

PYROLYSIS OF COALS LOADED WITH POLYCYCLIC AROMATIC HYDROCARBONS

Ripudaman Malhotra, Gilbert St. John,
Doris S. Tse, and Donald F. McMillen

Chemical Kinetics Department, Chemical Physics Laboratory
SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025

INTRODUCTION

The relative simplicity of pyrolysis offers significant advantages as a coal conversion approach. However, char yields are typically high and volatile products are generally distributed between low value light hydrocarbons and tars that can be very difficult to upgrade. Consequently, the pyrolysis of coals under conditions that would produce larger yields of condensable and readily upgradable hydrocarbons is clearly a desirable goal, and the literature contains many examples of approaches to augmenting pyrolysis yields. For this reason, it is desirable that additional efforts be conducted as much as possible in light of what is known about the mechanism of volatiles production.

A fundamental aspect of the problem that is well recognized is the desirability of carrying out the process under reducing conditions in order to meet the stoichiometric requirements of bond rupture (replacement of C-C bonds with C-H bonds) and the ultimate desire (for fuel purposes) for substantially aliphatic products. This desirability has resulted in various hydrolysis approaches involving heating in the presence of medium- or high-pressure hydrogen. These approaches generally result in improved yields only when the reaction time is long, or when the temperature exceeds roughly 600°C (1112°F).^(1,2) At short reaction times and temperatures below 600°C, the principal impact of H₂ pressure is to decrease volatile yields, apparently through the impeding of volatiles transport out of the coal and from the pyrolysis region. The lack of any enhancement in volatiles yield is a result of the fact that below 600°C, H₂, although thermodynamically powerful, is kinetically an ineffective reducing agent owing to the high strength of the H-H bond and the resulting difficulty in thermally achieving significant concentrations of hydrogen atoms. Unfortunately, the 400 to 600°C region is precisely where coals become very reactive, and need effective reducing agents to prevent retrograde processes.

Recent mechanistic work indicates that bond scissions occurring during liquefaction⁽³⁾ and pyrolysis⁽⁴⁾ are not simply spontaneous thermal rupture of inherently weak bonds, but include to a substantial extent hydrogen-transfer-induced scission of strong bonds as well. One potentially effective way of engendering scission of strong bonds is by H-transfer from hydroaromatic (cyclohexadienyl) radicals. This suggestion finds support in the work of Hutter and Sperling who have subjected several coals to rapid pyrolysis after loading with aromatics, hydroaromatics, or alkylaromatics and found increases in the tar yields and decreases in the char yields of 5 to 10 percentage points.⁽⁵⁾ In contrast, Solomon and Serio have not observed any increase in the tar yields upon pyrolyzing coals in an atmosphere of aromatic hydrocarbons.⁽⁶⁾ Earlier work by Mazumdar and coworkers with reduced coals shows significant enhancement in pyrolysis yields, but does not distinguish between the effect of hydroaromatic hydrogen introduction and bond cleavage that may have occurred during reduction.^(7,8)

Other work in this area appears to have focused on the impact of such additives on liquefaction yields, and on meso-phase formation during coke production. Mochida and co-workers have found some hydrogenated petroleum pitches to be effective liquefaction

agents.(2) These same researchers, as well as a number of other workers, have found additives rich in PCAH to markedly extend the range of fluidity in time and temperature and to promote the development of anisotropy during coke formation.

In order that the loading with aromatics be an effective pretreatment, the reaction conditions must allow for an opportunity for the aromatics to react with the coal before they are simply devolatilized. Liquefaction and coking provide ample opportunity for reactions between the added aromatics and the coal while pyrolysis conditions generally do not favor such interactions. In this paper we report our efforts at determining the range of conditions under which loading of coals with PCAH may result in beneficial effects during pyrolysis.

EXPERIMENTAL PROCEDURE

Coals and Coal Loading. Three coals were tested in this study: a Wyodak (WYO-1, courtesy Univ. of Wyoming), an Illinois No. 6 (PSOC 1098), and a Pittsburgh No. 8 (PSOC 1099). The coals were loaded either with a highly aromatic coal tar (Wt. Av. MW 310) or a vacuum residue derived from a hydroprocessed petroleum pitch (Wt. Av. MW 908).

A simple evaporative loading technique has been used for all of the experiments reported here. The additive was dissolved in THF (stabilized) to produce a 10 wt% "solution," which was filtered through a 0.45 μ m millipore filter. The filtrate was added to the ground coal, and then removed, with periodic stirring, using a stream of argon. In order to minimize removal of extractable materials by THF, and to maximize deposition of the additive within the pores of the coal, the solution was added only to the point of incipient wetness. Nevertheless, since it was anticipated that some extraction would inadvertently occur and perhaps have a deleterious effect (10), "blank" coal samples were prepared by carrying out the loading procedure with pure THF. These THF-treated coals were used as the basis for judging the impact of the additives on loaded additive.

Pyrolysis. The TGA pyrolyses under argon were performed using a Dupont 1090 TGA system. The "rapid heating TGA" pyrolyses were performed using a specially constructed TGA consisting of a vertical tube furnace with a Cahn microbalance. The pyrolyses were performed with the maximum heating rate possible in this apparatus by raising the furnace, preheated to 1000°C, around a quartz vacuum envelope containing ~ 60 mg of coal suspended from the microbalance in a -1-inch diameter quartz flask. This procedure provided a heating rate of about 600°C/min as measured by a thermocouple placed near the flask containing the coal sample. The PY-FIMS experiments were carried out in the programmed temperature inlet of a field ionization mass spectrometer (FIMS). This instrument provides molecular ion profiles and organic weight loss as a function of temperature up to 500°C, and has been extensively used for analysis of high boiling, complex mixtures.

RESULTS

Following the rationale cited above, we have begun a series of experiments designed to test the effect on pyrolysis yields of loading coals with PCAH mixtures. We have thus far used three different pyrolysis techniques with slow to moderate heating rates. These are: pyrolysis-FIMS at high vacuum, TGA in one atmosphere of argon, and rapid heating TGA in vacuum, at heating rates of 2.5°C/min, 20°C/min, and 600°C/min respectively. The results from these experiments are shown in Table 1. The yields have been adjusted for tar vaporization, assuming that the volatility of the tar is not changed by being loaded into the coal. This assumption is of course not strictly true;

the temperature profile of the coal tar components in the PY-FIMS experiments show that vaporization is retarded by about 50°C. However, because the total amount of tar used is only about 10% of the weight of the coal, the error in overestimating tar volatility leads to no more than a 2% underestimate of the coal devolatilization.

From the limited data given in Table 1, we note two significant results. First, with none of the three pyrolysis techniques did the addition of 5 to 13 wt% of coal tar, hydrogenated coal tar, or vacuum resid from a hydrotreated petroleum resid, significantly increase the volatiles yield over THF-treated "blank" coals. Second, the THF treatment itself appears to have a deleterious effect on the release of volatiles from Wyodak coal, particularly above 500°C.

Effect of Changing Pyrolysis Conditions. It was anticipated that the impact of PCAH-loading would tend to increase with increasing heating rate and/or ability to retain the additive through the region of maximum tar formation reactivity. Specifically, since the results of Hüttlinger and Sperling (5) were obtained at heating rates of 1000°C/s, we felt that increasing the heating rate from 20°C/min to 600°C/min would increase the chances of seeing substantial beneficial effect. Furthermore, rapid heating is known to increase the impact of coking additives on fluidity.(11) Although the data in Table 1 definitely show higher yields for the 600°C/min heating in vacuum as expected (12), there was no improvement in the response to tar treatment itself even at this higher heating rate.

Pre-Hydrogenation of the Tar. Although FIMS and nmr analyses show the coal tar to have essentially no hydroaromatic character and only a small amount of alkylaromatic of the fluorene type), the known and projected benefits of large PCAH in shuttling indigenous coal hydrogen for use in conversion led us to use the tar as is for one series of experiments. However, because the added benefit of hydroaromatic hydrogen is well known, the tar was also subjected to mild hydrogenation and used for the coal treatment. The FI mass spectrum of the reduced tar showed 10 to 20 percent of the various PCAH were converted to the respective dihydroaromatics; nevertheless, treatment with this tar still showed no impact on pyrolysis yields.

Use of a Higher Boiling Additive. Since the coal tar itself was found to be 70% volatilized by 350°C (i.e., before the region of maximum chemical reactivity of the coal) under the atmospheric pressure TGA conditions and 88% under the PY-FIMS vacuum conditions, a slightly higher boiling additive was judged to be desirable under these slow heating conditions. Accordingly, we tested the use of the vacuum resid portion of a hydrogenated atmospheric resid (72% volatile at 350 under PY-FIMS conditions), but found this switch to a higher boiling (but less aromatic) additive did not result in any benefit to the pyrolyses, under the conditions thus far used.

DISCUSSION

Further efforts to define the extent of improvement in pyrolysis yields to be gained from PCAH additives as a function of coal type and reaction conditions will focus on the use of higher heating rates, higher boiling PCAH mixtures, and variations in the degree of sample confinement. It seems reasonable to assume any benefits to volatiles production will be maximized at high heating rate for the following three reasons.

- Volatiles yields tend to increase with increasing heating rates;(1,12)
- Coals of high fluidity tend to benefit most from this increase in heating rate;(3)
- PCAH additives increase fluidity under coking conditions.(11)

The probable impact of pressure is less clear. On the one hand, volatiles yields are often substantially larger under vacuum, owing to improved volatiles

transport. (1,12) On the other hand, higher pressures (up to 5 - 10 atm) have been reported to accentuate fluidity increases brought about by pitch additives. (11) Thus, it is not clear what trend will be observed with changing pressure. The experiments of Hüttinger and Sperling (5) were performed under nominal vacuum, but with the sample moderately confined in a Curie point pyrolysis capillary. This combination, along with the rapid heating, apparently resulted in enough of the various naphthalene derivatives remaining with the coal till temperatures of high coal reactivity were reached. Thus beneficial effects were observed notwithstanding the low boiling point of the additives. It was for this reason that we originally thought that a higher boiling tar, with PCAH components known to be much better coal conversion agents (albiet liquefaction) than naphthalene derivatives, would likely show significant beneficial effects - even at the lower heating rates used in this study.

The apparent detrimental effect of THF in the treatment of Wyodak coal is potentially informative, since low rank coals are known to be particularly susceptible to retrograde reactions or other factors that can significantly decrease their convertibility. In the present case, comparison of the FI-mass spectra of the raw and THF-treated Wyodak samples reveals the the high mass envelope (which is never large in this coal) is significantly decreased by the THF treatment. Examination of the temperature profiles for the peaks in this range shows that these are evolved at substantially lower temperatures than the dominant peaks in the spectrum, the dihydroxybenzenes and the phenols. The devolatilization of the high mass materials is consistent with these materials being more aliphatic and pre-existing in the coal, whereas the low molecular weight phenols and dihydroxybenes are products of pyrolysis. With this difference in mind, it may be significant that substantial detrimental effect of the THF treatment was not observed until the temperature exceeded 500°C: aliphatics, though they have high hydrogen content and are potential sources of hydrogen for hydrocracking, cannot generally make this hydrogen readily available until the thermal hydroxyrolysis temperature range (i.e., ~ 600°C). The extent and nature of this detrimental effect will be further explored.

Acknowledgement: Financial support for this work by the U.S. Department of Energy, METC, under contract No. DE-AC21-87MC23286 is gratefully acknowledged.

REFERENCES

1. Howard, J. B., "Fundamentals of Coal Pyrolysis and Hyropyrolysis," in Chemistry of coal Utilization, Second Supplementary Volume, M. A. Elliott, Ed., John Wiley and Sons, New York, 1982, p. 665.
2. O'Brien, R. J.; Gibbins-Matham J. R.; Snape, C. E.; Kandiyoti, R. in Proceedings of the 1987 International Conference on Coal Science, J. A. Moulijn, K. A. Nater, and H.A.G. Chermin, Editors, Elsevier Science Publishers B. V., Amsterdam, 1987, p. 695.
3. McMillen, D. F.; Malhotra, R.; Chang, S.-J.; Hum, G. P., *Energy & Fuels*, 1987, **1**, 193.
4. McMillen, D. F.; Malhotra, R.; Nigenda, S. E., "The Case for Induced Bond Scission During Coal Pyrolysis," *Am. Chem. Soc.*, Div. Fuel Chem. Preprints, 1987, **32**(3), 180.
5. Hüttinger, K. J.; Sperling; R. E.; "Flash Hydroxyrolysis of Coals Doped with Aromatics," in Proceedings of the 1987 International Conference on Coal Science,

J. A. Moulijn, K. A. Nater, and H.A.G. Chermin, Editors, Elsevier Science Publishers B. V., Amsterdam, 1987, p. 699.

6. Solomon, P. S.; Serio; M. A., private communication.
7. Bhattacharyya, A. C.; Mazumdar, B. K.; Lahiri, A., Fuel, 1964, 43, 181.
8. S. Ganguly; Mazumdar, B. K., Fuel, 1964, 43, 281.
9. Mochida, I; Moriguchi; Y.; Korai; Y.; Fujitsu, H.; Takeshita, K., Fuel, 1981, 60, 746.
10. O'Brien, R. J.; Gibbins-Matham J. R.; Kandiyoti, R., Fuel Processing Technology, 1987, 15, 71.
11. Green, P. D.; Patrick, J. W.; Mark Thomas, K; Walker, A., Fuel, 1985, 64, 1431.
12. Gibbins-Matham, J. R.; Kandiyoti, R., "The Effect of Heating Rate and Hold Time on Primary Coal Pyrolysis Product Distribution," Am. Chem. Soc., Div. Fuel Chem. Preprints, 1987, 32(4), 318.
13. Reasoner, J. W.; Hower, J. C.; Yates, L. P.; Lloyd, W. G., Fuel, 1985, 64, 1269.

Table 1

WEIGHT LOSS FOR PYROLYSIS OF COALS AND TAR LOADED COALS

Coal Treatment	2.5°C/min/vac 500°C	% Wt. Loss*			
		20°C/min/Ar		600°C/min/vac	
		500°C	900°C	500°C	900°C
Wyodak					
Raw	30	27.9	63.1	-	-
Blank (THF)	32	22.0	43.8	41.8	61.7
Coal-Tar	34	22.0	44.8	36.6	54.5
H-Coal-Tar	32	-	-	40.4	53.4
Ill. No. 6					
Raw	-	12.0	30.3	-	-
Blank (THF)	32	16.5	31.9	-	-
Coal-Tar	29	8.7	30.3	-	-
H-Coal-Tar	-	-	-	-	-
H-Pet-Res	28	-	-	-	-
Pitts. No. 8					
Raw	-	-	-	-	-
Blank (THF)	-	-	-	30.0	46.8
H-Coal Tar	-	-	-	30.9	45.6
H-Pet-Res	-	-	-	-	-

* The %-volatility of the tars alone in vacuum and in Ar up to 500°C was 95 and 80% respectively. The volatilities shown above are for the whole coals. They are corrected for tar volatilities for the tar-loaded cases.