BCURA
2006 Robens Coal Science Lecture

Thermal Breakdown in Coals

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We will discuss thermal breakdown in…

Pyrolysis:

Heating coal in an inert gas environment

50-60 % char - solid

maybe 20-25 % tar

& maybe 15-20 % gas

and

Liquefaction:

Reacting and dissolving coal in a solvent

10-20 % char - solid

maybe 75-85 % coal extract

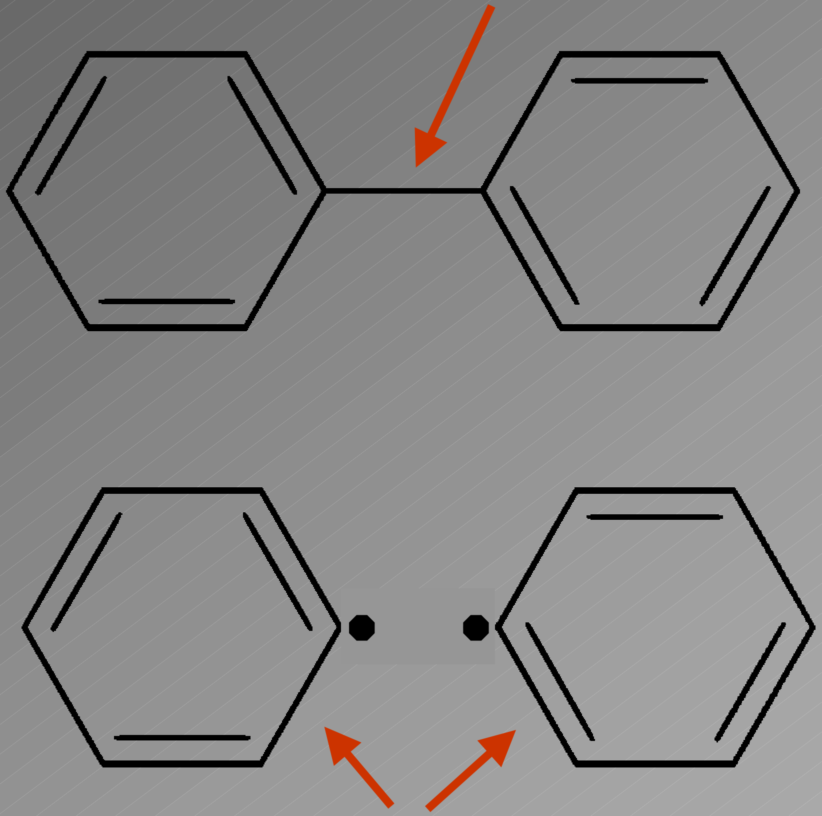
a little gas

We would like to explore

- When thermal breakdown actually begins…
- Similarities of reaction pathways in pyrolysis & liquefaction…
- When & how the reaction pathways begin to diverge?

Electron spin resonance spectrometry of Thermal Breakdown

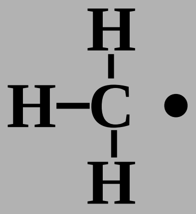
Coals normally contain ~10^{19} free radicals per gram



Chemical bond

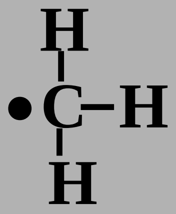
Rupture of a chemical bond

2 free radicals

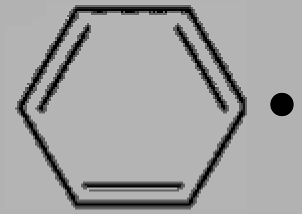


$\mathrm{H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}\bullet}$

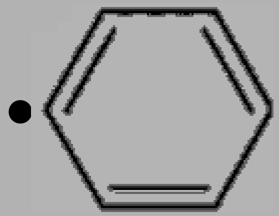
Very reactive

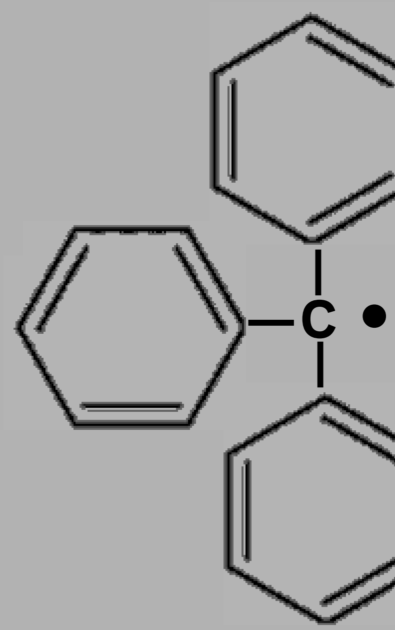


$\mathrm{\bullet\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H}$

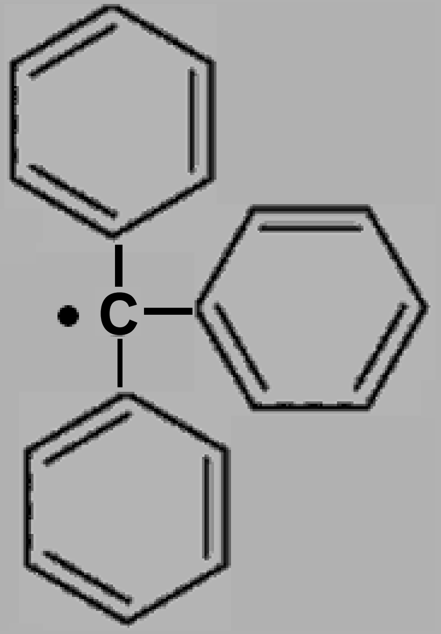


Reactive





Very stable



The electron spin resonance spectrum of a coal shows stable free radical populations embedded in the coal matrix

After thermal treatment, we observe accumulated fragments from completed covalent bond scission reactions.

Reactive free radicals in coals cannot be observed by *ESR**

***Fowler,Bartle & Kandiyoti; Energy & Fuels 1989 3 515**

& we will try to understand…

Why the product slate changes
when the heating rate is altered?

& how do retrogressive reactions work?

…questions relevant to understanding…

✱ combustion	power & steam generation
✱ gasification	power generation,chemicals
✱ liquefaction	liquid fuels & chemicals
✱ coking	iron making

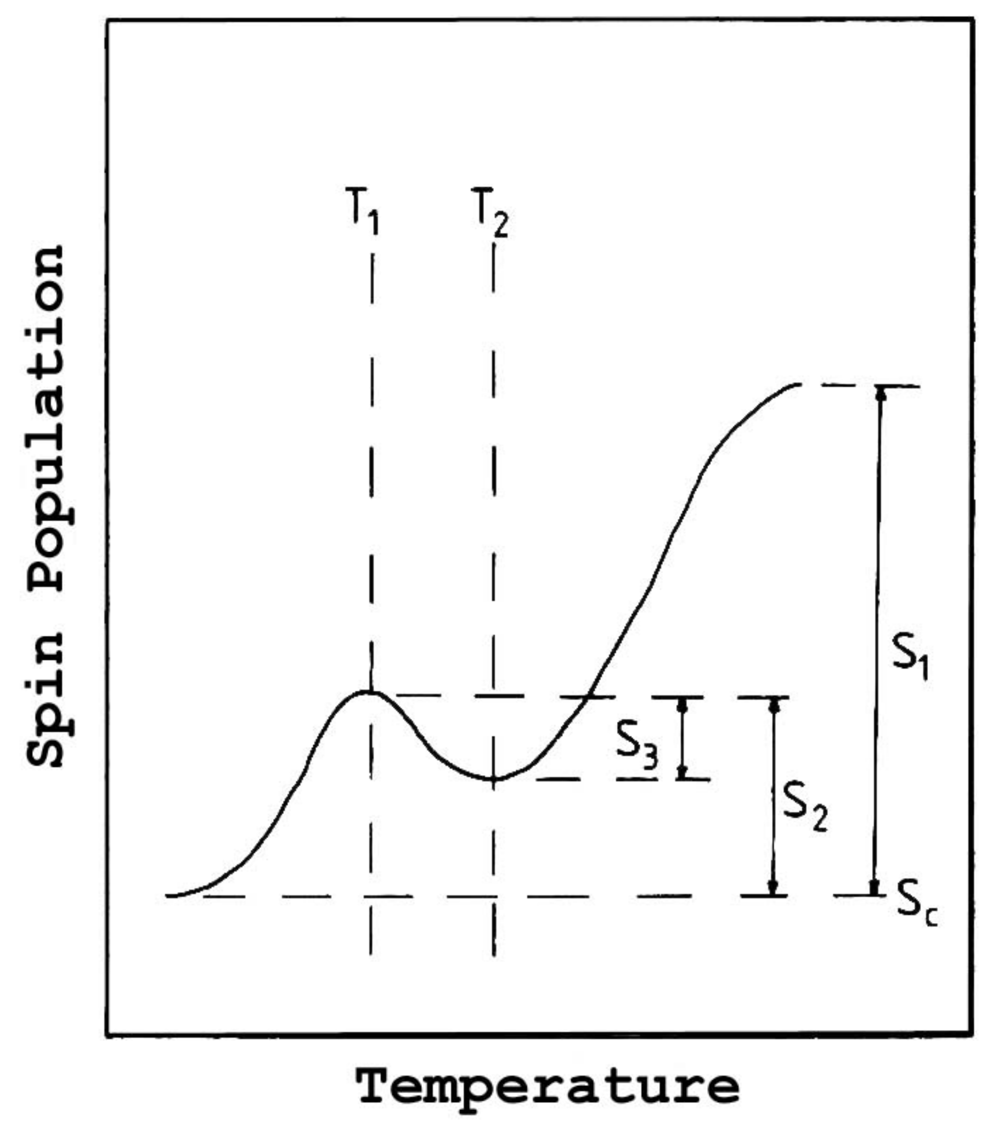
...of coals

Electron spin resonance spectra of pyrolysing coals (ESR)

up to T_1 – oxygen desorption

T1 -T2 – recombinations due to thermally induced mobility of occluded material

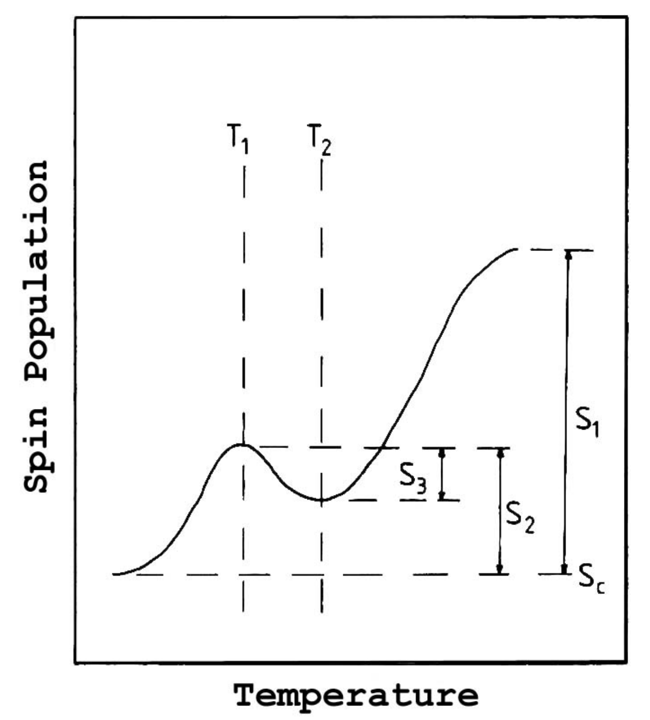
above T2 – Bond rupture



Pyrolysis in the ESR cavity

T_2 shows onset of bond scission reactions from 310 - 340 °C

Fowler, Bartle & Kandiyoti Carbon 1989 *27* 197



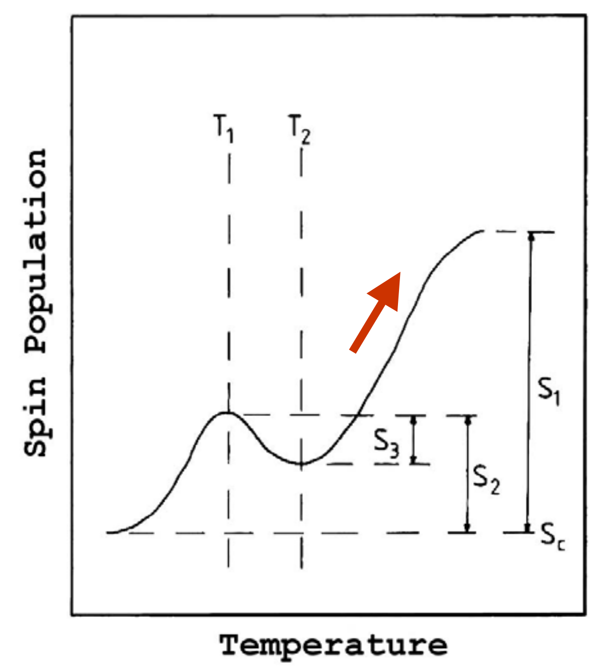
Coal	C-content (%, daf)	T_1 (°C)	T_2 (°C)
Can	54.2	250	310
Burning Star	75.5	220	310
Linby	83.0	205	310
Point of Ayr	85.4	220	325
Cortonwood	87.2	250	340
Cynheidre	95.2	-	-

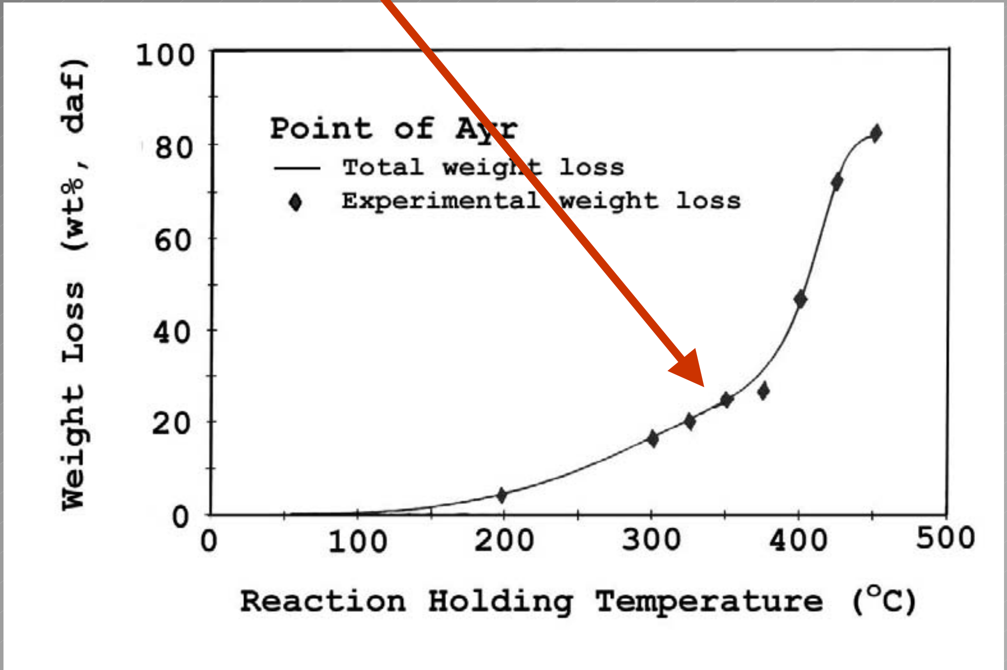
Note that...

- Coals climb high up the ESR curve before significant amounts of extract are released ~375-400 °C

  … showing that…

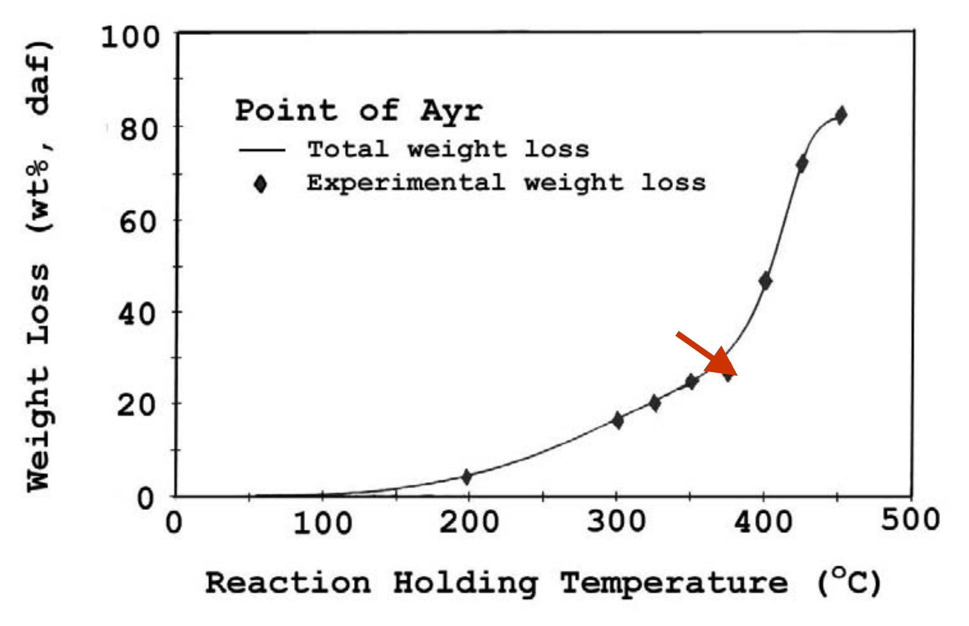
- Many co-valent bonds must rupture before large fragments are released from the solid matrix



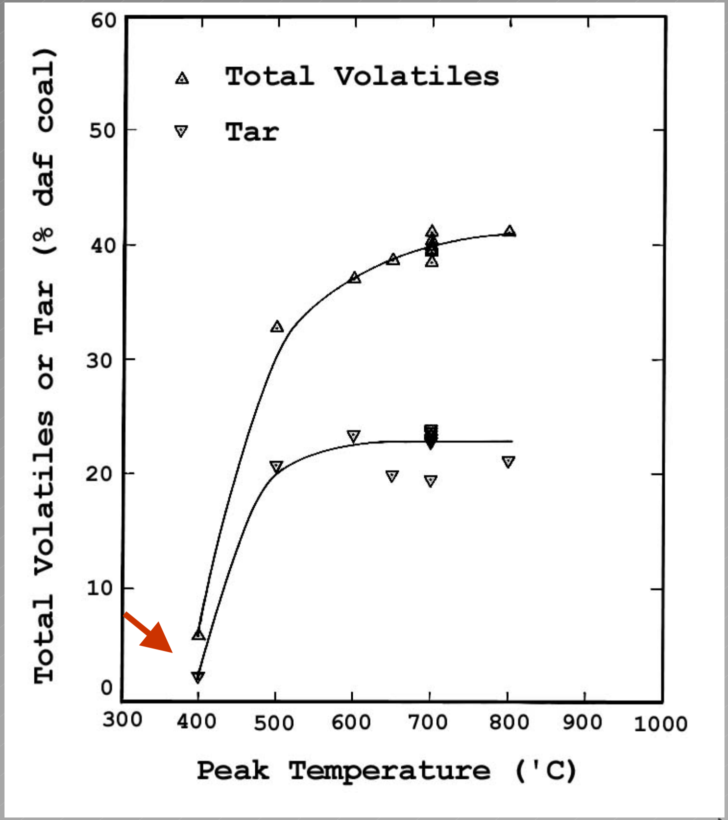


Point of Ayr coal shows this better than some other coals

During liquefaction, we can recover large amounts of extract above 350 - 375 °C in a good solvent

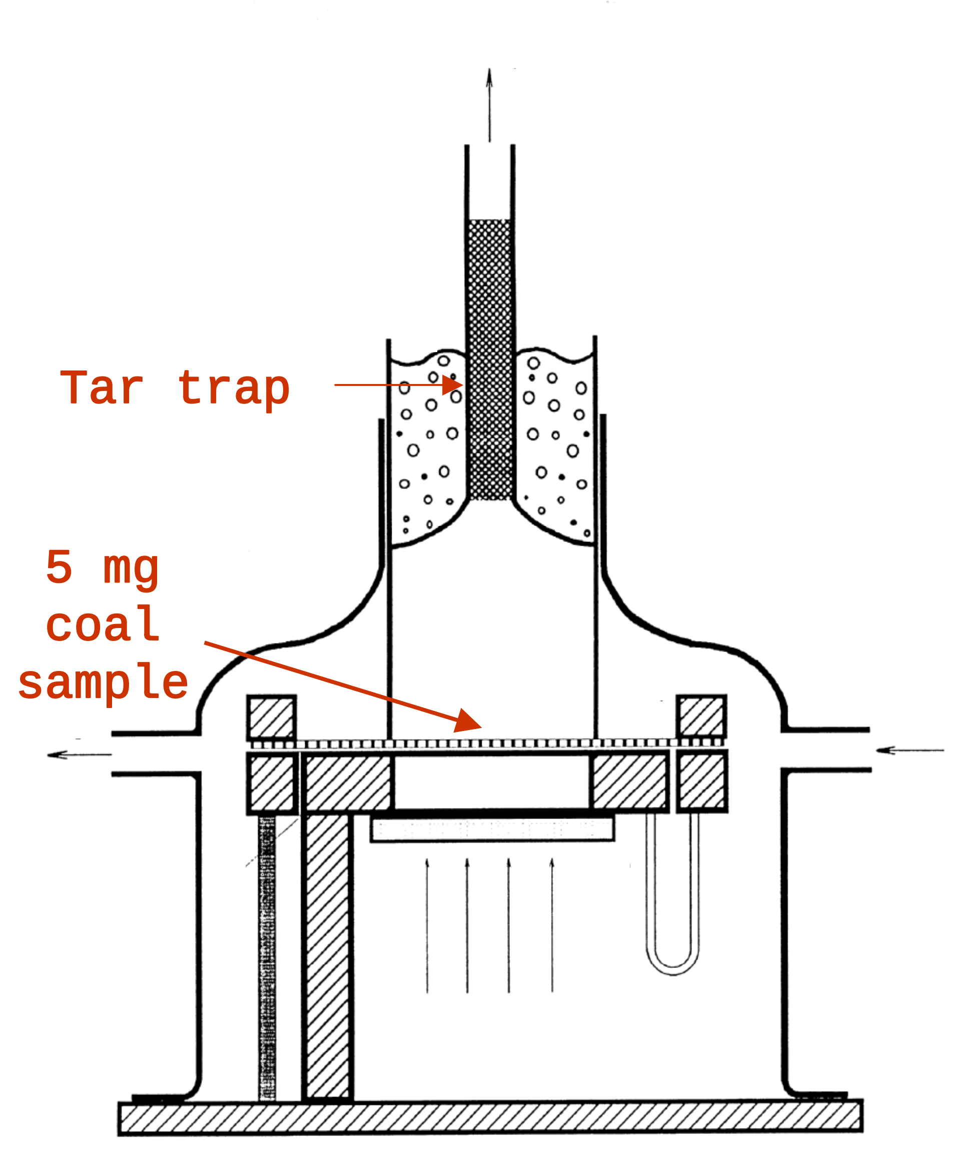


But not in "dry" pyrolysis!



In "dry" pyrolysis, bond scission is similar BUT material released from the solid matrix remains within the coal particles ➔

Pyrolysis experiments: Effect of heating rate



Wire-Mesh Pyrolysis Reactor

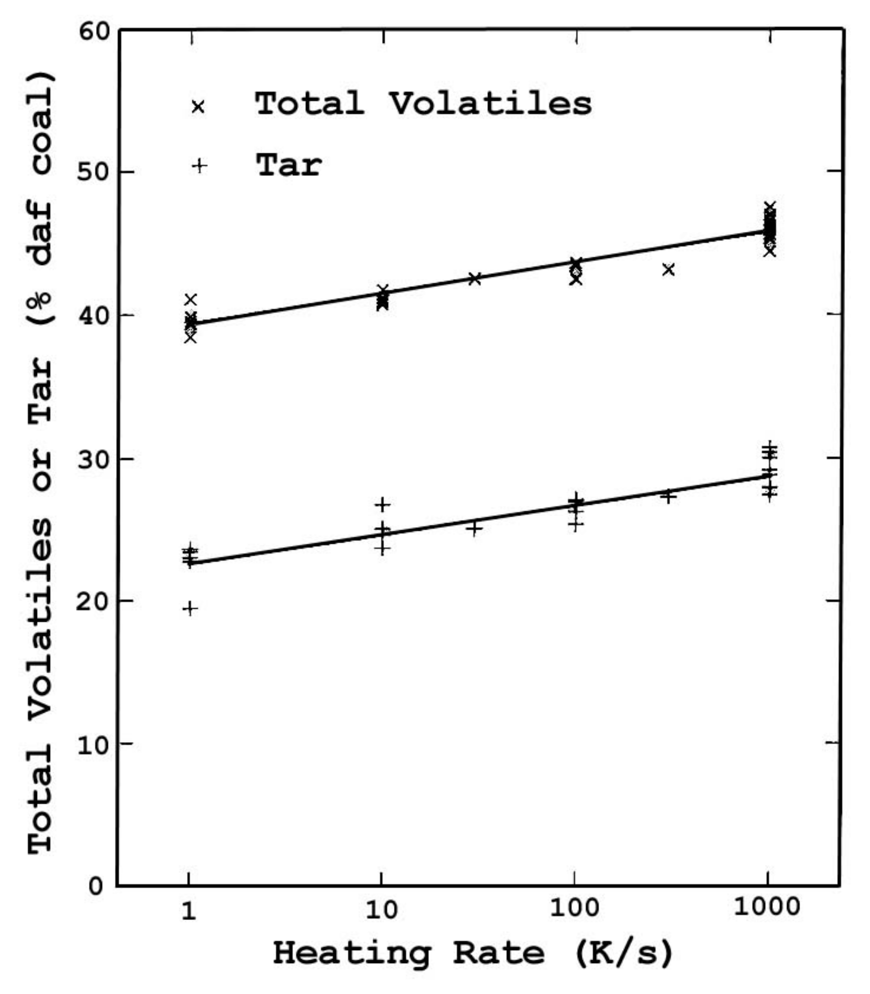
Heating rates variable between 1 °C/s - 10,000 °C/s

Maximum Temperature: 2,000 °C

Product distributions change when the heating rate is increased

Linby coal
700 °C in helium

Particle size
106-152 µm



Gibbins & Kandiyoti Fuel 1989, 68, 895

Extractables as a diagnostic tool for pre-pyrolysis phenomena

Extracting chars heated to 300 – 400 °C with a strong solvent

We know that…

Rapid preheating to ~ 400 °C improves coking properties of weakly-coking coals (pilot plant work,Nippon Steel)

Aramaki et.al.; Tetsu-to-Hagane 1996, *82*,5, 34)

We also know: weakly-coking coals melt *only* when heated rapidly

Example: heating at 1,000 °C s^{-1} to 700 °C

Gibbins & Kandiyoti; Energy & Fuels 2(1988), 505; Fuel 72, (1993), 3

We would like to explain how...

...plastic properties
& swelling ability
(→ coking ability)

of weakly coking coals are improved
by faster heating

~1,000 degrees per second vs. a few degrees per minute

Previous work has shown…

Brown & Waters: Fuel 1966 *45* 17

…that the coking properties of coals correlate with amounts of solvent extractable material found in chars heated to 300-400 °C

Experimental

Samples selected from three coals used by the Nippon Steel Corporation

Coal A Newcastle Blend Coal: weakly coking
Coal B Goonyella: strongly coking
Coal C K-9 Blend: v. strongly coking

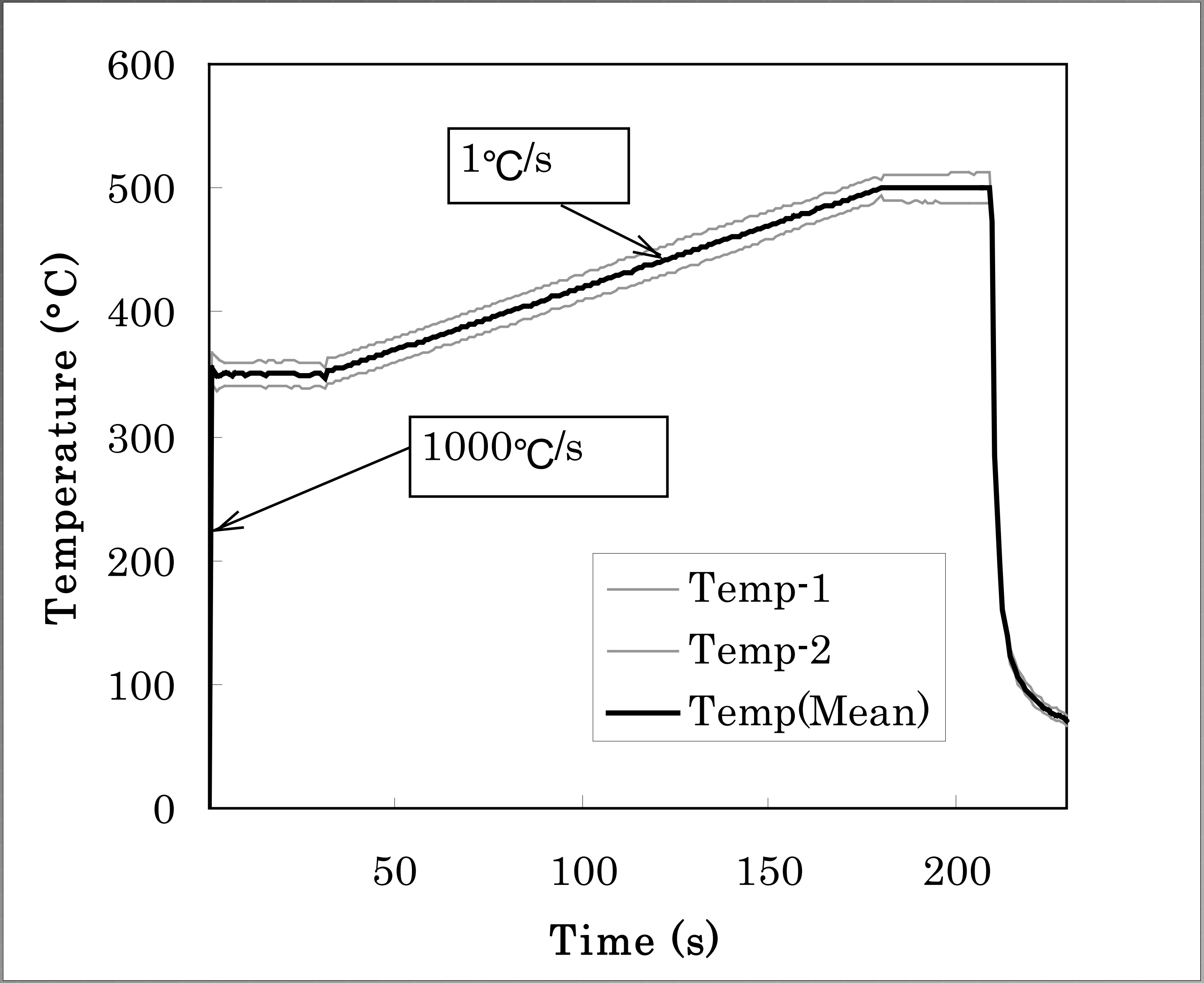
Characteristics of the Coals

	Coal A	Coal B	Coal C
VM	35.2	24.1	17.9
FC	52.4	65.1	72.3
Ash	9.0	9.3	8.9
Crucible SwNo	3.5	6.5	8.0
C (%, db)	83.6	87.7	90.7
H (%, db)	5.6	5.0	4.6
S (%, db)	0.55	0.57	0.15
N (%, db)	1.8	1.7	0.8
O (%, db)	8.3	4.8	3.3

We simulated rapid heating conditions in the laboratory, to examine the behaviour of the samples under near-plant conditions

Heating patterns in the wire-mesh reactor

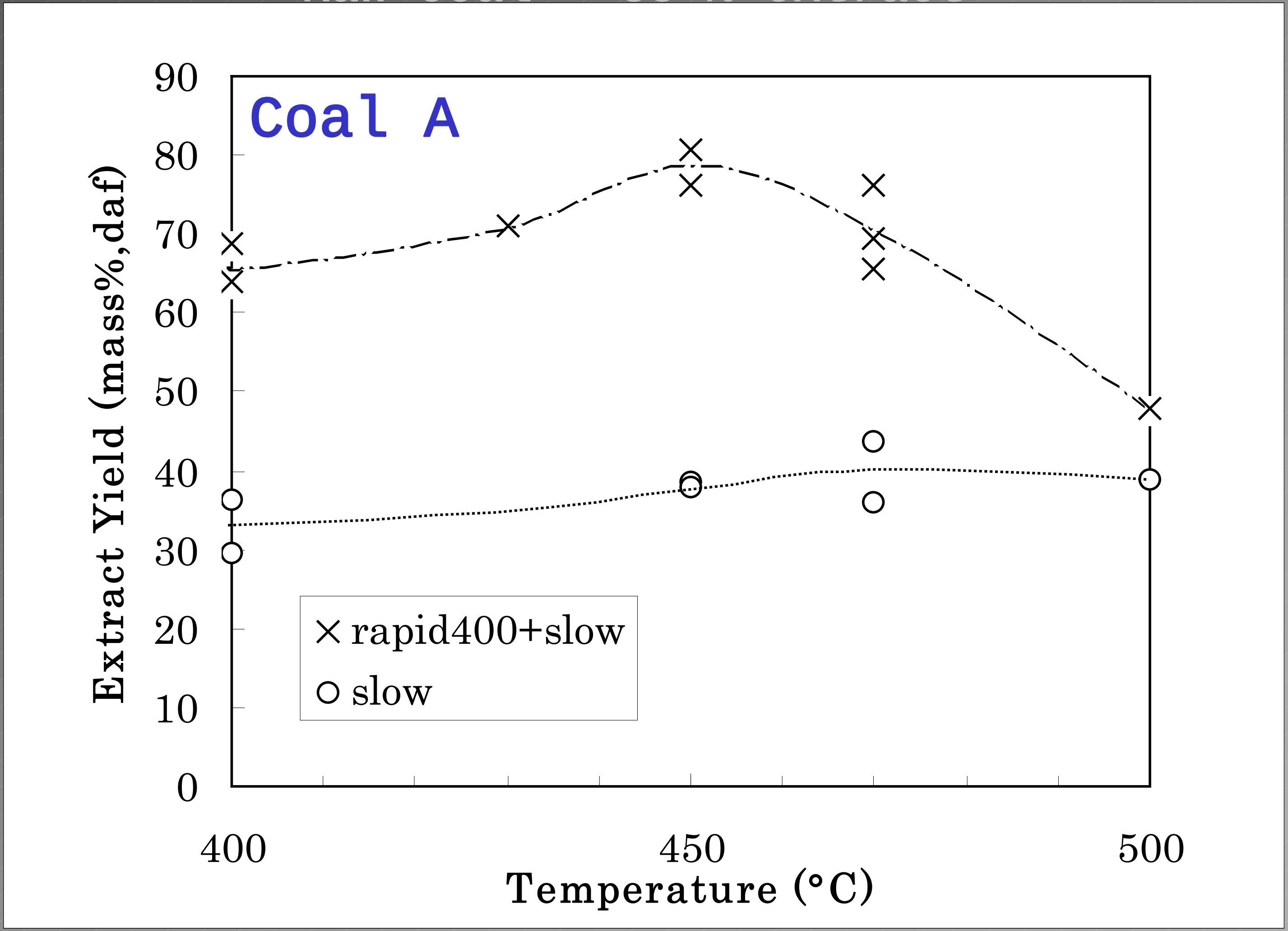
Fast - hold - *Slow* - hold



Experimental Results

Comparing NMP-extract yields for *‘rapid400+slow’* and *‘slow’* heating

Raw coal ~ 35 % extract



Fukuda, K. et.al. Energy & Fuels (2004) <u>18</u> 1140

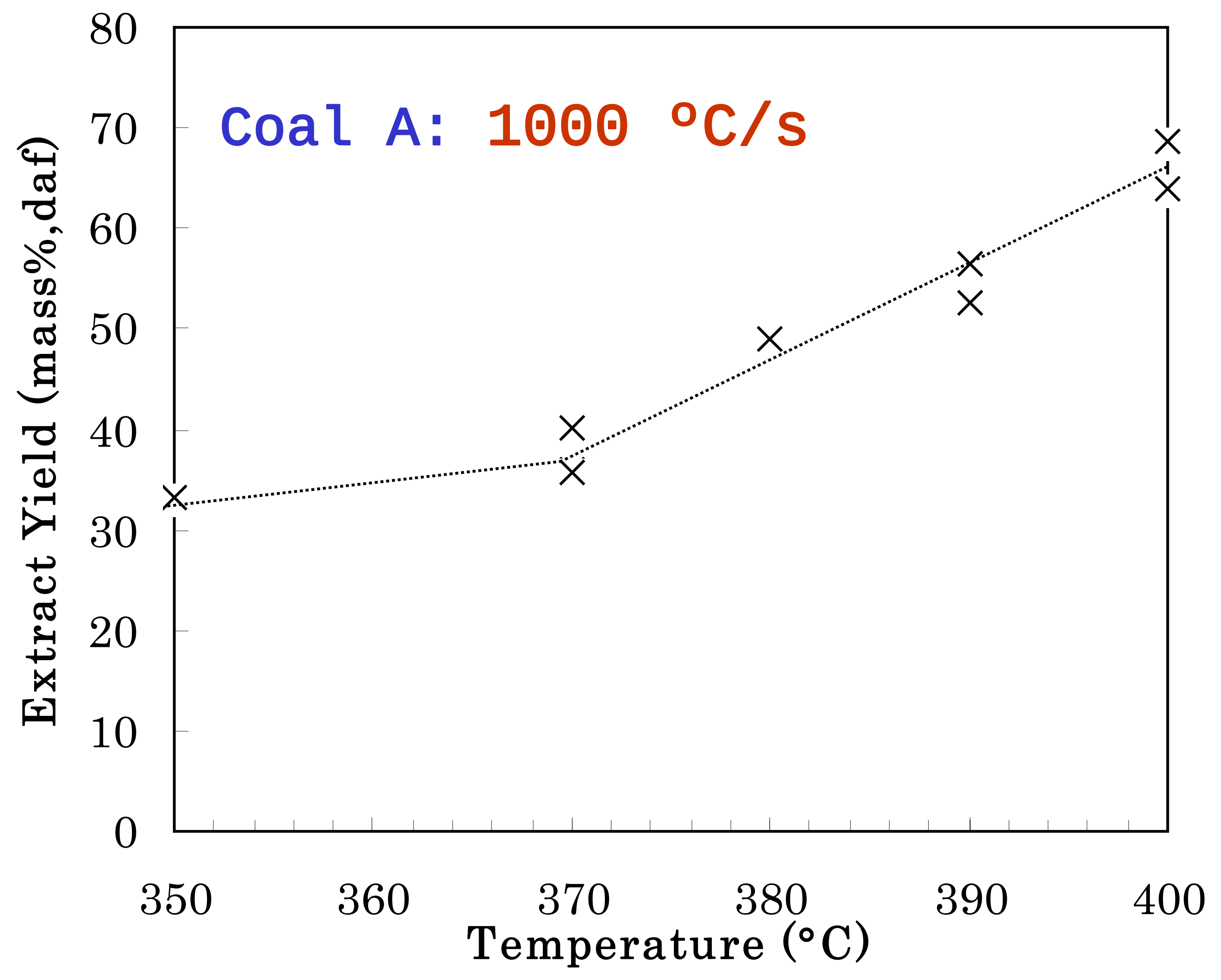
We would like to know whether

✱ there is a characteristic transition temperature?

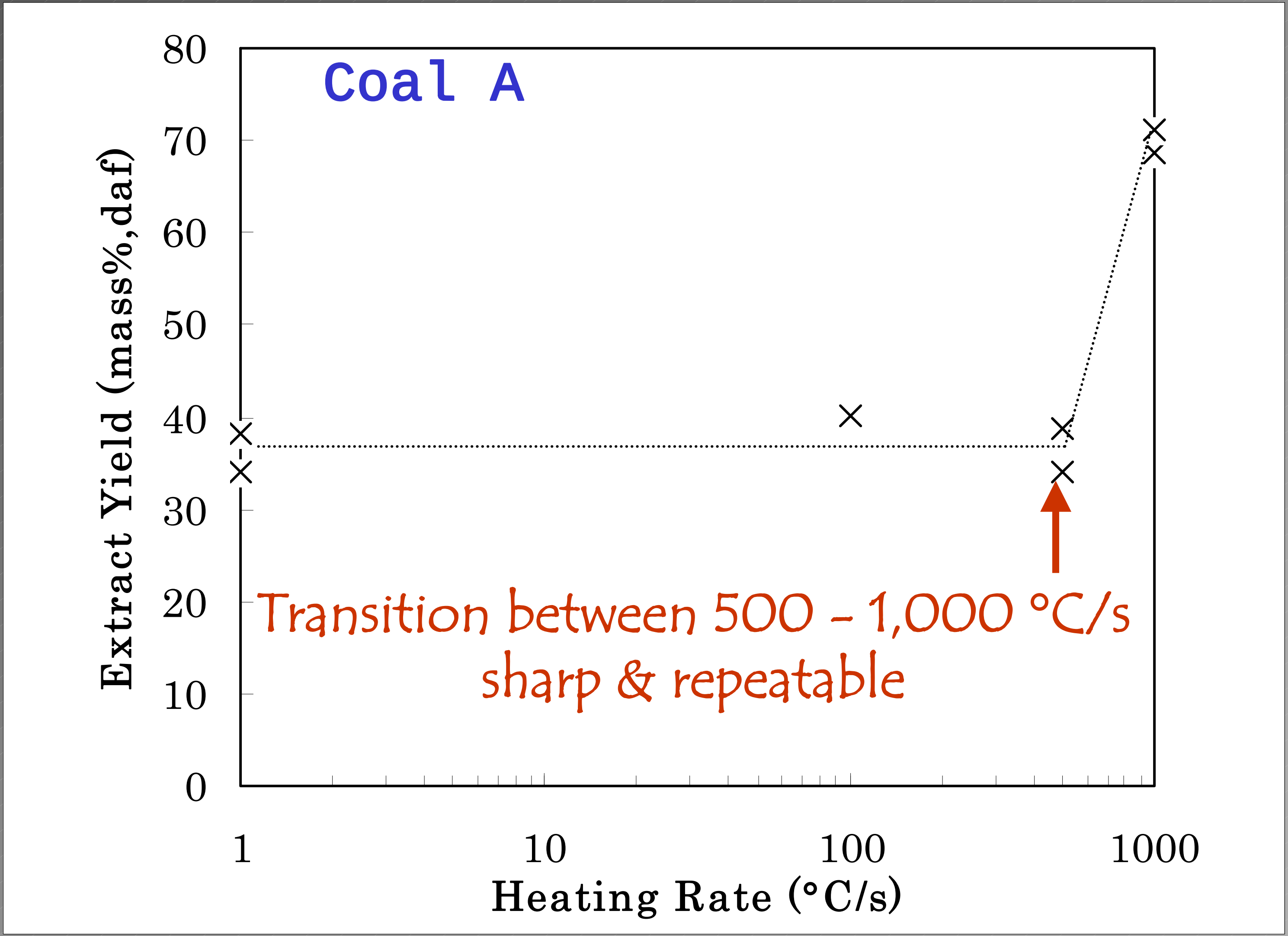
&

✱ what is the range of heating rates that cause the increase in extractables?

Effect of peak temperature on NMP-extracts

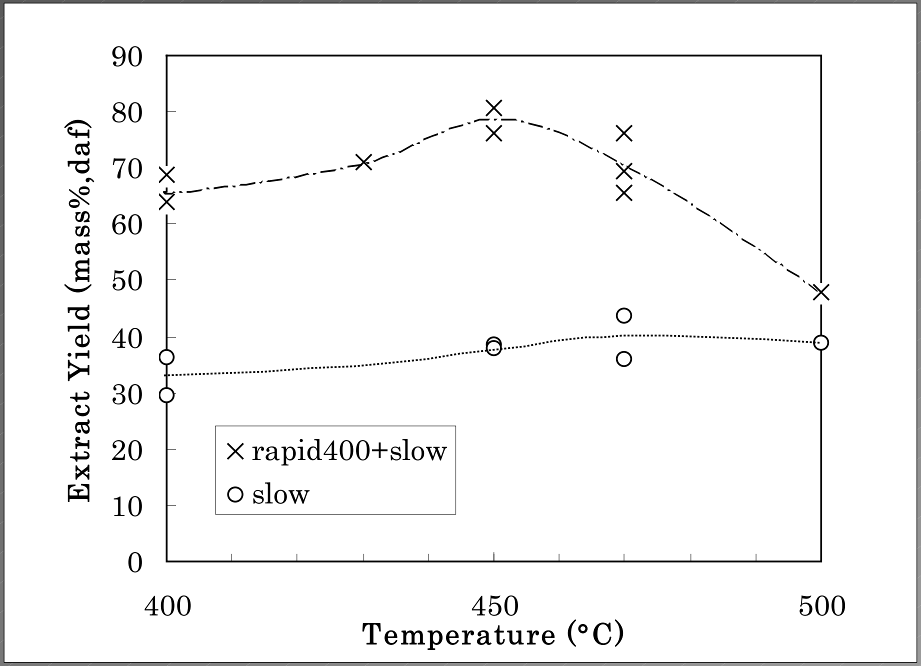


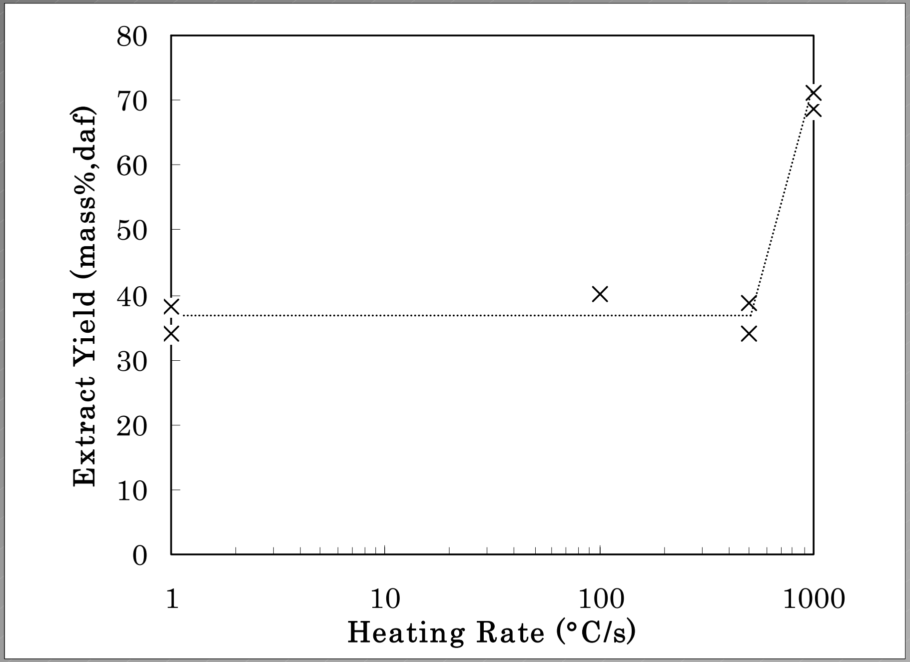
Effect of heating rate on NMP-extracts
Temperature : 400 °C



Transition between 500 - 1,000 °C/s
sharp & repeatable

original coal mass released within coal particles as NMP-extractables is thus a direct function of the heating rate

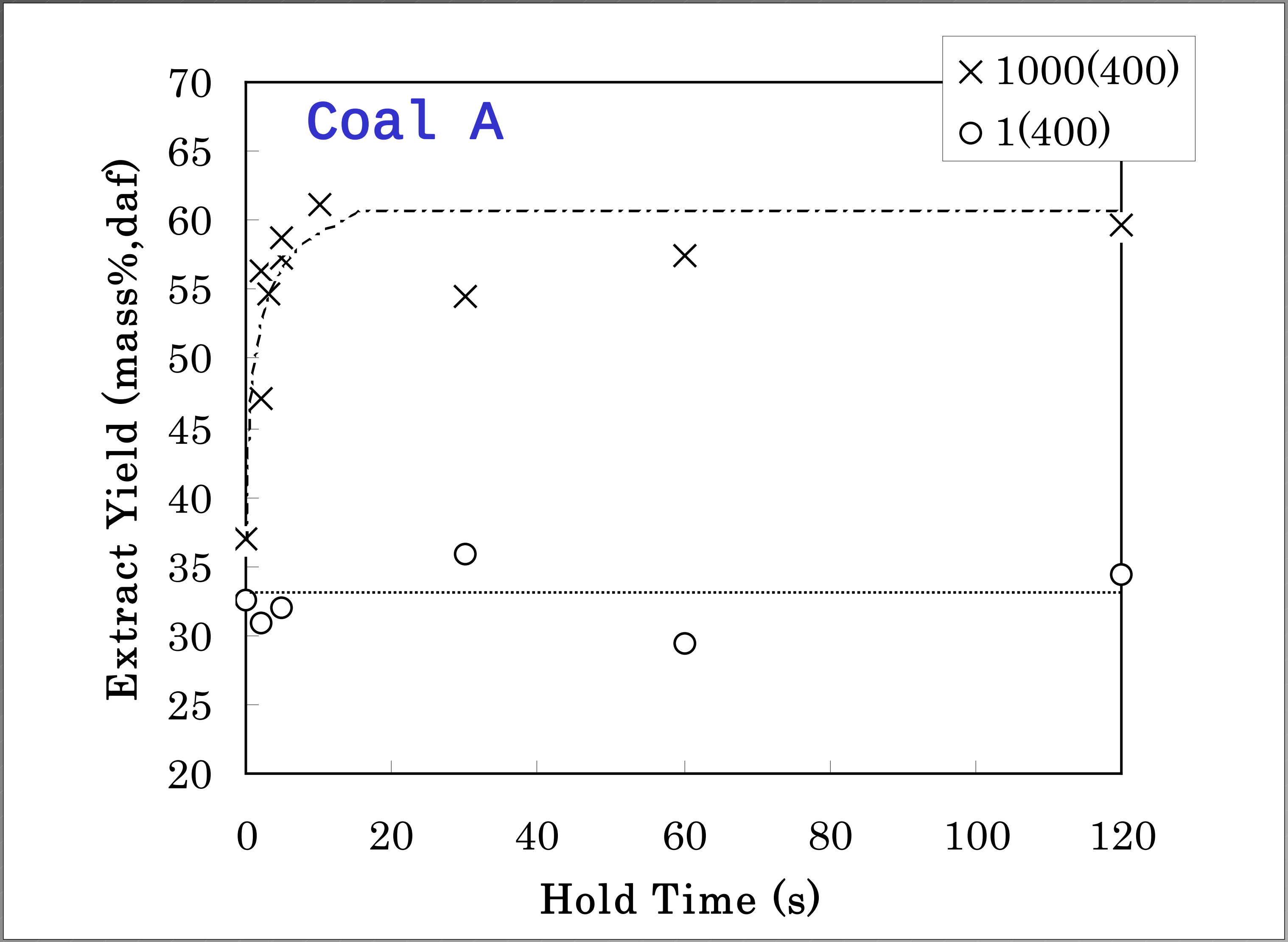




And the effective heating rates are between 500 – 1,000 °C per second for this coal !

… but we still need to explain
why excess extractable material
is formed
during faster heating!

Effect of time on NMP-extract yield
Heating at 1 and 1,000 °C s^{-1} to 400 °C



At 400 °C, repolymerization rate of NMP-extractables negligible during 120 s

… the stability of extractables during 2 minutes allows for agglomeration into lumps in coke ovens

We also know that:

Plasticity and extractable content are linked

The temperature of maximum extractables of Coal A was near the temp. of maximum thermo-plasticity found by Giesler plastometry

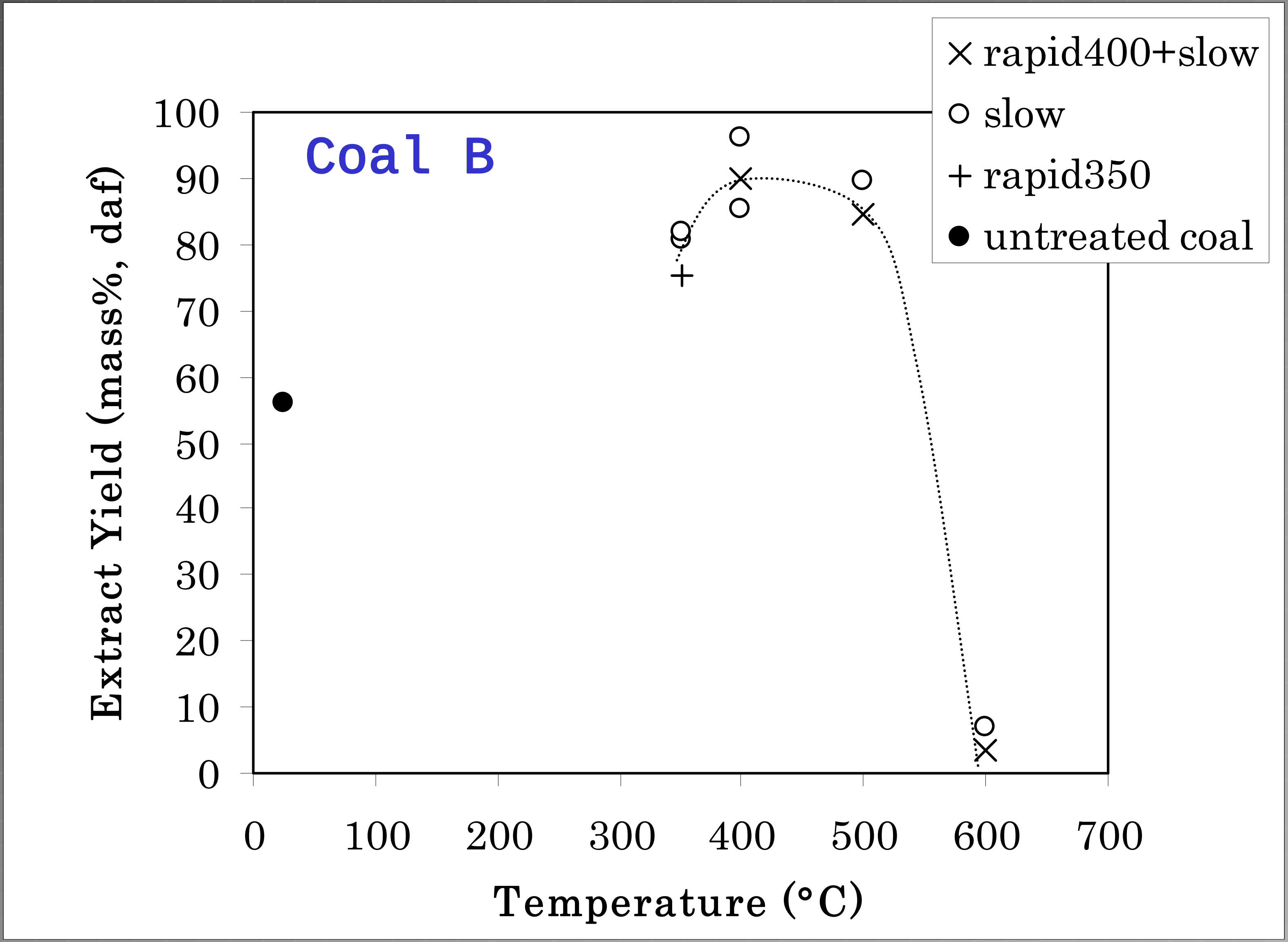
At higher temps, a correlation exists between minimum viscosity and maximum (pyridine) extractables content using a ‘fast-response plastometer’ Howard *et.al.* Fuel 65 (1986) 195

rapid heating thus leads to improved coke strength via a related increase in thermo-plasticity

Now let us examine the behaviour of “GOOD” coking coals

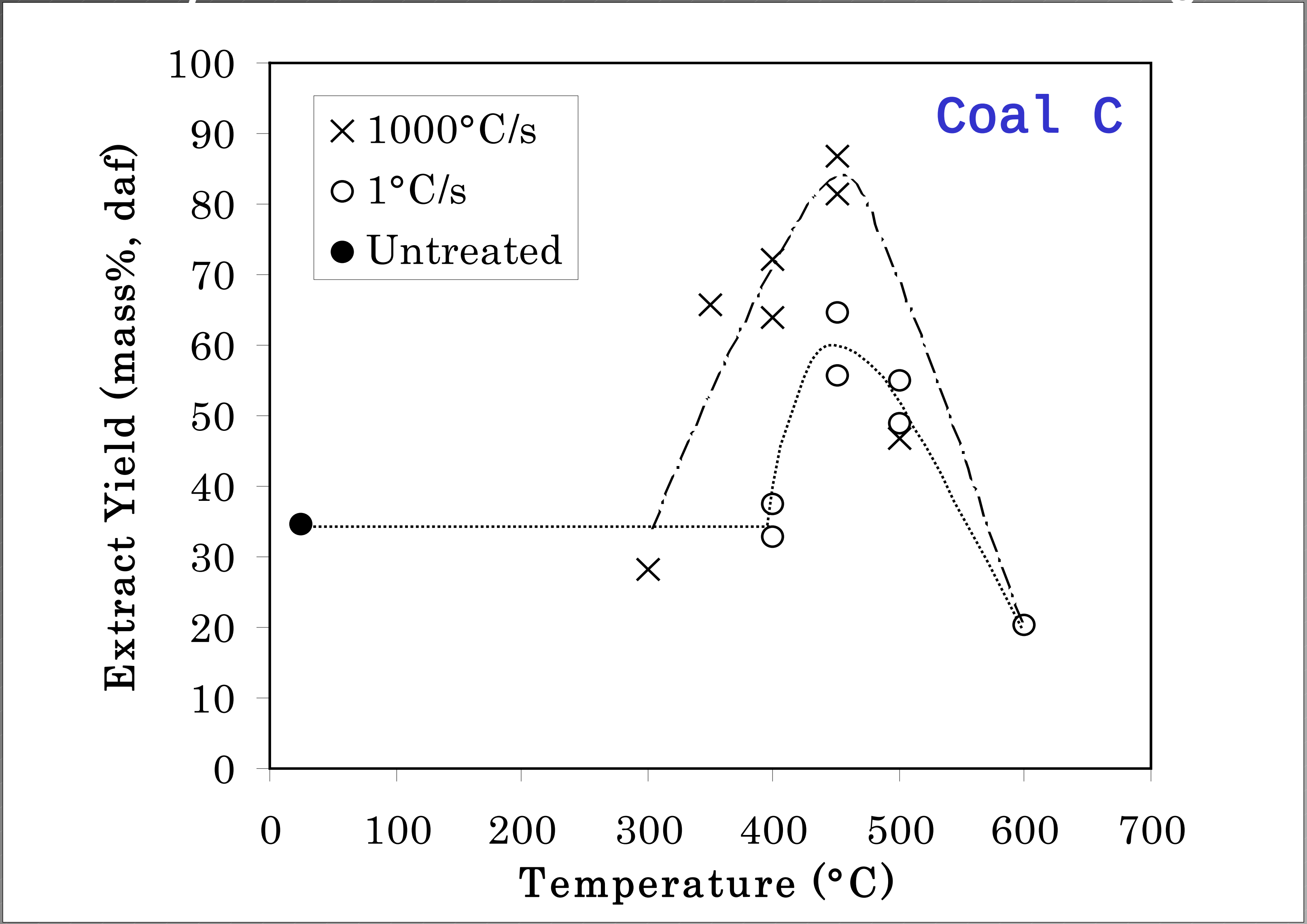
in analogous experiments

Comparing NMP-extract yields for *'rapid400+slow'* and *slow'* heating



Marked difference with behaviour of weakly coking Coal A

Comparing NMP-extract yields for *‘rapid400+slow’* and *slow’* heating



Behaviour of Coal C intermediate between Coal A and Coal B

We have observed that:
High heating rates promote plastic behaviour in weakly coking coals

Good coking coals show plastic behaviour anyway, … irrespective of heating rates

But why do high heating rates enhance the melting & coking properties of weakly coking coals?

Higher tar yields during fast heating was explained by the explosive ejection of tar precursors (i.e. extractables) … it helps reduce the probability of repolymerization reactions of tar-precursors

Grey V.R. FUEL 67, 1988, 1298

We observed (in Coal A), there is a larger amount of extractable material → a larger pool of tar pre-cursors which (according to Grey) gets explosively ejected, enhancing tar yields

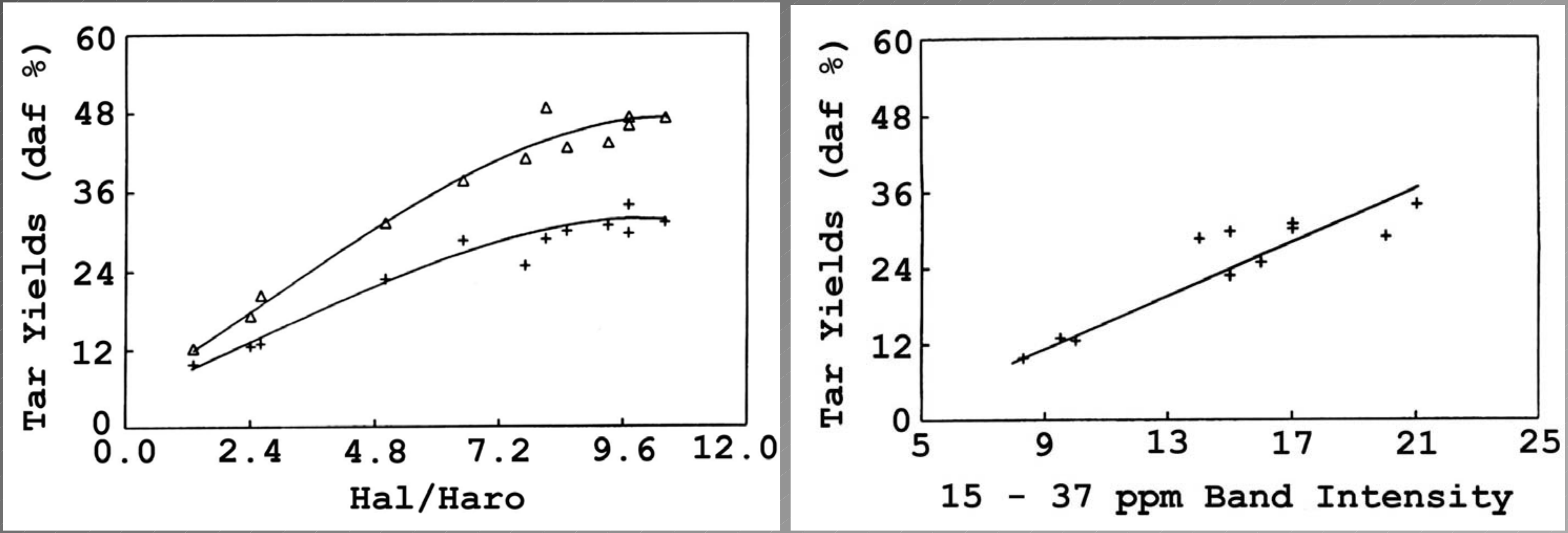
So all that hangs together!

However, we still need to explain why there was more extractable material in the rapidly heated chars!

Could we find a clue by looking at molecular structures that contribute to extractable (& tar) formation ?

We have some relevant spectroscopic data…

We have data showing correlations between tar yields and (Aliphatic + hydroaromatic) structures



We also know simple aliphatics do not assist liquefaction

***Left**: FT-ir-derived aliphatic: aromatic hydrogen ratio : + tar, Δ TV*
***Right**: ^{13}C-n.m.r-derived 15 – 37 nm aliphatic band intensity*
Rank-ordered series of Northern Hemisphere coals.

Pyrolysis in atmospheric pressure helium at 1000 °C/s to 700 °C with 30 s holding time.
Fuel 1994,73,851

We do not have a rapid & accurate method to measure hydroaromatic content in coals

…but we have just seen evidence

suggesting that

<u>hydroaromatic structures promote tar formation</u>

during pyrolysis!

There is a "consensus" view that*

* Before tar evaporation, pyrolysis works as an internal liquefaction process: free radicals are quenched & stabilised by internally released hydrogen

where

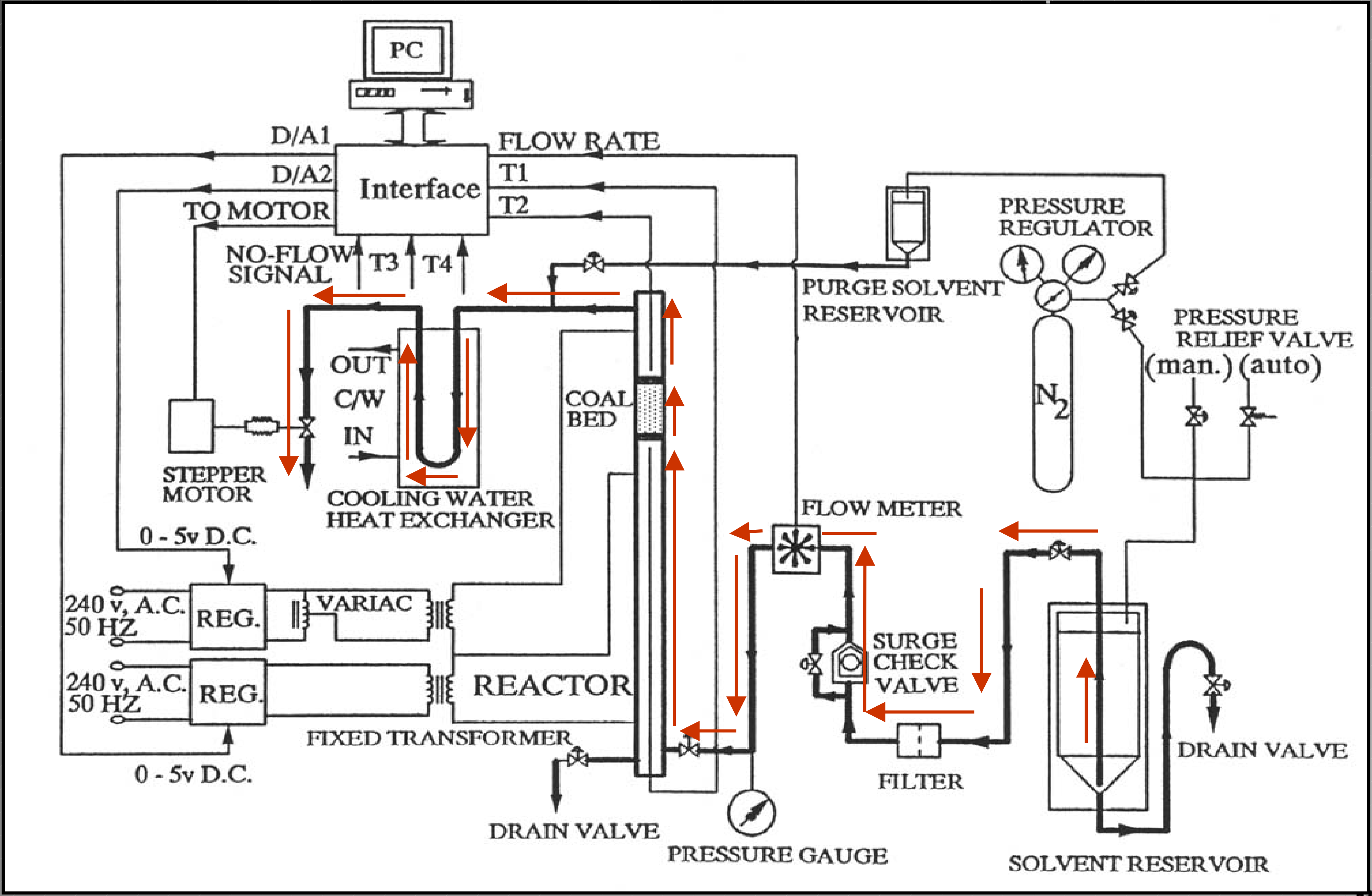
* H-donor ability resides in the hydroaromatic component of the coal

* Brown & Waters: Fuel 1966 *45* 17; Wiser: Fuel, 1968 *47*, 475

Neavel, R. C. Coal Science, Academic Press, 1981, 1-19

The flowing solvent liquefaction reactor

Solvent flow rate: 0.9 ml/second at 70 bar pressure



Xu & Kandiyoti, Energy & Fuels <u>10</u> (1996) 1115

Conversions in the Flowing Solvent Reactor

Liquefaction Experiments

(% w/w daf basis)

H.Rate °C/s	Hold time(s)	Solvent	Weight Loss 350°C	Weight Loss 450°C
Point of Ayr (vitrinite):				
1,000	**150**	**Helium**	**3.3**	**20.5**
5	400	Tetralin	28.8	77.6
5	400	Q/P*	38.0	73.8
5	400	Quinoline	---	72.7
5	400	Hexadecane	12.5	27.3
Point of Ayr (whole coal):				
5	400	Tetralin	24.6	82.5
5	400	Quinoline	39.5	74.7
5	400	Hexadecane	---	24.0

← Pyrolysis Experiment

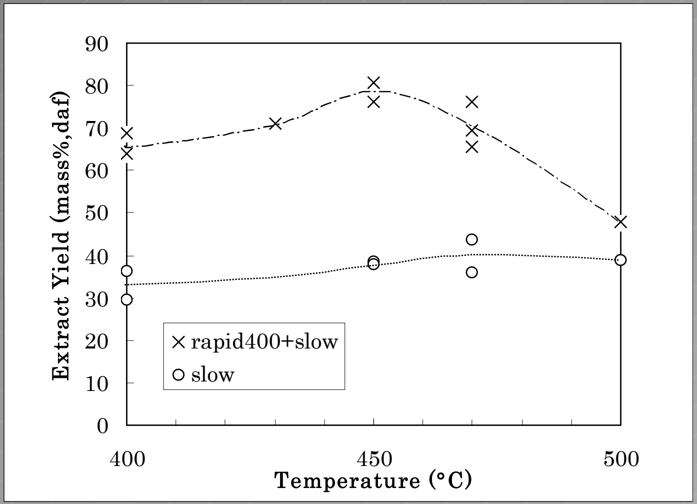
* Q/P: quinoline/phenanthrene (2.5:1 w/w) mixture.

Back to our pyrolysis/extraction data!

It is known that….

* Bond scission rates are dependent on temperature alone (broadly, independent of the heating rate)

* So…differences in extract yield between slow & fast heating for Coal A must arise from <u>more recombination reactions during slow heating !</u>



* In rapid heat-up, 25-28 % *more* of the coal mass, released as extractables into the particle, <u>survived</u> as extractable material … but why?

We know that…

* Fast heating telescopes the sequence of events into a narrower time frame and shifts the temperature scale upwards

* In fast heating, hydrogen released from pyrolysing solids from about ~ 300 °C* remains in contact with the pyrolysing mass up to higher temperatures…

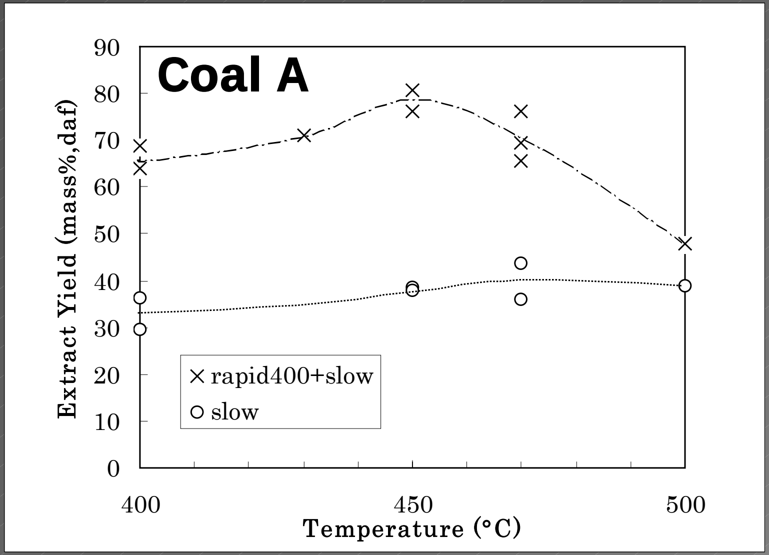
Here we must speculate a little…

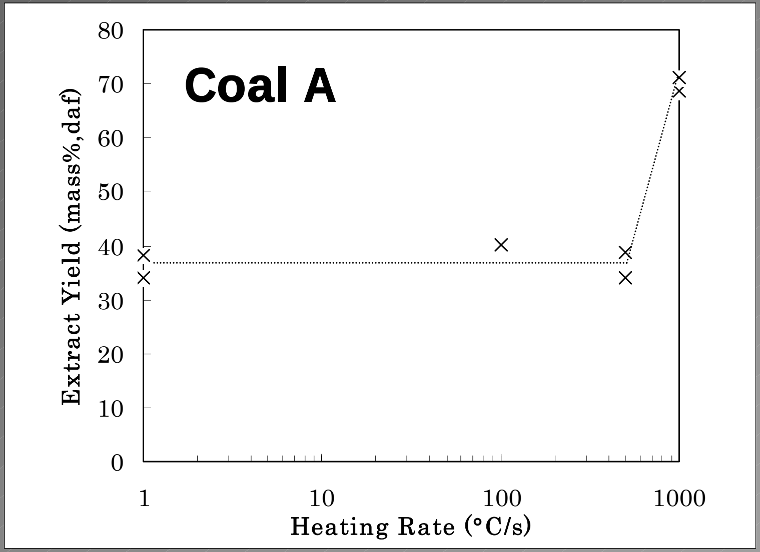
* If the evolving hydrogen reacts with some of the internally released free radicals and blocks recombination reactions, THAT would explain our data…

…and why…

Coal A retained more extractable material during heatup at 1,000 °C s^{-1} compared to 1 °C s^{-1}

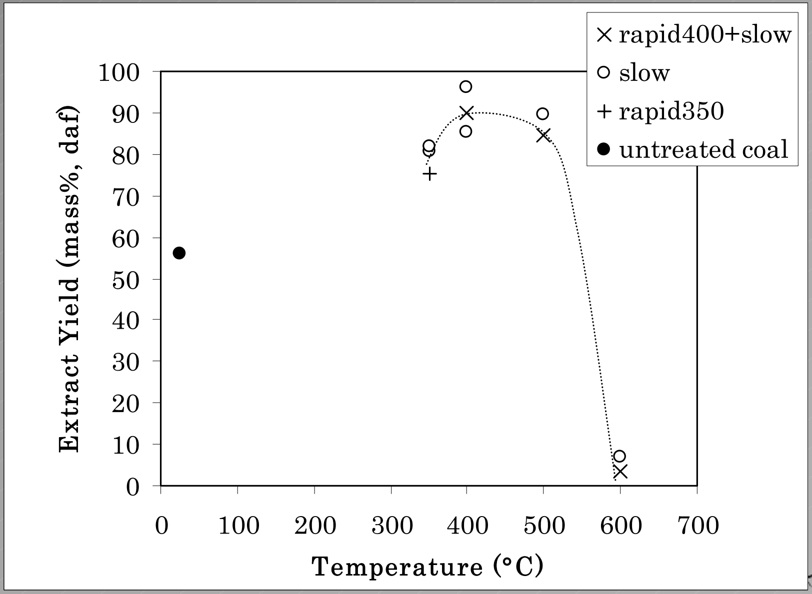
*** e.g. Fuel, 1987, *66*, 486**



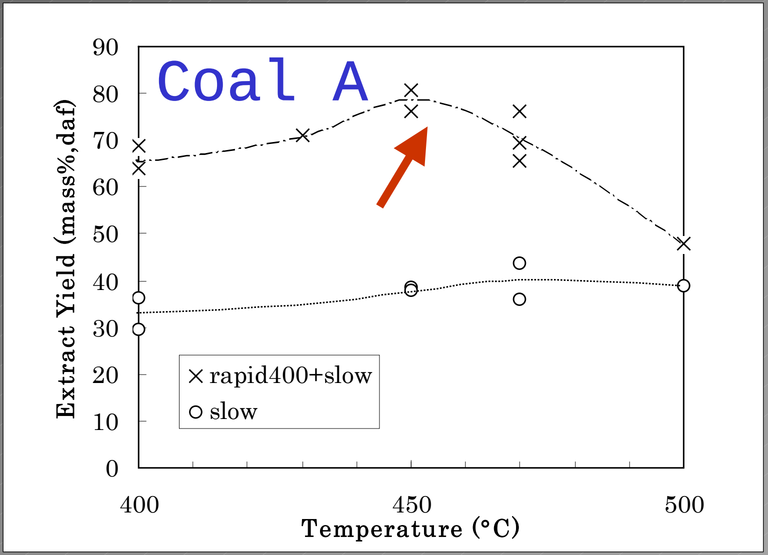


Data show … large proportion of the coal mass converted to solvent extractables, released from the ‘solid’ matrix – & not yet expelled from the particle

AND that a good coking coal did not need high heating rates to do this!
because it already had more H_2 available and less O_2 to scavenge hydrogen

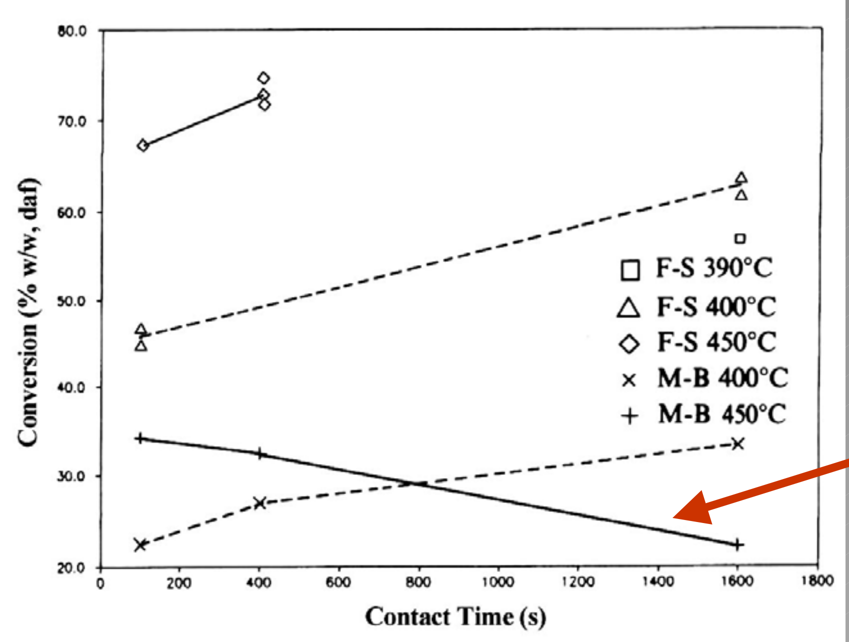


Free radical quenching reactions during heatup must be **RAPID** and different from other recombination reactions we have been able to track→(I)



Also distinct from reactions described by the (II) rate eqn. by Howard et.al. for 600 - 800 °C range

Fuel (1986) *65* 195



←AND distinct from (III) evidence of *slow* recombination reactions during liquefaction at 450 °C in a **batch reactor**, in non-donor solvent 1-methylnaphthalene

Fuel 70, (1991), 380

Taken together these data suggest two sets of events occurring in parallel during heatup :

(i) fast free radical quenching (stabilizing) reactions of reactive free radicals created during heat-up, (probably corresponding retrogressive reactions are also rapid; we have circumstantial evidence for that)

and,

(ii) slower repolymerization/recombination reactions taking place between the more stable (less reactive) free-radicals … → forming char at higher temps!

Again comparing liquefaction conversions in

helium	20 %
hexadecane	27 %
strong solvents	72-74 %
tetralin	78 %

The manner of releasing depolymerized material from particles depends not only on density (i.e. gas or liquid) but also on chemical nature of solvent (solvent power and/or donor ability)

The difference between 72-74% and 78 % (or 75 and 82.5 %) shows material that has rapidly repolymerized)

Summarising our findings…

* Initial thermal breakdown reactions during pyrolysis & liquefaction in coals are similar, occur ~ 310-350 °C

* Several bonds must break before the solid matrix releases tar precursors into solid particle

* Exit of depolymerized material from particles depends on the chemical characteristics of the medium: Conversions in hexadecane (a liquid) and helium (a gas) were not much different!

* Liquefaction in a good (non-donor) solvent does not allow all depolymerized material to be carried away.

on the other hand, during "dry" pyrolysis …

at 400 °C, most of the extractables are still intact within the coal particle

When the temperature is raised further,

- some of the lighter components evaporate
- most of the extractables crack, producing lighter tar & light gases
- but a significant amount of the extractables recombines to form char

That is why we get 50-60 % char during dry pyrolysis!

…and going back to coking

* The effect of heating rate is only noticeable when the sample coals are marginally deficient in donatable hydrogen

* Similarly liquefaction in hydrogen donor solvent shows no effect of heating rate (nor does Goonyella coal)

More generally…

* There appear to be <u>very rapid</u> and <u>very slow</u> radical recombination reactions ~ corresponding to the more stable & more reactive free radicals formed during thermal Breakdown!

Why have we done all this work?

Does coal have a place in our future energy mix ?

Thank you for your attention!

It is with pleasure and appreciation that I acknowledge the work and help of all my friends, associates and students…

Tim Fowler, Keith Bartle, Alan Herod, Koichi Fukuda, Denis Dugwell, Nigel Paterson, James Harrison, David McCaffrey, Jon Gibbins, Xu Bin, Cai Haiyong, Li Chunzu, Trevor Morgan, Raymond Chan, Alec Gaines, Geoff Kimber, Sam Moore, Shebnem Madrali, Dick Wood, Malcolm Dix, Robert King, Tony Meredith
… and so many others who have contributed to this work…