



Ethylene
Middle East
Technology
Conference

Effective fouling protection for Olefins Plant



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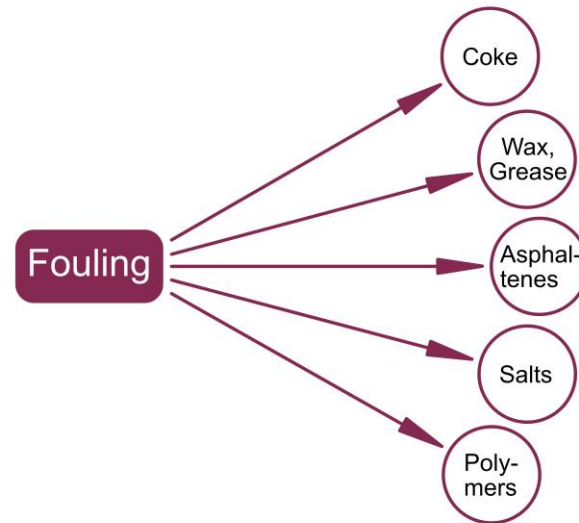
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- Polymer formation mechanisms
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- Case studies
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Kinds of Fouling

1. Petrochemical industry observes a number of different types of fouling.
2. At the same time different fouling mechanisms can be initiated.
3. Radical polymerization almost always happens.

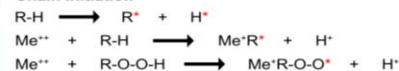


Polymer Formation Mechanisms

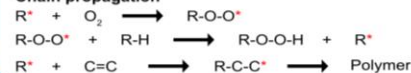
Unwanted formation of insoluble polymers

Free
radical
polymeri-
sation

Chain initiation



Chain propagation

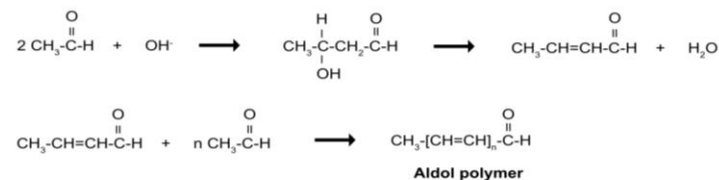


Chain termination



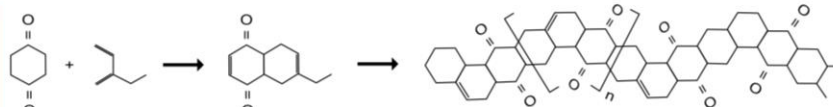
Aldol
condensa-
tion

Aldol condensation



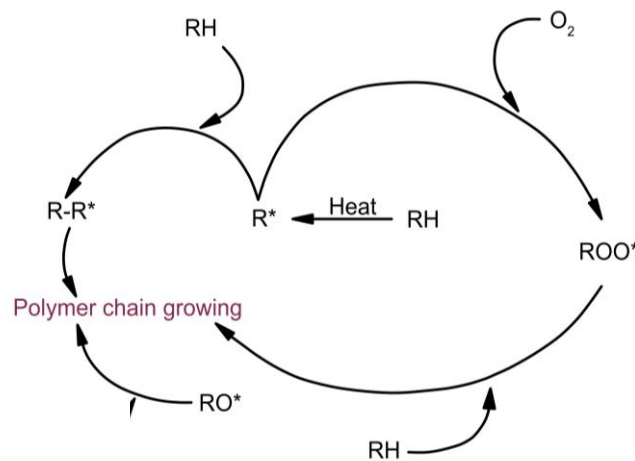
Diels
Alder
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tion

Diels Alder condensation



Free Radical Polymerization

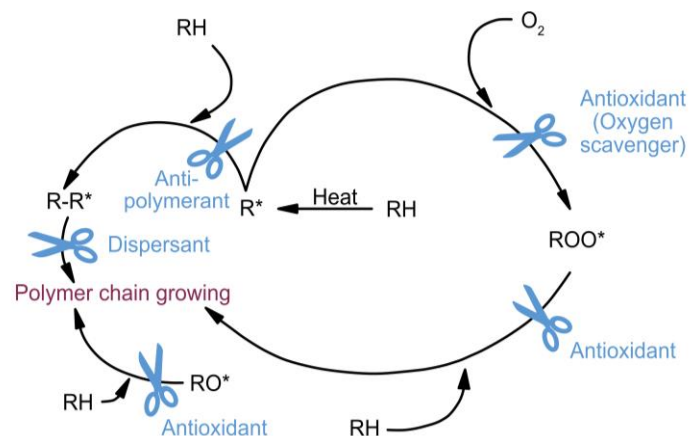
1. Unwanted polymer chain-growing processes.
2. Radical polymerization requires an initiation step to form an active center.
3. Heat, peroxides, oxidation-reduction (redox) reactions, etc. promote the initiation step.



Polymerization Inhibition

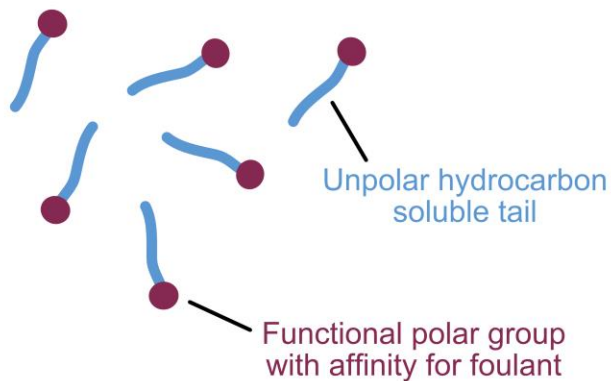
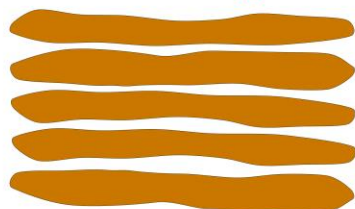
1. Antifoulant programmes stop or decelerate polymer chain-growing.
2. Formulations with different active materials are required:

- Oxygen scavengers
- Antioxidants
- Antipolymerants
- Dispersants
- Metal deactivators
- Retarders

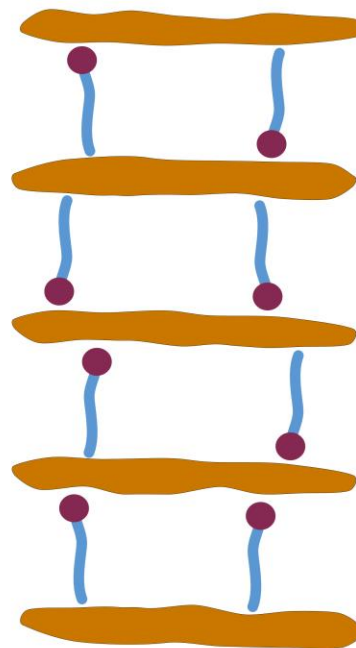


Dispersant Function

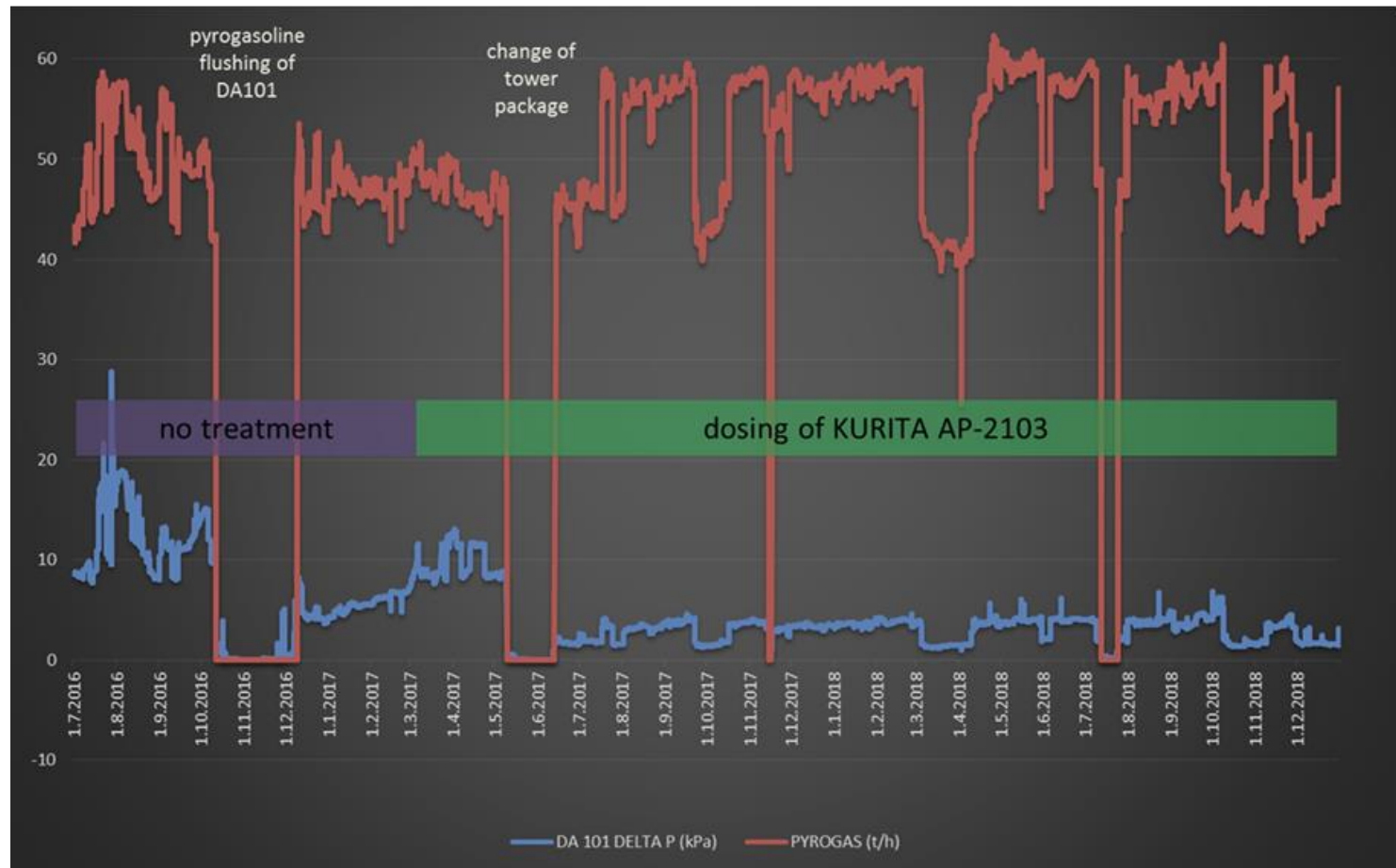
Fouling



Antifoulant with dispersant function

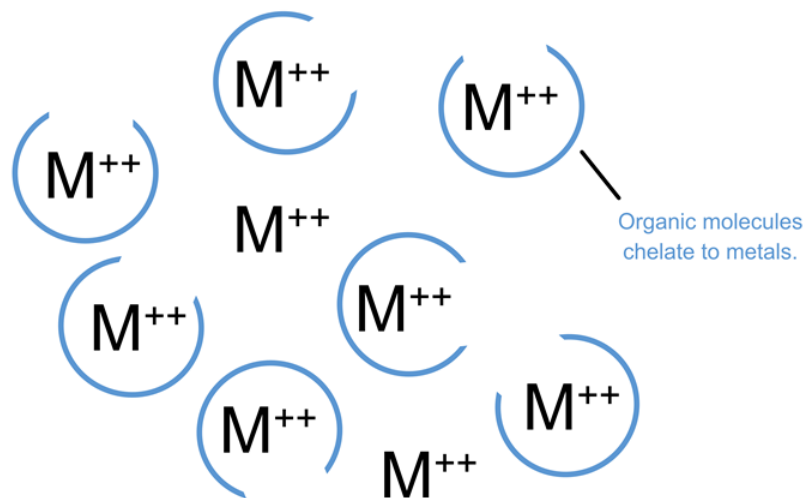


Quench Oil Column Treatment



Metal Deactivators

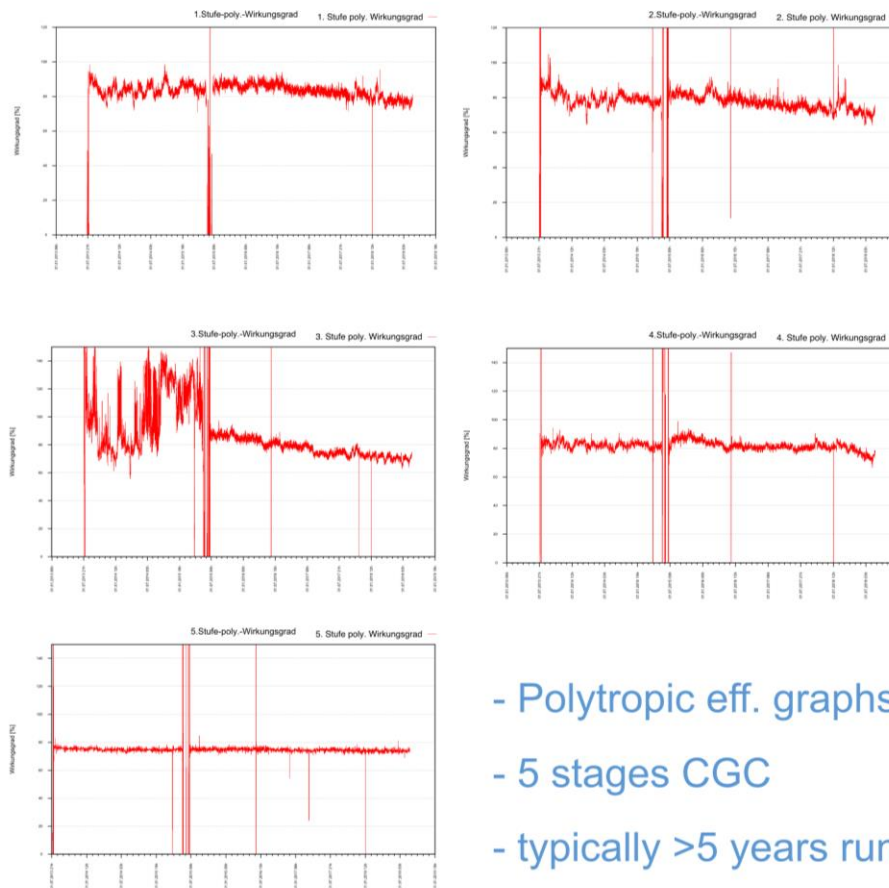
1. Deactivate the active centers of metals (Ni, V, Fe, Cr, ...).
2. Inhibit catalyzing reactions that form gums.



CGC & Cold Section Antifoulants

1. The best performing balance is essential.
2. Special attention, if active materials may increase the risk of blue gums formation in the cold box section.
3. Product selection with risk classification:
 - Formation of NO
 - Formation of N and O
 - Only N or O are part of the molecule
 - No N or O are formed

CGC & Cold Section Antifoulants



$$N_p = \left[\frac{K - 1}{K} \right] \times \frac{\ln(p_2 / p_1)}{\ln(T_2 / T_1)}$$

N_p = Polytropic efficiency
 $K = C_p / C_v$
 P_2 = Outlet pressure in Pa
 P_1 = Inlet pressure in Pa
 T_2 = Outlet temperature in K
 T_1 = Inlet temperature in K
 C_p = Heat capacity at constant pressure
 C_v = Heat capacity at constant volume



- Polytropic eff. graphs
- 5 stages CGC
- typically >5 years run time

Process Water Stripper

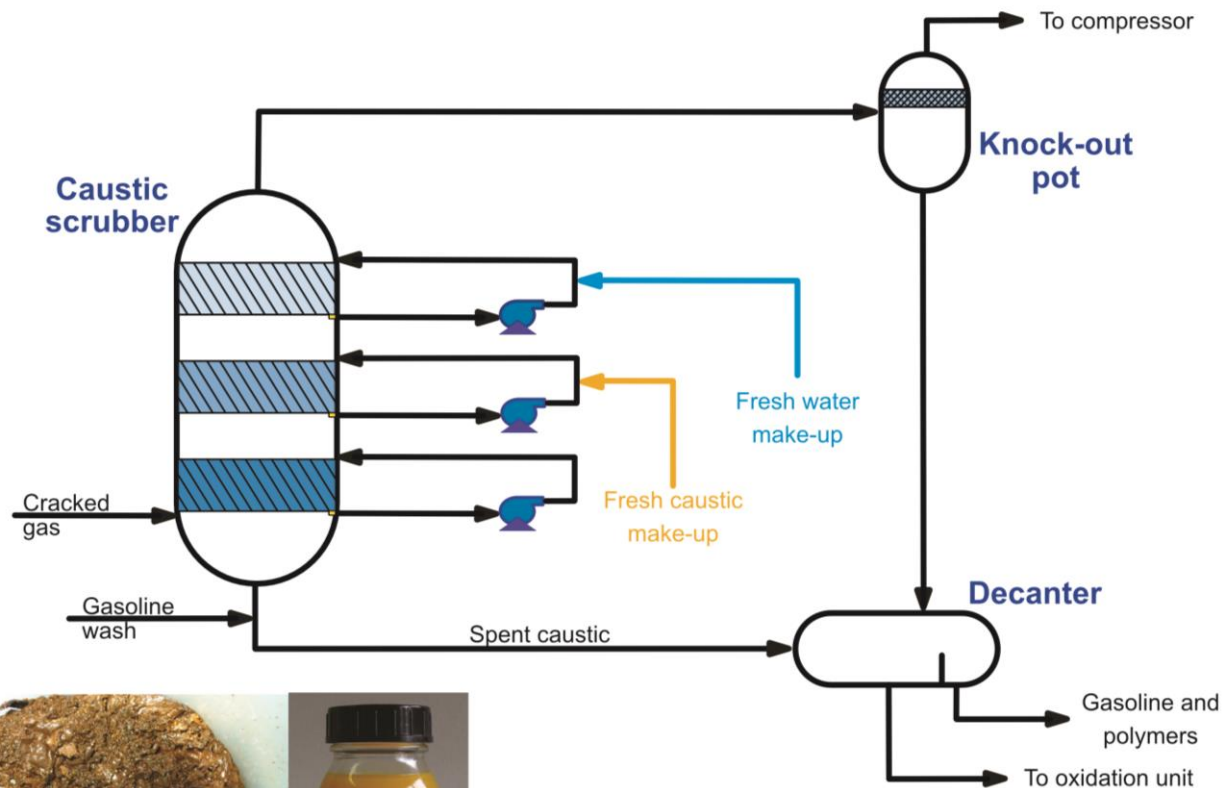
PWS are systems with mainly water, where acidic components, oxygen and remaining radicals may cause fouling (e.g. styrene, Indene, butadiene fouling).

Common oil-based antifoulants with aromatic solvents should not be used.

Requirements for a PWS antifoulant program:

- Water-soluble formulation
- Formulation with dispersants, radical catchers and antioxidants
- Reactive centers of formed radical have to be blocked
- Short-chain polymers are kept suspended
- Prevention of low-molecular polymers, agglomeration and precipitation

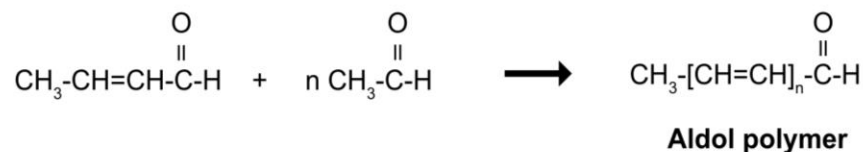
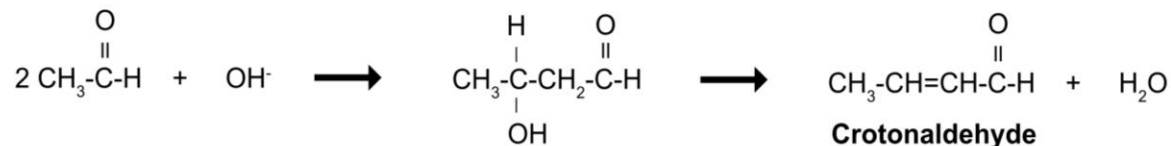
Caustic Tower Aldol Fouling



Aldol condensation

Aldol Condensation

Aldol condensation



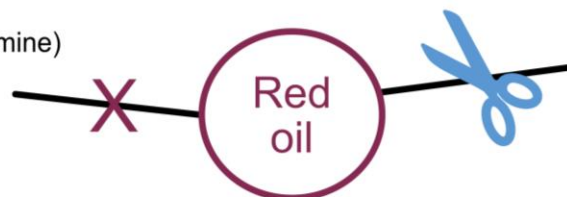
At higher temperature formation of Crotonaldehyde and Hexa-2,4-dienal.

Finally, polyacetalaldols are formed.

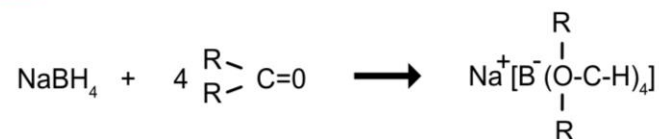
Antifoulant programmes

Carbonyl scavengers (e.g. Ethylene diamine)
stop Red Oil formation.

Reaction is reversible.



Sodium borohydride forms
a stable reaction product.
Reaction is not reversible.



Conclusion

1. Fouling, if not protected effectively, can cause major losses to an Olefins plant
2. To control fouling, it is essential to know the chemistry/ nature of the fouling
3. Solution approach and Product needs to be individually assessed based on impurities and process conditions of a plant.
4. Monitoring to appraise performance of the solution deployed is the key.
5. Kurita has decades of global experience to benchmark/ analyze each issue and recommend proven product accordingly.

Thank you for your attention!

We have

Concepts
Chemistry
Competence
Commitment

Imagine what we can achieve together

Let us do it!

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