STUDIES ON NON-CATALYTIC LIQUEFACTION OF WESTERN CANADIAN COALS

by

B. Ignasiak, D. Carson, A. J. Szladow* and N. Berkowitz
Alberta Research Council, Edmonton, Alberta, Canada

Though still only very incompletely explored, and subject to major revisions, Canada's coal resources are so extensive as to place this country among the half-dozen most richly coal-endowed nations (1-3). Recent appraisals (Table 1) set ultimate in-place resources in >2 1/2ft thick seams under less than 2500 ft of cover at some 518 billion tons; and preliminary estimates from deeper testhole logs suggest that similar, if not even larger, tonnages may lie in coal occurrences at depths between 2500 and 4500 feet.

But there are wide regional disparities with respect to distribution and coal type.

Except for a relatively small (<500 million ton) lignite deposit in northern Ontario's James Bay area, the Central region (i.e., Quebec, Ontario and Manitoba) which accommodates some 70% of the country's population and the greater part of its industry, is devoid of coal; and the Maritime Provinces (principally Nova Scotia) contain less than 2% of Canada's total coal - mostly Carboniferous hvb coal which closely resembles its Eastern US counterparts.

The great bulk of Canadian coal is concentrated in the three Western provinces (Saskatchewan, Alberta and British Columbia). In this region, it is of Cretaceous and/or Tertiary age, with rank generally increasing in a westerly direction toward the Rocky Mountains. Although contained in different geological formations (which, in Alberta, form three partially overlapping coal zones), the lignites of Saskatchewan thus give way to subbituminous coals in the Alberta Plains, and the latter successively to hvb, mvb and lvb coals in the Mountain regions further west.

Table 1 summarizes latest available data respecting reserves of these classes of coal.

As matters stand, the low-rank coals of Western Canada (as well as some hvb coal in the Maritimes) are now being increasingly used for

*Presently at Pennsylvania State University.

generation of electric energy, and metallurgical (mvb and lvb) coals are being primarily produced for export (notably Japan, though other markets are being developed in Korea, South America and Western Europe). But the large reserves of near-surface subbituminous coals and lignites are also being looked upon as future sources of synthetic fuel gases and liquid hydrocarbons, and could therefore augment production of synthetic crude oils from, e.g., Northern Alberta's oil sands (4).

A notable feature of the Western Canadian coals is their low sulphur content (usually, <0.5%) which tends, however, to be partly offset by higher mineral matter contents than are associated with the Eastern coals. As well, the bituminous coals in the mountain belts are typically deficient in vitrinite, which often represents less than 50% of the coal "substance" and only occasionally reaches 70-75%, but this is compensated by the fact that micrinites and semifusinites tend to be "reactive" constitutents when the coals are carbonized. Notwithstanding their low fluidity (rarely >1000 dd/min), Western mvb coals therefore make excellent metallurgical cokes when carbonized in suitably proportioned blends.

But, perhaps reflecting their unique petrographic make-up as much as a more basic chemistry which may set them apart from their Carboniferous equivalents, the Western coals also tend to respond differently to, e.g., oxidation and the action of solvents on them. Air-oxidation at 150°C, instead of developing acid oxygen functions, incorporates much of the chemisorbed oxygen in carbonyl groups, and solubility in $CHCl_3$ (after shock-heating to ~400°C) is substantially smaller than the FSI would lead one to expect from correlations for Carboniferous coals (5).

These, and other, behaviour differences have prompted initiation of several exploratory studies in order to elucidate the response of selected Western coals to liquefaction procedures, and the parameters that affect this response. This paper summarizes some of the more important observations recorded in the course of that work.

1. Liquefaction (Solubilization) by Interaction with H-Donors

To test initial solubilization, ~5 gm samples were reacted with 10-15 gm of tetralin at 390±2°C and autogenic pressures in helium-purged, sealed heavy-duty Pyrex capsules which were inserted into a stainless steel bomb charged with ~30 ml tetralin in order to counterbalance the pressures generated in the capsules. Reactions were carried to completion over 4 hrs, after which the capsules were cooled to room temperature and opened in a manner that permitted quantitative analysis of all reaction products (including gaseous products).

In one series of experiments, residual tetralin was removed by heating the solvolyzed samples at 70-80°C in vacuo (~0.05 mm Hg) to constant weight, and yields of non-volatile products and their solubilities in pyridine and in benzene were determined.

The solubilities thus recorded for 13 Western (Cretaceous) coals (with 69.6-91.5% carbon, daf) and 8 Carboniferous coals (80.6-90.9% C, daf) are shown in Figure 1, and indicate that

(a) the pyridine-solubilities of reacted Carboniferous subbituminous and bituminous coals are significantly higher than those of corresponding Cretaceous coals, and

(b) strongly caking Carboniferous coals (with 86-88% C, daf) tend to generate substantially more benzene-soluble matter under the reaction conditions of these experiments.

What is, however, still unclear is whether these effects arise solely from different chemical compositions (and molecular configurations) or are also, at least in part, a consequence of the Cretaceous coals generally containing almost twice as much mineral matter as the Carboniferous samples.

2. The Role of Ether-Linkages in Solubilization of Low-Rank Carboniferous Coals by H-Donors

There is some consensus that formation of asphaltenes in the early stages of solubilization of low-rank bituminous coals results from cleavage of open ether-bridges (6). But while the presence of such configurations in high- and medium-rank bituminous coals is well established (7), their existence in less mature coals remains to be unequivocally demonstrated. From reactions of low-rank bituminous coals with sodium in liquid ammonia or potassium in tetrahydrofuran, it has, in fact, been concluded that open ether-bonds are absent (8) or only present in negligible concentrations (9).

The failure to detect open ether-linkages through treatment with Na/liq. NH_3 could, of course, be due to formation of non-cleavable phenoxides (10). We note, in this connection, that low-rank coals, which contain much "unreactive" oxygen, are also characterized by relatively high concentrations of hydroxyl groups, and some "unreactive" oxygen could therefore be quite reasonably associated with phenoxy phenol configurations. However, whereas phenoxy phenols would be expected to resist cleavage by hydrogen-donors, low-rank coals are, as a rule, most easily solubilized by them; and in view of this seeming inconsistency, we thought it pertinent to reexamine the behaviour of oxygen-linkages during interaction with H-donors.

The reactions were carried out under the same conditions as solubilization (see sec. 1), except that a constant 2:1 donor:substrate (molar) ratio was used; and in some tests, 1,2,3,4-tetrahydroquinoline was employed instead of tetralin. The results obtained with different ethers are summarized in Table 2.

Detailed discussion of these findings will be presented elsewhere, and here we only wish to point out that responses to a hydrogen donor

tend to be quite critically affected by very minor structural differences (as well as by possible copolymerization of donor and substrate). Thus, while diphenyl ether remains substantially unaffected by exposure to a donor, its hydroxy-derivatives (phenoxy phenols) often display fairly high reactivity. Taken in conjunction with the failure of low-rank coals (7) and phenoxy phenols (10) to suffer reductive cleavage when treated with sodium in liquid ammonia, this lends some support for the existence of phenoxy phenol entities on these coals.

Other observations, however, indicate that this notion will require more direct evidence before it can be accepted.

The inertness of phenols and phenoxy phenols toward Na/liq. NH_3 can be attributed to the fact that phenols are powerful proton-donors in this system; and resistance of the resultant anions toward reduction is believed to result from stabilization by resonance (10). While alkylation of low-rank coals before treatment with Na/liq. NH_3 therefore offers means for establishing the presence of phenoxy phenol ethers in them, an alternative is afforded by the observation that some phenols can be reduced by concentrated solutions of lithium (11): if this latter reaction also reduces phenoxy phenols in coal, a second treatment should then cause ether-cleavage.

We found, however, that even highly concentrated lithium (9M) or sodium (3M) solutions did not reduce coal so that subsequent treatment increased its hydroxyl content; and in parallel tests, 100% unreacted p-phenoxy phenol was always recovered from the lithium solutions.

The failure to cleave p-phenoxy phenol by reduction and subsequent scission of the ether-bond prompted us to examine the possibility of splitting the C-O bond in the alkylated molecule (12). Attempts to alkylate p-phenoxy phenol with C_2H_5Br after treatment with lithium in liquid ammonia proved uniformly abortive; but ethylation in Na/liq. NH_3 yielded nearly 50% of the ethylated product, and ethylation in K/liq. NH_3 led to quantitative conversion - with ~40% of the reaction product recovered as p-diethoxybenzene. Protonation instead of ethylation furnished ~45% of p-dihydroxybenzene. In the light of these results, we believe that the ether-bond in phenoxy phenols can be cleaved without prior alkylation, and consider it significant that treatment of low-rank coal (or of a vitrinite fraction from such coal) with variously concentrated solutions of potassium in liquid ammonia did <u>not</u> cause an increased -OH content in the reacted material. Nor was the hydroxyl content affected by such treatment after prior exhaustive methylation of the coal with dimethyl sulphate and K_2CO_3 in acetone (13).

It appears to us therefore that cleavage of ether-bonds contributes little to solubilization (and consequent reductions of the molecular weight) unless the coal contains an appreciable proportion of open oxygen linkages in the form of dialkyl ethers. And since there are indications that such structures are generally absent (14) one might tentatively conclude that molecular weight reductions during solubilization by H-donors

accrue primarily from C-C bond scission or from structural realignments associated with elimination of oxygen. It should be possible to tests this by measuring molecular weight distributions in H-donor liquefied and non-destructively solubilized coal products (see sec. 3).

3. Non-Destructive Solubilization of Low-Rank Bituminous Coal

Present methods for solubilizing coal (including reductive alkylation in tetrahydrofuran (15) or liquid ammonia (8)) entail cleavage of oxygen ethers, scission of C-C bonds in certain polyaryl-substituted ethylenes and, in the case of reactions in tetrahydrofuran, extensive elimination of hetero-atoms (16).

We therefore draw attention to a novel technique which allows solubilization of coal without rupture of covalent bonds. This method utilizes the fact that the acidity of low-rank coals, which is thought to be largely due to their high -OH contents, can be enhanced by proper choice of a medium.

We selected liquid ammonia because of its pronounced solubilizing characteristics and powerful ionizing properties. At -33°C and atmospheric pressure, the pK_a-value for auto-ionization of liquid ammonia [$2NH_3 \rightleftharpoons NH_2^{\ominus} + NH_4^{\oplus}$] is 34; and since the equivalent value for water is only 14, many substances (with pK_a-values between 14 and 34) which are neutral in water should be capable of splitting off protons in liquid ammonia. Acidic properties in liquid ammonia can be further enhanced by increasing the concentration of $NH_2^{\ominus}$ at the expense of protonic $NH_4^{\oplus}$; and this can be achieved by adding potassium and/or sodium amides which will then also form the respective coal "salts".

To test this approach, ~5 g samples of low-rank vitrinite, each -300 mesh (Tyloer) were stirred for 6 hrs in liquid ammonia (150 ml; -33°C) containing ~5 gms of potassium amide and ~5 g of sodium amide. (The amides were formed in the medium, before introducing the coal, by action of anhydrous ferric oxide (1 g) or ferric chloride (1.5 g) on alkali metals.) Thereafter, 100 ml of anhydrous ethyl ether was added, the suspended coal material ethylated with C_2H_5Br (32 ml), and the reaction mixture stirred until all ammonia and ether had evaporated. Following acidification of the residue with 10% HCl, the product was thoroughly washed with distilled water, dried at 70-80°C in vacuo (0.05 mm Hg) and analysed. Table 3 summarizes the results of three consecutive alkylations, with each datum being the average of four independent test runs. The initial ethylation introduced 7-8 ethyl groups/100 C atoms into the coal, and the results of the second and third ethylations indicate that essentially only -OH groups were ethylated at this stage. Overall, however, over 50% of ethyl groups introduced into coal were <u>not</u> linked to hydroxyl functions. Since in higher-rank vitrinites no atoms other than hydroxyl-oxygens are susceptible to ethylation by this procedure, it is tentatively concluded that acidic carbon atoms exist only in low-rank coals.

The most interesting outcome of this work is the observation that low-rank vitrinites can be rendered substantially soluble in chloroform and pyridine by alkylating coal salts formed in a non-reducing medium and under conditions that effectively preclude cleavage of covalent bonds.

The solubility of coal treated as above can be further enhanced by introducing longer alkyl chains. While, on reductive alkylation, this could lead to dimerization and formation of other by-products, non-reductive alkylation is not accompanied by such side-effects. Moreover, because of a significant reduction in the number of acidic sites, acid-base associations are also essentially excluded, and the alkylated product should, therefore, be amenable to GPC fractionation. Such fractionation, conducted on Bio Beads S-X1 and S-X2, results in separation by molecular weight and indicates that both benzene and chloroform extracts contain substantial amounts of high (~6000) and fairly low (560-640) molecular weight fractions (Figure 2). While the extract yields from non-reductively ethylated vitrinite increase in the order benzene extr. → chloroform extr. → pyrid. extr., the molecular weights, determined by VPO in pyridine, decrease in this order.

Figure 3 shows GPC fractionation of the benzene extract of a vitrinite which, before a single non-reductive ethylation, was treated with tetrahydronaphthalene at 390°C. Although solvolysis reduced the -OH contents (from 4.9 to 1.7%), non-reductive alkylation increased the benzene-solubility of the solvolyzed material from 53% to 80.2%. It appears that this effect is due to ethylation of acidic carbon atoms.

The existence of a substantial number of acidic carbons in a product obtained by thermal treatment of a vitrinite in a reducing medium at 390°C, but absence of such carbons in higher-rank coals raises an interesting question about the role of temperature in coalification.

Analysis of the results presented in Figures 2 and 4 appears to indicate that solvolysis of the vitrinite is also accompanied by polymerization (see pyridine extract, Figure 4). If this can be confirmed, it would be worth investigating whether it involves specific fractions in the original vitrinite or has a random character. Solvolysis of different molecular weight fractions of a non-reductively alkylated vitrinite (or coal) may furnish some insight.

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Table 1. Ultimate in-place coal resources in Canada (Energy, Mines & Resources, Canada, Report EP 77-5, 1976 Assessment

Region	In-place, billion tons	Principal coal type
Maritime Provinces		
Nova Scotia		
New Brunswick	1.7	hvb (Carb.)
Western Region		
Saskatchewan	38.8	lignite (Tert.)
Alberta* - Plains	360.0	subbit. (U.Cret. & Tert.)
Foothills	10.0	lvb, mvb, hvb (Cret.)
Mountains	30.0	lvb, mvb, hvb (Cret.)
British Columbia	77.8	mvb, lvb (Cret.) subbit. (Tert.)
Canada Total	518.3	

*After Energy Resources Conservation Board, Report 77-31, December 1976

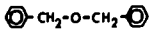
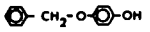
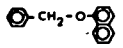
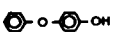
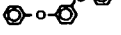
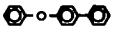
Table 3. Non-reductive ethylation of Carboniferous vitrinite* in liquid ammonia

	Ethyl groups intr. per 100 mg Cat.	Chloroform Solubility	Pyrioline Solubility	Ult. analysis (daf) %C	%H	%N	No of hydroxyl groups per 100 mg Cat.
I Ethylation	7-8	25	45-50	81.0	6.3	1.6	2.8
II Ethylation	8-9	45-50	55-60	81.3	6.8	1.8	2.0
III Ethylation	9-10	55-60	60-65	81.1	7.0	1.5	1.1

*Solubilities of untreated vitrinite: $CHCl_3$ - 1%; C_5NH_5 - 13%;

Elemental analysis of untreated vitrinite (daf): 80.8%C; 5.2% H; 1.5%N; 0.9% S; 5.0% O_{OH}

Table 2 Reactions of ethers with tetrahydronaphthalene and tetrahydroquinoline at 385°C

Ether	Structure	1,2,3,4 Tetrahydronaphthalene					1,2,3,4 Tetrahydroquinoline				
		% of Ether Conversion	Hydrogen Consumption Moles/Mole	Recovery of Tetrahydronapthalene + Naphth. [%]	Reaction Products Identification	Reaction Products Yield [Molar %]	% of Ether Conversion	Hydrogen Consumption Moles/Mole	Recovery of Tetrahydroquinoline + Quinoline [%]	Reaction Products Identification	Reaction Products Yield [Molar %]
dibenzyl ether		100	0.05	~100	toluene benzene benzaldehyde 1 methylindane	50 29 16 undetermined	100	~1	85	toluene water 3 methylpyridine(1) ethylbenzene(1) high mol.w.product(3)	51 10 undetermined undetermined undetermined
p(benzyloxy)phenol		-	0.8	~100	toluene	70	-	-	40	toluene high mol.w.product(3)	72 undetermined
benzyl 1-naphthyl ether		-	0.75	~100	toluene bibenzyl 1-naphthol 2-benzylnaphthalene 1-methylindane(1) 3 unidentified	73 7 74 undetermined undetermined -					
diphenyl ether		2	0.0	~100	no GC detectable prodts.	-	0	0.0	~100	no GC detectable prodts.	-
p-phenoxyphenol		7	0.04	88	phenol	7	50	-	62	phenol o-toluidine(1) high mol.w.product(4)	43 undetermined 90(2)
m-phenoxyphenol		0	0.0	~100	none	-	24	-	73	high mol.w.product(5)	90(2)
m-diphenoxybenzene		0	0.0	100	none	-	0	0.0	100	none	-
p-phenoxybiphenyl		0	0.0	100	none	-	0	0.0	100	none	-
furan		0	0.0	100	none	-	0	0.0	100	none	-
2,3-benzofuran		0	0.0	100	none	-	0	0.0	100	none	-
dibenzofuran		0	0.0	~100	1 unidentified	trace	0	0.0	~100	2 unidentified	traces
tetrahydrofuran		0	0.0	~100	1 unidentified	trace	0	0.0	100	none	-

1. probably originating from donor
2. % by weight
3. elemental analysis of the high molecular weight product unknown
4. elemental analysis: 82.3%C; 7.0%H; 4.2%N; 0.0%S; 0.0% ash; 6.5%O (by diff.)
5. elemental analysis: 79.0%C; 6.2%H; 1.8%N; 0.0%S; 0.0%ash; 13.0%O (by diff.)

Figure 1. Solubilities after treatment with tetrahydronaphthalene at 390°C for 4 hours

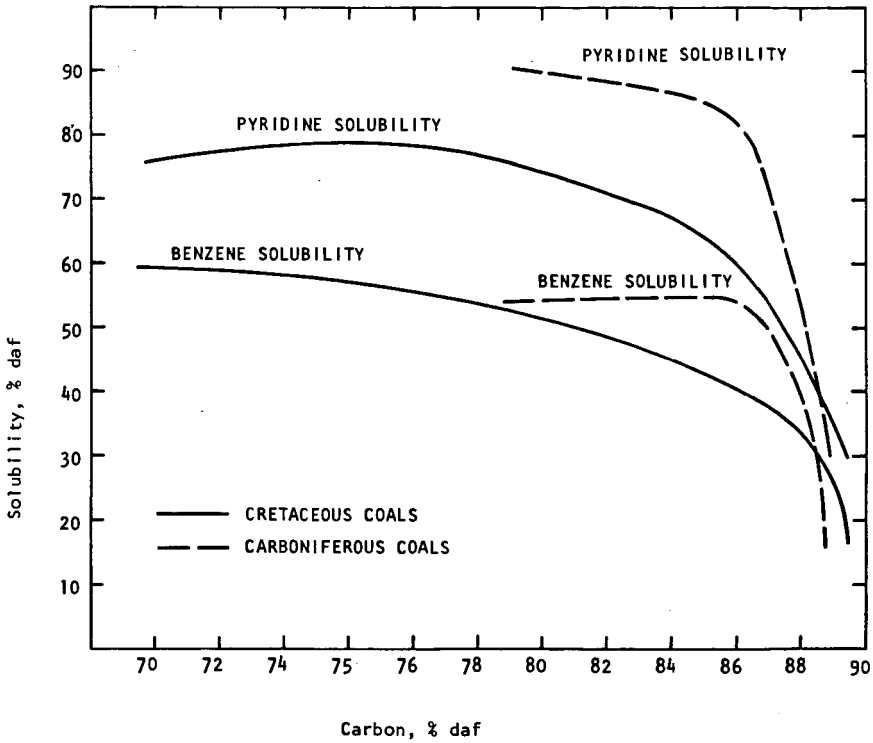
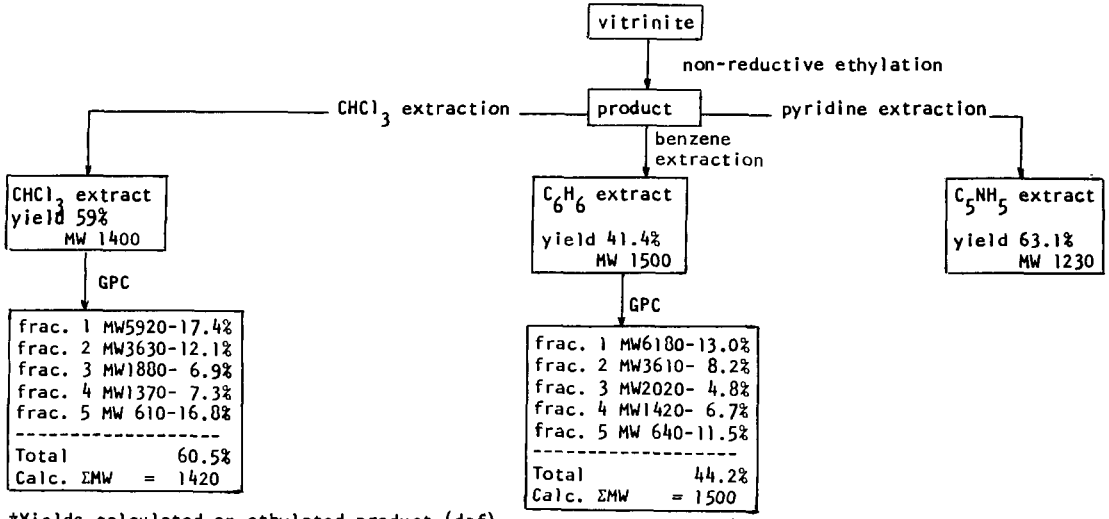
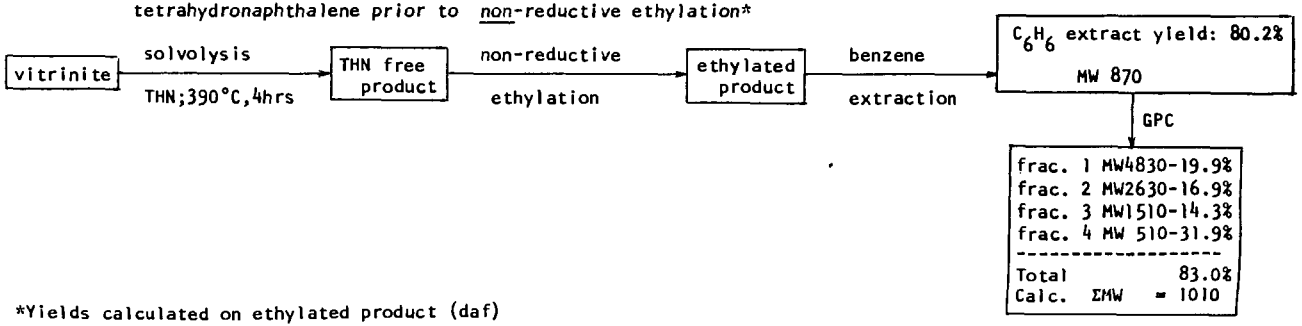


Figure 2. Solubilities and molecular weights of a vitrinite (80.8% C, daf) after non-reductive ethylation*



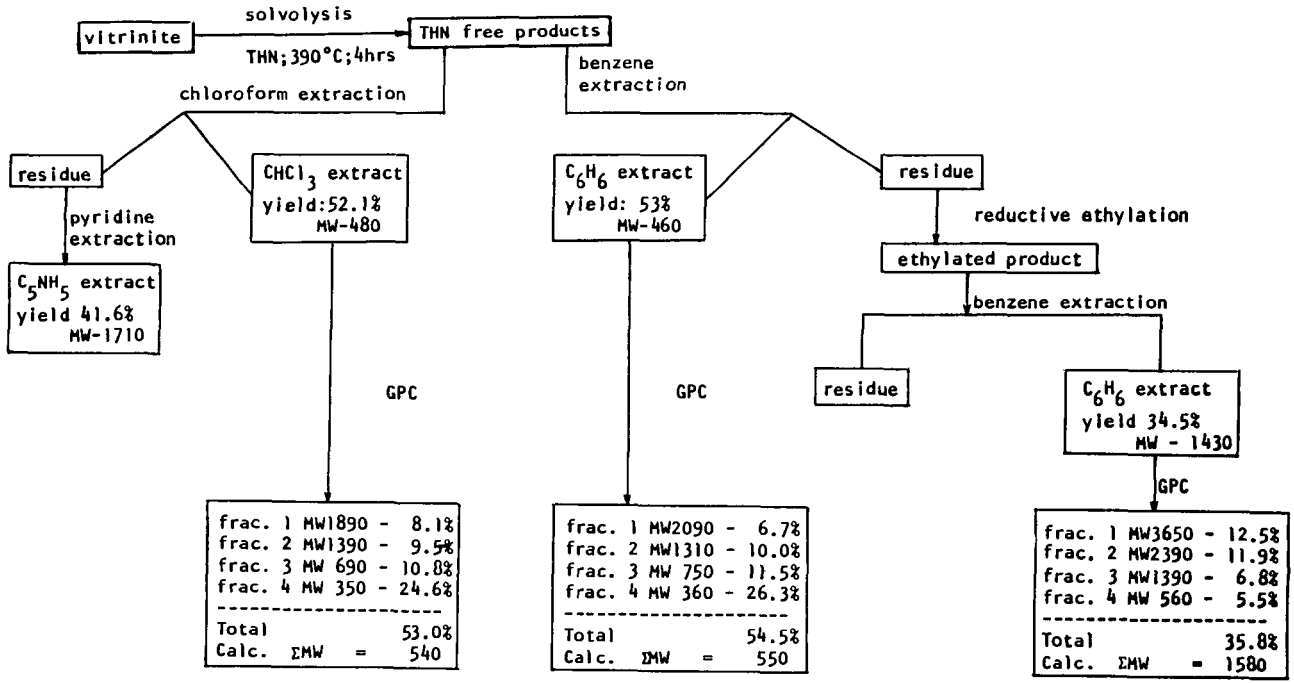
*Yields calculated on ethylated product (daf)

Figure 3. Solubilities and molecular weights of a vitrinite (80.8% C, daf) subjected to solvolysis in tetrahydronaphthalene prior to non-reductive ethylation*



*Yields calculated on ethylated product (daf)

Figure 4. Solubilities and molecular weights of a vitrinite, subjected to solvolysis in tetrahydronaphthalene*



* Yields calculated on THN free product (daf)