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Behaviour of Two Products Containing Film Forming Amines (FFA) in the Secondary Circuit Physico-Chemical Conditions of the Pressurized Water Reactor (PWR)

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Prague, 20-22 March 2018

International Conference on Film Forming Substances

Industrial Context

- **Lay-up of the secondary circuit of nuclear power plants (PWR)**
- **Secondary circuit chemistry: CHALLENGES**
  - *Health-environment: decrease the use of hydrazine*
  - *Safety: blockage and fouling limited*
  - *Cost: lay up implementation and follow up simplified*
  - *...*

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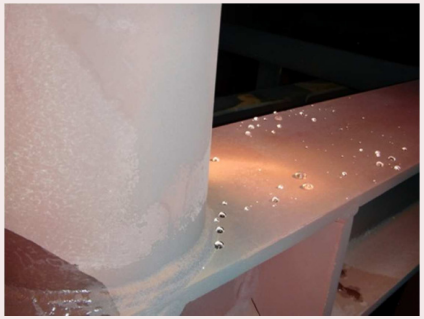
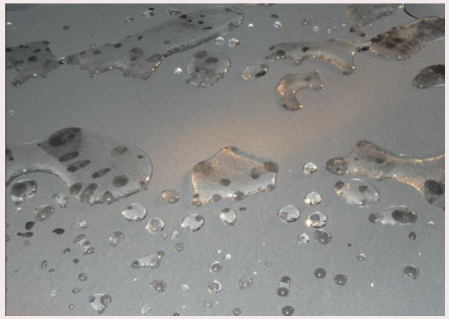
Expected Effects of FFA

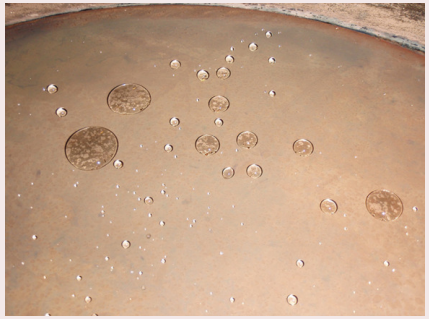
Protection against corrosion of all the secondary circuit (steam and liquid parts) during lay-up



Ramminger et al. 2012



Wagner et al. 2014



Anghel et al. 2014

⇒ Formation of a **protective and hydrophobic** film
⇒ Heat transfer performance seems to be improved

FFA Injection

- short duration / **intermediate duration** / continuous
- during normal operations, before lay up
- in the feedwater before the steam generator

Objectives of this study

- Study of the behaviour of 2 products containing FFA

1- Odacon® (Reicon)

Main FFA: $C_{18}H_{37}NH_2$ *(ODA)*

2- Cetamine® (Kurita)

Main FFA: $C_{18}H_{35}NHC_3H_6NH_2$ *(OLDA)*

⇒ *Evaluate the stability of the FFAs*

⇒ *Identify the decomposition products*

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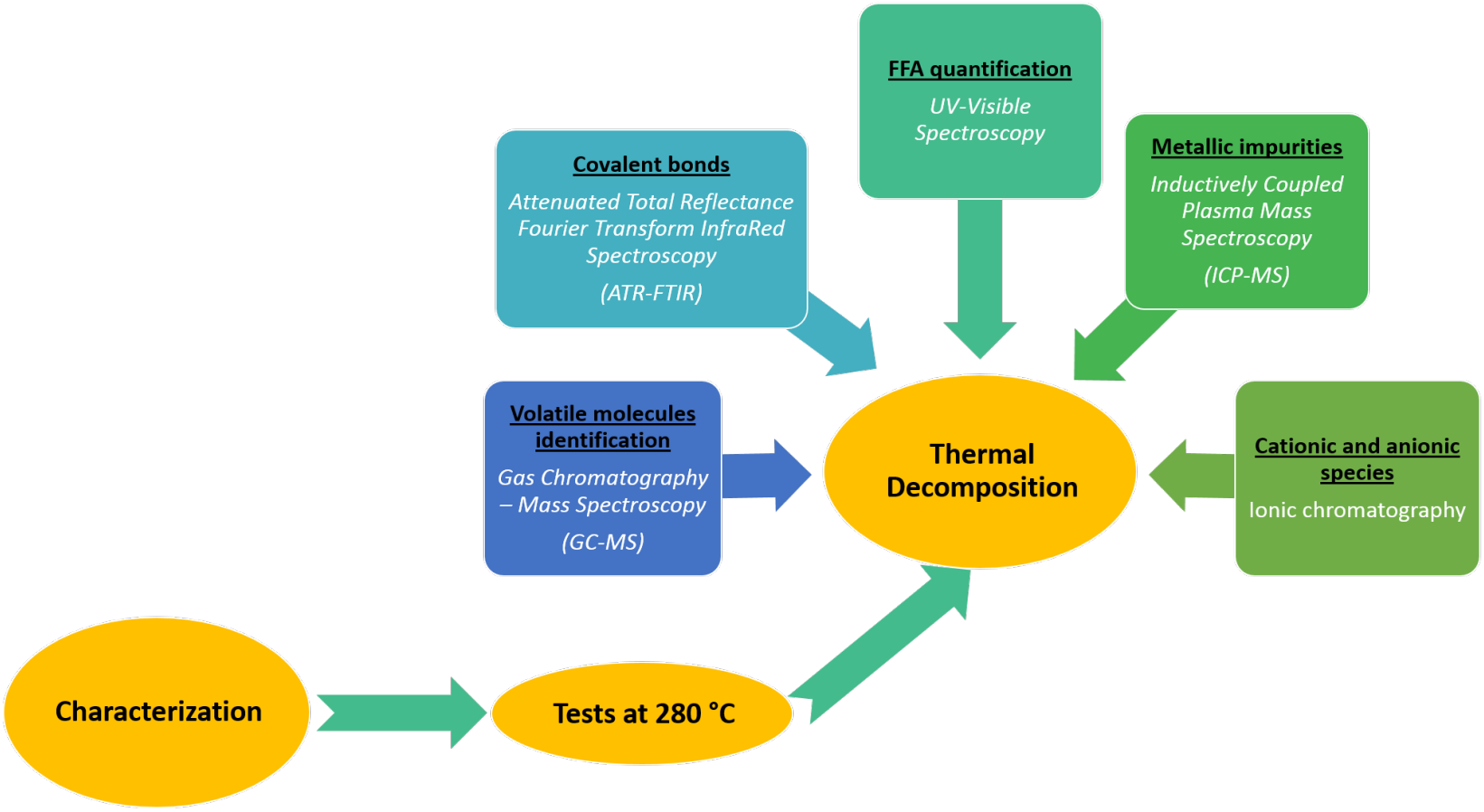
Same Methodology for Odacon® and Cetamine®



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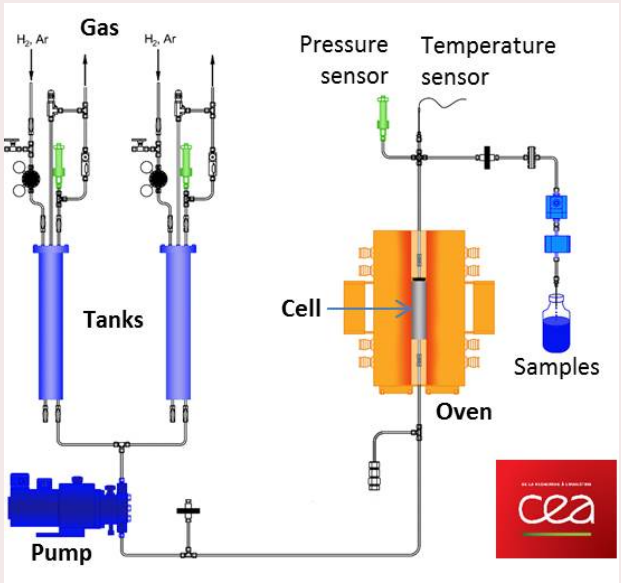
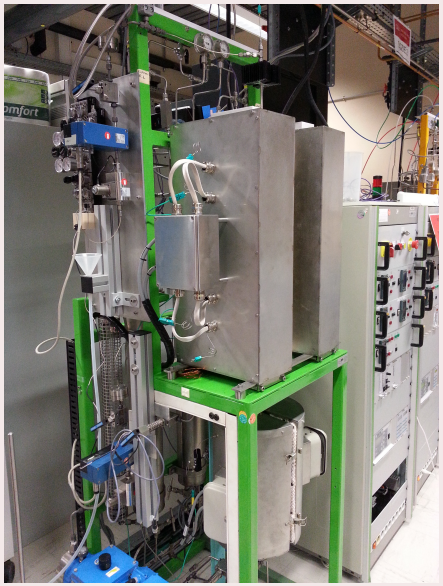
Experimental Test Device

- Specific device (GROZIE):
  - One-pass circulation system <=> the solution is constantly renewed ($t_{residence} = \rho(T) V_{cell} / Q_L$)
  - Or no circulation
- Designed to work in a one phase flow
  $25 < T(\,^{\circ}\mathrm{C}) < 360$ and $0.1 < P(\mathrm{MPa}) < 20$





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Experimental Conditions ~ physico-chemical conditions of the secondary circuit

Product	Duration	C_{FFA}	T	P	*p*H	C_{ETA}
-	-	$mg.kg^{-1}$	°C	10^6 Pa	at 25 °C	$mg.kg^{-1}$
Odacon®	20 min	32	280 ± 1	10 ± 0.2	9.8 ± 0.1	3.5
	1 week	38				3.5
Cetamine®	20 min	109	280 ± 1	10 ± 0.2	9.8 ± 0.1	-
	1 week	104				-

- pH is adjusted at 25 °C with diluted ammonia

Measured Parameters

- *T*, *P*
- C_{FFA} by UV-visible spectroscopy

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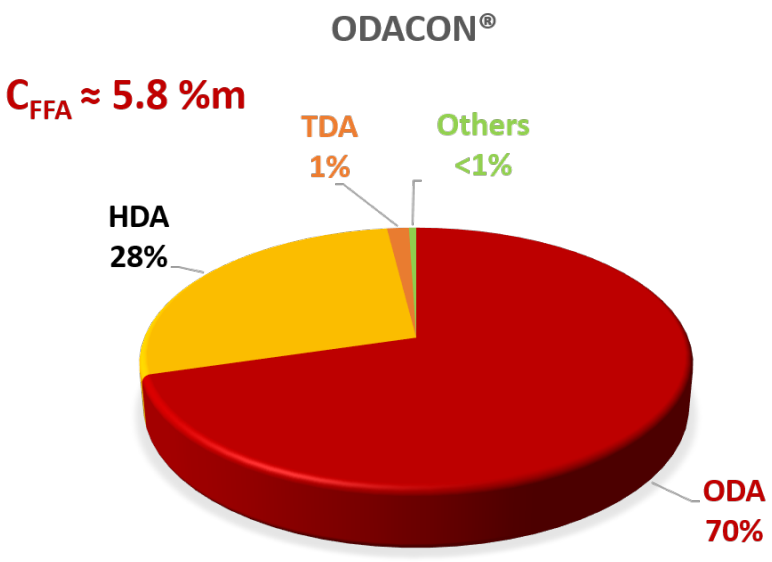
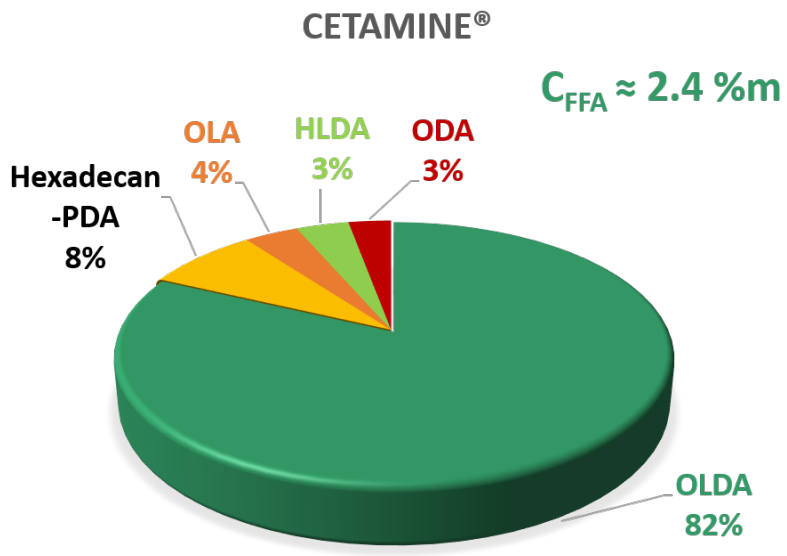
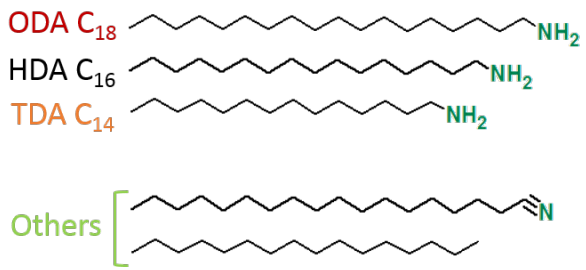
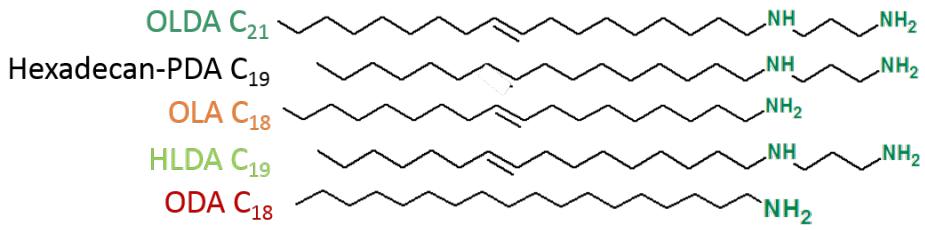
Characterization of the 2 FFA mixtures









→ No detection of metallic and ionic impurities in the 2 products except traces of Na in the Odacon®

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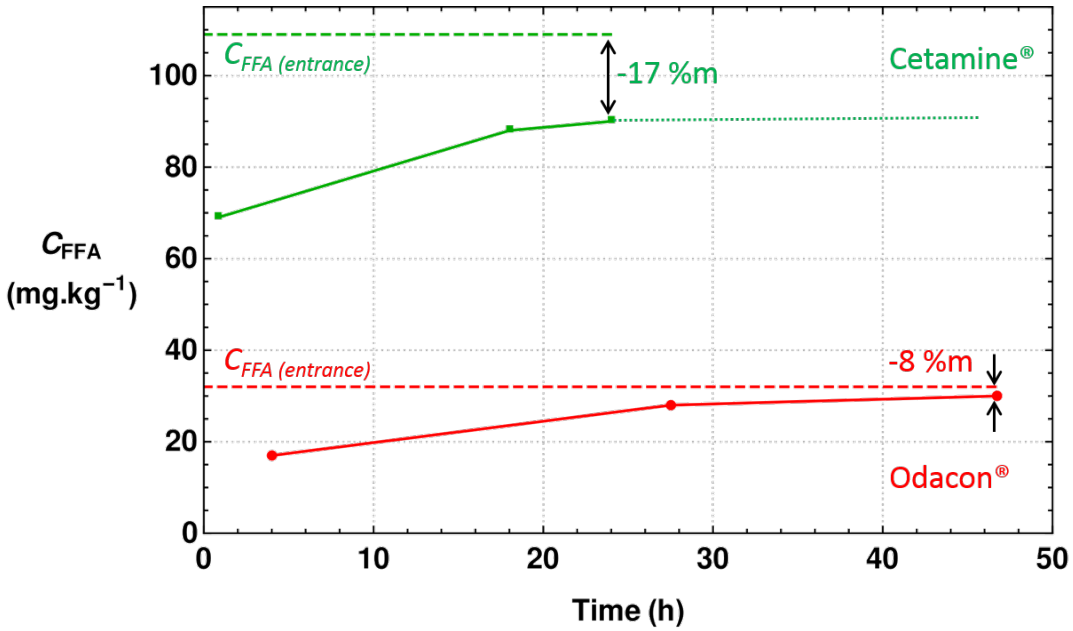
Thermal stability of the studied FFAs (1/2)

- After **20 min** of residence time at 280 °C



$\Delta C_{FFA} = -8\ \%m \Leftrightarrow 2$ mg.kg^{-1} adsorbed on the cell surface

$\Rightarrow$ no thermal decomposition of FFA in Odacon®

$\Delta C_{FFA} = -17\ \%m + 3$mg.kg^{-1} adsorbed on the cell surface

$\Rightarrow$ 14 $\%m$ of FFA seems to be decomposed

BUT

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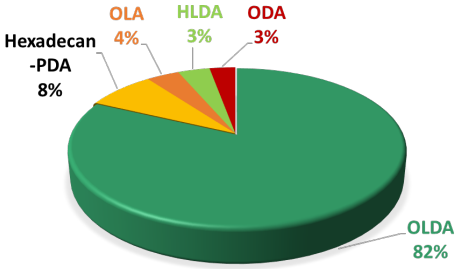
- For the Cetamine®

With the UV-visible spectroscopy analysis method:
Measured absorbance ≈ OLDA absorbance



⇒ 7 $\%m$ of FFA were thermally degraded *(not detected by the analyses)*

OR

⇒ $\Delta C_{FFA} \approx 0$ *(14 %m of FFA not detected by the analyses)*
but OLDA was decomposed in other FFAs

Thermal stability of the studied FFAs (2/2)

- After **1 week** of residence time at 280 °C
  ⇒ $\Delta C_{FFA} = -76\ \%m$ for the test with Odacon®
  ⇒ $\Delta C_{OLDA} = -84\ \%m$ for the test with Cetamine®

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FFA Identification in the thermally degraded solution

Analytical method: Gas Chromatography Mass Spectroscopy (GC-MS)

- Odacon®
  - → Detection of ODA and HDA (∈ initial product)
  - → Disappearance of TDA
- Cetamine®
  - → Disappearance of the main FFA: OLDA
  - → ↑ of OLA and ODA proportions
  - → Formation of HDA

⇒ Consistent with the decomposition of OLDA in FFAs with shorter alkyl chains.

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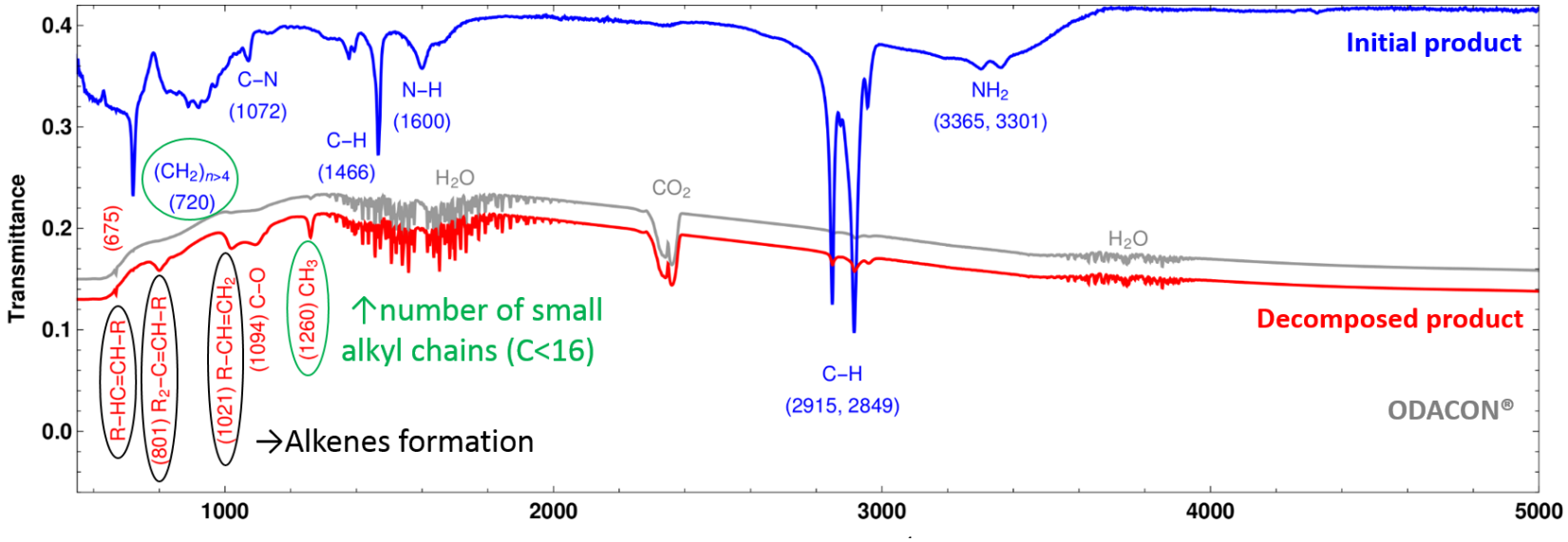
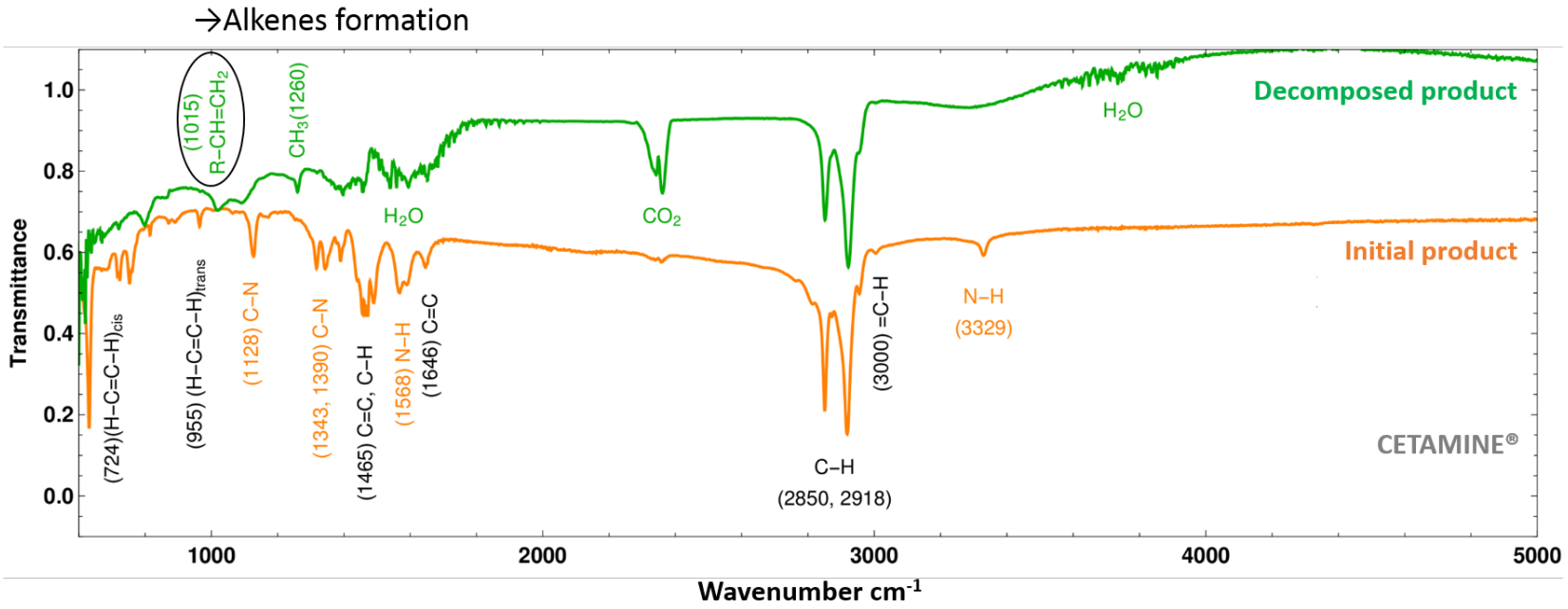

Initial product
Decomposed product
ODACON®
Transmittance
C–N
(1072)
N–H
(1600)
C–H
(1466)
$(CH_2)_{n>4}$
(720)
(675)
H_2O
CO_2
NH_2
(3365, 3301)
C–H
(2915, 2849)
R–HC=CH–R
(801) R_2–C=CH–R
(1021) R–CH=CH_2
(1094) C–O
(1260) CH_3
↑number of small alkyl chains (C<16)
→Alkenes formation


→Alkenes formation
Decomposed product
Initial product
CETAMINE®
Transmittance
(1015) R–CH=CH_2
CH_3(1260)
H_2O
CO_2
(724)(H–C=C–H)cis
(955) (H–C=C–H)trans
(1128) C–N
(1343, 1390) C–N
(1465) C=C, C–H
(1568) N–H
(1646) C=C
C–H
(2850, 2918)
(3000) =C–H
N–H
(3329)
Wavenumber cm-1

Ionic Species

Analytical method: Ionic chromatography

After **1 week** of residence time at 280 °C

- **Formation of ammonia NH_4^+** for both products
  ⇒ *Consistent with the detection of alkenes R-CH=CH$_2$ with ATR-FTIR spectroscopy analysis*

- Formation of carboxylates, mainly acetate CH_3COO^- only for Cetamine®

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Conclusions

- For 20 min residence time in the physico-chemical conditions of the secondary circuit

  ⇒ **No decomposition** of the Odacon®
  ⇒ **Very little decomposition** of the Cetamine®

- **Significative decomposition** for 1 week residence time

  ⇒ the products mainly formed are FFAs *which does not respond with the quantification protocol of FFAs*
  ⇒ formation of NH_4^+ and alkenes R-CH=CH_2

Perspectives

- Determination of the ***distribution coefficient*** of the 2 products at steam generator temperature *i.e.* 275 °C

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