

FOULING BEHAVIOR OF PYROLYSIS GASOLINE OVER CARBON STEEL AND STAINLESS STEEL ALLOYS

Michael Sprague[†], Patricio Herrera, Andrzej Krzywicki

NOVA Research and Technology Center, NOVA Chemicals Corporation
2928 – 16 Street NE, Calgary, Alberta, T2E 7K7 CANADA

[†]spragm@novachem.com

ABSTRACT

Chemical reaction fouling in petrochemical thermal processes (separation units, heat exchangers, and reboilers) is a serious and costly problem. One strategy being assessed to reduce fouling in separation units is to replace carbon steel column internals with stainless steel alternatives. Empirical evidence suggests fouling occurs to a lesser degree over stainless steel compared to carbon steel, however fundamental information regarding the influence of steel composition on chemical reaction fouling is lacking. In this work, four steel alloys of known composition are tested for fouling propensity of pyrolysis gasoline using the Hot Liquid Process Simulator (HLPS). Fouling rates are measured over each alloy to establish a ranking of fouling propensity. The HLPS results are rationalized based on the composition of the heater tube alloys, highlighting the influence of iron, nickel, chromium, and molybdenum content on fouling behavior.

INTRODUCTION

Fouling in petrochemical thermal processing units is a serious issue that can lead to some or all of the following:

- Separation efficiency problems,
- Reduced capacity,
- Greater energy consumption,
- Production losses,
- Increased cleaning costs during turn-around and the potential for fire during maintenance due to pyrophoric materials,
- Use of expensive chemical additive packages.

One approach to fouling mitigation in distillation units involves changing carbon steel column internals to stainless steel. Empirical evidence across the industry suggests that stainless steel can reduce the severity of fouling compared to carbon steel. Pictures of depropanizer column internals taken during a turn-around at a NOVA Chemicals' Plant show that polymer growth occurs preferentially on the vessel walls (carbon steel) as compared to trays (stainless

steel). Fundamental information in the open literature is lacking in regards to the impact of metallurgy on fouling rates, particularly with respect to chemical reaction fouling of intermediate petrochemical streams under temperature conditions common to distillation (<250°C). This work is aimed at expanding the knowledge available in this area.

A significant amount of information is available on the thermal stability of aviation fuels over various metal surfaces, however, most of the work done to date has been at temperatures where coking reactions predominate (>350°C), using feedstocks that have negligible olefin and diene content (Altin and Eser, 2001a, 2001b; Hazlett, 1991; Smith 1967; Stavinoha 1990; Taylor, 1968). Low temperature work was done by Faith *et. al.* (1971), evaluating the thermal stability of Jet A fuel using an Alcor JFTOT at 210°C. Various metallurgies were tested including 1015 carbon steel (CS), 304, 316, and 446 stainless steel (SS). The impact of metallurgy on fuel stability was significant, but the results may be valid only for aviation fuels. More recently, Isogai and Nakamura (2004) tested the fouling propensity of crude benzene using an Alcor HLPS over 1018CS, 304SS, 316SS and aluminum at 145°C and 41.6 psig. Their results show that carbon steel promotes crude benzene fouling in comparison to alloy surfaces. The fouling propensity of the different steels was attributed to the corrosion resistance of the material.

The objective of the present work is to establish fouling rates of pyrolysis gasoline over carbon steel and stainless steel alloys, at a temperature common to petrochemical thermal processing.

EXPERIMENTAL

Fouling experiments were carried out in an Alcor Hot Liquid Process Simulator (HLPS) utilizing heater tubes machined from 1018CS, 304SS, 316SS and 446SS. A simplified schematic of the Alcor unit is shown in Figure 1. Fouling is monitored as a function of differential pressure (dP) across a 17µm filter at the outlet of the test section.

Tests were carried out in a laminar flow regime, with recycled liquid flow. Pyrolysis gasoline was used as the test fluid, sampled from NOVA Chemicals' Corunna site.

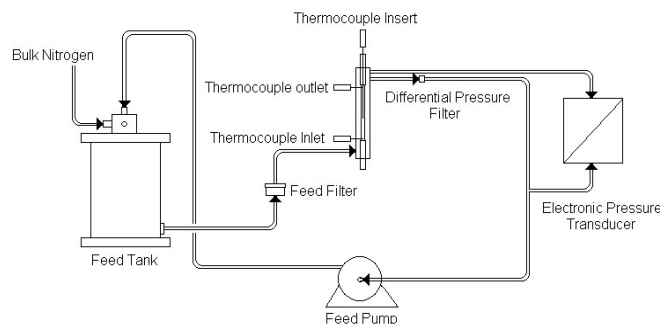


Fig. 1 Schematic of Alcor HLPS

HLPS tests can either be run by maintaining a constant liquid temperature at the outlet of the heated section (constant heat flux), or by maintaining constant heater tube surface temperature (at a single location along the length of the tube). Maintaining constant heat flux resulted in different surface temperature profiles and different maximum surface temperature for the various steel tubes. Since the catalytic activities of different metals should be compared at constant temperature, surface temperature was controlled such that the average tube surface temperature was approximately constant for each alloy. In all experiments the maximum heater tube surface temperature was maintained at 250°C. Heater tube temperature profiles were measured and are presented in (Figure 2).

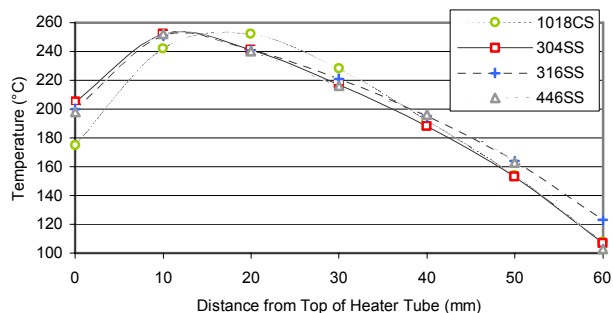


Fig. 2 HLPS Heater Tube Temperature Profiles for Various Alloys

Table 1 shows temperature data recorded for the HLPS experiments. Given the different thermal properties of the various metallurgies, maintaining constant surface temperature proved difficult. The average surface temperature ranged from 193°C (1018CS) to 199°C

(316SS). The liquid ΔT across the heated section also indicates some variation in heat flux to the liquid.

Table 1. Average heater tube surface temperature, fluid inlet and outlet temperatures, and ΔT of liquid across heated section.


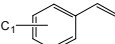
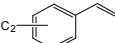

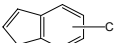
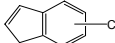
Alloy	$T_{\text{surface, ave}}$ (°C)	T_{inlet} (°C)	T_{outlet} (°C)	ΔT (°C)
1018CS	193	34	167	133
446SS	195	35	176	141
304SS	195	36	178	142
316SS	199	34	173	139

HLPS Test Procedure. 500cc of pyrolysis gasoline was gravity filtered using 8 μ m filter paper to remove pre-existing solids / gums, and was charged to the HLPS under 150 psig N_2 . Liquid flow was set to 3.0 ml/min, giving the liquid a residence time of \sim 11 seconds in the heated section. Differential pressure (dP) was used to monitor fouling and the test was stopped when the dP reached 200mm Hg. All experiments were run in duplicate.

RESULTS AND DISCUSSION

Characterization of Pyrolysis Gasoline. GC-MS analysis of pyrolysis gasoline revealed an abundance of styrene and indene derivatives (Table 2). Styrene and indene derivatives comprise \sim 44% of the total liquid, indicating the fouling mechanism is free-radical polymerization. 'Total inerts' refers to aliphatic and aromatic species that are not expected to participate in the fouling reaction.

Table 2. Composition of Pyrolysis Gasoline by Reactive Monomer Group

Compound Type	(%)
	17.4
	17.9
	1.4
	5.3
	1.5
	0.0
Total styrenes:	36.8
Total indenes:	6.7
Total inerts:	55.7
Sum:	99.2

Surface Roughness Analysis. A rough surface gives a much larger effective contact area than a smooth surface, potentially allowing strong adhesion of deposits (Rankin *et al.*, 1973). Surface roughness may also provide nucleation sites for deposits to grow, increasing initial deposition rates (Taborek *et al.* 1972). Based on this information, surface roughness testing was performed to ensure the heater tubes have comparable roughness. Tube surface roughness was analyzed using a Mitutoyo 402 SurfTest Series 178 Instrument (Table 3). Roughness, measured as (R_a), is the arithmetical mean of the roughness profile. The roughness for tubes used in this study ranged between 0.11 to 0.27 μm .

Table 3. Surface Roughness of HLPS Heater Tubes

	1018CS	304SS	316SS	446SS
Average Surface Roughness R_a (μm)	0.27±0.09	0.21±0.03	0.23±0.02	0.11±0.02

Studies by McGuire and Swartzel (1987) and Yoon and Lund (1994) independently demonstrate that no effect on surface roughness is observed in the R_a range of 0.04-2.31 μm and 0.08-0.60 μm respectively; therefore, the differences in surface roughness of tubes used in this study should not impact fouling rates.

Fouling Tests. Results of the fouling tests are summarized in Figure 3. The time required for the differential pressure to reach 200 mm Hg signified the end of a test. The dP curves in Figure 3 indicate the fouling induction period, given by the time where heat induced particulate formation results in differential pressure greater than zero. All steels were compared based on the induction period, and the time to reach 200 mm Hg dP. Depending on the heater tube material, we observe varying induction times and varying time periods to reach the 200 mm Hg cut-off. Note that all three stainless steel alloys have significantly longer induction periods than carbon steel. Note also that, despite having the lowest heat flux and highest average surface temperature (Table 1), 1018CS has the shortest induction period. Subtle differences exist between 446SS and 304SS, and both of these stainless steels show a slightly lesser propensity to foul as compared to carbon steel. With 316SS, we see a pronounced difference and extension of the induction period compared to the other alloys.

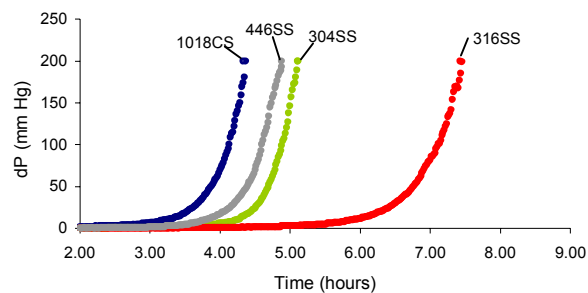


Fig. 3 Fouling Propensity of Pyrolysis Gasoline Over Various Alloys: 250°C, 150 psig N₂, 3.0 ml/min

Using the induction period and time to reach 200 mm Hg as a basis, a relative comparison of fouling propensity of the steels can be made. The induction period and time to each 200 mm Hg over 1018CS, 304SS, 446SS, and 316SS proceed according to the following scale:

Alloy	1018CS	> 446SS	≈ 304SS	> 316SS
Induction Period (hrs)	0.4	1.9	1.3	3.3
Time to 200 mm Hg (hrs)	4.3	4.9	5.1	7.4

The heated probe was examined at the end of each experiment. Pictures of the heater tubes are provided in Figure 4 for visual comparison. The most significant deposit was found on carbon steel in a single band centered on the tube hot spot. 446SS showed two bands of material just above and below the tube hot spot. The 300 series stainless steels gave a thin brown layer quite unlike the other two heater tubes. The deposits did not blister or form a mass like 1018CS and 446SS, but rather was spread in a thin layer around the tube hot spot. The difference in weight of the heater tubes before and after the experiment was negligible to within ±1 mg, attributed primarily to the short time-periods over which the fouling tests were conducted.

In an earlier study by Faith and coworkers (1971), the relative mass of deposits from Jet A fuel at 210°C over the same alloys follows according to:

Alloy	304SS	> 1015CS	> 316SS	> 446SS
Relative Deposit Mass	~70.0	~56.6	~3.0	1.0

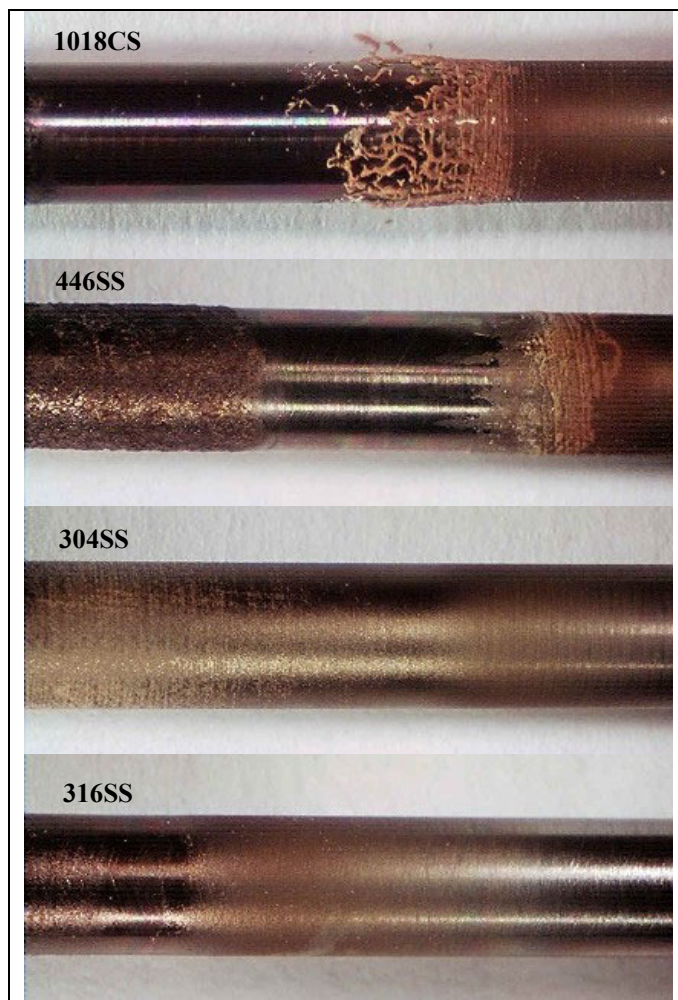


Fig. 4 Post-experiment Digital Pictures of HLPS Heater Tube Fouling Deposits (10× magnification)

In agreement to the current study, results from Faith and coworkers (1971) indicate that 316SS and 446SS have a lower fouling propensity as compared to carbon steel. In the same study however, 304SS shows a greater propensity to foul than carbon steel. This is in contrast to results from the current work, which shows that, in general, stainless steel has a lower propensity for foul as compared to carbon steel. The primary difference between the current work and that by Faith and coworkers (1971) is the nature of the hydrocarbon fluid. Jet fuel is predominantly a mixture of aliphatic, naphthenic and aromatic species, with very low olefinic content, which reacts predominantly via autoxidation. This is in contrast to pyrolysis gasoline, which contains upwards of 50% reactive olefins such as styrene, indene, and derivatives, and reacts via thermally and catalytically induced free-radical polymerization.

Effect of Metallurgy on Fouling. The trend in Figure 3 confirms empirical observations from our plant sites. Stainless steel is more inert to chemical reaction fouling compared to carbon steel for streams high in olefin and diene content. Since all other parameters are held constant, the information implies that the material or alloy is participating in the fouling reaction. It is thought that the surface of the alloy may act as a catalyst to varying degrees, depending on the surface composition.

Alloy compositions are provided in Table 4. The trend between alloy composition and fouling behavior is not well understood, however, there are indications that elements or oxides of iron, nickel, chromium and molybdenum are playing a role.

Table 4. Heater Tube Bulk Composition by ICP-MS

Element	1018CS	446SS	304SS	316SS
Al	0.4	0.0	0.0	0.0
Si	0.1	0.1	0.2	0.1
S	0.0	0.0	0.0	0.0
Cr	0.1	20.5	15.9	16.1
Mn	0.7	0.8	1.1	1.7
Fe	94.0	72.2	69.5	62.6
Co	0.0	0.0	0.2	0.1
Ni	0.1	0.4	8.9	12.4
Cu	0.1	0.1	0.3	0.3
Mo	0.0	0.1	0.3	2.5
Total wt. %	95.4	94.3	96.3	95.8

The composition data shows that decreasing iron content follows the trend in fouling propensity, whereby lower iron content gives lower fouling propensity. The influence of nickel follows the opposite trend. Fouling propensity of pyrolysis gasoline decreases with increasing nickel content. Thus, the presence of higher nickel content appears to have a mitigating effect on fouling. Although manganese is found in small quantities, <2%, it should be noted that fouling propensity of pyrolysis gasoline also decreases with increasing manganese content.

The effect of chromium is not as clear. Considering 1018CS and 446SS, 446SS has 20% higher chromium content. Since 446SS exhibits a slightly longer induction period compared to 1018CS, chromium may be more inert to the fouling reaction. In contrast to the suggestion that higher chromium content may be beneficial, comparison of

446SS with 300-series stainless steels indicates a lower fouling propensity with lower chromium content. Thus, it is not clear whether the presence of chromium is beneficial.

In comparing 304SS and 316SS, both alloys contain approximately the same chromium and manganese content; however, 304SS and 316SS show considerably different fouling propensities. The nickel content of 316SS (12%) is higher than 304SS (9%), which may be responsible for the differences in fouling behavior. Another subtle difference in composition between 304SS and 316SS, is that 316SS contains 2.5% molybdenum whereas 304SS contains 0.3% molybdenum. Thus, molybdenum may also contribute to the mitigating effect observed for 316SS.

Isogai and Nakamura (2004) fouled crude benzene over 1018CS, 304SS and 316SS and suggested the trend in fouling propensity is governed by a corrosion effect, whereby dissolved iron salts originating as a result of corrosion act as polymerization catalysts. Stavinoha *et al.* (1990) also suggest a similar mechanism where organic acids are believed to react with metal oxides to produce metal species soluble in the organic phase. These dissolved metal species can initiate autoxidation reactions or decompose existing hydroperoxides to free radicals, thus enhancing fouling rates. Thus, the corrosion properties of the steel may be related to the relative fouling rate over various metallurgies. Therefore the corrosion resistance of the particular alloy in contact with the liquid may also help explain these trends.

No simple correlation exists to explain the observed fouling behavior, however there are trends in the data. The effect of alloy composition appears to be the net result of not only individual elements and oxides, but also synergistic interactions among the various constituents and the liquid components in contact with the metal surface. More work is needed to identify the role of individual elements and their oxides. Furthermore, the corrosion resistance of the alloy in contact with the liquid may be a key parameter to consider when selecting metallurgies for equipment in fouling service.

CONCLUSIONS

Experimental evidence is provided to support the notion that stainless steel offers advantages over carbon steel in fouling mitigation for streams high in olefin and diene content. The results of this study lead to the following conclusions:

1. Chemical reaction fouling rates of pyrolysis gasoline vary according to the composition of metallurgy in contact with the liquid.

2. Thermal stressing of pyrolysis gasoline over 4 alloys shows that the fouling rate decreases according to:

$$1018CS > 446SS \approx 304SS > 316SS$$

3. Carbon steel has a higher propensity to foul compared to stainless steel. This trend was rationalized based on the composition of the alloys tested. In particular, pyrolysis gasoline has a lower fouling propensity over alloys containing nickel and molybdenum. To a lesser extent, chromium and perhaps manganese impact the fouling rate of pyrolysis gasoline.
4. The information gained in this study can be leveraged to select materials of construction in locations where fouling is an issue. Further work is underway to better understand the influence of alloy composition on fouling.

ACKNOWLEDGMENTS

Permission to publish this work is gratefully acknowledged. We would like to acknowledge the Alberta Research Council for performing characterization of heater tubes, and we would like to thank John Henderson, Chetan Anand and Andre Bernard for refining the content of this paper.

REFERENCES

Altin, O., Eser, S., 2001a, Analysis of Carbonaceous Deposits from Thermal Stressing of a JP-8 Fuel on Superalloy Foils in a Flow Reactor, *Ind. Eng. Chem. Res.*, 40, pp. 589-595.

Altin, O., Eser, S., 2001b, Analysis of Solid Deposits from Thermal Stressing of a JP-8 Fuel on Different Tube Surfaces in a Flow Reactor, *Ind. Eng. Chem. Res.*, 40 pp. 596-603.

Faith, L.E., Ackerman, G.H., Henderson, H.T., July 1971, Heat Sink Capability of Jet A Fuel: Heat Transfer and Coking Studies, *NASA Report CR-72951*, S-14115, Shell Development Company on contract, Cleveland, OH, July.

Hazlett, R.N., 1991, *Thermal Oxidation Stability of Aviation Turbine Fuels*, American Society for Testing and Materials, Philadelphia, PA.

Isogai, S., Nakamura, M., 2004, Analysis and Steps to Mitigate Heat Exchanger Fouling in an Aromatics Plant, *2003 ECI Conference on Heat Exchanger Fouling and Cleaning: Fundamentals and Applications*, Santa Fe, New Mexico, USA, Paper 30.

McGuire, J., Swartzel, K.R., 1987, Influence of Solid Surface Energetics on Macromolecular Adsorption from Milk, *AIChE National Meeting*, pp. 31.

Rankin, B.H., Adamson, W.L., 1973, Scale Formation as Related to Evaporator Surface Conditions, *Desalination*, 13, pp. 63-87.

Smith, J.D., April 1967, The Effect of Metals and Alloys on the Thermal Stability of Avtur 50, *Aircraft Engineering*, pp. 19-26.

Stavinoha, L.L., Naegli, D.W., McInnis, L., 1990, The Role of Surface Composition in Fuel Deposition, *ACS National Meeting, Fuel Chemistry Pre-prints*, 35, pp. 1315-1323.

Taylor, W.F., 1968, Kinetics of Deposit Formation from Hydrocarbons III. Heterogeneous and Homogeneous Metal Effects, *J. App. Chem.*, vol. 18, pp. 251-245.

Taborek, J., Aoki, T., Ritter, R.B., Palen, J.W., Kundsens, J.G., 1972, Predictive Methods for Fouling Behavior, *Chem. Eng. Prog.*, 68(7), pp. 69-78.

Yoon, J., Lund, D.B., 1994, Magnetic Treatment of Milk and Surface Treatment of Plate Heat Exchanger: Effects on Milk Fouling, *Journal of Food Science*, 59(5), pp. 964-969, 980.