Reaction-diffusion model for oxidative aging of bitumen

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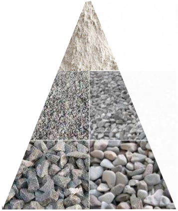

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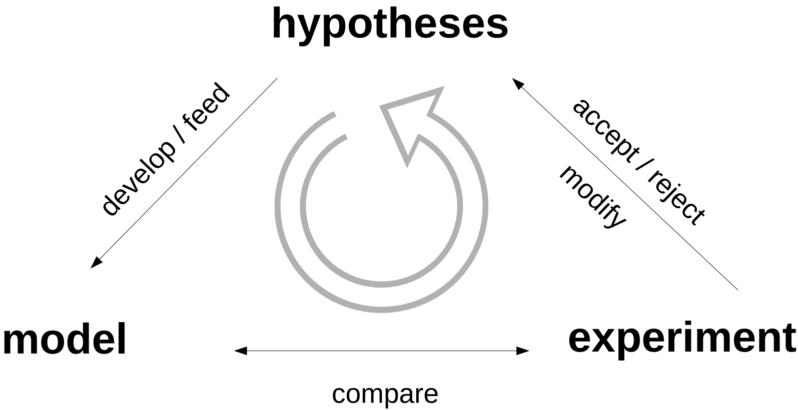
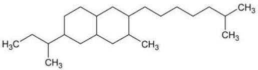
Uwe Mühlich

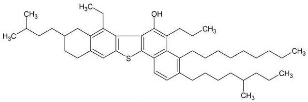

hypotheses
develop / feed
accept / reject
modify
model
experiment
compare

Molecular structure

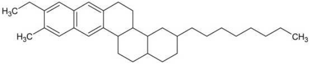
saturates[2]

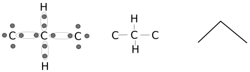


resins[2]

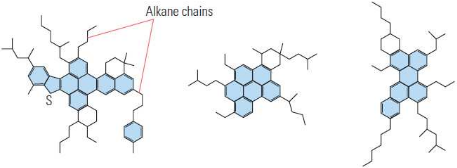


aromatics / naphtenics[2]





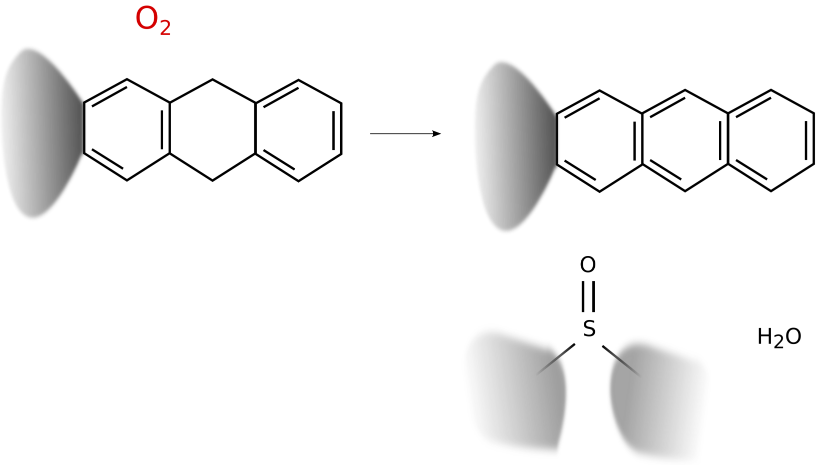
asphaltenes [1]



source: http://www.interchem.at

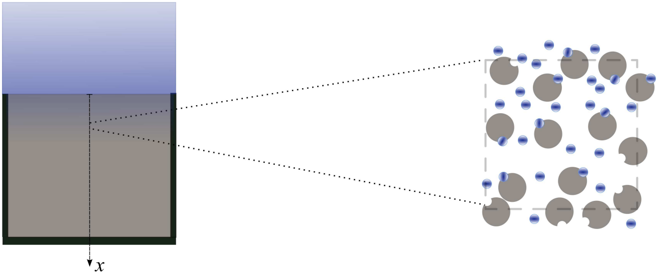
[1] [Akbarzadeh et al., 2007]
[2] [Soenen, 2017]

example: "spurt" oxidation[3] $\approx$ 40 hours



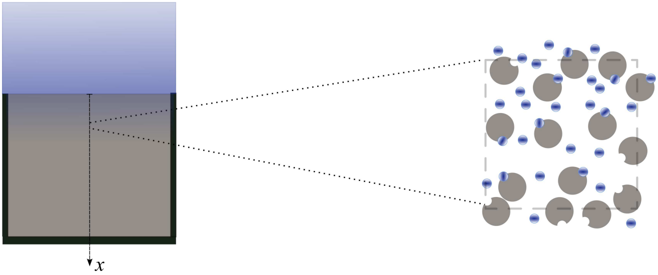
[3][Petersen and Glaser, 2011]

Mixtures - partial mass balances



$$\rho_1 \leftarrow \frac{n_1 m_1}{V} \qquad \rho_2 \leftarrow \frac{n_2 m_2}{V} \qquad \rho_3 \leftarrow \frac{n_3 m_3}{V}$$

Mixtures - partial mass balances



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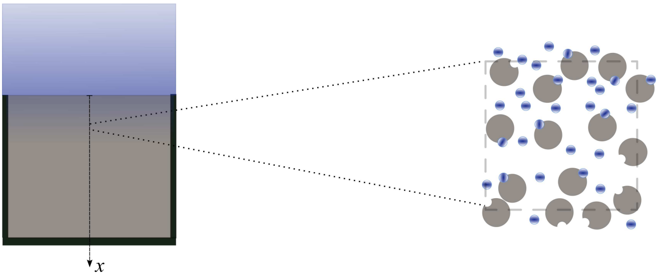
$$\partial_\tau \rho_1 + J_1' = r_1$$

$$\partial_\tau \rho_2 + J_2' = r_2$$

$$\partial_\tau \rho_3 + J_3' = r_3$$

Mixtures - partial mass balances



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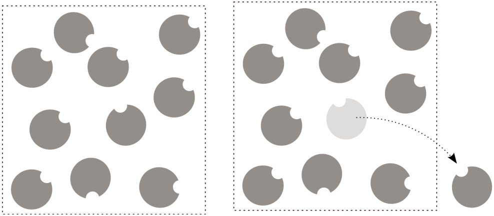
$$\partial_\tau \rho_\alpha + J_\alpha' \quad = \quad r_\alpha \quad , \quad \alpha = 1, ..., N$$

Mixtures - chemical potential

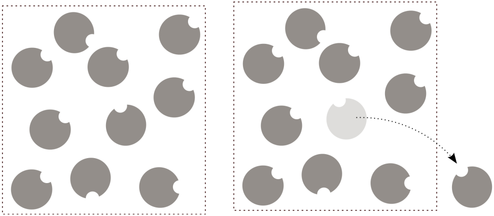


chemical potential

change in energy by
removing / adding
one unit of particles

pure substance

Mixtures - chemical potential



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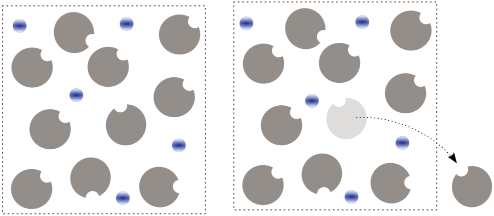


mixture

TIP - one reaction and isothermal conditions

mass balances

$$\partial_\tau \rho_\alpha + J'_\alpha = r_\alpha$$

diffusion fluxes

$$J_\alpha = -\frac{1}{T}\sum_{\beta=1}^{\nu-1} L_{\alpha\beta}\left[\mu_\beta - \mu_\nu\right]'$$

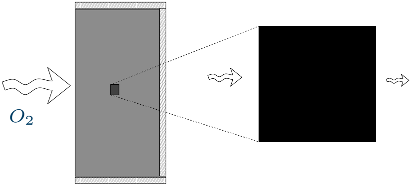
reaction kinetics

$$r_\alpha = \Lambda s_\alpha M_\alpha$$

chemical potentials

$$\begin{aligned}\mu_\alpha &= \mu_\alpha^0 + RT\ln a_\alpha \\ &= \mu_\alpha^0 + RT\ln \chi_\alpha\gamma_\alpha\end{aligned}$$

1. O_2
2. H_2O
3. aromatized (ARA*) with one S=O
4. aromatizable compounds with traces of sulfur (ARA)
    - resins
    - aromatics
    - asphaltenes
5. saturates



assumption:
every ARA member affected only once
$\Longrightarrow$ average compounds

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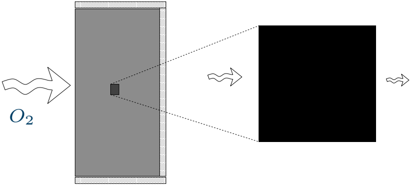

assumption:
every ARA member affected only once
$\Longrightarrow$ average compounds

Typical elemental composition for heavy oil[1] (Gateau *et al.*, 2004).

Fraction	Weight percentage (%)	Elementary composition based on C_{20} + (%)				
		C	H	N	O	S
Asphaltene	14.1	83.8	7.5	1.3	1.7	4.8
Resin	37.3	82.8	8.9	1.5	2.0	4.3
Aromatic	37.2	84.3	10.0	< 0.3	1.1	4.0
Saturate	11.4	86.6	13.0	< 0.3	< 0.2	< 0.1

[1] From Venezuela reserve.

stoichiometry

$$1\,O_2 + 1\,ARA \quad \rightleftarrows \quad 1ARA^* + 1\,H_2O$$

stoichiometric coefficients

$$s_1 = s_4 = -1,\ s_3 = s_2 = 1\,, s_5 = 0\,.$$

molar fraction relations

$$\begin{aligned} \chi_3 &= \chi_2\,, \\ \chi_5 &= \chi_5^0[1-\chi_1-\chi_2]\,, \\ \chi_4 &= [1-\chi_5^0][1-\chi_1-\chi_2]-\chi_2\,. \end{aligned}$$

mass balances

$$\begin{aligned} \partial_\tau c_1 + \bar{J}_1' &= -\Lambda \\ \partial_\tau c_2 &= \Lambda \end{aligned}$$

1	O_2
2	H_2O
3	ARA*
4	ARA
5	saturates

s_α	stoichiometric coeff's
χ_α	molar fraction $\frac{n_\alpha}{n_{\mathrm{tot}}}$
c_α	molar concentrations $\frac{\rho_\alpha}{M_\alpha}$
M_α	molecular mass
Λ	reaction rate density $\frac{r_\alpha}{s_\alpha M_\alpha}$

Regular solution type activity model

[Vidal, 2003]

$$\ln \gamma_\alpha = \frac{v^*_\alpha}{RT}\left[\delta_\alpha - \bar{\delta}\right]^2$$

with

$$\bar{\delta} = \sum_{\alpha=1}^{N} \delta_\alpha \Phi_\alpha$$

$$\Phi_\alpha = \frac{v^*_\alpha \chi_\alpha}{\sum_{\beta=1}^{N} v^*_\beta \chi_\beta} = \frac{v^*_\alpha \chi_\alpha}{V^*}\,.$$

1	O_2
2	H_2O
3	ARA*
4	ARA
5	saturates

χ_α	molar fraction $\frac{n_\alpha}{n_{tot}}$
M_α	molecular mass
v^*_α	molar volume of pure substance in liquid state
δ_α	solubility parameter
Φ_α	volumetric fraction

diffusion part (constant T)

$$\begin{pmatrix} J_1 \\ \cancel{J_2} \\ \cancel{J_3} \\ \cancel{J_4} \\ \cancel{J_5} \end{pmatrix} = -\frac{1}{T} \begin{pmatrix} L_{11} & L_{12} & L_{13} & L_{14} \\ L_{21} & L_{22} & L_{23} & L_{24} \\ L_{31} & L_{32} & L_{33} & L_{34} \\ L_{41} & L_{42} & L_{43} & L_{44} \\ L_{51} & L_{52} & L_{53} & L_{54} \end{pmatrix} \cdot \begin{pmatrix} [\mu_1 - \mu_2]' \\ [\mu_3 - \mu_2]' \\ [\mu_4 - \mu_2]' \\ [\mu_5 - \mu_2]' \end{pmatrix}$$

$$[\mu_2 - \mu_5]_{,j} = \beta_1 [\mu_1 - \mu_5]'$$
$$[\mu_3 - \mu_5]_{,j} = \beta_2 [\mu_1 - \mu_5]'$$
$$[\mu_4 - \mu_5]_{,j} = \beta_3 [\mu_1 - \mu_5]'$$

$$J_1 = -\frac{L_{11}^*}{T} [\mu_1 - \mu_5]'$$

1	O_2
2	H_2O
3	ARA*
4	ARA
5	saturates

μ_α	chemical potentials
$[]'$	$\frac{\partial []}{\partial x}$
L	$\frac{RL_{11}^*}{\chi_1}$ (mobility)

$$A_{15} = \ln \frac{\gamma_1}{\gamma_5}$$

$$J_1 = -L \left\{ \left[1 + \frac{\chi_1}{1 - \chi_1 - \chi_2} + \chi_1 \frac{\partial A_{15}}{\partial \chi_1} \right] \chi_1' + \left[\frac{\chi_1}{1 - \chi_1 - \chi_2} + \chi_1 \frac{\partial A_{15}}{\partial \chi_2} \right] \chi_2' \right\}$$

diffusion part (constant T)

$$\begin{pmatrix} J_1 \\ \cancel{J_2} \\ \cancel{J_3} \\ \cancel{J_4} \\ \cancel{J_5} \end{pmatrix} = -\frac{1}{T} \begin{pmatrix} L_{11} & L_{12} & L_{13} & L_{14} \\ L_{21} & L_{22} & L_{23} & L_{24} \\ L_{31} & L_{32} & L_{33} & L_{34} \\ L_{41} & L_{42} & L_{43} & L_{44} \\ L_{51} & L_{52} & L_{53} & L_{54} \end{pmatrix} \cdot \begin{pmatrix} [\mu_1 - \mu_2]' \\ [\mu_3 - \mu_2]' \\ [\mu_4 - \mu_2]' \\ [\mu_5 - \mu_2]' \end{pmatrix}$$

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approximate Λ by a polynomial in activities [Pekar M. and Samohyl I., 2014]

$$
\begin{aligned}
\Lambda \approx P_\Lambda = B_0 \quad &+ \quad \frac{1}{2}B_{11}a_1^2 + B_{12}a_1a_2 + B_{13}a_1a_3 + B_{14}a_1a_4 + B_{15}a_1a_5 \\
&+ \quad \frac{1}{2}B_{22}a_2^2 + B_{23}a_2a_3 + B_{24}a_2a_4 + B_{25}a_2a_5 \\
&+ \quad \frac{1}{2}B_{33}a_3^2 + B_{34}a_3a_4 + B_{35}a_3a_5 \\
&+ \quad \frac{1}{2}B_{44}a_4 + B_{45}a_4a_5 \\
&+ \quad \frac{1}{2}B_{55}a_5^2
\end{aligned}
$$

approximate Λ by a polynomial in activities [Pekar M. and Samohyl I., 2014]

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equilibrium

- affinity $A = -\sum_{\alpha=1}^{N} \mu_\alpha s_\alpha$ must vanish

  $$\ln\left(\frac{a_1^\ominus a_4^\ominus}{a_2^\ominus a_3^\ominus}\right) = \frac{\mu_A^\ominus}{RT} \quad \rightarrow \quad K = \frac{a_1^\ominus a_4^\ominus}{a_2^\ominus a_3^\ominus}$$

- $\Lambda^\ominus = \Lambda(a_\alpha = a_\alpha^\ominus)$ must vanish too

approximate Λ by a polynomial in activities [Pekar M. and Samohyl I., 2014]

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&+ \quad \frac{1}{2}B_{55}a_5^2
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- $\Lambda^\ominus = \Lambda(a_\alpha = a_\alpha^\ominus)$ must vanish too

$$\Lambda = B_{14}[a_1a_4 - Ka_2a_3]$$

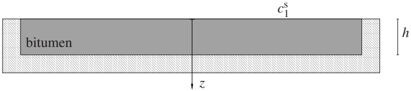
intermediate result:

$$\Lambda = B_{14}\Bigg[\ \chi_1\chi_4 \exp\left(\frac{v_1^*}{RT}\left[\delta_1-\bar{\delta}\right]^2+\frac{v_4^*}{RT}\left[\delta_4-\bar{\delta}\right]^2\right) \\ -\chi_2\chi_3 \exp\left(\frac{v_2^*}{RT}\left[\delta_2-\bar{\delta}\right]^2+\frac{v_3^*}{RT}\left[\delta_3-\bar{\delta}\right]^2\right)K\Bigg]$$

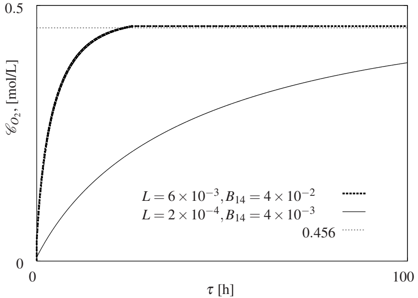
$$\Lambda = B_{14}\chi_1\chi_4 \exp\left(\frac{v_1^*}{RT}\left[\delta_1-\bar{\delta}\right]^2+\frac{v_4^*}{RT}\left[\delta_4-\bar{\delta}\right]^2\right)$$

final result:

$$\Lambda = B_{14}\chi_1\left[[1-\chi_5^0][1-\chi_1-\chi_2]-\chi_2\right]\exp\left(\frac{v_1^*}{RT}\left[\delta_1-\bar{\delta}\right]^2+\frac{v_4^*}{RT}\left[\delta_4-\bar{\delta}\right]^2\right)$$



$$
\begin{aligned}
h &= 0.1\text{cm} \\
c_1^s &= 8.10 \times 10^{-7}\ \frac{\text{mol}}{\text{cm}^3} \\
l_e &= 0.1/100 \\
\Delta t_{\text{LB}} &= \frac{1}{6L} l_e^2 \\
\chi_5^0 &= 0.35
\end{aligned}
$$



species		density $\frac{\text{g}}{\text{cm}^3}$	molecular weight $\frac{\text{g}}{\text{mol}}$	molar volume $\frac{\text{cm}^3}{\text{mol}}$	solubility $\sqrt{\text{MPa}}$	solubility $\sqrt{\frac{\text{g}}{\text{cm } s^2}}$
oxygen		1.114	32	28.0	14.0	44272.2
water		0.988	18	18.2	48.0	151790.4
ARA*				1709.0	20.0	63246.0
ARA	aromatics	1.006	440	437.0	21.0	
	resins	1.054	990	940.0	19.0	
	asphaltenes	1.200	4500	3750.0	20.0	
	average			1709.0	20.0	63246.0
saturates		0.887	370	417.0	16.5	52177.9

[Akbarzadeh et al., 2005, Powers, 2014]

$$
\begin{aligned}
\partial_\tau c_1 + \bar{J}_1' &= -\Lambda \\
\partial_\tau c_2 &= \Lambda
\end{aligned}
$$

$$
J_1 = -L\left\{\left[1 + \frac{\chi_1}{1-\chi_1-\chi_2} + \chi_1\frac{\partial A_{15}}{\partial \chi_1}\right]\chi_1' + \left[\frac{\chi_1}{1-\chi_1-\chi_2} + \chi_1\frac{\partial A_{15}}{\partial \chi_2}\right]\chi_2'\right\}
$$

$$
\Lambda = B_{14}\chi_1\left[[1-\chi_5^0][1-\chi_1-\chi_2]-\chi_2\right]\exp\left(\frac{v_1^*}{RT}\left[\delta_1-\bar{\delta}\right]^2 + \frac{v_4^*}{RT}\left[\delta_4-\bar{\delta}\right]^2\right)
$$

- only 2 purely phenomenological parameters (L, B_{14})
- able to distinguish between different compositions
- diffusion not significantly affected by the oxidation process
  supports hypothesis of additional processes at molecular level

Akbarzadeh, K., Alboudwarej, H., Svrcek, W. Y., and Yarranton, H. W. (2005).
A generalized regular solution model for asphaltene precipitation from n-alkane diluted heavy oils and bitumens.
Fluid Phase Equilibria, 232(1):159 – 170.

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Asphaltenes - problematic but rich in potential.
Oilfield Review, (22 - 43).

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Characterization and Asphaltene Precipitation Modeling of Native and Reacted Crude Oils.
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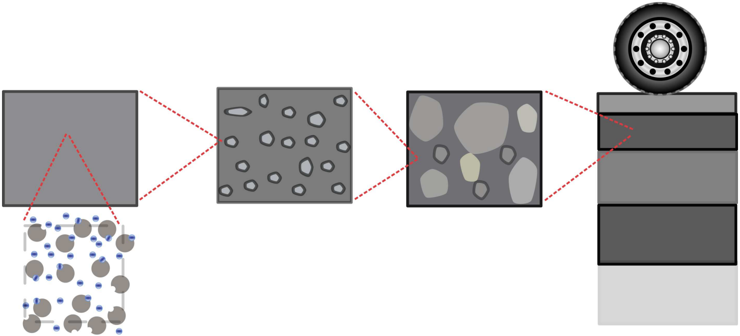

- second reaction C=O
- structure formation
- N_2 diffusion
- diffusion of rejuvenates
- mechanical part
- ...

- aging mortar
- diffusion rejuvenates
- mechanical properties

- aging asphalt
- diffusion rejuvenates
- mechanical properties