The Influence of Molecular Structure of Distillate Fuels on HFRR Lubricity

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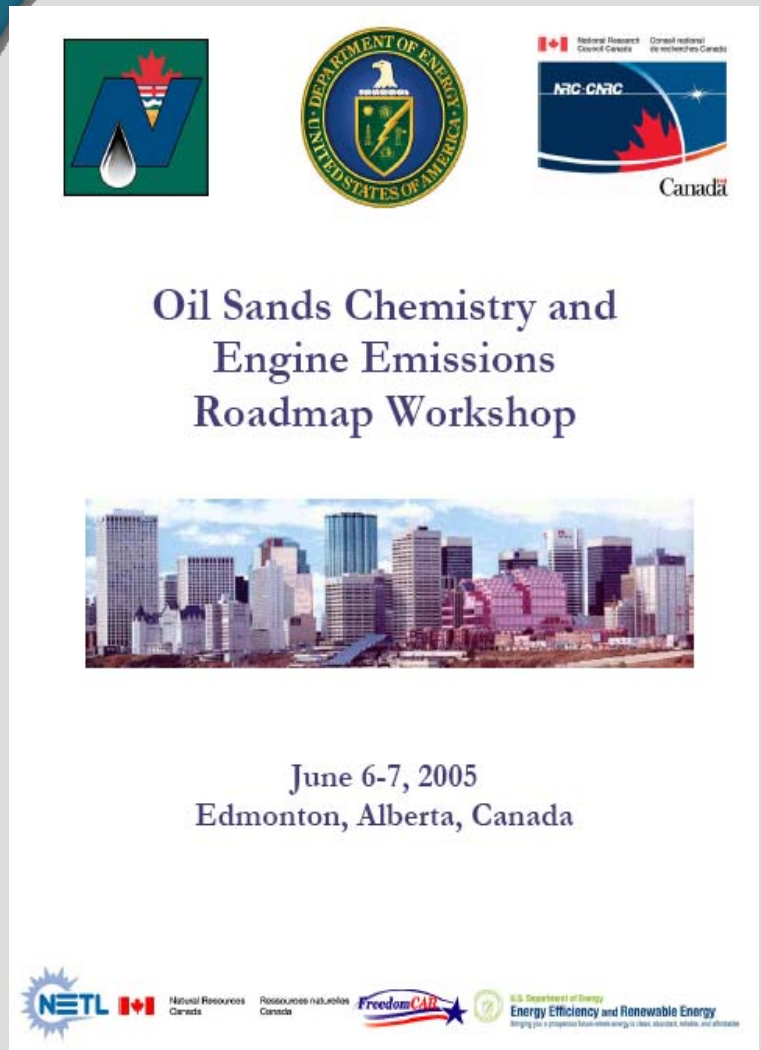
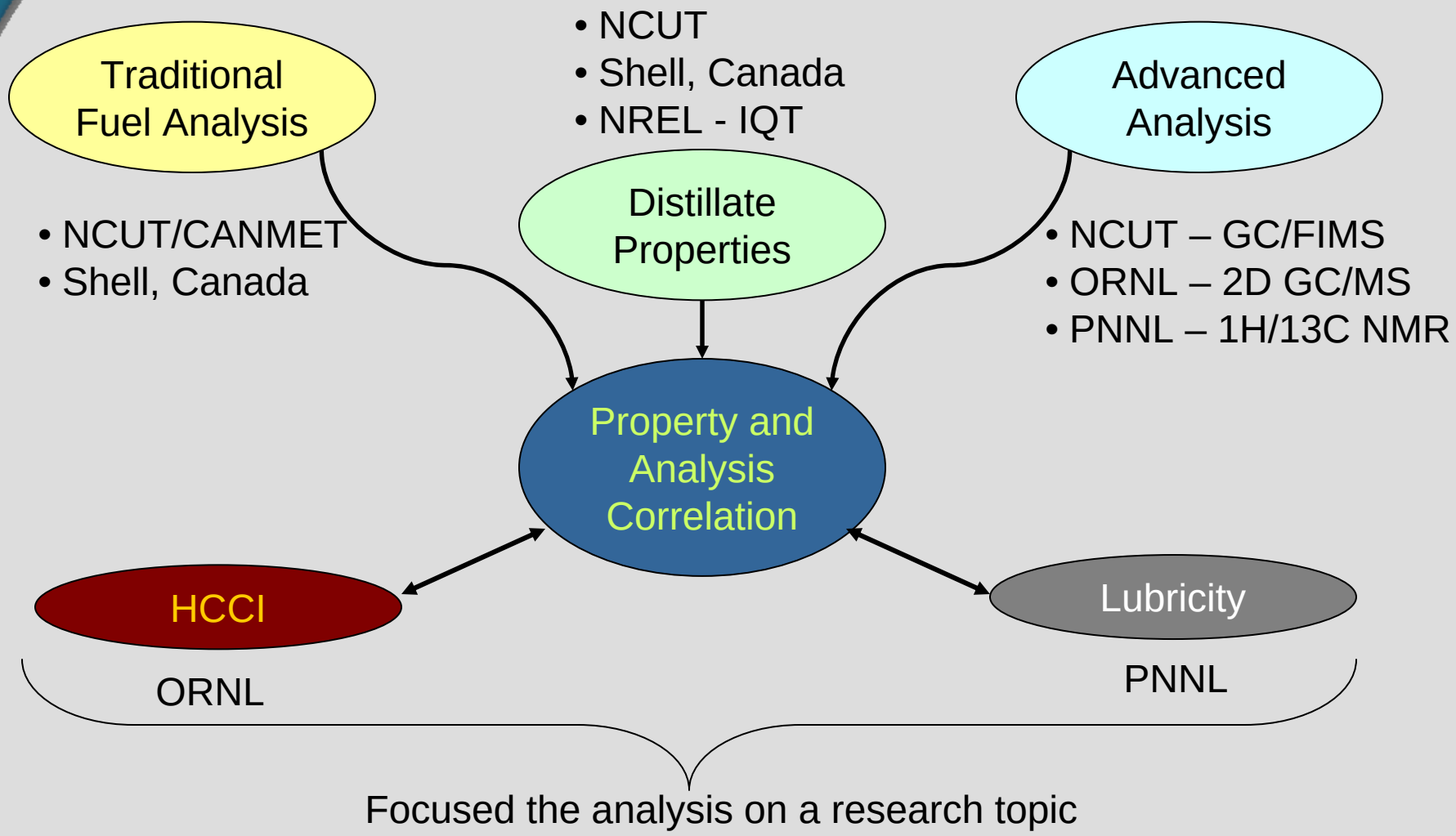
Distillate Fuel Knowledge Gaps



- During the joint DOE /CANMET workshop on Oil Sands derived fuels it was determined that our knowledge of distillate fuel chemistry was not adequate to support advanced engine research.
- Therefore, a collaboration was formed between CANMET/NCUT, ORNL and PNNL to:
  - Investigate analytical chemistry methods which would be applicable to distillate fuel chemistry, and
  - Demonstrate the value of these advanced analytical methods by identifying research areas, e.g., HCCI combustion, emissions, lubricity, or after treatment technologies, which the analytical data may provide improved understanding.

Collaborative Program Overview
Oil Sands Distillate Streams



Lubricity and Fuel Chemistry Background

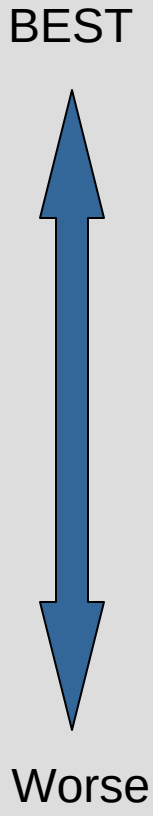
- Previous research identified numerous factors affecting lubricity, e.g.,
  - viscosity,
  - sulfur,
  - nitrogen and
  - Di-aromatics,
- However, none of these factors by themselves completely explain all the wear results.
- In addition, the two lubricity tests most commonly used, i.e., High Frequency Reciprocating Rig (HFRR) and the Scuffing Ball on Cylinder Lubricity Evaluator(S-BOCLE), did not correlate well.

Lubricity Collaboration

- PNNL , NCUT and Shell, Canada agreed to worked together to investigate the effect of molecular structure on lubricity, as defined by HFRR.
  - PNNL – 1H and 13C NMR
  - PNNL – HFRR (SwRI)
  - NCUT – GC-FIMS
  - Shell, Canada –Distillate Streams

Distillate Stream Selection Process

Sample ID	Nitrogen	Sulfur	Di Aromatics	Viscosity	Rating
F6-438	+	+	+	+	+4
F6-446	o	-	+	+	+1
F6-447	-	o	-	-	-3
F6-445	-	-	-	-	-4

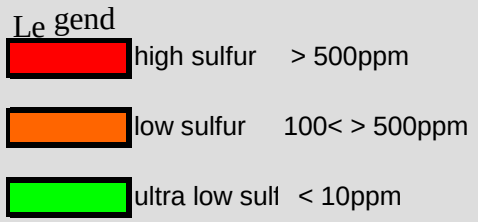


- From 8 distillate streams, the GC-FIMS data was used to select 4 streams that provided a wide range of chemistries.
- An arbitrate ranking scale was applied to each fuel as it related to lubricity components.

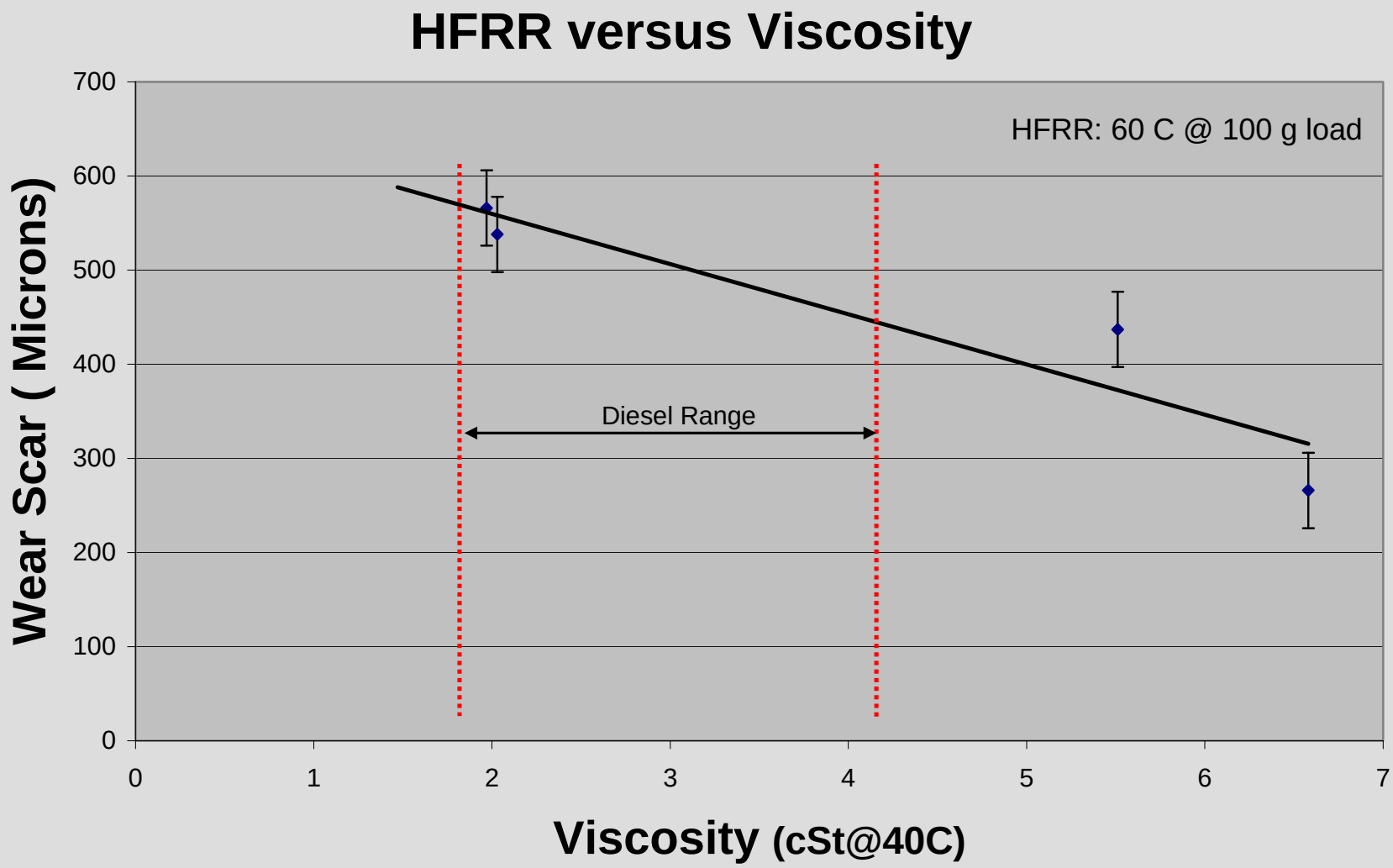
Distillate Stream Selection Process

Sample ID	Nitrogen	Sulfur	Di Aromatics	Viscosity	Bulk HFRR	Rating
F6-438	+	+	+	+	266	+4
F6-446	o	-	+	+	437	+1
F6-447	-	o	-	-	566	-3
F6-445	-	-	-	-	538	-4

- In general, the HFRR data follows the literature



Viscosity Effect
Viscosity versus Wear Scar



Lubricity HFRR

60 C @ 100 g Load

			Low Viscosity			High Viscosity		
			< C11	C11- C13	C13- C15	C15- C17	C17- C19	C19 - C21
Sample #		Bulk HFRR	< 200 C	200 - 235C	235 - 265C	265 - 300C	300 - 335C	335 - 360C
F6-438	+4	266				414	290	144
F6-446	+1	437				484	240	267
F6-447	-3	566	574	595	615	452		
F6-445	-4	538	627	593	543	510		

High Di-aromatics

Low Di-aromatics

Legend

high sulfur > 500ppm

low sulfur 100< > 500ppm

ultra low sull < 10ppm

Each distillate stream was fractionated by NCUT into a boiling point range that corresponded to a Carbon Number range to minimize the viscosity effect on lubricity.

Lubricity
High Frequency Reciprocating Rig (HFRR)
60 C @ 100 g Load

Low Viscosity | High Viscosity

Sample #		Bulk HFRR	< C11 < 200 C	C11- C13 200 - 235C	C13- C15 235 - 265C	C15- C17 265 - 300C	C17- C19 300 - 335C	C19 - C21 335 - 360C
F6-438	+4	266	Is there a molecular structure influence that overrides viscosity (chain length)?			**414**	**290**	**144**
F6-446	+1	437				**484**	**240**	**267**
F6-447	-3	566	**574**	**595**	**615**	**452**		
F6-445	-4	538	**627**	**593**	**543**	**510**		

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Legend

high sulfur > 500ppm

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ultra low sull < 10ppm

Is there a molecular structure influence that causes this scatter within a consistent viscosity range?

1H and 13C NMR Spectroscopy

1H NMR

Intensity	Region (PPM)	Significance
A	8.997 - 8.200	Tri-ring aromatics
B	8.200 - 7.551	Di-ring aromatics
C	7.551 - 7.182	Di-ring aromatics
D	7.182 - 7.130	Mono-ring aromatics
E	7.130 - 6.972	Mono-ring aromatics
F	6.972 - 6.785	Substituted mono-ring aromatics
G	6.785 - 6.425	Highly substituted mono-ring aromatics
H	4.184 - 3.306	Bridged CH2 groups in fluorene types
I	3.306 - 2.883	α-CH
J	2.883 - 2.641	α-CH2
K	2.641 - 2.292	α-CH2 + α-CH3
L	2.292 - 2.040	α-CH3
M	2.040 - 1.963	Allylic groups
N	1.963 - 1.570	CH and CH2 groups of naphthenes
O	1.570 - 1.391	CH groups of iso-paraffins
P	1.391 - 1.115	CH2 groups of paraffins (n-and iso)
Q	1.115 - 0.941	CH2 groups of paraffins (n-and iso)
R	0.941 - 0.254	CH3 groups of paraffins (n-and iso)

13C NMR

Peak	Region (PPM)	Significance
A	220 - 202	Ketone Carbonyl
B	202 - 195	Aldehyde Carbonyl
C	195 - 182	Quinone Carboxyl
D	182 - 175	Acid Carboxyl
E	175 - 165	Ester or Amide Carboxyl
F	165 - 143	Heteroatom (N, O, S) and alkyl (other than methyl) substituted aromatics.
G	143 - 137	Tertiary carbon in alkyl substituted aromatics.
H	137 - 131	Tertiary carbon in naphthalene units and methyl substituted aromatics.
I	131 - 127.5	Substituted carbon in alkenes (R2C=CR2) and orth and meta CH in toluene.
J	127.5 - 124	Substituted carbon in alkenes (RHC=CR2) and para CH in toluene.
K	124 - 115	Substituted carbon in alkenes (RHC=CR2)
L	115 - 95	Unsubstituted carbon in alkenes (CH2=CR2).
M	95 - 70	C, CH, and CH2 adjacent to oxygen halogen atoms.
N	70 - 60	CH2 adjacent to oxygen and C in tertiary alchols.
O	60 - 45	CH adjacent to Tertiary and isopropyl groups. Lso, CH3 in ether linkage.
P	45 - 40	CH in allylic and benzylic groups and in joining tetralin ring.
Q	40 - 36	CH2 adjacent to substituted double bonds and tertiary carbon.
R	36 - 33.5	CH, CH2 beta from secondary carbon and in cyclopentyl and cyclohexyl rings.
S	33.5 - 31	CH, CH2 gamma from CH3. CH2 alpa to allylic and beta to aromatic groups.
T	31 - 28.5	C in open chains. CH2 benzylic and CH2 not adjacent to CH in alkyl group.
U	28.5 - 26.5	CH, CH2 in open chains. CH2 in cyclohexyl groups and CH3 in Tert-buty ether.
V	26.5 - 24.5	Some naphthenic CH2. CH2 beta in propyl, indan and cyclopentyl groups.
W	24.5 - 22	CH2 gamma from terminal CH3. CH 2 beta in unsubstituted tetralin.
X	22 - 20	CH3 alpha in hydroaromatics and alkyls not shielded by adjacent rings or groups
Y	20 - 18	CH3 alpha in hydroaromatics and alkyls shielded by adjacent rings or groups
Z	18 - 15	CH3 in cyclohexanes and beta in ethyl aromatics and ethers.
Za	15 - 12.5	CH3 gamma to an aromatic ring or shielded by two adjacent rings or groups.
Zb	12.5 - 0	CH3 gamma to aromatic rings or ethyl substituted cyclohexanes.

Structural Distributions by 1H NMR Spectroscopy

Intensity	Region (PPM)	Significance
A	8.997 -8.200	Tri-ring aromatics
B	8.200 -7.551	Di-ring aromatics
C	7.551 -7.182	Di-ring aromatics
D	7.182 -7.130	Mono-ring aromatics
E	7.130 -6.972	Mono-ring aromatics
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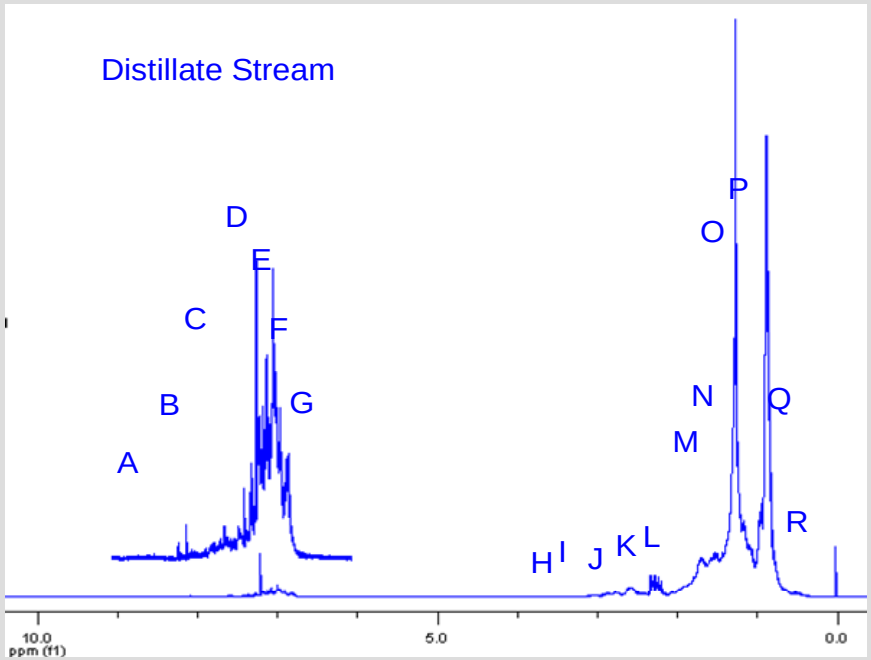
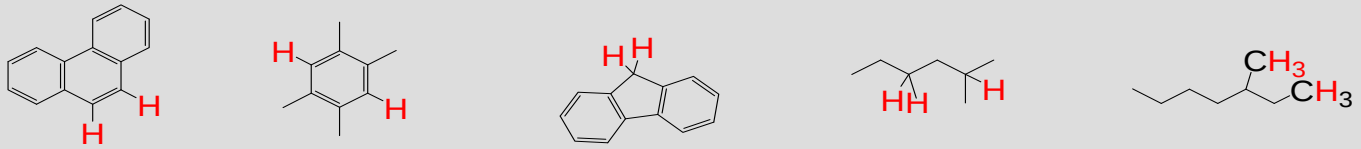
I	3.306 -2.883	α-CH
J	2.883 -2.641	α-CH2
K	2.641 -2.292	α-CH2 + α-CH3
L	2.292 -2.040	α-CH3
M	2.040 -1.963	Allylic groups
N	1.963 -1.570	CH and CH2 groups of naphthenes
O	1.570 -1.391	CH groups of iso-paraffins
P	1.391 -1.115	CH2 groups of paraffins (n-and iso)
Q	1.115 -0.941	CH2 groups of paraffins (n-and iso)
R	0.941 -0.254	CH3 groups of paraffins (n-and iso)



9.0 -7.50 **7.5-6.5** **4.0-1.8** **1.8-1.06** **1.06-0.5**



Typical Structures associated with 1 H NMR

Typical 1H NMR Fractionated Distillates

… 1H NMR Regions … / Peak Intensity (Normalized to 100%) for Distillate and Fractionated samples …

1H NMR Regions	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	
PPM	8.997-8.201	8.200-7.551	7.551-7.181	7.181-7.13	7.130-6.972	6.972-6.785	6.785-6.425	4.184-3.306	3.306-2.883	2.883-2.641	2.641-2.292	2.292-2.04	2.040-1.963	1.963-1.57	1.570-1.391	1.391-1.115	1.115-0.941	0.941-0.254	
	Peak Intensity (Normalized to 100%)																		%
Distillate																			total
F6-438	0.04	0.32	0.87	0.36	1.43	1.26	0.23	0.16	1.11	1.91	4.16	3.07	0.65	9.19	8.64	31.86	8.71	26.03	100.00
Fractionated																			
<200 C	0.02	0.1	0.56	0.4	1.62	0.74	0.07	0.05	0.43	0.92	3.11	3.42	0.5	8.09	7.09	28.69	9.92	34.27	100.00
200-235 C	0.06	0.24	0.52	0.26	1.24	0.96	0.08	0.17	0.77	1.58	2.98	3.34	0.64	9.52	7.86	27.84	10.2	31.74	100.00
235-265 C	0.01	0.16	0.55	0.27	1.11	0.97	0.16	0.06	0.65	1.61	3.39	2.74	0.66	9.98	8.05	28.13	11.02	30.48	100.00
265-300 C	0.32	0.39	0.72	0.25	1.14	1.04	0.17	0	0.71	1.88	3.74	2.73	0.62	9.79	8.07	30.9	10.09	27.44	100.00
300-335 C	0.06	0.46	1.15	0.3	1.29	1.21	0.21	0.14	0.93	1.94	4.03	3.02	0.58	8.8	7.94	31.96	8.97	27.01	100.00
>350 C	0	0.32	0.85	0.26	1.13	1.12	0.42	0.15	1.05	1.97	4.13	2.93	0.60	8.51	7.77	32.3	10.82	25.67	100.00
Distillate																			
F6-446	0.03	0.13	0.45	0.17	0.61	0.36	0.02	0.01	0.43	0.61	1.66	0.98	0.42	6.99	6.04	41.52	8.45	31.12	100.00
Fractionated																			
<200 C	0.04	0.16	0.62	0.38	1.41	0.7	0.08	0.01	0.42	1.03	2.53	2.8	0.56	9.06	7.6	25.47	9.51	37.62	100.00
200-235 C	0.06	0.33	0.75	0.27	1.41	0.99	0.1	0.05	0.71	1.96	3.48	2.98	0.58	8.84	6.78	28.59	9.45	32.67	100.00
235-265 C	0.03	0.34	0.76	0.18	0.97	0.83	0.13	0	0.48	1.53	3.09	2.38	0.41	8.28	6.37	32.4	9.96	31.86	100.00
265-300 C	0	0.2	0.52	0.19	0.63	0.43	0.04	0	0.49	0.89	2.27	1.07	0.41	7.73	6.33	39.18	8.31	31.31	100.00
300-335 C	0.01	0.17	0.43	0.14	0.4	0.25	0.04	0.01	0.3	0.34	1.24	0.61	0.32	6.08	6.22	42.82	8.88	31.74	100.00
>350 C	0.05	0.32	0.24	0.06	0.22	0.13	0.03	0.27	0.66	0.56	1.32	0.91	0.51	6.61	6.21	41.4	10.84	29.66	100.00

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Legend

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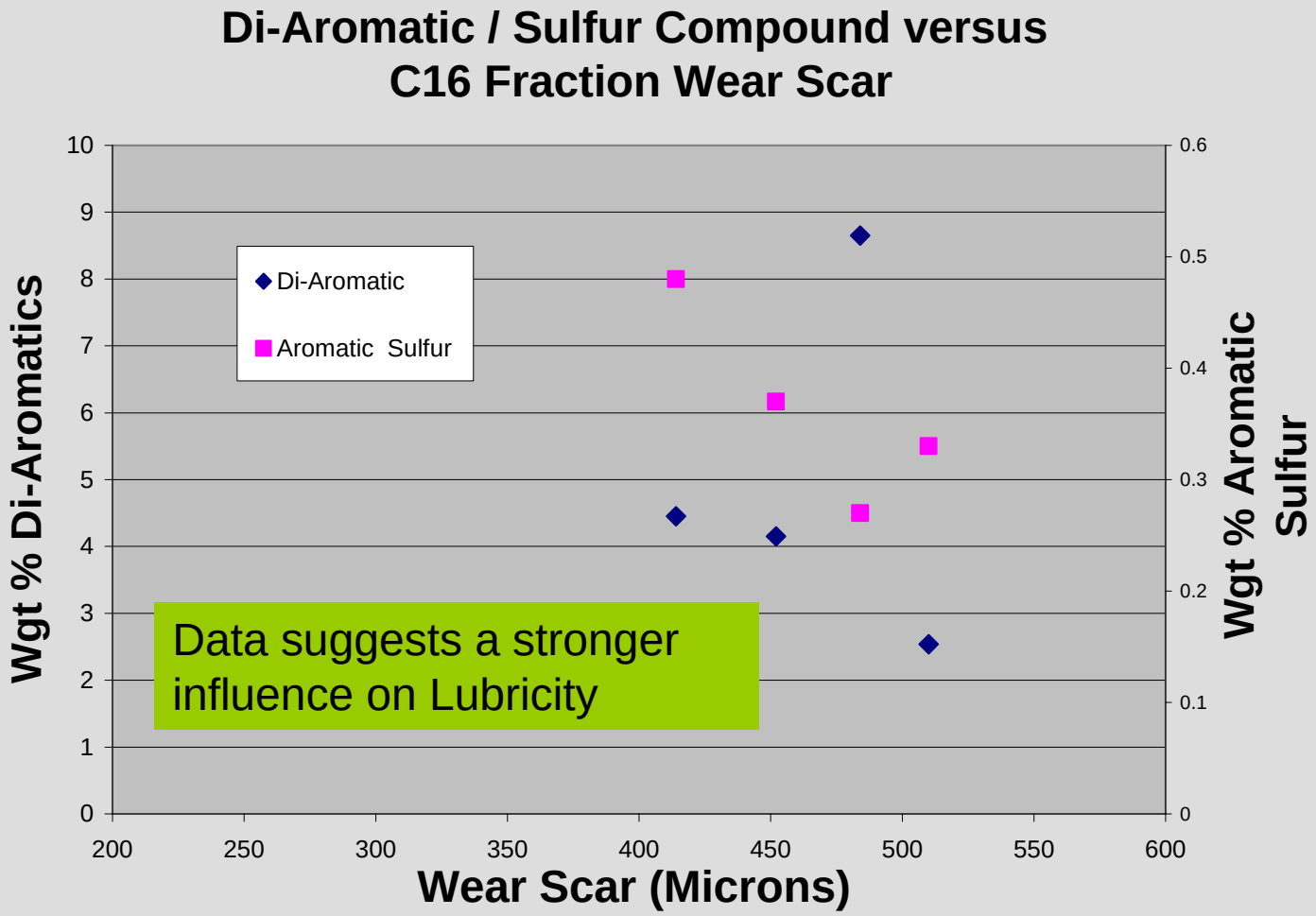
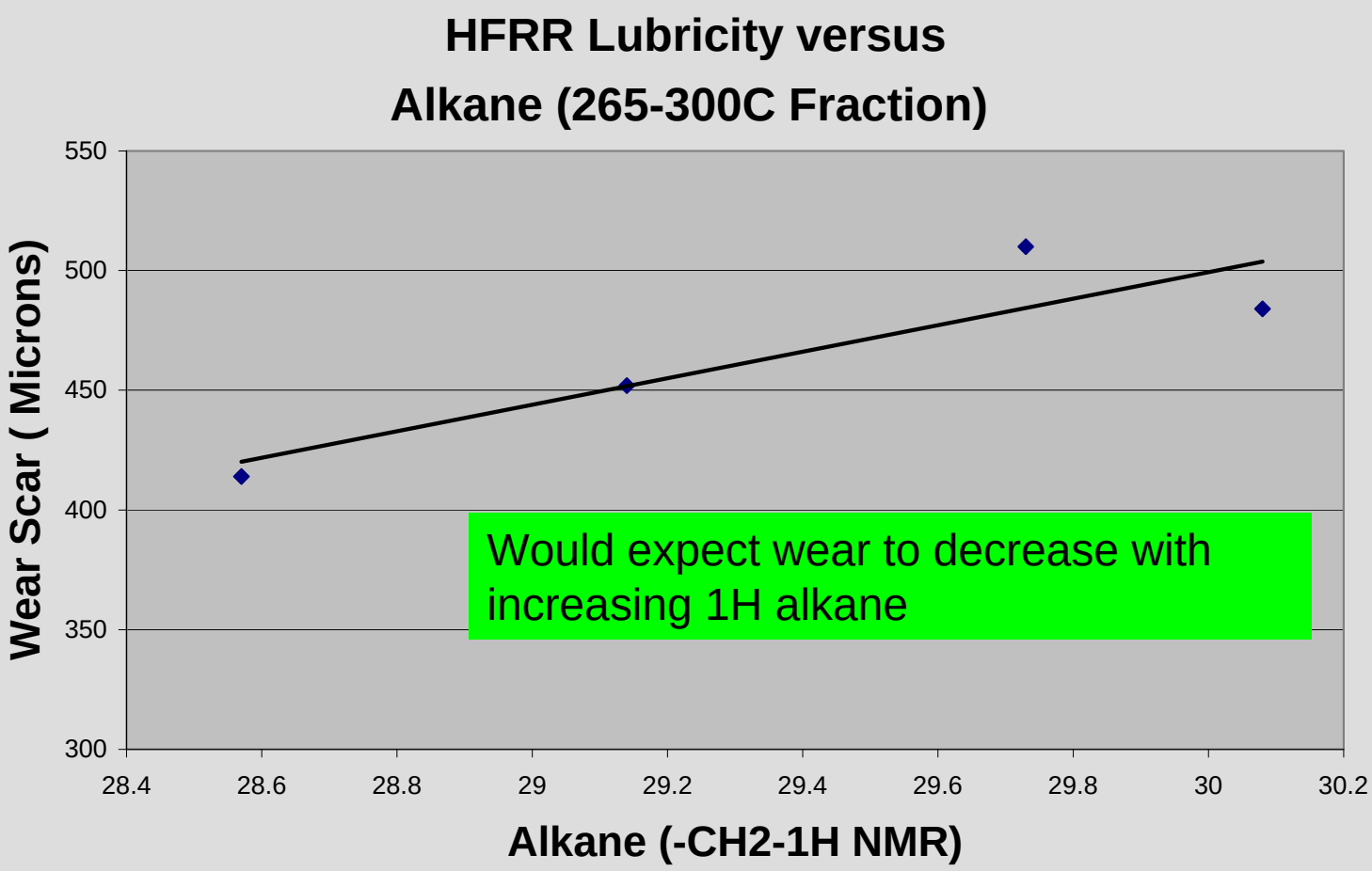
ultra low sull < 10ppm

Lets focus on this set of chemistries, as it demonstrates some unexpected HFRR results

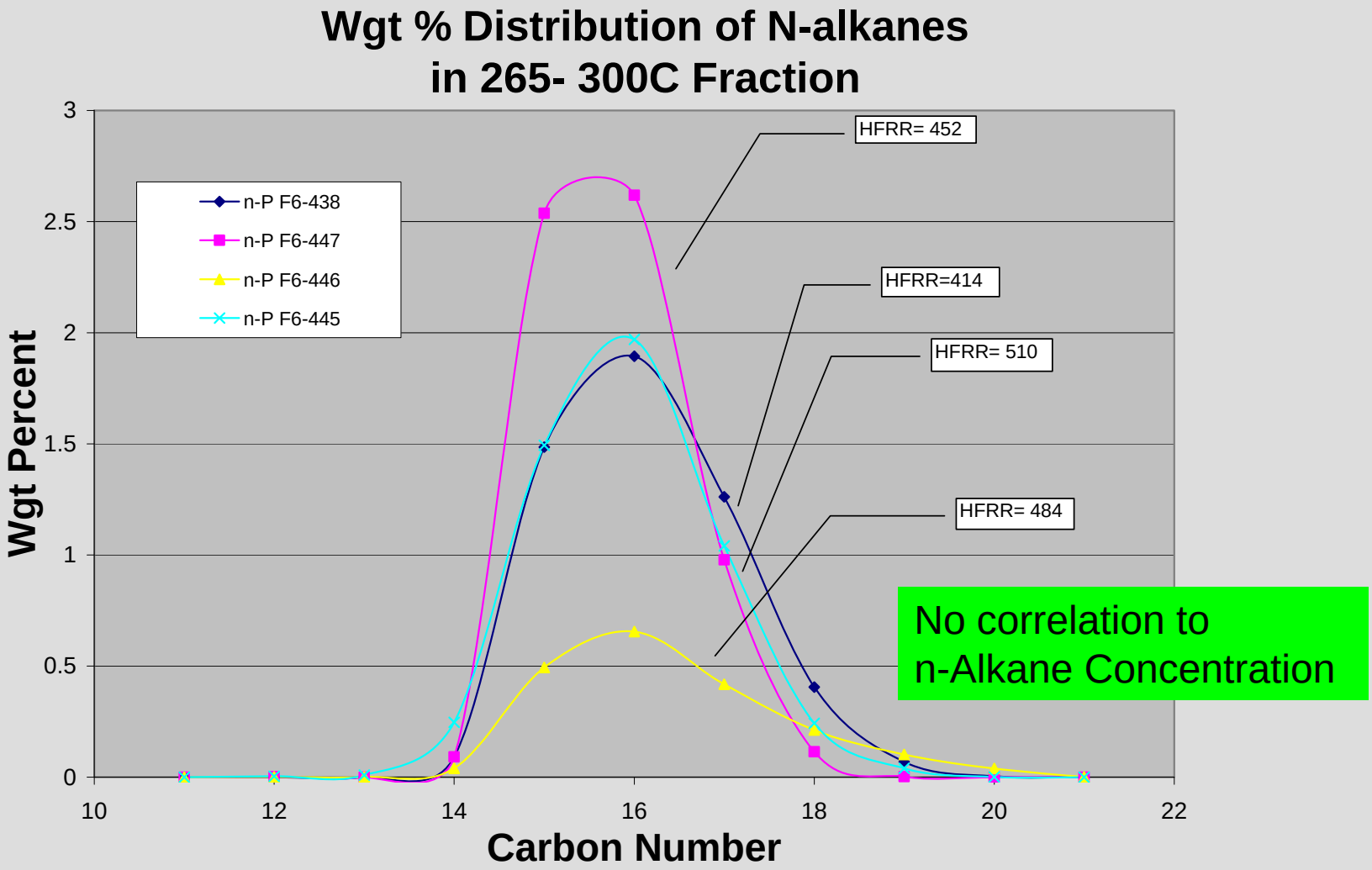
Di-Aromatic and Sulfur Compound Influence C16 Boiling Point range



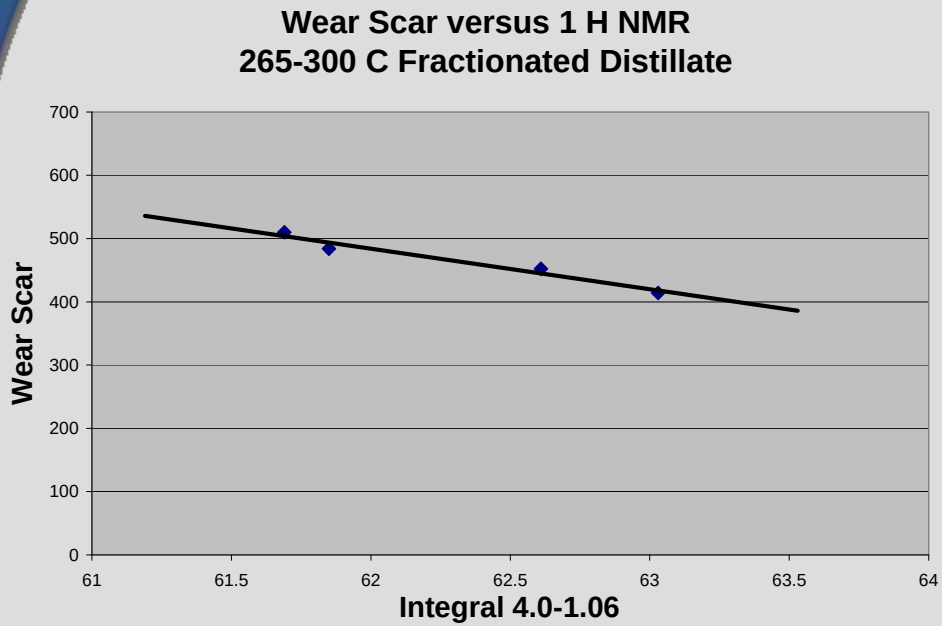
HFRR Lubricity Alkane

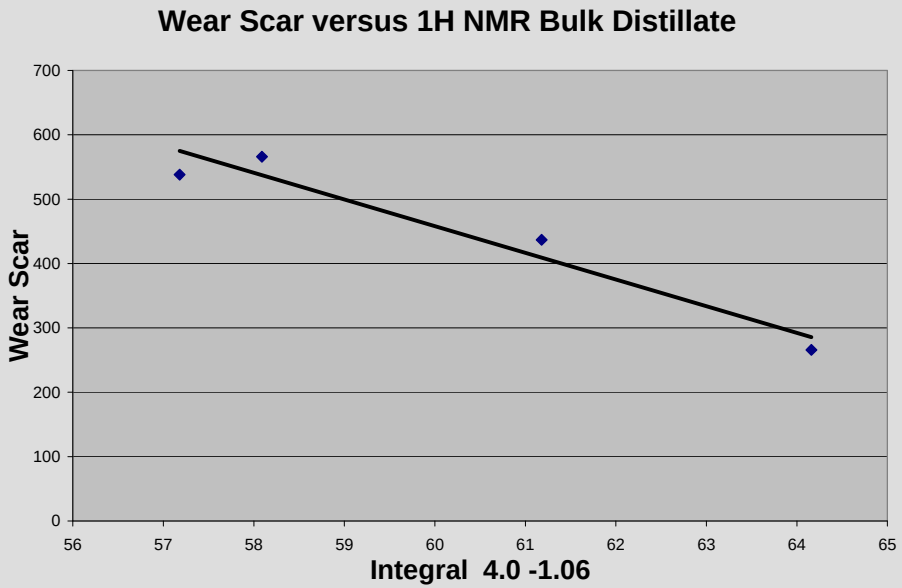


N-Alkane Distribution GC-FIMS Data



1 H NMR (4.0-1.06ppm Region)





- This 1H NMR region is typically associated with Cetane, implying a positive influence by long alkane chain and a negative influenceby Branched (iso-alkanes)
- Correlated well to both Bulk and the 265C- 300C fractionated samples.

Conclusions / Next Steps

- A variety analytical methods are required to adequately explore different theories regarding lubricity.
- Lubricity is a complex mechanism that has a molecular structure component.
- Viscosity influence may be an indirect measure of hydrocarbon chain length on boundary lubrication.
- The 13C NMR and GC-FIMS data needs to be explored to fully understand the molecular structure information of the 4.0 - 1.06 1H NMR region.