

“gel permeation chromatography is a separation technique based on molecular size. . .”

Gel Permeation Chromatography of Lignite Hydroliquefaction Products — An Exploratory Study *

by

Angela D. Escoto**

Background

The growing divergence between the world's demand for and supply of liquid fuels is one of the more important problems we face today. Consequently, it has become a must for us to develop technically and economically feasible means for alternative sources of energy. In the evolution of fossil fuel technology, production of liquid fuels from coal plays a major role in an attempt to meet the ever increasing demand for energy and at the same time provide protection against environmental pollution. Hence, a vast improvement in understanding coal structure and properties, the kinetics and mechanisms of coal liquefaction, as well as the nature of coal-derived liquids will be needed for the advancement of coal conversion technology.

A major important difference between coal and a liquid hydrocarbon fuel is the hydrogen-to-carbon ratio as compared in Fig. 1 (1). This H/C ratio determines the heating value per unit mass of the material wherein the higher the H/C ratio, the higher is the heating value. Conversion of coal to a liquid fuel, whether by liquefaction or by gasification and synthesis methods, therefore, requires addition of hydrogen to the coal and removal of ash, sulfur, oxygen and nitrogen.

The process used in the experiments conducted on lignite for the purpose of this work is a direct liquefaction process done in a 300 ml. batch autoclave reactor. This involves mixing of the pulverized coal (North Dakota Lignite) and catalyst (Cobalt molybdate on alumina) with a hydrogen donor solvent (Anthracene Oil) to form a slurry which is then fed into the reactor. The reaction is allowed to proceed in the presence of hydrogen at high temperature

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** Assistant Professor, Department of Chemical Engineering, University of the Philippines, Diliman, Quezon City.

and pressure for the desired residence time. The catalyst has been thought to aid in the depolymerization of the coal into molecular fragments which are further thermally cracked and hydrogenated to form stable compounds.

Coal Liquefaction Products:

The products of coal liquefaction consist of gases, liquids and solids. The gaseous products from lignite hydroliquefaction are methane, ethane, propane, butane, carbon dioxide, carbon monoxide, and hydrogen sulfide. The solid product consists mainly of char and unreacted coal.

The most desirable product of liquefaction is, of course, the liquid. In comparison to petroleum residue, coal liquids exhibit a lower H/C atomic ratio and a higher heteroatoms content. In general, these coal liquids are characterized by a high degree of aromaticity and more condensed ring structure. This is to be expected since coal is composed of mono-, di-, and triaromatic rings (2).

Coal liquids have been divided into three major fractions based on their solubility in specific solvents. These fractions are: oils, asphaltenes, and preasphaltenes, the definitions of which are given in Table 1.

Table 1. Definition of Coal Liquefaction Products Based on Solubility

Fraction	Soluble In	Insoluble In
Oils Asphaltenes Preasphaltenes	Pentane or Hexane Benzene or Toluene Tetrahydrofuran	Pentane or Hexane Benzene or Toluene

Objectives:

This work is an exploratory study aimed at using solvent fractionation as an analytical separation technique combined with gel permeation chromatography as a characterization method, to qualitatively measure the rate of depolymerization of lignite in a direct liquefaction process. By correlating the data obtained with reactor operating conditions, it is hoped that a better understanding of the depolymerization rate of lignite as a function of temperature and residence time will be gained.

Apparatus:

The analytical instrument used was a Water Associates Model ALC-201 Liquid Chromatograph equipped with a differential refractometer and a self-standing, fixed wavelength (254 nm) UV absorbance detector (LDC UV Monitor, Model 1205). The instrument has a septum injection port and a solvent delivery

system consisting of a Milton Roy single head, adjustable stroke, constant displacement pump capable of delivering 1000 psi and a flow rate which could be set by vernier adjustment up to a maximum stroke of 3 mls/min. The system set-up is shown in Fig. 2.

The stationary phase used is a Waters 100 angstrom microstyrigel column (30 cm. x 7.8 mm I.D.) with tetrahydrofuran as carrier solvent.

The Permeation Process:

Gel permeation chromatography is a separation technique based on molecular size. The permeation process is illustrated in Fig. 5. The chromatogram at the bottom of the chart shows peaks representing those molecules which come out first (the largest molecules), those which come out in the middle range, and those which are retained the longest (usually the smallest molecules). The plot of molecular size versus elution volume is a loglinear plot. At V_0 , known as the void volume in GPC, all molecules which are much larger than the gel pore of the stationary phase or the column, elute. There is also a point of total permeation, represented by V_t , wherein all molecules of a given size and smaller will elute. The distance between V_0 and V_t is the interstitial volume, V_i . This is the volume where separations take place. The larger this volume is, the more capacity you have for separation in a given range.

Calibration:

In this investigation, the column calibration was performed using the following materials as standards: 30,000 MW Polyvinyl pyridine, polyethylene glycol (973, 633, 402, and 234 MWs), toluene, hexane, and water. The data and the resulting plot are given in Table 2 and Fig. 3, respectively.

Results and Discussion:

Initially, it was attempted to inject the total THF soluble portion of the lignite liquid product into the system. This yielded molecular weight distributions which were masked by solvent or light oil-type materials. This, therefore, necessitated the use of successive extractions interspersed with solvent evaporation by vacuum. The separation scheme is shown in Fig. 4. This procedure allowed for the isolation of preasphaltene, asphaltene, and oil fractions. Each isolated fraction was then injected into the system for molecular weight determination. The corresponding peak heights on the UV response chart, which is a measure of UV absorbance, were used as concentration indicators.

A summary of results is presented in Tables 3 to 8. The data, as shown, give the UV detector response in terms of the elution volume and the corresponding peak height of the various sample fractions under consideration. More specifically, each table gives the results obtained for a particular temperature setting at varying reactor residence times. By using the calibration curve shown

in Fig. 3, the data for elution volume can be used to give the average molecular weight for a given sample. From the data, it can be said that there is no significant difference in the average molecular weight distribution of the various groups of substances making up the asphaltene and preasphaltene fractions with varying residence times and temperatures. For the oil fraction, the mean value of elution volumes at 425 degrees Celsius seem to increase slightly with increasing residence time, indicating a slight decrease in average molecular weight. At 440 degrees Celsius, the mean value of elution volumes for various residence times seems to indicate an increase in average molecular weight from 10 mins. to 30 mins. of reaction time and a decrease from 30 to 40 mins. However, statistical tests at 95% confidence level do not support a significant difference in the mean values of elution volumes (and hence, of molecular weights).

From the trends observed, this investigation, therefore, shows no significant time effects on the average molecular weights of the preasphaltene, asphaltene, and oil fractions with reactor residence time and temperature.

From the tabulated values of elution volume vs. peak height (Tables 7 and 8), it is noted that there are different groups of materials comprising the preasphaltene fraction. Most of these materials have average molecular weights of 600 and 900 (based on the calibration curve), and a smaller fraction at about 150 and 95. In some instances, a very small fraction comes out later than the elution volume of water. This phenomenon could be due to some adsorption on the column.

Similar observations were noted for the asphaltene fractions as in the case of the preasphaltenes. The asphaltenes also consisted of various subgroups having different molecular weights. The largest subgroup comprising the asphaltenes had a range of molecular weights of from 650 to 100. There were more instances in which the adsorption phenomenon was exhibited in the asphaltene case unlike in the preasphaltene case.

Finally, the oil fractions exhibited the smallest average molecular weights which fell in the range of 50-100. No adsorption effect was noted for this case.

Variations in peak heights of the various subgroups comprising the preasphaltenes and asphaltenes, and also the oil fraction against reactor residence time for a given temperature were studied.

According to Beer's Law, UV absorbance, as indicated by the peak height response, is proportional to concentration. In this study, it was shown that this holds true by investigating the variations of UV absorbance with concentration and sample load using naphthalene. In both cases, UV absorbance was found to relate linearly with these parameters. The peak height data were obtained on

Table 2. Microstyragel Column Calibration Table

Standard	Ave. MW	Log MW	V ^{*e}
Polyvinyl Pyridine	30,000	4.477	6.3
Polyethylene Glycol	973	2.988	6.3
Polyethylene Glycol	633	2.801	6.9
Polyethylene Glycol	402	2.604	7.45
Polyethylene Glycol	234	2.369	8.10
Toluene	92	1.964	9.65
Water	18	1.255	10.2

V^{*e} denotes the elution volume in ml.

Table 3. Residence Time Runs at 425 degrees Celsius

Sample Fraction:	Oil
Injection Volume:	2 microliters
Column:	Microstyragel
Solvent:	THF
Flow Rate:	1 ml/min
Chart Speed	0.5 inch/min
UV Detector Attenuation:	64
Residence Time (min)	10.00
Number Of Samples	4
Elution Volume (ml)	
Mean	Peak
95% C.L.	95% C.L.
Variance	Variance
9.338	+/- 0.119
0.075	66.00
*****	*****
Residence Time (min)	20.00
Number Of Samples	2
Elution Volume (ml)	
Mean	Peak
95% C.L.	95% C.L.
Variance	Variance
9.650	+/- 0.635
0.071	74.250
+/- 28.589	3.182
Residence Time (min)	30.00
Number Of Samples	4
Elution Volume (ml)	
Mean	Peak
95% C.L.	95% C.L.
Variance	Variance
9.800	+/- 0.000
0.000	118.100
+/- 27.910	11.234
Residence Time (Min)	40.00
Number Of Samples	2
Elution Volume (ml)	
Mean	Peak
95% C.L.	95% C.L.
Variance	Variance
9.950	+/- 0.635
0.071	88.800
+/- 1.271	0.141

Table 4. Residence Time Runs at 440 degrees Celsius

Sample Fraction:	Oil
Injection Volume:	2 microliters
Column:	Microstyragel
Solvent:	THF
Flow Rate:	1 ml/min
Chart Speed:	0.5 inch/min
UV Detector Attenuation:	64
Residence Time (min)	10.00
Number of Samples	3

Elution Volume (ml)		Peak	Height
Mean	95% C.L.	Variance	Mean
9.900	+/- 0.124	0.050	83.200
+/- 18.974	7.637		
Residence Time (min)	15.00		
Number Of Samples	4		
Elution Volume (ml)		Peak	Height
Mean	95% C.L.	Variance	Mean
9.750	+/- 0.159	0.100	112.900
+/- 15.559	9.780		
Residence Time (min)	30.0		
Number Of Samples	4		
Elution Volume (ml)		Peak	Height
Mean	95% C.L.	Variance	Mean
9.650	+/- 0.312	0.196	151.600
+/- 6.300	3.960		
Residence Time (min)	40.00		
Number Of Samples	5		
Elution Volume (ml)		Peak	Height
Mean	95% C.L.	Variance	Mean
9.860	+/- 0.081	0.065	135.000
+/- 9.290	7.483		

Table 5. Residence Time Runs at 425 degrees Celsius

Sample Fraction:	Asphaltene		
Injection Volume:	20 microliters		
Column:	Microstyragel		
Solvent:	THF		
Flow Rate:	1 ml/min		
Chart Speed:	0.5 inch/min		
UV Detector Attenuation:	64		
Residence Time (min)	10.00		
Number Of Samples	2		
Elution Volume (ml)		Peak	Height
Mean	95% C.L.	Variance	Mean
6.400	+/- 0.000	0.000	26.475
+/- 8.577	0.955		
8.150	+/- 0.635	0.071	42.425
+/- 11.753	1.308		
9.200	+/- 0.000	0.000	38.750
+/- 9.530	1.061		
10.250	+/- 0.635	0.071	36.925
+/- 8.577	0.955		
Residence Time (min)	20.00		
Number Of Samples	5		
Elution Volume (ml)		Peak	Height
Mean	95% C.L.	Variance	Mean
6.395	+/- 0.121	0.097	60.400
+/- 11.614	9.355		
9.415	+/- 0.169	0.137	172.480
+/- 5.785	4.660		
Residence Time (min)	30.00		
Elution Volume (ml)		Peak	Height
Mean	95% C.L.	Variance	Mean
6.388	+/- 0.040	0.025	45.175
+/- 5.290	3.325		
7.925	+/- 0.097	0.061	75.600
+/- 2.331	1.465		
10.062	+/- 0.151	0.095	40.175
+/- 0.855	0.538		
Residence Time (min)	40.00		
Number Of Samples	4		
Elution Volume (ml)		Peak	Height
Mean	95% C.L.	Variance	Mean
6.388	+/- 0.040	0.025	37.625
+/- 4.564	2.869		
7.981	+/- 0.237	0.149	74.875
+/- 1.640	1.031		
9.225	+/- 0.046	0.029	60.325
+/- 3.577	2.248		
10.212	+/- 0.040	0.025	60.625
+/- 1.193	0.750		

Table 6. Residence Time Runs at 440 degrees Celsius

Sample Fraction:	Asphaltene					
Injection Volume:	20 Microliters					
Column:	Microstiyragel					
Solvent:	THF					
Flow Rate:	1 ml./min.					
Chart Speed:	0.5 inch/min.					
UV Detector Attenuation:	64					
Residence Time (min)	10.00					
Number Of Samples	4.00					
Elution Volume (ml)		Peak		Height		
Mean	95% C.L.	Variance	Mean	95% C.L.	Variance	
6.400	+/- 0.065	0.041	34.000	+/- 1.299	0.817	
8.412	+/- 0.040	0.025	118.700	+/- 1.411	0.887	
9.238	+/- 0.040	0.025	99.200	+/- 1.071	0.673	
10.225	+/- 0.100	0.063	51.150	+/- 0.827	0.520	
10.225	+/- 0.080	0.050	77.850	+/- 0.950	0.597	
Residence Time (min)	15.00					
Number Of Samples	4					
Elution Volume (ml)		Peak		Height		
Mean	95% C.L.	Variance	Mean	95% C.L.	Variance	
6.238	+/- 0.076	0.048	36.150	+/- 2.148	1.350	
7.862	+/- 0.040	0.025	76.375	+/- 1.018	0.640	
10.112	+/- 0.100	0.063	51.150	+/- 0.827	0.520	
Residence Time (min)	30.00					
Number Of Samples	4					
Elution Volume (ml)		Peak		Height		
Mean	95% C.L.	Variance	Mean	95% C.L.	Variance	
6.260	+/- 0.028	0.022	44.700	+/- 2.345	1.474	
7.920	+/- 0.113	0.091	115.250	+/- 1.985	1.248	
9.860	+/- 0.102	0.082	43.400	+/- 4.083	2.566	
Residence Time (min)	40.00					
Number Of Samples	3					
Elution Volume (ml)		Peak		Height		
Mean	95% C.L.	Variance	Mean	95% C.L.	Variance	
6.300	+/- 0.124	0.050	39.400	+/- 8.985	3.617	
8.330	+/- 0.190	0.076	118.600	+/- 7.996	3.219	
9.083	+/- 0.190	0.076	109.530	+/- 10.730	4.319	
9.950	+/- 0.215	0.087	81.000	+/- 3.478	1.400	

Table 7. Residence Time Runs at 425 degrees Celsius

Sample Fraction:	Precasphaltene					
Injection Volume:	40 Microliters					
Column:	Microstiyragel					
Solvent:	THF					
Flow Rate:	1 ml /min					
Chart Speed:	0.5 inch/min					
UV Detector Attenuation:	64					
Residence Time (min)	20.00					
Number Of Samples	4					
Elution Volume (ml)		Peak		Height		
Mean	95% C.L.	Variance	Mean	95% C.L.	Variance	
6.262	+/- 0.076	0.048	64.700	+/- 9.712	6.104	
6.925	+/- 0.152	0.096	50.375	+/- 0.762	0.479	
9.256	+/- 0.211	0.133	21.375	+/- 3.003	1.887	

Residence Time (min)	30.00					
Number Of Samples	3					
Elution Volume (ml)		Peak		Height		
Mean	95% C.L.	Variance	Mean	95% C.L.	Variance	
6.300	+/- 0.000	0.000	69.200	+/- 6.969	2.805	
7.083	+/- 0.072	0.029	61.233	+/- 1.691	0.681	
8.600	+/- 0.000	0.000	35.467	+/- 1.597	0.643	
9.250	+/- 0.124	0.050	22.167	+/- 2.586	1.041	
10.267	+/- 0.143	0.058	9.900	+/- 0.896	0.361	
Residence Time (min)	40.00					
Number Of Samples	4					
Elution Volume (ml)		Peak		Height		
Mean	95% C.L.	Variance	Mean	95% C.L.	Variance	
6.325	+/- 0.079	0.050	86.525	+/- 4.299	2.702	
6.975	+/- 0.080	0.050	68.975	+/- 2.787	1.752	
8.575	+/- 0.080	0.050	39.850	+/- 12.168	7.648	
9.300	+/- 0.130	0.082	27.125	+/- 12.193	7.664	

Table 8. Residence Time Runs at 440 degrees Celsius

Sample Fraction:	Precasphaltene					
Injection Volume:	40 Microliters					
Column:	Microstiyragel					
Solvent:	THF					
Flow Rate:	1 ml /min					
Chart Speed:	0.5 inch/min					
UV Detector Attenuation:	64					
Residence Time (min)	10.00					
Number Of Samples	3					
Elution Volume (ml)		Peak		Height		
Mean	95% C.L.	Variance	Mean	95% C.L.	Variance	
6.283	+/- 0.072	0.029	74.900	+/- 4.601	1.852	
7.117	+/- 0.190	0.076	70.000	+/- 6.573	2.646	
8.517	+/- 0.190	0.076	38.933	+/- 15.206	6.121	
Residence Time (min)	15.00					
Number Of Samples	5					
Elution Volume (ml)		Peak		Height		
Mean	95% C.L.	Variance	Mean	95% C.L.	Variance	
6.210	+/- 0.092	0.074	69.160	+/- 5.876	4.733	
6.810	+/- 0.092	0.074	55.440	+/- 2.835	2.283	
8.430	+/- 0.113	0.091	28.880	+/- 3.078	2.479	
9.112	+/- 0.040	0.025	18.950	+/- 6.110	3.841	
Residence Time (min)	30.00					
Number Of Samples	4					
Elution Volume (ml)		Peak		Height		
Mean	95% C.L.	Variance	Mean	95% C.L.	Variance	
6.175	+/- 0.046	0.029	60.050	+/- 2.932	1.843	
6.975	+/- 0.080	0.050	37.800	+/- 0.566	0.356	
8.588	+/- 0.040	0.025	28.250	+/- 1.263	0.794	
10.125	+/- 0.080	0.050	6.700	+/- 3.991	0.627	
Residence Time (min)	40.00					
Number Of Samples	4					
Elution Volume (ml)		Peak		Height		
Mean	95% C.L.	Variance	Mean	95% C.L.	Variance	
6.150	+/- 0.159	0.100	43.225	+/- 2.274	1.429	
7.075	+/- 0.152	0.096	28.550	+/- 0.527	0.332	
8.563	+/- 0.119	0.075	26.650	+/- 2.265	3.604	
10.075	+/- 0.103	0.064	8.175	+/- 1.735	1.090	

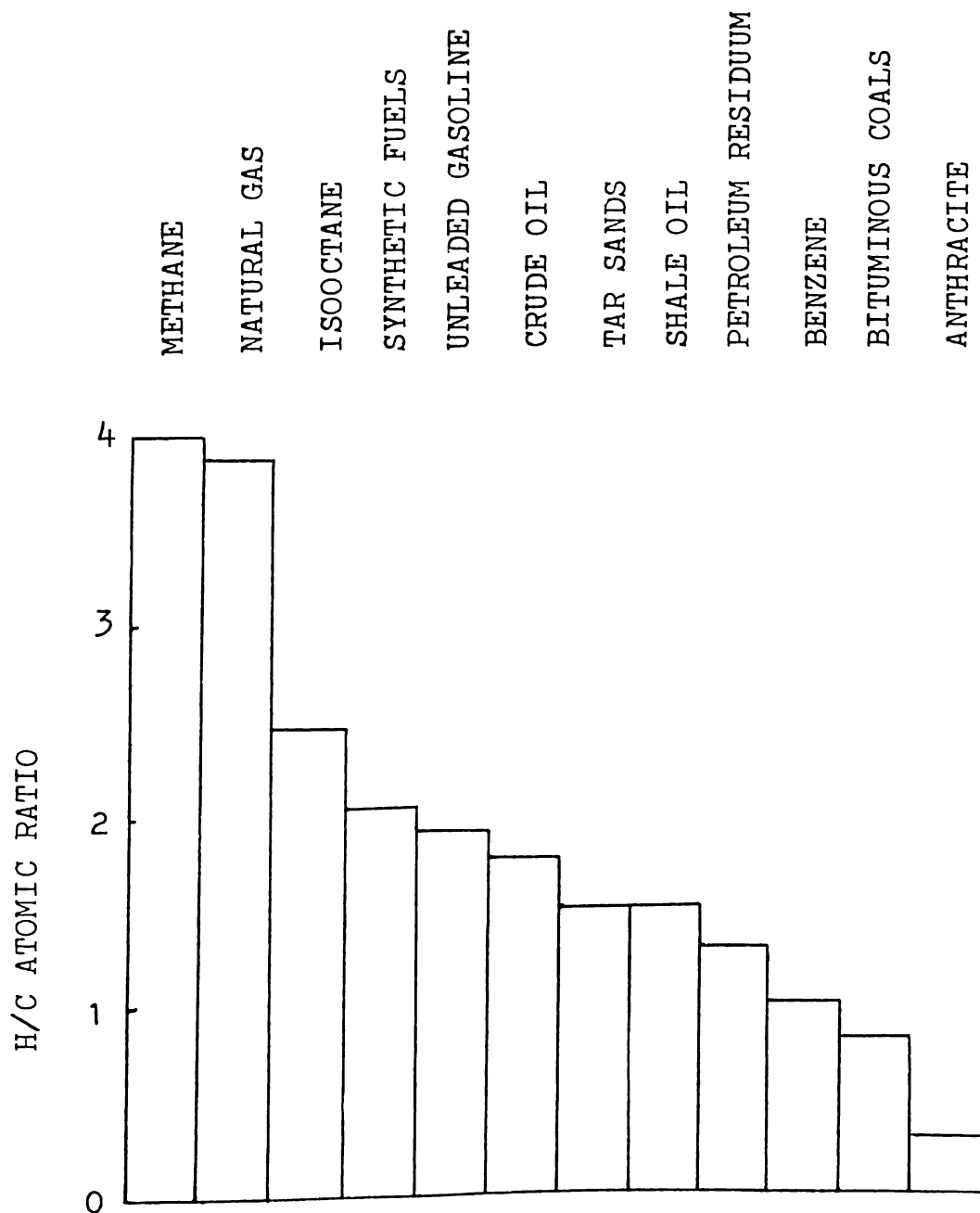


Fig.1. HYDROGEN/CARBON ATOMIC RATIO FOR SEVERAL HYDROCARBON FUELS (1)

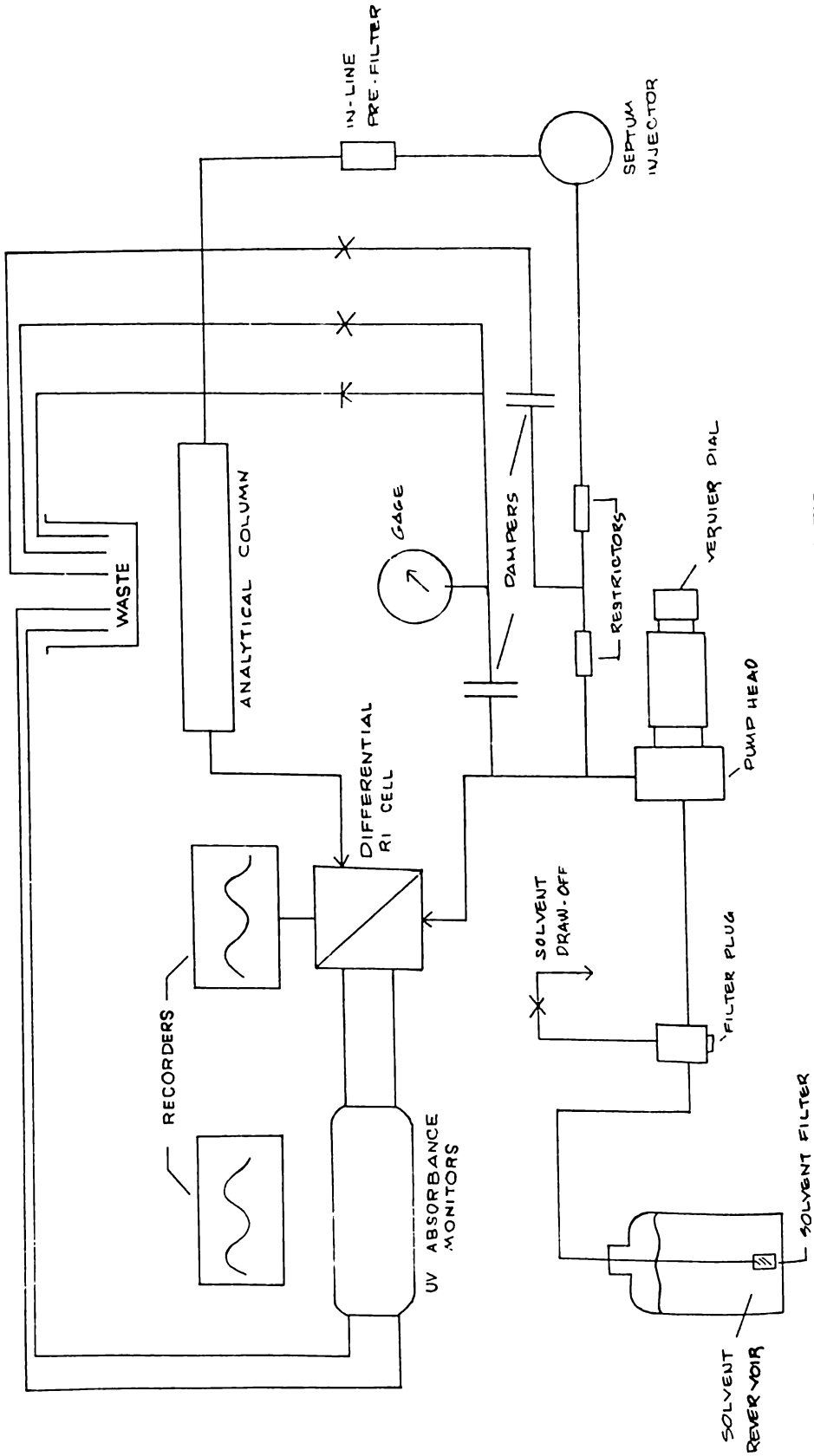


Fig. 2 SYSTEM FLOW SCHEMATIC

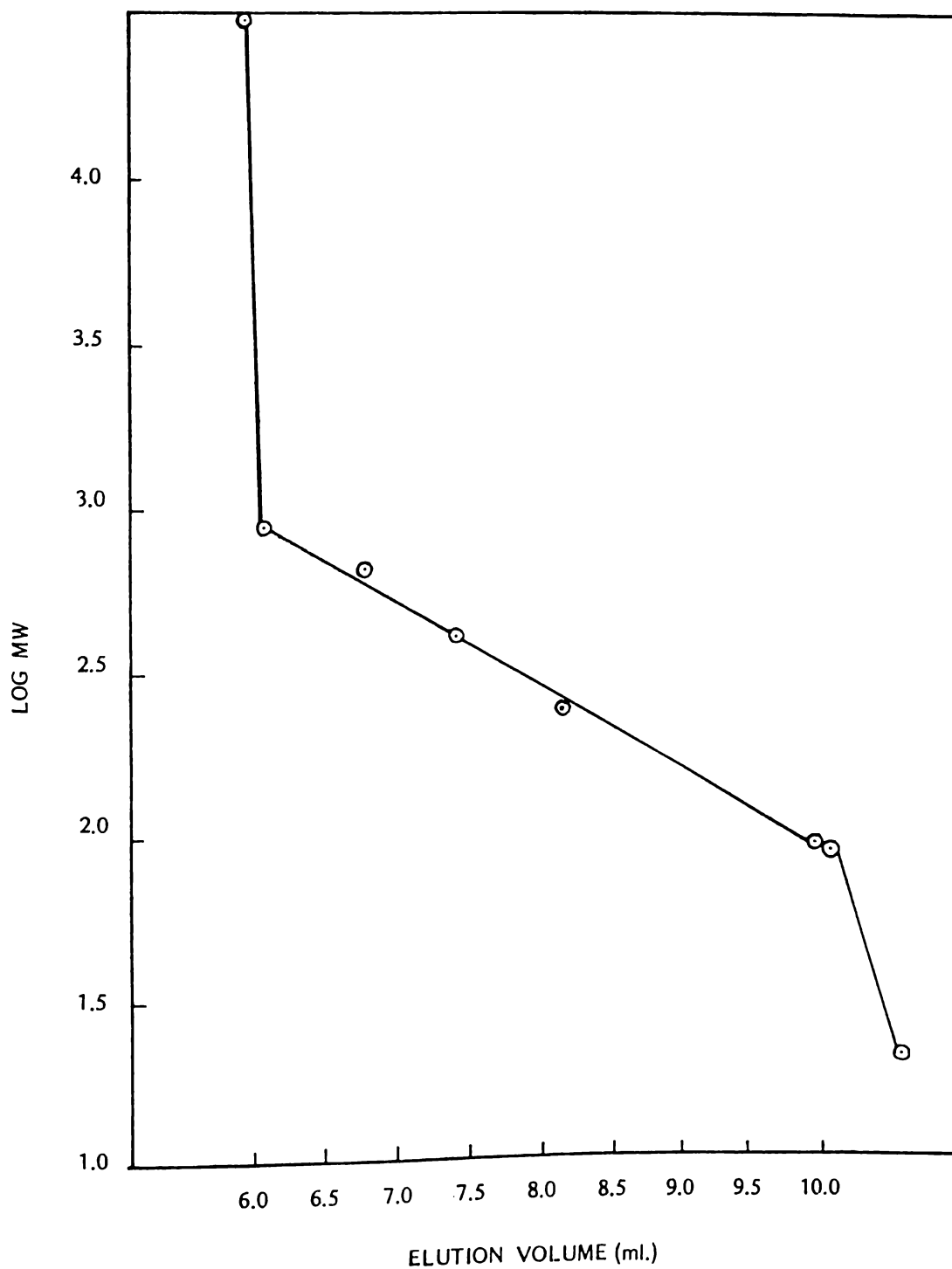


Fig. 3. GPC CALIBRATION CURVE

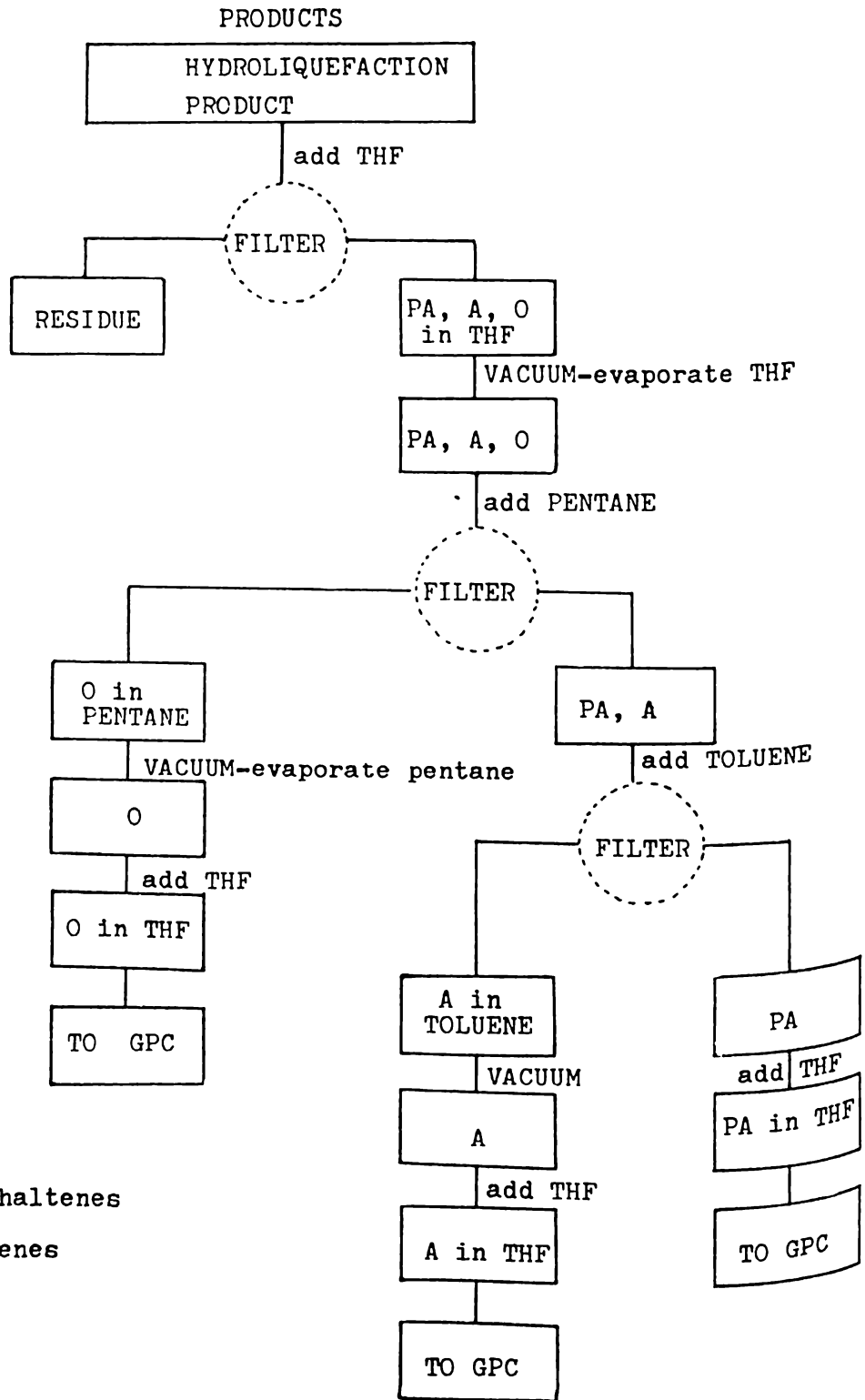


Fig.4. SEPARATION SCHEME FOR LIGNITE HYDROLIQUEFACTION

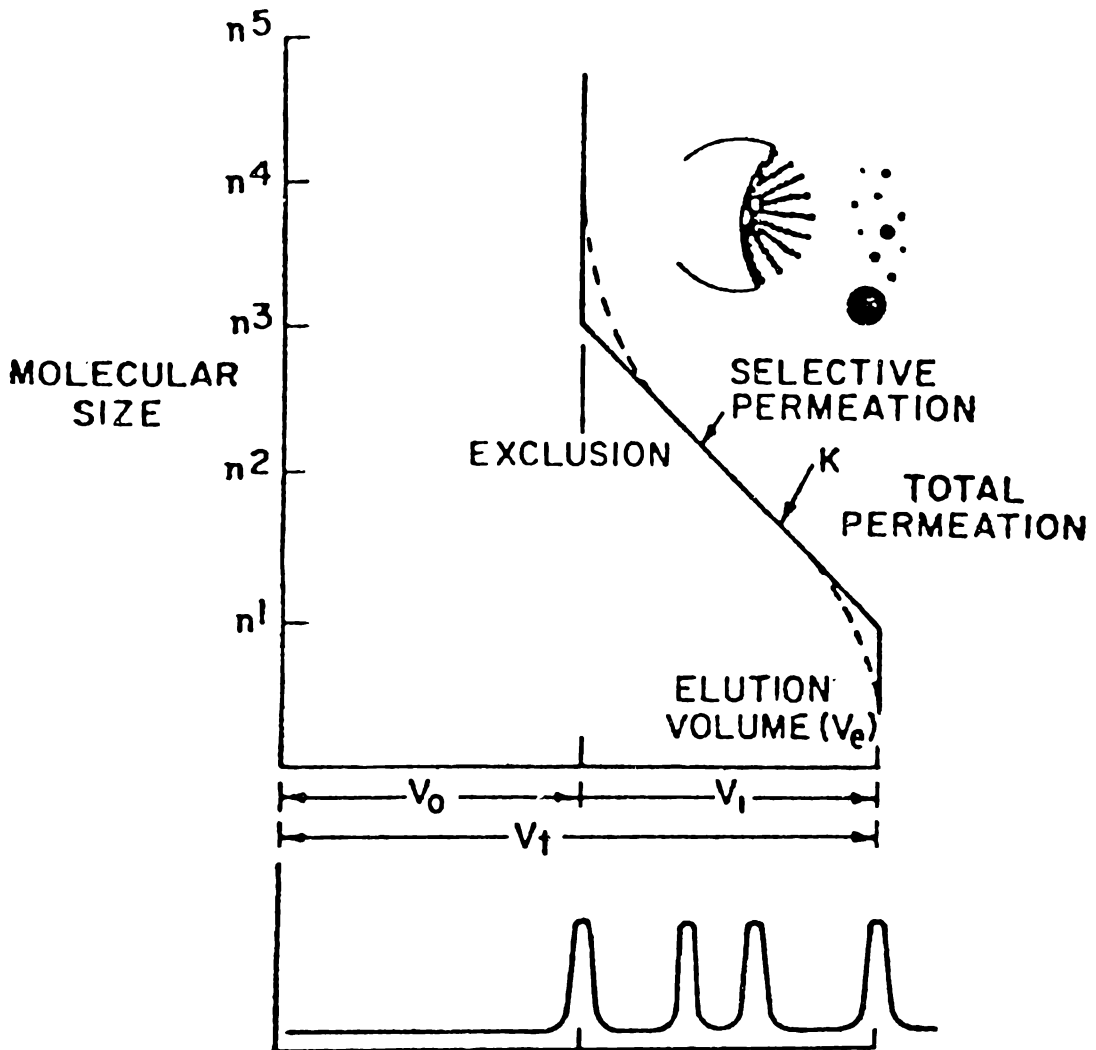


Fig. 5 THE PERMEATION PROCESS

the basis of the same injection volume for each of the groups under consideration. Hence, a direct comparison can be made.

At 440 degrees Celsius, the following residence time effects have been observed: all components of the preasphaltene fraction continuously decrease

in amount with increasing residence time. Some components of the asphaltene fraction at first seem to be consumed and then reappear after some time. The 650 molecular weight group, in particular, is generated during the first 30 mins., after which these compounds seem to react to form something else. The same trend is observed for the oil group at 425 degrees Celsius. From the above observations, it seems that the kinetic scheme followed for the type of reaction under investigation is one wherein all of the fractions considered are not end products in themselves. Rather, the preasphaltene, asphaltene, and oil fractions are all likely intermediate products of reaction.

Also, the data obtained show a definite increase in oil production with increasing temperature of operation.

Statistical analysis of the data presented in this study shows a reasonable accuracy only for the data on the elution volume of the material, and hence the average molecular weight distributions. Data for the peak heights remain questionable. For one thing, the resolution among peaks was poor, more specifically for the preasphaltene and asphaltene fractions. This will then make the peak height measurement subject to error. The actual individual peak heights could not be evaluated with accuracy for this case since tails and shoulders from adjacent peaks contribute to the peak height measurement of each peak. What could be done for this case is to deconvolute the chromatograms and come up with the pure individual peaks which when summed up will give back the original curve. This, however, is beyond the scope of this investigation.

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