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ANALYSIS OF EXXON CRUDE-OIL-SLIP STREAM COKING DATA *

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ABSTRACT: Exxon Research and Engineering Co. conducted a joint research project with the U. S. Department of Energy. One part of the research was to conduct coking experiments for crude oil subjected to heat fluxes greater than typical industrial conditions. In the present study, the coking data are re-analyzed and a simplified model is developed for predicting threshold fouling conditions. Recommendations are made for future experiments and analysis of the laboratory and field data.

INTRODUCTION

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Fouling of pre-heat train heat exchangers and process heaters used for the crude-distillation unit is a major unsolved problem which costs the industry in terms of energy inefficiency and productivity loss. The complexity of the fouling problem has prevented the industry from developing effective mitigation methods. In particular, the physical and chemical mechanisms associated with crude-oil fouling are complex. Coking is a general term used for fouling at high temperatures, because the structure of the deposition resemblance to coke. In general, single-phase flow is maintained in pre-heat train heat exchangers by applying an appropriate pressure, which is reduced before crude enters into heater tubes producing two-phase flow. The interactive effects of two-phase flow in tubes, outside combustion-heat transfer, and coking are the major sources of operational problems. Maldistribution of vapor and liquid phases produced in the U-bend region of the process heaters could promote localized coking that may eventually cause tube failure.

Several investigations have been carried out to characterize crude-oil fouling. Crittenden et al. [1992] obtained the performance data for selected individual pre-heat train heat exchangers and correlated the linear-fouling rate with the tube-wall temperatures. Lawler [1979] analyzed the effects of fouling on the overall performance of individual preheat-train heat exchangers and found that two commercial antifoulants they used were ineffective. Leach and Factor [1981] conducted a similar study to monitor performance of three high-temperature preheat-train heat exchangers for a period of 200 days. They found that the use of an antifoulant

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reduced the decline of the heat-exchanger performance and provided an economic analysis using the field data. They indicated that monitoring of the overall performance provides a practical tool for developing an effective fouling-mitigation method.

Investigations [Dickakian and Seay, 1988; Eaton and Lux, 1984] have been carried out to understand the mechanism of asphaltene deposition. Speight [1980], and Dickakian and Seay [1988] suggested that the molecular weight for asphaltenes can range from 1250 to 2000. Solubility of asphaltenes in different crudes is a major issue regarding fouling, because its presence is not necessarily an indicator of fouling propensity. The effects of other species (resins, brine, particulate, dissolved metals, and sulfur compounds) present in crude have not been fully characterized. The analysis of deposits collected by Eaton and Lux [1984] for three different crudes indicated that pentane soluble resins and toluene soluble asphaltene fractions were in the range of 12 to 31%, and 3 to 6%, respectively. The ash fraction was in the range of 9 to 54%, which indicates that inorganic compounds play an important role in the overall fouling process. Iron was found in all samples, along with sodium, chloride, and sulfur. Eaton and Lux [1984] investigated the effects of resin and asphaltene pitch on the relative rate of deposition. The results indicated that the deposition derived from the laboratory unit was representative of that obtained from refinery heat exchangers. A logical next step is to quantify the effects of physical parameters and determine threshold fouling conditions using a laboratory fouling unit that can simulate appropriate fluid dynamics of the field unit.

Fouling in crude process heaters is a major issue. Sprague and Roy [1990] summarized technical issues associated with fouling of process heaters. The fluid dynamics associated with two-phase flow and combustion heat transfer promote localized fouling deposition. The development of a methodology to use the laboratory data and predict threshold fouling conditions for process heaters is a crucial issue. Wood and Marino [1991] reported that the run time was significantly increased by adjusting operating conditions and making some design changes for a process heater used in the visbreaking operation. The case study of Wood and Marino [1991] may not be applicable to all processes, but it provides a clue that the fouling propensity can be significantly reduced by following appropriate design and operating guidelines.

The purpose of the present analysis is to examine the data obtained by Scarborough et al. [1979] in a joint research project with the US Department of Energy. The data were re-analyzed to develop a simple model to predict threshold fouling conditions. A model of this type should be able to predict threshold-fouling conditions after it is validated with a limited number of data points for a given crude quality. Also, such a model can predict the effects of change in operating conditions, such as heat flux and fluid velocity, on the relative rate of fouling deposition.

EXXON STUDY

The fouling study [Scarborough et al., 1979] was a part of the joint program between Exxon Research and Engineering Co. [1978] and the US Department of Energy for the development of fluidized-bed combustion (FBC). A crude-oil stream was obtained from a preheat-train heat exchanger at about 232 °C, pumped to 41.5 bar pressure to suppress boiling in the test section, heated to a temperature of about 343 °C in a gas-fired process heater, routed through four parallel-test sections (A,B,C and D) heated by radiant-electric heaters, and returned to the plant. Each test section was a 25.4 mm (1") scheduled XX stainless steel pipe (inner diameter of 15.2 mm) with nine thermocouples embedded near the inner surface at 0.3 m (1 ft.) apart from inlet to outlet.

Summary of Results

A summary of the test data is shown in Table 1. A series of four test runs was conducted with four parallel test sections. However, some of the test sections were not functional for all tests; therefore, the number of useful data points was 11 instead of 16. The fouling resistance was calculated as an average of all the locations. A detailed discussion of the observed fouling trends was reported by Exxon Research and Engineering Co. [1978] and a summary was presented by Scarborough et al. [1979]. Significant fouling was observed at calculated film temperatures in the range of 370 and 400 °C with velocities of 1.2 and 2.5 m/s. No detectable fouling was observed at similar wall temperatures but with velocities of 3.8 and 5.2 m/s. Fluid properties were not given in the original reports. However, on the basis of the calculated results, it was possible to calculate the properties. They are shown in Table 2.

TABLE 1
Summary of Exxon Coking Tests.

	Test 1			Test 2				Test 3	Test 4		
Test Section	A	C	D	A	B	C	D	D	A	C	D
Test Period, hr.	93	132	40	402	314	402	142	191	406	392	406
Temperature, °C											
Inlet	352	349	343	346	343	341	338	338	336	340	338
Outlet	366	377	399	358	358	362	382	367	353	365	352
Average wall	394	414	467	382	386	397	432	401	374	404	376
Velocity, m/s	5.2	2.5	1.2	5.2	3.7	2.5	1.2	1.2	1.3	2.5	2.5
Fouling rate, (m^2 K/kW)/hr	Nil	.0033	0.02	Nil	Nil	.0028	.0115	.0079	.0056	.0041	.0013

TABLE 2
Crude oil properties.

Properties	Values
Pressure	41.5 bar
Temperature	354 °C
Density	560 kg/m^3
Specific heat	3.35 kJ/kg K
Thermal Conductivity	0.1 W/m K
Viscosity	0.24 10^{-3} Pa.s

Pressure Drop

The pressure-drop data for Test 2D from Quarterly Report No. 8 [1978] were analyzed. The observed sharp increase in pressure drop during the first few hours of test run can be explained on the basis of rapid initial fouling and breaking of deposits that produce rough surfaces. The measured pressure drops at initial, start of run, and end of run were 2.8, 4.1 and 4.6 kPa respectively. The deposit roughness was estimated on the basis of the known thermal resistance, deposit thickness, pressure drop, and heat-transfer and friction-factor correlations. The calculated deposit roughness at the initial time and beginning of the test run were 0.1 and 0.3 mm respectively. The roughness remained relatively constant during the test period. The sharp increase in the surface roughness results in not only increase in the friction factor but also a reduction in the film temperature for a given heat flux. The roughness produced by the initial deposition seemed to be dependent upon the fluid velocity. The change in the surface roughness is of practical importance; therefore, pressure-drop measurements should be reported in a fouling research.

DEVELOPMENT OF THRESHOLD MODEL

The classical-fouling model [Kern and Seaton, 1959] is based on the assumption that the net rate of fouling is deposition minus removal. Applicability of such a model to crude-oil fouling needs to be established. Panchal and Watkisnson [1993] and Crittenden et al. [1987] showed that relatively complex model may be required to determine the effects of physical parameters on the fouling rate for petroleum products. Crittenden et al. [1987] assumed that a single-step reaction occurs at the fluid-solid interface. Panchal and Watkinson [1993] developed an analysis assuming reactions can occur in the bulk of fluid, in the thermal-boundary layer or at the interface. Such models are useful to determine the controlling mechanisms; however, determination of unknown constants is an elaborate task. They can be simplified by assuming limiting cases in which the mass-transfer resistance is negligible [Paterson and Fryer, 1988] or the kinetic rate for governing reactions is relatively high.

The present investigation is focused on the development of a simplified correlation for predicting threshold fouling conditions on the basis of the following assumptions:

1. The net deposion is given by formation minus removal of foulant from the thermal-boundary layer,
2. Foulant is formed in the boundary layer by reactions which can be grouped as one-step reaction,
3. Concentration gradients of reactants in the boundary layer is negligible,
4. Foulant is transported by diffusion and turbulence eddies from the boundary layer to the bulk flow,
5. Temperature profile in the boundary layer is linear, and
6. An integrated reaction term can be expressed by the film temperature in the boundary layer.

The Exxon data indicated that by increasing the mass velocity at constant film temperature, the rate of fouling deposition is reduced. This can be explained on the basis of the combined effects of reduced thickness of the boundary layer and increased removal of foulant. A simple diffusion type equation for foulant may not be justifiable. Several turbulence theories have been suggested for removal of particulate from the surface [Epstein, 1988]. These theories were developed for predicting removal of particulate from the surface. The focus of the present study is on foulant removal from the boundary layer. The mechanisms for removal of foulant from the boundary layer and surface may be different. Removal of foulant from the boundary layer can be explained on the basis of the transport mechanims; however, removal of deposists from the surface may be explained on the basis of a mechanism such as the turbulence-burst theory discussed by Epstein [1988]. A focused investigation is needed to understand the mechanism for removal of foulant from the boundary layer. In the absence of a detailed analysis, the wall-shear stress is used as a representative parameter.

The proposed correlation for predicting the linear rate of fouling and threshold film temperature and fluid velocity is as follows:

$$\frac{dR_f}{dt} = \alpha \, \mathrm{Re}^{\beta} \exp(-E / RT_f) - \gamma\tau \tag{1}$$

Foulant forming reactions are assumed to occur in the thermal-boundary layer at a mean film temperature T_f. Subsequently foulant is removed from the thermal-boundary layer by the transport mechanism, including the turbulent eddies. The net rate of deposition is difference between the rate of formation of foulant and removal. If the rate of removal of foulant from the thermal-boundary layer is greater than the rate of formation for a given set of operating conditions, negligible fouling is expected.

The correlation shown by Equation 1 differs from the Kern-Seaton correlation as follows:

1. The proposed correlation is intended for predicting the film temperature at which initiation of fouling would occur. The Kern-Seaton correlation is intended for predicting an asymptotic fouling resistance.
2. The rate of deposition and removal is assumed to be independent of the fouling-film thickness. The rate of removal of deposists is proportional to the fouling film thickness in the Kern-Seaton correlation.
3. In the proposed correlation, foulant is assumed to be removed from the thermal-boundary layer by the transport mechanisms. In the Kern-Seaton correlation deposits are assumed to be removed from the surface by a detachment process.
4. A term representing the formation of foulant is included in the proposed correlation, while the Kern-Seaton correlaiton does not have such a term.

Temperature is assumed to vary linearly in the thermal-boundary layer. Assuming constant reactant concentration, the local rate of reaction for an incremental boundary layer of dx and for an unit cross-section area can be expressed by the Arrhenius equation as follows:

$$r = A \exp(-E/RT)\, dx \tag{2}$$

This equation needs to be integrated for the boundary layer from film thickness of 0 to δ to obtain an integrated average kinetic constant, $\bar{k}$ as shown below:

$$\bar{k} = \frac{A}{\delta} \int_0^{\delta} \exp(-E / RT) dx \tag{3}$$

A simple analytical solution for Equation 3 is not possible; therefore, an appropriate numerical method is required to calculate an average kinetic constant. Alternatively, the Arrhenius equation can be linearized [Paterson and Fryer, 1988] for a reference temperature resulting into an analytical solution in the following form:

$$\bar{k} = \frac{R}{E} k(T_b)\left(\frac{T_b^2}{T_b - T_i}\left(1 - \exp(a(T_b - T_i))\right)\right) \tag{4}$$

where $a = E / RT_b^2$

In order to evaluate the relative errors in various assumptions, Equation 3 was evaluated by various methods. The methods and corresponding results are summarized in Table 3. For the sake of brevity, frequency factor, A was not included in the integration. The temperature range was divided into 20 increments for the Simpson's numerical integration method. The numerical value was used to compare the results from other methods. The first set of values in Table 3 is representative of the range of conditions for the Exxon data. A higher wall temperature was used for the second set of values. The integrated value using the linearized approach of Paterson and Fryer [1988] was about 5% greater than the reference value. Next the Arrhenius equation was evaluated at bulk, wall and midpoint temperatures and an average value was calculated. The two-point, bulk and wall, average gave significantly higher values; however, three point average was close to that predicted by the linearized method. The value calculated at midpoint was about 4% lower than the reference value. The Arrhenius equation calculated at the film temperature, T_f, shown by Equation 5, was generally close to the integrated value for two sets of conditions shown in Table 3. However, the other methods diverged significantly from the reference value for the wall temperature of 450 °C.

$$T_f = T_b + 0.55\,(T_i - T_b) \tag{5}$$

TABLE 3

Comparison of integrated and averaged value of the Arrhenius equation.

Parameters	Value			
Input Parameters				
Energy of activation, kJ/mol	69		69	
Bulk temperature, °C	343		343	
Wall temperature, °C	399		450	
Methods	value 10^{-6}	relative value	value 10^{-6}	relative value
Numerical integration	1.78	1.0	3.25	1.0
2 point average	1.94	1.09	4.10	1.26
3 point average	1.86	1.04	3.67	1.13
Linearized integration	1.86	1.05	3.91	1.21
Mid point temperature	1.71	0.96	2.83	0.87
Film temperature	1.80	1.01	3.13	0.96

The linear rate of fouling reported in the Exxon study was used to determine the four constants in Equation 1. A nonlinear regression analysis was used to minimize the error function and determine the four constants. The resulting values for the four constants are as follows:

α = 30.2 10^6 (K m^2/kW)/hr
β = -0.88
E = 68 kJ/mol
γ = 1.45 10^{-4} m^2/N (K m^2/kW)/hr

These constants are acknowledged as inexact because the number of data points was limited and the measurement accuracy could not be estimated. Nevertheless, constants β and E have a physical significance. The reported [Crittenden, 1992; Watkinson, 1988] activation energy E for crudes is in the range of 20 and 55 kJ/mol. The present value of 69 kJ/mol for the activation energy is greater than reported values in the literature, which include the combined effects of chemical reactions and physical processes. The physical processes are less dependent on the temperature than the chemical reactions; therefore, the calculated value of E is generally lower when the effects of physical processes are not separated out in the analysis of the data. A value of 0.88 for β validates the argument that the Reynolds number term in Equation 1 determines an effective-film thickness for the thermal-boundary layer. The interactive effects of fluid velocity and temperature distribution in the thermal-boundary layer is presented in the first term by a simplistic but representative manner. In a practical approach, constants are determined using the laboratory data for a wide range of conditions. Subsequently, a limited number of test runs from the field site will be used to validate the correlation. Applicability of such a simple correlation to determine threshold fouling conditions is quite appealing, provided it can be used for a practical range of operating conditions. If experimentally and analytically proved, the simple correlation shown in Equation 1 may be applicable to two-phase flows with inclusion of appropriate terms for calculating the thermal-boundary layer and the wall shear-stress.

The data and predicted rates of fouling are shown in Figure 1. It also shows the fouling rate for three velocities for which negligible fouling was detected. For a given velocity, the fouling rate remains negligible until a threshold temperature is reached above which it rapidly increases with temperature. The threshold temperatures for the fluid velocities of 1.2, 2.5, 3.8, and 5.2 m/s were about 255, 331, 410, and 466 °C, respectively. The results show that fouling deposition would be negligibly small, if the film temperature is maintained below the threshold value for a corresponding fluid velocity. Note that the threshold-film temperature increases sharply with velocity.

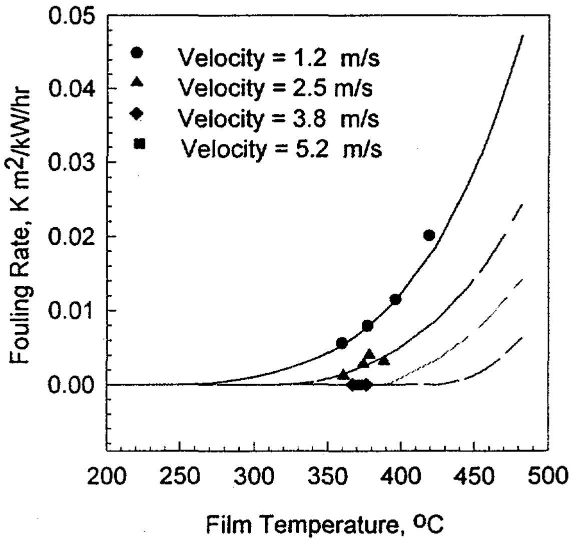

Figure 1. Comparison of experimental and predicted fouling rates.

Threshold temperatures can be estimated by equating Equation 1 to zero, and a plot similar to that shown in Figure 2 can be prepared. Negligible fouling is expected for film temperatures and fluid velocities to the right and below the threshold line. For industrial uses, this is an important kind of result that can be achieved from a fouling research, because defining the boundary between fouling and non-fouling conditions is a major design issue for the heat-exchange equipment. However, if the equipment cannot be designed to operate below threshold conditions, then appropriate chemical additives can be added or physical devices can be developed to change the threshold line. Therefore, the development of such threshold lines with different levels of chemical additives should serve the industrial needs to develop effective fouling-mitigation methods without excessive use of additives.

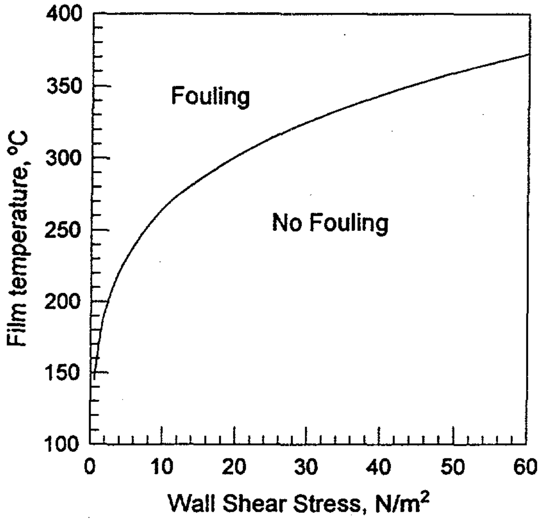

Figure 2. Threshold-film temperature as a function of wall shear.

EXPERIMENTAL EXPERIENCE

Important experience can be derived from the Exxon fouling research. The recent field tests by Crittenden et al. (1992) should also be useful for future experiments and ways to analyze the data. Some of the key observations made in the present re-analysis of the Exxon research project are summarized in this section.

1. Threshold-film temperatures increases sharply with increasing crude velocity.
2. In order to establish a correlation to predict threshold conditions, two or three fluid velocities, for which finite fouling rate can be determined, should be used in fouling experiments. Subsequently, few data points with negligible fouling should be used to validate the correlation.
3. Fluid properties used for analyzing the experimental data should be reported in the technical report.
4. The test apparatus must be checked with a non-fouling fluid to establish the measurement accuracy and the heat-transfer performance. The quality of the Exxon data may have suffered due to lack of these measures.
5. Simultaneous monitoring of heat-transfer resistance and pressure drop across the fouling zone are essential to assess the film temperature and shear stress.

6. Significant fouling deposition occurred during startup of some of the tests. This may have changed the surface characteristics of the wall surface, possibly creating unknown level of surface roughness.
7. Consistent startup procedure should be used. Starting with maximum possible velocity with low heat flux is highly recommended. The heat-transfer monitor should not be preheated to temperatures greater than the test value before the steady-state flow can be fully established. Starting with a cold heat-transfer surface may deposit wax or resin. A good approach is to preheat the monitor close to the fluid temperature before starting flow.
8. Preserving fouling deposits at the end of a test run requires a careful shut-down procedure. In the Exxon procedure, the heater power was first turned off, followed by a few minutes of flow before flow was stopped. The left over fluid was immediately displaced with nitrogen before significant cooling could occur.

SUMMARY

The analysis of the Exxon data provided general guidelines to obtain quality data from a field unit. A simple correlation for crude-oil fouling was developed on the basis of a limited number of data points. Such a correlation could serve as an analytical tool to develop a computerized procedure to monitor effects of change in operating conditions and the effectiveness of mitigation methods on fouling of preheat-train heat exchangers.

NOMENCLATURE

A = frequency constant in Equation 2, mol/s m^3
E = activation energy, kJ/mol
$\bar{k}$ = average kinetic constant, mol/s m^3
r = rate of reaction, mol/s
R = gas constant, kJ/mol K
Rf = fouling resistance, m^2 K/kW
T = temperature, K or °C
Re = Reynolds number
α, β, γ = undetermined constants in Equation 1
δ = boundary layer thickness, m
τ = wall shear stress, N/m^2

Subscripts

b = bulk
f = film
i = interface

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