

Formation of Gum and Deposits in an Oxygenated Naphtha Stream



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Abstract

- Chemical reaction fouling is a serious problem in petrochemical separators, heat exchangers, pumps and compressors.
- This research aims to investigate mechanisms in autoxidation fouling, a prime source of deposit formation in streams contaminated with oxygen.
- Blended naphtha, with reactive species such as branched hydrocarbons and alkyl-benzenes, was oxidized in batch experiments, and re-circulated through a heat exchanger.
- Rates of hydro-peroxide and gum formation were determined as functions of temperature and oxygen pressure.
- Deposits occurred where boiling could occur either at high probe surface temperatures (~185°C) or in dead zones of the heat exchanger.
- Both gums and deposits contain about 20 % oxygen.

Objectives

- Establish the formation rates of hydroperoxide, soluble and insoluble gum as functions of temperature, and dissolved oxygen content.
- Determine the rate of thermal fouling as functions of dissolved oxygen content, temperature, and fluid velocity using a fouling loop.
- Characterize gum and fouling deposits from both batch and fouling loop experiments using available analytical techniques.
- Identify controlling steps for fouling under isothermal and heated situations from above results.
- Recommend conditions to minimize fouling based on knowledge of the fouling mechanism.

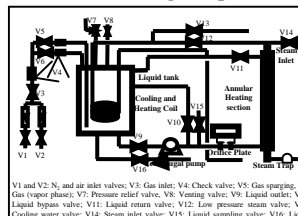
Project Benefits

- Generate key information on mechanisms governing fouling progress in different processing units.
- Permit identification of processing locations with the highest level of gum formation, and develop techniques to monitor auto-oxidation continuously and take corrective actions for fouling mitigation.
- Assist in optimizing operating conditions to minimize fouling problems.
- Provide guidance on employment of chemical or mechanical mitigation approaches.

Batch Reactor



Fouling Loop



Effect of Temperature on Peroxides Formation

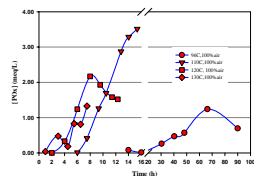
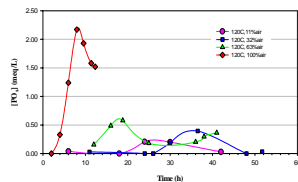


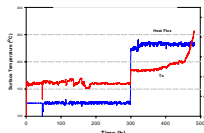
Table of Naphtha Fouling Runs

Heating Method	Steam Heating					Electrical Heating				
	1a	1b	2	3a	3b	4a	4b	5	6	7
Pre-heating	-	-	-	-	-	-	-	-	-	-
T (°C)	110	110	110	-	110	-	-	-	-	-
P(kPa)	-	585	650	-	650/720	-	-	-	-	-
t (h)	20	70	70	-	86	-	-	1	-	-
Heating										
T (°C)	66	66	95/94	90/95	90/95	80	90	90	-	-
P _{in} (kPa)	685	688	858/850	855/795	855/795	650/720	650/720	650/720	-	-
V (m/s)	1.21	0.80	0.79	0.75	0.21	0.12	0.12	0.12	-	-
Re	4750	31000	37000	37000	10000	18000	18000	18000	-	-
T (°C)	102	121	128	125	140	160	182	185-215	-	-
Q (kW)	2.8	2.6	2.0	2.0-2.5	1.0-1.1	0.19	0.40	0.5-1.2	-	-
U ₁ (kW/m ² K)	2.01	1.54	1.72	1.8-2.3	0.80-0.96	0.80	0.70-1.22	1.30-2.30	-	-
1-h)	8.6	20.8	147	187	260	300	182	805	-	-

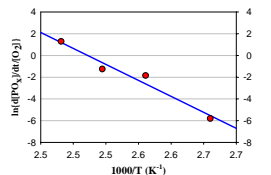
Effect of Oxygen on Peroxides Formation



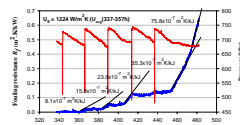
Probe Surface Temperature (Run 4)



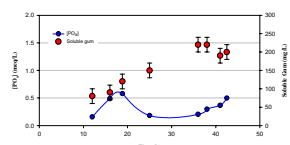
Arrhenius Plot for Peroxide Formation



Fouling Resistance Vs. Time (Run 4)



Gum and Peroxides Formation Vs. Time



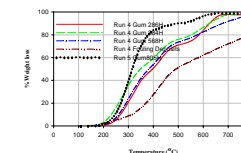
Fouling Deposits (Run 4)



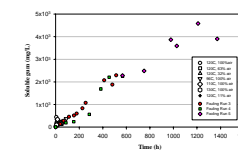
Elemental Analysis of Gum and Deposit Samples

Sample	C (%)	H (%)	O (%)	O/C**	H/C**
Run 3-Gum-260h	71.31	8.44	20.25	0.21	1.42
Run 4-Gum-384h	70.81	7.97	21.22	0.22	1.35
Run 4-Gum-568h	70.85	8.15	21.00	0.22	1.38
Run 5-Gum-805h	70.07	7.97	21.96	0.24	1.36
Gum Avg.	70.76	8.13	21.11	0.22	1.38
Run 3-deposit	71.45	6.82	21.73	0.23	1.15
Run 4-deposit	74.70	7.13	18.17	0.18	1.15
Deposit Avg.	73.08	6.98*	19.95	0.21	1.15

TGA Results



Gum Formation in Naphtha



Pyrolysis GC/MS Results

Species	Gums-Run 5 (Area %)	Deposits-Run 4 (Area %)
CO ₂	4.0	2.7
Ketones + Acetic acid	35.4	3.0 (acetone)
Light saturates (< C ₇)	5.4	23.1
Unsatur'd. fragments	25.8	12.4
Aromatics	29.4	34.0
Cycloparaffins	-	10.6
Alkanes > C ₇	-	11.3

Conclusions

- Reactive species in the naphtha are likely to be the alkyl-benzenes and branched alkanes.
- Deposition occurs only under conditions where the gum becomes insoluble either through vaporization of naphtha in the dead zones at the exchanger end, or under sub-cooled boiling conditions.
- At temperatures ranging from 96 to 130°C with air presence, blended naphtha undergoes oxidation slowly, leading to foulant formation by steps consistent with the model of Taylor and Frankentfeld (1986).
- A delay time, ranging from 1 to 30 hours, was observed, followed by a rise in peroxide concentration to levels of 1-4 meq/L, passing through a maximum over periods of 2-70 hours.
- At 120°C, a decrease in dissolved oxygen content from 70 to 10 ppm resulted in a decline of the average peroxide formation rate by a factor of 13.
- The ratio of [Avg. peroxide formation rate] / [Dissolved oxygen content] increases strongly with temperature.
- Under non-boiling conditions with 120-140°C surface temperature and Re = 10000 - 37000, no fouling was observed over periods of 260h at gum levels reaching 2280 mg/L. Deposits formed in the dead spaces at the ends of the double pipe exchanger.
- At 160°C surface temperature, no fouling was detected over more than 100h with Re = 15300 and gum concentrations below 1700 mg/L. At a surface temperature of 180°C (sub-cooled boiling conditions), and gum concentrations of 2300 mg/L, fouling occurred at a rapidly accelerating rate after 75-90h.
- Deposits from fouling loop experiments and recovered gum have H/C atomic ratios of 1.15 and 1.38, respectively, and have oxygen content of 20-21% wt.
- TGA analysis shows that deposits appear to originate from the soluble gums, which can reach concentrations as high as 2300 mg/L.
- Over 90-h experiments, the rate of gum formation increases weakly with dissolved oxygen content, and averaged 4 mg/L-h.

Acknowledgements

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