

A CONCEPTUAL MECHANISM FOR HOW CRUDE OILS FOUL IN HEAT EXCHANGERS

*H. M. Joshi¹

¹ Clean As New Gulf Coast, 1303 Thompson Park Dr., Baytown TX 77521 USA; hjoshi@cleanasnew.com

ABSTRACT

This paper presents a physical description of how crudes foul in heat exchanger tubes and the properties which influence fouling and provides suggestions for a properties-only based model. Such a model should be able to predict fouling without the need to fit constants based on historical data. The proposed mechanism is postulated based on several field-based observations and measurements -- fouling rates, crude chemistry, thermophysical properties, deposit analysis, and pilot-plant data. The fouling process consists of deposition on the tube wall of inorganic and organic solids, present in the laminar sublayer, and the conversion of the organics to coke-like material. However, many complicated interactions occur in this simple two-step process. They include precipitation of asphaltenes, the attraction between the solids and the tube surface (clean and fouled), the size of the solids relative to the sublayer, the effect of shear stress, and the transport of the solids into and away from the laminar sublayer. A successful simplified approach using an empirical correlation derived from pilot plant data is also described.

INTRODUCTION

The mechanism presented here is a simple two-step process of deposition and thermal conversion, which has been presented many times before. Ref. [1-5], and Ref. [6] describes an almost identical process as presented here. This paper puts new thoughts on this mechanism based on the observation of crude properties, the dominant effect of shear stress, and crude temperature only playing a role in the solubility of organic precursors. The terminology used and the field observations on which this paper is based are explained in this section.

Terminology

Crude (Fluid) Properties: The properties which play a major role in the fouling process – viscosity and Prandtl number, which determine the thickness of the laminar sublayer and the relative thicknesses of the velocity vs temperature boundary layer.

Crude (other) Properties: Corrosion related properties which have an impact on fouling. These

include TAN (Total Acid Number), nitrogen, and sulfur.

Crude Composition: Specifically refers to crude components which affect the solubility of asphaltenes at the operating temperature. Although the exact components have not been identified, generically aromatic fractions are good solvents and alkanes are poor solvents.

Inorganics: Inorganic contaminants which are part of the fouling deposit, and which may affect the rate of deposition. These include iron sulfide and salts (chlorides, carbonates, oxides), both of which are always found in fouling deposits.

Asphaltenes: Insoluble organic particles which deposit as part of fouling and which are presumed to be the main organic precursors. A typical definition of asphaltenes is that they are soluble in toluene and insoluble in heptane.

Crude Compatibility: A compatible crude is one in which the asphaltenes are in solution at room temperature. The term “Unstable” is sometimes used to denote incompatibility. This paper deals with compatible crudes only.

Shear Stress: Fluid shear at the tube wall, a function of viscosity and the velocity gradient at the wall. Shear stress in the laminar sublayer is constant due to a linear velocity profile.

$$\tau = \mu (\partial u / \partial y) \quad [\text{Pa}] \quad (1)$$

Basis of the proposed mechanism

As stated above, the mechanism shown here is the same as proposed many times before, but the ideas are modified to account for several observations from fouled heat exchangers. These are as follows:

Fouling trends (with steady and heat balanced data) consistently show linear trends over a 6-12 month period and show a strong dependence on shear stress.

Cold-end heat exchangers, approximately below 150°C crude bulk temperature, show minimal fouling on the crude side. At higher temperatures crude side fouling is similar in all heat exchangers depending on the shear stress.

The atomic H/C ratio of fouling deposits varies between 0.80-0.95 which is consistent with the starting material being asphaltenes which have H/C of 1.15-1.20. The deposit ratio is quite a bit higher

than what it would be for high temperature coke, such as that formed in a furnace or a coking process.

Some surfaces (for example coated surfaces) show a reduced rate of fouling over a 6-12 month period and this rate also depends on shear stress. The impact of the different surfaces is similar regardless of the crude properties.

Crudes with high TAN have very high compatibility presumed to be due to good asphaltene solvency at high temperatures. Nitrogen is suspected to have a similar impact.

FOULING MECHANISM

The deposition of solids and conversion of the deposit happens in a small Zone of Action (ZoA) near the wall, the laminar sublayer. In this layer the shear stress counteracts the tendency of solids to stick to the wall, and the temperature is at the highest which affects asphaltene solubility. The turbulent flow velocity profile and shear stress are shown conceptually in Fig. 1 and with actual dimensions in Figs. 2 and 3. Figs. 2 and 3 are for typical crude properties at two average velocities corresponding to shear stresses of 6 Pa and 10 Pa, and a wall temperature of 350°C. Fig. 4 shows a view of asphaltenes under a microscope.

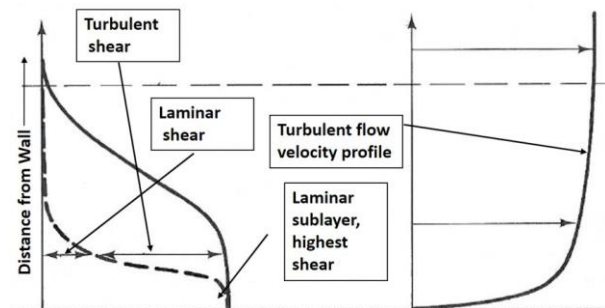


Fig. 1. Turbulent flow boundary layer showing shear stress (left) and velocity variation (right)

Fig. 1 shows velocity and temperature profiles in fully developed turbulent flow in a circular tube. The dark lines represent the magnitude of shear/velocity at a point along the flow length, as shown by the horizontal arrows. The profiles extend from the wall (the hatched base) to the center of the tube (top of the figure). The velocity is zero at the wall (right image) but the gradient and thus the shear stress is the highest in the laminar sublayer (left image). Laminar shear dominates in the sublayer and turbulent shear towards the center of the tube, and the total shear stress decreases from the wall to the center of the tube.

The dimensions of the proposed ZoA are shown in Figs. 2 and 3, lower graph. Note that the bottom

part of these figures is an expanded plot of the left side of the top. Particles, including asphaltenes, smaller in size than the sublayer thickness are more likely to stick to the wall compared to larger particles [7]. Fig. 4 shows that asphaltenes aggregates can be quite small, of the order of 5-10 μm , but can agglomerate to form larger particles. The agglomerated asphaltenes could become larger than the sublayer thickness and migrate out of the sublayer.

Fig. 5 shows the temperature profiles in the sublayer. The solubility of asphaltenes is a function of this temperature. It is not known how the variation of solubility with temperature should be quantified, but there is a temperature below which asphaltenes are totally soluble and therefore not present as solids in the sublayer, and deposition will be that of inorganics only.

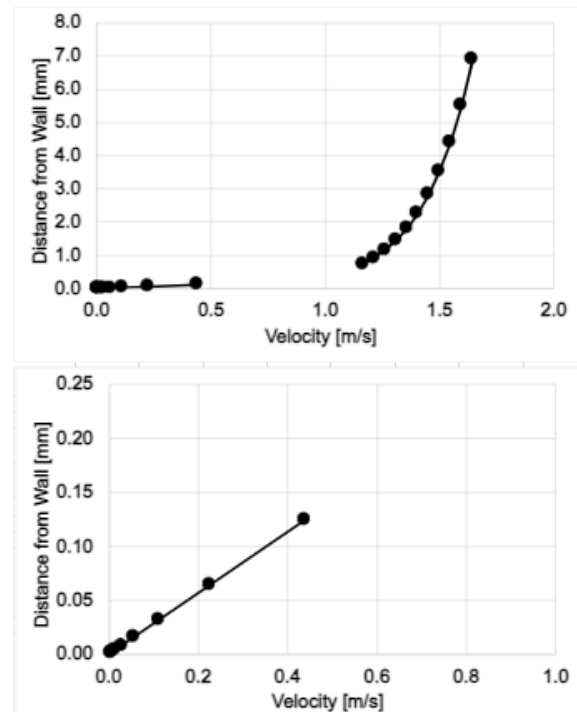


Fig. 2. Velocity profile in a 19.86 mm ID tube (full profile at top, laminar sublayer at bottom) Average velocity = 1.44 m/s, Wall shear stress = 6 Pa, sublayer thickness = 0.124 mm

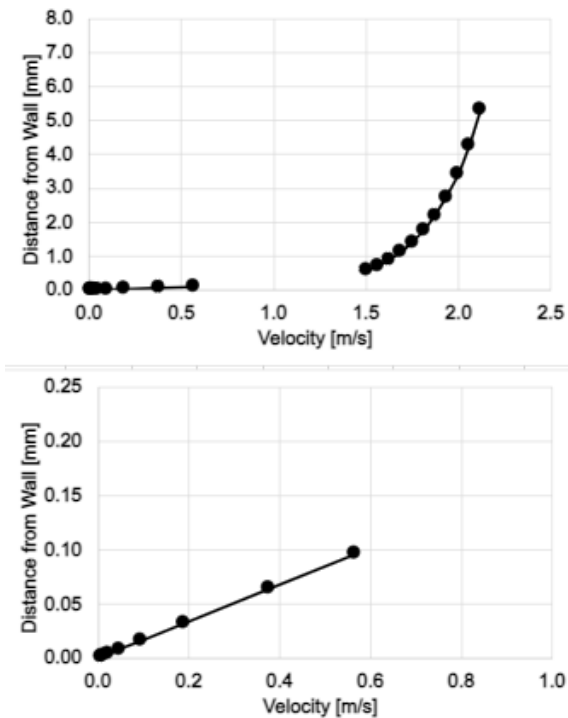


Fig. 3. Velocity profile in a 19.86 mm ID tube (full profile at top, laminar sublayer at bottom)
Average velocity = 1.93 m/s, Wall shear stress = 10 Pa, sublayer thickness = 0.0962 mm



Fig. 4. Asphaltenes in crude, 500X magnification, photo scale L to R is 150 μm

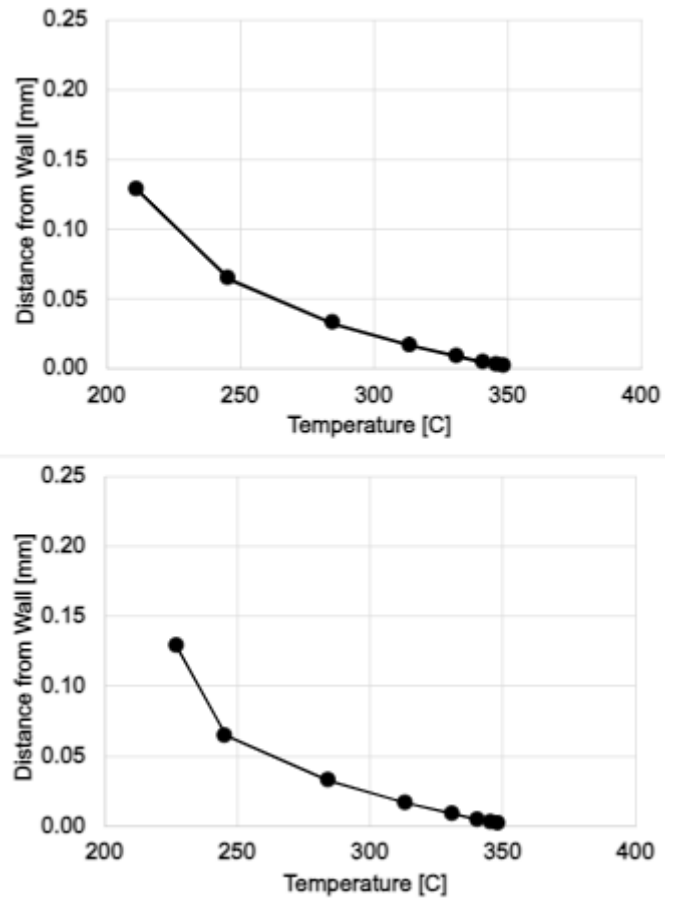


Fig. 5. Temperature profiles in the laminar sublayer

Figs. 6 and 7 (which are magnified versions of the left side of Fig. 1) depict the process of particle transport, deposition, and conversion. Fig. 6 (top) shows the scenario below the asphaltene precipitation temperature where only inorganics are available to deposit, and the bottom shows when both types of solids are present. The various possibilities for the particles to travel in or out of the sublayer are also shown. Fig. 7 shows a deposit on the tube wall which may be partially converted to coke-like material. New deposition occurs on top of this surface and the stickiness of the particles to this layer is likely different than that on the base tube metal, or on a partially covered surface. Which surface has a higher stickiness is not clearly known.

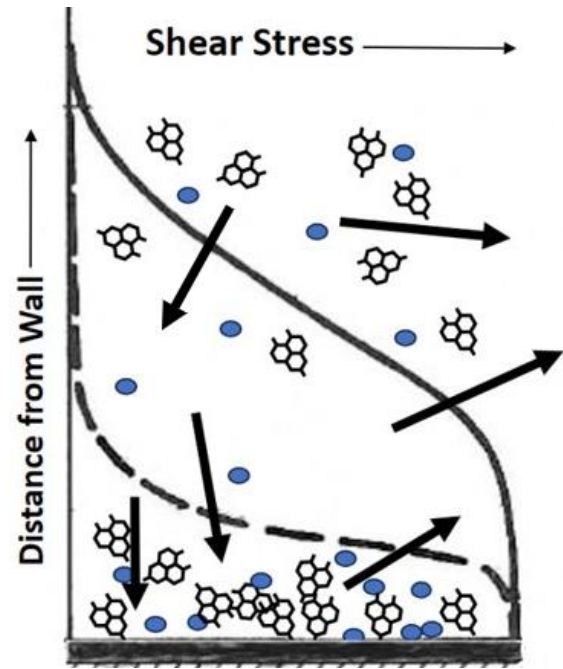
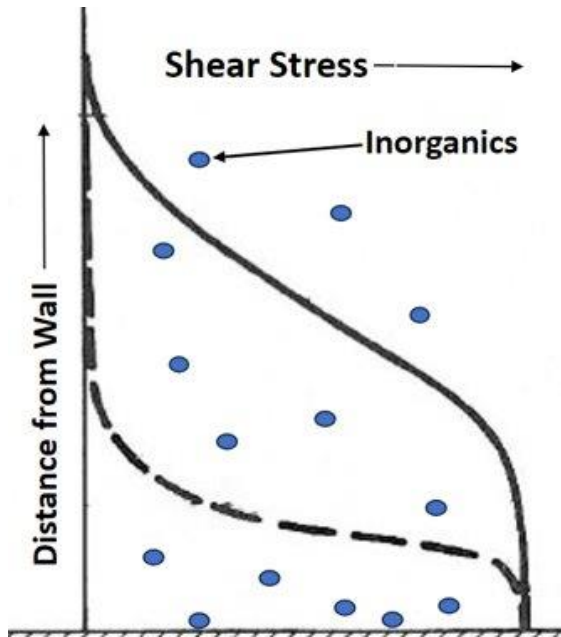


Fig. 7. Deposit layer added to Fig. 6

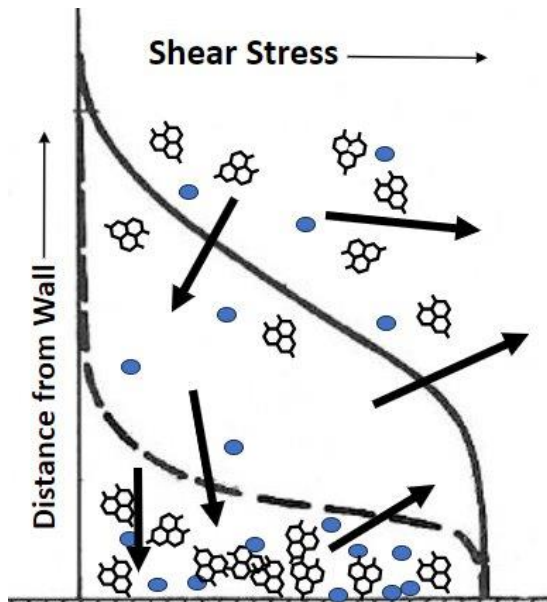


Fig. 6. Inorganic precursors only (top, “cold” heat exchangers), inorganic plus precipitated asphaltenes (bottom, “hot” heat exchangers)

FOULING MODEL

A mathematical model, which doesn't depend on curve-fitting of fouling resistance data, but only on crude properties, shear stress, temperature, and surface properties can be built using the mechanism described above. It requires a description of the following:

- Precursor availability: Concentration of inorganics, solubility of asphaltenes at the operating temperature, concentration of precipitated asphaltenes, and the proportion of the crude fraction containing asphaltenes
- Precursor transport: How they move in and out of the sublayer.
- Precursor stickiness: Surface properties which attract the most present precursors – asphaltenes, salts, FeS.
- Size of the sublayer (ZoA): Where deposition occurs and the relative size of the particles which deposit.
- Effect of shear stress: How does it counteract stickiness.
- Deposit removal: Effect of shear stress, other factors.
- Effect of temperature: How it changes the thermal conductivity and thickness of the deposit (aging), and how it affects asphaltene solubility.
- Aging reaction: The conversion of asphaltenes to coke-like material, which may not be like high temperature coking and needs a different kinetic model.

Surface and precursor properties: As they relate to sticking of the precursors.

To mathematically model all the above is a very complicated task, especially without data taken for this specific purpose and at the right scale of flows, temperatures, and geometry. A simple alternative, which showed very good success, is discussed next.

EMPIRICAL CORRELATION AS A SIMPLE MODEL

This section describes the development of a method to model and predict crude fouling by using a correlation of fouling data to fit the form shown in Eq. (2). The data itself and the numerical outcomes are not presented in this paper.

$$dRf/dt = SF * (FC) * (\tau)^n \quad [m^2-C/W/day] \quad (2)$$

On the left-hand side is the rate of fouling, FC is a Fouling Coefficient based only on crude properties, and the exponent 'n' is a negative number of the order of -1.0 to -1.2. SF is a factor to account for the effect of the surface (stickiness), with carbon steel assigned a value of 1.0.

Data from a pilot plant on a variety of crudes over a range of shear stresses and temperatures corresponding to the hot end of a crude preheat train was used to assign a value of FC for each crude. The data is displayed in Fig. 8. Several properties which are presumed to affect fouling (those considered critical for asphaltene availability and solubility and those which affect the boundary layer thickness) were selected and a correlation was developed for FC as a function of those properties. The correlation can now be used for any crude heat exchanger above a certain operating temperature, typically any heat exchanger past the desalter.

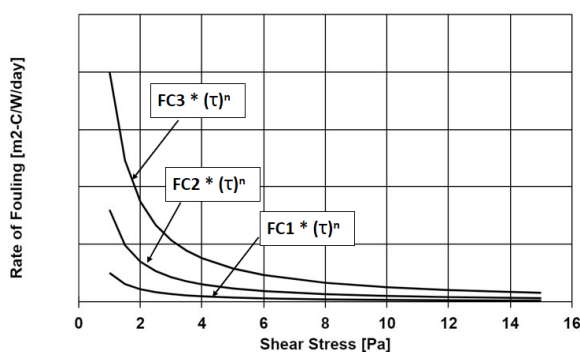


Fig. 8. Rate of fouling variation with shear stress in pilot plant data.

Use of the correlation

When tested against field data for 10 different crude preheat trains, the correlation was able to predict the daily fouling resistance variation with good accuracy, both in terms of the rate for a given crude blend, and the change of slope when there was a change in the blend. For example, the slope and changes in slope of Trend 1 in Fig.9. The validation data cannot be shown in this paper due to its proprietary nature.

The simplified correlation can be used by operating companies in a couple of ways. First, the ratio of FC can be used to directly compare one crude blend to another. For example, if $(FC2/FC1) = 2.0$, crude #2 will foul 2X as fast as crude #1, at the same shear stress, implying half the run length.

Secondly, predictions of future operations with a given crude blend can be made, enabling crude and blend selection. Using a crude preheat train simulation model the correlation can predict the future performance (heat duty) of the preheat train and the operator can decide whether a higher fouling blend (presumably cheaper) can be justified based on including the fouling impact in the economics. Note that this impact must include the effects on the furnace due to increased fuel consumption.

A major deficiency in this simplified approach is that the rate of fouling is always positive (Eq. 2), although in the field the fouling resistance sometimes declines or stays level, removal of deposit being one possible explanation. Trend 2 of Fig. 9 shows this scenario in which the simple correlation is not able to match or predict the negative slope between days 300-450.

A second limitation of the correlation is that it is not able to predict the slope of Trend 3 which is for an incompatible crude where the fouling rate is 5-10 times compared to a compatible crude.

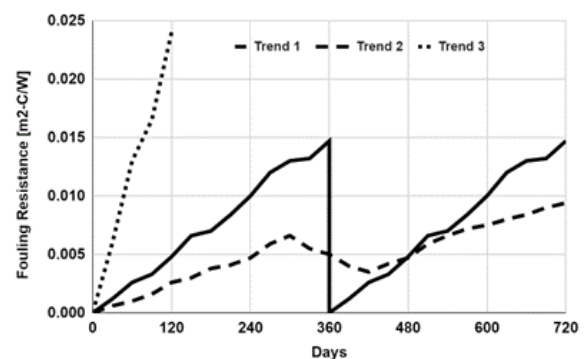


Fig. 9. Different fouling trends, (1 and 2) for compatible crudes, (3) for an incompatible crude.

The data on which the correlation is based was taken on carbon steel tubes (ASTM A179), and $SF=1.0$ is assigned for that material. Field data analysis showed that for different materials (e.g., stainless steels corresponding to ASTM A249 and A268) SF lower than one was needed to fit the field

data. But it was found that the same value of SF fits each material in different crude units, implying that the stickiness is a function of the surface and independent of crude properties.

CONCLUSIONS

A two-step model for fouling of crude oils in heat exchanger tubes was presented here. The steps are those of particle (precursor) deposition and the thermal conversion of the organic precursors. Very similar models have been proposed before, but this paper elaborated on details regarding crude properties, boundary layer and precursor dimensions, and the number of interactions which are part of the fouling process. A simple model for the rate of fouling using a fouling coefficient unique to each crude, derived from pilot plant data, has worked quite well to predict field fouling which increased with time. The simple approach fails when fouling slopes are negative or flat, possibly because it doesn't account for deposit removal.

Future studies based on this work could focus on two major aspects. First, identify the properties which affect asphaltene solubility at heat exchanger operating temperatures and quantify their impact. Secondly, the variation of solubility with temperature has not been studied, at least in the context of heat exchangers. In this proposed mechanism it is assumed that although asphaltenes might be more soluble as temperature increases from ambient, there is a point (around 200°C) when the solubility reverses and asphaltenes precipitate. A public reference to strengthen this assumption has not been located.

Further, it is necessary to develop a quantified understanding of how particles, organic and inorganic, stick to surfaces in tube side flow. Not only will that improve the model by getting a better prediction of SF, but it will also drive the development of surfaces less prone to sticking, such as coatings.

NOMENCLATURE

FC	Fouling Coefficient
n	Shear stress exponent, dimensionless
R_f	Fouling resistance, m^2-C/W
SF	Surface factor, dimensionless
t	Time, day
μ	Viscosity, Pa s
τ	Fluid shear stress, Pa
$(\partial u/\partial y)$	Velocity gradient at the wall, s^{-1}

REFERENCES

[1] Ebert, W. A. and Panchal, C. B., Analysis of Exxon Crude-Oil Slip Stream Coking Data, *Fouling Mitigation of Industrial Heat Exchange*

Equipment, Begell House, New York, pp. 451-460, 1997.

- [2] Polley, G. T., Review of the Development of Models for the Prediction of Fouling Rates in Exchangers Heating Crude Oil, *Proc. 11th Intl. Conf. Petroleum Phase Behavior and Fouling*, San Antonio, Texas, USA, pp. 13-17, 2010.
- [3] Epstein, N., A Model of the Initial Chemical Reaction Fouling Rate for Flow within a Heated Tube and its Verification, *Proc. 10th Intl. Heat Transfer Conf.*, Vol 4, pp. 225-229.
- [4] Watkinson, A. P., Deposition from Crude Oils in Heat Exchangers, *Heat Transfer Eng.*, Vol. 28, pp. 177-184.
- [5] Wilson, D. I., A Review of Predictive Models for Crude Oil Fouling, *Report F-23*, Heat Transfer Research Inc., Ciollege Station, TX, USA, 2014.
- [6] Coletti, F., Ishiyama E. M., et al., Impact of Deposit Aging and Surface Roughness on Thermal Fouling: Distributed Model, *AIChE Journal*, Vol 56 (12), 2010.
- [7] Bennett, C. A., A Theory Describing Sedimentation Particulate Fouling Thresholds Inside Heat Exchanger Tubes, *Heat Transfer Engineering*, Vol 37 (5), 2015.