Comments on Analogies for Correlated Heat and Mass Transfer in Turbulent Flow

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The Colburn analogy is a well-known analogy for predicting the heat and mass- transfer coefficients in turbulent pipe flow. However, this analogy (or other heat-mass transfer analogies) is not applicable for predicting the mass transfer rate in turbulent flows, where the concentration field is correlated to the temperature field. An example of such a situation is frost formation on the cold surfaces of heat exchangers that are exposed to moist air (Lee et al., 1997). Another example, is that of paraffin deposition in cold pipelines, which is a multimillion dollar problem faced during the transportation of "waxy" crude oils (Anonymous, 2001). In both of these processes, a temperature gradient is directly responsible for establishing a concentration gradient. In the latter process, paraffin molecules precipitate and deposit on the walls of cold pipelines restricting the flow of oil. It is necessary to quantify the convective mass flux of paraffin molecules while modeling this phenomenon. In this article, an approach based on solubility is developed to predict the convective mass-transfer rate. Although this article specifically describes the paraffin deposition process, the results shown here can be used for any process, where the heat and mass transfer are correlated.

Crude oil is a complex mixture consisting of paraffins, aromatics, naphthenics, resins, asphaltenes, and other impurities. The solubility of high-molecular-weight paraffins (interchangeably referred to as "waxes" in this article) in crude oil decreases drastically with decreasing temperature. At off-shore reservoir temperatures (70–150) and pressures, the solubility of these waxes is sufficiently high to keep them fully dissolved in the crude oil. However, as the oil is transported through subsea pipelines, where the ambient temperatures can be about 4°, the waxes precipitate out, due to their decreased solubility

and deposit on the cold pipe walls. The enormous economic impact of this problem has led to several studies of the paraffin deposition process (Bern et al., 1980; Brown et al., 1993; Burger et al., 1981; Holder and Winkler, 1965; Majeed et al., 1990; Patton and Casad, 1970; Prasad, 1987; Singh et al., 2000). A number of mechanisms have been considered, and in our previous work we have found that molecular diffusion, enhanced by convective mass flux, is the dominant mechanism responsible for wax deposition (Singh et al., 2000). In two of our previous articles published in the AIChE Journal (Singh et al., 2000, 2001), we have explored the wax deposition phenomenon using laboratory flow-loops, and developed a mathematical model to predict the deposition under the laminar flow regime. It is necessary to extend the results of wax deposition under laminar flow conditions to deposition under turbulent flow, because many oil pipelines operate under turbulent flow conditions. One of the challenges that arise when developing a model for turbulent flow deposition, is the determination of the mass-transfer coefficient of paraffin molecules. As explained later, analogies, such as the Colburn analogy, can not be used to predict the mass-transfer rate in this situation. Hence, the mass-transfer coefficient has to be derived by different means.

Wax Deposition

Figure 1 shows the wax deposition process in a subsea pipeline (or a laboratory flow-loop, which is used to study the deposition in the lab scale). Due to the difference between the bulk oil temperature and the pipe wall temperature, a radial temperature profile is established. If the pipe wall temperature is less than the "cloud point" temperature (which is the saturation temperature for the paraffins), then paraffin molecules close to the wall precipitate and adhere onto the cold wall. This precipitation generates a radial concentration gradient of the dissolved paraffins, which leads to a radial mass flux, resulting in further precipitation. Thus, the amount of wax deposited increases

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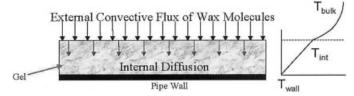


Figure 1. Wax disposition process on a cold wall.

The radial-temperature profile across the deposit, and the bulk flow is also shown.

with time. The total amount of wax deposited can be calculated by the following mass balance equation (Singh et al., 2000)

$$\frac{d}{dt} \left(\pi \cdot (R^2 - r_i^2) \cdot F_w \cdot \Delta L \cdot \rho_{gel} \right)
= (2\pi \cdot r_i \cdot \Delta L) \cdot k_M \cdot (C_b - C_i) \quad (1)$$

where R is the clean pipe radius (m), r_i is the opening radius available for flow (m), F_w is the solid wax fraction of the gel deposit, $\rho_{\rm gel}$ is the density of the gel (kg/m³), k_M is the convective mass-transfer coefficient (m/s), and C_b and C_i are the dissolved paraffin concentrations (kg/m³) in the bulk and at the oil-gel interface, respectively. Internal diffusion of wax within the "porous" gel deposit results in an increased solid wax content of the deposit, in a process termed "aging" (Singh et al., 2000). This article specifically explores the external convective mass flux of paraffins.

To determine the temperature profile, the convective heat-transfer coefficient, h (W/m²/K) has to be calculated. For the laminar flow deposition model, we calculated the Nusselt number using the Hausen correlation and Seider-Tate correlation for the thermally developing region . (Singh et al., 2000, 2001). For laminar flow with fully developed temperature profile, the Nusselt number is: Nu = 3.657 (Deen, 1998). Similarly, the Sherwood number for convective mass transfer for laminar flow with fully developed concentration profile is: Sh = 3.657.

Model for Turbulent Flow Deposition

In order to estimate the transport rates under turbulent flow without resorting to computational techniques, transport analogies are frequently used. A famous heat-transfer analogy for turbulent flow through pipes, is the Colburn equation. According to this equation, the Nusselt number is equated to the Reynolds and Prandtl numbers as

$$Nu = 0.023 \text{ Re}^{0.8} \text{ Pr}^{1/3} \tag{2}$$

It may be noted that more accurate correlations such as the one proposed by Gnielinski (1976), are available (Deen, 1998). The Colburn analogy is shown for simplicity; the analysis shown in this article can be used with any other correlation as well. The analogous correlation for mass transfer is

$$Sh = 0.023 \text{ Re}^{0.8} \text{ Sc}^{1/3}$$
 (3)

where Sc is the Schmidt number.

However, this heat-mass transfer analogy is valid only when

the temperature and concentration fields are independent. During the wax deposition process, the temperature gradient is directly responsible for establishing the concentration gradient as explained earlier. Thus, these fields are not independent. The concentration boundary layer thickness is not independent of the temperature boundary layer thickness. As a result, the heat-mass transfer analogy as described earlier is not expected to hold. Hence, we use an approach based on solubility to derive the mass-transfer coefficient.

For heat transfer

$$h \cdot \Delta T = -k_{oil} \frac{dT}{dr}$$
 (4)

For mass transfer

$$k_{M} \cdot \Delta C = -D_{\text{wo}} \frac{dC}{dr} \Big|_{i} \tag{5}$$

In the above equations, ΔT (K) is the temperature difference between the bulk (same as the center-line value in the flow-loop), and the deposit-oil interface, ΔC (kg/m³) is the dissolved wax concentration difference between these two points, $D_{\rm wo}$ (m²/s) is the diffusivity of wax in oil, and the differentials in temperature and concentration are evaluated at the deposit-oil interface.

Since Nu = $(h \cdot (2R))/k_{\text{oil}}$ and Sh = $(k_M \cdot (2R))/D_{\text{wo}}$, from Eqs. 4 and 5

$$Nu = \frac{2R}{\Delta T} \cdot \left(-\frac{dT}{dr} \right)$$
 (6)

$$Sh = \frac{2R}{\Delta C} \cdot \left(-\frac{dC}{dr} \right) \Big|_{i} \tag{7}$$

Hence

$$\frac{\mathrm{Sh}}{\mathrm{Nu}} = \left(\frac{dC/dr|_i}{dT/dr|_i}\right) \cdot \frac{\Delta T}{\Delta C} \tag{8}$$

In the case of independent heat and mass transfer, the ratio of Sh to Nu can be obtained from the correlations of Eqs. 2 and 3 as

$$\frac{Sh}{Nu} = \left(\frac{Sc}{Pr}\right)^{1/3} \tag{9}$$

This ratio can also be arrived at by estimating the gradients in Eq. 8 using computational techniques. Typically for oils, $Sc \gg Pr$ (that is, the Lewis number). Equation 9, thus indicates that the Sherwood number is higher than the Nusselt number. However, in the case of wax deposition, since the concentration at the interface is determined by the temperature (C=f(T)), the ratio of the gradients in Eq. 8 can be written as

$$\left(\frac{dC/dr|_{i}}{dT/dr|_{i}}\right) = \left(\frac{dC}{dT}\right)\Big|_{i} \tag{10}$$

The term on the righthand side of Eq. 10 is the slope of the wax solubility curve (C vs. T) at the interface temperature. An assumption made in taking this ratio is that the system is at thermodynamic equilibrium, that is, the kinetics of paraffin precipitation are much faster compared to the transport rates. We have observed this assumption to hold for model wax-oil systems used in our laboratory. This assumption also holds for some crude oils that are subjected to slow cooling rates, such as in big pipelines. However, for some crude oils the precipitation rates may be much slower, in which case the analysis has to be extended to include the kinetics, and one has to resort to computational means.

From Eqs 8 and 10, we obtain

$$\frac{\mathrm{Sh}}{\mathrm{Nu}} = \left(\frac{dC}{dT}\right)\Big|_{r} \cdot \frac{\Delta T}{\Delta C} \tag{11}$$

This equation (Eq. 11) shows the correct way of calculating the mass-transfer coefficient for wax deposition. Thus, for the wax deposition process, the ratio of the Sherwood number to the Nusselt number is a function of the solubility curve, rather than a function of the Schmidt and Prandtl numbers. Note that the Nusselt number can still be calculated by the Colburn analogy in as much as the temperature profile is established independently.

Discussion

We consider a couple of examples where the application of Eq. 11 provides some interesting insights into the transport rates.

Example 1: A model wax-oil system

We have used a model system to study the deposition process in a flow loop. A "food grade" paraffinic wax with a carbon-number distribution ranging from C23 to C40 was used as the model wax, and a mixture of mineral oil and kerosene was used as the model solvent. For this model mineral oil-wax

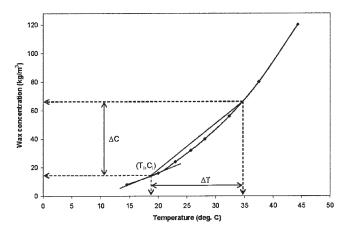


Figure 2. Solubility curve of the model wax-oil system.

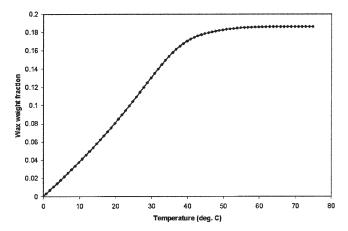


Figure 3. Solubility curve of a typical Indonesian waxy crude.

system, the shape of the solubility curve is "concave upwards" as shown in Figure 2.

Hence, when the system is subcooled, that is, the center-line temperature is less than, or equal to the cloud-point temperature

$$\left(\frac{dC}{dT}\right)\bigg|_{i} < \frac{\Delta C}{\Delta T} \tag{12}$$

Hence, for this case, the Sherwood number is *less* than the Nusselt number (Sh < Nu), although the Schmidt number is much higher than the Prandtl number. For this system, Sc \approx 2,3000 and Pr = 68. Hence, if the Colburn analogy were to be applied for mass transfer, the predicted Sherwood number will be

$$Sh = Nu \left(\frac{Sc}{Pr}\right)^{1/3} \approx 7 \text{ Nu}$$
 (13)

When a 3 wt% (~wax-in-oil mixture is used in the flow loop with the inlet temperature equal to its cloud point of 23, and the pipe wall temperature maintained at 4, then the ratio predicted by Eq. 11 is calculated to be

$$Sh = 0.4 \text{ Nu} \tag{14}$$

Use of the Colburn analogy would thus, over-predict the mass-transfer rate more than 17 times. The wax deposition model using Colburn analogy for mass transfer would, hence, over-predict the amount and rate of wax deposition, leading to unnecessarily conservative remediation strategies.

Example 2: An Indonesian crude oil

The solubility curve of a typical Indonesian waxy crude oil is shown in Figure 3. Note that this figure shows the solubility in terms on weight fraction rather than the concentration. The weight fraction can, however, be linearly scaled-up to the concentration because the densities of the wax and the oil are very similar. The solubility curve is practically linear at lower-

temperatures and then it is "concave downward" Hence, for this oil

$$\left(\frac{dC}{dT}\right)\Big|_{i} \ge \frac{\Delta C}{\Delta T} \tag{15}$$

Therefore, the Sherwood number is greater than or equal to the Nusselt number for this case. Sh \approx Nu when the centerline temperature is lower than about 35 in as much as the solubility curve is essentially linear up to this temperature. However, when the centerline temperature is higher than this value Sh > Nu. For example, if the centerline temperature is 55, and the pipe wall temperature is 4, then the ratio predicted by Eq. 11 is calculated to be

$$Sh = 1.3 \text{ Nu}$$
 (16)

Hence, the use of Colburn analogy for mass transfer will once again provide incorrect predictions (over-prediction) over the entire range of temperatures.

Conclusions

In processes, such as wax deposition in cold pipelines and frost formation on heat exchanger surfaces, the temperature gradient results in the establishment of a concentration gradient. Hence, the usual heat-mass transfer analogy by which a heat transfer correlation for the Nusselt number is used to obtain the Sherwood number by replacing the Prandtl number with the Schmidt number, is not valid for this system. An approach based on the solubility of wax in oil has been developed to derive the Sherwood number, that is appropriate for the wax deposition process. Using the Colburn analogy for mass transfer has been shown to overestimate the mass transfer rate for a model system by a factor as high as 17, which would result in overly conservative design in the oil field.

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