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A CRITICAL LOOK AT THE USE OF ACTIVATION ENERGY IN CRUDE OIL FOULING MODELS

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ABSTRACT

The assumption that the fouling process can be modeled as a chemical reaction has made activation energy a central component of many crude oil fouling models. Inclusion of activation energy and the associated semantics in fouling models imply that fouling phenomena are better understood than they actually are.

This approach does provide the basis of a semitheoretical model. However, while the approach is wellintended and rational, this paper makes the case that activation energy cannot be measured in an accurate and physically relevant manner. Using the well-established term "activation energy" forces a line of thinking consistent with the false assumption that fouling is a single, well-defined chemical reaction.

The implications of using activation energy are discussed. Additionally, fouling dependence on the exponential of reciprocal temperature is challenged, and literature data are reviewed to demonstrate that normal temperature dependence fits fouling data equally well, if not better. Until an experimental method is developed to directly and indisputably measure the activation energies involved independent of the influence of other fouling phenomena, the term "activation energy" should be avoided in future fouling models.

INTRODUCTION

Fouling deposition in crude oil preheat trains results in reduced heat recovery, which causes increased fuel consumption in furnaces and greater pressure drop, increasing pumping cost and/or reducing throughput. Fouling models, which predict the rate of fouling, can help determine optimum cleaning cycles and thus mitigate the detrimental impact of fouling. They can also be used to predict the expected fouling behavior of new crudes.

The challenge in developing fouling models is that crude oil fouling is not a simple process. To illustrate the complexity of fouling, Fig. 1 categorizes factors that influence fouling into three groups: fluid properties, surface properties, and the interface conditions between the fluid and the heat transfer surface. Each of these categories can be further expanded.

An ideal fouling model would represent the impact of *all* these factors. However, the seemingly infinite

complexity and the lack of supporting data and characterization methods require simplifications.



Fig. 1. Factors that influence fouling behavior

Activation energy is appealing because it provides a theoretical foundation for modeling fouling as a chemical reaction. However, as activation-energy based fouling models continue to be applied to increasingly complex scenarios such as crude oil fouling, the activation energy term loses its physical meaning and is in practice just another variable that is fitted to the data. Continuing to include the term "activation energy" in fouling models is detrimental to development of future crude oil fouling models because doing so implies that fouling mechanisms are better understood than they actually are.

ACTIVATION ENERGY

Brief History of Activation Energy in Fouling Models

Since the late 1960s, fouling models have contained an activation energy term (Watkinson and Epstein, 1969). In these early works, well-defined chemical reaction fouling mechanisms (indene in kerosene, styrene in kerosene, protein degradation from milk) were studied (Wilson and Watkinson, 1996; Paterson and Fryer, 1988; Crittenden et al., 1987; Epstein, 1994). These "ideal" studies included a single fouling component whose concentration was measurable. The mechanism/stoichiometry was known, and the solution is otherwise void of other physical fouling precursors, compared to crude oil. For these well-defined fouling experiments, the rationale for an Arrhenius-style rate model is a straightforward extension of chemical reaction principles, assuming that the reaction is kinetically dominated (i.e., no transport limitations) and removal is assumed to be negligible. Even in these cases, the application of the activation-energy based model is not fully consistent with the definition of activation energy, but it is an acceptable approximation.

As fouling model work progressed, authors combined the activation energy concept with the deposition-removal form of Kern and Seaton (1959) to create a second generation of models, which attempt to account for removal and transport dependence (Ebert and Panchal, 1996; Nasr and Givi, 2006; Yeap et al., 2004). These second generation models, are applied to crude oil fouling that is significantly more complex. These models have helped advance our knowledge by attempting to account for more of the factors in Fig. 1.

However, the newer models are still relevantly simple compared to the complex phenomena involved in crude oil fouling. Because these new models have multiple terms, the model constants (including activation energy) are determined, not from an Arrhenius plot, but through regression to fit a data set. Regression of parameters for any model has a compensating effect; errors and discrepancies for phenomena not captured in the model are incorporated into the resultant values.

The activation-energy parameter has become a legacy term whose value cannot accurately reflect its definition. For this reason, the authors feel the term *activation energy* should no longer be used, as it leads to misleading interpretation and comparison of activation energy values in the context of its perceived physical meaning. To illustrate this detriment, an example of a misleading interpretation is provided.

The following sections provide detailed point-bypoint arguments against the use of activation energy, supported by data from the literature.

What is Activation Energy and How is it Measured?

In the most general terms, activation energy is the minimum energy required to form or break a bond (Ebbing and Gammon, 1999; McMurry, 1999). Deposition fouling may result from a variety of mechanisms, some physical changes (precipitation, crystallization, and absorption), and some chemical reactions (adsorption, polymerization, autoxidation, coking). Regardless of the mechanisms, bonds must be formed for the material to attach. Each mechanism is dominated by different types of bonding (van der Waal interactions, ionic bonds, pi bonds, etc.) and will have an associated activation energy.

For a single-phase chemical reaction, the activation energy is determined by measuring the concentration of the products and/or reactants with time at different temperatures. These data are used to calculate the rate constant, k, for the reaction. The natural logarithm of the rate constant is plotted vs. the reciprocal absolute temperature. The activation energy is determined from the slope of a best-fit straight line through the data. Because reaction rate is a strong function of temperature, it is critical that the reaction temperature be *constant* for the duration of a given experiment.

An example is the decomposition of acetaldehyde, shown in Eq. (1) (Atkins and de Paula, 2002). In excess oxygen, the reaction is second-order (per stoichiometric coefficient of acetaldehyde), shown in Eq. (2). The rate constant is defined by the Arrhenius relationship, shown in Eq. (3). The activation energy is determined from the slope of the Arrhenius plot shown in Fig. 2.

$$5O_2 + 2C_2H_4O \rightarrow 4CO_2 + 4H_2O \tag{1}$$

$$r = k \left[C_2 H_4 O \right]^2 \tag{2}$$

$$k = A e^{\frac{-L_A}{RT}}$$
(3)



Fig. 2 Arrhenius plot for the decomposition of acetaldehyde (Atkins and de Paula, 2002)

Implications of Activation Energy

Activation energy has a well-established definition and measurement technique. Thus, adding activation energy to a fouling model initiates several implied assumptions. The following list briefly discusses each implication in the context of crude oil fouling models.

- 1 Fouling is solely a chemical reaction. This is not a bad assumption. Dominant fouling mechanisms in crude oil fouling, such as coking/aging, polymerization, and autoxidation, are chemical reactions. However, fouling is not necessarily always a chemical reaction (e.g., sedimentation, particulate embedment). Regardless of whether or not the fouling mechanism is a chemical reaction, attachment of matter to the heat transfer surface involves the formation of bonds that have an associated activation energy.
- 2. Fouling is caused by a single chemical reaction mechanism. Many fouling mechanisms, each with activation energy and temperature unique dependence. contribute can to fouling simultaneously. Each mechanism will have a unique activation energy and temperature dependence. The composite activation energy varies based on the mechanisms active for the given operating conditions. For example, it is known that around 340 °C fouling transitions from asphaltene adhesion to coking. At best, the activation energy in a fouling

model is a lumped average approach. Ideally, each mechanism could be modeled, if a method existed to properly measure each reaction's activation energy.

- 3. The reaction stoichiometry is known. The reaction stoichiometry is useful in predicting the reaction order (i.e., concentration dependence). Crude oil is composed of 10^5 to 10^6 compounds. Identifying the exact molecular details of the compounds that are responsible for fouling is an ongoing area of research.
- 4. Fouling is a single-step chemical reaction. For a complex liquid like crude oil, fouling occurs in a myriad of ways, including multi-step reactions. Watkinson and Wilson (1997) provide a summary of several proposed pathways for deposition of asphaltenes. Polymerization reactions are inherently multi-step processes. Each reaction step has a unique activation energy. Further, the factors affecting each reaction step are different (e.g., concentration, flow, temperature).
- 5. The chemical reaction rate is measured. Fouling is measured as a thermal resistance, not in chemical reaction terms (mole/time-volume). The argument that the fouling rate is proportional to the chemical reaction rate causing the fouling is straightforward and well documented (Crittenden et al., 1987). This conversion requires knowledge of the deposit density (ρ), deposit thermal conductivity (k_d), and fouling concentration in the fluid. Obtaining accurate measurements of these properties is not trivial. Simplifications assume these values are constant; however, they are likely functions of temperature, thus further complicating the accurate conversion of fouling resistance to reaction rate.
- The amount/concentration of reactants and products is quantifiable in terms of moles. Without properly measuring a chemical reaction rate in terms of moles, how can a physically meaningful activation energy reported in terms of kJ/mol be determined? An alternate approach to measuring the reaction rate of fouling is to monitor the concentration of reactants (fouling precursors) with time. As stated in item 3, identification and quantification of fouling species is an ongoing area of research. Further, it has been demonstrated that more sophisticated methods are needed as the concentration of "bad" oil components, such as asphaltenes, alone are not a reliable indicator of fouling as is evident by the concept of the colloidal instability index (Smith, 2013; Asomaning and Watkinson, 2000).
- 7. *The reaction temperature is known.* In a heat exchanger, the temperature varies from the coolest bulk temperature to the hottest wall temperature; thus, the error associated with an average value for field data is very high. Even for experimental fouling rigs, the uncertainty in wall temperature can be significant.

Cross-section wise there is a temperature gradient from the hot surface to the cooler bulk fluid. The temperature that governs fouling is a matter of debate (Epstein, 1994; Yeap et al., 2004; Crittenden

et al., 1987; Srinivasan and Watkinson, 2003). For example, the impact of bulk temperature remains unresolved. Researchers have demonstrated that increasing bulk temperature can both increase and decrease the fouling rate. There appears to be a tradeoff in solubility and transport effects. Yet bulk temperature and these other phenomena have yet to be incorporated into fouling models. Further, some precursors may require formation/reaction in the bulk fluid before attaching to the surface. Current methods offer only a best estimate, and the temperature of fouling continues to have a relatively high degree of uncertainty.

- 8. The reaction rate is measured at constant temperature. Atkins and de Paula (2002) emphasize that temperature control is paramount, as reaction rates are very sensitive to temperature. This requirement puts "severe demands" on the design of the experiment. As fouling occurs, the temperature profile through the deposit and fluid changes with time. Many fouling apparatuses operate under constant heat flux; thus, the surface temperature of the deposit is nominally constant (assuming the heat transfer coefficient is constant) throughout the test. Provided bulk temperature is well controlled, most experiments can adequately approximate constant temperature conditions.
- 9. The measured reaction rate is not diffusion limited. To measure the activation energy of a heterogeneous reaction, the reaction must not be transport/diffusion limited. For example, to measure the activation energy of a catalyst, the catalyst is pulverized to increase surface area and minimize the diffusion limitations. For fouling, this assumption is valid only at high velocity/Reynolds numbers. However, at conditions where transport is not limited (i.e., highly turbulent flow), shear stress becomes a factor. Thus, the apparent measured activation energy is a function of shear stress, whereas a true activation energy should be independent of flow conditions. Further Barrie et al (2013) demonstrated there are mathematical factors that can lead to artificial trends of activation energy with velocity.
- 10. The activation energy is specific to the reaction. In the example shown in Eqns. (1)-(3), the activation energy is specific to the decomposition of acetaldehyde with oxygen. If we presume crude oil fouling to be a reaction, it is specific to the oil and the heated surface. In literature, the activation energy is always associated with the oil, and the influence of the metallurgy is ignored. Researchers have demonstrated that surface finish and metallurgy impact fouling rate (Kukulka and Devgun, 2007; Wang and Watkinson, 2013).

Starting with a clean surface, deposition transitions from foulant attaching to the metal surface to foulant attaching to the deposit, thus, changing the chemistry of the stationary phase as fouling progresses. None of the listed implications of activation energy are fully satisfied, and few are reasonably approximated.

Conundrum of Measurement Techniques

In the literature, workers report activation energies for crude fouling that have been determined either from an Arrhenius plot or from regressing model constants to best fit a data set. Both methods have merits, but the associated caveats preclude determination of physically meaningful activation energies.

Arrhenius Plot. For well-defined chemical reactions, like the textbook example discussed previously, activation energy is measurable from an Arrhenius plot. However, when used to calculate activation energies for fouling, this method does not account for other significant phenomena that impact fouling rate such as transport, shear/removal, and asphaltene solubility. To illustrate this problem, Ebert and Panchal (1996) collected fouling data at coking temperatures (350–425 °C) over several velocities (1.2, 2.5, 3.8, and 5.2 m/s). Fig. 3 is an Arrhenius plot of the data with resulting activation energy shown (3.8 and 5.2 m/s data had zero fouling rates and cannot be plotted on a logarithmic plot). From Fig. 3, it is clear that each velocity set creates a unique trend.



Fig. 3 Arrenhius plot of Ebert and Panchal (1996) data with 1.2 and 2.5 m/s data fit together



In Fig. 4, each velocity set is fit separately, and the resulting activation energy of each is shown.

Fig. 4 Arrhenius plot of Ebert and Panchal (1996) data with 1.2 and 2.5 m/s data fit separately

It is tempting to conclude from Fig. 4 that activation energy is increasing with increasing flow. While the constant represented by activation energy seems to increase with increasing velocity, it does not make sense that velocity has a fundamental impact on the true activation energy of the reaction. The Arrhenius plot method ignores the impact of flow (shear stress and transport) on fouling. Thus, the resulting value is not the activation energy but the logarithmic rate of change of fouling rate with reciprocal temperature, which is a composite of the true activation energy, shear rate, transport dependence, solubility dependence, and any other factor influencing the fouling rate (Crittenden et al., 2007).

All that can fairly be concluded from Fig. 4 is that increasing shear stress due to increased flow results in decreasing the fouling rate.

Regression. To address flow impacts, the second generation of fouling models merged the concepts of chemical reaction fouling (Crittenden et al., 1987; Paterson and Fryer, 1988) and deposition and removal (Kern and Seaton, 1959). Ebert and Panchal (1996) modeled removal as a linear function of shear stress and included the Reynolds number in the deposition term to help account for transport phenomena. Others have followed this equation form as it accounts for three major phenomena that contribute to fouling: wall temperature, shear stress, and flow regime (Panchal et al., 1999; Polley et al., 2002a; Nasr and Givi, 2006; Polley, 2010). Joshi (2013) proposed a model for tubeside fouling test data that combines the effects of shear stress, surface, and deposit ageing. Ageing was modeled using an ageing rate parameter and normal (i.e., not reciprocal) temperature dependence.

Because these models are more complex, regression must be used to determine the constants (including activation energy) to best fit the data set. The model more accurately reproduces the data set; however, when the activation energy is regressed in an equation other than the unadulterated Arrenhius equation, the new equation dictates the definition of the activation energy. Thus, the activation energy obtained for different fouling rate models is not comparable. Data provided by Yeap et al. (2004) illustrate this drawback in their comparison of three different models (see Table 1). Each model produced a different activation energy for the same data set. Also, the method used to solve for the regressed constants and the initial guesses used can impact the resulting values. Although these models intend for the activation energy to be accurate and physically meaningful, it simply cannot be so.

When model constants are regressed to a data set, the phenomena not captured by the model are compensated in the resulting values of the constants. For example, the influence of asphaltene solubility and phase behavior, which is also temperature dependent, is incorporated into the model constants including activation energy.

Because the activation energy is nothing more than a regression constant, it seems that dividing the value by the gas constant, R, is unnecessary. Combining E_A/R into a single value (e.g., G) is a simpler and more transparent approach. The Ebert-Panchal model can then be rewritten:

$$\frac{dR_f}{dt} = \alpha \operatorname{Re}^{\beta} e^{\frac{-G}{T}} - \gamma \tau \tag{4}$$

The combined value has the same mathematical impact and is representative of the chemicalreaction/activation-energy term. However, it avoids the semantics of activation energy and any tendency to overstate the physical meaning and/or misrepresent the constant and its value for something it is not.

RECIPROCAL ABSOLUTE TEMPERATURE VS. TEMPERATURE

The adoption of activation energy brings with it the exponential reciprocal temperature dependence. In this section, the authors challenge the assumption of the exponential of reciprocal temperature dependence and argue that the exponential of normal temperature dependence is as good, if not better, for correlating fouling data. Throughout this discussion, all temperature dependences are intended as an exponential form. *Reciprocal temperature* and *normal temperature* are used to simplify the language.

Exponential Trends are Similar at High Temperature

Fig. 5 plots the exponential of $-E_A/RT$ vs. temperature for a wide range of activation energies. As shown, at the temperature range relevant to crude oil fouling, the exponential of the reciprocal temperature expression is approximately linear on a logarithmic scale.



Fig. 5. Semi-log plot of the exponential of $-E_A/RT$ with temperature for different values of E_A

Fig. 6 shows the relative error between the exponential using the reciprocal temperature and a best-fit linear trend line (i.e., a normal temperature approximation). These curves were obtained by subtracting the curves in Fig. 5 from a best-fit linear trend line and the dividing by the curve in Fig. 5 to obtain the relative error.





Experimental Error

Fouling data reported in the literature shows a high degree of scatter (Panchal et al., 1997; Yeap et al., 2004; Yang et al., 2009; Yang et al., 2011; Crittenden et al., 2007; Srinivasan and Watkinson, 2003; Bennett et al., 2009; Watkinson, 2007; Ebert and Panchal, 1996, Joshi 2013). As discussed, the temperature measurement may exhibit a high level of uncertainty. Beyond temperature measurement error, analysis of fouling rates is not straightforward, and different rates can be obtained from a single fouling curve. There is a high degree of error in both the fouling temperature and rate. Smith (2013) presented an approach using objective criteria to help standardize the fouling rate analysis; however, these techniques are an ongoing area of research at HTRI.

While crude oil fouling data are correlated to reciprocal temperature, they do not clearly demonstrate reciprocal temperature dependence. Typically, Arrhenius plots are provided with a small number of "noisy" data (< 5) over a narrow temperature range (< 100 °C). These data are equally well correlated with normal temperature (Yang et al., 2009; Yang et al., 2011; Crittenden et al., 2007; Srinivasan and Watkinson, 2003; Bennett et al., 2009; Watkinson, 2007; Ebert and Panchal, 1996, Joshi 2013). As an example to support this claim, Fig. 7 plots the data in Fig. 4 vs. temperature. Comparison of the trends and R^2 values illustrate these data are equally well fit to normal temperature. Petkovic and Watkinson (2014) presented data spanning ~200 °C that are better correlated with an exponential of normal temperature than reciprocal temperature.



Fig. 7 Natural logarithm of Ebert and Panchal (1996) plotted vs. wall temperature

Comparative graphs are shown in Fig. 8 and 9. While the R^2 values are similar, the average absolute error between the measured and predicted fouling rate is ~30% (Fig. 8) and ~20% (Fig. 9).



Fig. 8 Plot of the natural logarithm of mass deposition rate vs. reciprocal absolute film temperature (data from Petkovic and Watkinson (2014))



Fig. 9. Plot of the natural logarithm of mass deposition rate vs. absolute film temperature (data taken from Petkovic and Watkinson (2014))

The above comparison has been between linear reciprocal and normal temperature dependences. Consideration of non-straight-line dependences of either reciprocal or normal temperature would like improve the fit to the data, however, the noisy data presents challenges with confidently identifying these curves.

Temperature Dependence is More than Reaction Kinetics

If chemical reaction fouling were the only temperature dependent phenomena, there may be little room for debate about reciprocal temperature dependence. However, asphaltene solubility and aggregation are significant temperature dependent phenomena that impact the fouling rate.

Lambourn and Durrieu (1983) show that asphaltene solubility varies with temperature and that a maximum solubility temperature exists, above which asphaltenes are less soluble. Studies investigating the role of bulk temperature on fouling have presented seemingly contradictory results, suggesting there is a tradeoff in solubility and transport-related phenomena (Ramasamy and Deshannavar, 2012; Srinivasan and Watkinson, 2003).

Closely related to asphaltene solubility is asphaltene aggregation (Hoepfner, 2013). As asphaltenes precipitate, they can associate to form aggregates of varying size and complexity. Bennett (2012) presented a theory stating that for an asphaltene particulate to deposit, the bonding force has to be greater than or equal to the hydrodynamic force. Thus, for a given flow, there is a threshold particle size above which particles are too large to attach. Temperature affects the precipitation and aggregation of asphaltenes and, depending on the change in the particle size distribution, fouling can be significantly impacted. Thus, bulk temperature plays a role in fouling that is not captured explicitly by current fouling models.

Normal Temperature Dependence Offers Conveniences

Use of reciprocal temperature creates an inverse relationship with activation energy and fouling behavior (i.e., lower activation energy means greater fouling tendency and vice versa). This inverse relationship can be cumbersome compared to a direct relationship that allows a more intuitive interpretation. The authors suggest that the temperature coefficient for normal temperature dependence be called *temperature sensitivity*, defined as the natural logarithmic rate of change of fouling rate with respect to wall temperature. In contrast to activation energy, temperature sensitivity is an explicitly empirical value whose definition and measurement are congruent. Both activation energy and temperature sensitivity quantify the change in fouling rate with temperature; however, temperature sensitivity does not impose the rigid criteria of a well-established scientific term that activation energy has. The authors believe temperature sensitivity has more value to users as it explicitly informs them of how rapidly fouling accelerates per degree temperature.

EXAMPLE

Yeap et al. (2004) provide an excellent review of two leading fouling rate models [Panchal et al., 1999 (Model I); Polley et al., 2002b (Model II)] and present a new, more accurate model (Model III). Their model's equation form is significantly different, including three explicit temperature dependencies.

To aid discussion, Table 1 summarizes the pertinent data for this discussion from Crittenden et al. (1992) and Yeap et al. (2004).

			E_A , kJ/mol			
Data set	<i>T</i> _w , K	<i>V</i> , m/s	Arrhenius plot	Model I	Model II	Model III
Crittenden et al.	433-553	1.1–2.1	33	_	_	_
Н	469-543	1.37-2.55		—		68
Ι	290-491	2.08-3.94	_			32
J	381-530	0.63-1.42	_	31	48	86

Table 1 Summary of data from Crittenden et al. (1992)and Yeap et al. (2004)

This original work from Yeap et al. provides original thought and helps advance fouling modeling efforts; however, a quote from their publication illustrates a primary concern:

The value of E_A obtained for data set I [model III], near 30 kJ/mol, is similar to that reported by Crittenden et al (1992) in their analysis of refinery fouling. This value suggests a physical element to the fouling process, which could be due to diffusion or temperature dependencies in the terms within the constants. The E_A values for sets H and J are larger, suggesting that fouling in these units is more strongly linked to reaction, or that the temperature dependencies have been accounted for more successfully.

In the quote, Yeap et al. (2004) interpret the activation energy values with the assumption that the values are accurate and "suggest a physical element." They fail to acknowledge that the value was determined via regression of Model III whereas Crittenden et al. (1992) determined the activation energy from an Arrhenius plot. The method of determination results in different activation energy values, as demonstrated in the Conundrum of Measurement Techniques section. This point is also well illustrated by comparison of the E_A values for the different models for data set J in Table 1. The data set provided by Crittenden et al. (2004) was taken at a higher temperature range and at a lower velocity than data set I. As shown above, the velocity of the data set affects the resulting activation energy value determined from an Arrhenius plot. If Model III were fit to the Crittenden et al. (1992) data set, the resulting activation energy would likely be higher than 33 kJ/mol and change the conclusion made by Yeap et al. (2004). Thus, based on the information available, the authors see the similarity as a coincidence, with further effort required to make a fair comparison.

In the second half of the quote, Yeap et al. (2004) state that the large values of E_A (Model III) indicate stronger reaction dependence. The reality is actually the opposite. Fig. 5 shows that as activation energy value increases, the value of the exponential decreases; thus,

contribution from the reaction term of the model is decreased (not increased). The improved accuracy of Model III is presumably due to increased accounting for other temperature-dependent phenomena. It makes sense that the contribution of the reaction term decreases as other terms account for non-reaction, temperaturedependent phenomena.

The study by Yeap et al. (2004) is just one example in which activation energies from different sources and methods have been compared. The authors recognize the natural tendency to compare one's results against those of peers. However, comparisons must be made on the same basis; researchers should not place too much physical significance on any regression constant.

CONCLUSIONS

The authors do not dispute that chemical reactions are involved in crude oil fouling, and therefore activation energies associated with those reactions play a role in fouling. However, fouling is a complicated phenomenon, and simplifications are necessary to create a model for practical use. In making these simplifications, researchers should avoid terminology that is hard to segregate from the assumptions. *Activation energy* has a fixed scientific definition. As the authors have argued, the value represented by activation energy cannot physically or accurately represent the true activation energies involved. Continuing to use *activation energy* out of tradition only perpetuates a line of thinking congruent with these false assumptions and can lead to misinterpretation of data.

- 1. Clearly, chemical reactions and bonding are involved in the fouling process, thus, there are activation energies that describe these phenomena. However, given the extreme complexity of crude oil fouling, challenges obtaining good experimental fouling data, and deficits in thorough crude and deposit chemical characterizations, current methods do not allow activation energy, as defined by Arrenhius, to be measured from fouling data in an accurate and meaningful way. The term *activation energy* should be avoided until a technique is developed to appropriately measure the activation energy in an accurate and physically relevant manner.
- 2. Functionally, activation energy as used in current fouling rate models is a regression constant, whose definition and meaning are dictated by the respective equation.
- 3. The logarithmic fouling rate correlates equally well (if not better) with normal temperature than with reciprocal temperature.
- 4. Future fouling models should not use activation energy because the term forces a line of thinking consistent with a false assumption that fouling is a single, well-defined chemical reaction. Its use can lead to the unwarranted assignment of physical relevance to regressed values.

RECOMMENDATIONS FOR FUTURE FOULING MODELS

- 1. Combine the ratio of activation energy and the gas constant, *R*, into one appropriately labeled value [for example, *G*, Eq. (4)] so that it cannot be confused with a well-established scientific term (e.g., *fouling energy, attachment energy, temperature dependence constant*).
- 2. Include bulk temperature dependence and reevaluate the wall temperature dependence. The data reviewed in this paper indicate normal wall temperature dependence is a better fit for the data for a single temperature dependence. However, the best fit for wall temperature dependence needs to be reevaluated. Normal wall temperature dependence should be considered. Experiments should include a wider range of bulk and wall temperatures.
- 3. Devise an experimental procedure to independently and indisputably measure activation energy (not via regression) to satisfy more of the criteria described in this paper. The requirements of reducing transport limitations *and* shear stress impact lead to the idea of a stirred fouling apparatus with a very high surfacearea-to-volume ratio. Although this alone does not satisfy all the concerns the authors raised, it is a step in the right direction.
- 4. Account for key phenomena presently not modeled such as asphaltene solubility, particulate content, and particulate size distribution.

NOMENCLATURE

- *A* Pre-exponential factor, dimensionless
- E_A Activation energy, kJ/mol
- G Constant, K^{-1}
- k Reaction rate constant, $t^{-1}mol^{-1}L^{-1}$
- k_d Thermal conductivity of deposit, W/m K
- *R* Universal gas constant, kJ/mol K
- *r* Reaction rate, mol/t Vol
- R_f Fouling resistance, m² K/W
- Re Reynolds number, dimensionless
- t Time, hr
- T Temperature, K or °C
- T_{film} Film temperature, K
- T_w Wall temperature, °C
- $T_{w,abs}$ Absolute wall temperature, K
- V Velocity, m/s
- α Constant, dimensionless
- β Constant, dimensionless
- ρ Density, kg/m³
- τ Shear stress, Pa
- *γ* Constant, dimensionless

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