

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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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

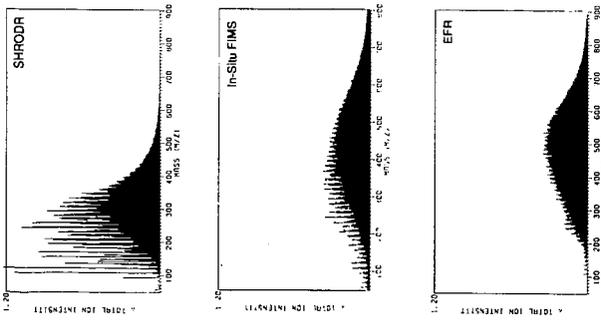


Fig. 1 - FIMS Spectra from Upper Freeport Coal

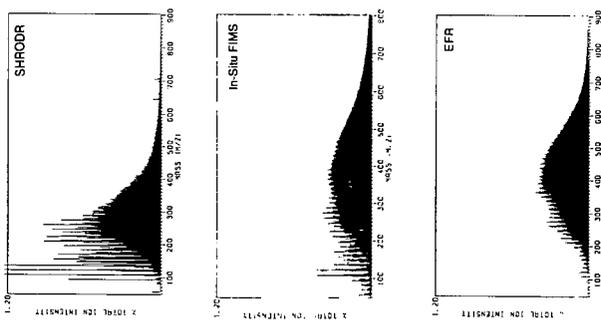


Fig. 2 - FIMS Spectra from Pittsburgh No. 8 Coal

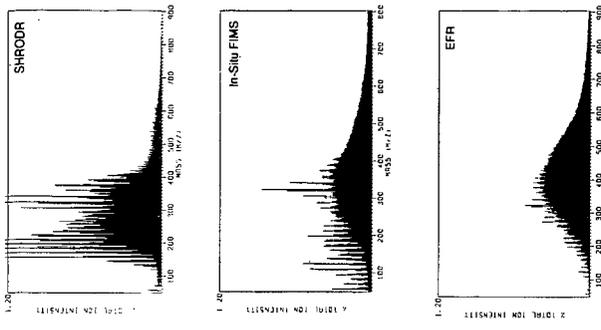
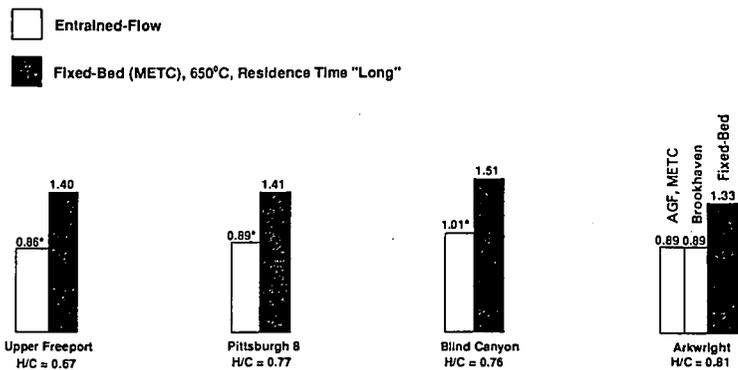


Fig. 3 - FIMS Spectra from Utah Blind Canyon Coal

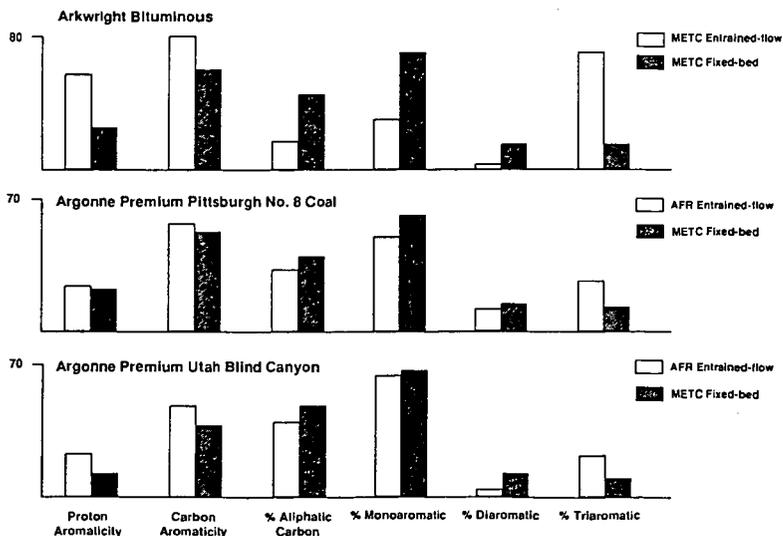
Fig. 4 - Comparison of H/C of Coal Pyrolysis Liquids Generated in Fixed-Bed and Entrained-Flow Reactors



* 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)



C89-0869-3 AA5

Coal volatiles post pyrolysis in a two staged reactor

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INTRODUCTION

The aim of this paper is to present some new results about volatiles post pyrolysis of the low rank, french, Gardanne coal. Direct pyrolysis of this peculiar coal has been earlier described, with special consideration of light gases release (1)(2) and solid evolution (3)(4). Focusing now on volatiles transformation, we use a two staged reactor where volatiles, produced in the first stage, undergo post pyrolysis in the second stage. After a first study where second stage temperature was kept close to first stage temperature (5), one observation is enlarged here to a wider second stage temperature range.

Compared to other coal tar pyrolysis studies where products are collected at the end of experiments (6)(7)(8)(9), one experimental device is designed as to follow light gases flow rates during post pyrolysis experiments as a function of volatiles production temperature in first stage and of post pyrolysis temperature in second stage.

EXPERIMENTAL

The Gardanne, or Provence, french coal studied here is a low rank one, from Upper Cretaceous, with following characteristics :

Prox. anal. (wt %) - Moisture : 9.6, Ash : 7.4, VM : 45.1

Ult. anal. (wt %, daf) - C : 74.9, H : 5.3, O : 11.3, N : 2.0, S : 5.4

The two staged reactor has been already described (2)(5). It is composed of two stainless steel cylindrical stages series connected and independently heated. Coal sample of 10 g were placed as a thin bed in middle of first stage, supported by carborundum particles deposited on the steel grid present at the bottom of each stage. Carborundum particles also filled second stage as to ensure thermal equilibrium. Coal particles were sized between 0.4 mm and 0.5 mm so that coal bed was formed, on an average, of four particles layers. Carrier gas was N₂ which entered first stage with 33 cm³min⁻¹ flowrate. Gaseous effluent was cooled in two successive traps and, after partial condensation, introduced into GC for analysis.

For each experiment, once the reactor was filled and fitted as above described, second stage was heated up to the predetermined T₂ value while N₂ flowed across the whole reactor and first stage remained at ambient temperature. When the predetermined T₂ value was

reached, it was held constant and first stage began to be heated at $3^{\circ}\text{C min}^{-1}$ heating rate : temperature T_1 of first stage was then measured at the same time that gases were introduced in GC.

RESULTS AND DISCUSSION

General features and results presentation

In one stage experiments, it was found that among the nine gases studied, four were largely predominant (CO , CO_2 , H_2 , CH_4) and five appeared as minor gases (C_2H_4 , C_2H_6 , C_3H_6 , C_3H_8 , H_2S). For the last three gases, flow rate which was already very low in one stage experiments became lower in two stages experiments and rapidly undetectable with increasing T_2 values. In sake of illustrating T_2 influence upon gases flow rate, results are presented as flow rate v.s. T_2 curves for CH_4 , H_2 , CO , CO_2 , C_2H_4 and C_2H_6 (fig. 1 to 6) and as flow rate v.s. T_1 curves for C_3H_6 , C_3H_8 and H_2S (fig. 7 to 9).

When flow rates are plotted against second stage temperature for different T_1 values, post pyrolysis of volatiles, main purpose of these experiments, is only concerned by T_2 values higher than T_1 . However results for T_2 lower than T_1 are also quoted : they show how volatiles cooling in second stage may influence gases flow rates, keeping in mind that this cooling always maintain volatiles above 600°C .

Increasing first stage temperature, T_1 became equal to T_2 and situation occurred where volatiles were kept in second stage at their production temperature in first stage. Compared to one stage experiments, two stages experiments lead thus to increase residence time of volatiles at their production temperature, giving indication upon residence time influence on gases flow rate.

Although main purpose of this study was volatiles post pyrolysis on an, as possible, inert solid, when second stage temperature exceeded 700°C , coke was found in second stage, deposited on carborundum particles and internal reactor walls. In conditions described in experimental part, and taking into account that apparatus was not conveniently suitable for quantitative solid recuperation, coke traces are observed at 800°C and averaged weights of 40 mg and 500 mg respectively measured at 900°C and 1000°C .

Carbon dioxide

Before coke deposition, T_2 rise has a positive effect on CO_2 flow rate (fig. 1). With coke present in second stage, at T_2 higher than 800°C , two different effects are observed according to first stage temperature range : the effect of T_2 rise is positive for low values of T_1 (500 to 600°C) and negative for higher T_1 values. Cooling volatiles from 700°C and 800°C to lower temperatures decreases CO_2 flow rate.

Volatiles are assumed to contain CO₂ precursors which require for decomposition temperatures higher than their production temperature in first stage. Decomposition into CO₂ is also enhanced by longer residence time, as we observed positive effect of residence time upon CO₂ flow rate at 700°C and 800°C. These decomposition reactions appear to be reversed when cooling volatiles from 700°C and 800°C to lower temperature. Above 800°C, T₂ value, CO₂ flow rate increase is related to reaction with deposited coke, this reaction being less complete when volatile are produced at low T₁ (500°C to 600°C).

Carbon monoxide

In absence of coke, CO flow rate is little changed by post pyrolysis temperature rise. Compared to one stage experiments, two stages experiments lead to CO flow rate decrease of about 25 % for 600 to 800 common values of T₁ and T₂. Inversely cooling volatiles from 600°C to 700°C increases CO flow rate (fig. 2). In presence of coke, CO flow rate increases with T₂ rise, for all T₁ values and this increase is more important the lower the volatiles production temperature T₁.

These results do not allow definitive conclusions about predominance of CO production or consumption reactions involatiles below 800°C: we may only conclude to existence of such reactions from decrease of CO flow rate for higher residence time and from CO increase when cooling volatiles. At higher temperature of second stage, when coke is deposited, CO flow rate increase is partly ascribed to reaction of CO₂ with coke, what explains also CO₂ flow rate decreases observed on figure 1. Other part of CO production increase is assumed to reaction between coke and water produced in primary pyrolysis and present in volatiles released below 600°C.

Hydrogen

Variations of H₂ flow rate with second stage temperature seem qualitatively like CO ones, with H₂ flow rate about twice CO one (fig. 3). Below 800°C, effect of T₂ rise is weakly positive, effect of residence time is negative except for 800°C where it becomes unappreciable and cooling volatiles decreases H₂ flow rate. Above 800°C, T₂ has positive effect upon H₂ flow rate and this effect is more important when volatiles are produced below 600°C than when produced above 600°C.

In absence of coke, H₂ flow rate variations result from competition between H₂ producing and H₂ consuming reactions which may be mainly hydrocarbons cracking, deshydrogenation and aromatisation of H₂ production and hydrocracking for H₂ consumption. From our observations, in this competition H₂ producing reactions would be favoured by higher post pyrolysis temperature while H₂ consuming ones would be promoted by longer residence time and lower temperature. In presence of coke (at the end of experiment), as for CO, H₂ flow rate increase may be partly ascribed to water reaction with coke, forming simultaneously CO and

H₂, when volatiles are produced below 600°C and contain thus quantity of water. For T₁ value above 600°C, volatiles do not contain more water and H₂ production is only related to aromatisation and cokefaction.

Methane

CH₄ flow rates are in the range of H₂ ones, but evolution with T₂ is quite different (fig. 4). Up to 650°C T₁ value, CH₄ flow rate show two maxima, for T₂ values of 700°C and 850°C, and a minimum between 750°C and 950°C. For T₁ higher than 650°C, CH₄ flow rate decreases when T₂ varies from 800°C to 1000°C. Cooling volatiles from 700°C and 800°C to lower temperature in second stage decreases CH₄ flow rate and residence time has positive effect upon this flow rate, of 60 % at 700°C and 480 % at 800°C.

CH₄ production in second stage is ascribed to cracking and hydrocracking reactions below 800°C T₂ value and to cokefaction above 800°C. Parallel to cracking and hydrocracking reactions, aromatisation occurs when T₂ rises above 700°C, decreasing thus CH₄ flow rate after the maximum shown at 700°C. Above 800°C, cokefaction occurs and releases CH₄, what increases CH₄ flow rate till maximum at 950°C, above which temperature cokefaction does not release more CH₄. CH₄ precursors chemical groups appear to be different for cracking reactions and cokefaction, as first maximum related to cracking reactions increases for higher T₁ values and second maximum, related to cokefaction, decreases for higher T₁ values.

C₂ hydrocarbons

C₂H₄ flow rate evolution looks like CH₄ one when T₂ increases with two maxima, at 700°C and 950°C, for T₁ lower than 700°C and with a rapid decrease for T₁ higher than 700°C (fig. 5). Maximum at 700°C is assumed to result from competition between cracking and deshydrogenation reactions, predominant below 700°C, and aromatisation reactions which prevail above 700°C.

C₂H₆ evolution is different from C₂H₄ one, specially by shifting of maximum flow rate to higher T₂ values when T₁ increases (fig. 6). Assuming that C₂H₆ decomposition reaction is the same, very probably deshydrogenation, for all T₁ values, maximum shifting is ascribed to difference in chemical nature of C₂H₆ precursors when volatiles production temperature varies.

C₃ hydrocarbons and hydrogen sulfide

C₃ hydrocarbons and hydrogen sulfide rapidly disappear from volatiles when second stage temperature increases (fig. 7, 8, 9). For C₃ hydrocarbons, it is evident that disappearance is related to numerous consumption reactions like cracking, deshydrogenation and aromatisation. H₂S is known to decompose in the temperature range of second stage operating.

CONCLUSION

The above experiments of coal volatiles post pyrolysis in a two staged reactor give informations upon respective influence of pyrolysis and post pyrolysis temperatures on light gases production. Such two stages experiments allow to relate light gases production to volatiles composition and to distinguish between temperature ranges where solid coke is, or not, deposited. Results confirm influence of residence time upon post pyrolysis reactions and go further in details of peculiar effects. Slow cooling of volatiles, in temperature range where they remain reactive, modify gaseous flow rates, indicating thus volatiles evolution between reacting place and analysis inlet.

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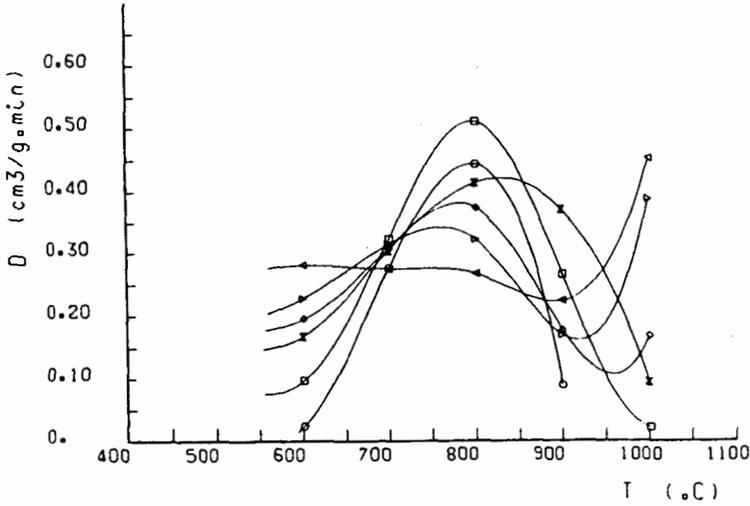


FIG 1 CO₂ FLOW RATE VS SECONO STAGE TEMPERATURE
 FIRST STAGE TEMPERATURE:
 ▲ 500°C, ▷ 550°C, ○ 600°C, ⊗ 650°C, ◻ 700°C, ○ 800°C

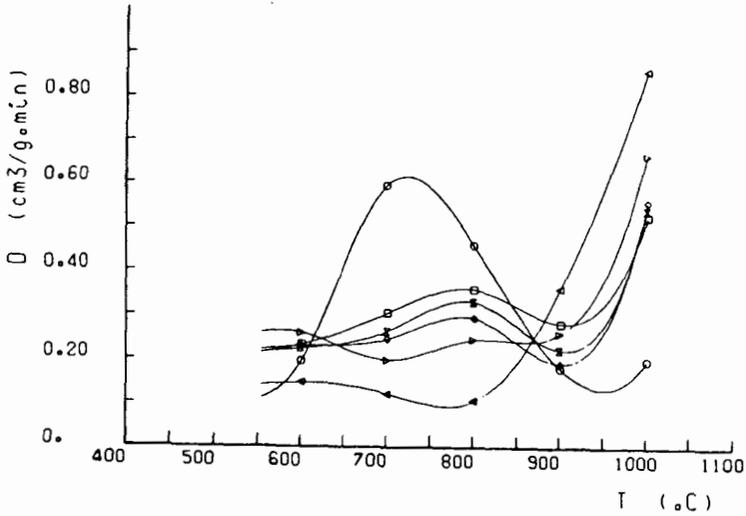


FIG 2. CO FLOW RATE VS SECOND STAGE TEMPERATURE
 FIRST STAGE TEMPERATURE:
 ▲ 500°C, ▷ 550°C, ○ 600°C, ⊗ 650°C, ◻ 700°C, ○ 800°C

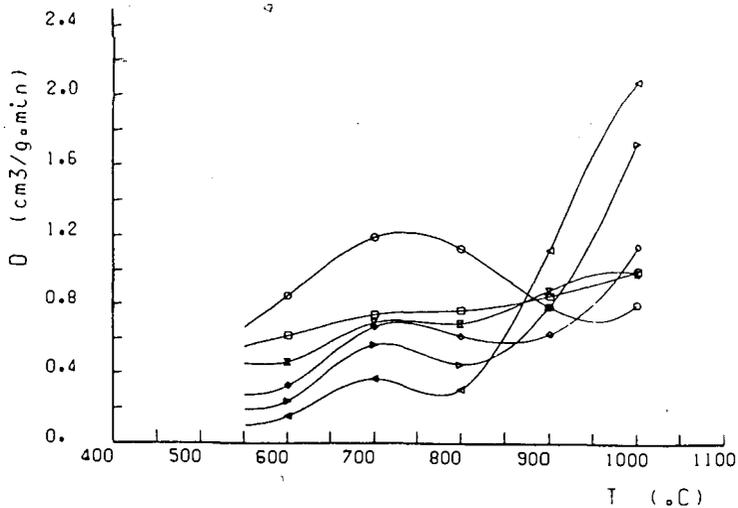


FIG 3 H₂ FLOW RATE VS SECOND STAGE TEMPERATURE
 FIRST STAGE TEMPERATURE:
 ◀ 500°C, ▷ 550°C, ○ 600°C, ⋈ 650°C, □ 700°C, ○ 800°C

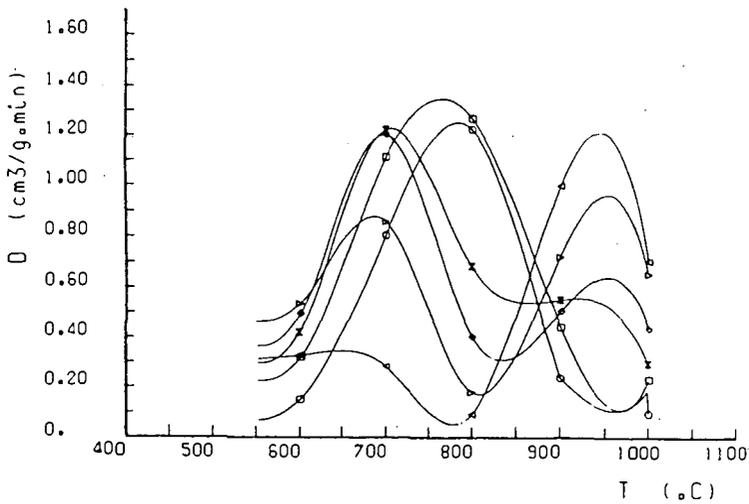


FIG 4 CH₄ FLOW RATE VS SECOND STAGE TEMPERATURE
 FIRST STAGE TEMPERATURE:
 ◀ 500°C, ▷ 550°C, ○ 600°C, ⋈ 650°C, □ 700°C, ○ 800°C

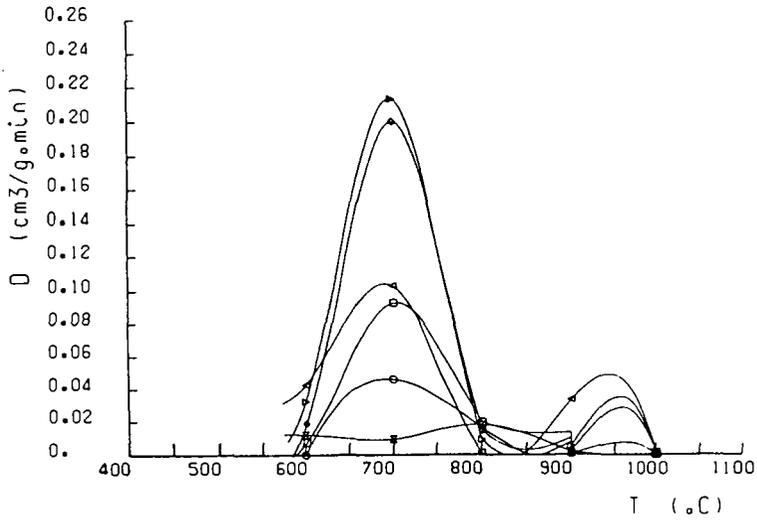


FIG 5 C₂H₄ FLOW RATE VS SECOND STAGE TEMPERATURE
 FIRST STAGE TEMPERATURE :
 △ 500°C. ▽ 550°C. ○ 600°C. × 650°C. □ 700°C. ◇ 800°C

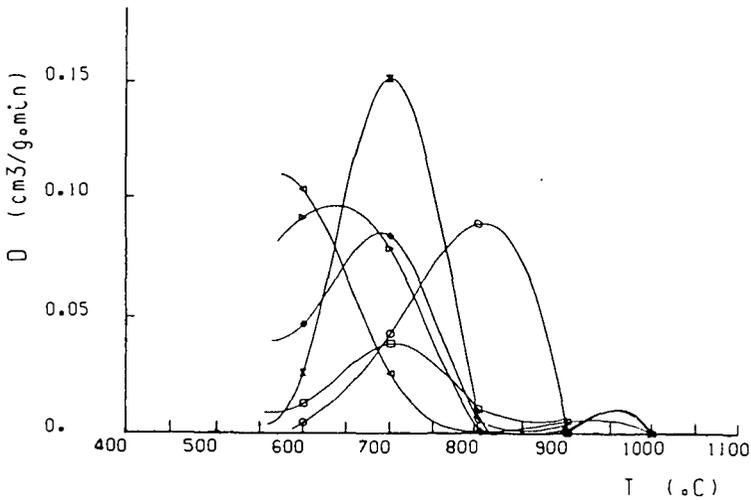


FIG 6 C₂H₆ FLOW RATE VS SECOND STAGE TEMPERATURE
 FIRST STAGE TEMPERATURE :
 △ 500°C. ▽ 550°C. ○ 600°C. × 650°C. □ 700°C. ◇ 800°C

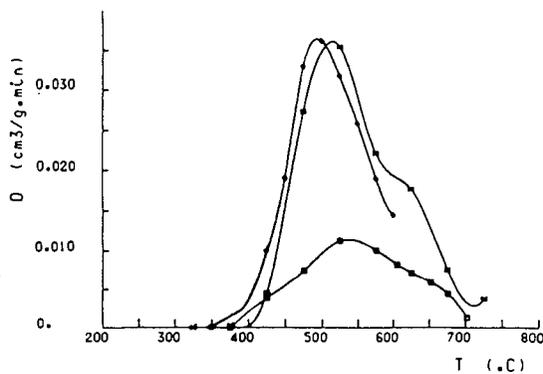


FIG 7 C_2H_4 FLOW RATE VS FIRST STAGE TEMPERATURE
SECOND STAGE TEMPERATURE
 \circ $600^{\circ}C$, \square $700^{\circ}C$, ONE STAGE $2\text{-}n$

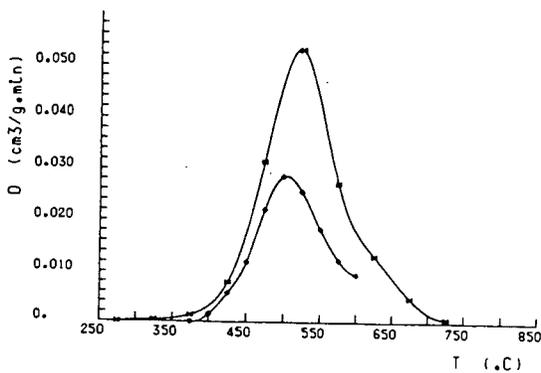


FIG 8 C_2H_4 FLOW RATE VS FIRST STAGE TEMPERATURE
SECOND STAGE TEMPERATURE
 \circ $600^{\circ}C$, \square $700^{\circ}C$, ONE STAGE $2\text{-}n$

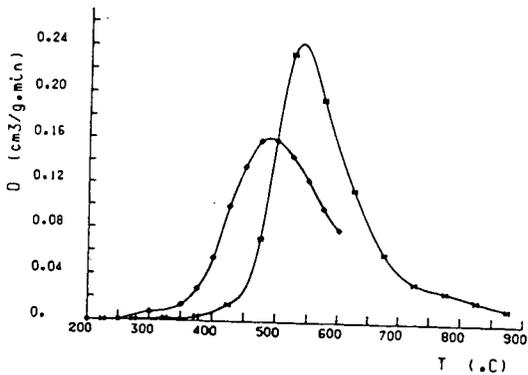


FIG 9 H_2S FLOW RATE VS FIRST STAGE TEMPERATURE
SECOND STAGE TEMPERATURE
 \circ $600^{\circ}C$, \square $700^{\circ}C$, ONE STAGE $2\text{-}n$

A NOVEL METHOD FOR FLASH PYROLYSIS OF COAL

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Introduction

Flash pyrolysis of coal is a promising process for producing chemicals such as benzene, toluene and xylene (BTX). But, the yield of liquid products including BTX (tar) is limited because of low hydrogen to carbon ratio in coal. It is necessary to supply hydrogen to coal efficiently for increasing the tar yield. Hydropyrolysis is one of the means to supply hydrogen to coal. This is, however, realized under only severe reaction conditions: high hydrogen pressure, high temperature and long residence time.

Recently, several attempts have been made to supply atomic hydrogen or radicals from super critical steam^{1,2)} or solvents³⁾ to coal. This paper presents a new efficient method for increasing both the conversion and the tar yield in which the coal swollen by solvents was pyrolyzed in a flash mode in an inert and a hydrogen atmospheres. We will show drastic increase of coal conversion and tar yield are brought about by a physical effect and effective hydrogen transfer from/via tetralin.

Experimental

Sample Preparation

A Japanese coal, Taiheiyo coal, was used as a raw coal. Its properties are given in Table 1. The coal was ground and the particles less than 74 μm were used. The coal was dried in vacuo at 110 °C for 1 h before use.

The coal particles were mixed with tetralin by the ratio of 10 to 6 by weight, then heated to the temperatures between 25 and 350 °C under the 1 MPa of nitrogen. By this treatment coal particles were swollen, and tetralin was retained in the coal matrix. This sample is abbreviated to tetralin treated coal (TTC).

The tetralin treated coal was degassed at 70 °C in vacuo for 1 h to completely remove the retained tetralin (vacuum dried coal; VDC). When the swelling is irreversible, swollen but tetralin free coal is obtained. This sample was pyrolyzed to examine the physical effect of swelling on the pyrolysis. Several partially degassed samples were also prepared to examine the effect of the amount of tetralin retained on the pyrolysis.

Char produced under a high temperature pyrolysis of Taiheiyo coal, this is not pyrolyzed further, was also treated by tetralin in the same manner as was employed to prepare TTC. This sample was pyrolyzed

to obtain the yield of each component from tetralin. This result was utilized to estimate the contribution of pyrolysis of tetralin on the product yields from TTC. Thus, four kind of samples were prepared from the Taiheiyo coal.

Flash pyrolysis of samples

Samples prepared above were pyrolyzed in an inert and high-pressure hydrogen atmospheres. Pyrolysis in the inert gas of atmospheric pressure was performed using a Curie-point pyrolyzer (Japan Analytical Ind., JHP-2S). About 2 mg of sample were wrapped in a ferromagnetic foil, and heated up to a temperature between 650 to 920 °C at the rate of 3000 °C/s by induction heating coil to be pyrolyzed rapidly. The products were immediately cooled down by the inert gas of high flow rate. Then, the tar was trapped completely by the silica wool placed just below the foil. The inorganic gases and hydrocarbon gases were led to gas chromatograph and analyzed. On the other hand, the pyrolysis under high pressure was performed using a specially designed Curie-point pyrolyzer. This reactor consisted of high pressure vessel and a quartz reactor as shown in Fig. 1. This was designed to keep the inner and outer pressure of the reactor same. About 5 mg of sample were pyrolyzed at 764 °C under 0.1 to 7.5 MPa of hydrogen. Produced tar was again trapped by the silica wool, but produced gases were collected in a gas holder once. Then a part of gas was introduced to a gas chromatograph to be analyzed. The column used was Porapak Q. The yields of char and tar were measured from the weight changes of the foil and the reactor. The same experiment was performed several times to check the reproducibility of experiment.

Analysis of structure change of coal by swelling

The swelling ratio, elemental composition, the pore volume and the surface area were measured to examine the change of coal structure by swelling. The swelling ratio of tetralin-treated coal was measured by volumetric method^{6,7)}. The pore volume and surface area of raw coal and TTC were calculated from the adsorption isotherm of CO₂ measured at 0 °C. Furthermore, to estimate the interaction between coal surface and tetralin, the thermal desorption curve of tetralin from the TTC was measured under the heating rate of 5 °C/min using a thermobalance (Shimazu Co. Ltd., TGA 50).

RESULTS AND DISCUSSION

Effect of pretreatment temperature on product distribution

Figure 2 shows the change of swelling ratio of TTC and VDC against swelling temperature. Taiheiyo coal began to swell by tetralin at 70 °C, and the swelling ratio reached 1.34 at above 170 °C. Taiheiyo coal swollen at below 100 °C shrank reversibly to its original state by vacuum drying, but the coal swollen at above 100 °C did not shrink completely, and the swelling at 250 °C was almost irreversible. At 250 °C, the coal structure was expected to change as mentioned in earlier works^{6,7)}. The micropore volume and the internal surface area of VDC of coal swollen at 250 °C were larger than those of raw coal

as shown in Table 2.

Figure 3 shows the curves of the thermal desorption of tetralin from TTC. Since tetralin desorbs at higher temperatures from the coal treated above 100 °C as compared with that treated at 25 °C, the interaction between coal and tetralin is stronger for the coals treated above 100 °C. Coals treated by tetralin at several temperatures were pyrolyzed at 764 °C under 0.1 MPa of He. The product yield of each component of treated coal, Y_i , was represented based on daf coal excluding the yield from the pyrolysis of tetralin. The yield, Y_i , is defined by

$$Y_i = \{(\text{Yield from TTC}) - w(\text{Yield from solvent})\} / (1-w) \quad (1)$$

where w is the weight fraction of tetralin in TTC.

Figure 4 shows the tar yield against the swelling temperature. The tar yield was same as that of raw coal at the swelling temperature of 25 °C, but it reached about 1.5 times larger than that of raw coal at 100 to 250 °C. This result and Figure 3 show only the tetralin retained strongly by coal is effective to increase the tar yield.

The tar yield decreased at the swelling temperature of 350 °C, because the coal was almost decomposed during the treatment at this temperature. From above results, the swelling temperature was decided to be 250 °C.

Effect of the amount of tetralin in the coal

The effect of the amount of tetralin retained in the coal on the tar yield was examined at the pyrolysis temperature of 764 °C. The amount of tetralin was varied by changing the vacuum drying time of TTC prepared at 250 °C. Figure 5 shows the tar yield during the flash pyrolysis against the amount of tetralin retained in the coal. The sample of zero tetralin content was completely dried one (VDC). Even a trace of tetralin was not detected in this sample, judging from the mass balance during the vacuum drying and the FTIR measurements. Since the VDC is still swollen by 30 %, this coal has much larger pore volume than the raw coal. The tar yield of the VDC was about 4 wt.% larger than that of raw coal. This means that the pore enlargement by swelling increases the tar yield. This is just a physical effect. On the other hand, the gradual increase of the tar yield with the increase of tetralin content is the chemical effect produced by tetralin. These are discussed in more detail in relation to the yields of the other products in the next section. The tar yield of the coal treated at 25 °C is almost same as that of raw coal as stated earlier.

Flash Pyrolysis in an Inert Atmosphere

Figure 6 shows the char yields of TTC, VDC and raw coal against the pyrolysis temperature. The char yield of TTC is lower than that of raw coal at all the temperature by 4 to 10 wt.%. The char yield of VDC is also 4wt.% lower than that of raw coal. These results show the swelling of coal by tetralin is effective to increase the conversion

of coal into gas and liquid. This effect was brought about from the pore enlargement and the tetralin retained strongly in the coal as stated earlier.

Figure 7 shows the tar yield. The tar yield of TTC increased drastically up to 30 wt.% daf at the pyrolysis temperature of 764 °C, which was 1.5 times larger than that of raw coal. This indicates the effectiveness of the proposed method for increasing the liquid product. The tar yield of TTC at 920 °C, however, was almost equal to that of raw coal. The trend of tar yield of TTC with the temperature is similar to that of the H₂ yield from the pyrolysis of tetralin. On the other hand, the tar yield of vacuum dried coal increased by 4 wt.% irrespective of pyrolysis temperature, as compared with that of raw coal. Figures 8 and 9 show the yields of other products. The inorganic gas (IOG) yield was nearly equal between three samples. The hydrocarbon gas (HCG) yield and the total yields of benzene, toluene and xylene (BTX) were nearly equal at the temperatures lower than 764 °C. These yields of TTC at 920 °C, however, were larger than those of the other two samples. The H₂ yield of TTC was smaller than that of raw coal at temperatures lower than 800 °C, but exceeded that of raw coal at 920 °C. The H₂ yield of VDC was almost same as that of raw coal at all temperatures.

The physical effect and the effect of hydrogen donability of tetralin are summarized from above results as follows: The increase of micropore caused by tetralin pretreatment facilitated the escape of the tar vapor, which would be stabilized as char, from coal particles. Then the tar yield of VDC was increased at all the temperatures. On the other hand, the effect of hydrogen donability from the tetralin to coal depends on the pyrolysis temperature.

The conversion of coal to volatile matter is expected to increase when hydrogen atom is supplied timely to the reactive fragments of coal which would be stabilized as char without hydrogen supply. At both 670 and 764 °C, the char yield of TTC was smaller than that of VDC. So, hydrogen atom was effectively transferred from tetralin to the coal fragments at these temperatures. This is substantiated by the small H₂ yield and large tar yield of TTC at these temperatures. This indicates that the rates of the dehydrogenation of tetralin and the formation of coal fragments matched well at these temperatures. Then the mechanism of the pyrolysis of TTC is schematically represented as given in Fig. 10.

On the other hand, the char yield of TTC was almost same as that of VDC at 920 °C. So, tetralin did not contribute to increase the conversion of coal at this temperature, but contributed to increase the yields of light hydrocarbons as shown in Fig. 8. This was supposed to be brought about by the radicals produced by the decomposition reaction of tetralin, which was prevailing over the hydrogenation reaction at this temperature. The radicals were very reactive, and decomposed primary pyrolysis products of coal, though the reaction mechanism is not clear now.

Pyrolysis in hydrogen atmospheres

It has been reported that the yield of volatile matter during flash pyrolysis decreases with increasing hydrogen pressure⁸⁻¹⁰. This is said to be because the escape of tar vapor from coal particles is suppressed under pressurized conditions. The flash hydrolypyrolysis of TTC, however, is, as it were, liquefaction within the pore space. Therefore, the increase of tar yield is expected under pressurized hydrogen.

Figure 11 shows the hydrogen pressure dependency of the char yields of TTC, VDC and raw coal at the pyrolysis temperature of 764 °C. The char yield of VDC was smaller than that of raw coal by 2 to 4 wt.%. This was considered to be brought about by the pore enlargement. The char yield of TTC was smaller than that of VDC and tended to decrease with increasing hydrogen pressure. This means that the tetralin treatment is more effective for the pyrolysis in high pressure hydrogen. This is because molecular hydrogen is expected to be transferred to the reactive coal fragments via tetralin as is transferred in coal liquefaction. The char yields of both VDC and raw coal did not decrease with increasing hydrogen pressure contrary to previous works⁸⁻¹⁰. We examined the effect of hydrogen flow rate on the char yield, and found that the char yield increases significantly with increasing pressure under low hydrogen flow rate as reported previously. The increase of char yield was suppressed with increasing hydrogen flow rate. So, our experiments were all performed under high hydrogen flow rate. This is the reason that our char yield did not decrease with increasing hydrogen pressure.

Figure 12 shows the tar yields corresponding to Fig. 11. The tar yield of TTC increased with the increase of hydrogen pressure, and reached up to 38 wt.% at 5 MPa, which was 1.8 times larger than that of raw coal. This clearly shows that proposed method is effective for increasing the tar yield as well as the coal conversion, especially in high pressure hydrogen atmospheres. Both tar yields of VDC and raw coal decreased with increasing hydrogen pressure. This was due to the decomposition of tar to lighter hydrocarbons under high hydrogen pressure.

CONCLUSION

A novel flash pyrolysis method of coal was developed for drastically increasing the tar yield, in which the coal swollen by solvents was pyrolyzed in a flash mode. The tar yield was increased by the factor of 1.5 for the flash pyrolysis, and by the factor of 1.8 for the flash hydrolypyrolysis. The increase of tar yield is brought about by the pore enlargement caused by swelling and by the effective hydrogen transfer from/via tetralin.

ACKNOWLEDGMENT

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Table 1 Properties of Coal

	Proximate Analysis (wt%)			Elemental Analysis (wt% daf)			
	FC	VM	ASH	C	H	N	S+O
Raw coal	43.2	45.8	11.0	74.5	6.0	1.3	18.20
Treated coal	-	-	11.0	72.7	5.9	1.5	19.90

Table 2 Change of Pore Volume and Surface Area during Swelling

Coal	Solvent	Temp. (°C)	Pore Volume (cc/g)	Surface Area (m ² /g)
Taiheiyō	Raw	-	0.039	108.2
	Tetralin	100	0.039	102.4
		170	0.040	102.5
		250	0.061	152.9

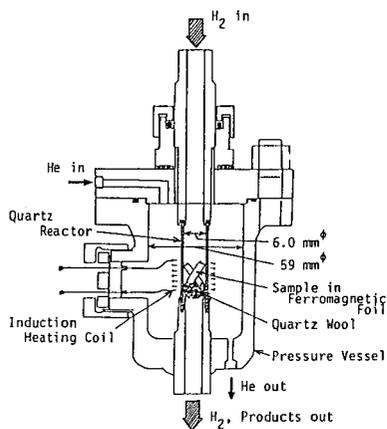


Fig.1 Schematic of a high pressure Curie-point pyrolyzer

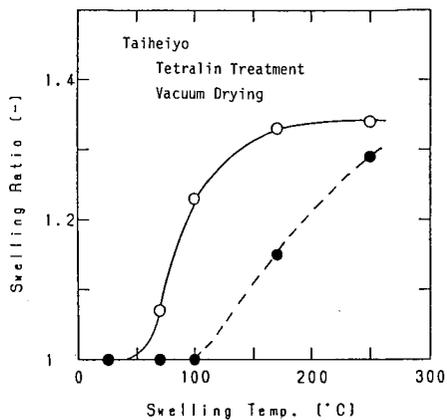


Fig.2 Change of the swelling ratio of tetralin treated coal and vacuum dried coal with the pretreatment temperature

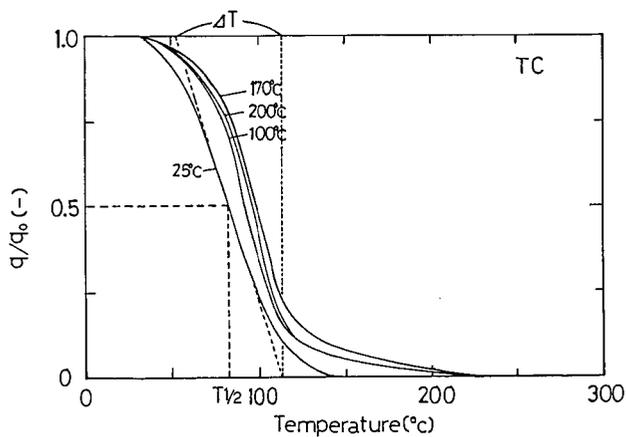


Fig.3 Thermal desorption curves of tetralin from the coal treated with tetralin at different temperatures

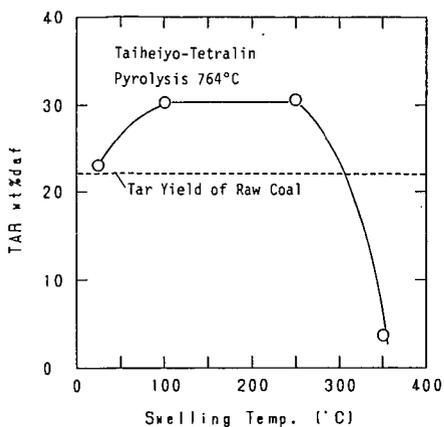


Fig.4 Effect of the pretreatment temperature on the tar yield during the pyrolysis of tetralin treated coal

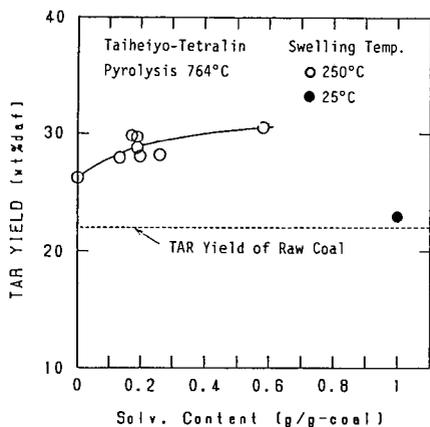


Fig.5 Effect of the amount of solvent remaining in the coal on the tar yield

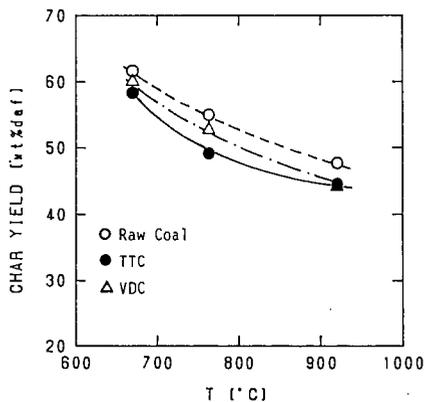


Fig.6 Effect of the pyrolysis temperature on the char yield during the pyrolysis for coal, tetralin treated coal and vacuum dried coal

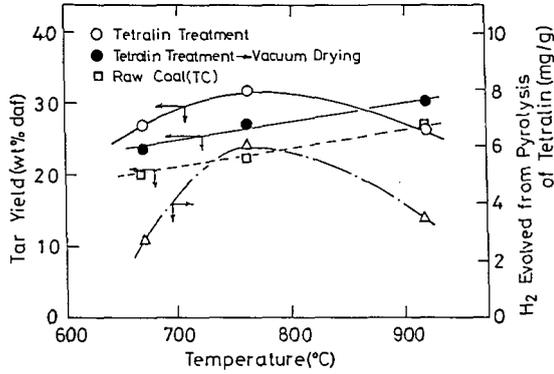


Fig.7 Effect of the pyrolysis temperature on the tar yield during the pyrolysis for coal, tetralin treated coal and vacuum dried coal

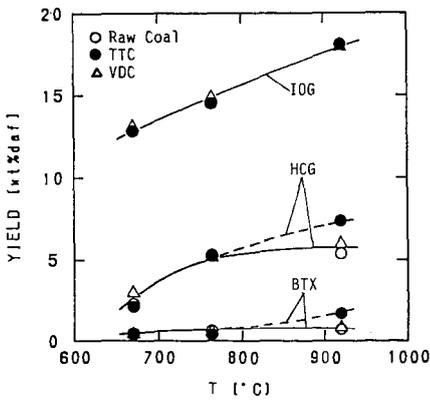


Fig.8 Effect of the pyrolysis temperature on the IOG, HCG and BTX yields during the pyrolysis for coal, tetralin treated coal and vacuum dried coal

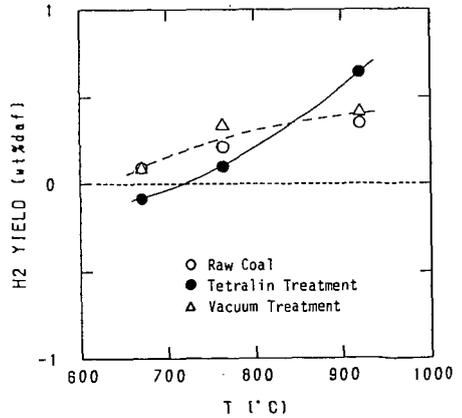


Fig.9 Effect of the pyrolysis temperature on the H₂ yield during the pyrolysis for coal, tetralin treated coal and vacuum dried coal

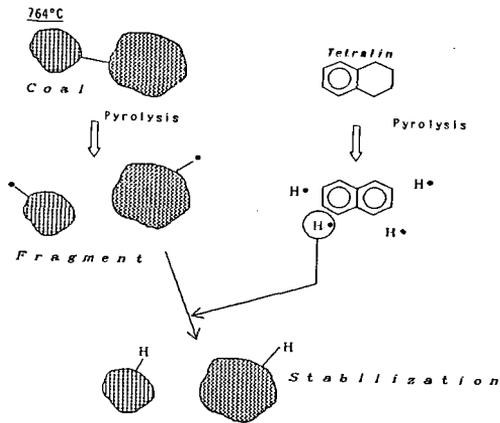


Fig.10 Presumed mechanism of pyrolysis of tetralin treated coal at temperatures lower than 764 °C

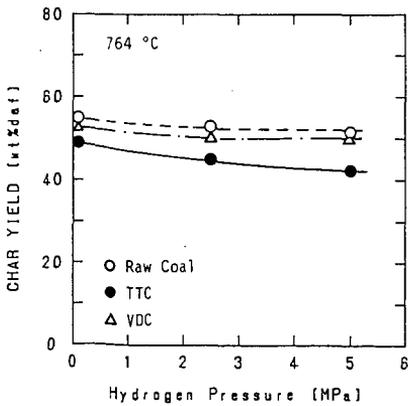


Fig.11 Change of the char yield during the pyrolysis with increasing hydrogen pressure

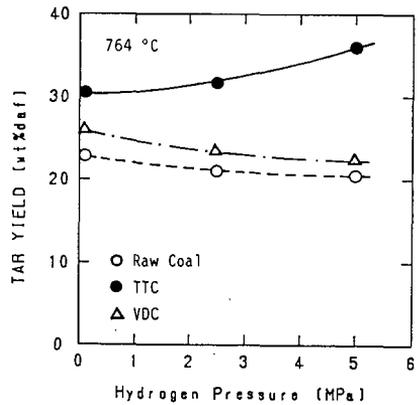


Fig.12 Change of the tar yield during the pyrolysis with increasing hydrogen pressure

THE ANALYSIS OF VOLATILE COMPONENTS FROM
PYROLYZED GASIFIER CARBON-RICH SOLID SAMPLES

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ABSTRACT

Samples of carbon-rich solid products, taken during the processing of coal in a Texaco Coal Gasifier, have been analyzed by flash-pyrolysis using the electrically-heated grid technique. Gas chromatography and mass spectrometry data were obtained on the composition of the gases and tars evolved.

SAMPLE PREPARATION

The coal gasifier solid products, consisting approximately of 51.2% carbonaceous material, 47.1% ash, and 1.7% water by weight, were pyrolyzed using a heated grid apparatus, which was similar to a procedure used by other workers.(1,2) The pyrolyzer consisted basically of two layers of wire mesh mounted between two electrodes, with a thin uniform layer of gasifier solid sample weighing about 50 mg placed between the two wire mesh screens. The sample was heated under vacuum for six seconds to a peak temperature of 1350°C. The heating rate was estimated to be in the order to 2000°C/s. The reaction products, consisting of gases, tars, and char were collected.

The gases were analyzed on-line by gas chromatography. The gases consisted of 0.5% hydrogen, 1.8% methane, 1.7% water, 0.2% ethylene, 1.0% carbon monoxide, 0.6% ethane, 0.3% propylene, 0.9% carbon dioxide, and 0.7% other olefins based upon the weight relative to the initial sample.

The tars, materials collected on filter paper at the reactor exit or condensed on other reactor surfaces at room temperature, were analyzed by mass spectrometry.

ANALYSIS OF TARS BY MASS SPECTROMETRY

The tar samples were analyzed by both direct insertion probe and direct exposure probe mass spectrometry, using a VG Analytical 7070HS instrument. The mass spectrometer was operated under the following electron impact conditions: 200 uA trap current, 70 eV electron energy, 4 kV accelerating voltage, 1200 resolution (10% valley), and a 250°C source temperature. Masses were magnetically scanned from 20 to 800 daltons, and subsequently from 25 to 300 daltons every four seconds.

For the direct insertion probe analysis, a 100 ug sample of tar was fractionally sublimed from a shallow (4 mm) quartz cup which was attached to the probe and positioned in the source just short of the electron beam. The probe temperature was controlled by both a water cooling line and an electrical heating element. The sample was initially heated from 20°C to 50°C in the first minute, and then increased by 50°C every 30 seconds, to a final temperature of 450°C for five minutes.

During the direct exposure probe analysis, the tar was dissolved in methylene chloride and then deposited onto a platinum emitter filament. After the evaporation of the solvent, the direct exposure probe was positioned in the source so that the sample was in actual contact with the electron beam. A current was ramped from 0 to 1.2 A in 50 seconds to flash vaporize the sample.

MASS SPECTROMETRY RESULTS

Approximately 75% of the tar sublimed from the quartz direct insertion probe cup into the mass spectrometer source. This was determined by weighing the probe cup after the analysis. Although the initial mass scanning range was from 25 to 800 daltons, few ions were observed above a mass of 250 daltons, even at the higher probe temperatures. The upper mass limit was then reduced to 300 daltons.

When using the second introduction technique, the emitter coil on the direct exposure probe was burnt clean. Although this technique generally allows better detection for high molecular weight molecules, again only an upper mass range of approximately 250 daltons was observed.(3)

A total ion chromatogram for a tar sublimation reveals that the tar was composed of a fairly uniform distribution of materials over the entire temperature range. (Figure 1) Each time the temperature was incremented by 50°C, there was a corresponding increase in total ion intensity which would then fall off after about 15 seconds. This periodic tendency continued even at the highest probe temperature of 450°C. There was still about 15% of the tar remaining after about five minutes at this temperature, although the ion intensity dropped off to only a few percent of this maximum level.

The mass spectra indicate mainly the presence of relatively simple hydrocarbons. The most prominent types of hydrocarbons observed were alkenes, dienes and some alkylated phenols. No substituted cycloalkanes, benzenes, polynuclear aromatics, or common biomarkers such as dicyclic terpanes, were observed. The major fragmentation series at 27, 41, 55, 69, 83, 97, and 111, having the empirical formula C_nH_{2n-1} , and the relative abundance of these peaks, represents the strong presence of alkenes. The fragmentation series 67, 81, 95, 109, 123, 137, 151, and 165,

having the empirical formula C_nH_{2n-3} , and the relative abundance of these peaks, represents the presence of dienes. Alkenes and dienes were prominent throughout the entire chromatogram, especially being dominant below 150°C. (Figure 2) The alkylated phenol fragmentation was represented in the 135, 149, and 163 series. The alkylphenols were most intense at about 250°C. (Figure 3) Peaks representing paraffinic molecules, having an empirical formula C_nH_{2n+1} , end very quickly at about 85 daltons indicating that this series probably only represents the alkylated regions in the parent molecules.

CONCLUSION

Overall the mass spectra indicate that the tars generally contained only relatively light alkenes, dienes, and alkylphenols. These components are somewhat less complex than materials typically associated with coal pyrolysis.(4) This simpler distribution is actually the result of a double pyrolysis. The coal was first pyrolyzed in a coal gasifier, and then the selected carbon-rich products were pyrolyzed in the screen-heater reactor.

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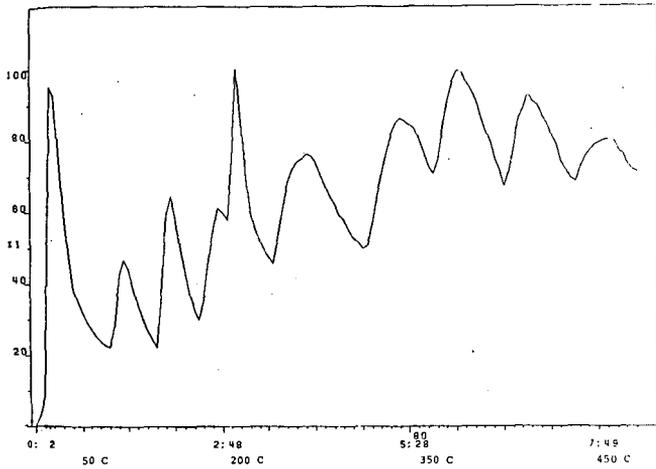


FIGURE 1. Total Ion Chromatogram of Tar

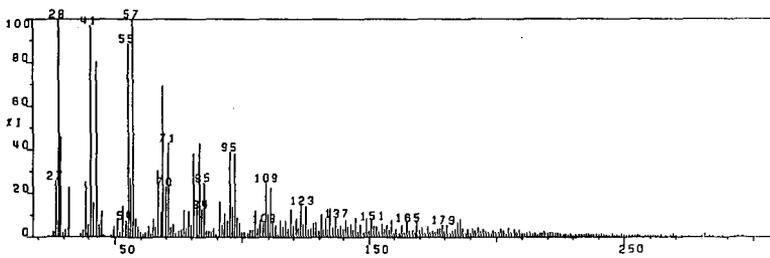


FIGURE 2. Mass Spectrum at 100°C

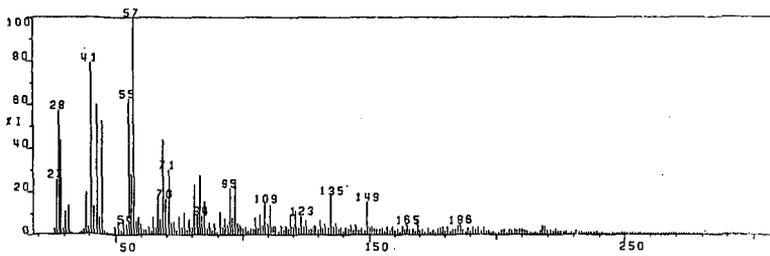


FIGURE 3. Mass Spectrum at 250°C

INFLUENCE OF HYDROGEN SULPHIDE PRETREATMENT
ON HYDROPYROLYSIS OF A BITUMINOUS COAL

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Abstract

The influence of 5% H_2S/H_2 pretreatment of a bituminous Beringen Belgian coal on HyPy is studied in a thermobalance. The presence of H_2S does not improve the total oil yield, but increases the oil evolution rate. Thus, HyPy can be performed at a temperature 60°C lower in H_2S/H_2 -HyPy than in normal HyPy, resulting in an increase in the efficiency of hydrogen utilization. Sulphur is added to coal during H_2S/H_2 pretreatment stage and is removed in the following HyPy stage, indicating that H_2S does not act as a real catalyst. A kinetic analysis shows that the activation energy in the initial stage of oil formation in H_2S/H_2 -HyPy is remarkably reduced as compared with that in H_2 -HyPy. It is suggested that H_2S acts as a hydrogen donor to improve hydrogen transfer and to generate the active sulphur radicals for easier saturation of free radicals formed pyrolytically.

Introduction

Hydrogen pretreatment of coal was reported to be effective in improving both the yield and the quality of the oil in the following hydropyrolysis (HyPy) (1). It is still interesting to find a way to accelerate the rate of oil formation at low temperature in order to increase the hydrogen utilization efficiency due to the decrease in the formation of light hydrocarbon gases.

It is known that H_2S can act as a hydrogen transfer catalyst and appears to be a hydrogen donor (2-5). The activation energy for hydrogen transfer and the temperature necessary to promote effective hydrogen transfer are bound to decrease (6,7). The reaction between H_2S and free radicals formed pyrolytically is much faster than that between H_2 and radicals, even with the addition of only a small amount of H_2S under lower temperature (8). According to several reports on coal liquefaction (9-11), 5% H_2S in H_2 seems to be enough effective to obtain the highest catalytic activity.

The purpose of this paper is to examine the influence of coal pretreatment with 5% H_2S in H_2 on HyPy using a thermogravimetry study. The comparison between the pretreatment under H_2 and H_2S/H_2 at 673 K and 3 MPa is investigated in detail while the effects of H_2S/H_2 pretreatment at other temperatures are simply compared. A kinetic analysis is attempted to obtain further information for the explanation of the H_2S function.

Experimental

A two-pin thermobalance with a sample of 0.1 g is used in this study. The apparatus has been described elsewhere (12). The on-line

gas analysis is carried out by gas chromatography with a methanizer using Ni as a catalyst for the quantitative detection of gas components CH_4 , C_2H_4 , C_2H_6 , CO and CO_2 .

Hydrogen pretreatment (H_2P) and $\text{H}_2\text{S}/\text{H}_2$ pretreatment ($\text{H}_2\text{S}/\text{H}_2\text{P}$) are performed under 3 MPa with a gas flow rate of 1 l/min and a heating rate of 5 K/min up to 673 K (or at other temperatures) for 30 min. In the H_2P -HyPy process, HyPy is run up to 1100 K directly after pretreatment, while in the $\text{H}_2\text{S}/\text{H}_2\text{P}$ -HyPy process, the reactor is first evacuated to remove H_2S for later analysis of the gas, HyPy is then operated under 3 MPa and a heating rate of 5 K/min with a gas flow rate of 1 l/min.

A bituminous Berigen Belgian coal is ground to less than 90 μm for this study. Its characteristics are given in Table 1.

The content of combustible sulphur in the pretreated coal and char is analysed by means of Carlo Erba Elemental Analyser (Model 1106) with a paropok column (1/4" X 0.8 m).

The data on gas composition obtained by G.C. is corrected in order to eliminate the influence of the time-lag in getting product gases to G.C.. The oil yield is given by carbon balance. The carbon content in char at various temperatures is analysed in our laboratory (13). The carbon content in oil is found to be $84 \pm 2\%$.

Kinetic analysis

The thermal decomposition of coal can be described as:

$$\frac{dx}{dt} = A \exp(-E/RT) (1-x)^n \quad 1)$$

Assuming first order for the rate of mass loss at a constant heating rate, we obtain:

$$\frac{dx}{dT} = \frac{A}{m} \exp(-E/RT) (1-x) \quad 2)$$

where m is the heating rate, x the decomposed fraction (on the decomposable basis, here based on the weight loss at 913 K at which oil evolution is ended) and A , E and R are the usual Arrhenius equation terms. The integration of equation (2), by using the integral approximation method (14), gives

$$\ln(-\ln(1-x)/T^2) = \ln\left(\frac{AR}{mE} / (1+2RT/E)\right) - E/RT \quad 3)$$

Since $2RT/E$ is much less than unity at moderate temperature and high activation energies, the value of $(1+2RT/E)$ is assumed constant. Thus, the kinetic parameters from equation (3) can be determined by plotting $\ln(-\ln(1-x)/T^2)$ versus $1/T$. For low activation energy, the value of $2RT/E$ can not be negligible. Equation (3) can be rewritten as:

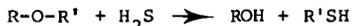
$$\ln(-\ln(1-x)/T^2) + \ln(1+2RT/E) = \ln\frac{AR}{mE} - E/RT \quad 4)$$

A more accurate value of E is obtained by using the first approximate E and plotting $\ln(-\ln(1-x)/T^2) + \ln(1+2RT/E)$ versus $1/T$.

Results and Discussion

1. Comparison of H_2P -HyPy and H_2S/H_2P -HyPy

The influence of pretreatment with 5% H_2S/H_2 on HyPy under 3 MPa and 5 K/min at 673 K for 30 min is first studied to compare the results obtained in H_2P -HyPy under same conditions. Figure 1 shows the comparison in yields of char, oil and gas. The conversion in H_2S/H_2P -HyPy is about 4% (wt%) higher than that in H_2P -HyPy. Before 880 K the higher conversion is mainly attributed to the higher oil yield while after 880 K it comes from the difference in gas yield. Figure 2 and 3 show the yields of CH_4 , C_2H_6 , CO and CO_2 . Before 1100 K the CH_4 yield is lower in H_2S/H_2P -HyPy than that in H_2P -HyPy, which may relate to the higher oil yield at lower temperature in H_2S/H_2P -HyPy because H_2S can change the route of cleavage of some bonds. Surprisingly, it is found that at higher temperatures, the difference in gas yield, which leads to higher conversion in H_2S/H_2P -HyPy, results from the increasing CO yield with an increase in temperature. In H_2P -HyPy, like HyPy, the evolution of CO is ended at about 1000 K. The reason why CO enhances with increasing temperature and more CO is formed might be that H_2S reacts with ether groups to form phenolic hydroxyl groups according to the following reaction(10):



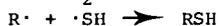
Then, hydroxyl groups decompose to CO at higher temperature(15,16).

Figure 4 shows the comparison of oil evolution rates in H_2P -HyPy and H_2S/H_2P -HyPy. It is clear that although the maximum oil yield is same in these two processes, the oil yield formed during the pretreatment stage is higher and the oil reaches the maximum yield more quickly in H_2S/H_2P -HyPy. This demonstrates that the reactions between H_2S and free radicals formed pyrolytically are much faster than that between H_2 and radicals. It is also observed that the oil evolution ends about 60°C earlier in H_2S/H_2P -HyPy as compared with H_2P -HyPy. Figure 5 gives the comparison of hydrogen utilization in H_2P -HyPy and H_2S/H_2P -HyPy. For the same oil yield, a high amount of total hydrogen in gaseous compounds means more hydrogen being consumed in the formation of hydrocarbon gases. One important factor in the economics of the coal hydrogenation process is the hydrogen consumption. For this reason, it is desirable that the formation of gaseous products which consume more H_2 be minimized while liquids are maximized. Thus, using H_2S pretreatment, HyPy can be performed at lower temperature, resulting in an increase in the efficiency of hydrogen utilization due to the decrease in the formation of light hydrocarbon gases. The study(17) on the reaction of H_2S with model compounds also found that the addition of H_2S reduced reductant consumption as much as three-fold whilst maintaining high oil yield levels when the reaction temperature was reduced by 60°C.

Table 2 gives the comparison of combustible sulphur content in H_2S/H_2 pretreated coal, H_2 pretreated coal and chars obtained in H_2S/H_2P -HyPy and HyPy. After H_2S/H_2 pretreatment the sulphur content in pretreated coal increases from 0.42% to 1.11% as compared with that in H_2 pretreated coal, showing that H_2S does not act as a real

catalyst. However, the sulphur content in char in H_2S/H_2P -HyPy is almost the same as that in HyPy. This implies that the additional sulphur in H_2S/H_2 pretreatment stage will be removed in the following HyPy stage, leaving the sulphur content in char unchanged. Thus, it is suggested that H_2S acts as a hydrogen donor to improve the hydrogen transfer and the reactions between H_2S and coal follow free radical chain mechanism, involving the active sulphur radicals $\cdot SH$ as intermediate as follows:

in H_2S/H_2 pretreatment stage,



in the following HyPy stage,



Figure 6 gives the comparison of kinetic curves in H_2P -HyPy and H_2S/H_2P -HyPy. Table 3 lists the kinetic parameters. HyPy can be roughly divided into three stages: the pyrolytic stage at temperature below 750 K; hydrogenation in temperatures ranging from 750 to 850 K; and the hydrocracking stage at higher temperatures. In the pyrolytic stage the free radicals are mainly saturated by internal hydrogen while at the hydrogenation stage they are stabilized by gaseous hydrogen. The presence of H_2S decreases the apparent activation energy as much as four-fold in the pyrolytic stage as compared with that in the absence of H_2S , while it has no effect on the apparent activation energy in higher temperature stages. It is known that the bond energy of H_2 is greater than that of most C-H bonds whereas that for H_2S is not (18). According to data on the relative bond strengths most C-S bonds are cleaved much more rapidly than almost all C-C bonds (5). Thus, the saturation of free radicals by H_2S and the cleavage of the saturated radicals are much faster at the low temperature stage in H_2S/H_2P -HyPy than that in H_2P -HyPy.

It should be noted that HyPy in fixed-bed reactor, due to the slow rate of hydrogen diffusion and without solvent, seems to be more subject to mass transfer limitation(1). During H_2S/H_2 pretreatment stage, a considerable amount of oil is produced, which results in a decrease in agglomeration ability. Therefore, more H_2 will penetrate the coal to saturate the free radicals in the following HyPy stage, leading to an increase in oil evolution rate.

The H_2S/H_2 pretreatment of coal can be easier performed because H_2S is generated within the process. The problem is whether the sulphur content in oil will be increased, which leads to an additional cost in the treatment of oil. The studies(5,10) in coal liquefaction using H_2S/H_2 showed a very small increase in total sulphur in liquids and a very large increase in total sulphur in the residue. It might be possible to obtain the same quality of oil in H_2S/H_2P -HyPy as in H_2P -HyPy, but this needs to be proved.

2. Influence of different pretreatment temperature

Figure 7 shows the influence of H_2S/H_2 pretreatment temperature

ranging from 573 to 723 K under 3 MPa for 30 min on oil yield. The oil yield obtained in H_2S/H_2P -HyPy indicates the same tendency as in H_2P -HyPy(1). After 623 K, the oil yields in H_2S/H_2P -HyPy and H_2P -HyPy are higher than that in HyPy. The same oil yield produced in H_2S/H_2P -HyPy and H_2P -HyPy shows that the presence of H_2S does not improve oil yield. However, the oil yield obtained during H_2S/H_2 pretreatment stage is much higher than that obtained during H_2 pretreatment stage. In H_2P at 673 K, little oil is produced while in H_2S/H_2P at the same temperature about 25% of total oil in H_2S/H_2P -HyPy is already formed. This further demonstrates that H_2S can reduce the activation energy for hydrogen transfer and the temperature necessary to promote effective hydrogen transfer.

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Table 1. Beringen Coal Analysis

Proximate Analysis (wt%, as received)		Ultimate Analysis (wt%, daf)	
Moisture	1.49	C	84.74
Ash	4.72	H	4.86
Volatile Matter	34.52	N	1.70
		O+S (by difference)	8.70

Table 2. Combustible sulphur Contents in Pretreated Coal and Char

Coal	Pretreated Coal 3 MPa, 673 K, 30 min		Char 3 MPa, 1073 K		
	H ₂ P	H ₂ S/H ₂ P	HyPy	H ₂ S/H ₂ P-HyPy	
S (wt%, daf)	1.17	0.42	1.11	0.12	0.18

Table 3. Comparison of Kinetic Parameters in H₂S/H₂P-HyPy and H₂P-HyPy under 3 MPa and 5 K/min. Pretreatment: 3 MPa, 673 K

Process	Tem. Range (K)	Ea° (KJ/mol)	A (1/min)	Coef. Correlation
H ₂ P-HyPy	673-750	79.99	7.58x10 ⁶	0.979
	750-850	43.08	45.71	0.980
	850-913	74.31	5.10x10 ³	0.991
H ₂ S/H ₂ P-HyPy	673-750	20.17	0.71	0.977
	750-850	43.08	45.71	0.980
	850-913	74.31	5.10x10 ³	0.991

* Apparent activation energy obtained by $\ln(-\ln(1-x)/T^2) + \ln(1+2RT/E)$ versus $1/T$.

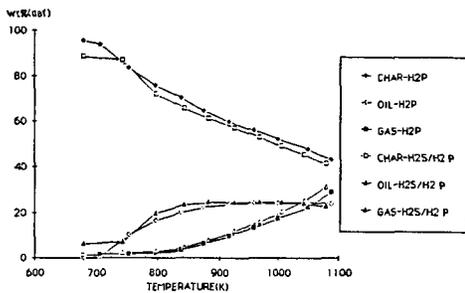


FIG. 1 COMPARISON BETWEEN H₂P-HyPy AND SX H₂S/H₂ P-HyPy IN YIELDS OF CHAR, OIL AND GAS. PRETREATMENT: 3 MPa, 673 K, 30 min

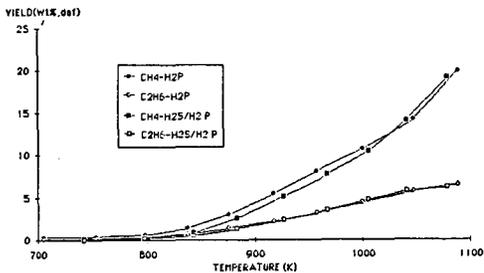


FIG. 2 COMPARISON ON YIELDS OF CH₄ AND C₂H₆ BETWEEN H₂P AND SX H₂S/H₂ P. PRETREATMENT CONDITION: 3 MPa, 673 K, 30 min

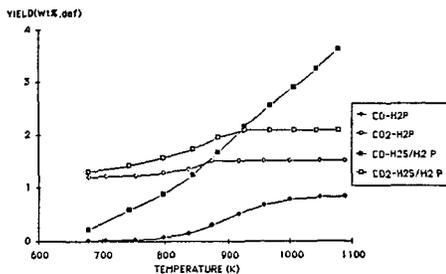


FIG. 3 COMPARISON ON YIELDS OF CO AND CO₂ BETWEEN H₂P AND SX H₂S/H₂ P. PRETREATMENT CONDITION: 3 MPa, 673 K, 30 min

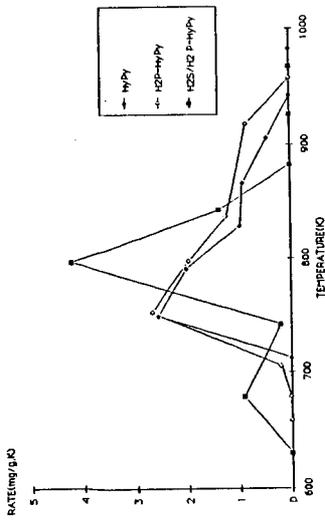


FIG 4 COMPARISON ON OIL EVOLUTION RATE IN H₂P-mPy, H₂P-H₂P, AND H₂S/H₂P-mPy AT 3 MPa, 5 K/min, 673 K, 30 min.

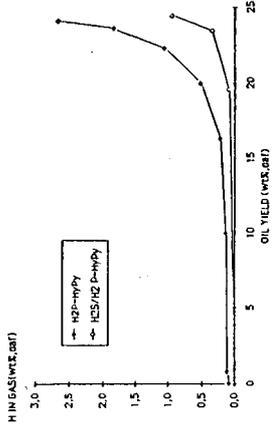


FIG 5 COMPARISON OF HYDROGEN UTILIZATION IN H₂P-mPy AND H₂S/H₂P-mPy PRETREATMENT CONDITIONS 3 MPa, 673 K, 30 min.

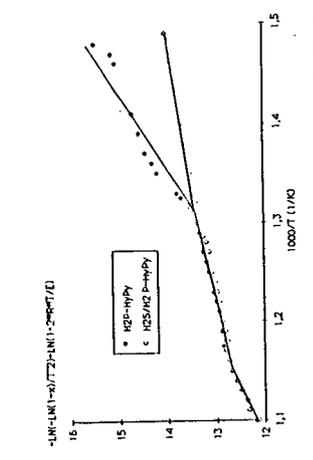


FIGURE 6 COMPARISON OF KINETIC CURVE BETWEEN H₂P-mPy AND H₂S/H₂P-mPy UNDER 3 MPa, 5 K/min, PRETREATMENT CONDITION 3 MPa, 673 K, 30 min

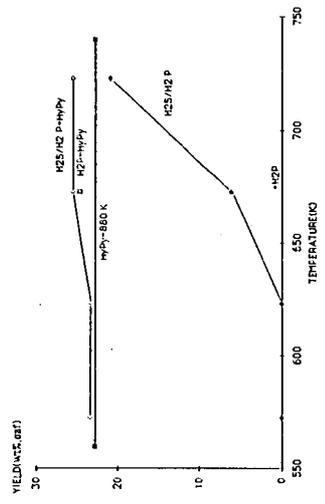


FIGURE 7 INFLUENCE OF PRETREATMENT TEMPERATURE ON OIL YIELD PRETREATMENT: 3P, 5 K/min, 30 min

**Influence of Reactor Configuration/Type on the
Composition of Mild Gasification Liquids***

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INTRODUCTION

Yield, quality, and the composition of coal liquids produced by devolatilization depend on the reactor configuration, pyrolysis temperature, and on the coal type used. In this investigation a fixed-bed, a fluidized-bed, and an entrained-flow reactor were used in which Pittsburgh No. 8, Illinois No. 6, and Montana Rosebud coals were pyrolyzed. In addition to the above-mentioned reactor configurations, the liquid produced in the fixed-bed reactor was passed through a reactor tube maintained at 500°C and then the sample was collected to investigate the effects of heat treatment on liquid composition/quality. Vapor phase reactions occurring in the pyrolysis liquids are an important consideration keeping in mind that in a mild gasification process, liquid may experience some hot or high-temperature surfaces.

The goals of this study were (a) to understand the chemical reactions induced in the thermal (tube) reactor and (b) to compare compositional differences of coal liquids produced in a fixed-, fluidized-, and entrained-flow reactors. To this end, devolatilization products were separated using gravity-flow liquid chromatography according to chemical functionality. Subsequently, the first fraction which contained mainly neutral aromatic compounds and the third fraction which was composed of phenolic compounds were analyzed using FIMS.

EXPERIMENTAL

The experimental procedure for coal pyrolysis liquid in a fixed-bed reactor is described by Khan (1). In this configuration liquids were generated at 500°C from the Pittsburgh No. 8 and Montana Rosebud coals. In a separate experiment, coal liquids thus generated were passed through a reactor tube (modified configuration) maintained at 500°C before the final collection. In addition, coal liquids from the pyrolysis of Illinois No. 6 coal in a fixed- and a fluidized-bed reactor at 500°C, of Pittsburgh No. 8 coal in a fixed-bed and an entrained-flow reactor at 650°C, and finally, of Pittsburgh No. 8 coal in an entrained-flow reactor at a reactor temperature of 850°C are included in this study. All experiments were performed in an inert atmosphere.

Open column liquid chromatographic (LC) separation was carried out on silica column with sequential elution of the sample with solvents of different polarity (2,3). Field ionization mass spectral data were obtained at SRI International (Menlo Park, California). Data in the tabular form spread over 14 columns contained relative intensity for each mass number. For each spectrum the relative intensities were normalized to 10,000. Details of instrumentation and data acquisition procedure are described by St. John, et al. (4). Data were reduced to identify homologous

*Work reported here was performed at Morgantown Energy Technology Center

series in each column and their relative concentration was expressed in mole percent of given fraction or of the total sample. Proton NMR spectra of the Pittsburgh No. 8 coal liquid from the fixed-bed and entrained-flow reactor (reactor temperature 850°C) were obtained at The Energy and Mineral Research Center in Grand Forks, North Dakota, from which average molecular parameters were derived (5). Elemental analysis for these samples were obtained in our laboratory.

RESULTS AND DISCUSSION

Comparison of Coal Liquids Produced in the Fixed-Bed and the Modified Fixed-Bed Reactors

The relative quantities of chromatographic fractions in Pittsburgh No. 8 and Montana Rosebud coal liquids produced in the fixed-bed reactor and in the modified configuration are given in Table 1. The separation results suggest certain gross compositional changes in liquids produced in the modified configuration relative to the raw liquids. The relative weight percent of the residue, which is mainly asphaltenes like materials are less abundant in the liquids produced in the modified reactor, whereas that of fraction 3 is higher than in the raw liquid. These two observations suggest that heavier polar compounds with multifunctional groups are cracked producing simple phenols. On the other hand, FIMS data for the first and the third fractions give details of certain chemical reactions induced in the tube reactor.

In our LC separation the first fraction is composed of alkanes, cycloalkanes, olefins, and neutral aromatic compounds whereas, the third fraction is made up of simple phenolic compounds. FIMS data for these two fractions were reduced to identify homologous series in compound class types mentioned above, using the procedure described by Whitehurst, et al. (6). Results are given in Tables 2 and 3.

According to the separation results one of the reactions in the modified fixed-bed reactor is the formation of simple phenols from heavier polar compounds. FIMS results agree with this conclusion; more importantly, they suggest that two parallel reactions are taking place involving phenols. One is the deoxygenation of simple phenolic compounds such as phenols, naphthols, and others; the other is the formation of hydroxy hydroaromatic and aromatic compounds with three or more condensed rings and hydroxy indenenes and benzofurans. Results of elemental analysis (Table 4), however, indicate that there is a decrease in elemental oxygen upon thermal treatment. The decrease in elemental oxygen is consistent with the separation as well as FIMS results. When simple phenols are deoxygenated, the decrease in the weight percent of oxygen is much larger than the percentage increase in elemental oxygen when heavier phenols are formed.

FIMS data for the first LC fraction were obtained without any further separation. Nevertheless, with the aid of certain definite compositional information, which are, that the first fraction of coal liquids produced in fixed-bed reactors contain about 15 weight percent of olefins and saturated compounds, that mono- and di-aromatic compounds are the two major ring systems in this fraction, and that in the present sample not more than two homologous series constitute each column of FIMS data, it was possible to identify all series with reasonable certainty. To illustrate the identification of series in a given column, Column 10 is taken as the example in which are included alkanes, naphthalenes, dibenzothiophenes, binaphthyls, and phenolic compounds. The distribution of relative intensity of molecular ions as a function of carbon number suggest that only two series contribute to this column. The contribution of one series, whose parent compound begins with $m/e = 128$ to the total relative intensity in the column was 75 percent. Since phe-

nolic compounds were not eluted into this fraction, there are only two possible assignments to the parent compound; an alkane or an aromatic compound. Coal liquids contain mainly higher alkanes at a much lower concentration than aromatics. Therefore, the series beginning with $m/e = 128$ was assigned to naphthalenes and the other series to alkanes. In a similar manner, homologous series in the other columns were identified. The results suggest that alkanes and cyclic alkanes are cracked in the modified configuration of the fixed-bed reactor, while neutral aromatic compounds are practically unchanged, with the exception of naphthalene. A large increase in the concentration of naphthalene is probably due to its formation from cracking of larger molecules or deoxygenation of naphthols. These possible reactions do not explain why a concentration increase was observed only for naphthalene and not for other aromatic compounds commonly found in fixed-bed samples.

The influence of modified reactor configuration on tar and char yield, gas composition and elemental composition of tar and char are presented in Table 4. In the modified reactor, the tar yield is decreased and the total gas yield is increased. In gaseous products, the increase in the level of C_1 - C_8 alkanes is significant. These observations are consistent with some of the reactions induced in the modified reactor, identified based on FIMS data. Cracking of saturated compounds, including alkanes and cyclic alkanes would enhance the total gas production, in particular those of short-chain hydrocarbons.

Compositional Comparison of Pittsburgh No. 8 Coal Liquids Produced in the Entrained-Flow Reactor and the Fixed-Bed Reactor

A primary objective of this comparison was to assess whether coal tars produced in the entrained-flow reactor at elevated temperatures can serve as feedstocks for high energy density fuels. To this end, the first fraction of the LC separation of entrained-flow reactor liquid was analyzed using FIMS, data were reduced and finally, specific chemical structures were assigned to parent members of homologous series. The separation and mass spectral results along with those for the fixed-bed sample are given in Tables 5 and 6, respectively. The pyrolysis temperature in the fixed-bed reactor was 500°C; although the entrained-flow reactor was heated to 850°C, the particle temperature was much less, but at least 100°-150°C higher than 500°C.

Results included in Table 6 are presented in a different format in Figure 1 to highlight the difference in the naphthenic carbon content in the two samples. The first column of this figure contains names of identified compounds along with their structures. In the next two columns, the total number of carbon atoms and naphthenic carbons, respectively, contributed by each structure to the LC fraction-1 of fixed-bed liquid are given. The other two columns contain the same information for the entrained-flow reactor sample. The total number of carbons contributed by aromatic compounds and cyclic alkanes were obtained assuming that on the average that each structure is substituted with three carbon atom side chains. The average number of carbon atoms in normal and branched alkanes was assumed to be 20.

Elemental analysis indicated that the fixed-bed sample was hydrogen rich relative to the EFR sample. According to average molecular parameters derived from the proton NMR spectra, the EFR sample was more aromatic, contained less naphthenic carbons, had a higher concentration of polycyclic aromatic compounds, and the aromatic structures were substituted with shorter alkyl chains relative to the fixed-bed sample. These gross structural features are in agreement with the results of elemental analysis. FIMS results, on the other hand, gave details of structural changes.

Two important compositional differences were reduced concentration of monoaromatic and increased concentration of polycyclic aromatic compounds in the EFR sample relative to the fixed-bed sample. Tetralin, a monoaromatic compound, was probably first changed to butyl benzene and eventually to volatile BTX. Side chains in alkyl benzenes were severely cracked. Elevated temperatures favor ring condensation reactions and in this process certain hydroaromatic compounds were formed. Therefore, EFR samples also contain reasonable amounts of naphthenic carbons, although tetralins and octahydronaphthalenes were substantially depleted at elevated temperatures. However, the total population of naphthenic carbons in the first fraction of fixed-bed sample was higher than in the EFR sample. Also the weight percent of first fraction in the total fixed-bed sample was about 50 percent higher than in the EFR sample. Therefore, coal liquids produced in a fixed-bed reactor have a definite edge as a high energy density fuel feedstock over the EFR liquids.

Compositional Comparison of Coal Liquids Produced from a Fixed-Bed, Fluidized-Bed, and Entrained-Flow Reactors

Coal liquids produced from Pittsburgh No. 8 coal in the fixed-bed and entrained-flow reactors at 650°C and from Illinois No. 6 coal in the fixed-bed and in the fluidized-bed reactors at 500°C were separated using LC and the results are given in Table 7. Unlike for the previously discussed samples, field ionization mass spectral data were obtained for the total sample. Therefore, assignments of chemical structure to the parent compound of each homologous series is based solely on m/e values. Despite this limitation, assignments appear to be reasonable. Results are presented in Tables 8 and 9.

A survey of the composition of fluidized-bed and entrained-flow reactor samples relative to the composition of fixed-bed liquids suggest that cracking of simple hydroaromatic compounds such as tetralins, deoxygenation of simple phenolic compounds, and ring fusion are the reactions induced by rapid pyrolysis both at moderate and elevated temperatures. The ring fusion reaction results in neutral polycyclic aromatic, polycyclic hydroaromatic, and oxygen-containing polycyclic aromatic compounds.

SUMMARY AND CONCLUSIONS

Coal pyrolysis liquids produced by slow heating at moderate temperatures in fixed-bed and modified fixed-bed reactors and by rapid pyrolysis at moderate or elevated temperatures in fluidized-bed or entrained-flow reactors were separated by adsorption chromatography. Pertinent fractions thus generated and total liquids in some cases were analyzed using field ionization mass spectroscopy. The mass spectral data were deconvoluted and each homologous series was associated with a chemical structure. In data analyses for fractions, it was possible to assign definite chemical structures to the parent compound of each series. Identification of components in the total sample is tentative, nevertheless reasonable.

The thrust of this study was to understand compositional differences among coal liquids produced in different reactor configuration and to decide the best configuration for the production of high energy density fuels. In the modified fixed-bed reactor the primary pyrolysis liquid was post-heated to 500°C to understand the influence of heat treatment on liquid quality.

Separation and FIMS results have shown that slow pyrolysis in the modified fixed-bed reactor and rapid pyrolysis both at moderate and elevated temperatures induce

some common reactions, in particular deoxygenation of phenolic compounds and cracking of heavier polar compounds.

Rapid pyrolysis depletes the concentration of simple hydroaromatic compounds and alkyl benzenes, and reduces the length of alkyl side chains on aromatic structures. Ring condensation is another reaction induced during rapid pyrolysis and results in polycyclic aromatic, polycyclic hydroaromatic, and oxygen-containing polycyclic aromatic compounds.

Based on compositional data for liquids produced in different reactor configurations, mild gasification liquids produced in the fixed-bed reactor appear to be the suitable feedstock for high energy density fuels.

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TABLE 1. Fractions of Coal Liquids Produced in Fixed-Bed and in the Modified Configuration from Pittsburgh No. 8 and Montana Rosebud Coals

Fraction No.	Weight-Percent in Sample			
	A	B	C	D
1	42.8	42.6	42.8	46.1
2	13.8	4.9	7.5	6.2
3	14.8	24.7	12.1	23.0
4	1.0	2.1	1.4	0.6
5	8.5	12.4	4.3	4.7
6	6.3	7.1	2.5	6.2
Residue	12.8	6.2	27.1	13.5

A -- Pittsburgh No. 8 Fixed-Bed (FB) Reactor
 B -- Pittsburgh No. 8 Modified FB Reactor
 C -- Montana Rosebud FB Reactor
 D -- Montana Rosebud Modified FB Reactor

TABLE 2. Composition of LC Fraction-1 of Montana Rosebud and Pittsburgh No. 8 Coal Liquids Produced in Fixed-Bed and Modified Fixed-Bed Reactors

Compound	MR	MRM	PGH	PGHM
<u>Alkanes and Cyclic Alkanes</u>				
Alkanes, Normal and Branched	4.54	2.10	6.45	4.36
Monocyclic Alkanes	2.39	0.66	3.81	2.69
Tetracyclic Alkanes	2.93	2.07	4.15	2.85
Pentacyclic Alkanes			1.76	0.46
<u>Aromatics</u>				
Benzenes	9.45	9.98	9.43	10.23
Naphthalenes	15.82	19.34	9.63	12.94
Tetralins	12.51	13.76	4.96	4.29
Acenaphthenes/Biphenyls	13.24	13.63	12.59	14.29
Fluorenes	11.87	10.99	9.41	10.53
Anthracenes/Phenanthrenes	11.45	11.08	12.66	12.04
Dibenzothiophenes	0.92	1.12	2.78	1.64
Octahydroanthracenes	8.20	9.72	4.68	4.69
Fluoranthenes	2.80	1.79	8.41	10.52
Dihdropyrenes	--	--	0.74	0.72
Tetrahydro Fluoranthenes	0.80	0.81	1.59	1.44
Chrysenes	3.02	2.89	6.97	6.25

TABLE 3. Composition of LC Fraction-3 of Pittsburgh No. 8 and Montana Rosebud Coal Liquids Produced in Fixed-Bed and Modified Fixed-Bed Reactors (Mole Percent)

Compound	PGH	PGHM	MR	MRM
2-Indenols	3.1	7.0	5.8	7.2
Unidentified	3.8	3.4	2.9	3.0
Hydroxybenzofurans	7.4	11.1	10.9	10.7
Hydroxypyrenes	6.2	4.9	4.7	2.7
Phenols	31.9	27.8	26.1	24.7
Hydroxyphenylnaphthalenes	3.6	4.1	3.2	5.5
Catechols	2.4	1.0	--	--
Phenanthrols	5.2	6.7	7.3	8.3
1-Hydroxy 9,10-Dihydroanthracenes	8.0	9.1	9.48	10.34
Hydroxypentacenes	1.5	1.4	0.74	0.38
Hydroxybiphenyls	10.9	8.5	11.6	9.8
9-Hydroxytetrahydroanthracenes	1.8	1.9	0.2	3.0
Naphthols	9.9	8.2	15.9	12.4
9,10-Dihydroxytetrahydroanthracenes	2.1	3.7	1.3	2.0
Unidentified	1.7	0	--	--

PGH -- Pittsburgh No. 8 Liquid Produced in the FB Reactor
 PGHM -- Pittsburgh No. 8 Liquid Produced in the Modified FB Reactor
 MR -- Montana Rosebud Liquid Produced in the FB Reactor
 MRM -- Montana Rosebud Liquid Produced in the Modified FB Reactor

TABLE 4. Influence of Fixed-Bed Reactor Configuration on Product Composition (Pittsburgh No. 8 Coal)
(All Data on Dry Coal Basis)

	Fixed-Bed Reactor	Modified Fixed-Bed Reactor
Wt Sample (g)	50.0	50.0
Total Gas (l)/100 g Dry Coal	10.0	12.5
Char (Wt %)	71.2	72.0
Tar (Wt %)	18.0	9.0
<u>Gas Composition (Vol %)</u>		
H ₂	10.51	8.29
CO	4.54	4.46
CO ₂	6.81	7.43
H ₂ S	6.58	5.78
COS	0.16	0.23
H ₂ O	0.03	0.08
CH ₄	48.32	43.22
C ₂ H ₄	1.52	1.79
C ₂ H ₆	9.91	10.80
C ₁ -C ₈	71.10	73.69
<u>Tar Composition (Wt %)</u>		
C	77.62	81.68
H	8.93	8.69
S	0.74	0.93
N	0.94	0.86
O	11.77	7.84
H/C (atomic)	1.38	1.28
Btu/lb	14,926	15,626
<u>Char Composition (as received, Wt %)</u>		
C	78.56	78.73
H	2.89	2.86
N	1.76	1.73
S	1.66	1.71
Ash	10.51	10.77
VM	10.61	11.26
H ₂ O	0.30	0.81
H/C	0.44	0.44
O (By Difference)	15.13	14.97
Btu/lb	13,121	13,101

TABLE 5. Fractions of Pittsburgh No. 8 Coal Liquids in Fixed-Bed and Entrained-Flow Reactors

Fraction No.	Fixed-Bed	Entrained-Flow Reactor
1	42.8	33.1
2	13.8	3.5
3	14.8	26.5
4	1.0	9.1
5	8.5	8.6
6	6.3	14.0
Residue	12.8	5.2

TABLE 6. Composition in Mole Percent of LC Fraction-1 of Fixed-Bed and Entrained-Flow Reactor Liquids Generated From Pittsburgh No. 8 Coal

Compound	Fixed-Bed	Entrained-Flow
Tetralins	5.0	1.0
Pyrenes/Fluoranthenes	8.4	12.0
Cyclic alkanes	1.8	2.0
Benzenes	4.1	0.9
Dihdropyrenes	9.3	7.4
Tetracyclic alkanes	0.7	4.2
Phenanthrenes	--	9.6
Tetrahydropyrenes	1.6	5.6
Octahydronaphthalenes	12.7	--
Acenaphthylenes	9.4	7.1
Hexahydropyrenes	3.0	--
Octahydrobenzanthracenes	--	6.9
Acenaphthenes	12.6	6.1
Monocyclic alkanes	3.8	--
Benzopyrenes	--	9.3
Naphthalenes	9.6	8.3
Alkanes	6.4	7.5
Binaphthyls	--	0.5
Indenes	4.7	1.8
Chrysenes	6.9	8.3
Unknown	--	1.4

TABLE 7. Fractions of Fixed-Bed and Fluid-Bed (Illinois No. 6) and Fixed-Bed and Entrained-Flow Reactor (Pittsburgh No. 8) Liquids

Fraction No.	Weight Percent in			
	Fixed-Bed Illinois No. 6 500°C	Fluid-Bed Illinois No. 6 500°C	Fixed-Bed Pittsburgh No. 8 650°C	Entrained-Flow Reactor Pittsburgh No. 8 650°C
1	28.6	12.9	39.2	4.7
2	4.6	5.0	14.3	10.3
3	23.8	20.0	14.3	28.3
4	19.7	23.2	5.3	30.0
5	14.1	37.8	9.0	11.4
6	11.29	0.0	5.5	6.2
Residue	9.0	1.1	17.9	9.0

TABLE 8. Relative Weight Percent of Neutral Aromatic and Phenolic Compounds in 500°C Fixed-Bed and Fluid-Bed Liquids (Illinois No. 6 Coal)

Compound	Fixed-Bed	Fluid-Bed
Benzenes	6.1	--
Phenols	11.4	3.6
Catechols/Hydroquinones	--	1.6
Indenes	7.7	--
Naphthalenes	4.5	8.8
Tetralins	7.2	3.8
Benzo thiophenes	--	3.1
Naphthols	--	3.7
Acenaphthenes/Biphenyls	10.5	7.5
Fluorenes	9.1	9.7
Hydroxybiphenyls	7.7	--
Octahydronaphthalenes	10.8	--
Anthracenes/Phenanthrenes	--	7.9
Octahydrophenanthrenes	4.5	4.6
Hexylbenzenes	5.1	--
Pyrenes	--	8.6
Dihdropyrenes	--	8.6
Hydroxytetralins	9.3	--
Benzopyrenes	--	2.7
Binaphthyls	1.75	2.6
Chrysenes	--	6.2
Hydroxypentacenes	--	4.2
Dibenzopyrenes	--	2.5
Pentacenes	--	3.1
Dihydrobenzopyrenes	--	2.7

TABLE 9. Composition of Fixed-Bed and Entrained-Flow
Reactor Liquids Generated from Pittsburgh
No. 8 Coal (650°C)

Compound	Fixed-Bed	Entrained-Flow
Indanes/Tetralins	4.31	0.75
Pyrenes	2.48	5.98
Dihydrobenzanthracenes	1.83	--
Hydroxybenzanthracenes	--	2.20
Hexacenes	--	0.40
Benzenes	5.32	--
Benzofurans	--	1.04
Phenyl naphthalenes or Hydroxypyrenes	4.74	5.76
Dihydroxy Benzanthracenes	--	2.54
Phenols	7.92	0.79
Anthracenes	3.60	5.87
Phenanthrenes		
Dihydroxytetralins		
Hydroxyphenyl	0.99	2.74
Naphthalenes		
Tetrahydropyrenes	1.87	--
Catechols	2.17	--
Acenaphthylenes	5.42	2.84
Phenanthrols	--	1.84
Dihydroxytetrahydro Benzanthracenes	--	3.74
Octahydrotetracenes	0.74	--
Pentacenes	--	0.28
Cyclohexanes	1.06	--
Acenaphthenes/Biphenyls	6.50	3.26
Benzopyrenes	1.01	5.09
Tetrahydronaphthyl Phenyl Ether	0.81	--
Hydroxypentacene	--	1.21
Naphthalenes	9.24	2.04
Hydroxytetrahydroanthracenes	--	1.32
Binaphthyls	1.81	3.69
Unknown	--	1.17
Tribenzopyrenes	0.17	1.39
Indenes	3.90	1.00
Octahydrophenanthracenes/ Dibenzofuran	3.50	--
Dihydroxy Tetrahydro Anthracenes	--	6.41
Bianthryls	--	1.86
Dinaphtho Thiophene	0.58	--

FIGURE 1. Relative Composition of LC Fraction-1 of Fixed-Bed and Entrained-Flow Reactor Coal Liquids (Pittsburgh No. 8)

Compound/Structure		Fixed Bed		Entrained-Flow Reactor	
		Total Carbon	Naphthenic Carbon	Total Carbon	Naphthenic Carbon
Octahydronaphthalenes		165.1	101.6	0.0	0.0
Tetralins		65.0	20.0	13.0	4.0
Benzenes		36.9	0.0	8.1	0.0
Naphthalenes		124.8	0.0	107.9	0.0
Acenaphthylenes		141.0	0.0	106.5	0.0
Acenaphthenes		189.0	25.2	91.5	12.2
Phenanthrenes		0.0	0.0	163.2	0.0
Pyrenes		159.6	0.0	228.0	0.0

FIGURE 1. Relative Composition of LC Fraction-1 of Fixed-Bed and
 Entrained-Flow Reactor Coal Liquids (Pittsburgh No. 8)
 (Continued)

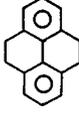
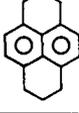
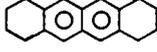
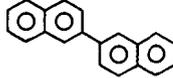
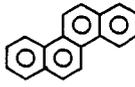
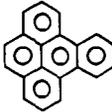
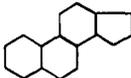
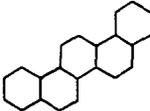
Compound/Structure	Fixed Bed		Entrained-Flow Reactor	
	Total Carbon	Naphthenic Carbon	Total Carbon	Naphthenic Carbon
Dihydroxyrenes 	176.7	18.6	140.6	14.8
Tetrahydroxyrenes 	30.4	6.4	106.4	22.4
Hexahydroxyrenes 	57.0	18.0	0.0	0.0
Octahydrobenzanthracenes 	0.0	0.0	144.9	55.2
Binaphthyls 	0.0	0.0	7.5	0.0
Indenes 	56.4	4.7	21.6	1.8
Chrysenes 	144.9	0.0	174.3	0.0

FIGURE 1. Relative Composition of LC Fraction-1 of Fixed-Bed and Entrained-Flow Reactor Coal Liquids (Pittsburgh No. 8)
(Continued)

Compound/Structure	Fixed Bed		Entrained-Flow Reactor	
	Total Carbon	Naphthenic Carbon	Total Carbon	Naphthenic Carbon
Benzopyrenes 	0.0	0.0	213.9	0.0
Alkanes (n- and branched)	128.0	0.0	150.0	0.0
Monocyclic alkanes 	34.2	22.8	0.0	0.0
Tetracyclic alkanes 	14.0	11.9	84.0	71.4
Pentacyclic alkanes 	45.0	39.6	50.0	44.0
Total	1568	268.8	1811.4	225.8
% Naphthenic Carbon in LC Fraction-1		17.1		12.4
% Naphthenic Carbon in Total Liquid		7.3		4.1