What is Special About My Asphalt?

New Characterization Approaches to Better Capture it

J-P. Planche (PHD), Jeramie Adams (PHD), Ryan Boysen, Michael Elwardany (PHD), Joe Rovani - WRI

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AMAP The Association of Modified Asphalt Producers
Better Roads from Better Technology

jplanche@uwyo.edu

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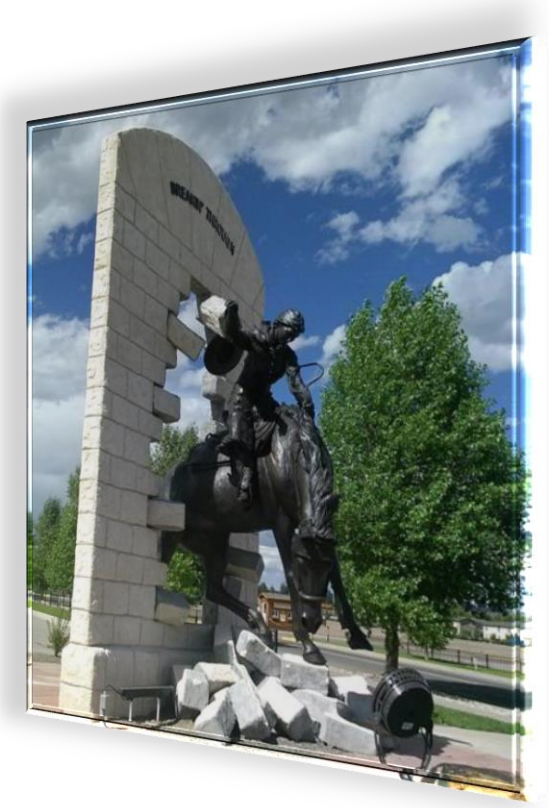
  - E. Harrigan and the Panel
  - The Project Team
- **Partners**
  - WRI-Asphalt Industry Research Consortium
  - Paving and Roofing actors



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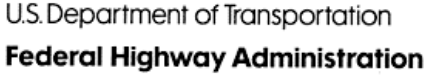
WRI partners -Asphalt / Coal / Petroleum / Biomass materials



- ***Others incl. DOE, MIT, ORNL, Solvay, SRI…***

Outline

- What is special about my asphalt?
- What is really special about my asphalt?
- Why? Industry Context
- Examples from an industry study
- Summary and perspectives

What is special about my Asphalt?

- **Example:** 4 same PG grades (PG 70-22), **but**…
- Different ΔTc's and Black Space behaviors
- Known production process – different crudes and base asphalts

Sample ID	Source/Description
A	SBS Modified
B	Straight Run
C	Air Blown (Lloydminster)
D	SBS Modified

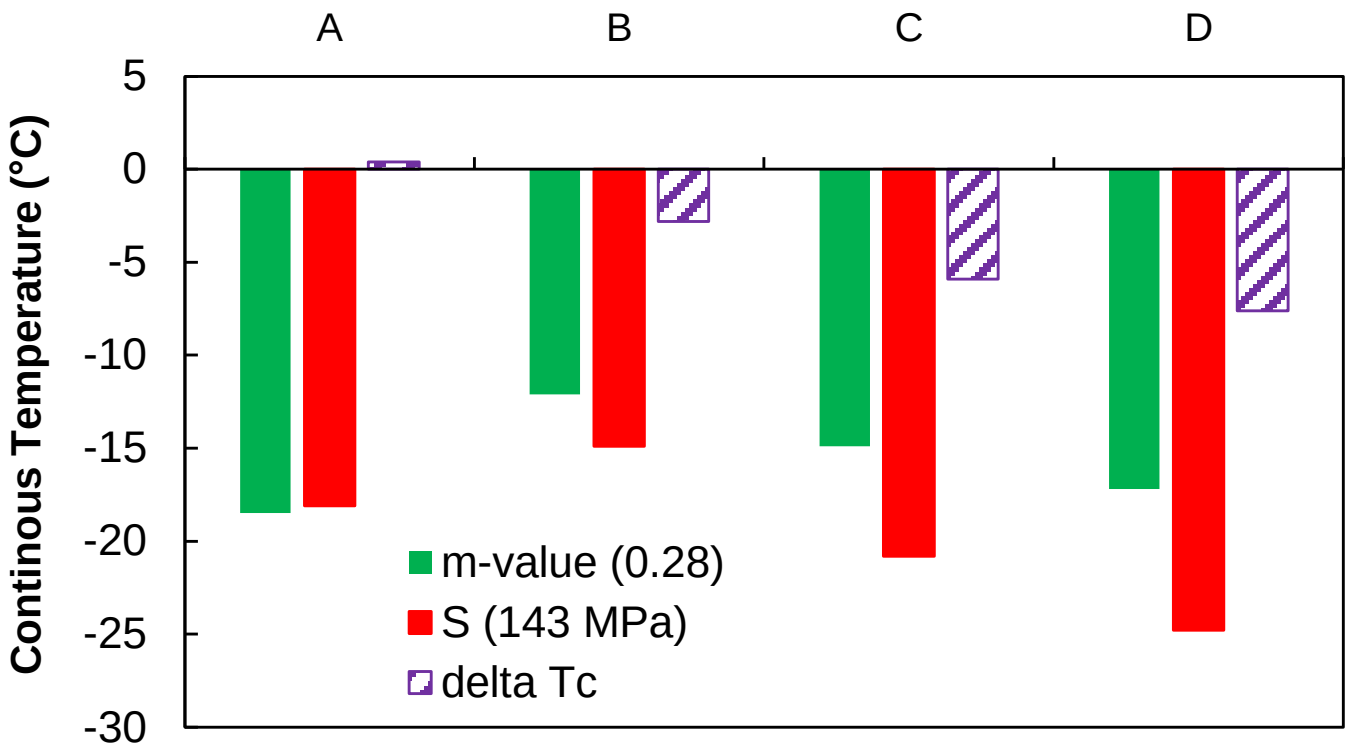



WRI-AIRC data

What is special about my Asphalt?

A	SBS Modified
B	Straight Run
C	Air Blown (Lloydminster)
D	SBS Modified

Low temperature rheological behavior – from PG specs



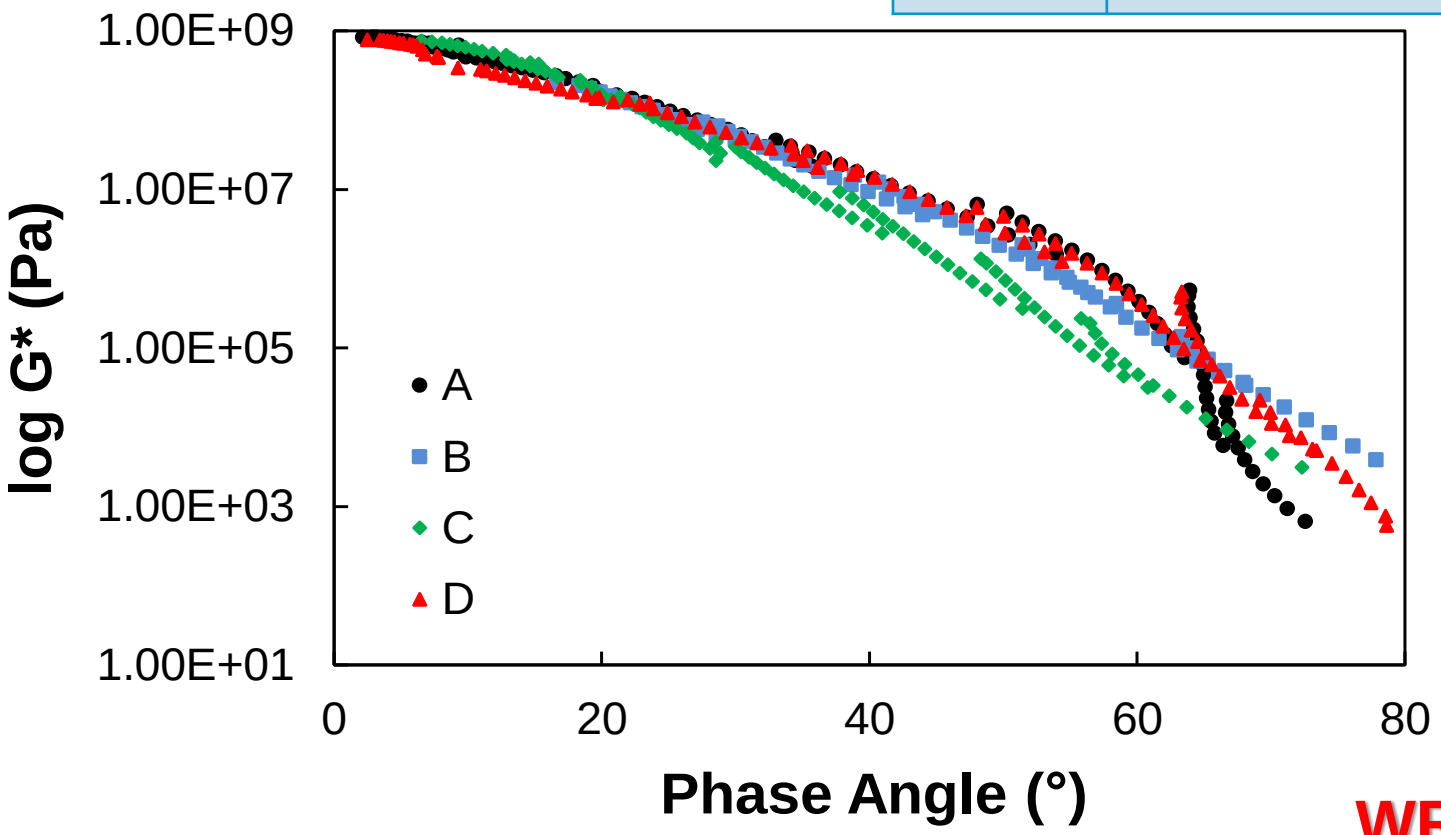
BBR or 4mm DSR Data

WRI-AIRC data

What is special about my Asphalt?

A	SBS Modified
B	Straight Run
C	Air Blown (Lloydminster)
D	SBS Modified

Whole temperature, frequency rheological behavior – beyond PG



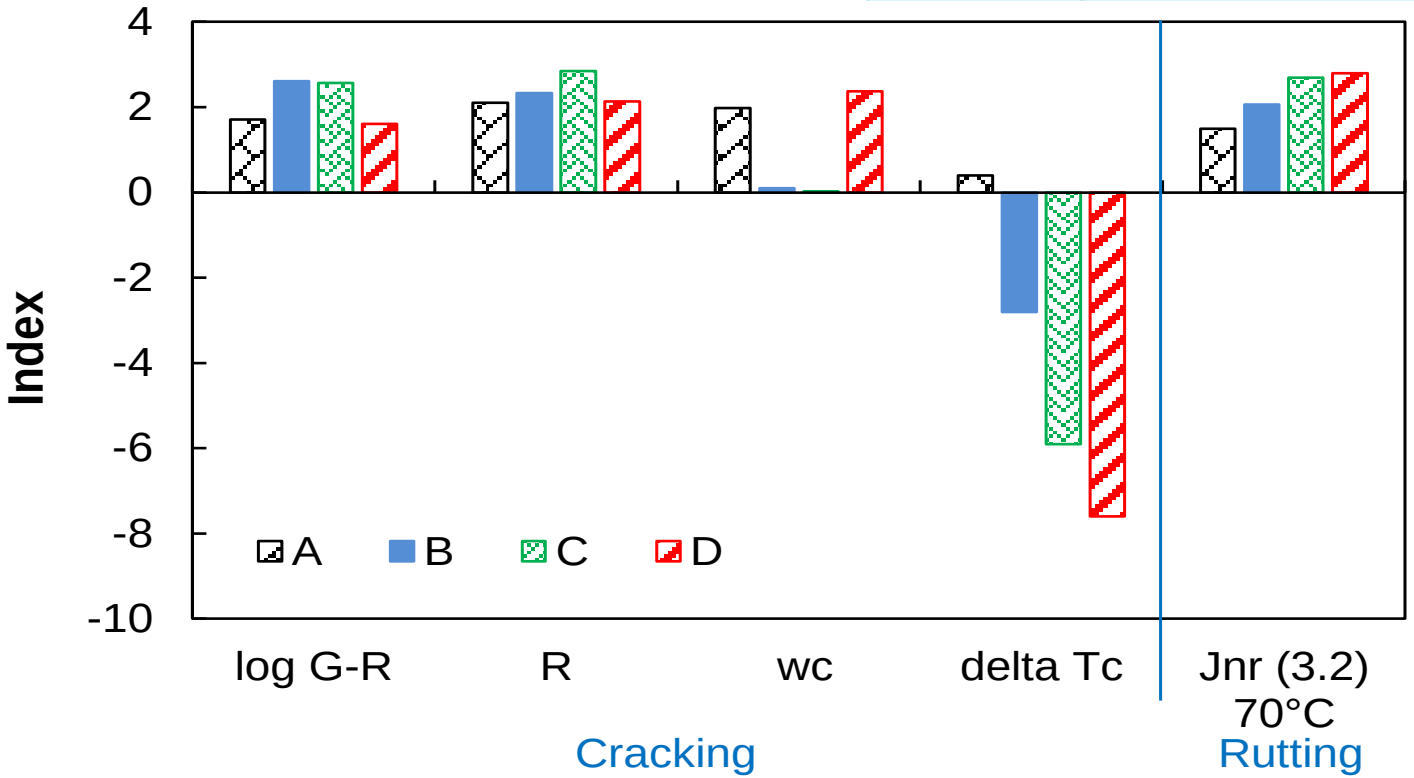
25 and 4mm DSR Data

WRI-AIRC data

What is special about my Asphalt?

"Buzz performance parameter"
Binder behavior – beyond PG
G-R, R, Crossover f, ΔTc
- **Not equivalent**

A	SBS Modified
B	Straight Run
C	Air Blown (Lloydminster)
D	SBS Modified



25 and 4mm DSR – BBR Data

WRI-AIRC data

What is special about my Asphalt?

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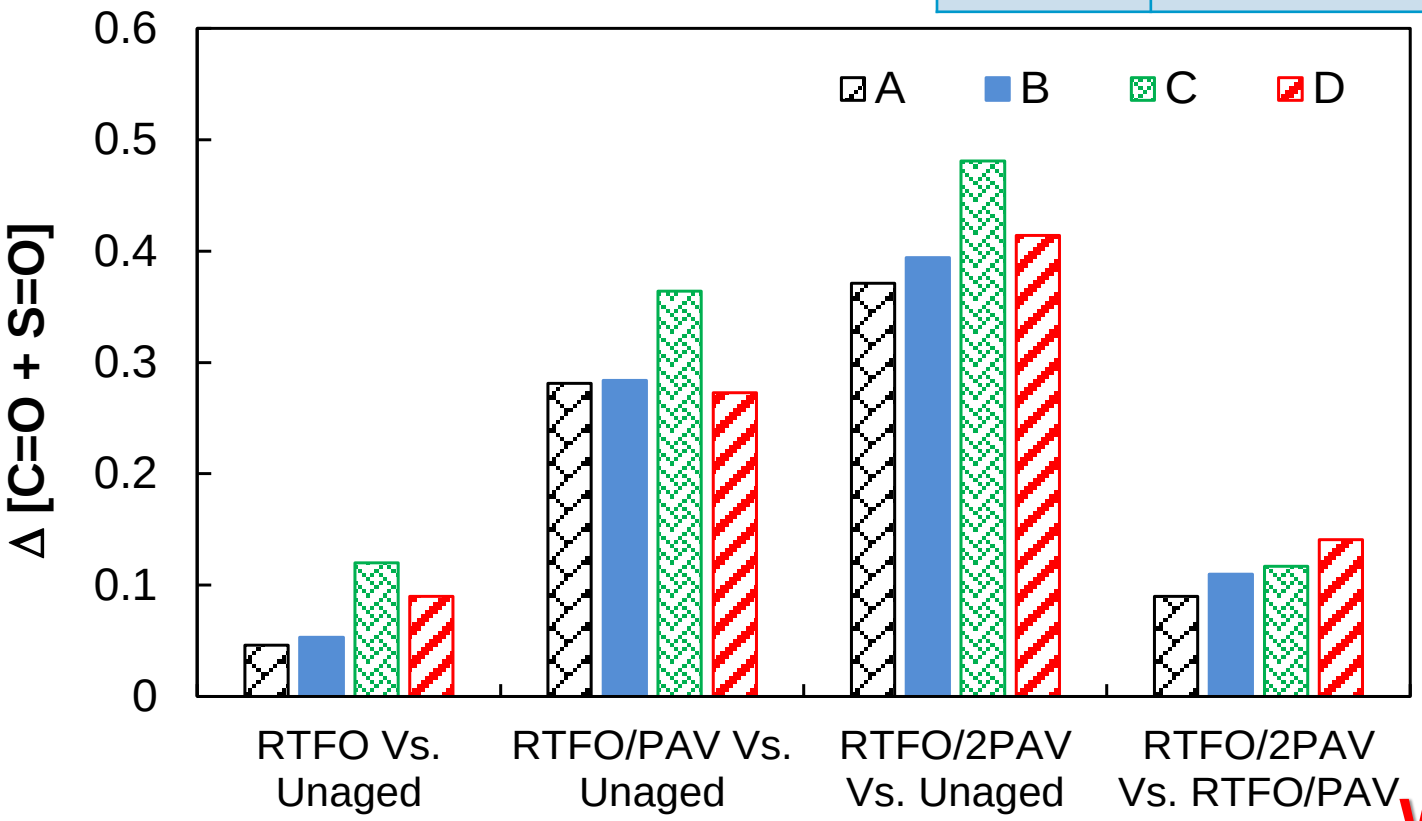
D	SBS Modified

Oxidation behavior – Chemical Analysis



FTIR Data

WRI-AIRC data

What is really special about my Asphalt?

A	SBS Modified
B	Straight Run
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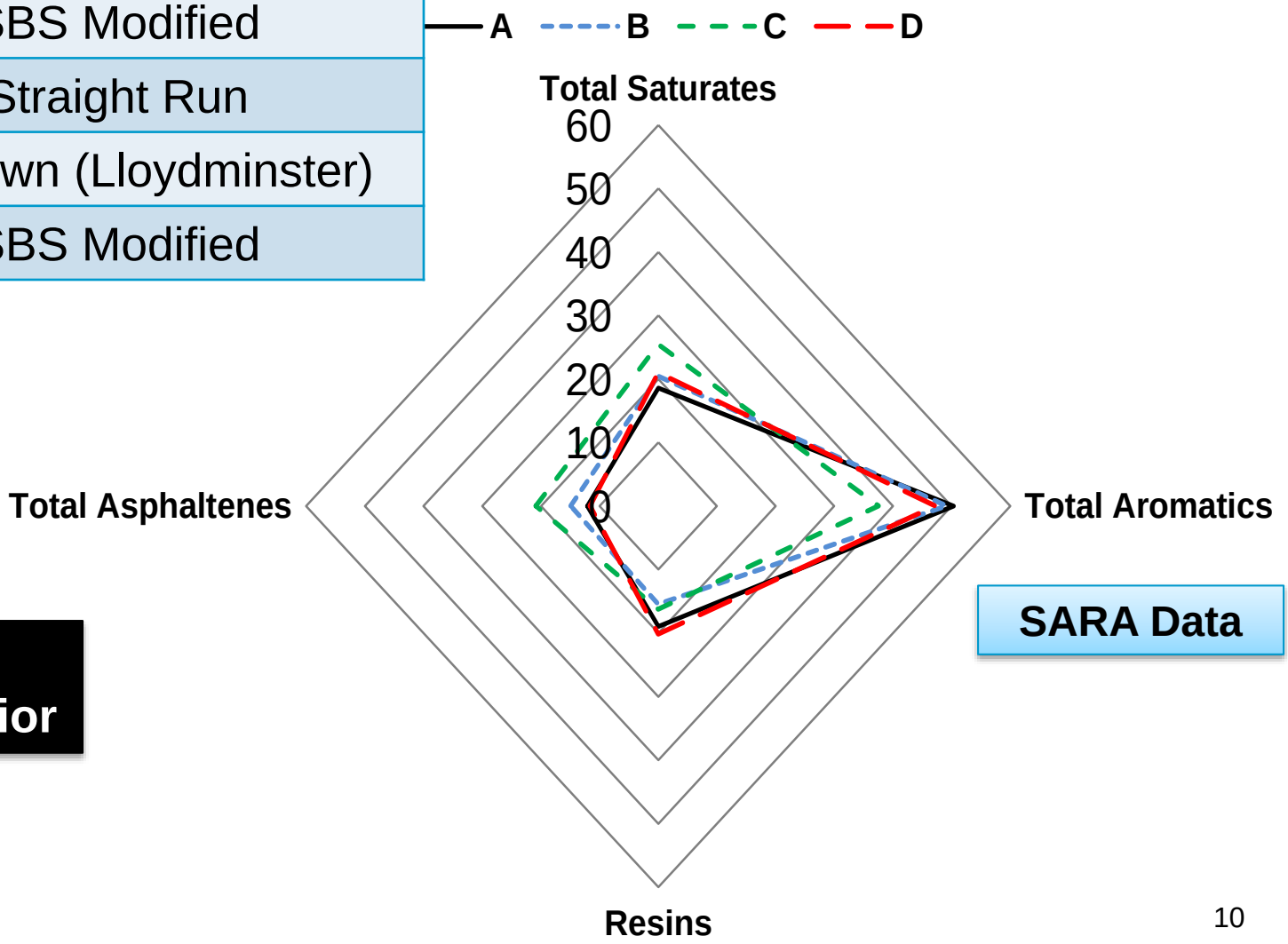

SARA Data

Composition - fraction behavior

WRI-AIRC data

What is really special about my Asphalt?

A	SBS Modified
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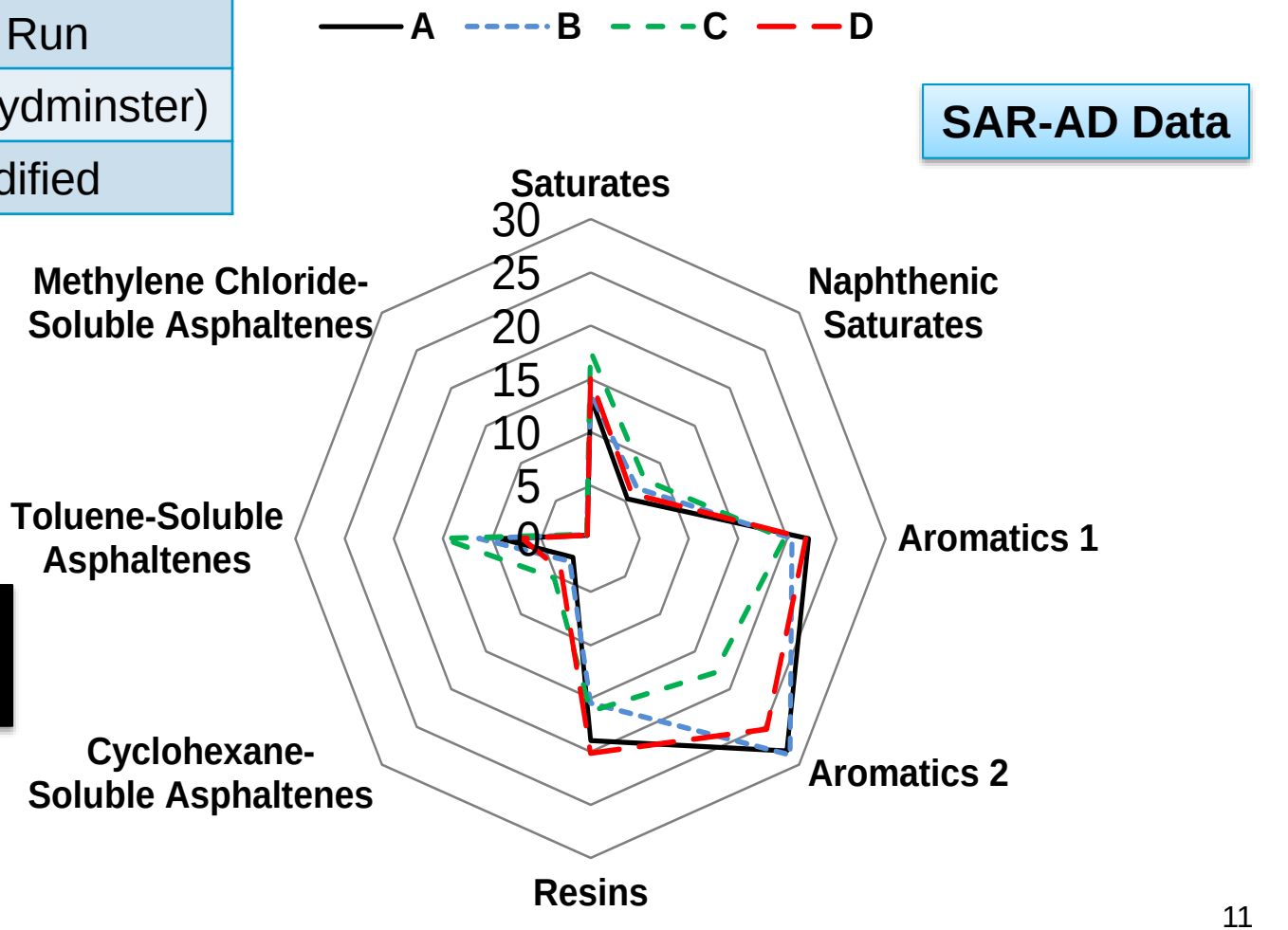

Composition - fraction behavior

WRI-AIRC data

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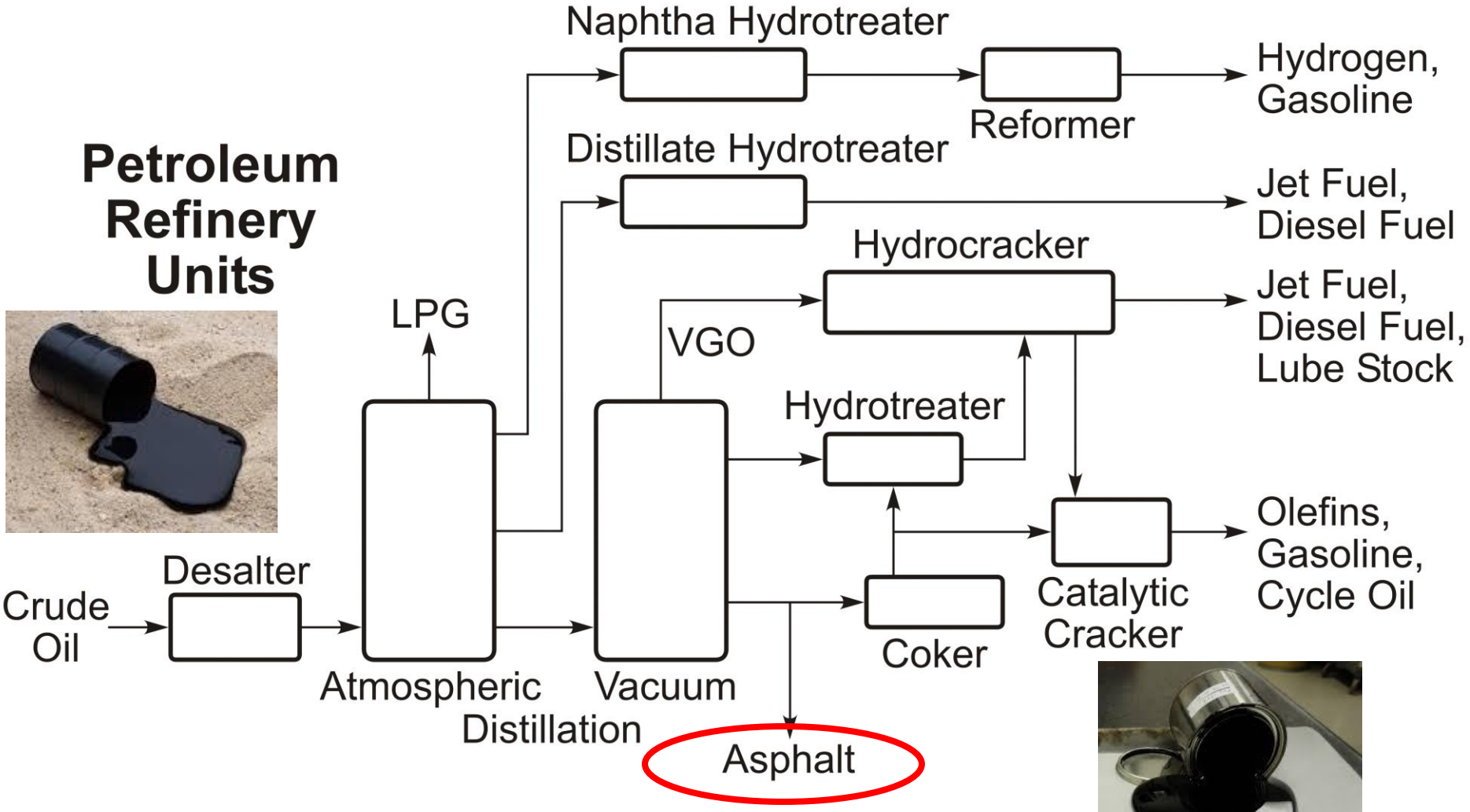
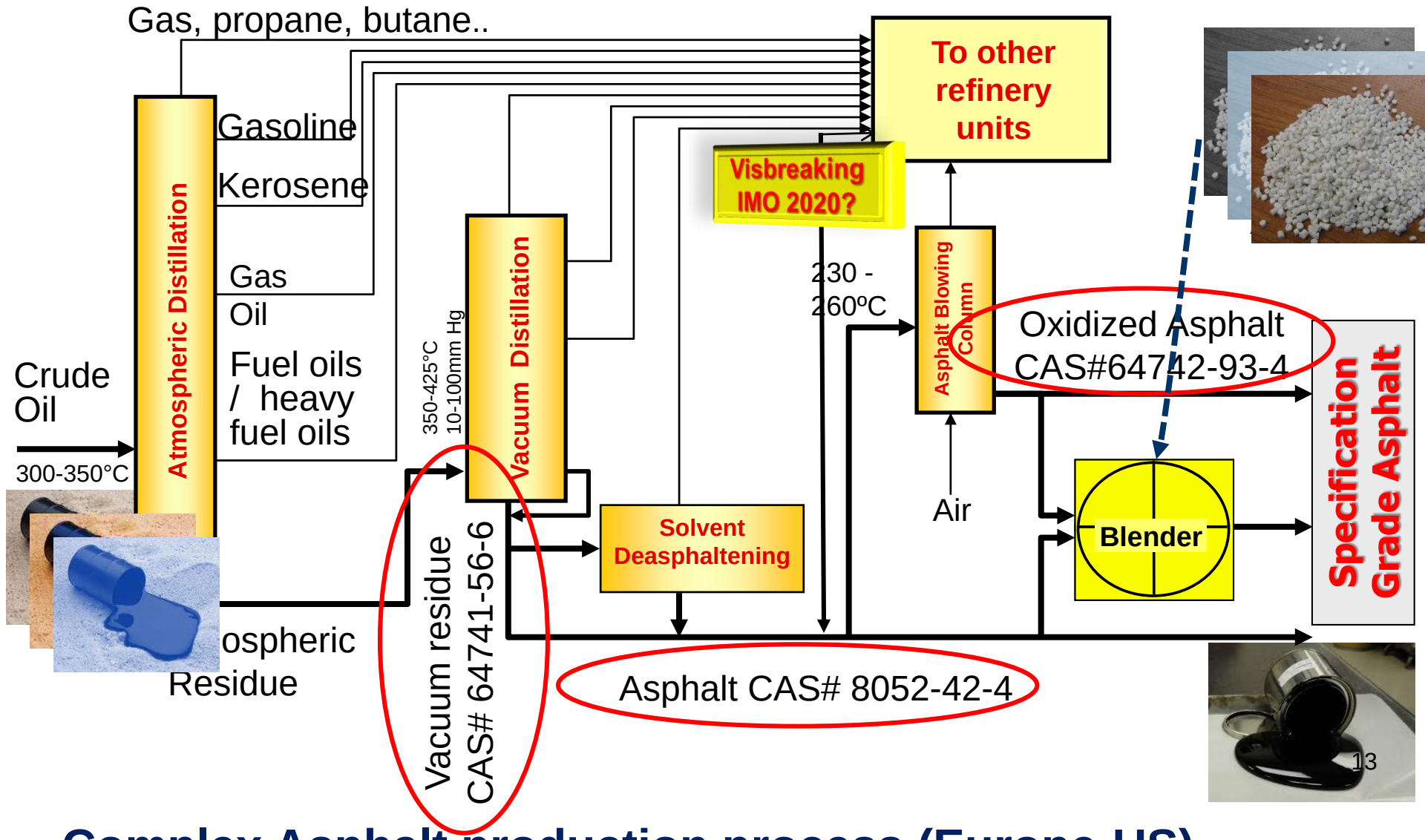
Why is my asphalt special? Refinery Block Diagram - 1



"Simple" asphalt production process (US)

Adapted from AI-Eurobitume document

Why is my asphalt special? Refinery Block Diagram -2



Complex Asphalt production process (Europe-US)

Why is my asphalt special?

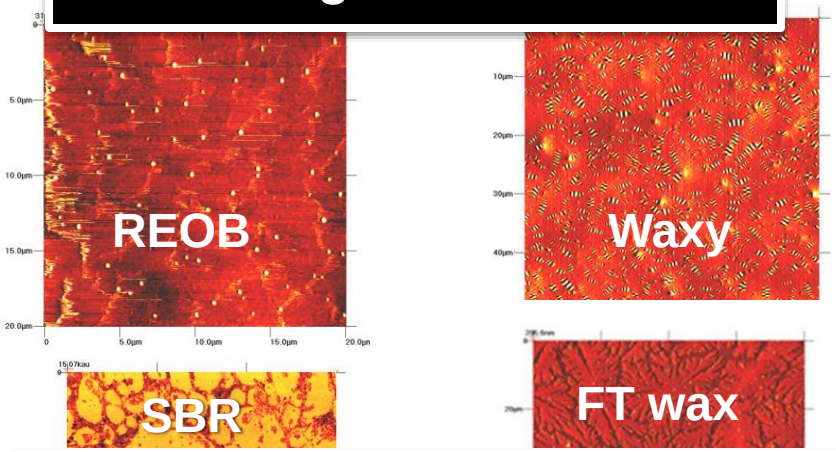
- **Context: economics, geopolitics, societal, regulatory**
  - **Changes** in crude oils and processes
  - **Blends** of various refining bases
  - **New world of additives** - polymers, biomass molecules, …
  - **High rate recycling**
    - RAP / RAS / REOB / GTR / Plastics, …
  - **Impact of specifications**
    - **Asphalt**: Superpave and empirical – no true performance related
    - ***Other petroleum products specs***: 2020 IMO on Marine fuel % Sulfur
- **Consequences: New problematic binders appearing**
  - **High ΔTc, sensitive to aging**
  - **"Out of balance" composition - incompatible, inhomogeneous blends (NCHRP 9-60 literature review)**

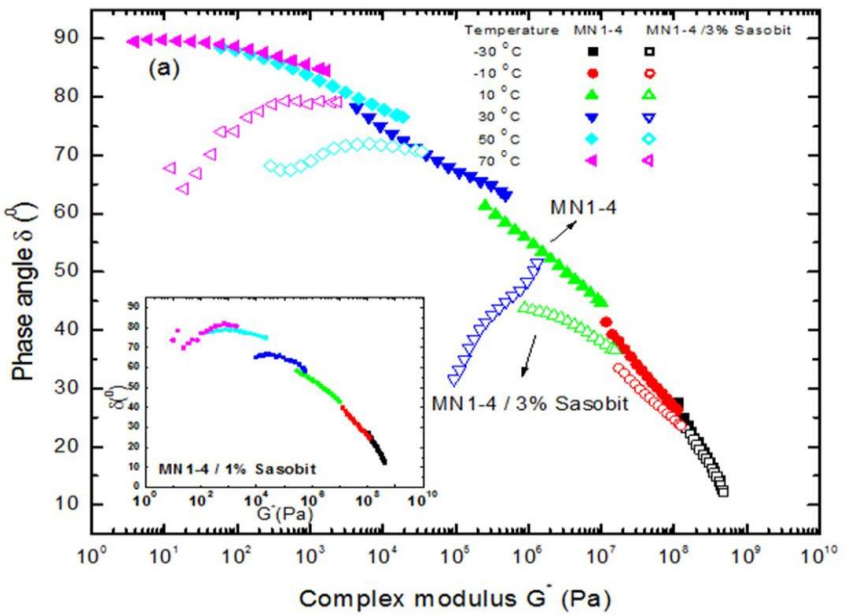
Why is my asphalt special? Changes in binders / SHRP era

- **Examples of problematic binders**
  - Incompatible blends – fracking crudes / heavy crudes
  - Airblown, oxidized blends
  - High RAP / RAS
  - Hard SDA / soft blends
  - Visbroken residues (IMO 2020)
  - Waxy binders
  - REOB blends
  - Inhomogeneous modified binders
    - Polymers - EVA, SBS, Terpolymers
    - Additives - PPA, wax, biomass

- **Note: these blends can be made suitable too!**

Complex structure and rheological behavior





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Why is my asphalt special? Is this important?

- **Field consequences**
  - Pavement issues: lower durability
- **Superpave binder specs**
  - Binder variability - inconsistent quality, not captured by current specs
  - PG specs and test methods, designed in the 90's for asphalt from the 90's
  - Not for today's / tomorrow's binders
- **→NCHRP 9-58,-59,-60,-61 projects**
- **NCHRP 9-60**
  - Improve current performance graded asphalt binder specifications & tests
  - To prevent premature thermal cracking and raveling

Raveling - WI: Year 3

Cracking - ON: Year 5: 9% REOB

Block cracking - WY - Parking lot

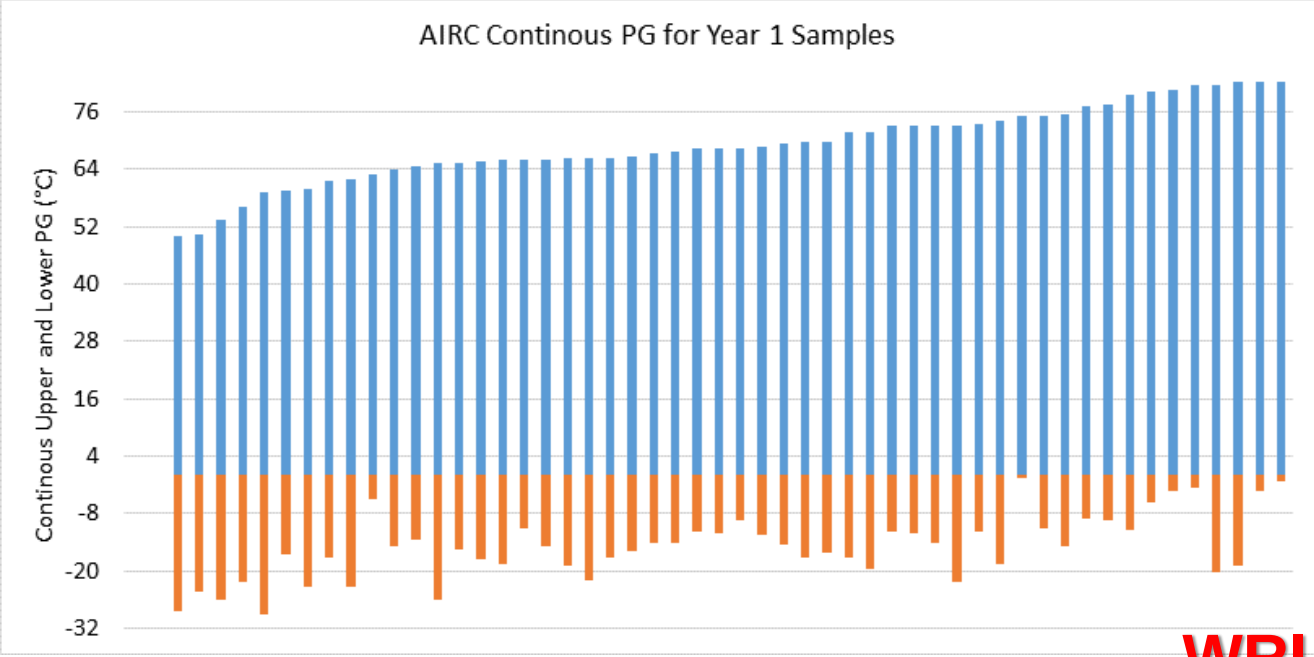
Examples from an industry study

- **WRI-AIRC (Asphalt Industry Research Consortium)**
  - **Goal: Asphalt binder fingerprinting to Understand and assess the source variability**
  - **8 partners: BE, CA, FR, MX, SP, US**
    - **Road administration**
    - **Road contractors**
    - **Additive supplier**
    - **Asphalt suppliers / producers**

WRI-AIRC data

Examples from an industry study

- **WRI-AIRC (Asphalt Industry Research Consortium)**
  - **Asphalt binders: 52 samples (Year-1) - worldwide**
    - **SHRP and ARC asphalts - references**
    - **Unmodified – straight run, airblown, SDA, and VB blends**
    - **Modified with polymers / additives /…**
    - **Biobinder**

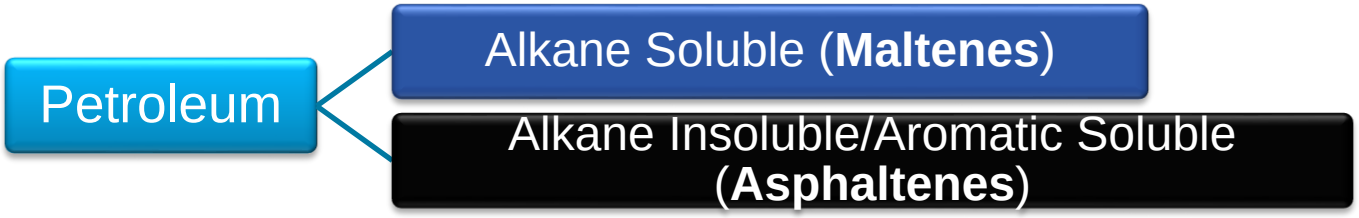


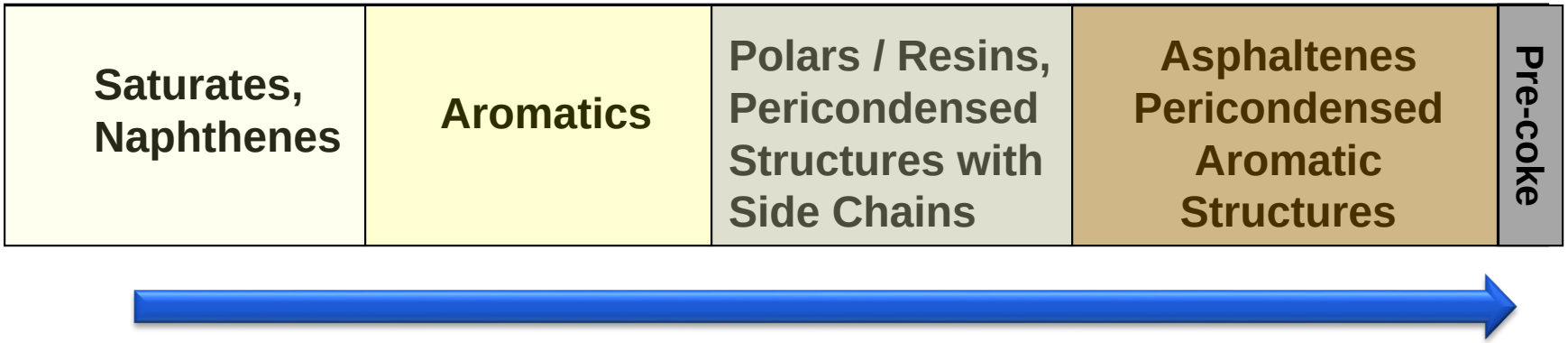
WRI-AIRC data

What is really special about my asphalt?

Background on Asphalt Chemistry – Help understand

- Asphalt (Petroleum): a very complex mixture of molecules (100,000s)
- Continuum of molecules from hydrogen-saturated to H-deficient
- Molecules with a continuum of solubility parameters





Assessing hydrocarbons

Saturate, Aromatics, Resins-Asphaltene Determinator (SAR-AD)

Asphaltene

Polarity and Aromaticity

Cyclohexane (1) → Toluene (2) → CH_2Cl_2:MeOH (3)

Asphaltene Determinator

Saturate

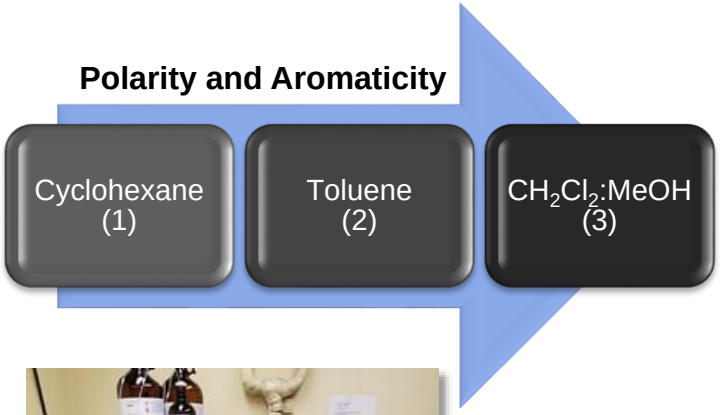
Aromatic

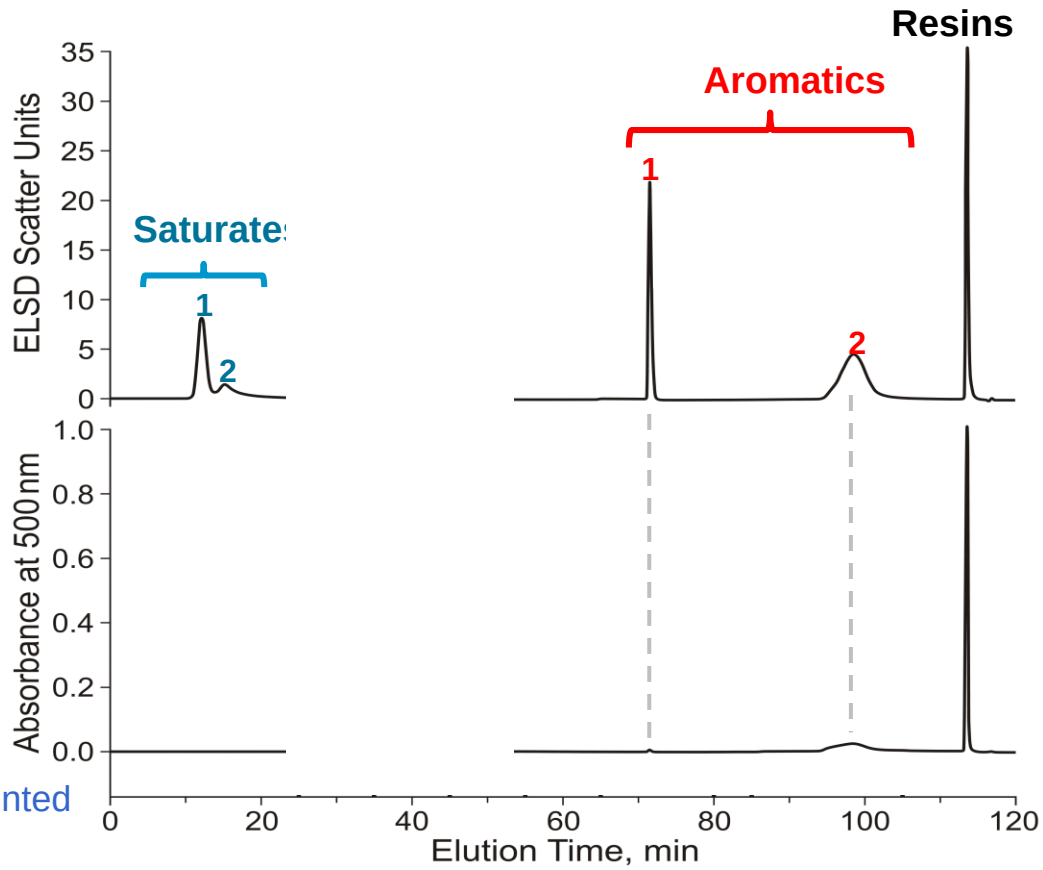
Resin

Assessing hydrocarbons

Saturates, Aromatics, Resins-Asphaltene Determinator (SAR-AD)™

Fully automated SAR separation (chromatography) coupled to AD asphaltene fractionation (solubility)

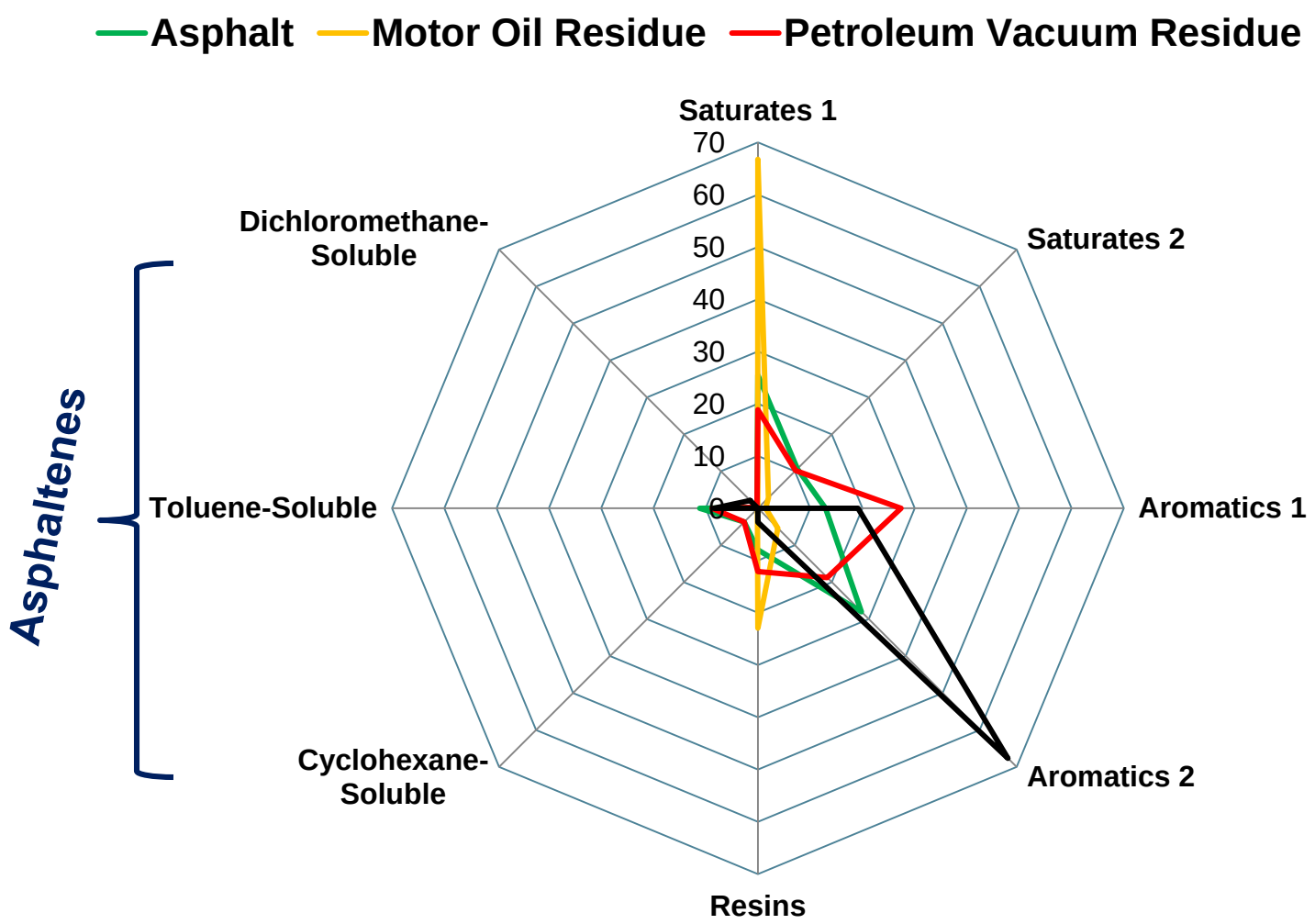




Patented

Assessing hydrocarbons

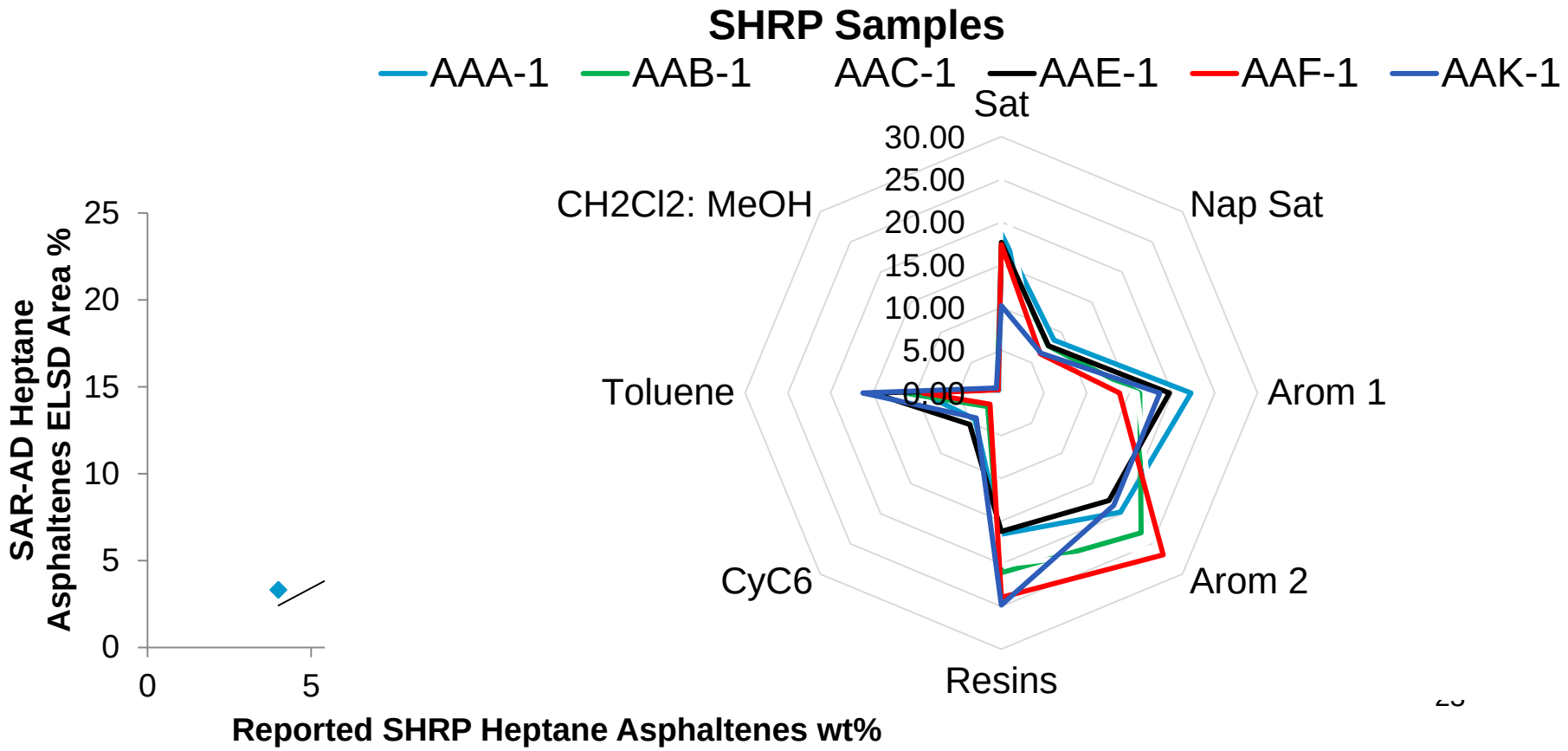
SAR-AD Fractions: ELSD Area Percent = Weight %



Assessing asphalt bases

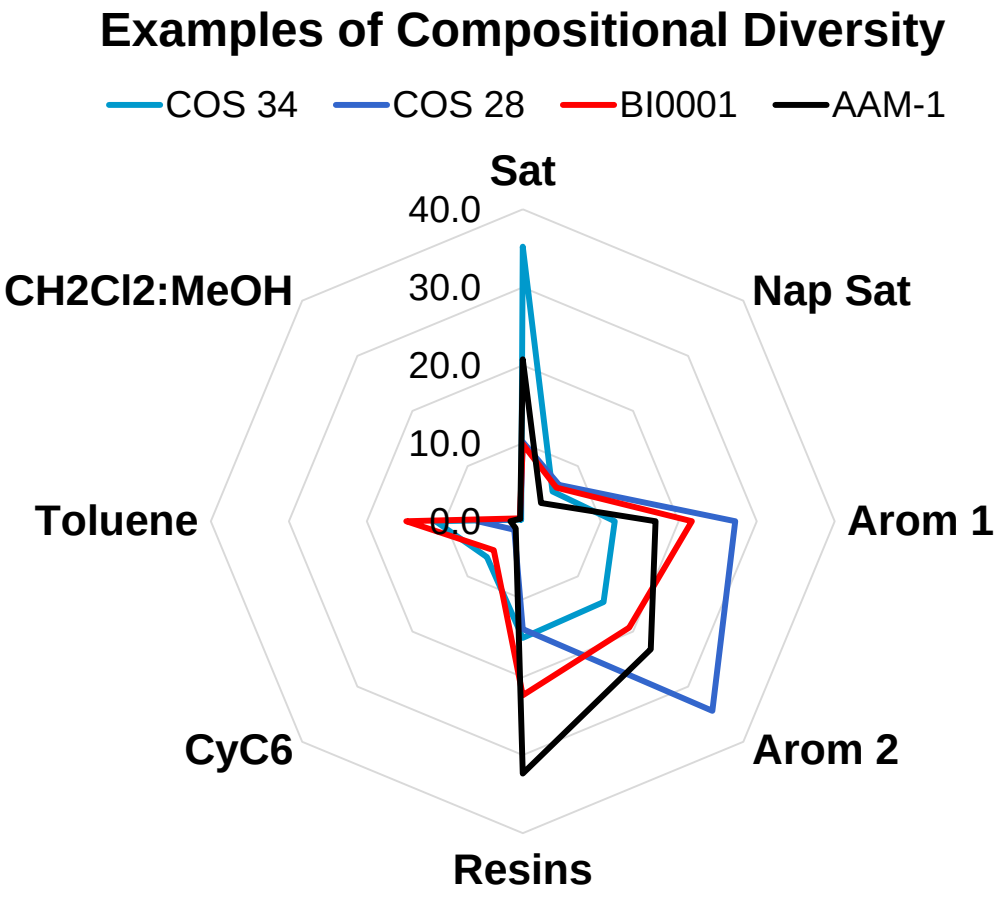
SAR-AD and SARA

- **Similarities:** Correlation Gravimetric vs. SAR-AD Asphaltenes
- **Differences:** more and different information on subfractions



SAR-AD – Asphalt Finger Printing – Today's Asphalts

Polar asphaltenes
- ↗ With visbreaking
- ↗ With oxidation



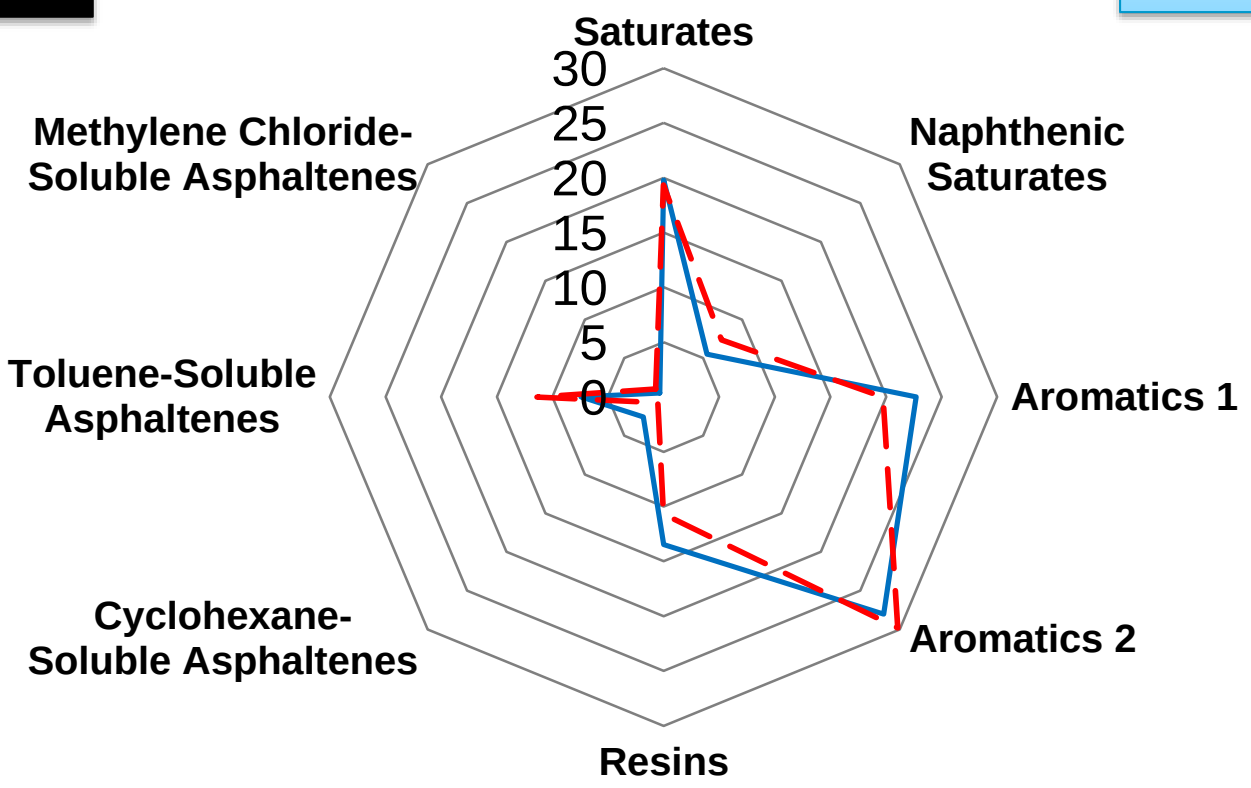
WRI-AIRC data

Assessing special asphalt bases

Example of a visbroken residue - IMO 2020 possibility

Composition - fraction behavior

SAR-AD Data

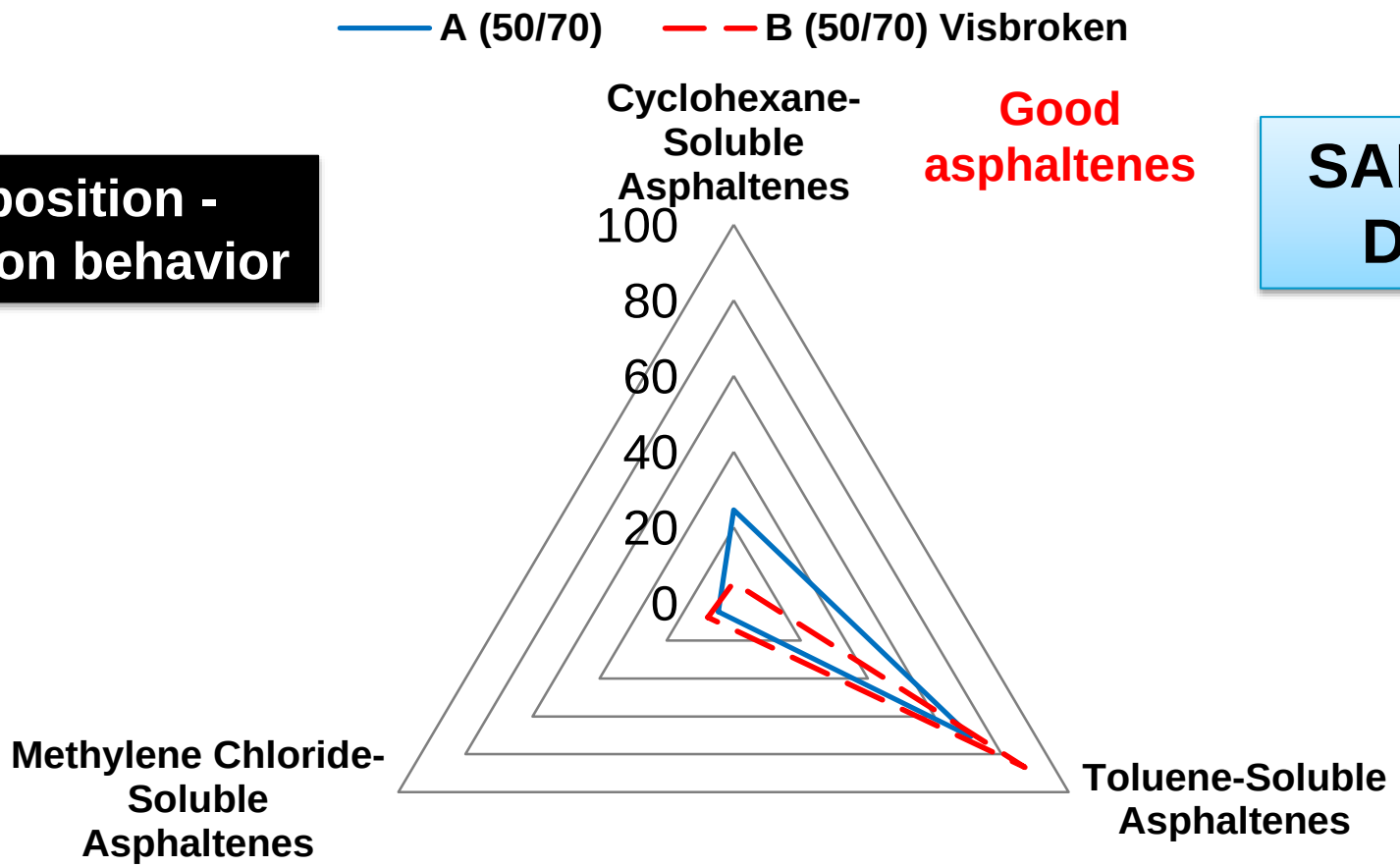


WRI-AIRC data

Assessing special asphalt bases

Example of a visbroken residue

Composition - fraction behavior



Good asphaltenes

Bad asphaltenes

SAR-AD Data

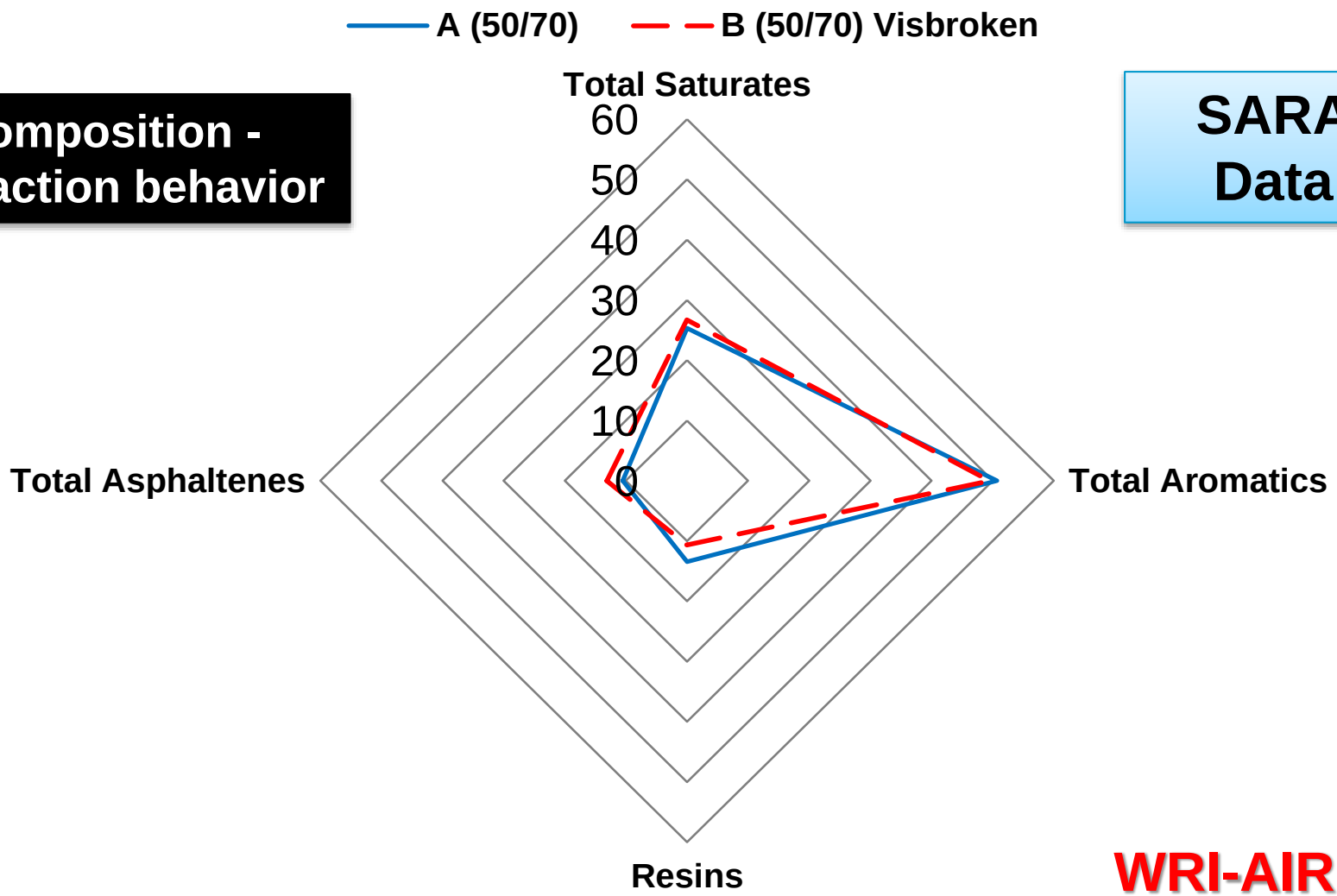
WRI-AIRC data

Assessing special asphalt bases

Example of a visbroken residue

Composition - fraction behavior

SARA Data

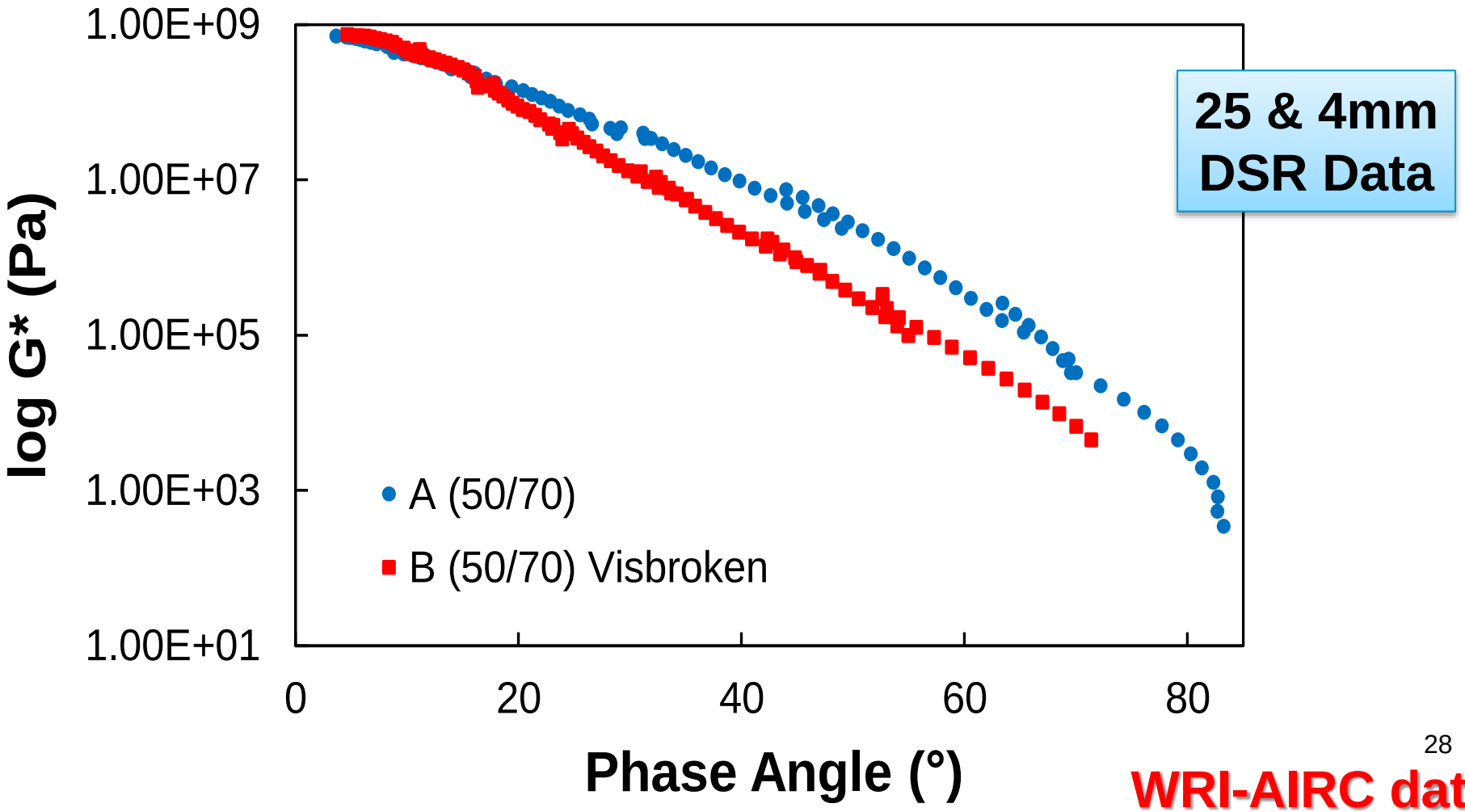


WRI-AIRC data

Assessing special asphalt bases

Example of a visbroken residue

Whole temperature, frequency rheological behavior – beyond PG

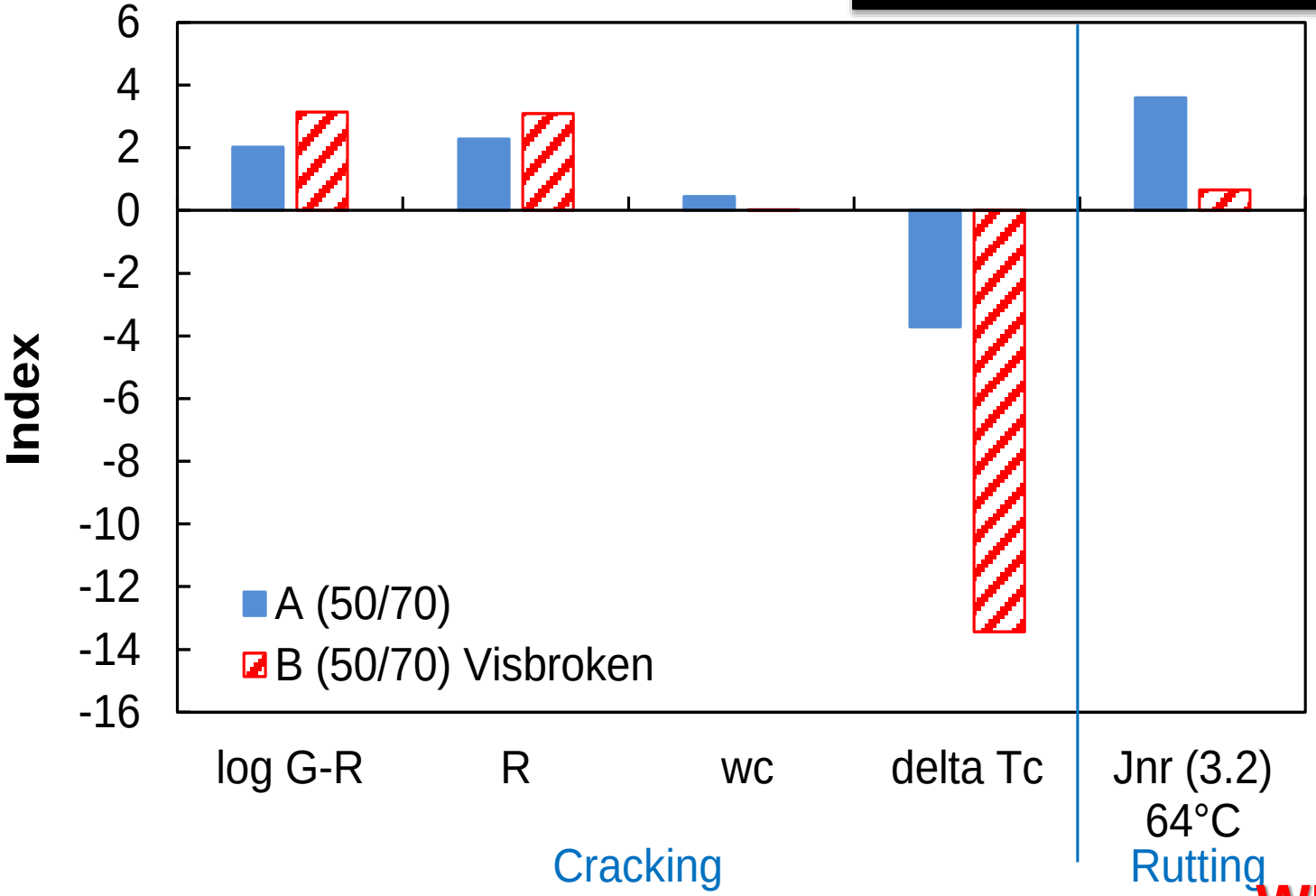


WRI-AIRC data

Assessing special asphalt bases

Example of a visbroken residue

"Buzz performance parameter"
Binder behavior – beyond PG



25 & 4mm DSR – BBR Data

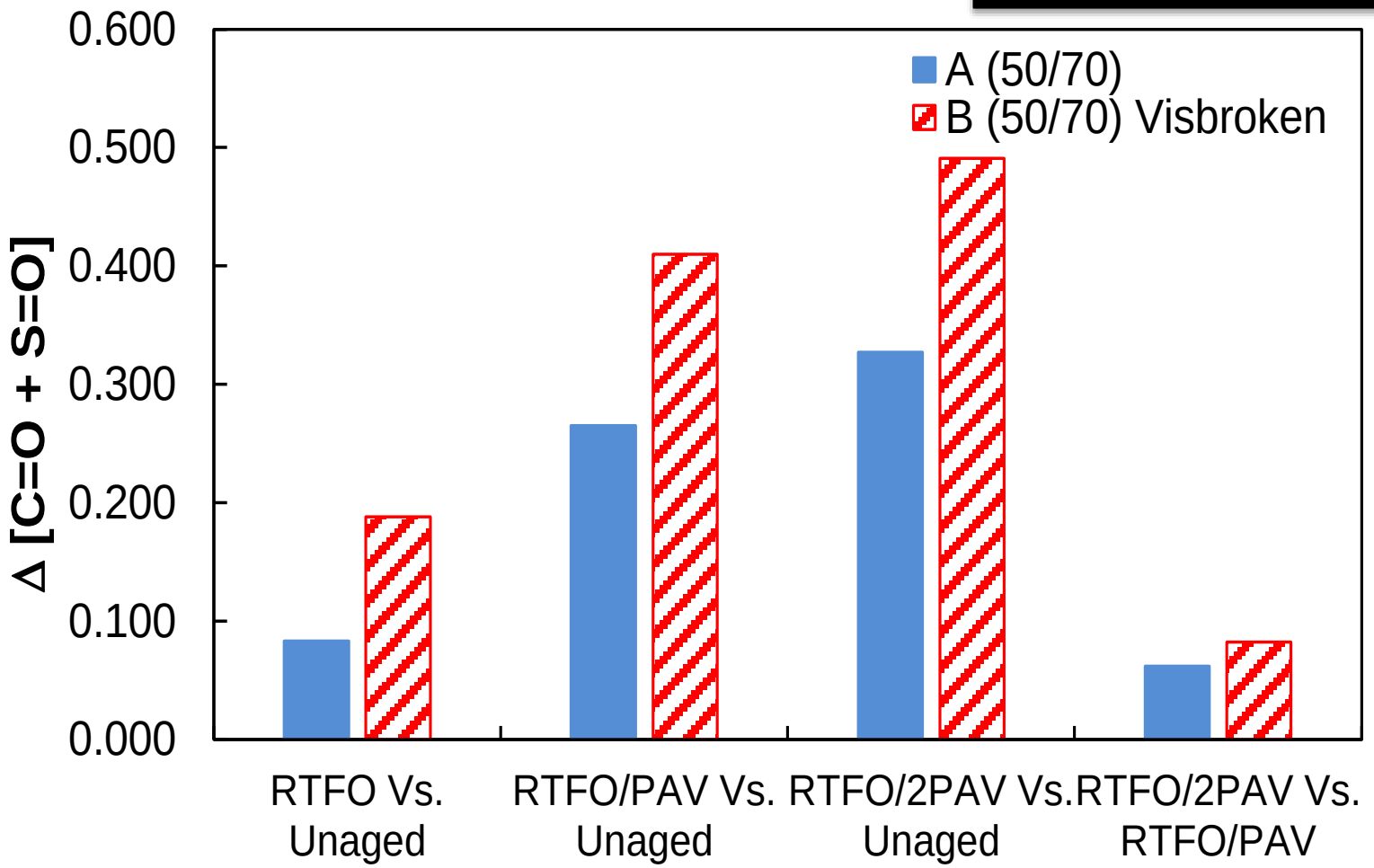
WRI-AIRC data

Assessing special asphalt bases

Example of a visbroken residue

FTIR Data

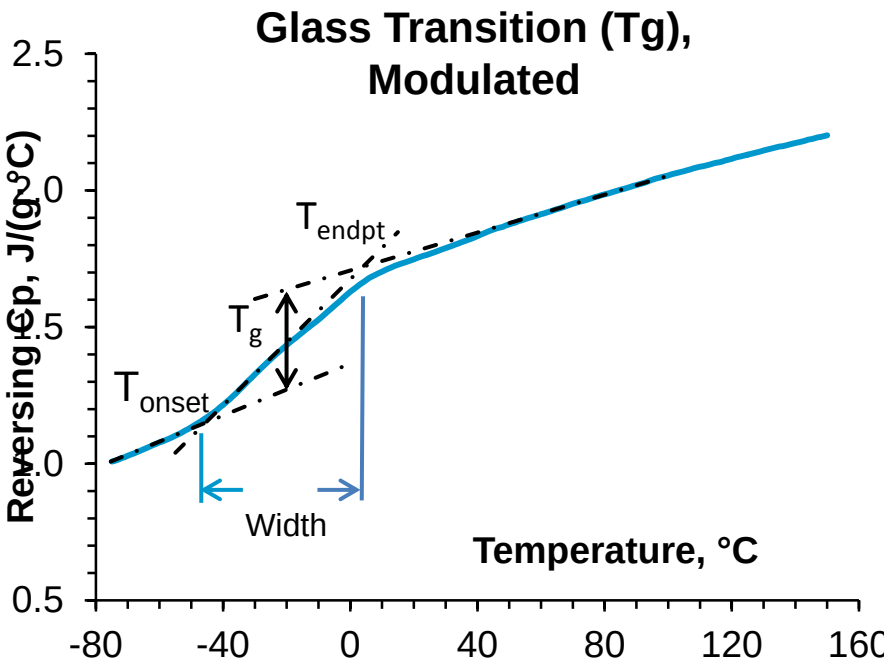
Oxidation behavior – Chemical Analysis

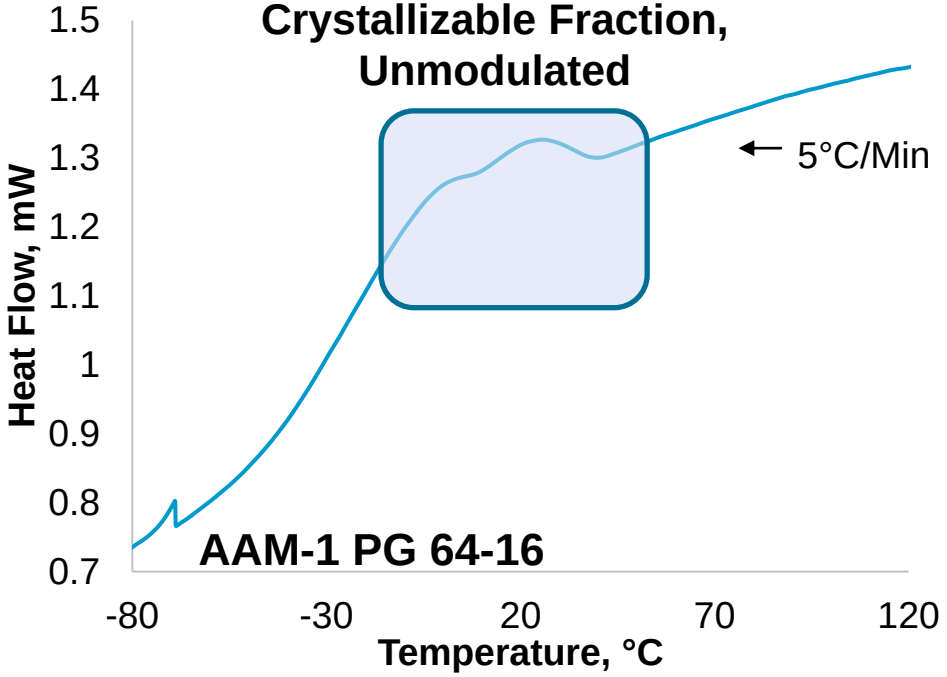


WRI-AIRC data

Assessing asphalt bases

Physical – Chemical Test: Differential Scanning Calorimetry (DSC) to capture waxes and glass transition

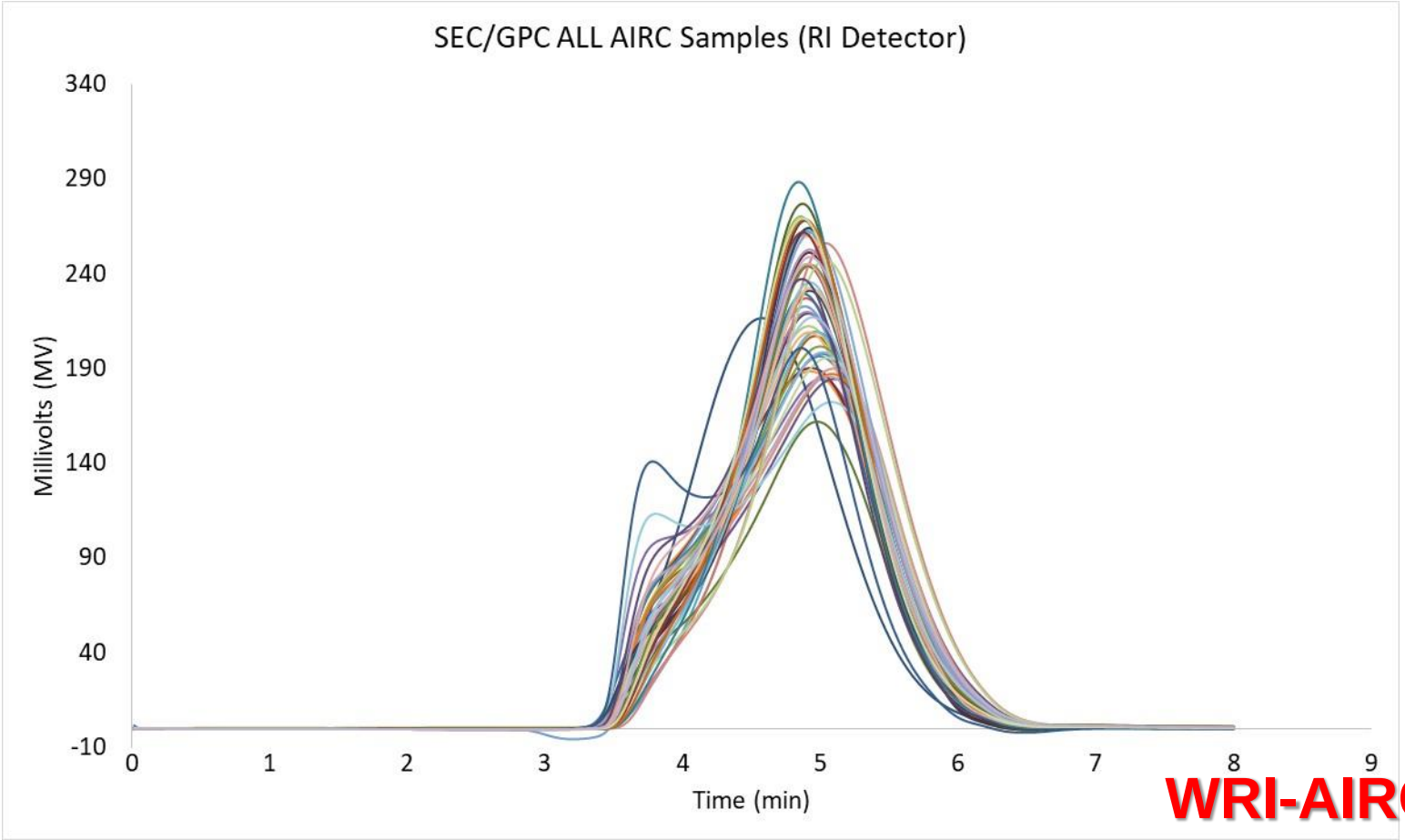




- **Glass transition** – Heat capacity change
- **Crystallization/precipitation** – Exotherms
- **Melting/Dissolution** – Endotherms

- **Tg sensitive to**
  - **Maltenes/softeners** (onset)
  - **Asphaltenes/stiffeners** (endpoint)
  - **Modifiers (polymers, REOB)**

Size Exclusion Chromatography / Gel Permeation Chromatography (RI Data)
– Molecular weight and associations

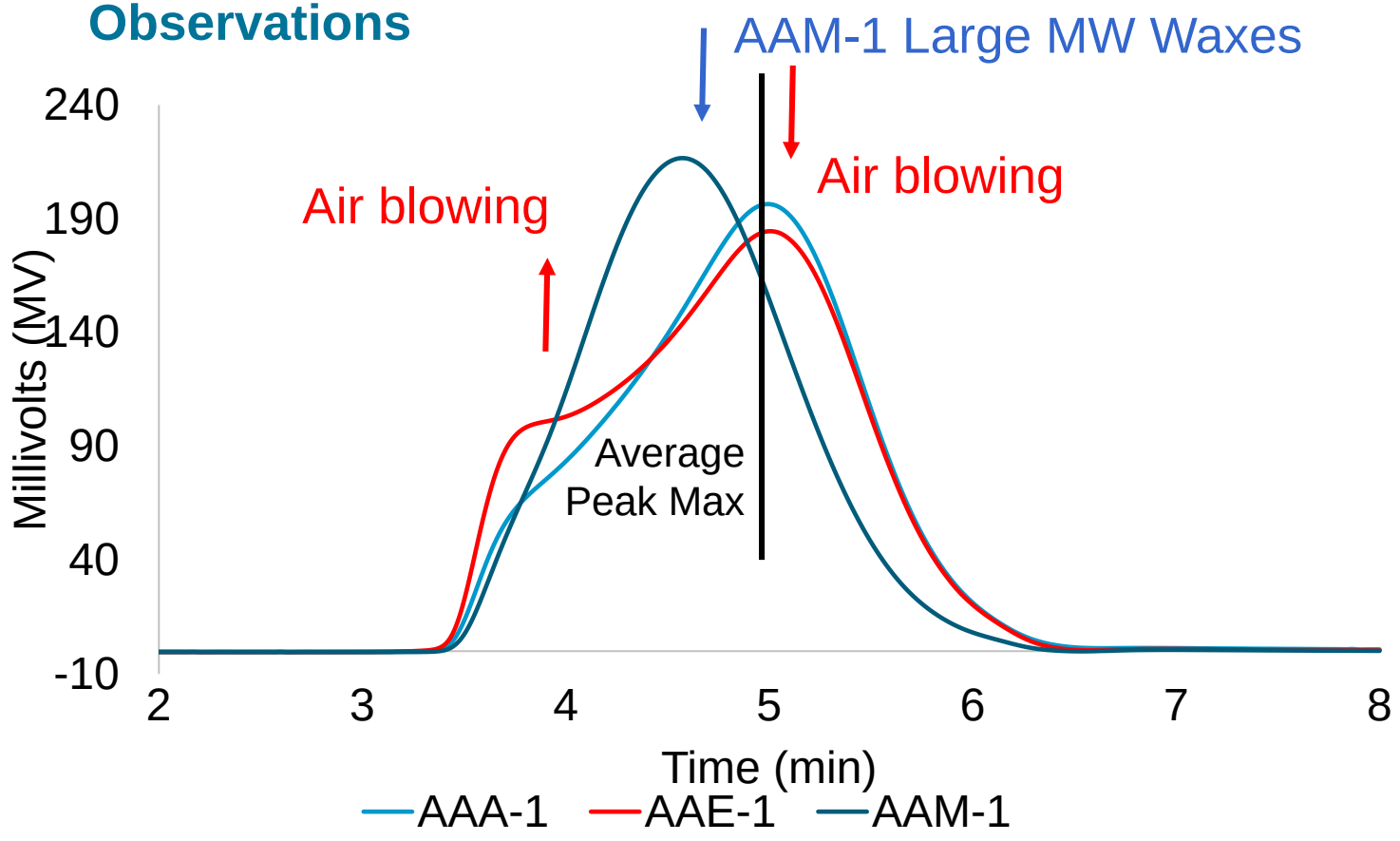


WRI-AIRC data

Assessing asphalt bases

Size Exclusion Chromatography / Gel Permeation Chromatography
To capture air-blowing / polymers…

Observations

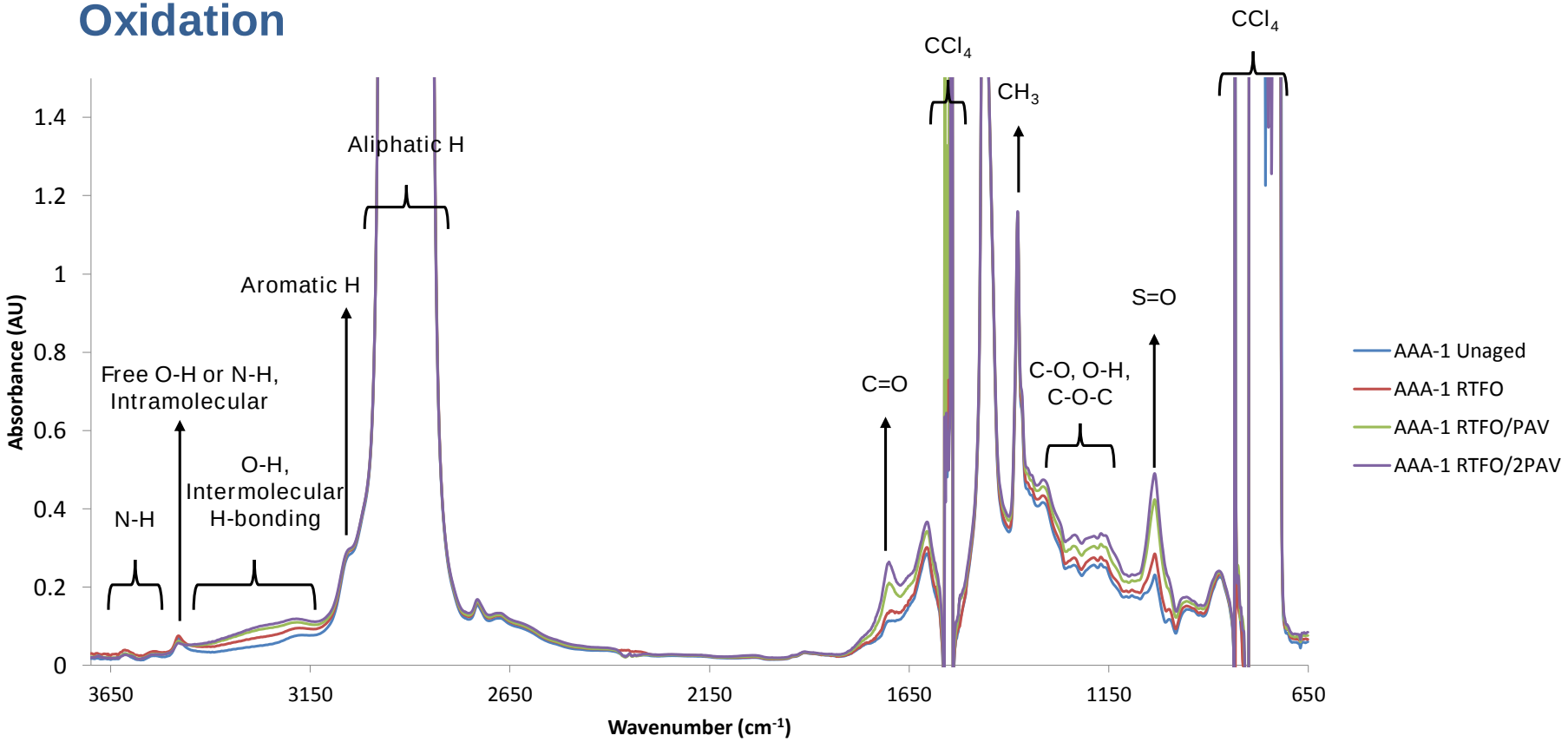


WRI-AIRC data

Assessing asphalt bases oxidation and additives

FTIR

Oxidation



FTIR in multiple solvents to get the full picture

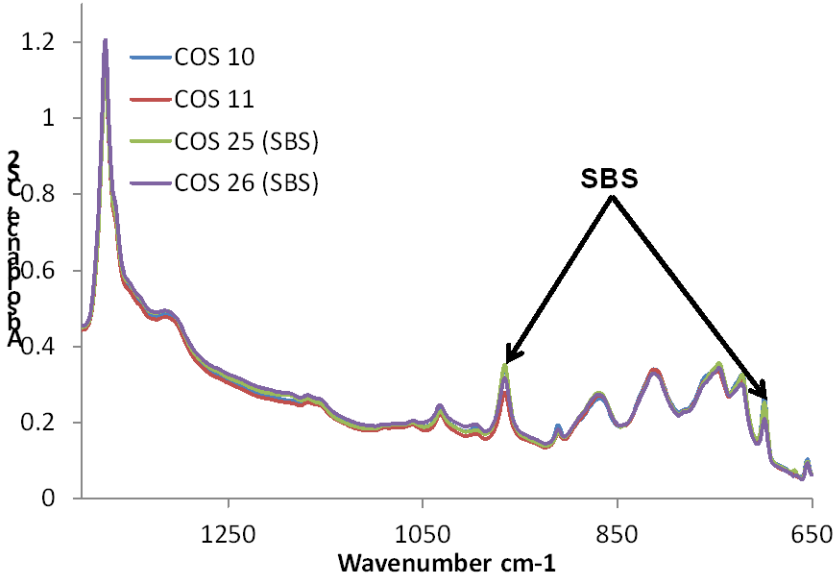
- Capture asphalt /additive molecule functions and associations

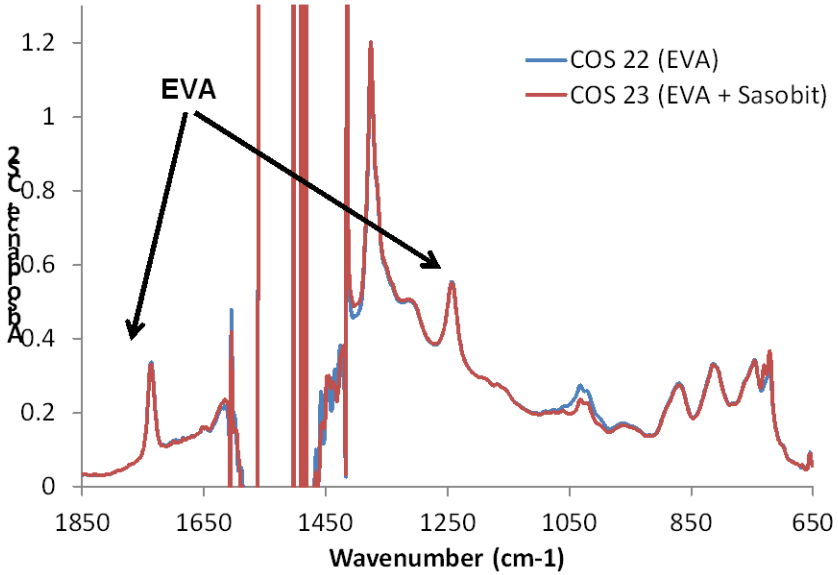
WRI-AIRC data

Assessing polymers in PMA's

FTIR

Polymers





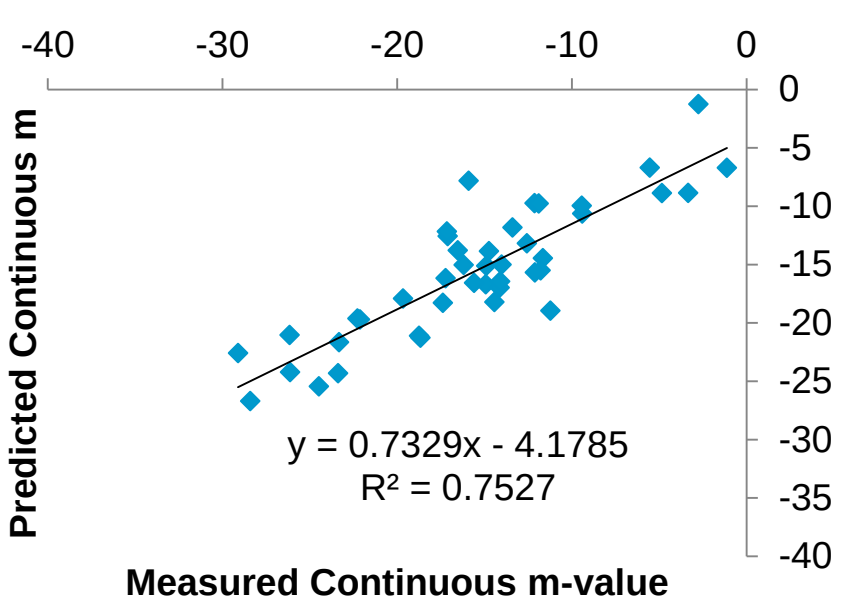
COS 30 and 31 also contain SBS

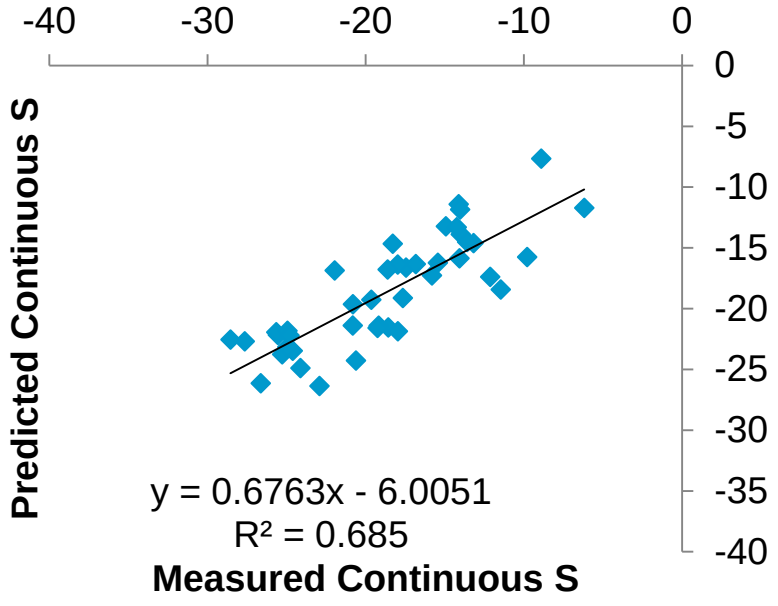
- Capture polymer nature / molecule functions – cases of SBS and EVA

WRI-AIRC data

So what? Quantitative Data towards Formulation Guidelines

SAR-AD – DSR Tm and TS Correlations using ExpliFit™





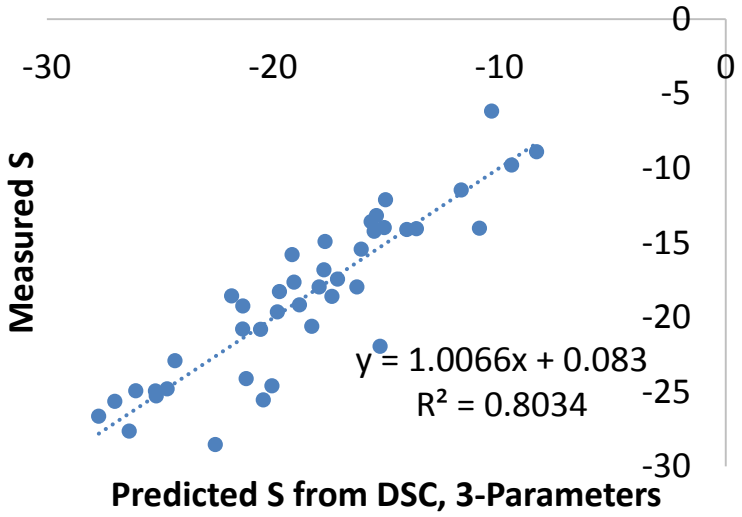
Fractions	Effect
• Naphthene saturates	Positive
• Aromatics 1 / 2	Positive / Negative
• Toluene asphaltenes	Negative

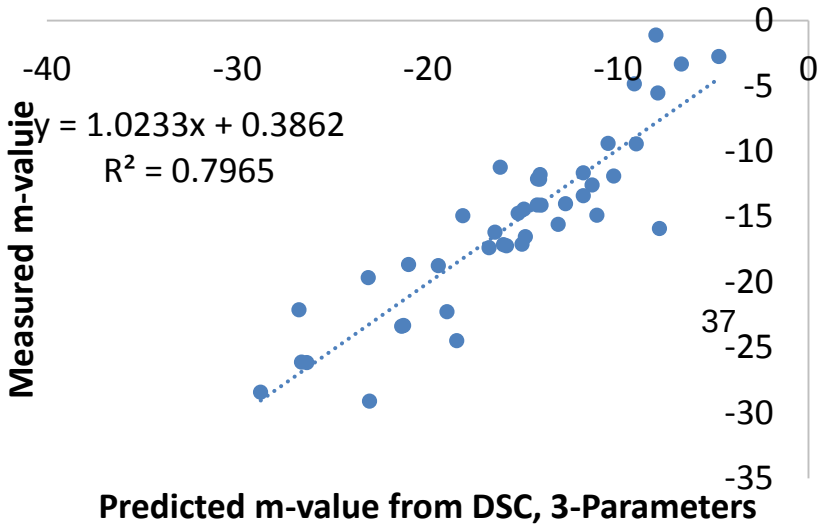
➢ **Note: Essentially reverse for Upper PG temperature**

WRI-AIRC data

So what? Quantitative Data towards Formulation Guidelines

DSC - DSR Tm and TS Correlations using ExpliFit™





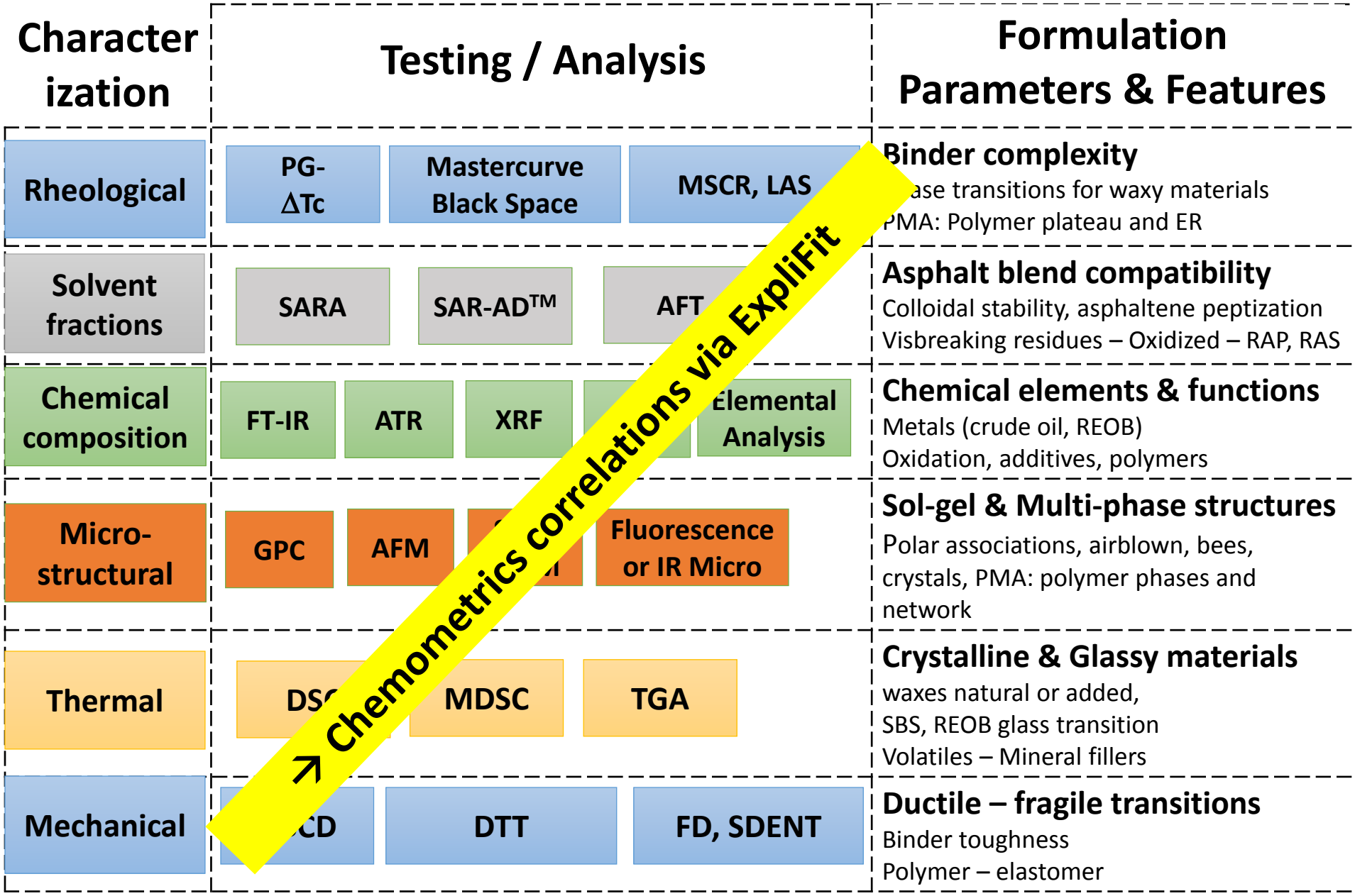
Interpretation

- S: more controlled by the middle temperature of the Tg (Tg(I) or Tg(H))
- m-value: more controlled by the Tg end point (sensitive to asphaltenes, increases upon oxidation – consistent with aged binder m-control)

WRI-AIRC data

Work in progress !

Summary: Matrix of Tools and Binders



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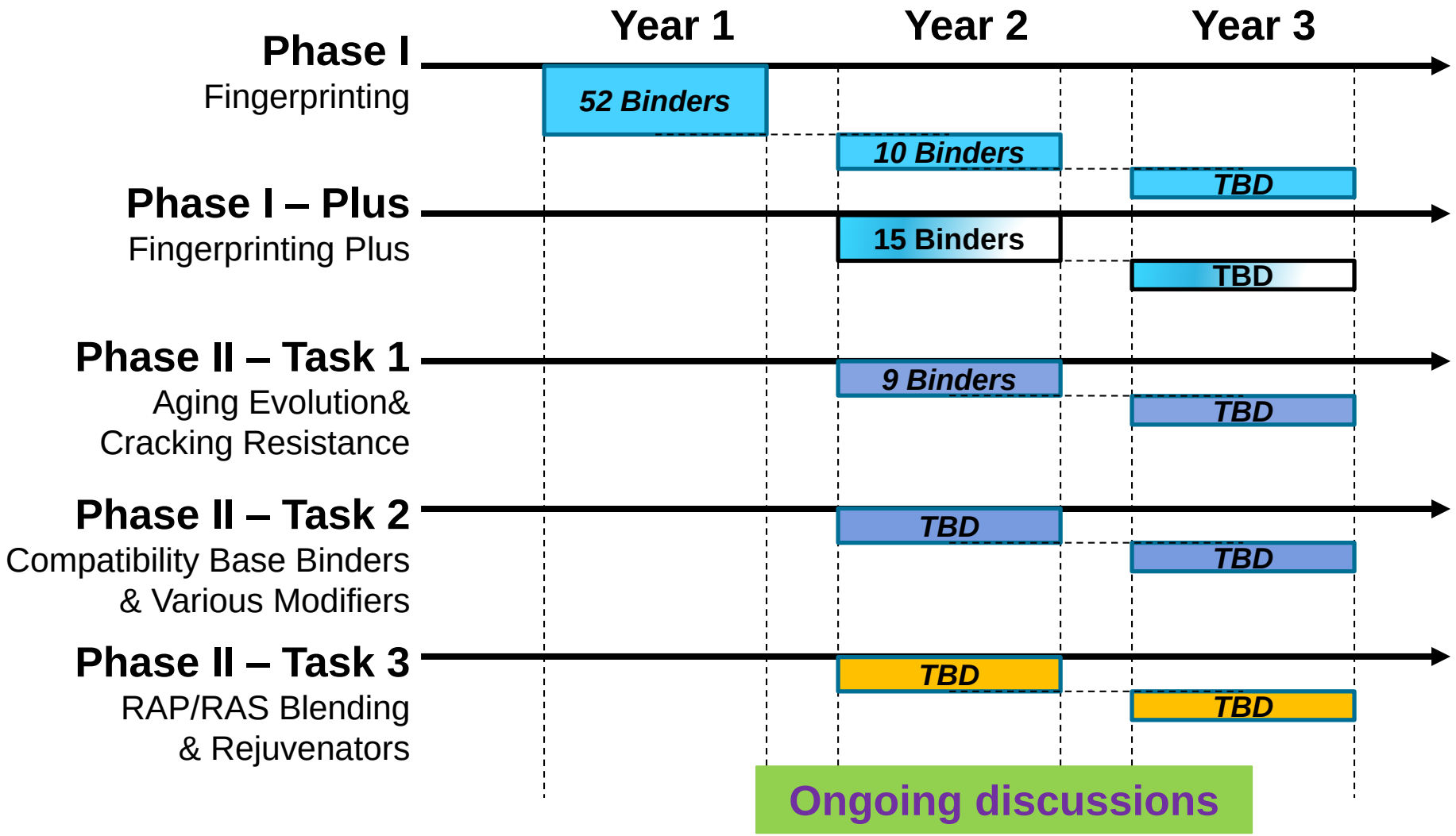
Summary and Perspectives

- **Asphalt production changes since SHRP: crudes, refining processes, blends, additives, higher recycling**
- **Superpave is not enough to assess the changes**
- **Rheological assessment beyond Superpave can give important insights: Black space representation, ΔTc, …**
- **Analyzing asphalt binder composition is powerful but tricky: requires association of several techniques**
  - ✓ Slight differences between bases
  - ✓ Additives / asphalt interferences: need for calibration
- **Need to know what to look for to use relevant tools**
- **New tools are already here and more are coming**
  - **Quantitation – possibilities of correlations and predictions**
  - **More universal** - combining various conditions, detectors
  - **Or more specifically designed** - to assess specific formulation

Stay tuned!

Perspectives
AIRC Year-2 and above



Thank You!
Questions?

Come to the 55th PARC
2018 - July 15-18
in Laramie!