

Comments on

“RELATE CRUDE OIL FOULING RESEARCH TO FIELD FOULING OBSERVATIONS” by Joshi et al., Schladming Conference, 2009

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Recently, a plot of tube-side fouling rate, \dot{R}_f , vs. wall shear stress, $\tau_w (= f\rho u^2/2)$, based on 30 data points from six crude oil preheat trains was presented by Joshi et al. (2009) to show that \dot{R}_f decreases as τ_w , and hence velocity u , increases. The plot, Fig. 1, also was purported to show no close relationship between \dot{R}_f and the hot-side inlet temperature, taken “as a representation of the tube surface temperature in the exchanger.”

There are at least two problems with respect to the apparent absence of a surface temperature effect. Firstly, the hot-side inlet temperature is a rather crude representation of the tube-side surface temperature, T_s , which it will always exceed and which varies along the length of the tube. Secondly, and perhaps more importantly, there is another key variable that has been neglected in the plotting procedure, at least if one pays attention to the following mathematical model, developed originally (Epstein, 1994) to simulate the initial fouling rate due to the polymerization of styrene from kerosene solution (Crittenden et al, 1987). The model, which in the case of chemical reaction fouling, assumes that the initial fouling rate, \dot{R}_{fo} , is governed by mass transfer of a precursor from the bulk to the surface followed by chemical attachment to the surface, takes the following generalized form (Vašák and Epstein, 1996):

$$\frac{k_1 \dot{R}_{fo}}{k_m} + \left[\frac{k_2 \dot{R}_{fo} \tau_w e^{E/RT_s}}{\mu} \right]^{1/n} = C_b \quad (1)$$

Eq. (1) has been variously validated, not only for other instances of chemical reaction fouling (Wilson and

Watkinson, 1996; Rose et al., 2001), but also for colloidal particle deposition under attractive double-layer conditions (Vašák et al., 1995) and for precipitation fouling of $CaSO_4 \cdot 2H_2O$ (Fahiminia et al, 2007). It has also received some support for crude oil refinery fouling (Yeap et al., 2004, 2006) in its first order ($n=1$) form,

$$\dot{R}_{fo} = \frac{C_b}{\frac{k_1}{k_m} + \frac{k_2 \tau_w e^{E/RT_s}}{\mu}} \quad (= a e^{-E_f/RT_s}) \quad (2)$$

where the first term in the denominator denotes the mass transfer resistance and the second the resistance due to chemical reaction induced attachment to the wall. The bracketed equality added on to Eq. (2) defines, at any given fluid velocity, the fouling activation energy E_f , which should not be confused with the chemical-kinetic activation energy E , in the equation proper (Rose et al, 2001). Further discussion of E_f occurs below.

When the mass transfer resistance, dominance of which would yield an increase of \dot{R}_{fo} with fluid velocity and hence with τ_w , becomes negligible relative to that of attachment, which occurs eventually as the velocity is increased, then Eq. (2) for constant C_b simplifies to

$$\dot{R}_{fo} = k_3 \frac{\mu}{\tau_w} e^{-E/RT_s} \quad (3)$$

which shows the fouling rate to be decreasing as τ_w increases, consistent qualitatively with Fig. 1. What

differentiates this model from others is the term μ/τ_w , which has the dimensions of time and is proportional to the residence time of the fluid near the hot wall (i.e. within the viscous sublayer) over any fixed length of tube (Epstein, 1994). \dot{R}_{fo} thus increases as this residence time increases, i.e. Eq. (3) implies that the shear stress τ_w becomes less effective in resisting fouling when the fluid residence time near the wall increases due to increased viscosity.

The presence of the viscosity μ in Eq. (3) adds a new dimension to the problem since the temperature effect on μ for most liquids can be represented by the Andrade (1930) equation,

$$\mu = Ae^{B/T} = Ae^{E_\mu/RT} \quad (4)$$

where E_μ can be interpreted as a viscosity de-activation energy. If μ in Eq. (4) is evaluated at $T = T_s$, then combination of Eqs. (3) and (4) leads to

$$\dot{R}_{fo} = k_4 e^{-(E-E_\mu)/RT_s} / \tau_w \quad (5)$$

E_μ thus exerts a diminution of the measured activation energy when μ is not separately evaluated in Eq. (3) at the value of T_s for each experimental point, or when it is omitted altogether as in Fig. 1. The diminution effect for the data of Fig. 1 can be gauged approximately by consideration of both E and E_μ .

Yeap et al. (2004, 2006) evaluated the chemical-kinetic activation energy in Eq. (2) for fouling of ten crude oils, with the result that $E = 48 \pm 18 \text{ kJ/mol}$ (18 is the standard deviation) for $T_s = 290 - 649 \text{ K}$. Assuming values of T_s about 50 Celsius degrees below the hot-side inlet temperature range (141-360°C) of Fig. 1, i.e. $T_s = 363 - 583 \text{ K}$, making use of the kinematic viscosity data from 40°C to 200°C for two Arab crude oils provided by Puttagunta et al. (1992), the absolute viscosity data at 90°C for a Syncrude sweet blend measured by Sundaram (1998), and a generalized chart for extrapolating such data to higher temperatures recommended in the Chemical Engineers' Handbook (Perry and Chilton, 1973), E_μ was estimated to be in the range 21–30 kJ/mol .

Thus $E - E_\mu$ is considerably less than E and, depending on the crude oil, could be close to or even equal to zero. If we add to this the fact that \dot{R}_{fo} in Eqs. (1), (2), (3) and (5) is a localized initial fouling rate for which T_s is a measure of the corresponding wall temperature in immediate contact with the crude, while the \dot{R}_f

measurements of Fig. 1 are "rates of fouling over several years of operation" (Joshi et al., 2009) during most of which the surface temperature that the heated crude experiences will not be that of the wall but rather the progressively diminishing surface temperature of the thickening fouling deposit, then it is not at all surprising that, in a plot simply of \dot{R}_f vs. τ_w , there is no "clear relationship between these fouling rates and the hot side temperature."

Turning now to the commonly determined (e.g. Crittenden et al., 1992) E_f in the bracketed portion of Eq. (2), its value at low velocity is normally relatively small due to the dominance of mass transfer over attachment, mass transfer rates being almost unaffected by T_s . As the velocity is increased, E_f will increase (Rose et al., 2001) as the contribution of mass transfer becomes negligible relative to attachment. However, it will never approach E since the contribution of μ is neglected in the bracketed portion of Eq. (2), as it was neglected in Fig. 1. This could explain retroactively why E_f increased with velocity but never approached E (as originally expected) in the work of Rose et al. (2001).

Finally, it is of interest to note that while Eq. (3) shows \dot{R}_{fo} as inversely proportional to τ_w (i.e. to $f\rho u^2/2$), the best line in Fig. 1 is approximated by $\dot{R}_f \propto 1/\tau_w^{1.6}$, a result that is completely consistent with the results of protein fouling (Rose et al., 2001), which showed similar deviations from Eq. (3) at the higher fluid velocities.

NOMENCLATURE

A	pre-exponential factor in Eq. (4), $Pa \cdot s$
a	pre-exponential factor in bracketed portion of Eq. (2), $m^2 \cdot K / kJ$
B	exponential constant in Eq. (4), K
C_b	bulk concentration of precursor, kg / m^3
E	chemical-kinetic activation energy, kJ / mol
E_f	fouling activation energy, kJ / mol
E_μ	viscosity de-activation energy, kJ / mol
e	natural exponent, -
f	Fanning friction factor, -
k_1, k_2, k_3, k_4	dimensional constants
k_m	mass transfer coefficient, m/s
R	universal gas const. = $0.008314 \text{ kJ}/(\text{mol} \cdot \text{K})$
\dot{R}_f	fouling rate, $m^2 \cdot K / (W \cdot \text{day})$
\dot{R}_{fo}	initial fouling rate, $m^2 \cdot K / kJ$
T	absolute temperature, K
T_s	absolute surface temperature, K
u	bulk fluid velocity, m/s

Greek letters

μ	fluid viscosity, $Pa \cdot s$
ρ	fluid density, kg/m^3
τ_w	wall shear stress, Pa

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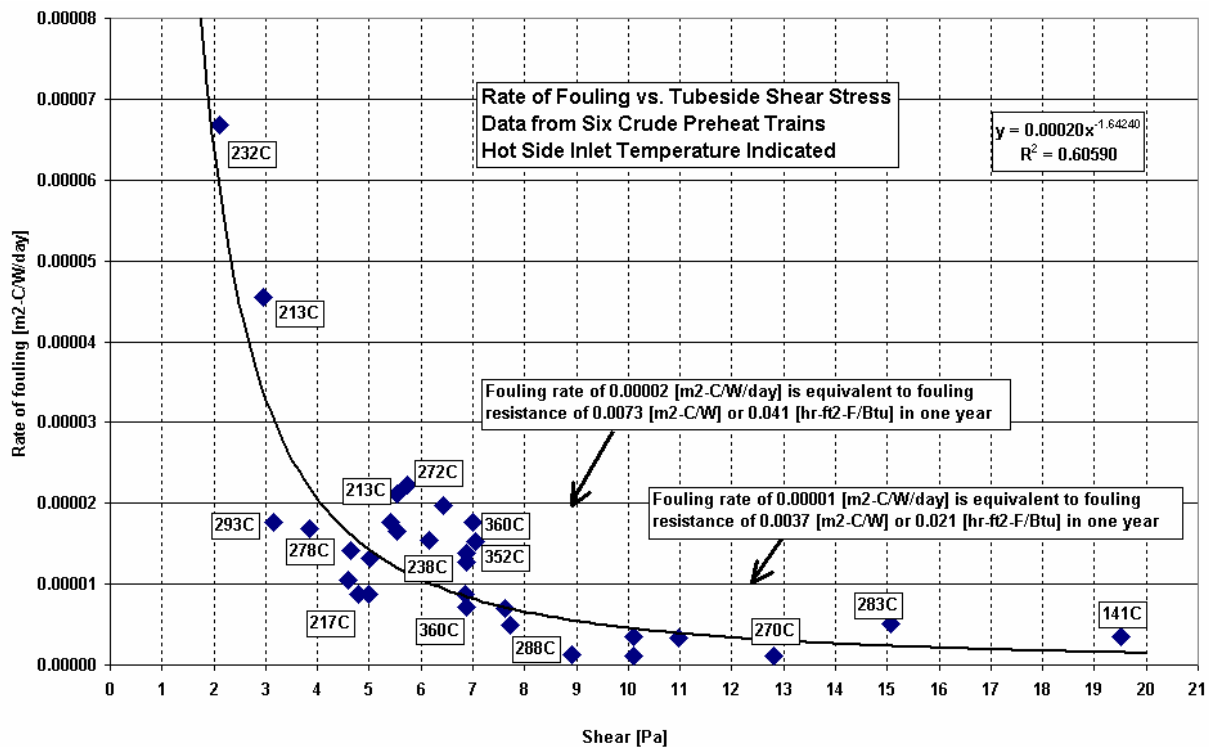


Fig. 1 Rate of tubeside fouling vs. shear stress and velocity (Joshi et al. 2009).