# Measurement of H/C Ratio in Petroleum Samples by GC-AED


**Y. Briker, T.J.W. de Bruijn, W.S. Yip, Z. Ring**

**National Centre for Upgrading Technology**
**1 Oil Patch Drive, Suite A202**
**Devon, AB, T9G 1A8, Canada**



**PITTCON 2006**
**March 12-17, 2006**
**Orlando, Florida**

# H/C Ratio Measurement

## Objectives

**Detailed analysis of petroleum feedstocks and products:**

- **provides knowledge useful for improving and optimizing the upgrading process**
- **gives valuable insight into processing characteristics**
- **makes possible correlation between composition and fuel properties**

# Method Development

At NCUT we developed a method for the analysis of hydrogen to carbon ratio (H/C) for full-range petroleum samples by gas chromatography-atomic emission detection (GC-AED) coupling.

It requires installation of the kit for automated hydrogen linearization and measurement, containing hardware (a methane bleed regulator) and software (recipe files and macros).

Hydrogen linearization is done by generating a pseudo chromatogram with pressure programming of the methane AED "Aux" reagent gas.

This pseudo chromatogram is processed by a macro to calibrate out the non-linearity in the AED hydrogen response.

A second pseudo chromatogram is generated and used to calibrate the relative response factors of carbon and hydrogen. This data is then used to calculate the percent total carbon and hydrogen when samples are analyzed.

# Method Development, Continued

## Sample method for running diesel range samples

| | |
|---|---|
| GC Column | 25m x 0.32mm i.d. x 0.17 um HP-1 |
| Injector (split/splitless) | 300$^{o}$C, split ratio 50:1, constant flow mode at 2.0 mL/min, 0.5ul injection volume |
| Oven Temperature | 40$^{o}$C to 340$^{o}$C at 20$^{o}$C/min (hold 5 min) |
| AED Reagent Gases | Oxygen 55 psi, Hydrogen 45 psi |
| | **Methane 7psi** |
| AED Makeup Gas | 100 mL/min |
| AED Data Rate | 5 Hz |
| AED Solvent Vent | None |
| AED Transfer Line Temp | 340$^{o}$C |
| AED Cavity Temp | 375$^{o}$C |
| AED Element Group | **"Hydrogen Linearization with Aux"** |
| AED Elements Selected | **Carbon 496, Hydrogen 486[L]** |

# Method Development continued

## Calculations

The macros do a simple calculation of the carbon and hydrogen (ignoring other elements) by comparison of the areas measured for the methane pseudo peak with the areas for the unknown.

$$\%C = \frac{(A_{C\ unk}/A_{C\ CH4}) \times (M_C/M_{CH4}) \times 12.01115}{((A_{C\ unk}/A_{C\ CH4} \times (M_C/M_{CH4} \times 12.01115 + (A_{H\ unk}/A_{H\ CH4}) \times (M_H/M_{CH4}) \times 1.00797}$$

$\%H = 100 - \%C$

Where

- $A_{C\ unk}$ = Area of carbon from the unknown
- $A_{C\ CH4}$ = Area of carbon from methane
- $M_C/M_{CH4}$ = Moles of carbon per mole methane
- 12.01115 = atomic weight of carbon
- $A_{H\ unk}$ = Area of hydrogen from the unknown
- $A_{H\ CH4}$ = Area of hydrogen from methane
- $M_H/M_{CH4}$ = Moles of hydrogen per mole methane
- 1.00797 = Atomic weight of hydrogen

This calculation ignores the presence of any other elements. If the amounts of sulphur, nitrogen and oxygen are measured by AED or any other means, the data for C and H are easily renormalized

# Method Development, Continued

## H/C Ratio Distribution by Boiling Point

**The H/C ratio by-boiling-point distribution is generated using an HP 6890 gas chromatograph coupled with an atomic emission detector, Model G2350A, from HP (GC-AED). The carbon and hydrogen emissions of 496 nm and 486 nm, respectively, are used to collect the signals (in a single injection), and the distribution calculation is performed with the help of software for simulated distillation, SDE60 (by Separation Systems, Inc.) using the ASTM D2887. The H/C ratio distribution is calculated by using the calibration parameters obtained from running the mixture of paraffin standards (C5 to C44) at the same conditions as for the analyzed samples.**

**In the second injection, using the sulphur emission of 181 nm to collect the sulphur signal, the by-boiling-point distribution of sulphur is calculated. In this case the paraffin calibration is obtained by analyzing the mixture of paraffin standards using a carbon emission of 179 nm. A similar distribution can be obtained by analyzing the sample by the GC-SCD (sulphur chemiluminescent detector).**

**The nitrogen distribution is obtained from the GC-NCD (nitrogen specific detector) analysis of the sample or from the GC-AED analysis using a nitrogen emission of 388 nm.**

**To correct the H/C distribution, the sulphur and nitrogen distributions are subtracted from the corresponding carbon distribution.**

# Sulphur Table (wt%), ASTM D2887, AED sulphur(181) Channel

| WT % | BP(C) | | WT % | BP(C) | | WT % | BP(C) |
|---|---|---|---|---|---|---|---|
| 0.019 | 111.9 | | 1.261 | 316.3 | | 2.523 | 411.6 |
| 0.037 | 134.8 | | 1.299 | 319.6 | | 2.560 | 414.2 |
| 0.074 | 139.6 | | 1.336 | 322.6 | | 2.597 | 417 |
| 0.111 | 158.2 | | 1.373 | 326 | | 2.634 | 419.7 |
| 0.148 | 162.4 | | 1.410 | 329.7 | | 2.671 | 422.3 |
| 0.186 | 169.9 | | 1.447 | 332.8 | | 2.708 | 424.9 |
| 0.223 | 180.7 | | 1.484 | 335.7 | | 2.745 | 427.7 |
| 0.260 | 185.1 | | 1.521 | 337.9 | | 2.783 | 430.5 |
| 0.297 | 195.8 | | 1.558 | 340.7 | | 2.820 | 433.3 |
| 0.334 | 203.6 | | 1.595 | 343.8 | | 2.857 | 436.2 |
| 0.371 | 211.2 | | 1.632 | 346.7 | | 2.894 | 439.1 |
| 0.408 | 221.2 | | 1.670 | 349.3 | | 2.931 | 442.3 |
| 0.445 | 226.7 | | 1.707 | 351.8 | | 2.968 | 445.3 |
| 0.482 | 230.9 | | 1.744 | 354.2 | | 3.005 | 448.5 |
| 0.519 | 240.6 | | 1.781 | 356.9 | | 3.042 | 451.8 |
| 0.557 | 245.4 | | 1.818 | 359.4 | | 3.079 | 455.1 |
| 0.594 | 248.2 | | 1.855 | 362.2 | | 3.116 | 458.5 |
| 0.631 | 250.7 | | 1.892 | 364.8 | | 3.154 | 462 |
| 0.668 | 257.0 | | 1.929 | 367.5 | | 3.191 | 465.5 |
| 0.705 | 262.6 | | 1.966 | 370.2 | | 3.228 | 469.1 |
| 0.742 | 265.6 | | 2.003 | 373 | | 3.265 | 472.7 |
| 0.779 | 268.0 | | 2.041 | 375.8 | | 3.302 | 476.5 |
| 0.816 | 272.0 | | 2.078 | 378.5 | | 3.339 | 480.5 |
| 0.853 | 276.5 | | 2.115 | 381.1 | | 3.376 | 484.8 |
| 0.890 | 279.5 | | 2.152 | 384.1 | | 3.413 | 489.4 |
| 0.928 | 282.5 | | 2.189 | 387.1 | | 3.450 | 494.5 |
| 0.965 | 286.4 | | 2.226 | 390 | | 3.487 | 500.1 |
| 1.002 | 290.6 | | 2.263 | 392.8 | | 3.525 | 506.3 |
| 1.039 | 294.1 | | 2.300 | 395.5 | | 3.562 | 513.6 |
| 1.076 | 297.6 | | 2.337 | 398.2 | | 3.599 | 522.5 |
| 1.113 | 301.5 | | 2.374 | 400.9 | | 3.636 | 533.8 |
| 1.150 | 305.5 | | 2.412 | 403.8 | | 3.673 | 550.1 |
| 1.187 | 309.4 | | 2.449 | 406.5 | | 3.691 | 562.8 |
| 1.224 | 312.8 | | 2.486 | 409.1 | | | |
| **TOTAL SULFUR (wt.%** | | **3.71** | | | | | |

# Nitrogen Table (Wt%), ASTM D2887, NCD Detector

| WT % | BP(C) | | WT % | BP(C) | | WT % | BP(C) |
|---|---|---|---|---|---|---|---|
| 0.0007 | 190.2 | | 0.0484 | 377.7 | | 0.0968 | 441 |
| 0.0014 | 215.3 | | 0.0498 | 379.8 | | 0.0983 | 443 |
| 0.0028 | 241.4 | | 0.0513 | 381.9 | | 0.0997 | 445 |
| 0.0043 | 255.8 | | 0.0527 | 383.9 | | 0.1011 | 447 |
| 0.0057 | 266.3 | | 0.0541 | 385.9 | | 0.1025 | 449 |
| 0.0071 | 276.5 | | 0.0555 | 387.9 | | 0.1040 | 451 |
| 0.0085 | 287.3 | | 0.0570 | 389.8 | | 0.1054 | 453 |
| 0.0100 | 294 | | 0.0584 | 391.6 | | 0.1068 | 455.1 |
| 0.0114 | 299.9 | | 0.0598 | 393.5 | | 0.1082 | 457.2 |
| 0.0128 | 305.1 | | 0.0612 | 395.4 | | 0.1096 | 459.4 |
| 0.0142 | 309.6 | | 0.0627 | 397.2 | | 0.1111 | 461.6 |
| 0.0157 | 313.6 | | 0.0641 | 399 | | 0.1125 | 463.8 |
| 0.0171 | 317.4 | | 0.0655 | 400.9 | | 0.1139 | 466.1 |
| 0.0185 | 321.4 | | 0.0669 | 402.7 | | 0.1153 | 468.5 |
| 0.0199 | 325.2 | | 0.0684 | 404.4 | | 0.1168 | 471 |
| 0.0214 | 328.4 | | 0.0698 | 406.2 | | 0.1182 | 473.7 |
| 0.0228 | 331.7 | | 0.0712 | 408 | | 0.1196 | 476.4 |
| 0.0242 | 334.7 | | 0.0726 | 409.7 | | 0.1210 | 479.2 |
| 0.0256 | 337.7 | | 0.0740 | 411.5 | | 0.1225 | 482.2 |
| 0.0271 | 340.4 | | 0.0755 | 413.2 | | 0.1239 | 485.3 |
| 0.0285 | 343.1 | | 0.0769 | 415 | | 0.1253 | 488.7 |
| 0.0299 | 345.8 | | 0.0783 | 416.8 | | 0.1267 | 492.2 |
| 0.0313 | 348.4 | | 0.0797 | 418.6 | | 0.1282 | 496 |
| 0.0328 | 351.2 | | 0.0812 | 420.4 | | 0.1296 | 499.8 |
| 0.0342 | 353.8 | | 0.0826 | 422.2 | | 0.1310 | 503.9 |
| 0.0356 | 356.3 | | 0.0840 | 424 | | 0.1324 | 508.4 |
| 0.0370 | 358.9 | | 0.0854 | 425.8 | | 0.1339 | 513.4 |
| 0.0384 | 361.3 | | 0.0869 | 427.6 | | 0.1353 | 519 |
| 0.0399 | 363.8 | | 0.0883 | 429.5 | | 0.1367 | 525.4 |
| 0.0413 | 366.3 | | 0.0897 | 431.4 | | 0.1381 | 533.1 |
| 0.0427 | 368.6 | | 0.0911 | 433.3 | | 0.1396 | 542.6 |
| 0.0441 | 371 | | 0.0926 | 435.2 | | 0.1410 | 555 |
| 0.0456 | 373.3 | | 0.0940 | 437.2 | | 0.1417 | 562.8 |
| 0.0470 | 375.6 | | 0.0954 | 439.1 | | | |
| **TOTAL NITROGEN (%)** | | **0.1424** | | | | | |

# Sulphur and Nitrogen Distributions by 10$^{o}$C intervals

| | Cumul. S | Diff. S | | Cumul. N | Diff. N |
|---|---|---|---|---|---|
| Temp., oC | WT% | WT% | Temp., oC | mg/kg | mg/kg |
| 110 | | | 110 | | |
| 120 | 0.0251114 | **0.025111** | 120 | | |
| 130 | 0.0332118 | **0.008100** | 130 | | |
| 140 | 0.0749978 | **0.041786** | 140 | | |
| 150 | 0.0949441 | **0.019946** | 150 | | |
| 160 | 0.1272 | **0.032256** | 160 | | |
| 170 | 0.1858435 | **0.058644** | 170 | | |
| 180 | 0.2201954 | **0.034352** | 180 | | |
| 190 | 0.2766897 | **0.056494** | 190 | | |
| 200 | 0.3167769 | **0.040087** | 200 | 0.00099 | **0.000990** |
| 210 | 0.3651421 | **0.048365** | 210 | 0.0012737 | **0.000284** |
| 220 | 0.403648 | **0.038506** | 220 | 0.0016804 | **0.000407** |
| 230 | 0.47435 | **0.070702** | 230 | 0.002226 | **0.000546** |
| 240 | 0.5171052 | **0.042755** | 240 | 0.0027716 | **0.000546** |
| 250 | 0.620312 | **0.103207** | 250 | 0.0036984 | **0.000927** |
| 260 | 0.687675 | **0.067363** | 260 | 0.0048416 | **0.001143** |
| 270 | 0.79765 | **0.109975** | 270 | 0.0062125 | **0.001371** |
| 280 | 0.8965833 | **0.098933** | 280 | 0.0075815 | **0.001369** |
| 290 | 0.9964 | **0.099817** | 290 | 0.0091179 | **0.001536** |
| 300 | 1.0987308 | **0.102331** | 300 | 0.0114194 | **0.002302** |
| 310 | 1.1937471 | **0.095016** | 310 | 0.0143824 | **0.002963** |
| 320 | 1.3034467 | **0.109700** | 320 | 0.0180136 | **0.003631** |
| 330 | 1.4133903 | **0.109944** | 330 | 0.0220504 | **0.004037** |
| 340 | 1.548925 | **0.135535** | 340 | 0.026845 | **0.004795** |
| 350 | 1.679888 | **0.130963** | 350 | 0.0321417 | **0.005297** |
| 360 | 1.82585 | **0.145962** | 360 | 0.0376767 | **0.005535** |
| 370 | 1.9635519 | **0.137702** | 370 | 0.0435507 | **0.005874** |
| 380 | 2.0990038 | **0.135452** | 380 | 0.0499756 | **0.006425** |
| 390 | 2.226 | **0.126996** | 390 | 0.0571182 | **0.007143** |
| 400 | 2.3620333 | **0.136033** | 400 | 0.0648295 | **0.007711** |
| 410 | 2.499056 | **0.137023** | 410 | 0.0728613 | **0.008032** |
| 420 | 2.6383808 | **0.139325** | 420 | 0.0808516 | **0.007990** |
| 430 | 2.775875 | **0.137494** | 430 | 0.0886627 | **0.007811** |
| 440 | 2.9042344 | **0.128359** | 440 | 0.0960825 | **0.007420** |
| 450 | 3.0219636 | **0.117729** | 450 | 0.10324 | **0.007157** |
| 460 | 3.1323 | **0.110336** | 460 | 0.1100364 | **0.006796** |
| 470 | 3.236975 | **0.104675** | 470 | 0.1161984 | **0.006162** |
| 480 | 3.3343625 | **0.097388** | 480 | 0.1214197 | **0.005221** |
| 490 | 3.4175647 | **0.083202** | 490 | 0.1258409 | **0.004421** |
| 500 | 3.4867375 | **0.069173** | 500 | 0.1296535 | **0.003813** |
| 510 | 3.5433041 | **0.056567** | 510 | 0.1328877 | **0.003234** |
| 520 | 3.5882787 | **0.044975** | 520 | 0.1355025 | **0.002615** |
| 530 | 3.6233239 | **0.035045** | 530 | 0.1375547 | **0.002052** |
| 540 | 3.6499117 | **0.026588** | 540 | 0.1391623 | **0.001608** |
| 550 | 3.6726724 | **0.022761** | 550 | 0.1404018 | **0.001240** |
| 560 | 3.6873602 | **0.014688** | 560 | 0.1414324 | **0.001031** |
| 570 | **3.71** | **0.022640** | 570 | **0.1424** | **0.000968** |
| 580 | **3.71** | **3.710000** | 580 | **0.1424** | **0.142400** |

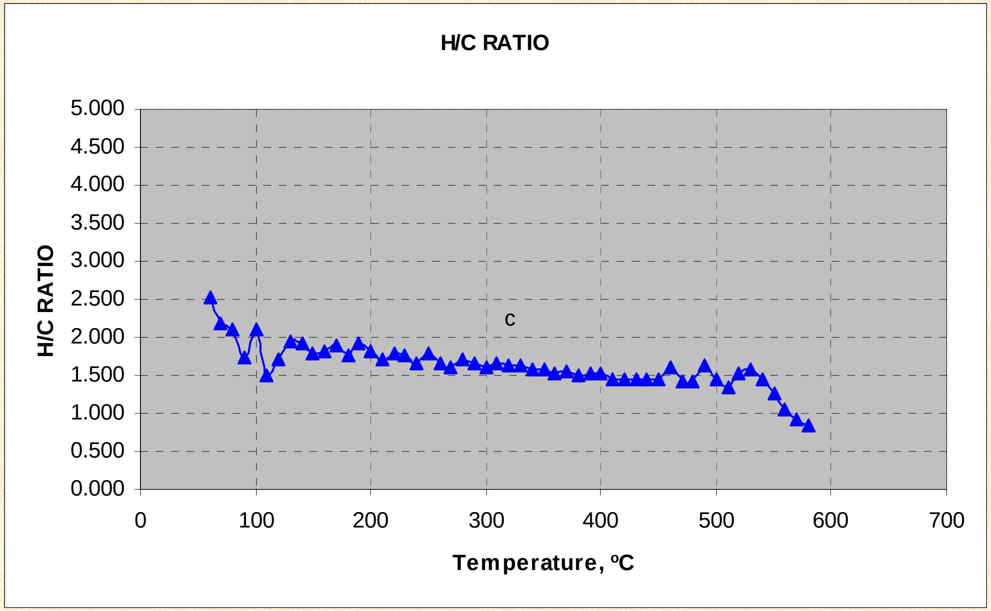
# H/C Ratio Distribution Calculated in Discrete Temperature Intervals

| Temp. °C | Calculated from AED Wt.%C | Calculated from AED Wt.%H (100-Wt.%C) | Recalcul. C-(S+N) Wt.%C | Recalcul. 100-(C+S+N) Wt.%H | Calculated wt%H/1.00797/(wt%C/12.01115) H/C Ratio |
|---|---|---|---|---|---|
| 60 | 82.57 | 17.43 | 82.57 | 17.43 | 2.516 |
| 70 | 84.44 | 15.56 | 84.44 | 15.56 | 2.196 |
| 80 | 85.03 | 14.97 | 85.03 | 14.97 | 2.098 |
| 90 | 87.26 | 12.74 | 87.26 | 12.74 | 1.739 |
| 100 | 84.93 | 15.07 | 84.93 | 15.07 | 2.115 |
| 110 | 88.78 | 11.22 | 88.78 | 11.22 | 1.506 |
| 120 | 87.40 | 12.60 | 87.38 | 12.60 | 1.718 |
| 130 | 85.89 | 14.11 | 85.89 | 14.11 | 1.957 |
| 140 | 86.10 | 13.90 | 86.06 | 13.90 | 1.925 |
| 150 | 86.89 | 13.11 | 86.87 | 13.11 | 1.799 |
| 160 | 86.74 | 13.26 | 86.71 | 13.26 | 1.823 |
| 170 | 86.33 | 13.67 | 86.28 | 13.67 | 1.888 |
| 180 | 87.06 | 12.94 | 87.02 | 12.94 | 1.772 |
| 190 | 86.10 | 13.90 | 86.05 | 13.90 | 1.924 |
| 200 | 86.75 | 13.25 | 86.70 | 13.25 | 1.822 |
| 210 | 87.38 | 12.62 | 87.33 | 12.62 | 1.722 |
| 220 | 86.93 | 13.07 | 86.89 | 13.07 | 1.792 |
| 230 | 87.08 | 12.92 | 87.01 | 12.92 | 1.769 |
| 240 | 87.79 | 12.21 | 87.75 | 12.21 | 1.657 |
| 250 | 86.95 | 13.05 | 86.84 | 13.05 | 1.791 |
| 260 | 87.83 | 12.17 | 87.77 | 12.17 | 1.652 |
| 270 | 88.20 | 11.80 | 88.09 | 11.80 | 1.596 |
| 280 | 87.54 | 12.46 | 87.44 | 12.46 | 1.698 |
| 290 | 87.85 | 12.15 | 87.75 | 12.15 | 1.649 |
| 300 | 88.10 | 11.90 | 88.00 | 11.90 | 1.611 |
| 310 | 87.82 | 12.18 | 87.72 | 12.18 | 1.655 |
| 320 | 88.01 | 11.99 | 87.89 | 11.99 | 1.626 |
| 330 | 88.05 | 11.95 | 87.93 | 11.95 | 1.620 |
| 340 | 88.26 | 11.74 | 88.12 | 11.74 | 1.588 |
| 350 | 88.27 | 11.73 | 88.13 | 11.73 | 1.586 |
| 360 | 88.59 | 11.41 | 88.44 | 11.41 | 1.537 |
| 370 | 88.55 | 11.45 | 88.40 | 11.45 | 1.544 |
| 380 | 88.84 | 11.16 | 88.70 | 11.16 | 1.499 |
| 390 | 88.74 | 11.26 | 88.60 | 11.26 | 1.515 |
| 400 | 88.71 | 11.29 | 88.56 | 11.29 | 1.520 |
| 410 | 89.24 | 10.76 | 89.10 | 10.76 | 1.438 |
| 420 | 89.18 | 10.82 | 89.03 | 10.82 | 1.448 |
| 430 | 89.20 | 10.80 | 89.05 | 10.80 | 1.445 |
| 440 | 89.22 | 10.78 | 89.08 | 10.78 | 1.442 |
| 450 | 89.22 | 10.78 | 89.09 | 10.78 | 1.442 |
| 460 | 88.22 | 11.78 | 88.10 | 11.78 | 1.594 |
| 470 | 89.42 | 10.58 | 89.30 | 10.58 | 1.412 |
| 480 | 89.27 | 10.73 | 89.17 | 10.73 | 1.434 |
| 490 | 87.93 | 12.07 | 87.84 | 12.07 | 1.637 |
| 500 | 89.12 | 10.88 | 89.04 | 10.88 | 1.456 |
| 510 | 89.93 | 10.07 | 89.87 | 10.07 | 1.335 |
| 520 | 88.64 | 11.36 | 88.59 | 11.36 | 1.529 |
| 530 | 88.32 | 11.68 | 88.28 | 11.68 | 1.577 |
| 540 | 89.10 | 10.90 | 89.07 | 10.90 | 1.459 |
| 550 | 90.50 | 9.50 | 90.48 | 9.50 | 1.251 |
| 560 | 91.86 | 8.14 | 91.84 | 8.14 | 1.056 |
| 570 | 92.91 | 7.09 | 92.89 | 7.09 | 0.909 |
| 580 | 93.39 | 6.61 | 93.39 | 6.61 | 0.843 |

# Comparison of GC-AED and Lab Results

| Analytical method | Calculation method | Wt.%C | Wt.%H |
|---|---|---|---|
| AED | by integrating total area of the chromatogram | 88.1 | 11.9 |
| AED | by summing up 10°C slices of the chromatogram | 88.2 | 11.8 |
| AED | renormalized for presence of Sand N | 84.4 | 11.2 |
| LAB | ASTM methods | 84.4 | 11.2 |

# H/C Ratio Distribution



# Applications

**Bitumens have high viscosities and densities. They are mixed with diluents to meet the specifications for pipeline transportation. Due to the large projected increase in bitumen production, diluent shortages are forecast.**

## Visbreaking

**Visbreaking is one of the cost-effective ways to reduce the viscosities of the heavy oils and bitumens. It is a low severity thermal cracking process (<500$^{o}$C) by which large oil molecules are converted into lower boiling material, therefore lowering viscosity, with minimum coke formation.**

## Coking

**Coking is a process for the thermal breaking of bonds in heavy oils and bitumens under more severe conditions, which result in the formation of a complete range of products, from solids to gases.**

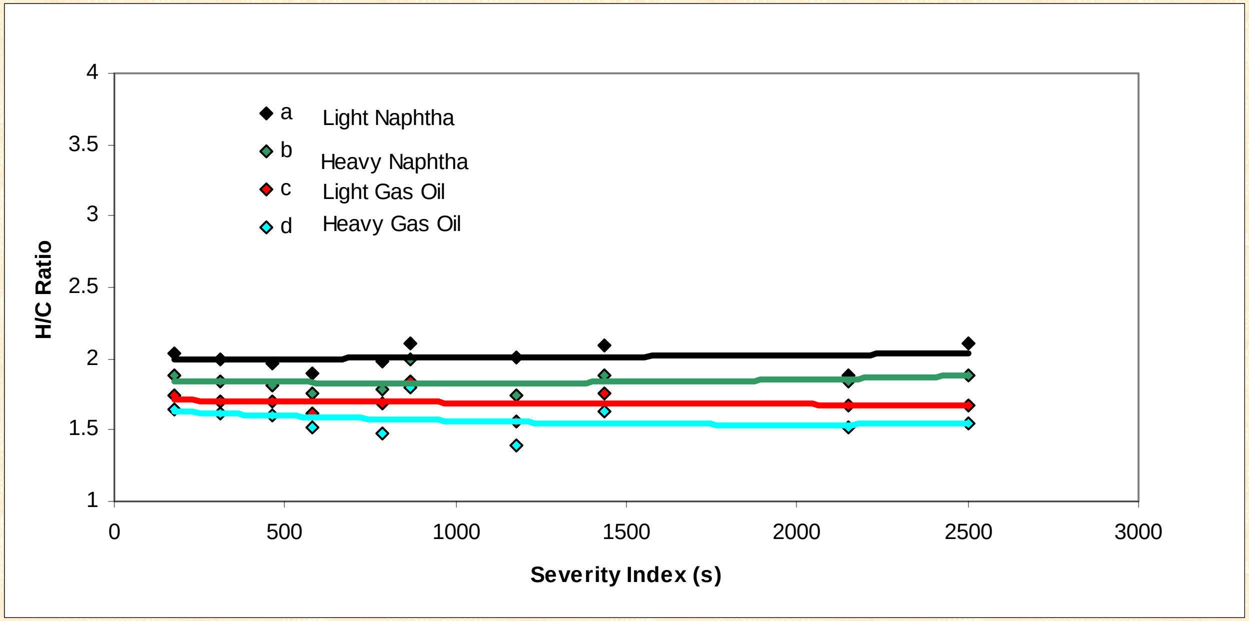
## Objectives

**To study the change in bitumen characteristics during visbreaking and coking using the H/C Ratio data obtained from the GC-AED analysis of TLPs, and compare these data with the hydrocarbon type composition analysis.**

# H/C Ratio VS Severity Index Calculated for Pseudo-components of TLP from Visbreaking and Coking of Athabasca Bitumen

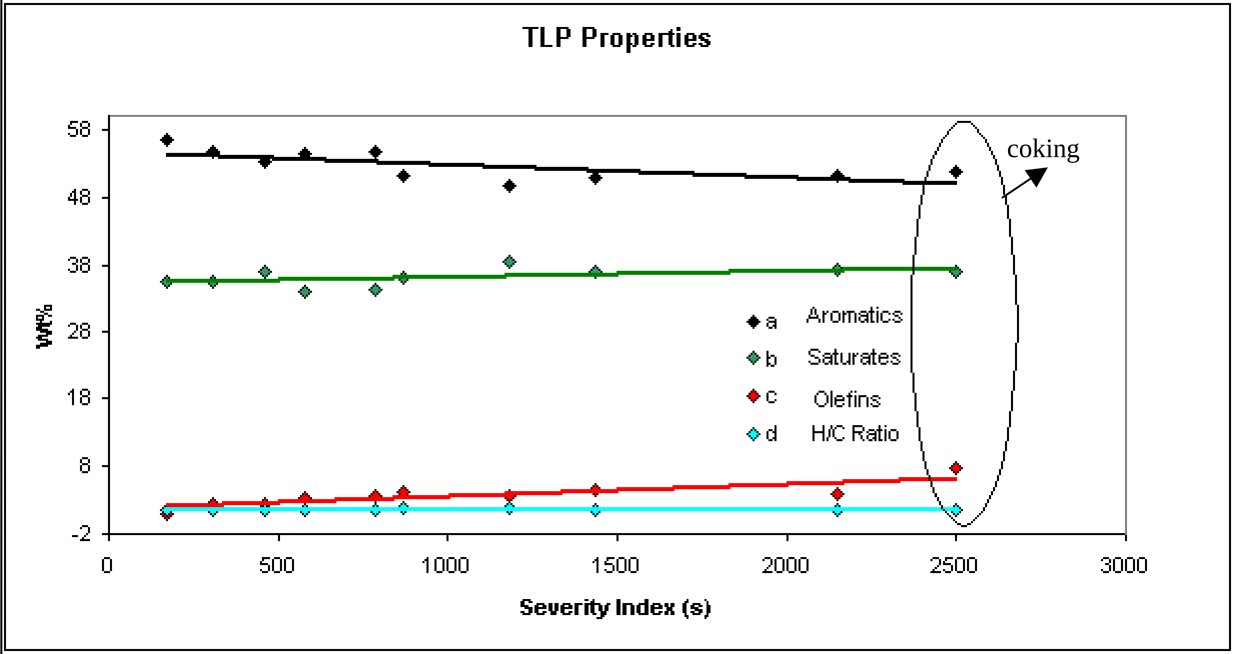
| | Process | Severity Index | Light Naphtha | Heavy Naphtha | Light Gas Oil | Heavy Gas Oil | Flow | Temp. |
|---|---|---|---|---|---|---|---|---|
| | | | IBP-120 | 120-220 | 220-340 | 340-FBP | Kg/h | °C |
| Run1 | visbreaking | 174.2 | 2.042 | 1.879 | 1.740 | 1.647 | 2 | 390 |
| Run2 | visbreaking | 308.7 | 1.989 | 1.841 | 1.701 | 1.618 | 3 | 405 |
| Run3 | visbreaking | 463 | 1.974 | 1.819 | 1.697 | 1.608 | 2 | 405 |
| Run4 | visbreaking | 578.4 | 1.902 | 1.752 | 1.616 | 1.522 | 3 | 415 |
| Run5 | visbreaking | 786.3 | 1.979 | 1.779 | 1.683 | 1.475 | 3 | 420 |
| Run6 | visbreaking | 867.5 | 2.111 | 1.995 | 1.836 | 1.804 | 2 | 415 |
| Run7 | visbreaking | 1179.5 | 2.005 | 1.748 | 1.565 | 1.399 | 2 | 420 |
| Run8 | visbreaking | 1434.6 | 2.092 | 1.887 | 1.761 | 1.636 | 3 | 430 |
| Run9 | visbreaking | 2151.9 | 1.886 | 1.838 | 1.670 | 1.519 | 2 | 430 |
| Run1 | coking | >10000 | 2.114 | 1.890 | 1.676 | 1.553 | - | - |

# H/C Ratio VS Severity Index Calculated for Pseudo-components of TLP from Visbreaking and Coking of Athabasca Bitumen



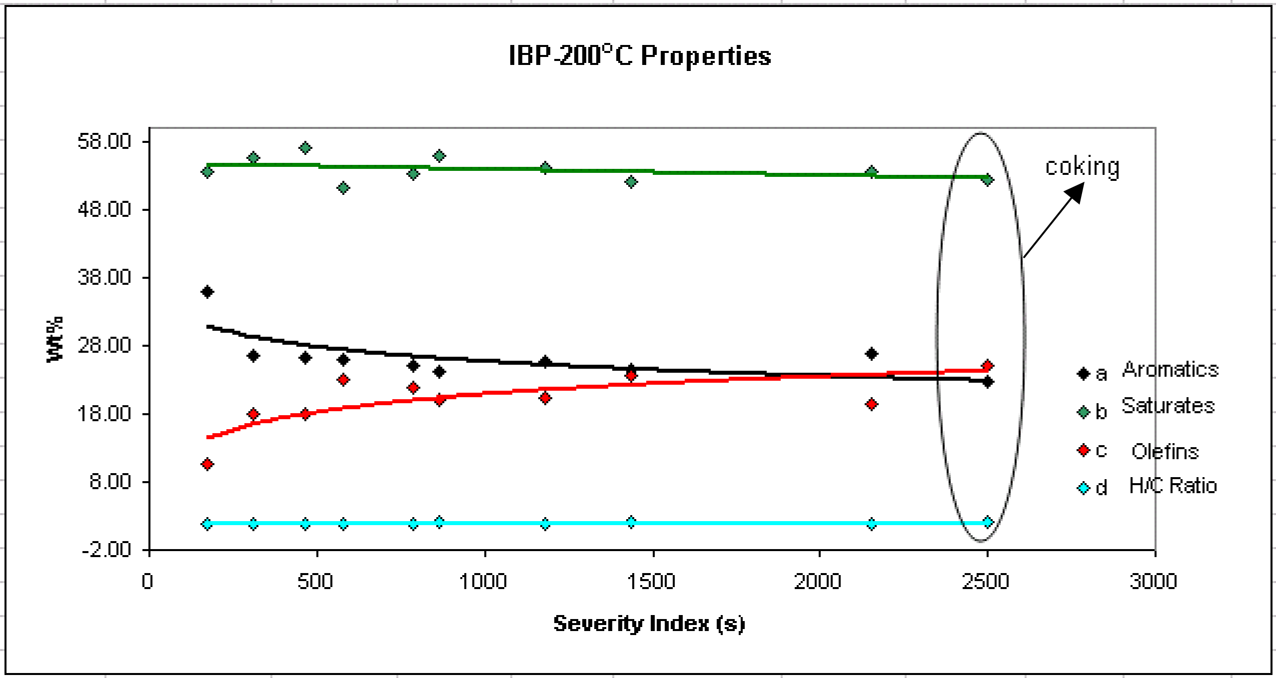
# Properties of TLP

| | Process | Severity Index | Aromatics | Saturates | Olefins | Polars | H/C |
|---|---|---|---|---|---|---|---|
| Run1 | visbreaking | 174.2 | 56.47 | 35.57 | 1.06 | 6.91 | 1.641 |
| Run2 | visbreaking | 308.7 | 54.66 | 35.41 | 2.46 | 7.48 | 1.656 |
| Run3 | visbreaking | 463.0 | 53.20 | 36.92 | 2.53 | 7.34 | 1.619 |
| Run4 | visbreaking | 578.4 | 54.52 | 33.97 | 3.28 | 8.23 | 1.582 |
| Run5 | visbreaking | 786.3 | 54.71 | 34.32 | 3.58 | 7.40 | 1.605 |
| Run6 | visbreaking | 867.5 | 51.27 | 36.14 | 4.06 | 8.52 | 1.724 |
| Run7 | visbreaking | 1179.5 | 49.59 | 38.34 | 3.68 | 8.39 | 1.776 |
| Run8 | visbreaking | 1434.6 | 50.83 | 36.92 | 4.50 | 7.75 | 1.621 |
| Run9 | visbreaking | 2151.9 | 51.26 | 37.19 | 3.90 | 7.65 | 1.587 |
| Run1 | coking | >10000 | 51.75 | 36.97 | 7.60 | 3.68 | 1.657 |



# Properties of Naphtha

| | | Wt.% of Total | | | | Weighted by SimDist | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Process | Severity Index | Aromatics | Saturates | Olefins | SimDist Yield | Aromatics | Saturates | Olefins | Sum | H/C |
| visbreaking | 174.2 | 1.76 | 2.62 | 0.52 | 4.89 | 35.99 | 53.58 | 10.63 | 100.00 | 1.938 |
| visbreaking | 308.7 | 1.69 | 3.53 | 1.14 | 6.35 | 26.61 | 55.59 | 17.95 | 100.00 | 1.908 |
| visbreaking | 463 | 2.15 | 4.69 | 1.47 | 8.22 | 26.16 | 57.06 | 17.88 | 100.00 | 1.894 |
| visbreaking | 578.4 | 2.23 | 4.38 | 1.97 | 8.58 | 25.99 | 51.05 | 22.96 | 100.00 | 1.819 |
| visbreaking | 786.3 | 2.34 | 4.99 | 2.03 | 9.35 | 25.03 | 53.37 | 21.71 | 100.00 | 1.743 |
| visbreaking | 867.5 | 2.92 | 6.76 | 2.42 | 12.11 | 24.11 | 55.82 | 19.98 | 100.00 | 2.054 |
| visbreaking | 1179.5 | 2.79 | 5.85 | 2.19 | 10.83 | 25.76 | 54.02 | 20.22 | 100.00 | 1.855 |
| visbreaking | 1434.6 | 3.06 | 6.52 | 2.93 | 12.51 | 24.46 | 52.12 | 23.42 | 100.00 | 1.981 |
| visbreaking | 2151.9 | 3.17 | 6.31 | 2.29 | 11.77 | 26.93 | 53.61 | 19.46 | 100.00 | 1.873 |
| coking | >10000 | 4.63 | 10.71 | 5.13 | 20.47 | 22.62 | 52.32 | 25.06 | 100.00 | 2.002 |



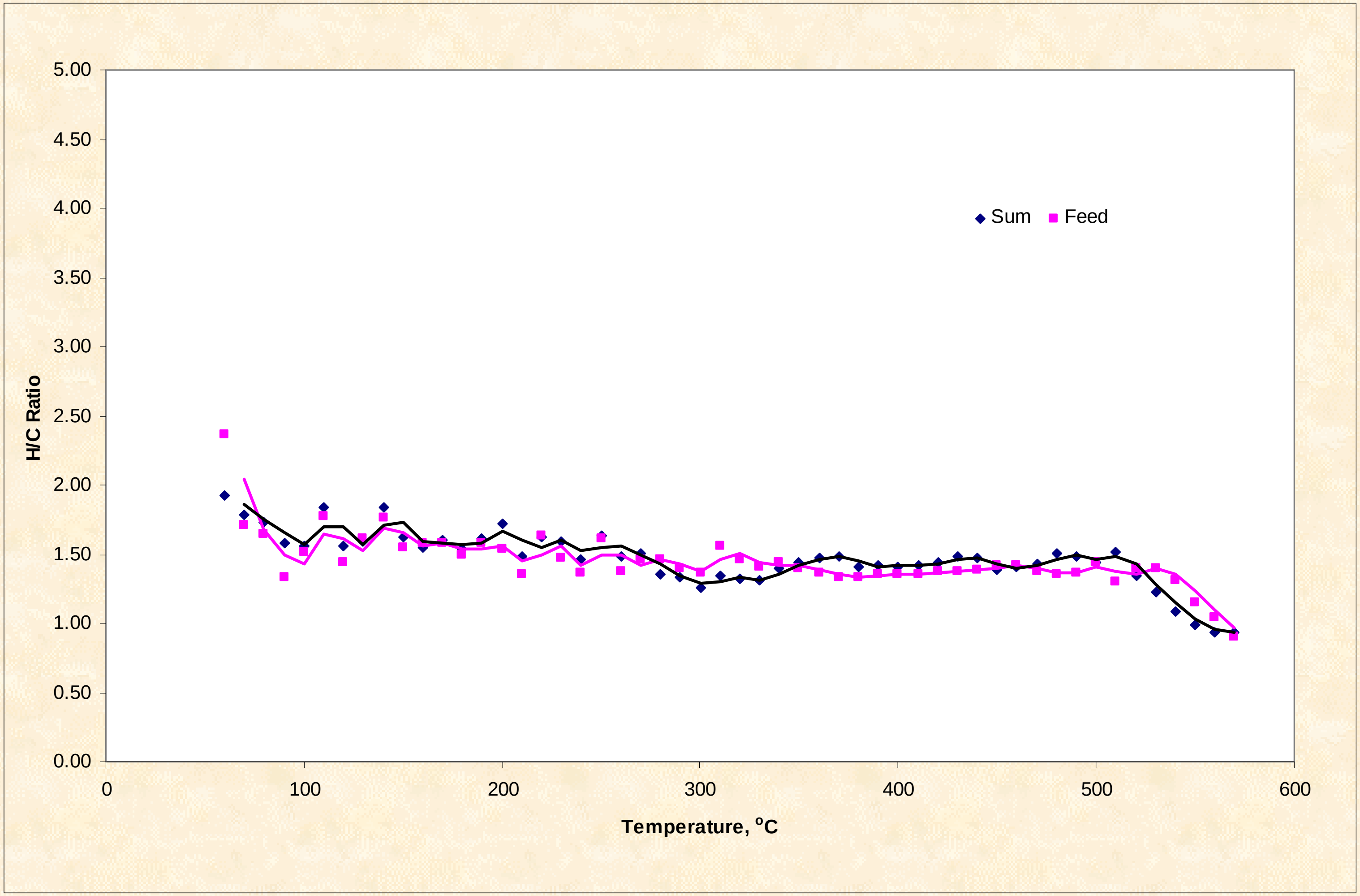
# Analysis of Total Feed and Its Distillation Fractions

| | IBP | FBP | SimDist Yield |
|---|---|---|---|
| | °C | °C | Wt.% |
| **Feed** | 56.7 | 560.4 | 100.00 |
| **Fraction1** | 36.0 | 287.1 | 20.70 |
| **Fraction2** | 166.9 | 371.0 | 40.10 |
| **Fraction3** | 276.0 | 567.3 | 39.20 |

# H/C Ratio for Total Feed and Distillation Fractions

| | Carbon | | | | | | Hydrogen | | | | | H/C Ratio | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temp., °C | Total Feed | Fraction1 | Fraction2 | Fraction3 | Sum of fractions | | Total Feed | Fraction1 | Fraction2 | Fraction3 | Sum of fractions | Sum of fractions | Total Feed |
| 60 | 83.43% | 86.07% | | | 86.07% | | 16.57% | 13.93% | | | 13.93% | 1.928 | 2.366 |
| 70 | 87.43% | 86.97% | | | 86.97% | | 12.57% | 13.03% | | | 13.03% | 1.785 | 1.713 |
| 80 | 87.89% | 87.32% | | | 87.32% | | 12.11% | 12.68% | | | 12.68% | 1.731 | 1.642 |
| 90 | 89.90% | 88.31% | | | 88.31% | | 10.10% | 11.69% | | | 11.69% | 1.577 | 1.339 |
| 100 | 88.74% | 88.42% | | | 88.42% | | 11.26% | 11.58% | | | 11.58% | 1.560 | 1.512 |
| 110 | 87.01% | 86.66% | | | 86.66% | | 12.99% | 13.34% | | | 13.34% | 1.835 | 1.779 |
| 120 | 89.18% | 88.45% | | | 88.45% | | 10.82% | 11.55% | | | 11.55% | 1.557 | 1.446 |
| 130 | 88.10% | 88.23% | | | 88.23% | | 11.90% | 11.77% | | | 11.77% | 1.590 | 1.610 |
| 140 | 87.13% | 86.65% | | | 86.65% | | 12.87% | 13.35% | | | 13.35% | 1.836 | 1.761 |
| 150 | 88.50% | 87.99% | | | 87.99% | | 11.50% | 12.01% | | | 12.01% | 1.627 | 1.549 |
| 160 | 88.32% | 88.48% | | | 88.48% | | 11.68% | 11.52% | | | 11.52% | 1.552 | 1.576 |
| 170 | 88.26% | 86.93% | 88.77% | | 88.14% | | 11.74% | 13.07% | 11.23% | | 11.86% | 1.603 | 1.584 |
| 180 | 88.88% | 87.92% | 88.90% | | 88.57% | | 11.12% | 12.08% | 11.10% | | 11.43% | 1.538 | 1.491 |
| 190 | 88.25% | 87.52% | 88.36% | | 88.07% | | 11.75% | 12.48% | 11.64% | | 11.93% | 1.614 | 1.586 |
| 200 | 88.56% | 87.16% | 87.52% | | 87.39% | | 11.44% | 12.84% | 12.48% | | 12.61% | 1.719 | 1.539 |
| 210 | 89.79% | 87.52% | 89.62% | | 88.90% | | 10.21% | 12.48% | 10.38% | | 11.10% | 1.487 | 1.354 |
| 220 | 87.92% | 88.16% | 87.98% | | 88.04% | | 12.08% | 11.84% | 12.02% | | 11.96% | 1.619 | 1.637 |
| 230 | 88.99% | 88.50% | 88.11% | | 88.24% | | 11.01% | 11.50% | 11.89% | | 11.76% | 1.588 | 1.474 |
| 240 | 89.73% | 88.26% | 89.47% | | 89.05% | | 10.27% | 11.74% | 10.53% | | 10.95% | 1.465 | 1.364 |
| 250 | 88.07% | 88.40% | 87.74% | | 87.96% | | 11.93% | 11.60% | 12.26% | | 12.04% | 1.631 | 1.614 |
| 260 | 89.66% | 88.31% | 89.25% | | 88.93% | | 10.34% | 11.69% | 10.75% | | 11.07% | 1.484 | 1.375 |
| 270 | 89.07% | 88.72% | 88.83% | | 88.79% | | 10.93% | 11.28% | 11.17% | | 11.21% | 1.504 | 1.463 |
| 280 | 89.07% | 88.74% | 88.84% | 91.25% | 89.76% | | 10.93% | 11.26% | 11.16% | 8.75% | 10.24% | 1.359 | 1.462 |
| 290 | 89.50% | 89.16% | 88.98% | 91.32% | 89.93% | | 10.50% | 10.84% | 11.02% | 8.68% | 10.07% | 1.334 | 1.399 |
| | | | | | | | | | | | | | |
| 530 | 89.54% | | | 90.71% | 90.71% | | 10.46% | | | 9.29% | 9.29% | 1.221 | 1.393 |
| 540 | 90.09% | | | 91.65% | 91.65% | | 9.91% | | | 8.35% | 8.35% | 1.086 | 1.310 |
| 550 | 91.17% | | | 92.35% | 92.35% | | 8.83% | | | 7.65% | 7.65% | 0.988 | 1.154 |
| 560 | 91.97% | | | 92.72% | 92.72% | | 8.03% | | | 7.28% | 7.28% | 0.936 | 1.040 |
| 570 | 92.94% | | | 92.74% | 92.74% | | 7.06% | | | 7.26% | 7.26% | 0.932 | 0.906 |

# H/C Ratio for Total Feed and Distillation Fractions



# Hydrocarbon Type Distribution by Boiling Point - IBP-FBP

| Start BP Deg. C | | | IBP | | 200 | 210 | 220 | 230 | 240 | 250 | - | 510 | 520 | 530 | **Sum** | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| End BP Deg. C | | | 200 | | 210 | 220 | 230 | 240 | 250 | 260 | - | 520 | 530 | 540 | | |
| Weight Percent | | **SimDist** | | **SimDist** | 0.554 | 0.708 | 0.799 | 0.968 | 1.077 | 1.997 | | 1.073 | 0.912 | 0.552 | | |
| **Hydrocarbon Types** | **Z** | **PIONA** | | **GC-MS** | | | | | | | | | | | | |
| **Saturates** | | **PIONA** | **2.020** | **SPE/FID** | **0.362** | **0.478** | **0.520** | **0.662** | **0.722** | **0.926** | | **0.252** | **0.200** | **0.061** | **31.141** | **33.161** |
| **Total Paraffins** | | **PIONA** | **1.400** | **ASTM2786** | **0.098** | **0.157** | **0.080** | **0.140** | **0.096** | **0.147** | | **0.032** | **0.024** | **0.007** | **4.500** | 5.900 |
| iso-Paraffins | **2** | **PIONA** | 0.690 | - | | | | | | | | | | | | |
| n-Paraffins | **2** | **PIONA** | 0.710 | - | | | | | | | | | | | | |
| **Cycloparaffins** | | **PIONA** | **0.620** | **ASTM2786** | **0.265** | **0.321** | **0.440** | **0.522** | **0.626** | **0.951** | | **0.220** | **0.176** | **0.053** | **26.641** | 27.261 |
| **Olefins** | **0** | **PIONA** | **1.050** | **SPE/FID** | **0.129** | **0.215** | **0.204** | **0.279** | **0.236** | **0.311** | | **0.129** | **0.107** | **0.086** | **10.700** | **11.750** |
| Monocycloparaffins | **0** | | | **ASTM2786** | 0.081 | 0.072 | 0.089 | 0.093 | 0.106 | 0.187 | | 0.035 | 0.026 | 0.008 | 5.770 | |
| Dicycloparaffins | **-2** | | | **ASTM2786** | 0.179 | 0.220 | 0.298 | 0.324 | 0.359 | 0.368 | | 0.069 | 0.050 | 0.014 | 8.971 | |
| Tricycloparaffins + | **-4** | | | **ASTM2786** | 0.005 | 0.029 | 0.053 | 0.105 | 0.162 | 0.395 | | 0.116 | 0.100 | 0.031 | 11.900 | |
| **Aromatics** | | **PIONA** | **1.530** | **SPE/FID** | **0.191** | **0.230** | **0.279** | **0.306** | **0.355** | **0.576** | | **0.821** | **0.712** | **0.491** | **45.959** | **47.489** |
| **Monoaromatics** | | | | **ASTM3239** | **0.191** | **0.221** | **0.257** | **0.240** | **0.286** | **0.358** | | **0.205** | **0.153** | **0.081** | **15.753** | |
| Alkylbenzenes | **-6** | | | **ASTM3239** | 0.149 | 0.127 | 0.126 | 0.080 | 0.084 | 0.090 | | 0.108 | 0.118 | 0.078 | 4.395 | |
| Benzocycloalkanes | **-8** | | | **ASTM3239** | 0.034 | 0.078 | 0.095 | 0.101 | 0.135 | 0.158 | | 0.041 | 0.012 | 0.000 | 5.092 | |
| Benzodicycloalkanes | **-10** | | | **ASTM3239** | 0.007 | 0.016 | 0.036 | 0.059 | 0.068 | 0.109 | | 0.057 | 0.023 | 0.004 | 6.265 | |
| **Diaromatics** | | | | **ASTM3239** | **0.000** | **0.009** | **0.022** | **0.036** | **0.041** | **0.092** | | **0.343** | **0.494** | **0.285** | **12.083** | |
| Naphthalenes | **-12** | | | **ASTM3239** | 0.000 | 0.009 | 0.013 | 0.032 | 0.033 | 0.081 | | 0.051 | 0.144 | 0.017 | 3.410 | |
| Naphthocycloalkanes | **-14** | | | **ASTM3239** | 0.000 | 0.000 | 0.009 | 0.003 | 0.003 | 0.004 | | 0.038 | 0.027 | 0.016 | 3.437 | |
| Fluorenes | **-16** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.001 | 0.005 | 0.007 | | 0.254 | 0.322 | 0.252 | 5.235 | |
| **Triaromatics** | | | | **ASTM3239** | **0.000** | **0.000** | **0.000** | **0.000** | **0.000** | **0.000** | | **0.000** | **0.000** | **0.000** | **4.001** | |
| Phenanthrenes | **-18** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.000 | 0.000 | 0.000 | 2.314 | |
| Phenanthrocycloalkanes | **-20** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.000 | 0.000 | 0.000 | 1.687 | |
| **Tetraaromatics** | | | | **ASTM3239** | **0.000** | **0.000** | **0.000** | **0.000** | **0.000** | **0.000** | | **0.011** | **0.000** | **0.000** | **2.888** | |
| Pyrenes/Benzofluorenes | **-22** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.011 | 0.000 | 0.000 | 2.041 | |
| Chrysenes | **-24** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.000 | 0.000 | 0.000 | 0.847 | |
| **Pentaaromatics** | | | | **ASTM3239** | **0.000** | **0.000** | **0.000** | **0.000** | **0.000** | **0.000** | | **0.002** | **0.000** | **0.000** | **1.223** | |
| Benzpyrenes/Perylenes | **-28** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.002 | 0.000 | 0.000 | 1.130 | |
| Dibenzanthracenes | **-30** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.000 | 0.000 | 0.000 | 0.094 | |
| **Unidentified** | | | | **ASTM3239** | **0.001** | **0.000** | **0.000** | **0.000** | **0.000** | **0.000** | | **0.118** | **0.001** | **0.092** | **1.729** | |
| CnH2n-32/CnH2n-46 | **-32** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.001 | 0.001 | 0.000 | 0.210 | |
| CnH2n-36/CnH2n-26S | **-36** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.000 | 0.000 | 0.000 | 0.042 | |
| CnH2n-38/CnH2n-28S | **-38** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.117 | 0.000 | 0.092 | 1.426 | |
| CnH2n-40/CnH2n-30S | **-40** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.000 | 0.000 | 0.000 | 0.015 | |
| CnH2n-42/CnH2n-32S | **-42** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.000 | 0.000 | 0.000 | 0.002 | |
| CnH2n-44/CnH2n-34S | **-44** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.000 | 0.000 | 0.000 | 0.034 | |
| **Aromatic Sulfur** | | | | **ASTM3239** | **0.000** | **0.000** | **0.000** | **0.030** | **0.028** | **0.126** | | **0.142** | **0.065** | **0.033** | **8.283** | |
| Benzothiophenes | **-10S** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.030 | 0.028 | 0.126 | | 0.094 | 0.065 | 0.032 | 4.849 | |
| Dibenzothiophenes | **-16S** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.049 | 0.000 | 0.001 | 2.775 | |
| Benzonaphthiophenes | **-22S** | | | **ASTM3239** | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | | 0.000 | 0.000 | 0.000 | 0.659 | |
| **Polars** | | | | **SPE/FID** | | | | | | | | | | | | **7.400** |
| **Asphaltenes** | | | | **SE** | | | | | | | | | | | | **0.200** |
| **Total** | | | | | | | | | | | | | | | | **100.000** |

# Comparison of Detailed Hydrocarbon Type Analysis and H/C Ratio Analysis

**Hydrocarbon type analysis**

- PIONA analysis for IBP-200°C fraction
- Class-type separation into saturates, aromatics, olefins and polars using SPE (solid phase extraction) chromatography
- Analysis of SPE fractions by GC-FID to calculate the mass balance and simulated distillation of the fractions (200°C-FBP)
- Analysis of saturate, aromatic fractions, and the retention time callibrant by the GC-MS
- Calculation of the by-boiling-point distribution of hydrocarbon types
- Analysis of TLP by the GC-AED for S181, or by the GC-SCD (both require separate injections for the retention time callibrant)
- Analysis of TLP by the GC-NCD (require separate injections for the retention time callibrant)

**H/C ratio analysis**

- Analysis of total TLP by the GC-AED for C496 and H486 (single injection)
- Analysis of the retention time callibrant by the GC-AED for C496
- Analysis of TLP by the GC-AED for S181, or by the GC-SCD (both require separate injections for the retention time callibrant)
- Analysis of TLP by the GC-NCD (require separate injections for the retention time callibrant)
- Calculation of the by-boiling point distribution of H/C Ratio

# Conclusions

**The H/C Ratio by GC-AED is a relatively inexpensive technique for the analysis of various petroleum liquids in a distillable boiling range.**

**The results obtained by the GC-AED, if renormalized for the presence of other elements, are comparable with the lab results for C and H.**

**The by-boiling-point distribution of H/C Ratio by GC-AED shows the potential for the application of this type of analysis for characterization of distillation fractions of a petroleum sample without the need for physical distillation. H/C ratios for distillation fractions were calculated from the distribution generated for the corresponding full-range sample and compared with measured values. The comparison was satisfactory.**

**The H/C ratio analysis by GC-AED represents an alternative technique to detailed hydrocarbon analysis of fractions from physical distillation.**

# Acknowledgement

NCUT would like to thank Bruce D. Quimby from Agilent Technologies for assistance provided during method development and for supplying a complimentary software package for hydrogen linearization.

NCUT would like to thank Dr. Terry Ramus from Diablo Analytical for guidance and assistance in the development of GC-AED methods.