM method, and for sulfur using a Fisher Model 470 sulfur analyzer. The gases were subjected to chromatographic analysis using thermal conductivity detection, flame ionization detection, or flame photometric detection, depending on the species analyzed. Complete descriptions of the analysis are given in the report.

**Table 2.** Proximate Analysis of As-Received NMNM Coal<sup>a</sup>

Moisture	9.6
Volatile Matter	33.3
Fixed Carbon	37.7
Ash	19.4

<sup>a</sup>All units are Wt. %.

## Pyrolytic Weight Loss

For both coals in both reactors, no devolatilization occurred at temperatures below 400°C, except for the moisture in the feedstock. Between 400 and 700°C, the major fraction of volatile material was released. Increases in temperature above 700°C produced marginal increases in asymptotic weight loss. A greater extent of devolatilization was found in the fluidized bed than in the fixed bed, probably attributable to readsorption of volatiles on the particles in the fixed bed.

Asymptotic weight loss data obtained for slow pyrolysis in this study, and for slow and rapid (10<sup>3</sup>-10<sup>5</sup>°C/s) pyrolysis for several other published studies, are plotted versus temperature in Figure 1. The data for each heating regime show a surprising independence of coal rank; apparently, the fractional asymptotic weight loss depends only on temperature and whether the heating is slow or fast, but not on the particular coal being pyrolyzed. Moreover, the curves for the two regimes are distinctly different: apparent weight losses for fast pyrolysis are lower than those for slow pyrolysis at temperatures below 900°C; but, between 900 and 1000°C, apparent weight losses are similar.

Linear regression was used to obtain a polynomial fit of the slow pyrolysis data shown in Figure 1, with the following result:

$$\text{Weight Loss (d.a.f)} = -49.0 + 0.20T - 1.066 \times 10^{-4}T^2 \quad (1)$$

where T = temperature in degrees Celsius. The data for rapid pyrolysis shown in Figure 1 were fitted by nonlinear regression to obtain the following formula:

**Table 1.** Ultimate Analysis of NMNM Subbituminous Coal<sup>a</sup>

	As-Received	Dry Basis	Dry Ash-Free Basis
Carbon	54.4	60.1	76.6
Hydrogen	3.5	3.9	4.9
Sulfur	0.8	0.9	1.1
Oxygen	12.3	13.6	17.4
Ash	19.4	21.5	---
Moisture	9.6	---	---

<sup>a</sup>All units are Wt. %.

**Table 3.** Ultimate Analysis of Partially Dried Montana Knife River Deposit Lignite<sup>a</sup>

	As-Received	Dry Basis	Dry Ash-Free Basis
Carbon	57.1	63.3	72.1
Hydrogen	2.7	3.0	3.4
Sulfur	0.6	0.6	0.7
Oxygen	18.7	20.9	23.8
Ash	11.0	12.2	---
Moisture	9.9	---	---

<sup>a</sup>All units are Wt. %.

**Table 4.** Proximate Analysis of Partially Dried Montana Knife River Deposit Lignite<sup>a</sup>

Moisture	9.9
Volatile Matter	41.0
Fixed Carbon	38.1
Ash	11.0

<sup>a</sup>All units are Wt. %.

$$\begin{aligned} \text{Weight Loss (d.a.f)} &= 165 \exp(-0.000714T) \\ &- 846 \exp(-0.00310T) + \\ &1350 \exp(-0.00587T) \quad (2) \end{aligned}$$

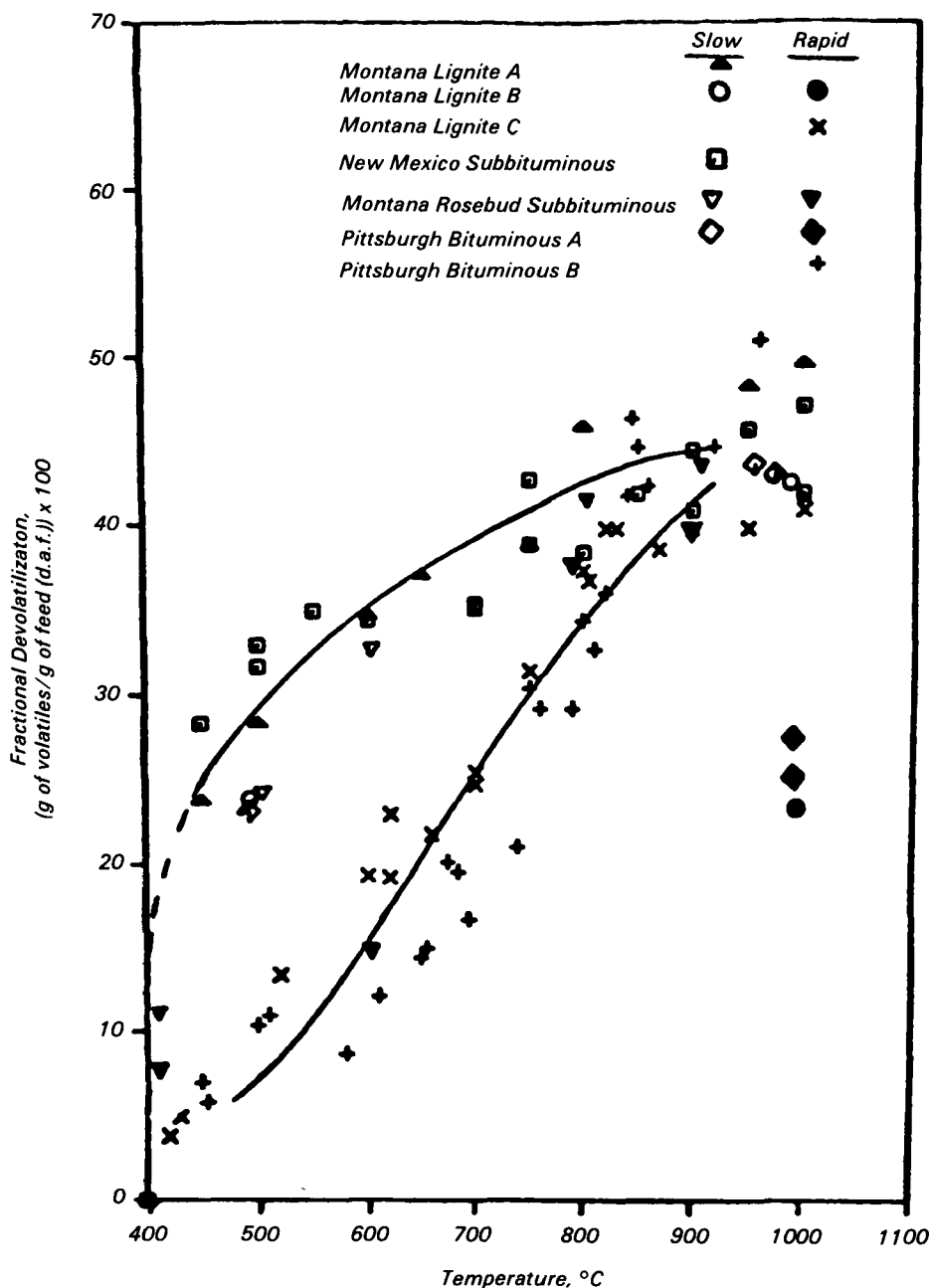
### Elemental Release

The fractional release of both oxygen and hydrogen increased with temperature over the range 400-1000°C; 80% of the elements were volatilized at 800°C, and 90% were volatilized at 900°C. A lower fractional volatilization of carbon was found than was observed for either hydrogen or oxygen. The maximum volatilization of carbon, approximately 35% by weight of the feed carbon, was observed at 1000°C for the subbituminous coal. At slow heating rates, a greater fraction of the feed carbon was volatilized from subbituminous coal than from lignite. Comparison of the results with literature data shows that rapid pyrolysis produced lower volatilization of carbon than did slow pyrolysis for similar lignite feedstocks.

Plots of fractional sulfur volatilization in the fluidized-bed pyrolysis of lignite and subbituminous coal exhibit maxima in the temperature range 600-800°C. This result is consistent with an earlier observation that the sulfur content of coke reaches a minimum around 700 to 800°C. The production of hydrogen sulfide, the major volatile sulfur species, recommences only around 1100°C.

Several factors might account for the observed maxima in the sulfur volatilization curves for the fluidized bed. At temperatures above about 750°C, internal sintering of coal begins to take place, leading to a lowered porosity and a decreased ability of the hydrogen sulfide evolved to escape. At the same time, the evolved hydrogen sulfide reacts to an increasing extent with such mineral constituents of coal as calcium, iron, and magnesium oxides and carbonates, forming sulfides and thereby retaining the sulfur in the char.

In the pyrolysis of subbituminous coal in the fixed-bed reactor, the asymptotic sulfur volatilization did not exhibit a



**Figure 1.** Fractional devolatilization in the slow and rapid pyrolysis of several coals.

maximum, but increased monotonically with temperature, approaching a release of 50% above 900°C. The same behavior was observed earlier for the crucible pyrolysis of lignite and bituminous coals. Further experiments to clarify the differences in behavior between the fixed- and fluidized-bed reactors are currently under way.

### Production of Tar and Water

The yields of tar and the principal pyrolysis gas species are shown in Figure 2. For clarity of presentation, data points are omitted in this and subsequent figures. They are in plots in the report.

As Figure 2 shows, tar was the major volatile species formed in the pyrolysis of the subbituminous coal, with production reaching a maximum at 600-700°C. Significantly less tar was evolved from the lignite. Above 700°C, the drop in tar production due to the cracking of the tar resulted in an increase in the gas fraction of the volatiles. The relatively low tar yield from the lignite, taken in conjunction with the relatively high oxygen content of this coal, supports an earlier observation that the oxygen content of the feedstock sup-

presses tar yields by a phenolic condensation mechanism.

The production of water from the pyrolysis of lignite in the fluidized bed was found to be greater than that from subbituminous coal. A similar result was obtained earlier in the rapid pyrolysis of lignite and bituminous coal. The production of pyrolytic water for the fluidized-bed pyrolysis of lignite decreased at temperatures above 800°C, paralleling an earlier result for the rapid pyrolysis of a lignite.

Overall mass, oxygen, and hydrogen balances for fluidized-bed pyrolysis of lignite support the observation that volatilized oxygen shifts from pyrolytic water to carbon monoxide as the temperature increases, reflecting the increasing rate of the steam/char reaction yielding carbon monoxide and hydrogen.

### Pyrolytic Gases

Plots of asymptotic yields of major pyrolytic gas species vs. temperature for the fluidized-bed pyrolysis of subbituminous coal and lignite are given in Figure 2. For both coals, asymptotic yields of

hydrogen, carbon monoxide, and methane increased with temperature. Carbon dioxide was the principal gaseous product at most temperatures studied. The carbon dioxide production increased with temperature up to 900°C, and then leveled off for subbituminous coal and decreased for lignite. Carbon monoxide was the most abundant gas species above 900°C.

Comparing carbon oxide yields from the fluidized-bed pyrolysis of the two feedstocks shows that greater yields of carbon monoxide and carbon dioxide were obtained from lignite than from subbituminous coal. Earlier, similar results were reported for rapid pyrolysis. Heating rate apparently has little effect on carbon monoxide formation, while more carbon dioxide is obtained in slow pyrolysis.

Yields of aliphatic hydrocarbons are shown in Figure 3. Methane was the predominant aliphatic hydrocarbon produced from the fluidized-bed pyrolysis of subbituminous coal and lignite. The production of methane in the fluidized bed increased with temperature, with greater yields from subbituminous coal than from lignite. The yields of methane

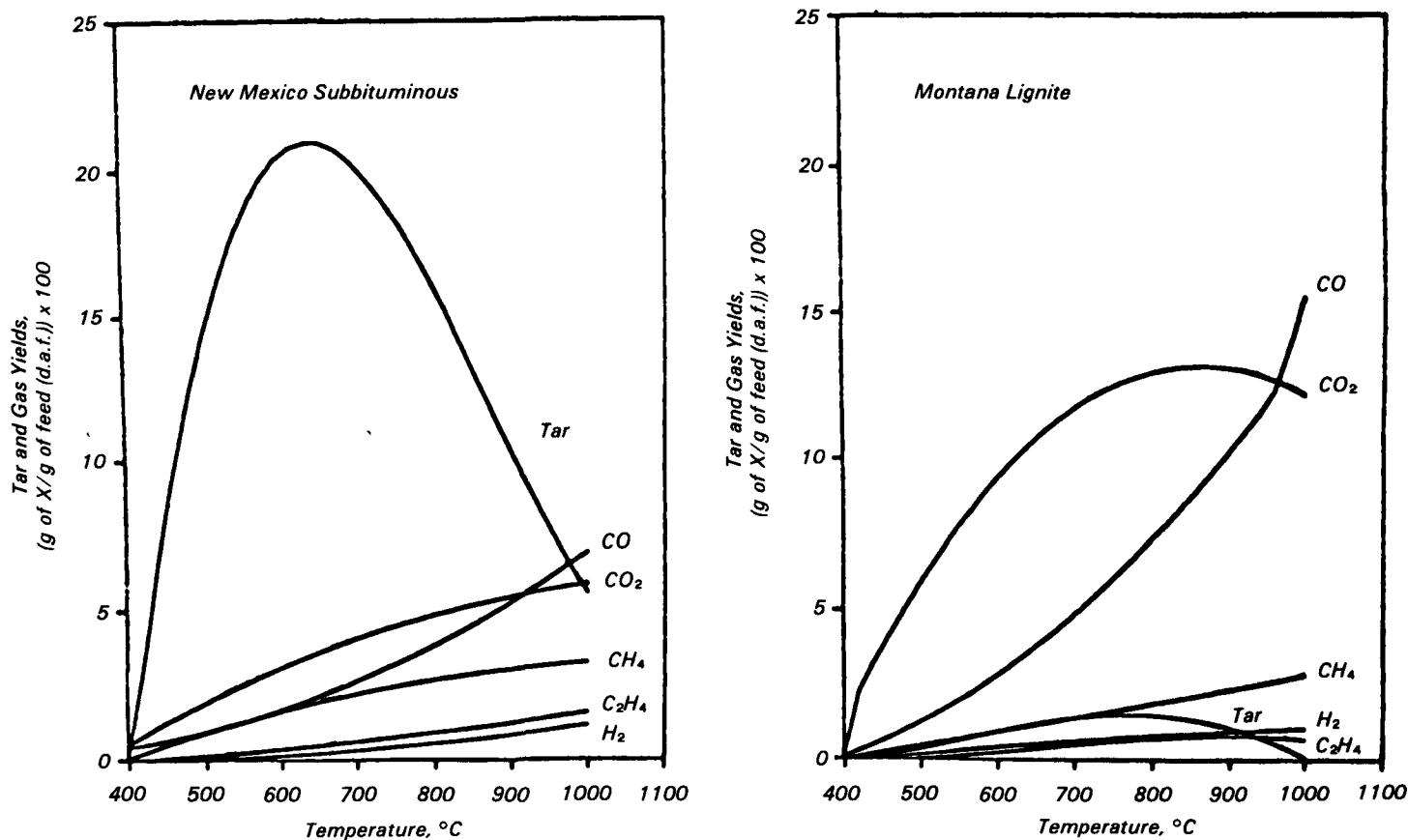


Figure 2. Yields of tar and gases from the pyrolysis of two coals.

from slow pyrolysis were greater than reported yields from fast pyrolysis.

The results shown in Figure 3 indicate that the asymptotic yields of aliphatic hydrocarbon species were greater for subbituminous coal than for lignite, and the yield of each alkene was greater than that of the corresponding alkane for the same coal. Ethylene yields increased with temperature for fluidized-bed pyrolysis of subbituminous coal, but decreased for lignite at temperatures above 900°C. Yields of all aliphatics larger than ethylene were maximized between 700 and 800°C.

At temperatures below 700°C, yields of benzene, toluene, and xylene were similar for both subbituminous coal and lignite feedstocks. (See Figure 4.) The production of benzene increased dramatically at temperatures above 700°C. For both feedstocks, the yields of toluene and xylene at temperatures above 700°C showed marginal increases relative to the benzene yields. At 1000°C the yield of benzene was about 10 times greater than that of xylene and 3 times greater than that of toluene.

Sulfur gas species found in the pyrolysis products include hydrogen sulfide, carbonyl sulfide, methyl and ethyl mercaptans, and carbon disulfide. Yields of these species are shown in Figures 5 and 6. Hydrogen sulfide was by far the predominant sulfur species formed. The decrease in the hydrogen sulfide yield for the slow pyrolysis of both coals at temperatures above 800°C is consistent with an earlier view that the volatilization of sulfur at these temperatures is limited by mass transfer.

Yields of carbonyl sulfide were two to three times greater for the subbituminous coal than for the lignite. At temperatures above 700°C, further carbonyl sulfide production was marginal. Yields of thiophene were similar for both feedstocks. Yields of methyl mercaptan for both coals showed maxima at about 700°C.

Carbon disulfide was produced from the pyrolysis of subbituminous coal in both the fluidized- and fixed-bed reactors at temperatures above 800°C. It was not produced in the fluidized-bed pyrolysis of lignite. Conversely, ethyl mercaptan was

produced in the fluidized-bed pyrolysis of lignite, but did not appear in the products of either the fixed- or fluidized-bed pyrolysis of subbituminous coal.

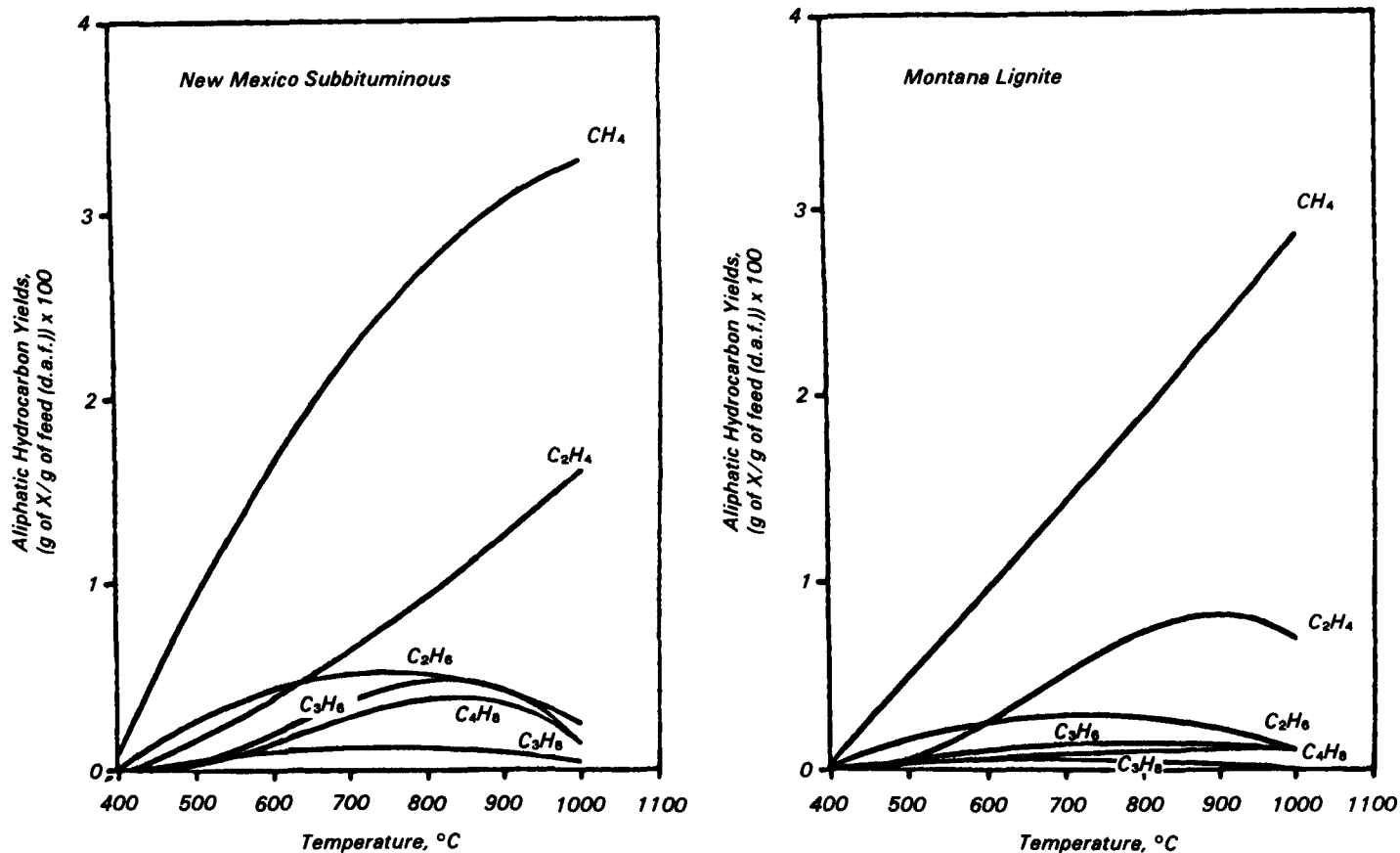
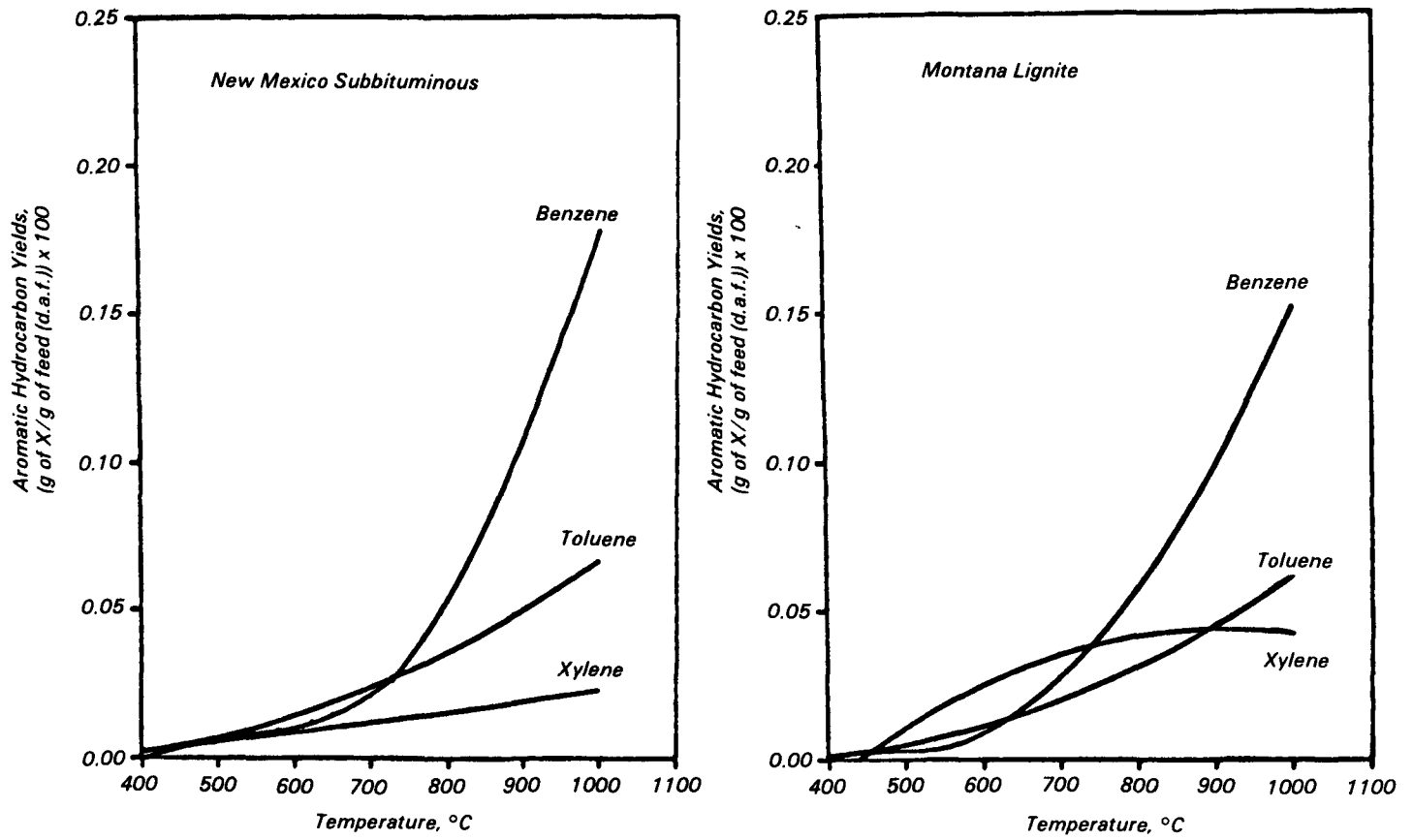


Figure 3. Yields of aliphatic hydrocarbons from the pyrolysis of two coals.



**Figure 4.** Yields of aromatic hydrocarbons from the pyrolysis of two coals.

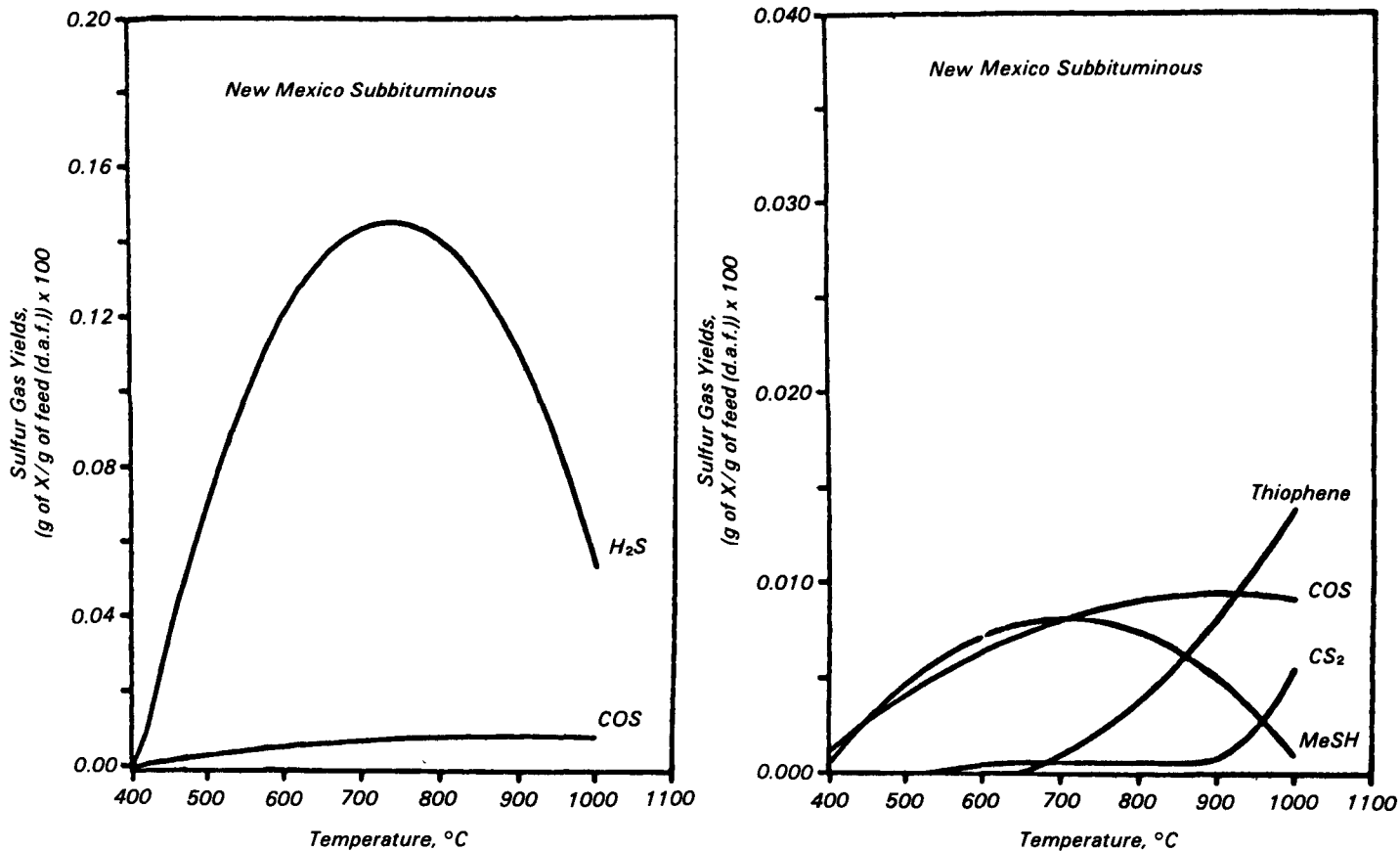


Figure 5. Yields of sulfur gases from the pyrolysis of two coals.

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N. Dean Smith is the EPA Project Officer (see below).

The complete report, entitled "Analysis of Volatile Products from the Slow Pyrolysis of Coal," (Order No. PB 84-230 036; Cost: \$11.50, subject to change) will be available only from:

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The EPA Project Officer can be contacted at:

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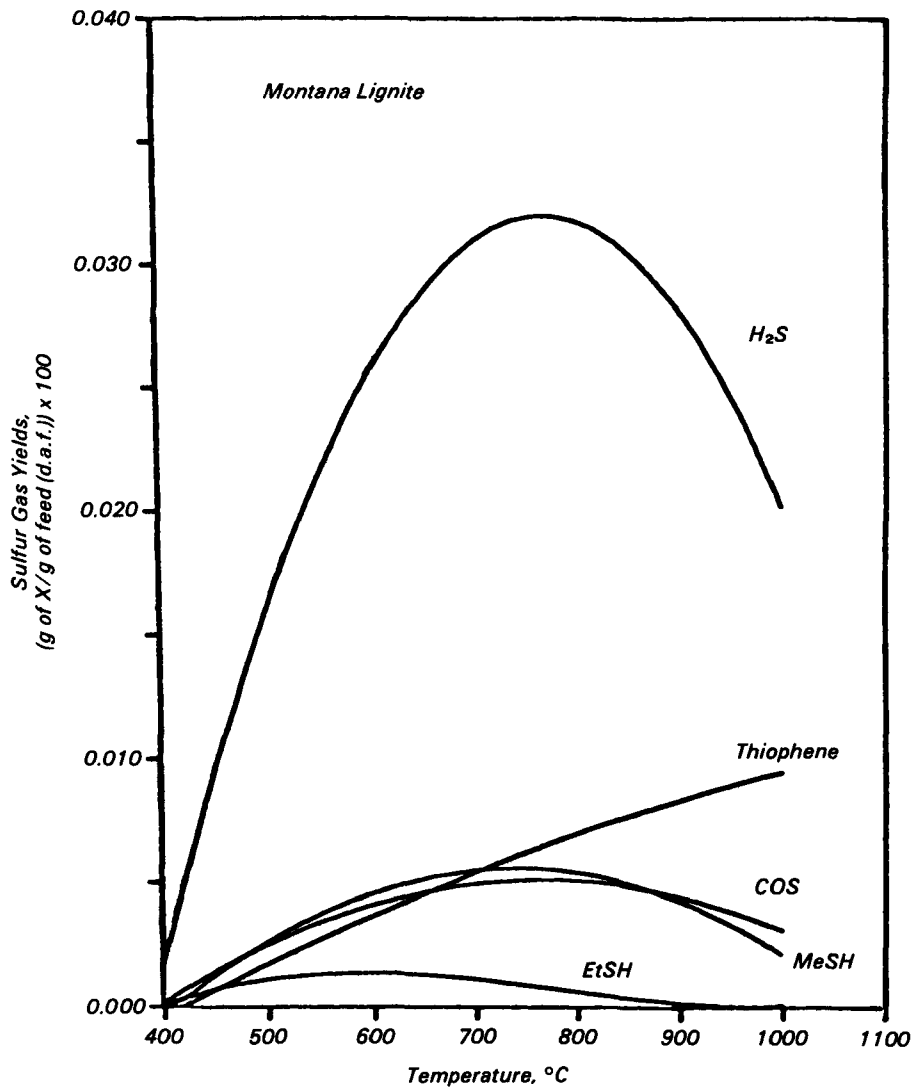


Figure 6. Yields of sulfur gases from the pyrolysis of lignite.

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