PORLA Heavy and Crude Oil Stability and Compatibility Analyzer as a Tool to Improve Profitability of Oil Industry

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WOULD YOU LIKE TO MAKE MILLIONS OF USD MORE PROFIT !!!!! BY HEAVY FUEL OIL STABILITY ANALYZERS ?

NO

YES !
HOW MUCH MORE PROFIT

• ASSUMPTIONS
  – OPTIMIZED OIL REFINERY, ANNUAL FEED 10 MTON, VISBREAKER PROCESS, MANUAL HEAVY OIL STABILITY ANALYSIS

• ACTION
  – FROM MANUAL TO AUTOMATIC STABILITY ANALYSIS

• ANNUAL INCREASE IN PROFITABILITY
  – REPRODUCIBILITY MANUAL 0.2, AUTOMATIC 0.05 PV UNIT
  – 0.1 P-VALUE UNIT - 1 000 000 USD ANNUALLY

0.2-0.05=0.15PV ==> 1 500 000 USD !!!
PORLA Automatic Laboratory Analyser

- Determination of Stability and Compatibility
- Introduction of Automatic PORLA Analyser
- Case studies of costs of compatibility problems
- Results of Visbreaker Products
- Results of Hydrocracking Products
- Results of Crude Oils
- Conclusions
STABILITY and COMPATIBILITY

• **Instability** – Tendency of a Liquid Material to Form (or Initially Contain) Sediment upon Storage or Heating
  – Mechanism could be Asphaltene Precipitation or Oxidation and Polymerization Reactions

• **Incompatibility** – Tendency of a Liquid Material to Form Sediment upon Mixing with Another Liquid
WHAT IS SEDIMENT?

- Sediment Measured during Stability and Compatibility Testing are:
  - Precipitated Asphaltenes
  - Fines Particulates (Catalyst, Scale) Possibly Acting as Precursor of Sediment and Aggregating the Asphaltenes
  - Carboneous Materials Dispersed in the Effluents or Feed
How are Stability and Compatibility Determined Manually?

- Dilution of OIL with an AROMATIC solvent
- Precipitation of Asphaltenes with a PARAFFINIC solvent
- Visual detection of precipitation by manual spot test or microscopy

![ML Parraffin / g oil](chart)

- 0.1
- 0.2
- 0.3
- 0.4
- 0.5
CALCULATION OF STABILITY FIGURES

\[ \text{FR} = \frac{\text{Varom}}{\text{Varom} + \text{Vpara}} \]

\[ \text{TE} = \text{FR5/1} \times 100\% \]

\[ \text{X} = \frac{\text{Varom} + \text{Vpara}}{\text{Moil}} \]

\[ \text{P} = 1 + X_{\text{min}} \]
CALCULATION OF STABILITY FIGURES

\[ P = 1 + X_{\text{min}} \]

\[ P_a = 1 - FR_{\text{max}} \]

\[ P_o = (FR_{\text{max}}) \times P \text{ or } P_o = (FR_{\text{max}}) \times (1 + X_{\text{min}}) \]

\[ P_a = \text{peptizability of asphaltenes} \]
\[ P_o = \text{peptizing power of the oil matrix} \]
\[ FR_{\text{max}} = \text{maximum flocculation ratio (at 1/X=0)} \]
Why stability analyses are so important in resid. conversion processes?

- Improve monitoring and profitability of conversion unit
  - Increased yield of valuable components by maximizing conversion v/s converted fuel oil stability
  - Decreased consumption of aromatic cutter stocks (not always available)
  - Minimized amount of Off-Spec. products in the final heavy fuel pool (compatibility)
  - Increased operability of key equipments such as feed/product heat-exchanger
ASSUMPTIONS
- **OPTIMIZED** OIL REFINERY, ANNUAL FEED 10 MTON, VISBREAKER PROCESS, MANUAL HEAVY OIL STABILITY ANALYSIS

ACTION
- FROM MANUAL TO AUTOMATIC STABILITY ANALYSIS

ANNUAL INCREASE IN PROFITABILITY
- REPRODUCIBILITY MANUAL 0.2, AUTOMATIC 0.05 PV UNIT
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\[0.2 - 0.05 = 0.15PV \Rightarrow 1 500 000 USD !!!\]
COMPATIBILITY PARAMETERS

\[ I_N = \frac{TE}{(1 - \frac{V_H}{25d})} \]

\[ S_{BN} = I_N \left( 1 + \frac{V_H}{5} \right) \]

TE = toluene equivalent

\( V_H = \) maximum n-heptane can be added to 5 ml of oil

\( d = \) density of oil
COMPATIBILITY MODEL

Compatibility criterion

\[ S_{BNmix} > I_{Nmax} \]
Blends are compatible when the volumetric average solubility blending number is greater than the insolubility number of any component of the blend.
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PORLA Method Input/Output

INPUT:
- OPERATOR NAME
- SAMPLE NAME
- METHOD
- STOCK SOLUTION DATA
- DENSITY
- SAMPLE QUANTITIES
- MEASURING PROFILE

OUTPUT:
- PARAFFIN CONSUMPTION
- EXTRAPOLATION LINE
- CORRELATION COEFF.
- P-VALUE, Pa, Po
- SOLVENT EQUIVALENT
- COMPATIBILITY PARAM.
Detection Principle of PORLA

LIGHT SOURCE

OIL sample + Aromatic solvent

DETECTOR

Paraffinic solvent
TITRATION CURVE OF HFO

Heavy Fuel Oil

Paraffin feeding Step

Inflection Point

Rel.Int.

Deriv.
TITRATION CURVE OF CRUDE OIL

Crude Oil

Paraffin feeding Step

Inflection Point

Rel. Int.

Deriv.
TITRATION CURVE OF CRUDE NA

Crude Oil with no Asphaltenes

Paraffin feeding Step

Rel. Int.

Deriv.
SOME FEATURES OF PORLA

• Automatic, Simple and Easy Operation
• Applicable for Research and Refinery Operations
• Asphaltene Sensitive Detector
• One Variable and Three Fixed Dilution Ranges
• Fast Screening Option
• Measurement Mode for Light Samples
• Heavy and Crude Oil Compatibility Application
• Use of Different Aromatic and Paraffinic Solvents
• Aromatic Solvent Evaporation Correction
• Operation at Elevated Temperatures
• Can Analyze Low Asphaltene Content Oils (<0.1%)
PORLA Analyzer

• **Automatic Measurement of P-Value, Solvent Equivalent and Flocculation Ratio**
• **Accurate Estimation of Stability and Compatibility Parameters**
• **Analytical Procedure Used:**
  – Variable Combination of Solvent Aromatic (Xylene, Toluene, etc.) and Paraffinic (Heptane, iso-octane, Cetane, etc.)
  – Automatic Titration of the Three Solutions (Oil, Aromatic, Paraffin)
  – Detection of Asphaltene Particles by Selective Detector (Back-Scattering) : Onset of Flocculation Is Called FR
  – Automatic Calculation of Stability and Compatibility Figures
Benefits of PORLA

- No Need For Tedious Filtering
- No Need For Experienced Operators
- High Automation Level - Proven Technology
- Low Labor Requirements
- Easy To Use And Maintain
- Less Time Consuming versus Manual Reference Method
  - 1/6 of Manual Method Time
- PORLA Pay-out Time is 6 - 8 Months
WHY ASTM STANDARDIZATION (D 7112)

• The present trends in oil refining require more accurate process control and analytical methods
• Poor reproducibility of manual methods may lead to confusions in the process control
• There was no universal method to determine stability and compatibility figures - only in-house methods
• New regulations on sulfur content of marine fuels in Europe will increase compatibility risks fuel oil blender of ships
• Internationally accepted standard method would minimize unexpected surprises in use of products
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Crude or fuel instability (in the form of asphaltenes flocculation resulting in sludge formation and fouling) can be caused by several factors:

a) an upset in a residue conversion unit, leading to a less stable visbreaker bottoms stream (e.g. P value 1.1 instead of 1.3) and an unstable fuel oil blend (P value < 1) upon dilution with normal cutter stocks

b) blending of two stable fuels or crudes with strongly differing chemical composition (e.g. a visbroken residue with highly aromatic asphaltenes and a paraffinic straight run long residue)

c) blending in the wrong order: when adding an aromatic, asphaltene rich stream to a paraffinic stream, the asphaltenes will initially encounter a high concentration of hydrocarbons with poor solubility, so that flocculation occurs, even if the final blend is theoretically stable.
Main causes of unstable fuel oils

1. Upset in a residue conversion unit, resulting in a less stable bottoms stream and an unstable blend after dilution with normal diluents

2. Blending of two stable fuels of completely different origin (e.g. Middle East residue with paraffinic residue)

3. Blending in the wrong order
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THERMAL CRACKING UNIT

- FEED → MIDDLE DISTILLATES → LIGHT ENDS
- HEAVY BOTTOM → CUTTER STOCK
- STABILITY ANALYSIS → HEAVY FUEL OIL

STABILITY vs TIME graph
CORRELATION OF P-VALUE AND PROCESS TEMPERATURE OF VB-UNIT
## Fortum Oil and Gas Ltd Data

<table>
<thead>
<tr>
<th>Run</th>
<th>Residue (450ºC)</th>
<th>Residue (435ºC)</th>
<th>Residue (420ºC)</th>
<th>Feed Stock</th>
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<tbody>
<tr>
<td></td>
<td>FR5/1 P-Val</td>
<td>FR5/1 P-Val</td>
<td>FR5/1 P-Val</td>
<td>FR5/1 P-Val</td>
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<tr>
<td>1</td>
<td>0.56 1.24</td>
<td>0.39 1.92</td>
<td>0.29 2.48</td>
<td>0.05 5.50</td>
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<tr>
<td>2</td>
<td>0.57 1.32</td>
<td>0.39 1.98</td>
<td>0.30 2.45</td>
<td>0.07 5.14</td>
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<tr>
<td>3</td>
<td>0.58 1.27</td>
<td>0.38 1.98</td>
<td>0.28 2.40</td>
<td>0.08 4.92</td>
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<tr>
<td>4</td>
<td>0.58 1.29</td>
<td>0.38 1.98</td>
<td>0.28 2.49</td>
<td>0.08 5.02</td>
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<tr>
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<td>0.28 2.52</td>
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<tr>
<td>6</td>
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<td>0.38 1.98</td>
<td>0.29 2.47</td>
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<td>Aver.</td>
<td>0.578 1.268</td>
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<td>0.287 2.468</td>
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<td>0.008 0.041</td>
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<td>r.</td>
<td>0.010 0.028</td>
<td>0.004 0.019</td>
<td>0.006 0.033</td>
<td>0.010 0.182</td>
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</tbody>
</table>
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Optimization of H-Oil Using PORLA

• Maximizing Conversion versus Fuel Oil Stability
• Decreased Consumption of Aromatic Cutter Stocks
• Increased Operability of Key Equipment Such As Feed/Product Heat Exchanger
(1) typical feed. : SR VR from Conventionnal Crude, SR AR from extra heavy crude
H-Oil PROCESS

- Catalytic Hydroconversion Process for Upgrading Petroleum Residue
- Utilizes an Ebullated-Bed Reactor
- Long Cycle Length (over 3 years)
- Temperature: 410 - 440°C
- High Hydrogen Pressure: 100 - 200 bar
- Space Velocity: 0.25 - 1.5 hr⁻¹
- On-line Catalyst Addition: 0.3 - 2.5 kg/m³
<table>
<thead>
<tr>
<th>Performance Item</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resid. conversion</td>
<td>45 to 90% v/v</td>
</tr>
<tr>
<td>S Removal</td>
<td>65 to 90% m/m</td>
</tr>
<tr>
<td>Metals (Ni, V) Removal</td>
<td>65 to 90% m/m</td>
</tr>
<tr>
<td>CCR Conversion</td>
<td>45 to 75% m/m</td>
</tr>
<tr>
<td>Chemical H2 Consumption</td>
<td>130-300 Sm$^3$/m$^3$</td>
</tr>
<tr>
<td>Conversion main limitation</td>
<td>Resid. Stability</td>
</tr>
</tbody>
</table>

Conversion main limitation: Resid. Stability
PORLA precision study v/s time: repeatability/intra labo. reproducibility

<table>
<thead>
<tr>
<th>level</th>
<th>method</th>
<th>intra. Lab. repeatability ( r_L )</th>
<th>intra. Lab. Reproducibility ( R_L )</th>
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<tr>
<td>1,5</td>
<td>manual</td>
<td>not det.</td>
<td>0,20</td>
</tr>
<tr>
<td>1,5</td>
<td>PORLA</td>
<td>0,08</td>
<td>0,08</td>
</tr>
<tr>
<td>0,5</td>
<td>manual</td>
<td>not det.</td>
<td>0,06</td>
</tr>
<tr>
<td>0,5</td>
<td>PORLA</td>
<td>0,014</td>
<td>0,019</td>
</tr>
</tbody>
</table>

- PORLA precision 3 times better than manual method
- PORLA measurement very stable v/s time \( (r_L = R_L) \)
- PORLA: precision not dependant on operator
Utilization of PORLA on H-Oil Product

- Extensive comparison with the manual method
  - 4 very different feedstocks:
    - Arabian Heavy Conventional V.R.
    - 3 A. R. from extra heavy crudes from Venezuela (Boscan, Morichal) and Canada (Cold Lake)
Utilization of PORLA on H-Oil Product

- Parameters to be compared:
  - FR5/1 (manual method): 0.35 (very stable) to 0.80 (border-line/unstable)
  - p-value: 1.8 (very stable) to 1.0 (unstable)

- Net V.R. Conversion: 50 to 65% m/m
Utilization of PORLA on H-Oil Products

Extensive study of all H-oil streams, wide variation of feed stocks and stabilities. The key points found were:

- P-Values by Porla and manual method were equal and Porla results were 3 times more accurate than manual method results (confidence interval +/-0.06 Porla v/s +/- 0.14 manual)

- Between Porla and manual method FR5/1 values there was a constant correlation (FR5/1PORLA = 0.84 FR 5/1 Manual) and Porla results were 3 times more accurate (+/- 0.014 Porla v/s +/- 0.043 manual)

- No feed stock effect between Porla and manual method
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## STABILITY AND COMPATIBILITY ANALYSES OF ATHABASCA BITUMEN

<table>
<thead>
<tr>
<th>QC</th>
<th>P-Value</th>
<th>In</th>
<th>SBN</th>
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<tbody>
<tr>
<td>1</td>
<td>3.66</td>
<td>28.1</td>
<td>102.1</td>
</tr>
<tr>
<td>2</td>
<td>3.61</td>
<td>26.9</td>
<td>96.4</td>
</tr>
<tr>
<td>3</td>
<td>3.80</td>
<td>26.3</td>
<td>99.3</td>
</tr>
<tr>
<td>4</td>
<td>3.79</td>
<td>26.1</td>
<td>98.2</td>
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<tr>
<td>5</td>
<td>3.89</td>
<td>26.9</td>
<td>103.6</td>
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<tr>
<td>6</td>
<td>3.67</td>
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<td>91.8</td>
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<td>7</td>
<td>3.85</td>
<td>25.3</td>
<td>96.7</td>
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<tr>
<td>8</td>
<td>3.86</td>
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<td>9</td>
<td>3.64</td>
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<td>10</td>
<td>3.81</td>
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<tr>
<td><strong>Average</strong></td>
<td><strong>3.76</strong></td>
<td><strong>26.1</strong></td>
<td><strong>97.2</strong></td>
</tr>
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<table>
<thead>
<tr>
<th></th>
<th>s</th>
<th>r</th>
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<tr>
<td>s</td>
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<td>1.0</td>
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<tr>
<td>r</td>
<td>0.06</td>
<td>0.6</td>
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---
## ANALYSES OF RUSSIAN CRUDES

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<tr>
<th>Oil</th>
<th>S&lt;sub&gt;BN&lt;/sub&gt;</th>
<th>I&lt;sub&gt;N&lt;/sub&gt;</th>
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<tr>
<td>HFO</td>
<td>76</td>
<td>45</td>
<td>1.7</td>
</tr>
<tr>
<td>PEB</td>
<td>63</td>
<td>23</td>
<td>3.0</td>
</tr>
<tr>
<td>Novosergie</td>
<td>66</td>
<td>28</td>
<td>2.6</td>
</tr>
<tr>
<td>Novokievsk</td>
<td>77</td>
<td>29</td>
<td>2.9</td>
</tr>
<tr>
<td>Usinsk</td>
<td>44</td>
<td>20</td>
<td>2.3</td>
</tr>
<tr>
<td>Aktyubinsk*</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zagorskaya*</td>
<td>45</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Rkondkargi*</td>
<td>35</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DUC*</td>
<td>94</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Rkondakzai*</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zaikinsk*</td>
<td>13</td>
<td>-</td>
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</tr>
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</table>

* Analyzed indirectly by mixing with FHO
## REPETITIVE ANALYSES, SYNCRUDE

<table>
<thead>
<tr>
<th>Test No.</th>
<th>FR5/1</th>
<th>P-value</th>
<th>$S_{BN}$</th>
<th>$I_N$</th>
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<tbody>
<tr>
<td>1</td>
<td>0.21</td>
<td>2.78</td>
<td>91.7</td>
<td>33.0</td>
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<tr>
<td>2</td>
<td>0.21</td>
<td>2.71</td>
<td>86.5</td>
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<tr>
<td>3</td>
<td>0.24</td>
<td>2.57</td>
<td>89.6</td>
<td>34.8</td>
</tr>
<tr>
<td>4</td>
<td>0.21</td>
<td>2.71</td>
<td>86.5</td>
<td>32.3</td>
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<td>89.2</td>
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<tr>
<td><strong>Mean</strong></td>
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<td><strong>2.71</strong></td>
<td><strong>88.7</strong></td>
<td><strong>32.8</strong></td>
</tr>
<tr>
<td>s</td>
<td>0.012</td>
<td>0.073</td>
<td>1.99</td>
<td>1.03</td>
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<tr>
<td>r</td>
<td>0.010</td>
<td>0.058</td>
<td>1.59</td>
<td>0.83</td>
</tr>
</tbody>
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Conclusions (1)

- Substitution of manual stability analyses by Porla in monitoring of optimized visbreaker process:
  => 1500 kUSD more profit annually
  => real pay-back within 1 month

- 3 times better precision v/s ref. manual method in H-Oil process optimization:
  => about 3% more V.R. net conversion
  => real pay-back within 1-2 months
Conclusions (2)

- Preventing instability/incompatibility cases in blending of fuel oils:
  => profit 250,000 - 1,000,000 USD per case

- Monitoring of processes and compatibility of crude oil blends in industrial plants is important to prevent plugging trouble and unit shut downs:
  => savings as result of minimized fouling problems and more economically selected blends of crudes
Conclusions (3)

- PORLA determines $P$-value, $P_a$, $P_o$, FR5/1 (solvent equivalent), $FR_{\text{max}}$, $X_{\text{min}}$, $I_N$ and $S_{\text{BN}}$
- Poor reproducibility of manual methods may lead to confusions in the process control
- PORLA method is very stable with time, not operator dependant
- The present trends in oil refining require more accurate process control and analytical methods
- Uniform stability determination method minimize unexpected surprises in use of products
- PORLA method is ASTM Standard Method D 7112
Conclusions (4)

- PORLA can analyze low asphaltene content (<0.1%) heavy and crude oils
- Detection not sensitive to interfering film on the optical parts of the detector
- PORLA can be used in auto-control
- Visbreaker monitoring easy application for PORLA
- PORLA adapted on unstable H-Oil products (spot very difficult to read for FR5/1 >0.8 on manual method)
- PORLA is used for monitoring of IFP H-OIL pilot plant on the full FR5/1 range: 0.20 to > 0.80
Conclusions (5)

- Detection of asphaltene precipitation for wide range of materials including crude oils, heavy fuel oils, process residues and bitumen
- Heavy and crude oil compatibility program is powerful tool in marine fuel and crude oil blending
- Porla can be used for preventing plugging troubles in oil production pipelines/blenders
- Latest application: Determination of three dimensional solubility parameters of bitumen
WOULD YOU LIKE TO MAKE MILLIONS OF USD MORE PROFIT !!!!! BY HEAVY FUEL OIL STABILITY ANALYZERS ?

YES !

PROFITABILITY