

STAINLESS STEELS Cost-Efficient Materials for the Global Biofuels Industries

By Kristina Osterman



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STAINLESS STEELS COST-EFFICIENT MATERIALS FOR THE GLOBAL BIOFUELS INDUSTRIES

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Environmental Note:

Stainless steels and nickel alloys offer important environmental benefits. Their durability ensures long life: replacement, and the resource demand that makes, is minimized as operating efficiencies are improved. At the end of the life of the structure, the nickel alloys are completely recyclable. Overall, stainless steels and nickel alloys are exceptional life cycle performers in both the environmental and economic senses.

by Kristina Osterman Consultant to the Nickel Institute

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The Nickel Institute

The Nickel Institute is an international non-profit industry association actively involved with, and with key focus on, the development of sustainable and responsible usage of stainless steel and other nickel containing materials. The organization is active in all key end-use industries for stainless steel, offering guidance and neutral technical advice regarding their cost-efficient usage. The Nickel Institute has offices in Europe, North America, Japan and China.

This Publication

We are issuing this publication to help ethanol, biodiesel and biogas producers, process technology providers, developers as well as plant designers and operators, recognize those applications where economic benefits can be realized from selecting the appropriate grade of stainless steel.

Stainless Steels -Economic Benefits and Costefficiency for the Biofuels Industry

Executive Summary

Stainless steels are widely used in the global biofuels industry. Stainless steels have an excellent track record and are the materials of choice for numerous applications in bioethanol, biodiesel and biogas production facilities. Stainless steels offer excellent corrosion resistance in the biofuels industry's various process conditions, coupled with good strength, ductility, toughness and ease of fabrication.

Stainless steels are readily available worldwide in a wide variety of product forms. In addition, stainless steels are easily maintained to give an attractive, hygienic, high-tech appearance. The 100% recyclability of stainless steel supports the biofuels industry's long term sustainability concepts and goals.

Although the cost of stainless steel products such as pipe, weight for weight, is significantly higher than for carbon steel and other possible materials, there is sometimes a perception that they are "too expensive", and that they should be confined only to the most corrosive applications. However, the advantages of stainless steels allow them to be used cost-effectively. This has been demonstrated extensively and successfully in both ethanol and biodiesel plants in all main geographic producing regions.

An increasing number of biofuels process engineering companies specify stainless steel for a considerable share of the production equipment. Often using stainless steels allows designers to use lighter walled piping systems, or thinner walled tanks and process vessels. This results in construction, handling and fabrication costs which are frequently lower when stainless steels are used compared to much heavier carbon steels.

Standard austenitic stainless steels Type 304(L) and Type 316(L) are capable of meeting most of the corrosive conditions encountered in ethanol, biodiesel and biogas production and handling equipment, and are therefore widely used and recognized as cost-effective and reliable materials solutions. For superior corrosion resistance in certain more corrosive applications, duplex, super-austenitic and nickel alloys will be suitable. Some high temperature applications in cellulosic ethanol production may also require special stainless or nickel alloys.

The ethanol industry is dynamic, fast changing and ambitious, with ongoing research and process development. Optimizing and adjusting existing corn, wheat and other feedstock-based production technologies while finding ways to minimize production costs and maximize yields are key issues within the ethanol industry. For its future growth and long term potential this industry must develop efficient and cost competitive cellulosic/biomass ethanol process designs, based on the use of sustainable, nonfood supply interfering, ecologically friendly feedstocks. In recent years, considerable progress has been made and promising technologies for producing ethanol from cellulose have started to emerge. Commercial-scale cellulose ethanol plants are now in operation as well as under construction.

The challenges and the objectives of the biodiesel industry are similar. Existing soya bean, rapeseed and canola technologies keep evolving and producers are looking for ways to optimize quality and maximize yields, and for cost-savings and cost-efficiency improvements. In parallel to this, the biofuels industry is developing new technologies based on non-food feedstocks, such as algae and jatropha. Ecological issues, sustainability and profitability are key issues and long term drivers.

The biogas industry can present numerous shining examples of profitable biogas plants operating in various parts of the world, principally producing methane by anaerobic digestion or fermentation of biomass, manure, animal and farm waste, sewage, municipal waste and other waste product feed-stocks. The biogas plants naturally produce all their required operating power and in addition, the required power to light up and heat nearby communities and towns.

There is no doubt that the growth prospects of these industries are considerable. Laws, mandates and government policy and incentives facilitating their development and growth are in place in numerous countries in the world, in various ways. Global ethanol production in 2011 was 105.6 billion liters (33.5 billion liters in 2003) and market analysts predict compound annual growth (CAGR) of 4.4% in the next 8 years.



Biodiesel production in the world reached 23.6 million liters and is forecast to grow at 3.5% CAGR, translating into some 32 million liters by 2020 (source: Global Data).

Many industry participants believe that the future lies in bio-refineries which integrate biomass conversion processes and equipment to produce fuels, power and chemicals from biomass. Industrial bio-refineries have been identified as the most promising route to the creation of a bio-based industry in many countries.

The trend is clearly towards stronger awareness of costefficiency in these industries, which will take more and more notice of such issues as it grows and develops. Biofuels plants will be looking for reliability, low maintenance costs and long lasting production equipment. Stainless steels actively contribute to these objectives and bring considerable value to the biofuels industry.

Panel 1:

top: Neste Oil Biodiesel Plant, Rotterdam © Neste Oil **middle:** Verbio Biofuel and Technology Biodiesel plant, Germany © Verbio Biofuel and Technology **bottom:** Transesterification Plant in South America © Crown Iron Works

Panel 2:

top: Advanced steam system in lignocellulosic ethanol pretreatment system, © Adritz Ltd middle: Steam reactor for lignocellulosic ethanol, plant

middle: Steam reactor for lignocellulosic ethanol plant, © Andritz Ltd

bottom: Scale reactor feed unit for lignocellolosic ethanol system, © Andritz Ltd

Panel 3:

top: Inside logen Corporation's ethanol plant © logen Corporation

middle: Stainless steel tank for the US ethanol industry © Apache Stainless Equipment Corporation

bottom: Storage tanks, exhuast chimney, Ethanol plant, Canada, iStock photo © SimplyCreativePhotography

Applications for stainless steel and the many benefits

Stainless steels perform well under the conditions of the ethanol, biodiesel and biogas industries. Table 1 here below, lists proven applications for stainless steel in the biofuels industries.

| TABLE 1: PROVEN APPLICATIONS OF STAINLESS STEELS IN ETHANOL, BIODIESEL AND BIOGAS PLANTS | | | |
|--|-----------------------------------|-------------------------|--|
| Ethanol Plants | Biodiesel Plants | Biogas Plants | |
| Corn steepers in wet mills | Acid pretreatment systems | Fermenters | |
| Liquefaction tanks | Caustic pretreatment systems | Digesters | |
| Fermentation tanks | Reactors | Pumps | |
| Yeast slurry tanks | Acid tanks | Slurry processing | |
| Beer well tanks | Decanters | Gas piping systems | |
| Fermentation washing tanks | Centrifuges | Air pollution control | |
| Distillation columns | Slurry tanks | Liquid fertilizer tanks | |
| Whole stillage tanks | Flash tanks | Gas holders | |
| Centrate surge tanks | Receiving tanks | Air piping systems | |
| Centrifuges | Condensate tanks | Steam systems | |
| Thin stillage tanks | Buffer tanks | Fittings | |
| Syrup tanks | Internal process tanks | Gas turbines | |
| Dryers | Dryers | Gas engines | |
| Evaporators | De-acidification columns | Storage tanks | |
| Evaporator condensate tanks | Rectification columns | Various tanks | |
| Pumps | Distillation columns | Heat exchangers | |
| Mixers | Methanol recovery tanks | Mixers | |
| Valves | Pumps | Pumps | |
| Filters | Mixers | Agitators | |
| Regulators | Agitators | Valves | |
| Piping systems & required fittings | Valves | Modules | |
| Heat exchanger tubes | Filtration & purification systems | | |
| Skid systems | Regulators | | |
| Emission control equipment | Piping, tubing | | |
| Pre-treatment systems | | | |

Combined with their corrosion resistance are stainless steel's excellent mechanical properties - good strength, ductility and toughness. These attributes result in several advantages:

- Properly chosen, the corrosion rates in most applications are close to zero, allowing for design without any additional increase in thickness as a "corrosion allowance". With very low corrosion, the products are not contaminated by the material of construction. With low corrosion rates, there are minimal maintenance requirements.
- There is no dependence upon applied coatings for corrosion protection. No constituents of the coatings are lost into the ethanol and biodiesel and there is no coating maintenance.
- Their strength and ductility mean that the weight of a component can be reduced in many cases and resistance to impact damage during operations is enhanced.
- The clean smooth inner surface of the stainless steel is useful in piping systems, allowing for free and easy flow with minimal friction losses. There can be many tens of thousands of linear metres of pipe in an ethanol or biodiesel plant

| TABLE 2: RELEVANT ATTRIBUTES OF STAINLESS STEELS FOR THE BIOFUELS INDUSTRY | | | |
|--|---|--|--|
| Characteristics | Advantages conferred | | |
| High corrosion resistance | Low maintenance, long life and consistent operation | | |
| Smooth surface | Resists formation of deposits, no contamination, lower energy consumption in pumping, lower cleaning costs, good for conveying wet solids | | |
| Good weldability | Most fabricators have experienced stainless steel welders, suitable for in-shop and on-site welding | | |
| Low weight/Thinner wall thickness* | Simpler construction and erection – an advantage both for tank construction and piping systems | | |
| Good mechanical properties, good ductility at all temperatures | Strong, durable, suitable for all extremes in weather | | |
| Good wear and fatigue resistance | Low maintenance and long life | | |
| Materials covered by well-defined international standard specifications. | Easy to specify and ready availability globally in most product forms | | |
| Recyclable with residual value at end of life | Low environmental impact, compatibility with long term industry sustainability goals | | |
| Attractive appearance | Clean, hygienic, high-tech image | | |
| No corrosion or leachant products, no organoleptic or turbidity problems (in food grade ethanol) | Do not contaminate the food or animal product, do not change the flavor and are approved and standard material worldwide in food production | | |

*compared to carbon steel

Stainless steels offer excellent corrosion resistance. In many cases, the life cycle cost of a plant can be reduced by using stainless steels, arising from a combination of installation, reduced maintenance and extended life benefits. The low level maintenance requirements associated with using stainless steel makes the material highly appealing to the biofuels industry. With the use of stainless steel comes peace of mind and the economic benefit associated with consistency in operations, instead of sporadic shut downs in order to deal with maintenance or corrosion prevention issues. The smooth surface of stainless steel over its lifetime comes with many advantages. It resists the formation of deposits, resulting in no contamination issues and low cleaning costs. It also results in low energy consumption in pumping and benefits for conveying wet solids.

In addition, stainless steels exhibit good weldability. Most fabricators have experienced stainless steel welders on staff and the welding can easily be performed both in-shop or on-site.

Ethanol

General Process Conditions

Ethanol production processes can be considered moderately corrosive. In an ethanol plant, the pH ranges from about 5.8 to 2 (slightly to moderately acidic) in most parts of the production process. Temperatures are often relatively low, with a few exceptions where they may reach 115°C (240°F). (The pre-treatment stage of cellulosic ethanol production will be discussed separately.) Standard austenitic stainless steels are therefore widely used and recognized as cost-effective and reliable materials solutions.

We estimate that close to 90% of stainless steel used in existing ethanol plants is accounted for by Type 304 (UNS S30400) or its low carbon version, 304L (S30403) stainless steel. The "L" grade is preferable where welding will be done. These popular stainless steel grades often



meet the required corrosion resistance and are readily available in all required product forms all over the world. For the purpose of this report, the designation 304(L) will indicate either 304 or 304L and 316(L) will indicate either 316 or 316L.

304 (L) UNS S30400 is the most suitable stainless steel grade and accounts for the largest share of all stainless steel usage. Where the operating conditions in the ethanol production process are more corrosive due to higher temperatures and the presence of acids and other potentially corrosive agents, 316(L) UNS S31600 stainless steel will often be specified. Specialty stainless and a range of other stainless steel grades are also regularly specified and used in today's ethanol plants.

When to Select 304(L), 316(L) or one of the Specialty Grades?

Dry milling – Wet milling

There are some differences between the stainless steel requirements for a dry milling and those for a wet milling corn ethanol plant. In dry milling, the stainless steel used is primarily Type 304(L). In the milling section of the wet milling process, Type 316(L) stainless will be specified for equipment as the corn will be steeped in a more corrosive solution, containing sulfur dioxide (SO₂) and lactic acid.

| TABLE 3: MAJOR STAINLESS STEEL GRADES USED IN BIOFUELS (ETHANOL) PLANTS | | | |
|---|--------|--------------------|---|
| Common name | UNS | EN | Attributes |
| 304 | S30400 | 1.4301 | Good general corrosion resistance to slightly acidic as well as caustic media. Minimum strength level slightly higher than for the "L" grades. |
| 304L | S30403 | 1.4307 | As above, but L" grades are preferred for welded constructions. Material can be usually purchased "Dual Certified" meeting the requirements of both 304 and 304L. |
| 316 | S31600 | 1.4401 / 1.4436 | Improved corrosion resistance in most acidic conditions, especially at higher temperatures and/or with chlorides present |
| 316L | S31603 | 1.4404 / 1.4432 | As above, but L" grades are preferred for welded constructions. Material can be usually purchased "Dual Certified" meeting the requirements of both 316 and 316L. |

There is a similar scenario regarding materials used for evaporators and dryers. In a dry milling ethanol plant, this equipment will typically be made from Type 304(L). The same equipment used in wet milling plants will be preferably made of Type 316(L) stainless steel, which offers improved corrosion resistance.

The Pre-treatment Phase in Cellulose Ethanol Production Technologies

The pre-treatment phase of cellulosic ethanol process designs can be considerably more corrosive than the rest of the production process. This is particularly the case in plants using acid hydrolysis to break down the lignin, where the biomass is treated with diluted sulfuric acid at high temperatures (up to 240°C / 460°F) and under high pressure. This operating environment is highly corrosive and often nickel alloys such as Alloy C276 (UNS N10276) and other C-type nickel alloys must be used.

A somewhat less corrosive process is the concentrated acid hydrolysis process, using higher sulfuric acid concentrations but much lower temperatures.

Many pre-treatment process technologies are based on enzymatic hydrolysis, which require some kind of pre-treatment process to break-down the crystalline structure of the lignocellulose and to remove the lignin to liberate the cellulose and hemicellulose molecules. Depending on the biomass feedstock, physical or chemical methods will be used. Some of the most costeffective technologies may involve a combination of an acid pre-treatment stage and enzymatic hydrolysis. Various stainless steel grades and nickel alloys have been tested and used for the pre-treatment production equipment in both pilot plants and commercial plants. These include Types 316(L) and 316Ti (S31653) and specialty stainless grades, such as 904L (N08904), duplex 2205 (S32205) and super duplex grades such as 2507 (S32750). Super-austenitic 6% molybdenum alloys have been tested and used, the proprietary names for these grades include 254SMO® and AL-6XN®.

Thermochemical technologies can also be used for biomass pre-treatment processing. Specialized high temperature alloys may be required for equipment used in the related operating environments.



Inside logen Corporation's ethanol plant © logen Corporation

Stainless Steel Usage in Brazil's Sugarcane Ethanol Industry

Stainless steels are also increasingly used in the integrated sugar/ethanol plants in Brazil. Carbon steels are more commonly used in the sugar plants, while the distilleries typically use stainless steel. The use of carbon steel in sugar plants causes frequent wear and corrosion issues, which many plants have eliminated by switching to stainless steels.

For example, where sugar cane is fed on a conveyor to be transported to the crushing mill, carbon steel suffers severe erosion and wear. Donnelly chutes are often made from Type 304(L) or S20400. A 12% Cr stainless steel called 410D (S41003) in Brazil has sometimes been used because it has improved erosion and abrasion resistance over carbon steel and lower cost than the higher alloyed stainless steel grades.

In several other areas of sugar plants where corrosion is more severe, Type 304(L) will be used. In South America, ferritic stainless steel S43932 (a modified Type 439 type) and Type 444 (S44400) are commonly available, especially in thinner sheet thicknesses, and therefore often used.

Types 304L, S43932 and/or 444 stainless steels are suitable for most applications in a sugar mill, such as in the cane juice extraction process (ducts, diffuser top), steam generation process, cane juice treatment and evaporation process, and in the sugar milling. Types 444 and S43932 are not recommended for the sulphitation (addition of SO₂) stage of the process, where columns require 316(L) stainless. The distillation columns are also typically made of either Type 304(L) or 316(L) stainless steel.

Stainless Steels

Piping, Tubing and Fittings

Ethanol plants require substantial amounts of pipe, tubes and fittings – an estimated 75% of which is stainless steel. The amount of piping in an ethanol plant varies by plant design and size. One leading process technology provider's design uses 15,500 linear metres in a 200 million liters/year ethanol plant and 29,000 linear metres in a 400 million liters/year plant. Another major process technology company, on the other hand, uses some 15,000 linear metres in a 200 million liters/ year plant but 20,000 linear feet in a 380 million liters/ year plant. The diameter of the piping will depend largely on the capacity of the ethanol plant.

Type 304(L) accounts for the vast majority of the stainless steel pipe and fittings required. In the US, some 80-90% of the pipe used is ASTM A 778 as-welded pipe, together with ASTM A 774 as-welded fittings, also in Type 304(L). Ethanol plants in Canada have opted for a higher quality of product, using ASTM A 312 (welded and annealed) in Type 304(L) but also Type 316(L) where required. The Types 304(L) and 316(L) fittings used in Canada are specified to ASTM A 403 Class WP, similarly welded and annealed.

Heat exchangers in ethanol plants require Type 316(L) stainless tubes. Tubing for evaporators can be either type 304(L) or 316(L). Brazil's sugar cane ethanol industry also uses Types 444 and S43932 for evaporator tubing. In Europe Type 304(L) is commonly used and at times Type S43932 will also be suitable. The cleaning systems and chemicals used, which may contain strong chemicals, will impact material choices for evaporators.

The power washing CIP (Cleaning-In-Place) systems required in ethanol plants to clean fermentation tanks use caustic soda with an acid rinse. The evaporators require regular cleaning due to scale build up. Stainless steels are used within the CIP system, with Type 316(L) in heat exchangers and in the associated piping systems. Various components within the sulfuric acid skid systems typically use N08020 (Alloy 20).

Other Applications for Stainless Steel

The numerous mixers in ethanol plants are mostly made from Type 304(L) stainless steel but also from Type 316(L) or Alloy 20. It is expected that the usage of the Type 316(L) alloy will increase when commercial scale cellulosic ethanol plants will be built.

Decanter centrifuges are mostly made from Type 316(L), but also from Type 317L (S31703) and 2205 duplex.

The numerous processing pumps at ethanol plants are made from cast Type 316 (ACI CF8M) or Type 316L (CF3M) stainless steel, but increasingly also from duplex cast alloys, such as ASTM 890 Grade 1B (ACI CD4MCuN), 3A (CD6MN) or 4A (CD-3MN).

Leading pump manufacturers indicate that some 60-70% of pumps supplied to ethanol plants are made of Type 316(L) and 30-40% of one of the duplex alloys. There has been a clear increase in the use of duplex grades in the last 5 years. Duplex alloys are more erosion-corrosion resistant, performing well where solid particles are present.

Ethanol plants also use stainless steel valves, filters, regulators, quills, thermo-compressors, steam ejectors, screens and various other parts and components, mainly made from Types 304(L) and 316(L). Alloy 20 is also used in sulfuric acid environments. Applications for Type 304(L) stainless can also be found in emission control equipment used by ethanol plants to control air pollutants and odor emissions.



Discharge device made from a nickel alloy, pretreatment system, Andritz Ltd

| TABLE 4: SPECIALTY STAINLESS STEELS AND NICKEL ALLOYS USED IN ETHANOL PLANTS. | | | |
|---|---------|---------|--|
| Common name | UNS | EN | Attributes |
| 316Ti | S31635 | 1.4571 | Similar to 316 in corrosion resistance, higher strength at elevated temperatures |
| 317L | S31703 | 1.4438 | Slightly more corrosion resistant than 316L |
| 904L | N08904 | 1.4539 | Excellent corrosion resistance in sulfuric acid |
| Alloy 20 | N08020 | 2.4460 | Excellent corrosion resistance in sulfuric acid |
| 6% Mo alloys | various | various | S31254, N08367 - used in very acidic or high chloride conditions |
| N30 | S20400 | - | Improved sliding abrasion wear properties over 304 |
| 2101 | S32101 | 1.4162 | One of several lean duplex alloys with high strength, suitable for large tanks |
| 2205 | S32205 | 1.4462 | Duplex alloy, higher strength and better corrosion-erosion resistance than 300-series alloys |
| 2507 | S32750 | 1.4410 | One of several superduplex alloys, higher corrosion resistance than 2205 |
| 410D | S41003 | 1.4003 | Very low alloyed stainless steel, improved wear resistance over carbon steel, especially used in Donnelly chutes |
| 439-modified | S43932 | 1.4510 | Somewhat close to 304 in corrosion resistance, used especially in Brazil |
| 444 | S44400 | 1.4521 | Somewhat close to 316 in corrosion resistance, used especially in Brazil |
| Alloy C-276 | N10276 | 2.4819 | Nickel-base alloy used in extremely corrosive conditions |

Tanks for food-grade ethanol will be constructed using stainless steels, typically Type 304(L). Some of the new high strength lean-duplex grades such as S32101 will be suitable for the very large tanks that use heavier plate.

Summary

Stainless steels are used extensively in the current ethanol industry, providing a long, maintenance-free life. As new processes are commercialized, their usage will only increase. Properly chosen and fabricated, stainless steels will be the material of choice for generations to come.

Biodiesel

General Process Conditions

The biodiesel production processes can be considered moderately corrosive. Although the base catalyzed transesterification process runs at low temperatures of around 50°-70°C up to 120°C (250°F) and low pressure, the process environment becomes quite corrosive due to the presence of free fatty acids (FFA) from feedstocks, as well as acids (hydrochloric and sulfuric), solvents and chemical catalysts (sodium or potassium hydroxide or methylate) injected into the process. In addition, the presence of any chlorides can further increase the corrosiveness.

The operating environment will be impacted by the type of feedstocks used and by the FFA levels that the various feedstocks contain. Soybean, canola, rape seed, palm and jatropha oils have lower FFA content than waste cooking oils and animal fats, such as used frying oil, trap grease, yellow grease, chicken fat, leather fat etc. Waste oils and animal fats (among others)also may contain chlorides.

Biodiesel process engineering companies design their plants for a blend of feed-stocks and must choose materials accordingly. Stainless steels meet the materials requirements of biodiesel plants, offer ease of maintenance and longevity. Our estimate is that approximately 80% of the production equipment in today's biodiesel plants is made from stainless steel. Most leading biodiesel process engineering companies specify stainless steel for the vast majority of the biodiesel production equipment.

However, depending on the particular process technology, some biodiesel process engineering companies specify more stainless steel than others. The material requirements for large plants using a continuous process can be somewhat different (e.g. larger equipment, more stainless steel, more duplex and specialty alloys) from smaller biodiesel plants using batch technology. Batch technologies are more suitable for waste oils etc. Many U.S. firms have used batch technology. Continuous processes used in Europe and in industrial processes in the U.S. (to produce methyl esters for uses other than fuel) can use raw oils or may require refined oils. Batch processes provide excellent opportunities for quality control if variations in feedstock quality are common, such as with yellow grease and animal fats. Cost-efficient large scale



Neste Oil Biodiesel plant in Rotterdam

production of biodiesel requires continuous processes, which is the long term trend.

The general manager of a biodiesel plant in Canada recently made the following statement:

"Stainless steel was chosen as the most costeffective material as the biodiesel plant was designed for a 25 year life expectancy. Stainless steel offers ease of maintenance and longevity. When material and equipment costs were assessed, the cost difference between carbon steel and stainless steel was insignificant."

Standard austenitic stainless steels are widely used in biodiesel plants and are generally recognized as costeffective and reliable materials solutions. We estimate that 55-60% of stainless steel used in biodiesel plants is accounted for by Type 304 (UNS S30400) or its low carbon version, 304L (S30403) stainless steel. The "L" grade is preferable where welding will be done. These popular stainless steel grades often meet the required corrosion resistance and are readily available in all required product forms everywhere.

Type 316(L) stainless steel is also a popular grade



and is widely used in biodiesel plants (some 35% of stainless steels used). Specialty stainless steels, such as duplex 2205 and 2507 are also commonly used. A range of other stainless steel grades and some nickel alloys are also regularly specified and used in today's biodiesel plants.

Type 304(L) versus Type 316(L) and Specialty Stainless Steels

Type 304(L) is typically used in a wide range of applications in the more alkaline operating media of the biodiesel production processes. Depending on the process design, these may include storage, receiving, decanter and buffer tanks, batch process distillation columns and reactors with associated piping systems, other piping and tubing systems, methanol recovery and recycling systems etc.

Type 316(L) stainless steel is used in any of the environments where acids are present and when temperatures are higher. In the highest temperature acidic conditions, duplex 2205 and 2507 are used (see later).

Production equipment linked to the pretreatment or neutralizing process of high FFA containing feed-stocks typically requires Type 316(L) and/or duplex 2205 and 2507. Type 316(L) stainless steel is also used, for example, in pressure vessels, acid storage tanks, reactors and associated piping systems, separators, decanters, flash tanks, distillation columns, rectification columns and various other equipment. For many applications, the choice between Types 316(L) or 304(L) may depend on the process engineering company, as some have a preference for Type 316(L) over Type 304(L) and vice versa.

Duplex (austenitic-ferritic) alloys 2205 and 2507 offer excellent corrosion resistance in many acidic environments. The superior strength and increased stress corrosion cracking resistance enable wall thickness savings in large tanks and pressure vessels while increasing their reliability.

Duplex 2205 and 2507 are used where weak hydrochloric or sulfuric acids are present. In addition to the pretreatment systems, other areas of application for duplex stainless steels are in the washing and the glycerin removal process. Here temperatures can be in the 95°C to up to 160°C (200°F to up to 330°F) range. Combined with the presence of hydrochloric acid, high chloride content this becomes quite a corrosive operating environment.

Piping, Tubing and Fittings

Biodiesel plants require substantial amounts of pipe, tubes and fittings, the vast majority of which is stainless steel. The amount of piping in a biodiesel plant varies by plant design and capacity but 15 -20,000 linear metres of pipe and heat exchanger tube are certainly required. For the larger biodiesel plants requirements are in the range of 25 - 30,000 linear metres.

| TABLE 5: MAJOR STAINLESS STEEL GRADES USED IN BIODIESEL PLANTS | | | |
|--|--------|--------------------|---|
| Common name | UNS | EN | Attributes |
| 304 | S30400 | 1.4301 | Good general corrosion resistance to slightly acidic as well as caustic media. Minimum strength level slightly higher than for the "L" grades. |
| 304L | S30403 | 1.4307 | As above, but L" grades are preferred for welded constructions. Material can be usually purchased "Dual Certified" meeting the requirements of both 304 and 304L. |
| 316 | S31600 | 1.4401 / 1.4436 | Improved corrosion resistance in most acidic conditions, especially at higher temperatures and/or with some chlorides present |
| 316L | S31603 | 1.4404 / 1.4432 | As above, but L" grades are preferred for welded constructions. Material can be usually purchased "Dual Certified" meeting the requirements of both 316 and 316L. |
| 2205 | S32205 | 1.4462 | Duplex alloy, higher strength and better corrosion-erosion resistance than 300-series alloys, higher resistance to chlorides than 316L. |
| 2507 | S32750 | 1.4410 | One of several superduplex alloys, higher corrosion resistance than 2205 |

Stainless Steels

Both Type 304(L) and Type 316(L) are used in piping and tubing systems for biodiesel plants. Some process designs use up to 80% Type 316(L), while others limit the usage of 316(L) to some 50-60% of pipes and tubes and also use large amounts of Type 304(L). The piping systems linked to the reactor system are mostly Type 316(L).

Heat exchangers in biodiesel plants require Type 316(L) stainless tubes. Alloys 20 and C 276 are used in piping systems operating in hot sulfuric acid.

Other Applications for Stainless Steel

Leading pump manufacturers indicate that a large share of pumps supplied to biodiesel plants use Type 316(L) and duplex alloys 2205 and 2507. At times there are requirements for high alloyed grades such as 904L or the super-austenitic 6% molybdenum alloys (e.g. ALX6N®) and their cast equivalents. There can also be requirements for very hard and very high strength martensitic alloys, such as EN.14418 also known as 16Cr-5Ni-1Mo. Another such grade is S41500, also known as 410NiMo. The martensitic stainless steel grades have much lower corrosion resistance than even Type 304, but are useful in environments where the corrosion component is not so severe, but abrasion or erosion become important issues.

The numerous agitators and mixers in biodiesel plants are mostly made of Type 316(L). Biodiesel plants also contain stainless steel valves, filters, regulators, instrumentation and various other components and hardware, mainly from Types 316(L) and 304(L).

Biodiesel plants are equipped with several heat exchangers, which are made from Type 316(L), and at times from Type 304(L). Centrifuge decanters for biodiesel plants are made from Types 316(L), 317L and often also from duplex 2205.

Skids and frames can be stainless steel or carbon steel, depending on the plant.

Some of the new high strength lean-duplex grades such as S32101 will be suitable for the very large tanks that use heavier plate.



Biodiesel plant, Germany © Verbio Biofuel and Technology

Cost-efficient materials for the global biofuels industries

| TABLE 6: SPECIALTY STAINLESS STEELS AND NICKEL ALLOYS USED IN BIODIESEL PLANTS. | | | |
|---|---------|---------|--|
| Common name | UNS | EN | Attributes |
| 316Ti | S31635 | 1.4571 | Similar to 316 in corrosion resistance, higher strength at elevated temperatures, mostly used in Europe |
| 317L | S31703 | 1.4438 | Slightly more corrosion resistant than 316L |
| 904L | N08904 | 1.4539 | Excellent corrosion resistance in sulfuric acid |
| Alloy 20 | N08020 | 2.4460 | Excellent corrosion resistance in sulfuric acid |
| 6% Mo alloys | Various | Various | S31254, N08367 - used in very acidic conditions with high chloride |
| N30 | S20400 | - | Improved sliding abrasion wear properties over 304 |
| 2101 | S32101 | 1.4162 | One of several lean duplex alloys with high strength, suitable for large tanks |
| 2205 | S32205 | 1.4462 | Duplex alloy, higher strength and better corrosion-erosion resistance than 300-series alloys |
| 2507 | S32750 | 1.4410 | One of several superduplex alloys, higher corrosion resistance than 2205 |
| 410D | S41003 | 1.4003 | Very low alloyed stainless steel, improved wear resistance over carbon steel, especially used in Donnelly chutes |
| 439-modified | S43932 | 1.4510 | Somewhat similar to 304 in corrosion resistance, used especially in Brazil |
| 444 | S44400 | 1.4521 | Somewhat similar to 316 in corrosion resistance, used especially in Brazil |
| 16Cr-5Mo- 1Mo | - | 1.4418 | High hardness, very high strength |
| 410NiMo | S41500 | 1.4313 | High hardness, very high strength |
| Alloy C-276 | N10276 | 2.4819 | Nickel-base alloy used in extremely corrosive conditions |

Summary

Stainless steels are used extensively in the current biodiesel industry, providing a long, maintenance-free life. Properly chosen and fabricated, stainless steels will be the material of choice for generations to come.

Biogas

General Process Conditions

Biogas, principally methane and carbon dioxide is produced by the anaerobic digestion or fermentation of biomass, manure, sewage, municipal waste, green waste or energy crops. It can be considered moderately corrosive in nature, with the operating temperatures being relatively low and the operating conditions being mostly quite mild. However, during the biogas production by anaerobic digestion process, hydrogen sulfide and ammonia are formed in the digester, which increases the corrosivity. Also, when feedstocks such as municipal waste, manure and litter that contain chlorides are used, the operating environment becomes more corrosive. Some feedstocks can also cause issues with corrosion and erosion due various levels of sand content.

Standard austenitic stainless steels are widely used and recognized as cost-effective and reliable materials solutions in a wide range of biogas production equipment. In addition to stainless steels, tanks can be made from concrete or from coated or stainlessclad steel. The dominant share of stainless steel used in existing biogas plants is Type 304 (UNS S30400) or its low carbon version, Type 304L (S30403). The "L"



Biogas fermenters at Verbio Biofuel and Technology in Germany

grade is preferable where welding will be done. These popular stainless steel grades often meet the required corrosion resistance and are readily available in all required product forms everywhere.

Examples of applications for Type 304(L) are fermenters, slurry tanks, liquid fertilizer tanks and air pollution control systems. Piping and tubing systems in more alkaline operating media will be made from Type 304(L) stainless steel or from carbon steel. (Small scale agricultural biogas plants also use concrete and plastics).

Where the operating conditions in biogas production processes are more corrosive due to the presence of chlorides, acids and other potentially corrosive agents,

| TABLE 7: MAJOR STAINLESS STEEL GRADES USED IN BIOGAS PLANTS | | | |
|---|---------|--------------------|---|
| Common name | UNS | EN | Attributes |
| 304 | \$30400 | 1.4301 | Good general corrosion resistance to slightly acidic as well as caustic media. Minimum strength level slightly higher than for the "L" grades. |
| 304L | S30403 | 1.4307 | As above, but L" grades are preferred for welded constructions. Material can be usually purchased "Dual Certified" meeting the requirements of both 304 and 304L. |
| 316 | S31600 | 1.4401 / 1.4436 | Improved corrosion resistance in most acidic conditions, especially at higher temperatures and/or with chlorides present |
| 316L | S31603 | 1.4404 / 1.4432 | As above, but L" grades are preferred for welded constructions. Material can be usually purchased "Dual Certified" meeting the requirements of both 316 and 316L. |
| 316Ti | S31635 | 1.4571 | Similar to 316 in corrosion resistance, higher strength at elevated temperatures, mostly used in Europe |
| 904L | N08904 | 1.4539 | Excellent corrosion resistance in acid conditions including hydrogen sulfide |
| Alloy 20 | N08020 | 2.4460 | Excellent corrosion resistance in acid conditions including hydrogen sulfide |
| 6% Mo alloys | Various | Various | S31254, N08367 - used in very acidic conditions with high chloride |

Type 316 (UNS S31600) or Type 316L (S31603) stainless steel will often be specified. Examples of applications are digesters and its auxiliary equipment as well as all associated piping systems, whether in contact with liquid or with gas. Digestate tanks and gas piping systems are also very common applications for Type 316(L) stainless steel. For selected applications in high chloride process conditions with low pH value, some industrial scale biogas plants use higher alloyed stainless steels such as 904L or one of the superaustenitic 6% Mo alloys (e.g. ALX6N®or 254 SMO®).

Stainless steels are also widely used in various multi-fuel gasification technologies. An example is a plasma gasification system, which uses a variety of feedstocks: tires, municipal waste, sludge, biomass or coal to produce syngas. Stainless steels will be used in the equipment required for converting syngas into steam and power, fuels, hydrogen and other liquids and chemicals.

Stainless steels are also widely used in an innovative integrated multi-fuel gasification technology, enabling the production of syngas from any calorific waste, where the gas will further be used to generate energy by the use of a gas engine or turbine.

Many biogas plants are equipped with gas turbines, which contain stainless steels and nickel alloys.

Other Applications for Stainless Steel

Biogas plants will be equipped with pumps handling fluid media as well as gas pockets. All parts of the pumps that are in direct contact with either liquid or gas will be made from Type 316(L) or 316Ti. Agitators and mixers used at biogas plants are made from both Type 316(L) and 316Ti. There will be several tubular heat exchangers in the biogas production process. The most commonly used stainless steel in this application is Type 316(L); however, specialty stainless steels have also been used occasionally.

In addition, biogas plants use stainless steel fittings, valves and other parts and components.

Some of the new high strength lean-duplex grades such as S32101 will be suitable for the very large tanks that use heavier plate.

Summary

Major investment in large scale anaerobic digestion capacity expansion is anticipated in the time period 2012-2020, especially in Europe but also in North America and in the rest of the world. The use of stainless steels in current and future biogas plants will provide a long, maintenance-free life. Properly chosen and fabricated, stainless steels will be the material of choice for generations to come.



Verbio Biogas plant, Germany © Verbio Biofuel and Technology

Stainless Steels

For additional information on stainless steels and other nickel-containing alloys:

Nickel Institute – www.nickelinstitute.org ISSF (International Stainless Steel Forum) – www.worldstainless.org EuroInox (European Stainless Steel Development Association) – www.euro-inox.org BSSA (British Stainless Steel Association) – www.bssa.org.uk SSINA (Specialty Steel Industry of North America) – www.ssina.com ASSDA (Australian Stainless Steel Development Association) – www.assda.asn.au NZSSA (New Zealand Stainless Steel Development Association) – www.hera.org/nz/nzssda/ ISSDA (Indian Stainless Steel Development Association) – www.stainlessindia.org SASSDA (South African Stainless Steel Development Association) – www.sassda.co.za

Other Stainless Steel Development Associations include:

Brazil – www.nucleoinox.org.br China – www.cssc.org.cn France – www.construiracier.fr Germany – www.edelstahl-rostfrei.de Italy – www.centroinox.it Japan – www.jssa.gr.jp Mexico – www.cendi.org.mx Poland – www.cendi.org.mx Poland – www.cedinox.es Switzerland – www.swissinox.ch Thailand – www.tssda.org Turkey – www.turkpasder.com

Other associations:

IMOA (International Molybdenum Association) – www.imoa.info/ ICDA (International Chromium Development Association) – www.icdachromium.com



The Nickel Institute is an international, non-profit organization which promotes the production, use and re-use (through recycling) of nickel in a socially and environmentally responsible manner. We offer free technical knowledge about nickel, its properties and uses to ensure optimum performance, safe handling and use.

We are supported by most of the world's producers of nickel and have offices in Belgium, Canada, China, Japan and U.S.A.

For contact details, please visit our website www.nickelinstitute.org