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## FUNDAMENTALS OF COAL PYROLYSIS AND LIQUEFACTION

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**ABSTRACT.** This chapter describes what is known of the dependence of the pyrolysis and liquefaction of solid fuels on the chemical structure of their constituent maceral groups, on the design of the reactors and on the parameter defining their operation. The role of catalysts is not considered.

### 1. Introduction

In the progression from the mining of coal to processing a clean synthetic fuel, this chapter considers the basic chemistry and chemical engineering of pyrolysis and liquefaction. In particular, it will be shown how starting from the chemical structure of coal, the yields of liquid products are determined by the parameters regulating pyrolysis and liquefaction and how this regulation arises naturally from the mechanism of the process. It will also be shown how reactor design influences both the yields and characteristics of the liquid products, emphasis being given to the distinction between primary and retrogressive reactions. In this chapter, the effects of solid catalysts -save as they are inherent in coal- will not be considered either as they influence the primary conversion or as they are used to refine the technological properties of the liquid products. Much of the material discussed will be taken from the author's own research and some familiarity with the subject will be assumed. It is hoped that the understanding generated by the chapter will lead to better and even novel syntheses of clean fuels. The need for such processes is urgent. The motivation for using solid fuels, despite the environmental and health hazards pointed out in other chapters, is the human desire for increased comfort. Tables 1 and 2 show the annual consumption of energy and electricity per head of population. It is the difference in these figures between different parts of the world which distinguishes developed from developing societies.

TABLE 1. Energy consumption per head of population in 1981 (tons of coal equivalent)

USA	UK	USSR	CHINA	INDIA
10.2	4.6	5.7	0.6	0.2

TABLE 2. Electricity consumption per head of population in 1984 (kw hrs.)

ASIA	EUROPE	N.AMERICA	S.AMERICA	AFRICA
550	14800	7341	1186	393

(Russia is not included in this table. The statistics are from United Nations Year Books.)



It is clear that India, Africa and especially China, with its large reserves of coal, will wish to increase their energy consumption ten-fold. Given the size of their populations, the global environmental consequences could be grotesque. One is faced either with having to persuade developing societies to forego the use of solid fuels or with transferring the best engineering design of which we are capable.

## 2. The Starting Material

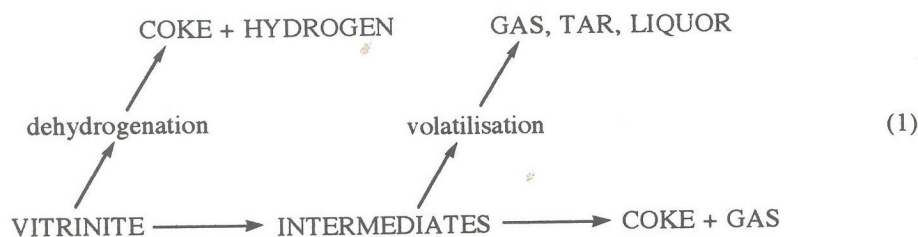
In this chapter coal will be considered as consisting of three groups of organic mineral (maceral):

- Vitrinite, composed of aromatic, often phenolic, nuclei associated through hydroaromatic linkages (1).
- Liptinites, formerly termed exinites, composed of aliphatic chains substituted by alkyl hydroxy aromatics (1).
- Inertinites which, in the absence of detailed knowledge, may be considered to have similar structures to high rank vitrinites.

Chemical structures of fragments of solubilised material are listed in reference (2). It will sometimes be useful to regard coals and their constituent maceral groups as organic matrices containing extractable material. Further details of coal structure will be introduced as they are needed.

## 3. Pyrolysis and Hydropyrolysis at Slow Rates of Heating

The archetypal apparatus for the study of coal pyrolysis at low rates of heating, prompted by the need to understand the formation of metallurgical coke, was the Gray-King furnace (3). Experiments in such apparatus established that coal pyrolysis starts at about 350°C and that whilst the total yield of volatile material always increases with temperature, prolonged heating at 600°C is sufficient to give the maximum yield of tar. The pyrolysis of vitrinites and of vitrinite rich material in the Gray-King furnace may be represented by the following sequence of consecutive and parallel reactions (4):



Hydroaromatic structures dehydrogenate to give an extended aromatic network which becomes transformed into coke or char. This is not only consistent with the pyrolysis of such model compounds as tetralin (5) and of partially deuterated coals (6), it has been observed in lignites by infra-red spectroscopy (7). The hydrogen released by the dehydrogenation diffuses through the pyrolysing solid and causes rupture of aliphatic bonds. This reaction, which may be represented by



requires little activation energy and to form gas, the formation of water and linkages between aromatic nuclei complete that significant quantities (In another chapter, Schobert describes knowledge, perhaps equally valuable, hydroaromatic material and bond transferred by radicals. The consequences be essentially the same as those of radicals formed by reaction 2 have yield extended structures which even presence of mobile intermediate confers fluidity (9), relatively small making large changes to the fluid static bed, reaction 1 is sufficient and also the loss of weight complex schemes, reviewed by developed to model the formation. Mass transfer processes play a prominent of volatiles obtained during pyrolysis development of fluidity plays a especially in controlling the transition zone. Table 3 shows results from caking and gave little fluidity in atmospheres.

When pyrolysis produced little pore structure and led to an increased generated fluidity which slowed mass

TABLE 3. Microporosities and surface

Sample	Initial H/coal ratio, KPa/g	Final M
Coal	—	—
Nitrogen coke	—	—
Nitrogen coke	—	—
Hydrogen coke	20	—
Hydrogen coke	80	—
Hydrogen coke	140	—
Hydrogen coke	190	—
Hydrogen coke	140	—
Hydrogen coke	140	—
Hydrogen coke	140	—
Hydrogen coke	140	—

The original coal containing 83.3% C at 500°C for two hours.

Of course, pyrolysis in hydrolysis yields of gas appear to be generated at pressures but maximum yields of gas but not excessive pressure since coal ratio generates gas from the

The tars obtained from slow pyrolysis furnace are complex mixtures



requires little activation energy and results in the elimination of alkyl groups to form gas, the formation of water from hydroxyl groups and the scission of aliphatic linkages between aromatic nuclei and it is not until such reactions are nearly complete that significant quantities of hydrogen gas are evolved from the pyrolysis. (In another chapter, Schobert describes a different - but with our present experimental knowledge, perhaps equally valid - mechanism in which dehydrogenation of hydroaromatic material and bond scission occur simultaneously, the hydrogen being transferred by radicals. The consequences of such a radical hydrogen transfer would be essentially the same as those of the description of pyrolysis given here). The free radicals formed by reaction 2 have been observed (8). Some radicals recombine to yield extended structures which eventually form coke or char together with gas. The presence of mobile intermediate material (metaplast) of moderate molecular mass confers fluidity (9), relatively small changes in the concentration of intermediates making large changes to the fluidity (10). If vitrinites are pyrolysed slowly in a static bed, reaction 1 is sufficient to model both the rate of development of fluidity and also the loss of weight measured by thermogravimetric analysis (9). More complex schemes, reviewed by Gavalas, Howard and Solomon (12) have been developed to model the formation of individual compounds during the pyrolysis. Mass transfer processes play a prominent role in determining the amount and composition of volatiles obtained during pyrolysis of coals, particularly of softening coals (11). The development of fluidity plays a key role in the regulation of mass transfer (12), especially in controlling the transfer of hydrogen into, within and out of the reaction zone. Table 3 shows results from the pyrolysis of a coal which was but weakly caking and gave little fluidity in nitrogen but which gave much fluidity in hydrogen atmospheres.

When pyrolysis produced little fluidity (in nitrogen) volatilisation unlocked the pore structure and led to an increase in char microporosity. Pyrolysis in hydrogen generated fluidity which slowed mass transfer and led to a decrease in coke microporosity.

TABLE 3. Microporosities and surface areas of cokes formed under pressure at 500°C (4).

Sample	Initial H/coal ratio, KPa/g	Final pressure, MPa	Surface area, m <sup>2</sup> /g	Microporosity volume, ml/g
Coal	—	—	162.3	0.0614
Nitrogen coke	—	1.90	181.5	0.0629
Nitrogen coke	—	2.95	206.2	0.0742
Hydrogen coke	20	4.45	96.6	0.0334
Hydrogen coke	80	5.75	57.5	0.0199
Hydrogen coke	140	6.66	61.0	0.0214
Hydrogen coke	190	10.03	33.7	0.0115
Hydrogen coke	140	2.50	102.8	0.0376
Hydrogen coke	140	4.50	68.5	0.0239
Hydrogen coke	140	6.66	61.0	0.0214
Hydrogen coke	140	13.20	33.0	0.0115

The original coal containing 83.3%C daf., was heated to 500°C at 4.2K/minute and was held at 500°C for two hours.

Of course, pyrolysis in hydrogen caused increased tar and gas yields. Maximum yields of gas appear to be generated by high ratios of hydrogen to coal and high pressures but maximum yields of tar require an optimum ratio of hydrogen to coal but not excessive pressure since further increase in the pressure and the hydrogen to coal ratio generates gas from the tar (4).

The tars obtained from slow pyrolysis in a static bed such as a Gray-King furnace are complex mixtures of alkanes, alkyl phenols, alkyl aromatics and



heterocyclic material. They are even more complex than coke oven tars and the "high temperature" Gray-King assay simulates the process in a coke oven by the addition of a secondary cracking furnace arranged such that tars issuing from the primary furnace at 600°C pass through a static bed of carbon at 900°C. This results in a diminution of the tar yield and a simplification of the chemical structures present in the tar. The high temperature tars, like coke oven tars, contain polynuclear aromatics, the low temperature tars having become dealkylated and alkanes having cracked, as have such reactive compounds as polyhydric phenols. The role of the second "cracking" Gray-King furnace introduces the concept of secondary reactions which are "retrogressive" in the sense that they may counter the primary reactions of pyrolysis and reduce yields of liquid products. These retrogressive reactions are not necessarily confined to the second Gray-King furnace; investigation of the primary static bed shows that retrogressive reactions occur below 600°C as the products of pyrolysis diffuse through the bed, especially when mass transfer is limited by the development of fluidity (4).

#### 4. Rapid Pyrolysis

As interest in steel making was overtaken by curiosity about combustion and electricity generation, and as chemical engineering developed fluidised and entrained beds, coal scientists forsook slow rates of heating and considered the design of the reactors. In a Gray-King furnace bituminous coals, rich in vitrinite, pyrolyse to yield about 70% of coke or char and about 10% of each of tar, liquor (water) and gas. It is clear that retrogressive reactions reduce the yield of tar and one realises that, in order to maximise the tar yield one requires a reactor in which liquid products are removed from the hot zone as rapidly as they are formed. This implies

a. fine particles of coal-so that liquid products may escape readily and so that problems of heat transfer are minimised.

b. a bed in which particle contact is avoided-for the same reasons as in (a).

c. rapid heating-to encourage liquid products to 'explode' out of the coal and to minimise their residence time in the bed.

d. a "carrier" to remove pyrolysis products from the hot reaction zone.

Table 4 shows pyrolysis yields from a reactor-a "wire mesh" reactor- which embraces these principles (13). The design of the reactor consists of a stainless steel sample holder comprised of a sandwich of two layers of wire-mesh stretched between two electrodes. The mesh acts as an electrical resistances heater. About 7 mg of particles of 100-150 microns diameter form a monolayer of nontouching particles between the wire-mesh sandwich. Gas sweeps through the wire-mesh at 0.1 m/s to carry pyrolysis products from the bed. Linear heating rates of 1000 K/s (still orders of magnitude slower than those achieved in combustion) take the temperature to its final value which may then be held for specified lengths of time.

There can be no guarantee that no retrogressive reactions at all occur in the wire-mesh reactor though this is believed to approximate to the truth. Figures 1 and 2 compare pyrolysis yields from the wire-mesh reactor with those obtained, using the same coal, from two other laboratory reactors designed for rapid heating, one, a fluidised bed and the other, a "hot rod" (14). In the hot rod reactor a shallow plug of coal is maintained within a metal cylinder. The cylinder is used as the electric resistance heater-hence the name "hot rod"- and gas flows through the plug of coal.

Table 5 compares the parameters of the three designs of reactor. Table 4 and Figures 1 and 2 show that tar yields from vitrinite rich material at rapid rates of heating may exceed those from a Gray-King furnace by a factor of two or three and that total yields of volatile material may easily exceed those obtained from a standard volatile test. The maximum yields of tar from the wire-mesh and fluidised

bed reactors are very similar-with fluidised bed reactor generally exhibiting yields which suggests the occurrence of lower temperatures. Even under optimum conditions yields remain lower than those obtained from a hot rod reactor significant quantities of tars. A detailed discussion of the effects of retrogressive reactions, given in a paper on rapid pyrolysis, depend on the design of the reactor perhaps one would expect, fast Gray-King pyrolyses in that tar yields are substantially complete around 600°C used to interpret Gray-King pyrolysis yields of rapid pyrolyses.

TABLE 4. Pyrolysis yields in a wire mesh reactor

Fuel	%C	Maceral %V
POINT OF AYR		
whole coal	85.2	83.8
clarain	82.6	93.0
durain	84.9	30.0
vitrinite	84.8	91.0
liptinite 1	85.7	30.0
liptinite 2	84.8	29.5
inertinite	84.2	17.0
LINBY		
whole coal	82.3	73.0
vitrinite	77.6	85.0
liptinite	79.1	16.0
inertinite	78.2	35.0
CORTONWOOD		
whole coal	86.5	63.2
vitrinite	85.9	97.0
liptinite	85.1	0
inertinite	85.7	7.0
FREYMING		
whole coal	82.3	93.0
vitrinite	83.5	99.2
DINNINGTON		
vitrinite	81.4	96.0
liptinite	84.3	32.0

%C: % carbon w/w daf

Maceral group analysis, %V, %L, %I

T1: Tar yield, %w/w daf coal; heated

V1: Total volatile yield, %w/w daf coal

T1000: Tar yield, %w/w daf coal; heated

V1000: Total volatile yield, %w/w daf coal

All pyrolyses were conducted in a fluidised bed

held for 30 seconds.



bed reactors are very similar - within experimental error - but the tar yields from the fluidised bed reactor generally exhibit a maximum as a function of peak temperature which suggests the occurrence of retrogressive reactions, at least at the higher temperatures. Even under optimum conditions tar yields from the hot rod reactor remain lower than those obtained from the wire mesh reactor, indication that in the hot rod reactor significant quantities of tar are removed by retrogressive reactions. A detailed discussion of the experimental parameters controlling the extent of retrogressive reactions, given in reference (14), convinces one that the kinetics of pyrolysis depend on the design of the reactor. Figures 1 and 2 confirm that, as perhaps one would expect, fast rates of heating eg. 1000K/s give similar results to Gray-King pyrolyses in that tar formation appears to start near to 350°C and is substantially complete around 600°C. This is comforting, it implies that the chemistry used to interpret Gray-King pyrolyses, such as the reactions 1, can also be applied to rapid pyrolyses.

TABLE 4. Pyrolysis yields in a wire-mesh reactor (13).

Fuel	%C	Maceral group analysis %V	%L	%I	T1	V1	T1000	V1000
POINT OF AYR								
whole coal	85.2	83.8	6.0	10.2	20.7	33.6	26.1	42.4
clarain	82.6	93.0	5.0	2.0	18.1	34.7	24.4	40.8
durain	84.9	30.0	27.0	43.0	26.8	40.5	30.1	44.2
vitritine	84.8	91.0	5.0	4.0	20.5	33.9	24.6	40.1
liptinite 1	85.7	30.0	61.0	9.0	43.4	56.8	47.1	62.0
liptinite 2	84.8	29.5	52.3	18.2			47.9	62.5
inertinite	84.2	17.0	3.0	80.0	15.4	30.4	16.1	31.3
LINBY								
whole coal	82.3	73.0	15.0	12.0	26.7	37.6	29.8	40.9
vitritine	77.6	85.0	6.0	9.0	20.3	37.8	29.5	45.2
liptinite	79.1	16.0	70.0	14.0	45.5	59.9	48.9	64.9
inertinite	78.2	35.0	4.0	61.0	19.6	35.8	26.3	42.4
CORTONWOOD								
whole coal	86.5	63.2	15.4	21.4	26.7	37.6	29.8	40.9
vitritine	85.9	97.0	3.0	0	24.7	39.2	26.5	42.1
liptinite	85.1	0	90.0	10.0	54.9	65.5	53.7	70.7
inertinite	85.7	7.0	0	93.0	21.0	33.4	22.5	35.8
FREYMING								
whole coal	82.3	93.0	3.5	3.7	20.3	36.7	28.4	44.2
vitritine	83.5	99.2	0.4	0.4	18.2	34.4	26.3	43.0
DINNINGTON								
vitritine	81.4	96.0			14.3	31.0	21.2	34.2
liptinite	84.3	32.0	68.0	0	47.3	58.9	48.8	63.1

%C: % carbon w/w daf

Maceral group analysis, %V, %L, %I = % vol/vol dmmf vitritine, liptinite, inertinite.

T1: Tar yield, %w/w daf coal; heated to 700°C at 1K/s

V1: Total volatile yield, %w/w daf coal; heated to 700°C at 1K/s

T1000: Tar yield, %w/w daf coal; heated to 700°C at 1000K/s

V1000: Total volatile yield, %w/w daf coal; heated to 700°C at 1000K/s

All pyrolyses were conducted in a flow of helium and the peak temperature of 700°C was always held for 30 seconds.



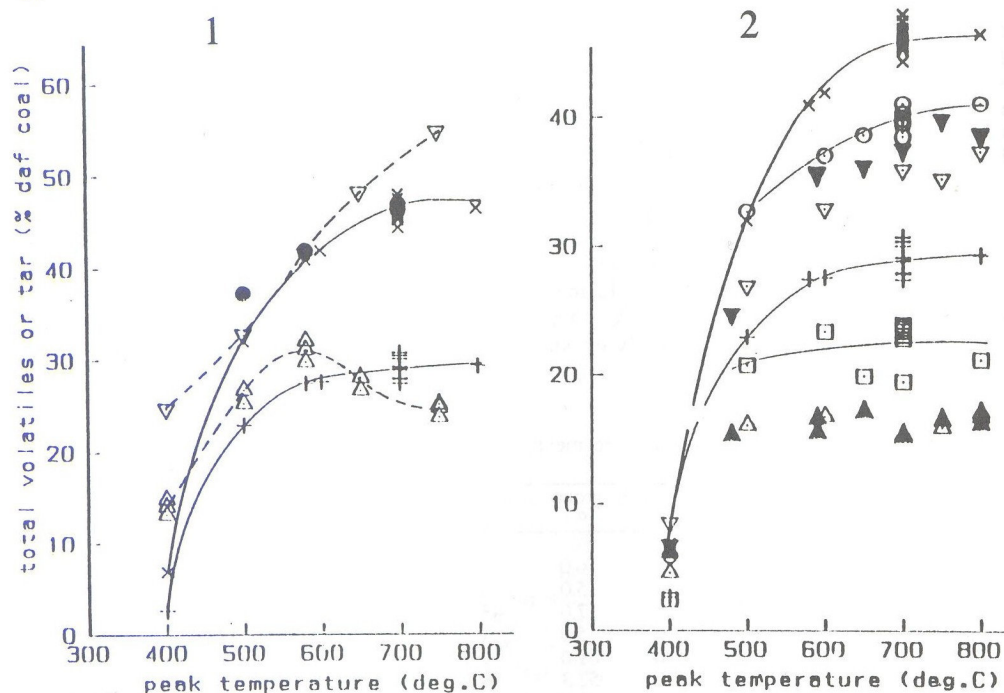


Figure 1. Pyrolysis of Linby coal in fluidised-bed and wire mesh reactors (14):

Fluidised-bed:  $\Delta$ : tar yields,  $\nabla$ : total volatile yields.

Wire mesh: (1000K/s, 30s hold, helium flow 0.1m/s), +: tar yields, X: total volatiles (1000K/s, 1000s hold, helium flow 0.1m/s),  $\bullet$ : total volatiles.

Figure 2. Pyrolysis of Linby coal in wire mesh and hot rod reactors (14):

Wire mesh: (1000K/s, 30s hold, helium flow 0.1m/s), +: tar yields, X: total volatiles, (1K/s, 30s hold, helium flow 0.1m/s),  $\square$ : tar yields,  $\circ$ : total volatiles.

Hot rod: (5K/s, 200s hold, helium flow 0.1m/s),  $\Delta$ : tar yields,  $\nabla$ : total volatiles (5K/s, 200s hold, hydrogen flow 0.1m/s) solid symbols as above.

TABLE 5. Comparison of the parameters of three reactors (14)

Reactor type	Fluidised Bed	Wire-Mesh	Hot Rod
Size of sample	1-15 g	5-25 mg	50 mg-1 g
Maximum temperature (°C)	900	1200	900
Pressure (bar)	1	0-160	1-150
Rate of heating	slow to flash	slow to 5000 K/s	slow to 20 K/s
Flow of carrier gas	3-5(fluidisation)	slow to 0.3 m/s	slow to 10 m/s
Retrogressive reactions	in bed and in freeboard	minimal but non-zero	may be minimised at very high flows
Accuracy/repeatability	tar + 2-3% char + 5%	tar + 2-3% char + 1-2%	tar + 2-3% char + 3-4%

Table 4 and Figures 1 and 2 show the effect of temperature on the yields of tar and volatiles. These are amongst those which demonstrate the maximum yields obtainable at atmospheric pressure. It is well known that under reduced pressure but it is already known that reactions leads to greatly increased tar yields. The tar group concentrates increase in the tar yields, that, if one assumes that the tar and volatiles are additive sums of the tar and volatiles, one can deduce a consistent set of yields. These may vary with rank. The above data require careful interpretation. Evidently, the yields of each other. There is a sense in which it is different if it is pyrolysing as an individual (i.e. non-coherent solid powder) to when it is pyrolysing as part of a fluidised bed (i.e. circumscribed). What Table 6 is concerned with is the organic matrix of each macerene. The presence of crosslinked aliphatic chain substituents leads to the breakage of the aliphatic chain, which results in relatively high yields of liquid products. This may be observed to become fluidised bed pyrolysis (15). Vitrinites disrupt the fluidised bed obeys reactions 1. The formation of coke/char with the formation of coke or char is inevitable. As a result the tar yields and coke/char being determined by the hydrogen donor, the reduction of coke/char is inevitable. The attack on it by hydrogen and the reaction 4. In consequence, about 10% of the tar is formed by the dehydrogenation of the tar. The simultaneous reactions forming tar and coke/char are a good explanation of the variation of tar yields with temperature but other explanations of the variation of tar yields from liquefaction of heating.

## 5. The Liquefaction of Solid Fuels

The liquefaction of solid fuels may be achieved by hydrogenation and the refining of the coal. It will be said about the second stage of the process to produce a clean synthetic fuel.

The criteria for minimising retrogressive reactions may also be applied to their solubilisation. The original Bergius and Pott Broche processes for the liquefaction of coal products have been constrained to operate at high pressure (17). Such circumstances clearly affect the nature of the liquid products. The liquefactions are performed at moderate temperatures.



Table 4 and Figures 1 and 2 show the effect of the rate of heating and the peak temperature on the yields of tar and volatile matter in the wire-mesh reactor. These results are amongst those which demonstrate that the tar yields quoted at 1000K/s are the maximum obtainable at atmospheric pressure. It is quite possible that larger yields might be obtained under reduced pressure but it is already abundantly clear that minimisation of retrogressive reactions leads to greatly increased tar yields. Table 4 shows that the tar yields of maceral group concentrates increase in the order inertinite < vitrinite < liptinite. Table 6 shows that, if one assumes that the tar and the volatile yields from a solid fuel are the additive sums of the tar and volatile yields of its maceral group components, then one can deduce a consistent set of yields for 'pure' maceral groups (13). Obviously these may vary with rank. The additivity of the yields of the maceral groups needs careful interpretation. Evidently, the maceral groups are not pyrolysing independently of each other. There is a sense in which the pyrolysis of inertinite, for example, is different if it is pyrolysing as an inertinite concentrate (when it is pyrolysing as a non-coherent solid powder) to when it is pyrolysing as part of a coking coal (when it is pyrolysing as part of a fluid or plastic mass in which mass transfer is circumscribed). What Table 6 is indicating is that the chemical skeleton of the organic matrix of each maceral group disrupts in a characteristic manner independently of the presence of other maceral groups. Thus, in liptinites, a crosslinked aliphatic chain substituted by alkyl hydroxy aromatics (1), disrupts by breakage of the aliphatic chain (possibly by a random scission process) to give relatively high yields of liquid products and volatile material. Liptinite concentrates may be observed to become fluid and relatively limpid throughout most of the pyrolysis (15). Vitrinites disrupt differently; the pyrolysis of their aromatic skeleton obeys reactions 1. The formation of tar by the scission of the skeleton competes with the formation of coke or char following dehydrogenation of the hydroaromatic linkages. As a result the tar yield is less than that from liptinite, the proportions of tar and coke/char being determined by the experimental conditions. In the absence of a hydrogen donor, the reduction of tar yields because of the simultaneous formation of coke/char is inevitable. The scission of the skeleton occurs because of attack on it by hydrogen and this hydrogen is generated by the coke/char forming reaction 4. In consequence, about as much aromatic material forms tar as forms coke by the dehydrogenation of the hydroaromatic network (16). Competition between simultaneous reactions forming tar and coke respectively provides a straightforward explanation of the variation of tar yields with heating rate observed in vitrinite rich material but other explanations are possible and Tables 4 and 6 show some examples of tar yields from liptinites and inertinites which also varied with the rate of heating.

### 5. The Liquefaction of Solid Fuels in Tetralin

The liquefaction of solid fuels may be divided into two; the primary solubilisation, usually by hydrogenation and the refining of the soluble products by further hydrogenation. Little will be said about the second stage though it is of great importance to the production of a clean synthetic fuel.

The criteria for minimising retrogressive reactions during the pyrolysis of solid fuels may also be applied to their solubilisation. Most of the recent laboratory developments of the original Bergius and Pott Broche processes have used closed reactors in which liquefaction products have been constrained to remain in the hot reaction zone for appreciable periods of time (17). Such circumstances clearly favour the modification both of conversions and of the nature of the liquid products by retrogressive reactions, especially since most liquefactions are performed at moderate pressure. Retrogressive reactions may be minimised



by carrying out liquefactions in a flowing solvent reactor (18) in which a small, fixed bed of powdered coal is permeated by a hot hydrogen donor solvent which flows through the bed and carries products out of the reaction zone.

The results to be discussed in this chapter were obtained from a cylindrical, metallic, tubular reactor in which a plug of powdered (100-150 micron) coal, diluted tenfold with sand of the same size in order to minimise contact between the coal particles and prevent the development of fluidity, was swept by hot tetralin (18). Liquefactions were carried out with tetralin flowing at 0.9 ml/second at a pressure of 70 bar; the coal was heated at 5 K/second to a selected temperature between 300 and 450°C for a pre-set period of time. Minor variations in the tetralin flow rate, the pressure or the rate of heating caused little change in conversions. The tetralin flow rate of 0.9ml/second was always sufficient to remove solubilised liquefaction products continuously from the reaction zone and into a heat exchanger within 10 seconds.

TABLE 6. Calculated and experimental pyrolysis yields (13).

Fuel		T1	V1	T1000	V1000
POINT OF AYR					
100% liptinite	calculated yield	59.7	73.3	64.2	78.4
100% vitrinite	calculated yield	19.4	31.8	22.5	38.8
100% inertinite	calculated yield	12.9	28.5	12.9	27.9
whole coal	calculated yield	21.2	34.0	24.0	40.1
	experimental yield	20.7	33.6	26.1	42.4
clarain	calculated yield	21.3	33.8	24.4	40.6
	experimental yield	18.1	34.8	24.4	40.9
durain	calculated yield	27.5	41.6	29.6	44.8
	experimental yield	26.8	40.5	30.1	44.2
LINBY					
100% liptinite	calculated yield	58.2	71.1	59.1	75.1
100% vitrinite	calculated yield	17.9	35.9	28.2	44.0
100% inertinite	calculated yield	17.7	33.6	23.1	39.3
whole coal	calculated yield	23.9	40.9	32.2	48.1
	experimental yield	24.2	40.2	30.7	46.6

The pyrolysis conditions, the fuels and the symbols are those used in Table 4. Calculated yields have been deduced assuming that yields are additive sums of the yields of the component maceral groups.

Detailed comparison of the liquefaction of the same sample of Point of Ayr coal in the flowing solvent reactor and in a minibomb reactor operated at the same temperature for the same duration of time (19) has demonstrated the success of the design of the flowing solvent reactor in minimising retrogressive reactions. When tetralin was used as the hydrogen donor solvent conversions in the flowing solvent and the minibomb reactors were found to be quite similar. When, however, a less powerful hydrogen donor solvent, 1-methyl naphthalene, was used secondary char formation was observable in the minibomb but not in the flowing solvent reactor. As Figures 3 and 4 illustrate, size exclusion chromatography suggested that the relative proportions of higher molecular mass material in the liquefaction products from the flowing solvent reactor increased as a function of increasing reaction temperatures and hold times. This is what one expects if liquefaction is the disruption and subsequent solubilisation of a cross-linked network. The opposite effect was observed with samples from the minibomb reactor, the products becoming relatively lighter with increasing temperature and hold time and this was clearly the consequence of retrogressive reactions. Thus, one may write

COAL  $\longrightarrow$  SOLUBLE PRODUCT

PRODUCT MOLECULE +  
PRODUCT MOLECULE  $\longrightarrow$  C  
or PARTICLE

though this is an over simplification depicted as reaction 4 and observable were slow. In the minibomb reactor 10-100 seconds which increased to insufficient time for these retrogressive but, as reaction 4 predicts, the enhance reactor decreases the rate of the retro

absorbance - arbitrary units

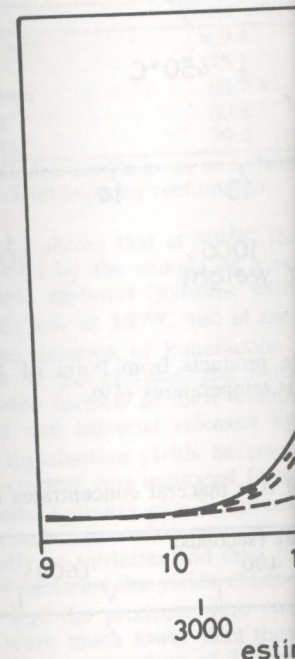


Figure 3: Size exclusion chromatogram of Point of Ayr coal liquefied in a flowing solvent reactor at various peak temperatures (19).

Tables 7 and 8 illustrate how concentrations vary with the temperature. Table 9 shows yields of liquefaction compared with the tar and volatile displayed in Table 4.



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42.4  
40.6  
40.9  
44.8  
44.2

75.1  
44.0  
39.3  
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COAL  $\longrightarrow$  SOLUBLE PRODUCTS

(3)

PRODUCT MOLECULE +  
PRODUCT MOLECULE  $\longrightarrow$  CHAR PRECURSOR + LIGHTER PRODUCT  
or PARTICLE

(4)

though this is an over simplification. The major retrogressive char forming reactions, depicted as reaction 4 and observable in the minibomb but not the flowing solvent reactor, were slow. In the minibomb reactor at 450°C these reactions had a characteristic time of 10-100 seconds which increased to over 1600 seconds at 400°C. Not only was there insufficient time for these retrogressive reactions to develop in the flowing solvent reactor but, as reaction 4 predicts, the enhanced dilution of the products inherent in the design of the reactor decreases the rate of the retrogressive reactions even further (19).

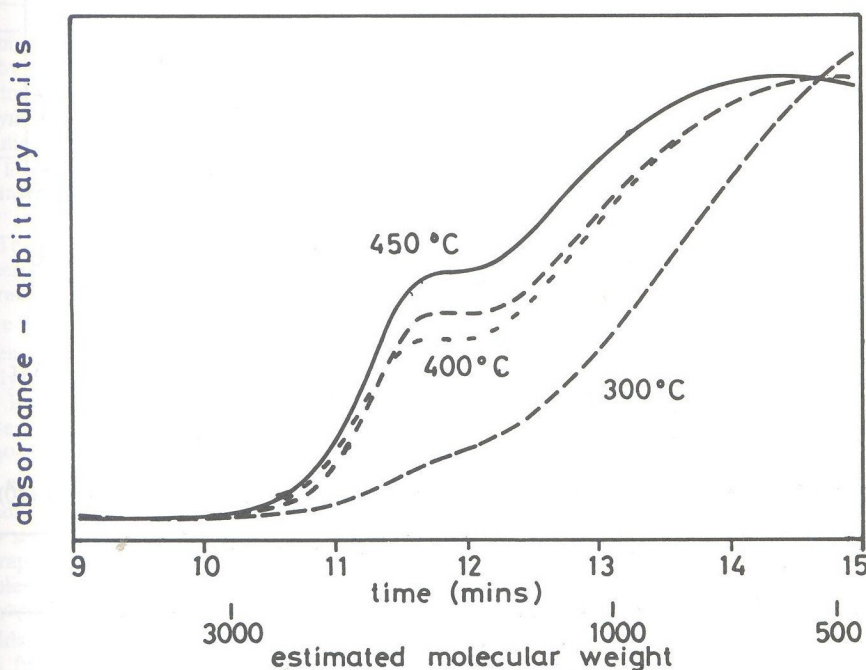


Figure 3: Size exclusion chromatograms of tetralin/cold THF soluble products from Point of Ayr coal liquefied in a flowing solvent reactor under standard - Table 9 - conditions with various peak temperatures (19).

Tables 7 and 8 illustrate how yields of liquefaction products from maceral group concentrates vary with the temperature and the hold time in the flowing solvent reactor (20). Table 9 shows yields of liquefaction products under standard conditions which may be compared with the tar and volatile yields obtained from the wire-mesh pyrolyser and displayed in Table 4.



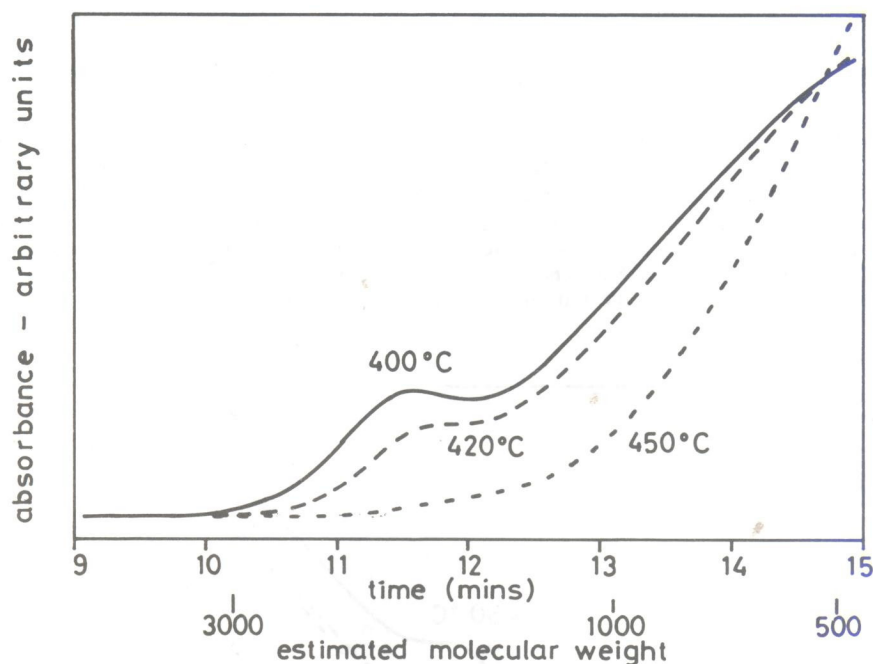


Figure 4: Size exclusion chromatograms of THF soluble products from Point of Ayr coal liquefied with tetralin in a minibomb for 1600 s at various temperatures (19).

TABLE 7. Total liquefaction yields (% daf) from Point of Ayr maceral concentrates (20).

Peak Temperature	Hold time at peak temperature (seconds)							
	0		100		400		1600	
	V	L	V	L	V	L	V	L
300°C	15.9	.	19.2	.	19.0	.	.	.
350°C	18.2	.	29.2	.	29.0	24.7	.	.
400°C	25.3	.	42.6	22.4	54.6*	34.7	.	65.9
450°C	37.2	.	73.7	48.1	84.1	85.7	.	.
450CH	.	.	17.1	35.6	.	.	.	.

V = Vitrinite concentrate used in Table 4.

L = Liptinite 2 concentrate used in Table 4.

Standard heating rate of 5 K/s to the peak temperature, standard pressure of 70 bar and standard tetralin flow of 0.9 ml/s.

\* = 500 seconds.

450CH = Hexadecane used as solvent.

TABLE 8. Total li

whole coal  
vitrinite  
liptinite  
inertinite

Vitrinite, liptinite and  
solvent reactor as in T

TABLE 9. Total l  
reactor (20).

Point of Ayr  
Linby  
Cortonwood  
Freyning  
Dinnington

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TABLE 8. Total liquefaction yields (% daf) from Linby coal and maceral concentrates (20).

	Peak Temperature (°C)			
	350	400	420	450
whole coal				75.1
vitritinite	22.3	33.2	61.9	70.4
liptinitite	29.4			70.1
inertinitite		27.4	46.3	53.4

Vitritinite, liptinitite and inertinitite are the concentrates used in Table 4. Standard conditions in the flowing solvent reactor as in Table 7. Hold time at peak temperature = 100 seconds.

TABLE 9. Total liquefaction yields (% daf) under standard conditions in flowing solvent reactor (20).

	Whole coal	Vitritinite	Liptinitite	Inertinitite
Point of Ayr	69.4	73.7	48.1	38.7+
Linby	75.1	70.4	70.1	53.4
Cortonwood	68.7	79.6	82.7	65.8
Freyning	60.8	75.1	52.7	17.1
Dinnington	79.4	70.1	63.5	unexamined

The liquefaction conditions are as in Table 8. The samples are those in Table 4.

+: single result requiring confirmation.

Table 7 shows that at 300°C the total liquefaction yield (that is, the total loss in weight experienced by the sample as a result of liquefaction) was barely larger than the yield of extractable material (pyridine extracts some 18% of Point of Ayr Vitritinite). Conversions were still low at 350°C and at these temperature there was little increase in the conversion when the duration of liquefaction was prolonged. Little pyrolysis occurs below 350°C but analyses by gas chromatography/mass spectrometry discussed later in the chapter show that the liquids formed at these comparatively low temperatures consisted of both extractable material and material released by hydrogenation. Tables 7 and 8 show that at 400 and 450°C liquefaction yields became substantial and increased significantly as the duration of the experiment was increased from 100 to 400 seconds. It is often observed that, under mild conditions, liptinites give lower conversions than vitritinites, whilst at 450°C and hold times of 400 seconds conversions are comparable. In other words liptinites do not appear to solubilise as rapidly as vitritinites and their activation energy for liquefaction appears to be higher (20). Table 7 includes the yields obtained when pyrolysis, and not liquefaction, was carried out at 450°C and the products were swept away in a stream of hexadecane. As one expects, the yields were much lower than those obtained under the same conditions in tetralin. Pursuing this further, comparison of Tables 4 and 9 demonstrates that liquefaction yields, even when the liquefaction was prolonged for the comparatively short time of 100 seconds, were generally higher than the total volatile yields generated by pyrolysis in a wire-mesh reactor.

It is apparent from the results illustrated in Tables 7, 8 and 9 that liquefaction yields vary from one coal to another- and clearly with rank- and that much work will be needed before one can unravel all the chemistry involved. It is already obvious, however, that, not surprisingly, inertinites give low liquefaction yields and that the effects of liquefaction - when compared with pyrolysis - are more dramatic for vitritinites than for liptinites. The difference between the liquefaction and pyrolysis yields shown in Tables 4 and 9 is always greater for a vitritinite than for its associated liptinitite. Partly this is simply because liptinitite pyrolysis gives rather high yields of volatile products. It is more interesting to consider the effect of liquefaction on the vitritinites. It has already been shown that tar and volatile yields from the pyrolysis of vitritinites are necessarily low since char formation is essential to provide the hydrogen needed for the generation of liquid products by reaction 2. When, in liquefaction,



hydrogen is provided by tetralin, the rates of the subsequent bond scission reactions are greatly increased and are no longer dependent on simultaneous char formation. Indeed, dehydrogenation reactions, precursors of char formation, might be expected to be inhibited by the pressures employed in liquefaction. This is the chemical explanation of how much larger yields of volatile material are given by vitrinites on liquefaction than on pyrolysis.

## 6. Liquefaction Products and the Mechanism of Liquefaction

Those liquefaction products obtained from the flowing solvent reactor which were soluble in hot tetralin but not in pentane, LPIP, comprised some 25-50% of the original fuel. Since retrogressive reactions have been minimised, the chemical structure of this material should be similar to that of the original fuel, as the infrared spectrum shown in Figure 5 illustrates, any differences being indicative of the chemistry of the liquefaction reactions. LPIPs being pitch-like solids, detailed information of the course of liquefaction may be obtained from their  $^{13}\text{C}$  CPMAS nmr spectra. Illustrative  $^{13}\text{C}$  CPMAS nmr spectra are shown in Figure 6. The spectra are similar to those of the starting material, the differences being quantitative but not qualitative. Figure 6 reminds one, however, that the differences in the chemical structures of vitrinites and liptinites is reflected in their  $^{13}\text{C}$  nmr spectra. In particular, liptinites have a large, often spiky, peak between 29 and 30 ppm, characteristic of long methylene chains, which is not present in vitrinites spectra. Nevertheless, it is convenient to describe the spectra by dividing them into eight chemical shift regions; four - (a), (b), (c) and (d) - in the aromatic region, and four - (w), (x), (y) and (z) - in the aliphatic region (Figure 6). The regions (b), (c) and (d) embrace the chemical shifts of aromatic carbon atoms attached to hydrogen, carbon and oxygen atoms respectively (1, 21). Region (a) includes substituted phenols and certain heterocyclic structures including indoles (1, 21). Region (w), 0 to 15 ppm, includes methyl groups on the ends of alkyl chains (liptinites) and alpha to aromatic rings but shielded by two adjacent chemical groups (vitrinites) (21). Region (x), 15 to 24 ppm, contains methyl groups alpha to an aromatic ring (21) which are comparatively unshielded. Region (y), 24 to 40 ppm, contains methylene groups in long chains (liptinites) and also in hydroaromatic structures alpha to an aromatic ring (vitrinites) (21). Region (z), from 40 ppm onwards, contains methines, diarylmethanes and methylenes both alpha to an aromatic ring and adjacent to a methine group.

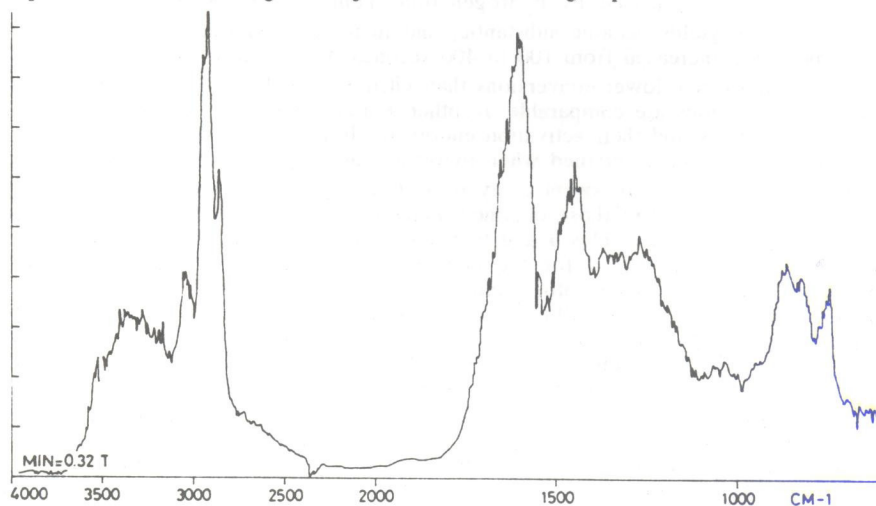


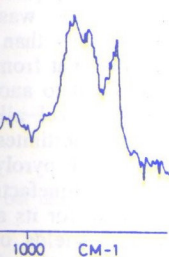
Figure 5: Infrared spectrum of LPIP from Point of Ayr vitrinite liquefied in the flowing solvent reactor at 450°C under standard -Table 9- conditions.

Figure 6:  $^{13}\text{C}$  CPMAS nmr spectra of LPIP from Point of Ayr vitrinite liquefied in the flowing solvent reactor at 450°C under standard conditions (iii) LPIP from standard conditions.



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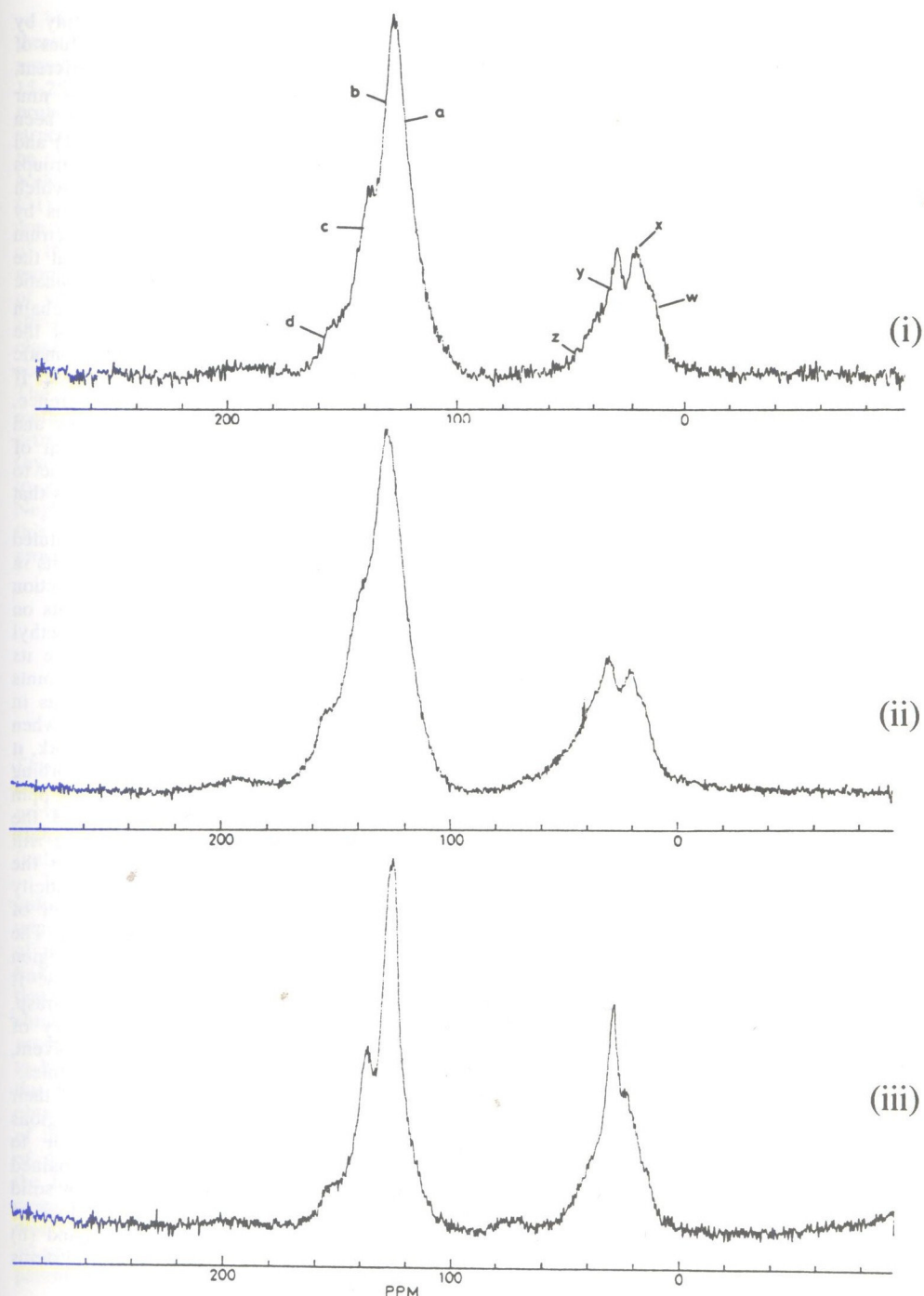


Figure 6:  $^{13}\text{C}$  CPMAS nmr spectra: (i) LPIP from Point of Ayr vitrinite liquefied in the flowing solvent reactor at  $450^\circ\text{C}$  under standard conditions. (ii) Point of Ayr vitrinite. (iii) LPIP from Dinnington liptinite liquefied in the flowing solvent reactor at  $450^\circ\text{C}$  under standard conditions.



The liquefaction of liptinites in the flowing solvent reactor was accompanied not only by a small loss in the atomic H/C ratio but also by a consequent small increase in the values of the aromaticity,  $f_a$ . Davis et al., (1), observed the aromatic structures present in four different, pyridine-extracted liptinites (sporinites) to be virtually identical. Accordingly, the nmr spectra show the aromatic structures present in LPIPs obtained from liptinites to have been little affected by liquefaction. Liptinites contain much long chain aliphatic material, (1) and much of the 0-15 ppm region (w) of aliphatic absorption will be due to the methyl groups on the ends of the chains and the dominant peak near 29 ppm, in region (y) which distinguishes the shapes of vitrinite and liptinite nmr spectra, consists of absorptions by methylene groups delta and further from an aromatic nucleus. Comparison of the spectrum of the LPIP from Cortonwood liptinite with that of the original liptinite suggests that the increase in the value of  $f_a$  caused by liquefaction was due to the removal of long aliphatic chains: that is, absorption by methylene groups in the 24-40 ppm region and by chain terminating methyl groups in the 0-15 ppm region diminished. Gain in region (x) of the Cortonwood spectrum suggests that liquefaction created methyl groups alpha to an aromatic ring. The proportion of absorption in the region from 40 ppm onwards also increased. If one uses the spectra obtained from liptinite residues by Davis et al. (1) as a reference, comparison of the aliphatic portions of the spectra from LPIPs from Dinnington, Linby and Point of Ayr liptinites also suggests that liquefaction was accompanied by removal of methylene chains and the formation of methyls alpha to aromatic rings. Absorption due to methines and diaryl methanes also appears to have increased in these LPIPs but it seems that Dinnington and Linby liptinites gave increased absorption in the 0-15 ppm region.

Liptinites (sporinites) consists of an essentially aliphatic network with pendant substituted aromatic nuclei. Pyrolysis occasions the disruption of the aliphatic network and this results in the observed high yields of volatiles and the development of marked fluidity. Liquefaction and pyrolysis appear to follow a similar course. The hydrogenation of alkyl substituents on the aromatic rings connotes the removal of methylene and the formation of alpha methyl groups as we have observed. The hydrogenation of the aliphatic network would cause its disruption and the formation of liquid products. The hydrogenation would occur at points of structural weakness (in the bond energetic sense) such as alpha methine groups (as in polystyrene). This would lead to the formation of additional alpha methyl groups but, when hydrogenation is less extensive or when it occurs at branch points in the aliphatic network, it will result in the formation of methyl groups on the ends of shortened chains and absorbing in the 0-15 ppm range. The net loss or gain of methyl groups absorbing in the 0-15 ppm region clearly depends on the balance between the loss of alkyl substituents and the formation of terminal methyl by hydrogenation of the aliphatic network. Such a balance will vary from liptinite to liptinite. As one has seen, the removal of alkyl chains provides the mechanism for the decrease in the atomic H/C ratio and the small increase in aromaticity which accompanies the formation of LPIPs from liptinites even though it is transfer of hydrogen atoms from tetralin which is causing the disruption of the aliphatic network. The only nmr feature remaining unexplained is the creation of structures absorbing in the region where methines and diarylmethanes usually absorb and this demands further study. It suggests that there may be some feature of sporinite structure which still eludes our grasp. Everything which has been written so far implies that the details of the chemistry of liquefaction will apply also to pyrolysis. Since no hydrogen is supplied by a donor solvent, one expects the pyrolysis of liptinites to be accompanied by the formation of some olefines.

Liquefaction of vitrinites caused little change in the features of the aromatic part of their nmr spectra. There appeared to have been an interchange of carbon atoms between regions (a) and (b) of the nmr spectra but the number of aromatic carbon atoms attached not to hydrogen but to carbon and oxygen atoms - regions (c) and (d) of the spectra - remained unchanged in LPIPs. When oxygen groups are removed during the liquefaction of a solid fuel this must therefore occur through retrogressive reactions or during the refining stage of the hydrogenation. The apparent interchange of carbon atoms between regions (a) and (b) may be explicable by the transfer of hydrogen atoms between different aromatic systems during the liquefaction process eg. between diaromatic and polyaromatic rings.

Vitrinites are therefore supposed to have an aromatic ring and 15-25 ppm range probably most, of structures and alpha be close, often alpha both alpha to an aromatic nucleus (21). Inspection of the nmr spectra of concentrates was accompanied liquefaction. The formation of alpha methylenes) appears in the vitrinites in the form of (hydrogenation) of the to give fragments in Negligible numbers of this liquefaction, and process is symbolised

R Ar CH

This is presumably the reaction 1. The significance of the previous discussion is the alpha position to an aromatic nucleus.

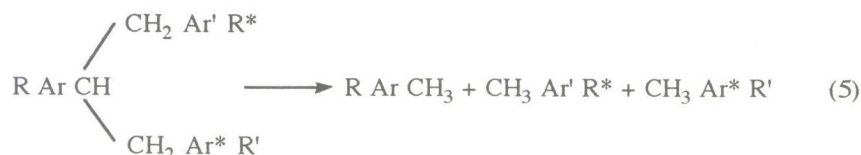
The nmr spectrum indicated that solubility of LPIP material was due to the removal of methyl groups and the formation of linkages. The increase in the proportion of aromaticity that at least some methylenes are shielded by adjacent aromaticity. The proportion of aromaticity to have been redistributed. The Linby concentrate obtained from Point of Ayr inertinite repectively of Ayr inertinite was the formation of methylenes corresponding vitrinite was also reduced but 30 ppm. Although this parent concentrate con



accompanied not only by an increase in the values of the absorption in four different regions, (1) and (2) to the methyl groups in region (y) which suggests that the removal of long aliphatic chains and by chain branching in region (x) of the spectrum also increased. If (1) as a reference, Linby and Linby (2) noted the absorption due to LPIPs but it seems that the process is symbolised in reaction 5:

with pendant substituted alkyl substituents on the network and this results in a loss of fluidity. Liquefaction of alkyl substituents on the network would cause its rupture at points where methine groups (as in LPIPs) but, when the aliphatic network, if broken, chains and absorbing in the 0-15 ppm region. Such a balance will be achieved when the increase in aromaticity is offset by the transfer of aliphatic network. The process is further study. It still eludes our grasp. of the chemistry of the refining stage of the parent aromatic systems.

Vitrinites are essentially hydroaromatic, containing little long chain alkyl material. One therefore supposes that, in LPIPs, the methyl groups in the 0-15 ppm range were alpha to an aromatic ring and shielded by two adjacent chemical groups and the methyl groups in the 15-25 ppm range were alpha to an aromatic ring and comparatively unshielded; many, probably most, of the methylene groups in the 24-40 ppm range will be in hydroaromatic structures and alpha to an aromatic ring whilst the methine groups in the 40 - end region will be close, often alpha, to an aromatic ring though diarylmethanes and methylenes which are both alpha to an aromatic ring and adjacent to a methine group can also absorb in the region (21). Inspection of the aliphatic regions indicated that the formation of LPIPs from vitrinite concentrates was accompanied by marked increases in region (y) and decreases in region (z) of the nmr spectra and thus liquefaction appears to have led to the formation of methyl groups alpha to an aromatic ring and the concomitant destruction of methine groups (or of certain methylenes alpha to an aromatic ring). Comparison of the Point of Ayr LPIP spectrum with that from a supercritical pyridine extract of the same vitrinite concentrate clearly indicated that the changes in the aliphatic region of the  $^{13}\text{C}$  nmr spectra which accompanied liquefaction were due, not to selective solubilisation, but to chemical reaction. The formation of alpha methyls by the hydrogenation of methines (or of certain alpha methylenes) appears to have been the major chemical reaction during the liquefaction of vitrinites in the flowing solvent reactor. Thus LPIPs were formed by the rupture (hydrogenation) of hydroaromatic material containing methine and alpha methylene groups to give fragments in which previous linkages had been replaced by methyl groups (20). Negligible numbers of aliphatic carbon atoms were lost as simple volatile molecules during this liquefaction, aromaticities remained constant and atomic H/C ratios increased. The process is symbolised in reaction 5:



This is presumably the major pathway during which radicals and intermediates are formed in reaction 1. The significance of methines in vitrinite structures has not received much previous discussion though Doğru et al. (2) noted the preponderance of branching at the alpha position to an aromatic ring during their investigations of reductively ethylated solid fuels.

The nmr spectrum from LPIP obtained by liquefying the Linby inertinite concentrate indicated that solubilisation had followed the same (or a very similar) mechanism as that by which LPIP material had been formed from vitrinites. There was an increase in the formation of methyl groups and a marked decrease in the presence of methine (or alpha methylene) linkages. The increase in methyl groups in the 0-15 ppm region was noteworthy, suggesting that at least some methyl groups formed by liquefaction were alpha to an aromatic ring but shielded by adjacent substituents (21). Liquefaction appeared to cause little change in the proportion of aromatic carbons substituted by carbon or oxygen atoms but there appeared to have been redistribution of aromatic carbons between regions (a) and (b). Unfortunately, the Linby concentrate contained but 61% of inertinite and spectra from LPIP material obtained from Point of Ayr and Cortonwood inertinite concentrates containing 80 and 90% of inertinite respectively, showed inconsistent patterns. The spectrum of the LPIP from Point of Ayr inertinite was consistent with the scission (hydrogenation) of methine linkages and the formation of methyl groups alpha to aromatic rings but to a much lesser extent than the corresponding vitrinite LPIP. The methine content of the LPIP from Cortonwood inertinite was also reduced but the aliphatic part of the spectrum was dominated by a peak close to 30 ppm. Although this is close to the chemical shift where long alkyl chains absorb, since the parent concentrate consisted of 90% inertinite it seems more reasonable to suppose that the



peak arose from methylene groups in tetralin structures with substituents at the alpha position (21). Such structures could obviously have been formed by hydrogenation of aromatic - or, more probably, hydroaromatic - material. There is little in these spectra to indicate why inertinites give low liquefaction yields and, clearly, it is the unexamined residues which resisted hydrogenation.

Gas chromatography/mass spectrometry of the volatile components of liquefaction products from the flowing solvent reactor showed them to consist of a complex mixture containing significant concentrations of alkanes and of alkylated/hydroxylated/aromatics. These compounds apparently embraced a variety of branched and cyclic structures and certainly at high conversions, simple sequences of *n* alkanes, alkyl benzenes, alkyl phenols or alkyl naphthalenes etc. were not, in fact, distinguishable by their intensity. Though probably present such compounds were submerged by the large numbers of more complicated structures. Products obtained by liquefaction of Point of Ayr coal in tetralin - or in 1-methyl naphthalene - in a minibomb reactor at the same temperatures as liquefactions in the flowing solvent reactor produced not only lower molecular mass (lighter) products, as discussed earlier in this section, but volatile material which was less diverse than that from the flowing solvent reactor. Thus, branched chains were less apparent and *n* alkanes dominated gas chromatography/mass spectrometry spectra. Similarly, the aromatic material from minibomb liquefactions was less varied in structure. These mass spectral results are supported by many similar product analyses obtained by previous workers, (17), whose reaction conditions one now realises to have been retrogressive. It is apparent that the relatively lower molecular mass, but doubtless hydroaromatic, primary material produced by the liquefaction of vitrinites is readily degraded to leave simpler structures as liquefaction products. More extensive retrogression - caused by even longer reaction times and lower concentrations of available hydrogen - would be expected to simplify product structures even more. Analogy with pyrolysis would suggest the further loss of alkanes, of complex phenols and of side chains from aromatic structures (3). Fine tuning of retrogression could be significant in refining the technological properties of a clean synthetic fuel. By this stage of retrogression, it may no longer be possible to discern dominant reaction pathways. One is generating a multitude of radicals and polarisable molecules from the original hydroaromatic material and virtually all possible combinations of these radicals and molecules take place, eventually resulting in randomised 'scrambling' of all the hydrogen atoms (22).

## 7. Acknowledgments

Although I am guilty of providing a restricted list of references, I hope that the extent to which this chapter is indebted to the many pioneers of coal science will be perfectly obvious. I am personally grateful to my colleagues and students who participated in the work. My especial thanks are due to Drs. J. R. Gibbins and R. Kandiyoti who taught me all I know about reactor design. The work has been funded by the National Coal Board, the British Gas Corporation, Shell, British Petroleum, the scientific research councils of Britain and Turkey (SERC and TUBITAK) and, most recently, [Research Contract No. EN3V.0052:UK(H) directed by Dr. R. Kandiyoti] by the European Community.

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