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OPTIMIZATION CHEMISTRY AND PRODUCT ANALYSIS OF SUPERCRITICAL GAS EXTRACTION FOR THE LIQUIFACTION OF CANADIAN COALS

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OPTIMIZATION CHEMISTRY AND PRODUCT ANALYSIS OF SUPERCRITICAL GAS EXTRACTION FOR THE LIQUIFACTION OF CANADIAN COALS

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ABSTRACT

Supercritical gas extraction was carried out on Forestburg subbituminous coal. The presence of excess solvent during the heat-up period favoured the yield of coal derived liquids (cdl). The yield of cdl was sensitive to the temperature and pressure conditions employed during the extraction with higher yields being obtained at high temperatures and higher pressures.

A series of supercritical toluene extractions were carried out using temperatures ranging from 350 to 450°C and pressures ranging from 1100 to 1900 psig. A simple mathematical model for predicting yields of cdl was derived from the results.

Supercritical gas extractions using oxygenated solvents lead to solvent degradation. The yield of cdl decreased relative to toluene when paraffinic solvents were used. Tetralin used in conjunction with toluene resulted in an increased yield of cdl and highly altered char.

Analysis of cdl showed that aromatic content increased with increasing temperatures of extraction.

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TABLE OF CONTENTS

Table of Contents continued

I. INTRODUCTION

The Department of Supply and Services awarded a contract (23440-9-9069) to Raylo Chemicals Limited to investigate the feasibility of supercritical gas (scg) extraction of Canadian coals. The contract period extended from April 1, 1980 to December 10, 1980. This contract was a continuation of a previous contract (23440-8-9091) (November 1979 to March 1980).

A simple semi-continuous extraction apparatus was designed and constructed and samples of bituminous, subbituminous and lignitic coals were extracted with supercritical toluene during the first contract period. The yields of coal derived liquids (cdl) obtained by supercritical toluene extractions at 400°C and 1500 psig from high volatile bituminous C coal was 19% on a dry ash free (daf) basis, 17% for Forestburg subbituminous coal and 17% for the lignitic coal. These results were encouraging and justified the continuation of the feasibility study in this contract period.

The work in this summary report was originally reported in Raylo Progress Reports numbers VI through XIV.

II. OBJECTIVES

The purpose of this project was to investigate the feasibility of using scg extraction techniques for the liquefaction of Canadian coals. The objectives were:

1. to provide data about the relative importance of pyrolytic and extraction processes in the scg extraction of coal;
2. to evaluate the effects of temperature, pressure, solvent and flow rate on the efficiency of scg extractions of samples of lignitic, subbituminous and high volatile bituminous coals;
3. to investigate the chemical interactions between toluene and the intermediates generated by pyrolysis of the coal during the course of scg extraction;
4. to provide sufficient analytical data on the coal liquefaction products obtained under optimized extraction conditions to enable their evaluation; and
5. to provide recommendations to E.M.&R. about the further steps required to assess the economic potential of the scg extraction technique on the basis of the published information and the data generated during the project.

Although the overall objective of the project was to determine the effectiveness of scg extraction for the liquefaction of several ranks of coal, it was agreed with the Scientific Authority (Dr. A.E. George) that it would be efficient to carry out most of the experiments with only one rank of coal. Once experimental trends were established and the reaction conditions defined, the other ranks would be examined. The experiments relating to the general properties of scg extraction were performed on samples of subbituminous coal. This coal has properties intermediate between bituminous and lignitic coals and is the most abundant rank of coal in Western Canada. The ultimate in-place reserves in the Alberta Plains Region are estimated at some 360 billion tons and the ultimate recoverable reserves totals approximately 80 billion tons (1). This coal is the most likely candidate for scg extraction on a commercial scale.

III. EXTRACTION OF SUBBITUMINOUS COAL

A. Experimental Methods

1. Method A:

The coal sample (12 - 24 mesh - 400 grams) was placed in the autoclave, the apparatus assembled and evacuated and 350 millilitres of solvent were introduced. The autoclave was isolated and heating started. Pressure increased, slowly at first, but rapidly in the 225 to 300^{o} range due primarily to the release of water from the coal. Pressure in excess of the chosen operating pressure (1000 to 2000 psig) was released as the autoclave continued to heat to the chosen extraction temperature (350 to 450^{o}). The time required to reach the operating temperature ranged from 90 to 120 minutes. Release of pressure was usually required at 275°. Solvent was lost with the release of pressure resulting in nearly total loss of solvent before the desired operating temperature was reached especially if the temperature was 400° or higher. With the loss of solvent, the coal in effect underwent pyrolysis in the dry state during the latter part of the heat-up period. When the desired operating temperature was reached, three litres of solvent (2.6 kilograms, if the solvent was toluene) measured at room temperature was pumped through the system at a pumping rate of 27 to 32 millilitres per minute (23 to 28 grams per minute, if the solvent was toluene).

2. Method B:

The above procedure was modified so that dry heating of the coal would be eliminated. As venting to control pressure became necessary during the heat-up period, fresh solvent was introduced into the autoclave by simultaneously starting the solvent feed pump. The chosen operating pressure was maintained by operating the pressure control valve. After the desired operating temperature was reached, an additional three litres of solvent was pumped through the system at a pumping rate of 27 to 32 millilitres per minute. The heat-up times were increased to between 105 and 195 minutes due to this procedural modification.

B. Extraction With Supercritical Toluene

1. Effect of experimental method on cdl yield:

Table I summarizes the effect of the experimental method on the isolated yield of cdl. At low reaction temperatures, the operational method has little effect on the isolated yield of cdl. Little venting was required to maintain the pressure while reaching the extraction temperature and the difference between the two operating methods was minimized. At 400°, differences in yields become more pronounced especially at low pressures. To maintain the low pressure, much of the solvent was lost during the heat-up period. To maintain high pressure, less venting was required thereby minimizing the essential difference between the operational methods. The effect was most dramatic at 450° and 1500 psig in which instance 3.4 times as much cdl was isolated using Method B compared with Method A. In general, the material balance was better using Method B with the most pronounced effect observed at 450°. The amount of char isolated was dependent on temperature but essentially independent of the extraction method.

These results tend to show that the extent of coal pyrolysis was dependent only on temperature. The different amounts of cdl isolated reflected the heat lability of cdl under the pyrolysis-extraction conditions. If the cdl are not efficiently removed from the reaction zone, they undergo secondary reactions forming gaseous and heavy polymeric materials. Since the gas evolution was not measured, the material balance is lower for extractions in which there would be larger amounts of gas formed. Deposition of the high molecular weight material on the autoclave wall was not generally observed except in the 450° - 2000 psig extraction run using Method A. This deposited material could not be collected and weighed thus further contributing to the lower material balance relative to the extraction at 450° and 1900 psig using Method B.

2. Optimization studies:

Having established the effect of pyrolysing coal in the presence or the (partial) absence of solvent on the isolated yield of cdl, the effect of temperature and pressure was studied using extraction Method B. This extraction method eliminated the drying out effect. A set of experiments was designed so that the greatest amount of information could be gained from the least possible number of experimental runs. The two independent variables were each specified at five levels (modified Box-Wilson design). The temperature range was set from 350° (30° above the critical temperature of toluene) to 450° (limited by equipment). The pressure range was set from 1100 psig (yield is known to be low at this pressure) to 1900 psig (limited by equipment). With five levels of two independent variables, 25 runs would be required to test all the conditions. A satisfactory regression analysis can, however, be made on a partial factorial set of nine experiments with a replicate of the central experiment to check the experimental error. The results are shown in the following table which illustrates the effects of temperature and pressure on the percent isolated yield of cdl and also the layout of the factorial set (numbers in brackets indicate the grams of char remaining after extracting 400 grams of coal). The complete results are given in Table II.

Pressure (psig)	Temperature (°C) 350	375	400	425	450
1100			14.5 (235)		
1300		14.3 (242)		17.9 (237)	
1500	11.0 (257)		17.8+0.5 (226±8)		24.7 (221)
1700		16.6 (247)		21.3 (224)	
1900			19.3 (223)		

The amount of cdl isolated increased with increasing temperature while the amount of char decreased with increasing temperature confirming a greater degree of coal pyrolysis at higher temperature. The amount of cdl isolated increased with increasing pressure at any given temperature indicating better extraction efficiency at higher pressure.

Table III shows the amount of cdl isolated in various temperature ranges during the heat-up period. One-third of the total cdl was isolated during the heat-up period for the extraction at 350° and two-thirds was isolated during the heat-up periods of the extractions at 450°. These results indicate that cdl were formed at relatively low temperatures (less than 300°) and that more than one-half of the cdl were isolated at temperatures below 400° in this set of extractions.

3. Mathematical analysis:

a) Objectives

1. To find the relationship between the yield of cdl and the temperature and pressure of the scg extraction in order to find as simple a physical/chemical explanation of the effects as possible. The most accurate mathematical fit was not desired.
2. To find out if the overall yield could be interpreted as a pyrolysis of the coal (temperature dependent) with a separate measure of the efficiency of the extraction (temperature and pressure dependent).

b) Computer program

The experimental set was devised to measure the effects of temperature and pressure on the yield of cdl. Before the extractions were performed, it was expected that the temperature effect could be expressed as a single variable (absolute temperature) but that it might be necessary to consider both a linear pressure effect and a pressure squared term. The basis for this assumption was that supercritical gas extraction efficiency is usually considered to be a function of the density of the extracting fluid and the density of the fluid requires a pressure squared term to obtain a good regression. Therefore a computer program was written, for a TRS-80 computer, to calculate all the linear and quadratic regressions necessary to evaluate a cubic level multiple linear regression. The results obtained from this program allows the effects of each of the variables to be evaluated and in all possible combinations with the others. The program was also used to obtain equations for the density of the extracting fluid and for the release of volatiles in thermogravimetric analysis.

c) Results of the mathematical analyses

i. Observed yield as a function of temperature and pressure:

The observed yield (Y, %) of cdl obtained at a temperature (K, ^{o}K) and a pressure (P, psig) is given by:

$$Y = -72.1395 + 11.9\ (K/100) + 6.375\ (P/1000).$$

The standard error of the estimate is 0.93%. The precision of the estimate is not improved significantly by introduction of a pressured squared term.

The yields calculated from the formula are compared with the observed yield in Table IV and Figure 1.

ii. Solvent density as a function of temperature and pressure:

The density of the extracting fluid (D, g/ml) was estimated from generalized compressibility charts using the reduced temperature and pressure (see Appendix I). The density can be represented by:

$$D = 0.8317 - 0.1967\ (K/100) + 0.8916\ (P/1000) - 0.2292\ (P/1000)^2$$

The standard error of the estimate is 0.01. All the variables are significant and the regression is excellent.

iii. Observed yield as a function of fluid density:

These variables gave a scatter diagram without a significant regression.

iv. Estimation of pyrolysis yield:

The results for a thermogravimetric analysis (see below) were used to estimate the yield which could be obtained by a perfectly efficient extraction. The volatile matter (V, %) at a temperature (K, °K) is given by:

$$V = 325.293 - 162.802\ (K/100) + 26.3495\ (K/100)^2 - 1.2995\ (K/100)^3$$

The standard error of the estimate is 0.91%. In this case, the precision of the estimate is improved by the inclusion of all three terms of the equation. The amount of volatile matter released is greater than the possible yield of cdl because some of the weight loss observed in the thermogravimetric analyses over this temperature range (548 - 873°K) is due to dehydration. Various, somewhat arbitrary, corrections have been applied to correct for the liberation of water and so estimate the hypothetical yield.

v. Extraction efficiency as a function of temperature and pressure:

The extraction efficiency (S, a decimal fraction), was defined as the observed yield divided by the hypothetical yield.

Based on a rough measurement of the amount of water liberated during the supercritical toluene extraction at the extraction temperature, it was decided that the most reasonable correction of the hypothetical yield was given by V-4. Using this value to calculate extraction efficiency, it was found that the extraction efficiency can be represented by:

$$S = 0.3459 + 0.2772\ (P/1000).$$

The standard error of the estimate is 0.04. There was no significant regression in temperature nor did the introduction of a temperature term in the quadratic equation improve the precision.

vi. Extraction efficiency as a function of fluid density:

These variables gave a scatter diagram without a significant regression.

d) Discussion of the mathematical analyses

i. Regression analysis:

The yield of cdl which can be isolated by scg extraction of coal would be expected to increase with temperature, since greater amounts of volatiles are formed by pyrolysis, and with pressure, since higher fluid density leads to greater solubility power of the extracting fluid. The variation of the yield would not necessarily be linear with these variables. However, the observed yield, based on the available experimental data, is well represented by a regression linear in both temperature and pressure. The accuracy of the regression is commensurate with the experimental error and closely predicts the actual yield of cdl in an extraction carried out at 450° and 1900 psig (Table IV). This is very satisfactory but gives little insight into the actual extraction and pyrolysis mechanism.

ii. Simple model:

To obtain further insight into these processes, an attempt was made to estimate a maximum possible yield, the hypothetical yield, and hence obtain a measure of extraction efficiency. The hypothetical yield was expected to increase with temperature, since this is dependent on the degree of pyrolysis, but not with pressure. The extraction efficiency was expected to be proportional to the density of the extracting fluid and therefore decrease with temperature and increase strongly with pressure.

Thermal lability of the cdl was also expected to be a factor in view of the results obtained while carrying out the extraction using experimental Method A.

Considerable difficulty was experienced in assigning a reasonable value to the hypothetical yield. In order to keep to an experimental base, thermogravimetric analysis of the coal was used as an indication of the amount of volatile material which could be released from the coal at a given temperature and make an allowance for part of these volatiles being water. By testing a range of corrected volatility estimates, it was shown that the effect of temperature and pressure on the efficiency of extraction were similar for all the cases tested. There was no significant temperature effect and there was a positive linear pressure effect. Using the best estimate of hypothetical yield, percent volatiles minus four, the extraction efficiency ranged from 0.63 to 0.86.

The simple model which emerges from this admittedly rough analysis is shown below. As the hypothetical yield is independent of pressure, each column shows the hypothetical yield for the corresponding temperature. As the extraction efficiencies were independent of temperature, each row shows the extraction efficiency corresponding to its pressure. The entries in the table are the yield of cdl calculated from the model and, in brackets, the yield found experimentally.

	Temp (C)	350	375	400	425	450
	Hypo yld (%)	15.5	19.2	23.0	26.8	30.5
Pressure (psig)	Extraction efficiency (fract)					
1100	0.65			15.0 (14.5)		
1300	0.71		13.6 (14.3)		19.0 (17.9)	
1500	0.76	11.8 (11.0)		17.5 (17.8)		23.2 (24.7)
1700	0.82		15.7 (16.6)		22.0 (21.3)	
1900	0.87			20.0 (19.3)		26.5 (25.4)

iii. Further development of the model:

The simple model gives a good representation of the experimental results but the simplicity is probably deceptive. The bulk of the cdl were obtained early in the extraction, much of it being obtained before the working temperature was reached (Table III). In each case the cdl were being extracted as they were formed by a fluid of decreasing density since the temperature is increasing while the pressure is kept constant. As the experiments covered a range of pressures and temperatures, the fluid densities during the heat-up periods were different in different experiments. Further work will be necessary to design, construct and operate an experimental unit with a high heat-up rate in order to investigate the process in more depth.

4. Other extraction experiments:

a) Continuous cdl removal

In one experiment, the solvent flow and the heater were simultaneously started and the coal was extracted at 1500 psig with toluene throughout the temperature range from 25 to 394°. The extract was collected every ten minutes and the weight of cdl determined. The results are shown in Figure 2. Each fraction represents the passage of 240 grams of toluene through the coal bed. The yield of char was 226 grams, comparable with all the extractions carried out at 400°; the yield of cdl was 56.9 grams (21% on a daf basis), somewhat greater than for other extractions at 400°, and the material balance was 98.2%.

The results show that 18.8% of the total cdl was extracted before the critical temperature of toluene (321°) was reached. The coal starts to undergo significant pyrolysis at 140° as shown by the increasing yield of cdl. In the range of 234 to 267°, a large amount of cdl is liberated indicating the release of a large amount of a specific class of compound. The greatest amount of pyrolysis takes place in the 350 to 380° range. An additional observation was that the bulk of the water was released in the 250 to 280° range.

The highest yield of cdl for an extraction carried out at 400°C and 1500 psig occured in this experiment. This gives a further indication that cdl are heat labile materials and efficient removal from the reaction zone is necessary to maximize their isolated yields.

b) Effect of fluid feed rate on isolated cdl yield

An extraction was carried out using Method A at 400° and 1500 psig employing a toluene feed rate of 36 grams/minute. The results are compared with those obtained for an extraction employing the same experimental conditions except that the toluene feed rate was the usual rate of 24 grams/minute in Table V.

The char yield was insensitive to flow rate. The isolated cdl yield was significantly greater for the extraction employing the faster feed rate. These results are indicative of the lability of cdl and the necessity of efficient removal of these materials from the reaction zone in order to maximize the isolated yield.

c) Extraction of dewatered coal

Subbituminous coal (400 grams) was heated to 275° under 1500 psig nitrogen pressure. The water present in the coal came off as a liquid and the coal particles remained intact under these conditions (vapour pressure of water is 865 psia at 275°). The heated coal was swept with nitrogen, while maintaining the pressure, to remove the water. The amount of water isolated was 85 grams (21.2%), an amount which agreed very well with the moisture content of this coal as determined by proximate analysis (21.5%). The reactor was cooled, the nitrogen was released and the reactor was charged with 350 millilitres of toluene and reheated. The rate of pressure increase during the heat-up period was considerably slower than for the as received coal and a pressure of 1500 psig was reached at 375° (compared with 275° for the as received coal). The extraction was carried out using Method B.

The amount of char remaining was 234 grams which compares with the extractions of as received coal carried out under similar extraction conditions (234 and 218 grams). An additional 25 grams of water was isolated to bring the total water liberated to 110 grams, the same as for extractions of as received coal. This indicates the initial 85 grams was physically held water while the remaining 25 grams is chemically formed water. The amount of cdl was 39 grams, lower than for extractions of as received coal under similar extraction conditions (49.4 and 47.0 grams). The lower yield may be caused by degradation of the coal during the dry heating period or may indicate that water is a beneficial co-solvent for scg extractions of coal, a property alluded to by other workers (2).

C. Supercritical extraction using solvents other than toluene

Toluene was chosen as the base solvent for the investigation of the effect of various parameters on the scg extraction of coal because this solvent is known to be a good solvent for dissolving cdl and is generally thought to be inert under the extraction conditions. The effects of solvents other than toluene on the liquefaction of coal and the isolation of cdl were briefly studied.

The following solvents were chosen for study following consultation with the Scientific Authority, Dr.A.E. George:

- tetralin (tetrahydronaphthalene) since it is known to be a relatively effective hydrogen donating solvent;
- isopropyl alcohol because the hydride donation chemistry associated with it is said to have a beneficial effect on coal liquefaction (3);
- methyl ethyl ketone because this solvent is known to readily dissolve cdl;
- 90% p-cresol/10% water is a polar solvent known to be a reactive liquid phase solvent for coal (water was added to make the p-cresol liquid);
- the paraffinic solvents n-decane and n-heptane since these are probably inert solvents not entering into or influencing the coal thermolysis reaction. The paraffinic solvents would be expected to have similar solvent powers for cdl but would have different densities under the scg extraction conditions, which could offer an indication of the effect of solvent density on cdl isolation.

Results of extractions carried out with the above solvents are summarized in Table VI.

1. Extraction with tetralin

The high critical temperature of tetralin (516°C) precluded the use of this material as an extraction solvent. It can, however, be used in conjunction with toluene.

In this extraction experiment, the subbituminous coal was heated with 370 grams of tetralin. During the heat-up period, the external reference temperature of the autoclave increased steadily. The internal autoclave temperature, however, showed sharp temperature increases at temperatures higher than 200°, the temperature at which coal starts to undergo active thermal decomposition. This contrasts sharply with the behaviour during the heat-up in the presence of toluene. In the presence of toluene, the internal autoclave temperature increased steadily, paralleling the reference temperature (see Figure 3), and no sharp temperature increases are noted. The difference in thermal behaviour provides strong evidence for several exothermic reactions taking place above 200° between tetralin and the coal.

Rapid pressure fluctuations accompanied the rapid temperature fluctuations. At 300°, the increase in pressure ranged from 150 to 500 psi per minute making pressure control at 1500 psig difficult. The pressure fluctuation subsided at 330°, the point at which internal and reference temperatures coincide. The autoclave was probably "dry" at this point.

Extraction with toluene was started at 400°. Table VI shows that the amount of char remaining was 176 grams, considerably lower than the amount of char remaining after scg extraction in which toluene was the solvent present during the heat-up period. This indicates that the coal had undergone a greater degree of pyrolysis. Analysis of the char (see below) indicates changes not evident in the chars of coal extracted with other solvents. Coking of the char was noted.

The crude cdl contained unreacted tetralin and the product of its dehydrogenation, naphthalene. A gas chromatographic analysis, to estimate the content of these materials in the mixture, was developed so that the amount of isolated cdl could be determined. The amount (85 grams) was 31.4% of the coal on a daf basis.

The results show that the amount of cdl can be strongly influenced by the presence of a reactive solvent.

2. Extraction with isopropyl alcohol (IPA)

The extraction with IPA (T_c = 235°; P_c = 47 atm) was carried out using experimental Method A. No extraordinary temperature or pressure effects were noted (see Figure 3). The weights of char and cdl are similar to those obtained by toluene extraction. The char was very soluble in pyridine and had an atomic hydrogen to carbon ratio similar to that of the starting coal (see below). This suggests that the solvent does take part in the thermolysis reaction. The low density of IPA under the extraction conditions (0.16 g/ml) may have resulted in the redeposition of cdl on the char.

A large amount (170 millilitres) of volatile material was condensed in a dry ice cold trap during the extraction. The bulk of this liquid evaporated when the trap was allowed to warm to room temperature. Based on this observation, this by-product was tentatively identified as propylene (b.p. -47.4^{o}) resulting from the dehydration of IPA. If this tentative conclusion is correct, then IPA would not be suitable as an extraction fluid.

3. Extraction with methyl ethyl ketone (MEK)

The extraction with MEK (Tc = 262^{o}; Pc = 41 atm) was carried out using experimental Method B. This extraction lead to excessive amounts of tars the bulk of which were solvent derived. The amount of char (252 grams) was high, possibly due to high molecular weight polymers derived from solvent polymerization being deposited in the char. No further work using this solvent is anticipated.

4. Extraction with 90% p-cresol/10% water

The addition of water (Tc = 374^{o}; Pc = 218 atm) to p-cresol (Tc = 432^{o}; Pc = 50.8 atm) was required to facilitate pumping of the solvent. The critical temperature and pressure of the mixed solvent was estimated to be 420^{o} and 80 atmospheres. The extraction was carried out employing experimental Method B at 450^{o} and 1900 psig. The amount of char (199 grams) was less than that obtained for toluene extractions but more than that obtained for the tetralin/toluene extraction (176 grams). This would indicate that p-cresol is more effective than toluene as a solvent for coal liquefaction but less effective than the tetralin/toluene system. A considerable amount of coking was observed in the char.

The isolated cdl were contaminated with p-cresol. The amount was estimated by a gas chromatographic technique similar to that developed to estimate the amounts of tetralin and naphthalene. An estimated amount of 226 grams of produced liquid was isolated. The material balance of 132% clearly indicated that a substantial amount of the liquid was solvent derived.

A large difference between the internal autoclave temperature and the external reference temperature was observed when 90% p-cresol/10% water was subjected to the extraction conditions in the absence of coal. The presence of a positive peak at temperatures exceeding 230^{o} (Figure 4) indicated that an exothermic reaction was taking place. Samples of the recovered solvent condensed after passage through the autoclave taken at 15 minute intervals were spotted on thin layer silica gel plates and eluted with 15% ethyl acetate/hexane. Each sample had a component with a lower Rf value than the p-cresol as well as a spot at the origin, both of which were absent when the unheated p-cresol/water mixture was spotted on the plate. Both these observations indicate that p-cresol reacts with itself in the absence of coal at the extraction conditions. These reactions would probably be enhanced in the presence of coal. The reactivity of p-cresol has also been observed by workers at the British National Coal Board (4).

All the oxygenated solvents studied have reacted under the extraction conditions. Therefore these solvents cannot be considered useful as supercritical extraction fluids. They may, however, be useful in modifying a base solvent resulting in a more efficient liquefaction/extraction process.

5. Extraction with paraffinic solvents:

Subbituminous coal was extracted with the paraffinic solvents, n-heptane (Tc = 267°; Pc = 27 atm) and n-decane (Tc = 344°; Pc = 21 atm), using experimental Method B. The amounts of char remaining were similar to that obtained by toluene extraction. The amounts of cdl isolated were considerably lower than the amounts obtained by toluene extraction. This probably reflects the weaker solvating power of paraffinic solvents for cdl. Deposition of cdl in the tubing and the catch pot was observed when paraffinic solvents were used but was never observed when toluene was employed. The weaker solvating power of paraffinic solvents results in less efficient removal of cdl from the reaction zone leading to secondary reactions.

The amount of cdl isolated from the n-decane extraction was larger than the amount isolated from the n-heptane extraction showing that decane is a better solvent for dissolving and solvating cdl possibly because it is a more dense fluid under the extraction conditions employed (density for n-decane 0.40 g/ml; for n-heptane 0.28 g/ml).

IV. ANALYSIS OF PRODUCTS

A. Coals and Chars

1. Proximate and ultimate analysis:

All the chars submitted for proximate and ultimate analysis were derived from scg extractions carried out using extraction Method A. The results are summarized in Tables VII and VIII. After toluene extraction, the residual volatile matter in the char was lower than the volatile content of the coal. The volatile content of the chars decreased with increasing extraction temperature and with increasing extraction pressure. The temperature effect can be explained by increased pyrolysis of the coal and the pressure effect by improved extraction with denser solvent.

The residual volatile matter was lower after the IPA and tetralin/toluene extraction. Both these solvents are reactive solvents and may have altered the coal structure. The tetralin/toluene extraction had also resulted in much greater amounts of isolated cdl.

All the extracted dry chars showed an increase in calorific value over the dry coal. This increase was greatest for the char resulting from toluene extraction at 450° and 1500 psig and least for the char resulting from the tetralin/toluene extraction. There does not seem to be any obvious relationship between changes in volatile matter and changes in calorific value.

There were decreases in oxygen and sulfur content and increases in carbon and nitrogen content in the chars from all sources relative to the coal. The hydrogen content decreased for the chars resulting from toluene and tetralin/toluene extractions and the atomic hydrogen to carbon ratio decreased significantly relative to the coal. The hydrogen content increased for the char resulting from IPA extraction and the atomic hydrogen to carbon ratio decreased only slightly. This indicates that IPA donates hydrogen to the coal and suggests that this solvent, or others like it, may be useful co-solvents for maximizing the isolated cdl yield or for upgrading cdl quality in scg extractions.

2. Thermogravimetric analysis (TGA):

Figures 5 through 8 show the TGA of the three types of coal and of chars obtained from supercritical toluene extractions of these coals. The extractions on the high volatile bituminous C (HVBC) and lignitic coals were reported in the summary report of the previous contract period. These curves show the thermal characteristics of each individual coal. A number of conclusions may be drawn.

a) All the coals start to lose weight immediately (Figure 5). This is most pronounced for HVBC coal and least pronounced for the lignite. This rapid initial loss is due to loss of surface moisture.

b) Active thermal decomposition, characterized by an increased rate of weight loss, starts at 270° for the subbituminous and lignitic coals. This stage is characterized by rapidly increasing pressure during the extraction of these coals. Active thermal decomposition starts at 310° for the HVBC coal.

c) The chars from all the coals obtained by supercritical toluene extraction at 400° show immediate weight loss during the initial heating stage. The weight loss up to 110°, the temperature at which moisture is determined in proximate analysis, correlates well with the "moisture content" of the chars as determined by proximate analysis. Both measurements of weight loss are probably due to desorption of adsorbed solvent.

d) The char obtained from HVBC coal starts to undergo an increased rate of weight loss at 300°, about the same temperature as the coal. However, weight loss is not as rapid. The char obtained from toluene extraction of the subbituminous coal starts to undergo an increased rate of weight loss at about 350° compared with 270° for the feed stock while the char obtained from the lignite shows an increased rate of weight loss at 400° as compared with 270° for the starting coal. These observations suggest that the pyrolysis and scg extraction of lignite was most complete while that for the HVBC coal was least complete. The percent loss of volatile matter (proximate analysis) were 43% for lignite and 39% for subbituminous coal. Unfortunately, the proximate analysis of the char obtained from the HVBC coal extracted at 400° is not available. However, a char obtained by supercritical toluene extraction at 350° and 1500 psig showed only a 5% loss of volatile material. By way of comparison, the char obtained by extraction of subbituminous coal under the same conditions showed a 17% loss of volatile matter (Table VII).

e) The thermogravimetric curve of the char derived from heating subbituminous coal in the presence of tetralin is drastically altered compared with the curve obtained for the starting coal showing that a significant change had taken place in this instance (Figure 6). This was evident from a 55% reduction in volatile matter and further confirmed by petrographic studies (see below). This shows the influence a reactive solvent can have on the liquefaction/extraction process.

3. Petrographic analysis:

The petrographic analysis of coals and chars were carried out by Mrs. Judith Potter at the University of Saskatchewan, Regina. Her complete report was attached as an Appendix to one of Raylo's monthly progress reports (5).

The samples submited for petrography were three coal samples:

22/230-SQ-8-30019-H- HVBC;
-S- subbituminous;
-L- lignite;

and a number of chars:

22/230-SQ-8-30019-HCT- supercritical toluene extraction of HVBC at 400° and 1500 psig;
-LCT- supercritical toluene extraction of lignite at 400° and 1500 psig;
-SCT- supercritical toluene extraction of subbituminous coal at 400° and 1500 psig;
-SCL- subbituminous coal heated to 400° in the presence of tetralin followed by extraction with toluene at 400° and 1500 psig;
-SCD- supercritical *n*-decane extraction of subbituminous coal at 400° and 1500 psig.

Taking the degree of vesiculation as an indication of devolatilization and, therefore, a measure of degradation, supercritical toluene extraction at 400° and 1500 psig was most effective for HVBC coal, of intermediate effectiveness for lignite and least effective for subbituminous coal. The daf yield of cdl from these extractions were 19.0%, 17.4% and 18.2% respectively (see Table IX). The degree of vesiculation does not appear to correlate with percent cdl yield, nor with the changes in volatile matter as determined by proximate analysis, nor with the TGA curves (see above) when comparing different ranks of coal. On the other hand, if degree of vesiculation is indeed a measure of the completeness of formation and extraction of volatiles, then the cdl yield from HVBC coal is about as complete as can be expected while the yield from subbituminous coal could be and indeed can be improved a great deal.

Supercritical n-decane extraction of subbituminous coal at 400° and 1500 psig showed only 22% vesiculation, none of it highly vesicular, indicating that the decane extracted coal had undergone less devolatilization than the toluene extracted coal (32.6% vesiculation). The yields of cdl were 11.8% and 18.2% respectively, showing, in this case, correlation with petrographic results (see Table X).

The residue from tetralin/toluene extraction was most highly altered showing coking of the char, a highly vesicular char and possibly redeposition of cdl on the char. The latter could be due to the "dry" heating of the coal before toluene extraction was started (see above).

Additional observations suggest that penetration of the coal particles by supercritical gas is good, agreeing with a literature statement (6). The results also suggested that some coal particles had not been contacted with supercritical gas indicating uneven gas distribution within the reactor.

4. Pyridine soluble materials:

Blessing and Ross have suggested that coal thermolysis rates are enhanced in the presence of a solvent and took the increase in the amount of pyridine soluble material in the coal products as an indication of this phenomenom (3). Pyridine is a specific coal solvent which can dissolve up to 40% of a coal under certain conditions. The extraction yields are strongly dependent on coal composition and extraction procedures (7).

Table XI summarizes the amounts of pyridine soluble material from Forestburg subbituminous coal and of the products derived from this coal by supercritical solvent extraction. The cdl were totally soluble in pyridine and the column "cdl" represents the percent yield of cdl obtained from daf coal. The solubility of the daf char was substantially lower than the solubility of the coal except for the char derived from supercritical isopropyl alcohol extraction. The ultimate analysis of this char (Table VIII) showed an increased amount of hydrogen compared with the coal and an atomic hydrogen to carbon ratio similar to that of the coal. These results may be indicative of redeposition of cdl on the char due to the very low density (0.16 g/ml) of the supercritical gas and hence expected poor solvent power of IPA for cdl at the extraction conditions. With the exception of this case, the char solubility contributed very little to the total product solubility. There was no correlation between extraction conditions and char solubility for the chars derived from supercritical toluene extraction. The amount of pyridine solubles in these chars is 1.08% with a standard deviation of 0.37%. The total amount of pyridine soluble material in the products was greater than the amount of pyridine soluble material in the starting coal in every instance.

For supercritical toluene extraction, Blessing and Ross obtained from five to twelve percent pyridine soluble materials from their chars, considerably more than the pyridine soluble material obtained from our chars (less than two percent). These workers used a batch mode for supercritical gas extraction resulting in a liquid-solid separation of cdl. This procedure has a very high potential for redeposition of cdl on the char. A semi-continuous supercritical gas extraction mode removes cdl from the coal as it is formed resulting in an efficient gas-solid separation having little potential for redeposition of cdl. Determination of the total amount of pyridine soluble material in the coal products would be an important indicator of coal conversion when operating in a batch mode but has little value when operating in a semi-continuous or fully continuous mode.

B. Analysis of cdl

1. Fractionation:

The cdl isolated from the extraction process always contain some solvent. To ensure that cdl were solvent free, they were placed in a short path distillation apparatus and the flask was heated to 200 ±

10° for 30 minutes. Gas chromatographic analysis of the distillate indicates the presence of a number of volatile components (b.p. less than 200°) in the cdl. No attempt was made to identify or quantify these components. The residue was then fractionated into benzene insoluble material (preasphaltenes), benzene soluble but pentane insoluble material (asphaltenes) and pentane soluble material following a published procedure (8).

Since only the pentane soluble portion was suitable for spectroscopic analysis, the above procedure was streamlined to fractionate the cdl into pentane soluble and pentane insoluble fractions using a procedure very similar to a published procedure (9). The effect of the supercritical gas extraction conditions on the relative amounts of pentane soluble and pentane insoluble fractions are tabulated in Table XII. The data shows that there is relatively more pentane soluble material in the cdl derived from supercritical n-decane extraction than there is in cdl derived from supercritical toluene extraction. The data is too sparse to show any trend in the relative amounts of these fractions with extraction conditions for the toluene extractions.

2. Infrared spectroscopy:

An infrared (ir) spectroscopic analytical method for the estimation of the percent paraffinic, naphthenic and aromatic carbon present in heavy oils has been described in the literature (10).

The absorbance at 2850 cm^{-1} (methylene C-H stretching frequency) is used to calculate the amount of paraffinic carbon and the absorbance at 1600 cm^{-1} (aromatic double bond stretching frequency) is used to calculate the aromatic carbon content. Regression equations are given for both these relationships and the naphthenic content is calculated by difference. Figures 9 and 10 show typical ir spectra obtained for the pentane soluble fractions of cdl and Table XIII summarizes the results of the ir analysis. In cdl, the absorbance at 2850 cm^{-1} is small resulting in zero or negative paraffinic carbon content when the absorbance value is substituted into the equation. The cdl contain substantial amounts of carbonyl containing material which absorb at about 1700 cm^{-1} and large amounts of aromatic C-O bonds which absorb in the 1600 cm^{-1} region. Both these absorbance bands interfere with the aromatic carbon double bond stretching frequency at 1600 cm^{-1}. These interfering absorbance bands make the absorbance measurement at 1600 cm^{-1} unreliable leading to high estimates of the amount of aromatic carbon (Table XIII).

The ir spectra of cdl are compared with the ir spectra of oil obtained by supercritical propane extraction of Athabasca oil sands (Figures 11 and 12). These spectra do not contain significant carbonyl absorbance in the 1700 cm^{-1} region and show a stronger absorbance at 2850 cm^{-1}. The amounts of the various carbon types estimated from the ir spectra are reasonable.

The ir method calibrated for heavy oils is not valid for cdl samples. The ir data does appear to show an increase in aromatic character as the temperature of supercritical toluene extractions increase. Conventional ir methods are of limited value for the analysis of cdl. However Fourier Transform ir techniques, having the capability of "eliminating" interfering bands by normalizing the spectra followed by successive subtraction of interfering ir absorbances, may in future prove to be a valuable tool for cdl and coal analysis.

3. Nuclear magnetic resonance (nmr)

a) Proton magnetic resonance:

Various types of protons can be distinguished in the proton magnetic resonance spectra of cdl as summarized in Table XIV (11).

Figure 13 shows a typical nmr spectrum of a pentane soluble fraction of cdl. Aromatic protons are readily observed but there are no olefinic protons. Fluorene type methylene protons are detectable at $\delta 4$ (by integration), hydrogens on carbons alpha to aromatic rings are abundant and naphthenic protons are detectable by integration but no fine structure is evident. The bulk of the protons are present as methylene or methyl groups (most likely methylene groups because of the sharpness of the resonance at δ 1.25) beta or more remote from aromatic rings. Methyl groups gamma or further removed from aromatic rings also make up a significant portion of the total protons present. The sharp singlet at δ 2.92 is due to the benzylic protons of bibenzyl. The ratio of the broadly grouped paraffinic-naphthenic protons to the aromatic-phenolic protons, taking into account the contribution of bibenzyl protons [toluene degradation is assumed to be the major source of bibenzyl (12)], is calculated from the integration and summarized in Table XV. These results show that:

1. more aromatic material is isolated when toluene is used as the supercritical extraction gas than when n-decane is used;
2. the relative amount of aromatic material increases with increasing extraction temperature;
3. bibenzyl is not detectable by nmr when supercritical toluene extraction is performed at 350°;
4. the amount of bibenzyl formed increases with increasing extraction temperature;
5. with hydrogen donors present (tetralin or toluene at high temperature - implicated by bibenzyl formation), the relative amount of aromatic material in the extract is enhanced;
6. the pentane soluble fraction of cdl from subbituminous coal are more aromatic than heavy oil from the Athabasca oil sands.

These preliminary results show that nmr analysis is useful for determining the composition of cdl and may be useful in elucidating the factors affecting coal thermolysis in the presence of various supercritical media.

b) Carbon-13 magnetic resonance:

Figures 14 and 15 show the aromatic and aliphatic regions of a 50.32 MHz C^{13} nmr spectrum of pentane soluble cdl obtained from the extraction of subbituminous coal at 450° and 1500 psig with toluene. The aromatic region is dominated by signals at δ_{TMS} 128.8, 128.6, 128.4, 128.2 and 125.8. The first set of these signals are associated with unsubstituted carbon of benzene or naphthalene aromatic systems while the latter is associated with carbons para to the substituted carbon of naphthalenic systems (13). This signal could also be associated with cycloalkenes but this assignment is less likely since there were no olefinic hydrogens observed in the proton nmr of the same sample. The aliphatic region is dominated by signals at δ 37.8 and 29.7. The first of these is associated with carbons alpha to an aromatic ring whereas the second resonance is associated with methylene carbons which are beta or further removed from an aromatic ring (14). This resonance appears as a triplet in the proton coupled spectrum with a coupling constant of 126 Hz confirming that this signal is due to methylene carbon. Smaller signals at δ 22.9 and 22.7 are associated with methylene groups of chain terminating ethyl groups while the signal at δ 14.1 is associated with chain terminating methyl groups (14). Signals for saturated cyclopentanes and cyclohexanes appear in the δ 26 to 28 range. Very few signals are observed which coincides with the proton nmr spectrum in which only small amounts of naphthenic hydrogen was observed.

Quantitative C^{13} nmr combined with H^1 nmr would result in a powerful tool in the estimation of the amounts of hydrocarbon types present in cdl.

C. Analysis of gaseous products

The volume of gas liberated during the scg extraction of subbituminous coal was crudely measured for some of the toluene extractions and found to be about 15 litres for extractions at 375°, 18 litres for extractions at 400°, 23 litres for extractions at 425° and 30 litres for extractions at 450°. These volumes represent from 0.7 to 1.3 moles of gas.

In other experiments, the evolved gas was passed through a dry ice (-78°) cold trap. The volumes of the condensable portion of the gas was about ten millilitres. More than half of this material evaporated on warming to 0° and probably consisted primarily of hydrogen sulfide (b.p. -60.7°) as indicated by its distinctive odour. The remainder of the material was analyzed by gas chromatography (six foot by quarter inch, 10% SE-30 from 40° to 100°, 40 ml/min helium flow rate). Figure 16 shows a typical chromatograph obtained for a toluene extraction of subbituminous coal. The chromatograph displays four major products (greater than 1.5% by peak area) and traces of eight minor components. Toluene (66.4%) was identified by retention time and methyl sulfide (19.8%) by retention time and nmr (single peak at δ 2.15 - identical to that of the authentic sample). Chromatographic analysis of the contents of the cold trap after extractions with n-heptane, n-decane and MEK revealed the presence of methyl sulfide, small amounts of benzene and significant amounts (up to 40%) toluene.

D. Analysis of recovered toluene

Toluene recovered from the extraction of subbituminous coal at 400° and 2000 psig was fractionally distilled through a one foot by three-quarter inch Vigreaux column. The fractions were analyzed by gc and where possible by nmr. The results are shown in Table XVI. Besides toluene, the major volatile component isolated and identified is methyl sulfide (b.p. 38°). Besides methyl sulfide, there were traces of six other compounds which elute before toluene and, from the distillation residue, only one compound which eluted after toluene. No attempt was made to identify these minor components which could not account for a significant proportion of the products derived from coal.

V. CONCLUSION

The work reported in this summary report was carried out in a space of eight months and meets all the major objectives put forward at the beginning of the contract period. The yield of cdl isolated from subbituminous coal by scg extraction was sensitive to the procedure followed during the heat-up period, temperature, pressure and to some degree on the flow rate of the extracting gas. The yield was also dependent on the solvent used for extracting, with toluene being much better than paraffinic solvents. Oxygenated solvents generally underwent extensive degradation and cannot be considered as scg extraction media. However, these types of solvent, especially alcohols, may be very useful as a reactive co-solvent for increasing the yield of cdl or for upgrading the quality of cdl. The use of a hydrogen donating solvent such as tetralin greatly improves the yield of cdl and drastically alters the characteristics of the char. The chemical composition of cdl was sensitive to temperature of the extraction with the material becoming more aromatic at high temperatures.

VI. FUTURE WORK

The extractions carried out using solvents other than toluene, indicated the influence extraction solvents can have on the yield and composition of cdl. Much more work is necessary to define these solvent effects.

The effect of extraction procedure pointed to the important influence conditions during the heat-up period have on the isolated cdl yield. Heating rate is expected to have a major influence on extraction yield. The heating rate cannot be altered using the current equipment. Therefore, an apparatus must be designed and constructed which will reduce the heat-up rate from a matter of hours to a matter of minutes.

The effects of temperature and pressure were conducted over a very narrow range, the upper limits being defined by current equipment limitations. The design of a new apparatus should also incorporate the capability to reach temperatures of 600° and pressures to possibly 6000 psig.

These proposals have already been developed and a research proposal has been sent to the Department of Energy, Mines and Resources.

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TABLE I

The effect of extraction procedure (see text) on the isolated yield of cdl when extracting 400 grams of subbituminous coal with supercritical toluene.

Experimental Conditions			Products (g)		% cdl	% Material
Method	Temp (^{o}C)	Pressure (psig)	Char	cdl	daf	Balance a)
A	350	1500	257	27.7	9.4	97.2
B	350	1500	257	29.8	11.0	98.7
A	400	1000	235	17.2	6.2	90.6
B	400	1100	235	39.4	14.5	96.1
A	400	1500	223	24.2	8.7	89.3
B	400	1500	218	47.0	17.3	93.8
B	400	1500	234	49.4	18.2	98.4
A	400	2000	227	42.3	15.0	93.1
B	400	1900	223	52.7	19.3	96.4
A	450	1500	227	19.7	7.2	90.7
B	450	1500	221	67.1	24.7	99.5

a) Takes into account the amount of water isolated (110 g) but not the amount of gas liberated.

TABLE II

Supercritical toluene extraction of 400 grams 12-24 mesh subbituminous coal at various temperatures and pressures using extraction Method B.

Temp °C	Pressure psig	Solvent a)			Products b)		% cdl daf	% Material Balance
		Flow ml/min	Space Time min	Density g/ml	Char g	cdl g		
450	1900	76	7.2	0.33	217	68.8	25.4	94.2
450	1500	77	7.1	0.28	221	67.1	24.7	99.5
425	1700	59	9.3	0.36	224	57.7	21.3	97.9
425	1300	102	5.4	0.27	237	48.5	17.9	98.9
400	1900	54	10.1	0.43	223	52.7	19.3	96.4
400	1500	69	8.0	0.39	218	47.0	17.3	93.8
400	1500	72	7.6	0.39	234	49.4	18.2	98.4
400	1100	107	5.1	0.26	235	39.4	14.5	96.1
375	1700	57	9.7	0.45	247	44.9	16.6	100.5
375	1300	72	7.6	0.39	242	38.8	14.3	97.7
350	1500	48	11.5	0.47	257	29.8	11.0	98.7

a) Estimation based on compressibility factors (see Appendix I).

b) Water estimated at 110 g.

TABLE III

Cumulative amount of cdl isolated during the heat-up period in toluene extraction of 400 grams 12-24 mesh subbituminous coal at various temperatures and pressures.

Temp °C	Pressure psig	Total cdl	cdl isolated (g) Cumulative wt. in temp range 275-300	300-325	325-350	350-375	375-400	400-425	425-450	% of total cdl
450	1900	68.8	2.2	8.5	12.0	18.7	27.6	38.1	46.1	67.0
450	1500	67.1	4.7	9.1	14.5	21.7	30.6	39.2	45.0	67.1
425	1700	57.7	---	7.3	12.1	17.4	26.9	36.6	----	63.4
425	1300	48.5	4.2	8.6	12.5	18.2	25.3	32.5	----	67.0
400	1900	52.7	---	4.1	12.7	19.0	28.1	----	----	53.3
400	1500	47.0	3.7	8.2	12.3	18.8	27.5	----	----	58.5
400	1500	49.4	3.8	6.0	9.1	16.5	27.3	----	----	55.0
400	1100	39.4	0.3	6.1	10.8	16.9	24.4	----	----	61.9
375	1700	44.9	4.8	9.4	13.4	19.1	----	----	----	42.5
375	1300	38.8	3.2	9.2	13.1	19.0	----	----	----	49.0
350	1500	29.8	3.2	5.5	9.1	----	----	----	----	32.8

TABLE IV

Comparison of Calculated Yields of cdl[a)] with Experimental Yields at Various Temperatures and Pressures.

Pressure (psig)	Temp C	% Yield (daf)		Pressure (psig)	Temp C	% Yield (daf)	
		Calc'd	Found			Calc'd	Found
1100	325	6.0	--	1700	325	9.9	--
	350	9.0	--		350	12.8	--
	375	12.0	--		375	15.8	16.6
	400	15.0	--		400	18.8	--
	425	17.9	--		425	21.8	21.3
	450	20.9	--		450	24.7	--
	475	23.9	--		475	27.7	--
1300	325	7.3	--	1900	325	11.1	--
	350	10.3	--		350	14.1	--
	375	13.3	14.3		375	17.1	--
	400	16.2	--		400	20.1	19.3
	425	19.2	17.9		425	23.0	--
	450	22.2	--		450	26.0	25.4
	475	25.2	--		475	29.0	--
1500	325	8.6	--	2100	325	12.4	--
	350	11.6	11.0		350	15.4	--
	375	14.5	--		375	18.4	--
	400	17.5	17.3/18.2		400	21.3	--
	425	20.5	--		425	24.3	--
	450	23.5	24.7		450	27.3	--
	475	26.4	--		475	30.3	--

a) $Y = -72.1395 + 11.9\ ({}^{o}K/100) + 6.375\ (psig/1000)$

TABLE V

Effect of toluene feed rate on the isolated yield of cdl when extracting 400 grams of subbituminous coal at 400° and 1500 psig using extraction Method A.

Feed Rate g/min	Solvent Flow Rate ml/min a)	Space Time min	Products (g) Char	Products (g) cdl	% cdl daf	% Material Balance b)
36	92	6.0	229	39.7	14.6	94.7
24	62	8.9	223	24.2	8.7	89.3

a) At 400° and 1500 psig; toluene density is 0.39 g/ml.

b) Includes 110 ml water.

TABLE VI

Effect of solvent on the isolation of cdl derived from supercritical gas extraction of 400 grams subbituminous coal at 400° and 1500 psig.

Experimental Method a)	Solvent				Products		% cdl daf	% Material Balance b)
	Material	Flow Rate ml/min	Space time	Density g/ml	Char g	cdl g		
A	Tetralin c)	---	---	---	176	85.0	31.4	92.8
A	IPA	131	4.2	0.16	222	48.3	17.8	95.1
B	MEK d)	87	6.3	0.22	252	----	----	----
B	90% p-cresol 10% water e)	44	12.5	0.64	191	226	----	132
B	n-decane	52	10.6	0.40	234	32.1	11.8	94.0
B	n-heptane	64	8.6	0.28	237	20.5	7.6	91.9
B	toluene	72	7.6	0.36	234	49.4	18.3	98.4

a) See text for explanation.
b) Includes 110 g water but not amount of gas evolved.
c) Tetralin present during heat-up period followed by toluene extraction.
d) Solvent degradation occurs leading to 263 g of tar.
e) Solvent degradation occurs; extraction took place at 450° and 1900 psig.

TABLE VII

Proximate analysis and calorific value for subbituminous coal and char derived from scg extraction using experimental method A.

Sample a)	Deter'd as b)	Moisture %	Ash %	Volatile Matter		Fixed Carbon %	Calorific Value	
				%	% decrease c)		Btu/lb	% increase c)
A	1	21.5	4.7	33.7	---	40.0	10,510	---
	2	--	6.0	42.9	---	51.1	12,122	---
B	1	3.1	6.6	34.6	---	55.7	13,030	---
	2	--	6.9	35.7	17	57.5	13,447	10.9
C	1	1.7	7.8	29.3	---	61.2	---	---
	2	--	7.9	29.8	31	62.3	---	---
D	1	1.3	6.8	25.9	---	66.0	13,206	---
	2	--	6.9	26.2	39	66.9	13,380	10.4
E	1	1.0	7.4	21.9	---	69.7	13,813	---
	2	---	7.5	22.1	48	70.4	13,953	15.1
F	1	2.1	11.7	19.0	---	67.2	12,987	---
	2	---	12.0	19.4	55	68.6	13,266	9.4
G	1	2.7	8.7	23.5	---	65.1	13,502	---
	2	---	8.9	24.2	44	65.9	13,877	14.5

a) A - subbituminous coal; B - Toluene at 350° and 1500 psig; C - Toluene at 400° and 1000 psig; D - Toluene at 400° and 1500 psig; E - Toluene at 450° and 1500 psig; F - Tetralin/toluene at 400° and 1500 psig; G - IPA at 400° and 1500 psig.

b) 1 - Air dried sample; 2 - dry basis.

c) Relative to dry coal.

TABLE VIII

Ultimate analysis of subbituminous coal and chars remaining after scg extraction at 400° and 1500 psig using experimental method A.

Sample a)	Deter'd as b)	Moisture %	Ash %	C %	H %	N %	S %	O %	H/C
A	1	(13.25)	3.60	62.09	5.54	1.32	0.69	26.76	---
	2	---	4.15	71.57	4.68	1.52	0.80	17.28	---
	3	---	--	74.67	4.88	1.59	0.83	18.03	0.78
B	1	(1.30)	6.81	78.45	4.03	1.67	0.56	8.48	---
	2	---	6.90	79.48	3.93	1.69	0.57	7.43	---
	3	---	--	85.37	4.22	1.82	0.61	7.98	0.59
C	1	(2.09)	11.73	76.98	3.80	1.78	0.55	5.16	---
	2	---	11.98	78.62	3.65	1.82	0.56	3.37	---
	3	---	--	89.32	4.15	2.07	0.64	3.83	0.56
D	1	(2.69)	8.65	76.82	4.89	1.64	0.33	7.67	---
	2	---	8.89	78.94	4.72	1.69	0.34	5.42	---
	3	---	--	86.64	5.18	1.85	0.37	5.95	0.72

a) A - subbituminous coal; B - toluene; C - tetralin/toluene; D - IPA.

b) 1 - air dried sample; 2 - dry basis; H and O do not include sample moisture (ASTM D-3180, Nov. 1974); 3 - dry ash free basis.

TABLE IX

Petrographic results obtained for chars derived from different coal ranks after supercritical toluene extraction at 400° and 1500 psig.

Coal Rank	% Vesiculation	% Highly Vesicular a)	% cdl (daf)	% loss of volatile matter b)
HVBC c)	72	90	19.0	---
Subbituminous	32.6	0	18.2	39
Lignitic	85	10.5	17.4	43

a) % of total vesiculation.

b) Obtained by comparing proximate analysis of coals and chars.

c) High volatile bituminous C.

TABLE X

Petrographic results obtained for chars derived from supercritical gas extraction at 400°C and 1500 psig of subbituminous coal.

Gas	% Vesiculation	% Highly Vesicular a)	% cdl (daf)
Toluene	32.6	0	18.2
n-Decane	22.0	0	11.8
Tetralin/Toluene b)	62.0	95	31.4

a) % of total vesiculation.

b) 34% of the char was semi-coke, ranging from fine grained to flow type over one-half of which was vesicular.

TABLE XI

Pyridine solubles in products derived from supercritical solvent extraction of subbituminous coal.

Extraction Conditions			% of coal products soluble in pyridine on a daf basis		
Solvent	Temp	Psig	cdl a)	Char	PS b)
Feed Stock			--	7.0	7.0
Toluene	350	1500	11.0	1.23	12.1
Toluene	375	1300	14.3	1.30	15.4
Toluene	375	1700	16.6	0.75	17.2
Toluene	400	1100	14.5	0.63	15.0
Toluene	400	1500	17.3	1.26	18.3
Toluene	400	1500	18.2	1.85	19.7
Toluene c)	400	1500	14.4	0.76	15.1
Toluene	400	1900	19.3	1.18	20.3
Toluene	425	1300	17.9	1.31	19.0
Toluene	425	1700	21.3	0.64	21.8
Toluene	450	1500	24.7	0.99	25.4
Toluene	450	1900	25.4	1.03	26.2
Tet/Tol	400	1500	31.4	0.89	32.0
Heptane	400	1500	7.6	2.00	9.2
Decane	400	1500	11.8	1.67	13.6
IPA	400	1500	17.4	7.87	23.9

a) The cdl obtained from an extraction was totally pyridine soluble.

b) PS = Product Solubility = % cdl + (100 - % cdl/100) (% pyridine solubility of solids). See Appendix II for a sample calculation.

c) Coal dewatered before extraction.

TABLE XII

Effect of extraction conditions on the relative amounts of pentane soluble and pentane insoluble materials in cdl derived from supercritical gas extraction of subbituminous coal.

Extraction Conditions					
Gas	Temp C	Pressure psig	% Pentane Insoluble	% Pentane Soluble	Soluble/ Insoluble
Toluene	450	1500	52.3 a)	47.7	0.91
Toluene	425	1700	52.8	47.2	0.89
Toluene	400	1500	62.5	37.5	0.60
Toluene	350	1500	59.4	40.6	0.68
n-Decane	400	1500	35.5	64.5	1.81

a) CDL from this run was fractionated into benzene insoluble (35.8%) pentane insoluble (16.5%) and pentane soluble (47.7%) fractions.

TABLE XIII

Infrared analysis of pentane soluble oil obtained from supercritical gas extraction of subbituminous coal.

Extraction Conditions			% Carbon Type a)		
Gas	Temp C	Pressure psig	Paraffinic	Aromatic	Naphthenic
Toluene	450	1500	-16	127	-11
Toluene	400	1500	-2	191	-89
Toluene	350	1500	0	73.6	26.4
n-Decane	400	1500	0	62.0	38.0
n-Propane b)	110	1900	12.5	63.1	24.4

a) $\% C_p = 62.93 A_{2850}/c \times a - 31.54$ $\% C_A = 710.19 A1600/c \times a - 11.55$

$\% C_N = 100 - (\% C_A + \% C_p)$ A = absorbance, c = concentration in g/l
a = path length in cm.

b) Oil obtained from Athabasca oil sands.

TABLE XIV

Hydrogen types distinguishable in cdl by proton magnetic resonance a).

δ Range (ppm)	Assignment	Symbol
5.5 - 9.0	Aromatic and phenolic	H_A
4.7 - 5.5	Olefinic	H_O
3.3 - 4.5	Methylene groups α to two aromatic rings (e.g. fluorene)	$H_{\alpha 2}$ or H_F
2.0 - 3.3	Hydrogen on carbon atoms α to an aromatic ring	H_α
1.6 - 2.0	Naphthenic methylene and methine (other than α to an aromatic ring)	H_N
1.0 - 1.6	Methylene β or more remote from an aromatic ring; methyl groups to an aromatic ring	H_β
0.5 - 1.0	Methyl γ or further from an aromtic ring	H_γ

a) Adapted from reference 11.

TABLE XV

Nmr spectral data showing the relative amounts of paraffinic-naphthenic and aromatic protons in the pentane soluble fractions of cdl obtained from supercritical gas extraction of subbituminous coal.

Extraction Conditions			Bibenzyl a)		% Proton type b)		$\frac{H_p+H_N}{H_A}$ b)
Gas	Temp	Pressure	H_p+H_N	H_A	H_p+H_N	H_A	
Tetralin/ toluene	400	1500	---	---	63.0	37.0	1.70
Toluene	450	1500	8	28	63.7	36.3	1.75
Toluene	425	1700	5.8	26.5	69.7	30.3	2.30
Toluene	400	1500	2.2	19.7	81.8	18.2	4.47
Toluene	350	1500	---	--	81.1	18.9	4.29
n-Decane	400	1500	---	--	92.6	7.4	12.5
n-Propane c)	110	1900	---	--	95.9	4.1	23.4

a) Percent contribution of bibenzyl protons to the integration of paraffinic-naphthenic (H_p+H_N) and aromatic (H_A) protons.

b) Corrected for bibenzyl contribution.

c) Oil obtained from Athabasca oil sands.

TABLE XVI

Fractional distillation and gas chromatographic analysis of toluene recovered from the supercritical toluene extraction of subbituminous coal at 400°C and 2000 psig.

Fraction	b.p.	Products
1	52 - 57	Toluene and CH_3SCH_3 (nmr)
2	78 - 88	---
3	92 - 95	---
4	95 - 100	Toluene & traces of 4 compounds a)
5	100 - 102	Toluene & traces of 6 compounds a)
6	102 - 105	Toluene & traces of 4 compounds a)
7	105	Toluene & traces of 3 compounds a)
Residue	105	Toluene & traces of 1 compound b)

a) Eluted from 6' x 1/4", 10% S.E. -30 column at 60°C before toluene.

b) Eluted after toluene.

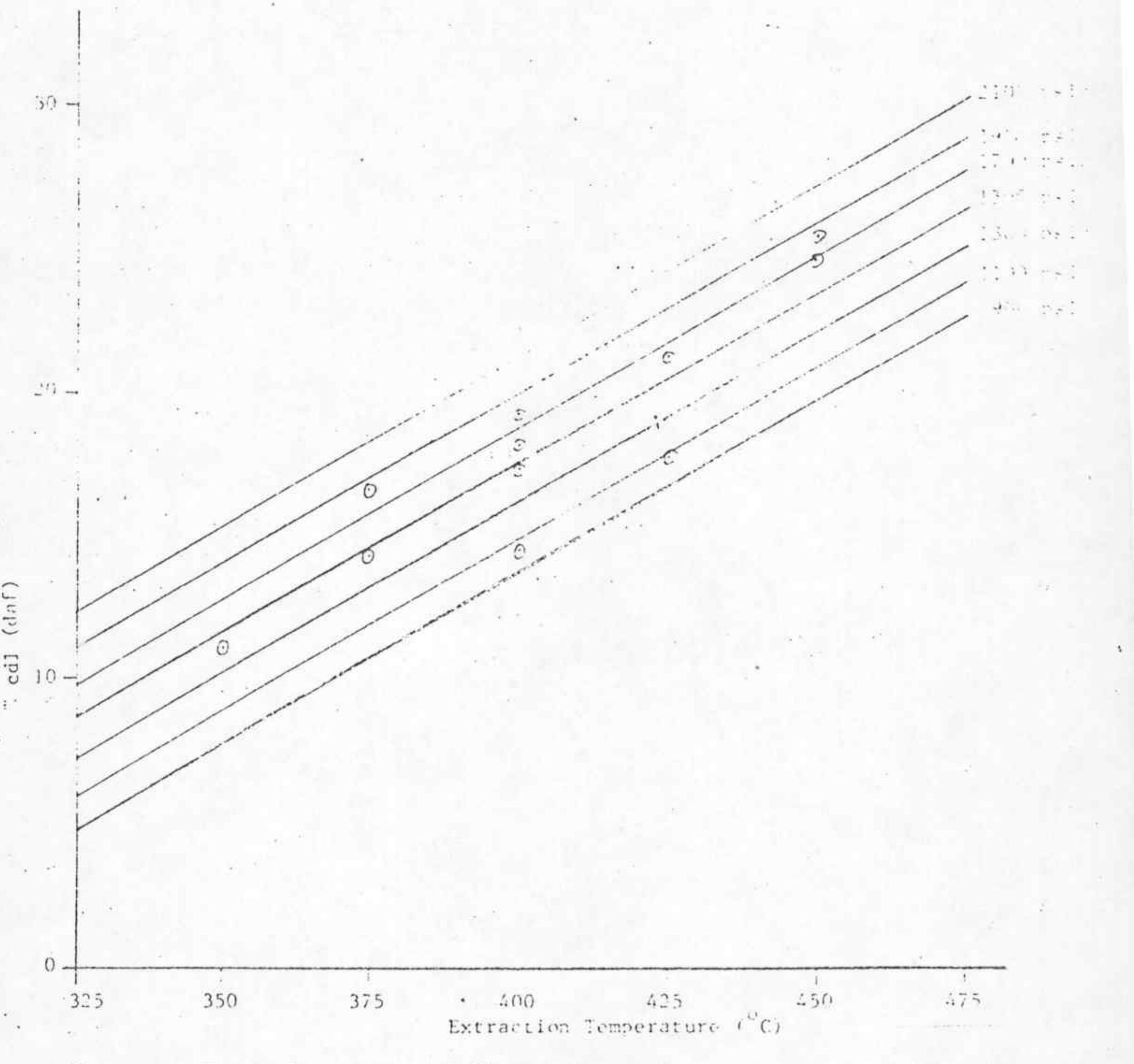


Figure 1: Increasing percent yield with increasing temperature and pressure. Lines represent calculated yields while θ represents experimental yields (see Table II).

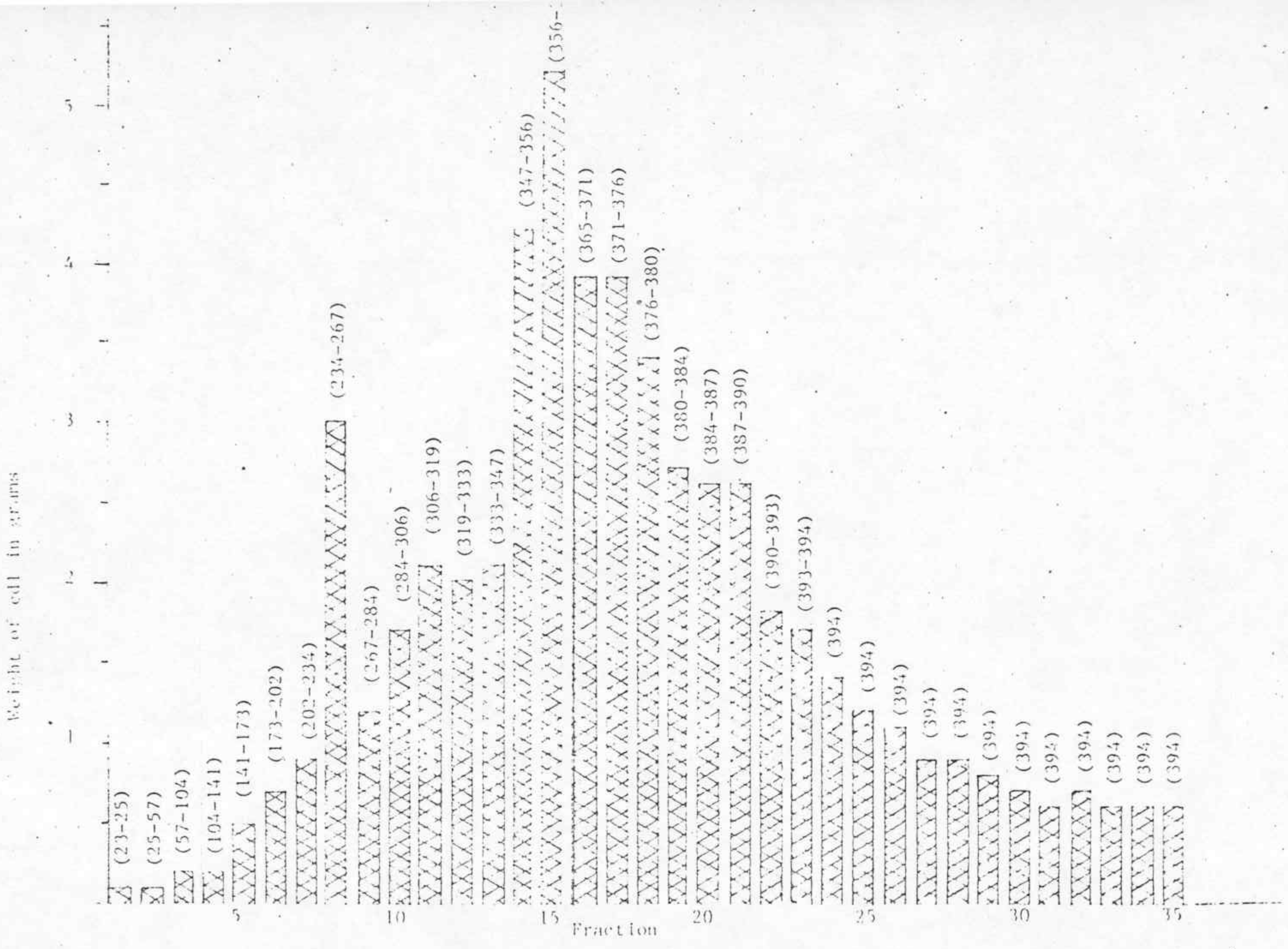


Figure 2: The weight of cdl extracted by the same weight of toluene during the continuous extraction of subbituminous coal at 1500 psig. Numbers in the brackets represent the temperature range over which the fractions were collected.

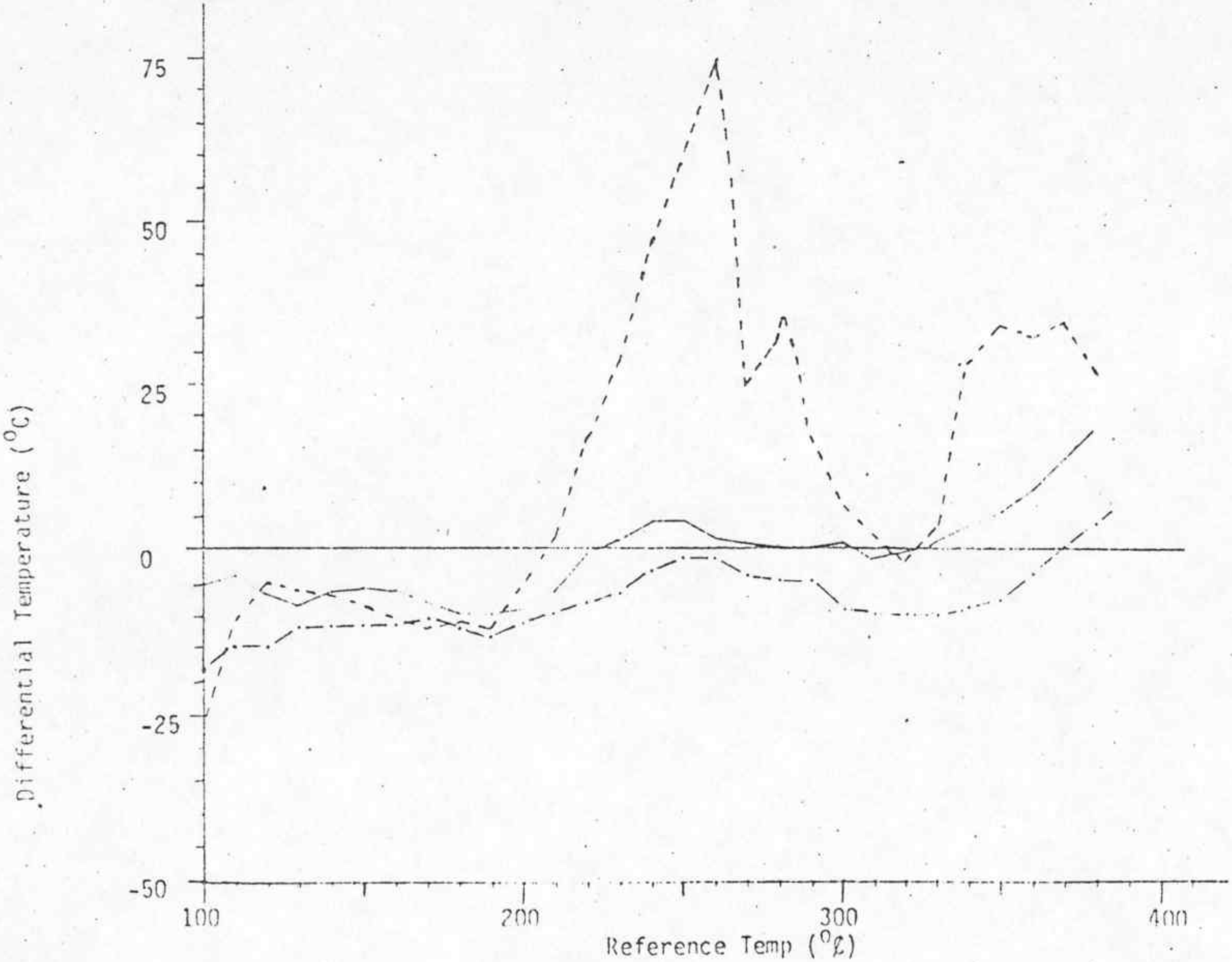


Figure 3. Deviation of the internal autoclave temperature from the reference temperature when subbituminous coal is heated with various solvents. Toluene (—); Tetralin (---); Isopropyl alcohol (-.-).

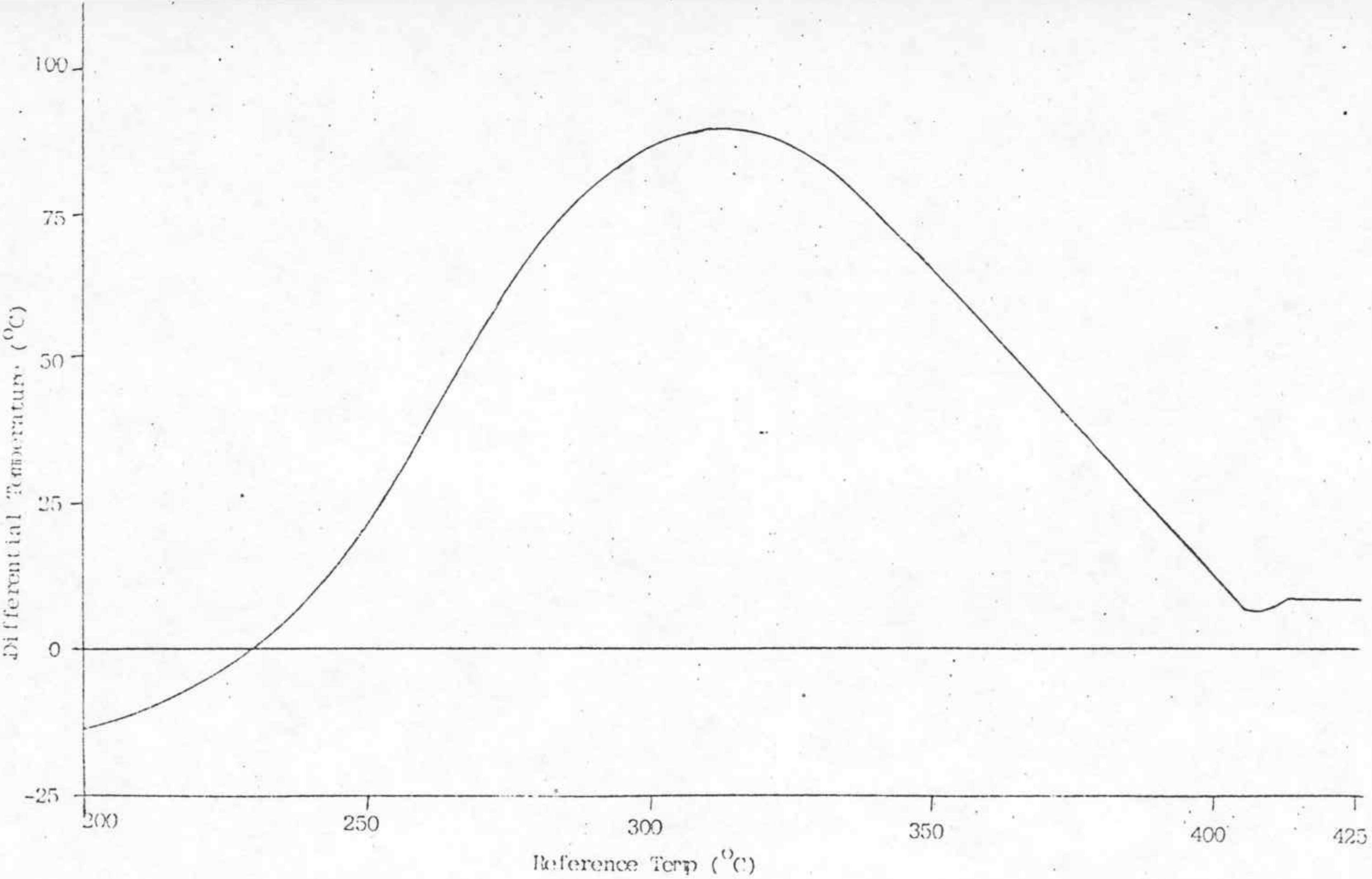


Figure 4 : Deviation of the internal autoclave temperature from the reference temperature when heating 10% water/p-cresol.

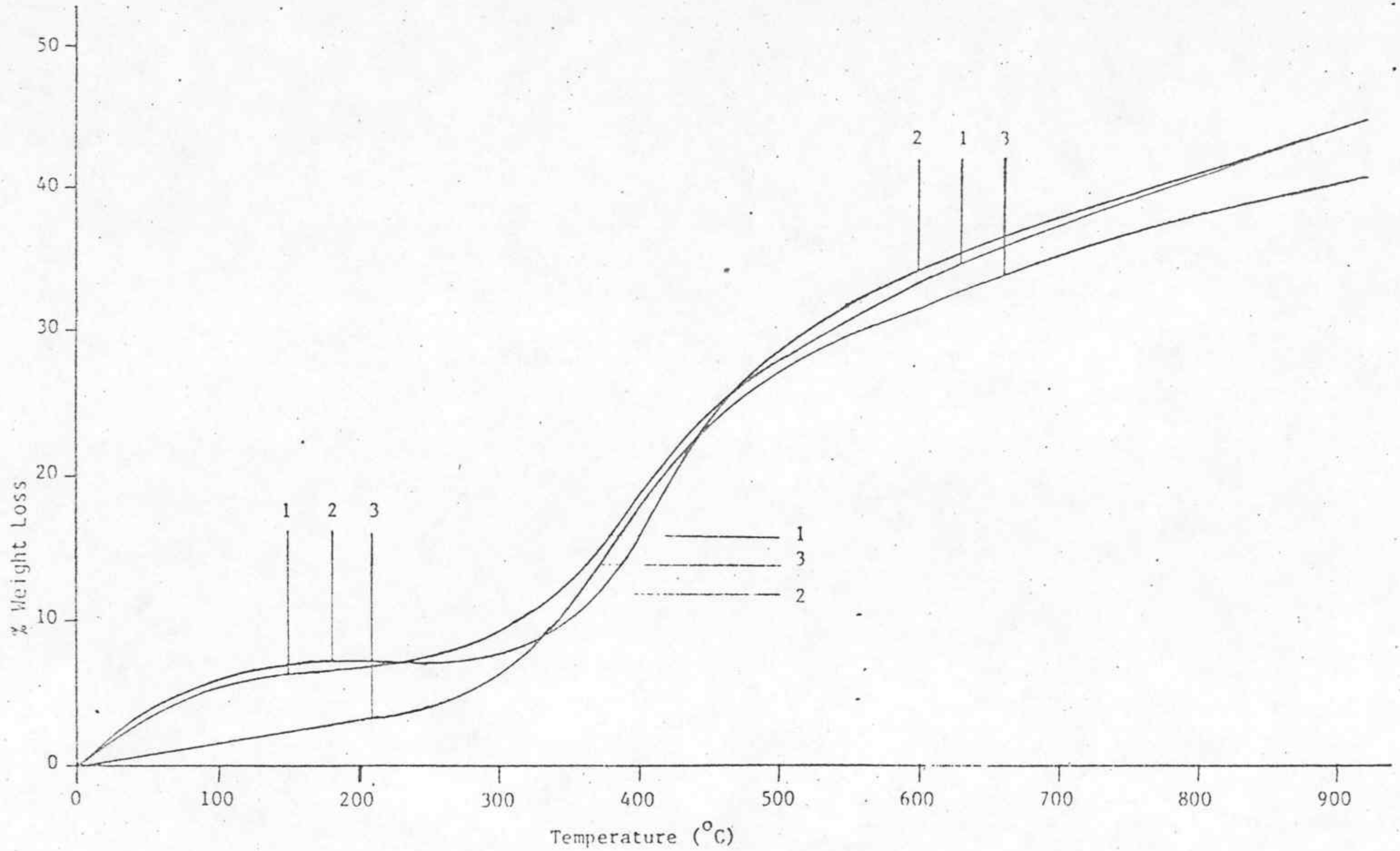


Figure 5 : Thermogravimetric analysis; heating rate 5°C/min. Curve 1 - subbituminous coal; Curve 2 - high volatile bituminous C coal; Curve 3 - lignite.

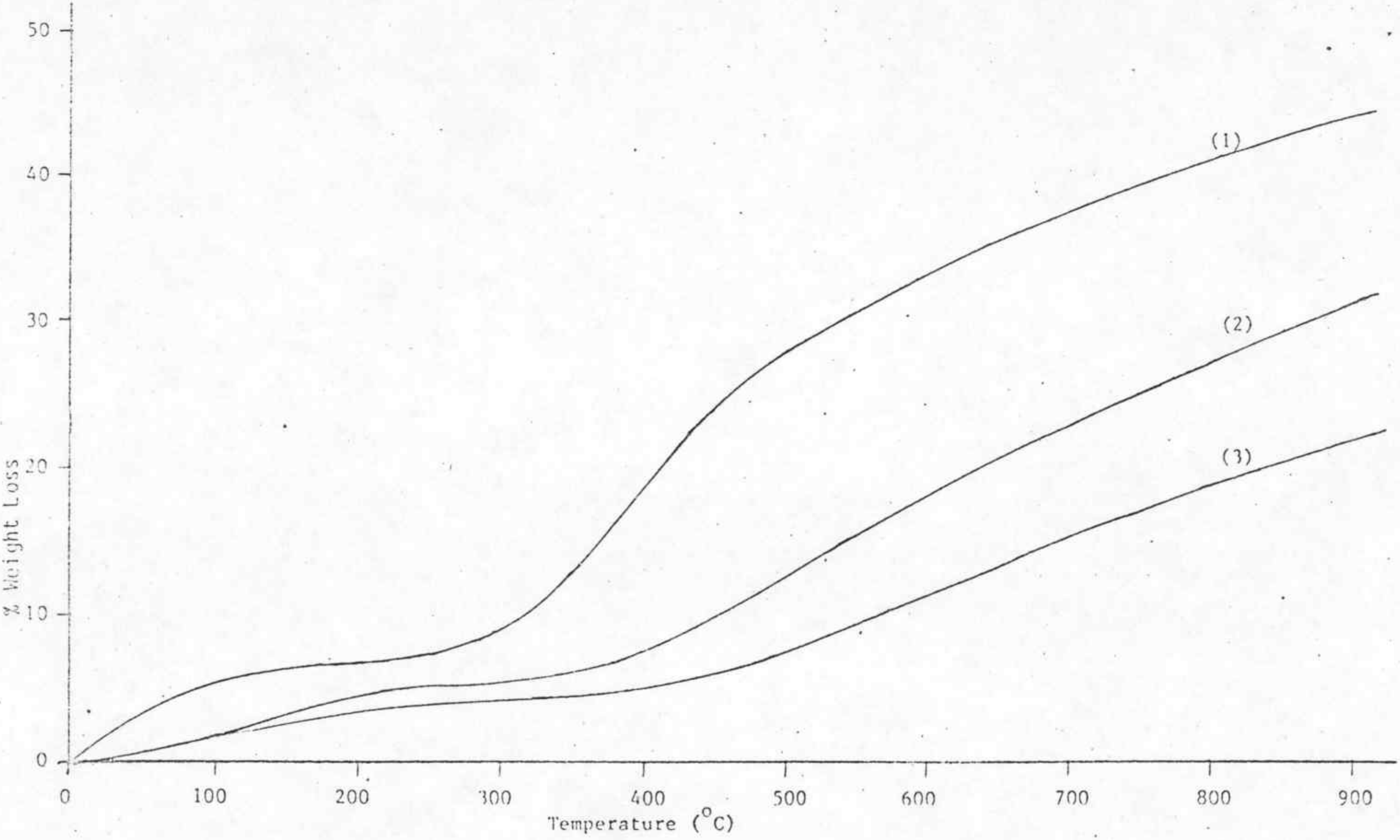


Figure 6: Thermogravimetric analysis; heating rate 5°C per min. Curve 1 - subbituminous coal; Curve 2 - char from supercritical toluene extraction at 400°C and 1500 psig; Curve 3 - char resulting from preheating coal with tetralin followed by supercritical toluene extraction at 400° and 1500 psig.

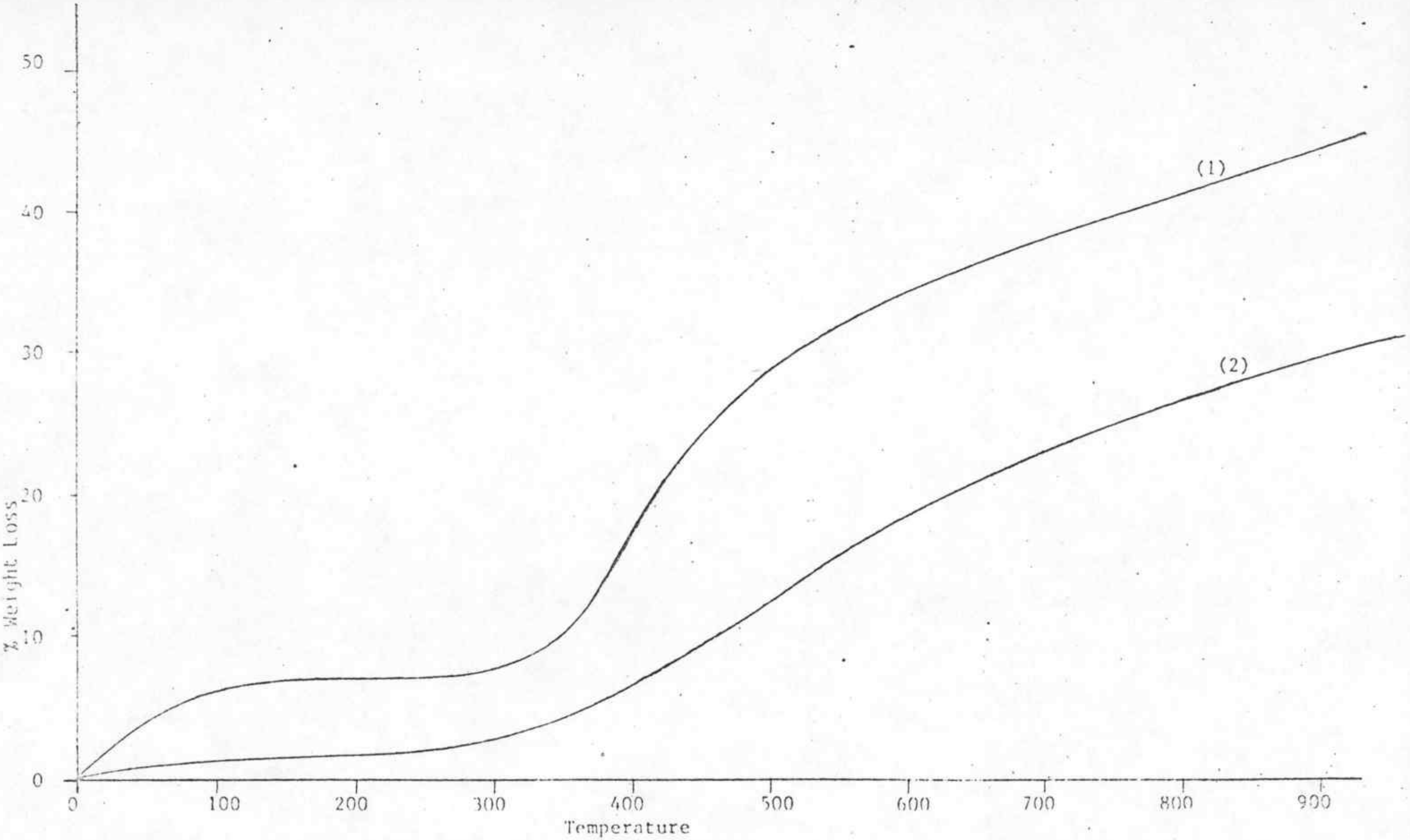


Figure 7 : Thermogravimetric analysis; heating rate 5°C/min. Curve 1 - high volatile bituminous C coal; Curve 2 - char remaining after supercritical toluene extraction at 400°C and 1500 psig.

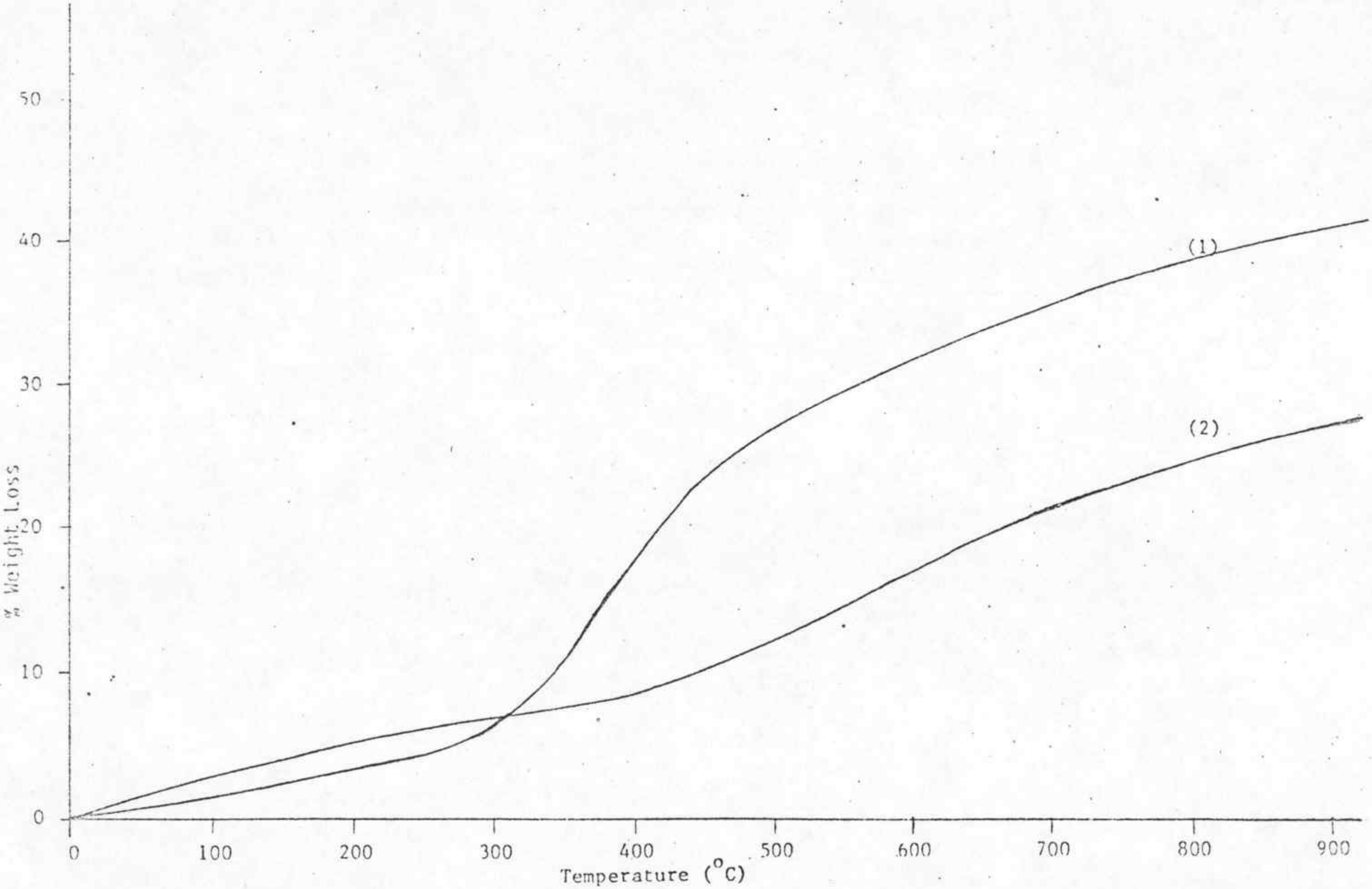


Figure 8 : Thermogravimetric analysis; heating rate 5°C/min. Curve 1 - lignite; Curve 2 - char from supercritical toluene extraction at 400°C and 1500 psig.

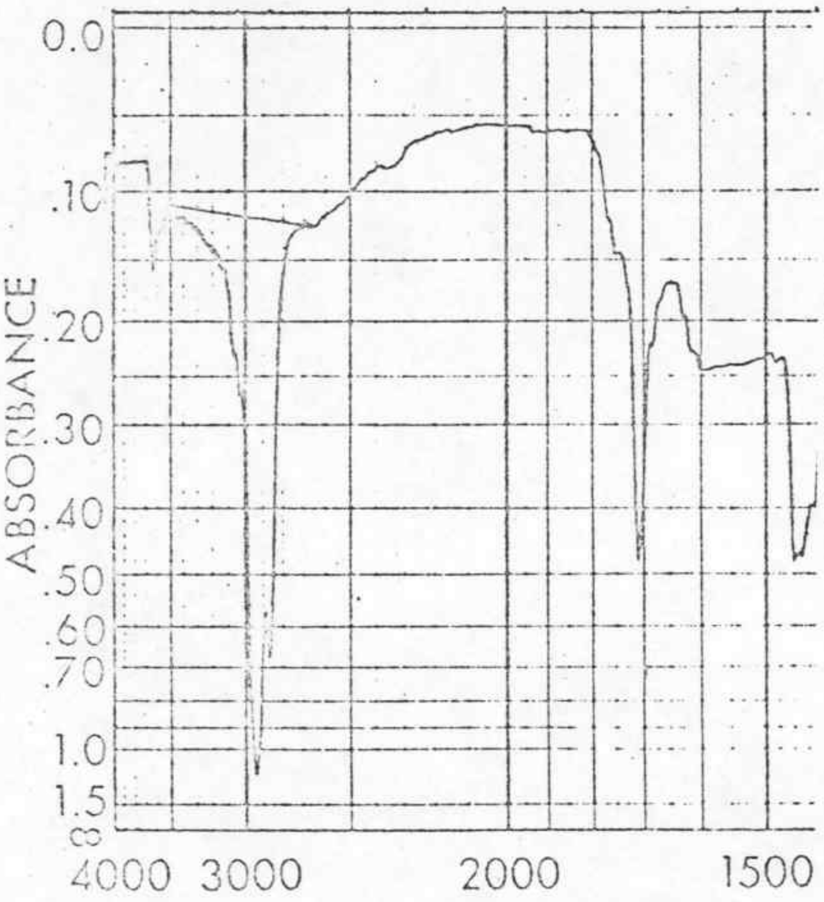


Figure 9

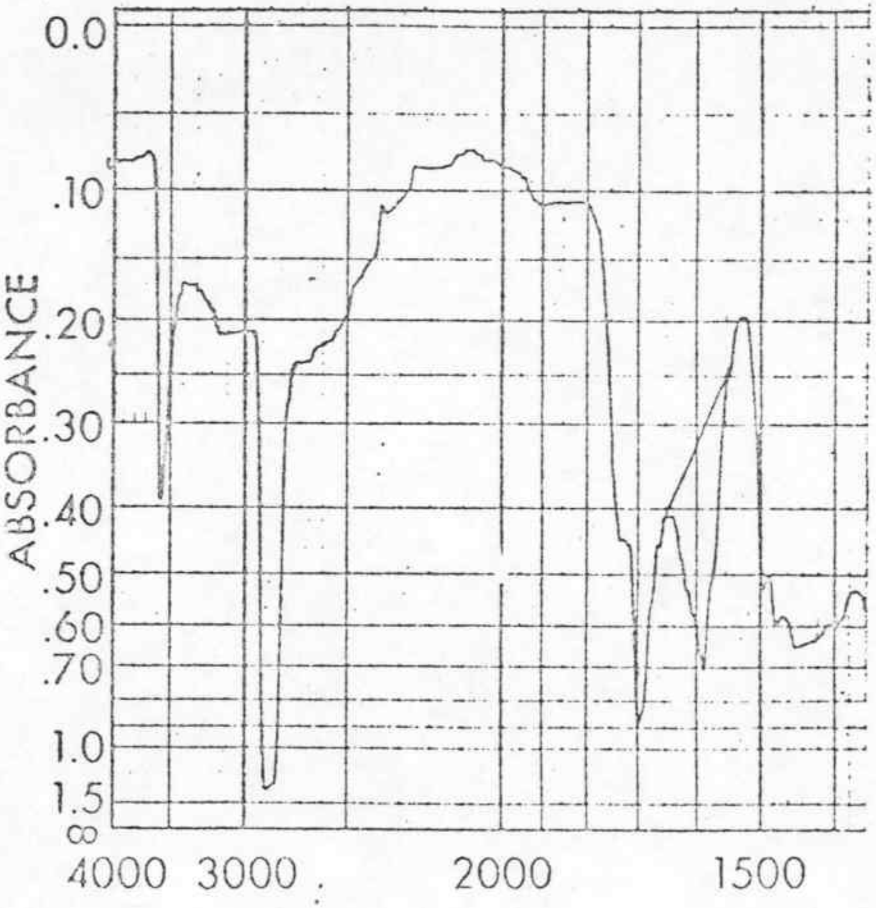


Figure 10

Infrared spectra in carbon tetrachloride (Fig. 9) and methylene chloride (Fig.10) of the pentane soluble fraction of CDL obtained from supercritical toluene extraction at 350°C and 1500 psig of subbituminous coal.

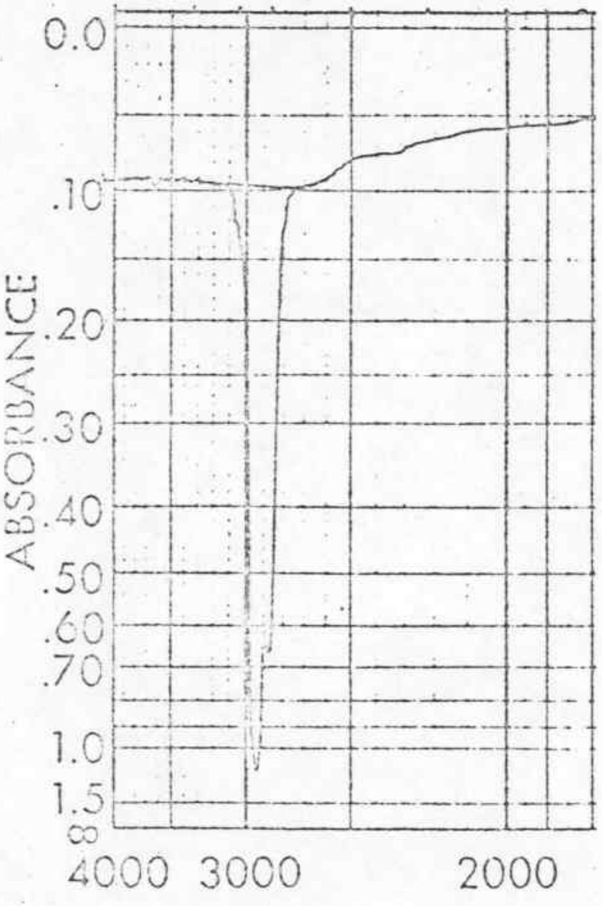


Figure 11

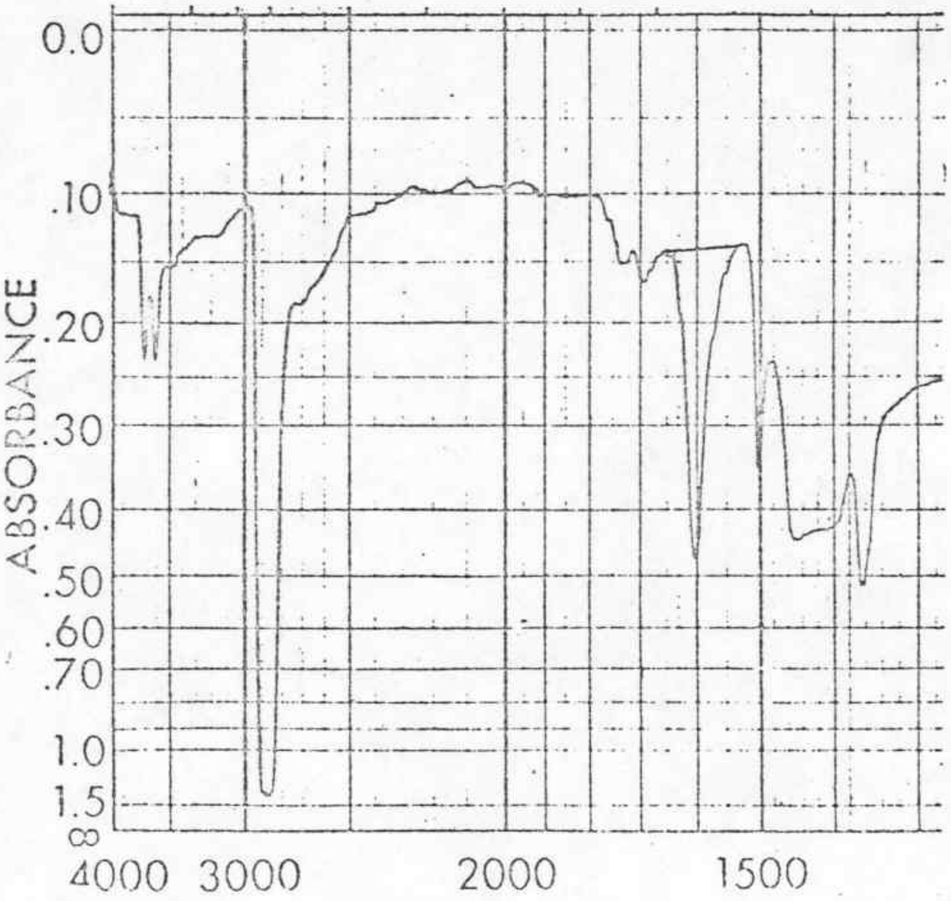
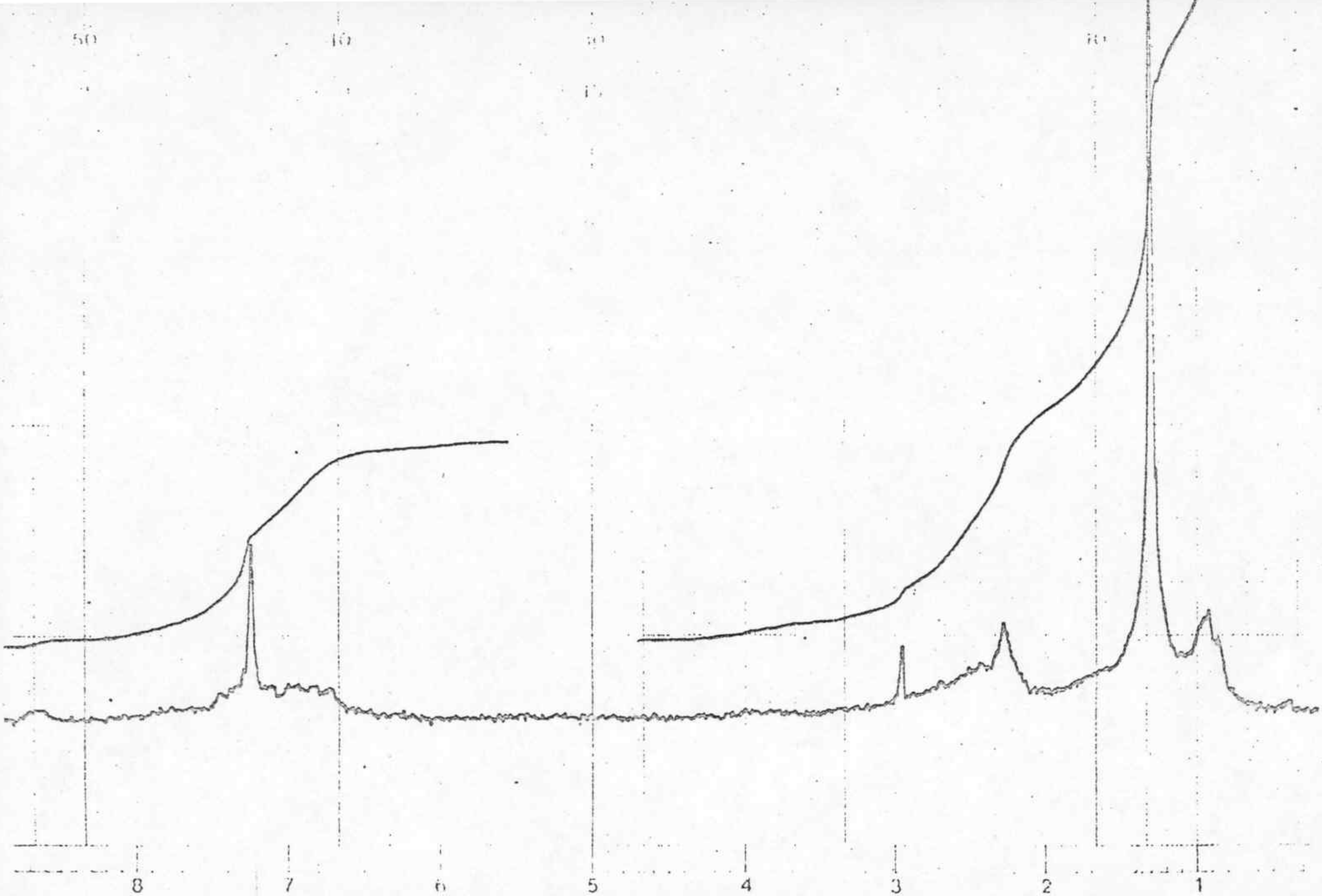


Figure 12

Infrared spectra in carbon tetrachloride (Fig. 11) and methylene chloride (Fig. 12) of oil obtained from supercritical propane extraction at 110°C and 1900 psig of Athabasca oil sands.



ure 13: 60 MHz nmr of pentane soluble fraction of cd1 obtained from supercritical toluene extraction at 400°C and 1500 psig of subbituminous coal.

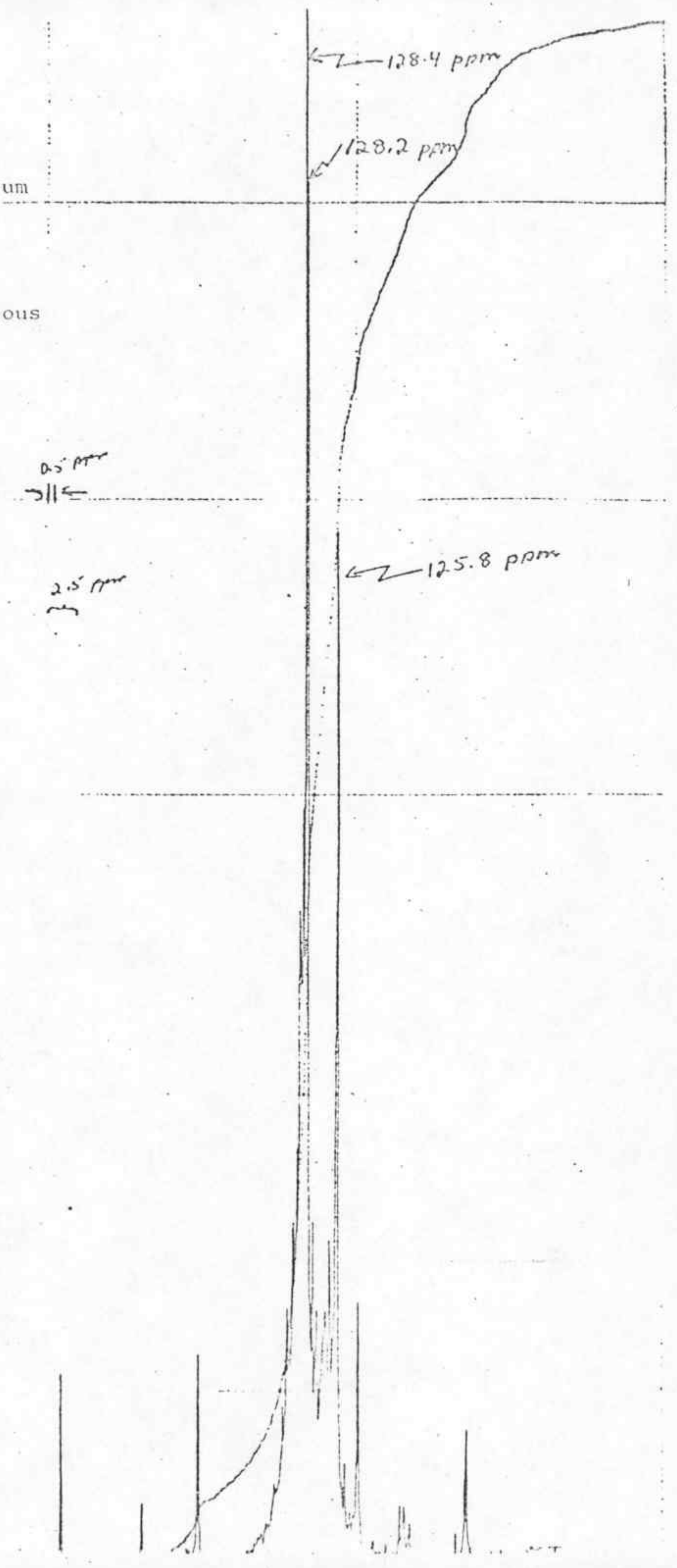
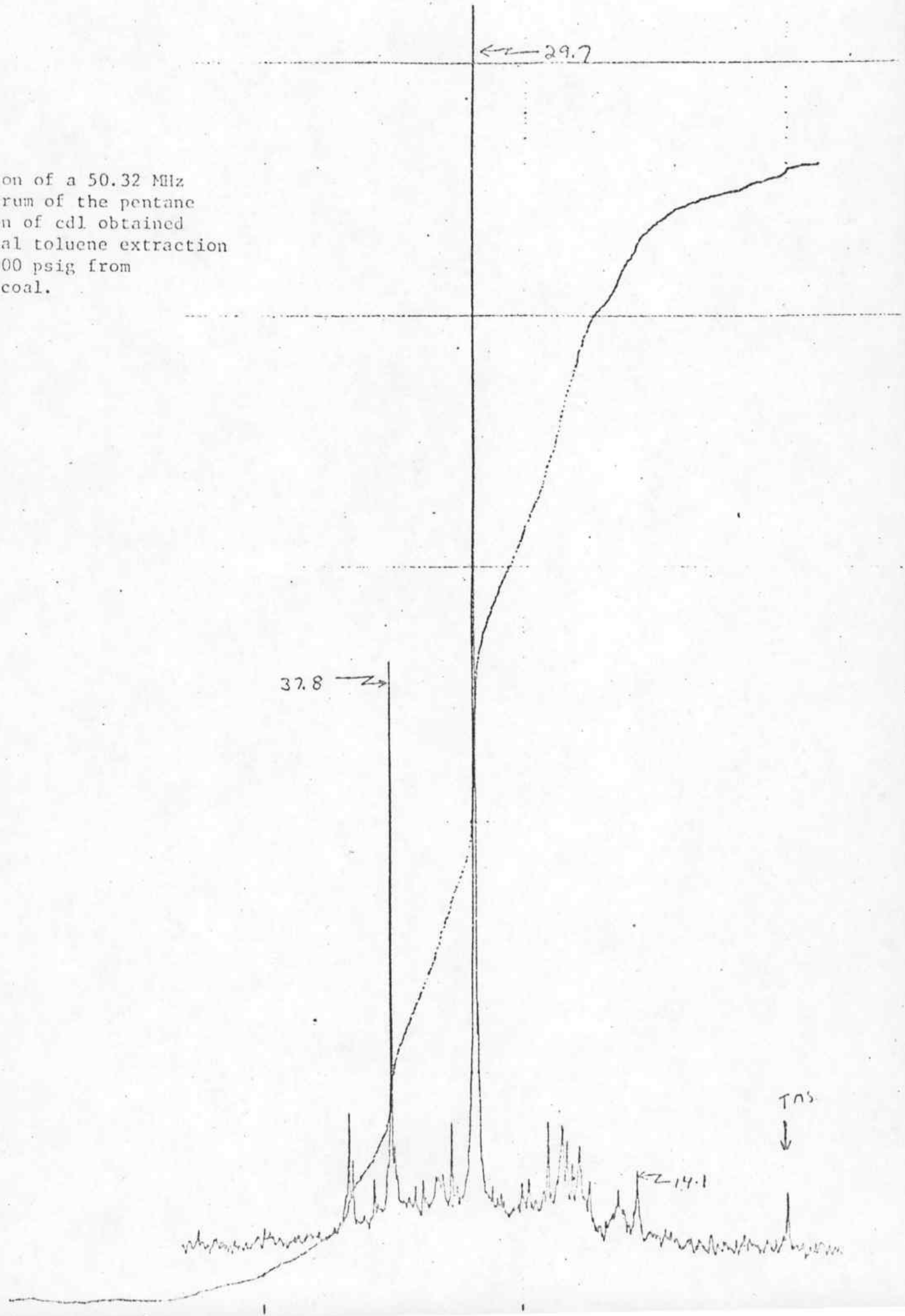


Figure 14: Aromatic region of a 50.32 MHz C-13 nmr spectrum of the pentane soluble fraction of cdl obtained by supercritical toluene extraction at 450° and 1500 psig from subbituminous coal.

igure 15:

liphatic region of a 50.32 MHz
-13 nmr spectrum of the pentane
oluble portion of cdl obtained
y supercritical toluene extraction
t 450° and 1500 psig from
ubbituminous coal.



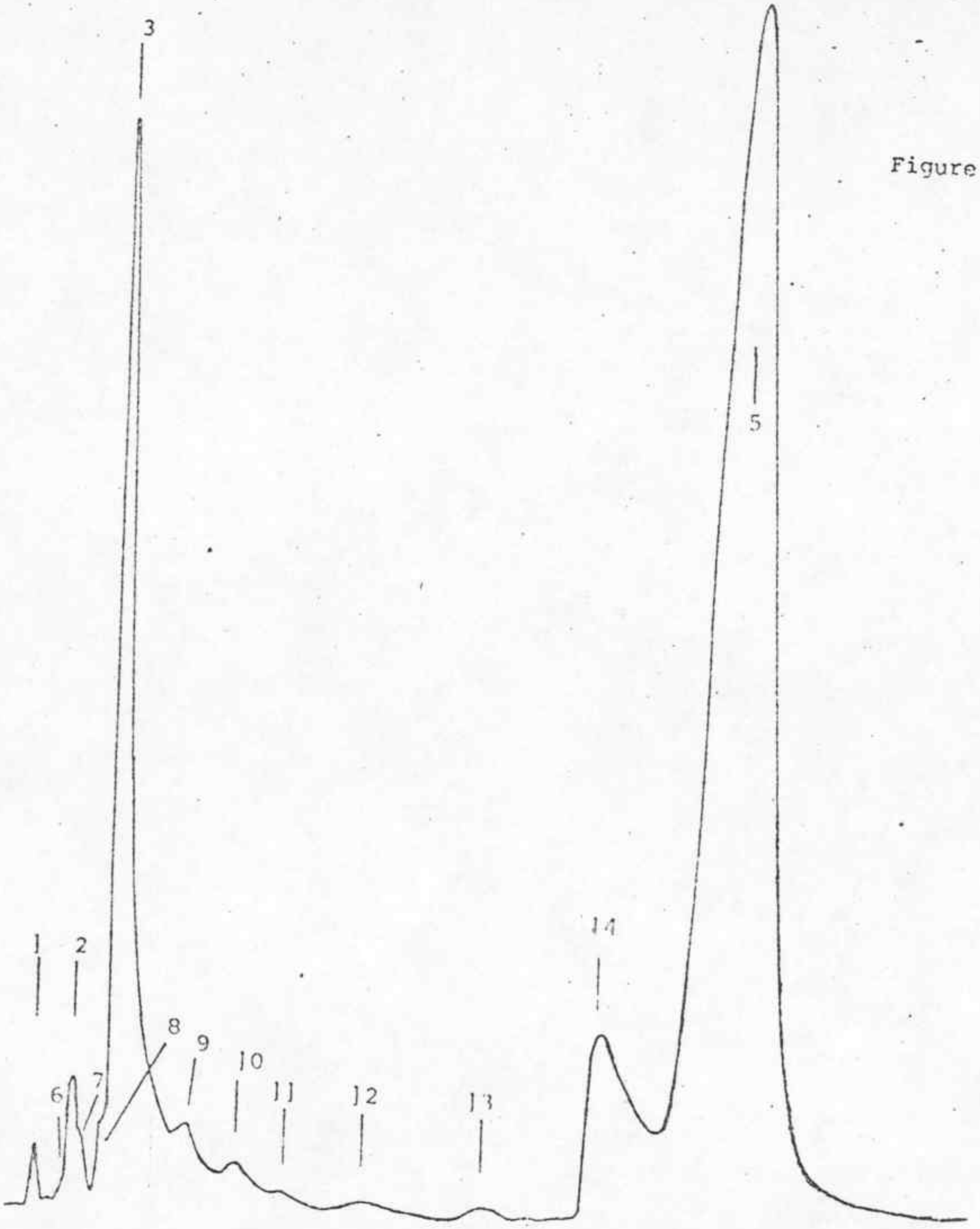


Figure 16: Gas chromatographic trace of the contents of the cold finger after supercritical toluene extraction of subbituminous coal at 330°C and 1500 psig.

Peak #1 - air; 2 - unknown 1.5%, 3 - methyl sulfide 19.8%; 4 - unknown - 12.3%; 5 - toluene 66.4%; 6 through 13 - unknowns.

APPENDIX I

Molar volumes of non-ideal gases may be calculated from

$$V = \frac{ZRT}{P}$$

Z = Compressibility factor
V = Molar volume

Z may be determined from standard plots like those appearing in "Chemical Engineers Handbook", R.H. Perry and C.H. Chilton, McGraw-Hill Company, 5th Ed., p.3-232, and from the following parameters.

P = actual pressure
T = actual tempeature
Pc = critical pressure (41.6 atm for toluene)
Tc = critical tempeature (320.6°C 593.6°K for toluene)
Pr = reduced pressure = P/Pc
Tr = reduced temperature = T/Tc

At 1500 psig and 400°C

Pr = 103/41.6 = 2.48
Tr = 673/594 = 1.13
Z = 0.48 (above source).

$$V = \frac{0.48 \times 82.05 \times 673}{103} = 257 \text{ cm}^3\text{/mole}$$

A flow rate of 36 g/min = 36/92 x 257 = 101 cm^3/min.

Likewise a flow rate of 23.6 g/min = 66 cm^3/min.

These calculations generally give values accurate within 3 to 5%.

Space Time = time taken for one bed volume of fluid to pass through the system. Conventionally the volume of the bed occupied by the solids is neglected.

Residence Time = Average time during which individual portions of the feed are in the reaction zone.

Space Velocity = Inverse of the space time generally expressed in hr^{-1}, that is the number of times the bed volume is changed per hour.

To calculate space velocity

$S = \frac{v^0}{V}$ where v^0 = fluid flow rate (ml/min)

V = volume of bed (ml)

36 g toluene/min = 101 ml/min at 400°C and 1500 psig.

400 g coal occupies 550 ml

$$S = \frac{101}{550} = 0.184\ \text{min}^{-1} = 11.0\ \text{hr}^{-1}$$

Corresponding space time . $\theta = 1/S = 1/0.184 = 5.43$ min

The corresponding values of 23.6 gm/min are

$$S = \frac{66}{550} \quad 0.120\ \text{min}^{-1} = 7.20\ \text{hr}^{-1}$$

$$\theta = \frac{1}{0.120} = 8.33\ \text{min.}$$

APPENDIX II

Sample Calculation for Determination of Pyridine Soluble Products

Extraction conditions: Toluene, 350°C, 1500 psig, 400 g coal.

Ash content of coal = 0.047 x 400 = 18.8 g (proximate analysis)

Products: 29.8 g cdl = 11.0% (daf basis)

257 g char which contains 18.8 g ash but no moisture.

0.5250 g char contained 0.0060 g pyridine soluble material.

$$PS = 11.0 + \frac{100 - 11.0}{100} \times \frac{0.0060 \times 100}{0.5250 - 0.5250 \times 18.8/257}$$

$$= 11.0 + 0.89 \times 1.23 = 12.1\%$$

Char contains 1.23% pyridine soluble material on a daf basis.