

Internal and External Mass Transfer Limitations in Coal Pyrolysis

Phillip E. Unger*

Dept. of Chem. Eng., Carnegie-Mellon University, Pittsburgh, Pa. 15213

Eric M. Suuberg

Division of Engineering, Brown University, Providence, R.I. 02912

Introduction

The recent work of Professor Howard and colleagues at MIT has helped focus attention upon the significant role that mass transfer limitations can play in shaping the pyrolysis behavior of coals (see, for example, the review by J.B. Howard, 1981). Despite having learned a great deal from these and earlier studies, it is fair to say that much remains to be learned on this topic. The present paper outlines some recent results of relevance. The focus here will be mainly on studies of high heating rate pyrolysis of finely ground coals (less than a millimeter in diameter) in low particle concentration environments. Such conditions of course exist in an enormous variety of coal conversion processes. The present focus is narrowed further by considering only the tar products of pyrolysis. Not only are these species central in discussions of mass transfer limitations, but they are of considerable interest as dominant products of most coal pyrolysis processes. Also, the topic of tar chemistry fits in well with Professor Howard's own discussion in this session, since tars have been suggested as key intermediates in certain soot formation processes during combustion of coal (Seeker et al., 1981; Mclean et al. 1981).

Background

It is customary to explore for internal mass transfer limitations in gas-solid reaction systems by performing experiments at various particle diameters. Unfortunately, data on the variation of pyrolysis product yields with particle diameter are often influenced by unintentional variations in heat transfer conditions (J.B. Howard et al., 1981). In addition, even in situations in which heat transfer to particles is relatively well defined (as in the heated wire mesh technique described below), there are sometimes difficulties in particle size characterization, since particles soften, swell, and/or flow on the surface of solid supports during pyrolysis. Consequently, most reliable information on mass transfer effects during rapid pyrolysis of fine particles has come from experiments in which the primary variable is external gas pressure.

It is well established that pyrolysis of coals under reduced pressures leads to increased volatile matter yields, compared to pyrolysis under atmospheric pressure (H.C. Howard, 1945, 1963; Anthony and J.B. Howard, 1976; J.B. Howard, 1981). There also remains little question that an increase in tar yield is mainly responsible for this increase in volatile matter yields (see above reviews and Suuberg et al., 1979a). Tar

* Present Address: Shell Development Corp., Houston, Texas

is here crudely defined as any room temperature condensable products of pyrolysis; water is excluded, but small amounts of product that is sometimes categorized as "oil" may be included. The increase in tar yields under reduced pressure has been qualitatively explained in the following terms. When heated, the coal "depolymerizes", yielding tar-like species. If these species are quickly transported away from the particle, they are observed as part of the tar products of pyrolysis. If, however, the species are given long times in the hot environment of the particles, they may be "repolymerized" into the mass of the particle, and later be counted in with the char.

While there is little debate over this qualitative picture, the development of quantitative models has revealed a great diversity of opinion concerning the nature of volatiles transport. Some have modeled the controlling transport processes by use of empirical external mass transfer coefficients (Anthony et al., 1974; Reidelbach and Summerfield, 1975), some by postulating internal pore transport to be limiting (Russel et al., 1979; Melia and Bowman, 1982, the latter allowing for bubble formation), one by considering nucleation and motion of bubbles within softened coal particles (Lewellen, 1975) another by considering the motion of volatiles in pseudo-bubbles (not accounting for particle swelling, James and Mills, 1976), and some by employing both a crude model of pore diffusion and an external film coefficient (Chen and Wen, 1979). Other models have more explicitly considered how product compositions may vary during pyrolysis. Of these, several have represented gas film diffusion as controlling, much as in classic droplet evaporation models (Suuberg et al., 1979b; Unger and Suuberg, 1981; and Zacharias, 1979). In other cases, pore transport models have again been developed (Gavalas and Wilks, 1980; Cheong, 1977). Finally, in one case, mass transport limitations have been handled through the use of a pseudo-chemical kinetic model (Solomon and Colket, 1979).

It is apparent that there continues to be considerable disagreement as to the true nature of mass transfer limitations which are responsible for the observed effects of pressure. Part of the disagreement concerns the location of the main transport limitation—whether it is internal or external to the pyrolyzing coal particle. Another source of the apparent disagreement between different workers concerns the nature of the starting coal—whether it is softening or non-softening (in the former case, it makes more sense to model the particle as essentially a droplet). In this paper, some of these issues are readdressed in the context of newly available data on the nature of coal tars.

General Observations Concerning Mass Transfer Limitations During Pyrolysis

There is a paucity of information concerning the effect of pressure on product yields observed during pyrolysis. Figure 1 presents an attempt at summarizing the majority of relevant data concerning pressure effects on tar yields during pyrolysis. It is a plot of reported tar yield vs. pressure, which illustrates the general feature of decreasing tar yield with increasing pressure. In order to compare the results for a wide range of ranks in a single figure, the data for

each coal have been "normalized" by dividing tar yield at a particular pressure by the maximum tar yield which can be obtained with that coal. This maximum tar yield naturally occurs at the lowest pressure examined during the series of experiments on the particular coal. Table 1 summarizes the conditions under which the data in Figure 1 were obtained. Where actual tar yield data were not available, a correlation based on all the available tar yield data was used to estimate normalized tar yields from weight loss data. This correlation was of form:

$$\text{Normalized tar yield} = 1 - 0.55((v_0 - v)/(v_0 - v_H))$$

where v_0 is the weight loss at the lowest pressure employed in the study, v_H is the weight loss at the highest pressure employed in the study, and v is the actual weight loss at the pressure of interest.

A rather consistent trend of decreasing tar yield with increasing pressure is observed in Fig. 1. Note that the data include both softening coals and non-softening coals, ranging in rank from lignite to low volatile bituminous. It is noteworthy that the points which seem to fall above the general trend are mainly those which were normalized with respect to 0.1 atm tar yield data. Both the data of Anthony et al. (1974) and Arendt and van Heek (1981) imply that 0.1 atm is still a high enough pressure such that an additional decrease in pressure might tend to increase tar yields further; thus the normalization factor applied to the data of Arendt and van Heek (1981) and Cavalas and Wilks (1980) might be relatively higher than that applied to the other data. Were lower pressure data available in these latter two cases, it is possible that normalization with respect to such data would pull these groups' results into even better agreement with the general trend.

On the basis of the general agreement between the diverse sets of data shown in Fig. 1, it might be concluded that the effect of external pressure is similar in all ranks of coal. Of course the coals that produce the largest amounts of tar are likewise those whose product yields are most sensitive to variations in pressure. The actual nature of the mass transfer process responsible for such behavior is still unknown, however. Some order of magnitude analyses have been advanced to eliminate a few possibilities.

If a particle is non-softening and ordinary gas phase diffusion were solely responsible for transport of tar, Russel et al. (1979) have pointed out that internal pore diffusion would almost certainly be controlling. It is possible that either pressure driven bulk flow or Knudsen diffusion might play a role in pore transport (though it must be recalled that the latter does not depend upon pressure). Niksa (1981) concludes that bulk flow must control flow out of the pores, so long as the particle retains its identity as a solid; however, the possible role of an external gas film limitation is not considered.

If the coal particle softens, Attar (1978) has proposed that a competition exists between liquid phase diffusion and bubble nucleation within particles. While plausible, it seems equally likely that bubbles are formed by gas pressure swelling pores originally present within the particle. It is not clear how important bubble transport of tar species is. A small bubble breaking the surface of the particle only serves to increase the surface area of the particle slightly, but a large bubble swelling the particle into a cenosphere increases its surface area

enormously. The extent to which bubbles aid in diffusion of species from bulk to surface is also unclear. In addition, it is possible that bubble growth and motion could be a source of internal mixing. It is difficult to make any general statements about the effect of bubbles or their significance, except that it is likely that their presence will enhance transport rates. The remainder of the discussion on transport in the case of softening coals will disregard the role of bubbles.

Softened coal particles have been previously viewed as analogous to multicomponent liquid droplets (Unger and Suuberg, 1981). Consider the ratio of characteristic time for internal liquid phase diffusion of tars from the bulk to the particle surface (t_i) to the characteristic time for external diffusion of the tar through a stagnant vapor film which surrounds the particle (t_e):

$$t_i/t_e = D_v C_v y / D_L C_L x$$

where D_v and D_L are vapor and liquid diffusivities, respectively; C_v and C_L are vapor phase and particle phase molar densities; y is the vapor phase mole fraction of a tar species at the particle surface, and x is the liquid phase mole fraction of a tar species at the particle surface. By use of Raoult's Law, if P^0 is the vapor pressure of the tar species, $y/x = P^0/P_{tot}$. In the case of atmospheric pressure pyrolysis, P_{tot} is 1 atm. and (C_v/C_L) is of order 10^{-2} to 10^{-3} . Neither P^0 nor D_v/D_L is known a priori. In particular, D_L is difficult to estimate, even to an order of magnitude.

It has been suggested that D_L can be estimated by use of the Stokes-Einstein equation to be of the order of 10^{-14} sq. cm/sec (Cavalas, 1982). Unfortunately, such estimates are based on having a knowledge of coal viscosity, which is itself unknown to even an order of magnitude under the high heating rate, high temperature conditions of interest here. In addition, recent measurements of the diffusivity of naphthalene in high viscosity oils have shown the Stokes-Einstein equation to be invalid (Hiss and Cussler, 1973). This is not surprising, since this equation has been derived assuming a large disparity in the size of solvent and solute, a condition which is met in neither coal melts nor the experiments described above. Although it is impossible to make even a crude estimate of D_L , it is reasonably certain that it will be smaller than 10^{-5} sq. cm/sec, implying that (D_v/D_L) is larger than 10^5 or 10^6 . Hence, unless P^0 is of order 10^{-3} or less, internal diffusion will definitely control.

Again, P^0 is difficult to estimate, because there exist no vapor pressure data for the type of coal tars of interest. To make a crude estimate, we have improved a previously used (Suuberg et al., 1979) simple correlation for vapor pressures of high molecular weight hydrocarbons:

$$P^0(\text{atm}) = 3756 \cdot \exp(-253 \cdot MW^{0.586}/T)$$

where MW is molecular weight and T is temperature in K. See Table 2 for a comparison of the predictions of the correlation to vapor pressure data. Note that the correlation does not include any structural information, nor has it been tested against data on high molecular weight materials with significant heteroatom contents. Considering "typical" tar molecular weights in the range 500 to 2000 (Unger and Suuberg, 1983a), at temperatures around 1000K, then apparently P^0 is of order 10^{-1} to 10^{-6} atm. On the basis of this range of values, it is impossible to draw a firm conclusion regarding the relative importance of internal and external mass transfer limitations. It is possible that

the escape of light species is limited by internal diffusion rates, but the escape of heavy species is limited by external film diffusion.

In this paper, we explore some new experimental evidence which sheds some light upon the nature of the transport limitations which exist during coal pyrolysis. Other important aspects have been presented elsewhere (Unger and Suuberg, 1983a, 1983b).

Experimental

Data will be presented on the molecular weight distributions of tars produced under a variety of pyrolysis conditions. The experimental technique has been described in detail elsewhere (Unger and Suuberg, 1983a). The widely used heated wire mesh technique was used to pyrolyze small (10-20mg) samples of coal. In these experiments, a thin layer of coal is uniformly spread on a wire mesh which is heated electrically at a predetermined rate to a peak temperature, from which the sample is then immediately recooled without an intervening isothermal period. The mesh is contained inside of a reactor shell which is filled with helium at the desired pressure; the helium remains relatively cold throughout the experiment, as the mesh is the only part of the apparatus which is heated. Since the mesh offers little resistance to escape of volatile products from the thin layer of particles which rest upon it, the volatiles may be assumed to be immediately quenched upon escape from the particle (this point is discussed further below).

Tars are gathered by washing the reactor with tetrahydrofuran (THF) and are analyzed by liquid chromatography for molecular weight distribution. In a few cases, extracts of the chars were obtained by soaking the chars in boiling THF for at least 15 minutes, in an ultrasonic bath. These extracts were analyzed in the same manner as tars for their molecular weights.

In a few cases, tars which had previously escaped the coal particles were reheated in the wire mesh. The sample sizes were roughly 10mg, and the run procedures were identical in every respect to the coal pyrolysis runs.

Finally, a few coal pyrolysis experiments were performed in an atmosphere of pure nitric oxide (NO). Again, the technique was otherwise identical to that used in normal coal pyrolysis experiments.

Table 3 gives elemental compositions of all coals examined in this study.

Results and Discussion

Figure 2 displays molecular weight data for Bruceton standard high volatile bituminous coal tars and extracts. These data will be discussed at length elsewhere (Unger and Suuberg, 1983a) and are shown here only as a framework for subsequent discussion. It should be emphasized that the Bruceton coal is a softening coal. Results for non-softening coals will be given below. Several conclusions have been drawn from these data:

-Tars produced at atmospheric pressure are significantly lighter in molecular weight than tars produced at vacuum. The number average molecular weight for the atmospheric pressure tars is typically

between 330 and 350, whereas for vacuum tar it is 430 to 460.

-Both vacuum and atmospheric pressure tars are significantly lighter than the extractable tars left behind in the particle; there is clearly a selective distillation.

-Neither vacuum nor atmospheric pressure tar molecular weight distributions show much sensitivity to temperature.

Subsequent work has revealed several other points (Unger and Suuberg, 1983b):

-There is a low inventory of extractable material present in the particle over the period of most active tar evolution.

-The large difference in yields of atmospheric pressure and vacuum tars develops mainly at peak temperatures in excess of about 550°C. Above this temperature, vacuum tar continues to be evolved, whereas atmospheric tar evolution is virtually complete at this temperature.

The generality of these conclusions is being tested by examining the behavior of a number of other coals. The temperature dependence of the molecular weight distributions of tars from an Illinois No. 6 high volatile bituminous coal, a Pocahontas low volatile coal and a North Dakota lignite are shown in Figures 3 through 5, respectively. Of these other coals, only the Illinois No. 6 softens during pyrolysis. The behavior of the Illinois No. 6 is very similar to that of the Bruceton coal, including the fact that the molecular weight distribution is relatively independent of temperature. The tar from the North Dakota lignite is likewise very similar in molecular weight range to the tar from the two softening coals. Again, the molecular weight distribution shows little sensitivity to temperature of evolution.

The tar from the Pocahontas coal shows a markedly lower molecular weight range than the tars from the other coals. The number average molecular weight of the Pocahontas tar is 240 at 464°C and 200 at 810°C. As of this writing, no extract molecular weight distribution data are yet available for this coal.

The data which are presently in hand suggest that the evolution of tar during coal pyrolysis is a complex combined transport and reaction process. Clearly, a pure internal liquid phase diffusion limitation cannot explain the trends observed in the softening coals, since it would be impossible to predict a pressure dependence of molecular weight distribution on this basis alone. A simple "batch distillation" transport model is inappropriate, since it would predict increasingly high tar molecular weights with increasing temperature. This has not been observed in any of the coals tested, except over very limited parts of the process (Unger and Suuberg, 1983a). The fact that the tars are apparently a light fraction of the extractable molecules present within the particle nevertheless seems to support an evaporation controlled mechanism. On this basis, a hypothesis that the evaporation process might be essentially analogous to a continuously fed distillation is currently being tested. Other data recently suggested that the pool of evaporating tar is continually being replenished by chemical reactions whose products are basically in a narrow range of molecular weight (Unger and Suuberg, 1983b).

As a further test of the hypothesis that evaporation rate controls tar escape from the particle, additional experiments were performed which involved evaporation of pure tars from the wire mesh.

Several milligrams of tar were collected by ordinary methods from the pyrolysis of the Illinois No. 6 coal. This tar was dried and spread in a pure state over the same type of wire mesh as used for coal pyrolysis. Figures 6 and 7 show the results of reheating the tar samples.

Figure 6 shows the molecular weight distribution of the "raw" tar and the molecular weight distributions of the re-evaporated tar fractions. The "raw" tar in Figure 6 differs from the tar products shown in Fig. 3 because drying of any tar sample promotes condensation of light fractions into heavier fractions (as does exposure of tar solutions to light or peroxides). It is apparent from Fig. 6 that tars up to 2000 in molecular weight can indeed evaporate, since no other transport processes were likely to be important in this experiment. It is interesting that upon repyrolysis, the molecular weight distribution of the re-evaporated tar is similar to the original molecular weight distribution of the Illinois No. 6 tar, prior to drying (see Fig. 7).

The above data imply that some degree of true pyrolysis also occurs in the tar re-evaporation experiments. Note in Fig. 6 that there is more light molecular weight material evaporated than was originally present. It is possible that the destruction of high molecular weight species (>2000 in molecular weight) explains why there is relatively much less of this material in re-evaporated tar than in the original coal tar. Alternatively, the presence of such high molecular weight material in the original tar might imply some role of physical entrainment mechanisms during coal pyrolysis, which do not exist in the tar re-evaporation experiments. The physical entrainment picture receives some support from a crude calculation; from the previously presented vapor pressure correlation, the vapor pressure of a 2000 molecular weight species is less than a microtorr at about 450°C. Yet there is a significant amount of such material present in the low temperature tars of all coals studied at that temperature. Of course, there is a great deal of uncertainty in the use of this correlation (derived for considerably lighter, pure hydrocarbons) for coal tars.

Finally, there was some concern that the observed molecular weight distributions might be influenced by secondary gas phase reactions of tar fragments. It was thought that free radical processes were the most likely pathway for such processes, so a crude attempt was undertaken to trap free radicals that might exist in the gas phase. This involved performing the coal pyrolysis experiments in an atmosphere of nitric oxide (NO, a well-known radical trap) rather than helium. It was postulated that if small free radicals were recombining to give larger tar molecules, there would be evidence of a downward shift in the tar molecular weight in NO. The results in Fig. 8 show no such evidence; in fact the average molecular weight of tar species appears to go up in NO. Unfortunately, the test is not clean by any means, since the NO obviously participated in the solid phase chemistry as well.

Conclusions

It now seems apparent that there is a great deal of similarity in the mechanisms of escape of tar from both softening and non-softening coals. The weight of evidence presently appears to favor an evaporation controlled escape of tar from the particle. A simple "batch distillation" model is obviously inappropriate for describing the process. Instead, it seems that a model which allows for simultaneous

tar precursor formation reactions, evaporation processes, and repolymerization reactions is necessary.

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Table 1
Conditions for Figure 1

<u>REFERENCE</u>	<u>SYMBOL</u>	<u>COALS⁺</u>	<u>PARTICLE SIZE (μ)</u>	<u>HEATING RATE/MAX. TEMP.</u>	<u>PRESSURE (ATM)</u>	<u>METHOD</u>
ARENDR & VAN HECK (1981)	+	HVB(26), HVB(25), MVB(17), LVB(9)	200-315	200 °C/s 1000 °C	0.1-90	HWM
CAVALAS & WILKS (1980)	⊙	HVB(19), SUBB(6)	110	600 °C/s 500 °C	0.1-2	HWM
SUUBERG ET AL. (1978, 1979)	•	LIGNITE(8) 53-88 HVB(36)		1000 °C/s >900 °C	10 ⁻⁴ -69	HWM
UNGER & SUUBERG (1983b)	⊠	HVB(36)	62-88	1000 °C/s >900 °C	10 ⁻⁴ -1	HWM
H.C. HOWARD (1945)	Δ	HVB(20)	400-800	1 °C/s 525 °C	10 ⁻⁴ -1	RETORT
*ANTHONY ET AL. (1974)	■	HVB	70	>650 °C/s 1000 °C	10 ⁻³ -69	HWM
*NIKSA (1981)	×	HVB	125	1000 °C/s 750 °C	10 ⁻⁴ -100	HWM

* Tar yield data estimated

+ Maximum observed tar yields under vacuum shown in parentheses

HWM= Heated Wire Mesh

Table 2
Comparison of Predicted and Measured Temperatures
for a Vapor Pressure of 0.5mmHg ($^{\circ}$ C)

<u>Compound</u>	<u>MW</u>	<u>Meas. Temp.</u>	<u>Calc. Temp.</u>
1-t-Butyldecahydro-naphthalene	198	59.5	71.2
1,2-Diphenylbenzene	231	124.0	115.3
Perhydroperylene	262	150.5	145.1
3-n hexylperylene	336	198.0	210.8
2-n octylchrysene	339	242.5	213.3
3-n decylpyrene	342	235.5	215.8

MW=Molecular Weight

Vapor pressure data from G. Smith, J. Winnick, D. Abrams, and J. Prausnitz, Can. J. Chem. Eng., 54, 337(1976).

Table 3
Ultimate Analyses of Coals Examined

<u>COAL</u>	<u>C</u>	<u>H</u>	<u>O</u>	<u>N</u>	<u>S</u>	<u>ASH</u>	<u>MOISTURE</u>
BRUCETON PITTS. NO. 8 BITUMINOUS	80.4	5.3	6.7	1.6	1.0	4.6	1.7
HILLSBORO ILL. NO. 6 BITUMINOUS	67.2	4.6	12.3	1.2	3.4	11.7	8.6
W. VA. POCAHONTAS LOW VOLATILE BITUM.	84.4	4.2	3.7	0.3	0.5	6.8	0.2
NORTH DAKOTA LIGNITE	66.7	3.7	19.5	0.9	0.8	9.3	32.4

All results on a dry basis except moisture, which is reported on an as-received basis. North Dakota lignite is dried prior to use.

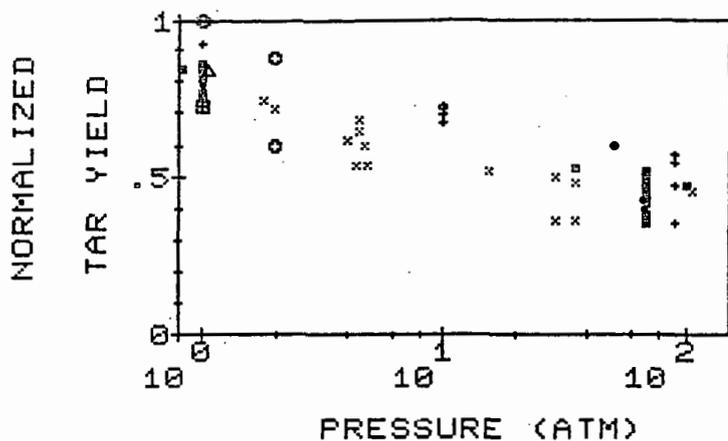


FIGURE 1. VARIATION OF TAR YIELD WITH PRESSURE OF INERT GAS EXTERNAL TO THE PARTICLE DURING PYROLYSIS. SEE TABLE 1 FOR EXPLANATION OF SYMBOLS.

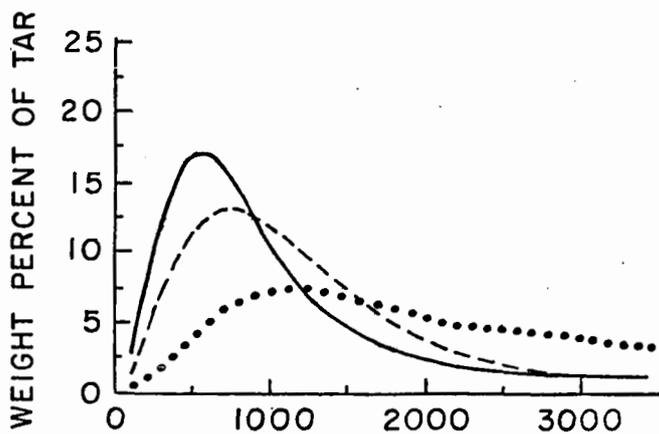


FIGURE 2. MOLECULAR WEIGHT DISTRIBUTIONS OF BRUCETON COAL TARS AND EXTRACTS. SOLID CURVE-ATMOSPHERIC PRESSURE TAR; DASHED CURVE-VACUUM TAR; DOTTED CURVE-COAL EXTRACT. ALL FOR SAMPLES HEATED AT 1000°C/s TO 546°C, FOLLOWED BY COOLING AT 200-400°C/s.

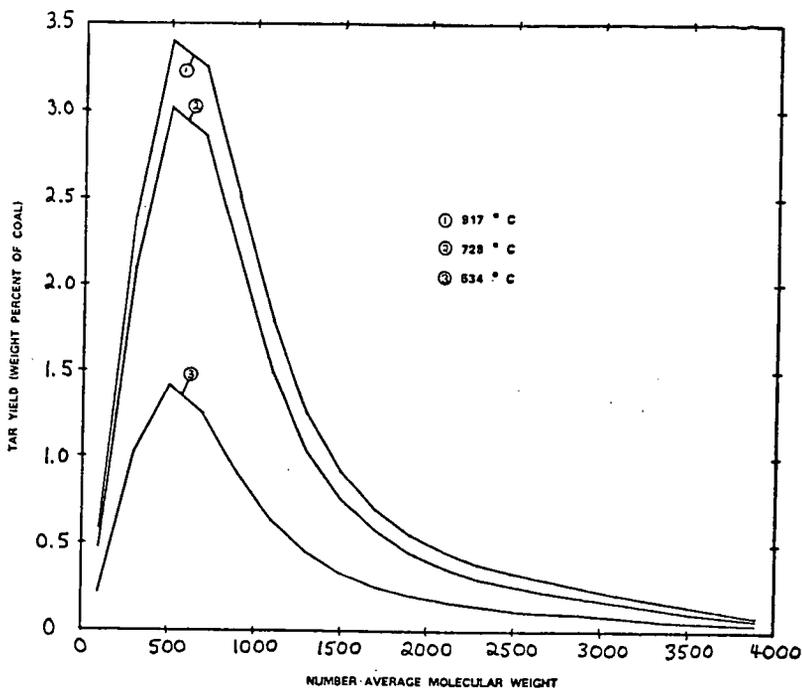


FIGURE 3. MOLECULAR WEIGHT DISTRIBUTIONS OF ILLINOIS NO. 6 ATMOSPHERIC PRESSURE TAR. SAMPLES HEATED AT 1000°C/S TO INDICATED TEMPERATURES.

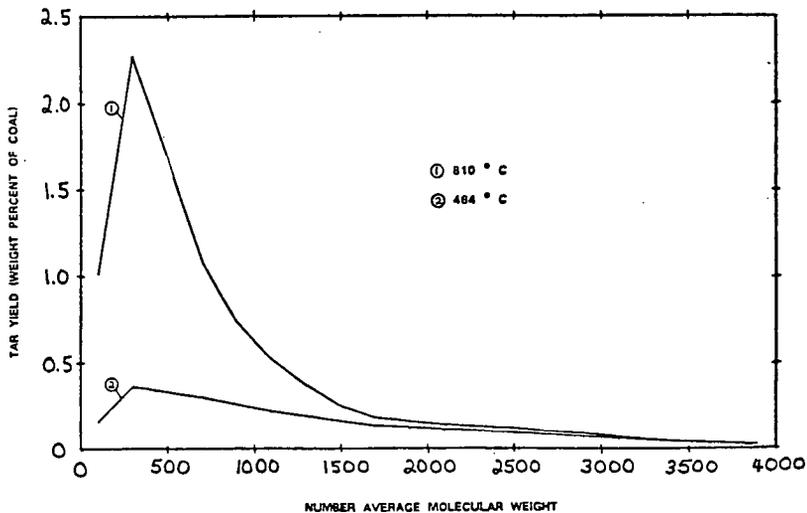


FIGURE 4. MOLECULAR WEIGHT DISTRIBUTIONS OF POCAHONTAS LOW VOLATILE COAL ATMOSPHERIC PRESSURE TAR. SAMPLES HEATED AT 1000°C/S TO INDICATED TEMPERATURES.

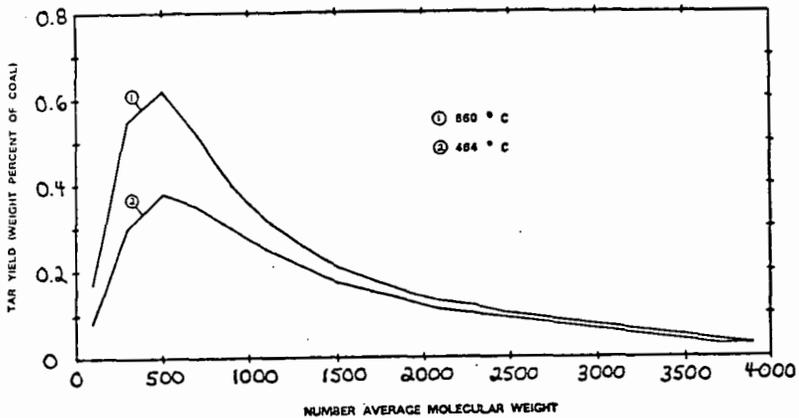


FIGURE 5. MOLECULAR WEIGHT DISTRIBUTIONS OF NORTH DAKOTA LIGNITE ATMOSPHERIC PRESSURE TAR. SAMPLES HEATED AT $1000^{\circ}/s$ TO INDICATED TEMPERATURES.

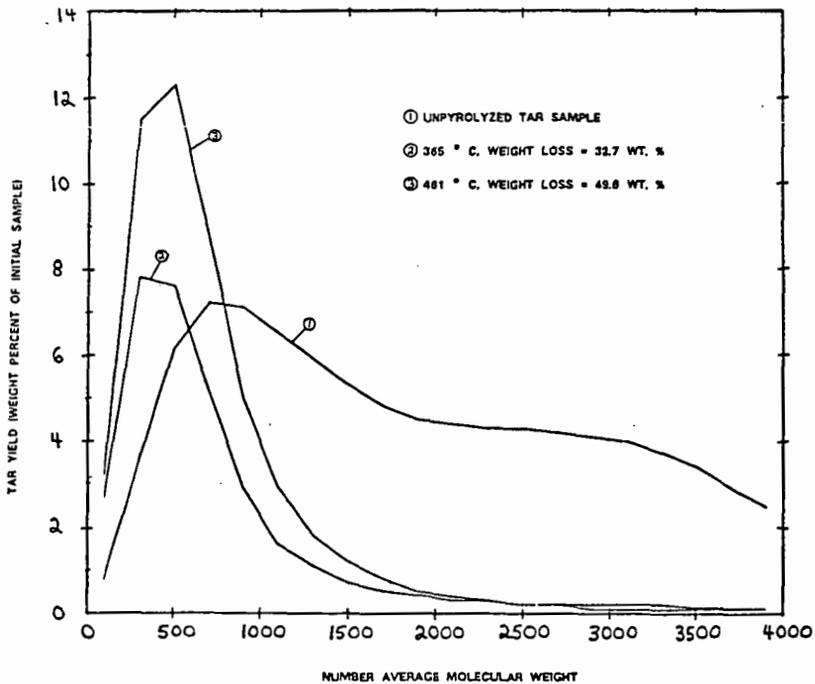


FIGURE 6. MOLECULAR WEIGHT DISTRIBUTIONS OF DRIED "RAW" ILLINOIS NO. 6 TAR, AND RE-PYROLYZED (RE-EVAPORATED) FRACTIONS OF THAT TAR. SAMPLES HEATED AT $1000^{\circ}C/s$ TO THE INDICATED TEMPERATURES.

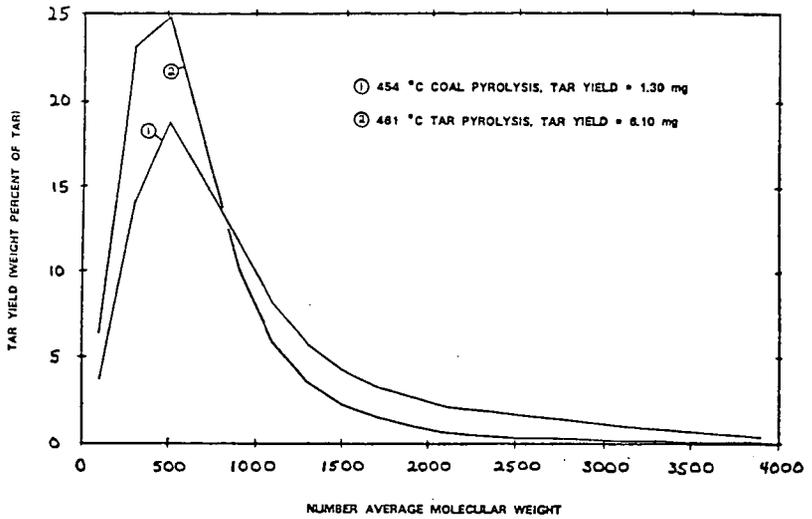


FIGURE 7. A COMPARISON OF THE MOLECULAR WEIGHT DISTRIBUTIONS OF FRESH ILLINOIS NO. 6 TAR (FROM COAL PYROLYSIS) AND RE-PYROLYZED TAR. THESE SAMPLES WERE FORMED UNDER NEARLY IDENTICAL HEATING CONDITIONS (1000°C/S HEATING RATES).

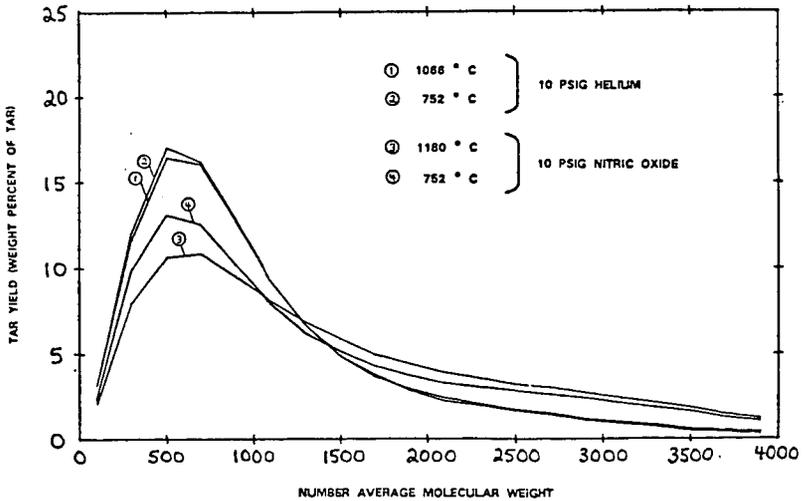


FIGURE 8. A COMPARISON OF MOLECULAR WEIGHT DISTRIBUTIONS OF TARS PRODUCED BY PYROLYSIS OF BRUCETON COAL UNDER HELIUM AND NITRIC OXIDE.