

FOULING CHARACTERISTICS OF A HEAVY VACUUM GAS OIL IN THE PRESENCE OF DISSOLVED OXYGEN

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ABSTRACT

Dissolved oxygen can lead to gum and deposit formation in hydrocarbon systems, as has been shown in prior work with crude oils, naphthas, gas oils and mixtures containing model organic compounds. In this work, a heavy vacuum gas oil (HVGO) was re-circulated through an annular heat transfer probe and the decline in heat transfer coefficient measured over periods of up to 200 hours, at bulk temperatures of about 85°C, and initial surface temperatures in the range 260-322°C. The HVGO was saturated with nitrogen-air mixtures to yield oxygen pressures up to 106 kPa. Soluble gum concentration in the re-circulating system, which was determined by precipitation in n-heptane at 0°C, increased over time reaching a maximum of 300 mg/L after 300-hours. Initial experiments with unfiltered HVGO which contained suspended solids, gave fouling rates an order of magnitude higher than subsequent experiments using filtered oil. Complex fouling behaviour, including induction periods, negative thermal fouling resistances, and partial deposit spalling were observed in this complex system. The rate of fouling increased linearly with oxygen pressures from 20 to 100 kPa. At velocities above 0.75 m/s, fouling rate decreased with increasing velocity. At 106 kPa oxygen pressure, rates increased strongly with surface temperature, corresponding to a fouling activation energy of 130 kJ/mol. Analyses of soluble gum and deposits, suggest that the labile soluble gum is the precursor, and undergoes some thermal decomposition to form more stable deposits.

INTRODUCTION

Autoxidation resulting in formation of oxidized polymeric gum species is considered to be one among many causes of fouling in organic fluids such as petroleum fractions. Dissolved oxygen (O₂) effects have been studied in hydro-desulphurizer feedstocks (Braun and Hausler, 1976) model systems containing olefins (Asomaning and Watkinson, 1992 ; Wilson and Watkinson 1995), crude oils (Watkinson, et al., 2000), and unstable heavy oil-diluent mixtures (Asomaning and Watkinson, 2000) and in naphthas (Li *et al.*, 2007).

Gum formation mechanisms can be described in a simplified manner as done by Taylor *et al.*, 1967, or in more detail through the free-radical reactions of the basic autoxidation scheme. Where propagation occurs via addition reactions, polymeric peroxides are formed which cause fouling through some combination of wall reaction of dissolved gums, and transport plus adhesion of insoluble gums (Wilson and Watkinson, 1995). Ervin *et al.*, 1996 present a model of aviation fuel fouling based on these ideas. Certain species are susceptible to autoxidation, and because of their structure give rise to autoxidative polymerization (Wallace, 1964). For example, Wu and Chung (2007) have shown that pyrrolic species in coker gas oils can undergo autoxidative polymerization, as was outlined in the review by Watkinson (1992).

Gum solubility, and hence precipitation, will depend on the structure and polarity of the gum, and the temperature and solubility parameter of the surrounding fluid.

Autoxidation fouling requires the presence of some oxygen in the system, and good design and operating practices should keep dissolved oxygen concentrations to a minimum, however as stated by Vadekar (2002), for vacuum systems in particular, oxygen ingress will occur unless equipment is sealed unfaillingly at all times.

The objectives of this work were to explore operating parameter effects on autoxidative fouling of a heavy vacuum gas oil (HVGO), which gave little fouling under inert atmospheres, and to characterize the deposits.

EXPERIMENTAL

Table 1 lists properties of the HVGO. This asphaltene-free oil contained roughly 68 % paraffins and equal amounts of aromatics and resins. It had an average molecular mass of 285, and a solubility parameter of 16.8 (MPa)^{0.5}. It also contained some suspended solids, as will be discussed below.

Fouling experiments were done in a re-circulating system (Li *et al.*, 2007), equipped with an HTRI-type annular probe. The feed tank held 9-L of sample oil at 85°C and was pressurized to 410 kPa, with air-nitrogen (N₂)

mixtures to fix the partial pressure of dissolved oxygen in the system. Oxygen solubility at atmospheric pressure and room temperature was expected to be of the order of 10 ppmw. Fouling resistance was calculated as

$$R_f = [T_s - T_{s,i}] / q \quad [1]$$

Initial rates were calculated from a linear fit of R_f vs. t , after any induction period. In selected cases an asymptotic or sigmoidal fit was used.

Suspended solids were determined by filtration at 85°C through a 1.2 micron pore-size filter, and washed by n-heptane after cooling. Dissolved gum was determined by adding n-heptane at 150/70 volumetric ratio to the HVGO, cooling for 3-h in an ice-water bath, and filtering through 1.2 micron pore size filter at 0°C.

Table 1 Properties of Heavy Vacuum Gas Oil

% Saturates	68.3	Mol. Wt (g/mol)	285
%Aromatics	15.9	Spec. Gravity	0.869
%Resins	15.8	ν 25°C (m ² /s)	10.8E-06
% Asphaltenes	0.0	ν 85°C (m ² /s)	2.5E-06
C wt %	86.55	Boiling %wt off	T (°C)
H wt%	12.65	10	277
S wt %	0.98	50	336
N wt %	0.03	90	372
H/C Atomic	1.76	99	408

RESULTS AND DISCUSSION

Fouling resistance versus time behaviour was in general, complex, showing for different run conditions an induction period followed by either constant or falling rates, or even the presence of negative R_f values due to the pattern of deposit structure. These complicating issues will be discussed further below in section (d).

a) Effects of Oxygen Partial Pressure and Solids Content

Figure 1 shows effects of O_2 partial pressure at fixed conditions of velocity and initial surface temperature for oils which had been pre-filtered. The time axis is corrected for the induction time, before which negligible fouling could be detected. Both the extent of fouling at 24-h, and the initial rate of fouling evidently increase with the oxygen pressure. At O_2 pressures of ~20 kPa, fouling is barely detectable at a velocity of 0.75 m/s and an initial surface temperature of 260-270°C.

Figure 2 shows effects of filtration, and O_2 pressure on the initial rate of fouling for the same velocity and initial surface temperature conditions as in Figure 1. Two full curves are evident, with the fouling rate for non-filtered feed being over an order-of-magnitude higher than with pre-filtered feed, at a given O_2 pressure. The un-filtered feedstock contained about 35 ppmw of insoluble material, which upon thermogravimetric analysis (TGA) was found to be 3.3% ash, and the remainder organics volatile at temperatures over 230°C. For the filtered HVGO, initial fouling rates increase from virtually undetectable

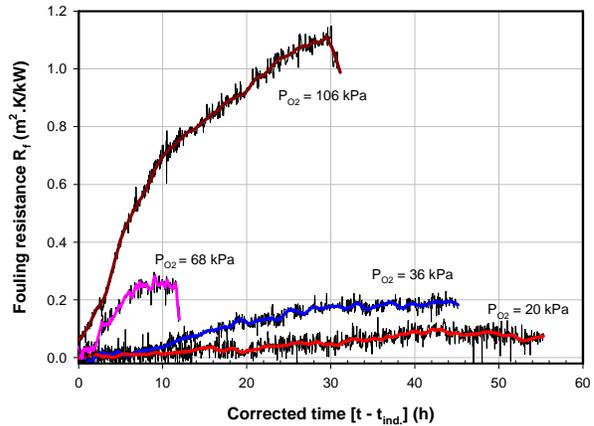


Fig. 1 Fouling resistance vs corrected time for filtered oils under different O_2 partial pressures at $V = 0.75$ m/s, and $T_{s,0} = 260-270^\circ\text{C}$

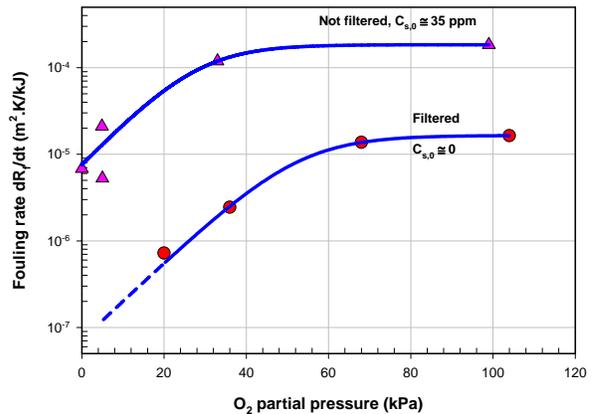


Fig. 2 Effect of O_2 partial pressure on initial fouling rate for non-filtered and filtered oils with different levels of suspended solids at $V = 0.75$ m/s, $T_{s,0} = 260-270^\circ\text{C}$

($dR_f/dt = 1\text{E-}07$ m² K/kJ) under N_2 , to over $1\text{E-}04$ m² K/kJ when O_2 pressure is 106 kPa, at fixed temperature. For both filtered and non-filtered oils (not shown), the rate of fouling increase with O_2 pressure is nearly linear (Fig. 3).

b) Effects of Velocity

Velocity effects for filtered oils are shown in Figures 4 and 5 at O_2 pressure at 106 kPa. Fouling was nearly undetectable at $V = 1.28$ m/s, and increased as the velocity was lowered to about 0.74 m/s. This velocity effect was to be expected for fouling due to gum deposition, where deposits are well bonded to the surface. There is some evidence of an increase in fouling rate with velocity at the low range of 0.6 to 0.8 m/s. However given the errors and uncertainties in the data, too much should not be read into the single data point in Fig. 5 to the left of the maximum. These data were taken at relatively low Reynolds number of 4000-8000.

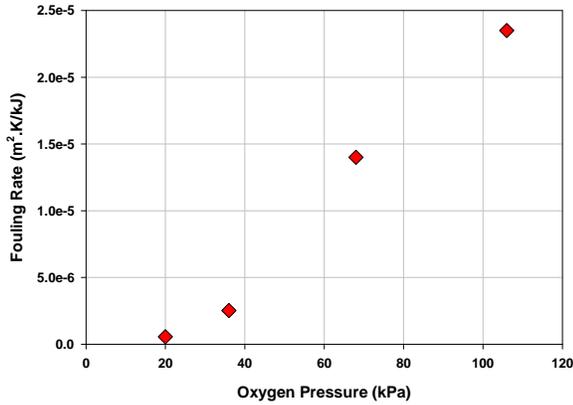


Fig. 3 Effect of O₂ pressure on fouling rate of filtered oils (Conditions of Fig. 2)

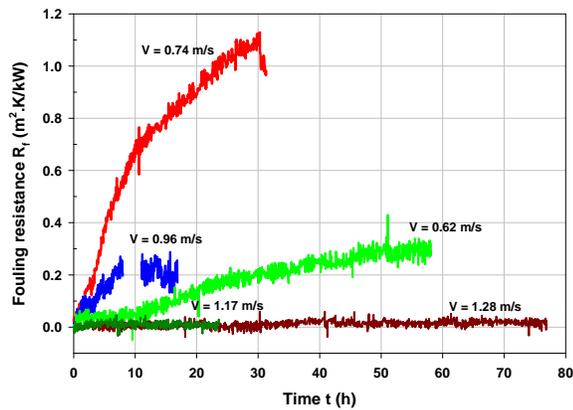


Fig. 4 R_f vs. time for different velocities at $T_{s,o} \sim 260$ - 270°C and $P_{O_2} \sim 106$ kPa

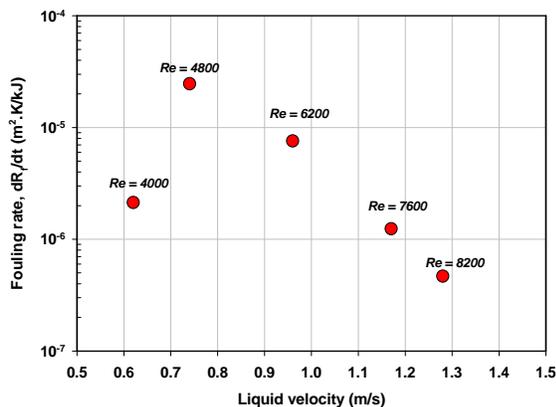


Fig. 5 Initial fouling rate as function of velocity

c) Effects of Surface Temperature

Surface temperature effects were explored in a series of runs at initial surface temperatures of about 265°C to 322°C, and fixed velocity, oxygen pressure and bulk temperature. Plotting all data in the fouling Arrhenius form of $\ln[dR_f/dt]$

vs. $1/T_{s,o}$ (K), as seen in Figure 6 shows a wide scatter, particularly at low surface temperatures; the fouling activation energy based on surface temperature over the range 265 to 322°C was 130 kJ/mol at $V = 1$ m/s.

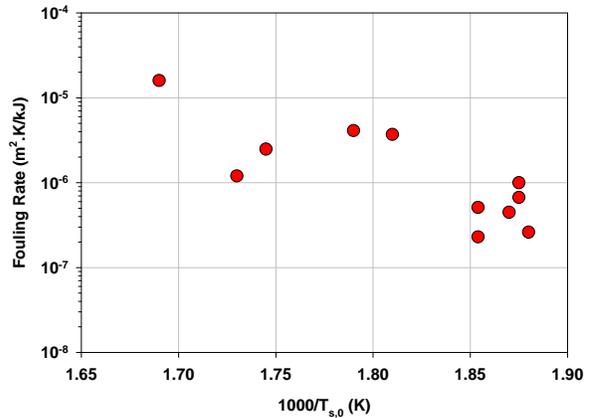


Fig. 6 Plot of initial rate vs. inverse of initial surface temperature (rates corrected to $V = 1$ m/s).

d) Complicating Factors in Interpretation of Results

In terms of dissolved gum concentration, these experiments were run under non-steady conditions, as the concentration built up over duration of the run. Given the complex nature of free-radical gum forming reactions in autoxidation, it is perhaps not surprising that several types of complicating behaviour were observed.

With filtered oil, at surface temperatures above 275°C, induction times before measurable fouling occurred were near zero. However at lower surface temperatures a broad range of induction times of about 70-140 hours were found (Fig. 7).

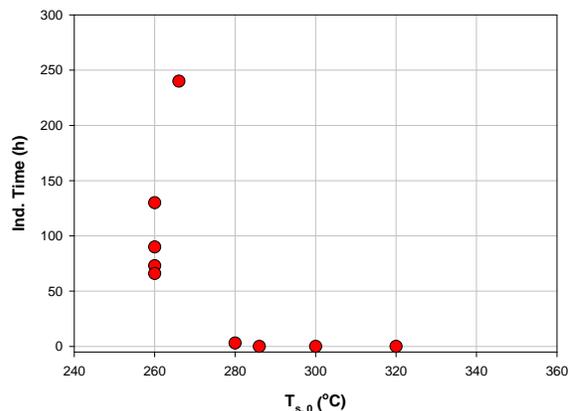


Fig. 7 Induction times as a function of initial surface temperature at $P_{O_2} = 106$ kPa.

Another anomaly which occurred after one case of long induction time is shown in Fig. 8(a), where a negative fouling resistance began after some 120-h of operation. The reason for the negative R_f values is evident in Fig. 8(b),

which shows the isolated gum deposits of the order of 0.5 mm high, which were well spaced to generate roughness effects to increase the heat transfer coefficient. At the end of a typical run, rough granular deposits eventually covered the whole heated section of the probe, as shown in Fig. 8(c).

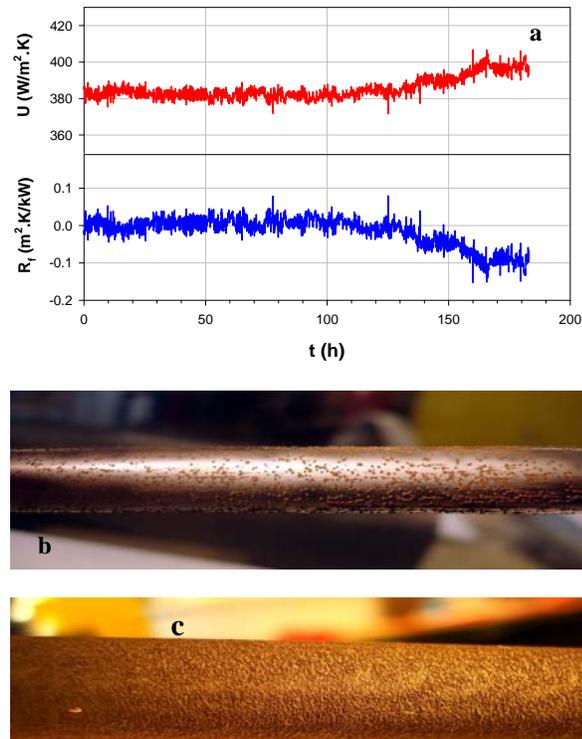


Fig. 8 (a) “Negative” fouling resistances due to sparse, rough deposit shown in Fig 8(b), and final well-covered probe in Fig. 8(c) [$V= 0.75$ m/s, $T_{s,o} = 260^{\circ}\text{C}$, $P_{O_2} = 106$ kPa].

Partial deposit removal was found under highest surface temperature conditions. In Fig. 9(a) the R_f vs t plot shows a marked drop in R_f after 16-h. This is attributed to the evident spalling of part of the deposit as shown in Fig.9(b). Spalling may have been caused by partial boiling at the surface.

Fig. 10 shows that the soluble gum present in the feed tank at 85°C , increased with run duration. The average rate of gum formation was $\sim 1\text{mg/L-h}$, over the first 300-h, after which little further increase was noted. For runs of very long re-circulation times, at which the highest gum concentrations were reached, fouling rates increased with time, as shown in Fig. 11. This accelerating-rate behaviour might be expected when the foulant concentration is increasing with time. When gum reaches its solubility limit, fouling will occur not only from dissolved gum reacting on the surface, but also by particulate gum deposition, as has been shown for model compound studies by Watkinson and Wilson (1997). Fouling rates plotted in earlier figures (Figs. 2, 4, 6, 7) were representative of short runs, where dissolved gums were typically, 100 mg/L .

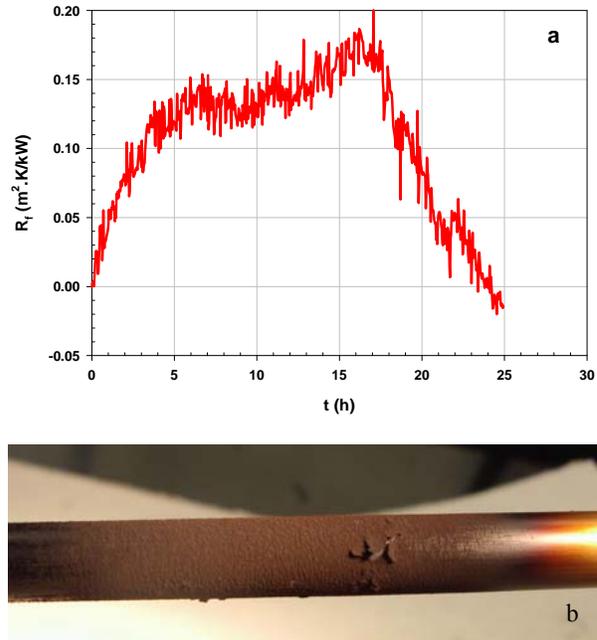


Fig.9 (a) R_f vs. time behaviour at high surface temperature ($T_{s,o} = 322^{\circ}\text{C}$, $V=0.95$ m/s); (b) evidence of spalling of deposits

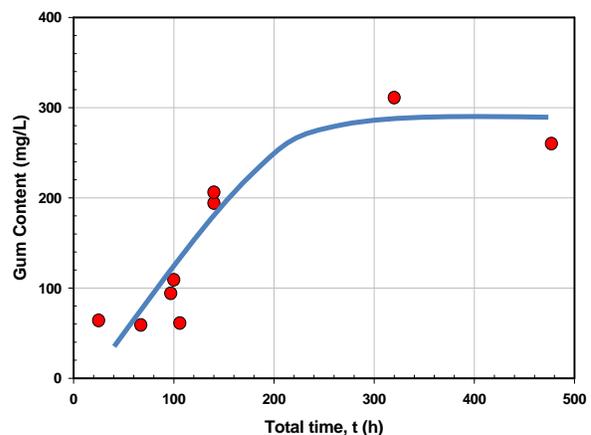


Fig.10 Soluble gum concentration in feed tank at end of fouling runs of different durations.

e) Deposit Compositions

Table 2 compares the deposit analyses from the non-filtered oil, where fouling rates were high (Fig. 2), with the analysis of the suspended solids. The suspended solids appear to be gum-like material with a high O/C ratio and ash content. Deposits from experiments with wall temperature $260\text{-}270^{\circ}\text{C}$, are lower in oxygen, nitrogen and ash content compared to the suspended solids.

Table 3 compares the compositions of deposits from the filtered oil experiments with those of the dissolved gum recovered by precipitation in cold n-heptane. Gums are highly oxygenated and also very high in nitrogen content, which is also partially reflected in the deposit compositions.

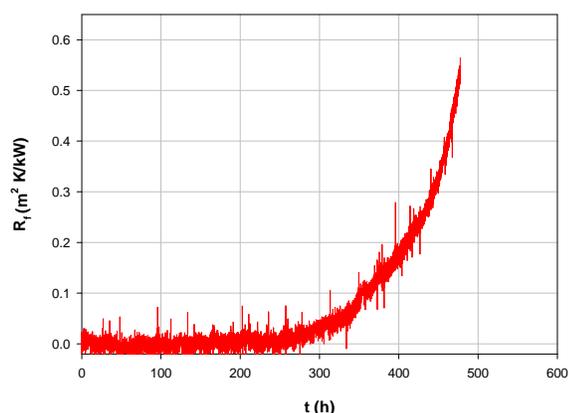


Fig. 11 Accelerated fouling after long re-circulation time.

This nitrogen content may be due to the presence of reactive pyrroles, as has been noted by Wu and Chung (2007). Deposits from experiments with wall temperatures 260 to 320 °C, are also fairly high in oxygen content, but are lower than the dissolved gums in oxygen, nitrogen, and H/C ratio.

Table 2 Deposits and Suspended Solids Composition for Experiments with Non-filtered Oil

	C	H	N	S	O	H/C	O/C	Ash
	%					-	-	%
D*	78	9.2	0.4	ND	7	1.4	0.07	4
S#	47	5.6	1.5	4.2	27	1.4	0.4	14

No. of samples * n=5 ; # n=2

Table 3 Deposits and Soluble Gum Composition for Experiments with Filtered Oil

	C	H	N	S	O	H/C	O/C	Ash
	%					-	-	%
D*	65	2.8	1.9	2.0	25	0.5	0.3	4.0
G#	58	5.7	3.9	ND	32	1.2	0.4	-

No. of samples * n=5, # n=3

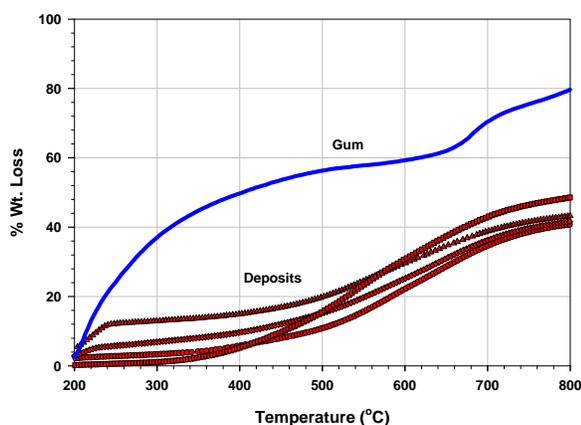


Fig. 12 Thermogravimetric analyses of gum and deposits

Fig. 12 shows the weight loss vs. temperature for a gum sample, and four deposit samples determined by heating the solid in N₂ in TGA. The weight loss traces vs. temperature for all the deposits are fairly similar. It is clear that the gum, however, is a much more volatile material than the deposits, which have aged on the surface. At 300°C, the gum has partially decomposed to lose 40% of its weight, whereas the more stable deposits lose less than 12% of weight at this temperature, and only reach 40% weight loss when heated to about 800°C. This trend supports the data in Table 3 where H/C levels and % oxygen levels are significantly lower in the deposits than in the gums.

CONCLUSIONS

Studies with a heavy vacuum gas oil in the presence of oxygen have shown that:

1. The fouling rate increases almost linearly with oxygen pressure over the range 20 kPa to 106 kPa for both filtered and non-filtered oils. Oils containing suspended particles fouled at much higher rates than filtered oils.
2. At surface temperatures in the range 260-320°C, fouling rates increased with temperature according to a fouling activation energy of ~ 100 kJ/mol. At velocities over 0.7 m/s, fouling rate decreased as velocity was increased.
3. Soluble gums formed at ~1 mg/L-h at 85°C, and oxygen partial pressures of 106 kPa. Recovered gums were more labile than deposits, which appeared to form from gum particulates. Both were highly oxygenated at O/C ~ 0.3-0.4, although deposits showed lower H/C ratios.
4. Induction periods were of the order of a few hours, at temperatures above 275°C, but were scattered and much higher in magnitude at lower temperatures.

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NOMENCLATURE

P	Pressure (kPa)
Q	Heat flux (kW/m ²)
R _f	Thermal fouling resistance (m ² K/kW)
Re	Reynolds number based on Equivalent diameter and T _f
T	Temperature (°C) or K
V	Bulk Velocity (m/s)
N	Kinematic viscosity (m ² /s)

REFERENCES

Asomaning, S, Watkinson, A.P., 2000, Petroleum Stability and Heteroatom Species Effects in Fouling by Asphaltenes, *Heat Trans. Eng.* 21, 10-16.

Braun R., and Hausler, R.H., 1976, Contribution to Understanding Fouling Phenomena in the Petroleum Industry, *16th National Heat Transfer Conf., St. Louis, Mo., USAPaper 76-CSME/CSCHE-23*, 14pp.

Ervin, J.S., Williams, T.F., Katta, V.R.,1996, Global Kinetic Modeling of Aviation Fuel Fouling in Cooled Regions in a Flowing System, *Ind. Eng. Chem. Res.* 35, 4028-4036

Li, YH., Watkinson, A.P., Herrera, P., Fahiminia, F., James, M., 2007, Formation of Gum and Deposits in an Oxygenated Naphtha Stream, *Heat Exchanger Fouling and Cleaning VII, ECI Conference, Tomar, Portugal, 1-6 July 2007*, pp80-89.

Taylor, W.F. and Wallace, T.J., 1967, Kinetics of Deposit Formation from Hydrocarbon Fuels at High Temperatures-General Features of the Process, *IEC Proc. Res. Dev.* 6, 258-62

Vadekar, M., 2003, Oxygen Contamination of Hydrocarbon Feedstocks, *Petroleum Technology Quarterly*, Winter 2002-3 pp87-93

Wallace, T.J., 1964, Chemistry of Fuel Instability, *Adv. Petrol. Chem. & Refining Vol. IX, Chapt.8* J.J. McKetta Jr.(Ed.) Interscience, pp353-403.

Watkinson, A.P., 1992, Chemical Reaction Fouling of Organic Fluids, *Chem. Eng. Technol.* 15, 82-90.

Watkinson, A. P. and D. I. Wilson, 1997, Chemical Reaction Fouling -A Review *Experimental Thermal and Fluid Science* 14, 361-374.

Watkinson, AP, Navaneetha-Sundaram, B., Posarac, D., 2000, Fouling of a Sweet Crude Oil under Inert and Oxygenated Conditions *Energy & Fuels* 14(1) 64-69.

Wu, X.A. and Chung, K.H., 2007, Solving a Hydrotreater Feed Filter Fouling Problem, *Heat Exchanger Fouling and Cleaning VII, ECI Conference, Tomar, Portugal, 1-6 July 2007*, pp436-438.