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COMPARISON OF BITUMENS FROM OIL SANDS WITH DIFFERENT RECOVERY PROFILES

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3. Syncrude Canada Ltd.

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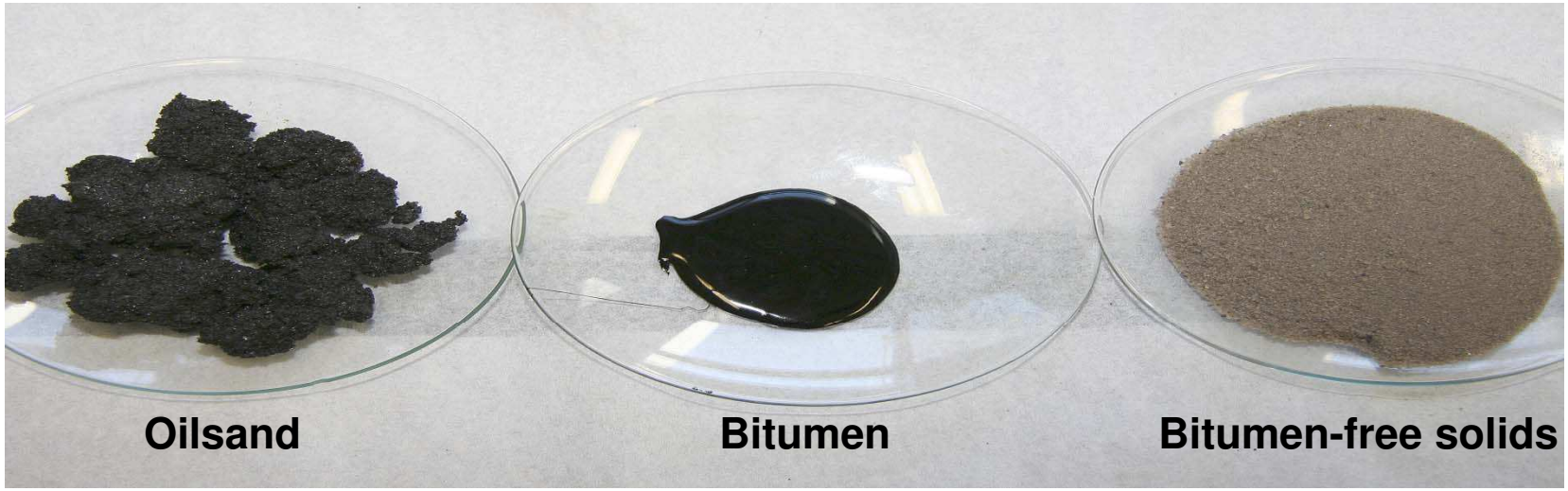
Introduction

- Aspects of predicting processability from key marker components of oil sands ores is needed in order to assess appropriate operating conditions for commercial extraction of bitumen
- Potential contributions from minerology of inorganic fractions, chemistry of bitumen and then the interfaces and surface property effects between these
- Research was conducted to fractionate various samples to determine if correlation between fractions and processability

- Question to be addressed: “Does bitumen composition influence and therefore correlate with bitumen recovery in water extraction processes?”

Objective

- Various lab techniques were used separate oil sand into bitumen and bitumen free solids, although this is not easily achieved in commercial operations
- Bitumen was then fractionated from corresponding oil sands samples using high performance liquid chromatography (HPLC) and then carry out further analyses on bitumen fractions as well as overall composition of original oil sands samples.



Oil Sands Samples

- Four oilsands from a previous bitumen recovery study were selected (Energy & Fuels **2008**, 22, 3174–3193).

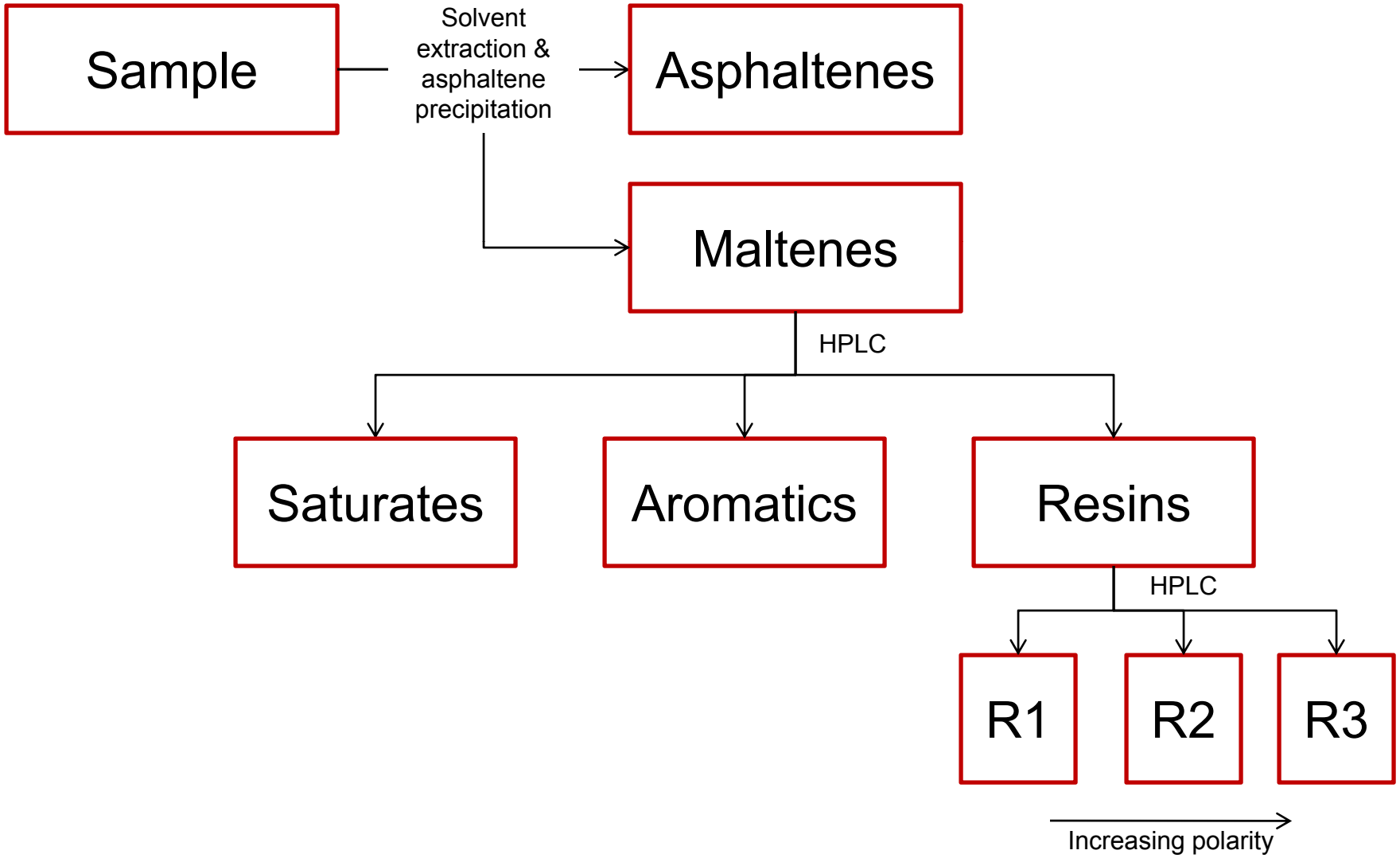
Sample ID	Component (% of Oilsands)			Bitumen Recovery %
	Bitumen	Fines	Clay	
E7	14.6	4.9	1.6	93.3
E3	9.8	29.9	3.8	91.5
M13	9.9	25.8	6.3	31.7
M18	7.9	41.8	5.2	57.5

- Estuarine (E7) processed with high recovery with a high bitumen content and low fines and clay content
- Estuarine (E3) and marine (M13) oil sands have similar bitumen and fines (<44μm) contents, but high and low bitumen recoveries respectively.
- Marine (M18) oilsand has a very high fines content but intermediate bitumen recovery.

Characterization Approach

- Extracted bitumen was separated into asphaltenes (asp) and maltenes.
- Application of HPLC to maltenes yields saturates (sat) aromatics (ar) and resins fractions.
- The resin component is divided into three fractions (R1, R2 and R3) based on increasing polarity (Fuel **2004**, 83, 1907-1914).

Characterization Approach



Characterization Methods

Molecular weights:

GPC

Elemental analysis:

C,H,N,S with LECO analyzer

Nitrogen and sulfur types:

X-ray photo electron spectroscopy

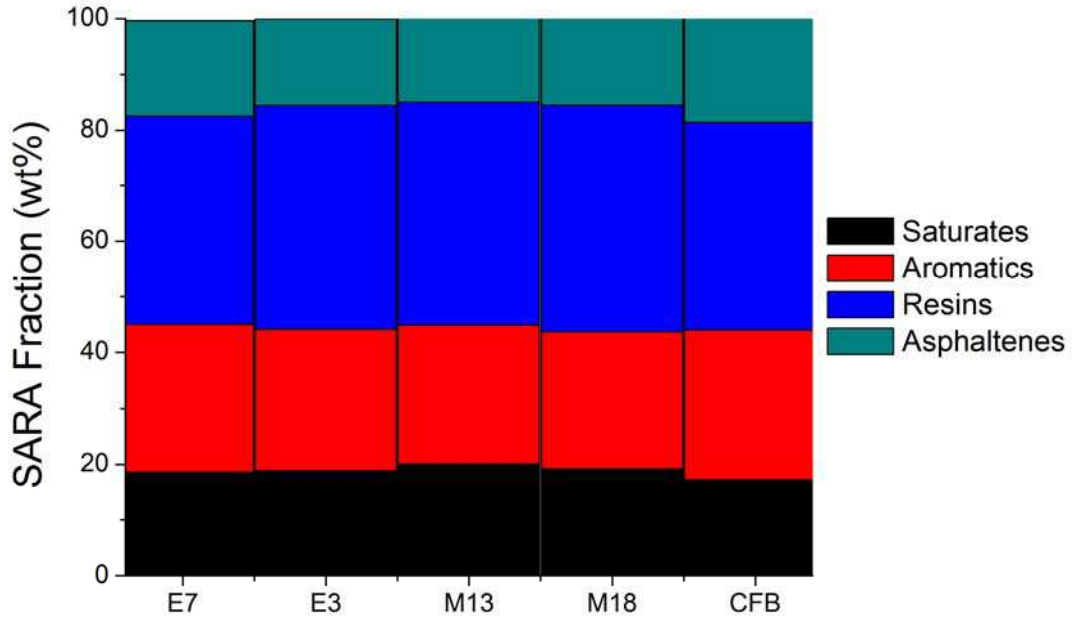
Carbon and proton types:

^{13}C NMR, ^{1}H NMR

Average structural parameters:

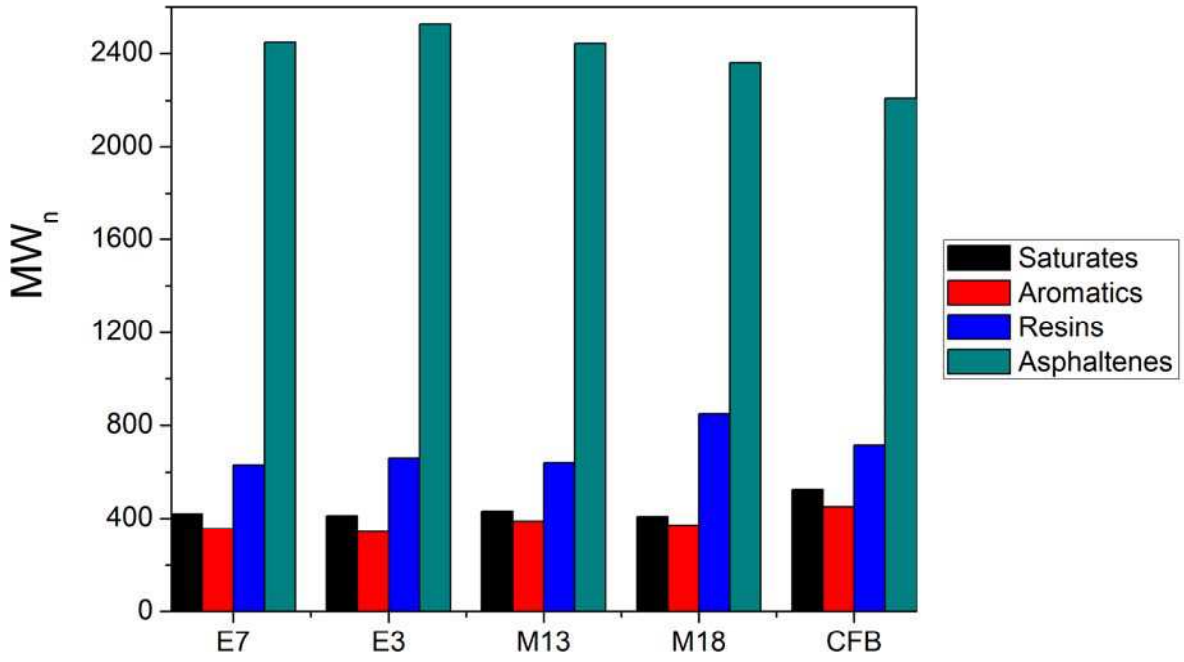
Calculated based on elemental analysis, MW and NMR results.

Results from SARA analysis



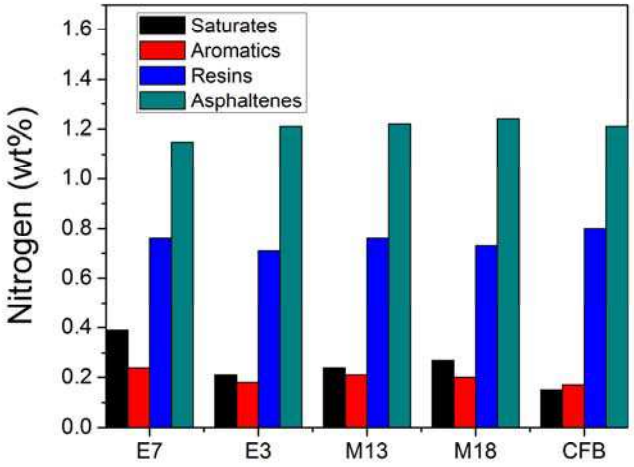
Samples E3, E7, M13 and M18 compare in composition to typical coker feed bitumen (CFB).

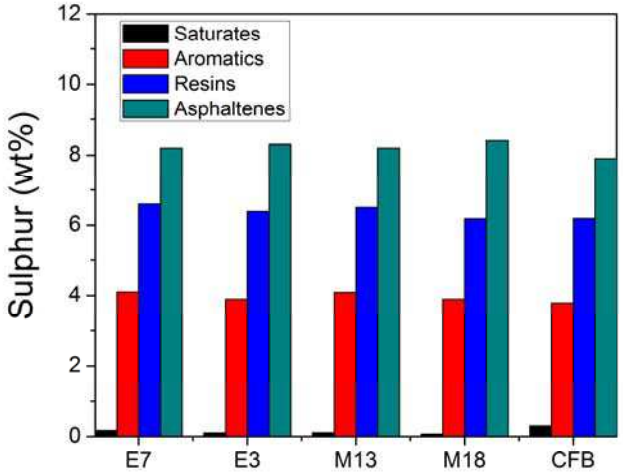
Molecular weights for coker feed bitumen fractions compared to other samples



Molecular weights similar for all samples except slightly higher for resins in M18.

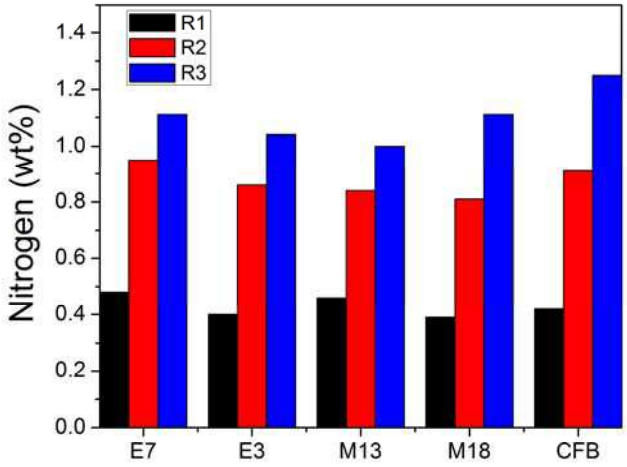
Nitrogen and sulfur contents for fractions of samples

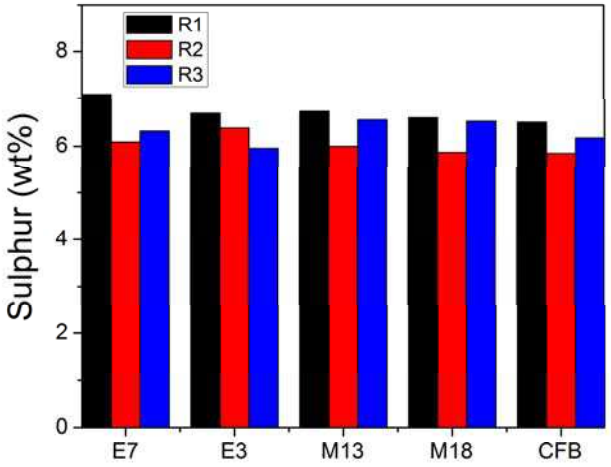




- Nitrogen and sulfur content is similar for corresponding fractions of each sample and similar to CFB content.

Nitrogen and sulfur contents for R1, R2 and R3 fractions





- Nitrogen content increases in increasing HPLC column polarity for separating R1, R2 and R3 fractions
- Nitrogen content in R3 approaches levels measured for asphaltene fraction
- Sulfur content similar in all sample fractions

Average structural parameters
(Fuel 1982, 61, 402-410)

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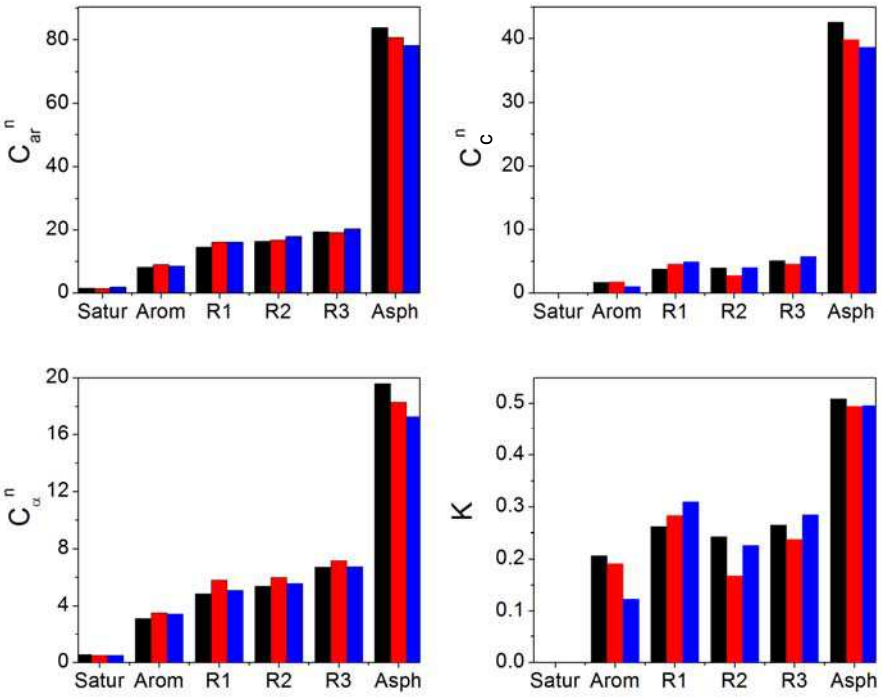
Calculations based on molecular weights, elemental analysis, ^{13}C NMR and ^{1}H NMR.

Symbol	Parameter
C_{ar}^{n}	Number of aromatic carbon atoms in average single molecule
C_{alfa}^{n}	Number of alkyl substituents on aromatic ring system in an average single molecule
C_{c}^{n}	Number of carbon atoms at condensed points in aromatic ring in an average single molecule
K	Degree of condensation of aromatic ring system (C_{c}^{n} / C_{ar}^{n})
L	Average paraffinic straight chains. Estimated from the ratios of the ^{13}C NMR resonances at 29.7ppm and 14.2ppm.

Average structural parameters
(Fuel 1982, 61, 402-410)



- Sample and fractions derived from them are similar in composition

E3
M13
M18

Sample ID	Component (% of Oilsands)			Bitumen Recovery %
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Conclusions

- Bulk properties of each extracted bitumen sample and corresponding SARA fractions were similar
- C_{ar}^{n} , C_{alpha}^{n} and other structural parameters determined from NMR results in conjunction with MW and elemental analyses show little difference between the samples

- **Correlation of sample properties reported here *did not* correlate with observed bitumen yield… another factor must be effecting recovery rates**

- Other factors therefore must be contributing (for example, surface properties of solids, mineralogy of solids and particle size distribution)

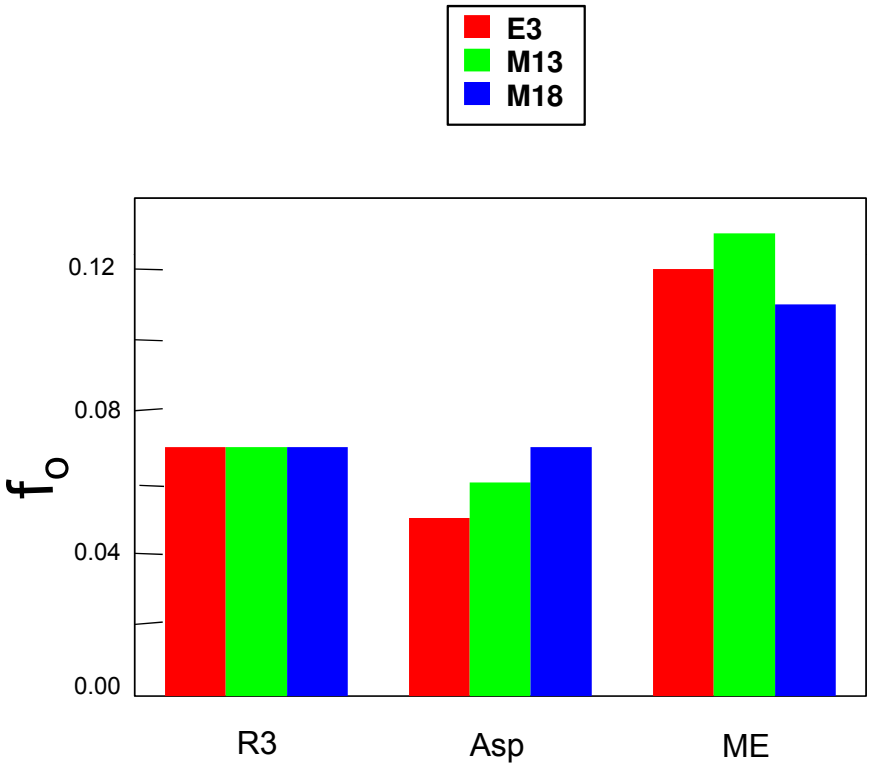
Questions

Thank-you ....
Questions?

XPS results for nitrogen and sulfur types for selected fractions from bitumen and methanol extracts (ME)

- While pyrrole was always the primary nitrogen species, pyridine groups were also present in each case; the greatest contributions from pyridine species occurred in the ME samples.
- In every case the sulphur species were predominantly thiophenic with some contribution from sulphides.
- The sulphoxide and sulphone species occurred in only some of the asphaltene fractions from the parent bitumens; the highest concentrations of this species were found in the ME samples.
- Concurrently with this observation the thiophenic sulfur contents in the methanol extracts are lower than those for the corresponding fractions from bitumen.

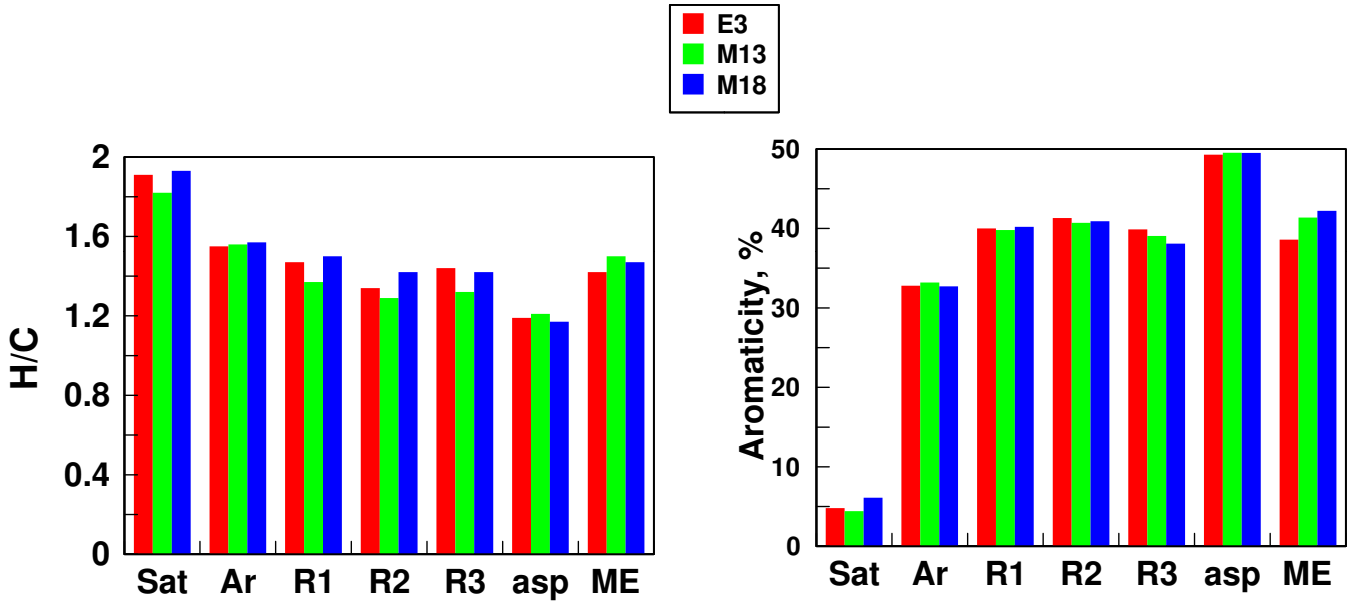
Fraction of carbon associated with oxygen for bitumen fractions & methanol extracts (ME) from C^{13} NMR



f_o estimated from the integration of the following ^{13}C NMR regions (ppm)	
50-70	Aliphatic C-OH, C-OR
145-160	Aromatic C-OH, C-OR
160-190	COOH, COOR, acid, ester

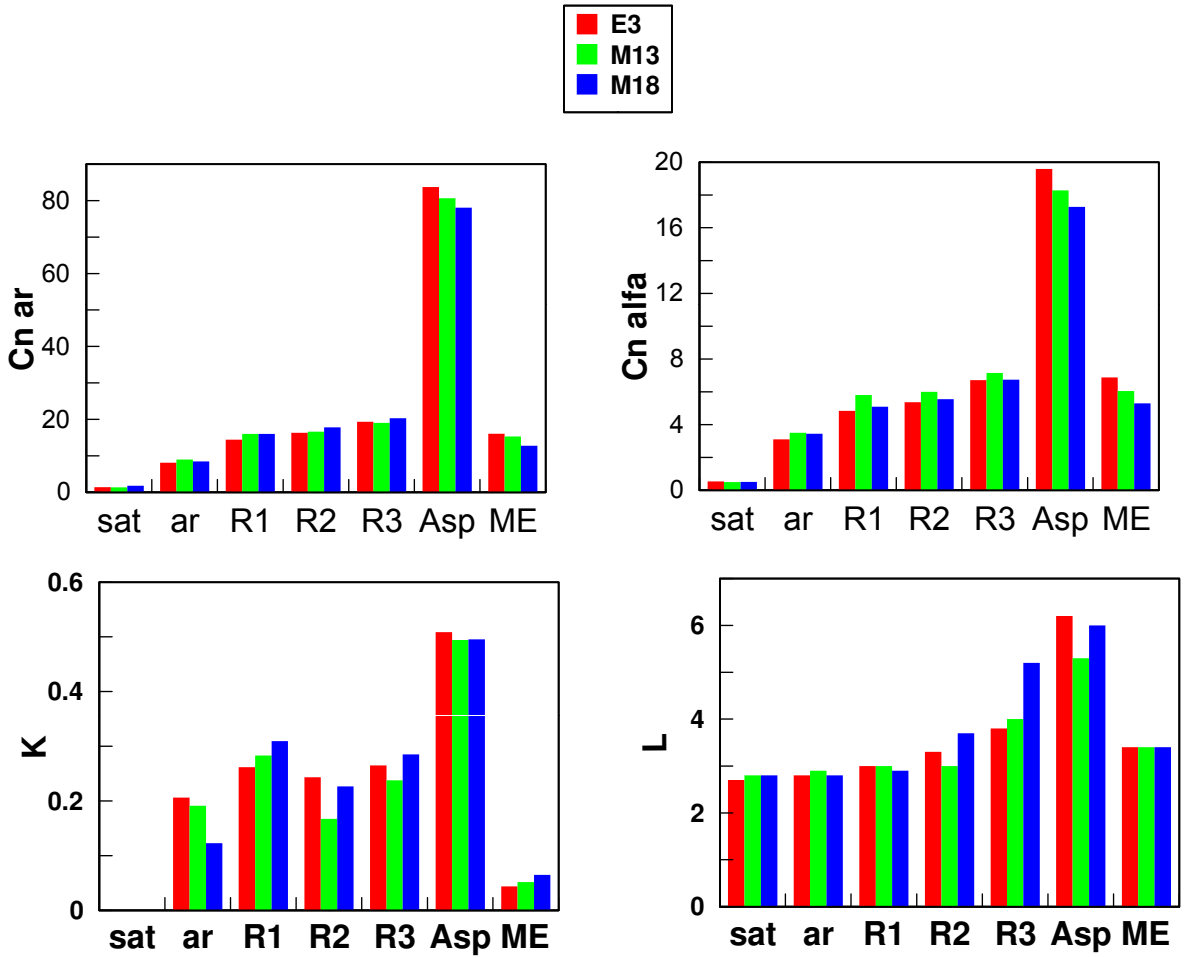
ME has a higher amount of carbon associated with oxygen compared to R3 and asphaltenes.

Atomic H/C ratios and ^{13}C aromaticities for bitumen fractions and methanol extracts (ME)



Differences are small when comparing H/C atomic ratios and aromaticities between ME and resins.

Average structural parameters for bitumen fractions & methanol extracts (ME)



Conclusions

- Molecular weights for methanol extracts from bitumen free oilsands solids are close to those for resin fractions, and much lower than those for asphaltenes.
- Only minor differences exist between H/C atomic ratios, aromaticities for ME and resins.
- Number of aromatic carbon atoms in molecule; number and chain lengths of alkyl substituents on aromatic rings were among parameters pointing to similarities between the methanol extract and resins.
- Degree of condensation of aromatic ring systems for the ME samples are much lower than the values for the corresponding resin fraction.
- Both elemental sulfur content and the contribution of thiophenic sulfur in the methanol extract samples is lower than those in the bitumen components.

Conclusions

- The contributions of elemental nitrogen and carbon associated with oxygen for the methanol extract are higher than those for the resin and the asphaltenes.
- Owing to its polar nature TIOM may be responsible for increased interaction with bulk bitumen leading to associated difficulties with oil release during conventional water based separation processes.
- In all cases the nitrogen species are predominantly pyrrolic. Pyrolle rich organic matter is known to undergo oxidative polymerization to form the adhesive material with high a propensity to fouling.