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ASPHALTENE FRACTIONATION

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Martin Fossen

Summary of PhD work at NTNU, 2004-2007

Extraction and Analysis of Asphaltene Fractions

Based on two papers

Paper 1: Energy&Fuels 2007

Asphaltenes Precipitated by a Two-Step Precipitation Procedure. 1. Interfacial Tension and Solvent Properties

Martin Fossen,*,† Harald Kallevik,‡ Kenneth D. Knudsen,§ and Johan Sjöblom†

Ugelstad Laboratory, Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway, Statoil ASA, R&D Center, Trondheim, Norway, and Institute for Energy Technology, Kjeller, Norway

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Paper 2: Energy&Fuels 2011

Asphaltenes Precipitated by a Two-Step Precipitation Procedure. 2. Physical and Chemical Characteristics

Martin Fossen,*,† Harald Kallevik,‡ Kenneth D. Knudsen,§ and Johan Sjöblom‖

†SINTEF Petroleumsforskning AS, NO-7031 Trondheim, Norway

‡Research and Development Centre, Statoil ASA, NO-7005 Trondheim, Norway

§Institute for Energy Technology, NO-2007 Kjeller, Norway

‖Ugelstad Laboratory, Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway

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Objective/Research Question

- How will asphaltenes fractionate upon successive dilution and filtration off?
- What are the differences between solubility fractions?
- Can the same differences be seen for different oils?

What was new?

- Direct precipitation and fractionation from the crude oil
- Most previous work had precipitated the whole asphaltene fraction and then fractionated that afterwards.
- We tried to do it more realistic by extracting different solubility fraction directly.

Fractionation procedure

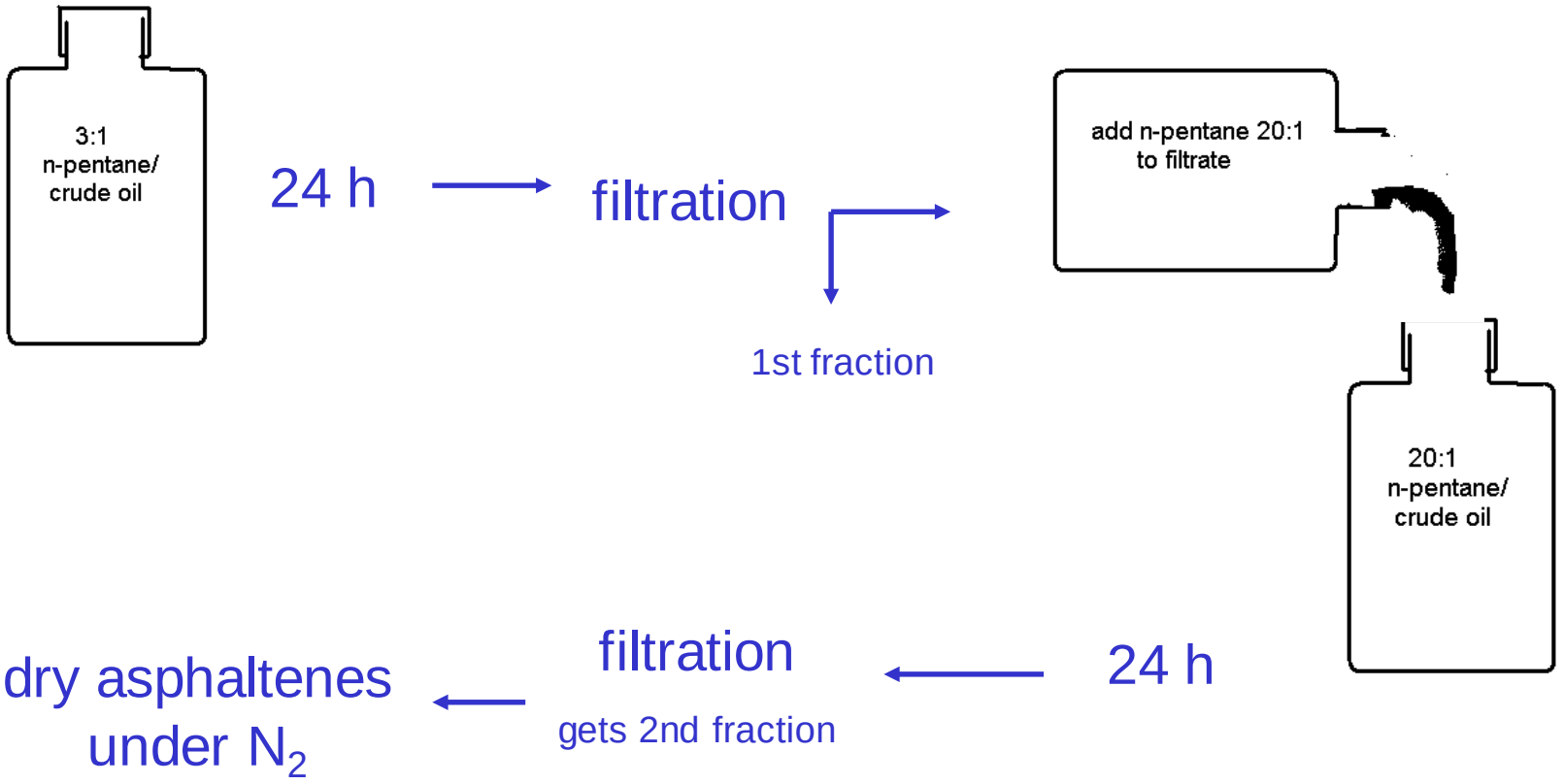
- 1. Dilute with 3:1 of *n*-pentane – first / 1st fraction
  - Filtrate off precipitated asphaltenes
- 2. Dilute with 18:1 of *n*-pentane – second / 2nd fraction
  - Filtrate off precipitated asphaltenes
- In addition, we precipitated by standard method the whole asphaltene fraction by 40:1 *n*-pentane.

- Gave three fractions: 1st., 2nd, and whole

Analytical chemistry

- **FT-NIR**
  - Onset of precipitation
- **Pendant Drop**
  - Interfacial tension
- **Smal Angle Neutron Scattering (SANS)**
  - Radius of gyration / aggregate size
  - 1 wt% (10 000 ppm)
- **Elemental composition (ASTM D5291)**
  - Percentage of C, H, N, O and S elements.
- **LDI-MS**
  - Molecular weight
- **FT-IR**
  - Quantification of functional groups
- **NMR (^{1}H, ^{1}C, and DEPT-135**
  - Structural parameters like aliphatic chain lengths, aromaticity, branchiness index, bridged/non-bridged carbon etc

Two-step precipitation



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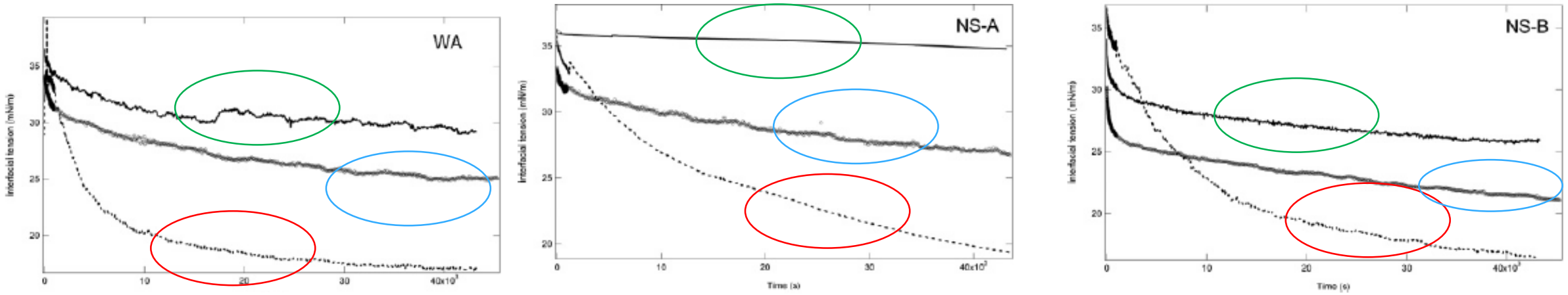
Interfacial activity



3:1 diluted fraction

Whole Asphaltenes

18:1 diluted fraction

- Pendant drop
- The 18:1 fraction was most interfacial active for all oils
- The 3:1 fraction was less interfacial active than the Whole Asphaltene fraction

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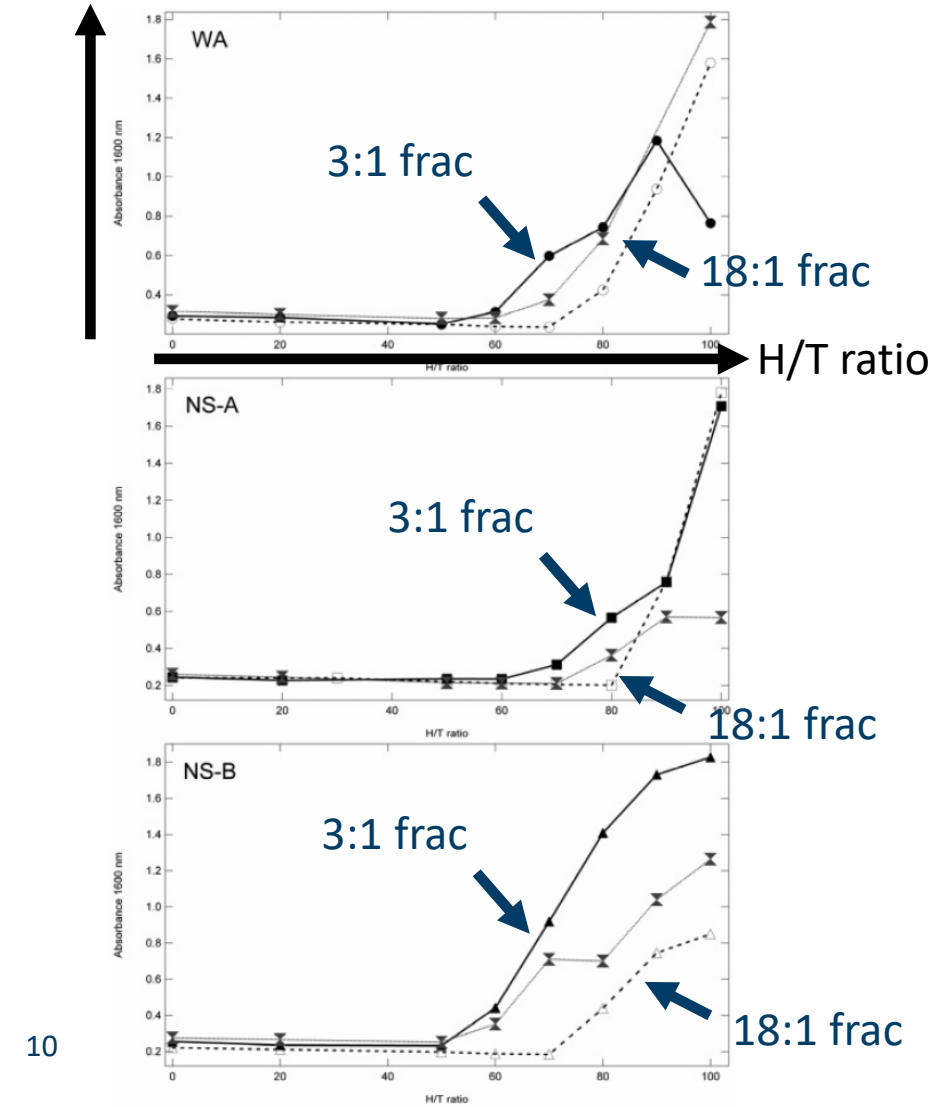
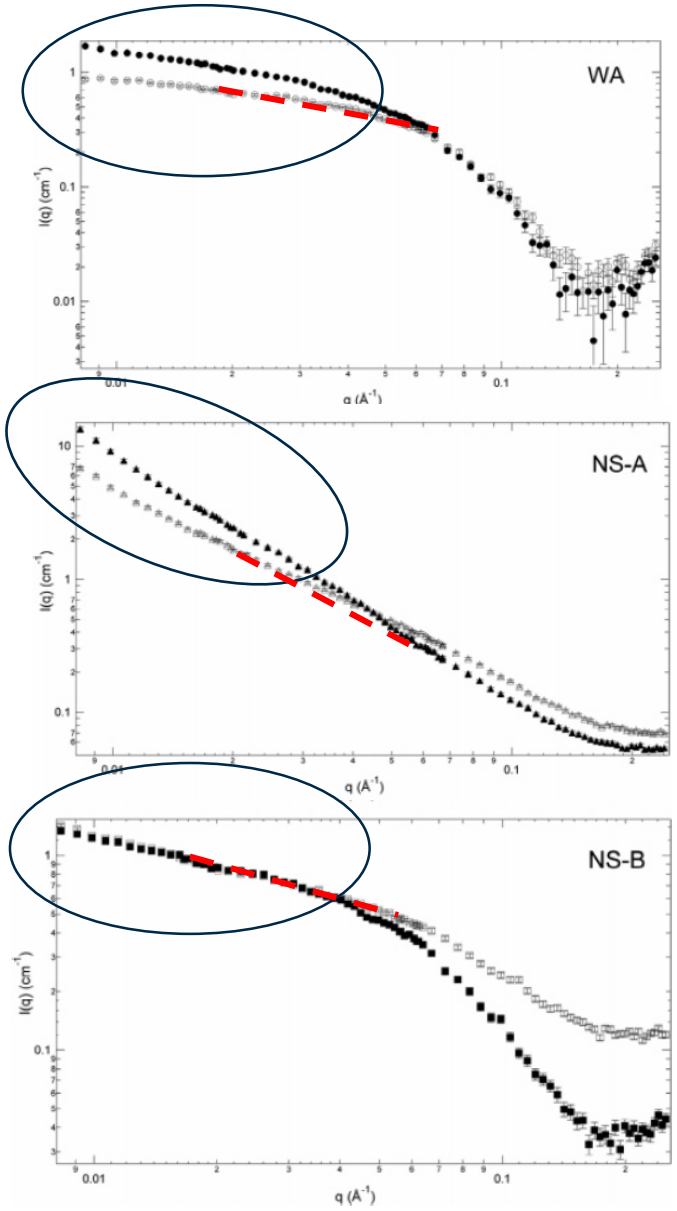
Onset of Precipitation



- Asphaltenes in Heptane-Toluene
- Concentration: 2300 – 2900 ppm (wt/wt)
  - Quite high asph. Conc. In order to detect aggregation.

- 18:1 fraction – more soluble
  - More heptane needed to detect preciptiation
- Whole and 1st fraction has approx same onset point (as would be expected)

Radius of gyration



Guinier approximation: $I(q) = I_0 \exp(-q^2 R_G{}^2/3)$

- By fitting a straight line between 0.02 Å and 0.08 Å (ex. Red line)
1 wt% asphaltene in deuterated toluene (toluene-d_8).

18:1 Asph. Lower aggregate size

Table 4. Calculated R_G from the SANS Measurements Using the Guinier Approximation[a]

asphaltene fraction	R_G (Å)	
WA first	30	
WA second	25	
NS-A first	ND	> 700 Å
NS-A second	ND	> 700 Å
NS-B first	26	
NS-B second	21	

First > second frac.

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FT-IR

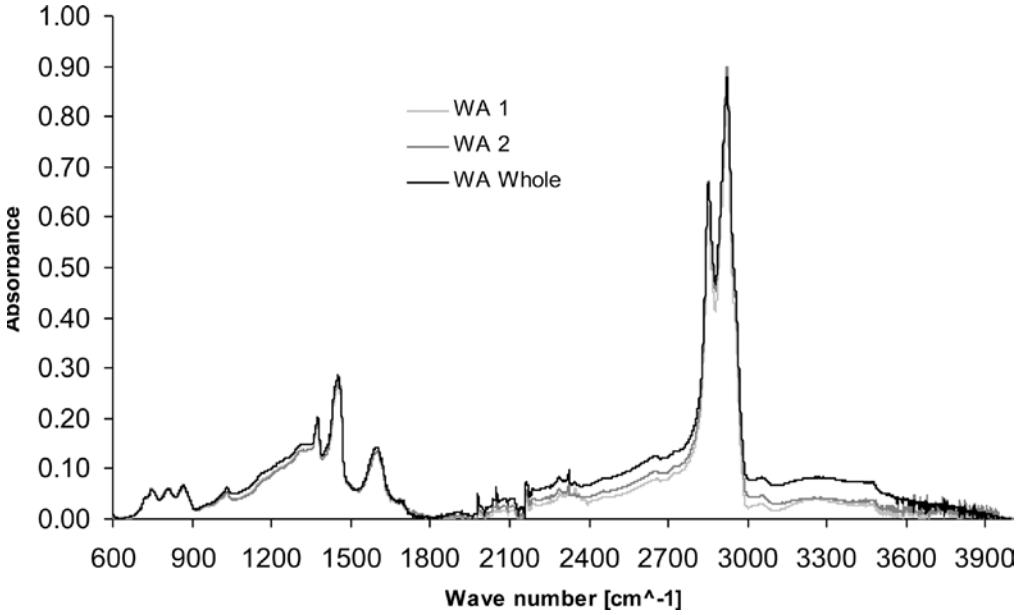

Figure 1. Absorbance spectra from FTIR measurements on powder asphaltene samples of WA whole, WA 1, and WA 2. The spectra were corrected for peaks because of CO2 and H2O (atmospheric correction) and were baseline-corrected using three points (4000, 1800, and 600 cm1).

- 1st fractions more aromatic
- 2nd fractions had higher degree of substitution
- 1st fraction: C-H oop indicated more condensed aromatic ring structure
- 2nd fraction: more –OH and –COOH groups
  - Supported by DEPT-135 NMR

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Amounts precipitated

Table 1. Percent Weight (wt %) of Asphaltenes for the First Fraction (3:1), Second Fraction (18:1), and the Asphaltenes Precipitated by the Standard Procedure of Excess (40:1) *n*-Pentane (Whole Fraction)[a]

oil	wt % first fraction (3:1)		wt % second fraction (18:1)	sum wt % first and second fractions	wt % whole fraction (40:1)
WA	0.8	40%	0.9	1.7	2.0
NS-A	1.0	55%	0.8	1.8	1.8
NS-B	0.4	25%	0.5	0.9	1.6

[a] The first and second fractions did not sum up to the whole, as shown for the WA and NS-B asphaltenes. While for the NS-A, the fractions did sum up to the whole fraction.

A large amount of the asphaltenes are easily precipitated. From 25% to 55 wt% of the total amount of asphaltenes precipitated when diluting with 3:1

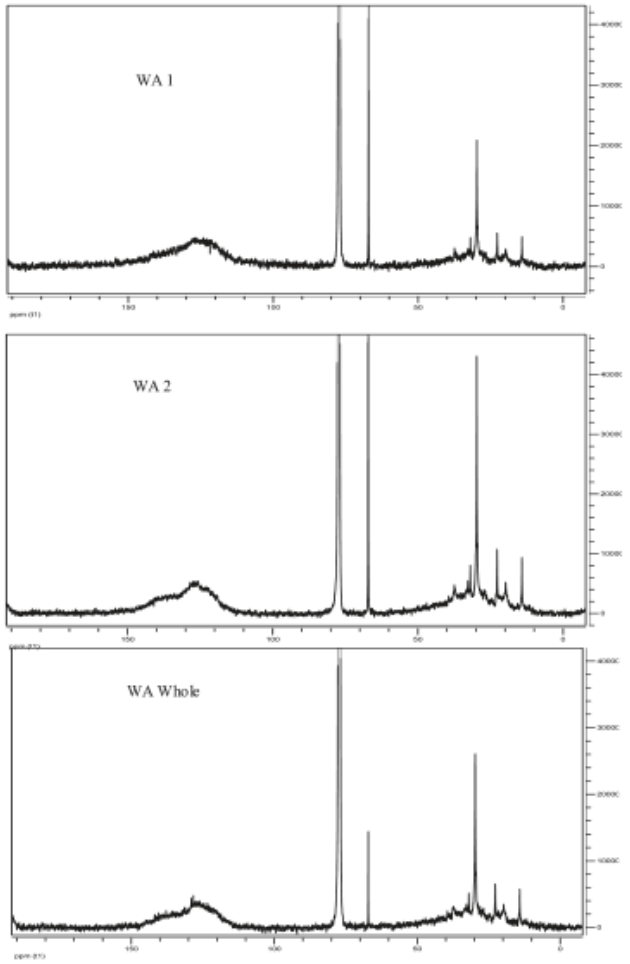
LDI-MS

Table 5. Number Averaged MW ($W_{averaged}$) Values in g/mol of the Asphaltenes Obtained by LDI–MS Using a Laser Pulse with an Energy of 20 μJ

fraction	WA	NS-A	NS-B
first fraction (3:1)	825	840	470
second fraction (18:1)	720	745	460
whole fraction (40:1)	500	700	445

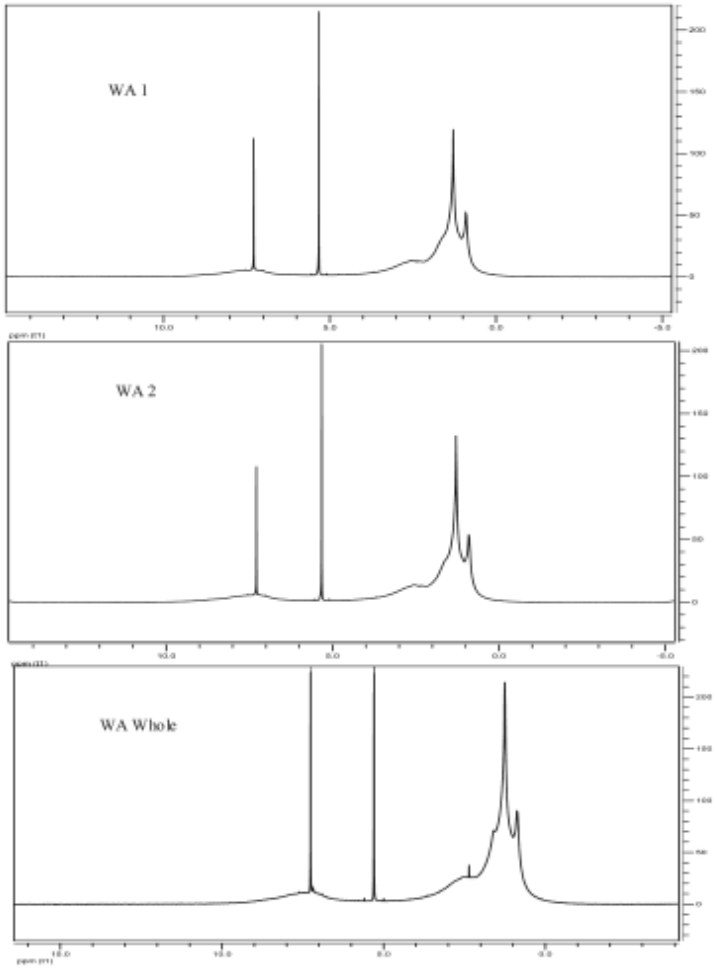
NMR Spectra

Proton



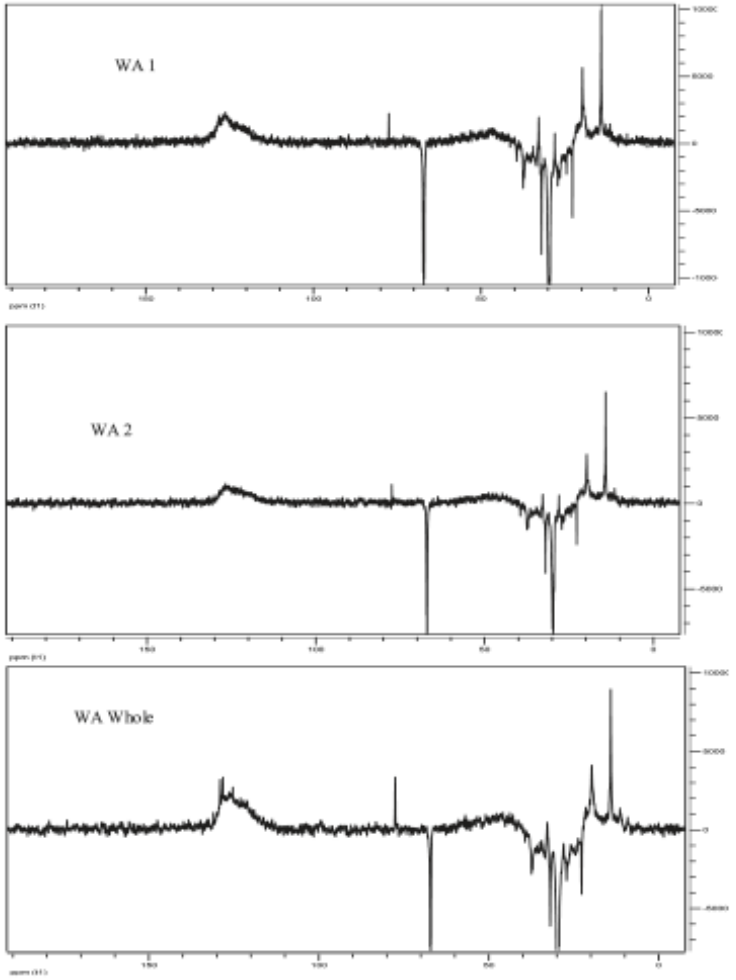
obtained for WA asphaltenes from the ^{13}C NMR measurements. There were differences in both the shape and
e samples.

Carbon



tained for WA asphaltenes from the ^{1}H NMR measurements. There were differences in both the shape and intensiti

DEPT-135



obtained for WA asphaltenes from the DEPT-135 NMR measurements. There were differences in both the sh
n the samples.

Deduced *average* structural parameters

Table 12. Average Structural Data Obtained by NMR of the Whole and Fractionated Asphaltenes of the NS-A Crude Oil

property	NS-A whole	NS-A first	NS-A second
total H	37	40	40
aromatic H	5	6	5
aliphatic H	32	35	35
aliphatic H in the α position	9	11	9
aliphatic H in the β position	17	19	20
aliphatic H in the γ position	5	5	6
total carbon	31	33	32
aromatic carbon	15	17	17
tertiary aromatic carbon	5	6	5
quartemary aromatic carbon	10	11	12
substituted aromatic carbon	4.8	5.1	4.1
bridged aromatic carbon	4	4	6
nonbridged aromatic carbon	11	13	11
aliphatic carbon	17	16	16
naphtenic carbon	2.2	2.0	2.3
n-alkyl carbon	1.6	1.4	1.3
aliphatic carbon in CH_3 group	3.8	4.2	3.6
average number of C atoms on chains, *n*	3.4	3.2	3.9
total number of aromatic rings per molecule	3.2	2.8	3.8
total number of naphtenic rings per molecule	0.63	0.58	0.65
branchiness index, BI	0.31	0.29	0.32
aromaticity, f_a	0.47	0.51	0.51
degree of substitution of aromatic carbon, σ	0.49	0.47	0.46
degree of condensation of aromatic carbon, γ	0.29	0.22	0.34
average C/H weight ratio of alkyl groups, f_c	6.2	5.6	5.4
total sulfur	0.30	0.54	0.47
total nitrogen	0.45	0.50	0.46
total oxygen	0.73	0.97	0.89
empirical formula	$C_{31}H_{37}N_{0.4}O_{0.7}S_{0.3}$	$C_{33}H_{40}N_{0.5}O_{1.0}S_{0.5}$	$C_{32}H_{40}N_{0.5}O_{0.9}S_{0.5}$
formula MW (g/mol)	435	475	461

- Aromaticity
- Number of aliphatic chains
- Average chain length
- Etc…

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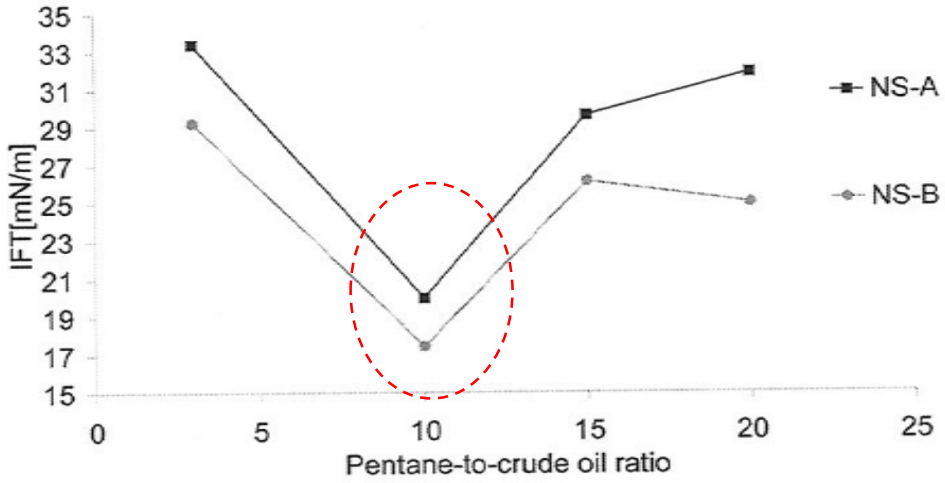
Conclusions

- 3 Crude oils; NS-A, NS-B and WA
- 2 solubility fractions + whole asphaltenes
- NS-B and WA followed the same trend.
- Least soluble asphaltenes (3:1 fraction)
  - Higher average MW
  - Larger aggregate size
  - Less interfacially active
  - More aromatic
  - More condensed (higher degree of quarternary carbons in the aromatic region of the spectra)
- More soluble fraction (18:1)
  - Smaller and lower R_g
  - Higher degree of branching of the substituted alkyl chains
  - Higher amount of carboxyl and hydroxyl groups
  - More soluble; i.e more heptane was needed to detect aggregation

However…

4-step fractionation ->

- 3:1, 10:1, 15:1 and 20:1 successive dilution and filtration off
  - For two crude oils
- Precipitiation onset test 0-100% H/T: As expected
- IFT: 10:1 fraction was much more interfacially active!
  - Why?
  - Asphaltenes as a solubility fraction is not homogenous
  - Some asphaltenes may be worse than other for specific operational problems
    - Deposition and plugging
    - Emulsion stability
    - Viscosity?



A New Procedure for Direct Precipitation and Fractionation of Asphaltenes from Crude Oil

Martin Fossen and Johan Sjøblom
Ugelstad Laboratory, Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway
Harald Kallevik
Statoil ASA, R&D Center, Trondheim, Norway
Joakim Jakobsson
Department of Chemical Engineering, Aabo University, Turku, Finland

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Teknologi for et bedre samfunn