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High temperature corrosion in various grades of vegetable and waste oils used for bio-fuel production

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Abstract:

Corrosion experiments were conducted at 220 °C in vegetable and waste oils used to produce biofuels. Industrial oils and model solutions with controlled concentrations of free fatty acids (FFA) were used. Corrosion of carbon steel and low alloy steel increased with FFA concentration up to several millimeters per year. AISI 316L stainless steel was immune to corrosion in all FFA concentrations used in this study. Test solution analysis with various techniques allowed identifying corrosion mechanisms involving consumption of FFAs and the formation of highly soluble metal complexes.

Keywords: A. Low alloy steel, A. Stainless steel, B. Weight loss, C. Acid corrosion, C. High temperature corrosion

Highlights:

- Corrosion tests on stainless steel, low alloy steel, and carbon steel are carried out at 220°C in vegetable and waste oils
- AISI 316L presents perfect corrosion resistance in all test solutions
- For carbon and low alloy steels, linear correlations are obtained between the oil's initial acidity and corrosion rate
- Corrosion mechanism involves direct reaction with free fatty acids and the formation of organo-metallic complexes

Nomenclature and units:

AV: Acid Value CPO: Crude Palm Oil DTO: Distilled Tall Oil DG: Diglycerides FFA: Free Fatty Acid HDT: Hydrotreatment MG: Monoglycerides PFAD: Palm Fatty Acid Distillate SAM: Self Assembled Monolayer TG: Triglycerides TOFA: Tall Oil Fatty Acid WCO: Waste Cooking Oil TAN: Total Acid Number NAC: Naphthenic Acid Corrosion

1. Introduction

In the ultimate goal of improving industrial sustainability for years to come, the transition from fossil fuel-based energies to renewable biomass-based energies has incorporated new conditions to refining processes. One of the applications involves the hydrotreatment of lipidic feedstock of various grades such as oils and fats issued from dedicated agriculture crops (vegetable oils) or process wastes (animal fats, waste cooking oils, tall oils, etc.) into high quality drop-in-fuels, namely jet and diesel fuels with good cold flow properties ^[11]. Hydrotreatment of these lipidic feedstocks can be done in new grassroot dedicated units or by co-processing with fossil fuels in a refinery existent facility. This type of biomass feedstock significantly differs from conventional fossil feeds. Thus, specific corrosion problems related to these feeds are likely to occur in bio-refineries ^[2]. While those phenomena are not necessarily similar throughout the entire plant, feedstock characterization is important to identify the potential contaminants present in the fresh feed and assess the possible reactions which can evolve during the process.

Oils and fat composition can differ depending on the origin, method of extraction, refining level, and their applications. For example, conventional vegetable oils are extracted by pressing the seeds or oil-bearing fruits (trituration process) or by solvent extraction in the case of those with low fatty matter. During the extraction process, oils are susceptible to degradation reactions and contaminations. As these products are frequently used in consumption as edible oils, they are forced to undergo stabilization and purification treatments to remove contaminants such as heavy metals, water, and other undesirable products. As the use of edible oils for fuel production is quite controversial, the tendency is to increase the use of alternative feedstock with complex compositions that are often difficult to trace back to a single source. These types of feeds are often designated as waste oils, such as those products (e.g. distilled fatty acid fractions) where their composition is highly variable and requires deeper characterization. Other feeds are not plant based but have animal origins such as slaughterhouse wastes which include, but are not limited to, beef tallow, poultry fats, and fish oils.

The overall composition of oils and fats used to produce biofuels is commonly summarized using the scheme in *Figure 1*.



Figure 1. Typical composition of vegetable oils and animal fats used to produce biofuels

Vegetable and waste oils are mainly composed of triglycerides and free fatty acids while minor components are commonly found with an average concentration of 1-5%. Fatty acids are carboxylic acids with an aliphatic chain of 4-24 carbons and most often with an even number of carbon atoms. They can be saturated or unsaturated, including one or more C=C double bond, and can be unbranched as Free Fatty Acids (FFA) or branched in an ester structure. Triglycerides are esters of three similar or different molecules of fatty acids and are the major components found in vegetable oils and animal fats. High temperature or prolonged contact with air causes degradation reactions such as hydrolysis, oxidation, and polymerization that deteriorate the esters into less stable species, namely FFA. Although FFA can be naturally occurring in oils and fats, they are mainly produced from the hydrolysis of triglycerides during the extraction phase but are also known as end-products of thermo-oxidation and frying reactions ^{[3], [4]}. Therefore, the concentration of FFAs varies between different types of oils and depends on multiple factors, namely the quality, the extraction process, the storage, and the exposure to air and temperature ^{[5],[6]}. During the production of edible oils, post extraction treatment of raw vegetable oils to remove FFAs produces by-products of concentrated acidic cuts which can also be used in the production of fuels. For example, purification and deodorization of crude palm oil (CPO) give rise to a waste distillate of concentrated palm oil fatty acids (PFAD). The acids are stripped from the oil by steam distillation at elevated temperatures (180-220°C) and under vacuum or low pressures (2-6 mbar). Heating of cooking oils also produces free fatty acids by dissociation of ester bonds through auto-catalytic radical chain reactions and thermo-oxidation phenomena. Prolonged atmospheric exposure to high temperatures promotes the hydrolysis and oxidation reactions of triglycerides to increase the FFA content in the oil ^[7]. Disposal of non-consumable oils creates blends of degraded lipids with relatively high concentrations of acids that can readily evolve and generate problems during future processing stages. Other contaminants can also exist due to further degradation

of the free fatty acids and triglycerides in the form of more complex and unstable oxygenated species (peroxides, aldehydes, ketones, alcohols, alkoxy radicals, acrolein) [8],[9],[10].

Experience in the refining of conventional hydrocarbons can help in the identification of corrosion risks for bio-refineries. One of the major parameters governing corrosion risks for conventional refining is associated with the presence of naphthenic acids (NAC). The damage incurred by these organic compounds is especially prominent in high temperature settings of the vacuum distillation unit. Similarly to free fatty acids, naphthenic acids are carboxylic acids, except that they include a cyclopentane or cyclohexane ring in their alky structure, and generally vary in molecular weight between 300 and 400 g/mol. Corrosion by these compounds is usually observed through localized corrosion and flow induced corrosion (in high velocity areas). Uniform and localized weight loss can also be found in low velocity conditions for low alloy and carbon steels. Based on ASTM D664 [11], the total acid number (TAN) is used to quantify the total amount of naphthenic acids present in a crude without discrimination of structure and stability. Peihl [12],[13] suggests a distribution profile of TAN in function of the true boiling point (TBT) of an acidic crude to identify the areas within a process potentially vulnerable to naphthenic acid corrosion. The observed trend propose that acids are the most corrosive at temperatures close to their boiling points. Further investigation determined that corrosion is most crucial in the range between 180 and 400°C as below the kinetics are too slow, and beyond acids decompose and deposit as coke on metal surfaces [14],[15],[16],[17]. Based on many laboratory studies and field experience, threshold values have been established: crude oils with TAN greater than 0.5 mgKOH/g and distillate sub-fractions with TAN greater than 1.5 mgKOH/g are considered to be corrosive for low alloy steels [12],[16],[18],[19]. Given the similarity between the fatty acids in bio-based oils and the naphthenic acids in crude hydrocarbon oils, analogous corrosion phenomena might take place in biorefineries.

This study hereby focuses on the impact of free fatty acids on the corrosion of various alloys in process settings. The experimental approach consists of corrosion experiments in various types of vegetable and waste oils accompanied by extensive ex-situ analysis of the solutions before and after test to better understand the corrosion mechanisms. In a first step, experiments are conducted in industrial feedstocks of diverse quality and composition with focus on free fatty acid concentration. Information amassed by the ample characterization tools is used to build chemical profiles of the different solutions to develop categorical attributions of the feeds. Identification of those key chemical species furthered the investigation by implementing a second set of experiments in model mixtures with controlled concentrations of free fatty acids.

2. Experimental methods

2.1. Batch autoclaves

Two types of high-temperature autoclaves were used for this study.

The first test unit is composed of a 600 ml reactor made of Hastelloy[™] C-276 alloy with maximum operating conditions of 138 bar and 500 °C. Heating is achieved by an electric heating collar regulated by PID (Proportional Integral Derivative) controllers and monitored with a thermocouple placed in the reactor. Periodic renewal of the gas phase can be carried out. In this study, nitrogen blanketing was applied throughout the tests. Sampling ports allow collecting aliquots of gas and liquids for further analysis. Due to their amphipathic properties, FFAs have the ability to reduce surface tensions and increase diffusion of oxygen into the bulk by means of the hydrophilic carboxylic end-group ^{[20],[21]}. To minimize dissolved oxygen

concentration in the test solutions, nitrogen purging was carried out for at least 4 h to ensure complete removal of dissolved oxygen before each test. Temperature and pressures are monitored in real time to assess system control. At the end of the tests, aliquots of test solutions are kept under argon blanketing to prevent oxidation before proceeding to the analytical phase. This test unit is used for experiments on industrial grade vegetable and waste oils. Results are obtained by conducting batch operations for five days at 220 °C with no feed renewal and no intermittent sampling. Preliminary evaluation of the impact of test duration and test solution renewal was carried out through ten days exposures at the same temperature of 220 °C and daily renewal of the test solution. No differences were seen in comparison with five days batch exposures, so this duration was selected as it allowed conducting more tests. The temperature of 220 °C was selected as it is representative of the industrial process. In addition, the analogy with crude oil refining and naphthenic acids corrosion suggests that corrosion by carboxylic acids might start to be significant in this temperature range.

The second test unit is composed of six individual reactors with a capacity of 100 ml each. The main advantage of this test unit is its ability to operate six tests in parallel, thus allowing multiplying test conditions in a single run. All reactor components are made of 316L and can operate at maximum conditions of 183 bar and 330 °C. The test protocol for this unit is similar to that used for the 600 ml autoclave which include prior oxygen expulsion of the test solution, nitrogen blanketing of the autoclave, and final sampling of oil for analysis. Heating is achieved by placing the cells in heating stations which accommodates three reactors per station. Great care was taken to ensure homogeneous heating between the different autoclaves and minimize calorific losses. Temperature is recorded throughout the tests using type-J thermocouples connected to a data logger.

2.2. Steel coupons

The tested steels include AISI 316L stainless steel, AISI 1018 carbon steel, and A387 Gr11 low alloy steel. AISI 1018 was selected as a model carbon steel grade that is very often used in laboratory experiments. The other grades are commonly used in refineries or bio-refineries for transfer lines and reactors. A387 Gr11 low alloy steel is often employed for its better resistance to high-temperature hydrogen attack provided by chromium and molybdenum additions. AISI 316L is also used for these types of applications: in crude oil refineries, austenitic stainless steel grades with 2% molybdenum are often employed to resist naphthenic acid corrosion.

AISI 316L coupons were extracted from a 2 mm thick solution annealed cold rolled plate. AISI 1018 coupons were supplied by Metal Samples and no information on the thermomechanical history is available. A387 Gr11 coupons were obtained from a 10 mm thick normalized and tempered plate. The chemical composition of these steel coupons is presented in **Table 1**. Optical microscope observations of their microstructure are presented as supplementary material attached to this article.

Steels		Composition (wt%)								
	С	Mn	Si	Cr	Ni	Мо	Р	S	Ν	Fe
AISI 316L	0.019	1.26	0.45	17.75	10.19	2.02	0.035	0.001	0.051	68.01
AISI 1018	0.18	0.84	0.02	0.02	0.01	<0.01	0.01	<0.005	-	99
A387 Gr 11	0.1	0.5	0.7	1.25	-	0.50	0.02	0.02	-	97

Table 1. Chemical composition of tested steels

Corrosion coupons have dimensions of 76 mm x 15 mm x 2 mm for AISI 1018 and AISI 316L and 55 mm x 10 mm x 2 mm for A387 Gr11. The smaller size of A387 Gr11 coupons was only due to availably from a previous work but this difference might not affect the test results. Before the tests, steel coupons are polished up to 2000 grit papers, 30 s per side. All coupons are subjected to ultrasonic cleaning in heptane for 3 min, rinsed in ethanol and finally dried by air before weighing. The coupons are then suspended using quartz rods and fully immersed in the test solution.

After the tests, coupons are cleaned to remove deposits. Then, they are weighed to calculate the weight-loss corrosion rate. Microscopic observations are also carried out to detect the presence of localized attacks.

2.3. Analytical methods

2.3.1. Chemical composition

To understand the corrosion mechanisms associated with organic mediums, it is useful to carry-out thorough analysis of test solutions to identify corrosive species and corrosion products. This is achieved by conducting a chemical profiling of all the selected feeds while focusing on essential chemical properties suspected to influence the corrosiveness of the matrix. These techniques are based on standard analytical methods casually adapted from the nutritional sector with emphasis on fatty acid profile, oil stability and quality, and contaminant inclusion. The techniques used for the assessment of the chemical composition are summarized in *Table 2*.

Measured property	Method Reference	Information obtained
Acid value	NF EN ISO 660	Total concentration of FFA
Fatty acid composition	NF EN ISO 12966-2 and - 4	Quantifies and identifies fatty acid methyl esters
Glyceridic profile	Internal ITERG/GC method	Identifies and quantifies families (TG, DG, MG, FFA, glycerol and sterol)
lodine value	NF EN ISO 3961/EN 14111	Measures an average degree of unsaturation
Peroxide index	NF EN ISO 3960	Identifies secondary oxidation products (peroxides, aldehydes, ketones)
Karl Fischer	NF EN ISO 12937/6296	Water content. Link to FFA production

Table 2. Measured chemical properties of the solutions

The acid value is determined according to NF EN ISO 660 which uses potentiometric titration to measure the amount of KOH (expressed in milligrams) needed to neutralize the acids in one gram of oil (mg_{KOH}/g). The value obtained represents the total amount of free fatty acids contained with no distinction of the structure and type of acid. Since carboxylic acids play a crucial role in the corrosion of steels, quantifying the amount of free fatty acids is thought to be a key indicator of impact assessment. A fatty acid profile for all feeds is conducted based on standardized analytical tests NF EN ISO 12966-2 and 12966-4 which allows for the identification and quantification of the different fatty acids contained in the oils. It is

important to mention that this type of profile characterizes all fatty acids, i.e. those composing the glyceridic esters as well as the free fatty acids. This provides a better insight on the different species forming the chemical matrix of the solutions which is essential to unveil the reactions that are likely to occur during corrosion tests. Additionally, a glyceridic profile is conducted with a gas chromatography method which determines the different chemical families, notably esters and free fatty acids. Finally, some chemical properties are measured to characterize oil stability and resistance to oxidation and thermal degradation. These properties include the iodine index (NF EN ISO 3961) which measures the average unsaturation of the lipids. This is particularly important as the number of double bonds directly affects the stability of the esters to oxidation. The peroxide index (NF EN ISO 3960) evaluates the extent of oxidation undergone by an oil by measuring the amount of secondary oxidation products that can eventually impact the corrosion activity. The water content (Volumetric Karl Fischer titration, NF EN ISO 12937/6296) is also measured as lipids can undergo hydrolysis to produce additional free fatty acids and alter the initial acidity of an oil as well as influence the activity of soluble oxygenates. Before the tests, all the oils are stored at 6 °C with no exposure to light to avoid photooxidation and thermal deterioration during storing.

2.3.2. Simulated distillation (SIM-DIS)

A gas chromatography-flame ionization detector (GC-FID) method is conducted in all solutions, before and after the corrosion tests. This GC-FID method is based on the conditions of the standard ASTM D2887-16a broadly used for the hydrocarbon product analysis and known as Simulated Distillation GC (SIM-DIS) [22]. Moreover, the temperature range covering the eluted species is 35-650°C. Measurements were conducted using a Restek chromatography nonpolar column (10 m x 0.53 mm x 0.88 μ m) and helium is used as the gas vector (flow rate = 26 ml/min). Each sample is diluted in CS_2 while ensuring proper miscibility at ambient temperature as injecting a pure sample that freezes at STP conditions might cause contaminations further in the column. Although CS₂ is typically used in the ASTM D2887 for the dissolution of nonpolar hydrocarbon samples, another option could be the use of a solvent that incorporates a larger plethora of more polar samples containing fatty acids and triglycerides (chloroform is a suitable replacement $\frac{[22]}{2}$). 80 µl of the sample is diluted in 1 ml of CS₂ which is then injected using an on-column injector. Injection is made from 100 to 400 °C at a gradient of 50 °C/min and temperature plateau of 0.5 min at 100°C and 15 min at 400 °C. Heating is performed in an oven with a ramp from 60 to 400 °C at a gradient of 35 °C/min and by maintaining a final temperature level during 15 min. The species are separated by increasing boiling points and correlated with the retention times in the GC column through a calibration curve obtained by running a calibration mixture of hydrocarbon normal paraffins. Although this method is specific to hydrocarbon species, identification of other organic compounds can also be achieved by assessment of major individual peaks in the chromatogram in combination with complementary information obtained from other chemical characterization techniques (glyceridic profile, acid value, fatty acid composition) and the use of standards. As for corrosion test products, an entire method should be developed using representative oxygen species standards and turning to more complex, fastidious and expensive analytical tools coupling separation and identification techniques such as GC-MS and/or LC-MS for a more precise analysis. Although GC-FID SIM-DIS method lacks for accurate identification of unknown chemical structures, it can be used as a powerful quantification and monitoring tool for the species identified in the initial solutions.

2.3.3. Attenuated total reflectance-fourier transform infrared spectroscopy (ATR-FTIR)

Infrared spectra are recorded using a Nicolet iS50 spectrometer with an MCT detector module (cooled using liquid nitrogen) and adapted with a Golden Gate ATR diamond crystal. The measurements are conducted before and after the experiments by adding a droplet of the solution on the diamond crystal at 20°C without any specific preparation prior to the measurement. All absorbance spectra are obtained in the mid-infrared region at 4000-650 cm⁻¹ and with a resolution of 4 cm⁻¹. Background acquisition is made with a blank crystal. Based on the interactions between the electromagnetic radiations in the infrared domain and the molecules in the solution, the non-destructive technique allows for an identification of species based on functional groups having specific bond vibrations. This is particularly useful as the detection of some species and products might not be possible with the standard analytical techniques used in the profiling phase. The information extracted is used for the identification of some key chemical components. All presented spectra are corrected by removing the signals of atmospheric contaminations.

2.3.4. Inductively coupled plasma – optical emission spectroscopy (ICP-OES)

The technique makes it possible to obtain a quantitative elemental composition of metals dissolved in the tested solutions. Quantifying the corrosion products is necessary to validate the acid attack mechanism by linking with the information obtained from the pseudoquantification by DS data and the qualitative characterization by ATR-IR. The samples are prepared by mineralization in an acidic medium and then injected by nebulization into the plasma where temperatures of 9000 K are reached allowing the solution to vaporize and the analytes to atomize, ionize and thermally excite. The OES coupling allows to detect and quantify elements by measuring the intensity of the emitted rays in relation to the characteristic wavelength of the element under the form of excited atoms or ions. The measurements are then converted to elemental concentration following calibration standards.

2.4. Test solutions

2.4.1. Industrial feeds

Industrial oils and fats are supplied by Daudruy Van Cauwenberghe, Dunkirk (France) to use in immersion tests. The detailed characterization of the samples is done at ITERG (Canéjan, France). A complete chemical profile of the oils used in this study is illustrated in **Table 3** and **Table 4**.

Table 3. Physical-chemical properties of the industrial feeds

Physical-chemical	properties	Refined Rapeseed	Refined Sunflower	Refined Soja	Refined Palm	Animal fat	Fish oil	wco	PFAD	TOFA	DTO
Fatty acid esters ¹	[wt%]	>99	>99	>99	>99	96.7	98.5	93.9	6.2	-	-
Free fatty acids	[wt%]	0.1	<0.1	<0.1	<0.1	3.3	1.5	6.1	93.8	96.7 ²	77.6 ²
Acid value	[mg _{KOH} /g]	0.06	0.06	0.06	0.16	10.2	4.6	16	185	196	192
Peroxide index	[meqO ₂ /kg]	0.6	2.1	0.7	1.1	13.4	3.4	1.2	1.2	7.2	-
Water content	[mg/kg]	150	170	150	100	709	1000	3310	1468	240	640
lodine index	[g/100g]	115	126	132	53.5	78	136	87	61	146	166
Density (15°C)	[g/cm ³]	0.921	0.923	0.923	0.916	0.917	0.923	0.921	0.897	0.909	0.940

¹Fatty acid esters: Triglycerides, diglycerides, monoglycerides

²Values do not include rosin acids

Table 4. Fatty acid composition of the industrial feeds

Fatty acid compositio	n (wt%)¹	Refined Rapeseed	Refined Sunflower	Refined Soja	Refined Palm	Animal fat	Fish oil	wco	PFAD	TOFA	DTO
Lauric acid	12:0	<0.05	<0.05	<0.05	0.47	0.14	0.09	0.12	0.22	-	-
Myristic acid	14:0	0.07	0.07	0.07	1.1	1.6	2.8	0.7	1.3	-	-
Palmitic acid	16:0	4.8	6.3	<u>10.7</u>	<u>42.9</u>	<u>21.1</u>	11.0	<u>17.4</u>	<u>48.9</u>	0.6	0.3
Palmitolei c acid	16:1	0.2	0.1	0.1	0.2	3.9	4.2	1.3	0.2	-	-
Margaric acid	17:0	0.06	<0.1	0.1	0.1	0.3	0.4	0.2	-	0.2	0.1
Stearic acid	18:0	1.9	3.7	3.9	4.6	5.9	2.8	6.3	3.9	0.7	0.6
Oleic acid	18:1	<u>57.9</u>	<u>29.8</u>	<u>23.6</u>	<u>40.1</u>	<u>49.6</u>	<u>34.6</u>	<u>45.3</u>	<u>36.2</u>	<u>24.4</u>	<u>17.1</u>
Linoleic acid	18:2	<u>24.6</u>	<u>57.8</u>	<u>52.5</u>	9.4	<u>12.6</u>	<u>11.6</u>	<u>24.1</u>	8.4	<u>34.4</u>	<u>33.4</u>
Linolenic acid	18:3	7.7	0.5	7.2	0.2	1.0	4.9	1.6	0.3	0.7	4.5
Arachidic acid	20:0	0.5	0.3	0.3	0.4	0.2	0.3	0.3	0.3	0.3	0.6
Gondoic acid	20:1	1.1	0.2	0.2	0.1	1.0	4.9	0.5	0.1	1.8	2
EPA	20:5	-	-	-	-	0.05	4.1	-	-	-	-
Erucic acid	22:1	0.2	<0.1	<0.05	<0.05	0.1	4.2	0.06	<0.05	0.1	-
DPA	22:5	-	-	-	-	0.1	1.4	-	-	-	-
DHA	22:6	-	-	-	-	0.07	5.3	-	-	-	-
Rosin acid		-	-	-	-	-	-	-	-	3.3	22.4

¹Only the major fatty acids and fatty acid isomers are illustrated to facilitate the data

²The formula "X:Y" represents the number of carbons and the number of double bonds respectively

Samples identified as "refined" are vegetable oils that have undergone post-extraction treatment (physical and/or chemical refining). These refined vegetable oils commonly have low concentrations of FFA (<1 mg_{KOH}/g) and high levels of fatty acid esters (mainly under the form of triglycerides). These oils differ mostly in their iodine index which is highly dependent on the nature and origin of the oil. Refined sunflower, refined soja and refined rapeseed have relatively high iodine index due to the large presence of oleic and linoleic fatty acids which include one and two double bonds in their alky chain, respectively. Conversely, refined palm oil is characterized by high amounts of palmitic acid which explains the lower iodine value. Additionally, impurities such as oxidation products and water are low in these types of feeds (peroxide index < 15 meqO₂/kg and water content < 200 ppm). These properties might evolve with storage conditions and exposure to light and oxygen. Additionally, the level of unsaturation influences the stability of oils. Polyunsaturated vegetable oils are less resistant than mono and saturated oils particularly regarding their oxidative stability. It is generally agreed upon that vegetable oils are thermo resistant at temperatures up to 280 °C but onsets for thermo-oxidation can occur as early as 200 °C if exposed to enough oxygen [10], [23]. Studies show that the induction period for unsaturated oil oxidation is significantly smaller than saturated oils when exposed to similar environments [24]. The natural presence of antioxidants, such as tocopherols, ferulic acid, citric acid, and vitamin E allow for a better resistance of the oils even highly unsaturated ones [10],[23]. Based on the principles of decreased stability in function of unsaturation, it should be assumed that oils with high iodine values are most prone to deteriorate. However, operations under inert atmospheres and in controlled temperatures below threshold values reduce the probability of thermal oxidation to occur for these initially stable oils.

Animal fat and fish oil are feeds extracted from animal wastes produced mainly from the agrifood industry. One main difference from refined vegetable oils is the water content. Karl Fischer titration shows that animal fat and fish oil include 709 ppm and 1000 ppm of water, respectively, compared to the refined oils in which water content ranges between 100 and 170 ppm. Another major difference relates to the free fatty acid content which varies between 4.6 mgKOH/g (fish oil) and 10.2 mgKOH/g (animal fat). The peroxide index of these feeds is also significantly higher, reflecting a higher degree of oxidation.

The remaining samples, WCO, PFAD, TOFA, and DTO, are feeds obtained from industry and consumer wastes. These oils are the most complex out of the entire series and their characterization using analytic methods, like those for vegetable oils, might not be entirely accurate since most tools were developed for edible vegetable oils. Nevertheless, a complete profile is constructed for these oils in which major compositional features are distinguished from the other sources. While the waste cooking oil is still mainly composed of fatty acid esters (93.9 %), the acid content is greater than previous feeds. It also has the highest water content of all test solutions (3000 ppm). The other oils share the common feature of a very low fatty acid ester content (i.e. triglycerides, diglycerides, monoglycerides). While WCO derive from a mixture of degraded vegetable oils with fatty acids commonly varying between C12-C18, others are obtained as industrial process by-products. PFAD which results from the distillation of CPO is mainly composed of palmitic acid (C16:0) and oleic acid (C18:1). TOFA (Tall Oil Fatty Acids) and DTO (Distilled Tall Oil) are cuts of tall oil distillates obtained from the Kraft process in the paper manufacturing industry. While they differ from the typical oleaginous sources, they contain intense concentrations of free fatty acids (oleic, linoleic, and palmitic) as well as

rosin acids (abietic, dehydroabietic, pimaric etc.). Rosin acids also belong to the family of carboxylic acids, but while free fatty acids are composed of a linear alkyl chain, rosin acids contain three condensed naphthenic and/or aromatic rings. TOFA are obtained from the fractionation of tall oil under vacuum distillation and are characterized by having important concentrations of oleic acid C18:1 and linoleic acid C18:2. The composition of DTO is quite similar to that of TOFA, except for the rosin acid content which is significantly higher (22 wt% compared to 3.3 wt% in TOFA).

2.4.2. Model mixtures

2.4.2.1. Preparation of the model solutions

To investigate the impact of free fatty acid concentration, model solutions are prepared by adding oleic acid (C18:1) to rapeseed oil (high erucic acid). High erucic rapeseed oil is a refined vegetable oil which distinguishes itself from the other industrial feeds by having near 50 wt% erucic acid (C22:1) in its original fatty acid ester structures. This vegetable oil is selected for this study since it was readily available at the time of the test program, and its low corrosiveness was verified during preliminary tests. Additionally, it is representative of the lipidic feeds similarly used in the industrial applications. A chemical profile for the reference is detailed in *Table 5*.

Fatty acid composition (wt%)						
Lauric acid	12:0	<0.05				
Myristic acid	14:0	<0.05				
Palmitic acid	16:0	3.01				
Palmitoleic acid	16:1	0.25				
Margaric acid	17:0	0.06				
Stearic acid	18:0	0.99				
Oleic acid	18:1	<u>14.76</u>				
Linoleic acid	18:2	<u>12.89</u>				
Linolenic acid	18 :3	<u>10.44</u>				
Arachidic acid	20:0	0.77				
Gondoic acid	20:1	5.22				
Erucic acid	22:1	<u>47.34</u>				
Physical-chemical propert	ties					
Fatty acid esters	[wt%]	>99				
Free fatty acids	[wt%]	0.1				
Acid value	[mg _{кон} /g]	0.76				
Peroxide index	[meqO ₂ /kg]	21				
Water content	[mg/kg]	350				
lodine index	[g/100g]	104				
Density (15°C)	[g/cm ³]	0.913				

Table 5. Composition profile of erucic rapeseed oil (model mixture solvent)

Analytical grade oleic acid is supplied by Merck with a purity >90 %. Impurities include other free fatty acids of carbon chains close to that of the major acid, notably palmitic acid (C16:0). Oleic acid is miscible with rapeseed oil at normal conditions with only one phase appearing, hence no additional modifications are added to the system. Model solutions of varying oleic acid content from 0 to 70 wt% are used in this study. The exact acid value is determined by potentiometric titration based on the standard NF EN ISO 660. The values corresponding to various mixing ratios are reported in **Table 6**.

ble 6. Free fatty acid content (acid value) of the model mixtures used for the study
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Mass % oleic acid added	0	10	20	30	40	50	70
Acid value (mg _{KOH} /g)	0.76	19	38	58	77	97	152

2.4.2.2. Additional characterization with SIM-DIS and ATR-IR

Since the composition of model mixtures is better controlled than industrial feeds, additional analytical techniques are used to monitor alterations in solutions after the tests. This is achieved by first conducting an initial screening of the model mixtures using SIM-DIS and ATR-FTIR techniques.

The approach is initially made first to identify the effect of oleic acid doping on the reference solvent oil and to obtain information on the major lipidic groups forming the matrix. The GC-FID chromatograms obtained under SIM-DIS conditions are illustrated in *Figure 2.a* for rapeseed oil (high erucic) and *Figure 2.b* for the doping agent. The relative intensities of the species are presented as a function of their retention times in the column. Different regions are easily identified.



Figure 2. (a) SIM-DIS chromatogram of the reference solvent showing the main lipidic components in high erucic rapeseed oil (TG, DG, MG). (b) SIM-DIS chromatogram of pure doping agent showing major peaks for oleic acid (C18:1) and minor peak for palmitic acid (C16:0).

For the rapeseed oil matrix (*Figure 2.a*), the region with the longest retention times (9-11 min) is attributed to triglycerides. It is composed of several peaks corresponding to different chain lengths of fatty acids within the ester structure. The highest peak at 10.5 min can be attributed to triglycerides of erucic acid (C22:1) which represents 47 wt% of the total fatty acids in the glyceridic matrix (*Table 5*). The other peaks can be associated to triglyceride structures with gondoic acid (C20:1), linolenic acid (C18:3), linoleic acid (C18:2), and oleic acid (C18:1). As

shown in **Table 5**, high erucic rapeseed oil also contains small fractions of diglycerides (1.8 wt%) and monoglycerides (0.2 wt%), which correspond to the weaker signals found in the region between 6-9 min. *Figure 2.b* shows the chromatogram of the doping agent used for the preparation of the model mixtures. Its main constituent is oleic acid (90 wt%), but it also contains other acids such as palmitic acid (10 wt%). The major peak at 4.4 min can thus be attributed to oleic acid (C18:1), while the smaller one at 3.7 min corresponds to palmitic acid (C16:0).

The retention time domains for each type of species are summarized in **Table 7** as well as the equivalent boiling temperature range given by the normal paraffins calibration mixture. It must be noted that these values might differ based on the type of column, the preparation method, and the species retention inside the column. For reference, Morgan et al. ^[22] obtained different retention time values for the same type of species.

COMPOUND	RETENTION TIME (MIN)	BOILING POINT (°C)
Triglyceride	9-10	580-620
Diglyceride	7-8	520-570
Monoglyceride	6-7	360-430
Free fatty acids:	2-5	280-380
Palmitic acid (C16:0)	3.5-4.0	339-348
Oleic acid (C18:1)	4.0-4.5	360-368

Table 7. Characteristic SIM-DIS values for compounds identified by SIM-DIS chromatograms of model mixtures

SIM-DIS chromatograms are also obtained for model mixtures with various amounts of acid value. The time domain corresponding to the evolution of free fatty acid concentration is presented in *Figure 3* and expressed in function of weight percent acid inclusion. As expected, the peak intensities of C16:0 and C18:1 increase with the percentage of added acid in the refined oil matrix. Interestingly, integration of the peak area proved to be proportional to the total acid value, showing that the analysis of SIM-DIS chromatograms can be used to determine the amount of free fatty acids in the test solutions. As will be seen later, this method is superior to potentiometric titration for post-test measurements as titration does not discriminate between free fatty acids and other related structures.



Figure 3. Characteristic retention time peaks of the model mixtures in SIM-DIS chromatograms *for (a) 0, 10 and 20 wt% free fatty acid, and (b) 30, 40 and 50 wt% free fatty acid.* Minor peak at 3.7 min for palmitic acid (C16:0) and major peak for oleic acid (C18:1) at 4-4.5 min

In addition to SIM-DIS measurements, infrared spectroscopy is also used. **Figure 4** shows the effect of acid inclusion on the reference oil.



Figure 4. Infrared spectra showing the effect of oleic acid doping on high erucic rapeseed oil

Doping with oleic acid C18:1 has a significant impact on the spectra, particularly in the regions specific to the carboxylic vibration modes. A decrease of the peak intensity at 1744 cm⁻¹, which is attributed to the vibration mode of carbonyl in the esters, is due to the relative decrease of ester concentration in the solution as the concentration of oleic acid is further increased in the mixture. This feature is accompanied by an increase of the peak intensity at 1711 cm⁻¹ belonging to the vibration mode of carbonyl in oleic acid. Additionally, the absorbance region attributed to O-H vibration modes between 3400 and 3000 cm⁻¹ evolves as FFA concentration

increases which is linked to the increase of hydroxyl intensity in the carboxylic group of oleic acid. Without additions of oleic acid, the reference rapeseed oil is composed mainly of triglycerides, the O-H functionality of fatty acids is absent due to the ester C-O-C type bonding. The peak intensity at 3009 cm⁻¹ corresponds to the vibration modes of C-H in cis double bonds which increases coherently with the acidity of the mixtures as oleic acid includes one double bond predominantly in the cis configuration. The peak increase at 966 cm⁻¹ also indicates the presence of a trans configuration in the acid mixtures.

Figure 5 focuses on the absorption bands specific to carbonyl vibrations of fatty acids for the various mixing ratios of model solutions. As expected, the absorbance level of the carbonyl group for free fatty acids (1711 cm⁻¹) increases with the acid content. Simultaneously, a decrease of the peak at 1744 cm⁻¹ is seen, which is attributed to the vibration mode of carbonyl in the fatty acid esters (TG, DG, MG). Additionally, the absorbance region attributed to O-H vibration modes between 3400 and 3000 cm⁻¹ evolves as FFA concentration increases which is linked to the increase of hydroxyl intensity in the carboxylic group of oleic acid.



Figure 5. Characteristic wavelengths of oleic acid doping on high erucic rapeseed oil *for (a) 0, 10 and 20 wt% free fatty acid, and (b) 30, 40 and 50 wt% free fatty acid.* Increase of carbonyl C=O vibrations in FFA at 1710 cm⁻¹ and decrease of carbonyl C=O vibrations in fatty acid esters at 1740 cm⁻¹ with increasing acid values.

Contrary to SIM-DIS, it is not possible to differentiate between the acid structures in ATR-FTIR as the vibration bands specific to the free fatty acids cannot be used to discern between individual acid structures. However, a summary of the main absorption bands of the detected functional groups in the mid-infrared region can be used to obtain some information of the general behavior of the solutions (*Table 8*).

Table 8. Absorption band values of functional groups in MIR (4000-400 cm⁻¹)

Functional Group	Wavenumber (cm ⁻¹)	Reference
Stretching of O-H group	3400-3000	[25] [26] [27]
Symmetric stretching of C-H in cis double bonds (HC=CH)	3009	[25] [27] [29] [30] [31]
Asymmetric and symmetric stretching of C-H in CH_2	2922 and 2853	<u>[27] [32] [33] [34]</u>
Stretching of carbonyl group in triglyceride esters (O-C=O)	1744	[26] [27] [31] [33] [35]
Stretching of carbonyl group in FFA (C=O)	1711	<u>[31] [34]</u>
Stretching of cis olefins (cis RHC=CHR)	1654	<u>[27] [30] [31] [36]</u>
Bending C-H in CH₂ and CH₃	1463 and 1458	<u>[25] [31]</u>
Rocking C-H in disubstituted cis-olefins	1418	[25] [31]
Symmetric bending of C-H in CH ₂	1378	[25] [31]
Stretching and rocking of ester C-O, CH ₂	1237 and 1160	<u>[25] [29] [31]</u>
Stretching of ester C-O	1118 and 1099	<u>[25] [31] [37]</u>
Out-of-plane bending of trans HC=CH in disubstituted olefins	966	[25] [27] [29] [33] [37]
Out-of-plane bending of cis HC=CH	914	[31]
Superposition rocking of CH ₂ and out-of-plane disubstituted cis-olefins	722	<u>[25] [27] [31] [36]</u>

3. Results

The experimental study is carried out in two complementary steps. The first one consists in exposing the steel coupons to industrial feeds of various quality and grades (*Table 4*). Cross analysis was conducted on corrosion rates and composition of test solutions to determine the key physical-chemical parameters governing corrosiveness.

The second step focuses on the impacts of free fatty acid concentration. Here, experiments are conducted in model solutions prepared with a non-corrosive matrix (erucic rapeseed oil, composition given in *Table 5*) and various amounts of oleic acid. Post-test analysis were also carried-out to monitor the evolution of the composition of test solutions and identify the specific components involved in the corrosion process.

3.1. Tests in industrial feeds

These tests were carried out in the batch reactor (section 2.1) for five days, under 220 °C, under 10 bar of N_2 , and in the presence of AISI 316L, AISI 1018, and A387 Gr11 steel coupons. Corrosion rates are summarized in **Table 9**. The presented corrosion rates are the average value of two coupons and the corresponding deviation. For all the tests of this study, including those in model solutions, no corrosion product deposits were observed at the surface of the coupons. The values in **Table 9** are complemented by iron content values obtained from ICP-OES measurements.

Industrial ails	AV		Corrosion rate (µm/y)	[Fe]			
industrial ons	(mgкон/g)	316L	AISI 1018	A387Gr11	(wt. ppm)			
		Veg	etable oils					
Refined Soja	0.06	<5	<5	<5	N/A			
Refined Sunflower	0.06	<5	44 +/- 2	6 +/- 4	N/A			
Refined Rapeseed	0.06	<5	41 +/- 4	<5	N/A			
Refined Palm	0.16	<5	<5	<5	N/A			
Animal fats and oils								
Fish oil	4.6	<5	179 +/- 3	132 +/- 12	265			
Animal fats	10.2	<5	307 +/- 18	247 +/- 8	459			
		Industrial pr	ocess by-products					
wco	16	<5	1187 +/- 28	1355 +/- 56	1935			
PFAD	185	<5	7270 +/- 3	1522 +/- 151	8420			
TOFA	196	<5	10324 +/- 78	5514 +/- 406	12800			
DTO	192	<5	6451 +/- 16	6054 +/- 50	9210			

Table 9. Weight-loss corrosion rate results and dissolved iron counts from industrial feed after immersion tests

The first major finding from these tests is the high corrosion resistance of AISI 316L stainless steel grade. Weight losses below the detection limit were measured and no localized corrosion was observed on the coupons after the tests.

In comparison, carbon and low alloy steels suffer multiple levels of corrosion attack which varies based on the type of feed. It must be noted that surface observations carried out after the tests revealed that corrosion mechanism was always uniform, without any evidence of localized attack. As inferred from the literature study, the level of corrosiveness seems to be strongly correlated to the acid value of the feeds. Three categories of test solutions can be distinguished based on the corrosiveness towards carbon steel and low alloy steel. Category 1 (non-corrosive) presents corrosion rates that are not exceeding 0.1 mm/y. It is composed of refined vegetable oils with acid values close to zero. Category 2 (mildly-corrosive) includes animal-based waste oils with acid levels from 4 to 10 mg_{KOH}/g. Here, corrosion rates of a few tenth of mm/y are observed. Category 3 (highly-corrosive) is constituted of waste cooking oil (AV = 16 mg_{KOH}/g) and fatty acid distillates (AV above 185 mg_{KOH}/g). These feeds are highly aggressive with corrosion rates recorded above 1 mm/y.

In the first category, four types of refined vegetable oils are compared. For most of the tests, corrosion rates of carbon and low alloy steels are below the detection limit (5 μ m/y). Measurable corrosion rates are only measured for carbon steel in rapeseed (41 μ m/y) and for carbon steel and low alloy steel in sunflower (respectively 6 μ m/y and 44 μ m/y). These trends do not seem to be directly correlated to the acid value since the least corrosive oil (palm) is the one with the highest acid value in the category. It is assumed that the differences in acid

content are insignificant. The slightly higher corrosiveness of sunflower and rapeseed could be explained by the larger amounts of unsaturated fatty acids, as shown by their higher iodine index values (Table 3). These unsaturated bonds attribute to an increasing availability of highly abstractable allylic hydrogens at high temperature where bond cleavages lead to the formation of scission radicals which can introduce reactive oxygen to the system and initiate lipid oxidation chain reactions [38], [39], [40]. However, this trend is not observed for refined soja which presents an iodine index of 132 g/100g which is very close to that of refined rapeseed (115 g/100g) and refined sunflower (126 g/100g). Here, we believe that the lower corrosiveness of refined soja is explained by the presence of natural antioxidants [41], [42], [43]. Category 2 (mildly corrosive) is composed of animal oils and fats. Here, there is a notable increase of the corrosion rates of AISI 1018 carbon steel and A387 Gr11 low alloy steel compared to the results in category 1. The amount of free fatty acids can no longer be neglected as an active corrosiveness parameter. As the acid value increases from 4.6 mgKOH/g in fish oil to 10.2 mgKOH/g in animal fat, corrosion rates of carbon steel are also nearly doubled, from respectively 179 μ m/y to 307 μ m/y. The same trend is observed for A387 Gr11 low alloy steel which exhibits a 20-30% reduction of corrosion rates compared to AISI 1018 carbon steel.

The corrosiveness is further increased in the oil fractions produced as distillate cuts of industrial processes and unrefined mixtures of consumer wastes. Category 3 (highly corrosive) incorporates these feeds. Exposure to wasted cooking oil (WCO) results in a corrosion rate of 1189 μ m/y for AISI 1018 carbon steel and 1355 μ m/y for A387 Gr11. This was the only test condition where the low alloy steel suffered more severe weight-loss than carbon steel. A possible explanation may be linked to the larger amount of impurities present in WCO. As shown in **Table 3**, the water content in WCO is the highest of all tested feeds. It is very likely that other impurities such as salts are also present, which might have affected the protectiveness associated with chromium and molybdenum additions in A387 Gr11. As expected, tests in feeds with the highest acid values showed even higher corrosion rates. Tests carried out in PFAD (AV = 185 mg_{KOH}/g) results in corrosion rates of 7270 μ m/y for AISI 1018 and 1522 μ m/y for low alloyed steel A387. Immersion in DTO (AV = 192 mg_{KOH}/g) results in corrosion rates of 6451 μ m/y for AISI 1018 and 6054 μ m/y for A387 Gr11, while corrosion rates results from exposure to TOFA (AV = 196 mg_{KOH}/g) are 10324 μ m/y and 5514 μ m/y, respectively. For AISI1018 carbon steel, the proportionality between the corrosion rate and the acid value previously observed in category 2 is generally confirmed. Interestingly, the gap in corrosion rate values between the AISI 1018 and A387 Gr11 does not seem to remain uniform in the highly corrosive solutions. While A387 Gr11 always presents lower corrosion rates compared to AISI 1018, the difference varies between 6 % in DTO and 79 % in PFAD. At this stage, no clear explanation of the interactions between corrosive species and alloying elements could be proposed. However, from the industrial standpoint, these results do not conclude differently for the applicability of carbon and low alloy steel. When it comes to these types of feeds, investigation should be made on each system separately. Other factors, besides FFA content, can cause the discrepancy in the corrosion rates of AISI 1018 and A387 Gr11. Additionally, it is still unclear what the impact of acid structure and impurities has on the corrosion mechanisms in complex mediums such as these.

Interestingly, dissolved iron concentration generally follows the same trend as corrosion rates, reaching values as high as tens of grams per liter. For the tests exhibiting high corrosion rates and dissolved iron, a significant change of the aspect of the solution was observed between

the beginning and the end of the test turning from light yellow to dark brown. On the contrary, non-corrosive refined vegetable oils present similar visual aspect before and after the tests. A selection of pictures of the test solutions before and after the tests are provided as supplementary material.

Fundamentally, these tests indicate that like naphthenic acid does for conventional oils, the concentration of carboxylic acids in vegetable and waste oils plays a major role in corrosion. As such, the investigation is further developed into evaluating the impact of free fatty acids alone on corrosion phenomena by focusing on carbon steels.

3.2. Tests in model mixtures

A model mixture approach is used to assess the effect of free fatty acid concentration alone on corrosion behaviors. This is achieved by mixing a reference, non-corrosive, refined rapeseed oil with increasing concentrations of oleic acid. Selection of oleic acid is due to the ample presence of that fatty acid in all tested industrial feeds (*Table 4*) while rapeseed oil is chosen based on the observations that refined vegetable oils having low initial acid value exhibit low corrosion on steels in given conditions (*Table 9*). Based on corrosion results obtained previously, only AISI 1018 carbon steel was used as it was the grade most severely affected.

3.2.1. Evolution of corrosion rates and dissolved iron

Table 10 presents the corrosion rates obtained after immersion tests for 5 days at 220 °C. Reported values of corrosion rates represent the average and deviation of two identical coupons. The concentration of dissolved iron measured after the test by ICP-OES is also presented. Acid values presented in this table were measured before each test with the potentiometric titration method.

FFA content	Acid value (mgкон/g)	Corrosion rate AISI 1018 (μm/y)	[Fe] (wt. ppm)
0 wt%	0.76	197 +/- 7	529
10 wt%	19	856 +/- 185	N/A
20 wt%	38	1792 +/-12	4990
30 wt%	58	2763 +/- 20	17900
40 wt%	87	4229 +/- 103	N/A
50 wt%	97	5205 +/- 120	26700
70 wt%	152	7027 +/- 203	N/A

Table 10. Corrosion rate results and dissolved iron counts for corrosion tests in model mixtures

Similarly to the observations made in section **3.1** for industrial feeds (*Table 9*), the linear trend of corrosion rate of carbon steel with the acid value is confirmed. Interestingly, the correlation aligns well with the one obtained from industrial feeds (*Figure 6*). This is a clear indication that acid value plays a major role compared to other minor variables such as acid structure, impurities, degree of unsaturation, etc.



Figure 6. Relationship between corrosion rate of AISI 1018 after immersion tests in model mixtures and industrial feeds

In addition to direct measurements of the weight change of coupons, it is also quite usual to study corrosion by indirect means through dosing of dissolved metals. From the data presented in **Table 9** (industrial feeds) and **Table 10** (model mixtures), dissolved iron measurements were carried-out after each test. The total amount of dissolved iron is then compared to the weight change of corrosion coupons, which is assumed to be composed mainly of iron (*Figure 7*). For the sake of consistency of units, dissolved iron is expressed in mass. ppm, while the weight-loss of coupons (mg_{Fe}) is related to the total mass of test solution expressed in kg. This normalization permits a direct comparison between the tests in industrial feeds carried out in a 500 ml autoclave and the tests in model mixture conducted in 100 mL reactors. It is important to note that free fatty acids do not appear to have preferential selectivity to the submerged steels and that each coupon is likely to act as an independent system with regards to unreacted acids.



Figure 7. Relationship between iron concentration measured by ICP-OES and total weight loss of all steel coupons in industrial feeds and model mixtures

The correlation in Figure 7 shows a good linear trend between iron content and total weight loss with a slope close to unity. This indicates that all corroded iron remains dissolved in the test solution without forming further precipitation. Compared to solubility limits of iron in aqueous solutions which commonly vary from few mg/L to few hundreds of mg/L, the values are exceeding tens of g/L here. This suggests that soluble organo-metallic complexes are formed.

After the corrosion tests, noticeable changes are observed in the physical properties of the model oil samples. While the initial visual aspect of model mixtures is light yellow, it turns to dark brown after 5 days of exposure at 220 °C. Besides the variation of color, the solutions also undergo an increase in viscosity, and emit a rancid smell. To characterize the changes in test solution composition and to better understand corrosion mechanisms, a thorough analytical survey of test solution before and after the tests was carried-out, whose results are presented in the next sections.

3.2.2. Evolution of acid values during tests

As a clear correlation is observed between free fatty acid content and corrosion rate, then an attempt at measuring acid consumption would reveal more on the mechanisms. At first, potentiometric titrations were conducted after the tests following the same procedure applied on the initial solutions. The results did not reveal significant modifications between measurements before and after the tests. It appears that this analytical method is not capable of discriminating between unreacted free fatty acids and products formed from reactions with these molecules^[44]. To overcome these limitations, simulated distillation is employed as a pseudo-quantification tool. *Figure 8* shows the evolution of the SIM-DIS chromatograms before and after the tests in pure rapeseed oil (a) and in model mixture containing 50 % oleic acid (b).



Figure 8. (a) SIM-DIS chromatograms showing the evolution of 0 wt% oleic acid mixture after immersion test. Appearance of peaks in the FFA region and minor changes in the fatty acid ester region. (b) SIM-DIS chromatograms showing the evolution of 50 wt% oleic acid mixture after immersion test. Decrease of the peak intensities of oleic acid and triglycerides and increase of peak intensities in the mono- and diglyceride region.

Significant changes are observed, primarily in the solution with 50 wt% acid. First, the intensity of the oleic acid (C18:1) peak (4-4.5 min) is much lower at the end of the test compared to its initial value. The same trend is observed for all model mixtures comprising oleic acid. This

suggests that this free fatty acid is directly involved in the corrosion mechanism. The evolution of acid concentration between the beginning and the end of the test was further assessed by conducting an analysis based on surface integration of the appropriate peaks (i.e. C16:0 and C18:1 since they are the only ones already present in the initial model solution). Since SIM-DIS is developed for hydrocarbon species the response factor for FFA and fatty acid esters is not known. Therefore, an empirical response factor was obtained from comparison between acid values measured according to NF EN ISO 660 and the quantitative analysis of SIM-DIS chromatograms. This analysis consisted in calculating the integral of the peaks associated with FFA acids, as shown in Figure 3. The amount of oleic acid consumed during the tests (expressed in moles C18:1) is obtained and compared to the quantity of iron dissolved (expressed in moles Fe) (*Figure 9*).

A good correlation is found between the total metal mass loss and the variation of initial acid value. This is a clear indication of a direct implication of free fatty acids in the corrosion process. In addition, results interpretation suggests that 2 moles of acid react with one mole of iron.



Figure 9. Relationship between total coupon weight loss and consumption of the initial acids in the model mixtures after immersion tests

Other changes in the composition of test solutions are revealed from the SIM-DIS chromatograms particularly for that of AV = 97 mg_{KOH}/g (*Figure 8.b*). The region of short retention times (3-5 min), which contains the peaks of palmitic acid (C16:0) at 3.75 min and oleic acid (C18:1) at 4.3-4.4 min shows that new peaks are formed at 4.7 and 5 min. Since the retention times are slightly longer than those of C16:0 and C18:1 acids, then these peaks are presumably associated with free fatty acids of longer chains, newly formed from the decomposition of the original triglycerides. This decomposition is further confirmed by the decrease of the group of peaks at 9-10 min (attributed to triglycerides), and the rise of new peaks in the intermediate region (7-8 min) that would relate to mono- and di-glycerides.

The last evolution of SIM-DIS chromatograms relates to the region of retention times between 5 and 7 min. Here, no clear peak is detected, but a continuous hill that represents several compounds with nearly similar boiling points, present in co-elution, and impossible to separate and identify using this GC-FID method. These results also suggest that the alteration

of triglycerides is enhanced by corrosion activity. Indeed, the relative decrease of the triglyceride peaks and subsequent increase of mono- and di-glyceride peaks is far less pronounced for the tests in solutions with a lower initial acid value such as presented in *Figure* **8.***a*. It is likely that dissolved metals have acted as catalyzers for free radical chain reactions leading to intense thermal decomposition of the esters.

3.2.3. Identification of metal complexes by ATR-FTIR

ATR-FTIR analysis of model mixtures carried out after the tests reveals significant changes of the initial spectra, notably in the regions specific to the carboxylic acid absorption bands. *Figure 10.a* and *Figure 10.b* respectively illustrate the evolution of IR spectra for the tests in pure rapeseed oil (AV = 0 mg_{KOH}/g) and in the model mixture with 50 wt% oleic acid (AV = 97 mg_{KOH}/g).



Figure 10. (a) ATR-FTIR spectra showing the evolution of 0 wt% oleic acid mixture after immersion test. No major changes except increase of peak at 966 cm⁻¹ suggesting cis/trans inversion of fatty acids. (b) ATR-FTIR spectra showing the evolution of 50 wt% oleic acid mixture after immersion test. Decrease of peak intensities of -OH vibration (3400-3000 cm⁻¹) and C=O vibration (1711 cm⁻¹) of FFA. Appearance of vibration modes at 1567 and 1605 cm⁻¹ suggesting new coordination structures.

Major changes are observed. An important decrease in the peak intensities occurred at the hydroxyl and carboxyl bands of oleic acid, at 3400-3000 cm⁻¹ and 1711 cm⁻¹ respectively. As previously concluded from simulated distillation measurements, this result confirms that freefatty acid is consumed during the corrosion process. The stretching vibration of the triglyceride carbonyl (1744 cm⁻¹) is also affected, indicating changes at the fatty acid level of the ester chain. Focusing on the region 1700 cm⁻¹ - 1500 cm⁻¹, a newly formed absorption band is observed. This band is characterized by a split peak at 1567 cm⁻¹ and 1605 cm⁻¹ which is attributed to the asymmetric vibration of carboxylate COO⁻. This band is most intense in the mixture with the highest initial acidity amongst the series and nonexistent in pure rapeseed oil with no added oleic acid. A similar increase occurring at 1462 cm⁻¹ is attributed to the symmetric vibration of carboxylate, indicating additional modifications of the acid function. These types of vibrations exist in chemical structures composed of organo-metallic ligands found as coordination complexes [45],[46],[47],[48],[49]. The produced vibration bands could indicate that these complexes are in the form of a carboxylate chelating agent bound to one or more central iron atoms forming stable oil soluble structures. Changes of the dipole moment caused by the presence of the metal increases the asymmetric stretching vibrations of the molecule and hence becomes highly polar. A unit of measure is used to estimate the changes in bond angles expressed by $\Delta = V_{asym}$ - V_{sym} . The overall effect is for Δ to decrease as the O–C–O bond angle becomes more acute. The presence of a split peak at the asymmetric carboxylate stretching band is tied to the structure of the complexes and the coordination of the central atom. It could suggest the presence of different configurations which can be hypothesized using the Δ factor. Based on the principles established by Bronstein et al. ^[46], Lin et al. attribute different modes of ligand coordination by linking the carboxylate absorption values in IR with threshold values of Δ ^[47].

These values are displayed in *Table 11*.

Table 11. Suggested threshold values for structural identification of organo-metal complexes by ATR-FTIR [46],[47]

STRUCTURE	Δ (V _{ASYM} -V _{SYM})
Unidentate	> 200 cm ⁻¹
Bidentate chelating	$110 < \Delta < 200 \text{ cm}^{-1}$
Bidentate bridging	< 110 cm ⁻¹

In the measured spectra, the major peak intensity of the split band is at 1567.2 cm⁻¹ and the minor peak at 1605.8 cm⁻¹ while the symmetric vibration appears at 1462.6 cm⁻¹. The Δ values for the major and minor peaks are 104.6 cm⁻¹and 143.2 cm⁻¹ respectively indicating a dominating bidentate bridging mode and to a lesser extent a bidentate chelating mode.

Solubility of these structures in the organic matrix is insured by the hydrophobic alkyl chain of the free fatty acids forming the coordination complexes which seems to have been unaltered. This assumption is further supported by the vibration bands of the asymmetric and symmetric stretching of C-H in CH₂ at 2922 cm⁻¹ and 2853 cm⁻¹ which are similar to the initial intensities in all solutions.

Combining the SIM-DS results with the information obtained by ATR-FTIR, the corrosion products appear to be soluble in the solution and involve a direct consumption of FFA thus reinforcing a mechanism of direct acid attack of the metallic structures.

4. Discussion

The results presented in this paper suggest that the reaction mechanism occurring at the surface is a direct chemical reaction between the steel and free fatty acids.

Connatser et al. ^[50] investigated the role of chelation as a possible chemical reaction. The process includes the dynamic interactions of mobilized metals with deconstructed chemical compounds at interfacial levels. Chelation is a type of bonding that occurs when an ion or molecule (called ligands) forms a coordination complex with a single or multiple central atoms (in this case a metal cations) by creating 2 or more separate covalent bonds with the electrons donated by that atom. In the case of FFA, it is suggested that large acids and oxygenated groups act as chelating agents and have the ability to form charge transfer complexes with surface metals (or metal oxide passive layers) increasing the solubility of the charged metal thus contributing to mobilization of the surface and allowing further acid attack. Connatser et al. approach the subject of ligand formation by assessing the similarity of electronic levels between a metal and an organic compound of interest. They attribute two types of coordination groups arising from carboxylic acids depending on the electron donating site of the molecule ^{[50], [51]}:

1- <u>Metal-bounded surface complexes (MBSC)</u>: direct interaction between the lone electron pair of the donating carbonyl oxygen [C=O] and the charged surface metal through Lewis-like acid base mechanism

2- <u>Hydrogen-bounded surface complexes (HBSC)</u>: hydrogen-bonding type between the oxygen of the hydroxyl termination group [OH] and the charged metal surface via protonation (Bronsted like mechanism).

Given these options, four structures can arise from the carboxylate metal binding phenomena [48],[52] (Figure 11).



Figure 11. Suggested mechanism for the formation of organo-metallic coordination complexes

Similar studies conducted on the identification of such mechanisms have noted that the transport and the adsorption of reactive acid to the metal surface is the initial step prior to complexation ^[14]. The parameters which are critical for this step are the chemical configuration of the molecule (weight, size, chain length...) and the temperature. It was also noted that metals, such as iron copper and zinc, have a high affinity to form complexes with free radical states of carboxylic acids, i.e. carboxylate ligands, which is facilitated at increased temperatures ^[15].

The corrosion mechanism in presence of organic acids in non-aqueous solution is further developed by Patrick ^[15] who studied the effect of varying the types of naphthenic acids on corrosion in high temperature environments. A microgravimetric approach was used to model the corrosion kinetics of carbon steel by measuring the mass evolution of in-situ deposited iron when exposed to acid rich crudes at high temperatures (220-320 °C). The model of metal ligand formation has been verified by measuring the depletion of both the iron and the naphthenic acid present in solution. A combination of Raman spectroscopy and FT-IR provided information on the type of complexes formed. The resulted corrosion product [Fe(RCOO)₂] is highly soluble in non-polar, non-aqueous oil media. Even if naphthenic acids and free fatty acids differ in the type of hydrocarbon chain, both are carboxylic acids with the capacity to form chelating products with similar mechanisms.

Diffusion of the organic species from the bulk is an integral part of the phenomenon. In fact, even if acid concentration is a limiting parameter for the reaction, the structure of the

hydrocarbon chain impacts the kinetics of diffusion and thus the overall net attack. Research conducted on the properties of sustainable lubricants include studies of layer formation by fatty acid additives (mainly oleic, stearic, and linoleic) in bio-oil like synthetic organic mediums (poly-alpha-olefin base oils) [53], [54], [55], [56]. Loehle et al. [55] investigated the mechanisms of fatty acid adsorption and film stability in single and mixed environments. They state that the chemical structure is a predominant factor in the diffusion of molecules and that adsorption occurs through the acid group regardless of the acid. This is based on the ability of fatty acids to spontaneously organize into self-assembled monolayers (SAMs) on steel surfaces through physisorption and chemisorption. Depending on the temperature and the type of acid forming the layer, the stability of these SAMs is different and usually deforms beyond a certain temperature threshold. Loehle shows that in the ranges of 50-150 °C the layers formed individually by stearic, oleic, and linoleic acids do not desorb from the surface, even at 150 °C, and that stearic acid shows the best tribological behavior. However, the stability of the film at high temperatures depends on the desorption of the products which is highly dependent on the nature of the complex formed. The transition temperature can also vary depending on the surface properties of the steel, i.e. irregularities, thickness of oxide layer, composition of passive film for stainless steels. In all cases, desorption is accelerated at high temperatures as the increase in the thermal agitation of the molecules distorts the stability of the adsorbed acids and subsequently that of the film. Also, the presence of unsaturated acids has been found to have an anti-synergic effect on layer stability, especially at high temperatures, which is suggested to be caused by steric hindrance effects induced by the double bonds. This was verified by S. Loehle, who carried out molecular dynamic simulations suggesting that unsaturated fatty acids diffuse faster than saturated acids [56]. This author found that as the temperature increased in the medium, the dispersion between the diffusion coefficients of stearic, oleic, and linoleic acids increased with that of linoleic acid being the highest. These results might explain the intense corrosion in mixed environments as all the acids compete for the same active sites and the resistant SAMs formed by fatty acids such as stearic acid is inhibited by the steric hinderance effects of the unsaturated fatty acids such as linoleic and oleic acid. Investigation of the effect of acid structure on the corrosion of steels might show that linoleic acid alone might be more corrosive than oleic and stearic acid under similar concentrations, temperatures, and exposure times but this will be subject to future experimentation.

Based on the principles provided, the suggested corrosion model involves the following steps: 1- Diffusion of the acids to the oil-metal interface.

- 2- Adsorption of the acids onto active sites (physisorption or chemisorption)
- 3- Formation of SAM (stability depending on acid type and temperature)
- 4- Metal dissolution through the formation of soluble complexes

5. Conclusion and perspectives

This study focuses on corrosion phenomena encountered in the refining of vegetable or waste oils to produce biofuels, upstream of the hydrotreatment process.

Corrosion rate values are measured using weight loss coupons AISI 316L, AISI 1018, A387 Gr11. Two types of solutions are tested: 1) industrial feedstocks, including a range of refined vegetable oils and various waste oils and fats; 2) model solutions composed of a non-corrosive vegetable oil doped with controlled concentrations of oleic acid. Standard analytical techniques are applied to the test solutions, before and after exposure, to study compositional changes. After conducting batch tests under 220 °C for 5 days, the following conclusions can be drawn:

- While the impact of naphthenic acids on corrosion is well documented from the experience of crude oil refining, this study brings new knowledge on the impact of FFA in a broad range of concentrations.
- AISI 316L stainless steels shows strong resistance to free fatty acid corrosion even in high acidity oils.
- The corrosion rate of AISI 1018 carbon steel and A387 Gr11 low alloy steel exhibit a linear trend of uniform corrosion rate with the initial acid value of the feed.
- The same linear correlation is found for industrial feeds and model solution with well controlled FFA content.
- At 220 °C, corrosion rates of AISI 1018 and A387 Gr11 exceed 0.1 mm/y as soon as the acid level reaches a few mg_{KOH}/g.
- Simulated distillation analysis shows a good correlation between the amount of corroded metal and the decrease in FFA concentration.
- The solubility of iron is important in these mediums, reaching several tens of g/L.
- ATR-FTIR analysis confirms that metal solubility is associated with the formation of coordination complexes between FFA ligands and iron central atoms. Initial measurements suggest a dominating bidentate bridging coordination mode.
- Vegetable and waste oil composition evolves during heating potentially releasing additional FFA and other corrosive species.

Recommendations for future research on this area can also be provided. Two important axes are highlighted. First, it would be important to evaluate the effect of temperature on the corrosiveness of these types of oils. For carbon and low alloy steels, this would allow constructing engineering diagrams to determine safe operating envelopes related to temperature and acid values. The second axis is associated with the corrosion resistance of stainless steels and the impact of molybdenum as alloying element. Indeed, austenitic grades without Mo such as AISI 321 or AISI 347 are also commonly found in refineries. Furthermore, the good corrosion resistance of AISI 316L was demonstrated up to 220 °C, but higher temperatures can be found during hydrotreatment of vegetable and waste oils. For the industrial application, material compatibility needs to be verified up to temperatures of 300 - 350 °C.

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Supplementary material

Several pictures are provided as supplementary material, as they are not essential for the understanding of the test results. They include:

- metallographic observations of the steel specimens
- pictures of a selection of industrial oils taken before and after the tests illustrating changes of visual aspect

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