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REVIEW

Thermal stability of film forming amines-based corrosion inhibitors in high temperature power plant water solutions

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Abstract

Film forming amines (FFA) are corrosion inhibitors added to power plant water. The major concern associated with their application is the thermal stability in the high temperature power plant water medium, along with the risk of decomposition into low molecular weight organic acids that can cause corrosive damages in the water/steam cycle. However, there is still a lack of sufficient data on the thermal stability of FFA corrosion inhibitors. This paper presents a comprehensive critical review and state-of-the-art assessment of the results obtained from studying the thermolysis of FFA corrosion inhibitors in power plant water/steam cycle conditions, highlighting the relevance for practical application and research needs. Temperature, exposure time, initial concentration, and alkalizing agents were identified as key factors influencing the thermal stability of FFA in high temperature power plant water. Organic acids are found in concentrations harmless to metal tubes. Advanced scientific background information and additional research are required on this topic.

KEYWORDS

corrosion, corrosion inhibitors, FFA, film forming amines, power plant water, thermal stability

1 | INTRODUCTION

Appropriate chemistry practices significantly improve the efficiency and performance of power plant components in the water/steam cycle. Film forming amine (FFA) have been used as organic feedwater additives in the power industry for several decades due to their advantageous anticorrosion film forming properties. Over the last two decades, the application of FFA corrosion inhibitors has been expanding and they are now successfully applied in hundreds of nuclear and fossil plant water cycles around the world as an alternative to conventional treatment programs for steam generators. Successful application practices have been reported for both layup conditions and continuous operations.[1–5] Details about the layup conditions are given by Rziha.[6] FFA are added to the boiler feedwater to form a non-wettable film[7] on metal surfaces which functions as a physical barrier preventing contact between the metal wall and water or moisture containing corrosive impurities (e.g., oxygen). Consequently, this protects the steam generating equipment, such as feedwater, steam, and condensing systems, against corrosion and deposits formation.

Corrosion incurs substantial expenses and raises the cost of electricity. To illustrate, the estimated annual direct cost of corrosion in electricity-generating plants in the USA amounts to $6.9 billion, of which the largest share consists of the nuclear power cost of $4.2 billion, followed by fossil fuel plants costs of $1.9 billion.[8] Besides, the deposition of corrosion products, most notable in boilers and steam turbines, is an issue of concern in many power and industrial plants, as it is the main cause of efficiency loss and decreased safety. Deposits of the corrosion products can lead to overheating and failure of boiler tubes, reduced heat transfer, shutdowns of steam generators, detrimental underdeposit corrosion, and damages to power plant equipment including turbines.[9] Overall, the deposits have a substantial negative impact on plant performance,[10] resulting in considerable economic implications. In addition, in nuclear plants, corrosion products adsorb radioactive elements[11–13] and cause increased radiation fields that lead to complications of the maintenance operation. Consequently, FFA have a significant positive impact on power plant performance,[14] reliability, availability, efficiency, and the profitability of the fossil power plant unit operation, thus reducing boiler tube failures, increasing components life and integrity, and decreasing power generating costs.

FFA have therefore been utilized both in nuclear water reactor systems and in conventional power plants. In conventional electricity generating plants, FFA are dosed as solutions, emulsions, or suspensions at a single point of the water/steam cycle, primarily in the condensate.[15] The possible dosing points for all conventional power plants are the condensate pump discharge (CPD) or condensate polisher plant outlet (CPP), and alternatively the deaerator outlet for fossil plants. Stabilizing the film requires a permanent maintenance of a residual concentration in water and steam. The dosage is independent of the concentrations of corrosive agents because FFA is not reactive with them but rather only with the metal surface, which explains the low consumption of FFA corrosion inhibitors.[16] FFA circulates through the entire water/steam cycle and gradually creates a film on all metal components. The water/steam cycle contains high-purity water (with the cation conductivity below 0.2 μS/cm), previously demineralized in the water treatment plant, then heated to a high temperature in low and high pressure heaters, and pumped into the boiler where it is transformed into steam, which is transferred to the turbine,[17] producing electricity. A detailed explanation of the water steam cycle in a thermal power plant was provided by Vidojkovic et al.[18] A simplified scheme of the water/steam cycle for a conventional fossil-fired plant is shown in Figure 1. Although FFA are also used in nuclear power plants,[19] this work primarily focuses on the conventional fossil-fired power plants due to the wider range of pressures and temperatures at which they operate (from 200°C and 2.0 MPa to supercritical parameters). Nevertheless, the results of this study are applicable to all other power and numerous industrial steam raising plants.

The most commonly used FFA with a long history of successful applications in the power industry is octadecylamine (ODA). Some of the other FFA applied for corrosion inhibition in the power industry are hexadecylamine (HDA), oleylamine (OLA), and oleilpropylendiamine (OLDA) (Table 1). Some power plants utilize film forming amine products (FFAP)[15] which are blends composed of FFA, neutralizing amines,[15,20,21] and other additives.

The primary issue of concern in many power plants associated with FFA is their thermal decomposition in the water/steam cycle into low molecular weight acids that can cause corrosion and inflict damage to the constructional material of power units.[22–25] Therefore, the thermal stability of FFA is the most important property that determines the limits of their application in the water/steam cycle of power plants. For utilization at high temperatures, FFA should exhibit a high level of thermal stability to be applicable to the next generation of steam cycle power plants. Thus, while FFA have a long history of application in nuclear power plants, their application in fossil-fired plants remains the object of debate due to higher operating temperatures.

Despite FFA having been increasingly applied in numerous power plants over the last two decades, the thermal decomposition of FFA, together with the consequences of breakdown products formation for metal components in the water/steam cycle, is a poorly investigated phenomenon, undergoing a scarcity of fundamental scientific background. So far, the utilization of FFA is mostly based on practical experience. Scientific knowledge, understanding, and prediction of FFA decomposition behavior are crucial for the safe and effective application of these compounds, as well as for proper selection. This prevents misapplications that could lead to subsequent damages to power plant equipment.

Therefore, this paper provides a critical review of FFA thermolysis under power plant water/steam cycle conditions. Additionally, it provides a state-of-the-art overview, summarizes, systematizes, and discusses the current knowledge concerning the thermal decomposition of FFA and FFAP, and identifies the influencing factors and research needs. The importance of existing data for practical application was also considered and

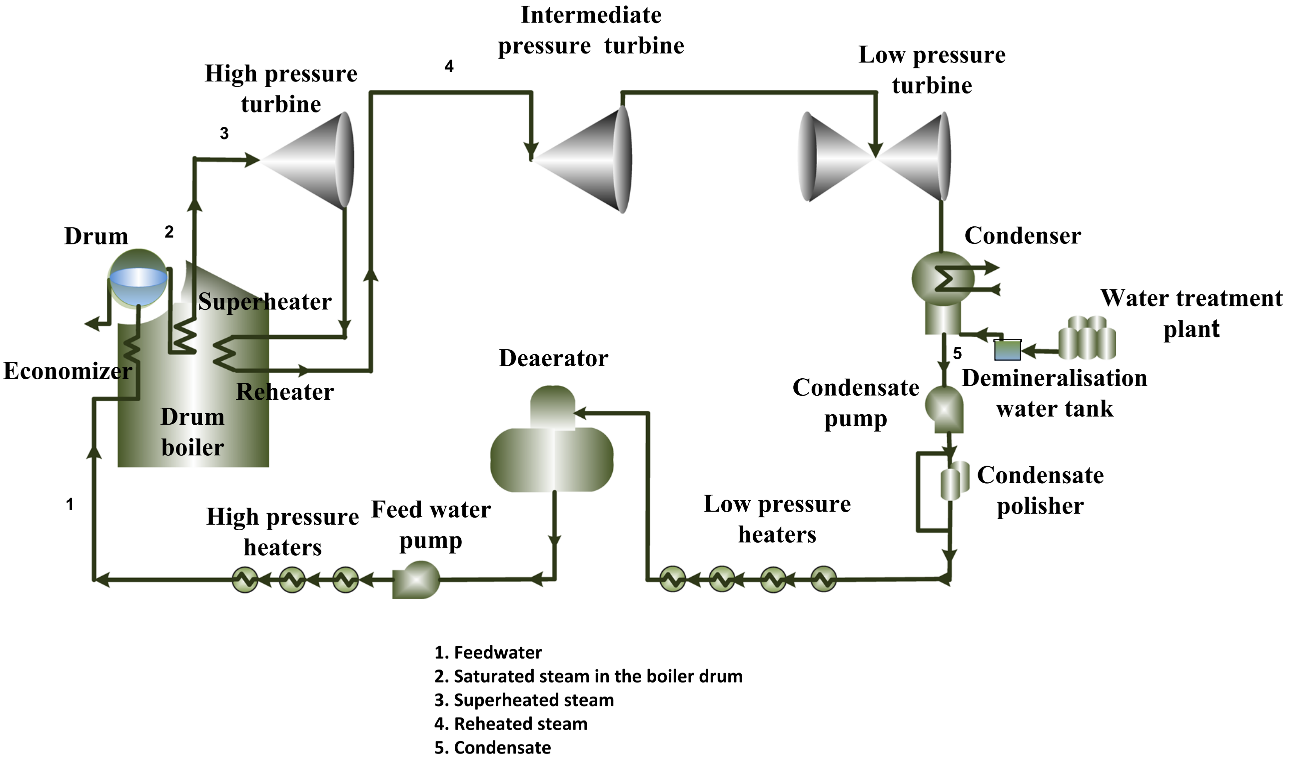

FIGURE 1 A simplified plant cycle diagram for a drum unit: 1—feedwater; 2—saturated steam in the boiler drum; 3—superheated steam; 4—reheated steam; 5—condensate.

TABLE 1 Commonly used FFA corrosion inhibitors.

Chemical name	Abbreviations	Structural formula	CAS number
Octadecylamine	ODA	$CH_3(CH_2)_{17}NH_2$	124-30-1
Oleylamine	OLA	$CH_3\ (CH_2)_7{=}CH(CH_2)_8NH_2$	112-90-3
Oleyl Propylendiamine	OLDA	$CH_3(CH_2)_7CH{=}CH(CH)_8NH(CH_2)_3NH_2$	7173-62-8
Hexadecylamine	HDA	$CH_3(CH_2)_{15}NH_2$	143-27-1

research directions of interest for science and practical applications in power plant systems were suggested.

2 | PHYSICAL AND CHEMICAL PROPERTIES OF FFA

Chemical structure plays an important role in the reactivity, behavior, and consequently, the application of FFA under conditions of power plant water/steam cycles. Like all compounds belonging to amines, FFA represent the products of the replacement of one, two, or three hydrogen atoms of ammonia (NH_3) with hydrocarbon substituent, R (such as alkyl, alkenyl, or the aryl group), and contain a basic nitrogen atom with a lone pair. Depending on the number of hydrogen atoms that are replaced by substituents, they can contain the primary, secondary, and tertiary functional amino group, which is a fast-reacting, active, and polar part determining the characteristics of the compound, while the substituent, R, is a slow-reacting, inactive, and non-polar part[26] of the molecule.

The most common FFA are composed of an aliphatic carbon chain (open, straight, or branched, without rings of any type) with 10–22 saturated (connected by one bond) or unsaturated (connected by double or triple bonds) carbon atoms and one or several primary and/or secondary amino groups.[15] A frequently used general chemical formula for FFA is $R1–[NH–R2–]_n–NH_2$[27] where n is an integer between 0 and 7, R1 is an unbranched aliphatic chain (such as alkyl or alkenyl) with 12–22 carbon atoms, and R2 is a short aliphatic chain (such as alkyl or alkenyl group) that usually contains 1–4 carbon atoms.

The simplest FFA is ODA, $n = 0$, $R1 = C_{18}H_{37}$, which is also the most widespread in the energy sector[4,15,28–32] and has the longest history of utilization. It belongs to the primary aliphatic amines with a saturated carbon chain. The general chemical formula is $C_nH_{2n+1}NH_2$, where C_nH_{2n+1} represents the general formula of an alkyl group (R1). HDA consists of one saturated carbon chain and a primary amino group, OLA contains one long unsaturated (double bond) carbon chain and one primary amino group, and OLDA contains one long unsaturated (double bond) and one short, saturated carbon chain, as well as one primary and one secondary amino group (Table 1).

FFA are liquid or solid substances with a characteristic odor. Their reactivity and behavior stem from a lone electron pair of the nitrogen atom in the functional amino group. This pair is responsible for the high affinity of the FFA molecule to the metal surface, as well as their alkali properties. Consequently, FFA are known to be alkalinizing agents[29] and generally weak bases. Considering the low concentrations of FFA applied to the water/steam cycle of power plants, the pH increase is expected to be insignificant.

The tendency of the hydrophilic amino group to bond with the negatively charged metal (iron) surface[6,27] (or magnetite layer through an interaction between the polar N–H and Fe–O bonds of the FFA and the magnetite layer, respectively) leads to the formation of monomolecular protective films on these surfaces.[27] The aliphatic carbon chains, characterized by hydrophobic ends and oriented towards the water, as shown,[27] impart a non-wettable feature to the film formed on the metal surface. This film remains stable and unaltered for an extended period (over 2 years) after dosing,[29,33] enabling the conservation of power plant equipment during short or long shutdown periods.[3,4,29,32,34–36] The aliphatic groups are interconnected through attractive van der Waals forces, which enhance the adhesion of FFA onto the metal surface. Considering the lack of sufficient data and the existence of different theories, with some supporting a monolayer[27] and others favoring a multiple layer[7] adsorption mechanism, further research on this subject is warranted. According to the Technical Guidance Document,[15] the initial rapid formation of monomolecular layer is succeeded by a gradual development of a multilayer. Experimental research has shown that ODA was also adsorbed on iron powder to the extent of 70%–80%, of which 90% was adsorbed within 10 min, and an adsorption equilibrium was reached within 6 h.[37]

Due to the long hydrophobic radical carbon chain, ODA (and other FFA) exhibits a relatively poor solubility in water, even at the high temperatures at which it is present in colloidal form,[37] and can thus be applied in the form of an emulsion. Poor solubility can be ascribed to the fact that the attractive forces between the molecules of the solvent (water) are always stronger than those between the molecules of the solvent and the non-polar hydrocarbon chain. However, the solubility in ether, acetic acid, ethanol, isopropyl alcohol, and acetone facilitates handling FFA in the laboratory, particularly for removing adsorbed FFA from vessel walls. The large relative molecular mass of an FFA (for instance, Mr (ODA) = 269.52)) contributes to its high boiling point, which makes it favorable for film formation, in comparison with amines with shorter aliphatic carbon chains. This occurs due to the fact that breaking down intermolecular bonds in a longer hydrocarbon chain requires more energy as a result of stronger intermolecular forces. FFA exhibit no reaction with copper,[38] unlike ammonia,[39] even in the presence of oxygen, which also makes them suitable for the protection of condensate trains[40] that are usually composed of copper alloys.

3 | EFFECT OF THERMAL DECOMPOSITION OF FFA ON CORROSION AND DEPOSITION

In a high temperature aqueous thermal power plant environment, FFA are subjected to thermal decomposition into low molecular weight organic acids (mostly present in anionic forms) known to initiate a corrosion of metal components.[41–43] This poses a challenge to power plant engineers and chemists in the successful application of FFA. The consequences of the presence of organic acids in the water cycle, techniques for their removal, and the methods to effectively increase FFA concentration are still gaps in FFA utilization that need to be further addressed. Acids contribute to the dissolution of the protective magnetite layer on the metal tubes and thus increase the corrosion rate.[13,41,44–53] Acidic decomposition products[15,42] could also increase the acid conductivity after cation exchange (CACE) and obstruct the detection of anionic contamination (chloride, sulfate) in the water/steam cycle. The increase in the acid conductivity in the steam beyond the normal range leads to early condensate corrosion and damage to the turbine.[23,41,42,54] In addition, acetate was found to increase the distribution coefficient of dissolved species (for instance, chloride, sulfate, and fluoride) between boiling water and saturated steam,[55] causing an increase in steam contamination. The decomposition process of FFA at various pressures and temperatures involves the formation of not only simpler organic molecules, but also corrosive carbon dioxide (CO_2) and ammonia. Ammonia formation increases corrosion in systems made of copper alloys.[39,56] Carbon dioxide decreases the pH of the condensed steam and can cause stress corrosion cracking[42] in the turbine.

Along with a direct impact, breakdown products can have an indirect effect on constructional material, causing the deposition of corrosion products on metal surfaces. Corrosion products, mainly composed of iron oxides formed on internal steel surfaces, are released into the water in the form of a colloidal suspension and subsequently transported through the water/steam cycle.[3] The colloidal surface characteristics of the suspended particles (surface charge, zeta potential) play a crucial role in the formation of deposits by creating an electrostatic interaction between the internal wall surface and the suspended colloidal particles.[15,27] The breakdown products of FFA may affect the surface properties and the subsequent deposition behavior of colloidal corrosion products present in water, such as magnetite (Fe_3O_4),[57–77] known to be the predominant corrosion product forming deposits in water/steam cycles in all types of power plants.[14,59] Namely, the presence of the breakdown products could weaken the electrostatic repulsion between the metal surface and the suspended colloidal particles, trigger the deposition on heat transfer surfaces, and increase the deposition rate. Unfortunately, there is no published data on the effect of the products of FFA thermal decomposition on the surface properties and the deposition of iron oxides at elevated temperatures corresponding to a power chemistry cycle, to the authors' knowledge. The potential of FFA breakdown products to modify the surface charge of suspended material in the heat transfer fluid and, subsequently, alter electrostatic forces between the particles and the boiler's inner surfaces, emphasizes the need for a detailed study of this phenomenon in the future.

4 | EXPERIMENTAL APPROACH FOR STUDYING THE THERMAL STABILITY OF FFA AND FFAP

The earliest data on the thermal stability of FFA dates back to 1971.[78] It was the beginning of comprehensive studies on the properties of ODA, initiated by the growing utilization of ODA in thermal power plants, which started in the early 1960s. The experimental study was conducted in an ampoule made of steel 1X18H9T (GOST 5632-51), containing 72% iron, 17%–19% chromium, 9%–12% nickel, 0.08% carbon, 0.7%–1%, titanium, 2% manganese, 0.035% phosphorus, 0.02% sulfur, 0.75% silicon, and 0.2% antimony. The ampule was equipped with a thermocouple, filled with ODA and water, and placed in a high temperature furnace. The ODA was subjected to high temperatures up to 500°C and pressures of 4.0, 9.8, and 14.7 MPa. After each run, the percent of decomposed ODA was calculated. A later study on ODA thermolysis in water emulsion[79] was carried out at temperatures of 85°C, 120°C, and 160°C and corresponding pressures. The experiments were conducted in a high-temperature high-pressure vessel made of steel 1X18H10T, with a residence time of 100 h, which is the longest residence time for pure FFA tested to date. In a recent study on the decomposition of ODA at temperatures ranging from 350°C to 560°C,[80] an autoclave with an online sampling system was used to simulate a power plant water/steam system. In contrast to the above mentioned studies, Dubrovski et al.[33] and Martinova et al.,[81] used a unique high pressure dynamic test rig made of steel 1X18H10T to study the thermal stability of ODA. These two studies were conducted with saturated steam bubbling through the boiling water containing ODA (emulsion) at saturation temperatures of 233°C and 343°C and pressures of 2.9 MPa and 15.2 MPa, respectively, with a residence time of 5 h. This experimental approach had advantages over the other published studies in an improved construction and more accurate approximation of real conditions as the unique dynamic test rig more thoroughly simulated the processes in a thermal power plant drum boiler. This construction also enables the creation and variation of a wide range of dynamic and quasi-static experimental conditions, such as steam consumption and residence time. It additionally permits the permanent and simultaneous sampling of the emulsion and condensed steam to determine the concentration of ODA and breakdown products in both the liquid and steam phases. The techniques and methods used in performed experimental studies on the thermal decomposition of FFA are given in Table 2. For analysis of ODA concentrations, ultraviolet spectrophotometry was used.[1,33,79–83] The thermal stability and thermal decomposition products of some FFAP (Table 3) were studied in real life conditions in steam generators at steam temperatures of 400°C and 510°C and pressures of 4 and 9.8 MPa,[82] respectively, and also at 400°C and 4.2 MPa.[1] For other FFAP studies, experimental autoclaves were used at the temperatures of 175°C, 400°C, 520°C,[83] and 275°C.[84] For studying the decomposition products of FFAP in water and steam simultaneously, Rudasova and Sajdi[85] employed a circuit assembled from an interconnected storage tank (liquid phase) simulating a boiler and autoclave (steam phase) simulating a superheater at 570°C and 17 MPa.

5 | RESULTS AND DISCUSSION

The results on thermal stability for pure FFA-based corrosion inhibitors have only been published for ODA and are presented in Table 2.

TABLE 2 Published results of thermal stability for FFA.

Temperature (°C)	Pressure (MPa)	FFA	Technique	Decomposition product	Experimental installation	Results and conclusions/ comments	References
350, 400, 430, 450, 480, 500, 520, 540, and 560	–	ODA	• Gas chromatography–mass spectrometry (GC/MS) (for sample composition) • Ultraviolet–visible spectrophotometry (for ODA concentration)	–	Autoclave with an online sampling system	• Decomposition began at over 450°C. • No low molecular organic acids were found.	Cao et al.[80]
325–500	4, 9.8, and 14.7	ODA		• Hydrocarbons • Ammonia	Ampoule made of steel 1X18H9T and placed in a high temperature furnace.	• Decomposition started over 350°C • Exposure time was 30 min. • The rate of decomposition does not change noticeably with the residence time. • The rate of thermal decomposition of ODA was quite high at the beginning. • The extent of decomposition was governed by temperature, not exposure time.	Ivanov and Klimanov[78]
233 and 343	2.9 and 15.2		• Photometry (for measurement of ODA and ammonia concentrations) • Chromatography (for detection of dissolved gases) • Potentiometry (for pH measurement)	• Ammonia (in the liquid and steam phases) • Gases (in the liquid and steam phases): ○ Hydrogen (H_2) ○ Carbon monoxide (CO) ○ Methane (CH_4)	• High pressure test rig made of steel 1X18H10T, with steam bubbling through the boiling water containing ODA (emulsion)	• 40% of ODA had been decomposed. • Exposure time was 5 h. • After 5–6 h thermolysis was not completed at the given parameters. • Decomposition of ODA began at the temperature of 95°C. • The process of methane formation takes place under noticeably high temperature conditions.	Martinova et al.[81]; Dubrovski et al.[33]

TABLE 2 (Continued)

Temperature (°C)	Pressure (MPa)	FFA	Technique	Decomposition product	Experimental installation	Results and conclusions/comments	References
85, 120, and 160	Corresponding pressures	ODA	• Photometry (for measurement of ODA and ammonia concentrations) • Gas chromatography (for detection of dissolved gases) • Potentiometry (for pH measurement) • Colorimetry for oxygen concentration	• Ammonia (NH_3) • Hydrogen (H_2) • Carbon monoxide (CO) • Methane (CH_4)	Steel autoclave made of 1X18H10T	• Exposure time was 100 h. • The intensity of ODA decomposition at high temperatures depended on initial concentration, temperature, and the time of exposure to those temperatures.	Dubrovski et al.[79]

5.1 | Effect of temperature

Temperature was found to be one of the most important factors producing a significant effect on the intensity of the thermal decomposition of ODA.[33,78–81] According to the results obtained by Cao et al.[80] and Ivanov and Klimanov,[78] in the absence of air, decomposition started at over 450°C and 350°C, respectively. However, according to Dubrovski et al.[33] and Martinova et al.,[81] thermolysis started at 95°C, which conclusion was reached based on products such as ammonia discovered at that temperature. A later investigation by Babler et al.[28] showed that the decomposition of ODA began at the temperature of 80°C, thus supporting the results obtained by Dubrovski et al.[33] and Martinova et al.[81] The reported data on the beginning of ODA decomposition are presented in Figure 2. The inconsistency between the data referring to the temperature at which the decomposition of ODA starts can be partly attributed to the different experimental methodologies and conditions. Thus, the dynamic conditions were only applied in the studies conducted by Martinova et al.[81] and Dubrovski et al.[33] Furthermore, they monitored water samples throughout the high-temperature experiments described above, as well as complementary low-temperature experiment conducted at the temperature of 100°C and 0.1 MPa. This monitoring enabled the detection of the trace concentrations of decomposition products, indicating that decomposition had begun. Other authors,[78–80] however, were focused on the difference between the starting and final concentrations of ODA, which provides limited possibilities to precisely determine the start of the decomposition process. The accuracy of these experiments can be additionally diminished by the adsorption of FFA on the walls of the reactor vessel. Nonetheless, this approach can still provide fairly good evidence of the temperature at which significant decomposition starts. Thus, in spite of the discrepancies, all these studies are in agreement that below ~350°C, the application of ODA in the water/steam cycle is safe, successful, and without the formation of dangerous decomposition products for power plants.

Figure 3 shows the published results obtained by various authors concerning the effect of temperature on the amount of decomposed FFA. Despite the different experimental methodologies and parameters, there is a reasonable agreement between the obtained results, referring to the temperatures corresponding to the feedwater and economizer (below 400°C) as well as the superheater. Since the temperature in superheaters and reheaters is typically over 400°C, it may be stated that the study of Cao et al.[80] conducted in the range from 350°C to 560°C covers the highest temperature range of the

TABLE 3 Published results of thermal stability for FFAP.

Temperature (°C)	Pressure (MPa)	FFAP	Technique	Decomposition product	Experimental installation	Sampling points	Results and conclusions/comments	References
400 and 510 (refers to the superheated steam)	4 and 9.8	No name given	• Liquid chromatography–organic carbon detection (LC-OCD) (for low molecular weight acids) • Ion chromatography (IC) (for low molecular weight acids)	• Carbon dioxide (in the feedwater) • Ammonia (in the feedwater) • Glycol (in the boiler water) • Acetate in all sampling points	Industrial steam generators	• Condensate • Feedwater • Boiler Water • Superheated steam	• Very low concentrations of low molecular mass acids; the highest concentration of acetate was measured in the boiler water and amounted to 40 μg/L • The highest concentration of acetate in the steam was found to be 23 μg/L, in the feedwater 34 μg/L, and in the condensate 28 μg/L. • The pH values were below target values. • No formate and propionate were detected.	Sollner et al.[82]
–		No names given	–	• Ammonia • Small organic acids • Carbon dioxide • Low molecular weight amines • Octadecylamine • Substituted diamines. • Propionate • Glycolate • Oxalate • Citrate • Benzene	–	–	Propionate, glycolate, oxalate, citrate, and benzene were minor decomposition products.	TGD8-16, 2019[15]

TABLE 3 (Continued)

Temperature (°C)	Pressure (MPa)	FFAP	Technique	Decomposition product	Experimental installation	Sampling points	Results and conclusions/ comments	References
Max. 400 (in live steam)	4.2	Cetamine® V211	LC-OCD IC (for acetic acid) Photometry for FFAP	• Ethylene glycol (in a nondissociated form) in the feedwater, main steam, and condensate • Methanolamine • Cyclohexamine • Acetic acid in the steam	Refuse-derived fuel thermal power plant	Various locations in the water/ steam cycle	Concentrations of acetic acid in the steam equaled 28, 30, and 20 µg/L.	Kolander et al.[1]
400		Helamin® and Helamin® 906 H	• Photometry (for polyamines) • GC/MS (for polyamines) • Infrared spectroscopy (IR) (for poly-α-olefin)	• Acetic acid • Formic acid • Propionic acid • Ammonia • Short-chain amines • Volatile amines • Substituted diamines • ODA • Low molecular weight hydrocarbons with up to 18C atoms (poly-α-olefin)	Experimental set-up containing autoclave		• Both diluted and highly concentrated amine solutions were used. • For 24 h, 2%–5% of acetic, formic, and propionic acids were formed from a 10% solution of polyamines and amines (some polyamines and amines produced only 1% of these acids). • Helamin® produced ≪1% of volatile low molecular weight organic acids. • From 1 mg/kg of Helamin® 10 µg/kg was produced. • Helamin® 906H was tested under different	Frahne and Blum[83]

(Continues)

TABLE 3 (Continued)

Temperature (°C)	Pressure (MPa)	FFAP	Technique	Decomposition product	Experimental installation	Sampling points	Results and conclusions/ comments	References
							experimental conditions.	
570	17	C_1 and C_3 (no names given)	Mass spectrometry (MS) for butanolamine	• Acetic acid • Formic acid • Butanolamine	A steam circuit assembled from an interconnected storage tank (liquid phase) and autoclave (steam phase)		• The starting concentration of FFAP was 300 mg/L. • The residence times were 189 and 150 h. • No acetic acid was found for FFAP with a higher concentration of FFA than alkalizing components. • FFAP with a higher content of alkalizing components produced a small concentration of acetic acid (0.19% of the tested FFAP). • FFAP with more FFA produced more formic acid (on average 5.3 mg/L in the steam) as compared to that with more alkalizing amines (on average 2.43 mg/L in the steam).	Rudasova and Sajdi[85]
275		ODA-based FFAP		–	Autoclave		• 80% of ODA- based product was decomposed at 275°C during 6 h.	Baux et al.[84]

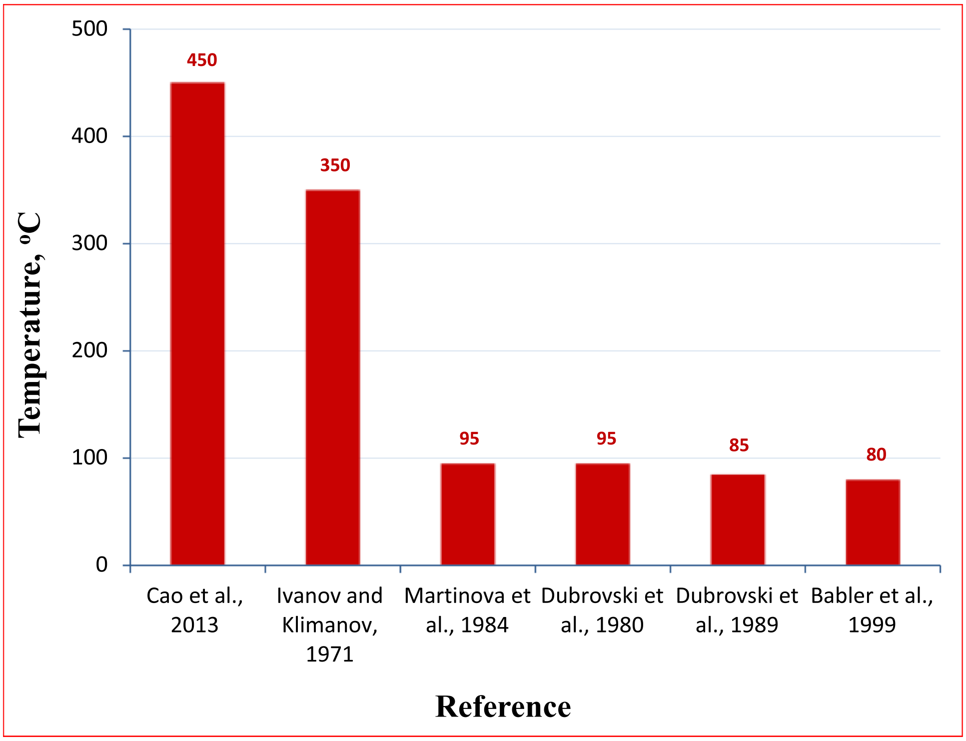

FIGURE 2 Beginning of ODA decomposition.

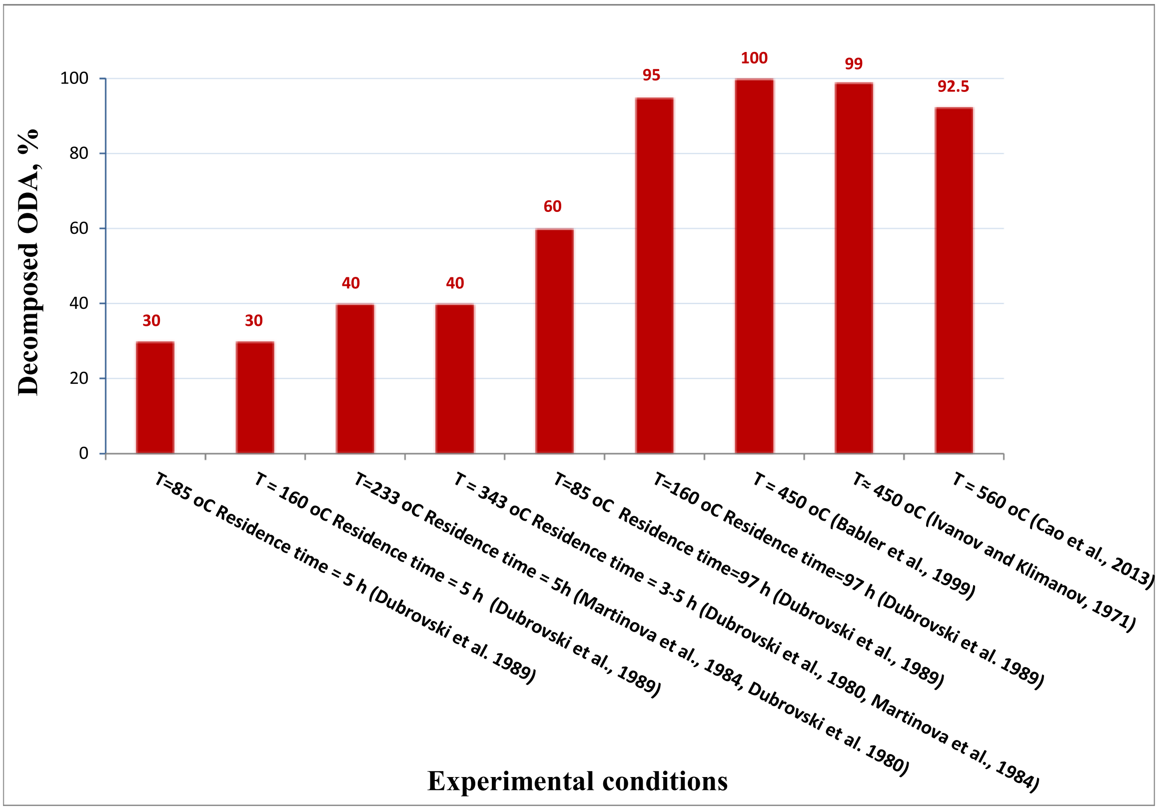

FIGURE 3 Decomposition of ODA for different experimental conditions.

power chemistry cycle, thus providing useful information for power plant operation. This study showed that the concentration of ODA declined slightly in the temperature range from 350°C to 430°C, which was attributed to the film formation on the inner surface of the autoclave. From 450°C to 500°C the concentration of ODA decreased rapidly due to its decomposition. Above approximately 500°C, the decrease in the concentration of ODA was slower and at the temperature of 560°C, this concentration was only 7.5% of the initially measured ODA concentration. Ivanov and Klimanov[78] showed that the decomposition of ODA became faster from 300°C and at approximately 450°C almost 99% of the ODA was decomposed, while Babler et al.[28] reported that at temperatures over 450°C, a complete degradation occurred. Cao et al.,[80] Ivanov and Klimanov,[78] and Babler et al.[28] failed to give clear information on the residence time of the ODA at these temperatures. Based on the experimental approach, the assumption can be made that the heating stopped after the aforementioned temperatures were reached.

Dubrovski et al.[79] further found that temperature influenced the decomposition of ODA only after 5 h of exposure time and at low concentrations of ODA, and that the rate of thermolysis increased with the increase in temperature (Figure 4). Accordingly, the intensity of ODA decomposition increased 1.5 times with an increase in temperature from 85°C to 160°C in the same conditions, implying a residence time of 97 h and an initial concentration of ODA < 20 mg/kg (which is equal to its solubility in water at 160°C). Thus, the amount of decomposed ODA varied between 90% and 95% at 160°C, while it was below 60% at 85°C. At the concentrations that exceeded the solubility of ODA, the examined temperatures had no influence on thermolysis except in the region when ODA was transferred from dispersed to dissolved form, which occurred after 80 h, and only at temperatures above 160°C. Based on the decrease in FFA concentration, it is possible to assume that the temperature also determines the amount of the decomposition products.

5.2 | Effect of residence time

The information on the rate of the FFA thermal decomposition is important for practical application in the utility industry, as it allows the personnel to anticipate the exposure time in the steam generator, at which the FFA-based corrosion inhibitor still preserves its positive properties at specific thermal parameters.

The aforementioned study by Ivanov and Klimanov[78] offers data on the rate of ODA thermolysis. The experiments were carried out at a temperature of 350°C

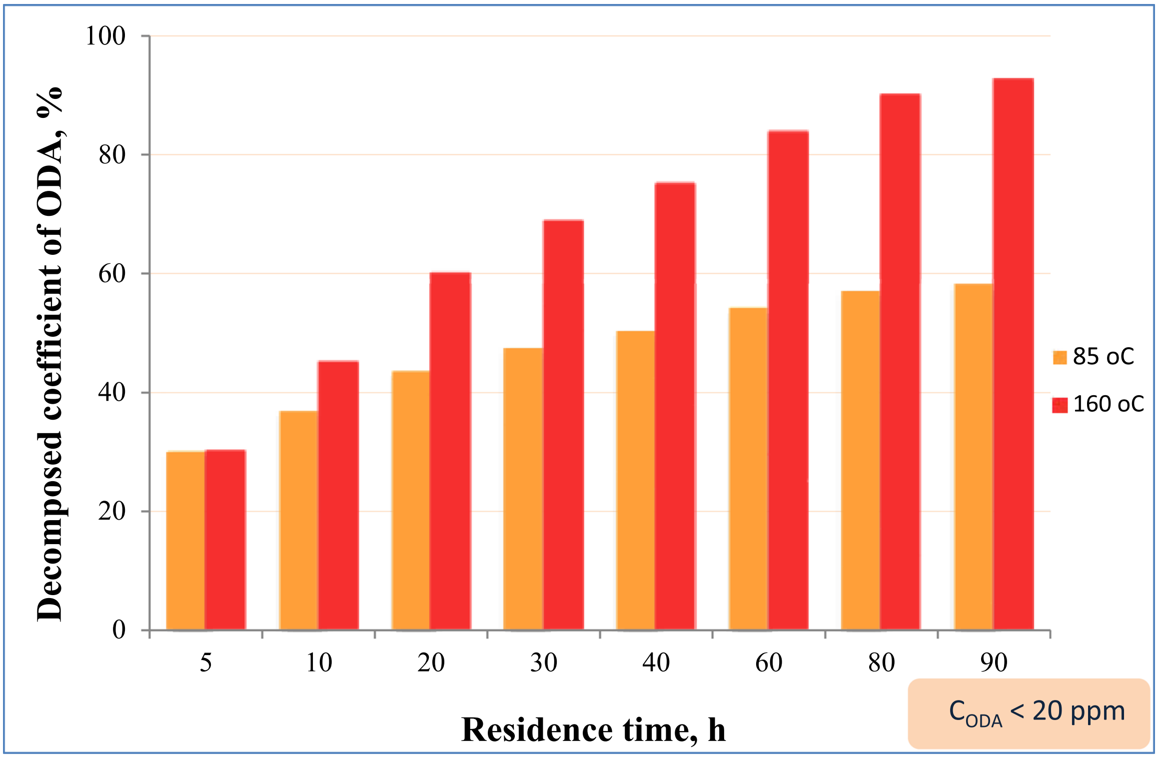

FIGURE 4 Change of the decomposition coefficient of ODA with residence time at different temperatures. Figure is adapted with permission from Dubrovski et al.[79]

for period ranging from 0.5 to 30 min. From the results, it can be concluded that the rate of the thermal decomposition of ODA remained almost the same regardless of residence time, i.e., the amount of ODA decreased by approximately 2.5% over the 30 min. Consequently, the authors reached the conclusion that the extent of decomposition was governed by temperature and not exposure time, as the majority of the decomposition occurred very rapidly at the beginning of the experiment. From the experimental results, it may be stated that the first sample was taken after approximately 30 s, by which time the amount of ODA had already decreased to roughly 33%, and it remained largely unchanged over the following 30 min, amounting to around 30.5%. Therefore, according to this study, only the operating temperature of the water/steam cycle component subjected to ODA treatment should be taken into account for practical application in the power plant water cycle.

However, these results are not completely consistent with those obtained later[33,79,81] which show that the decomposition rate was not a function of the temperature in the first 3–5 h. The discrepancy arose from the differing experimental approaches, including set-ups constructions, ODA concentrations, etc. For instance, an experimental study[79] demonstrated intensive decomposition during the first 5 h, which was dependent on neither the initial concentration nor the temperature, amounting to approximately 30%. However, at a later stage, it slowed down considerably and the rate of degradation depended on both the temperature and the initial concentration (Figures 4 and 5). It was further shown that, at a temperature of 160°C and an initial concentration below the solubility of ODA in water, the intensity of decomposition increased continually until full decomposition was reached, as explained in the previous chapter.

The intensity of thermolysis can be explained by the duration of the existence of a compound before its decomposition, while still maintaining its positive features under concrete thermal parameters. In the work of Dubrovski et al.,[79] the intensity of decomposition (in the literature sometimes presented as the amount of decomposed ODA) was described by the coefficient of decomposition, K (%), which is determined as the ratio between the concentrations of the decomposed, C_{dec} (mg/kg), and initial C_{in} (mg/kg) ODA:

$$K = (C_{\mathrm{dec}}/C_{\mathrm{in}})100. \quad (1)$$

Results obtained by Dubrovski et al.[79] are in full correlation with the work of Dubrovski et al.[33] and Martinova et al.[81] who obtained very similar results to each other on the dynamic test rig, also showing that after 3–5 h of exposure at the temperatures of 233°C and 343°C the thermolysis of ODA was not completed and the decomposed amount of ODA was 40% (Figure 6). The obtained results convincingly lead to the conclusion that, owing to a fairly good thermal stability at tested temperatures, ODA can be safely applied for conservation and conditioning in the electric generating power plant water/steam cycle. These investigations are also described elsewhere.[86]

Taking into account that the residence time of chemicals in a drum boiler is about 1 h (the percentage

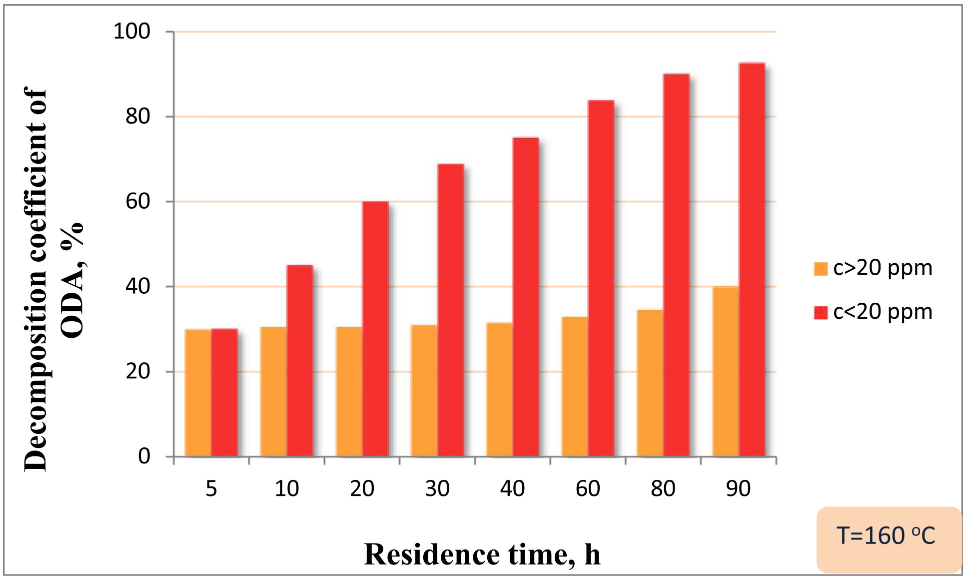

FIGURE 5 Change of the decomposition coefficient of ODA with residence time at different initial concentrations. Figure is adapted with permission from Dubrovski et al.[79]

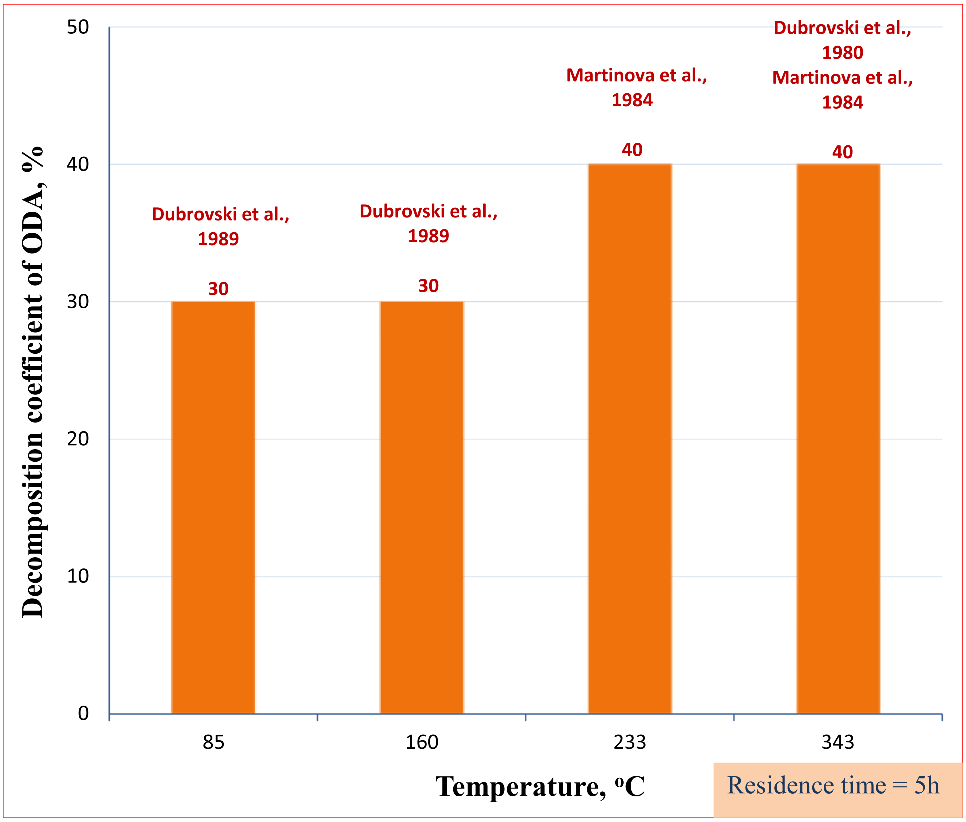

FIGURE 6 Decomposition coefficient of ODA at different temperatures and a residence time of 5 h.

of blowdown determines the exact residence time) and much shorter in once-through boilers, the residence time applied in these experiments,[33,79,81] fully covered all the cases in the real power plants. Furthermore, it may be stated that the anticipated decomposed amount of ODA in feedwater systems and boilers should not be over 30%.

5.3 | Effect of initial concentration

Dubrovski et al.[79] were the first to determine the effect of different concentrations of ODA on decomposition. However, there are no other published studies considering initial concentrations, to the authors' knowledge. The chosen concentrations at the temperature of 160°C were within the range of 7.5–43 mg/kg to ensure that a substantial or complete amount of ODA could be dissolved. The authors obviously took into account the temperature dependence of ODA solubility, which exhibits an increasing trend.[26] The concentration of 20 mg/kg represents the value at which the authors observed abrupt alterations in the character of the coefficient of ODA decomposition.

These authors found that up to 160°C, the decomposition rates for low and high ODA concentrations differ after 5 h of residence time. At high concentrations (ODA ˃ 20 mg/kg) that exceed the solubility of ODA, the decomposition rate increased rapidly during the first 5–10 h, resulting in the amount of decomposed ODA ranging from 25% to 40%, which aligned with the concentration of ODA < 20 mg/kg. However, after that time, while the decomposition rate for the concentration of ODA < 20 mg/kg was continuously increasing, the decomposition rate for the concentrations of ODA > 20 mg/kg remained almost constant at all examined temperatures, with the exception of a repeated slight increase exhibited after 80 h at the temperature of 160°C (Figure 5).

According to the authors'[79] interpretation, this effect can be explained by the fact that at low concentrations, the entire or a significant amount of ODA is dissolved at a specific temperature, and the rate of decomposition is determined by the rate of the transformation of initial ODA molecules into final products, which occurs through intermediate products. In this case, ODA decomposition occurs quickly and tends to reach 100%. Conversely, when the initial concentration is high, and exceeds the solubility concentration, ODA forms an emulsion. In this instance, the process of decomposition occurs in three stages. In the first stage, the decomposition of dissolved ODA happens relatively quickly with the formation of the system ODA-unsaturated solution, and lasts 5–10 h (Figure 5). In the second stage, undissolved ODA dissolves converting into a solution, with the dissolved ODA decomposing simultaneously. Accordingly, the decomposition coefficient varies little, as the decomposition rate then depends on the ODA dissolution rate, which is lower than the decomposition rate of a dissolved form of ODA. As explained in Section 2, the hydrophobic nature of the ODA molecule plays a crucial role in its low solubility, preventing an effective interaction between polar water molecules and a non-polar hydrocarbon chain. In the third stage, the dissolved ODA passes through the decomposition process relatively quickly and *K* tends toward 100%. These decomposition phases are shown in Figure 7.[79] From the results, it may be stated that the initial ODA concentration produced no effect on the decomposition intensity during the first 5 h, however after that period, an effect of the initial concentration on the decomposition intensity was observed. The results are of great importance for practical application in power plants as they clearly lead to the conclusion that ODA decomposition takes place only in a dissolved form. Even though the dosed concentrations of ODA are usually low, the experiments considering different concentrations allow for the estimation of the ODA decomposition rate in a broad range of concentrations.

5.4 | Effect of power cycle chemistry

One of the factors that influence the decomposition of organic corrosion inhibitors in the plant cycle involves other compounds in the water/steam cycle. To the authors' knowledge, only one study which considers this effect has been performed thus far. Ivanov and Klimanov[78] produced data relating to the influence of alkalizing agents, such as ammonia and sodium hydroxide, on ODA thermal stability. As a result of the study, it was observed that alkalizing agents, particularly ammonia, strongly influence ODA thermal decomposition. The effect of alkalizing agents may be attributed to the reaction of hydrolysis, which presumably contributes to decomposition and yields an alcoholate (alkoxide) and ammonia:

$$\mathrm{R-CH-NH_2} \xrightarrow{\mathrm{H_2O,NaOH}} \mathrm{R-CH_2-ONa} + \mathrm{NH_4OH}. \tag{2}$$

This is evidence that alkaline reagents in the steam lead to an additional degradation of the active molecule of the ODA inhibitor. The results suggest that the applied plant cycle chemistry is an important factor influencing FFA decomposition and therefore, it should be taken into account in future experiments.

5.5 | Decomposition products of ODA

Knowledge of potential FFA decomposition products is of great consequence for preventing and controlling their negative effects in the power water cycle. Thus, this knowledge is important for choosing monitoring techniques, providing correct water treatment concept, making the right selection of amines, as well as adjusting their dosing concentrations and working parameters. The compounds produced as a result of ODA thermolysis are ammonia,[15,28,33,35,78–81] hydrogen (H_2),[15,28,33,35,79,81] carbon monoxide (CO),[33,79,81] methane (CH_4),[15,28,33,81] and carbon dioxide.[15,28] Dioctadecylamine and trioctadecylamine are formed by releasing ammonia from ODA molecules and the reactions between them.[26,35,79,86] Harmful low molecular organic acids were neither reported in the mentioned papers nor in the work later

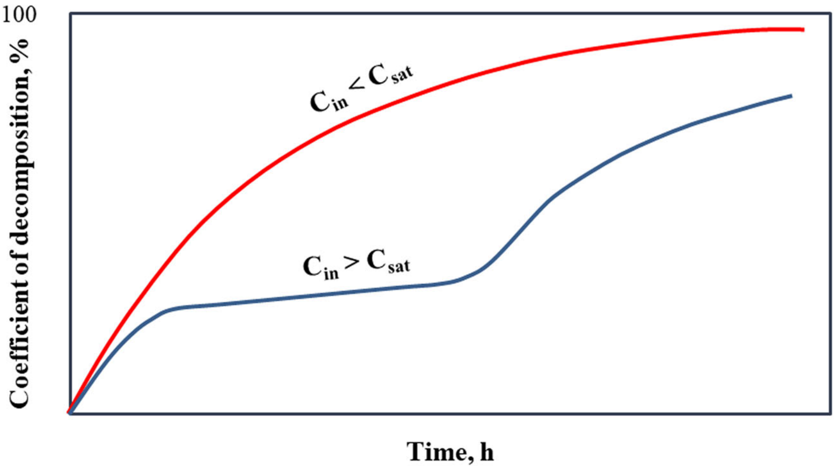

FIGURE 7 Scheme of the decomposition phases of ODA for the concentrations below and above the saturation concentration (C_{sat})[79] (figure is reused with permission from the respective journal).

published by Cao et al.[80] who analyzed samples obtained between 350°C and 560°C.

Regarding the quantities of breakdown products, it was calculated that 5 mg of completely decomposed ODA produced roughly 0.3 mg of ammonia.[26,87] Furthermore, at 343°C and 15.2 MPa, the total amount of hydrogen, carbon monoxide, and methane equaled 1% of the initial ODA amount.[33,81] Considering that the applied FFA concentrations in power plants are normally quite small and vary between 1 and 5 ppm, it may be stated that the total concentration of hydrogen, carbon monoxide, and methane is negligible and therefore they cannot have an effect on the corrosion development and the protective layer on the metal tubes. Small amounts of decomposition products such as ammonia, hydrogen, and others, were observed already at 95°C,[33,35,81] and also served as indicators of the beginning of the decomposition process. Based on the results obtained, the authors stated that the implementation of ODA was harmless for power equipment. Unfortunately, the lack of published results on FFA apart from ODA restricts the analysis of how the FFA structure influences the formation of decomposition products.

In the framework of the comprehensive experimental study by Ivanov and Klimanov,[78] the authors found that ODA pretreated at 350°C at a pressure of about 4 MPa provided no protection against corrosion, while ODA pretreated at 290°C provided only short-term protection. These results confirmed the supposition that the thermal decomposition converted the FFA molecules into compounds without protective features.

5.6 | Decomposition reactions of ODA

As mentioned in Section 5.5, the decomposition of primary amines at high temperatures is known to result in the formation of secondary and tertiary amines, while releasing ammonia. On the basis of the literature data,[28,78,79,86,88] the decomposition of ODA in steam generators in the presence of metal catalysts[26] leads to the formation of dioctadecylamine and ammonia, as follows:

$$2C_{18}H_{37}-NH_2 \rightarrow C_{18}H_{37}-NH-C_{18}H_{37}+NH_3. \tag{3}$$

According to this equation, one molecule of dioctadecylamine and one molecule of amine result from two molecules of ODA. The formation of dioctadecylamine can be explained by the following intermediate stages:

$$R-CH_2-NH_2 \rightarrow R-CH=NH+H_2. \tag{4}$$

$$R-CH=NH+R-CH_2-NH_2 \rightarrow R-CH=N-CH_2-R+NH_3. \tag{5}$$

$$R-CH=N-CH_2-R+H_2 \rightarrow R-CH_2-NH-CH_2-R. \tag{6}$$

The next stage is the formation of trioctadecylamine from one molecule of ODA and one molecule of dioctadecylamine:

$$C_{18}H_{37}-NH_2+C_{18}H_{37}-NH-C_{18}H_{37} \rightarrow (C_{18}H_{37})_3N+NH_3. \tag{7}$$

However, the reaction forming dioctadecylamine provides no explanation for the release of gases (hydrogen, carbon monoxide, methane) in the process of thermolysis, which has been demonstrated in the aforementioned studies.[79,81,86] Therefore, Dubrovski et al.[79] were the first to propose an explanation of the formation of gases by making the assumption that, ODA is transformed into alkenes during the decomposition process, as illustrated in the Figure 8A. Hydrolysis of alkenes leads to the formation of alcohols which are transformed into aldehydes and acids in the presence of metals or metal oxides as catalysts. If formic acid is an intermediate product of oxidation, thermolysis will occur according to the reaction (B) in Figure 8. The reactions (C) and (D) presented in Figure 8 produce hydrogen and methane.

The decomposition products may generally react amongst each other or with structural materials, which consequently may lead to corrosion.[22,23,25] In general, decomposition reactions are very complex,[79] creating numerous intermediate products with different properties such as volatility, a distribution coefficient, etc. These intermediate and final decomposition products most likely react with chemical additives, corrosion products, impurities, and their breakdown products in the water/steam cycle, forming new compounds. This in turn complicates the study of FFA thermolysis, especially in real conditions. Consequently, the FFA decomposition mechanism is a poorly investigated area that should be addressed in future research to generate a scientific foundation that can be implemented in practice.

6 | THERMAL DECOMPOSITION OF FFAP

FFAP are commercially available materials containing FFA and other substances such as alkalizing amines, reducing agents, dispersants, and emulsifiers. It is

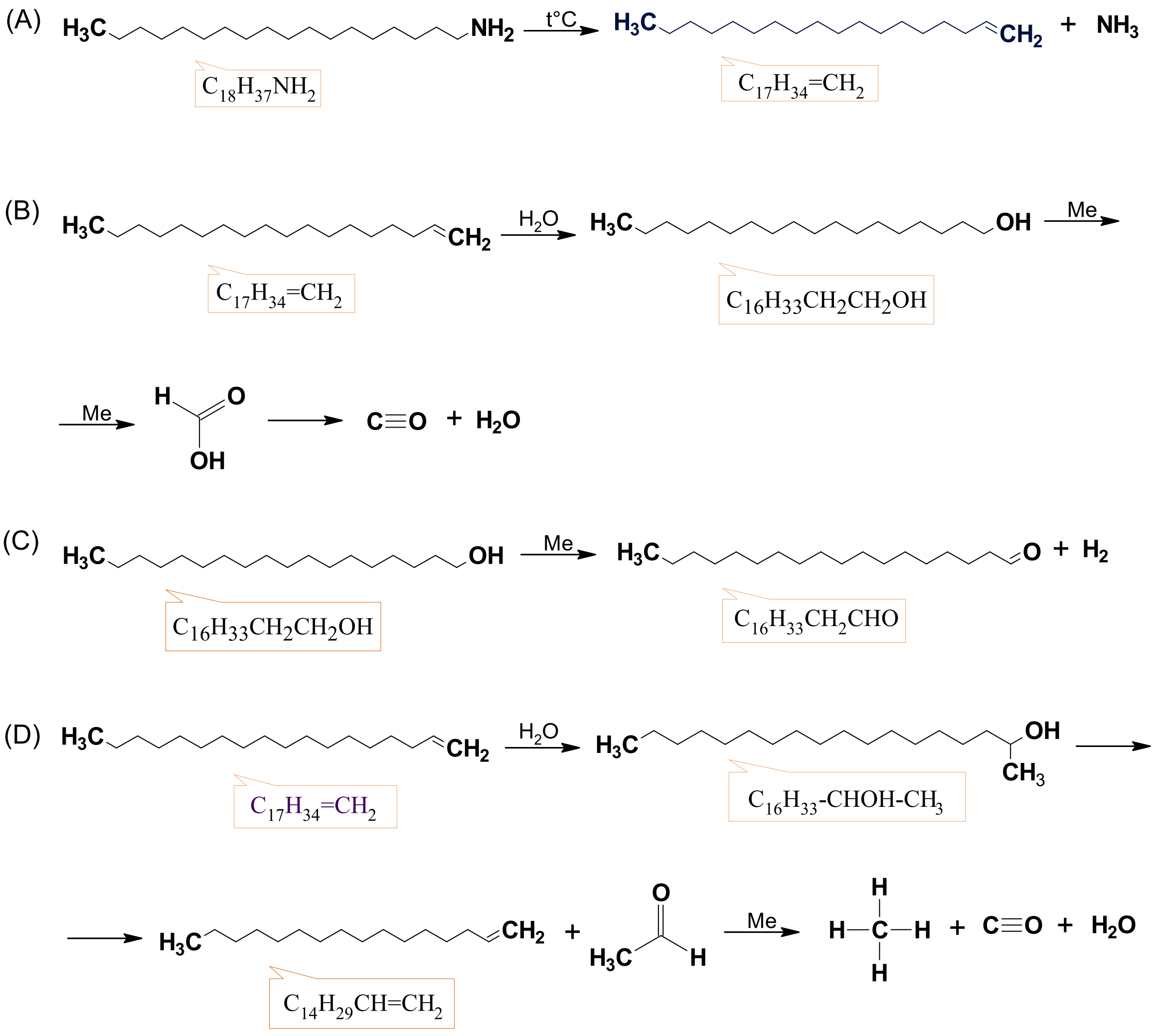

FIGURE 8 Formation of gaseous decomposition products (Dubrovski et al.[79]).

indispensable to know the decomposition products of FFAP to determine the necessity and the extent of their removal in the condenser polishing plant, as well as estimate their content in the first condensate, and assess the corrosion risk.

The published results for FFAP decomposition obtained by different authors are presented in Table 3. The results were observed to be consistent regarding low molecular mass organic acids found in minor concentrations among the thermolysis products. Sollner et al.[82] conducted a study on the contents of acetate, formate, and propionate (the decomposition products of FFAP) in water samples from four industrial steam generators with drum boilers and condensate polishing plants, located in the Netherlands, Germany, and Switzerland. The temperatures of the superheated steam equaled 400°C and 510°C and pressures were 4 and 9.8 MPa, respectively. The sampling points for all steam generators were condensate, feedwater, boiler water, and superheated steam. Based on Sollner et al.'s work,[82] under given conditions, the tested FFAP is harmless with regard to corrosive acids formation as the acquired values for the concentration of low molecular mass acids were very low. Thus, low concentrations of acetic acid, being recognized as the most thermally stable low molecular weight acid,[55] were found in tested samples. The highest concentration of acetate was measured in boiler water, amounting to 40 μg/L, while in the steam, the highest concentration of acetate was found to be 23 μg/L, in the feedwater 34 μg/L, and in the condensate 28 μg/L. However, it is difficult to judge the presented concentrations since the initial concentrations of FFAP were not given. In addition, based on the authors' statement, the origin of the acetates in this study remained unclear, as they could also be produced as a result of the decomposition of organic compounds in the makeup water, which is usually the main source of organic impurities entering the plant water/steam cycle from raw surface water.[18] Furthermore, pH values were below the target values (according to VGB guidelines), no formate and propionate were detected, but carbon dioxide and ammonia were found in the feedwater and condensate, as well as glycol with the highest concentration in the boiler water. The presence of glycol was ascribed to the decomposition of the ethanolamine present in FFAP, but its concentration was not specified. This study showed that the applied organic conditioning was satisfactory for the tested power plant.

One of the most serious limitations of this publication is that the composition of FFAP is unknown and the results can neither be applied to other FFAP to predict their decomposition nor compared with other published results. The results of the described study referred to a commercially available FFAP containing FFA and other constituents, which means that the decomposition products stem from all these components together and are specific for each compound. Therefore, it is necessary to know the decomposition behavior of each compound under steam generator operating parameters, though these data are exceedingly rare. For instance, there are some data on the decomposition of the alkalizing amine dimethylamine (DMA) produced at various locations in the secondary circuit of an advanced gas-cooled reactor power plant,[89] where the steam temperature exceeded 500°C. These data revealed that the decomposition products included ammonia, methylamine, carbon dioxide, unidentified organic species, and formic acid, with the concentration at the superheated outlet surpassing the expected values, i.e., 50 μg/kg of formic acid when DMA concentration was 450 μg/kg. Information on all other FFA components would enable foreseeing the decomposition products resulting from the blend.

Another disadvantage of the study published by Sollner et al.[82] is the incompleteness of the experimental dataset due to which the interpretation of the results and conclusions are limited and not fully reproducible. The absence of the initial concentration of tested FFAP makes it not only impossible to estimate the decomposition rate, but also to predict the quantity of the breakdown products (especially corrosive organic acids) in the power generators and consequently, their possible impact on the tube walls. Besides, comparison with other studies is not possible. In addition, due to a lack of information on the temperatures in all the examined sample points (except for the superheated steam), it is impossible to establish a relationship between the temperatures and the formed thermolysis products.

Moreover, in the study conducted by Sollner et al.,[82] the tested steam generators were additionally conditioned with other additives (cyclohexylamine, sodium hydroxide, ammonia) that interfere with FFAP decomposition and obstruct the accuracy of the obtained results in terms of products formed and their concentrations. Findings demonstrating a significant impact of ammonia and sodium hydroxide on ODA thermolysis[78] convincingly support this assumption. On the other hand, the real conditions under which the measurements were carried out offer an advantage by taking into account all the possible factors that influence FFAP decomposition and providing information to the power plant personnel about the FFAP behavior in the same or similar operational conditions. It further enables an efficient management of FFAP utilization and prediction of their impact on plant reliability and performance.

There are published data on the thermal decomposition of a FFAP Cetamine® V211,[1] which represents a conditioning agent used in some power plants. Cetamine® V211 is a blend of FFA and alkalizing amines. This investigation has also been performed in real conditions in the Nehlsen Stavenhagen refuse-derived fuel power plant, with sampling points at different locations in the water/steam cycle. The highest temperature of live steam equaled 400°C and the steam pressure was 4.2 MPa. FFA were not detected but alkalizing amines were found: monoethanolamine in the boiler water, and cyclohexylamine in the steam, feed water, and condensate. Ethylene glycol, as a decomposition product, was detected in the feedwater, main steam, and condensate. The authors stressed that it was present in a non-dissociated form that has no effect on acid conductivity. Of the low molecular weight acids, only acetic acid was detected, with concentrations in the steam of 28, 30, and 20 μg/L. The same as in the previous FFAP study,[82] the fact that temperatures in other sampling points were not given imposes a limitation on this research, as it has made it impossible to associate decomposition products with temperatures.

From the described experiments, it can be inferred that the acetate concentration was very low when it was found in the samples. Furthermore, the examined FFAP yielded glycolate, which originates from alkalizing amines. Thus, these results appear to be relatively consistent in all the examined plants.

Frahne and Blum[83] conducted experiments on the thermal stability of polyamines by using an experimental set-up containing an autoclave. At 400°C, and with the exposure time of 24 h, 2%–5% of the acetic, formic, and propionic acids were formed from a 10% solution of polyamines and volatile amines (no names were given) but some solutions of polyamines and volatile amines produced only 1% of these acids. Helamin®, containing both polyamines and volatile amines, yielded ≪1% of volatile low molecular weight organic acids. From 1 mg/kg of Helamin® (the typical dose for high pressure power plants), less than 10 μg/kg of organic acids were produced as a result of thermal decomposition. This is quite a small amount, especially in comparison with acids originating from natural organics estimated at 10% and varying between 50 and 500 μg/kg. The series of experiments with Helamin® led to the conclusion that the tested amine/polyamine additives can be applied in high temperature water environment without concern in terms of the quantities of corrosive thermal decomposition products formed. In support of the obtained results, the authors reported the data from a once-through high pressure boiler water (22 MPa) treated with Helamin®, confirming that the concentration of volatile organic acids only varied within the range of 20–40 μg/kg.

Further experiments[83] conducted with Helamin® 906 H (an amine/polyamine/polyacrylate blend) heated in an autoclave under different experimental conditions provided evidence for the formation of ammonia, ODA (intermediate product of polyamine synthesis), low molecular weight amines, substituted diamines as predominant decomposition products, low molecular weight hydrocarbons up to 18 C atoms (poly-α-olefin), and unknown volatile amines in small concentrations. The authors concluded that this polyamine, along with an accurate application, could be applied in high temperature water environments without any negative consequences for the metal. Moreover, they also stated that slowly releasing ODA exhibited better solubility and homogeneous distribution than the one injected directly into the power plant water/steam cycle.

A study of two different FFAP (nospecific names were provided) conducted by using a storage tank-autoclave circuit at 570°C and 17 MPa with an FFAP concentration of 300 mg/L and a residence time of 189 and 150 h[85] indicated that the concentration of acetic acid resulting from the decomposition was negligible, amounting to a maximum of 0.19% (in the steam phase) of the FFAP content and originating from alkalizing amines, while the concentration of formic acid was higher at a maximum of 2.79% (in the steam phase) of the total FFAP concentration. Small concentrations of low molecular weight acids, particularly acetic acid, are in fairly good correlation with other published data. The advantage of this study is a set-up capable of measuring the decomposition products in both the liquid and steam phases, which also gives possibility of estimating their partition coefficients. Another decomposition product confirmed in the mentioned study was butanolamine found in the liquid phase.

There is a recent study of the thermal stability of an ODA-based product (a commercial emulsion) providing evidence for 80% of the initial amount decomposed at 275°C during the 6 h.[84] However, the identification of the decomposition products was not an objective of this study.

The Technical Guidance Document dealing with film forming substances application[15] confirmed that small organic acids, carbon dioxide, low molecular weight amines, ODA, and substituted diamines could be produced as a result of FFA decomposition, while propionate, glycolate, oxalate, citrate, and benzene were classified as minor decomposition products.

7 | IMPORTANCE FOR PRACTICAL APPLICATION IN THE POWER WATER CYCLE

From the obtained data on the ODA thermolysis,[33,79,81] it may be inferred that the effect of temperature was not an issue for layup and feedwater conditioning, where the temperatures are typically below 300°C. Studied temperatures below 100°C[33,79,81] correspond to the condensate system, those of 160°C[79] and 233°C[33,81] to the feedwater in the subcritical thermal power plants, and the temperature of 343°C[33,81] matches the temperature in the economizer, which constitutes a first heat transfer section in the boiler.[18] The dosing points of FFA are typically in the condensate system where the water temperature is below 30°C. With the passage of ODA through the power plant, the temperature of water increases, normally reaching around 240°C in front of the boiler in the subcritical thermal power plants. Therefore, based on the obtained results, significant decomposition of ODA is not expected in the condensate and at the beginning of the feedwater systems. In the close proximity to the boiler, the decomposition probably occurs to some extent, however, a sufficient amount of undecomposed ODA will form a protective film on the metal tube walls. Allowing for the fact that, at one temperature point in the feedwater, the residence time is of the order of a few seconds, the assumption can be made that the decomposed amount of ODA in the feedwater and economizer will be significantly lower than that obtained after 5 h at the tested temperatures of 160°C, 233°C, and 343°C.[33,79,81] On the other hand, the amounts of decomposed ODA observed by Ivanov and Klimanov,[78] Babler et al.,[28] and Cao et al.[80] at the temperatures corresponding to the superheaters (above 450°C) in the subcritical power plants, point out the high influence of temperature on the stability of ODA, consequently affecting its applicability to the high temperature components in the water/steam cycle. In addition to that, with an increase in the temperature and a simultaneous decrease in the ODA concentration,[78–80] the concentration of the decomposition products rises, and it is easy to infer that their amount will be highest inside the superheater. Therefore, quantitative data on the increase in concentrations of organic acidic anions with an increase in temperature should be obtained for all FFA used in the power industry. In fact, it is one of the most important objectives for future investigations.

To obtain reliable results, it is important to understand the role of both laboratory experiments and those conducted in real power plant conditions. For the investigation of FFA and FFAP thermolysis, both laboratory and experiments in real plants are useful and only combined data can provide the basis for generating scientific knowledge. The real power plant conditions under which some of the described measurements were carried out are valuable because they take into account all the factors influencing the decomposition and provide useful information on concrete power plants as well as power plants with the same process conditions. These types of examinations are important due to the fact that the entire prediction of the decomposition reactions, the kinetics, quantity, and the type of decomposition products is possible only if the process conditions are known. However, it is difficult to use the obtained data for drawing conclusions about different operational conditions or other power plants and it is unreliable to match the thermal degradation from different industrial plants with respect to either the quality or the quantity of degradation products. These conditions are specific for each power plant and comprise the temperature, pressure, metal surface, residence time, heating rate, reducing and oxidizing conditions, water chemistry, pH, oxygen concentration, metallurgy, contaminants, and other parameters. Therefore, laboratory experiments are useful, since impeding factors can be avoided and the effect of specific influencing factors of interest or a combination of factors on decomposition can be studied. Consequently, this makes it possible to establish the fundamental principles, relations, and trends, and also predict the decomposition kinetics or the breakdown products under various power plant conditions. However, to produce reliable laboratory results under the specified conditions for industrial application, it is indispensable to take into consideration the maximum number of influencing parameters and simulate the real operational conditions in the power plant chemistry cycle. This is also an important direction towards the advancement of the experimental concept for studying FFA involving realistic solution compositions and extended temperature ranges. This approach will open up new frontiers in FFA decomposition studies that are both technically challenging and technologically important, enabling the results to be directly translated into practice. Since thermolysis is a complex function with many variables, the main disadvantage of the existing experimental studies using the laboratory setups is the difficulty to fully create real conditions. Nevertheless, the results can at least demonstrate general tendencies and provide an improved understanding of thermolysis reactions. A subsequent investigation of industrial steam generators and positive practical observations are the best confirmation of the results obtained in the laboratory.

Reliable experimental results are fundamental for the development of a model for predicting the temperature dependence of FFA thermolysis in feedwater, boiler, superheater, and reheater conditions allowing for residence time, pressure, applied type of water cycle chemistry, and other influencing parameters. The effect of all power plant water/steam cycle conditions on FFA decomposition is a research need that should be considered in future experimental studies to build a thermolysis model with a variety of parameters, enabling the prediction of the decomposition behavior of FFA and FFAP. Amongst others, this model would show the intensity of decomposition in simulated superheater conditions, as compared to simulated boiler conditions.

Also, in future work, it will be necessary to provide information on the effect of other FFA on the decomposition of the tested FFA that would contribute to the development of a practical mixed amine water chemistry optimized for corrosion prevention and fouling mitigation. Generally, to obtain accurate data, the composition of the examined solutions should include the complexity of multicomponent solutions and the combination of impurities and additives that are of interest to power plant application. In the study conducted by Sollner et al.,[82] four tested steam generators were conditioned with products based on FFA (dosed into the feedwater), and in addition, steam generator 1 was conditioned with alkalizing amine cyclohexylamine (injected after the condensate polishing plant), steam generator 3 with caustic (dosed into the drum boiler), and steam generator 4 with a small amount of ammonia (added after the condensate polishing plant). All of the compounds present in the water solution can affect the reaction mechanism and kinetics of FFA decomposition.

It may be noted that the existing published research results were limited to only one pure FFA and a few FFAP, which indicates the necessity of testing the other types of FFA under simulated power chemistry cycle conditions. This will help to establish the relationship between the chemical structure of FFA and the decomposition products, their concentrations, as well as degradation kinetics. Establishing these relationships will also allow the prediction of FFAP decomposition, which is strongly dependent on the present ingredients.

For instance, the study by Rudasova and Sajdi[85] gave strong evidence for the difference between FFAP containing more FFA and less alkalizing components, and those containing more alkalizing components than FFA. No acetic acid was produced as a result of the thermal decomposition of the FFAP with a higher concentration of FFA components, while FFAP with a higher content of alkalizing components yielded a small concentration of acetic acid detected at levels up to 0.56 mg/L in the steam phase, which represents 0.19% of the concentration of tested FFAP. Further, FFAP with more FFA is decomposed to a higher concentration of formic acid whose average concentration was 5.3 mg/L in the steam as compared to 2.43 mg/L of formic acid (in the steam) originating from FFAP with more alkalizing amines. This example clearly pointed out the necessity of knowing the composition of FFAP. Therefore, the operator should obtain information from the supplier regarding the constituents of the FFAP used, their limitations, the thermal stability under the given power plant conditions, the benefit for the power plant, and the influence of their decomposition products on power plant operation, particularly on the pH of early condensate[90] and conductivity after CACE.

The proper application of FFA corrosion inhibitors is the key element providing a benefit for power plants. In general, the application of FFA in power plants requires special attention from the operator and therefore, it is important to carefully follow the guidance in order to prevent damages. For instance, it is necessary to prevent overdosage and the subsequent formation of gel-like clumps that could block the tubes and other equipment. Experiments have also confirmed that maintaining the correct pH minimizes the corrosion risk that could result from organic treatments and their breakdown products.[91]

In the preceding chapters, the main factors affecting the thermal decomposition of FFA were identified and discussed. Further studies should allow for a wider range of compounds present in water, higher temperature ranges, realistic solutions of interest for power plant application, identification of other factors that could affect decomposition, and the detection of all decomposition products. Besides, attention should be given to the optimization of analytical methods for the detection of FFA. The selection and optimization of methods ought to correspond to the specific molecular structure of FFA, the demanded accuracy and sensitivity (limit of quantification), adequate selectivity, the potential presence of interfering substances in the solution, the required measurement range, available time constraints, the rapid measurement of series of samples when needed, toxicity and other relevant criteria. Generally, these methods are subjects of continuous development and improvement, as discussed in the text below.

The most widespread approach for determining the concentration of FFA today is the photometric technique. The concentration of FFA is determined by measuring the optical density of colored FFA complex compound at corresponding wavelengths. The drawback of the presented published papers is insufficient information provided concerning the analytical methods and procedures employed for determining FFA concentration. Certain papers failed to divulge the methodologies used to analyze the concentration of FFA,[78,84,85] others provided a brief indication of technique[80] or method[83] used, devoid of additional explanatory details, while some papers[1,33,79,81] only referenced the source where the method was previously described. Dubrovski et al.,[33,79] Martinova et al.[81] and presumably Cao et al.[80] analyzed the concentration of pure ODA using the well-established standard photometric methyl orange extraction method, exhibiting a sensitivity of 0.1 mg/L.[92] This method is based on measuring the optical density of an orange colored complex formed through the interaction of ODA and the methyl orange indicator, subsequently extracted into the organic phase by chloroform. The optical density is measured in an acidic environment at a wavelength of 430 nm, and the concentration is determined by referencing a calibration curve. Lower aliphatic and aromatic amines, ammonia, hydrazine, and metal ions like iron and copper do not interfere with measuring ODA concentration, which is the advantage of this approach.[92,93] The method utilizing methyl orange is applicable for experimental studies, as well as during the operation and conservation of power plants. The main drawback of the method is the utilization of a wide range of reagents, a toxic organic solvent, and possible losses due to extraction that can influence measurement accuracy. To counter the drawbacks, novel methyl orange-based methods were developed, including a rapid nonextraction method,[93] an approach to differentiate primary, secondary, and tertiary amines while addressing interference issues,[94] a method to determine primary and secondary amines in each other's presence,[95] and the replacement of toxic chloroform with dichloromethane.[15] The Bengal Rose photometric method used by Kolander et al.[1] and Frahne and Blum[83] was developed for determining the content of polyamines in water solutions. The Bengal Rose indicator is a fluorescein derivative containing xanthene rings. The method relies on the interaction between FFA and the Bengal Rose indicator in acidic medium, followed by the measurement of the optical density of the resulting colored water-soluble complex at a wavelength of 560 nm.[96] The concentration is subsequently determined using a calibration curve. This method exhibits sensitivity below 0.02 mg/L.[96] Due to the combination of its favorable characteristics, this method is now extensively used in both laboratory settings and real plant conditions. The advantages of the Bengal Rose method include acceptable accuracy and sensitivity, simplicity, measurement speed, rapid measurement of series of samples, and sufficient tolerance towards interfering substances such as monoethanolamine, cyclohexylamine, ammonia, and iron.[96] In addition to the described methods, the approach based on eosin indicator, which is also based on a xanthene dye, has proven to be reliable for determining FFA concentration[97,98] due to its sensitivity, accuracy, and reasonably good resistance to short chain organic amines and ammonia. However, the complex preparation process, extended reaction time, and short expiration period render it suitable only for periodic FFA concentration determinations.

Dubrovski et al.[33,79] and Martinova et al.[81] applied a photometric method specifically developed for determining ammonia concentration in the presence of ODA.[99] These are the only FFA thermolysis experimental studies that employ such a sensitive and accurate method, making it the most suitable choice for these experimental conditions. This method allows the precise detection of the onset of ODA decomposition. The essence of the method involves a reaction between ammonia, sodium hypochlorite, and sodium phenolate in the presence of acetone as a catalyst, resulting in the formation of a gray compound, in which the concentration of ammonia is measured at a wavelength of 630 nm. This approach prevents ODA from affecting the accuracy of the ammonia measurement up to an ODA concentration of 10 mg/L, while at higher ODA concentrations, the sample is recommended to be diluted. The method has a sensitivity of 0.005 mg/L, making it applicable for detecting low concentrations of ammonia irrespective of the presence of ODA. In other discussed studies carried out in power plant conditions, ammonia was determined either indirectly through its contribution to the acid conductivity measured by an online instrument,[1] or using a mV meter (model Orion EA 940, method AV 1015),[82] with a detection limit of 0.05 mg/L. The mV meter measures voltage signals and transforms them to actual ammonia concentrations using the established calibration curve. The well-established standard technique for analyzing low molecular organic acid anions in power plant water chemistry, both in science and practice, is ion chromatography (IC).[15,100] The sensitivity of the method is approximately 1 μg/kg. Some authors[1,82] conducted measurements using liquid chromatography–organic carbon detection (LC-OCD), with the results subsequently corroborated by IC. It is worth mentioning the method used to determine the concentration of hydrogen, carbon monoxide, and methane,[33,79,81] with an accuracy of ±5%. A special set-up was built,[99] allowing to establish a state of equilibrium between the liquid and gas phases, take sample from the gas phase, and insert it into the gas chromatograph. The total gas concentration was derived from the concentration of the inserted gas. The achieved lowest detectable concentration was 0.01 μg/kg for hydrogen and 0.2 μg/kg for carbon monoxide and methane, owing to the differences in solubility compared to hydrogen. Based on its characteristics and results obtained, this approach is proven to be valuable for identifying the mentioned gases released during the thermolysis of FFA.

8 | CONCLUSIONS

The following conclusions can be made based on the collected results: (1) The published results on thermal stability for pure FFA only refer to ODA. (2) The main factors influencing the intensity of the decomposition process of ODA in the power plant water/steam cycle are the temperature, residence time, initial concentration of ODA, and plant cycle chemistry (conditioning). (3) ODA decomposition occurs between 80°C and 450°C, with complete decomposition above 450°C. (4) During the first 5 h, only 40% of ODA is thermally decomposed, with a high decomposition rate independent of temperature and initial concentration, while subsequent decomposition was slow and dependent on temperature and initial concentration. (5) The following ODA decomposition products have been observed: ammonia, hydrogen, carbon monoxide, methane, hydrocarbons, and additionally produced di-and three-octadecylamine. (6) No acetic acid and other low molecular weight organic acids were reported in ODA decomposition studies. (7) Only dissolved ODA can undergo decomposition. (8) At high ODA concentrations, the decomposition process is slow, with the maximum amount of decomposed ODA estimated at 40% for ODA concentration >20 mg/kg at the temperature of 160°C, while for ODA concentrations <20 mg/kg, the decomposed amount reached 95%, at the same temperature. (9) Alkalizing agents accelerate the thermal decomposition of ODA. (10) ODA poses no harm to the structural materials of a power plant water cycle. (11) FFAP, containing different types of amines and other additives, decompose into carbon dioxide, ammonia, ethylene glycol, acetate in low concentrations, propionate, glycolate, oxalate, citrate, other low molecular weight organic acids, diamines, low molecular weight amines, benzene, ODA, low molecular weight hydrocarbons, and etc. (12) Prior information of the FFAP composition is necessary before application.

Further investigation allowing for the complexity of multicomponent solutions, higher temperatures, and different types of amines is needed to improve the understanding of the thermolysis of FFA under power generation plant conditions.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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