

PAPER 47: REVIEW ON THE ROLE OF SULFUR IN BITUMEN PROPERTIES



Sayed Nahar, TNO

Liz Mensink, Rijkswaterstaat

Xueyan Liu, Peng Lin, Delft University of Technology

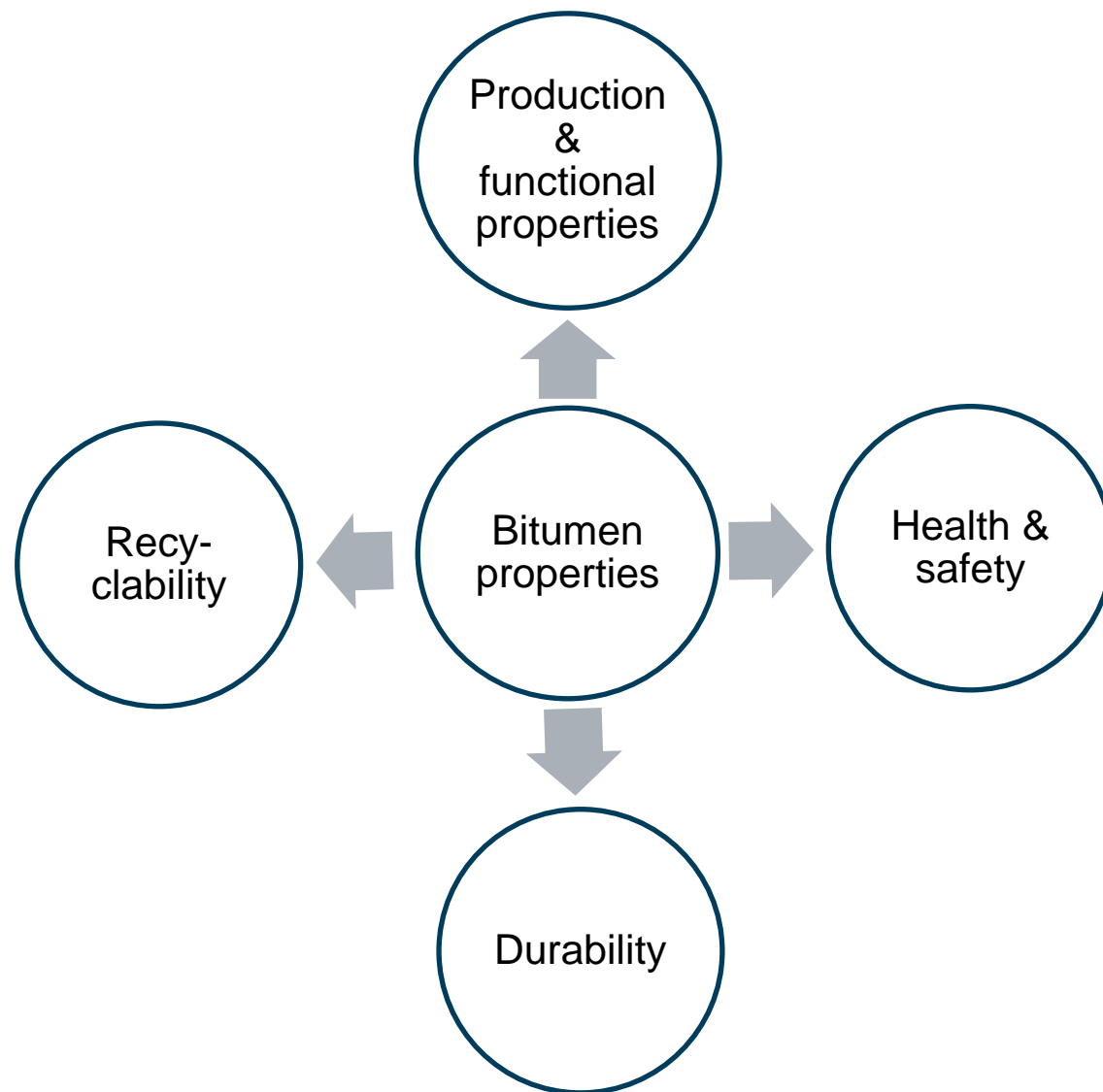


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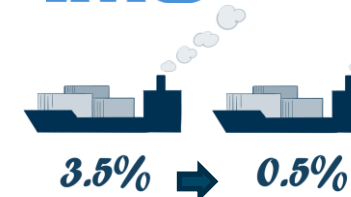
ASPECTS OF BITUMEN PROPERTIES



- › Refinery transitions
- › Closure of bitumen production

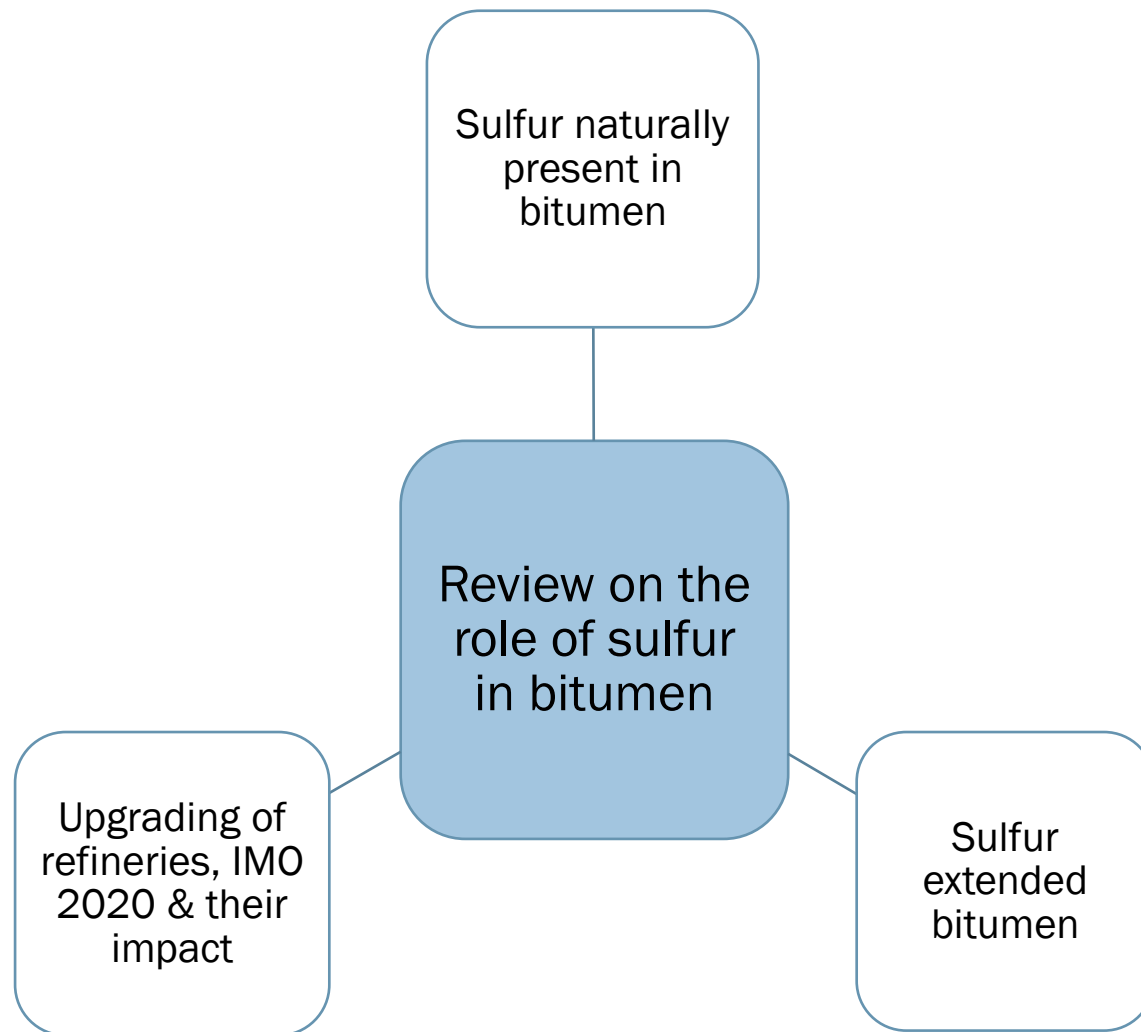


- › Reduction of sulphur in marine fuel



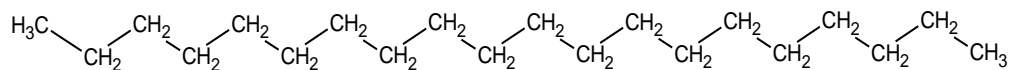
- › Diverse additives

› SULFUR IN BITUMEN

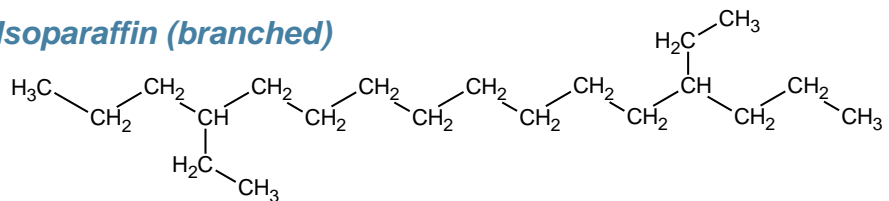


Saturates

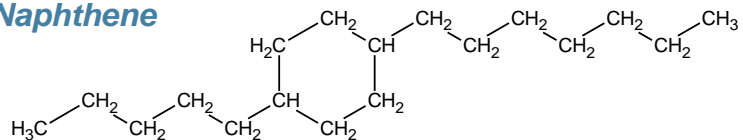
Paraffin



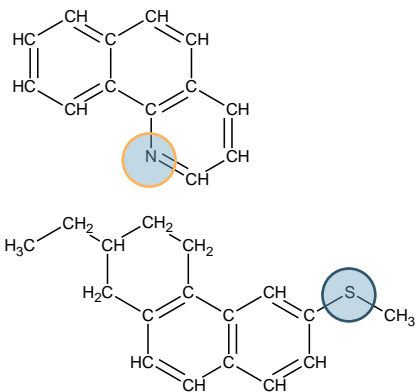
Isoparaffin (branched)



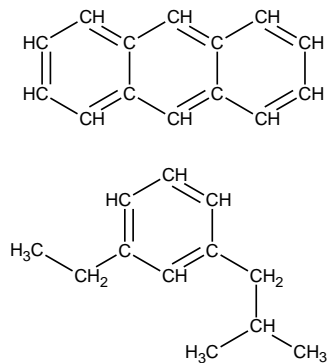
Naphthene



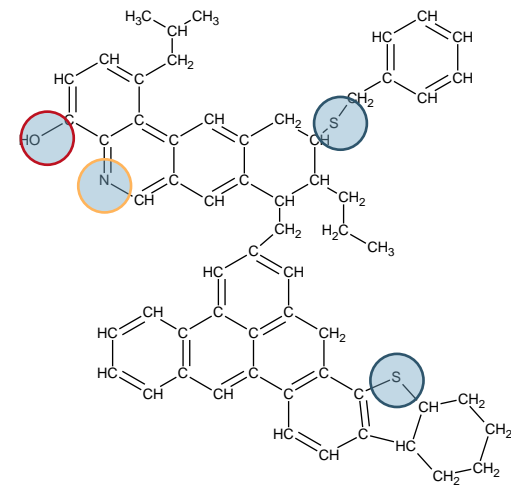
Resins



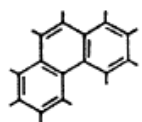
Aromatics



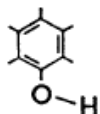
Asphaltenes



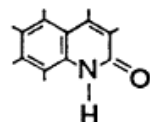
FUNCTIONAL GROUPS IN NEAT AND AGED BITUMEN



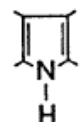
Poly-Nuclear Aromatic (1)



Phenolic (1)



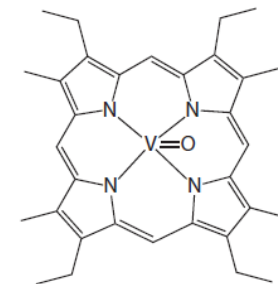
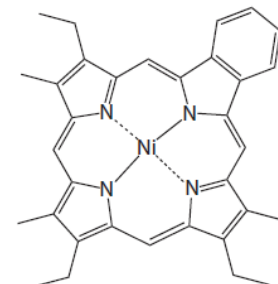
2-Quinolone Type (1)



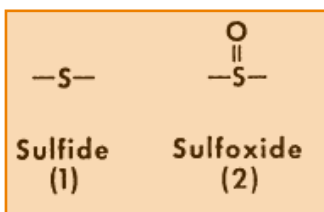
Pyrrolic (1)



Pyridinic (1)

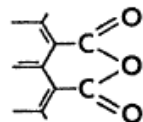


Nickel and Vanadium porphyrin structures in bitumen

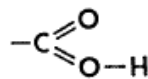


Sulfide (1)

Sulfoxide (2)



Anhydride (2)



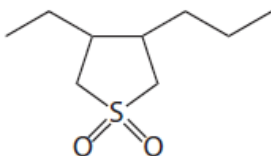
Carboxylic Acid (1,2)



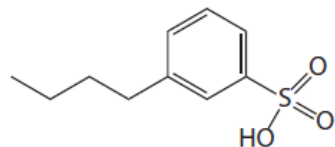
Ketone (2)

(1) Naturally Occurring
(2) Formed on Oxidative Aging

Cyclic sulfone

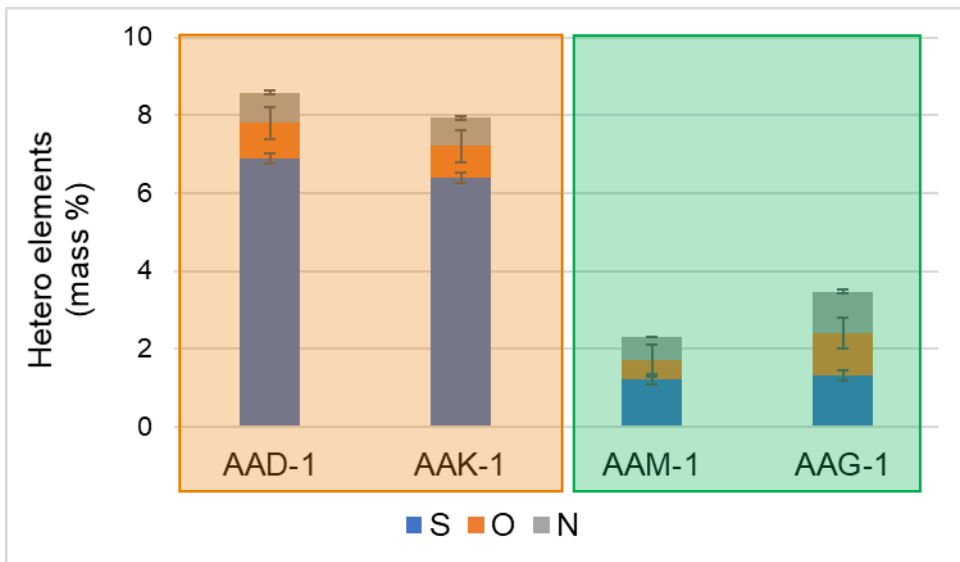


Sulfonic acid

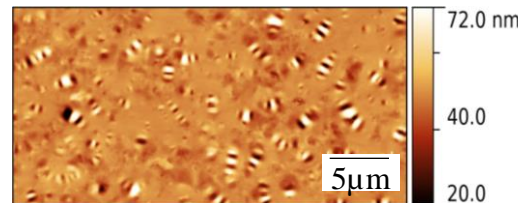


› aliphatic sulfides into sulfoxides,

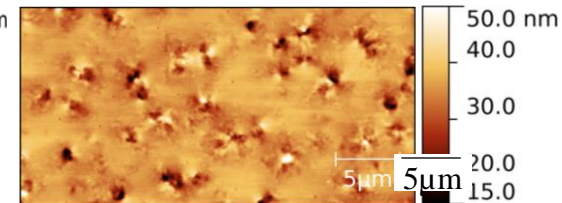
STRATEGIC HIGHWAY RESEARCH PROGRAM (SHRP) BITUMEN



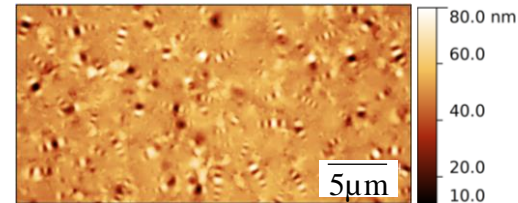
High sulfur content
AAD-1



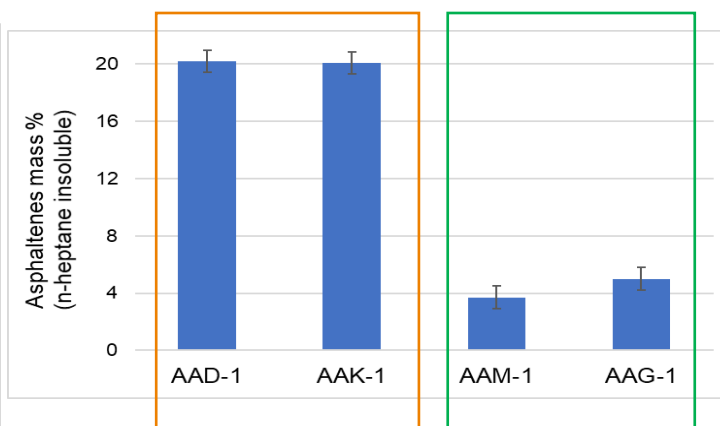
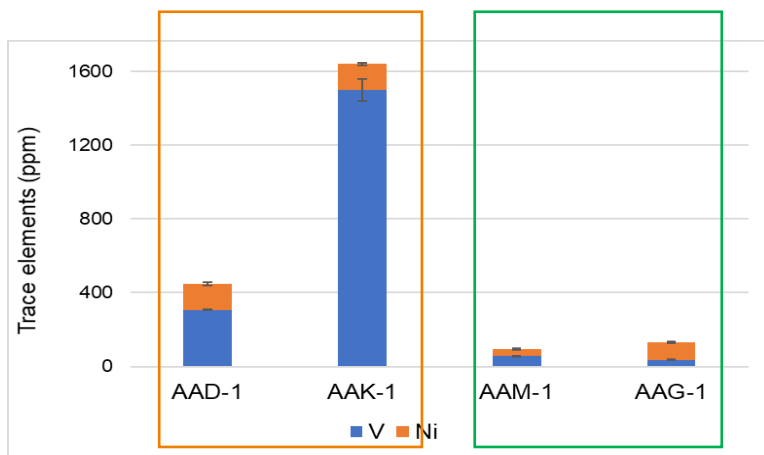
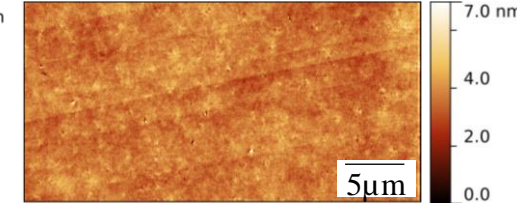
Low sulfur content
AAM-1



AAK-1

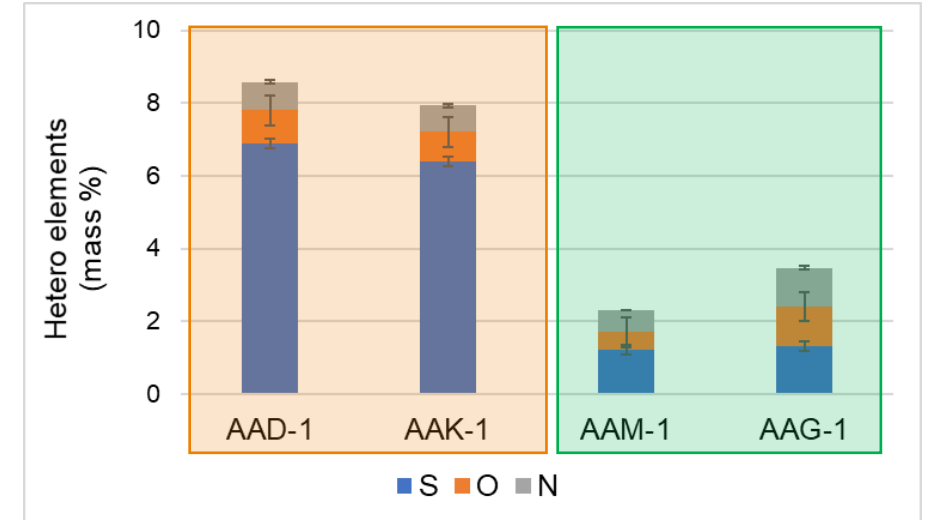
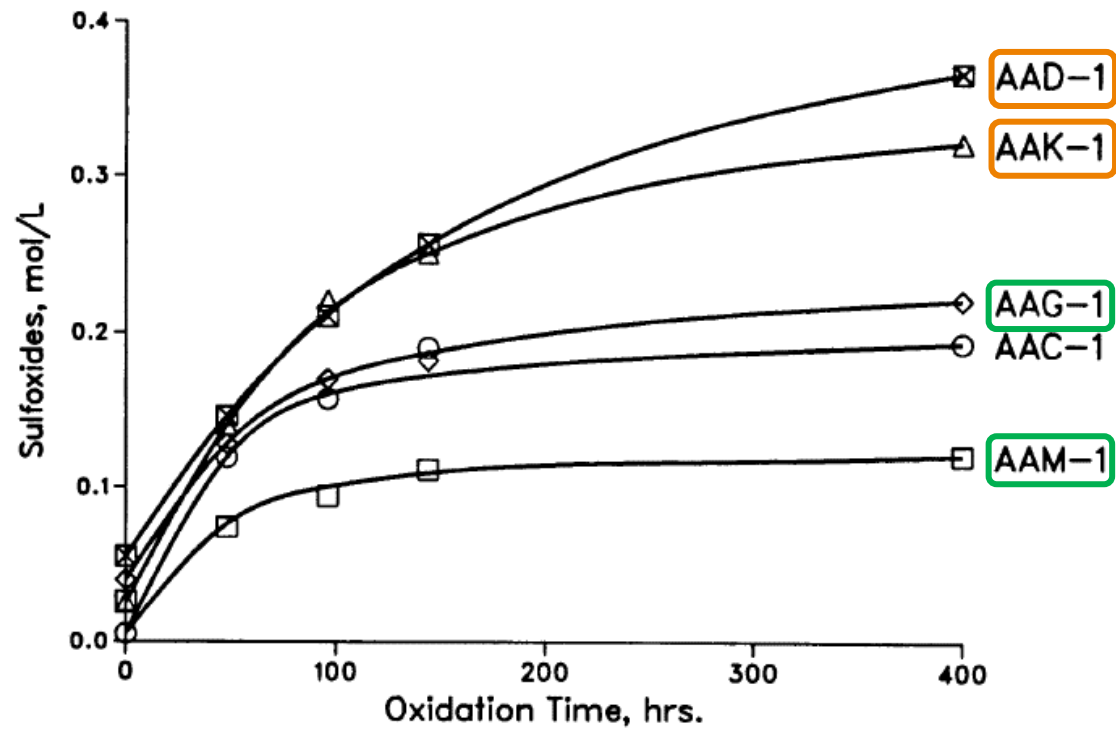


AAG-1

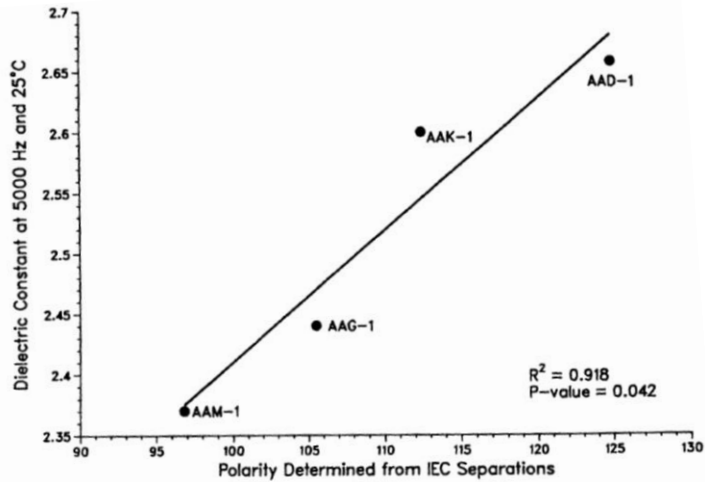


- › asphaltene fraction hosts most of the trace metals: influence the size and agglomeration
- › The influence of sulfur alone to facilitate agglomeration is limited

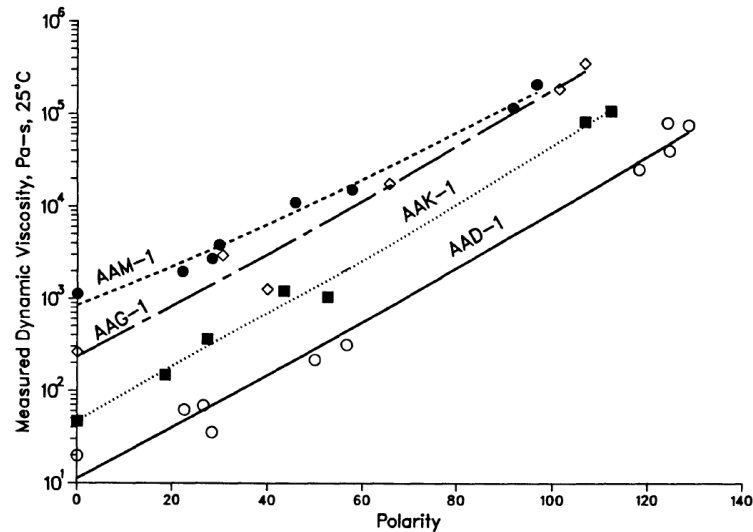
SULFOXIDE FORMATION AS A FUNCTION OF (PAV) AGEING @ 60 °C



PROPERTIES

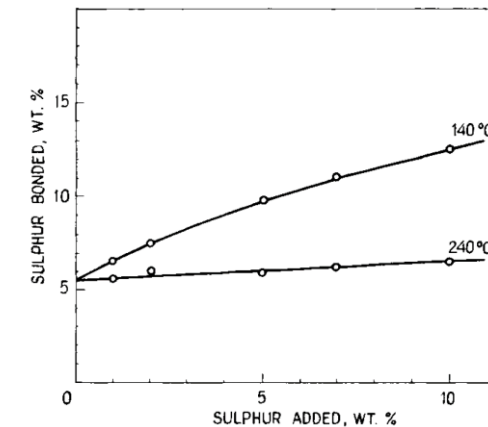


- › Higher sulfur-containing bitumen shows higher polarity
- › Viscosity as a function of polarity: linear relationships
- › High sulfur-containing bitumen is more susceptible to moisture damage and low temperature cracking.

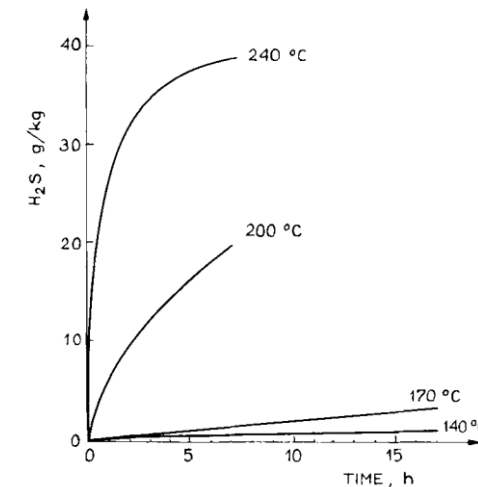
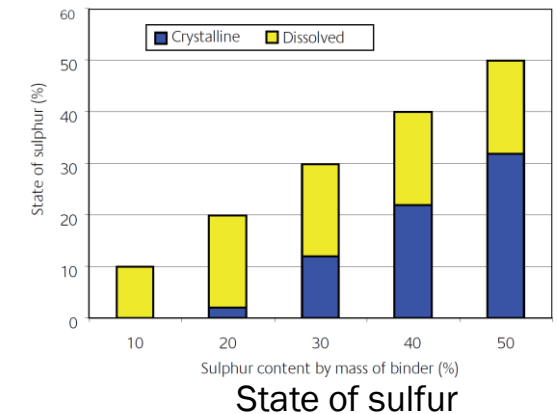


› SULFUR-EXTENDED BITUMEN (SEB)

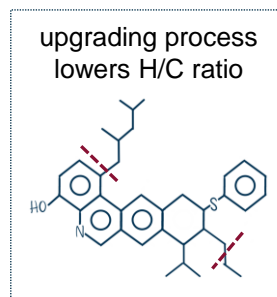
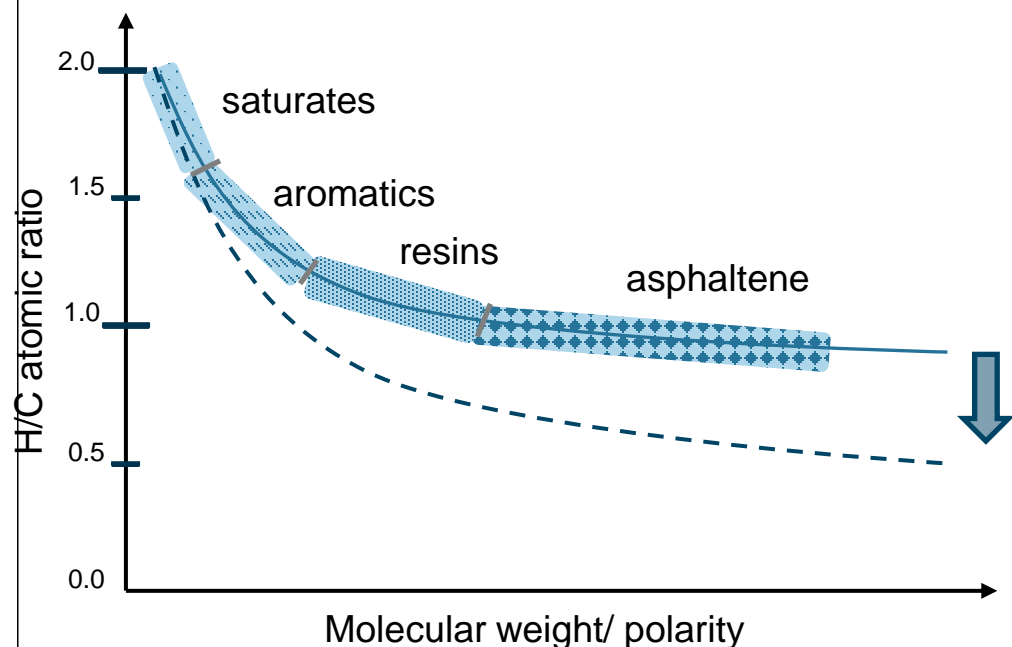
- › Treating bitumen with sulfur
- › The concept is available since 1930s and reported improved properties (i.e. stiffness, rutting resistance) over conventional bitumen
- › Sulfur in SEB can be found in three different forms: (1) chemically bonded, (2) 'dissolved' in bitumen, and (3) crystalline sulfur
- › low modification, sulfur incorporates well and extends the binder rheological properties;
- › higher modification, acts as a filler
- › Viscosity and softening point of SEB increase with the processing time
- › Emission: Below 140 °C the formation of hydrogen sulphide and sulfur dioxide is negligible



Influence of temperature on chemically bonded sulfur



› BITUMEN COMPOSITION IN RELATION TO PRODUCTION PROCESS



Upgrading of vacuum residue:

- › Deasphalting: Solubility based separation
- › Oxidation: Passing air through bitumen at elevated temperature → Oxidized/Blown bitumen
- › Thermal cracking
 - › Breaks the long paraffinic side chains attached to aromatic rings to form shorter molecules (above 420 °C to break C-C bonds)
 - › C-S bond is weaker than other aliphatic bonds.
 - › Thermal processing results in hydrogen sulfide (H₂S), even at temperatures below 250 °C
- › Hydrotreating/desulfurization
 - › hydrogen is introduced into this specific process usually resulting in desulfurization

› CONCLUSIONS

- › Discussed the presence of sulfur in bitumen, and its relation to other bitumen components, most prominently the asphaltenes and trace metals.
- › Most sulfur groups tend to oxidize more allowing for even more polar interactions.
- › Sulfur in bitumen molecules induces polar interactions, promoting agglomeration of asphaltenes.
- › Increased polarity, shows an increase in viscosity.
- › By adding sulfur into bitumen (SEB), at low concentrations influences the rheological properties, and at high concentrations partly act as a filler, also changing the mechanical properties.
- › Discussed changes in refining process, upgrading trends where increasingly harder grades bitumen are being available.

› **ACKNOWLEDGEMENT**

- › KPE- program: Characterization and Evaluation of Asphalt Binder Properties (CEAB)