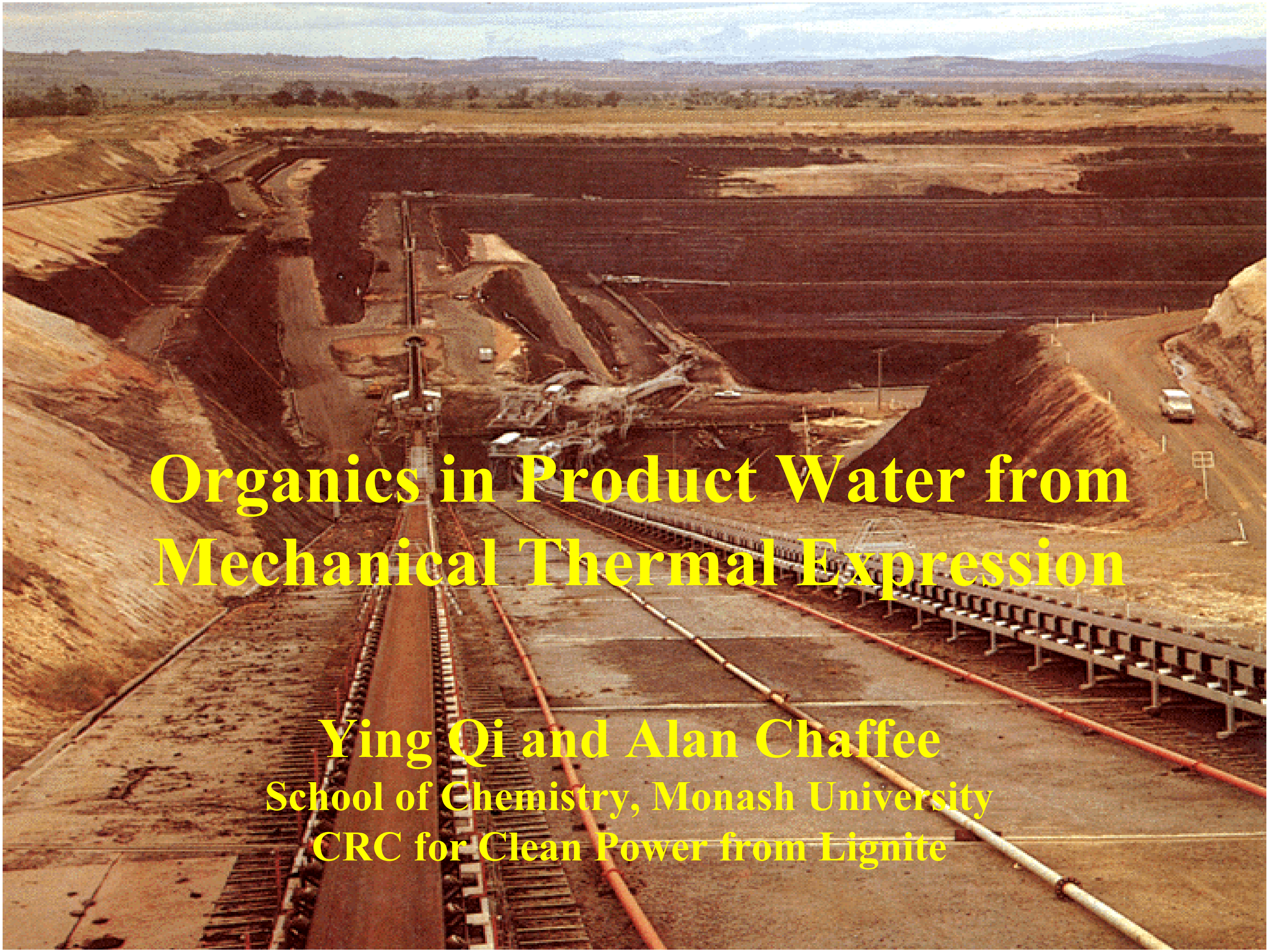

Organics in Product Water from Mechanical Thermal Expression

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School of Chemistry, Monash University
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TtH • Story • Digs to Offer*
Faith still had one arm locked around **Professor Snape's** neck. **...** They placed their hands on the shoe though, **dirt**, gum, and hair be damned. **...**
www.tthfanfic.com/Story-4658/echo+Digs+to+Offer.htm - 30k - Cached - Similar pages

A little **dirt** with your tea, sir or The Story of Buh Buh Bobbin
"**Dirt**. I know." she smiled. "I often accused Elrond of trying to pull one **...** Stop chewing on **Professor Snape**'s stool." The wolf took one long look at the **...**
memnet.tripod.com/tellindar10.htm - 41k - Cached - Similar pages

Occlumency :: A Severus **Snape** archive
Professor Severus **Snape** reflects back on his past, both the hate and the painful **...** Severus **Snape** sat, staring out of the **dirt** streaked window of his cold **...**
occlumency.sycophanthex.com/viewstory.php?sid=1100 - 12k - Cached - Similar pages

Occlumency :: A Severus **Snape** archive
... Morgan felt blood there. This was all she needed: to be conked out on a forsaken **dirt** road. **...** "Of course, **Professor Snape**, it's just a little cut. **...**
occlumency.sycophanthex.com/viewstory.php?sid=4108 - 35k - Cached - Similar pages

Harry Potter and the Idolatry of Yore
Your **Professor Snape** knew this." Madam Pomfrey's jaw fell open as she suddenly **...** **Snape** looked down at the **dirt** before continuing. "I found her, Harry. **...**
www.dprophet.com/iofy/chap33pg2.html - 11k - Cached - Similar pages

Professor Snape {er}... Answers Your Questions
Professor Snape {er}. **...** **Snape** and Sarah are sitting at the kitchen table, twiddling their thumbs and whistling nonchalantly. When you're stuck in a house **...**
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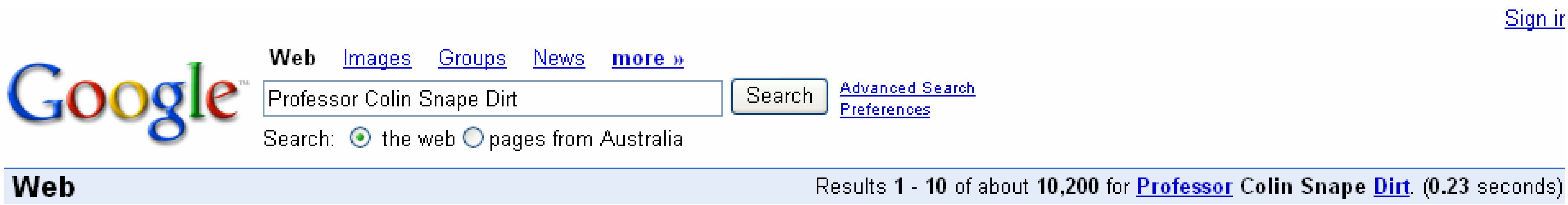
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The oil and **steroid** detector. We don't normally put oil exploration and **steroid** abuse. detection in the same box, but **Colin Snape** and team at the ...
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Colin E. **Snape**. 1. , Will Meredith. 1. and Gordon D. Love ...
colin.snape@nottingham.ac.uk. 2. Department of Earth, Atmospheric and Planetary Sciences, ...
www.nerc.ac.uk/funding/thematics/ oceanmargins/regform/Snape_abs.pdf - Similar pages

Asteroids and **Steroids**
Ida **Steroids** and asteroids have now got more in common than just seven letters. ... a team led by Prof **Colin Snape** at the University of Nottingham,have used ...
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Scientists make step forward in drug detection - News Archive ...
The research, being led by Professor **Colin Snape** in the University's School ... even the new designer **steroid** specifically manufactured to avoid detection ...
research.nottingham.ac.uk/ NewsReviews/newsDisplay.aspx?id=137 - 12k - Cached - Similar pages

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City leads field in drug testing

A new detection system to test athletes for performance-enhancing drugs is being developed.

Scientists at the University of Nottingham believe their research will provide a more reliable way of detecting drug molecules in the body.

The technique they are studying is normally used to aid oil exploration by splitting small fragments of organic matter fro petroleum rock.

Scientists think the system could allow them to pinpoint banned substances.

The modified technique can recognise the origin of any carbon-based molecules, including fatty acids and steroids, in the body.

> **"In effect, you are what you eat plus a little bit of what you might inject"**
>
> Professor Colin Snape

Previous testing techniques have been unable to offer a precise detection method.

Professor Colin Snape, based at the university, said: "In effect, you are what you eat plus a little bit of what you might inject.

"In their natural form, however, the body's molecules are too 'sticky' for accurate measurements by our laboratory equipment."

"In effect, you are what you eat plus a little bit of what you might inject"

Professor Colin Snape

drug
01 Feb 05 | SOL
- Team GB get clean bill of health
11 Nov 04 | SOL

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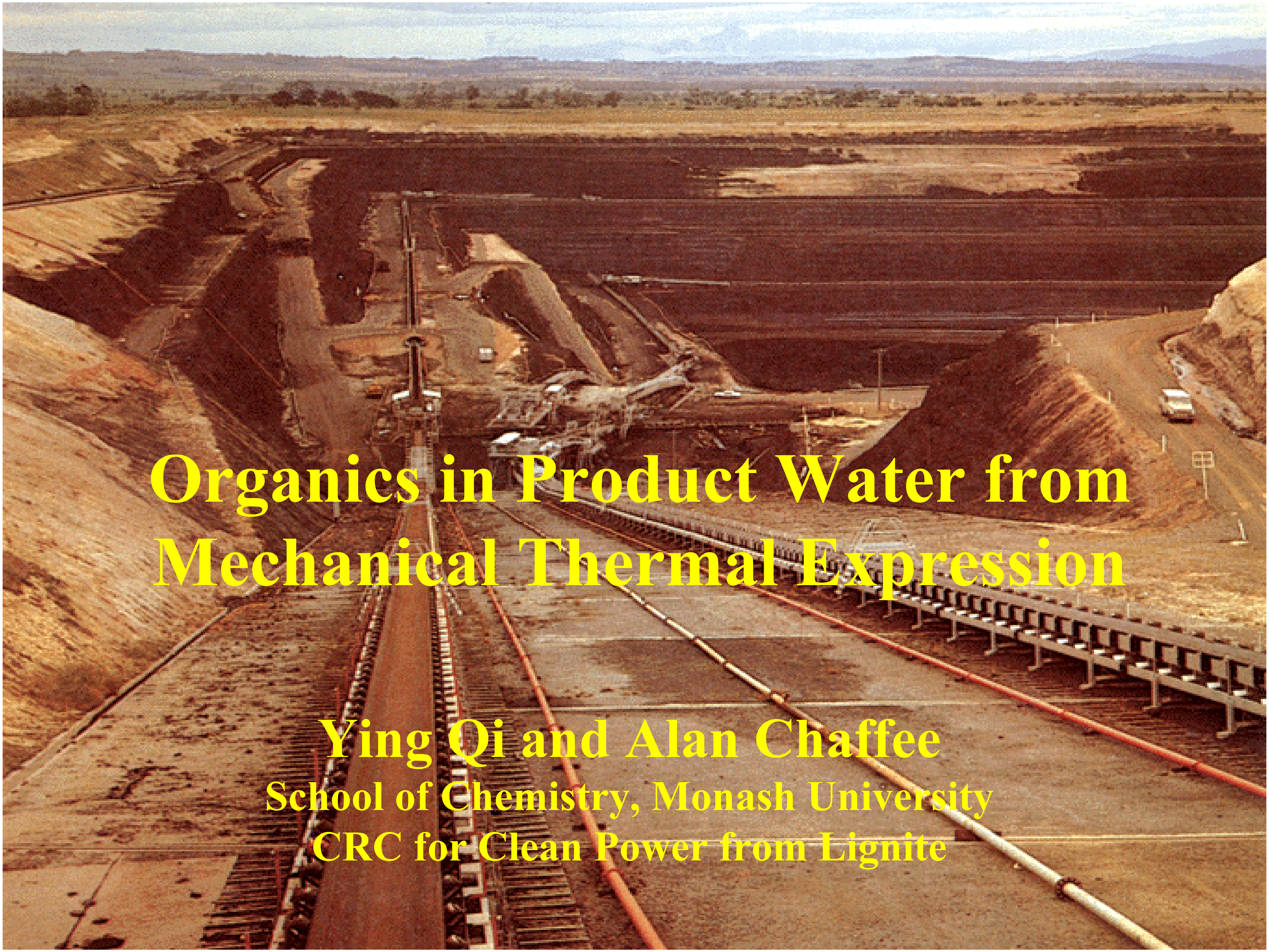
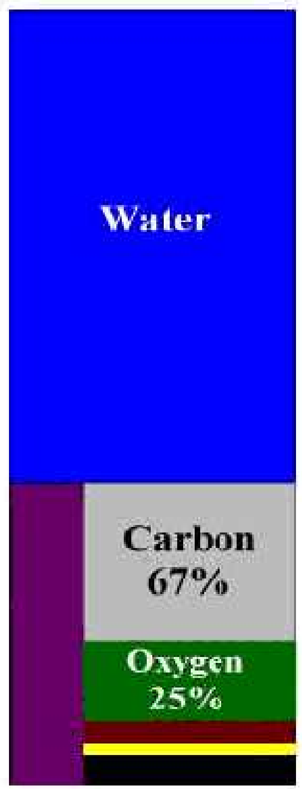


Organics in Product Water from Mechanical Thermal Expression

Ying Qi and Alan Chaffee
School of Chemistry, Monash University
CRC for Clean Power from Lignite

WATER PROBLEM IN BROWN COAL

DRY BASIS		WET BASIS
Water 150 g		Water 60%
Coal 100 g		Coal 40%



More Water than Coal

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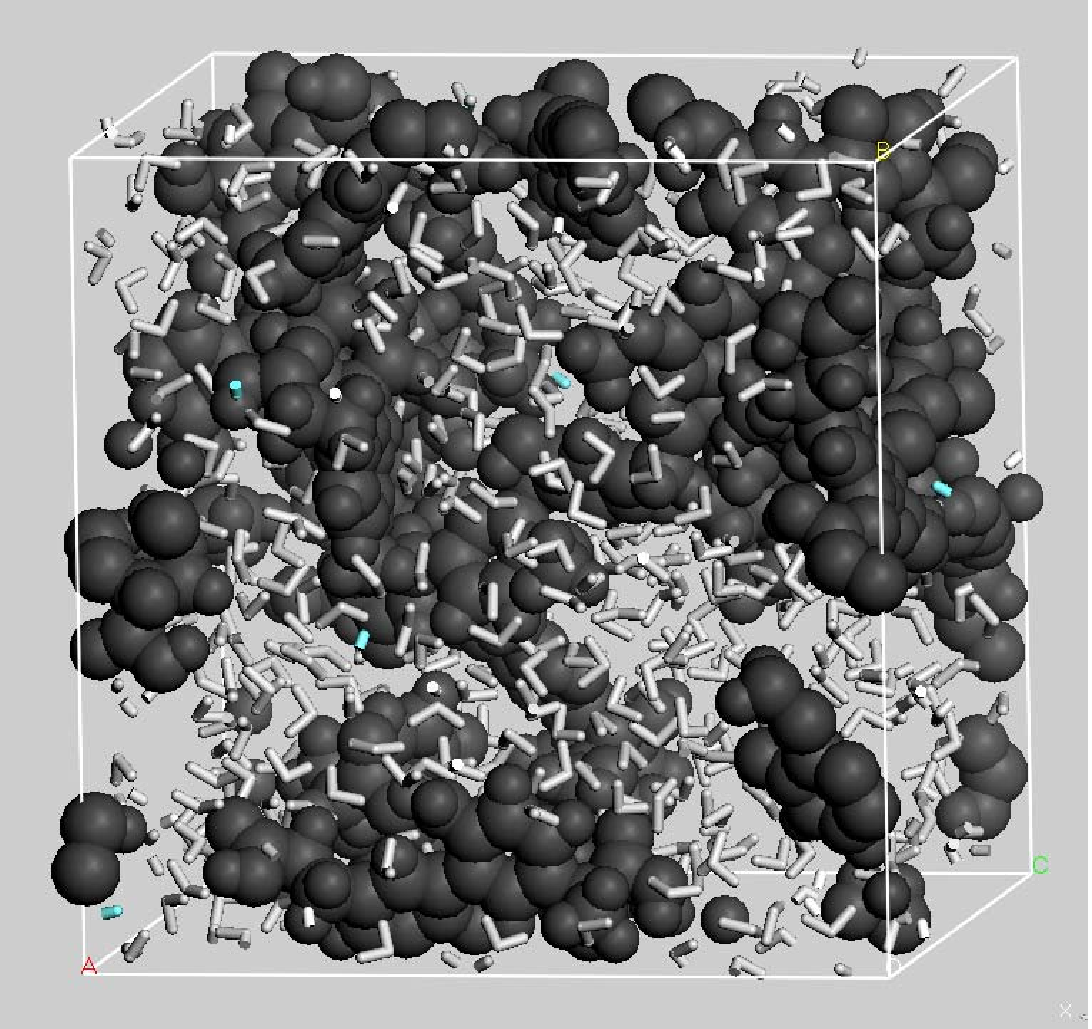
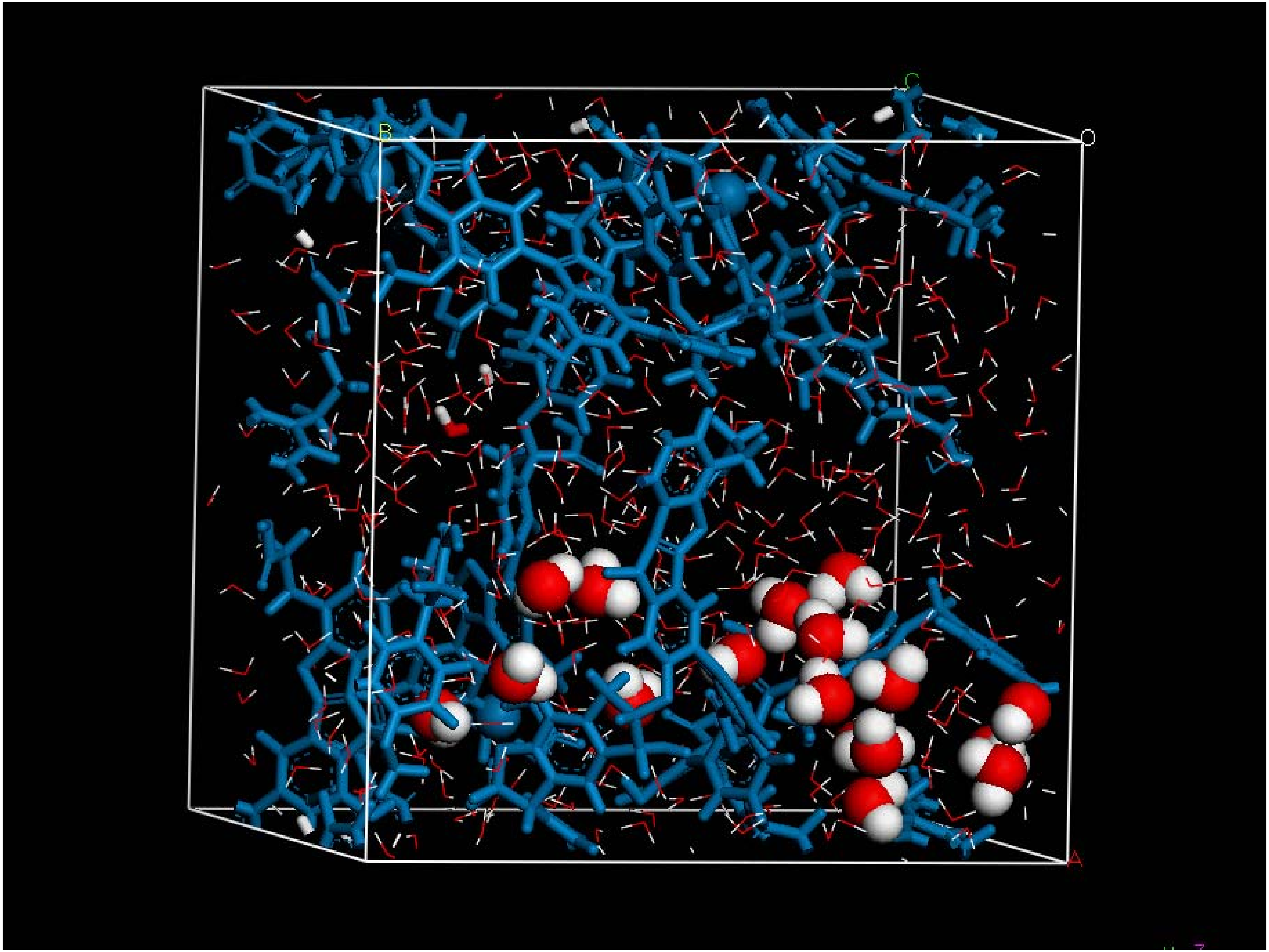
Lignite-Water Interactions

3-D molecular model of fossil wood (*Podocarpus sp*) from Loy Yang OC. The simulation box is (2.73 nm)^3.

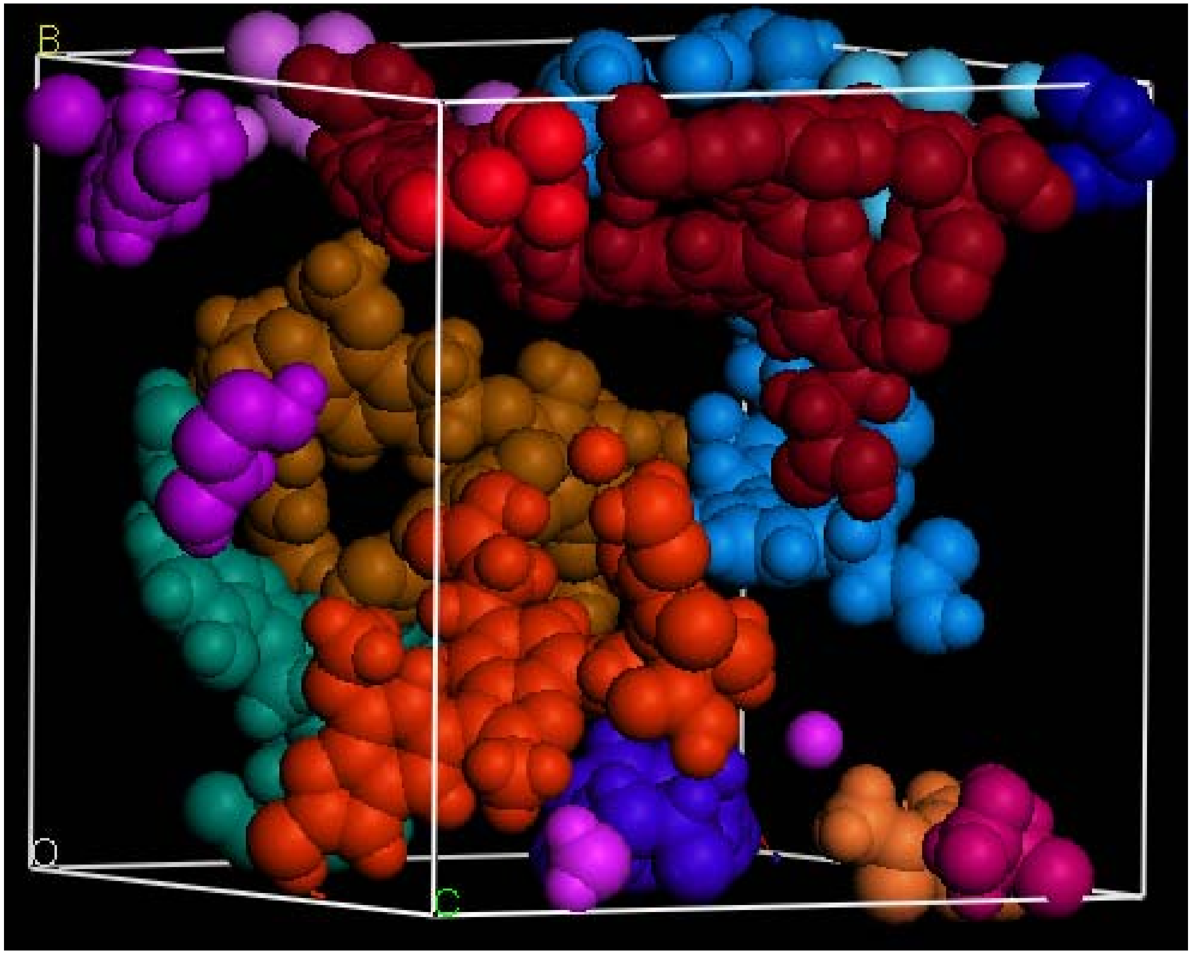



B
C
O
A

Lignite-Water Interactions

Water removed to illustrate pore volume

Porosity: 45.4%



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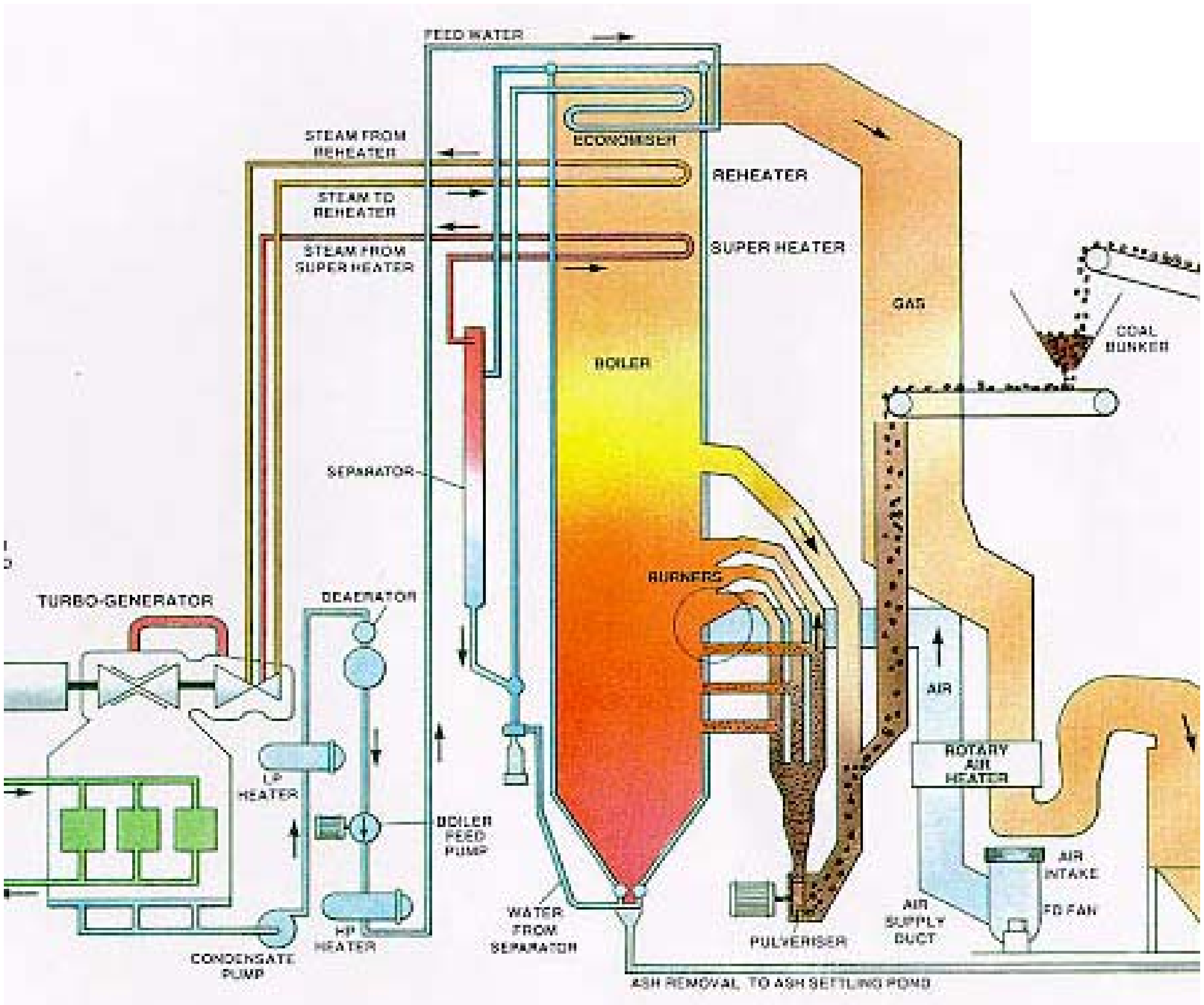
Current Practice



Water is removed by evaporation

VERY INEFFICIENT

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Non-Evaporative Drying Processes

Include:

- Mechanical Thermal Expression (MTE)
- Hydrothermal Dewatering (HTD)
- Pressurised Steam Drying

Water is removed as a liquid rather than steam

Heat of evaporation is saved -
leading to more efficient electricity production

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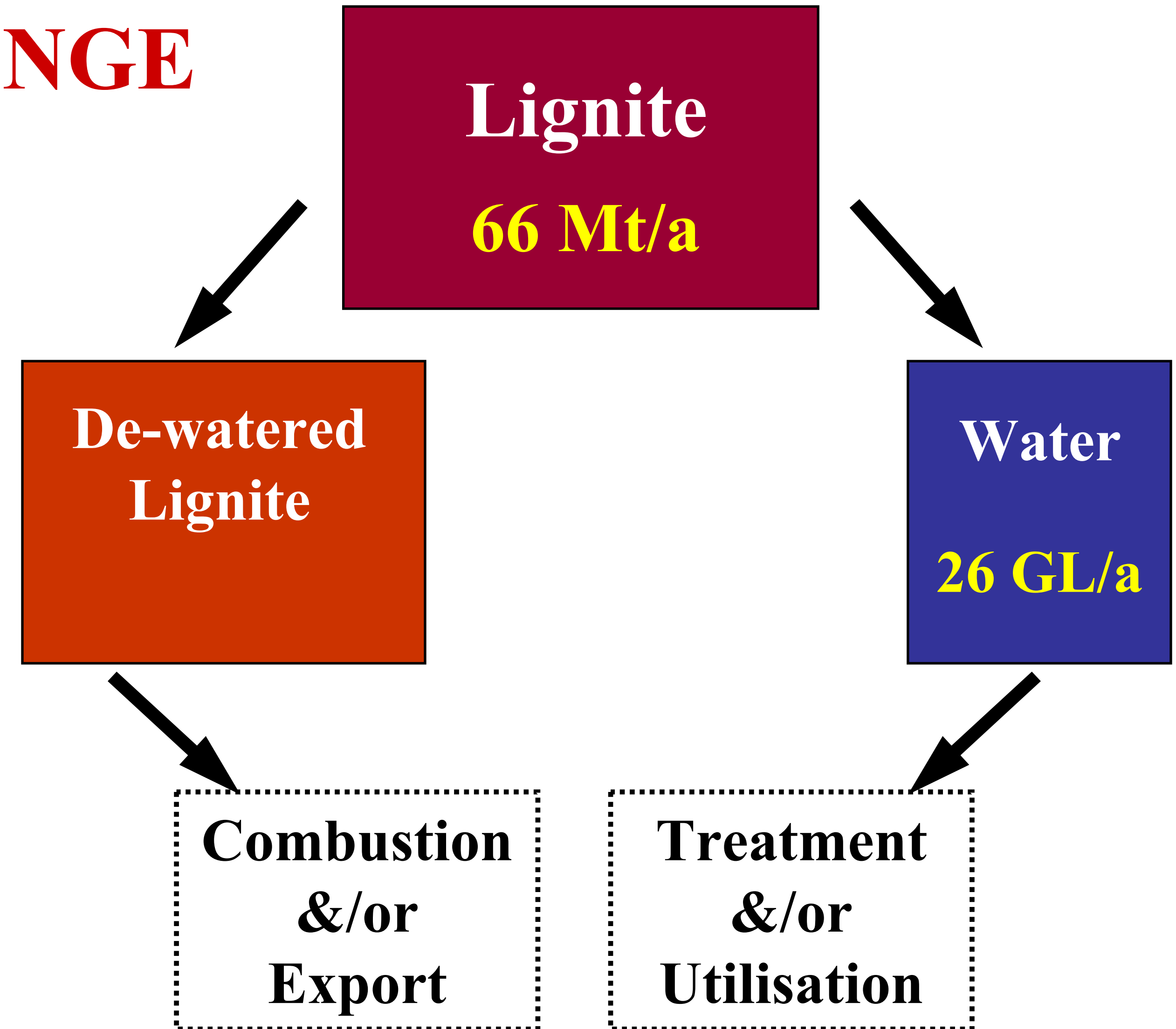
THE CHALLENGE



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Possible Applications

Industrial

- Power Station: Condensate water
- Power Station: Cooling water
- Power Station: Fire and ash water
- Paper plant

Environmental Recharge

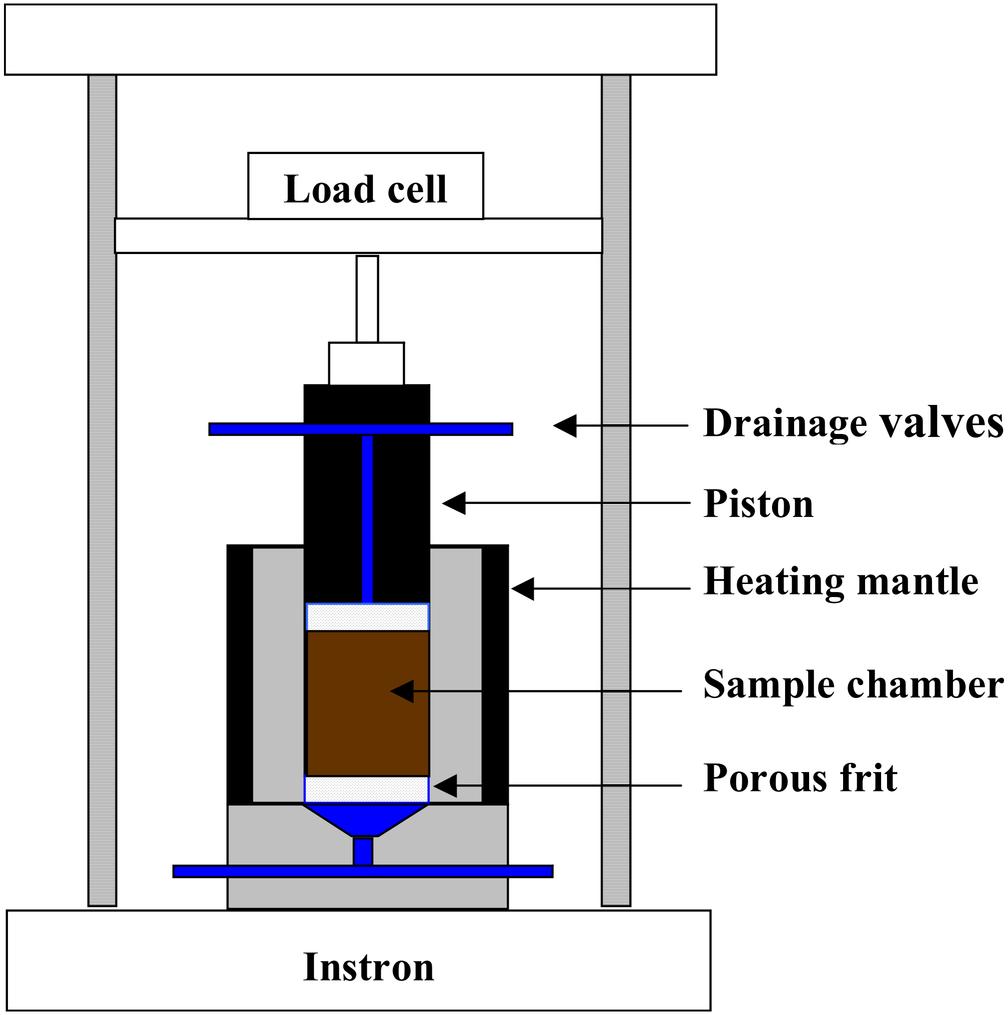
- Surface waters: lowlands, uplands, lakes, marine
- LV industrial area
- Groundwater

Primary Industries

- Irrigation
- Livestock
- Aquaculture

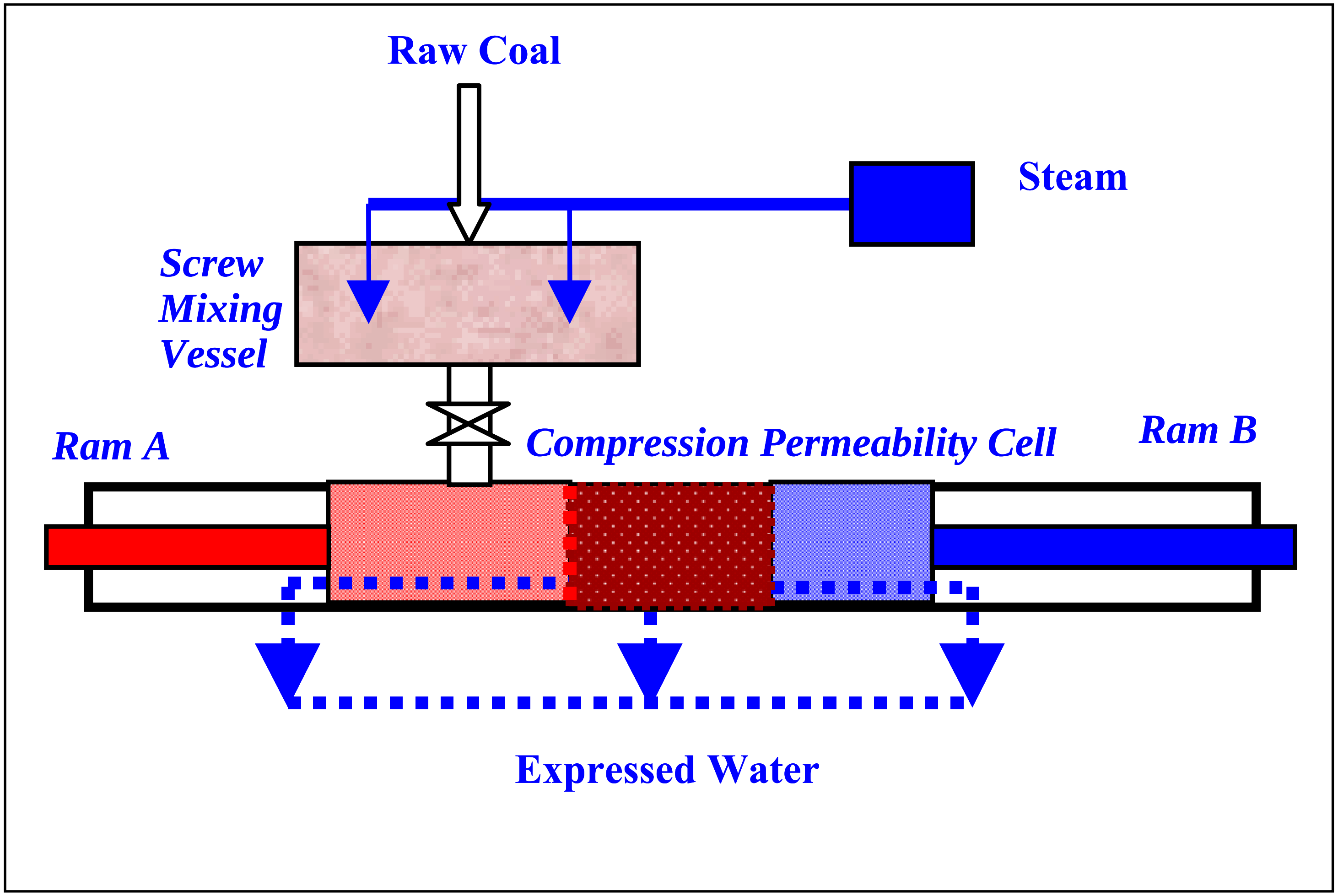
Recreation

MTE Processing



100g coal (wb)
T=180-250 °C
P_{mech}= 0-25 MPa

Schematic of MTE Pilot Plant



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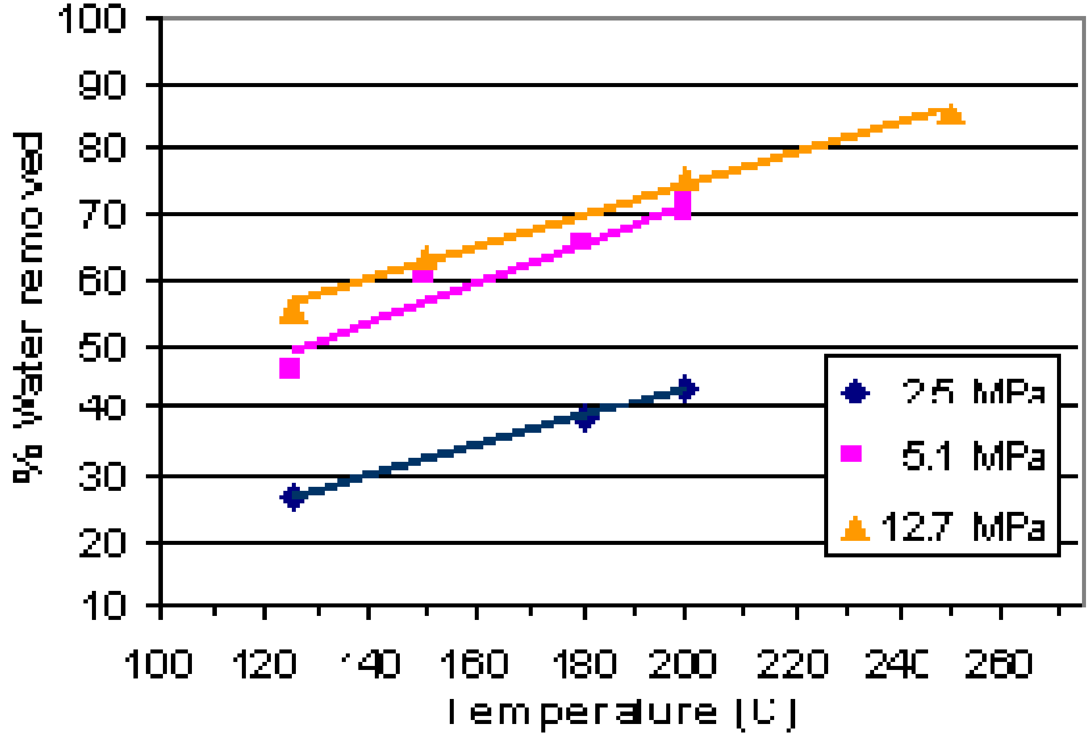
MTE Dewatering

Effect of Process Conditions



Harsher conditions (T, P) lead to greater water removal
Pressure becomes less significant as it increases

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Comparison of Dewatering Methods

Organic Carbon in Product Water

	MTE	Batch HTD	HTD pilot plant	Pressurised steam dewatering
Temperature (°C)	120 – 200	250 – 350	300	182 – 222
Lignite	Loy Yang	Loy Yang	Loy Yang	Loy Yang
Total Organic Carbon (g/L)	0.08 – 0.4	0.3* – 7	1.32	NA
Organic Carbon (g/kg dry coal)	0.4 – 2.2	2* – 50*	NA	0.1* – 2.3

Organic Carbon in product water is predominantly determined by process temperature
MTE releases less organics to the product water

MTE Water Quality

From Rig

After Settling

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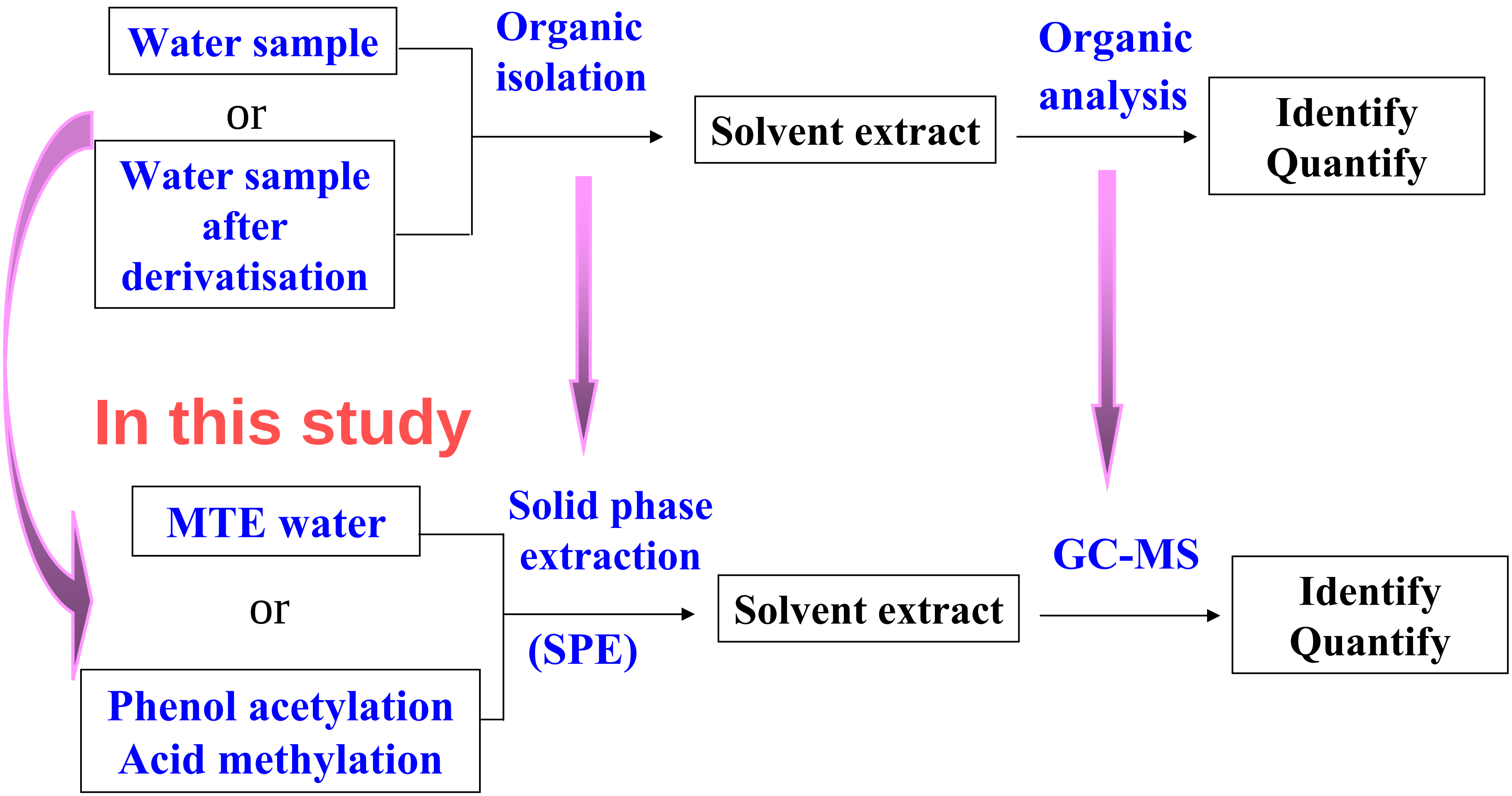
MTE Water Quality

Physical Properties vs Guideline Levels

Water type	pH	Conductivity (µS/cm)	Turbidity (NTU)	TDS (mg/L)	TSS (mg/L)
Loy Yang MTE water	3.46	2000	2600	2200	1700
Morwell MTE water	3.63	3890	726	5300	800
Yallourn MTE water	3.48	2080	1230	3000	920
Lowland rivers	6.5-8	125-2200	6-50	-	-
Latrobe Valley Waters	6-8.5	-	50	770	90
Cooling water make up	6.4-7.7	500	40	200	30
Agricultural irrigation	6-9	-	-	800	-
Saline Water Outfall Pipeline (SWOP)	6.5-8.5		25	25000	20
Regional Outfall Sewer	6.0-9.0				40

Physical properties do not generally meet guideline levels
Remediation will be required.

General analytical procedure for Organics



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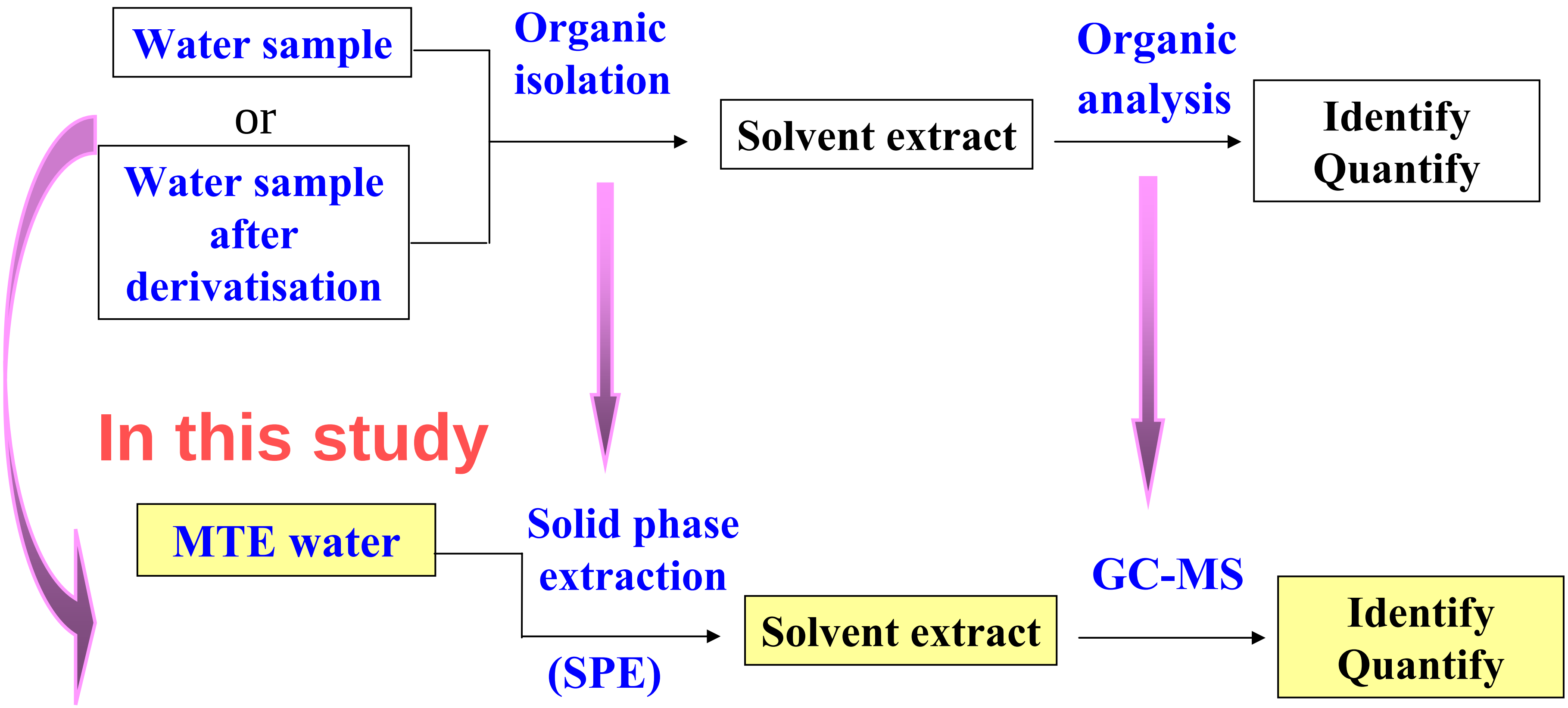

Direct SPE-GC-MS

- Method
  - Solid phases – PPL
  - Elution solvent – ethyl acetate
- Recoveries (ppm level)
  - Mono-phenols – >90%
  - Di-phenols – <80%
  - Tri-phenol – undetectable at < ~45ppm
  - LMW polar carboxylic acids not detectable at < ~250 ppm
- Conclusions
  - Low GC sensitivity of phenols and carboxylic acids
  - High detection limits
  - Poor recoveries for di and triphenols

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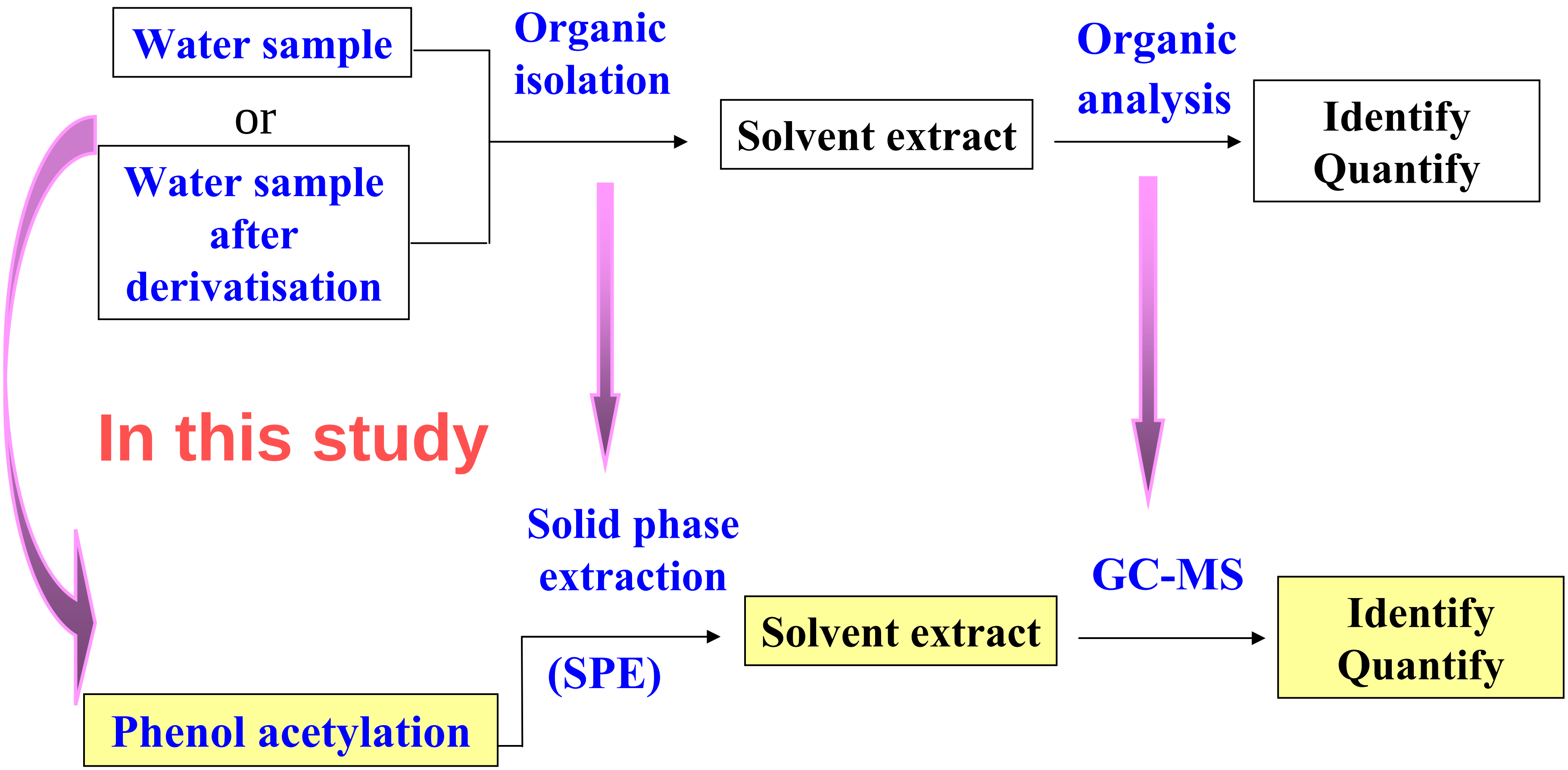
General analytical procedure for Organics



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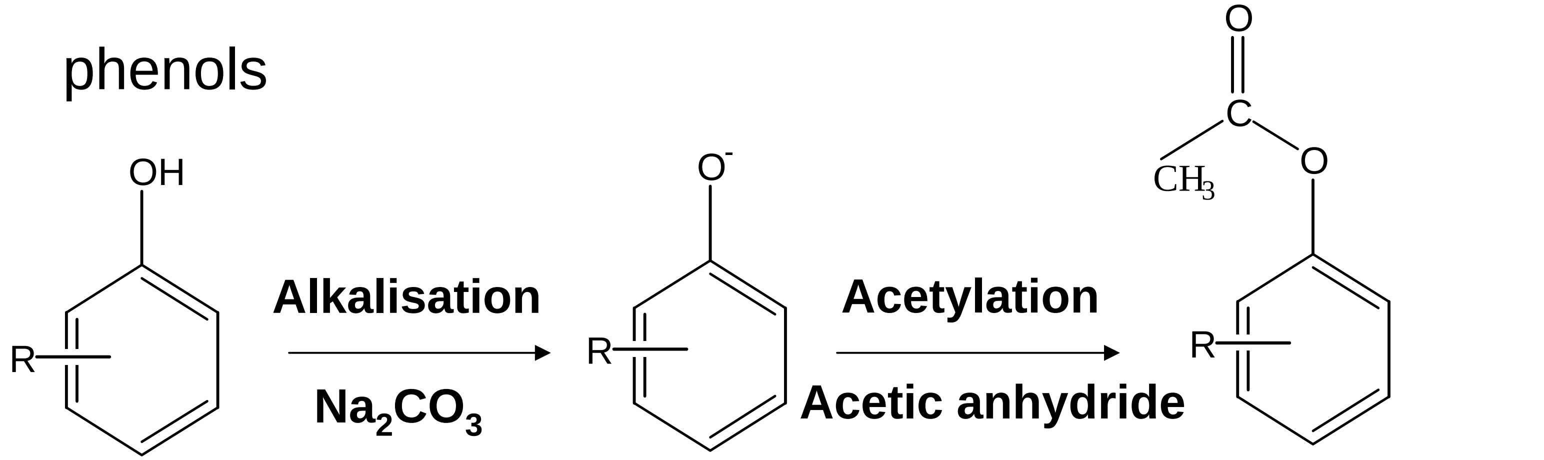
Phenol acetylation - SPE

phenols

phenol acetates



Polar, non-volatile, low GC sensitivity

Less polar, volatile, higher GC sensitivity

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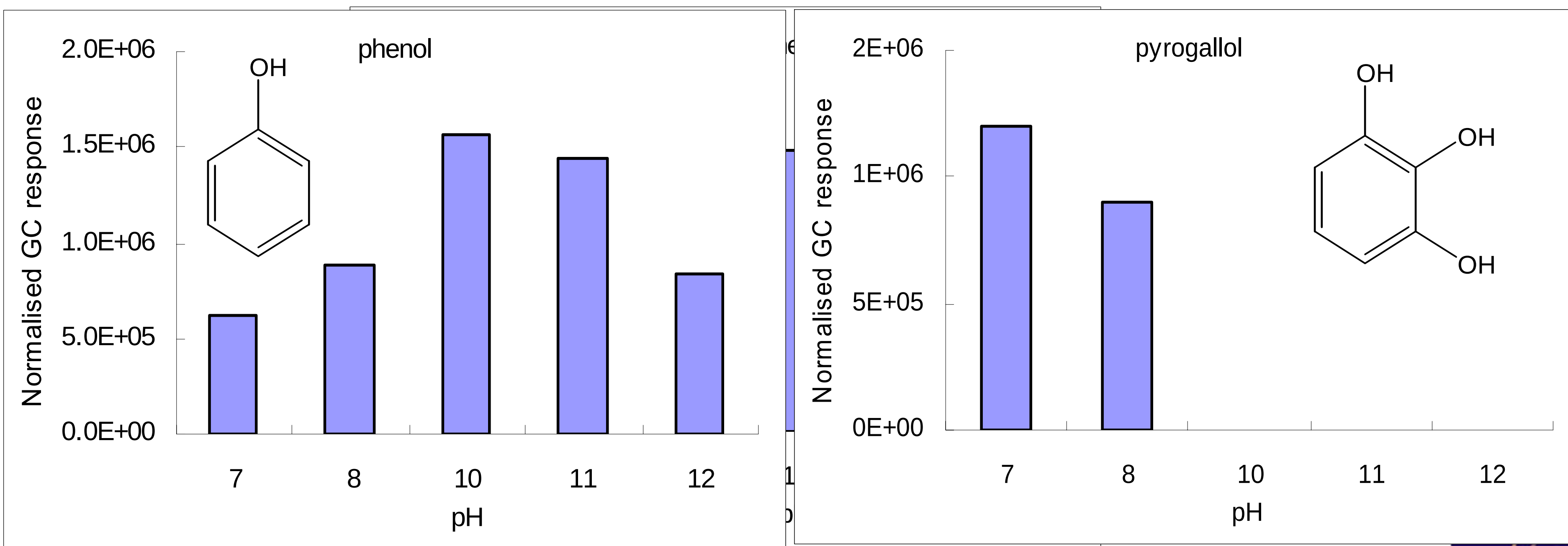
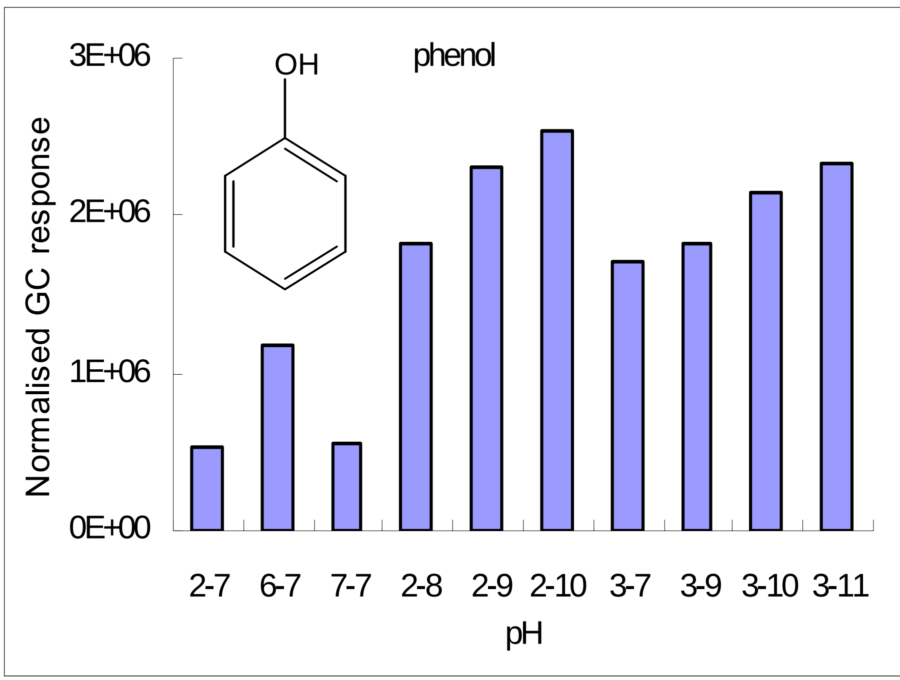
Phenol acetylation - SPE

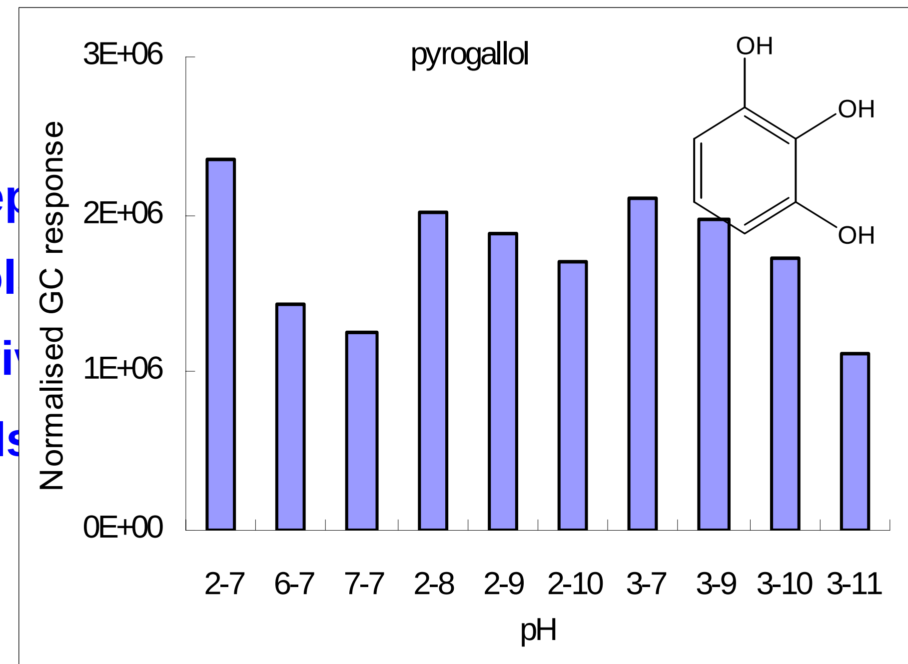
- Acetylation method evaluation
  - One step acetylation – in literature
    - •Substituted mono phenols and diphenol – low acetylation yield at low pH
    - •Phenol – low yield at low pH and high pH
    - •Tri-hydroxy phenol – low yield at high pH



Phenol acetylation - SPE

- Acetylation method evaluation
  - Two step acetylation – developed
    - First – low pH for tri-hydroxy phenol
    - Second – high pH for the rest of phenols (mono-, di-)





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Phenol quantification – method validation

Loy Yang 200°C/25MPa	Amount in MTE sample (μg/L)	Amount added (μg/L)	Total amount in spiked MTE sample (μg/L)	Recovery %	Recovery RSD%
Phenol	76 ± 1	195	280 ± 16	105	7.9
4-methyl-phenol	3.6 ± 0.3	192	208 ± 3	104	1.4
2,4-dimethyl-phenol	0.9 ± 0.0	203	212 ± 2	104	0.92
2-methoxy-phenol	98 ± 3	215	321 ± 1	104	0.25
2-methoxy-4-methyl-phenol	3.5 ± 0.1	199	215 ± 0	107	0.17
Catechol	627 ± 19	211	824 ± 17	93	8.7
2,6-dimethoxy-phenol	43 ± 1	208	244 ± 16	97	8.0
Vanillin	118 ± 5	213	345 ± 29	107	13
Pyrogallol	153 ± 4	223	290 ± 13	62	9.4

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Phenols identified in MTE water from Loy Yang coal (200°C, 25MPa)

Total organic carbon 0.15g/L	Estimated total phenols ~4mg/L
Phenol	1,2-dihydroxy-4-methyl benzene
4-methyl-phenol	2-methyoxy-4-ethyl-phenol
2,4-dimethyl-phenol	4-[1-methylethyl] phenol
2-methoxy-phenol	1-[4-hydroxy-3-methoxyphenyl] ethanone
2-methoxy-4-methyl-phenol	[4-hydroxy-3,5-dimethylphenyl] ethanone
Catechol	phenyl] ethanone
2,6-dimethoxy-phenol	ethylethylphenyl]} ethanone
Vanillin	5-dimethoxy benzaldehyde
Pyrogallol	nzaldehyde
3-methoxy-4-ethoxy phe	nzaldehyde
1,4-dihydroxy-2-methoxy-benzene	2,5-dihydroxy-benzaldehyde
1,4-dihydroxy-2,3,5-trimethyl benzene	3-hydroxy-4-ethoxy-benzaldehyde

Phenolics
Carboxylic acids
Others
GC-MS non-detectables

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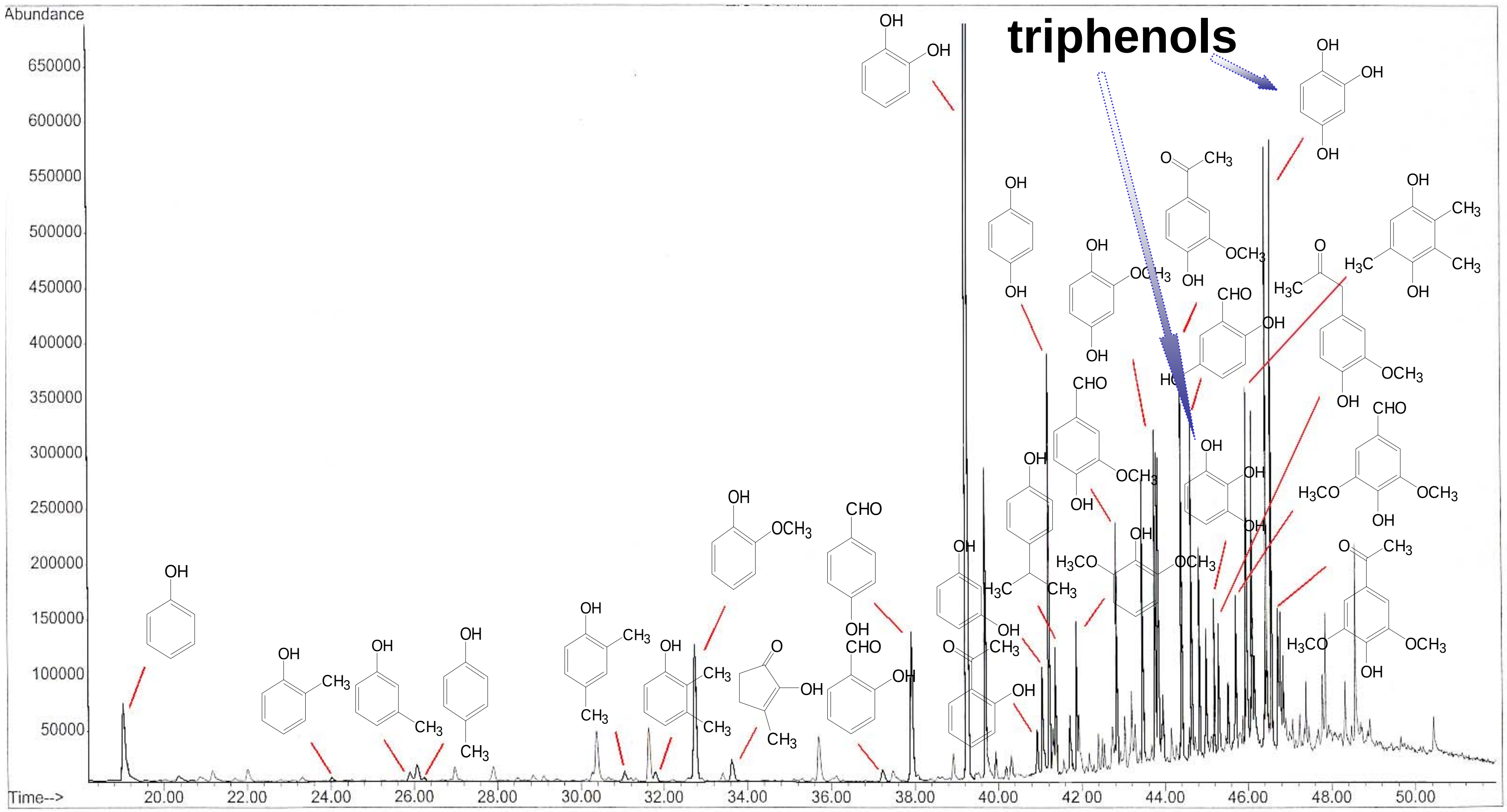
GC-MS TIC of an acetylation-SPE extract



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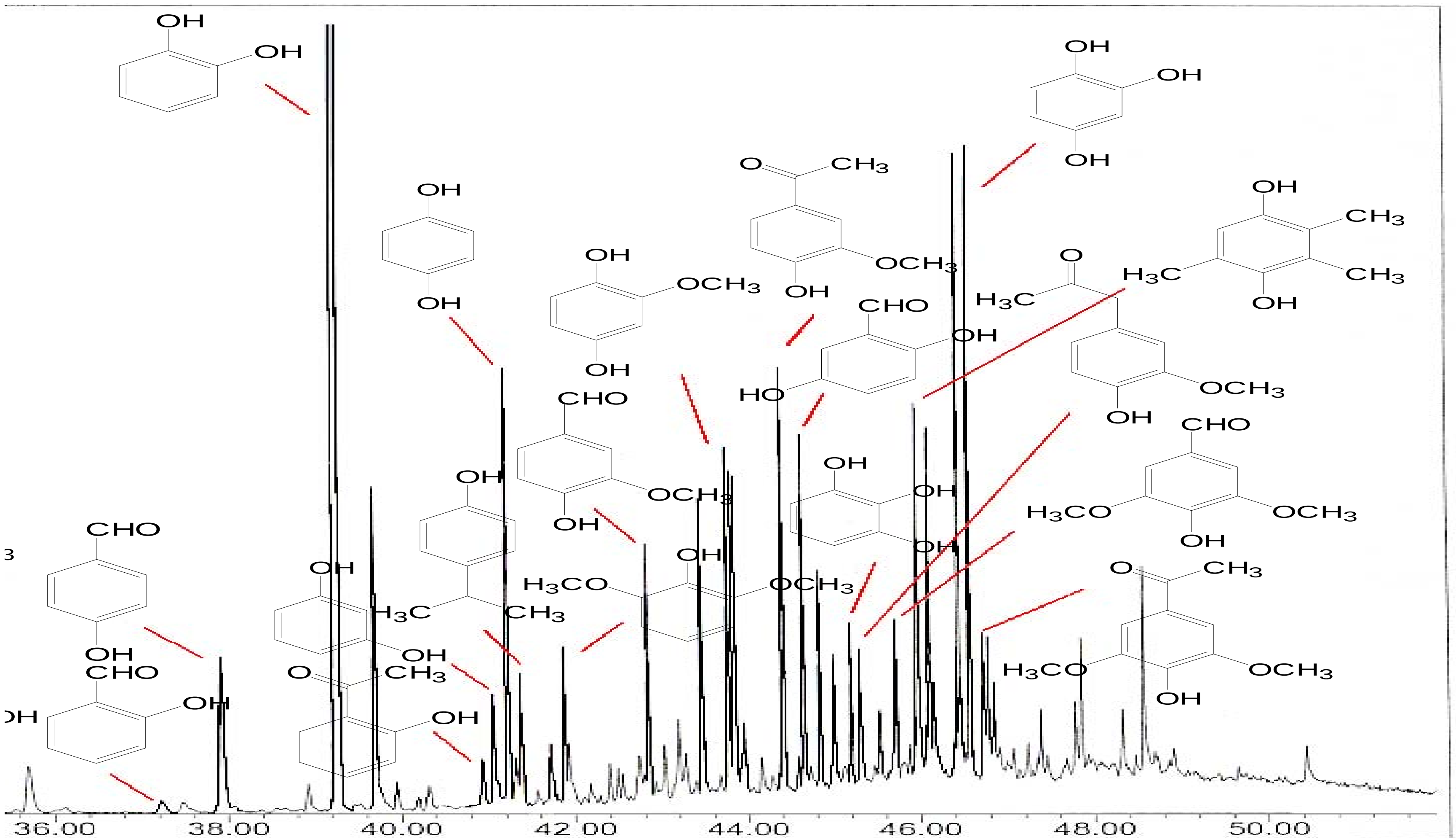
GC-MS TIC of an acetylation-SPE extract



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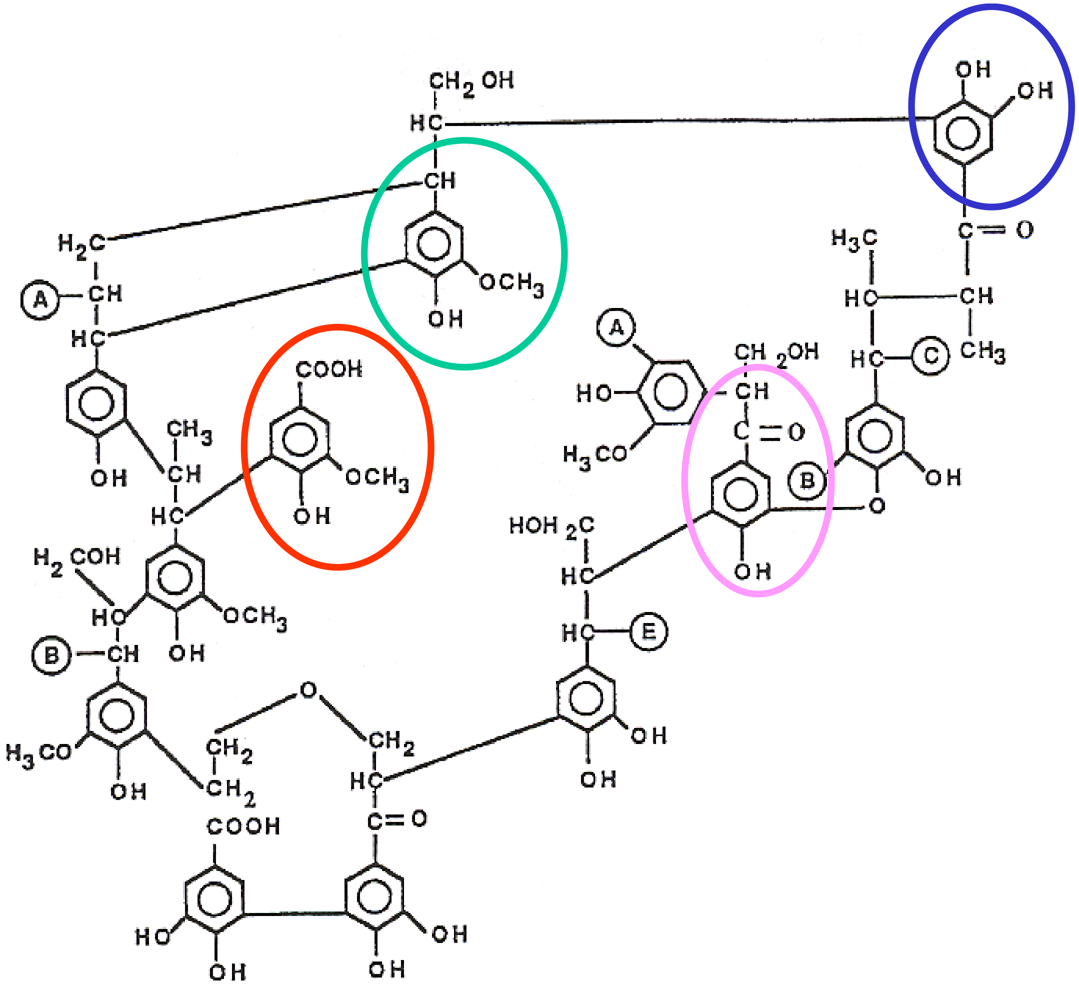
Model of Lignitic Wood



Hatcher, *Org Geochem*, **16**, 959 (1990)

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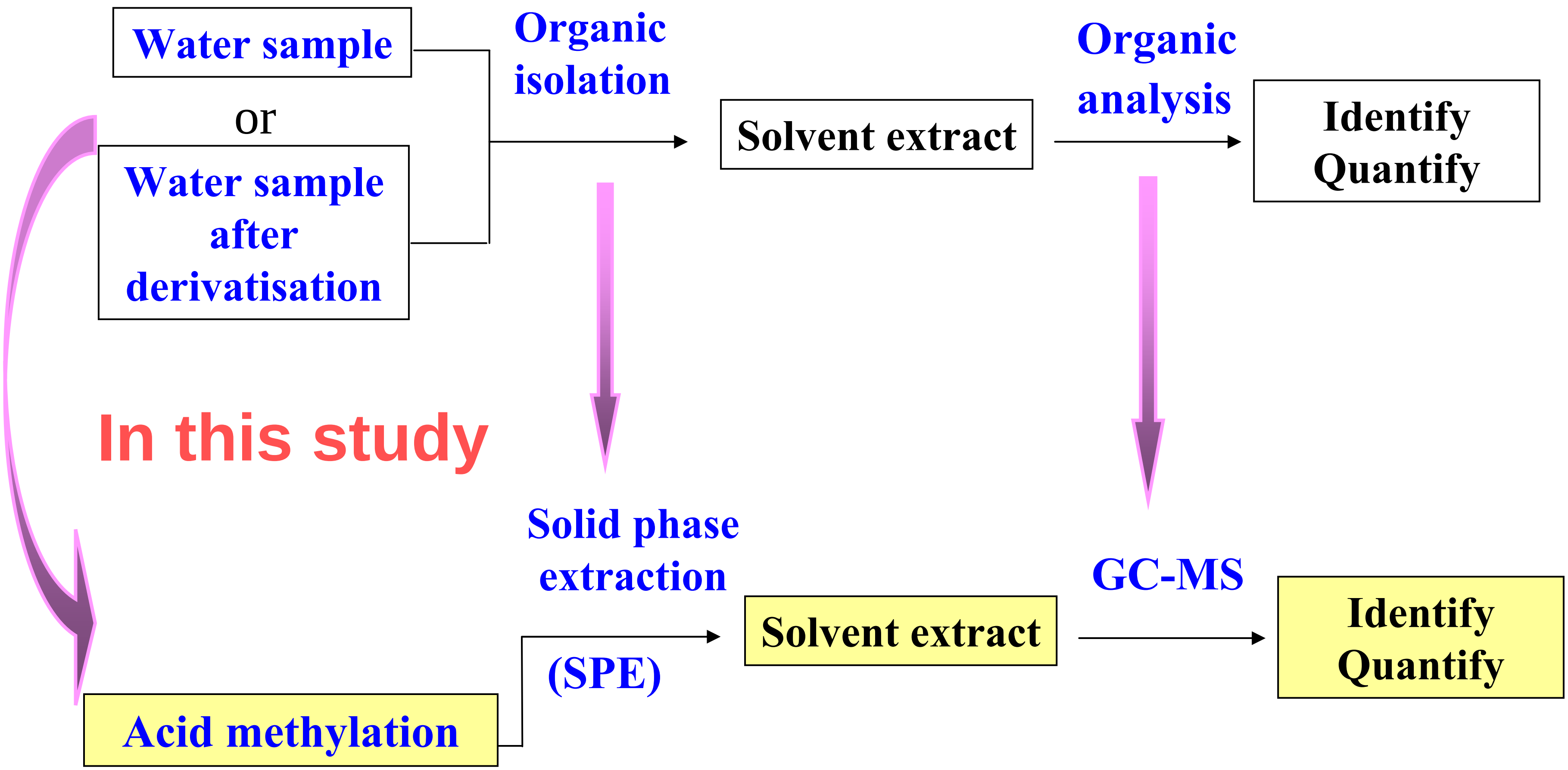
General analytical procedure for Organics



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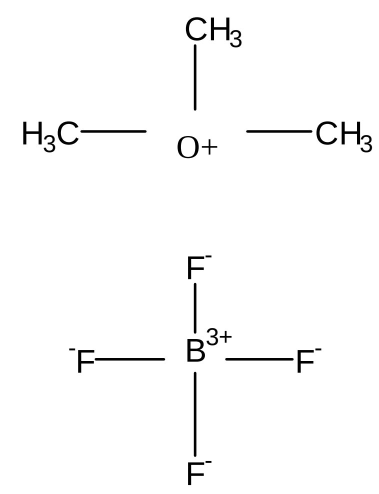
Carboxylic acid methylation

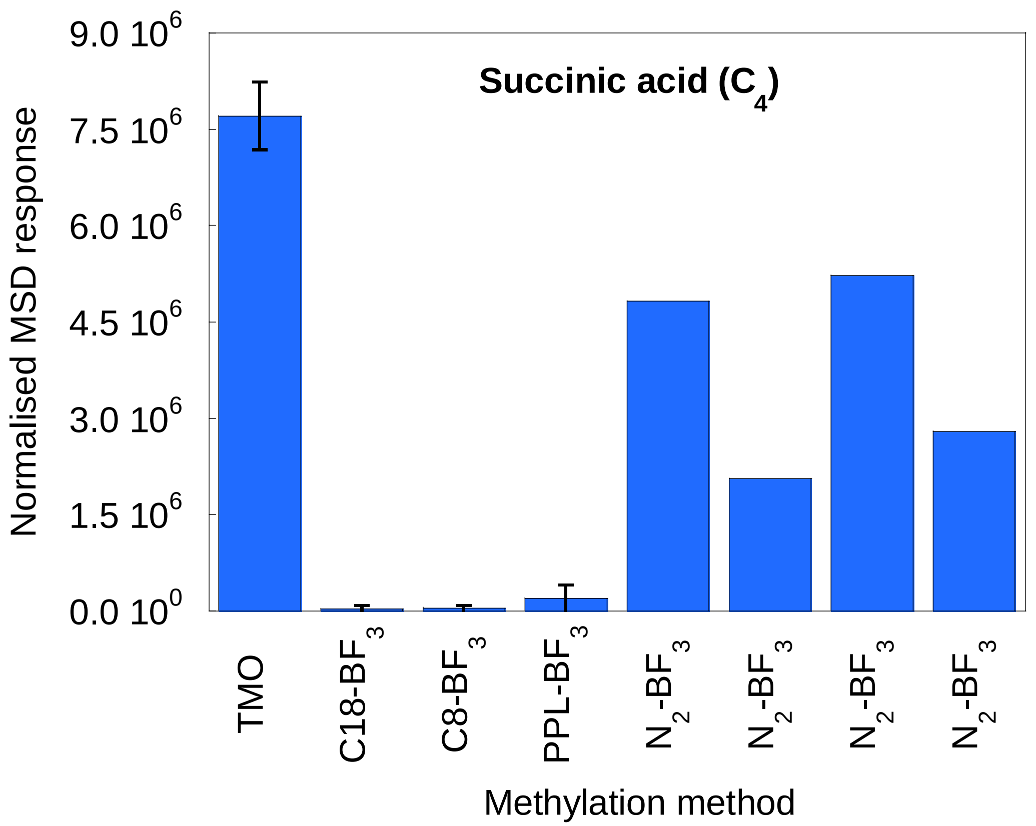
Common Reagents:

- **Diazomethane**
- **BF_3/MeOH**
- **Acetyl chloride/ MeOH**
- **Trimethyloxonium tetrafluoroborate (TMO)**



TMO

Acid methylation – comparison of methods



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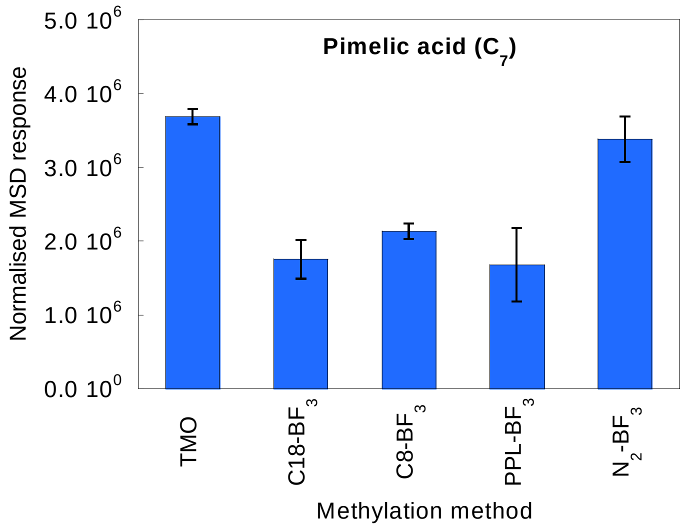
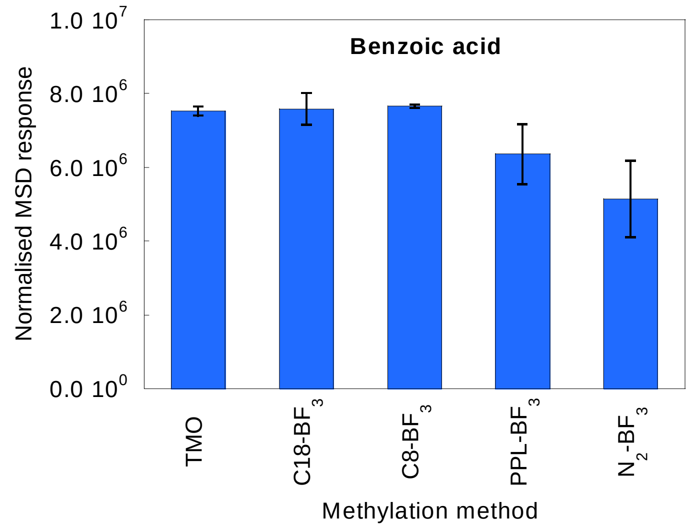
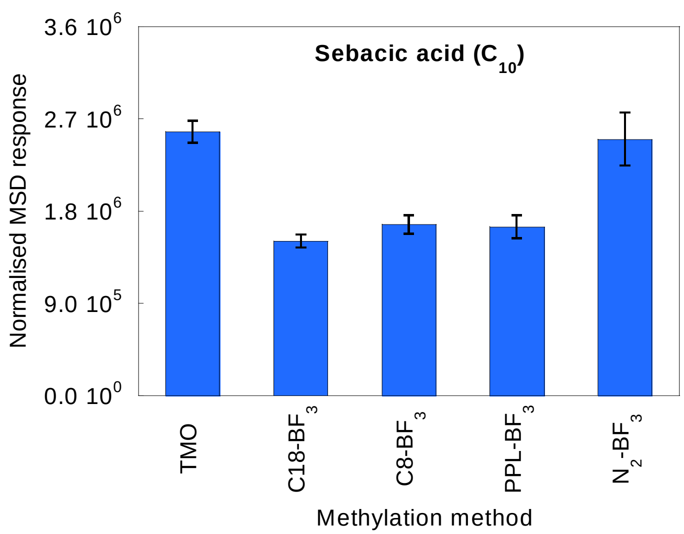
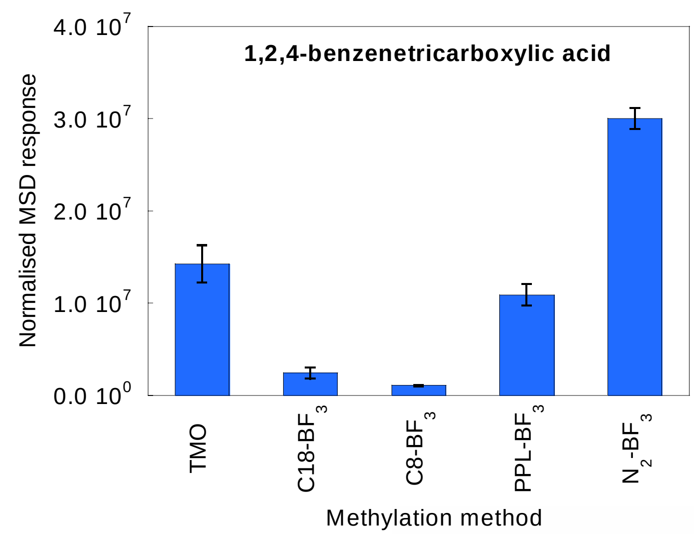
Acid methylation – comparison of methods









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Methylation with TMO in Aqueous Solution

$$RCOO^{-} + CH_3\text{-}O\text{-}(CH_3)_2^{+} \rightarrow RCOOCH_3 + CH_3\text{-}O\text{-}CH_3$$

Procedure must promote reaction between TMO and acid:

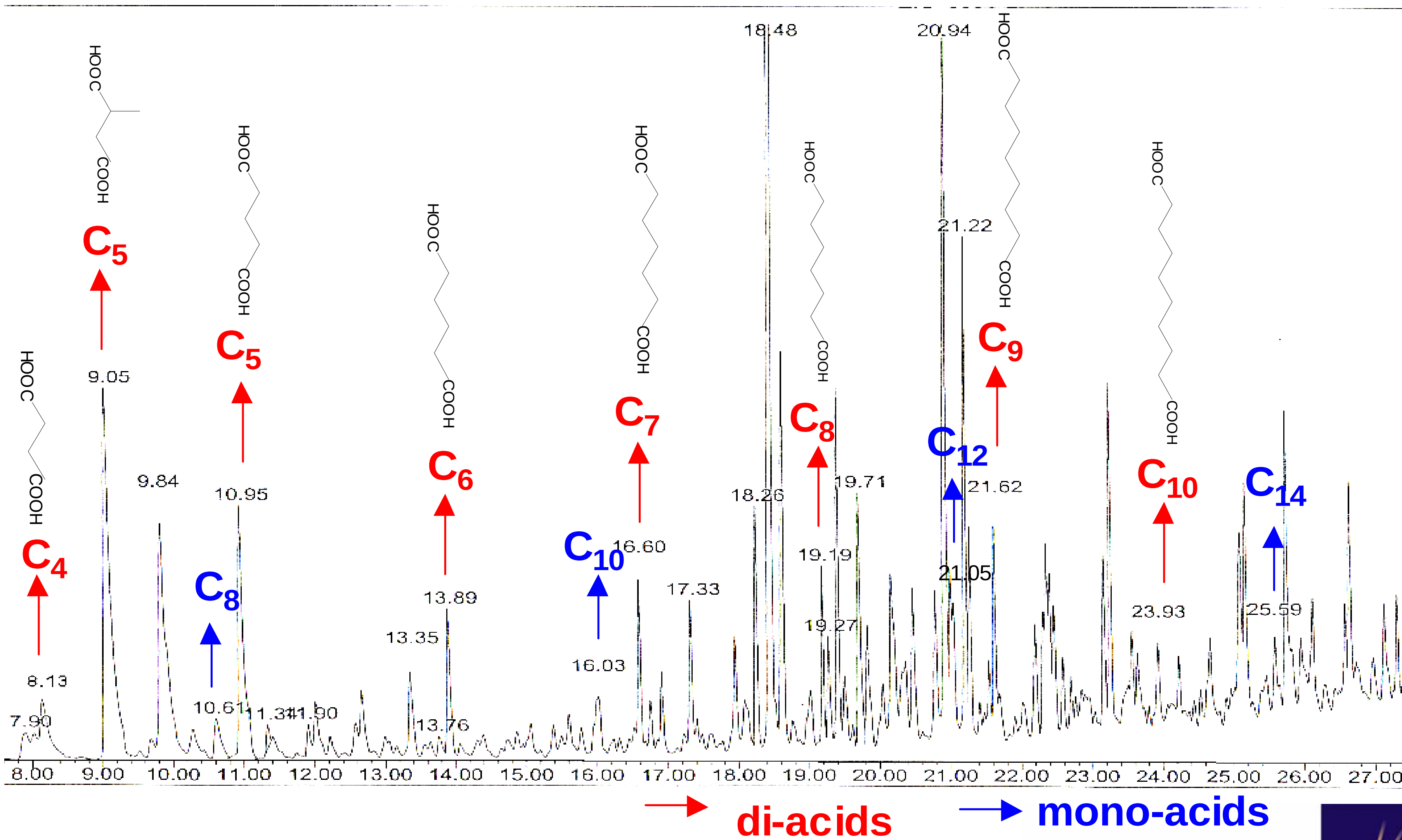
- **staged addition of TMO (5x)**
- **repeated alkalisation ($NaHCO_3$, Na_2CO_3)**
- **sealed and incubated at 100C (2 min)**

TMO methylation - SPE

Conclusions:

- Lengthy acid isolation step by N_2 drying or SPE is avoided
- Methylation efficiency and reproducibility high
- Final isolation of methyl esters using C18 / ethyl acetate

Carboxylic Acids in MTE water by GC-MS



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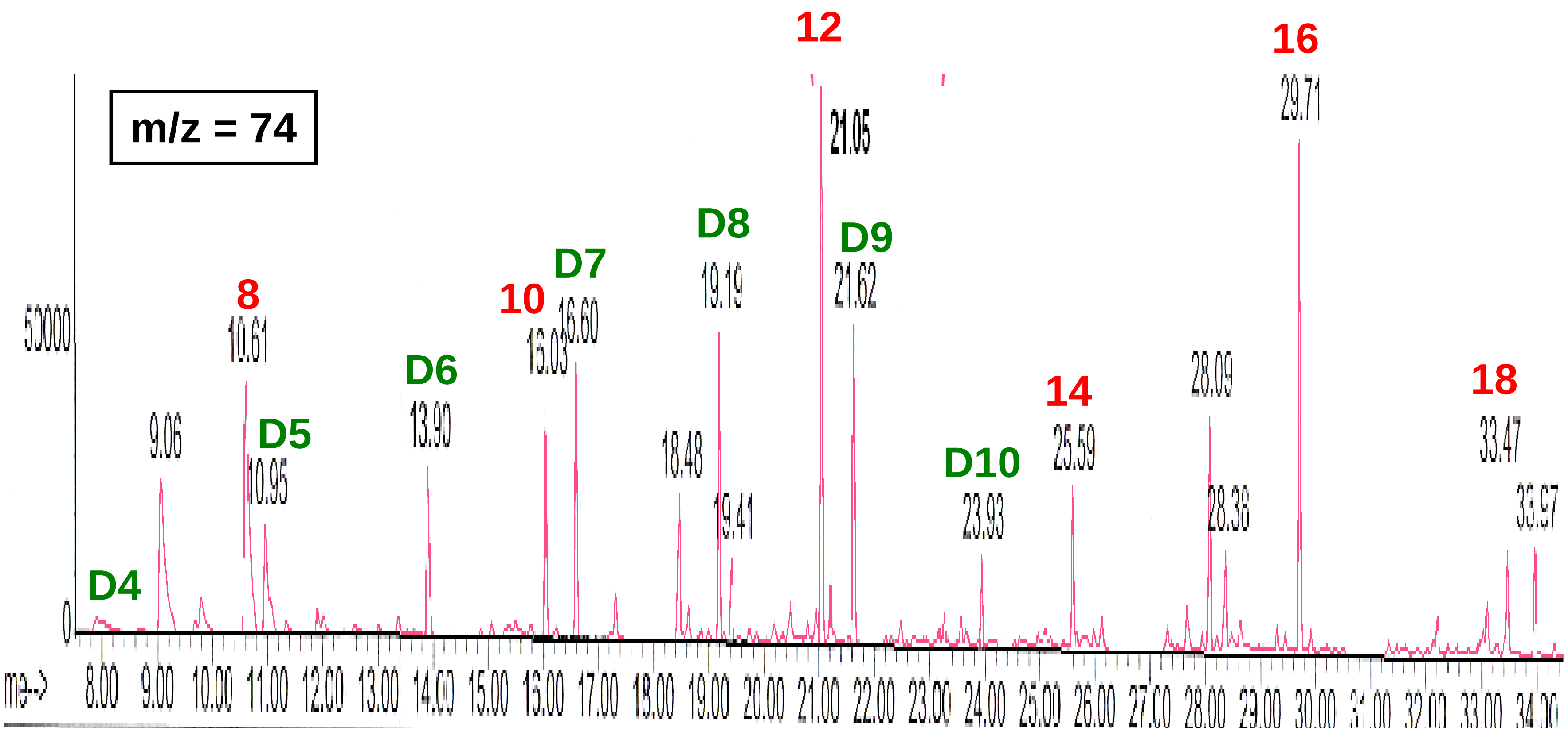
Carboxylic Acids in MTE water by GC-MS



XX – monocarboxylic acids

XX – dicarboxylic acids

Carboxylic Acids in MTE water by GC-MS

Aromatic acids		
Benzeneacetic acids	Benzoic acids	
benzeneacetic acid	benzoic acid	4-hydroxyl-3-methoxy-benzoic acid
4-methoxy-benzeneacetic acid	4-methyl-benzoic acid	?-hydroxyl-?-methoxy-benzoic acid
3,4-dimethoxy-benzeneacetic acid	4-methoxy benzoic acid	4-hydroxy-2-methoxy-3,5,6-trimethyl benzoic acid
4-hydroxy-3-methoxy-benzenacetic acid	3-methoxy-4-methyl-benzoic acid	2,4-dihydroxy-3,6-dimethyl-benzoic acid
Benzenedicarboxylic acids	2,4-dimethoxy-6-methyl-benzoic acid	3,4,5-trihydroxy benzoic acid
4-methyl-1,2-benzenedicarboxylic acid	?,?-dimethoxy-?-methyl benzoic acid	
4-methyl-1,3-benzenedicarboxylic acid	3-ethoxy-benzoic acid	
?-methyl-?,?-benzenedicarboxylic acid	2-hydroxy benzoic acid	
benzenetricarboxylic acids		
1,2,4-benzenetricarboxylic acid	1,3,5-benzenetricarboxylic acid	5-methyl-1,2,4-benzenetricarboxylic acid

MTE Water Quality

Organics Composition

	Loy Yang A			Morwell		
	150º 25 MPa	200º 6 MPa	200ºC 25 MPa	200º 6 MPa	200º 6 MPa	200º 25 MPa
Total phenols (mg/kg, db)	0.34	3.8	14	21	25	71
Total acids (mg/kg, db)	161	620	980	1210	1280	1970
Total compounds identified by GC-MS (mg/kg, db)	161	625	1000	1300	1310	2040
Total organic carbon (mg C/kg, db)	710	1300	2200	2500	2900	3600

Detectable organics are mostly small molecular weight carboxylic acids, not phenols as observed for HTD and SD

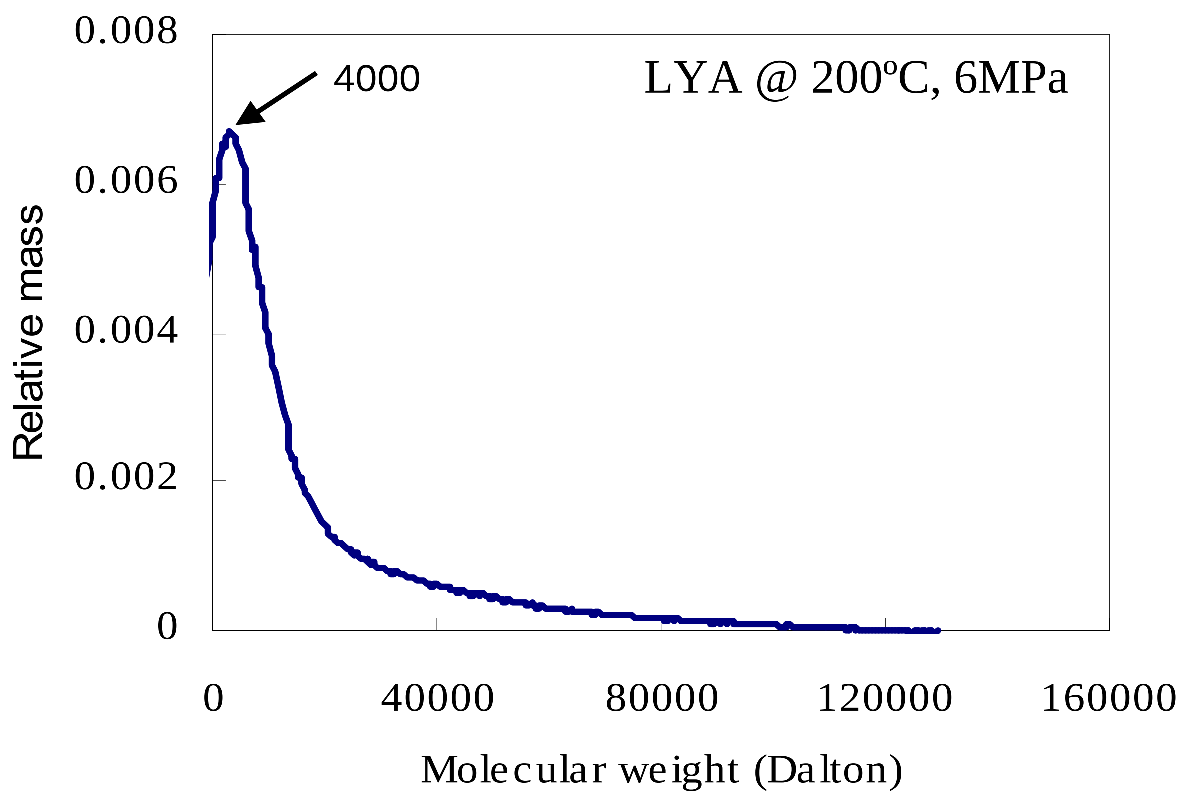
MTE Water Quality

Organics % observed by GC-MS

	Loy Yang A			Morwell		
	150º 25 MPa	200º 6 MPa	200ºC 25 MPa	200º 6 MPa	200º 6 MPa	200º 25 MPa
Total phenols (as carbon) in OC (%)	.037	.023	.48	.62	.65	1.4
Total acids (as carbon) in OC (%)	12	24	24	27	23	28
Total identified organics (as carbon) in OC (%)	12	24	24	27	24	29

GC-MS detectable components account for 25-30% of the organics in MTE water

Higher Molecular Weight Organics in MTE Water



By Field Flow Fractionation

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Conclusions

- MTE is effective for removing ~75% of the water in low rank coals like those from Victoria
- By-product water is 'clean' relative to that produced by other dewatering methods
- It will still require remediation for most foreseeable uses
- It contains inorganics as well as organics
- ~25-30% of the organics can be identified and quantified by GC-MS
- HMW components are also present
- Identifiable components are biomarkers and, considered as a whole, are not particularly nasty.

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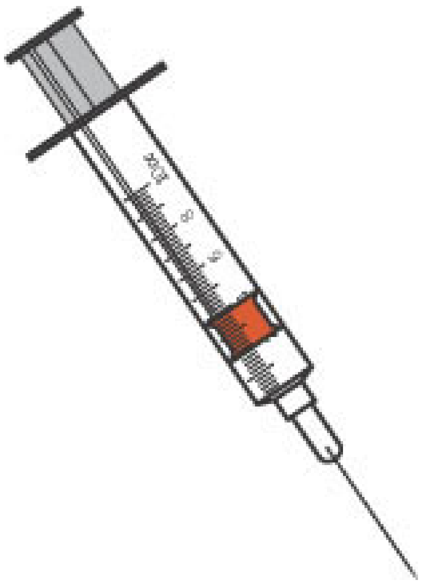
"In effect, you are what you eat
- plus a little bit of what you might inject"

Professor Colin Snape

BBC News



MTE Water	300^{o}C SV 5	300^{o}C SV 1.5	350^{o}C SV 5	350^{o}C SV 1.5

Quality Criteria

- Total Dissolved Solids (TDS): mg/L
- Suspended Solids (SS): mg/L
- pH
- Colour: Pt/co
- Turbidity: NTU^2
- Conductivity: (µS/cm)
- Biological Oxygen Demand (BOD): mg/L

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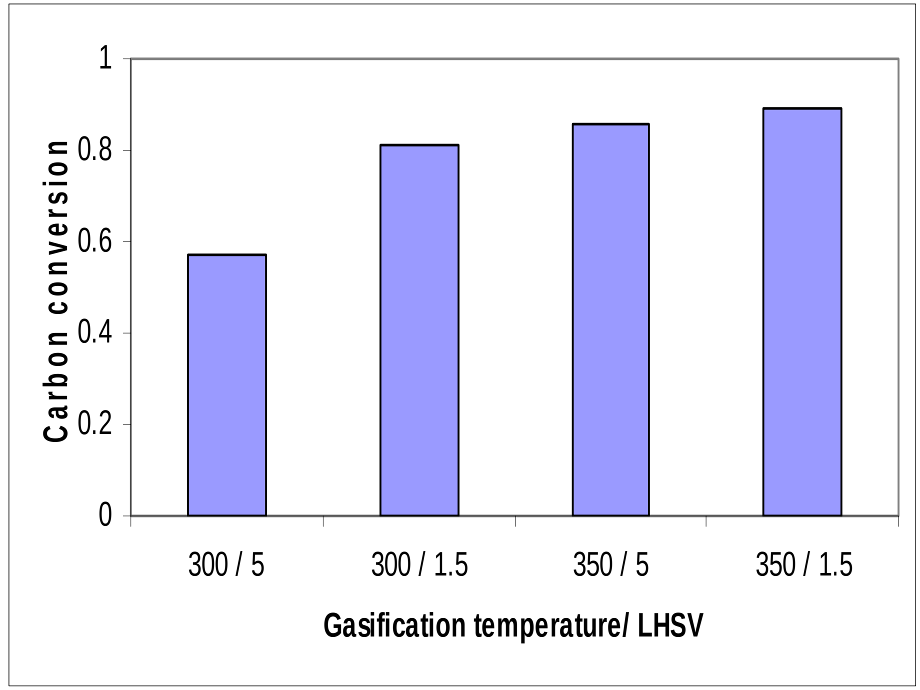
MTE Water Remediation

2. Gasification of Organics

Approach is moderately effective at 300-350C.
This approach is ineffective for inorganics.



MW MTE Raw water	300ºC SV 5	300ºC SV 1.5	350ºC SV 5	350ºC SV 1.5

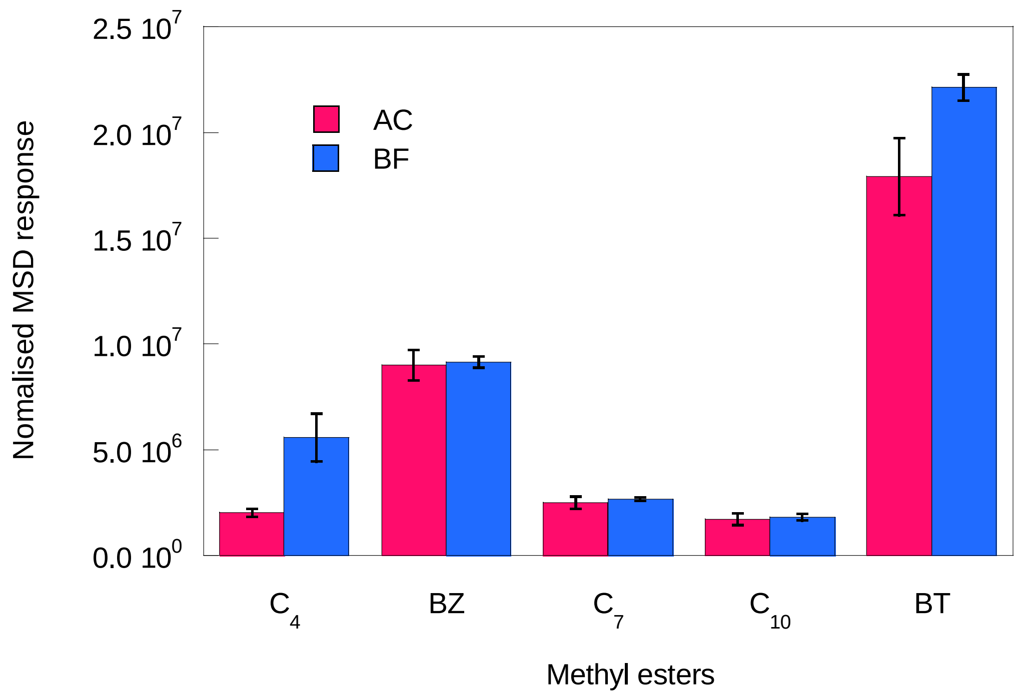
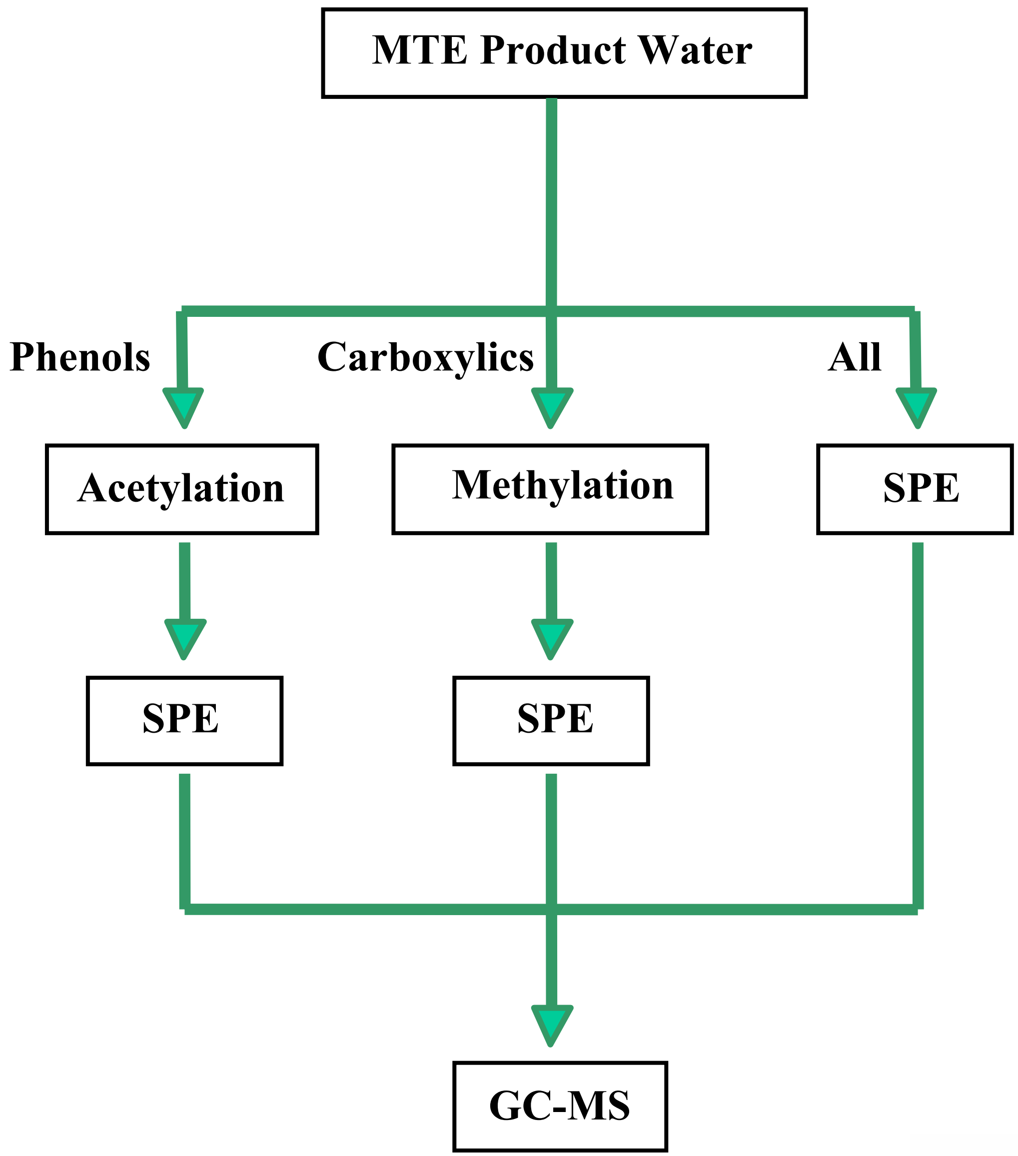


Figure 3-16. Comparison of acetyl chloride (AC) and BF_3 (BF) for methylation of carboxylic acids


MTE Product Water
Phenols
Carboxylics
All
Acetylation
Methylation
SPE
SPE
SPE
GC-MS

Mono-hydroxy phenols			
Alkyl phenols		Methoxy phenols	Phenolic ketones
phenol	4-[1-methylethyl] phenol	2-methoxy phenol	1-[2-hydroxyphenyl]-ethanone
2-methyl phenol	2-methyl-5-[1-methylethyl]-phenol	4-methoxy phenol	1-[3-hydroxyphenyl]-ethanone
3-methylphenol	5-methyl-2-[1-methylethyl]-phenol	2-methoxy-4-methyl phenol	1-[4-hydroxyphenyl]-ethanone
4-methyl phenol	2,4-bis[1-methylethyl]-phenol	2-methoxy-4-ethyl phenol	1-[4-hydroxy-3,5-dimethoxyphenyl]-ethanone
2,4-dimethyl phenol	4-[1-methylpropyl] phenol	2,6-dimethoxy phenol	1-[4-hydroxy-3-methoxyphenyl]-2-propanone
2,5-dimethyl phenol	2- or 4-[2-methylpropyl] phenol	2,4-dimethoxy phenol	Phenolic benzaldehydes
2,3-dimethyl phenol	?-methyl-?-propyl phenol	1-[4-hydroxy-3-methoxyphenyl] ethanone	2-hydroxy benzaldehyde
3-ethyl phenol	4-[1,1-dimethylpropyl] phenol		3-hydroxy-benzaldehyde
	4-[3-methyl-2-butenyl]-phenol		4-hydroxy benzaldehyde
			4-hydroxy-3-methyl benzaldehyde
			4-hydroxy-3-methoxy benzaldehyde (vanillin)
			4-hydroxy-3,5-dimethoxy-benzaldehyde

Di-hydroxy phenols			
1,2-benzenediol (catechol)	?-dimethyl-1,3-benzenediol	1-[2,4-dihydroxyphenyl]-ethanone	1-[2,4-dihydroxy-3-methylphenyl]-propanone
1,3-benzenediol	2,3,5-trimethyl-1,4-benzenediol	1-[2,5-dihydroxyphenyl]-ethanone	2,4-dihydroxy benzaldehyde
1,4-benzenediol	a methoxy benzenediol	1-[2,4-dihydroxyphenyl]-propanone	2,5-dihydroxy benzaldehyde
2-methyl-1,4-benzenediol		1-[2,5-dihydroxyphenyl]-propanone	3,4-dihydroxy benzaldehyde
a methyl benzenediol			?,?-dihydroxy-4-methoxy-benzaldehyde
Tri-hydroxy phenols			
1,2,3-benzenetriol (pyrogallol)	1,2,4-benzenetriol	1,3,5-benzenetriol	a tri-hydroxy phenol (MW=182)