Note Title 9/22/2016

# COMPOSITIONS OF PETROLEUM FLUIDS

- Compounds / Component :

  • Heptanes & heavier $C_{7+}$

  (Ch. 5)

± ↓

- Amounts (mass | molar | volumetric) ±

  ⊙ Molar Distribution Model (Gamma | Exponential)

  v ± Acentric Factor

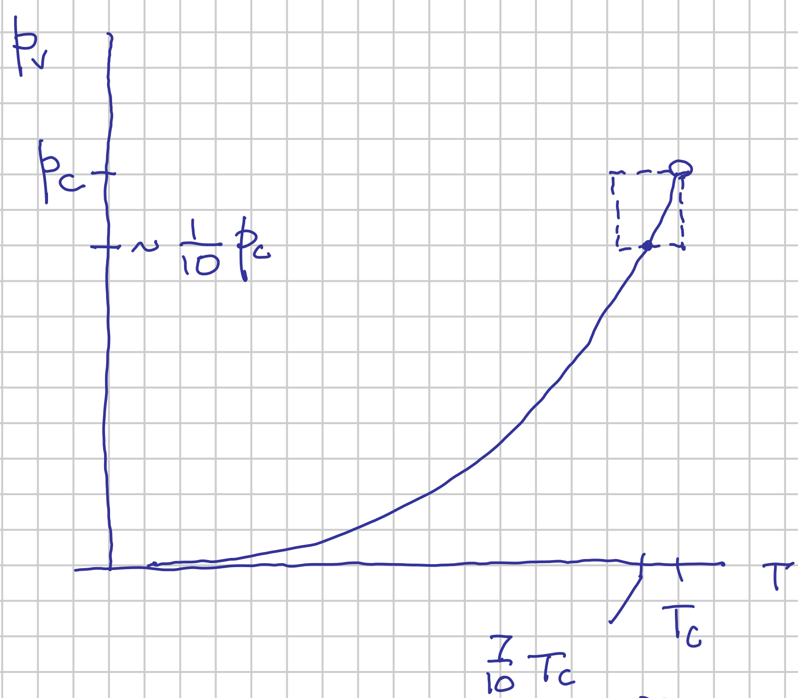
- Properties $(\underbrace{\bar{M},\ \bar{\gamma},\ \bar{T}_b}\ ;\ \underbrace{\bar{T}_c,\ \bar{P}_c,\ \bar{\omega},\ \bar{s}}_{\text{EOS}})$

$ ± > TBP data | Crude Assay ($T_b - \gamma$)

($M - \gamma - T_b$) data

↓

Custom Correlations




Pitzer:

30% below $T_c$

$\omega = 0$ for "spherical" compounds $\quad p_v = \frac{1}{10} P_c \ (0.7 T_c)$

$\quad = 1 \quad p_v = \frac{1}{100} P_c \ (0.7 T_c)$

$= 2$

$$p_v = \frac{1}{1000} p_c (0.7 T_c)$$

$$\omega = -1 - \log_{10} \left( \frac{p_v (0.7 T_c)}{p_c} \right)$$

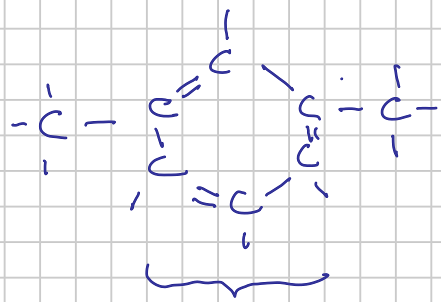
Compositions : $C_{7+}$

- Compounds

Paraffinics (Alkanes) P

Napthenes N

Aromatics A



Benzene Ring

1 atm

20°C

$\rho_{n-C_6}$ vs $\rho_{benzene}$

$660 \frac{kg}{m^3}$ $876 \frac{kg}{m^3}$

Normal Boiling Point

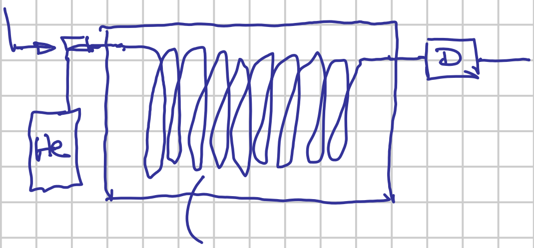
@ 1 atm

| | |
|---|---|
| $T_b$ n-$C_6$ | 69°C |
| Bz | 80 °C |
| $T_b$ n-$C_7$ | 98 °C |

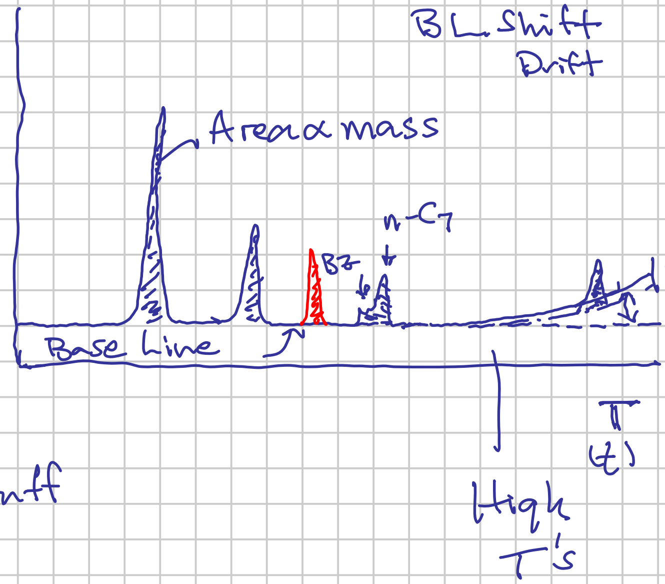
All compounds boiling in between n-$C_6$ n-$C_7$ are call SCN $C_7$

Add a sample @ $T_{sc}$

$C_1 + C_2$
+
$n-C_{30}$
+
$SCN\ C_7$ (TBP)
+
$C_{30+}$ (TBP Residue)




Column
Packed
porous permeable stuff




$$w_{C_1} = \frac{m_{C_1}}{m_{sample}} = \frac{A_{C_1}}{A_t}$$

| Comp | $A_i$ | $w_i$ |
|---|---|---|
| $C_1$ | $A_{C_1}$ ✓ | $A_{C_1}/A_t$ ✓ |
| $C_2$ | ✓ | ✓ |
| $C_7$ | ✓ | ✓ |
| $n-C_{30}$ | ✓ | ✓ |
| Residue | $\boxed{?}$ | $\boxed{=1-\sum w_i}$ |
| Internal Standard | ✓ | $0.1/(0.9+0.1)$ |

$$w_{IS} = \frac{m_{IS}}{m_t} = \frac{A_{IS}}{A_t} = 0.1 \Rightarrow A_t = \frac{A_{IS}}{0.1}$$

?

Summary of Compositional Analysis of Petroleum Fluids:

① Pressurized Liquid up to
Pressurized Gas $p \gtrsim 100$ bar } (a) Can NOT inject directly into the GC

Ambient oils ($p_b \sim 1$ atm)
Lower-p gases ($p \lesssim 100$ bar) } (b) Inj directly to the GC

(a) Flash Sample to 1 atm (any $T_{ambient}$)

Flash Gas $\longrightarrow$ GC $\quad w_{\bar{g}i} \quad y_i$ ✓ $\quad V_{\bar{g}} \quad n_{\bar{g}}$

Flash Oil $\longrightarrow$ GC $\quad w_{\bar{o}i} \quad \left(\begin{matrix}\text{I.S.}\\ \text{BLS}\end{matrix}\right) \quad V_{\bar{o}} \quad m_{\bar{o}} \quad M_{\bar{o}}$

$\bar{g}$ = gas @ $p_{sc}, T_{sc}$

$\bar{o}$ = oil @ $p_{sc}, T_{sc}$

$w_i$ weight frac.

$y_i$ gas mol frac

$x_i$ oil mol frac

$z_i$ total mol frac

Helps estimate "reasonable" $M_i$ $C_{7+}$ fractions

$$\underset{\text{measured}}{(M_{\bar{o}})} = \frac{w_{\bar{o}i}/M_i}{\sum w_{oj}/M_j}$$

j ~ mostly $C_{7+}$

(b) Math. Recombine

Sample

$$w_i = (m_{\bar{g}} \cdot w_{\bar{g}i} + m_{\bar{o}} \, w_{\bar{o}i}) / (m_{\bar{g}} + m_{\bar{o}})$$

$\downarrow$

$M_i$ (?)

$z_i$

EOS ($z_i$)

$$z_i = \frac{w_i / M_i}{\sum_{j=1}^{N} w_j / M_j}$$

Est. $M_j$ $C_{10}$ $C_{11}$ . . . . ? ±

① Most labs use Katz-Firoozabadi table (1978)

Table 5.2 SCN $M_i$ $i \in C_6$ $C_{45}$

$\gamma_i$

$T_b$

But beware your fluid may not be well represented by KF table!

$M_{N+}$ < Back-calculate from $w_{\bar{o}i}$ $M_{\bar{o}}$ $M_{i\,KF}^{est}$

Mystery (SLB) | CL*

"N" end of the GC analysis (7 , 10|12, 20-21, 30-36

→1980 1980s 90's >2000

$$* \quad v_{Li} = \frac{M_i}{\rho_i} = a_o + a_1 M_i$$

$$\text{measured } M_{\bar{o}} = \frac{\sum w_{\bar{o}i}}{\sum w_{\bar{o}i}/M_i} = \frac{1}{\sum}$$

$$\text{measured } \gamma_{\bar{o}} = \frac{\sum w_{\bar{o}i}}{\sum \frac{w_{\bar{o}i}}{\gamma_i}} = \frac{1}{\sum}$$

<u>Molar Distribution Model</u> : $z_i(M_i) \Leftrightarrow w_i(M_i)$

Alani-Kennedy : $\ln z_i = a M_i + b M_i^2 + c$

1980 Gamma Probability Dist. Model (continuous PDF)

81? Exponential Discrete (SCN) Model [PVTsim]

$$z_i = z_{c_n} \cdot \exp\left[A(i-n)\right]$$

$$M_i = 14 \cdot i + \boxed{h}$$

$h = +2$ P

$h = 0$ N

$h = -6$ A

PVTsim : $\underbrace{h = -4}$

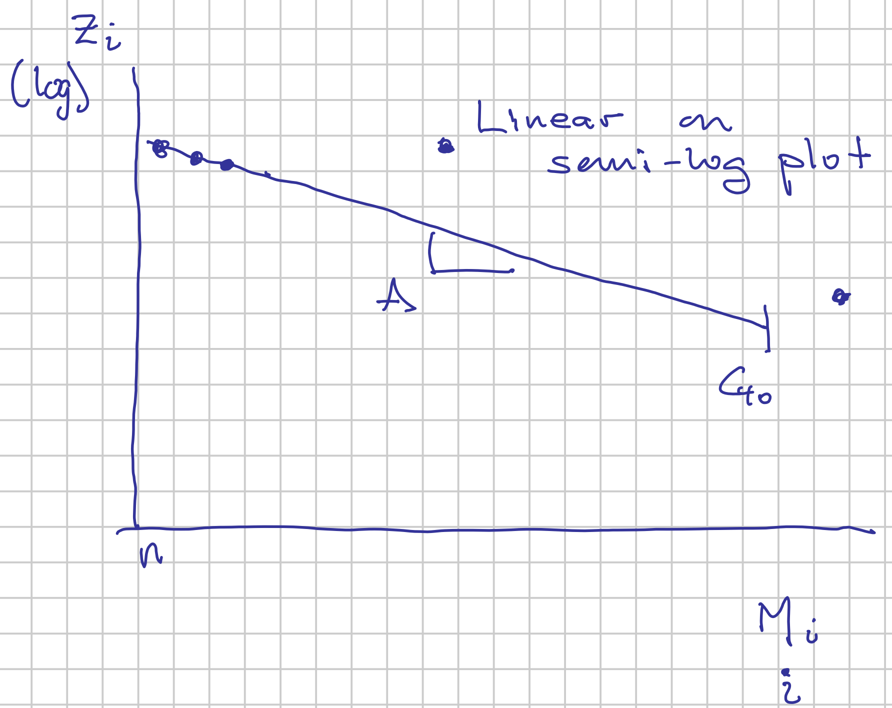
$A(M_{n+})$

Ch. 5 $\boxed{\hat{z}_i \equiv \frac{z_i}{z_{n+}}}$

$\hat{z}_n(M_{n+}) = \boxed{0.1}$ 10% $C_{n+}$ is $C_n$

$$\hat{Z}_n = \frac{\hat{Z}_{i+1} - \hat{Z}_i}{\hat{Z}_i} \qquad i \ge n$$

| $i$ | $\hat{Z}$ |
|---|---|
| $7 = n$ | 10% |
| 8 | 9% |
| 9 | 8.1% |




Gamma Distribution Model

All PDM's : $p(x)$

Lower Bound $\eta$

BOUND

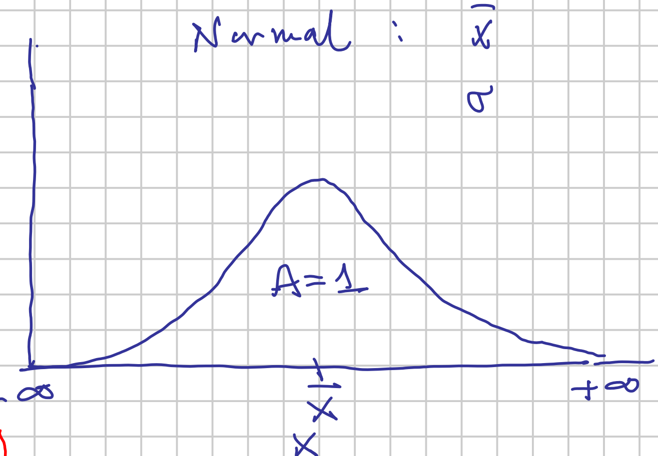
Shape $\alpha$ (SHAPE)

$\alpha = 1$ : Exponential

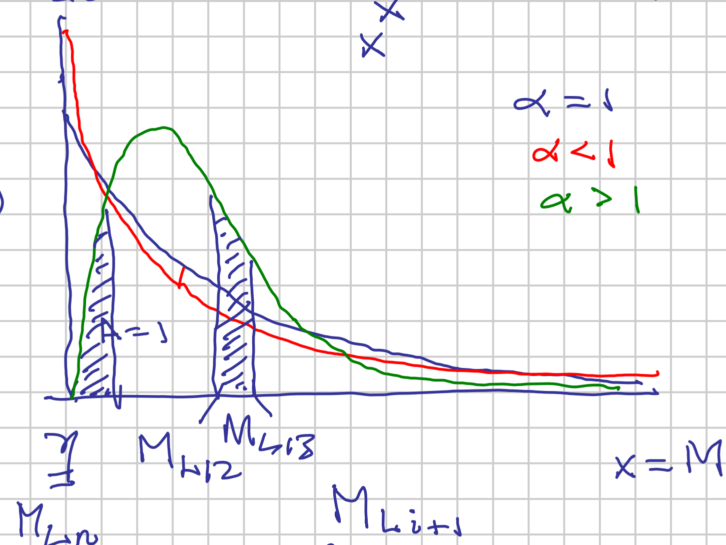
$\alpha = \infty$ : Folded Log-normal

$0 < \alpha \le \infty$

Normal : $\bar{x}$, $\sigma$




$p(M)$




Average $\bar{M}$ (AVERAGE)

$$\bar{M} = \frac{\int_{\eta}^{\infty} p \cdot M \, dM}{\left[\int_{\eta}^{1} p \, dM\right] \equiv 1} \qquad \begin{matrix} \text{mass} \\ \text{moles} \end{matrix}$$

$$\hat{Z}_i \equiv \int_{M_{Li}}^{M_{Li+1}} p \, dM$$

$$\bar{M}_i = \frac{\int_{M_{Li}}^{M_{Li+1}} p \cdot M \, dM}{\int_{M_{Li}}^{M_{Li+1}} p \, dM} \quad \begin{matrix} \text{mass} \\ \text{moles} \end{matrix}$$

Gamma Model:

1) $\bar{M}_{n+}$ AVERAGE
2) $\eta$ BOUND
3) $\alpha$ SHAPE
4) $M_{Li}$ LMW

$\Big\}\ p(M)$

Lower MW boundaries each "cut"

$\Rightarrow$ Slices $p(M)$ into "cuts"

$$\underbrace{\qquad\qquad}_{\tilde{z}_i \quad \bar{M}_i \quad w_i}$$

$M_{Ln} = \eta$ (usually)

How to apply the $\Gamma$ Distribution Model?

- Flashed oil GC data $\overline{w_i}^{\,\text{Lab}}$ for $C_{n+}$ ($C_{7+}$)

Norm. for $C_{n+}$

$$w_i = \frac{\hat{z}_i \, \bar{M}_i}{1 \cdot \bar{M}_{n+}} =$$

$$\frac{\hat{z}_i(\bar{M}_{n+}, \alpha, \eta, M_{Li}, M_{Li+1}) \cdot \bar{M}_i(\bar{M}_{n+}, \alpha, \eta, M_{Li}, M_{Li+1})}{\bar{M}_{n+}}$$

DATA
Lab

$\overline{\dot{i}}$ $\quad$ $\underline{(\underset{\delta}{W}_i)_{GC}}$ $\quad$ $\underline{(\underset{\delta}{W}_i)_{\Gamma}} = f(\underbrace{\overline{M}_{n+}, \alpha, \eta}_{\text{3 model parameters}}, M_{L_i})$

7

Assume $\underbrace{M_{L_i}}_{\text{Set (fix)}} \overset{\text{e.g.}}{=} M_{P_{i-1}}$ or another way

8

9

minimize

10 mismatch

$\Downarrow$

$(W_i)_{GC}$ vs $(W_i)_{\Gamma}$

31+

$$\min \quad SSQ = \sum \frac{(w_i)_{\Gamma} - (w_i)_{GC}}{(w_i)_{GC,\,max}}$$

SOLVER