A systematic study of the fouling characteristics of organic fluids was conducted in an annular test section. The study consisted of four main parts. First, the effect of key factors such as surface temperature, velocity, concentration, and oxygen on fouling from the system styrene-heptane-polystyrene was investigated. While surface temperature increased fouling considerably, higher velocities limited it. At high temperature and low velocity, higher concentrations of precursor increased the fouling rates while at low temperature and high velocity, concentration had no effect. Fouling rates and delay times were lower with oxygen present.

Second, the effect of a variety of organic sulfur compounds on fouling from the styrene-heptane-polystyrene system was studied. With 100 ppm sulfur, sulfides in general, lowered the extent of fouling while thiols completely inhibited it. A disulfide showed an
intermediate action. With only 10 ppm sulfur from n-dodecanethiol added, the fouling rate approached that of the sulfur-free system.

Third, chemical reaction fouling under subcooled boiling conditions was modeled. The new model was applied and tested with the fouling data and the independent kinetic data obtained for the system studied in part one. Deviations between model predictions of the initial fouling rate and the experimental values varied from 13% to over 100%.

Fourth, fouling from two batches of crude oil residuum was investigated. The threshold surface temperature for fouling to occur was about 790°F for the first batch while it was only between 575 and 600°F for the second batch. Higher temperatures increased fouling but the effect of velocity was complex.
Fouling Characteristics of Organic Fluids

by

Lounes Oufer

A THESIS
submitted to
Oregon State University

in partial fulfillment of
the requirement for the
degree of

Doctor of Philosophy

Completed February 2, 1990
Commencement June 1990
ACKNOWLEDGMENTS

Behind every accomplishment, I believe there is lots of hard work but there are also lots of help and encouragement from others. This, in my opinion, can change things to the point where hard work may even seem to become just fun. I therefore would like to express my sincere gratitude to the following:

My advisor, Dr. Knudsen, who not only gave me the opportunity to carry on this research, but also allowed me to jump above the usual advisor-student relationship. Thanks, Boss.

The Algerian government for its financial support in the form of a scholarship.

Heat Transfer Research Inc. (HTRI), Alhambra, California, for their funding of this project.

The faculty members in the Chemical Engineering Department, in particular, Dr. Mrazek, Dr. Levien and Dr. Sproull for their very valuable suggestions related to this work and Dr. Wicks and Dr. Levenspiel whose help I have never been denied.

Dr. McGuire and Dr. Thomas for their valuable time and effort.

Belaid Mahiou and Michele Croghan whose company I will always miss.
Nick Wannenmacher, not only for his invaluable technical assistance but for his very special everlasting friendship. Thanks Nicki for being yourself and for the wonderful times we shared.

Vi Campbell, for typing this thesis in such a short period of time.

Finally, my family, especially my mother who a long time ago already did the largest part of the hard work which allowed me to start my education and my brother, who always encouraged me to go farther.
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k  reaction rate constant, $L^{1-n}mol^{1-n}hr^{-1}$ or 
    $ft^{3(n-1)}lb_m^{1-n}hr^{-1}$

$k_c$  mass transfer coefficient, $ft/hr$

$K_m$  constant in Eq. G.4

$K^*$  constant in Eq. 3.20

L  heated length, $ft$

m  mass of deposit per unit area, $lb_m/ft^2$

m  exponent in Eq. 8.22

M  molecular weight

n  reaction order

N  mass flux, $lb_m/hr ft^2$

P  pressure, $lb_f/in^2$

P  degree of polymerization

q  heat to be transferred, $Btu/hr$

-r  reaction rate, $mol L^{-1}sec^{-1}$

R  universal gas constant

$R^2$  regression coefficient of determination

$R_b$  deposit bond resistance

Re  Reynolds number

$R_f$  fouling resistance of deposit, $hr ft^2 °F/Btu$

$R_f^*$  asymptotic value of $R_f$, $hr ft^2 °F/Btu$

$R_{f0}$  initial fouling rate, $ft^2 °F/Btu$

$R_w$  wall thermal resistance, $hr ft^2 °F/Btu$

Sc  Schmidt number

t  time, hr
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</tr>
<tr>
<td>$x$</td>
<td>thickness, ft</td>
</tr>
<tr>
<td>$x$</td>
<td>vapor quality</td>
</tr>
<tr>
<td>$x_i$</td>
<td>independent variable</td>
</tr>
<tr>
<td>$X$</td>
<td>chemical conversion of reactant</td>
</tr>
<tr>
<td>$Y$</td>
<td>dependent variable</td>
</tr>
<tr>
<td>$Y$</td>
<td>mole fraction</td>
</tr>
</tbody>
</table>

**Greek symbols:**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>constant in Eq. G.4</td>
</tr>
<tr>
<td>$\Delta h_v$</td>
<td>latent heat of vaporization, Btu/lb$_m$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>thickness of laminar sublayer, ft</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>relative error, %</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>parameter in Eq. 3.22</td>
</tr>
<tr>
<td>$\mu$</td>
<td>dynamic viscosity, lb$_m$/hr ft or cP</td>
</tr>
<tr>
<td>$[\mu]$</td>
<td>intrinsic viscosity, cc/g</td>
</tr>
<tr>
<td>$\mu_{sp}$</td>
<td>specific viscosity</td>
</tr>
<tr>
<td>$\Pi_1$</td>
<td>quantity given by Eq. 3.22</td>
</tr>
<tr>
<td>$\Pi_2$</td>
<td>quantity given by Eq. 3.23</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density, lb$_m$/ft$^3$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>shear stress, lb$_m$/hr ft$^2$</td>
</tr>
</tbody>
</table>
\( \phi_d \) deposition rate of foulant, \( \text{lb}_m/\text{hr ft}^2 \)

\( \phi_r \) removal rate of foulant, \( \text{lb}_m/\text{hr ft}^2 \)

\( \phi_{Td} \) fouling rate increase by deposition of tar-like products (Eq. 3.27), \( \text{ft}^2 \ °\text{F/Btu} \)

\( \phi_{Tr} \) fouling rate decrease by back convection of tar-like products to bulk fluid (Eq. 3.28), \( \text{ft}^2 \ °\text{F/Btu} \)

\( \phi_{CT} \) net fouling rate decrease by conversion of tar-like products to coke (Eq. 3.29), \( \text{ft}^2 \ °\text{F/Btu} \)

\( \phi_{Fr} \) fouling rate decrease by removal of tar-like products by fluid shear forces (Eq. 3.30), \( \text{ft}^2 \ °\text{F/Btu} \)

\( \psi \) parameter function of deposit structure

**Subscripts:**

A refers to reactant A

b bulk

b boiling

d dissociation

f foulant

f film

i solid-fluid interface

i initiation

l liquid

M monomer

p propagation
P  precursor
s  surface
S  solvent
t  termination
v  vapor
w  wall
0  at initial conditions
2  refers to second order reaction
5/2 refers to 5/2 order reaction
FOULING CHARACTERISTICS OF ORGANIC FLUIDS

CHAPTER 1

INTRODUCTION

The formation of deposits on heat exchanger surfaces in contact with hydrocarbon streams may have disastrous consequences for process industries such as the petroleum, chemical, and food industries. In the early 1980's the total costs related to fouling for the non-communist world refineries alone were evaluated at 4.41 billion dollars [1]. The various cost penalties include a drop in the efficiency of heat transfer equipment, higher pumping costs, chemical and/or mechanical cleaning and loss of production.

Although numerous studies have been reported in the field of organic fouling (also known as chemical reaction fouling), the phenomenon is still not well understood. There is a need for more thermal studies where a model fluid should be used. Only if the precursor-foulant system is well known would a good understanding of the overall process be possible. It is believed that a system with simple kinetics is the best way of investigating the role of key parameters such as surface temperature, velocity, and stream concentration on fouling. Further, there is
also a need for fouling research under boiling conditions.

The objective of this research is to help understand organic fouling in general by focusing on the mechanism in which a single reaction takes place. The work was sponsored by Heat Transfer Research Inc., Alhambra, CA. The effects of major variables on fouling rates were experimentally investigated, mainly under subcooled boiling conditions. These variables were respectively the surface temperature of the heating element, the bulk fluid velocity and the bulk fluid precursor concentration. For most of the study, the precursor-solvent-foulant system was chosen as styrene-heptane-polystyrene. The effect of oxygen and a variety of organic sulfur compounds on the fouling tendencies of this system were also investigated. Finally, fouling of a heavy crude oil residuum (Crude Resid) supplied by the Chevron Corporation was tested.

This thesis is divided into ten chapters. Chapter 2 presents some background on fouling heat transfer in general. Chapter 3 is a literature review of the most relevant work reported in the area of chemical reaction fouling. A separate kinetic study on the solution of polymerization of styrene in heptane was conducted to determine the kinetics of this system. This experimental investigation was performed in a mixed stainless steel batch reactor and is reported in Chapter 4 before the fouling studies.
Chapter 5 consists of a detailed description of the experimental apparatus which was built specifically to carry on organic fluid fouling research. The study presented in Chapter 6 deals with chemical reaction fouling occurring from the formation and deposition of a polystyrene film on a heat transfer surface. The bulk fluid stream consisted of small amounts of styrene monomer dissolved in heptane. The investigation was carried out in both the presence and the absence of oxygen to test its possible effect on fouling. Local boiling on the heat transfer surface prevailed in all experiments.

The effect of a variety of organic sulfur compounds having different chemical structures on fouling from the polymerization of styrene dissolved in heptane was studied. The results are given in Chapter 7. In Chapter 8, chemical reaction fouling under boiling conditions is modelled for the first time to the best of the author's knowledge. The special case of the second order chemical reaction presented in Chapter 4 is applied. The model takes into account the effect of the extra turbulence created by bubble formation on mass transfer of precursor to the reaction zone adjacent to the wall. The model is then tested with the experimental data reported in Chapter 6.

Fouling from an Alaskan North Slope crude oil residuum supplied by the Chevron Corporation was investigated and the results are reported in Chapter 9. The threshold
surface temperature for fouling to occur was determined for the two different batches of crude resid received from the supplier. The effect of fluid velocity was also studied.

Finally, in Chapter 10 the various results of this work are summarized. From the given conclusions, recommendations for future work are included. At the same time, some design suggestions are given which would help limit the extent of fouling resulting from chemical reactions.
CHAPTER 2
BACKGROUND ON FOULING

Introduction

As interesting as it seems to be and despite all the damage and inconvenience that may result from it, fouling still remains the least understood phenomena in the field of heat transfer [2]. If one were to ask the meaning of fouling to most undergraduate or even graduate students, the response expected would be a mention of a heat exchanger being covered by a deposit of some kind. Awareness of the fouling problem in general only seems to be directed toward purely industrial applications and therefore there is a lack of intensive research on the subject.

It is critical for the future of research related to the fouling phenomena to provide some incentives to engineers and researchers to work in this area. Chemical engineers can for example be involved in studying fouling of human lungs by cigarette smoke. How about fouling of our skin in an environment containing chemical pollutants. Our body is a complicated heat exchanger. We need to make people think more about fouling.

If human skin may be easily irritated by a small temperature difference of 30°C or less between our body and ambient, then think what it will be for a heat exchanger in
which the surface temperature can be higher than that of
the bulk fluid by a few hundreds of degrees. It is
important that chemical engineers be aware of the fouling
problem to provide ideas on how the problem can be solved.
Even without a complete solution, the losses due to fouling
would be reduced because of a much better understanding of
the situation.

2.1 General Classification of Fouling

Because problems arising from fouling occur in so many
different areas whether as part of the chemical process
industries or just as part of mother nature's behavior,
researchers in the field have in general agreed on an
overall classification of fouling [3,4,5]. Six major types
of fouling have been defined which are briefly described
below:

a. Chemical Reaction Fouling

This class involves the most diverse situations in
fouling. Chemical reaction fouling deals with material
deposition on a surface after a chemical reaction has
occurred. The surface itself is not a reactant but may act
as a catalyst. This type of fouling may be encountered in
a wide range of applications from nuclear energy to
chemical production and from petroleum refining to food
processing.

b. Particulate Fouling
Considerable interest has been given to this category of fouling over the years. It involves the deposition of suspended particles in a fluid onto a heat transfer surface. These particles can be anything from air-borne dust to coal to corrosion products.

**c. Precipitation Fouling**

Also referred to as crystallization fouling, this class is mainly the domain of deposition of dissolved salts on a heat transfer cold surface. Cooling tower water is perhaps the most investigated area related to precipitation fouling.

**d. Corrosion Fouling**

This class differs from chemical reaction fouling because the metal surface itself participates in the chemical reaction that results in corrosion products. In this case and in contrast to most other categories of fouling, periodic cleaning of the surface is not sufficient to restore the original heat transfer efficiency. Instead, the equipment has to be replaced completely because of severe degradation of the heat transfer duty and the structural integrity of the equipment.

**e. Freezing Fouling**

This type of fouling occurs by solidification of a fluid on a cold surface. Not very much work has been done in this area probably because of its limited applications.
f. Biological Fouling

This is in essence the area where as mentioned previously nature plays an important role. Marine microorganisms may adhere strongly to any surface such as that of a boat, oil platform, or any part of a cooling system in a power generating station using sea water as a coolant. Biological organisms can also be present in fresh water exposed to any extent to the surrounding environment.

2.2 Mechanism of Fouling

2.2.1 Introduction of Fouling Quantities

In practical situations the extent of fouling, which is defined as the deposition of any type of solid material onto a solid surface, can be followed in time in three different ways. These are based on measurement of either the thickness of the deposited material, the mass of material deposited or the rise in wall temperature (or decrease in overall heat transfer) as fouling takes place on the heat transfer surface. This last method, more generally referred to as thermal fouling, involves a quantity called the fouling resistance which is a thermal resistance with units of hr ft² °F/Btu (m² °C/W).

The various quantities involved in the three methods mentioned above are related as shown by Equation 2.1

\[ R_f = \frac{X_f}{k_f} = \frac{m_f}{\rho_f k_f} \]  

(2.1)

where,
Although the thermal method of studying fouling seems to be much more attractive than the other two for obvious reasons of simplicity and accuracy, it has also been criticized [6] for not being a direct physical method when in fact the problem which we are dealing with is a purely physical one.

For heat exchanger design purposes, the major source of fouling data are the well known TEMA tables [7] which list values of $R_f$ for various types of fluids. Despite their recognized lack of accuracy, these tables have been used for years to account for the effect of fouling which usually leads to oversizing the heat exchanger to be used for a specific heat duty. No such tables yet exist on either thickness or mass of deposit for any type of fouling categories. Knudsen [8] identifies that the basic problem in heat exchanger design lies in the inappropriate values of the fouling allowances used. The simple solution of overdesigning a heat exchanger to override fouling can be very detrimental [9].

2.2.2 Determination of the Thermal Fouling Resistance

In practice the determination of the fouling resistance $R_f$ relies on temperature and flow rate
measurements of the hot and cold fluids. Figure 2.1 defines the various terms used and shows the single resistances to heat flow from the metal wall to the flowing fluid for each situation. The subscript (o) is used to refer to the clean unfouled surface. In this analysis, the temperature of the wall, $T_w$, is known at some location below the surface of the metal. For example, it could be the temperature indicated by a temperature sensor embedded in a tube wall.

For the clean and fouled surfaces, the overall resistance (between the temperature sensor and the bulk fluid) to heat transfer is given by the expressions:

$$\frac{1}{U_o} = \frac{T_{wo} - T_{bo}}{(q/A)_o} = R_w + \frac{1}{h_o}$$ \hspace{1cm} (2.2)

$$\frac{1}{U} = \frac{T_w - T_b}{(q/A)} = R_w + R_f + \frac{1}{h}$$ \hspace{1cm} (2.3)

where,

$U = \text{overall heat transfer coefficient}$

$h = \text{convective heat transfer coefficient}$

$T_w = \text{temperature at the inner wall}$

$T_b = \text{temperature of the bulk fluid}$

$q = \text{heat to be transferred}$

$A = \text{heat transfer area}$

$R_w = \text{wall thermal resistance} = \frac{x_w}{k_w}$, where

$x_w = \text{wall thickness and } k_w = \text{wall thermal}$
Figure 2.1 Definition of various terms involved in thermal fouling
conductivity

\[ R_f = \text{fouling resistance} \]

Subtracting Equation 2.2 from Equation 2.3 leads to

\[
R_f = \frac{T_w - T_b}{(q/A)} - \frac{T_{wo} - T_{bo}}{(q/A)_o} - \frac{1}{h} + \frac{1}{h_o}
\]  

(2.4)

Equation 2.4 may itself be simplified in some cases of interest. For instance, assuming constant heat flux and bulk temperature, the expression of \( R_f \) simply becomes:

\[
R_f = \frac{T_w - T_{wo}}{(q/A)_o} - \frac{1}{h} + \frac{1}{h_o}
\]  

(2.5)

A further assumption that is usually made is that the local heat transfer coefficient \( h \) remains constant as the deposit builds up on the heat transfer surface. In such a situation, Equation 2.5 reduces to an even simpler form given by:

\[
R_f = \frac{T_w - T_{wo}}{(q/A)_o}
\]  

(2.6)

which only requires measurement of the wall temperature at time zero (when the surface is clean) and at time \( t \) (when the surface is fouled) along with the heat flux \( (q/A)_o \) in order to be able to compute \( R_f \) at the specific time \( t \).

Deviations between Equation 2.5 and Equation 2.6 are the result of a change in \( h \) from its initial value \( h_o \) as fouling proceeds. Such a change, when it occurs, is thought to be due to two possible reasons. The first reason is related to an increase in the roughness of the
surface as solid materials from the main fluid stream stick to it. The second reason is related to an increase in the fluid velocity as the thickness of the deposit layer increases, therefore reducing the cross-sectional area of the flow channel.

The effect of roughness as opposed to velocity seems to be more important shortly after the initial deposit on the heat transfer surface. Epstein [10] reports that the first explanation about the existence of negative fouling resistances recorded during the initial period was given as early as 1958 by Nunner [11] who mentioned the increase in roughness as the deposit starts building up on the surface. Similar experimental observations were later made by Hasson [12] and by Crittenden and Khater [13]. An interesting study on the effect of roughness on fouling was recently performed by Crittenden and Alderman [14]. Nevertheless, as significant as it can become and as explained by Melo and Pinheiro [15], any change in surface roughness can practically be corrected for through the friction factor only if very accurate pressure drop measurements are conducted as the fouling proceeds.

2.2.3 The Fundamental Steps of the Fouling Process

For most of the fouling categories mentioned in section 2.1, the process of fouling follows a succession of typical steps well recognized in the fields of heat and mass transfer, fluid flow, surface phenomena and reaction
kinetics. These events described by Hasson [12] and by Epstein [16] consist of initiation, transport to the surface, attachment, aging and removal.

Very briefly, initiation is a process that is related to an induction period that in some but not all instances precedes the onset of fouling on a heat transfer surface. Transport of foulant or foulant precursor from the bulk fluid to the solid surface governs the second step. Of course, both eddy transport and diffusion phenomena should in general be expected to play a role in this phase. In the special case where the overall process involves a chemical reaction, the foulant precursor or reactant first reacts on or nearby the surface to form reaction products or foulants which then attach to the surface.

Depending on the type of deposit formed, the effect of temperature on the characteristics of the film can have different consequences such as an increase or a decrease of its strength. In any case, however, the deposit is said to "age". Finally, either as a result of aging or of the strong action of fluid shear forces or even as suggested by Cleaver and Yates [17], due to the action of fluid turbulent bursts, the deposit may be removed partially from the surface back into the bulk fluid. Although both Hasson and Epstein seem to place the removal step before the aging step, it is believed here that either one could occur first depending on the overall system and conditions used.
In graphical form, the overall fouling process can be illustrated in the manner shown by Figure 2.2, where, as an example, the fouling resistance is plotted versus time. Several shapes of the so-called fouling curve can be seen. The general form of the curve is a function of the net fouling rate which, as defined by Kern and Seaton [18] is equal to the difference between a deposition rate and a removal rate,

$$\frac{dm_f}{dt} = d\left(\rho_f k_f R_f^*\right) = \phi_d - \phi_r$$  \hspace{1cm} (2.7)

where,

- $\phi_d$ = deposition rate of foulant
- $\phi_r$ = removal rate of foulant
- $R_f^*$ = asymptotic fouling resistance
- $t_d$ = induction time

and all other quantities are as defined in section 2.2.1.

Since the original work by Kern and Seaton, fouling research has basically focused on attempting to determine the effect of operating conditions such as wall temperature and velocity, surface characteristics and flow geometry on the two competing rates of material deposition and removal. Depending on the relative extent of these two terms, the overall fouling resistance-time curve may show different trends after the end of a possible induction period, during which time no significant fouling is observed.
Figure 2.2 Typical fouling resistance versus time curves
Induction periods may or may not be present in a fouling process. They were, for instance, observed experimentally in various investigations [19,20,21,22] but not in others [12,23,24]. The final asymptotic value in the fouling resistance-time curve occurs when the removal rate equals the deposition rate or when for some reason no more deposition nor removal of solid materials takes place. The values of fouling resistances given in TEMA tables are usually considered as asymptotic values.

Finally, it should be noted that fouling curves having a sawtooth shape have been reported in the literature [25]. However, it is thought that such curves are only special cases of the general ones, namely, linear, falling rate and asymptotic and are caused by the periodic sudden removal (sloughing) of the deposit from the heat transfer surface.

2.3 Importance of Fouling

It is obvious from the various reported estimations of the cost of fouling that the losses are significant. The total financial penalties associated with fouling may include the thermal efficiency decrease of heat transfer equipment, high fluid pressure drops, extra costs for antifoulant additives, physical and/or chemical cleaning and loss of production due to unscheduled plant shutdowns. Taking into account all of these factors, Van Nostrand, et al. [1] estimated an overall loss of about 10 million dollars per year for a hypothetical 100,000 barrels per day
crude unit. Based on these results, they then extrapolated the problem to the non-Communist world refineries to arrive at an astonishing number of 4.41 billion dollars annuities.

A more recent study undertaken by Garrett-Price, et al. [26] showed that the U.S. industry alone suffered an estimated yearly loss of 3 to 10 billion dollars as a consequence of fouling and corrosion. In the United Kingdom, Crittenden et al. [27] report that for 1979, Thackery [28] proposed a figure between 300 and 500 million pounds. All the given evaluations related to the problem of fouling are, of course, subject to fluctuations depending on the current energy rates. A paper by Pritchard [29] presents a good review of the economical problems of fouling.
CHAPTER 3

REVIEW OF CHEMICAL REACTION FOULING

Introduction

Chemical reaction fouling also referred to as organic fouling (since it often involves reactions of organic compounds) is the domain of fouling in which a chemical reaction is responsible for the production and deposition of solid products on a heat transfer surface. These products or foulants are either formed directly on the surface, in the region close to the wall or even in the bulk fluid. In the latter cases, they are transported to the surface by molecular diffusion and eddy transport before they are deposited on the wall. A proposed way for verifying whether the reaction occurs on the heat transfer surface is to have a long channel and then follow the variation in concentration of a given reactant as it passes along the heated surface.

Review papers on chemical reaction fouling may be found elsewhere [10,26,30-36]. In general, this area of fouling is of main concern in polymer production and hydrocarbon and food processing. Considering the complicated phenomenon involved, the solution to the fouling problem has yet to be found although more research work appears to be devoted to studying this type of fouling in the last decade. However, the review papers mentioned
above are of great interest because they offer insight about what has been achieved and what directions should be taken by the research. At this point, it should be mentioned that some papers such as those of Taborek et al. [2,37] and Knudsen [8], although not specifically aimed toward chemical reaction fouling alone, propose interesting suggestions that if followed would lead toward new developments in this field of research.

3.1 Parameters Affecting Chemical Reaction Fouling

Among the parameters known to greatly affect organic fouling are velocity of the main fluid stream past the heat transfer surface, the bulk fluid composition, surface temperature of the heat transfer surface and the bulk fluid temperature. Other factors, although not of negligible importance, are usually neglected as pointed out by Pinheiro [38]. These include the nature and type of surface, design of equipment, fluctuations during operation, properties of the deposit and so on. The following is a condensed review on the reported effect of some critical parameters to be considered in chemical reaction fouling.

3.1.1 Surface Temperature

It is well established that increases in temperature always increase the rate of chemical reactions. This dependence on temperature is usually expressed in terms of
an Arrhenius-type relationship which is of an exponential form. Because of this sensitive relationship between chemical reaction rates and temperature, it is essential that all other parameters affecting the fouling process be tightly controlled so that the effects of temperature may be determined. For organic fouling involving a series of unknown reactions, it is customary that the activation energy for the overall process be determined from a set of fouling experiments covering a range of surface temperatures.

For chemical reaction fouling, a wide range of activation energies (4.8 to 28.7 kcal/mol) have been reported [10]. In a study of fouling of a petroleum gas oil on a heated tube, Watkinson and Epstein [22] correlated data on the initial fouling rate as [24]:

\[
\dot{R}_{fo} = \frac{1.347 \times 10^9 \, e^{-28,730/RT_s}}{G^{1.07}}
\]  

(3.1)

where,

- \(T_s\) = surface temperature of the tube in K
- \(G\) = mass flow rate in lbm/sec
- \(R\) = gas-law constant in cal/mol K
- \(\dot{R}_{fo}\) = initial fouling rate in ft\(^2\) °F/Btu

The 28.7 kcal/mol activation energy seems to be one of the highest ever reported. Equation 3.1 was obtained for clean wall surface temperatures between 295 and 400°F.
Fouling of jet fuels on heat exchanger surfaces was thoroughly investigated by Taylor and co-workers [39-44]. While in general, fouling rates were found to increase with temperature, some very complex arrhenius plots were sometimes obtained. Activation energies ranged from less than 5 to 40 kcal/mol for the various fuels and simulated fuels investigated. Vranos et al. [45] also measured coking rates of a jet fuel under isothermal conditions on stainless steel metal strips of various roughnesses. They observed a relatively low activation energy of about 10 kcal/mol which they interpreted as being due to the physical processes taking place, namely, mass transfer and surface catalyzing effect. This activation energy was determined at a Reynolds number of 1130 and fluid temperatures between 250 and 500°F.

Hausler and Thalmeyer [46] used a hot wire technique to study fouling of three different petroleum feedstocks. They proposed a very simple form of relationship between temperature and fouling rate given by:

\[
\dot{R}_{f0} = \frac{1}{2.7 \times 10^6} \exp \left( \frac{T - 100}{100} \right)
\]

where \( T \) is in °F and \( \dot{R}_{f0} \) is in \( \text{ft}^2 \text{ °F/Btu} \). Braun and Hausler [47] extended the study to show that wire temperature sometimes offers unexpected results. For instance, irregularities similar to those observed by Hausler [48] for gas oil fouling appeared in their data as
the fouling rate sometimes shows a maximum with an increase in temperature. No explanation was given about these discrepancies which occurred in both the presence and absence of oxygen. Activation energies were evaluated between 356 and 735°F.

Fouling rates of various normal paraffins were measured by Taylor [49]. In the temperature range between 200 and 450°F, an activation energy of about 10 kcal/mol was observed. For binary blends of an aromatic compound (1-methyl-naphthalene) in a paraffin (n-decane), the activation energy increases with aromatic concentration to reach 20 kcal/mol at 90 wt% 1-methylnaphthalene. Steele et al. [50] studied mass deposition from used lubricating oils between 650 and 850°F. Their results agreed on a constant increase of coking rates with temperature in an Arrhenius fashion. For thermal fouling of kerosene in a horizontal tube, Crittenden and Khater [13] measured lower fouling rates at higher surface temperatures which were recorded at the top location of the tube.

Scarborough et al. [51] carried out a study of the coking tendencies of a virgin crude oil in a tubular heat exchanger. Their experimental data suggest that the fouling rate doubles for every 72°F (40°C) increase in the film temperature at a flow rate of 150 lbm/sec·ft² (750 kg/sec·m²). This rate was found to be relatively low compared to that observed in thermal cracking of
hydrocarbons which doubles about every 27°F (15°C). The so-called film temperature is the solid-fluid interface temperature which is usually referred to as the surface temperature. The calculated activation energy was found to be 12.5 kcal/mol for film temperatures between 708 and 860°F (375 and 465°C).

The first directly research oriented investigation on chemical reaction fouling was probably that of Crittenden et al. [52]. These workers investigated fouling from the dilute solution polymerization of 1% V/V styrene in kerosene in a 1-inch OD electrically heated stainless steel tube. Single reaction type studies are essential for better understanding of fouling phenomena [16]. Crittenden and his co-workers correlated their data to obtain an Arrhenius-type equation for each flow rate used. Their results show that the activation energy as given by the initial fouling rate is about 6 kcal/mol for flow rates below 102 lbm/sec*ft² (512 kg/sec*m²) and increases to about 9 kcal/mol above this flow rate. These values seem, however, to be somewhat lower than that for pure styrene which is about 20 kcal/mol. The temperature range investigated was between 72 to 480°F (22 to 249°C)

3.1.2 Bulk Fluid Temperature

The effect of bulk fluid temperature on chemical reaction fouling has not been studied as extensively as has wall surface temperature. Basically, only in some reports
such as the work of Vranos et al. [45] where hydrocarbon fouling was studied under isothermal conditions did bulk temperature play a major role. In general, it should be expected that this variable affects the rate of any chemical reaction that would possibly occur in the bulk fluid stream. In such a case, the reaction products will have to be transported to the hotter surface on which they may be deposited.

The effect of bulk temperature for non-isothermal systems is included in the general equation governing heat transfer between a hot surface and a colder stream or vice versa. In other words, bulk temperature is included in the temperature driving force. Eaton and Lux [53] found that deposition from a laboratory prepared hydrocarbon feedstock on a wire probe was zero for a zero wire-fluid temperature difference while fouling was so rapid when this difference was equal to 425°F (236°C) that the fouling resistance levelled off after only eight hours. Another experiment at a wire temperature of 484°F (251°C) and bulk temperatures of 160°F (71°C) and 291°F (144°C) showed a final asymptotic $R_f^*$ value about 3 times higher at the lowest bulk temperature probably due to a solubility effect.

3.1.3 Velocity

As mentioned previously, the effect of flow rate is in most cases directly connected with that of surface temperature. Besides the well known fact that high flow
velocities influence convective heat transfer as expressed by such heat transfer correlations as those proposed by Dittus and Boelter [54] or Sieder and Tate [55] for flow in tubes or those by Wiegand [56] or Monrad and Pelton [57] for flow in annuli, velocity seems to have a controversial effect on fouling.

Although it is well recognized that deposit removal from an already fouled surface can be promoted by the action of high wall shear stresses resulting from high flow rates, experimental data from various sources seem to differ when considering the effect of velocity on the overall deposition-removal fouling process. The original fouling model proposed by Kern and Seaton [18] which assumes asymptotic fouling predicts that the initial fouling rate is directly proportional to the mass flow rate.

Watkinson and Epstein [22] found that for gas oil fouling, the initial fouling rate is inversely proportional to the mass flow rate (Equation 3.1) for Reynolds numbers between 9800 and 41500. A very similar dependence of initial fouling rate on flow velocity was obtained by Paterson and Fryer [58]. Canapary [59] reports that for fouling of a gas oil, an increase of 0.3 ft/sec in velocity reduced fouling by as much as 50% in some cases.

Scarborough et al. [51] observed a decline in coking rates of a crude oil with an increase in oil mass flow
rate. While no fouling occurred at mass velocities equal to 600 lbm/sec*ft² (3000 kg/sec*m²), very little fouling took place at 450 lbm/sec*ft² (2250 kg/sec*m²) for surface temperatures as high as 734°F (390°C). For flow rates below 300 lbm/sec*ft² (1500 kg/sec*m²) deposit formation was evident and increased as the flow rate was decreased. Chantry and Church [60] looked at the design of forced circulation reboilers subject to heavy fouling from hydrocarbon streams. They found that velocities above 5 ft/sec decreased the fouling rates. In some cases, fouling was completely suppressed by a velocity of 20 ft/sec. For a given run length, an example was presented in which the fouling resistance was reduced by a factor of 10 as the velocity was increased from 5 to 15 ft/sec.

Chen and Maddock [61] derived a model to predict coking rates from hydrocarbon cracking based on experimental data obtained in ethylene plants. A log-log plot of the coking rate versus Reynolds number shows a horizontal line in the laminar regime and a straight line having a positive slope in the turbulent regime suggesting an increase in fouling rates with velocity only in turbulent flow.

Smith [62] measured fouling rates for kerosene fuels in a single tube heat exchanger. Fouling resistance-time curves were obtained at respectively 108, 170 and 216 lbm/sec*ft² corresponding to Reynolds numbers between 4500
and 10000. Fuel temperatures ranged between 341 and 406°F (171.5 and 207.5°C). It was found that at any given time, the thermal resistance of the deposit increased as flow rate increased. Various explanations were proposed among which a decrease in thickness of laminar sublayer, better availability of deposit forming species and decrease in deposit roughness as flow rate was increased.

Vranos et al. [45] correlated coking rate data of a jet fuel on stainless steel metal strips and found that the initial fouling rate increased with Reynolds number as given by the following equations:

\[ \dot{R}_f = 0.054 \ Re^{0.605} \text{ at } T = 500°F \]  
\[ \dot{R}_f = 0.006 \ Re^{0.566} \text{ at } T = 300°F \]  

Equations 3.3 and 3.4 were obtained for various tube diameters and for Reynolds numbers ranging from 600 to 12000.

A thermal fouling study induced by the polymerization of styrene contained in heptane on a heat transfer surface was carried out by Fetissoff and co-workers [63]. The purpose of this study was to compare the performance of two commonly used thermal fouling probes, namely the HTRI Portable Fouling Research Unit (PFRU) and a commercial hot wire probe. No general conclusions could be drawn regarding the effect of Reynolds number which for the PFRU
was well in the turbulent regime and for the wire only in the laminar regime.

The work of Crittenden et al. [52] has been mentioned. It presents a new way of looking at chemical reaction fouling for the purpose of a better understanding of the phenomenon. The workers performed an interesting study of the polymerization of 1% V/V styrene in kerosene in a single externally heated tube. Their findings on the effect of mass flow rate on initial fouling rates suggest that below a surface temperature of about 212°F (100°C), an increase in the flow rate slightly decreases the fouling rate. For temperatures above 248°F (120°C), a clear increasing effect on the fouling rate is observed. A slight criticism about this study is that it was carried out at relatively low Reynolds numbers which do not really reflect industrial applications. In fact, the range covered was between 1000 and 5200 which is in the hydrodynamically unstable transition region. Also, the use of kerosene as a solvent since it was not a pure solvent may have in some ways affected the fouling rate. A pure solvent may have given different results.

3.1.4 Concentration of foulant precursor

An extremely limited number of studies have been reported on the effect of foulant precursor concentration in the bulk stream on fouling involving a known single chemical reaction. In fact, the work done by Fetissoff et
al. [63] appears to be the only reference directly related to this subject. These authors studied fouling resulting from the polymerization of styrene contained in heptane flowing in an annular test section and over a coiled electrically heated stainless steel wire.

The concentration of styrene used was equal to about 3, 6 and 11.8 wt%. Because the aim of the study was to compare the two different fouling probes, placed in parallel in the flowing stream, the twelve experiments performed were not designed to determine the effect of the process variables. The experiments seem to be random and therefore do not really allow drawing a consistent conclusion since concentration is not the only variable between any pair of runs. However, from their overall plot comparing the initial fouling rates between the two probes obtained in all twelve experiments, Fetissoff and co-workers seem to imply that the effect of styrene concentration may be ascertained from these experiments. In such a case, high styrene concentrations in the bulk fluid are observed to generally enhance the rates of fouling.

It is reported that for all experiments with 3 wt% styrene concentrations, initial fouling rates were below $5.7 \times 10^{-4}\text{ft}^2 \, ^\circ\text{F}/\text{Btu} \ (0.1 \text{ m}^2 \text{ K/kWh})$. For the single run at 6 wt% styrene concentration, the rate was equal to about $11.4 \times 10^{-4}\text{ft}^2 \, ^\circ\text{F}/\text{Btu} \ (0.2 \text{ m}^2 \text{ K/kWh})$ and mostly ranged
between $14.2 \times 10^{-4}$ and $57 \times 10^{-4}$ ft$^2 \ \circ F/\text{Btu}$ ($0.25 - 1.0 \text{ m}^2 \text{ K/kWh}$) for the 11.8 wt% styrene concentration runs. For the PFRU, the data sometimes shows lower initial fouling rate at 11.8 wt% styrene concentration level that at 6 wt% concentration level. But again, no reason was given to explain such discrepancies.

In general, it can be said that concentration of reactant should be expected to have an effect on chemical reaction fouling based on the general idea that more reactant would lead to more reaction products. The latter would then lead to a higher possibility of a deposit buildup on the hot surface where the reaction most likely occurs. Nevertheless, the effect of concentration in a flowing system may not be as simple as in a batch system. It is also probable that the effect of this parameter may be coupled to those of other variables such as temperature and fluid velocity. Therefore, only a systematic study of all these factors would produce a better understanding of concentration effects.

3.2 Effect of Oxygen

The major role of oxygen on fouling from hydrocarbon streams relies on the strong oxidative action of this element to cause breakdown of organic compounds in general and under high thermal stresses in particular. Early work by Canapary [59] showed that complete removal of oxygen
from naphtha by purging it with nitrogen could improve heat transfer in a hydrodesulfurizer by as much as 80 to 90%.

Taylor [42] compared the rates of mass deposition of coke from jet fuels obtained in the absence of oxygen to those previously obtained under the presence of oxygen [40]. His conclusions agree that in general, coking rates are highly reduced if oxygen is eliminated from the liquid before it is exposed to high temperatures. In his first study on the effect of oxygen, Taylor [40] found that the initial coking rates all based on 4-hour period fouling runs were proportional to the oxygen partial pressure raised to the 0.2 power.

The work reported by Eaton and Lux [53] on crude oil fouling constitute the only known thermal study on the effect of oxygen. No regular trend was observed but instead their results were found to depend on the type of feedstock used. For instance, for one type of feedstock an increase in oxygen pressure resulted in a clear and sharp increase in the fouling rates with no fouling at all in a pure nitrogen environment. On the other hand, other types of crude oils showed consistent fouling in the presence of oxygen as well as under a nitrogen blanket with almost identical rates.

To explain these discrepancies, the authors advanced the idea of foulant precursor depletion which occurs in time with nitrogen but not with air. By performing two
distinct experiments, one under nitrogen pressure, the other under air pressure, they observed that the initial fouling rate decreased constantly as the feed was re-used with nitrogen whereas it constantly increased as the feed was re-used with air.

Gillies [64] proposed that the mechanism by which oxygen reacts with hydrocarbons to produce polymeric species which cause fouling may be as follows:

\[ \text{RH} + O_2 \rightarrow \text{ROOH} \rightarrow \text{RO}^+ + \text{OH} \quad (3.5) \]
\[ \text{RO}^- \rightarrow \text{ROR'} \rightarrow \text{ROR'R'} \text{ etc...} \quad (3.6) \]

where, RH is a hydrocarbon molecule and RO, ROR', etc... are free radical chain molecules. This mechanism seems however to be different than that previously considered to take place and which is [47]

**Initiation:** \[ \text{RH} + Z^\cdot \rightarrow \text{R}^\cdot + \text{HZ} \quad (3.7) \]
**Propagation:** \[ \text{R}^\cdot + \text{O}_2 \rightarrow \text{ROO}^\cdot \quad (3.8) \]
\[ \text{ROO}^\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}^\cdot \quad (3.9) \]
**Termination:** \[ \text{R}^\cdot + \text{R}^\cdot \rightarrow \text{RR} \quad (3.10) \]
\[ \text{ROO}^\cdot + \text{R}^\cdot \rightarrow \text{ROOR} \quad (3.11) \]

where Z can be any impurity in the system such as sulfur, metal ions or nitrogen compounds. At low temperatures, it is mentioned that the reactivity of oxygen is not sufficiently high to initiate the reaction as Gillies later suggested.
Another possible mechanism of hydrocarbon autoxidation reaction was reported by Hazlett and Hall [65] as:

Initiation: \[ 2RH + O_2 \xrightarrow{M} 2R^* + H_2O_2 \]  

(3.12)

Propagation: \[ R^* + O_2 \rightarrow RO_2^* \]  

(3.13)

\[ RO_2^* + RH \rightarrow ROOH + R^* \]  

(3.14)

Termination: \[ RO_2^* + RO_2^* \rightarrow \text{ketone + alcohol} + O_2 \]  

(3.15)

\[ RO_2^* + R^* \rightarrow ROOR \]  

(3.16)

\[ R^* + R^* \rightarrow RR \]  

(3.17)

where \( M \) symbolizes a metal surface.

The concentration of oxygen present greatly affects the rate of the propagation step as shown by Equation 3.13. For oxygen concentration of less than 20 ppm, Equation 3.13 is the slowest propagation step whereas a higher oxygen level makes Equation 3.14 the rate limiting step.

Crittenden and Khater [13] have investigated the effect of oxygen on thermal fouling of kerosene in a horizontal tube divided into four sections and with thermocouples installed at the bottom, side and top of each section. They concluded that with only 15% oxygen present in the vapor phase, very low values in the initial fouling rates were obtained and circumferential differences were almost absent. On the other hand, with 100% oxygen the rates of fouling were always higher than with low oxygen level but no systematic trend was observed.
3.3 Effect of Sulfur and Sulfur Compounds

The presence of sulfur compounds in hydrocarbon streams even at infinitely small concentration levels may trigger the fouling process and may increase the fouling rates quite considerably. Crude oils with high sulfur content are well known to create serious problems in heat transfer equipment during treatment. A direct effect of elemental sulfur or sulfur compounds is the formation of sludge and gum which with time and high temperatures degrade into a strong coke deposit layer very harmful to heat exchange.

Thompson et al. [66] carried out an investigation on the stability of oil fuels stored at 100°F to which free sulfur or sulfur derivatives were added. Their study showed that thiophenes, aliphatic mercaptans and aliphatic sulfides did not really increase the mass of sludge and soluble gum formed. However, sulfur and other sulfur compounds promoted such formation. For instance, disulfides such as hexyl, heptyl and octyl and polysulfides increased gum formation. Exceptions to the disulfides were the n-propyl and iso-propyl disulfides which gave very close fouling curves to those without an additive in the fuel. Of all sulfur compounds, thiophenol appeared to be the most active catalyst for gum formation during storage of oils. However, the general conclusion of the study was that no absolute quantitative results could be drawn
considering the many differences in the composition of the oils used.

Taylor and co-workers [41,43] did extensive work on the effect of trace sulfur compounds on fouling of jet fuels in both the presence and absence of oxygen. It was found that for oxygen saturated fuels, addition of 1000 ppm sulfur level from various sulfur based compounds including thiols, sulfides, disulfides and thiophenes was followed by an up to twenty fold increase in the rate of deposit formation. The exceptions were diphenyl sulfide and dibenzothiophene which showed no major effect. These two compounds are believed to be thermally stable at the temperatures used, which did not exceed 450°F. Thiols were again found to be the most active for enhancement of deposit formation. For the sulfur compounds used, the rate was found to be proportional to the square root of sulfur concentration level.

For deoxygenated systems, Taylor [43] demonstrated that addition of 3000 ppm sulfur level from compounds of the same type as those used previously with oxygen present also increased the deposition rates in general except for the condensed thiophenes. Based on experiments at 300 and 3000 ppm S level, the initial deposition rate was found to be proportional to the sulfur concentration raised to the 0.3 power.
Hausler and Thalmeyer [46] performed experiments which showed that fouling and corrosion in feed effluent heat exchangers do not necessarily occur together as was previously thought. They used a hot wire probe to simultaneously measure corrosion and fouling rates of three petroleum feedstocks. Their data showed that combinations of high fouling-low corrosion rates and low fouling-high corrosion rates are often obtained. The effect of sulfur was clearly experienced as the feed with higher initial sulfur content gave higher fouling rates. In the absence of oxygen, the sulfur compounds are believed to participate in reactions that produce the free radicals needed for polymerization initiation and propagation. With no oxygen present, it is postulated that the sulfur compounds attack the iron surface to form iron sulfide FeS which forms the corrosion product.

3.4 Effect of Boiling

The impact of boiling phenomena on heat transfer from a metal surface to a fluid has been one of the most extensively studied subjects in the area of heat transfer. However, when it comes to applications to chemical reaction fouling, it is as if boiling almost never existed. In most of the reported work on hydrocarbon fouling for example, reference to boiling was rarely made although the operating conditions used suggest that it was indeed often present. It is therefore possible to suspect that perhaps some of
the many controversies surrounding this research area may have some connection with boiling effects.

For boiling to occur, nucleation sites are needed. If one starts with an ideally smooth surface, then initial deposition of solid materials on the surface can offer the crevices that may initiate vapor bubble formation. The main effect of boiling on fouling rates from hydrocarbons is through the high turbulence created by the bubbles at the solid-fluid interface. This turbulence not only acts toward enhancement of heat transfer but also of mass transfer as well. The concentration of the foulant precursor species in the region close to the wall is constantly replenished as fresh supply is brought in more easily due to the reduction of the boundary layer resistance due to mixing from boiling.

For design of reboilers treating hydrocarbon streams in the chemical and petrochemical industries, Chenoweth [67] reports the fouling resistance values recommended by Palen and Small [68]. For the boiling side, these values seem to range between 0 and $51.3 \times 10^{-4}$ hr ft$^2$ °F/Btu (9 x $10^{-4}$ m$^2$ K/W) depending on the type of hydrocarbons involved. Low values correspond to n-paraffins with up to eight carbon atoms in their chains whereas the highest values are recommended for polymerizing species.

Hausler and Thalmeyer [46] observed that with their wire fouling probe, higher fouling rates were obtained when
boiling conditions prevailed in their fouling study with feedstocks. Fetissoff et al. [63] in their comparison study of two fouling heat transfer problems (annular versus wire) performed all their experiments under boiling conditions. The model fluids chosen were solutions of styrene in heptane recirculating in a heat transfer loop. High heat fluxes were used ranging from 93200 to 133500 Btu/hr ft$^2$ (294 to 421.1 kW/m$^2$). The study was carried out under a nitrogen environment at 95 psi (653 kPa). It was concluded that boiling influenced fouling rates. Because the annular probe was operated under turbulent flow regime and the wire probe under laminar flow regime, it was speculated that higher boiling intensity on the surface of the probes would bring the differences in fouling rates to very small values.

Crittenden and Khater [12] presented a detailed study of fouling occurring during the vaporization of kerosene in a 0.4-inch (1-cm) ID electrically heated horizontal stainless steel tube. Heat fluxes ranged from 17100 Btu/hr ft$^2$ (5.4 kW/m$^2$) for all-liquid phase runs to 103340 Btu/hr ft$^2$ (32.6 kW/m$^2$) for one all-vapor phase run. In general higher initial fouling rates were obtained at the bottom side of the tube where nucleate boiling is more likely to occur in the liquid phase. At this position, surface temperatures were however, found to be the lowest as opposed to the top and side positions. Around the
circumference of the tube, positions where surface temperature was close to the kerosene final boiling point showed lower fouling resistance values.

3.5 Existing Models

Modelling heat transfer fouling is not an easy task. The complexity of such a phenomenon as fouling almost makes it impossible to link the various factors involved in order to predict what would happen to a heat transfer surface exposed to a fluid under harsh operating conditions. Such a problem is evidently clear as no fouling model yet exists that could predict entirely the fouling process of a hydrocarbon stream [69].

In general, it can be said that most attempts to model fouling processes involving chemical reactions rely on Kern and Seaton's simple idea that the overall mechanism consists of two terms: deposition and removal. It then becomes clear that the next step is to determine the expressions of those two terms which may or may not depend on each other. Due to the difficulties encountered in the various analyses, assumptions are usually made to simplify the problem. Simple kinetics, no removal term, no change in surface roughness are some examples. An overview of chemical reaction fouling is shown in Figure 3.1. This figure is an attempt to summarize all the factors and steps considered in the reported models that were presented in
Figure 3.1 Generalized overview of chemical reaction fouling
the literature. A brief description of each model will then be given with a special emphasis on the assumptions made during the derivation of the models.

As early as 1934, Nelson [70] already advanced a model in which he related the fouling rate to the thickness of the liquid viscous boundary layer in direct contact with a heat exchanger surface. A little later Atkins [71] proposed a mechanism in which two distinct deposit layers, the inner a hard layer and the outer a soft layer, coexist together. Heat would then have to flow through the first layer which is formed by coke and then through the second layer which is softer since it is built up by recent material deposition.

While treating fouling originating from deposition of organic coolants in nuclear reactors, Nijsing [72] presented probably the first systematic study of fouling where the foulant products are allowed to diffuse back into the bulk stream. Assuming instantaneous first order reaction of foulant precursor, the rate of foulant deposition was found to be controlled by diffusion of precursor to the wall.

Watkinson and Epstein [24] adopted the first order release term of Kern and Seaton to which they added a deposition term involving a particle sticking probability $S$ which they defined as being proportional to the Arrhenius temperature factor and inversely proportional to shear
forces. Their final equation for the rate of fouling was given by:

\[
\frac{dR_f}{dt} = \frac{d(x_f/k_f)}{dt} = \frac{A_1(C_b-C_w)e^{-E/RT_s}}{v_f^{1/2}} - A_2fv^2x_f \tag{3.18}
\]

where:

- \(C_b, C_w\) = concentration of precursor in bulk fluid and at the solid wall
- \(f\) = friction factor
- \(v\) = bulk fluid velocity
- \(x_f, k_f\) = thickness and thermal conductivity of deposit film
- \(A_1, A_2\) = constants
- \(T_s\) = surface temperature
- \(E\) = activation energy

Equation 3.18 although derived for sand/water slurries was found to agree well with the experimental data obtained for gas oil fouling when correlating the initial fouling rate (see Equation 3.1). However, it did not predict accurately the asymptotic fouling resistance values. The authors cautioned regarding the use of the second term of the right hand side of equation 3.18 if hard deposits are obtained in a given fouling process such as coking.

Three models were developed for vapor phase pyrolysis of hydrocarbons in which no consideration of removal terms was made due to the strong nature of the deposit. The first attempt was made by Jackman and Aris [73] who tried
to model coke deposition occurring in pyrolytic reactors. The general picture was simplified to two single reactions: A first order reaction that describes the decomposition of the reactant in the tube to produce coke which then deposits on the tube walls through a zero order reaction. No mass transfer effects were included in the analysis. The second model was proposed by Fernandez-Banjin and Solomon [74] who considered a two step mechanism by which the reactant first diffuses to the wall then reacts by a first order reaction. The overall rate of coke formation was then found to be:

\[
\frac{dx_f}{dt} = k_c Y \left(1 - \frac{k_c}{kP + k_c} \right) \tag{3.19}
\]

where:

- \(k_c\) = mass transfer coefficient of reactant
- \(k\) = reaction rate constant
- \(Y\) = mole fraction of coke precursor in bulk fluid
- \(P\) = total pressure
- \(T\) = absolute temperature
- \(R\) = universal gas constant

Equation 3.19 may be simplified as in the case of pyrolysis where the temperature of the coil is so high compared to the temperature of the bulk fluid that mass transfer becomes the rate limiting step. In that case, the rate of coke deposition was given by:
\[
\frac{dm_f}{dt} = \frac{K^* G^{0.8}}{(D - 2x_f)^{1.8}}
\] (3.20)

where,

\begin{align*}
G & = \text{mass flow rate} \\
D & = \text{tube diameter} \\
K^* & = \text{constant function of feedstock}
\end{align*}

The model was tested under an industrial environment and was said to be in very good agreement with the experiment.

The third model was presented by Sundaram and Froment [75] and was developed for the cracking of propane. The model was applied to various consecutive mechanisms leading to coke formation from propane and was found to agree with experimental data. In all cases, the overall coke deposition rate was assumed to be controlled by kinetics. In other words, diffusion problems were not taken into account because the study was made in a mixed flow reactor.

Taborek et al.[2,37] presented a model which although mainly directed toward fouling of cooling tower water could be also used for chemical reaction fouling since the factors introduced may be determined. The main development brought in by these workers is in the expression of the deposit removal mechanism which they postulated was proportional to the fluid shear stress and inversely proportional to a new quantity called deposit bond resistance \(R_b\). \(R_b\) was defined as the adhesive strength of the deposit per unit area at the plane of weakest
adhesion. It is therefore expected to be high for uniform and strong deposits such as polymers and coke and low for weaker deposits.

In 1979, Crittenden and Kolaczkowski [76] published a more general study on modeling hydrocarbon fouling. They considered a single chemical reaction of first order occurring at the deposit-fluid interface. The deposition term included both kinetics and mass transfer of reactants while the removal term was formed by two terms: one related to shear forces and the other to back diffusion of the foulant into the bulk fluid. Using the Chilton-Colburn analogy [77] to express the mass transfer coefficients of precursor and foulant, they obtained the following equation for the overall fouling rate:

$$\frac{dR_f}{dt} = \Pi_1 - \Pi_2 R_f \quad (3.21)$$

where $\Pi_1$ = deposition rate

$$= \frac{1}{\rho_f k_f} \left\{ \frac{C_{PB}}{\rho(D-2x_f)1.8(Sc_p)^{0.67}} \left[ \frac{1.213 \lambda \mu^{0.2} G^{0.8}}{1.213 \lambda \mu^{0.2} G^{0.8} C_{fi}} \right] \right\} + \frac{1}{A e^{-E/RT}}$$

$$- \frac{1.213 \lambda \mu^{0.2} G^{0.8} C_{fi}}{\rho(D-2x)1.8(Sc_p)^{0.67}} \quad (3.22)$$

and $\Pi_2$ = Removal rate
\[
\begin{align*}
R_f(t) &= \frac{\Pi_1}{\Pi_2} \left( 1 - e^{-\Pi_2 t} \right) \quad (3.24)
\end{align*}
\]

where, 
\[
\begin{align*}
\lambda &= f \text{ (surface roughness)} \\
\psi &= f \text{ (deposit structure)}
\end{align*}
\]

Subscript (p) refers to precursor and subscript (f) refers to foulant. All other quantities are as previously defined.

Integration of Equation 3.21 for a given \( G \) and \( T_s \) yields the following fouling resistance-time relationship

\[
R_f^* = \frac{\Pi_1}{\Pi_2} \quad (3.25)
\]

The model as expressed by Equations 3.21, 3.22, and 3.23 seems to be very cumbersome although some simplifications are possible. The effect of flow rate is particularly complex along with that of tube diameter.

Crittenden and Kolacazkowski [78] further extended their model to the two-layer concept first mentioned by Atkins [71]. In this case, the final equation was given by:

\[
\frac{dR_f}{dt} = \phi_{Td} - \phi_{Tr} - \phi_{CT} - \phi_{Fr} \quad (3.26)
\]

where,
\[ \phi_{Td} = \text{rate of deposition of tar-like layer} \]
\[ \phi_{Tr} = \text{rate of back convection of tar-like products to bulk} \]
\[ \phi_{CT} = \text{net rate of conversion from tar-like product to coke product} \]
\[ \phi_{Fr} = \text{rate of deposit removal by shear forces} \]

The four terms forming the right hand side of Equation 26 were as follows:

\[ \phi_{Td} = \frac{1}{B_1 (D-2x_f)^{1.8} G^{0.8}} + B_2 e^{(E_t/RT_t)} \]  
\[ (3.27) \]

\[ \phi_{Tr} = \frac{B_3 G^{0.8}}{(D-2x_f)^{1.8}} \]  
\[ (3.28) \]

\[ \phi_{CT} = \frac{B_4}{e^{(E_c/RT_c)}} \]  
\[ (3.29) \]

\[ \phi_{Fr} = \frac{B_5 G^{1.8} R_f}{(D-2x_f)^{3.8}} \]  
\[ (3.30) \]

where,
\[ T_c = \text{temperature at interface between tar-like and coke layers} \]
\[ T_t = \text{temperature at interface between tar-like deposit and fluid} \]
\[ E_t, E_c = \text{activation energies corresponding to tar and coke formation, respectively} \]
\[ B_1 \text{ to } B_5 = \text{constants} \]
The initial fouling rate can then be easily obtained as

\[
\dot{R}_f^0 = \frac{1}{D_1 D_1^{1.8} G^{0.8}} e^{\frac{E_t}{RT_t}} - \frac{D_3 G^{0.8}}{D_1^{1.8}}
\]

(3.31)

where \(D_1, D_2,\) and \(D_3\) are constants.

The new model was tested using the gas oil fouling data obtained by Watkinson and Epstein [22]. Good agreement seems to have been obtained. The overall fouling rate was determined for that specific fluid to be:

\[
\frac{dR_f}{dt} = \dot{R}_f^0 - 4.63 \times 10^{-5} G^{1.8} R_f
\]

(3.32)

Crittenden et al. [32] used data obtained during the polymerization of 1% styrene in kerosene to test a three step model involving a known chemical reaction. Mass transfer of precursor to the wall, reaction at the wall and back convection of foulant to the bulk stream form the three steps. With no back convection considered, the predicted values of the initial fouling rate were much higher than the experimental values as the temperature is increased. Again, the relationship between initial fouling rate and flow rate appears to be of a complex nature. The foulant interfacial concentration was found to be independent of flow rate but it increases sharply with temperature.

Finally, Paterson and Fryer [58] adopted a reaction engineering approach to explain the decrease in initial
fouling rate with increasing velocity which they previously observed experimentally with fouling of milk. Although the original idea was proposed by Nelson [70] the authors were able to explain that the size of the boundary layer is really the key to many fouling problems.
CHAPTER 4
KINETICS OF THE THERMAL POLYMERIZATION OF STYRENE IN n-HEPTANE

Introduction

The commercial importance of polystyrene in the synthetic polymer industry has made styrene perhaps the most extensively studied monomer species. Not only are tremendous amounts of research papers available but even entire books have been written on styrene and its uses [79]. Nevertheless, there still does not seem to be general agreement on the kinetics of polymerization involved especially for the solution polymerization of styrene [80]. Therefore, this investigation has for intent to determine the overall kinetics (reaction order and rate constant) for the polymerization of styrene in heptane.

4.1 Background and Literature Review

4.1.1 Mechanism of the Thermal Polymerization of Styrene

As in all free radical chain polymerization reactions, the thermal polymerization of styrene follows the three major steps of initiation, propagation and termination as summarized in the example scheme given below,

\[ \text{Initiation: } 2M \xrightarrow{k_d} 2R' \]
\[ \begin{align*}
R' + M & \xrightarrow{k_i} RM' \\
\text{Propagation: } RM' + M & \xrightarrow{k_p} RMM' \\
RM_nM' + M & \xrightarrow{k_p} RM_{n+1}M' \\
\text{Termination: } RM_{n+1}M' + M_m & \xrightarrow{k_t} \text{Polymer}
\end{align*} \]

Where the rate constants \( k_d \), \( k_i \), \( k_p \) and \( k_t \) are respectively for dissociation, initiation, propagation and termination, \( M \) is a monomer molecule, \( R' \) a primary radical, \( RM' \) a chain initiating radical and \( RMM' \), \( ..., RMM_nM' \) are chain propagating radicals.

Both the initiation and termination steps still constitute an enigma as various schemes are presented by various investigators.

Flory [81] first reported the possible formation of a diradical \( \cdot CH\Phi-CH_2-CH_2-\cdot CH\Phi \) from the collision of two styrene molecules \( CH_2=C\Phi \) during initiation. However, other workers later ruled out this possibility, suggesting that only monoradicals were involved [82]. In what appears to be a detailed study of the thermal polymerization of styrene in bromobenzene, Mayo [83] suggested the occurrence of a termolecular reaction between styrene molecules to form two different types of monoradicals \( CH_3-\cdot CH\Phi \) and
CH$_3$-C=CH-CH=CH$_2$, which are capable of propagating the reaction. Again, Mayo's interpretation of the results was criticized by Burnett and Loan [84].

Odian [85] reports that initiation of the thermal polymerization of styrene occurs by combination of two styrene molecules to form a Diels-Alder dimer. The latter then reacts with another styrene molecule to form two free radicals which would propagate the reaction. Given that the initiation rate was found to be closer to third order with respect to monomer than to second order, it was deduced that the second step was rate-limiting.

The propagation step in the polymerization of styrene is quite well understood. It simply involves the successive linear addition of monomer molecules to the long-growing chain radical. The process of addition continues until termination occurs. For styrene, it has been shown that termination is by combination rather than by disproportionation. The long polymeric chain radical reacts with another radical formed in the initiation step to close the chain and hence lead to the final polymer product. In the presence of a solvent, this process may be complicated due to chain transfer. Discussions involving chain transfer may be found elsewhere [79,83].

4.1.2 Overall Kinetics of the Thermal Polymerization of Styrene
4.1.2.1 Effect of Styrene Concentration

At sufficiently high temperatures, some monomers such as styrene may undergo instantaneous thermal polymerization without the presence of an initiator. Bamford et al. [86] report on the first kinetic investigation carried out on the polymerization of styrene in various solvents by Breitenbach and Rudorfer [87]. At 212°F (100°C) and under vacuum, these authors found an overall second order dependency on monomer concentration. Almost at the same time, Suess and co-workers [88] also found a second order overall reaction for styrene molar concentrations below 60% in a multitude of solvents.

Gregg and Mayo [89] studied the thermal polymerization of styrene in thirteen different solvents including heptane. The investigation was carried out at 140 and 212°F (60 and 100°C) using various solvent/styrene ratios. The authors correlated the degree of polymerization with the concentration ratio by the following linear relationship,

$$\frac{1}{P} = \frac{1}{P_0} + C_{SM} \frac{C_S}{C_M}$$

(4.1)

where,

P and P₀ = degree of polymerization with and without solvent (usually determined by viscosity measurements)
\[ C_S \text{ and } C_M = \text{molar concentration of solvent and monomer} \]

\[ C_{SM} = \text{chain transfer constant for styrene in a given solvent} \]

The transfer constant \( C_{SM} \) was found to be highly dependent on the solvent used and increased exponentially with temperature giving a value of \( 4.2 \times 10^{-5} \) and \( 9.5 \times 10^{-5} \) for heptane at 140 and 212°F (60 and 100°C) respectively. However, \( C_{SM} \) was unaffected by a change in the initial concentration ratio. The authors noted irregularities with heptane which they speculated is due to the fact that this solvent precipitates the polymer as it forms. One such irregularity was that the second order rate constant was found to decrease with a decrease in styrene concentration.

It is also interesting that the values of \( C_{SM} \) obtained for heptane were higher than those of other aromatic solvents such as benzene, toluene and cyclohexane. This suggests, surprisingly, that a hydrogen abstraction from heptane is easier than from these aromatic compounds.

In the study by Mayo [83], it is reported that for the high molecular weight products formed during the thermal polymerization of styrene in bromobenzene over the range of styrene concentrations between 0.05 and 7.6M, the overall reaction order was closer to 5/2 than 2. This led the author to postulate a third order reaction for the initiation step as opposed to the usual second order found
by several other workers [90]. At the same time, Mayo postulates the independent formation of low molecular weight polymer materials which would follow a second order dependency on monomer concentration. In a later paper, Burnett and Loan [84] noted that based on Mayo's own data, the order of reaction seems to actually vary between a value of 2.0 at high styrene concentration to a value of 2.8 at low concentration. Recently, Crittenden and co-workers [52] also reported an overall value of 5/2 for the order of reaction for the polymerization of 1% V/V styrene in kerosene carried out in an agitated 300 cm$^3$ vessel and covering the range of temperatures between 86 and 349°F (30 and 176°C).

4.1.2.2 Effect of Temperature

The important effect of temperature on the thermal polymerization of styrene is two-fold. First, the reaction has to be initiated by heat and second the overall reaction rate depends on the temperature. High temperatures, although found to drastically increase the polymerization rates, have also been found to lower the molecular weight of the polymer formed.

For the bulk polymerization of styrene which was found to be second order in monomer concentration, Bamford and Dewar [91] gave the following equation for the overall reaction rate constant between 32 and 77°F (0 and 25°C):
\[ k_2 = 6.31 \times 10^6 e^{-23,200/RT} \text{ mol}^{-1} \text{ L. sec}^{-1} \]  \hspace{1cm} (4.2)

Based on data collected from various sources between 140 and 248°F (60 and 120°C), Rubens and Boyer [92] obtained the relation:

\[ k_2 = 1.17 \times 10^9 e^{-19,200/RT} \text{ mol}^{-1} \text{ L. sec}^{-1} \]  \hspace{1cm} (4.3)

These authors pointed out the fact that the value of 19,200 cal/mol for the activation energy is somewhat too low when compared to the 22.1 ± 2 kcal/mol value calculated from Mark and Raff's data [93] or the 23.5 kcal/mol deduced from individual reaction steps and calculated by the relation

\[ E_{\text{overall}} = \frac{1}{2}E_i + E_p - \frac{1}{2}E_t \]  \hspace{1cm} (4.4)

where subscripts i, p, and t respectively symbolize the initiation, propagation and termination phases of the reaction. For the data obtained by Mayo [83], the overall reaction constants for the postulated 5/2 and second order simultaneous but independent reactions occurring during the thermal polymerization of styrene in benzene are given by

\[ k_2 = 1.8 \times 10^5 e^{-22,600/RT} \text{ mol}^{-1} \text{ L. sec}^{-1} \]  \hspace{1cm} (4.5)

\[ k_{5/2} = 6.9 \times 10^5 e^{-21,020/RT} \text{ mol}^{1.5} \text{ L}^{1.5} \text{ sec}^{-1} \]  \hspace{1cm} (4.6)

In light of all the various results reported which obviously do not all seem to be in good agreement, the
activation energy for the polymerization of styrene appears to lie between 19.2 and 24.1 kcal/mol.

4.2 Experimental Apparatus and Procedure

Due to the differences encountered in published results concerning the kinetics of the polymerization of styrene, it was decided to perform our own experimental investigation. The objective of this investigation is mainly to determine the form of the overall rate equation which includes the order of reaction and the rate constant as a function of temperature. Of course, it is intended to reproduce in this study as much as possible, the conditions used in the fouling experiments of styrene dissolved in heptane. Such conditions include the solvent used, styrene concentration, temperature and pressure.

4.2.1 Apparatus

The apparatus used in this kinetic investigation is shown in Figure 4.1. It consists of a 10 cm ID, 13.5 cm high approximately one-liter capacity stainless steel cylinder. The reactor is equipped with an agitator which is controlled through a belt-pulley system. Walling [90] has mentioned that mixed flow vessels are useful tools for studying radical chain reactions.

Heating of the reactor is accomplished electrically through a high electrical resistance which surrounds the
Figure 4.1 Schematic of the high pressure stainless steel mixed batch reactor
reactor. The power supplied to the heating element can be set to either high or low whereas the reactor temperature measured by a thermocouple probe can be set to any desired value between 0 and 400°C. This is controlled automatically using on/off control as the temperature fluctuates around the setpoint valve.

Several ports are available on the cover top of the reactor. The cover is connected to the bottom cylinder with a set of six 5/16-inch bolts. A teflon seal between the two parts insures the absence of leaks. The main port is equipped with a tee and two valves which allow both sampling and pressurizing. It also contains a long 1/4-inch tube at the lower part of which is installed a porous stainless steel filter. The position of the filter is about 2 cm from the cylinder flat bottom. Nitrogen can also be supplied to the system through this same main port as shown in Figure 4.1. A vent port for the gas phase is also available.

4.2.2 Procedure

Prior to their use, the heptane purchased in 4L quantities from EM Scientific (New Jersey) was distilled and the styrene purchased in 4L quantities from JT Baker was distilled under vacuum for removal of the stabilizing agent. It was then kept under Argon in a glass flask completely covered with aluminum foil to avoid light. The flask was kept in the refrigerator until use.
Preparation of an experiment begins with the preparation of the styrene in heptane solution. Before use, the styrene was allowed to come to room temperature to minimize oxygen capture. The solution was prepared by introducing the desired volume of styrene into a 1000 ml glass flask and then filling to the desired level with heptane.

After the reactor was charged with 950 ml of the prepared solution, the cap was re-installed and the bolts firmly tightened. Heating was started without the reactor in place to heat up the remaining mass of the system. Nitrogen was bubbled into the solution to about 50 psig after which it was vented. This operation, the purpose of which was to remove as much dissolved oxygen in the solution as possible, was repeated three times for optimum results. When the reactor mantle was hot enough, the reactor was put in place and the mixing was started with the speed of rotation fixed at 100 rpm.

At the start of every experiment, an increase in pressure to values above the desired operating pressure which was 150 psig made it necessary to drain some liquid out of the vessel. In order to avoid concentration changes by venting the vapor phase, the sampling port was instead used to remove liquid instead of vapor. The sampling line was flushed with a few milliliters of liquid before a sample was obtained for analysis.
As soon as a sample was withdrawn into a 5 ml chilled vial, the cap was replaced and the sample chilled in iced water to rapidly stop the reaction. The sample was then allowed to come to room temperature before 1 ml was added to 1 ml of a 5% V/V ortho-dichlorobenzene-n-heptane solution. O-Dichlorobenzene was used as an internal standard for Gas Chromatography (GC) analysis of the samples from the polymerization reaction. The new solution was then quickly analyzed after it was well mixed.

4.3 Analysis

An HP 5840A gas chromatograph was used for sample analysis using helium as a gas carrier at 20 milliliters per minute. The column used was 6 feet in length, 0.085-inch ID, 1/8-inch OD and was made of stainless steel. The packing was Hayesep Q material with a mesh range of 80 to 160. A thermal conductivity detector (TCD) was used. Usually, two injections were made for each sample to be analyzed. However, more injections were often necessary when the results seemed to deviate by more than 2%. A period of 30 minutes was needed for a complete GC run.

For a given time, t, the conversion of styrene into polystyrene is obtained from the results of the corresponding GC run. The calculation involves the comparison of the area ratio between the styrene peak and the internal standard (o-dichlorobenzene) peak obtained for
that specific time and the similar ratio obtained at time
zero (start of the reaction). In other words,

\[ x\% = \left[ 1 - \frac{\text{Area ratio at time } t}{\text{Area ratio at time } = 0} \right] \times 100 \quad (4.7) \]

In general, the differential rate equation for an n-th
order chemical reaction of the type \( A \rightarrow \text{Products} \) may be
written for the reactant A as,

\[ -r_A = -\frac{dC_A}{dt} = kC_A^n \quad (4.8) \]

where,

- \( r_A \) = rate of reaction, \( \text{mol L}^{-1}\text{sec}^{-1} \)
- \( C_A \) = concentration of reactant A, \( \text{mol L}^{-1} \)
- \( k \) = reaction rate constant, \( \text{mol}^{1-n} \text{L}^{n-1} \text{sec}^{-1} \)
- \( n \) = order of reaction
- \( t \) = time, sec

**Note:** For convenience and since only one reactant is
involved, the subscript "A" will be omitted from here
on. However, it should be understood that all
concentrations or conversions refer to the reactant A.

Because our study is only intended to confirm whether
the reaction order for the thermal polymerization of
styrene in heptane is equal to 2 or 5/2, only the integral
method of solution will be used [94]. In brief, this
method consists of the integration of Equation 4.8 assuming
a value for the reaction order \( n \) and then a determination
of how well the experimental data fit a straight line. In
terms of conversion, \( X \), versus time, the final integrated form is given by

\[
\frac{1}{(1 - \frac{1}{X})^{n-1}} = (n-1) kC_0 t + 1
\]

(4.9)

where, \( C_0 \) = initial reactant concentration, mol/L. By applying Equation 4.9 to our two special cases we obtain the following expressions:

For \( n = 2 \)

\[
\frac{1}{(1 - X)} = k_2 C_0 t + 1
\]

(4.10)

For \( n = 5/2 \)

\[
\frac{1}{(1 - X)^{1.5}} = 1.5 k_{5/2} C_0 t + 1
\]

(4.11)

The data can then be plotted as \( 1/(1-X) \) versus time and as \( 1/(1-X)^{1.5} \) versus time. The best fit to a straight line determined by linear regression analysis would hence permit the determination of \( n \). From Equation 4.9, it can be seen also that the intercept of the line should be equal to 1. Deviation around this value is another indication besides the value of the coefficient of determination \( R^2 \) on how well the data fits a straight line as predicted by Equation 4.10 or 4.11.

4.4 Results and Discussion

A total of six kinetic experiments were carried out. A summary of the conditions used in each experiment along with the important results obtained are presented in Table 4.1. The detailed experimental data can be found in
Appendix A. Also presented in the same appendix is a sample output from the gas chromatograph.

All six experiments were performed at the same pressure and mixing speed namely 150 psig (10.2 atm) and 100 rpm. The first four experiments were performed at a styrene concentration of 0.41 mol/L corresponding to 6.0 wt % styrene in heptane. For these runs the temperature ranged from 130 to 190°C at 20°C intervals. The last two experiments, i.e., Nos. 5 and 6, were done at the same temperature as No. 3 (170°C) but at different styrene concentrations of 0.20 and 0.068 mol/L corresponding respectively to 3.0 and 1.0 wt % styrene in heptane.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>C&lt;sub&gt;0&lt;/sub&gt; mol/L</th>
<th>T °C</th>
<th>T&lt;sup&gt;-1&lt;/sup&gt;x10&lt;sup&gt;3&lt;/sup&gt;</th>
<th>k&lt;sub&gt;2&lt;/sub&gt;x10&lt;sup&gt;3&lt;/sup&gt; L/mol.sec</th>
<th>Y&lt;sub&gt;0&lt;/sub&gt; (1)</th>
<th>R&lt;sup&gt;2&lt;/sup&gt; n=2</th>
<th>R&lt;sup&gt;2&lt;/sup&gt; n=5/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.41</td>
<td>130</td>
<td>2.481</td>
<td>3.88</td>
<td>1.02</td>
<td>0.985</td>
<td>0.960</td>
</tr>
<tr>
<td>2</td>
<td>0.41</td>
<td>150</td>
<td>2.364</td>
<td>21.49</td>
<td>1.01</td>
<td>0.996</td>
<td>0.988</td>
</tr>
<tr>
<td>3</td>
<td>0.42</td>
<td>170</td>
<td>2.257</td>
<td>70.24</td>
<td>0.99</td>
<td>0.990</td>
<td>0.976</td>
</tr>
<tr>
<td>4</td>
<td>0.41</td>
<td>190</td>
<td>2.160</td>
<td>187.68</td>
<td>0.96</td>
<td>0.996</td>
<td>0.986</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>170</td>
<td>2.257</td>
<td>94.6</td>
<td>0.98</td>
<td>0.979</td>
<td>0.963</td>
</tr>
<tr>
<td>6</td>
<td>0.068</td>
<td>170</td>
<td>2.257</td>
<td>110.29</td>
<td>1.05</td>
<td>0.988</td>
<td>0.990</td>
</tr>
</tbody>
</table>

(1) Y<sub>0</sub> = Intercept

Table 4.1 Summary of kinetic data and results

Observation of the plotted data as shown in Figures 4.2, 4.3, and 4.4 and consideration of the results obtained from linear regression analysis confirm that the order of reaction for the thermal polymerization of styrene in heptane is closer to 2 than 5/2. The best linear fit as
Figure 4.2 Determination of best reaction order using the integral method (Runs Nos. 1 and 2)
Figure 4.3 Determination of best reaction order using the integral method (Runs Nos. 3 and 4)
Figure 4.4 Determination of best reaction order using the integral method (Runs Nos. 5 and 6)
symbolized by the higher values in $R^2$ as shown in Table 4.1 was in all cases obtained with $n=2$ except for Run No. 6 in which the smallest styrene concentration was used. Considering these results, further interpretation of the kinetic data will only be done for $n=2$.

At this point, it should be noted that for Run 1 performed at 130°C, the initial four data points were found to lie well above the line hence setting the intercept to 1.05 and giving $R^2=0.967$ for $n=2$. When these points were removed, the new intercept and $R^2$ improved considerably to 1.02 and 0.985, respectively. The reason for the relatively high conversions attained at the start of that specific experiment is probably due to the temperature having exceeded the set point by about 15°C before it was controlled at 130°C. The effect of temperature on the reaction rate can be seen on Figure 4.5 which is a composite plot of the integrated form of conversion versus time data for Runs No. 1, 2, 3, and 4.

Figure 4.6 shows a plot of the second order rate constant $k_2$ versus the inverse absolute temperature, $1/T$. This Arrhenius type plot leads to the equation

$$k_2 = 3.95 \times 10^{10} \ e^{-12,025/T}$$

(4.12) suggesting an activation energy $E$ of 23,890 cal/mol, which appears to lie in the upper range of values reported in the literature, which were between 19.2 and 24.1 kcal/mol.
Figure 4.5 Effect of temperature on polymerization rates of styrene in heptane ($C_0=0.41M$)
Figure 4.6 Effect of temperature on $k_2$ ($C_0=0.41M$)
Figure 4.7 Effect of initial styrene concentration on polymerization rates (T=170°C)
A comparison of experimental data between Runs No. 3, 5, and 6 shows the effect of initial styrene concentration on the reaction rates. In Figure 4.7, the integrated forms of the conversion-time data for the three runs which were all carried out at 170°C are presented. As expected, higher concentrations are found to substantially favor the polymerization rate.

4.5 Conclusion

In the light of the kinetic results obtained in this investigation, the thermal polymerization of styrene in heptane seems to follow more closely a second order dependency on monomer concentration than a 5/2 order. The overall reaction rate determined by the present investigation is given by

\[-r = -\frac{dC}{dt} = k_2 C^2\]

(4.13)

where \(k_2\) is given by Equation 4.2 as

\[k_2 = 3.95 \times 10^{10} e^{-23890/RT} \text{ mol.}^{-1}\text{L.sec}^{-1}\]

and \(C\) is the styrene monomer concentration.
CHAPTER 5

APPARATUS AND PROCEDURES OF FOULING STUDIES

Introduction

In all the fouling studies carried out in this work on hydrocarbon fluids, the thermal method of analysis which relies on temperature measurements was used. The fouling test rig was designed and built so as to handle safely and accurately the conditions under which it had to operate.

5.1 Apparatus

The system used for the determination of the fouling characteristics of organic fluids is a closed-loop circulation system shown in Figure 5.1. It consists of a storage vessel, a circulation pump, a test section, two flow measurement devices, a heating and a cooling system and an IBM personal computer for data acquisition and control along with a parallel manual data measurement system composed of electronic meters. A brief description of the various components in the system follows.

5.1.1 Storage Vessel

The storage vessel was constructed out of a 27-inch long, 6-inch schedule 80 (5.671-inch ID) 316 stainless steel pipe. To the bottom and top of the pipe were respectively welded a 6-inch schedule 80 stainless steel cap and a fifteen hundred pound stainless steel flange.
Three holes were drilled in the top part of the flange to which Swageloc fittings were welded: two 1-inch holes for the filling of the system and for the return line and a 3/4-inch hole for multipurpose use including pressurizing and venting of the system.

5.1.2 Circulation Pump

Due to the nature of the organic fluids to be handled, recirculation of flow was provided by a magnetically driven sealless pump. The pump was equipped with a 3HP, 3600 rpm explosion proof motor. Design specifications of the pump allow operation under fluid temperatures of up to 600°F and pressures of 750 psig.

5.1.3 Test Section

The test section consists of an annular duct formed by a 15-inch long, 1-inch OD, 0.771-inch ID stainless steel outer tube on the axis of which is located a 0.375-inch diameter plain heater rod. Figure 5.2 shows a schematic diagram of the test section. The rods used in the present investigation were purchased from Drew Industrial Division, Boonton, New Jersey, and were made of either stainless steel or carbon steel material.

In the core of each rod, about seven inches from the lower end is located an electrical resistance heater capable of heating a 3-inch long rod section at a constant
Figure 5.1 Flow diagram of heat transfer fouling rig
Figure 5.2 Schematic of annular test section
heat flux. At 120 volts AC, the heater is rated at 1200 watts.

A variable transformer allows control of the amount of energy supplied to the heated section of the rod. Each rod contains one chromel-constantan thermocouple embedded in its wall. Prior to their use, the heaters must be calibrated in order to determine the exact location of the thermocouple below the surface of the rod.

The calibration method is explained in Appendix B. It is based on a method described by Knudsen [95] which uses a Wilson-type [96] plot, the purpose of which is to determine the thermal resistance (or conductance) of the heater wall between the thermocouple junction and the surface of the heater. Such information allows determination of the surface temperature at the exact heater-fluid interface in a fouling experiment. The fluid temperature at the inlet and outlet of the test section is measured by two thermocouples of the same type as the thermocouple of the heater.

The heater rod is centered by a screen sandwiched between the lower end of the outer tube and the inside ring of a 1-inch union. This union also serves to increase the hydrodynamic entrance length that precedes the heated section of the rod to about twenty equivalent diameters. This permits a uniform flow of fluid around the perimeter of the heater rod as it approaches the heated section.
5.1.4 Heating and Cooling of Bulk Fluid

Heating of the process fluid to the desired bulk temperature is obtained through the use of resistance band heaters clamped around the storage vessel. The three pairs of band heaters purchased from Watlow, Inc. are presently connected to provide about 2300 watts at 120 volts AC with a density of 7 watts per square inch. The power input to these heaters is controlled by a Variac. The storage vessel and heater assembly are insulated by a 1.5-inch thick foam-glass layer.

Similar band heaters of appropriate size are also clamped around the bottom and top flanges of the storage vessel. The purpose of these heaters is to help in the heating of the large mass of the stainless steel flanges. In addition to the heating obtained from these band heaters, it was found necessary to provide extra heating of the overall piping of the system particularly for the studies involving crude oil vacuum residuum.

In these studies, it was crucial to avoid any cold regions in the system which would cause solidification of the fluid. Besides, operation of the system at high bulk fluid temperature also made this auxiliary heating necessary. Hence, silicon rubber heaters of various wattage capabilities of 200, 300 or 400 watts and having widths of either 1, 2, or 4 inches were used. These heaters are wrapped tightly around the 1-inch OD piping of
the heat transfer loop, the Swageloc fittings and the pump head and flanges. A separate Variac controls the power input to these heaters.

To avoid excessive heat losses, the whole system is insulated with fiber glass tape. Aluminum paper tape is then used to keep the insulation in place. When cooling of the system is desired, it can be obtained by manually controlling the city water flow rate to a cooling jacket installed in the bypass line to the test section.

5.1.5 Flow Measurement

Two independent flow measurement devices are installed in series in the system to determine the flow rate of fluid through the test section. Initially, only a venturi flow meter having two orifices of respectively 0.59 inch and 0.370 inch diameter was in place for the studies involving heptane. The venturi is connected to a differential pressure cell that converts volumetric flow rate into millivolts by two 1/4-inch stainless steel tube lines. These lines can be vented of gases or vapors by 1/4-inch stainless steel valved lines which connect the DP cell to the inlet side of the pump. Flushing of these lines is done before the bulk fluid temperature gets too high so as not to damage the electronics associated with the DP cell.

Calibration of the venturi flow meter for volumetric flow rate versus voltage relationship determination was
done with water. The best fit of the line is given by the equation:

\[ GPM = 0.3591 (mV - 200)^{0.5043} \]  

(5.1)

and the correlation coefficient is 99.9%. Equation 5.1 shows that a zero flow rate corresponds to a DP cell output voltage of 200 millivolts.

The venturi flow meter could not be used in the experiments involving crude oil vacuum residuum for two reasons. First, the high viscosity of that fluid even at relatively high temperatures causes plugging of the pressure transmitting tubing connecting the venturi to the DP cell. Second, the electronics associated with the DP cell would not withstand the high temperatures intended to be used in this study. Therefore, a mass flow meter was purchased from Micro Motion, Inc., Boulder, Colorado.

The mass flow meter is of the type D100S. It consists of a sensor unit which contains two U-shaped tubes, a drive coil and two position detectors and a remote electronics unit (REU). When fluid flows through the tubes, it produces a twist angle of the tubes proportional to the mass flow rate. The position detectors then send a signal to the REU where the information is processed and converted into voltage. Mass flow rates of gases, liquids or slurries can be measured to within ±0.4% independently of change in temperature or pressure. The operating
temperature is from -400 to +400°F and the operating pressure should be less than 2250 psi.

The analog output voltage from the remote electronics unit of the meter is 0-5 volts corresponding to 0-55 pounds per minute. However, the A/D converter of the Adalab data acquisition card uses a voltage range of ±1 volt for temperature, power and volumetric flow rate measurement. It was then necessary to use the electrical resistance divider shown in Figure 5.3 to scale down the output voltage to 0-1 volt in order for the computer to be able to record the mass flow rate. The two resistances $R_1$ and $R_2$ are such that the voltage signal from the meter is reduced by about five fold before it is sent to the computer.

Because the ratio of $R_2/(R_1 + R_2)$ is not exactly equal to 1/5, a DC power supply was used to find the exact correction factor. A 5 volt signal from the power supply resulted in an output of 1.0015 volt from the divider. Also calibration of the mass flow meter independently of the venturi showed that a correction factor of 1.474 had to be included. Hence, the final equation used to convert voltage in millivolts from the divider directly to mass flow rate in pounds per minute is

$$\text{lb}_m/\text{min} = \text{mV} \times \frac{55}{1001.5} \times 1.474 \quad (5.2)$$
Figure 5.3  Schematic of electrical divider to reduce output voltage from REU.

\[ V_{\text{out}} = \frac{R_2}{R_1 + R_2} \times V_{\text{in}} = \frac{102.5}{410.5 + 102.5} \times V_{\text{in}} = \frac{1}{5.005} \times V_{\text{in}} \]

R1 = 410.5 ohms
R2 = 102.5 ohms
5.1.6 Data Acquisition and Processing

The organic fouling heat transfer loop is monitored and controlled using an IBM PC personal computer. An Adalab-PC data acquisition and control board from Interactive Microwave, Inc. (IMI) was installed in the PC to permit following the course of an experiment in time and to automatically compile and process the acquired data through a computer program written in basic (Appendix C).

The information received by the computer from the process in the form of voltages comes from various measurement sensors. Among these sensors are the three thermocouples that measure the temperature of the bulk fluid in and out of the test section and the heater wall temperature. The venturi flow meter and the mass flow meter are the sensors for flow rate measurement while the power supply to the heater rod is sensed by a wattmeter.

All the voltage signals from the sensors are processed within the computer program into information in the form of temperature in degrees F, flow rate in the form of either gallons per minute, pounds per minute, or velocity in feet per second, and power in watts. The results from fouling calculations are constantly displayed on the computer screen. The data is then recorded on a floppy disk at given time intervals that depend on the fouling rates. This same data is also printed on a Panasonic KX P1091i dot matrix printer at the same time it is recorded on the disk.
This allows permanent screening of the data at any time during an experiment.

In addition to the computer system, the experimental data can also directly and manually be monitored through electronic analog instruments. These include a digital thermometer which displays any of the desired temperatures through an Omega thermocouple switch and a digital multimeter that displays, in volts, any of the measured flow rates or power supplied to the test section. These electronic devices are mainly used when a fouling experiment is to be started. At that time, a trial and error method is used to set the desired initial heater surface temperature by adjusting the power input to the heater rod. It is therefore necessary to read this power input and the heater wall temperature as quickly as possible and do the calculations to find the surface temperature. This will be described later in this chapter.

5.1.7 Safety Measures

Due to the nature of the study and the fluids to be used, various measures were taken to maximize safety and to avoid possible equipment damage. Excessive pressures in the system although very unlikely are prevented through installation of a pressure relief valve connected to a venting bucket by a 1/4-inch stainless steel tubing. Various electrical cut-off devices were also put in place in case of overheating, power failure or pump failure.
In case of excessive heater wall temperature as fouling becomes considerable, a signal will be sent from the computer to cut off the power to the heater rod. This is done to avoid burnout of the heater. If a pump failure occurs, then both the power to the heater rod and to the tank band heaters will be cut off. In case of pump overheating, an alarm is activated.

All the electrical wiring of the system follows the required safety rules. The open electrical circuits and devices are enclosed in a hermetically closed box. Inlet and outlet wiring are made through openings drilled at the bottom of the box. Inside the box is also installed the mass flow meter remote electronics unit and two voltage amplifiers for temperature measurement.

5.2 Procedure

5.2.1 Heptane-Styrene Experiments

Before the installation of the mass flow meter, the volume of feed used to initially fill the system was equal to 3.75 gallons. Prior to its use, the heptane purchased in twenty liter quantities from J.T, Baker, Inc. had to be distilled in a fifteen liter flask. The styrene which was purchased in four liter quantities also from J.T. Baker, Inc was distilled under vacuum for removal of the stabilizing agent. It was then kept in a glass flask under an inert gas environment. The flask was completely covered
with aluminum foil to avoid light and was kept in the refrigerator until use.

The heptane-styrene solution was prepared as quickly as possible to minimize oxygen uptake. For the studies involving sulfur compounds, the measured amount of a given sulfur compound is also added to the heptane-styrene solution. The system is then charged with the prepared solution by the use of a funnel. After tightly closing the cap of the filling opening, the system is pressurized with nitrogen to about fifty psig. It is then purged to the open air by opening the vent valve. Two more pressurizing-depressurizing actions are done in order to remove as much oxygen as possible from the system. Finally, the system is again pressurized to about fifty psig before the pump is started.

Heating of the fluid to the desired bulk temperature is performed with the external heating from the band heaters around the storage vessel. When the desired temperature is reached, the flow rate is adjusted and nitrogen supply is used to raise the pressure to the desired value. When all these conditions are met, the fouling experiment is ready to be started. To do so, the power to the heated section of the heater rod is slowly increased through a Variac and the rise in heater wall temperature closely observed.
The trial and error method to find the correct value of the power input needed to obtain a desired initial heater surface temperature is minimized in time. The method relies on the following equations:

\[(q/A)_o = U_o(T_w - T_{bo}) = h_o(T_{so} - T_{bo}) \quad (5.3)\]

and,

\[\frac{1}{U_o} = \frac{1}{h_o} + R_w \quad (5.4)\]

from which,

\[T_{so} = T_{wo} - (q/A)_o R_w \quad (5.5)\]

Hence, the surface temperature can easily be calculated by knowing the heat flux \(q/A\) (i.e., the power input \(q\) since the heat transfer area is known) and the heater wall temperature \(T_w\). As long as \(T_s\) is below the desired value, the heater power input is increased and the calculations repeated. Usually, the desired conditions are reached within less than five minutes.

As soon as the final heater power is found adequate, the computer program is started. Because of the extra heat supplied to the fluid by the heater rod, the heat input to the band heaters is decreased accordingly so as to keep the average bulk temperature of the fluid at the desired value. Usually, this is achieved by manually controlling the power supplied to the band heaters during the first hour of the experiment. After that, the bulk temperature usually remains constant within \(\pm 2^\circ F\).
Termination of a fouling experiment depends on many factors. If consistent fouling occurs, the run is terminated automatically by power cut off to the heater if its temperature reached a fixed value or manually if asymptotic value of the fouling resistance is thought to have been reached. If fouling is not so consistent or if no fouling seems to occur, the run is operated for a time believed to be sufficient for no fouling to occur.

After termination of the experiment, all external heating of the system is stopped. The heater rod is then allowed to cool down to the fluid temperature before the test section is then depressurized by draining the fluid trapped in it. This permits removal of the heater rod unit from the system without having to cool down the system completely. Such a procedure allows observation of the deposit as soon as the run is terminated.

The heater is then cleaned in an organic solvent which easily dissolves the polymer film formed. The system is cooled by opening the city water supply to the cooling heat exchanger jacket. It is then drained completely of the heptane-styrene solution before it is filled with an organic solvent which is circulated in the loop under pressure for a few hours in order to remove any polymer adhering to the piping walls. Before another experiment is started, the system is rinsed with pure heptane.
5.2.2 Crude Oil Residuum Experiments

The investigation of the fouling characteristics of a crude oil residuum diluted with a solvent (Penrenco Oil 2257) made it necessary to install a mass flow meter in the system for flow measurement. Such changes which also resulted in changes in the piping of the system increased somewhat the total volume of the system. It was therefore decided to use a charge of 4 gallons instead of 3.75 gallons.

Because the crude oil residuum supplied by Chevron Corporation in 5 gallon quantities is solid at room temperature, it is necessary to heat up the container first before the contents could become liquid. To do so, the 5 gallon bucket containing the residuum is immersed into a large cylinder filled with water in which a steam line was connected. It usually takes about 5 hours for the crude oil medium to melt. Meanwhile, another 5 gallon steel bucket is filled with the desired amount of solvent (amounts used were either 1 or 2 gal to make 75% or 50% V/V mixtures).

When the vacuum residuum is capable of flowing out of its original container, it is poured into the bucket containing the constantly mixed oil solvent until a total volume of 4 gallons is obtained. During this operation, the bottom of the bucket is kept in the hot water to ease the dissolution of the residuum. When the mixture is well
mixed, it is charged into the system. Prior to introducing the mixture into the system, it is important to first heat up all the system by supplying a small power input to the band heaters as well as the silicon rubber heaters while preparing the mixture. From this point, the method used to perform an experiment is similar to that described in the case of heptane-styrene.

Termination of a fouling experiment is also the same as for heptane-styrene runs. However, because the deposits obtained with the residuum are usually of a carbonaceous nature, mechanical cleaning of the heater rod is necessary for deposit removal. The method adopted is to install the heater in a lathe and use 400 grit 3M wet/dry sand paper to remove the carbon. At the end, the surface is polished with 600 grit 3M wet/dry sand paper which seems to give the same smoothness as the original heater.
CHAPTER 6

A STUDY OF CHEMICAL REACTION FOULING UNDER BOILING CONDITIONS USING STYRENE DISSOLVED IN n-HEPTANE

Introduction

In order to better understand the mechanisms involved in fouling of heat transfer equipment by organic fluids it is necessary to first investigate a simple system where only a single chemical reaction takes place. This approach is helpful when studying much more complicated systems such as those found in the petrochemical industries where perhaps hundreds of reactions occur simultaneously. In those cases, it is quite impossible to separate the various effects on each reaction.

6.1 Choice of the Styrene-Heptane System.

The polymerization of styrene as a model chemical reaction which results in the formation of a polymer film that deposits on the heat transfer surface was chosen for several reasons:
1. The reaction has been studied quite extensively.
2. The radical chain polymerization reaction of styrene can be initiated thermally without the use of an initiator.
3. The polystyrene deposit can be easily removed from the heat transfer surface using an organic solvent such as toluene which dissolves the polymer completely. This keeps
the surface identical from one experiment to the other since no mechanical cleaning is therefore necessary.

4. The physical properties of polystyrene are well known. The choice of heptane as a solvent was on the other hand, not so simple. In fact, hexane was first used but turned out to be very unstable. The solvent has to meet several requirements:

- It should not be subject to any chemical reaction in the temperature range to be used.
- It has to be relatively pure.
- Its boiling point should be in the medium range.
- It has to be relatively inexpensive.

Considering these requirements, heptane was found to be adequate and therefore was used in the investigation.

6.2 General Description of the Study

The investigation reported in this chapter includes a series of 65 fouling experiments using n-Heptane containing three different concentrations of styrene, namely, 1.0, 3.0, and 6.0 wt%. The nomenclature used to designate the various runs is as follows:

HEP - redistilled n-heptane
ST(X) - contains X wt% predistilled styrene
0 - oxygen present during a fouling test.

Hence, for example, Run No. 54 which used 6.0 wt% and was performed under oxygen present is designated HEP-ST (6.0)-0-54).
Besides the effect of styrene concentration on fouling, other variables were investigated as well. These variables are the heater surface temperature, the fluid velocity in the test section and, to a lesser extent, the bulk fluid temperature. Furthermore, the effect of the presence of oxygen was investigated. Fouling curves giving the thermal fouling resistance of the deposited polymer film versus time were obtained and the initial fouling rate was determined whenever significant fouling occurred. The method used to determine the initial fouling rate from a fouling curve is explained in detail in Appendix D where examples are also given.

A critical factor that must be known in each fouling experiment is whether the experiment occurred under local boiling or non-boiling conditions. In order to have this information, boiling experiments were performed on heptane free of styrene. The purpose of these experiments is to obtain boiling curves at the same operating conditions as the fouling runs. From these curves it is then possible to imply whether boiling was present in a given fouling test.

6.3 Boiling Experiments with Heptane

As previously mentioned, it is important to know if a given fouling experiment is performed under local boiling or non-boiling conditions. The six heat transfer boiling tests summarized in Table 6.1 were performed on pure redistilled heptane.
The boiling experiments have to be carried out at the same conditions of bulk fluid temperature, velocity and system pressure. The method is to gradually increase the power to the heated section of the heater rod, hence the heat flux, and to record the heater wall temperature at each power level. From this information and knowing the thermal resistance of the heater wall, it is possible to determine both the wall superheat \((T_s - T_b)\) and the convective heat transfer coefficient \(h\).

There are several ways of representing a boiling curve. Either the heat flux \(q/A\) or the convective heat transfer coefficient \(h\) is plotted versus the superheat \((T_s - T_b)\). In either case, the result is a curve which basically shows three heat transfer regions. At low
superheat, a straight line with a very small slope represents the region where heat transfer is by natural and forced convection. As the superheat increases, the curve shifts to another line having a very steep slope. This line is typical of the nucleate boiling zone. The transition region between the convective region and the nucleate boiling region is usually not easy to locate experimentally.

Figure 6.1 and Figure 6.2 show the various boiling curves obtained with heptane. The computer program used for heat transfer calculations along with the detailed experimental data are presented in Appendix E. Figure 6.1 and Figure 6.2 also show the effect of fluid velocity on the boiling curves at a given bulk temperature and pressure. The results indicate that in the pure convective region, the lines shift upward as the velocity increases. However, this effect disappears as boiling becomes predominant. At that point, the intense turbulence created by bubble formation overshadows the turbulence due to fluid flow and therefore all the data merge into a common line.

6.4 Results and Discussion of Fouling Experiments

Table 6.2 summarizes all the fouling tests performed with styrene in heptane along with the specific operating conditions. The various quantities given in the table and their dimensions are as follows:
Figure 6.1 Boiling curves for heptane (\(T_b=190^\circ\text{F}, P=110\ \text{psig}\))
Figure 6.2  Boiling curves for heptane ($T_b=210^\circ F$, $P=150$ psig)
t = duration time of run, hr
$v = \text{bulk fluid velocity, ft/sec}$
$T_s = \text{heater surface temperature, °F}$
$T_b = \text{bulk fluid temperature, °F}$
$P = \text{total static pressure, psig}$
$h_o = \text{value of convective heat transfer, Btu/hr ft}^2\text{°F}$
$R_f^* = \text{value of fouling resistance at end of run, hr ft}^2\text{°F/Btu}$
$\dot{R}_{fo} = \text{initial fouling rate, ft}^2\text{°F/Btu}$

In the last column of the table, some comments are included concerning the experiments. These comments are described below:

REU = re-used feed from previous run
B = boiling
NB = non-boiling
F = fouling occurred
NF = no fouling occurred
NSF = no significant fouling occurred

In the following discussion, the effect of styrene concentration, heater surface temperature, bulk fluid velocity, bulk fluid temperature and oxygen will be discussed. All the runs carried out in the absence of oxygen were done under an inert environment of nitrogen. On the other hand, the runs which are reported to include oxygen were carried out under a mixture of nitrogen and
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<th>T_b</th>
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<th>R_f^*</th>
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Table 6.2 Summary of fouling runs

RUNS WITH 6.0 wt% STYRENE (OXYGEN ABSENT)
Table 6.2 Summary of fouling runs (continued)

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**RUNS WITH 3.0 wt% STYRENE (OXYGEN ABSENT)**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp.</th>
<th>Conc.</th>
<th>Run Time</th>
<th>Efflux</th>
<th>Freq.</th>
<th>Fouling Rate</th>
<th>Stiffness</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEP-ST(3.0)-38</td>
<td>21.75</td>
<td>3.0</td>
<td>365</td>
<td>210</td>
<td>150</td>
<td>430</td>
<td>39.3</td>
<td>6.7</td>
</tr>
<tr>
<td>HEP-ST(3.0)-39</td>
<td>23.75</td>
<td>3.0</td>
<td>345</td>
<td>210</td>
<td>150</td>
<td>242</td>
<td>1.1</td>
<td>---</td>
</tr>
<tr>
<td>HEP-ST(3.0)-40</td>
<td>44.50</td>
<td>3.0</td>
<td>355</td>
<td>210</td>
<td>150</td>
<td>250</td>
<td>-2.7</td>
<td>---</td>
</tr>
<tr>
<td>HEP-ST(3.0)-41</td>
<td>2.45</td>
<td>3.0</td>
<td>374</td>
<td>210</td>
<td>150</td>
<td>532</td>
<td>28.8</td>
<td>22.4</td>
</tr>
<tr>
<td>HEP-ST(3.0)-42</td>
<td>3.75</td>
<td>3.0</td>
<td>373</td>
<td>210</td>
<td>150</td>
<td>534</td>
<td>29.0</td>
<td>23.8</td>
</tr>
<tr>
<td>HEP-ST(3.0)-43</td>
<td>41.75</td>
<td>5.5</td>
<td>373</td>
<td>210</td>
<td>150</td>
<td>673</td>
<td>9.2</td>
<td>0.9</td>
</tr>
<tr>
<td>HEP-ST(3.0)-44</td>
<td>60.75</td>
<td>5.5</td>
<td>362</td>
<td>210</td>
<td>150</td>
<td>639</td>
<td>22.8</td>
<td>0.9</td>
</tr>
<tr>
<td>HEP-ST(3.0)-45</td>
<td>25.75</td>
<td>8.0</td>
<td>364</td>
<td>210</td>
<td>150</td>
<td>544</td>
<td>-1.7</td>
<td>---</td>
</tr>
</tbody>
</table>

**RUNS WITH 1.0 wt% STYRENE (OXYGEN ABSENT)**

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Temp.</th>
<th>Conc.</th>
<th>Run Time</th>
<th>Efflux</th>
<th>Freq.</th>
<th>Fouling Rate</th>
<th>Stiffness</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEP-ST(1.0)-46</td>
<td>21.00</td>
<td>3.0</td>
<td>363</td>
<td>210</td>
<td>150</td>
<td>468</td>
<td>36.2</td>
<td>6.0</td>
</tr>
<tr>
<td>HEP-ST(1.0)-47</td>
<td>4.85</td>
<td>3.0</td>
<td>372</td>
<td>210</td>
<td>150</td>
<td>658</td>
<td>22.9</td>
<td>17.2</td>
</tr>
<tr>
<td>HEP-ST(1.0)-48</td>
<td>41.25</td>
<td>3.0</td>
<td>354</td>
<td>210</td>
<td>150</td>
<td>248</td>
<td>-6.2</td>
<td>---</td>
</tr>
</tbody>
</table>
Table 6.2 Summary of fouling runs (continued)

| HEP-ST(1.0)-49 | 24.50 | 5.5 | 363 | 210 | 150 | 415 | -1.2 | ---- | NF,B |
| HEP-ST(1.0)-50 | 18.50 | 5.5 | 373 | 210 | 150 | 385 | -2.8 | ---- | NF,B |
| HEP-ST(1.0)-51 | 3.50  | 5.5 | 383 | 210 | 150 | 508 | -0.1 | ---- | NF,REU,B |
| HEP-ST(1.0)-52 | 5.50  | 3.0 | 396 | 210 | 150 | 478 | 20.6 | 53.1 | F,REU,B |
| HEP-ST(1.0)-53 | 36.00 | 5.5 | 363 | 210 | 150 | 663 | 1.4  | 0.6  | NSF,B |

**RUNS WITH 6.0 wt% STYRENE (OXYGEN PRESENT)**

| HEP-ST(6.0)-0-54 | 2.25  | 3.0 | 373 | 210 | 150 | 479 | 34.5 | 98.0 | F,B |
| HEP-ST(6.0)-0-55 | 2.05  | 3.0 | 374 | 210 | 150 | 449 | 36.4 | 123.0| F,B |
| HEP-ST(6.0)-0-56 | 15.25 | 3.0 | 365 | 210 | 150 | 360 | 51.6 | 4.9  | F,B |
| HEP-ST(6.0)-0-57 | 116.75| 3.0 | 356 | 210 | 150 | 219 | 5.6  | 0.2  | F,NB |

**RUNS WITH 3.0 wt% STYRENE (OXYGEN PRESENT)**

| HEP-ST(3.0)-0-58 | 9.75  | 3.0 | 374 | 210 | 150 | 517 | 31.0 | 8.5  | F,B |
| HEP-ST(3.0)-0-59 | 25.75 | 3.0 | 364 | 210 | 150 | 356 | 7.6  | 0.6  | F,B |
| HEP-ST(3.0)-0-60 | 27.25 | 3.0 | 364 | 210 | 150 | 384 | 6.2  | 0.7  | F,B |
| HEP-ST(3.0)-0-61 | 10.00 | 3.0 | 384 | 210 | 150 | 525 | 26.6 | 6.7  | F,B |
| HEP-ST(3.0)-0-62 | 4.75P | 3.0 | 383 | 210 | 150 | 542 | 3.1  | ---- | F,B |

**RUNS WITH 1.0 wt% STYRENE (OXYGEN PRESENT)**

| HEP-ST(1.0)-0-63 | 8.00  | 3.0 | 373 | 210 | 150 | 551 | 28.8 | 8.7  | F,B |
| HEP-ST(1.0)-0-64 | 42.50 | 3.0 | 363 | 210 | 150 | 380 | 13.7 | 0.8  | F,B |
| HEP-ST(1.0)-0-65 | 38.50 | 3.0 | 363 | 210 | 150 | 540 | 1.4  | 0.3  | F,B |

(1) Btu/hr ft²°F  (2) hr ft²°F/Btu x 10⁴  (3) ft²°F/Btu x 10⁴

(4) F - fouling  
   NSF - no significant fouling  
   REU - re-used fluid from previous run  
   B - boiling  
   NF - no boiling  
   NB - no boiling
compressed air. The corresponding amount of oxygen initially introduced into the system was equal to about 0.05 mole.

6.4.1 Effect of Styrene Concentration

Various fouling runs were performed at styrene concentrations of either 1.0, 3.0 or 6.0 wt%. Figures 6.3 to 6.6 are composite plots which show the effect of initial styrene concentration on the fouling resistance. In each figure, the runs included were carried out under similar conditions of surface and bulk temperature, velocity and pressure. This then leaves the concentration of styrene in the bulk fluid as the only parameter.

Observation of these figures shows that the effect of styrene concentration affects fouling of the heat transfer surface in several ways all depending on both velocity and surface temperature. For instance, at high surface temperature and low velocity, as in Figure 6.3, styrene concentration seems to enhance fouling. However, as the surface temperature is decreased and the velocity increased, such as in Figures 6.4 and 6.5, the effect of concentration becomes insignificant. This is of course, an indication that mass transfer and kinetics are two concurring effects in the system.

The effect of styrene concentration on the initial fouling rate is summarized in Figure 6.7 which is deduced from the plots of Figures 6.3, 6.4 and 6.5. The top curve
Figure 6.3  Effect of initial styrene concentration on fouling. Comparison of runs Nos. 24, 41 and 47
Figure 6.4 Effect of initial styrene concentration on fouling. Comparison of runs Nos. 26, 38 and 46.
Figure 6.5 Effect of initial styrene concentration on fouling. Comparison of runs Nos. 37, 44 and 53.
Figure 6.6 Effect of initial styrene concentration on fouling. Comparison of runs Nos. 34, 43 and 50
Figure 6.7 Effect of initial styrene concentration on initial fouling rates
indicates that at a combined high surface temperature and low velocity, a linear relationship exists between $\dot{R}_f$ and $C_{Ao}$. The slope of the line is equal to $3.5 \times 10^{-4}$. For the curve in the middle, the slope drops about tenfold to $3.4 \times 10^{-5}$. This line was obtained at the same velocity as the top curve but at a surface temperature of 10 degrees less. For the lowest line which shows no slope whatsoever, the surface temperature was lower and the velocity higher than for the top line.

The depletion of styrene concentration during a fouling experiment may have an effect on the overall fouling curve. However, although the same styrene-heptane solution was constantly recirculated during a fouling run, concentration depletion was not in this case a problem. Analysis of various styrene-heptane solutions before and after a fouling experiment where heavy fouling occurred revealed that, in general, less than 6% of the initial styrene has reacted. Consequently, the assumption of constant bulk styrene concentration is justified. Higher concentrations of styrene do not necessarily lower the induction time preceding the onset of fouling.

6.4.2 Effect of Surface Temperature

Since chemical reaction fouling by definition involves a chemical reaction, which in this case is the thermal polymerization of styrene, a strong effect of the temperature of the heat transfer surface was expected. The
results obtained are presented in Figures 6.8 to 6.12. As opposed to concentration, higher surface temperatures seem to always increase fouling. In fact, the effect is clearly significant as long as the surface temperature is above 355°F.

Below surface temperatures of 355°F, it is noted that no significant fouling occurs even at the lowest velocity used (3.0 ft/sec). In terms of initial fouling rates, Figure 6.13 summarizes some of the important results obtained from Figures 6.8, 6.9, and 6.10. For the three cases shown, the experimental data points were fit to an Arrhenius-type equation of the form: \( R_{fo} = A \exp\left(-\frac{E_f}{RT_s}\right) \).

The statistical results are given in Table 6.3 (\( R = 1.9872 \) if \( E_f \) is in Btu/lb-mole and \( T_s \) in °R)

<table>
<thead>
<tr>
<th>Case</th>
<th>Reference</th>
<th>A</th>
<th>( E_f/R )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fig. 6.8</td>
<td>( 1.66 \times 10^{37} )</td>
<td>( 7.70 \times 10^4 )</td>
<td>0.984</td>
</tr>
<tr>
<td>2</td>
<td>Fig. 6.9</td>
<td>( 6.67 \times 10^{68} )</td>
<td>( 13.71 \times 10^4 )</td>
<td>0.934</td>
</tr>
<tr>
<td>3</td>
<td>Fig. 6.10</td>
<td>( 1.43 \times 10^{43} )</td>
<td>( 8.95 \times 10^4 )</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Table 6.3 Best parameter fit for the lines of Figure 6.13

The activation energy \( E_f \) in this case should be regarded as an activation energy for the overall fouling process. This activation energy which is obtained from the slopes of the straight lines in Figure 6.13 seems to be
Figure 6.8 Effect of surface temperature on fouling. Comparison of runs Nos. 5, 7, 10, 13 and 14
Figure 6.9 Effect of surface temperature on fouling. Comparison of runs Nos. 24, 26, 29 and 30.
Figure 6.10 Effect of surface temperature on fouling. Comparison of runs Nos. 33, 34 and 37
Figure 6.11 Effect of surface temperature on fouling. Comparison of runs Nos. 38, 39, 40 and 41
Figure 6.12 Effect of surface temperature on fouling. Comparison of runs Nos. 46, 47 and 48
Figure 6.13 Effect of surface temperature on initial fouling rates
very close for cases Nos. 1 and 3. However, case No. 2 deviates quite sensibly which cannot be explained at the moment from the limited data obtained. All three cases were performed with 6.0 wt% styrene concentration. Cases No. 1 and 2 used a velocity of 3.0 ft/s but a different bulk temperature of respectively 190°F and 210°F. Case No. 3, on the other hand, was performed at 5.5 ft/s velocity and 210°F bulk temperature.

6.4.3 Effect of Velocity

As with the heater surface temperature, velocity also plays a major role in fouling. The curves shown on the composite plots of Figures 6.14 to 6.17 indicate that higher fluid velocities past the heat transfer surface considerably reduce fouling in each case.

The effect of velocity is closely related to the surface temperature being used. Comparison of Figures 6.14 and Figure 6.15, for example, shows that at a higher surface temperature (374°F), a much higher velocity (8.0 ft/sec) was necessary to limit fouling. Instead, at 364°F a velocity of 5.5 ft/sec only was enough to inhibit the deposition of foulant on the heat transfer surface. Figure 6.14 also shows that at 8.0 ft/sec, no major deposit occurred even after almost 240 hours.

The effect of velocity on the initial fouling rate is represented by Figure 6.18. In this case however, the data is plotted in log-log format. Although only one set of
Figure 6.14 Effect of velocity on fouling.
Comparison of runs Nos. 24, 34 and 36
Figure 6.15 Effect of velocity on fouling.
Comparison of runs Nos. 26 and 37 and runs Nos. 47 and 50.
Figure 6.16 Effect of velocity on fouling.
Comparison of runs Nos. 38, 44 and 45
Figure 6.17 Effect of velocity on fouling.
Comparison of runs Nos. 41 and 43 and
runs Nos. 46 and 49
Figure 6.18 Effect of velocity on initial fouling rates
data has three observations while all four others have only two, this plot is mainly intended to show the existing trends between the five data sets. Initial fouling rates at 8.0 ft/sec are missing since at that velocity fouling rarely occurred.

Given that the top line, which was obtained at C = 6 wt% and T_s = 374°F, showed a reasonably good fit to a straight line, all other sets were also fit to a straight line. This means that the relationship to be expected between \( \dot{R}_{fo} \) and \( v \) is of the power law form, i.e. \( \dot{R}_{fo} = av^b \) where \( a \) and \( b \) are constants. Table 6.4 summarizes the statistical results. All the reported cases are for runs carried out at \( T_b = 210°F \) and \( P = 150 \text{ psig} \).

<table>
<thead>
<tr>
<th>Case</th>
<th>Reference</th>
<th>a</th>
<th>b</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6 wt%, 374°F</td>
<td>2.64</td>
<td>-5.78</td>
<td>0.951</td>
</tr>
<tr>
<td>2</td>
<td>3 wt%, 374°F</td>
<td>0.76</td>
<td>-5.30</td>
<td>1.000</td>
</tr>
<tr>
<td>3</td>
<td>6 wt%, 364°F</td>
<td>0.038</td>
<td>-3.54</td>
<td>1.000</td>
</tr>
<tr>
<td>4</td>
<td>3 wt%, 364°F</td>
<td>0.031</td>
<td>-3.50</td>
<td>1.000</td>
</tr>
<tr>
<td>5</td>
<td>1 wt%, 363°F</td>
<td>0.054</td>
<td>-4.10</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Table 6.4. Best parameter fit for the lines of Figure 6.18

Observation of the results obtained and particularly the value of the exponent \( b \) is rather interesting. It appears that the value of \( b \) which symbolizes the intensity
of the velocity effect on $R_{fo}$ is strongly related to the surface temperature but very slightly with styrene concentration. The value of $b$ is very close between cases 1 and 2 which both used $T_s = 374^\circ F$ but different concentrations and between cases 3, 4, and 5 which all used $T_s = 364^\circ F$ but different concentrations. In other words, as surface temperature increases, a higher velocity is needed to bring down the fouling rate. However, because of the different slope of the lines obtained for the same concentration and varying temperatures, this statement is only true up to a certain value of the velocity.

To illustrate more clearly, consider case No. 2 and 4, again represented in Figure 6.19. Both cases used 3 wt% styrene concentration but case No. 2 used a higher surface temperature. Hence, below a velocity of about 5.9 ft/sec, which is the abscissa of the intersection point obtained by extrapolation of the two lines, a higher velocity is required at $T_s = 374^\circ F$ to keep the initial fouling rate the same. For example, to limit $R_{fo}$ to $4 \times 10^{-4}$ ft$^2$°F/Btu at $T_s = 374^\circ F$ a velocity of about 4.2 ft/sec is needed compared to only 3.4 ft/sec at $T_s = 364^\circ F$.

For velocities above 5.9 ft/sec, and if extrapolation of the lines is attempted, the trend is reversed in the way that lower velocities are needed at higher temperatures than at lower temperatures to get the same fouling rate. Because such results are believed to be very improbable, it
Figure 6.19 Illustration showing the combined effect of velocity and surface temperature on initial fouling rates.
is concluded that extrapolation of the lines above the limits at which they were obtained should not be made. Furthermore, the experimental data has shown that in general, only a small change in the fouling rate occurs between 5.5 and 8.0 ft/sec. At such velocities, very low values of these rates are recorded making any comparison very doubtful due to the errors involved.

Finally, it should be noted that the value of 1.000 in the coefficient of determination $R^2$ given in Table 6.4 for cases 2, 3, 4 and 5 is only the result of using two single data points to draw the corresponding lines. Therefore, these coefficient values should not really be regarded as true values.

6.4.4 Effect of Bulk Temperature

The effect of bulk temperature on fouling was not really a focus in this study as were surface temperature and velocity. However, since a few runs were carried out at different bulk temperatures the results are discussed. Figure 6.20 shows the fouling curves obtained at $T_b = 175^\circ F$ and $T_b = 190^\circ F$ for four experiments. By comparison of runs Nos. 1 and 9 and of Runs Nos. 2 and 15, it can be clearly seen that the bulk temperature does affect fouling quite significantly.

In fact, at the lowest bulk temperature of the fluid stream used ($175^\circ F$), there is a definite lack of significant fouling. On the other hand, fouling was
Figure 6.20 Effect of Bulk temperature on fouling. Comparison of runs Nos. 1 and 9 and runs Nos. 2 and 15.
evident at 190°F. Although the initial fouling rates obtained are not very high due to the low surface temperatures used in these runs, they are not negligible. For Runs Nos. 1 and 9 which used $T_s = 360°F$, the initial fouling rate increased about 1.5 times as $T_b$ was increased from 175 to 190°F. For Runs Nos. 2 and 15 ($T_s = 355°F$), the initial rate was equal to $2.7 \times 10^{-4} \text{ft}^2 \text{°F/Btu}$ for run No. 15 ($T_b = 190°F$) and no fouling at all was observed at $T_b = 175°F$ after a relatively long period of 44 hours. The fact that more fouling was obtained in run No. 15 than in Run No. 9 is probably due to the re-used feed in Run 9.

The general effect of bulk fluid temperature on fouling is yet to be understood. However, it can be speculated that higher bulk temperatures enhance the rates of reaction in the bulk fluid. If this is the case, then the polymer products formed are transported to the heat transfer surface to which they adhere by adsorption. More experimental data are needed to explain these results.

6.4.5 Effect of Oxygen

In order to determine if the presence of oxygen has any effect on chemical reaction fouling leading to the deposition of a polystyrene film, twelve experiments were performed with oxygen present in the system. These runs are labeled from number 54 to number 65 in Table 6.2. Although an increased rate in fouling was expected due to possible formation of peroxy radicals from the action of
oxygen on the styrene monomers, this was not often observed. On the contrary, and as is shown in the composite plots of Figures 6.21 through 6.24, the presence of oxygen did in most cases inhibit the fouling process.

One single exception is presented in Figure 6.21 for Runs Nos. 24 and 55. For these runs, the initial fouling rates were respectively equal to $34.6 \times 10^{-4}$ ft$^2$F/Btu (oxygen absent) and $123.0 \times 10^{-4}$ ft$^2$F/Btu (oxygen present). In all other cases, the initial fouling rate was found to be less for the experiments that were performed under the presence of oxygen.

A possible explanation for such behavior is that since the oxygen present in the system is mainly in the gas phase, the formation of peroxy radicals occurs in the bulk fluid. These radicals then react with fresh monomer molecules to form a polymer product that is possibly precipitated by the n-heptane. At the same time, the reaction zone in the vicinity of the heat transfer surface finds itself deprived from fresh monomer molecules that would thermally react locally to form the deposit.

Another feature that may be deduced from Figures 6.21 to 6.24 concerns the induction time. In most cases, the presence of oxygen seems to lower the induction time. For instance, in Figure 6.21, $t_d$ is reduced from 12.0 to 1.5 hours between Runs Nos. 26 and 56. Whether such observation should be generalized to mean that actually...
Figure 6.21 Effect of oxygen on fouling. Comparison of runs Nos. 24 and 55 and runs Nos. 26 and 56.
Figure 6.22 Effect of oxygen on fouling. Comparison of runs Nos. 41 and 58 and runs Nos. 47 and 63
Figure 6.23 Effect of oxygen on fouling. Comparison of runs Nos. 38 and 59 and runs Nos. 46 and 64
Figure 6.24 Effect of oxygen on fouling. Comparison of runs Nos. 53 and 65
oxygen helps initiate the polymerization reaction but later somewhat acts to limit fouling is subject to speculation.

6.5 Accuracy of Experimental Data

6.5.1 Reproducibility

Fouling experiments are well known to lack reproducibility. This is because so many factors influence the fouling process that it is very difficult to control all these factors in order to reproduce exactly a complete fouling experiment. Consequently, perfect reproducibility was not obtained in this study as well. Some examples are presented in Figures 6.25, 6.26, and 6.27 to illustrate the problem.

The purpose of the first two figures is to show how reproducibility of experimental data was found to depend on surface temperature. In Figure 6.25 are presented the fouling resistance versus time curves for Runs Nos. 24 and 25 which were carried out at the same operating conditions among which the surface temperature was relatively high at 374°F. Except for the induction period which was about twice for Run No. 24, the other parts of the curves seem to agree quite well. In fact, the corresponding initial fouling rates were almost the same (34.6 x 10^{-4} versus 35.7 x 10^{-4} ft²°F/Btu).

On the other hand, at low surface temperatures, reproducibility was found to be very poor probably due to the low fouling resistance values reached. Figure 6.26 is
Figure 6.25 Reproducibility of experimental data at high surface temperature. Comparison of runs Nos. 24 and 25
Figure 6.26 Reproducibility of experimental data at low surface temperature. Comparison of runs Nos. 27, 28 and 29.
Figure 6.27 Reproducibility of experimental data in the presence of oxygen. Comparison of runs Nos. 54 and 55
an example of the scatter obtained in the data for Runs Nos. 27, 28 and 29 which used $T_S = 355^\circ F$. The relatively large negative values in $R_f$ observed at the beginning of those runs may be the result of perhaps being in the transition boiling region rather than in the completely developed nucleate boiling region. It is not believed that initial deposit formation is the reason for the obtaining of such negative values in $R_f$ as is usually interpreted in the literature.

The last figure regarding the problem of reproducibility is Figure 6.27. This figure compares two fouling runs which were conducted in the presence of oxygen. Although both runs were performed at a relatively high surface temperature which as mentioned before helps to obtain good reproducibility, Figure 6.27 actually shows that the presence of oxygen does not affect reproducibility. In fact, in the case shown even the induction periods for the two runs are very close in addition to the initial fouling rates.

6.5.2 Experimental Error

In addition to the problem of reproducibility which does not depend on the equipment constituents used to measure fouling, experimental error is of main concern as well. The method used to calculate the uncertainty on the fouling resistance $R_f$ is that of Kline and McClintock [97]
recommended by Holman [98]. This method is explained in
detail in Appendix F.

The relative uncertainties on the fouling resistance
computed with the method of Kline and McClintock showed
that it is dependent on how large the fouling resistance
is. For low fouling, the relative uncertainty could be as
high as 6%. However, for consistent fouling, hence large
values of \( R_f \), the relative uncertainty could be as low as
1%. Following these results and the discussion about
reproducibility of the experimental data, it is concluded
that the results reported in this study are best when
obtained under conditions at which heavy fouling occurred.
On the contrary, the results obtained when very little
fouling occurred should be considered as not so consistent.
For the very small initial fouling rates reported in Table
6.2, usually very scattered data was used.

6.6 Nature of Deposits

For all the fouling experiments where heavy fouling
was recorded a thin, smooth and glassy polymer film was
found on the 3-inch long heated section of the heater. The
deposit extended about three inches downstream from the
heated portion. This deposit on the unheated region was
thicker and softer than that on the heated region. The
presence of this film indicates that the shear forces are
responsible for causing polymer products to slide along the
rod. This phenomenon is probably enhanced when the heater
surface reaches high temperatures due to fouling which then results in the melting of the polymer.

Since the deposit can only be formed of polystyrene (at least for the experiments with no oxygen), a sample was recovered at the end of an experiment. The molecular weight of that polymer was then determined by viscosimetry using the method of Staudinger [99]. This method is outlined in Appendix G and is well explained in various text books such as [100]. An Ostwald-type viscometer was used to measure viscosities of prepared solutions of benzene containing various concentrations of the dissolved polymer. The viscosity average molecular weight of the polystyrene was then determined graphically to be about 88100.

A simple test of whether the polystyrene formed during the fouling experiments is of atactic or isotactic form was done. Such tests proposed by Natta [101] simply consists of checking if the polymer is soluble in boiling heptane. If it is not, then it is of the atactic form which is amorphous. Also, amorphous polystyrene appears rubbery at relatively high temperatures and glassy at low temperatures which the deposits showed. On the other hand, isotactic polystyrene which is crystalline is a white-like powder which was not observed.

These observations along with the low molecular weight value obtained indicate that the atactic form of the
polymer deposit obtained in the present investigation. In any case, Danusso and Moraglio [102] in studying properties of the two polystyrene forms mentioned that atactic polystyrene is formed by thermal free radical chain polymerization of styrene which agrees with the present findings. Some important properties of atactic polystyrene are presented in Table 6.5 [103].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Conductivity $k$ at 266°F, Btu/hr ft°F</td>
<td>0.0780</td>
</tr>
<tr>
<td>Density $C$, lb/ft³</td>
<td>65.5</td>
</tr>
<tr>
<td>Heat Capacity $C_p$, Btu/lb°F</td>
<td>0.3105</td>
</tr>
<tr>
<td>Melting Point $T_{MP}$, °F</td>
<td>459</td>
</tr>
<tr>
<td>Softening Point $T_{SP}$, °F</td>
<td>176-221</td>
</tr>
</tbody>
</table>

Table 6.5. Some properties of atactic polystyrene

The thermal conductivity is particularly important since it allows calculation of the deposit film thickness with the knowledge of the fouling resistance, $R_f$, at any time during a fouling run. The low range of the softening point was always exceeded in this investigation. However, the melting point was only reached at the surface of the heater when fouling was significant. It is suspected that as the polymer melts on the heater, the deposit becomes weaker and therefore responds to the shearing action of the flow. Irregularities observed on the fouling curves
presented in this chapter are believed to be related to such phenomena.
CHAPTER 7

THE EFFECT OF VARIOUS ORGANIC SULFUR COMPOUNDS
ON FOULING RESULTING FROM THE POLYMERIZATION
OF STYRENE DISSOLVED IN n-HEPTANE

Introduction

For many years, petroleum chemists have studied reactions involving organic sulfur compounds such as sulfides, disulfides, and thiols. The presence of such compounds can affect hydrocarbon fuel stability. For instance, the oxidation of thiols to disulfides by oxygen is a common practice used for sweetening jet fuels in order to avoid organic deposits that may form in the inside surfaces of aircraft tanks. Thiol oxidation with molecular oxygen at low temperatures is an extremely slow reaction [104]. However, in the presence of an olefin, the oxidation is fast. This type of problem is therefore, of concern because it leads to deposit (sediment) formation. The present investigation was conducted to determine the effect of a variety of organic sulfur compounds on a simulated chemical reaction fouling problem involving an olefin.

7.1 General Description of the Study

Since the polymerization of styrene was already used to investigate chemical reaction fouling (See Chapter 6), the same system (styrene in heptane) was used in this
study. Small amounts of various sulfur based additives were used with the styrene-heptane mixtures. Overall, six different sulfur compounds were added at 10, 100 or 1000 ppm S level to qualitatively determine their respective effects on the fouling rates resulting from the deposition of the polymerization reaction products on a heat transfer surface. The sulfur compounds were selected so that their chemical structure differ from each other.

The experiments performed in this study are of two types. The first set of experiments were done under an inert environment of nitrogen gas while the second set of experiments were performed in the presence of oxygen. At the same time, the first set utilized 1.0 wt% styrene in heptane whereas in the second set, the styrene concentration was equal to 3.0wt%. A stainless steel heater rod was used in all of the tests.

The nomenclature used to designate the various runs is as follows:

HEP - redistilled n-heptane
0 - test conducted in the presence of oxygen
ST(X) - X wt% distilled styrene added
SYCC - sulfur added in the form of compound "Y" to make a solution containing "CC" ppm of sulfur with respect to styrene. Y can have values from 1 to 6 as follows:
1 = methyl-phenyl sulfide (C₆H₅SCH₃)
2 = n-dodecanethiol \((CH_3-(CH_2)_{11}SH)\)

3 = phenyl-n-propyl sulfide
\((C_6H_5S-(CH_2)_{2}-CH_3)\)

4 = diphenyl sulfide \(((C_6H_5)_2S)\)

5 = dibenzyl disulfide \(((C_6H_5-CH_2)_2S_2)\)

6 = thiophenol \((C_6H_5SH)\)

and CC can be as follows:

\[
\begin{align*}
TH &= 1000 \text{ ppm sulfur} \\
HU &= 100 \text{ ppm sulfur} \\
TE &= 10 \text{ ppm sulfur}
\end{align*}
\]

A total of 29 fouling experiments were conducted among which 14 were done in the absence of oxygen. The heat transfer boiling experiments performed on heptane and reported in Chapter 6 also apply to the present study. Such experiments are necessary so that local boiling or non-boiling conditions during a fouling test could be identified.

7.2 Results and Discussion of Fouling Experiments

A summary of the 29 tests to investigate the effect of 6 different organic sulfur compounds on fouling resulting from the polymerization of an olefin, namely styrene, is shown in Table 7.1. Along with the operating conditions of each specific test are also given some results such as the final fouling resistance recorded at run termination and the measured initial fouling rate when applicable. The
Table 7.1  Summary of fouling runs

<table>
<thead>
<tr>
<th>Run No.</th>
<th>t</th>
<th>v</th>
<th>T_s</th>
<th>T_b</th>
<th>h_0</th>
<th>R_f</th>
<th>R_{f0}</th>
<th>REMARKS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hr</td>
<td>ft/sec</td>
<td>F</td>
<td>F</td>
<td>psig</td>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
</tr>
<tr>
<td>RUNS WITH 1.0 wt% STYRENE (OXYGEN ABSENT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HEP-ST(1.0)-S1TH-1</td>
<td>21.00</td>
<td>3.0</td>
<td>355</td>
<td>210</td>
<td>150</td>
<td>243</td>
<td>-5.2</td>
<td>---</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S1TH-2</td>
<td>7.00</td>
<td>3.0</td>
<td>355</td>
<td>210</td>
<td>150</td>
<td>338</td>
<td>-0.4</td>
<td>---</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S1TH-3</td>
<td>14.00</td>
<td>3.0</td>
<td>366</td>
<td>210</td>
<td>150</td>
<td>385</td>
<td>-0.3</td>
<td>---</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S1TH-4</td>
<td>4.75</td>
<td>3.0</td>
<td>395</td>
<td>210</td>
<td>150</td>
<td>489</td>
<td>2.3</td>
<td>6.8</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S1HU-5</td>
<td>15.50</td>
<td>3.0</td>
<td>355</td>
<td>210</td>
<td>150</td>
<td>240</td>
<td>-0.6</td>
<td>---</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S1HU-6</td>
<td>5.25</td>
<td>3.0</td>
<td>365</td>
<td>210</td>
<td>150</td>
<td>250</td>
<td>0.1</td>
<td>---</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S1HU-7</td>
<td>36.75</td>
<td>3.0</td>
<td>375</td>
<td>210</td>
<td>150</td>
<td>422</td>
<td>3.0</td>
<td>3.4</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S1HU-8</td>
<td>36.50</td>
<td>3.0</td>
<td>373</td>
<td>210</td>
<td>150</td>
<td>484</td>
<td>3.4</td>
<td>0.4</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S1HU-9</td>
<td>42.25</td>
<td>3.0</td>
<td>373</td>
<td>210</td>
<td>150</td>
<td>469</td>
<td>2.6</td>
<td>0.4</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S1TE-10</td>
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<td>3.0</td>
<td>373</td>
<td>210</td>
<td>150</td>
<td>476</td>
<td>2.7</td>
<td>0.5</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S2TH-11</td>
<td>17.50</td>
<td>3.0</td>
<td>356</td>
<td>210</td>
<td>150</td>
<td>240</td>
<td>-3.0</td>
<td>---</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S2TH-12</td>
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<td>3.0</td>
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<td>150</td>
<td>342</td>
<td>-1.3</td>
<td>---</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S2TH-13</td>
<td>5.50</td>
<td>3.0</td>
<td>365</td>
<td>210</td>
<td>150</td>
<td>462</td>
<td>-0.4</td>
<td>---</td>
</tr>
<tr>
<td>HEP-ST(1.0)-S2TH-14</td>
<td>14.00</td>
<td>3.0</td>
<td>373</td>
<td>210</td>
<td>150</td>
<td>633</td>
<td>-0.1</td>
<td>---</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>RUNS WITH 3.0 wt% STYRENE (OXYGEN PRESENT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEP-ST(3.0)-S1HU-O-15</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S1HU-O-16</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S2HU-O-17</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S2HU-O-18</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S2TE-O-19</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S3HU-O-20</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S3HU-O-21</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S3HU-O-22</td>
</tr>
</tbody>
</table>
Table 7.1  Summary of fouling runs (continued)

<table>
<thead>
<tr>
<th>Run</th>
<th>Temperature</th>
<th>Time</th>
<th>Flow</th>
<th>Fouling</th>
<th>Fouling</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEP-ST(3.0)-S4HU-0-23</td>
<td>14.45</td>
<td>3.0</td>
<td>384</td>
<td>210</td>
<td>150</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S4HU-0-24</td>
<td>26.75</td>
<td>3.0</td>
<td>374</td>
<td>210</td>
<td>150</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S5HU-0-25</td>
<td>26.00</td>
<td>3.0</td>
<td>384</td>
<td>210</td>
<td>150</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S5HU-0-26</td>
<td>23.25</td>
<td>3.0</td>
<td>374</td>
<td>210</td>
<td>150</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S6HU-0-27</td>
<td>42.00</td>
<td>3.0</td>
<td>394</td>
<td>210</td>
<td>150</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S6HU-0-28</td>
<td>41.25</td>
<td>3.0</td>
<td>384</td>
<td>210</td>
<td>150</td>
</tr>
<tr>
<td>HEP-ST(3.0)-S6HU-0-29</td>
<td>43.00</td>
<td>3.0</td>
<td>374</td>
<td>210</td>
<td>150</td>
</tr>
</tbody>
</table>

(1) Btu/hr ft²°F  (2) hr ft²°F/Btu x 10⁴  (3) ft²°F/Btu x 10⁴
(4) F - fouling  NF - no fouling
    NSF - no significant fouling  REU - re-used fluid from previous run
    B - boiling  TB - transition boiling
various quantities presented in the table are explained in Chapter 6, section 6.2.

7.2.1 Tests in the Absence of Oxygen

Fourteen tests labelled HEP-ST(1.0)-S1TH-1 to HEP-ST(1.0)-S2TH-14 in Table 7.1 constitute this group. All of these runs used 1.0wt% styrene. Bulk fluid temperature, velocity, and static pressure were fixed at 210°F, 3.0 ft/sec and 150 psig, respectively. Hence, the only variables to be considered are the surface temperature and the type and amount of sulfur compound used. The amount of oxygen in the system was limited to that eventually dissolved in the liquids added to the system.

The first series of runs (HEP-ST(1.0)-S1TH-1 to -4) was conducted with methyl-phenyl sulfide at 1000 ppm sulfur level. Figure 7.1 shows the results where the data obtained for Runs -2, -3, and -4 are translated in time accordingly since the feed was reused in each of them. Negative values of the fouling resistance are noted for Run -1 which was initiated in the transition boiling region as indicated by the value of the heat transfer coefficient. Fully developed nucleate boiling occurred very early in the test. Run -2 was initiated by increasing the heat flux at the termination of Run -1.

No fouling occurred for Run -2 nor -3 ($T_s = 355°F$ and $T_s = 366°F$, respectively). However, as soon as the surface temperature was increased to 395°F (Run -4), a relatively
Figure 7.1 Effect of surface temperature on fouling in the presence of methyl-phenyl sulfide (1000 ppm S). Comparison of runs Nos. 1, 2, 3 and 4 (no oxygen)
small but rapid increase in $R_f$ took place. The fouling resistance quickly stabilized at a value of $2 \times 10^{-4}$ hr ft$^2$F/Btu while the initial fouling rate was equal to $6.8 \times 10^{-4}$ ft$^2$ F/Btu. At the same operating conditions but without any sulfur additive, these two quantities were respectively found to be equal to $20.6 \times 10^{-4}$ hr ft$^2$F/Btu and $53.1$ ft$^2$ F/Btu for Run HEP-ST(1.0)-52 which is compared to Run HEP-ST(1.0)-S1TH-4 in Figure 7.2. It is postulated that, although the polymerization reaction of styrene is initiated rapidly by the sulfur free radicals, these free radicals then act as scavengers by reacting with the vinyl radicals of the styrene. Hence, the polymer growth is hindered by the excess of sulfur free radicals.

The next series of tests (Runs HEP-ST(1.0)-S1HU-5 through HEP-ST(1.0)-S1TE-10) had as an objective the determination of the effect of the amount of methyl-phenyl sulfide added to the system while the styrene concentration is maintained constant. The effect of surface temperature is shown in Figure 7.3 where Runs -5, -6, and -7 are plotted together in time sequence. Run -5 shows some small negative values of the fouling resistance but it ultimately returned to a zero value. Again, no fouling was obtained until the heat flux was increased to reach a surface temperature of 375°F at which a jump in the fouling resistance occurred almost immediately. After this rapid polymer deposition, which resulted in an initial fouling
Figure 7.2 Effect of organic sulfur compounds on fouling in the absence of oxygen. Comparison of runs Nos. 4 and 52 (blank run from Table 6.2)
Figure 7.3 Effect of surface temperature on fouling in the presence of methyl-phenyl sulfide (100 ppm S). Comparison of runs Nos. 5, 6 and 7 (no oxygen)
rate of $3.4 \times 10^{-4}$ ft$^2$°F/Btu, the fouling resistance then became constant at $3.0 \times 10^{-4}$ hr ft$^2$°F/Btu.

Figure 7.4 shows the effect of the addition of 10 and 100 ppm S from methyl-phenyl sulfide and 100 ppm S from n-dodecanethiol on fouling of 1.0wt% styrene in heptane solution. The blank run is for the sulfur free solution. Two tests (HEP-ST(1.0)-S1HU-8 and -9) were done at all similar conditions to show the reproducibility of experimental data when a sulfur compound is involved. As can be seen, the results are quite satisfactory as given also by the identical value of the initial fouling rates of $0.4 \times 10^{-4}$ ft$^2$°F/Btu. From the various fouling curves obtained, it can be concluded that for methyl-phenyl sulfide, an amount equivalent to 10 ppm S is sufficient to limit considerably the polymerization of styrene on the heat transfer surface. In fact, at 100 ppm S level, no difference is observed compared to the 10 ppm S level. For the thiol additive (n-dodecanethiol), fouling is completely eliminated with the addition of an amount equivalent to 1000 ppm S even at the relatively high surface temperature of 373°F used (Run HEP-ST(1.0)-S2TH-14).

The free radical addition of thiols to olefins, known to be an anti-Markovnikov addition, is extremely facile [105]. The formation of thiyl radicals RS· necessary to initiate the chain process by attacking monomer molecules is easily accomplished by heat or even by peroxide
Figure 7.4 Effect of organic sulfur compounds on fouling in the absence of oxygen. Comparison of runs Nos. 8, 9, 10, 14 and 47 (blank run from Table 6.2)
impurities in the reagents due to the very weak quality of the sulfur-hydrogen bond [106]. Back, et al. [107] proposed the following mechanism for the addition of thiols to olefins:

$$\text{Initiation: } \text{RSH} \xrightarrow{k_1} \text{RS}^*$$  \hspace{1cm} (7.1)

$$\text{RS}^* + \text{M} \xleftarrow{k_2} \xrightarrow{k_3} \text{A}^*$$ \hspace{1cm} (7.2)

$$\text{Chain transfer: } \text{A}^* + \text{RSH} \xrightarrow{k_4} \text{AH}^* + \text{RS}$$ \hspace{1cm} (7.3)

$$\text{Propagation: } \text{A}^* + \text{M} \xrightarrow{k_5} \text{AM}^*$$ \hspace{1cm} (7.4)

$$\text{Termination: } 2\text{RS}^* \xrightarrow{k_6} \text{RSSR}$$ \hspace{1cm} (7.5)

$$2\text{A}^* \xrightarrow{k_7} \text{AA}$$ \hspace{1cm} (7.6)

$$\text{A}^* + \text{RS}^* \xrightarrow{k_7} \text{ASR}$$ \hspace{1cm} (7.7)

Where \( \text{M} \) is a monomer molecule and \( \text{A}^* \) is the adduct radical. The fate of the overall reaction depends on the competition between the reactions given by Equations 7.3 and 7.4. Since usually chain transfer is more rapid than propagation and if the concentration of thiol is equal or greater than that of the monomer, the propagation step becomes negligible [108]. This therefore, explains the absolute absence of fouling with n-dodecanethiol. On the other hand, methyl-phenyl sulfide showed a much lower inhibitory effect. Moureux and Dufraisse [109] do claim that methyl-phenyl sulfide can be used to stabilize styrene.
7.2.2 Tests in the Presence of Oxygen

Fifteen fouling experiments were conducted with mixtures of 3.0 wt% styrene in heptane doped with quantities of sulfur compounds corresponding to 100 ppm of S by weight with respect to styrene. Only one test (Run HEP-ST(1.0)-S2TE-O-19) used 10 ppm of S. In order to be able to compare the effects of the various sulfur additives on the deposition rates, the surface temperature was kept constant at two levels (384 and 374°F) while the bulk temperature, velocity and pressure were maintained constant at 210°F, 3.0 ft/sec and 150 psig, respectively.

The two composite plots shown in Figure 7.5 and Figure 7.6 summarize the results obtained at $T_s = 384°F$ and $T_s = 374°F$, respectively. In each figure are plotted the corresponding fouling curves obtained with the six different organic sulfur compounds that were used at 100 ppm S level to dope solutions of 3.0 wt% styrene in heptane. Also are shown on the plots the fouling curves obtained at the same exact conditions but without any sulfur additive used. These runs were reported in Chapter 6, Table 6.2.

At $T_s = 384°F$ (Figure 7.5), it appears that the sulfides have no or little effect on fouling caused by the formation followed by the deposition of a polystyrene film on the heated surface. For instance, the experimental data obtained with added diphenyl sulfide (S4) virtually coincide with that of the undoped system (blank). The
Figure 7.5 Effect of organic sulfur compounds (100 ppm S) on fouling in the presence of oxygen at T_e=384°F. Comparison of runs Nos. 15, 17, 21, 23, 25, 28 and 61 (blank run from Table 6.2)
Figure 7.6 Effect of organic sulfur compounds (100 ppm S) on fouling in the presence of oxygen at \( T = 374^\circ F \). Comparison of runs Nos. 16, 18, 22, 24, 26, 29 and 58 (blank run from Table 6.2)
initial fouling rates for the two runs are nearly the same. Methyl-phenyl sulfide (S1) and phenyl-n-propyl sulfide (S3) show some slight effect since they both decreased the initial fouling rate from $6.7 \times 10^{-4}$ (blank) to $4.3 \times 10^{-4}$ (S1) and $4.8 \times 10^{-4}$ (S3) $\text{ft}^2\text{F/Btu}$. The effect of the disulfide (S5) appears to be intermediate between that of the mono-sulfides (S1 and S3) and that of the thiols (S2 and S6) which after 40 hours showed no sign of fouling.

At $T_s = 374^\circ\text{F}$ (Figure 7.6), the overall picture appears to be slightly different than at $T_s = 384^\circ\text{F}$ although the order of influence of the different sulfur compounds is in general preserved. In this case, either the sulfides are more active in limiting fouling or the rate of polymerization of styrene is slow enough that the reactivity of the sulfides becomes relatively important. On the other hand, the fouling curve obtained with the disulfide (S5) added is almost identical to that obtained at $T_s = 384^\circ\text{F}$. Since a decrease in temperature was in general, found to decrease fouling from undoped mixtures of styrene in heptane, it could be speculated that the reactivity of the disulfide also decreased to explain the unchanged form of the fouling curve. Again, both thiols used (S2 and S6) led to zero fouling as was the case at $T_s = 384^\circ\text{F}$ where flat fouling curves were observed up to 40 hours run time possibly due to chain transfer to the additive.
The effect of sulfur concentration using n-dodecanethiol as a source is shown in Figure 7.7. The data obtained at $T_s = 384^\circ F$ with 10 ppm and 100 ppm sulfur from that compound are compared to the corresponding blank run (HEP-ST(3.0)-0-61, Chapter 6). It is interesting to notice how determinant the amount of thiol used can be. The styrene:n-dodecanethiol molar ratios corresponding to 10 and 100 ppm of S are respectively 920:1 and 92:1. This indicates that although the amount of styrene is predominant, the thiol behaves very reactively to hinder the polymerization process. As the sulfur concentration is decreased to only 10 ppm, the polymerization reaction of styrene is able to proceed although at a smaller rate but at a relatively high temperature which should also be a factor.

To clearly examine the action of each of the organic sulfur additives that only partially lowered the extent of deposit formation at the two temperatures investigated several composite plots were prepared as shown in Figures 7.8 through 7.11. These figures are comparative plots for methyl-phenyl sulfide (S1), phenyl-n-propyl sulfide (S3), diphenyl sulfide (S4) and dibenzyl disulfide (S5). All the runs reported used 100 ppm of S. From these figures, it can be concluded that for the mono-sulfides, temperature seems to play a major role whether the compound is aromatic or aliphatic. On the other hand, very little change in
Figure 7.7 Effect of sulfur amount from n-dodecanethiol on fouling in the presence of oxygen. Comparison of runs Nos. 17, 19 and 61 (blank run from Table 6.2)
Figure 7.8  Effect of surface temperature on fouling in the presence of methyl-phenyl sulfide (100 ppm S). Comparison of runs Nos. 15 and 16 (with oxygen)
Figure 7.9  Effect of surface temperature on fouling in the presence of phenyl-n-propyl sulfide (100 ppm S). Comparison of runs Nos. 21 and 22 (with oxygen)
Figure 7.10 Effect of surface temperature on fouling in the presence of diphenyl sulfide (100 ppm S). Comparison of runs Nos. 23 and 24 (with oxygen)
Figure 7.11 Effect of surface temperature on fouling in the presence of dibenzyl disulfide (100 ppm S). Comparison of runs Nos. 25 and 26 (with oxygen)
fouling is observed between $T_s = 384^\circ F$ and $T_s = 374^\circ F$ when the disulfide is added to the system due to the well known higher stability of disulfides as opposed to mono-sulfides.

7.2.3 Discussion

An interesting feature that was observed in all the fouling tests performed in this study concerns induction times. In every case where a given sulfur compound was found to inhibit the overall polymer formation and deposition, the induction time preceding the start of the fouling process was unaltered by the presence of the sulfur additive employed. This observation may mean that the sulfur compounds do not really enter into play until some of the styrene is exhausted.

In the light of the results gathered, the free radical addition of the various organic sulfur compounds to styrene is hereafter discussed in a more general chemistry point of view. Many organic sulfur compounds may undergo decomposition at sufficiently high temperatures. For instance, thiols, disulfides and dialkyl sulfides were found to decompose at 300 to 750°F while diaryl sulfides only decomposed at 840°F [41]. The decomposition occurs by scission of the alkyl and/or the aryl C-S bond, the latter being much more stable. The experimental results support these findings as shown by Figure 7.5 and 7.6 in which the organic sulfur compound (S4) that did not decompose at the conditions used did not affect fouling.
Free radical addition of thiols to olefins such as styrene has been extensively studied. An early study of such a reaction was done by Kharasch, et al. [110] in the absence of oxygen:

\[ RS' + CH_2=CHR' \rightarrow RSCH_2-CHR' \] (7.8)
\[ RSCH_2-CHR' + RSH \rightarrow RSCH_2-CH_2-R' + RS' \] (7.9)

and in the presence of oxygen [111]:

\[ RS' + CH_2=CHR' \rightarrow RSCH_2-CHR' \] (7.10)
\[ RSCH_2-CHR' + O_2 \rightarrow RSCH_2-CHR'-O_2' \] (7.11)
\[ RSCH_2-CHR'-O_2' + RSH \rightarrow R-SOCH_2-CHR'O_2 + RS' \] (7.12)

which, therefore, leads to the formation of sulfoxides after going through the formation of peroxy radical intermediates.

In the present fouling experiments in which either n-dodecanethiol or thiophenol was used, no deposit formation occurred on the heated surface. In addition, the mixture at the end of the runs appeared to have become green while initially it was colorless. Only with the thiols did the heptane-styrene mixtures change color which is believed to be due to the formation of sulfoxides. The reactions involved can be summarized as follows:

\[ RSH + CH_2=CHR' + O_2 \rightarrow RSCH_2-CHR'-O_2H \rightarrow R-SOCH_2-CHR'-OR \] (7.13)

where \( R' \) is a phenyl group and \( R \) is either a phenyl or a \( C_7 \) alkyl group. Chain transfer to thiy radicals may have
affected considerably the polymerization reaction of styrene in the following manner by abstraction of a hydrogen from the thiol:

\[ R^\cdot + RSH \longrightarrow R_pH + RS^\cdot \]  
(7.14)

where \( R^\cdot \) is a possible chain propagating radical.

Considering the effect of the saturated monosulfides used (S1, S3, and S4) on fouling, it appears that structural effects are of importance as well. For a sulfide of the form Ph-S-R, the order of reactivity on oxygen uptake is [112]

\[ R = \text{Ph} > \text{Me} > \text{n-Pr} \]

Due to this difference in reactivity which translates into \( S_4 > S_1 > S_3 \), it is possible to explain the results obtained for the monosulfides in the following manner: If a given sulfur compound can quickly react with oxygen to form sulfoxides, the rate of the polymerization reaction of styrene is not decreased by the free radicals formed by decomposition of the sulfide. Therefore, the fouling process would be unaltered or only partially altered. This would then explain why more fouling was obtained with diphenyl sulfide (S4) than with methyl-phenyl sulfide (S1) than with phenyl-n-propyl sulfide (S3) as shown in Figures 7.5 and 7.6.

Finally, the overall results obtained in this thermal investigation seem to qualitatively agree well with those of Thomson, et al. [66]. In their study of fuel stability,
these workers found that the addition to a fuel oil of a variety of sulfur compounds resulted in different amounts of sludge formed. For instance, thiophenol was very effective in forming sludge while free sulfur, disulfides and polysulfides only promoted it. On the other hand, aliphatic sulfides, aliphatic mercaptans and thiophenes had no or very little effect on the formation of sludge in one gallon glass bottles stored at 100°F from which samples were withdrawn monthly.

7.3 Deposit characteristics

All the deposits obtained on the heat transfer surface appeared similar, at least visually, to those obtained when no sulfur compounds were added to the system. They were in the form of thin and transparent polymer films which seem to match the usual description of polystyrene. The polymeric materials were easily removed from the heater surface by immersing the heater in a cylinder containing toluene which completely dissolved the polymer.
CHAPTER 8
MODELLING CHEMICAL REACTION FOULING UNDER BOILING CONDITIONS

Introduction

As discussed in Chapter 2, several mathematical models have been developed for chemical reaction fouling but none has considered the effect of boiling. Despite the fact that several experimental investigations have been carried out under obvious boiling conditions it has not been consistent. In fact, according to Taborek, et al. [2], fouling under nucleate boiling conditions is one of the least investigated areas of fouling. One can speculate that there is a trade off associated with boiling heat transfer. On one hand, very good heat transfer can be accomplished due to the extra turbulence associated with the phenomenon. On the other hand, the high heat fluxes used and the extra turbulence may enhance mass transfer of foulants or foulant precursors to the heat transfer surfaces and hence resulting in unwanted material deposition on the metal surfaces.

In this chapter, an attempt is made to develop a model which could be used to possibly predict the rates of fouling in which a chemical reaction is the source of such deposited products. The successive events taking part in the overall fouling process will be taken into account.
These events are combined effects related to various transport phenomena, chemical kinetics and fluid dynamics. The model is derived on the basis of the results obtained with the deposition on a heat transfer surface of a polystyrene film formed by polymerization of styrene dissolved in n-heptane (Chapter 6). At the same time, the kinetic results obtained separately on the same system using a batch reactor (Chapter 4) will be used. These results mainly concern the order and the activation energy associated with the given reaction.

8.1 Development of Model

Applying the general idea of Kern and Seaton who first suggested that the net fouling rate is a combination of two opposing effects: deposition and removal, the fouling rate is given by

$$\dot{R}_f = \frac{dR_f}{dt} = \frac{1}{\rho_f k_f} (\phi_d - \phi_r)$$  

(8.1)

where, $\phi_d$ and $\phi_r$ are respectively the deposition rate and the removal rate of foulant. Equation 8.1 has been the initial step taken in basically every fouling model development. The next step is, therefore, to find ways of expressing $\phi_d$ and $\phi_r$ appearing in the right hand side of the equation.

In order to determine the expressions of $\phi_d$ and $\phi_r$, it is necessary to consider the various steps in the fouling process. Such steps include the following:
1. The foulant precursor (styrene) is brought adjacent to the reaction zone by convective flow.
2. The precursor molecules are then transported to the reaction sites through the liquid film by diffusion. In this step is also included the effect of boiling which enhances mass transfer due to the extra turbulence created by the boiling.
3. The monomer reacts in the reaction zone to form polymer products which form the foulant.
4. The polymer materials then either adhere to the heat transfer surface or return to the bulk fluid either due to solubility in the solvent or just by diffusion. For the case of polystyrene which is insoluble in heptane but soluble in styrene monomer, it is believed that no polymer is dissolved since the bulk styrene concentration is fairly small. However, removal of polystyrene is still possible due to wall shear forces which increase as the flow rate is increased. It is also believed that in the case of polymers such as polystyrene, the removal term is not only dependent on the velocity but also on the temperature reached by the deposit film as fouling proceeds. When the temperature at the metal-deposit interface gets close to the softening point of the polymer, the latter becomes more susceptible to the shearing action of the adjacent flowing fluid. This was experimentally observed since a thicker but softer polymer film was recovered downstream of the
heated length during the fouling experiments reported in Chapter 6 and Chapter 7.

Following the mechanism described above, some assumptions are made in order to analyze the process. Such assumptions include:

a. The concentration of styrene in the bulk fluid remains constant during the course of a fouling experiment. This was checked to be a valid assumption since only a small portion of the monomer has reacted even in the cases where heavy fouling occurred (Chapter 6.)

b. All styrene molecules that reach the reaction zone react to form polymer products. This assumes that no back diffusion of reactant to the bulk fluid is considered.

c. The polymer film is homogeneous along its thickness.

d. The bulk fluid temperature is constant.

e. The heat flux is constant.

f. The convective heat transfer coefficient remains equal to that recorded at clean conditions. This was also proven to be a valid assumption (See Chapter 6)

The rate of mass deposition on the heated length is given by:

\[ \phi_d = N_p - N_f \]  \hspace{1cm} (8.2)

where,

\[ N_p = \text{mass flux of precursor carried to the reaction zone} \]
\[ N_f = \text{mass flux of foulant possibly leaving the reaction zone} \]

The mass flux of precursor (styrene), \( N_p \), can be expressed in terms of the single mass transfer coefficient \( k_p \) and the concentration driving force \((C_{pb} - C_{pi})\) between the bulk fluid and the solid-fluid interface as

\[ N_p = k_p (C_{pb} - C_{pi}) \quad (8.3) \]

Equation 8.3 expresses the mass transfer diffusion of the reactant \( p \) through the liquid film to reach the interface where it can react. However, the axial velocity on which strongly depends \( k_p \) should not be the only important factor affecting mass transfer of reactant to the reaction zone. Because boiling has also a strong effect in disturbing the boundary layer next to the heat transfer surface, it does affect significantly the transport of the precursor to the reaction zone. To take this effect into account, a correction factor, \( E_b \), is included which depends on two dimensionless numbers: the Lockart-Martinelli parameter \( X_{tt} \) usually given in the form [113]:

\[ \frac{1}{X_{tt}} = \left( \frac{x}{1 - x} \right)^{0.9} \left( \frac{\rho_1}{\rho_v} \right)^{0.5} \left( \frac{\mu_v}{\mu_1} \right)^{0.1} \quad (8.4) \]

where \( x \) is the vapor quality, \( \rho \) and \( \mu \) are respectively the density and viscosity of the liquid (1) and the vapor (v), and the boiling number \( B_o \) given by

\[ B_o = \frac{(q/A)/\Delta h_v}{G/A_{cs}} \quad (8.5) \]
where \((q/A)\) is the heat flux, \(\Delta h_v\) the latent heat and
\((G/A_{cs})\) the total axial mass flux. Hence,

\[ E_b = f\left(\frac{1}{X_{tt}}, B_0\right) \tag{8.6} \]

A similar analysis was applied quite successfully by Gungor and Winterton [114] for the derivation of a two-phase flow heat transfer correlation for flow in tubes and annuli. These authors claimed improvement of an existing correlation proposed by Chen [115] for the prediction of duo-phase convective heat transfer by adding the boiling number as a parameter in the enhancement factor \(E_b\). The Lockart-Martinelli parameter accounts for the higher available velocities due to the formation of vapor, and the boiling number accounts for the extra turbulence created laterally by bubble formation. As Equation 8.5 shows, \(B_0\) is the ratio of the radial mass flux due to boiling over the total axial mass flux as it can also be argued that the correction factor \(E_b\) could include the effect of enhance mass transfer due to chemical reaction as indicated by Levenspiel [116].

The inclusion of the correction factor \(E_b\) results in modifying Equation 8.3 which simply becomes

\[ N_p = E_b k_p (C_{pb} - C_{pi}) \tag{8.7} \]

The enhancement factor \(E_b\) is assumed to be given by the same relation as that obtained by Gungor and Winterton, namely,
The mass flux of precursor to the reaction zone is balanced by the rate of chemical reaction. The reaction zone is considered to be the laminar sublayer which thickness can be determined using Equation 8.11 [118],

\[ \delta = \frac{5 D_e}{Re(f/2)^{0.5}} \]  \hspace{1cm} (8.11)

where,

- \( f \) = Fanning friction factor
- \( D_e \) = equivalent diameter of annulus
- \( Re \) = Reynolds number

Hence,

\[ N_p = E_b k_p (C_{pb} - C_{pi}) = k(C_{pi})^n \delta \]  \hspace{1cm} (8.12)

This relation is based on a quite large data bank on saturation boiling. Although the authors assumed that for subcooled boiling, there is no enhancement factor because there is no net vapor generation, it is believed here that an enhancement factor should be included as long as vapor is generated. For boiling in annuli, the equivalent diameter depends on the size of the annular gap as follows [117]:

\[ D_e = \frac{4 \times \text{flow area}}{\text{wetted perimeter}} \quad \text{for gap} > 4\text{mm (0.157in)} \]  \hspace{1cm} (8.9)

\[ D_e = \frac{4 \times \text{flow area}}{\text{heated perimeter}} \quad \text{for gap} < 4\text{mm (0.157in)} \]  \hspace{1cm} (8.10)

\[ E_b = 1 + 24000 B_0^{1.16} + 1.37 \left(\frac{1}{X_{tt}}\right)^{0.86} \]  \hspace{1cm} (8.8)
where,

\[ k = \text{reaction rate constant} \]
\[ n = \text{reaction order} \]

Since \( n = 2 \) for the polymerization of styrene in heptane (see Chapter 4), Equation 8.12 is used to solve for the unknown concentration \( C_{pi} \). The solution is therefore, obtained by solving the following second order polynomial in \( C_{pi} \)

\[ k \delta (C_{pi})^2 + E_b k_p C_{pi} - E_b k_p C_{pb} = 0 \]  
(8.13)

which solutions is

\[ C_{pi} = \frac{-E_b k_p + \left[ E_b^2 k_p^2 + 4 E_b k k_p C_{pb} \delta \right]^{1/2}}{2k \delta} \]  
(8.14)

Then, by substitution of Equation 8.14 in Equation 8.12, one obtains the mass flux \( N_p \) in terms of \( k, k_p \) and \( C_{pb} \) as

\[ N_p = \left[ \frac{-E_b k_p + \left[ E_b^2 k_p^2 + 4 E_b k k_p C_{pb} \delta \right]^{1/2}}{4k \delta} \right]^2 \]  
(8.15)

If back convection of foulant from the reaction zone to the bulk fluid is possible as assumed by Nijsing [72], then the mass flux of foulant is given by

\[ N_f = k_f E_b (C_{fi} - C_{fb}) \]  
(8.16)

where \( C_{fb} \) can usually be taken as zero.

Moreover, due to the relatively very low diffusivity of polystyrene which for example, is equal to \( 9 \times 10^{-7} \) cm\(^2\)/sec in methyl-ethyl ketone at 20°C [79], back diffusion
of polystyrene can be neglected. Therefore, Equation 8.2 reduces to:

\[
\phi_d = N_p = \left[ \frac{-E_b k_P + \left( E_b^2 k_P^2 + 4 E_b k_k p C_p \delta \right) / 4 k_P}{6} \right]^{1/2} \quad (8.15)
\]

The reaction rate constant \( k \) depends on the film temperature \( T_f \) in an Arrhenius fashion, i.e.,

\[
k = A e^{-E/RT_f} \quad (8.18)
\]

where \( E \) is the activation energy for the polymerization reaction of styrene and \( A \) a proportionality constant. On the other hand, the mass transfer coefficient, \( k_P \), of styrene monomer (precursor) through the liquid film can be determined by the use of a momentum and mass transfer analogy. For instance, the equation proposed by Metzner and Friend [119] is used to which the Sieder-Tate [55] viscosity correction factor is added as recommended by Metzner and Friend. Hence,

\[
k_P = \frac{f/2}{v \left( 1.20 + 11.8(f/2)^{0.5}(Sc - 1)Sc^{-1/3} \right) \left( \frac{\mu_b}{\mu_s} \right)^{0.14}} \quad (8.19)
\]

where, \( v \) = bulk fluid axial velocity

\( f \) = friction factor

\( Sc \) = Schmidt number = \( \mu / \rho D_{ps} \)

\( D_{ps} \) = diffusion coefficient of precursor p through the solvent s

\( \mu_b, \mu_s \) = dynamic viscosity of fluid at bulk and at surface temperature, respectively.
Equation 8.19 is valid for \(0.46 < S_c < 3000\). The diffusion coefficient \(D_{ps}\) of styrene in heptane is calculated from the Wilke-Chang equation as recommended by Reid, et al. [120] using a solvent association factor of 1.0. All physical properties were evaluated at the bulk fluid temperature except when mentioned otherwise. These properties were either taken from the literature [120,121,122] when available, or evaluated using the best methods recommended in those references.

Having assumed that no polystyrene product diffuses back to the bulk fluid after it is formed at the solid-liquid interface, the only possibility for polymer materials to reach the bulk flow is if they are removed from the fouled surface by fluid shear forces. This effect of velocity is believed to be important considering the usual asymptotic fouling curves observed experimentally (see Chapter 6). A removal process which depends on the hardness of the deposit material, and its force of adhesion to the wall on one hand, and on the possible strong removing action of the shearing forces on the other hand, was considered by Taborek et al. [37]. The removal term was expressed as

\[
\phi = C \frac{\tau}{R} \\
\tau_{r1b}
\]

(8.20)

where,
\[ \tau = \text{fluid shear stress} \]

\[ R_b = \text{deposit bond resistance opposing shear off} \]

\[ C_1 = \text{constant} \]

The fluid shear stress \( \tau \) is given by the relation

\[ \tau = \frac{1}{2} f v^2 \rho_f \]  
(8.21)

in which \( f \) is the friction factor, \( \rho_f \) the foulant density and \( v \) the velocity.

The resistance \( R_b \) was expressed as a function of both a parameter \( \psi \) dependent on the deposit structure and the fouling resistance \( R_f \) (or deposit thickness \( x_f \)) in the following manner:

\[ R_b = C_2 \psi / R_f^m \]  
(8.22)

where the exponent \( m \) is determined experimentally. For polymers (at least for polystyrene), it is suspected that the parameter \( \psi \) is dependent on perhaps velocity but more particularly on temperature. As the deposit film thickness increases, the thermal fouling resistance increases and as a result the temperature inside the deposit film also increases. This has the effect of softening the polymer deposit and even melting it as the melting point of polystyrene (about 482°F [101]) is exceeded. When the deposit becomes softer, it is more subject to the shearing action of the flow past the surface and therefore likely to be removed. This postulate follows from the experimental observation that consistent polymer deposit was found all
along the heater rod downstream of the 3-inch long heated length where the film was found to be thicker than on the hotter heated section.

Assuming the simple case \( m = 1 \) in Equation 8.22 and then substitution of Equation 8.22 in Equation 8.20, one obtains,

\[
\phi_r = C_3 \frac{T}{\psi} R_f
\]  

(8.23)

Finally, using Equations 8.1, 8.17, and 8.23, the following first order differential equation results

\[
\rho_f k_f \frac{dR_f}{dt} + C_3 \frac{T}{\psi} R_f = N_p
\]  

(8.24)

the solution of which is given by

\[
R_f = R_f^*(1-e^{-Bt})
\]  

(8.25)

with,

\[
B = \frac{C_3 \tau}{\rho_f k_f \psi}
\]  

(8.26)

and,

\[
R_f^* = \frac{\psi N_p}{C_3 \tau}
\]  

(8.27)

The form of the solution given by Equation 8.25 which agrees with the experimental fouling curves observed in this work indicate that the assumption of \( m = 1 \) is justified. However, this solution does not take into account the existence of induction or lag times which preceded the start of fouling in all experiments performed.
If such lag times had to be considered, then Equation 8.25 needs to be slightly modified to become

\[ R_f = R_f^* \left[ 1 - e^{-B(t - t_d)} \right] \tag{8.28} \]

where, \( t_d \) = induction time

For the present experimental data, there was not consistent reproducibility in the induction periods and because of this, no attempt is made to fit the model to the whole fouling curve. Instead, the model is used to predict the initial fouling rate. At this point some clarification concerning the development of Equation 8.25 is in order:

1. The mass flux \( N_p \) of precursor to the interface is assumed to remain constant.
2. The parameter \( \psi \) is assumed to be constant
3. The physical properties of the deposit are assumed to be constant.

The initial fouling rate is determined by differentiation of Equation 8.24 and by taking the limit at \( t = 0 \), hence

\[ \dot{R}_f(0) = \left. \frac{dR_f}{dt} \right|_{t=0} = BR_f^* = \frac{N_p}{\rho_f k_f} \tag{8.29} \]

which is equivalent to the rate of foulant deposition, \( \phi_d \).

The mass flux \( N_p \) is given by Equation 8.17 whereas the reaction rate constant \( k \) and the mass transfer coefficient of precursor \( k_p \) are expressed by Equations 8.18 and 8.19, respectively. The friction factor appearing in Equation 8.19 is evaluated using the Blasius equation,
\[ f = 0.079 \, \text{Re}^{-0.25} \quad 3 \times 10^3 < \text{Re} < 10^5 \]  
(8.30)

where,

\[ \text{Re} = \frac{\nu D_e \rho}{\mu} \]  
(8.31)

8.2 Testing of Model

In order to test the model, the experimental data obtained with the styrene-heptane-polystyrene system as the precursor-solvent-foulant is used. The reaction rate constant \( k \) is taken as the second order rate constant \( k_2 \) determined in the kinetic study described in Chapter 4. This rate constant is given by the relation:

\[ k_2 = 3.95 \times 10^{10} e^{-\frac{12025}{T_f}} \, \text{L}^{-1} \, \text{mol}^{-1} \, \text{sec}^{-1} \]  
(8.32)

where \( T_f \) is the film temperature which is equal to the arithmetic mean between heater surface temperature and bulk temperature in K. The rate constant \( k_2 \) can be converted to \( \text{ft}^3 \, \text{lb}^{-1} \, \text{hr}^{-1} \) by multiplying its value in \( \text{L}^{-1} \, \text{mol}^{-1} \, \text{sec}^{-1} \) by the constant 554.

The results are presented in Figure 8.1 where the experimental values of the initial fouling rate are compared with those predicted by the model. Good predictions are expressed by how close to the 45° line are the data points. As can be seen, quite large deviations are recorded in some cases while in others, the values of \( \dot{R}_{fo} \) match quite well. Therefore, deviations ranged widely from 13.0% to over 100% suggesting that some refinements
Figure 8.1 Comparison of measured initial fouling rates with model predictions.
are necessary.

The model was developed without any parameter fitting. It was, however, based on various assumptions which may not all be very accurate. Furthermore, the original introduction of the enhancement factor $E_b$ necessitated the use of the only a correlation (Equation 8.8) which was based on saturated boiling heat transfer data which may not be suitable for subcooled boiling. The use of the Metzner-Friend relation (Equation 8.19) possibly adds to the uncertainties involved in the evaluation of the physical properties of the system. As a result, it is concluded that although improvements are necessary, this model definitely offers an excellent basis for modelling of chemical reaction fouling under boiling conditions. Its application does, however, require knowledge of the kinetics of the fouling system involved.
CHAPTER 9
FOUling CHARACTERISTICS OF A CRUDE OIL RESIDUUM

Introduction

A problem that has been constantly faced by the petroleum industry is that of coking. This problem is encountered on heat exchanger surfaces as well as on the catalysts used in cracking of heavy hydrocarbons for the production of transportation fuels. In fluidized catalytic cracking (FCC) for example, high temperatures of up to 975°F are used which are responsible for causing coke deposition on the catalyst. In that case, continuous regeneration of the catalyst is accomplished by burning the coke in a contiguous regenerator. The fresh catalyst then returns to the reactor by circulation.

One of the main problems in this area is the knowledge of the extent of fouling before regeneration of the catalyst is necessary. Prediction of the rate of fouling is therefore of concern. This is further complicated by the fact that such rates are very highly dependent on the type of feed used and its composition as well as variables such as temperature and velocity. The following investigation was carried out to study the fouling characteristics of a Alaskan North Slope Vacuum Residuum (Crude Resid) supplied by the Chevron Corporation based in Richmond, California.
9.1 General Description of the Study

The main purpose of the study is to determine quantitatively the effect of two important variables on the fouling rates occurring during the deposition of solid materials from the crude resid on a heat transfer surface. These variables are namely, the heater surface temperature and the bulk fluid velocity. A first attempt to study the given resid undiluted resulted in several technical problems.

Before the undiluted resid could be charged into the system, it had to be heated in its original five gallon containers to make it more fluid. It was then introduced into the heat transfer loop which was preheated to avoid re-solidification. However, due to the high viscosity of the material even at relatively high temperatures (see section 9.2) the magnetically driven circulation pump in the circulation system was unable to provide any flow to the fouling test section.

Due to these unavoidable viscosity problems, it was decided to mix the crude resid with an organic solvent. The properties sought in such a solvent were a low content of unsaturated hydrocarbons and a sufficiently high boiling range. The former property was desired so that no polymerization reactions from foreign unsaturated organic compounds would occur. The latter property was needed so that very little evaporation of the solvent would occur.
during the mixing process with the crude resid. The solvent chosen was Penrenco 2257 oil which appeared to have such properties (See section 9.2).

Two different concentrations of the resid in solvent mixtures were used, namely, 50 and 75% by volume at about 150°F. The nomenclature used to designate the various tests using the crude resid/oil mixtures is as follows:

- **BO** - Boiling or heat transfer test
- **OIL** - Solvent (Penrenco 2257 oil)
- **0** - Test conducted in the presence of oxygen
- **RES(X)** - X% by volume of Alaskan North Slope Crude Oil Residuum (Resid) used.

A total of 55 fouling experiments and 6 heat transfer experiments were conducted. As explained in Chapter 6 (Section 6.2 and 6.3), the heat transfer experiments were necessary to determine if boiling conditions prevailed on the heat transfer surface during a fouling run.

The 55 fouling runs performed in the investigation included two different batches of crude resid and two heaters made of different materials, namely, stainless steel and carbon steel. The two heaters were of the same size. A few runs were carried out in the presence of oxygen. The crude resid was provided by the Chevron Corporation in five gallon containers. Two different batches of material were provided, each in 50 gallon lots.
The two lots were presumably the same material but as will be seen from the results displayed, quite different fouling characteristics were observed.

9.2 Specifications of the Crude Resid-Solvent System

The Alaskan North Slope Vacuum Residuum was received in five gallon containers from the Chevron Corporation. The specific gravity and kinematic viscosity versus temperature curves for the crude resid are given in Appendix H. Due to the very high viscous quality of the resid (about 32 centistokes at 400°F), it was decided to mix it with a Penrenco solvent before its fouling characteristics could be studied.

The Penrenco solvent "Oil 2257" was chosen as the desired solvent. Various properties of the solvent are given in Table 9.1 [123]. The high temperature boiling range and the absence of olefins were specifically of interest in choosing the solvent. In order to determine the bulk fluid velocity from mass flow rate measurement, it was essential to know the specific gravity of the new resid in solvent mixtures. For both the 50 and 75% V/V resid in oil mixtures, the specific gravity was experimentally determined at several temperatures below 160°F (Appendix H). The usual linear relationship between specific gravity and temperature enables extrapolation to higher temperatures.
Specific Gravity, 60/60°F  0.798
Viscosity at 100°F, Cst  2.18
Flash Point, °F  220
Initial Boiling Point, °F  430
End Point, °F  510
Aromatics Content, %  1.5
Olefins Content, %  0
Saturates Content, %  98.5
Carbon Numbering by GC  C\textsubscript{11} - C\textsubscript{16}

Table 9.1 Specifications of the Penrenco oil 2257

9.3 Boiling Experiments with Resid in Solvent

Six heat transfer experiments were carried out with a 75% V/V resid in oil mixture. A summary of the operating conditions at which these experiments were performed is presented in Table 9.1. Figure 9.1 shows the boiling curves obtained for Runs No. 1 and 2 which operated at the same conditions. Therefore, Figure 9.1 also shows the reproducibility of the heat transfer boiling data which is very good.

The heat transfer curves related to Runs No. 3, 4, 5, and 6 are shown in the composite plot of Figure 9.2. Since all the four runs were carried out at the same static pressure and bulk temperature, the only variable is the
Figure 9.1 Boiling curve for 75% V/V resid in Penrencos solvent ($T_b=310^\circ F$, $P=100$ psig, CS heater)
Figure 9.2 Boiling curves for 75% V/V resid in Penrenco solvent ($T_b=400^\circ\text{F}$, $P=200$ psig, CS heater)
velocity of the bulk fluid. As expected, it is observed that in the convection non-boiling region, higher heat transfer coefficients are attained at higher velocities for the same value of the superheat. On the other hand, such tendencies disappear in the nucleate boiling region where all the curves converge into a common line.

Table 9.2 Summary of boiling experiments with 75% V/V resid in Penrencol solvent.

<table>
<thead>
<tr>
<th>Run Name</th>
<th>T_b (°F)</th>
<th>P(psig)</th>
<th>v(ft/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OIL-RES(75)-BO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-1</td>
<td>310</td>
<td>100</td>
<td>1.0</td>
</tr>
<tr>
<td>-2</td>
<td>310</td>
<td>100</td>
<td>1.0</td>
</tr>
<tr>
<td>-3</td>
<td>400</td>
<td>200</td>
<td>1.0</td>
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<td>400</td>
<td>200</td>
<td>3.0</td>
</tr>
<tr>
<td>-5</td>
<td>400</td>
<td>200</td>
<td>5.5</td>
</tr>
<tr>
<td>-6</td>
<td>400</td>
<td>200</td>
<td>8.0</td>
</tr>
</tbody>
</table>

9.4 Results and Discussion of Fouling Experiments

Table 9.3 summarizes all the fouling experiments performed in the study. Also given in the same table are the operating conditions for each run along with some results and remarks. The various quantities and their corresponding units are the same as those described in Chapter 6, Section 6.4. The table is also divided so as to show which batch of resid (No. 1 or 2) and which heater (stainless steel or carbon steel) were used.
Table 9.3 Summary of fouling runs

<table>
<thead>
<tr>
<th>Run No.</th>
<th>t</th>
<th>v</th>
<th>T_s</th>
<th>T_b</th>
<th>P</th>
<th>h_0</th>
<th>R_f</th>
<th>R_f0</th>
<th>REMARKS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hr</td>
<td>ft/sec</td>
<td>F</td>
<td>F</td>
<td>psig</td>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
<td>(4)</td>
</tr>
<tr>
<td>RESID NO. 1</td>
<td>RUNS WITH STAINLESS STEEL HEATER</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>RESID NO. 1</td>
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<td>OIL-RES(75)-0-18</td>
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<td>OIL-RES(75)-21</td>
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<td>125</td>
<td>2.6</td>
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### Table 9.3 Summary of fouling runs (continued)

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<th>RESID NO. 2</th>
<th>RUNS WITH CARBON STEEL HEATER</th>
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<td>OIL-RES(75)-39</td>
<td>47 5.5 801 400 200 198 10.3 3.5 F</td>
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<td>6 8.0 789 400 200 245 9.4 39.3 F,REU</td>
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</tr>
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<td>151 8.0 651 400 200 224 24.4 2.3 F</td>
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<td>OIL-RES(75)-45</td>
<td>7 3.0 801 400 200 140 15.8 37.7 F</td>
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<td>OIL-RES(75)-46</td>
<td>19 3.0 802 400 200 138 16.3 32.0 F,REU,HC</td>
</tr>
<tr>
<td>OIL-RES(75)-47</td>
<td>23 3.0 802 400 200 139 16.1 18.3 F,REU,HC</td>
</tr>
</tbody>
</table>
Table 9.3 Summary of fouling runs (continued)

| OIL-RES(75)-48 | 62  | 3.0 | 701 | 400 | 200 | 134 | 3.2 | 1.3 | NSF |
| OIL-RES(75)-49 | 144 | 5.5 | 702 | 400 | 200 | 178 | 31.5| 2.7 | F   |
| OIL-RES(75)-50 | 179 | 8.0 | 600 | 400 | 200 | 215 | 10.2| 2.1 | F   |
| OIL-RES(75)-51 | 39  | 8.0 | 500 | 400 | 200 | 213 | 0   | ----| NF  |
| OIL-RES(75)-52 | 45  | 8.0 | 527 | 400 | 200 | 221 | 0   | ----| NF,REU |
| OIL-RES(75)-53 | 27  | 8.0 | 549 | 400 | 200 | 221 | 0   | ----| NF,REU |
| OIL-RES(75)-54 | 74  | 8.0 | 576 | 400 | 200 | 224 | 0   | ----| NF,REU |
| OIL-RES(75)-55 | 21  | 5.5 | 576 | 400 | 200 | 165 | 0   | ----| NF,REU |

(1) Btu/hr ft$^2$ °F  (2) hr ft$^2$ °F/Btu x 10$^4$  (3) ft$^2$ °F/Btu x 10$^5$

(4) F - fouling  NSF - no significant fouling  REU - re-used fluid from previous run
    HC - heater cleaned before run  NF - no fouling  P - power failure
9.4.1 Tests with Resid No. 1

At the start of the investigation, experiments were started using the resid from batch No. 1. Since some fouling research conducted by the Chevron Research Laboratories indicated that the Alaskan North Slope Crude Oil Residuum could foul a heat transfer surface if the temperature of the surface is at least 650°F, the first objective of the present study is to validate these findings.

9.4.1.1 Tests with Stainless Steel Heater

The stainless steel heater was initially used until the carbon steel heaters (on order) were received. Eleven Runs OIL-RES(50)-1 to -6 and OIL-RES(75)-7 to -11 were conducted with the stainless steel heater in absence of oxygen and two Runs OIL-RES(75)-0-12 and 0-13 in presence of oxygen (0.05 mole). All the runs were operated at a bulk fluid temperature of 300°F and a static pressure of 100 psig. The bulk fluid velocity was equal to 3.0 ft/sec except for Runs No. 10 and 11 for which it was respectively, 2.0 and 1.0 ft/sec.

The main variable in these tests was the surface temperature which ranged from 500 to 651°F. As indicated in Table 9.3, no major fouling occurred in any of the reported tests for run times of up to 50 hours. Since there was no fouling, the feed was constantly re-used from one experiment to the next but the heater was removed from
the system and cleaned any time the final fouling resistance in the previous run indicated some slight deposit formation. The initial heat transfer coefficient for this series of tests with the stainless steel heater is plotted versus superheat as shown in Figure 9.3. It appears that boiling occurred with the 50% resid mixtures but not with the 75% resid mixture as the slopes of the lines were respectively equal to 2.8 and 0.3.

9.4.1.2 Tests with Carbon Steel Heater

Since carbon steel is used in heat exchangers processing crude resid, a heater of similar material was suggested by the sponsor. Therefore, all further tests were done using a carbon steel heater in the test section. For the resid No. 1, 5 tests were carried out with 75% V/V resid in Penrenco solvent in the presence of oxygen (OIL-RES(75)-0-14 through -18). For these tests, bulk temperature and pressure were maintained constant at 300°F and 100 psig, respectively. Velocity and surface temperature were varied.

At surface temperatures below 653°F, no fouling occurred even at the lowest velocity of 0.5 ft/sec. When the surface temperature was increased to a value of 787°F, considerable fouling was observed. At this temperature, the initial fouling rate was determined to be 16.4 x 10^{-5} ft^2°F/Btu. The final fouling resistance value recorded at the end of the run was equal to 12.9 x 10^{-4} hr ft^2°F/Btu.
Figure 9.3  Heat transfer characteristics of 50% V/V resid in Penrenco solvent
($T_b=300^\circ F$, P=100 psig, SS heater)
However, this value was still increasing as the run was terminated.

The next series of tests OIL-RES(75)-19 through -27 was conducted without oxygen present in the system. The surface temperature was maintained around 787°F which appeared to be the threshold temperature for the fouling of this particular fluid. An exception was Run No. 24 which used a higher temperature of 798°F. All of the runs of this series were carried out at $T_b = 310°F$ and $P = 100$ psig.

The effect of re-using the feed on fouling is shown in Figure 9.4. While Run OIL-RES(75)-19 utilized a fresh mixture of crude resid in Penrenco solvent, Runs -20 through -23 each re-used the fluid from the previous run. Clearly, a strong effect exists. The initial fouling rate for Run -19 was $20.6 \times 10^{-5} \text{ ft}^2\text{ °F/Btu}$ whereas for the other runs no fouling was obtained. In Run -20, an unexplained sudden drop of the fouling resistance to rather large negative values was observed.

Similar results regarding the re-use of the fluid in subsequent tests are observed in Runs OIL-RES(75)-26 and -27 which were operated at $v = 5.5 \text{ ft/sec}$. The results of these two tests are shown in Figure 9.5. Using fresh fluid, Run -26 indicated an initial fouling rate of $30.5 \times 10^{-5} \text{ ft}^2\text{ °F/Btu}$ compared to only $4.2 \times 10^{-5} \text{ ft}^2\text{ °F/Btu}$ for Run -27. The values of the initial heat transfer
Figure 9.4 Effect of feed re-use on fouling from resid No. 1. Comparison of runs Nos. 19, 20, 21, 22 and 23.
Figure 9.5 Effect of feed re-use on fouling from resid No. 1. Comparison of runs Nos. 26 and 27
coefficient \( h_0 \) given in Table 9.3 also indicate that as a fluid is re-used, higher values of \( h_0 \) are obtained for the same operating conditions. A possible reason is that considerable changes take place in the fluid as it is circulated in the system at conditions under which fouling occurs. Perhaps, part of the foulant is removed during the fouling process which changes the characteristics of the bulk fluid so that it behaves differently when tested again under the same conditions.

The effect of heater surface temperature on fouling from the crude resid No. 1 is shown in Figure 9.6 in which Runs OIL-RES(75)-19 \( (T_s = 787^\circ F) \) and OIL-RES(75)-24 \( (T_s = 798^\circ F) \) are compared. With all other conditions being the same, the increase of 11°F in heater surface temperature results in a doubling of the initial fouling rate from \( 20 \times 10^{-5} \) to \( 40 \times 10^{-5} \text{ ft}^2 \text{ °F/Btu} \). This is consistent with the effect of temperature on the rate of chemical reactions which approximately doubles for every 10°F rise in temperature (See Chapter 6.)

Figure 9.7 is a composite plot of Runs OIL-RES(75)-19 \( (v = 1.0 \text{ ft/sec}) \), -25 \( (v = 3.0 \text{ ft/sec}) \) and -26 \( (v = 5.5 \text{ ft/sec}) \) that demonstrates the effect of velocity on the fouling of crude resid No. 1. Initial fouling rates are \( 20.6 \times 10^{-5}, 16.8 \times 10^{-5} \) and \( 30.6 \times 10^{-5} \text{ ft}^2 \text{ °F/Btu} \) for 1.0, 3.0 and 5.5 ft/sec, respectively. It also appears from Figure 9.7 that the final value of the fouling
Figure 9.6  Effect of surface temperature on fouling from resid No.1. Comparison of runs Nos. 19 and 24
Figure 9.7 Effect of velocity on fouling from resid No. 1. Comparison of runs Nos. 19, 25 and 26
resistance is affected quite significantly by velocity, having values of $20.4 \times 10^{-4}$ hr ft$^2$ °F/Btu (and still increasing rapidly), $9.0 \times 10^{-4}$ hr ft$^2$°F/Btu (increasing slowly) and $3.5 \times 10^{-4}$ hr ft$^2$°F/Btu (apparently constant) for velocities of 1.0, 3.0, and 5.5 ft/sec, respectively.

Finally, it should be mentioned that for the resid No. 1 the results were not always consistent as can be seen from Table 9.2. In particular, some very high negative values in the fouling resistance were observed with the 50% V/V mixtures of resid in Penrenco solvent (Runs -28, -30, and -31). It is suspected that in these cases, the experiments were initiated in the transition boiling region and then nucleate boiling occurred resulting in an increase in the heat transfer coefficient. The same type of observation can also be made concerning some of the mixtures containing only 25% of resid.

In the last series of tests using Resid No. 1 (Runs OIL-RES(75)-33 to -38), the bulk temperature was raised to 400°F. The pressure was raised to 200 psig. Again, somewhat strange results were obtained, probably due to the changes in the fluid. The high negative fouling resistance values obtained in Runs -34 and -37 which each re-used the feed from the previous run are believed to be due to transition boiling. This is further indicated by the relatively low values of the initial heat transfer coefficient. On the other hand, for Run -35 which used the
same operating conditions than Run -34 but fresh feed, no such negative values in $R_f$ were observed. The various discrepancies observed can only be attributed to either changes in the fluid as fouling proceeds or the local heat transfer state at which the test is started. In particular, if the test is started in the transition boiling zone, large negative values in the fouling resistance are experienced because if fully developed nucleate boiling occurs a significant increase in the heat transfer coefficient would result. More data on the fresh fluid is needed. Unfortunately, this is not possible since no more of this fluid is available.

9.4.2 Tests with Resid No. 2

When the experiments were started using the second batch of crude resid (referred to as Resid No. 2) received from the Chevron Corporation, no differences from the resid No. 1 were expected. Nevertheless, there were significant differences in the behavior of the two batches. All the tests performed with Resid No. 2 utilized a carbon steel heater.

The tests using Resid No. 2 are labeled from No. 39 to 55 in Table 9.3. This fluid was also diluted with 25% by volume of Penrenco solvent. Surface temperatures ranged from 500 to 800°F and velocities from 3.0 to 8.0 ft/sec. Bulk temperature and pressure were kept constant at respectively 400°F and 200 psig.
Initially, tests on Resid No. 2 were conducted at a surface temperature of 800°F since this appeared to be the threshold temperature for fouling with Resid No. 1. However, further tests at lower surface temperatures indicated that the threshold surface temperature for fouling was about 600 rather than 800°F as was obtained for Resid No. 1. This was the major difference identified between the two lots of crude resid.

The effect of re-using the feed is shown in Figure 9.8 which compares Runs OIL-RES(75)-45, -46, and -47 (Ts = 802°F). While Run -45 used fresh feed in Run -46, the feed was re-used from Run -45 and in Run -47 the feed was re-used from Run -46. It is interesting to notice that although there is an effect of re-using the feed, it is not as strong as with Resid No. 1 which had shown a completely different behavior as it was re-used. For the present case, the initial fouling rate values decreased in a regular fashion as the feed was re-used. The initial fouling rate decreased from $37.7 \times 10^{-5}$ to $32.0 \times 10^{-5}$ to $18.3 \times 10^{-5}$ ft$^2$°F/Btu from Run -45 to -46 to -47.

The important effect of surface temperature on fouling of Resid No. 2 was investigated. The results of five separate experiments which all used fresh feed are shown in Figure 9.9. The fouling curves shown are for Runs OIL-RES(75)-40, -43, -44, -50, and -51 (v = 8.0 ft/sec). The surface temperature range covered by these tests is from
Figure 9.8 Effect of feed re-use on fouling from resid No. 2. Comparison of runs Nos. 45, 46 and 47.
Figure 9.9  Effect of surface temperature on fouling from resid No. 2. Comparison of runs Nos. 40, 43, 44, 50 and 51 (v=8.0 ft/sec)
500 to 800°F. As expected for organic fouling which involves chemical reactions, higher surface temperatures enhance the fouling process by increasing the rates of chemical reactions taking place.

Although more runs were carried out at intermediate temperatures between 500 and 600°F, these were not shown since no fouling had occurred up to a surface temperature of 575°F (See Runs OIL-RES(75)-51 through -55 of Table 9.3). It appears that 600°F is about the threshold temperature for the Resid No. 2 since even at \( T_s = 575°F \) (OIL-RES(75)-54), no sign of any material deposition was observed on the heater. From the initial fouling rate measurement on the fouling curves of Figure 9.9 an Arrhenius-type plot was obtained as shown in Figure 9.10. The semi-logarithmic plot of the initial fouling rate versus the inverse of the surface temperature indicates a negative slope of 125.9 giving an activation energy of 25030 Btu/lb-mol (14.9 kcal/gmol). This value is typical of fouling processes reported in the literature in which organic fouling is involved.

At a velocity of 5.5 ft/sec the effect of surface temperature is shown in Figure 9.11 which is a composite plot of Runs OIL-RES(75)-39 (\( T_s = 800°F \)), -49 (\( T_s = 700°F \)) and -55 (\( T_s = 575°F \)). In this case, there does not seem to be a significant difference between 800°F and 700°F whereas at 575°F, no fouling is observed. The initial fouling
Figure 9.10 Effect of surface temperature on initial fouling rates from resid No. 2 (from Figure 9.9)
Figure 9.11 Effect of surface temperature on fouling from resid No. 2. Comparison of runs Nos. 39, 49 and 55 (v=5.5 ft/sec)
rates for the runs performed at 800 and 700°F were respectively equal to $3.5 \times 10^{-5}$ and $2.7 \times 10^{-5}$ ft$^2$ °F/Btu which are within 30% of each other for a temperature difference of 100°F. This is a small change in rate of fouling for such a large change in surface temperature.

The results obtained on the effect of surface temperature seem therefore to depend on the fluid flow rate past the heated surface where the products of the reaction accumulate. Obviously, the problem is directly related to mass transfer and chemical kinetics. At high fluid velocities, mass transfer is high. Therefore, the limiting step for the overall fouling process could be the chemical kinetics. Since chemical reaction rates are favored by high temperatures, an increase in the surface temperature should increase the fouling rates as was the case at 8.0 ft/sec.

On the other hand, although 5.5 ft/sec is already a relatively high velocity, the results indicate that for this fluid, mass transfer may be the controlling mechanism. The fact that there was only a small change in the fouling rates between 800 and 700°F is an indication that mass transfer is actually the rate-limiting step for the overall fouling process. Nevertheless, Figure 9.11 shows that even in this case, a threshold temperature for fouling exists.

Velocity appears to play a role in organic fluid fouling, hence, tests were conducted at various velocities
to determine the effect of this parameter. Figure 9.12 is a composite plot showing the variation of the fouling resistance with time for Runs OIL-RES(75)-39, -40, and -45 which were operated at a surface temperature of 800°F. The velocities for these runs were 5.5, 8.0, and 3.0 ft/sec, respectively. The initial fouling rates for these runs (at $T_s = 800°F$) are shown in Figure 9.14 plotted as a function of velocity. Figure 9.13 shows the fouling resistance-time curves for Runs OIL-RES(75)-43, -48, and -49 all conducted at $T_s = 700°F$ and velocities of 8.0, 3.0, and 5.5 ft/sec, respectively. The initial fouling rates for these runs are also shown in Figure 9.14 as a function of velocity.

There are some inconsistencies in the results. At both surface temperatures, the fouling curve for the highest velocity (8.0 ft/sec) lies between the other two velocities. This is somewhat unexpected. At $T_s = 800°F$, the greatest total fouling occurs at 3.0 ft/sec and the least at 5.5 ft/sec. The situation is reversed at $T_s = 700°F$ for which the greatest total fouling occurred at 5.5 ft/sec and the least occurred at 3.0 ft/sec. With respect to initial fouling rates at $T_s = 800°F$, a minimum fouling rate is observed at 5.5 ft/sec. At $T_s = 700°F$, the fouling rate is nearly independent of velocity.

Some of this behavior may be explained by considering processes that occur during fouling. The three processes that are involved in the overall fouling process are the chemical reaction, the mass transfer of the reactant to the
Figure 9.12 Effect of velocity on fouling from resid No. 2. Comparison of runs Nos. 39, 40 and 45 ($T_s=800^\circ F$)
Figure 9.13 Effect of velocity on fouling from resid No. 2. Comparison of runs Nos. 43, 48 and 49 (T_s=700°F)
Figure 9.14 Effect of velocity on initial fouling rates from resid No. 2 (from Figures 9.12 and 9.13)
heated surface and the removal of the deposit from the heated surface. The interactions of these three processes is likely very complicated. For example, at \( v = 8.0 \) ft/sec and \( T_s = 800\,^\circ F \), the chemical reaction rate is high, the mass transfer rate is high and the removal rate is high. The fouling rate is the result of these three processes. Since the data show that the initial fouling rate is quite high for these conditions (See Figure 9.14), it would suggest that the chemical reaction is the predominant rate limiting step while mass transfer is not limiting and removal is not rapid enough to reduce the rate of fouling significantly. At \( v = 5.5 \) ft/sec and \( T_s = 800\,^\circ F \), it is possible that the mass transfer has now become the rate limiting step and the removal rate is rapid enough to significantly reduce the initial fouling rate. At \( v = 3.0 \) ft/sec and \( T_s = 800\,^\circ F \), the mass transfer step is still the rate limiting step but the removal rate is low so that the resulting initial fouling rate is high. This could account for the minimum shown in the curve for \( T_s = 800\,^\circ F \) in Figure 9.14.

When the surface temperature is \( 700\,^\circ F \), it is possible that the chemical reaction is the rate limiting step at all velocities. This could explain the near independence of the initial fouling rate on the velocity. However, this postulate neglects consideration of the removal action of the velocity. When this is considered, it would be
expected that the initial fouling rate at 3.0 ft/sec would likely be higher than that at the higher velocities except for the fact that at 3.0 ft/sec the total fouling is very low and, hence, the removal rate might be small since removal rate is often proportional to the amount of deposit on the surface.

In the case of both surface temperatures, the fouling curves (not the initial fouling rates) are difficult to explain, i.e., the curve for \( v = 8.0 \) ft/sec lies between those for 3.0 and 5.5 ft/sec. This behavior again could be explained on the basis of the three processes of chemical kinetics, mass transfer, and deposit removal as was done above.

The reason for the reversal of the curves for 3.0 and 5.5 ft/sec at \( T_s = 700°F \) compared to those at \( T_s = 800°F \) cannot be explained. The interactions of chemical kinetics, mass transfer and deposit removal is probably very complicated and the above explanations are only conjecture.

The results indicate, that at very high surface temperatures (\( T_s = 800°F \)), significant fouling occurs such that very high fouling resistances are the result. At a lower surface temperature (\( T_s = 700°F \)), the results would indicate that perhaps an optimum velocity exists for which the ultimate fouling resistance is quite low. For example, from Figure 9.13, the fouling resistance at \( v = 3.0 \) ft/sec and \( T_s = 700°F \) appears to become relatively constant at a
reasonably low value of about 0.0003 hr ft² °F/Btu.

9.5 Deposit Characteristics

The fouling deposits were of two types. When a given test resulted in a very slight deposit (NSF - no significant fouling), the deposit was soft and gummy. In such cases, the heater was simply cleaned by immersing it in a glass cylinder containing toluene. This resulted in the complete removal of the slight deposit that was on the heater.

On the other hand, for tests in which heavy fouling occurred, the deposit was a thin, hard carbonaceous film. The hardness of this black deposit seemed to increase closer to the metal surface of the heater where higher temperatures existed. Removal of the deposit from the heater surface could only be accomplished by scraping the heater with a sharp blade. This operation had to be done very carefully so that the surface of the heater was not damaged.

After most of the deposit was removed mechanically, the heater was turned slowly in a lathe and buffed first with No. 400 and then with No. 600 grit 3M wet/dry sand paper. This cleaning method was used each time a hard deposit was formed on the heater in order to maintain uniformity of the surface condition between tests. After buffing, the surface was cleaned with toluene and the
heater was recalibrated to determine the new wall thermal resistance, $R_w$. 
Fouling of heat transfer surfaces by organic fluids was investigated. A model foulant system consisting of styrene-heptane-polystyrene was used to simulate chemical reaction fouling on a heated surface. A kinetic study was separately conducted on this system using a batch reactor. The fouling experiments carried out with this simple system had the purpose of investigating the effect on fouling of some key variables among which the temperature of the heated surface, flow velocity and bulk concentration of precursor. The effect of oxygen and a variety of organic sulfur compounds added to the bulk fluid (heptane and styrene) was studied. A mathematical model was developed for chemical reaction fouling under boiling conditions. Finally, the fouling characteristics of a heavy crude oil residuum supplied by the Chevron Corporation were investigated. The main results of this research are summarized hereafter.

10.1 Conclusions

The kinetics of the thermal polymerization reaction of styrene in heptane was investigated in a 1 liter stainless steel mixed batch reactor. Six kinetic experiments were performed at temperatures ranging from 130 to 190°C and styrene concentrations from 0.068 to 0.42M. The integral
method of analysis showed that the overall order of the reaction is closer to 2 than to 5/2. The second order reaction rate constant was found to be

\[ k_2 = 3.95 \times 10^{10} \, e^{-23890/RT} \, \text{L. mol}^{-1} \, \text{sec}^{-1} \]

where T is the absolute temperature and R the universal ideal-gas constant. The activation energy of 23890 cal per mole obtained is in accordance with the findings of other workers.

The experimental setup used to study fouling from hydrocarbon streams consisted of a heat transfer loop in which was circulated four gallons of a given test fluid. The test section was of annular geometry and was formed from a concentric 0.325 inch ID stainless steel rod jacketed by a 0.771 inch ID stainless steel tube. The electrically heated length of the rod was equal to 3 inches hence offering a heated area of about 3.53 square inches. Flow to the test section was provided by a magnetically driven pump and the flow rate through the test section could be measured by a venturi flow meter or a mass flow meter. The bulk fluid was heated using band heaters clamped on the outside surface of the loop. The overall system is made of stainless steel to avoid corrosion problems that can affect fouling. Data were recorded by an IBM PC and a direct output was provided during a fouling run on a parallel printer.
The first investigation on chemical reaction fouling was done with the system styrene-heptane-polystyrene. This system was chosen to simulate fouling involving a single chemical reaction of previously determined kinetics. The effect of operating conditions, mainly, heater surface temperature, velocity and styrene concentration in the bulk fluid was studied. Higher surface temperatures were found to always increase fouling rates as was expected from the known temperature dependency of chemical reaction rates. On the other hand, the effect of velocity was opposite in that higher velocities from 3.0 to 8.0 ft/sec limited the extent of fouling.

It appeared that the effects of these two variables may be closely inter-related. This suggests a competition between the kinetic rate and the mass transfer rate of reactant (precursor) to the reaction zones. Hence, depending on the value of surface temperature and velocity used, either chemical kinetics or mass transfer may become the rate limiting step. The third parameter to be considered was the styrene concentration in the bulk stream. By varying the concentration from 1.0 wt% to 6.0 wt%, it was shown that the effect of this variable depended also on surface temperature and velocity. At high temperature and low velocity, higher concentrations of styrene enhanced the fouling rates. However, at low
Various fouling experiments were performed using styrene in heptane in the presence of oxygen. In most cases, it was found that oxygen inhibited fouling. The initial fouling rates were generally lower when oxygen was present in the system probably due to reaction in the bulk fluid to form some polymer products that precipitate in the heptane, hence depriving the reaction zone from most of the styrene monomer. On the other hand, the induction times were generally smaller when oxygen was present in the system.

A fouling model based on principles of heat, mass and momentum transfer was developed for chemical reaction fouling under local boiling conditions. The model was tested with the experimental data obtained on the kinetics and fouling from a hydrocarbon stream consisting of small amounts of styrene monomer dissolved in heptane. The model predictions of the initial fouling rate were, in some cases, found to deviate significantly from the experimental values. In fact, these deviations ranged from about 13% to over 100%. However, considering the many assumptions that were made during the derivation of the model, the agreement is considered to be fairly good.

The effect of the addition to the styrene-heptane system of a variety of organic sulfur compounds including sulfides, disulfides and phenols was investigated. Thiols
were found to strongly inhibit fouling at the conditions studied. On the other hand, sulfides seemed to slightly decrease the extent of fouling. The only disulfide compound used had an intermediate action. The amount of thiol used was shown to have important consequences on fouling. For instance, while 100 ppm sulfur from n-dodecanethiol completely eliminated deposit formation, very heavy fouling occurred when only 10 ppm sulfur from the same compound were used. The different action of the sulfur compounds appear to be related to their reactivity toward olefins such as styrene.

Finally, the fouling tendencies of a crude oil residuum on a heat transfer surface were investigated. Due to its very high viscosity, the residuum was diluted in a paraffinic oil free of olefins and almost free of aromatics. Mixtures of 50% V/V and 75% V/V residuum in oil were studied. The two batches of the residuum received from the Chevron corporation proved to have very different fouling characteristics. For batch No.1, the threshold surface temperature for the occurrence of fouling was determined to be around 790°F. For batch No. 2, it was located between 575 and 600°F.

While the surface temperature constantly enhanced fouling in all cases, velocity had an unusual effect which, again, seemed to depend on the value of the surface temperature. At low values of the latter, velocity did not
appear to affect the initial fouling rate significantly. However, at high surface temperatures (around 800°F), there seemed to be an optimum value of velocity for the fouling rate. These results were explained on the basis of the usual competition mentioned previously between kinetics and mass transfer which are of concern in any chemical reaction fouling problem.

10.2 Future Work

Although the experimental data obtained in the course of this work was substantial, there is a definite need to investigate more clearly some of the discrepancies in the data. For instance, the effect of velocity and concentration on chemical reaction fouling deserves more attention. The various results obtained on the effect of oxygen also need to be clarified with more data. Following is a list of some points to be considered for future work and which would make this investigation of the fouling characteristics of organic fluids more complete:

1. Repeat the fouling study using styrene in heptane but under non-boiling conditions. This may probably answer the question of non-reproducibility of induction times between similar runs since nucleate boiling is very sensitive to the roughness of the heated surface.
2. Investigate more thoroughly the effect of bulk temperature on fouling.
3. Consider the combined idea of polymer melting and deposit removal by shearing forces. One way of investigating this point is, for example, to cover the heated surface of the rod by a product such as wax. Then for a given surface temperature and flow velocity, the decrease in the fouling resistance with time can be followed.

4. To generalize the problem, include more than one chemical reaction by adding another polymerizing species such as methylmetacrylate to the heptane-styrene system.

5. Possibly look at the effect of duct size on fouling. This could be achieved by either using heaters of different diameters or outer tubes of different diameters.

6. Use rods having heated lengths greater than 3 inches.


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APPENDICES
APPENDIX A

DETAILED KINETIC DATA FOR THE THERMAL POLYMERIZATION OF STYRENE IN n-HEPTANE

The following six tables present the experimental data obtained in the kinetic study of the thermal polymerization of styrene in n-heptane. The study which is reported in Chapter 4 was carried out in a stainless steel batch mixed reactor. In the given tables, $X$ refers to the conversion of styrene monomer while $1/(1-X)$ and $1/(1-X)^{1.5}$ are the integrated forms derived respectively for orders of reaction equal to 2 and 5/2.
Run No.1: \( C_0 = 0.41 \text{M} \quad T = 130^\circ \text{C} \quad P = 10.2 \text{ atm} \)

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Figure A.1 Typical output from Gas-Chromatograph (GC)

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| FID TEMP | 400 0 107 |
| TCD TEMP | 400 275 275 |
| CHT SPD | 0.20     |
| ZERO   | 10.0     |
| ATTN 2↑ | 10      |
| TCD SGNL | A       |
| SLP SENS | 0.05    |
| AREA REJ | 2000    |
| FLOW A | 0.0 32.0 |
| FLOW B | 0.0 30.9 |

DIL FACTOR: 1.0000 E+ 0

```

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<th>AREA %</th>
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<td>1.011</td>
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<tr>
<td>16.28</td>
<td>53030</td>
<td>3.115</td>
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</tbody>
</table>

HP RUN # 2
AREA %

START 0.23 2.80
2↑ 3.72
CS 16.28
ST 27.32
```
APPENDIX B

METHOD AND EXAMPLES OF HEATER CALIBRATION

The calibration method was used to both determine the wall resistance to heat flow, \( R_w \), and to experimentally evaluate the possible change in the local heat transfer coefficient, \( h \), between the solid surface and the fluid as deposit builds up on the surface.

The calibration of the heater rod is described by Knudsen [95]. The experimental setup used for calibration of the heaters is shown in Figure B.1. Again referring to the clean conditions by the subscript \((o)\), the overall resistances to heat transfer for the clean and fouled conditions are expressed in terms of the inverse of the overall heat transfer coefficient \( U \) by the expressions:

\[
\frac{1}{U_o} = \frac{T_{w0} - T_{b0}}{(q/A)_o} = R_w + \frac{1}{h_o} \quad (B.1)
\]

\[
\frac{1}{U} = \frac{T_w - T_D}{(q/A)} = R_w + \frac{1}{h} \quad (B.2)
\]

The determination of the fouling resistance \( R_f \) in Equation B.2 requires knowledge of the heat transfer coefficient \( h \) which itself can only be obtained from Equation B.1 by assuming \( h = h_o \). All other quantities appearing in Equation B.1 and B.2 are physically measurable with the exception of the wall thermal resistance, \( R_w \).
Figure B.1 Apparatus used for heater calibration
which is determined by calibration of the heater. For turbulent flow heat transfer between a fluid and the inner surface of a smooth annulus, Knudsen and Katz [123] recommend the equation proposed by Wiegand [56]:

\[
\frac{hD_e}{k} = 0.023 \left( \frac{D_e \rho v}{\mu} \right)^{0.8} \left( \frac{C_p \mu}{k} \right)^{0.4} \left( \frac{D_e}{D_i} \right)^{0.45}
\]  

(B.3)

Where, all the physical properties are that of the fluid and are evaluated at bulk temperature. \( D_o \) and \( D_i \) are respectively the outside and inside diameter of the annulus and \( D_e = D_o - D_i \) is the equivalent diameter.

For a given duct and constant bulk temperature, the relationship between the flow velocity \( v \) and the heat transfer coefficient \( h \) can be obtained from Equation B.3. Hence,

\[
h = 0.023 \frac{k}{D_e} \left( \frac{D_e \rho v}{\mu} \right)^{0.8} \left( \frac{C_p \mu}{k} \right)^{0.4} \left( \frac{D_e}{D_i} \right)^{0.45} v^{0.8}
\]  

(B.4)

or, \( h = \frac{1}{B} v^{0.8} \)  

(B.5)

where, \( B = f (\text{geometry, fluid physical properties}) \).

Substitution of Equation B.5 in Equations B.1 and B.2 leads to,

For clean surface:

\[
\frac{1}{U_o} = \frac{T_{w0} - T_{bo}}{(q/A)_o} = R_w + \frac{B}{v^{0.8}}
\]  

(B.6)
For fouled surface: \[ \frac{1}{U} = \frac{T_w - T_b}{q/A} = R_w + R_f + \frac{C}{v^{0.8}} \] (B.7)

The constants B and C depend on both the bulk temperature and the duct size and evaluation of the relative difference between the two quantities B and C (at constant physical properties) is also a measure of how much change in \( h \) occurs during fouling. It appears, therefore, from Equations B.6 and B.7 that a linear plot of \( 1/U_0 \) versus \( 1/v^{0.8} \) and of \( 1/U \) versus \( 1/v^{0.8} \) obtained with the clean and fouled heater respectively, would result in slopes B and C and in intercepts of \( R_w \) and \( (R_w + R_f) \). This value of \( R_f \) should correspond to that recorded at the end of the fouling experiment. Such plots of \( 1/U \) vs \( 1/v^{0.8} \) are called Wilson plots [96].

Two examples are presented on how the method was applied for two different types of deposit. The first one was obtained during the polymerization of styrene on a stainless steel heater and the second one for fouling from a vacuum residuum on a carbon steel heater. Figure B.2 shows the results of the comparisons between the calibrations of the clean and fouled heater for both cases. The results are also summarized below while the detailed data are given in the included tables following this section. So,
Figure B.2 Wilson plots for the clean and fouled heaters. Top: SS heater with polystyrene deposit. Bottom: CS heater with deposit from the resid.
FOR POLYSTYRENE:

<table>
<thead>
<tr>
<th></th>
<th>CLEAN</th>
<th>FOULED</th>
<th>CHANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>3.081 x 10^{-3}</td>
<td>3.285 x 10^{-3}</td>
<td>6.6%</td>
</tr>
<tr>
<td>Intercept</td>
<td>8.6 x 10^{-4}</td>
<td>13.1 x 10^{-4}</td>
<td>4.5 x 10^{-4}</td>
</tr>
<tr>
<td>R²</td>
<td>0.998</td>
<td>0.999</td>
<td>--</td>
</tr>
</tbody>
</table>

FOR CRUDE OIL RESIDUUM:

<table>
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<th>CHANGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>3.175 x 10^{-3}</td>
<td>3.340 x 10^{-3}</td>
<td>5.2%</td>
</tr>
<tr>
<td>Intercept</td>
<td>3.3 x 10^{-4}</td>
<td>14.8 x 10^{-4}</td>
<td>11.5 x 10^{-4}</td>
</tr>
<tr>
<td>R²</td>
<td>0.999</td>
<td>0.996</td>
<td>--</td>
</tr>
</tbody>
</table>

where,

\[
\text{CHANGE OF SLOPE (\%)} = \frac{\text{FOULED} - \text{CLEAN}}{\text{CLEAN}} \times 100
\]

\[
\text{CHANGE OF INTERCEPT} = \text{FOULED} - \text{CLEAN}
\]

Comparison of the fouling resistances recorded at the end of the two fouling experiments that produced the deposits of these two examples, namely, \( R_f = 28.8 \times 10^{-4} \) hr ft\(^2\)F/Btu for polystyrene and 13.3 x 10\(^{-4}\) hr ft\(^2\)F/Btu for the residuum, with the values given by the intercept change in the two tables shows some discrepancies that need a little clarification. For the residuum, the two values seem to agree quite well which suggests that the deposit
characteristics did not vary too much between the conditions of the fouling run and those of the calibration. On the other hand, for the polystyrene film, this argument seems to be invalid. The properties of the film seem to have changed considerably since the difference between the two values is as large as $24.2 \times 10^{-4}$ hr ft$^2\cdot$°F/Btu.

Variation in slope values between the clean and fouled surface suggests that no major change in the local heat transfer coefficient took place during the fouling process for both types of deposits. Although a change of 5 or 6% is within the experimental error associated with the calculations of the fouling resistance $R_f$, it is believed that any sensible variation in $h$ would be due to an increase in the surface roughness rather than an increase in the fluid velocity as the deposition of material proceeds. This is because no change in velocity was noticed during all of our fouling experiments and the thickness of the deposit was observed to be much smaller than the equivalent diameter of the annulus. The percent change in equivalent diameter during a fouling test was in the order of 5%.

In the given tables, the various quantities and their units are as follows:

- $Q = \text{volumetric flow rate, gal/min}$
- $q = \text{energy to be transferred, watts}$
- $T_b = \text{bulk temperature, °F}$
$T_w$ = wall temperature, °F

$U$ = overall heat transfer coefficient, Btu/hr ft$^2$ °F

CALIBRATION OF STAINLESS STEEL HEATER:

1. CLEAN

<table>
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<tr>
<th>$Q$</th>
<th>$q$</th>
<th>$T_b$</th>
<th>$T_w$</th>
<th>$U$</th>
<th>$1/U \times 10^3$</th>
<th>$1/Q \times 10^8$</th>
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</thead>
<tbody>
<tr>
<td>14.5</td>
<td>996</td>
<td>69</td>
<td>246</td>
<td>818</td>
<td>1.222</td>
<td>1.175</td>
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<tr>
<td>13.8</td>
<td>978</td>
<td>69</td>
<td>246</td>
<td>803</td>
<td>1.245</td>
<td>1.227</td>
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<td>962</td>
<td>69</td>
<td>245</td>
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INTERCEPT-----SLOPE-------$R^2$-------$k/x$-----
8.653E-04 3.081E-03 0.998 1.156E+03

2. FOULED WITH POLYSTYRENE

<table>
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<th>$T_w$</th>
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<th>$1/U \times 10^3$</th>
<th>$1/Q \times 10^8$</th>
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INTERCEPT-----SLOPE-------$R^2$-------$k/x$-----
1.308E-03 3.285E-03 0.999 7.645E+02
CALIBRATION OF CARBON STEEL HEATER:

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INTERCEPT——SLOPE———R^2———k/x———
3.354E-04 2.818E-03 0.999 2.982E+03

2. FOULED WITH RESIDUUM

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INTERCEPT——SLOPE———R^2———k/x———
1.475E-03 3.340E-03 0.996 6.778E+02
APPENDIX C
COMPUTER PROGRAM USED FOR DATA ACQUISITION, PROCESSING AND CONTROL

The following program was used to monitor fouling experiments and to record the extensive experimental data obtained. Fouling heat transfer calculations are carried out within the program as the original data is recorded. Some minor control of the apparatus including heater power shut off in case of excessive temperatures, is also performed by the program. The program listing is followed by an example output from the computer.
Program listing:

Program Foul. BAS

This program is used for data acquisition during fouling experiments. Heat transfer calculations are also performed.

*** VARIABLES DICTIONARY ***

ACS = Annular cross section area
FDATA = Flow rate variable
FLOW = Flow rate
FLUX = Heat flux
H = Convective heat transfer coefficient
HDATA = Temperature variable
HDATA = Temperature variable
I = Dummy variable
ITIMEM = Scan interval
J = Channel number
K = Inverse of heater wall thermal resistance
N = Dummy variable
PDATA = Heater power variable
POWER = Heater power
RF = Fouling resistance
RTIME = Data recording time
RW = Heater wall thermal resistance
SCTIME = Next data recording time
SPGR = Fluid specific gravity
TB = Bulk fluid temperature
TIME = Present time
TS = Heater surface temperature
TW = Heater wall temperature
U = Overall heat transfer coefficient
VEL = Fluid velocity through annular test section

*** CHANNEL ASSIGNMENTS ***

CHANNEL 0 = Bulk fluid inlet temperature
CHANNEL 1 = Bulk fluid outlet temperature
CHANNEL 2 = Tank temperature
CHANNEL 3 = Heater wall temperature
CHANNEL 4 = Flow rate measured by venturi
CHANNEL 6 = Heater power
CHANNEL 7 = Flow rate measured by mass flow meter

****** END OF SOURCE CODE ******

Load and initialize ADALAB-PC
ON KEY(4) GOSUB 3400

KEY(4) ON

REM Initialize program and heater status "ON"

REM

RTIME#=0
CHAHEAT=0
CHAPUMP=1
BITHEAT=1
BITPUMP=1

CALL DIGOUT(CHAHEAT,BITHEAT)
CALL DIGOUT(CHAPUMP,BITPUMP)

REM Collect base data

CLS
BFLOW#=0
BTB#=0
BNWATS#=0
BU#=0

FOR BASE=0 TO 9
PRINT "COLLECTING BASE DATA ":BASE
GOSUB 2070
BFLOW#=BFLOW#+AVDATA#(7)
BTB#=BTB#+(AVDATA#(0)+AVDATA#(1))/2
BNWATS#=BNWATS#+AVDATA#(6)
BTW#=BTW#+AVDATA#(3)
NEXT BASE

REM Collect base data

BFLOW#=BFLOW#/(BASE)
BTB#=BTB#/(BASE)
BNWATS#=BNWATS#/(BASE)
BTW#=BTW#/(BASE)

REM Set upper temperature setpoint for heater (Deg F)

INPUT SETHI#

REM Insert a formatted data disk into drive A: and press F5 when ready

STOP

ON ERROR GOTO 0
OPEN "A:RESID75.42" FOR OUTPUT AS #1
PRINT "ENTER THE SCAN INTERVAL IN MINUTES"
INPUT ITIKEMMI
1TIME#=ITIMEMM#*100
HH#=VAL(MIDS(TIMES,1,2))
MM#=VAL(MIDS(TIMES,4,2))
SSOKVAL(MIDS(T1MES,7,2))
T1MEORHH#*10000+MM#*100+SS#
LRTIME#=TIME#
SCTIMOmmITIMES+TIME#
SCTIMEHH=INT(SCTIMU/10000)
scrnemmwaNT(scTimEll/loo)
SCTIMESS=SCTIME#-SCTIMEMM*100
SCTIMED2401SCTIME3424SCTIMME*100
IF SCTIMEMM>=60 THEN
SCTIME#=(SCTIMENH+1)*10000+(SCTIMEMM-60)*100+SCTIMESS
IF SCTIMO=240000! THEN
SCTIME#=SCTIME#-240000!
REM Collect base data

CLS
BFLOW4)=0
BT151=0
DWATTS#=0
BTO4=0
BUIP=0
FOR BASE=0 TO 9
PRINT "COLLECTING BASE DATA ":BASE
GOSUB 2070
BFLOW#=BFLOWI+AVDATA#(7)
BTB#=BTB#+(AVDATA#(0)+AVDATA#(1))/2
BWATTS#=BWATTS#+AVDATA#(6)
ETW#=BTROAVDATA#(3)
NEXT BASE

BTW#=(BASE)
BTW#=(BASE)

REM Set upper temperature setpoint for heater (Deg F)

INPUT SETHI#

REM Insert a formatted data disk into drive A: and press F5 when ready

STOP

ON ERROR GOTO 0
OPEN "A:RESID75.42" FOR OUTPUT AS #1
PRINT "ENTER THE SCAN INTERVAL IN MINUTES"
INPUT ITIKEMMI
1TIME#=ITIMEMM#*100
HH#=VAL(MIDS(TIMES,1,2))
MM#=VAL(MIDS(TIMES,4,2))
SSOKVAL(MIDS(T1MES,7,2))
T1MEORHH#*10000+MM#*100+SS#
LRTIME#=TIME#
SCTIMOmmITIMES+TIME#
SCTIMEHH=INT(SCTIMU/10000)
scrnemmwaNT(scTimEll/loo)
SCTIMESS=SCTIME#-SCTIMEMM*100
SCTIMED2401SCTIME3424SCTIMME*100
IF SCTIMEMM>=60 THEN
SCTIME#=(SCTIMENH+1)*10000+(SCTIMEMM-60)*100+SCTIMESS
IF SCTIMO=240000! THEN
SCTIME#=SCTIME#-240000!
FOULING DATA FOR RESID IN OIL - RUN OIL-RES(75)-42: PRINT
FOULING DATA FOR RESID IN OIL - RUN OIL-RES(75)-42: LPRINT

INIT. H.T. COEFF. = ";CINT(BH#);"BTU/HR FT2 F"
INIT. H.T. COEFF. = ";CINT(BH#);"BTU/HR FT2 F"

TIME VELOCITY POWER TBULK TWALL TSURF RESISTANCE" HOURS FT/SEC WATTS DEG F DEG F DEG F HR FT2 F/ BTU
TIME VELOCITY POWER TBULK TWALL TSURF RESISTANCE" HOURS FT/SEC WATTS DEG F DEG F DEG F HR FT2 F/ BTU

CLS
REM Begin scan routine
REM Determine next scan
HH#=VAL(MIDS(TIMES,1,2))
MM#=VAL(MIDS(TIMES,4,2))
SS#=VAL(MIDS(TIMES,7,2))
TIME#=HH#*10000+MM#*100+S5#
IF SCTIME0=2400001 THEN
SCTIME#=SCTIMES-240000!
IF (TIME#>=SCTIME#) AND ((TIME#-SCTIME#)<10000) THEN GOSUB 2940
REM Begin scan routine
GOSUB 2070
REM Proceed with heat transfer computations
TB#=(AVDATA#(0)+AVDATA#(1))/2
FLUX#=POWER#*139.017
U#=(AVDATA#(3)-BTW#)/FLUX#
U2#=-1/(RW#+RF#)
TS#=(AVDATA#(3)-(FLUX#*U2#))
IF AVDATA#(6)=0 THEN RF#=0
IF AVDATA#(7)=0 THEN TS#=0 AND RF#=0
REM Turn heater power off if setpoint is exceeded
IF (AVDATA#(3)>SETHI#) THEN GOSUB 3920
REM End scan routine
PRINT "HEATER FLOW SURFACE POWER (W) RATE (LB/ MIN) VELOCITY (FT/ S) RESISTANCE"
PRINT USING "###.#####";POWERLAVDATA#(7),VELLRF#,
PRINT "UPPER SETPOINT (F)"
PRINT USING "###";SETHI#
NEXT SCAN

DATE CURRENT TIME NEXT SCAN

HOURS FT/SEC WATTS DEG F DEG F DEG F HR FT2 F/ BTU
HOURS FT/SEC WATTS DEG F DEG F DEG F HR FT2 F/ BTU
2000 PRINT
2010 PRINT "**************************************************************************"
2020 PRINT " F1. Change scan interval"
2030 PRINT " F2. Terminate program"
2040 PRINT " F3. Change heater setpoint"
2050 PRINT " F4. Change heater power"
2060 GOTO 1510
2070 REM
2080 REM Scan routine
2090 REM
2100 GAIN=64
2110 FOR N=0 TO 9
2120 AVDATA(N)=0
2130 NEXT N
2140 FOR J=0 TO 9
2150 FOR I=0 TO 9
2160 TDATA(I,J)=0
2170 NEXT I
2180 NEXT J
2190 FOR J=1 TO 2
2200 FOR I=0 TO 9
2210 CALL TRIGGER(TRIG,VALUE)
2220 CALL SLOWAD(J,GAIN,TDATA(I,J))
2230 NEXT I
2240 NEXT J
2250 FOR J=1 TO 2
2260 FOR I=1 TO 9
2270 AVDATA(I,J)=AVDATA(I,J)+TDATA(I,J)
2280 NEXT I
2290 NEXT J
2300 FOR J=1 TO 2
2310 AVDATA(I,J)=AVDATA(I,J)/(4095*GAIN*9)*1000
2320 NEXT J
2330 GAIN=1
2340 J=0
2350 AVDATA(I,J)=0
2360 FOR I=0 TO 9
2370 CALL TRIGGER(TRIG,VALUE)
2380 CALL SLOWAD(J,GAIN,HDATA(I))
2390 NEXT I
2400 FOR I=1 TO 9
2410 AVDATA(I,J)=AVDATA(I,J)+HDATA(I)
2420 NEXT I
2430 AVDATA(I,J)=AVDATA(I,J)/(4095*GAIN*9)*1000
2440 AVDATA(I,J)=AVDATA(I,J)/100
2450 GAIN=1
2460 J=3
2470 AVDATA(I,J)=0
2480 FOR I=0 TO 9
2490 CALL TRIGGER(TRIG,VALUE)
2500 CALL SLOWAD(J,GAIN,HDATA(I))
2510 NEXT I
2520 FOR I=1 TO 9
2530 AVDATA(I,J)=AVDATA(I,J)+HDATA(I)
2540 NEXT I
2550 AVDATA(I,J)=AVDATA(I,J)/(4095*GAIN*9)*1000
2560 AVDATA(I,J)=AVDATA(I,J)/10
2570 GAIN=1
2580 J=7
2590 FOR I=0 TO 9
2600 CALL TRIGGER(TRIG,VALUE)
2610 CALL SLOWAD(J,GAIN,FDATA(I))
2620 NEXT I
2630 FOR I=1 TO 9
2640 AVDATA(I,J)=AVDATA(I,J)+FDATA(I)
2650 NEXT I
2660 AVDATA(I,J)=AVDATA(I,J)/(4095*GAIN*9)*1000
2670 GAIN=1
2680 J=6
2690 FOR I=0 TO 9
2700 CALL TRIGGER(TRIG, VALUE)
2710 CALL SLOWAD(J, GAIN, PDATA#(I))
2720 NEXT I
2730 FOR I=1 TO 9
2740 AVDATA#(6)=AVDATA#(6)+PDATA#(I)
2750 NEXT I
2760 AVDATA#(6)=AVDATA#(6)/(4095*GAIN*9)*1000
2770 REM
2780 REM Convert thermocouple voltages
2790 REM GOSUB 3640
2800 REM
2810 REM Convert power voltages
2820 REM GOSUB 3780
2830 REM
2840 REM Convert flow voltages
2850 REM GOSUB 3850
2860 REM
2870 SPGR*=.7705
2880 VEL*=AVDATA#(7)/(SPGR#*62.4*ACS**60)
2890 CIS
2900 RETURN
2910 REM Record scan data
2920 RTIME40=RTIME#4.111MEMMV60
2930 CIS
2940 PRINT "RECORDING DATA"
2950 HH*=VAL(KIDS(TIMES,1.2))
2960 MM*=VAL(MIDS(T1MES,4,2))
2970 SS=VAL(MIDS(TIMES,7,2))
2980 SCTIME=INT(SCTIME*/10000)+MM*/100+SS
2990 IF SCTIME*>60 THEN SCTIME=(SCTIME*/10000)+MM*/100+SS
3000 IF $T1ME*>240000 THEN $T1ME=$T1ME-240000!
3010 IF IT1MEMM#>=15 THEN IT1MEMM#-3:GOTO 3190 ELS IF IT1MEMM#=-3 THEN IT1MEMM#-3:GOTO 3190 ELSE IT1MEMM#-15
3020 PRINT "ENTER SCAN INTERVAL IN MINUTES"
3030 INPUT IT1MEMM#
3040 ITIME=IT1MEMM*/100
3050 REM Change scan increment
3060 RETURN
3070 REM
3080 PRINT "ENTER SCAN INTERVAL IN MINUTES"
3090 INPUT IT1MEMM#
3100 ITIME=IT1MEMM*/100
3110 REM Change scan increment
3120 RETURN
3130 PRINT "ENTER SCAN INTERVAL IN MINUTES"
3140 INPUT IT1MEMM#
3150 ITIME=IT1MEMM*/100
3160 REM Change scan increment
3170 RETURN
3180 PRINT "ENTER SCAN INTERVAL IN MINUTES"
3190 INPUT IT1MEMM#
3200 ITIME=IT1MEMM*/100
3210 REM Change scan increment
3220 RETURN
3230 PRINT "ENTER SCAN INTERVAL IN MINUTES"
3240 INPUT IT1MEMM#
3250 ITIME=IT1MEMM*/100
3260 REM Change scan increment
3270 RETURN
3280 PRINT "ENTER SCAN INTERVAL IN MINUTES"
3290 INPUT IT1MEMM#
3300 ITIME=IT1MEMM*/100
3310 REM Change scan increment
3320 RETURN
3330 PRINT "ENTER SCAN INTERVAL IN MINUTES"
3340 INPUT IT1MEMM#
3350 REM Change scan increment
3360 RETURN
3370 IF SCTIME/>=60 THEN SCTIME=(SCTIME*/10000)+(SCTIME-60)*100+SCTIMESS
3380 IF SCTIME®>=240000! THEN SCTIME®=SCTIME®-240000!
3390 RETURN
3400 REM
3410 REM CHANGE HEATER POWER
3420 REM
3430 PRINT "ENTER NEW HEATER POWER (MILLIVOLTS)"
3440 INPUT POWER#
3450 POWER#=POWER#+25.115
3460 RETURN
3470 REM
3480 REM Escape scan routine
3490 REM
3500 PRINT
3510 PRINT
3520 PRINT "Scan routine terminated"
3530 CLOSE
3540 STOP
3550 REM
3560 REM
3570 REM Change heater setpoint
3580 REM
3590 CLS
3600 PRINT "Enter new upper temperature setpoint for heater in Deg F"
3610 INPUT SETHISI
3620 RETURN
3630 REM
3640 REM ******************************************
3650 REM Thermocouple voltage to temperature conversion
3660 REM
3670 FOR N=0 TO 3
3680 IF (AVDATA#(N)+4.72)<0 THEN AVDATA#(N)=0
3690 IF AVDATA#(N)>-1.029 THEN GOTO 3710
3700 AVDATA#(N)=32.583*(AVDATA#(N)+5.02)^.949:GOTO 3720
3710 AVDATA#(N)=38.529*(AVDATA#(N)+4.72)^.8765
3720 NEXT N
3730 AVDATA#(1)=AVDATA#(1)+3
3740 AVDATA#(0)=AVDATA#(0)+2
3750 AVDATA#(3)=AVDATA#(3)+3
3760 RETURN
3770 REM
3780 REM ******************************************
3790 REM Voltage to power conversion
3800 REM
3810 AVDATA#(6)=AVDATA#(6)*25.115
3820 IF AVDATA#(6)<0 THEN AVDATA#(6)=0
3830 RETURN
3840 REM ******************************************
3850 REM Flowrate Conversion
3860 REM
3870 REM
3880 REM
3890 AVDATA#(7)=AVDATA#(7)*(551/1001.5)*1.474
3900 RETURN
3910 REM ******************************************
3920 REM Turn heater power off
3930 BITHEAT=0
3940 CALL DIGOUT(CHAMHEAT,BITHEAT)
3950 TIMHTOFF=RTIME#
3960 RETURN
3970 END
3980 REM
3990 REM Turn pump off if needed
4000 REM BITPUMP=0
4010 REM CALL DIGOUT(CHAPUMP,BITPUMP)
4020 REM GOTO 3450
4030 END
Example of computer output:

FOULING DATA FOR STYRENE IN HEPTANE: RUN HEP-ST(6.0)-25

INIT. H.T. COEFF. = 554 BTU/HR FT2 F

<table>
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<tr>
<th>TIME (HOURS)</th>
<th>VELOCITY (FT/SEC)</th>
<th>POWER (WATTS)</th>
<th>TBULK (DEG F)</th>
<th>TWALL (DEG F)</th>
<th>TSURF (DEG F)</th>
<th>RESISTANCE (HR FT2 F/BTU)</th>
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APPENDIX D

METHOD AND EXAMPLES OF INITIAL FOULING RATE DETERMINATION

The initial fouling rates were determined from the plot of the fouling resistance versus time for each run that showed significant fouling. Consider, for instance, the example shown in Figure D.1 which represents the fouling curve obtained for Run HEP-ST(6.0)-1 reported in Table 6.2. The curve is divided into three zones with the central zone AB delineated from the two extreme ends of the plot. The region AB contains only the data points which appear to form a straight line which passes through the inflection point. The slope of this line is defined as the value of the initial fouling rate.

In order to determine the slope of the data in the region AB, a simple linear regression analysis of the data is conducted. The size of the zone AB is varied and the regression analysis is continued until a satisfactory (maximum) correlation coefficient is reached. Two graphical outputs from the regression analysis are shown in Figures D.2 and D.3. In some cases where fouling was very rapid, only a limited number of data points have been used in the statistical analysis. This occurred particularly when relatively high heater surface temperatures were used.
Figure D.1 Method of determining the initial fouling rate from a fouling curve
Figure D.2 Determination of the initial fouling rate for run HEP-ST(6.0)-1 (Table 6.2)

\[ R_f \text{ (hr ft}^2 \text{ °F/Btu x} 10^4 \text{)} \]

SLOPE=IFR=1.6 \times 10^{-4} \text{ ft}^2 \text{ °F/Btu}

\[ R^2=0.997 \]
Figure D.3 Determination of the initial fouling rate for run OIL-RES(75)-45 (Table 9.3)
during the fouling experiments performed with styrene as the foulant precursor.
APPENDIX E

BOILING HEAT TRANSFER DATA FOR n-HEPTANE AND
FOR CRUDE OIL RESIDUUM IN PENRENCO SOLVENT

In this appendix is presented the computer program used in the boiling heat transfer calculations followed by tables showing the detailed experimental data. First, the data obtained for boiling of pure n-heptane is given and then, the data obtained for 75% V/V crude oil residuum in penrenco solvent. In these tables, the indicated variables and their corresponding units are as follows:

\[
\begin{align*}
q & = \text{Power to the heater, Watts} \\
q/A & = \text{Heat flux, Btu/hr ft}^2 \\
v & = \text{Velocity, ft/sec} \\
T_b & = \text{Average bulk fluid temperature, } ^\circ\text{F} \\
T_w & = \text{Heater wall temperature, } ^\circ\text{F} \\
T_s & = \text{Heater surface temperature, } ^\circ\text{F} \\
T_s - T_b & = \text{Superheat, } ^\circ\text{F} \\
h & = \text{Convective heat transfer coefficient, Btu/hr ft}^2 \, ^\circ\text{F}
\end{align*}
\]
PROGRAM BOIL

CALCULATES BOILING DATA FOR ORGANIC FOULING UNIT

VARIABLE DICTIONARY

DT = Superheat (Ts - Tb), F

FLUX = Heat flux, F/hr ft2

H = Convective heat transfer coefficient, Btu/hr ft2 F

POW = Power to the heater, Watts

RW = Heater wall thermal resistance, hr ft2 F/Btu

TBI = Inlet bulk fluid temperature, F

TBO = Outlet bulk fluid temperature, F

TB = Arithmetic mean bulk fluid temperature, F

TS = Heater surface temperature, F

TW = Heater wall temperature, F

U = Overall heat transfer coefficient, Btu/hr ft2 F

INSTRUCTIONS: PRINT

INSTRUCTIONS APPEAR WHEN YOU EXECUTE PROGRAM, i.e. <RUN

LIST 340 AND PUT IN CORRECT FILE NAME"; PRINT

LIST 350 AND PUT IN CORRECT FILE NAME"; PRINT

LIST 420 AND 440 PUT IN CORRECT RUN INFO"; PRINT

WHEN STEPS 1 TO 3 HAVE BEEN COMPLETED PRESS <RUN>. THESE" INSTRUCTIONS WILL REAPPEAR WITH AN INDICATION THAT" EXECUTION HAS BEEN INTERRUPTED AT STATEMENT 300"; PRINT

PRESS <CONT> TO CONTINUE EXECUTION"; PRINT

STOP

CLS

DIM WATTS#(500), TBI#(500), TBO#(500), TW#(500)

DIM H#(500), FLUX#(500), TS#(500), DT#(500)

OPEN "BOIL400.6" FOR INPUT AS #1

OPEN "RESBOIL6" FOR OUTPUT AS #2

K = 0

IF EOF(1) THEN 410

K = K + 1

INPUT #1, WATTS#(K), TBI#(K), TBO#(K), TW#(K)

GOTO 370

N = K

RW# = 1/3760

PRINT #2, " BOILING DATA FOR RESID IN OIL - RUN OIL-RES(75)-BO-6

TB=400F  u=8.0ft/sec  P=200psig

LPRINT " BOILING DATA FOR RESID IN OIL - RUN OIL-RES(75)-BO-6

TB=400F  u=8.0ft/sec  P=200psig

LPRINT "

FOR K = 1 TO N

FLUX#(K) = (POW#(K))*139.017

TB#(K) = .5*(TBI#(K)+TBO#(K))

U#(K) = FLUX#(K)/TW#(K)-TB#(K))

XH#(K) = 1/(1/U#(K)-RW#)

TS#(K) = FLUX#(K)/H#(K) + TB#(K)

DT#(K) = TS#(K)-TB#(K)

NEXT K
590 PRINT #2,"," POWER FLUX TB TW TS DT h "
600 LPRINT ",", POWER FLUX TB TW TS DT h "
610 PRINT #2,", WATTS BTU/HR FT2 F F F F BTU/HR FT2 F"
620 LPRINT ",", WATTS BTU/HR FT2 F F F F BTU/HR FT2 F"
630 PRINT #2,"--------------------------------------------------"
640 LPRINT" "
650 FOR K = 1 TO N
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690 NEXT K
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BOILING DATA FOR RESID IN PENRENC OIL - RUN 05

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The method used to determine the uncertainty on the experimental values of the fouling resistance is that of Kline and McClintock [97] recommended by Holman [98]. This method suggests that the uncertainty of a dependent variable \( y \) can be found from the uncertainties of the variables \( x_1, x_2, \ldots, x_n \) by the relation,

\[
W_y = \left[ \left( \frac{\delta y}{\delta x_1} W_1 \right)^2 + \left( \frac{\delta y}{\delta x_2} W_2 \right)^2 + \cdots + \left( \frac{\delta y}{\delta x_n} W_n \right)^2 \right]^{1/2} \quad (F.1)
\]

where \( W_i \) stands for the uncertainty on the variable \( x_i \).

At a given time during the course of a fouling experiment, the fouling resistance \( R_f \) is calculated by Equation 2.6 as

\[
R_f = \frac{T_w - T_{wo}}{q/A} \quad (F.2)
\]

where,

\[
T_w = \text{heater wall temperature at time } t, \text{ °F}
\]
\[
T_{wo} = \text{heater wall temperature at time 0 (start of fouling experiment), °F}
\]
\[
q = \text{power to the heater, Btu/hr}
\]
\[
A = \text{heat transfer area, ft}^2
\]

Differentiation of Equation F.2 with respect to each of these variables gives:
Substitution of Equations F.3 through F.6 into Equation F.1 leads to

\[
\delta R_f \frac{\delta}{\delta T_w} = \frac{1}{q/A} 
\]  
\[\text{(F.3)}\]

\[
\delta R_f \frac{\delta}{\delta T_{wo}} = -\frac{1}{q/A} 
\]  
\[\text{(F.4)}\]

\[
\delta R_f \frac{\delta}{\delta q} = -\frac{T_w - T_{wo}}{q^2/A} 
\]  
\[\text{(F.5)}\]

\[
\delta R_f \frac{\delta}{\delta A} = \frac{T_w - T_{wo}}{q} 
\]  
\[\text{(F.6)}\]

The uncertainties on the variables \(T_w\), \(T_{wo}\), \(Q\), and \(A\) are as follows:

\[
W_{T_w} = W_{T_{wo}} = 1^\circ F 
\]

\[
W_q = 20 \text{ Btu/hr} 
\]

\[
W_A = 0.2454 \times 10^{-3} \text{ ft}^2 \text{ (1\% of the area } A \text{ which is equal to } 0.02454 \text{ ft}^2) 
\]

Hence, for a given power input \(q\) and from recordings of the heater wall temperatures of time zero and \(t\), the uncertainty on \(R_f\) can be computed by Equation F.7 from the uncertainties on the independent variables. The relative error on \(R_f\) can then be determined as
\[
\varepsilon = \frac{W_{RF}}{R_f} \times 100 = \%
\]

To illustrate these calculations, consider the data included in Appendix C for Run No. 25 of Chapter 6 (See Table 6.2). At \( t = 0 \) (start of the run), \( T_{Wo} = 447^\circ F \) and \( q = 649 \ W = 2215 \ \text{Btu/hr} \). This power to the heated section of the heater is kept constant during the whole experiment any deviation being due to fluctuations in the power supply lines. At \( t = 6.50 \ \text{hr} \), \( T_w = 496^\circ F \) and \( R_f = 5.3 \times 10^{-4} \ \text{hr ft}^2{^\circ F}/\text{Btu} \). So by Equation F.7

\[
W_{RF} = \left[ \frac{1}{(2215/0.02454)^2} \times \left(1^2 + 1^2\right) \right] \]
\[
+ \left[ \frac{447 - 496}{(2215)^2/(0.02454)} \times 20 \right]^2 \]
\[
+ \left[ \frac{496 - 447}{2215} \times 0.2454 \times 10^{-3}\right]^2 \right]^{1/2}
\]
\[
= 0.2 \times 10^{-4} \ \text{hr ft}^2{^\circ F}/\text{Btu}
\]

and

\[
\varepsilon = \frac{0.2 \times 10^{-4}}{5.3 \times 10^{-4}} \times 100 = 3.8\% 
\]

At high values of \( R_f \) such as at \( t = 8.00 \ \text{hr} \) (\( T_w = 760^\circ F \), \( R_f = 35.0 \times 10^{-4} \ \text{hr ft}^2{^\circ F}/\text{Btu} \), \( W_{RF} = 0.5 \times 10^{-4} \) and hence \( \varepsilon = 1.4\% \). For all the experimental data, relative errors ranged from 1\% to 6\% which is still acceptable.
APPENDIX G
DETERMINATION OF THE AVERAGE MOLECULAR WEIGHT OF
THE POLYSTYRENE DEPOSIT

The average molecular weight of polymers can be determined by measuring the viscosity of various solutions of a known solvent containing different polymer concentrations. This method initially proposed by Staudinger [99] relies on the fact that threadlike polymer molecules increase the viscosity of the solvent in which they are dissolved. At low polymer concentrations, the specific viscosity $\mu_{sp}$ given by Equation G.1,

$$\mu_{sp} = \frac{\mu - \mu_o}{\mu_o}$$  \hspace{1cm} (G.1)

where $\mu_o$ and $\mu$ are respectively the viscosity, in centipoise, of the pure solvent and the solution, can be approximated by the following equation,

$$\mu_{sp} = \frac{t - t_o}{t_o}$$  \hspace{1cm} (G.2)

where $t_o$ and $t$ are the corresponding flow times in a capillary viscometer.

The next step is to plot the reduced specific viscosity $\mu_{sp}/C$ in cc/g versus the polymer concentration $C$ in g/cc. Then by extrapolation of the curve to zero concentration, the intrinsic viscosity of the polymer is deduced, i.e.,
\[ [\mu] = \lim_{C \to 0} \left( \frac{\mu_{sp}}{C} \right) \]  \hspace{1cm} (G.3)

with [\mu] in cc/g. Finally, using the Mark-Houwink relation between intrinsic viscosity and molecular weight of polymer given by Equation G.4, the polymer average viscosity molecular weight is obtained (Equation G.5)

\[ [\mu] = K_m \cdot M^\alpha \]  \hspace{1cm} (G.4)

\[ M = \exp \left( \frac{\log [\mu] - \log K_m}{\alpha} \right) \]  \hspace{1cm} (G.5)

The constant \( K_m \) and exponent \( \alpha \) are tabulated for various polymer-solvent systems at given temperatures \([102, 125]\). For polystyrene in benzene at 20°C, the suggested values for \( K_m \) and \( \alpha \) are respectively \( 1.23 \times 10^{-2} \) and 0.72 \([102]\). For these values [\mu] is obtained in cc/g from Equation G.4.

The experimental technique used for determining the molecular weight of the polystyrene deposit obtained in the study reported in Chapter 6 is briefly explained below. One gram of the recovered polystyrene was dried and then dissolved in about 50 ml of benzene at 20°C. The solution was then filtered in a sintered glass and recovered in a 100 ml volumetric flask. Benzene was added to obtain 100 ml of a 0.01 g/cc solution of polystyrene in benzene. Three other solutions of respectively 0.005, 0.0025, and 0.00125 g/cc concentration were prepared by dilution of the mother solution. Using an Ostwald type viscometer, the
specific viscosity of each of the four solutions along with that of the pure benzene were determined by measuring their respective flow times. Table G.1 shows the results obtained.

Table G.1. Summary of viscosity measurements

<table>
<thead>
<tr>
<th>C (g/cc)</th>
<th>t (sec)</th>
<th>( \mu_{sp} )</th>
<th>( \mu_{sp}/C ) (cc/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>70.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.00125</td>
<td>74.5</td>
<td>0.0567</td>
<td>45.4</td>
</tr>
<tr>
<td>0.0025</td>
<td>79.5</td>
<td>0.1277</td>
<td>51.5</td>
</tr>
<tr>
<td>0.005</td>
<td>89.5</td>
<td>0.2695</td>
<td>53.9</td>
</tr>
<tr>
<td>0.01</td>
<td>115.0</td>
<td>0.6313</td>
<td>63.1</td>
</tr>
</tbody>
</table>

Figure G.1 is a plot of the reduced specific viscosity \( \mu_{sp}/C \) versus concentration. Extrapolation of the line to \( C = 0 \) gives a value of \( \mu_{sp}/C \) equal to 44.7 cc/g which by Equation G.3 is also equal to the intrinsic viscosity of the polystyrene. Using Equation G.5 and the values of \( K_m \) and \( \alpha \) for the polystyrene-benzene system at 20°C, the average molecular weight of the polystyrene can be computed:
Figure G.1  Plot of reduced viscosity versus concentration of polystyrene in benzene
\[ M = \exp \left( \frac{\log (44.7) - \log (1.23 \times 10^{-2})}{0.72} \right) \]

or \[ M = 88100 \]

The value of \([\mu]\) obtained graphically (44.7 cc/g) was checked using a single viscosity measurement using the equation proposed by Schulz and Blaschke [126] and recommended by Braun et al. [102],

\[ [\mu] = \frac{(\mu_{sp}/C)}{1 + K \cdot \mu_{sp}} \]  \hspace{1cm} (G.6)

where \(K = 0.28\) for low polymer concentrations. Hence, for \(C = 0.0025\) g/cc for example, \(\mu_{sp} = 0.1277\) and

\[ [\mu] = \frac{0.1277/0.0025}{1 + (0.28)(0.1277)} = 49.3 \text{ cc/g} \]

which is close to our 44.7 cc/g experimental value.
APPENDIX H

SPECIFICATIONS OF THE CRUDE OIL RESIDUUM-
PENRENCO SOLVENT- SYSTEM

In this appendix are given some physical properties of the crude oil residuum (RESID) and solvent (PENRENCO OIL 2257) system. The data shown in Figure H.1 and Figure H.2 for the undiluted resid were obtained from the Chevron Corporation. However, the curves for the specific gravity of the 50% and 75% mixtures of resid in the hydrocarbon solvent versus temperature had to be measured (Figure H.3).
Figure H.1 Specific gravity of crude resid versus temperature

\[ Y = 1.0174 - 3.6064 \times 10^{-4} X \]
Figure H.2  Viscosity of crude resid versus temperature
Figure H.3 Specific gravity of 50% and 75% V/V resid in Penrenco solvent versus temperature