THE EFFECTS OF SOLVENTS ON SUB-BITUMINOUS COAL BELOW ITS PYROLYSIS TEMPERATURE

Grens III., Edward A.

1979-12-01

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

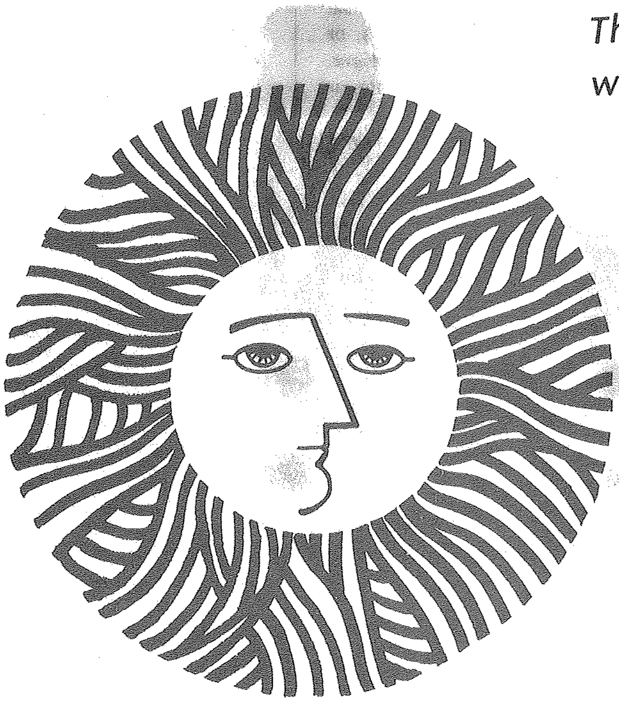
ENERGY & ENVIRONMENT DIVISION

Submitted to FUEL

THE EFFECTS OF SOLVENTS ON SUB-BITUMINOUS COAL BELOW ITS PYROLYSIS TEMPERATURE

Edward A. Grens II, Gary P. Dorighi, and David Lindsey

December 1979



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

THE EFFECTS OF SOLVENTS ON SUB-BITUMINOUS COAL BELOW ITS PYROLYSIS TEMPERATURE

Edward A. Grens II*, Gary P. Dorighi, and David Lindsey

December 1979

Energy and Environment Division, Lawrence Berkeley Laboratory
and Department of Chemical Engineering
University of California, Berkeley, California 94720

Abstract

The action of organic solvents on a sub-bituminous coal has been examined over the temperature range of 150-350°C. The solvents studied included benzene, tetralin, pyridine, quinoline, piperidine, and ethylenediamine. The yield of extracted material varied widely with solvent and temperature, exceeding 60% (daf) for ethylenediamine at 250°C. The extracts were anlayzed for molecular weight, elemental composition and proton aromaticity. When mixtures of strong amine-type solvents with toluene were used, the yield of extract was linearly related mol fraction of strong solvent in the mixture.

The action of various organic solvents on coal has been investigated since well before the beginning of this century, and solvent extraction has been extensively used in the characterization of coal and coal-derived materials. However, only relatively recently have the products of these solvent treatments been thoroughly analyzed or the effect of extraction conditions studied in any methodical way. The ranges of temperatures examined have remained limited, and very little investigation has been made of the effects of solvent mixtures.

The work described here was undertaken to provide a systematic study of the effects of a number of organic solvents, and of solvent mixtures, on a Wyoming sub-bituminous coal for temperatures from 150°C to 350°C. This temperature range was selected so that the interaction of the solvents with the coal itself, and not its thermal decomposition products, would be examined. The highest temperature used allowed the effects of coal pyrolysis to be noted (the initial pyrolysis temperature of the coal was 325°C). The solvents used included aromatic and hydroaromatic hydrocarbons, amines, and phenol. These span the range of categories of solvents (e.g. "non-specific," "reactive," "specific," etc.) identified by previous investigators.[1] The investigation of solvent mixtures was intended to determine if specific chemical interactions dominated the action of the more powerful coal solvents.

The early work on solvent dissolution of coal was conducted mainly at room temperature, or at the normal boiling point of the solvents; it has been well summarized by Dryden[2] and van Krevelen[3] among others. Many studies also concentrated on temperatures above 300°C, and thus primarily examined the effects of the solvents as vehicles for pyrolysis of coal (e.g. Orchin et al.[4]). The strong action, even at low temperatures, of certain organic solvents that have an oxygen or nitrogen atom with an unshared pair of electrons (specific solvents) was noted by Dryden[5]. It has been much studied since, but almost always in pure solvents.

Some solvent mixtures have been investigated at low temperatures and at their boiling points[6-10]. Usually extraction yields for mixtures were nearly equal to those for the most active solvent when mixtures of "specific" and "non-specific" solvents were used. Large effects from additions of small amounts of active solvents to other solvent vehicles have been reported at higher temperatures, where thermal decomposition of coal occurs[11,12]. However, no examination of mixtures of active amine-type solvents with hydrocarbons over wide composition ranges has been available.

EXPERIMENTAL

The coal investigated was from the Roland seam of the Wyodak mine in Gillette, Wyoming. It is a sub-bituminous C coal with proximate and ultimate analyses shown in Table 1. The coal was ground and sieved to -28, +150 (Tyler) mesh and stored under dry nitrogen. Before extraction it was dried for 24 hours at 105°C under 0.3 bar nitrogen swept through the oven. Solvents used were reagent grade from various suppliers.

The solvent extraction experiments were performed in two types of equipment. When pure solvents were used, most experiments were conducted in a pressurized Soxhlet-type apparatus. For mixed solvents, and for a few cases with pure solvents, the experiments were carried out in a stirred extractor with successive solvent batches. In the choice of these experimental arrangements, a primary consideration was the separation of dissolved materials from contact with the coal as rapidly as possible. Duplication of pure-solvent experiments in both types of equipment gave satisfactory agreement in yields and properties of extracted material.

Pressurized Soxhlet Extraction

The pressurized Soxhlet apparatus comprises a 2 liter solvent vessel connected through an approximately 1 cm internal diameter, water cooled reflux condenser to a 4 liter gas surge vessel. The reflux flows to a 200 cm^3 cup with 150 cm^3 siphon overflow volume. The entire apparatus is constructed of stainless steel. The solvent vessel is externally heated by electric resistance heaters, with heat input adjusted to control reflux rate. The solvent temperature is controlled to within 5°C by automatic pressure control on the gas surge space, maintained with a 10-30 cm^3/min flow-through of dry nitrogen or helium. The outlet gas is led to a vapor sampling system for gas analysis. The equipment is capable of operation at pressures from 0 to 35 bar (absolute) and at temperatures to 370°C. It is described more completely by Draemel[13] and by Dorighi[14].

In an experimental run, about 20 g of dried coal was weighed into a 200 mesh stainless steel basket (covered) and placed in the Soxhlet cup.

The extractor was then sealed and evacuated, and 400-600 cm^3 of solvent was introduced into the vessel and outgassed at about 0.3 bar. The system was then brought to extraction pressure (to fix temperature) and the heat input adjusted to give reflux rates of 2 to 4 liter/hour. After the desired contacting interval the equipment was cooled, the coal residue washed with room temperature solvent, and all solvent combined for analysis.

The extraction time used in this study was 4 hours. This was established on the basis of series of experiments with tetralin solvent at 200°C of from 1 to 200 hours duration[13]. These indicated that about 90% of ultimate extraction was achieved in 4 hours, and the increase in extract yield was very gradual after this time.

Successive Batch Extraction

The successive batch extractor consists of a 400 cm^3 stainless steel vessel. The coal is held in a 200 mesh stainless basket at the bottom of a vertical tube (25 cm diameter) in the center of the vessel, and solvent is circulated through the coal by an axial flow impeller. The solvent is maintained and the desired temperatures by an internal electric tube heater connected to a temperature controller, with a thermocouple sensor in the liquid. The equipment, capable of operation at pressures from 1 to 35 bar and at temperatures to 350°C, is described more completely by Lindsey and Grens[15].

The experimental procedure involved placing a sample of about 5 g of dried coal into the basket and evacuating the extractor vessel. Then about 150 cm^3 of premixed and preheated solvent was pressured into the vessel and extraction carried out for one or more hours. After this time the first solvent portion was forced out of the vessel (through a tube extending to the vessel bottom) by nitrogen pressure and another preheated solvent batch introduced. This procedure was repeated to give the desired batch extraction sequence. The solvent batches were all combined, together with solvent used to wash the residue, for analysis.

The solvent batch sequence used in this study usually employed three 150 cm^3 batches: two for one hour each followed by one for two hours. Very little material was extracted from coal in any subsequent solvent contacts, and this sequence (as well as a two batch sequence of 1 hour/3 hours) gave extract yields for pure solvents that were in good agreement with those obtained in the pressurized Soxhlet apparatus[15].

Extract Yield Determination

Combined solvents from an experiment were centrifuged (1 hour at 2000 rpm) and then vacuum filtered. The solid fines collected were combined on the filter with the residue in the coal baskets, washed with solvent and then water, and then dried under 0.3 bar nitrogen for 24 hr at 130°C (240°C when quinoline was the solvent used). Further drying had been found to give no additional change in sample weight. The total volume of solvent was measured and two 10 cm^3 aliquots were evaporated to dryness in petri dishes, again at 130°C under 0.3 bar of nitrogen (swept through oven at 0.8 gmol/hr).

The extract yield, in percent of daf coal, found from the average weight of dried extract in the petri dishes, was corrected for any incorporation of solvent in the extract. For solvents other than amines this incorporation was small, and was determined from the excess of extract plus residue over the coal sample, under the assumption that incorporation in the extract and residue was proportionate to the amount of these products. This is a crude assumption, but for the small incorporations involved it had very little influence on calculated extract yields.

For amine solvents, incorporation in the products was often more extensive. The degree of incorporation was determined from the nitrogen content of the extract and residue, under the assumption that the coal nitrogen divided between extract and residue according to the yields of the products. This assumption is also only a rough approximation; it was observed to hold reasonably well when solvents not containing nitrogen were used. Moreover, since the nitrogen content of the solvents is so much higher than that of the coal (e.g. 18% in pyridine compared to 1% in daf coal), it had a relatively small effect in yield calculations. Details of yield calculations are given elsewhere[13-15].

Analysis of Products

The extract and residue products from the solvent treatments were analyzed for elemental composition so that solvent incorporation could be calculated, elemental (C and H) balances made, and extract hydrogen to carbon (H/C) ratios determined. The extracts were further analyzed for solubility in hexane and toluene, for molecular weight by vapor pressure osmometry (VPO), and for hydrogen aromaticity by nuclear magnetic resonance (NMR). Gas samples collected for some pure solvent experiments were analyzed by mass spectrometry.

Elemental analyses of both extracts and residues were conducted for carbon, hydrogen, and nitrogen (and for ash) on a Perkin-Elmer Model 240 CHN Analyzer. Oxygen plus sulfur was determined by difference.

The extracts, for experiments where amine solvents were used and extract yields were relatively large, were fractionated into hexane-solubles ("oils"), toluene- but not hexane-solubles ("asphaltenes"), and pyridine- but not toluene- solubles ("preasphaltenes") by atmospheric Soxhlet extraction. For experiments using solvents other than amines (except those at 350°C) the extracts were completely soluble in toluene.

Number average molecular weights of extracts were measured in pyridine with a Hewlett-Packard Model 320B Vapor Pressure Osmometer. When the extract was not completely pyridine-soluble, the molecular weight found was for the pyridine soluble fraction.

Proton NMR spectra of extracts were determined to characterize the aromaticity of the hydrogen atoms present. The spectra were measured in d_5-pyridine on a pulsed 180 MH_z "Universal Mass Spectrometer" developed by the Department of Chemistry, University of California, Berkeley. The interpretation of spectra into aromatic and alpha, beta, and gamma aliphatic hydrogens was according to the method described by Andersen[16].

When gas analyses were conducted, helium was used as the inert gas in the pressure Soxhlet apparatus. A total gas sample was collected and then passed at 10^{-5} Torr through a trap at 77.4°K and then a 5 angstrom molecular sieve at the same temperature to separate out hydrocarbons and other gases (e.g. CO, CH_4, O_2) respectively. Suitable heating of these collectors eluted the trapped gases to a CEC Model 211103A Mass Spectrometer for analysis. Details are given by Derighi[14].

The coal residues were also examined to determine the effect of the solvents on the pore structure of the coal. This work has been reported separately by Petersen and coworkers[17].

RESULTS AND DISCUSSION

Extraction Yields With Pure Solvents

The solvents investigated in this work were benzene, toluene, tetralin, decalin, tetrahydrofuran, phenol, pyridine, piperidine, quinoline, and ethylenediamine. They include the classifications used by Oele[1] of non-specific (e.g. benzene), reactive (e.g. tetralin), and specific (e.g. pyridine). However, these classes, except for the classification of the amines as specific solvents, have little significance at the temperatures used in this work; for instance, benzene and tetralin produce very similar extraction yields at 150, 200, and 250°C. The extract yields for Roland seam coal with these solvents at temperatures from 100 to 350°C are given in Table 2, along with molar H/C ratios and solvent incorporation ratios for the extracts. Duplicate experimental runs were made in a number of these cases to establish the reproducibility of results; the standard deviation of extract yield,as a fraction of yield,was found to be less than 0.06.

Extract yields, at 250°C, range from less than 10% for benzene, toluene, decalin, tetralin, and tetrahydrofuran through 15 to 35% for pyridine, quinoline, and piperidine to over 60% for ethylenediame. The experiments with phenol behaved differently from those with other solvents,in that the extract yield continued to increase very significantly with time beyond 4 hours. Moreover, experiments run with phenol solvent without coal gave some higher molecular weight material on removal of the solvent. Thus the phenol results must be viewed with suspicion. The relative activity of the amine solvents agrees basically with that found by Dryden at room temperature, although here quinoline is a significnatly stronger solvent than pyridine[5]. As was found by Dryden, ethylenediame is an extremely powerful solvent for coal, dissolving 64.3% (daf) of Roland seam coal at 250°C. This solvent also incorporates into the extract to the extent of about 60% of the solvent-free extract weight and gives extracts with very low molar H/C ratios (about half that of the original coal).

The behavior of extract yields with extraction temperature is shown in Figure 1 for tetralin,pyridine, quinoline,piperidine, and ethylenediame. The solubility in tetralin increases markedly only as the initial pyrolysis temperature of the coal is approached, while solubilities in piperidine and ethylenediamine increase strongly at much lower temperatures. The solvent power of pyridine increases only modestly with temperature. This behavior, coupled with the relatively high incorporation of piperidine and ethylenediamine into the extract, is indicative of chemical associations being formed between coal materials and ethylenediame or piperdine that do not occur with pyridine. For tetralin it was determined from UV spectra that no hydrogen donation (naphthalene formation) took place at 300°C or below, while significant donor activity occurred at 350°C[13]. This is consistent with the well-known hydrogen donor action of tetralin to coal pyrolysis products.

Analyses and yields for gases formed during several experimental runs are shown in Table 3. There was very little content of hydrocarbons higher than methane in these gases, although some such hydrocarbons were undoubtedly removed with the solvent during vacuum drying of the extract. The analysis system did not permit water determinations in the gas, and ammonia determinations were only semi-quantitative. It can be seen that the primary gas products on a dry basis are CO_2 and CO, and that gas products constitute a significant fraction of the coal only at higher temperatures where pyrolysis occurs.

Characterization of Coal Extracts

The molar H/C ratios of extracts generally decreased with increasing extent of extraction, ranging from about 1.6 for small extract yields in benzene to about 0.9 for 30% extract yields in quinolene or piperidine, compared with a ratio of 1.0 in the coal. This trend is consistent with the most easily extracted material being more hydrogen-rich, and successively more carbon-rich material being extracted by stronger solvents or at higher temperatures. As noted earlier, the H/C ratios for extracts obtained with ethylenediame are anomalously low, about 0.5. Since the ratios in the residue was also below that of the coal (they were 0.6 to 0.7) this is indicative of a large hydrogen removal from the system. This must be as NH_3 or H_2O in the gas stream. The NH_3

concentrations observed seem too low to account for much of this hydrogen loss. Unfortunately the gas analysis system could not adequately determine H_2O contents of the gases produced, and the oxygen analysis (by difference) on the extract and residue had insufficient precision to permit any realistic estimate of H_2O production by oxygen balance. Nevertheless, it appears ethylenediamine must serve to remove some oxygen from this sub-bituminous coal to form H_2O in the gas products.

When the coal extracts were fractionated into oils, asphaltenes, and preasphaltenes, all of the extracts derived using the less active solvents were toluene soluble. Extracts obtained with amine solvents tended to be largely asphaltenes and preasphaltenes, and were not entirely soluble in pyridine at its normal boiling point,as illustrated in Figure 2 for 250°C extractions. Ethylenediamine extracts were again different in that they exhibited little or no hexane or toluene solubility and contained a considerable fraction of pyridine-insoluble material.

Number average molecular weights found for the extracts ranged from 580 to over 1500, varying with solvent as shown in Table 4. Since these molecular weights represent only the pyridine-soluble portion of the extracts, they can not properly characterize the extracts from the more active solvents. Moreover, they are influenced by the presence of incorporated solvent when there is significant solvent incorporation in the extract; these factors (with the high weighting given small molecules in number averages) probably account for the relatively low molecular weights measured for quinoline and ethylenediame extracts.

Proton distributions by NMR analysis are also shown in Table 4, and sample spectra given in Figure 3. These again represent only the pyridine-soluble fractions of the extracts and include the effect of incorporated solvent. Nevertheless the low fractions of aromatic protons, and the high beta-aliphatic porton contents are notable.

Extraction with Solvent Mixtures

The study of extraction of coal with mixtures of strong (specific) solvents and weaker (non-specific) solvents can give valuable insights into the nature of the coal/solvent interaction. As mentioned earlier, previous investigators have reported large increases in extraction for small additions of certain active components (e.g. tetrahydroquinoline) to less active solvents[9,11].

We have examined the effect on extract yields associated with the addition of several active amine-type solvents to toluene (a non-specific solvent) and to tetralin. The extractions were carried out at 250°C (150°C for ethylenediamine), and the complete range of solvent compositions was investigated. The results for mixtures of pyridine, quinoline, piperidine, tetrahydraquinoline, and ethylenediamine in toluene, and of pyridine in tetralin, are presented in Table 5. These extract yields are plotted against solvent composition (mol fraction) in Figure 4. It can be seen that, except where ethylenediamine is the active solvent used, the extract yield varies almost linearly with composition of the solvent between the yields in the pure solvents. Since the solvents were used in large ratios to the coal, this indicates that local continuum properties of the solvent, rather than specific chemical interactions with the coal, determine the extent of extraction. This behavior is in marked contrast to that reported at higher temperatures, where there is pyrolysis and hydrogen donation from the solvent can take place[11].

The action of ethylenediame is quite different from that of the other specific solvents used. High extract yields, comparable to those in pure ethylenediame, are obtained at relatively low addition fractions (in toluene). This is indicative of highly specific interactions of this solvent with the coal structure. When coupled with the high yields and very low H/C ratios for ethylenediame extracts described earlier, this provides additional evidence that ethylenediame is indeed quite an unusual coal solvent.

REFEREMCES

1. Oele, A. P., Waterman, H. I., Gvedkoop, M. L., and van Krevelen, D. W., Fuel 1951, 30, 169.
2. Dryden, I. G. C., Fuel 1950, 29, 197, 221.
3. van Krevelen, D. W., "Coal", Elsevier, New York, 1961.
4. Orchin, M., Golumbic, C., Anderson, J. E., and Storch, H. H., U. S. Bureau of Mines Bull. No. 505 (1951).
5. Dryden, I. G. C., Fuel 1951, 30, 39.
6. Bone, W. A., Pearson, A. R., Sinkenson, E., and Stockings, W. F., Proc. Royal Society A 1922, 100, 582.
7. Bakes, W. E., D. S. I. R. Fuel Research Tech. Paper No. 37, 1933, pg. 92.
8. Kuznetsoff, M. I., Fuel 1937, 16, 114.
9. Vahrman, R. S., Fuel 1970, 49, 5.

10. Rybicka, S. M., Fuel 1959, 38, 45.

11. Wise, W. S., "Solvent Treatment of Coal", Mills and Boon, London, 1971.

12. Hendry, D. G., and Hum, G. P., SRI International Quarterly Report, October, 1976.

13. Draemel, D. C., and Grens, E. A., Lawrence Berkeley Laboratory Report LBL-4434, 1975.

14. Dorighi, G. P., Lawrence Berkeley Laboratory Report LBL-6335, 1977.

15. Lindsey, D., and Grens, E. A., Lawrence Berkeley Laboratory Report LBL-7835, 1978.

16. Anderson, R. P., "Evolution of Steady State Process Solvents in the Pittsburgh and Midway Solvent Refined Coal Process", AIChE Symposium on Coal Processing, Salt Lake City, Utah, August 1974.

17. Harris, E. C. Jr., and Petersen, E. E., in press for Fuel, 1979.

This work was supported by the Basic Energy Sciences Division of the U.S. Department of Energy under contract No. W-7405-ENG-48.

Table 1. Roland seam coal analyses

Proximate analysis: (wt %, as received)	Moisture	1.0
	Ash	14.3
	Volatile matter	46.3
	Fixed carbon	38.4
Ultimate analysis (wt %, daf)	Carbon	70.0
	Hydrogen	5.9
	Nitrogen	1.2
	Chlorine	0.2
	Sulfur	0.5
	Oxygen (diff)	22.2
H/C Molecular ratio		1.01

Table 2. Extraction of Roland seam coal for 4 hours in pressure Soxhlet apparatus

Solvent	Temperature (°C)	Extract yield wt % daf[a]	Extract mol H/C ratio[a]	Solvent incorporation in extract wt ratio[b]
Benzene	150	5.1[c]	1.70	<.01
Benzene	200	4.2	1.65	<.01
Benzene	250	7.8	1.59	<.01
Toluene	250	7.2	1.61	<.01
Tetralin	150	5.3	1.35	.06
Tetralin	200	6.2	1.42	.07
Tetralin	250	8.3	1.44	.04
Tetralin	300	15.2	1.34	<.05
Tetralin	350	31.1	1.19	.02
Decalin	200	5.4	1.56	.01
Tetrahydrofuran	150	7.4	1.51	<.01
Tetrahydrofuran	200	9.0	1.46	<.01
Phenol	200	19.0[d]	1.44	--
Phenol	250	31.5	1.10	.08
Phenol	300	55.3	.99	.04
Pyridine	100	9.4	1.34	<.01
Pyridine	150	10.4	1.34	<.01
Pyridine	200	13.4	1.29	<.01
Pyridine	250	16.2	1.24	.02
Pyridine	300	20.5	1.20	.03
Piperidine	105	7.5	1.25	.24
Piperidine	150	8.6	1.13	.47
Piperidine	200	18.9	1.00	.38
Piperidine	250	35.4	.91	.60
Quinoline	200	15.0	1.08	.25
Quinoline	250	25.0	.99	.29
Quinoline	300	30.3	.86	.37
Quinoline	350	32.4	.75	.99
Ethylenediamine	150	42.4[c]	.43	.62
Ethylenediamine	200	48.0	.55	.58
Ethylenediamine	250	64.3	.46	.56

---

[a] Corrected for solvent incorporation.

[b] Weight ratio of incorporated solvent to solvent-free extract.

[c] Elemental material balances not well satisfied.

[d] Not corrected for solvent incorporation.

Table 3. Gas yield and analysis for extraction of Roland seam coal for 4 hours in pressure Soxhlet apparatus.[a]

Solvent	Tetralin	Tetrohydrofuran	Pyridine	Quinoline
Temperature (°C)	150	200	300	350
Gas yield, dry basis (wt %)	1.4	0.5	3.1	16.
Gas analysis (mol % dry)				
CO_2	48.	82.	85.	61.
CO	23.	16.	12.	22.
CH_4	28.	0.8	2.6	15.
H_2	0.	0.6	trace	1.0
NH_3	0.	0	trace	trace
Other	1.	0.4	0.4	0.9

---

[a] Dry basis - corrected for air present (average ∿ 5%) on basis of Argon.

Table 4. Molecular weights and proton distributions for some extracts of Roland seam coal - 4 hours extraction at 250°C (unless noted otherwise).

			Proton Distribution by NMR (%)[a]			
Solvent	Extract yield wt % daf	Number average molecular wt[a]	$H_{aromatic}$ 6.0-8.7 ppm[b]	H_{alpha} 2.0-3.3 ppm[b]	H_{beta} 1.0-2.0 ppm[b]	H_{gamma} 0.5-1.0 ppm[b]
Benzene[c]	4.2	810	-	-	-	-
Tetralin	8.3	780	8.	9.	61.	22.
Pyridine	16.2	880				
Quinoline	25.0	580	13.	12.	60.	15.
Piperidine	35.4	1200	4.	24.	62.	10.
Ethylenediamine	64.3	770	21.	31.	39.	9.

[a] Pyridine-soluble fraction of extract.

[b] Downfield shift of 180 H_z from tetramethylsilane = 1 ppm.

[c] 200°C.

Table 5. Extraction of Roland seam coal with solvent mixtures for 4 hours at 250°C (unless noted otherwise).

Solvent added to toluene	Mol fraction added	Extract yield wt % daf[a]	Extract mol H/C ratio[a]	Solvent incorporation in extract wt ratio[b]
None	0	7.5	1.67	<.01
Pyridine	.10	7.6	1.55	<.01
Pyridine	.50	11.0	1.45	<.01
Pyridine	.90	15.1	1.31	<.01
Pyridine[c]	1.0	16.2	1.24	.02
Quinoline	.10	5.9	1.43	<.01
Quinoline	.50	12.1	1.26	.11
Quinoline	.90	18.3	1.20	.14
Quinoline[c]	1.0	25.0	.99	.29
Piperidine	.10	11.5	1.23	.44
Piperidine	.50	17.9	1.03	.59
Piperidine	.90	28.0	.70	.99
Piperidine	1.0	35.5	.92	.50
Tetrahydroquinoline	.05	9.6	1.31	.38
Tetrahydroquinoline	.10	7.6	1.17	.58
Tetrahydroquinoline	.20	9.6	1.07	.65
Tetrahydroquinoline	.50	19.2	.67	1.86
Ethylenediamine[d]	.10	13.1	1.17	.25
Ethylenediamine[d]	.50	36.2	.81	.41
Ethylenediamine[d]	.90	36.7	.52	.49
Ethylenediamine[d]	1.0	34.6	.45	.66
Solvent added to tetralin				
None	0	9.0	1.44	<.01
Pyridine	.10	9.0	1.36	<.01
Pyridine	.50	10.4	1.31	<.01
Pyridine	.90	11.6	1.31	<.01

[a] Corrected for solvent incorporation.

[b] Weight ratio of incorporated solvent to solvent-free extract.

[c] Extraction in pressure Soxhlet apparatus.

[d] 150°C.

FIGURE CAPTIONS

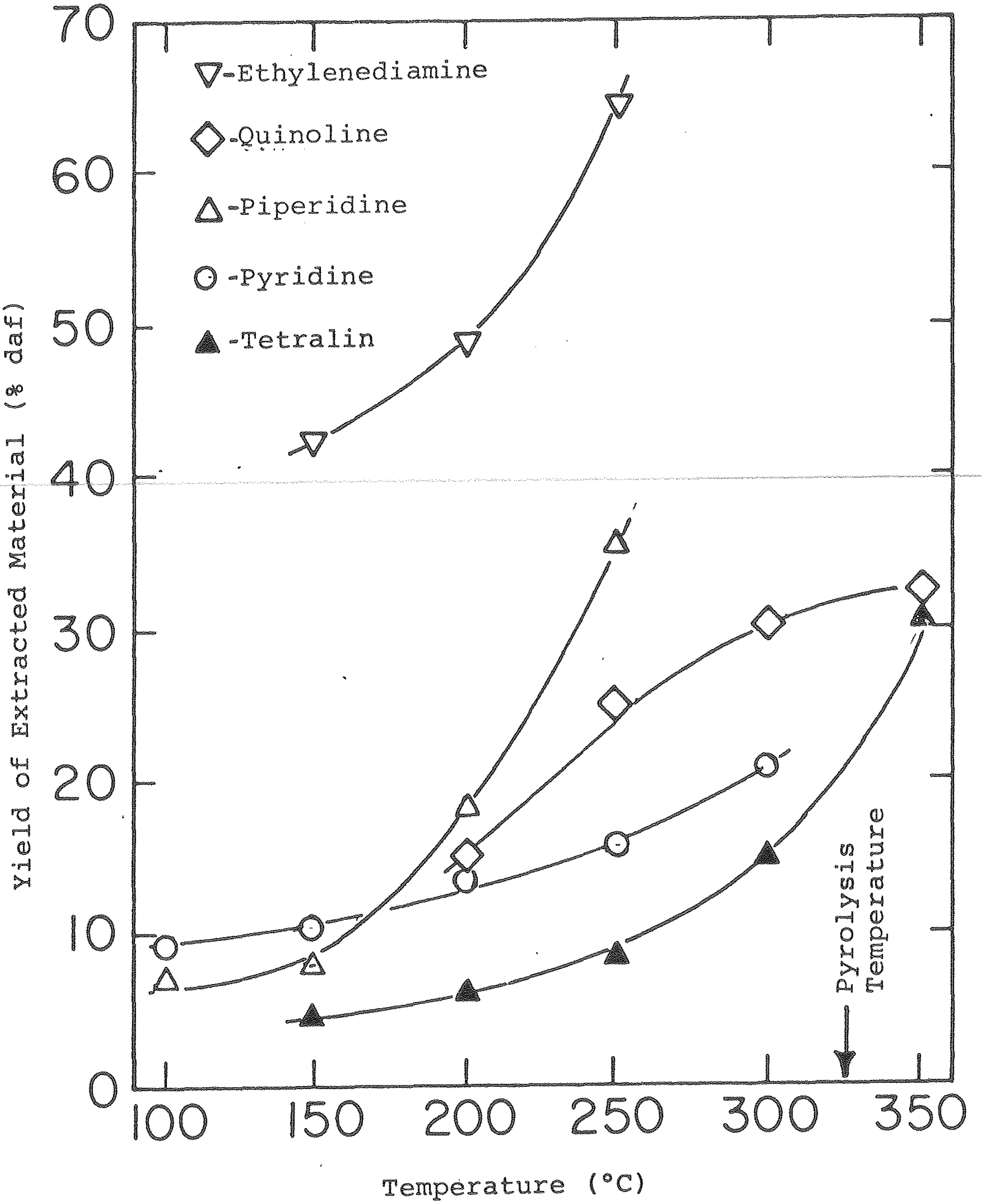
Figure 1. Effect of extraction temperature on yields for Roland seam coal extracted 4 hours in pressure Soxhlet apparatus.

Figure 2. Fractionation of Roland seam coal extracts derived from treatment with stated solvent for 4 hours at 250°C.

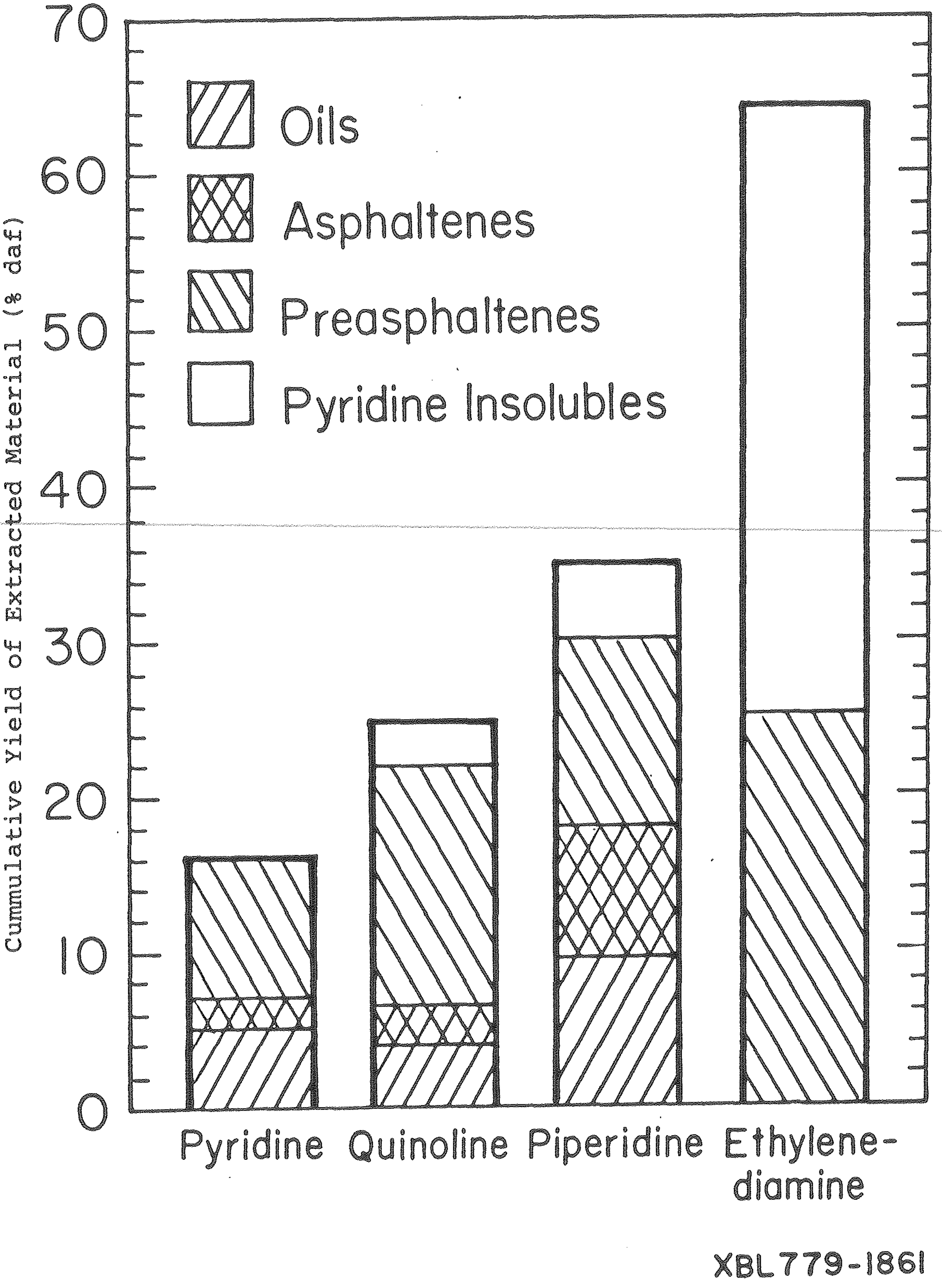
Figure 3. Proton NMR spectra of Roland seam coal extracts.
(a) Tetralin extract - 4 hours at 250°C.
(b) Piperidine extract - 4 hours at 250°C.

Figure 4. Effect of composition of mixed solvents in extraction yield for Roland seam coal. Extraction for 4 hours at 250°C (except 150°C for ethylenediamine).

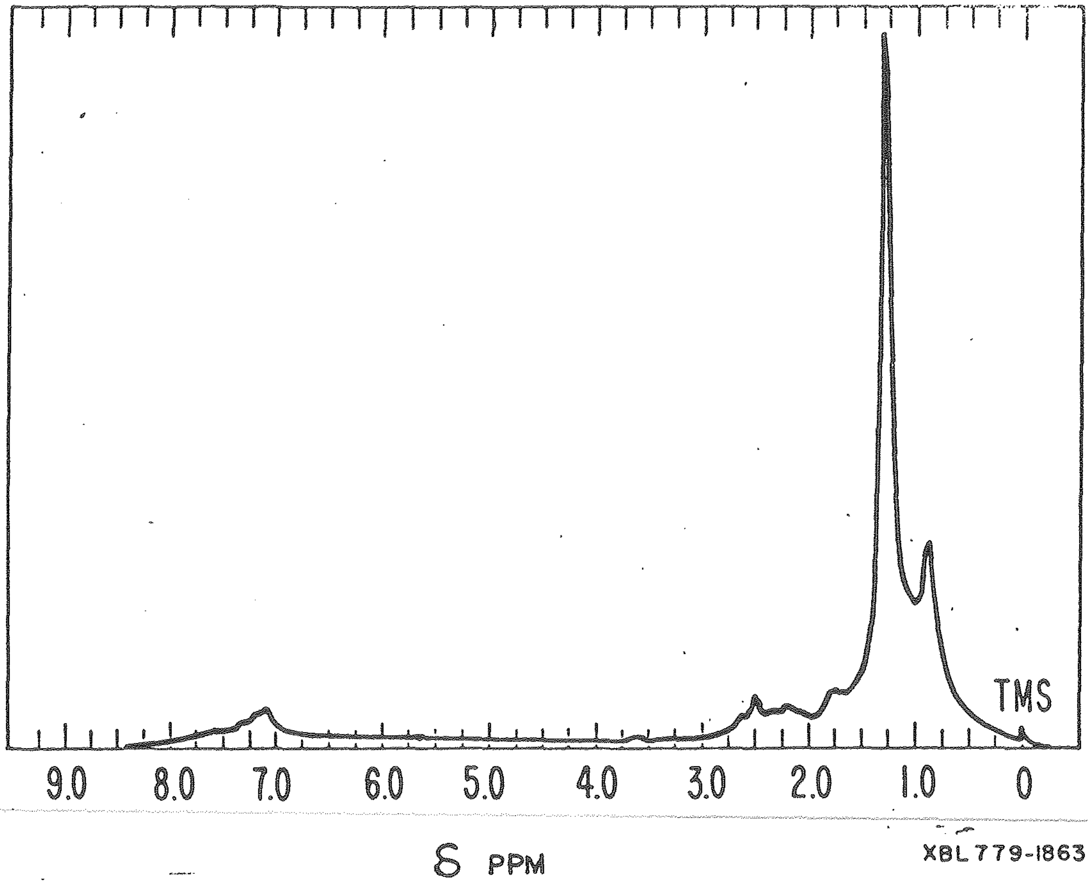
#1


▽-Ethylenediamine
◇-Quinoline
△-Piperidine
○-Pyridine
▲-Tetralin
Yield of Extracted Material (% daf)
0
10
20
30
40
50
60
70
100
150
200
250
300
350
Temperature (°C)
Pyrolysis Temperature

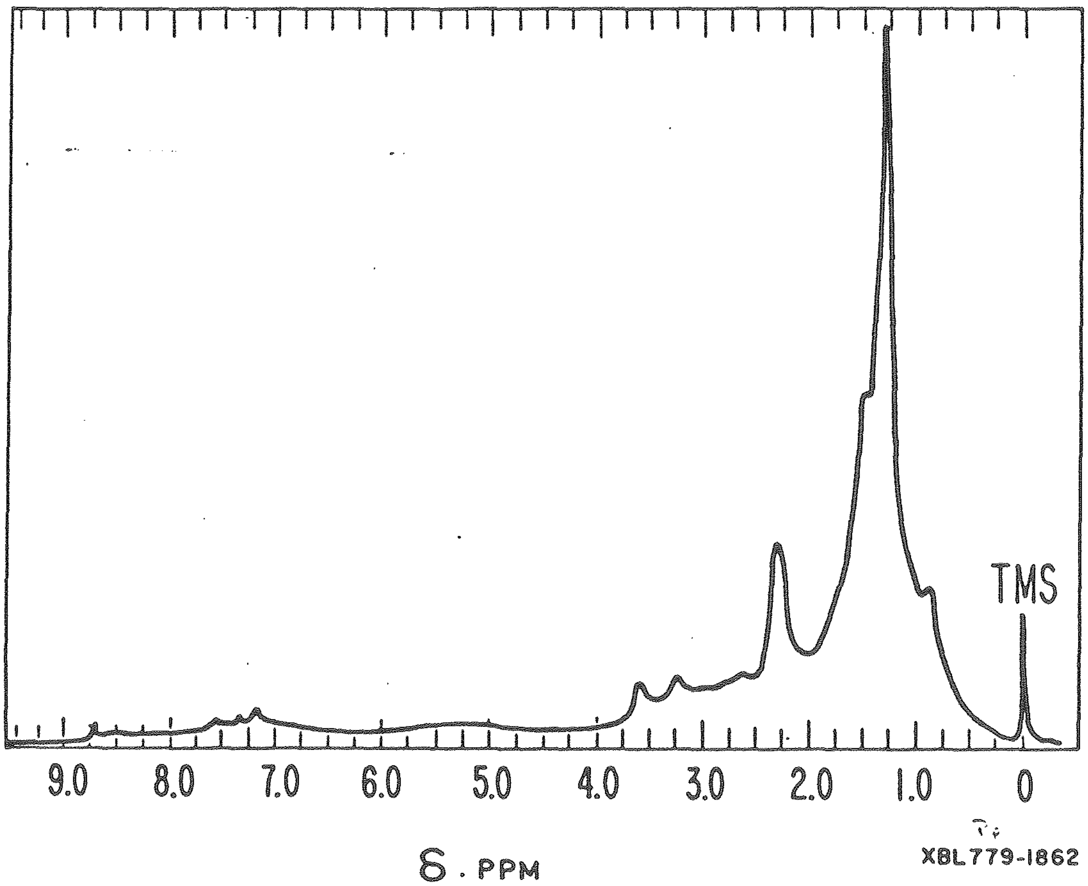
#2



XBL779-1861

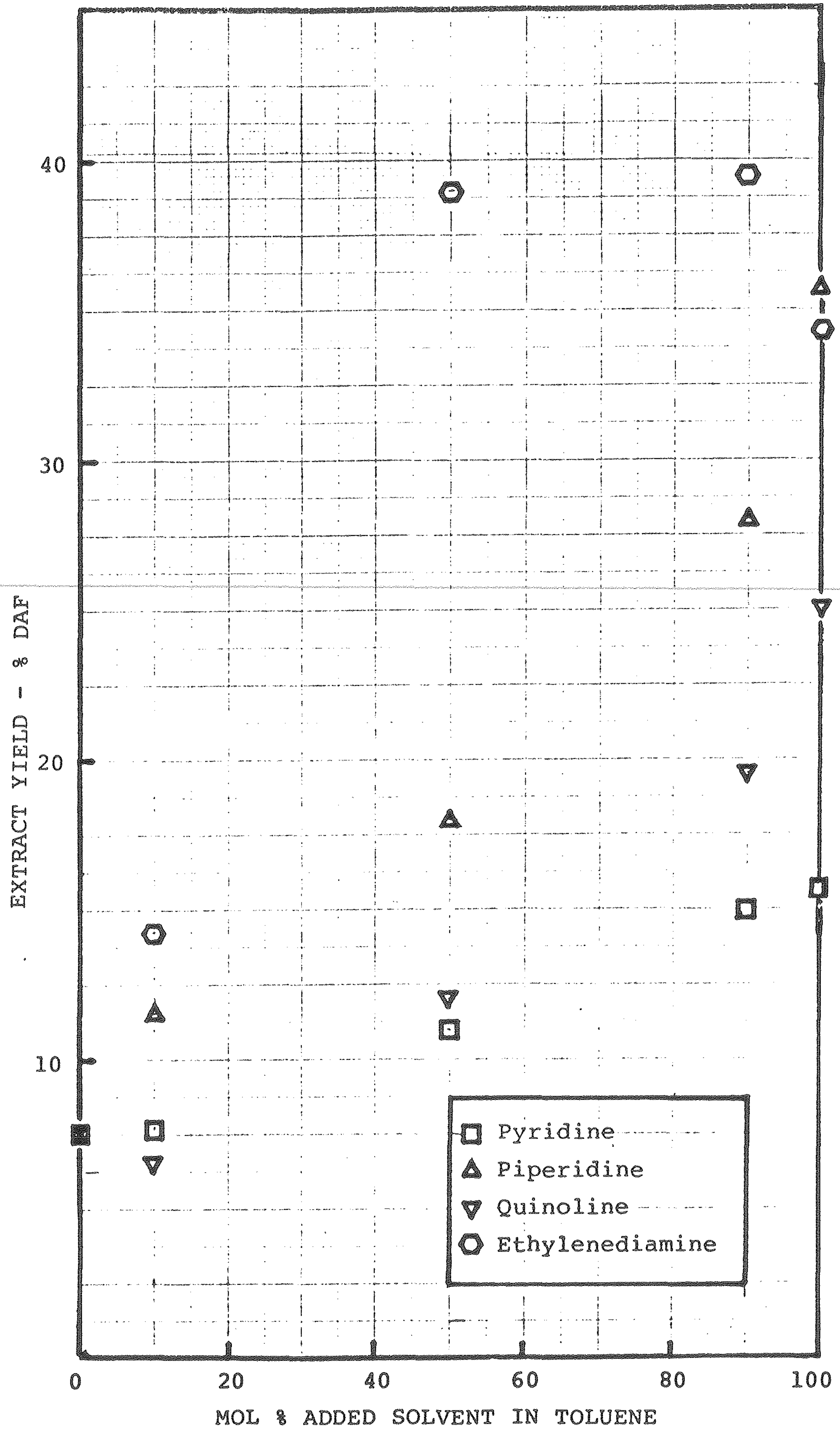


XBL 779-1863



XBL 779-1862

#4


EXTRACT YIELD - % DAF
40
30
20
10
0
20
40
60
80
100
MOL % ADDED SOLVENT IN TOLUENE
□ Pyridine
△ Piperidine
▽ Quinoline
⬡ Ethylenediamine