

Converting Hydroprocessing Equipment to Produce Renewable Diesel from Soybean and Corn Oil: Corrosion and Materials Considerations

Nathaniel Sutton, Ken Kirkham
E²G | The Equity Engineering Group, Inc.
20600 Chagrin Blvd., Ste. 1200
Shaker Heights, Ohio 44122
USA

ABSTRACT

Around the globe, refiners are seeking to convert an increasing portion of existing Hydroprocessing capacity to process renewable feedstocks. Facilities face economic pressure to bring renewables production online quickly, in order to take advantage of the current government incentives (credits) for renewable fuels. Simultaneously, however, materials and corrosion engineers face a lack of data-based guidance regarding the appropriate materials selection and expected damage mechanisms for renewables processing units. This paper discusses many of the major damage mechanisms which are considered most relevant in different areas of the RDU – Renewable Diesel Unit (e.g., feed, hot effluent, cooled effluent, etc.). Significant attention is devoted to fatty acid corrosion in the feed system, and lower-temperature aqueous acid corrosion in the cool effluent system. Specific considerations must be made when an existing unit is converted into an RDU, compared to new construction. The source and precise blend of renewable feeds and the extent (if any) co-processing with conventional petroleum feeds impact the susceptibility to certain damage mechanisms throughout the unit. Upstream pretreatment processes can have unique implications on the expected corrosion in the RDU.

Key words: Renewables, Fatty Acid Corrosion, Carbonic Acid Corrosion, Hydroprocessing, Corn Oil

INTRODUCTION

As governments around the world seek to promote the adoption of lower-carbon fuels, credits are available for fuels which satisfy various low-carbon or renewable fuels standards. In the United States, the most common standards discussed include California's Low Carbon Fuels Standard¹ and the US EPA's Renewable Fuel Standard². These standards define the acceptable methods (called pathways) for conversion of renewable feeds into consumer fuel products. In order for a producer to be eligible for credits, one of the acceptable pathways must be used. The most common pathway presently being used or considered by most facilities is hydrotreating.

A critical factor in determining the profitability of a new renewable diesel unit (RDU) is the speed with which the producer can bring their products to market in states or countries offering renewable fuels credits. Currently, credits incentivizing RDU projects are readily available, and the volume of renewable

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feedstocks being diverted from traditional consumers (namely livestock feed) has not significantly impacted feedstock prices. One of the advantages of hydrotreating renewable diesel over other low-temperature renewable fuel pathways (e.g., transesterification into biodiesel) is that the hydrotreating reaction is less sensitive to poor feed quality aspects, such as elevated organic chloride, free fatty acid content, or peroxidized (spoiled) lipids. As a result, RDU operators can take advantage of lower-cost feeds which are not suitable for other uses. A thorough discussion can be found in the next section.

As additional RDU units come online, however, there will simultaneously be greater demand for the feedstock oils, as well as increased competition for the available credits/incentives provided by various governments. Furthermore, once renewable infrastructure is established, the need for strong incentivization will decrease, causing the supply of credits to wane. Both factors could potentially reduce the profitability of RDU units.

CHARACTERISTICS OF RENEWABLE FEEDS & PRODUCTS

To facilitate an effective discussion of damage mechanisms in renewables processing, an understanding of the terminology related to renewable feeds and fuels is necessary. Furthermore, the fundamental characteristics and chemical nature of renewable feeds bears on their corrosion behavior and should be discussed

Renewable Feedstocks, defined

Feed oils for renewable fuels can generally be classified as bio-oils or bio-mass oils.

Bio-oils

Bio-oil typically refers to lipids from plants, animals, and algae. This includes vegetable oils, animal fats, greases, and other oils where the molecules exist in nature as lipids. These lipids are a mixture of triglycerides & free fatty acids (FFA). A triglyceride is simply a combination of 3 fatty acids, attached to a glycerol to form a larger molecule³. Another name for triglyceride is triacylglycerol⁴. In some bio-oils, phosphorous-containing groups replace one of the fatty acids of the triglyceride. These are referred to as phospholipids and are relevant since phosphorous can act to poison Hydroprocessing catalysts^{5,6}.

Conveniently, in many vegetable and animal lipids, the fatty acids have a hydrocarbon chain length comparable to that of distillate-range petroleum oils (C12-C20)^{7,8}. Bio-oils serve as the feedstock for *nearly all* renewable and bio-diesel production. The fatty acids which make up bio-oil triglycerides are named based on their carbon chain length and the number of double bonds along this chain (level of unsaturation). Unlike shorter-chain organic acids (formic [C1], acetic [C2], propionic [C3], etc.) which share the root of their name with the alkane of the same length, the names of the fatty acids which comprise bio-oil triglycerides do not obviously indicate the chain length. For example, palmitic acid has a 16-carbon chain and no double bonds (i.e., it is saturated), while palmitoleic acid has a 16-carbon chain and one double bond (i.e., it is mono-unsaturated)⁴. The predominant chain length in most vegetable oils is 18, and a variety of levels of unsaturation are observed including stearic (saturated), oleic (1 double bond), linoleic (2 double bonds) and linolenic (3 double bonds)^{7,8}. Bio-oil triglycerides are sometimes named with three letters to denote the three constituent fatty acids, e.g., LNO = Linoleic, Linolenic, Oleic or POO = Palmitic, Oleic, Oleic⁹.

Biomass-oils

Biomass oils, in contrast, originate from cellulosic material that does not have readily-extractable lipids. The molecules comprising biomass oil do not exist as lipids in nature, but rather must be made by breaking down larger cellulose molecules¹⁰. Sources of cellulosic material for biomass oil include crop residues, woody biomass, dedicated energy crops, and other plant-based agricultural wastes. Biomass-oils require different and additional pathways from those used to upgrade bio-oils. The most viable method is pyrolysis, during which high-temperature oxygen-free thermal cracking is used to decompose

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(crack) cellulosic material into smaller molecules¹¹. However, gasification and liquefaction pathways have also been explored, each with alternative challenges¹².

Biomass-oils have different corrosion properties than bio-oils. The former contain lighter organic acids in varying fractions which depend on their origin and processing pathway^{10,13}. The resulting oils vary in boiling point (LPG range through distillate range). Generally, biomass oil technologies have not been widely adopted at this point. Therefore, this paper will focus primarily on handling of bio-oil feeds.

Renewable Fuel Products, defined

Distinction must be made between renewable diesel and biodiesel. Biodiesel is produced through transesterification to convert the fatty acid feed into an ester (FAME – fatty acid methyl ester). Biodiesel must meet ASTM D6751¹⁴ and is approved for blending with petroleum diesel in limited amounts. B5 (5% biodiesel) is the most common blend for existing diesel engines¹¹.

In contrast, renewable diesel is a “renewable hydrocarbon biofuel.” Multiple pathways are defined by the US Dept. of Energy for renewable diesel production. However, the most common is hydrotreating. Renewable hydrocarbon biofuels are chemically identical to their petroleum-based counterparts: gasoline, diesel, or jet fuel. They must meet the same ASTM fuel quality standards as petroleum fuels (ASTM D975¹⁵ for petroleum diesel), and they can be used in existing engines and infrastructure without blending limits. For this reason, they are sometimes called “drop-in” biofuels.

Chemical Characteristics of Bio-Oils:

During the development of the diesel engine, its inventor, Rudolf Diesel envisioned that it could utilize pure vegetable oil as fuel, in addition to petroleum distillates¹⁶. In fact, as early as 1900 the French government sponsored research which led to the successful use of peanut oil in diesel engines. The motivation was to confirm the viability of vegetable oils as an alternative diesel fuel in remote areas where petroleum fuel may not be readily available, but vegetable oils were¹⁶. As petroleum-based diesel became ubiquitous, the need for vegetable oil fuel diminished, and the modern diesel engine evolved to the point that no longer burn unrefined vegetable oils. In the second half of the 20th century, various international political factors (wars, embargos) and, later, environmental concerns, prompted renewed interest in the use of vegetable oils as commercial fuel. The biodiesel transesterification process, developed decades prior, was revisited to make the first modern FAME-based biodiesel. The first US commercial production of biodiesel came online in 1991¹⁷.

Biodiesel transesterification processes are numerous, but generally use an aqueous catalyst with alcohol (e.g., methanol) to provide the methyl group for FAME¹¹. Pure vegetable oil with very low FFA content can be trans-esterified with alkaline catalysts. However, in bio-oil with more FFA, alkaline catalysts will result in saponification (i.e., formation of soap – technically, formation of carboxylate salts which dramatically stabilize the oil-water emulsion). Even the alternative acid catalyst esterification is challenged by high-free fatty acid feeds, requiring water removal and high alcohol-to-oil ratios¹⁸. Biodiesel is fundamentally limited by these feed quality restrictions as well as by its blending limits in the commercial diesel pool.

Both biodiesel and renewable diesel can be made from any number of vegetable oils, including soy, corn, canola (rapeseed), or animal lipids such as tallow and white grease. By far, the biodiesel feed stream is dominated by soybean oil, with 54% of all biodiesel coming from soybean oil in 2018, compared to 15% from corn oil¹⁹. Soybeans, by weight are about 80% meal and 20% oil. Soy meal is used almost exclusively for animal feed, with very little meal going to consumer food products; soybean oil primarily goes to food products (68%) and to a lesser extent, biodiesel (25% as of 2016), with minor other uses <10%²⁰ [. In contrast, in 2020, about half of corn produced in the US has gone to fuel ethanol production, and half to animal feed, with <10% going directly to other uses such as food, seed, and industrial applications²¹.

Fuel ethanol production results in vast quantities of spent distillers' grains, which have traditionally been used in animal feed. Increasingly, however, corn oil is being extracted as a co-product from distiller's grains. This co-product corn oil is not used for human consumption but can be used as an animal feed ingredient. The various milling, steeping/cooking, and extraction processes to which the grains are subjected affect the quality of the oil co-product, most noticeably its free fatty acid content. Subsequent handling and storage can result in peroxidation (spoilage) of some unsaturated fats in the oil^{7,22}. It was previously thought that high-FFA oils would have lower metabolic energy values when used as animal feed, but this may not be true⁸. In any case, concerns for low metabolic value of animal feed due to high FFA and peroxidation mean that there is a wealth of research on these aspects.

A major advantage of hydrotreating as a pathway for renewable diesel is its ability to accept high-FFA, even oxidized (spoiled) oils which cannot be used for biodiesel production or animal feed. The relatively severe hydrotreating conditions and catalysts will readily hydrogenate C-O bonds in FFAs and peroxidized lipids, as well as double bonds just as they do in triglycerides^{5,6}. The primary concern, then, lies in whether the process equipment can sufficiently resist corrosion from the lower-quality feeds. Unfortunately, given that interest in hydrotreating bio-oils is very recent (the first renewable diesel plant in the US, REG Geismar LLC came online in 2010²³), there is very little publicly available corrosion data for FFAs in hydrotreating environments.

Because of perceived similarities between vegetable oil FFA corrosion and conventional petroleum oil naphthenic acid corrosion (NAC), the total acid number (TAN) of renewable oils is used to describe its acid content. This is also done out of convenience: refiners looking to understand the general corrosivity of the renewable oil are familiar with TAN, and laboratories used to working with petroleum feeds are setup to run titrations for TAN. TAN and %FFA for a given oil can be converted if a representative molecular weight is known (or assumed)²⁴.

One of the challenges in testing the corrosivity of FFAs is that the TAN decreases over time²⁵ as the acid is converted into soluble iron naphthenate salts, no longer available to participate in corrosion. In an operating hydroprocessing unit, it may take an acid molecule only a few minutes to travel from the first feed effluent exchanger to the reactor inlet. Changes to the TAN of the oil stream may be irrelevant over this short duration. However, the decrease in TAN has had a significant impact on laboratory corrosion tests in fatty acids at high temperature. In particular, tests in petroleum oils with a finite number of naturally-occurring naphthenic acids (or a finite amount of added reagent organic acids) will experience a decrease in TAN over the test duration. Many benchtop corrosion tests use a duration of 24 hours or more, and the loss of acid can confound results and limit their applicability for plant decision making. For bio-oils, this is also true. At the same time, however, time at elevated temperature can result in lipid degradation²⁶. In this sense, while corrosion by fatty acids converts some into non-corrosive iron carboxylates, the lipid triglyceride provides a reservoir from which additional free fatty acids may be liberated²⁶. A more thorough discussion of free fatty acid liberation is found below.

For renewable diesel, the number of double bonds in a free fatty acid or in the constituent acids of a triglyceride is believed to have little direct effect on the corrosion characteristics, aside from the effect on the acid's boiling point. This is because the double bonds in bio-oil lipids are far-removed from the carboxylic acid; that is – the closest double bond to the acidic end of the fatty acid may be nine carbons away, as in the case of oleic acid^{6,27}. In contrast, shorter organic acids would be expected to be more acidic when a double bond is close to the carboxylic group of the molecule; for example, acrylic acid (C3), with a double bond only 2 carbons away from the carboxylic group, is significantly more acidic (based on a comparison of pKa values) than propionic/propanoic acid, with no double bonds²⁸. The double bonds in vegetable and animal lipids (C18-C20) are too remote⁴ to substantially increase the acidity of the molecule. Furthermore, the conventional understanding of boiling point vs corrosivity for petroleum naphthenic acid in crude/vacuum distillation units (low pressure) may not be applicable to high pressure hydrotreating streams. Generally, the number of double bonds is characterized by the iodine value (IV)⁷. Of course, the IV of particular acid, triglyceride, or bio-oil mixture may bear on the

expected hydrogen consumption. One caveat is that increasing numbers of double bonds can impact the corrosivity due to stearic hindrance²⁵, but at this time, to many gaps in the data exist for this to have a practical bearing on corrosion. In the opinion of the authors, the corrosion characteristics of oleic acid, for example, are not expected to be measurably different in practical operating scenarios, from those of lineoleic acid.

DAMAGE MECHANISMS IN RENEWABLE FUELS PROCESSING

Damage mechanisms in an RDU will differ substantially from those in conventional petroleum Hydroprocessing. With petroleum feeds, sulfur and nitrogen are the major feed impurities being removed. Some naphthenic acids if present, but naphthenic acid corrosion (NAC) is generally not a limiting damage mechanism. When NAC is a concern, sulfur-to-TAN ratios can often be maintained within an integrity operating window (IOW) to mitigate the phenomenon sometimes referred to as sweet-NAC corrosion. Materials selection in the high temperature section of most hydrotreaters is based on resistance to H_2/H_2S corrosion. This generally requires an 18Cr-8Ni stainless steel; to avoid sensitization, chemically stabilized grades such as 321 (18Cr-8Ni-Ti) or 347 (18Cr-8Ni-Nb). In the lower temperature effluent, ammonium chloride (NH_4Cl), ammonium bisulfide (NH_4HS) corrosion and wet H_2S damage become a concern.

In contrast, renewable feeds are very low in sulfur and nitrogen^{6,7}. High temperature FFA corrosion is the primary concern. Besides FFA, renewable feeds from certain sources (e.g., used cooking oil) can contain an appreciable amount of chloride, both organic and inorganic. In the lower temperature effluent, CO_2 corrosion and in some cases, condensing HCl corrosion can dictate material selection. Co-processing renewables with petroleum feeds has advantages and disadvantages, depending on the ratio and corrosive characteristics of the bio-oil and petroleum streams. In co-processed feeds where the renewable fraction has comparatively low FFA and the petroleum fraction sufficient sulfur, it may be possible to maintain a sulfur-to-TAN ratio of ≥ 0.5 {wt%-g/mg KOH}, i.e., $TAN/S \leq 2$ or more {mg KOH/g/wt%}. In co-processing effluents, sufficient ammonia may exist to neutralize carbonic acid. However, NH_4Cl , NH_4HS , and wet H_2S damage remain relevant mechanisms. Some of these are discussed in detail below.

It should also be emphasized that the RDU remains susceptible to many conventional Hydroprocessing damage mechanisms. During operation elevated temperature mechanisms such as High Temperature Hydrogen Attack H_2/H_2S corrosion and creep may affect equipment. During downtime, brittle fracture presents a concern. Brittle fracture is made more likely due to the effects of temper embrittlement and hydrogen embrittlement, for older-vintage hydroprocessing reactors. Polythionic acid stress corrosion cracking (PTASCC) may require special protections for 300-series stainless equipment.

High Temperature Fatty Acid Corrosion

Even in petroleum environments, naphthenic acid corrosion is difficult to predict. There is essentially no published data on the corrosion rates of common refinery alloys in high-TAN renewable feeds at the temperatures and pressures of concern for hydrotreaters. It is not the objective of this paper to present a comprehensive literature review. Indeed, other organizations, such as the Materials Technology Institute (MTI) are in the process of performing such reviews. Some operating companies or engineering & procurement contractors (EPC) have performed their own reviews of the literature to guide RDU projects. Much of the corrosion rate data yielded by such reviews is at conditions not relevant to Hydroprocessing units. Nonetheless, materials must be and have been selected by corrosion engineers with reasonable confidence that an acceptable service life will result.

One source of data is found in the forest products and soap industries. Although, by definition, the oils produced in pulp and paper operations are biomass oils, these must generally be refined in order to be used in other products. Tall oil, a co-product of Kraft pulp mills in the pulp and paper industry, and