Duplex Stainless Steels, a Cost Effective Option for Biofuel Facilities

Presenter:

Wachowiak, Devin
Academic Education and Degrees:
2005 Bachelor of Science in Mechanical Engineering,
University of Toledo, Toledo, OH
Presenter Professional Position:
Applications Engineer for Rolled Alloys, Temperance, MI

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Devin Wachowiak, Rolled Alloys, Temperance, MI

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Abstract:

The rising price of alloying components, such as nickel, have dramatically increased the costs for 304L and other high nickel bearing stainless steels, which are standard materials of construction in the design of ethanol and biodiesel plants.

Duplex stainless steels are a family of stainless steels that are lean in nickel and provide several distinct advantages as a material of construction in addition to their price stability. Lean duplex stainless steels, such as LDX 2101 and AL 2003 are leaner in nickel and molybdenum content in comparison to the duplex 2205 and superduplex 2507. The cost and availability along with the higher strength and corrosion resistance of duplex stainless steels has resulted in their use in several recent ethanol & biodiesel projects in North America and in Europe.

This session will review the importance of considering alternate materials of construction in plant design for ethanol and biodiesel tanks, process vessels, and other components in the biofuel process system during this period of time where metals prices and surcharges for stainless steels are at record levels. A review of the current and past projects that have opted to use duplex stainless steels as the material of construction will be discussed. Corrosion resistance and mechanical property comparisons between duplex stainless, 304L, and 316L will be reviewed along with examples of the cost savings that could be achieved with duplex stainless steel.

The conclusion of this session is that duplex stainless steels have many structural and corrosion resistant benefits to austenitic stainless steels that can provide a cost advantage in many different applications within an ethanol or biodiesel facility.

1 Introduction: The Rising Cost of Commodities Impact Stainless Steel Pricing

The rise in price of alloying components in stainless steel over the past several years, such as nickel, have dramatically increased the costs for 304L and other high nickel bearing stainless steels, which are standard materials of construction in the design of ethanol and biodiesel plants. With the increased amount of facilities being built and the cost of corn continuing to rise, another mean to reduce the cost of biofuel facilities is needed.

The number of ethanol and biodiesel facilities has been increasing considerably in the U.S. and around the world over the past several years with the price of oil rising every year. With the price of oil reaching over $140USD per barrel, one would think that ethanol and biodiesel manufacturing would be very competitive with gasoline. [1] However, with the increase in biofuel facilities, the demand of corn and other harvested crops has increased as well. This increased demand in crops has led to increased cost for the crops, high enough to raise the price of ethanol and other biofuels to levels approaching that of gasoline.

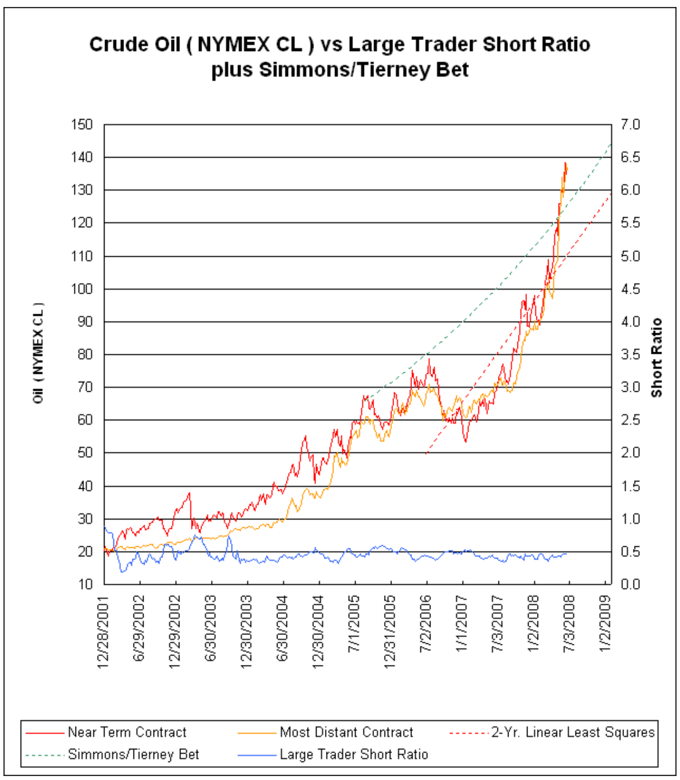

Fig. 1 Price of oil over past several years

Not only is the price of ethanol growing with the price of gasoline in the U.S., but also the number of fueling stations that offer E85 are still very low. In 2008, the number of U.S. fueling stations offering E85 surpassed 1,400 and continues to grow. Out of the 50 U.S. states, E85 stations are available in 45 of them. Out of those 45 states with E85 stations available, only 11 have over 50 stations in the entire state. As seen in Figure 2, only two states, Illinois and Minnesota, have over 100 E85 stations in the state. [2] According to the U.S. Census Bureau, as of 2002, there were 117,100 gas service stations in the U.S., meaning that 1 in every 84 gas stations now offer the E85 ethanol blended fuel.

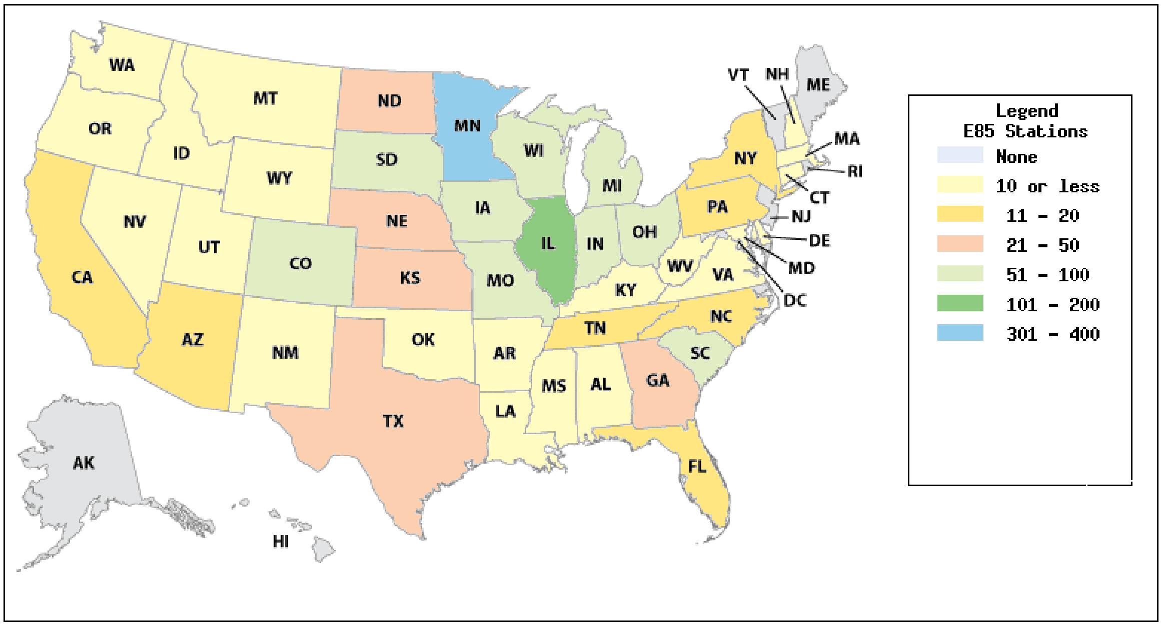

Fig. 2 Map showing the amount of E85 fuel stations in the 50 states

The price of nickel has rose from the $3 to $4 USD per pound range back in 2003 all the way up to $25 USD per pound and recently has fallen back down to around $10 USD per pound. Although the price of nickel has decreased significantly, it is still well above the historical price of nickel over the past few decades.

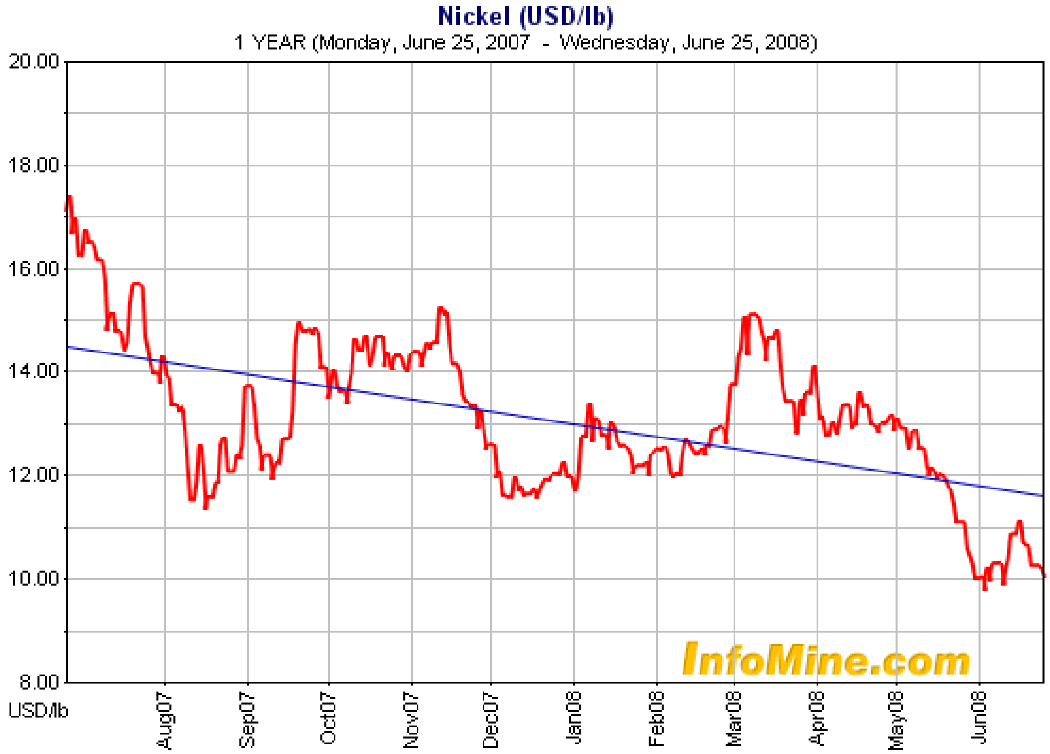

Fig. 3 Historical nickel price over last one year

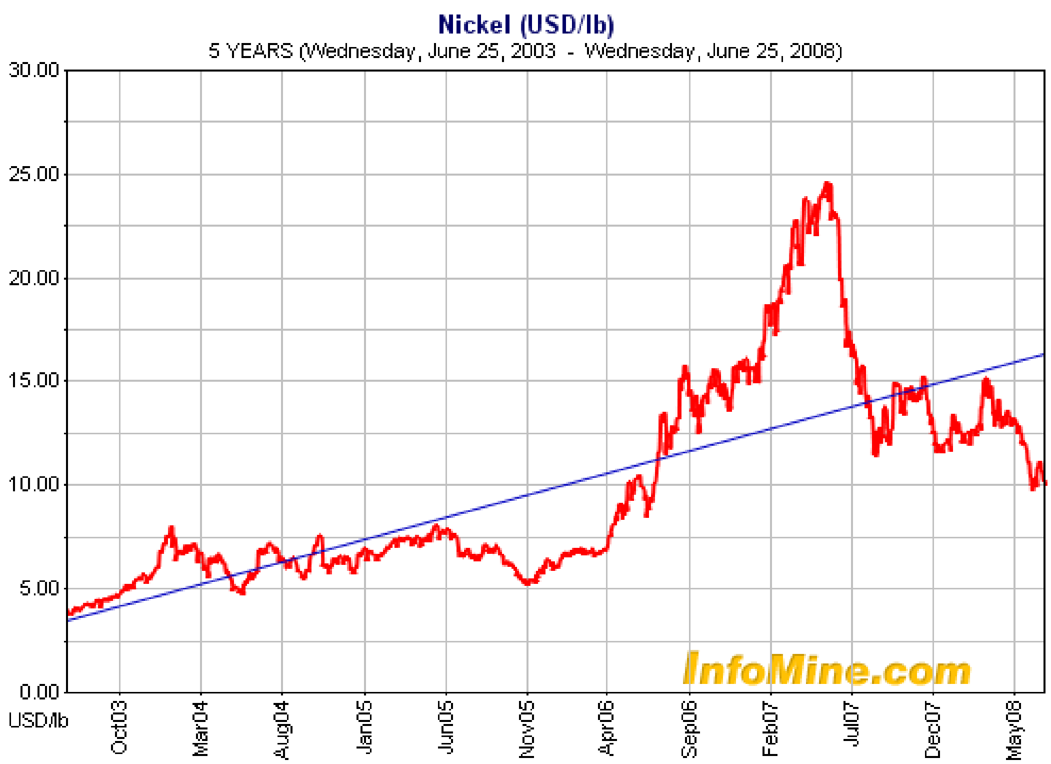

Fig. 4 Historical nickel price over past five years

As seen in Figures 3 and 4, the price of nickel has gone from an all time high of near $25 USD one year ago down to the current price of around $10 USD per pound of raw nickel. [3]

Although stainless steel is not composed of a majority of nickel, nickel prices can have a major effect on the total cost of stainless steel. With 8 to 10 percent nickel in stainless steel grade 304/L, the price of nickel strongly affects the total cost of the material.

Figure 5 shows how the price of nickel can increase the price of the austenitic and duplex stainless steels. This chart represents costs based on Molybdenum prices above $25 USD per pound. The shaded green area shows where the price of nickel has been over the past few months.

As seen in this graph, the price of 304/L and 316/L can have the tendency to double with the price of nickel rising from $5 USD to $25 USD. The duplex stainless grades LDX 2101, AL 2003, and 2205 only tend to increase less than 50% over this same nickel increase.

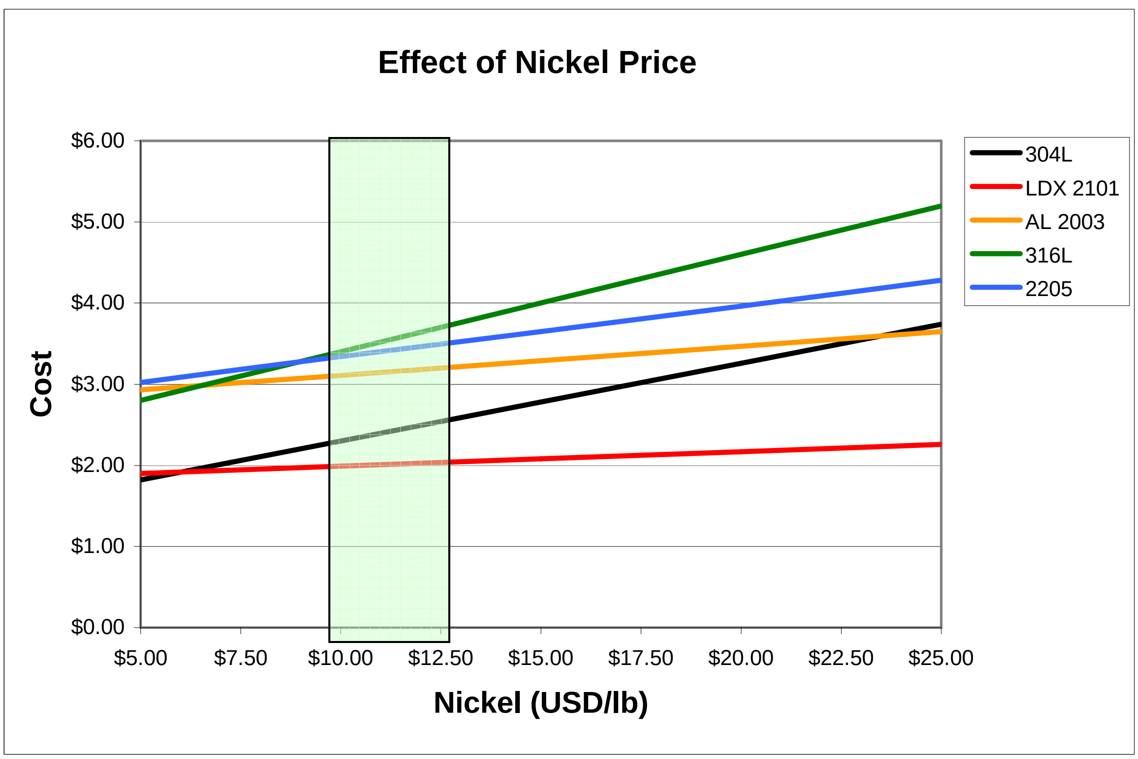

Fig. 5 Theoretical cost for a variety of austenitic and duplex stainless steels over a range of the cost of nickel

2 The advantages of Duplex Stainless Steel over Austenitic Stainless Steel in Biofuel Production

Duplex stainless steels are low nickel bearing stainless steels that offer many mechanical and corrosion resistant benefits over more popular 300 series stainless steels. LDX 2101 and AL 2003 are both lean duplex stainless steels that offer benefits over types 304/L and 316/L stainless steels. 2205 duplex stainless steel is a more common duplex stainless that offers corrosion resistance between 317/L and the 6% Mo alloys. Lastly, 2507 superduplex offers corrosion resistance similar to the 6% Mo alloys, better mechanical properties, at a fraction of the price. With nickel still priced above $10 USD per pound, these low nickel alternates offer far more stable pricing compared to the higher nickel austenitic alloys.

2.1 LDX 2101 Lean Duplex

LDX 2101 is a lean duplex stainless steel with 1.5 percent nickel that offers yield strength that is double the 300 series stainless, corrosion resistance superior to 304/L, and is priced similar to 304/L in the current market. In the recent ethanol boom, the alloy of choice for ethanol plants has always been 304/L with some areas requiring type 316/L stainless steel.

Alloy	Ultimate Tensile Strength, ksi	0.2% Yield Strength, ksi	Elongation %	Hardness Brinell
	Min	Min	Min	Max
LDX 2101	94	65	30	290
304/304L	75	30	40	201
316/316L	75	30	40	217

Fig. 6 Minimum mechanical properties for plate in thicknesses greater than 0.25 inch per ASTM A 240

As seen Figure 6, the minimum yield strength of LDX 2101 is over twice that of 304/L and 316/L stainless steels. The increased strength of LDX 2101 in comparison to 304/L and 316/L may allow for a lighter wall thickness for different tanks and vessels used in the production of biofuels. This leads to less material used for the application as well as less weld wire costs and even more importantly, less transportation costs.

LDX 2101 also has corrosion resistance superior to 304/L and more similar to that of 316/L in various environments. As seen below, the Pitting Resistance Equivalent number for LDX 2101 is similar to 316/L and higher than that of 304/L. Although the pitting resistance number is not always the best way to show alloy comparison in corrosive applications, it is a good measure to show how the alloys chemical content aids in its resistance in various environments.

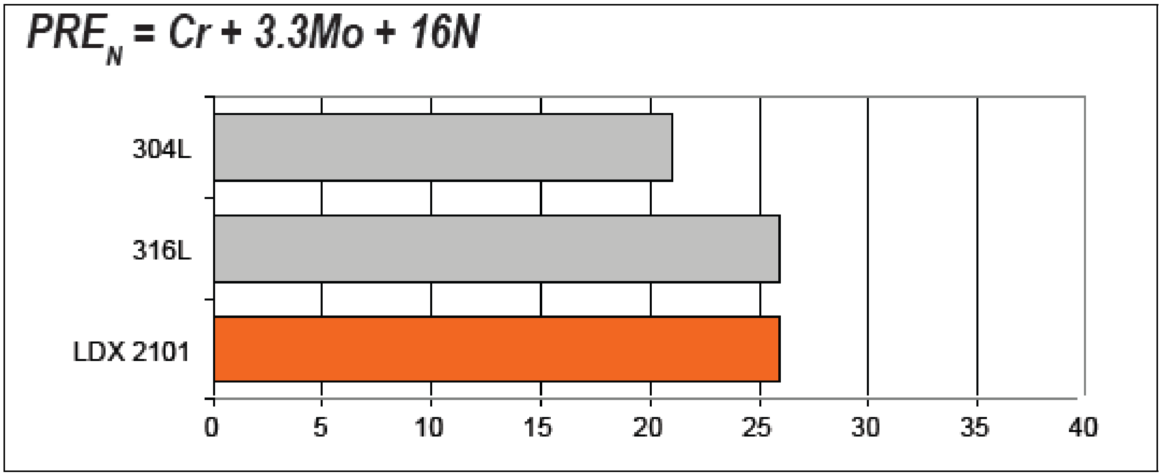

Fig. 7 Pitting Resistance Equivalent Number (PREN) of LDX 2101 compared to other stainless steels

Due to the lean chemistry of LDX 2101, in the current market, LDX 2101 is priced similar to 304/L in many product forms. When choosing between LDX 2101 and 304/L for ethanol applications, it is important to also know that LDX 2101 is a stronger and more corrosion resistant alloy than 304/L for about the same cost. Past projects where LDX 2101 has been used in place of 304/L for ethanol can be found in Section 3.

2.2 AL 2003 Lean Duplex

AL 2003 is also a lean duplex stainless steel that offers corrosion resistance superior than 316/L for a slightly lower cost. As a duplex stainless, it also obtains mechanical properties superior to 316/L, with minimum yield strength twice that of type 316/L stainless steel.

As seen in Figure 8, AL 2003 has twice the yield strength as 316/L and 317/L stainless steels. Due to this higher strength, lighter wall thickness design could be used to lower the total material weight used in the application.

Alloy	Ultimate Tensile Strength ksi (MPa) Min	0.2% Yield Strength ksi (MPa) Min	Elongation % Min	Hardness Brinell Max
AL 2003	95 (655)	65 (448)	25	293
316/316L	75 (517)	30 (207)	40	217
317L	75 (517)	30 (207)	40	217

Fig. 8 Minimum mechanical properties for plate in thicknesses greater than 0.25 inch per ASTM A 240

AL 2003 also has similar corrosion resistance to a type 317L stainless steel and is superior to a type 316/L stainless steel. The PREN of AL 2003, seen in Figure 9, is around 30. Type 316/L is around 25 and type 317L is also right around 30.

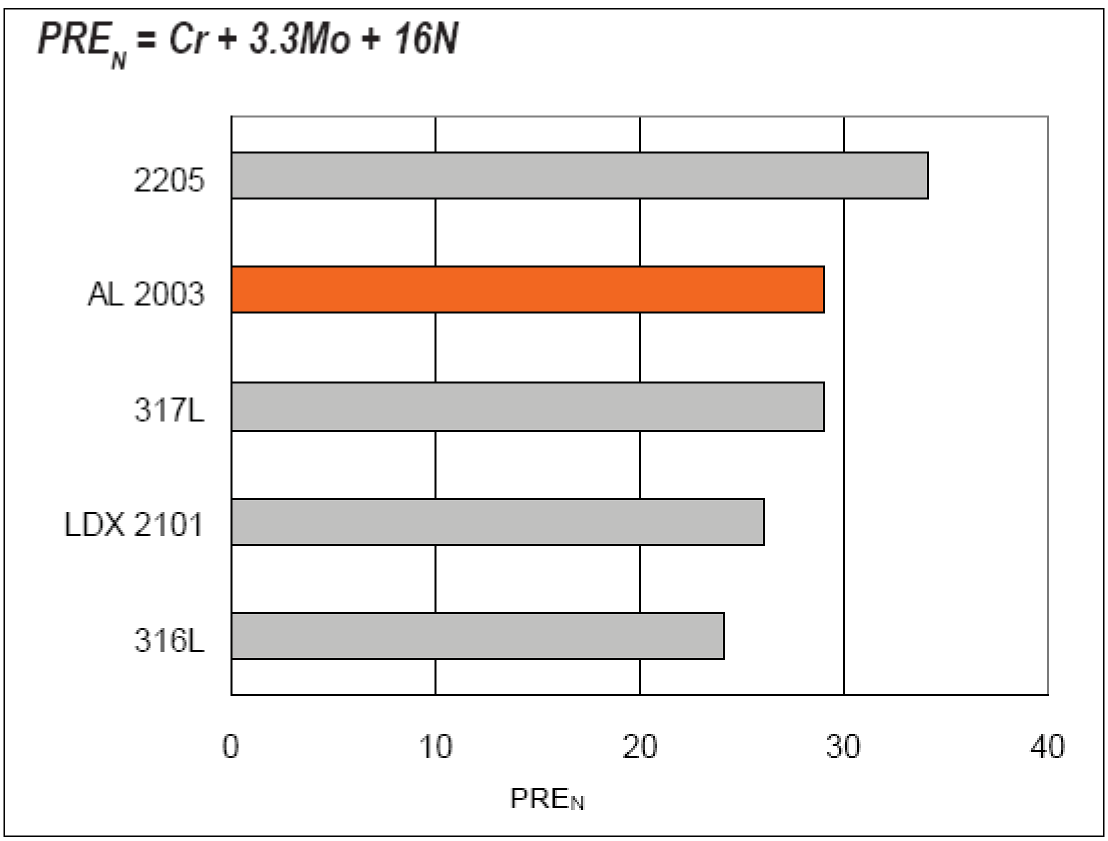

Fig. 9 Pitting Resistance Equivalent Number (PREN) of AL 2003 compared to other stainless steels

2.3 2205 Duplex Stainless

2205 duplex stainless is the most common duplex stainless steel in the market and currently the most widely used duplex stainless steel. 2205 duplex stainless also has similar mechanical properties as seen in the lean duplex stainless steels, but has a higher molybdenum content and therefore has better corrosion resistance to chloride and general corrosion environments.

2205 stainless, due to its mechanical properties, corrosion resistance properties, and experience in several industrial applications, has been and will continue to be an alloy alternate to types 317L and 317LMN stainless steels.

Alloy	Ultimate Tensile Strength UTS, ksi Minimum	0.2% Yield Strength YS, ksi Minimum	Hardness Maximum
2205	95	65	31 R_c
AL 2003™	95	65	31 R_c
316(L)	75	30	95 R_b
317(L)	75	30	95 R_b
317LMN	80	35	96 R_b
904L	71	31	90 R_b
Alloy 20	80	35	95 R_b
AL-6XN®	95	45	100 R_b

Fig. 10 Minimum mechanical properties for plate in thicknesses greater than 0.25 inch per ASTM A 240

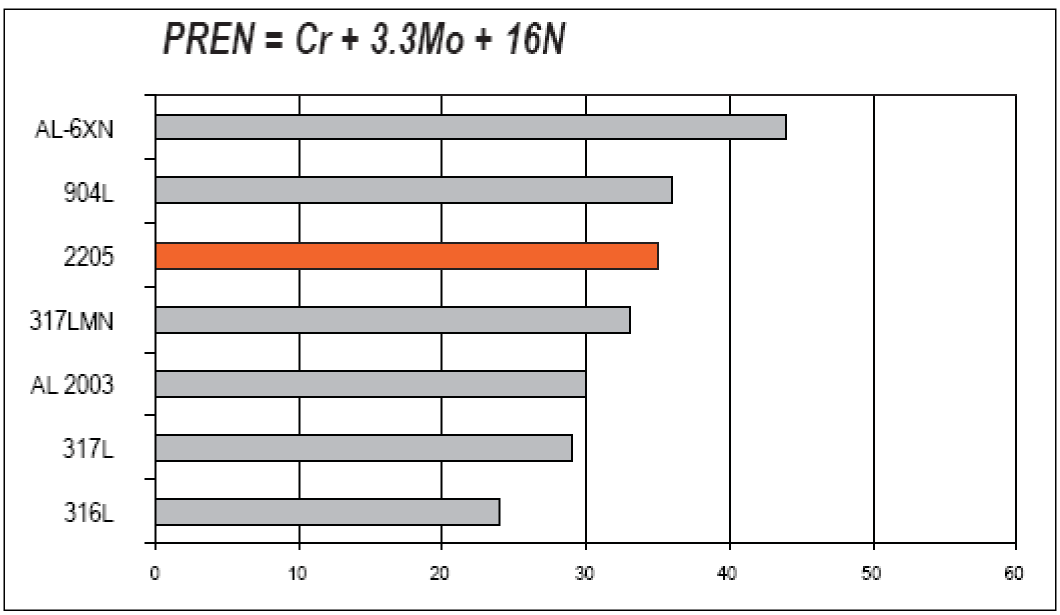

Fig. 11 Pitting Resistance Equivalent Number (PREN) of 2205 compared to other stainless steels

Figures 10 and 11 show how 2205 duplex compares to other austenitic stainless steels for both its mechanical properties as well as its corrosion resistance. Currently, 2205 is priced slightly above 316/L in many product forms. Therefore, it can be used as not only an alternate to 317L and 317LMN, but can also be used as an upgrade to 316/L stainless steel for not a large increase in cost.

2.4 2507 Super Duplex

2507 super duplex stainless offers corrosion resistance in comparison to the 6 percent molybdenum alloys and can also be considered as an alternate to higher nickel alloys. 2507 is a 25 percent chromium, 7 percent nickel, and 4 percent molybdenum duplex stainless steel that offers nearly twice the yield strength of 6 percent moly alloys for a fraction of the cost.

Alloy	Ultimate Tensile Strength, ksi Minimum	0.2% Yield Strength, ksi Minimum	% Elongation Minimum	Hardness Brinell Maximum
2507	116	80	15	310
AL-6XN®	95	45	30	241
625	110	55	30	—
2205	95	65	25	293
Alloy 255	110	80	15	302

Fig. 12 Minimum mechanical properties for plate in thicknesses greater than 0.25 inch per ASTM A 240

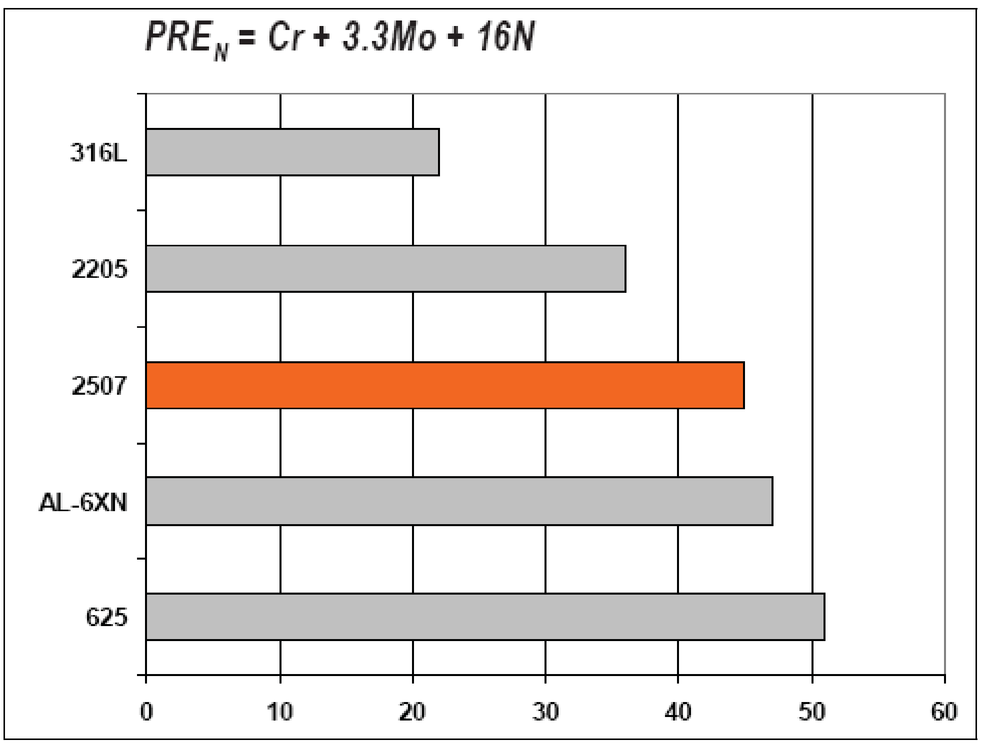

Fig. 13 Pitting Resistance Equivalent Number (PREN) of 2507 compared to other stainless steels and nickel alloys

Figures 12 and 13 show how 2507 super duplex compares to other austenitic stainless steels for both its mechanical properties as well as its corrosion resistance. Currently, 2507 is priced well below the 6 percent moly alloys in many product forms. It can also be used an alternate to alloy high nickel alloys, even though there may be a slight sacrifice in performance, there may be a large enough reduction in cost to make it beneficial.

3 Lean Duplex used in the production of Ethanol

3.1 LDX 2101 used at the Greater Ohio Ethanol Facility

LDX 2101 has been marketed in the ethanol industry over the past couple years and although the corn based ethanol industry has seemed to have been put on hold with corn prices where they currently are, other forms of ethanol may yield the use of LDX 2101 or other duplex stainless steels based on the corrosivity of the environment.

To date, there are two ethanol plants that have either used are or planning on using LDX 2101 for various applications inside the ethanol plant. One facility in the U.S. has chosen to use LDX 2101 to construct all of their storage and fermentation tanks. LDX 2101 was chosen over 304L stainless steel, which is the typical material of construction for ethanol facilities in the U.S. [4]

Fig. 14 View of the GO-Ethanol facility in Lima, OH during construction. All large tanks shown were constructed from the LDX 2101 lean duplex stainless

Fig. 15 View of the GO-Ethanol tanks further into construction.

3.2 Agroetanol Planning to Expand its Facility Using the LDX 2101 Lean Duplex

Agroetanol AB operates an ethanol plant on Handelo, an island some 10 kilometers from the city of Norrkoping in Sweden. The plant produces 55 million liters of ethanol per year to be used as gasoline replacement. Biofuel sector observers assess the need for ethanol as fuel on the Swedish market to increase from 270 million to 500 million liters within the next two years. To help meet the increase, Agroetanol is building an expansion on the existing plant, approved for production of 210 million liters.

Ethanol processes largely take place in stainless steel vessels and pipes. As the stainless supplier for the Agroetanol expansion, Outokumpu will be delivering for the project both flat and piping products. The pipes and fittings, representing close to the full Outokumpu size range, are mainly of the austenitic grade 304L. As a breakthrough in the ethanol business, the sheets and plates are of duplex LDX 2101. This proprietary duplex grade offers many benefits that make it a superior alternative to traditional, austenitic grades in a variety of industrial applications. The high mechanical strength of LDX 2101, characteristic of all duplex grades, provides considerable weight and therefore cost savings. Owing to its very low nickel content, LDX 2101 is today similar in price in absolute terms than austentic grades with similar corrosion resistance properties.

Deliveries for the Agroetanol plant expansion started in the early autumn of 2007. The current expansion will likely pave the way of the future in duplex LDX 2101 in ethanol production. Agroetanol has announced an interest to make an even wider use of LDX 2101 in possible future projects.

Agroetanol's production is based on 150,000 tons of wheat per year at the current level of output, which also produces 45,000 tons of protein feed in addition to ethanol. The company is owned by Swedish Farmers' Supply & Crop Marketing Association. [5]

Fig. 16 Agroetanol facility before expansion

3.3 2304 Lean Duplex used for Biodiesel production

2304 lean duplex stainless steel was used to construct the Rape Seed Biodiesel facility. This facility will produce roughly 42 million gallons of biodiesel every year. 2304 lean duplex was used as a cost benefit compared to 304L stainless steel. Over 120 tonnes of 2304 plate was used in this facility. By using the 2304, approximately 30 percent less material was used in comparison to 304L stainless. [6]

Fig. 17 Rape Seed Biodiesel facility

3.4 Other Application for Lean Duplex in Biofuel Production

Fig. 18 Ethanol manufacturing facility during construction. Lean duplex was used for the process tanks. [6]

Fig. 19 Ethanol fermentation tank constructed from lean duplex stainless steel

Fig. 20 LDX 2101 was used by Oostwouder Tank- & Silobouw BV of the Netherlands to fabricate these tanks used in the production of biodiesel for a project named Greenmills [6]

Fig. 21 LDX 2101 Tank being erected for the project Greenmills. LDX 2101 saved nearly 25% on total material used in comparison to type 304L stainless steel.

3.5 Other Opportunities for Lean Duplex in Biofuel Production

Due to the chloride stress corrosion cracking resistance of duplex stainless steels, there is no need for coating or painting of piping that will end up being insulated. Types 304L and 316L stainless steel are typically coated when insulated to protect the material from chloride stress cracking during service.

Figures 22 and 23 show some examples of insulated piping at Wyoming Ethanol. These pipes run outdoors and throughout the uninsulated metal buildings at the facility. Ingredients and eventually processed ethanol are delivered to tanks at expected temperatures with the help of the molded pipe insulation. [9]

Fig. 22 Insulation of biofuel process piping

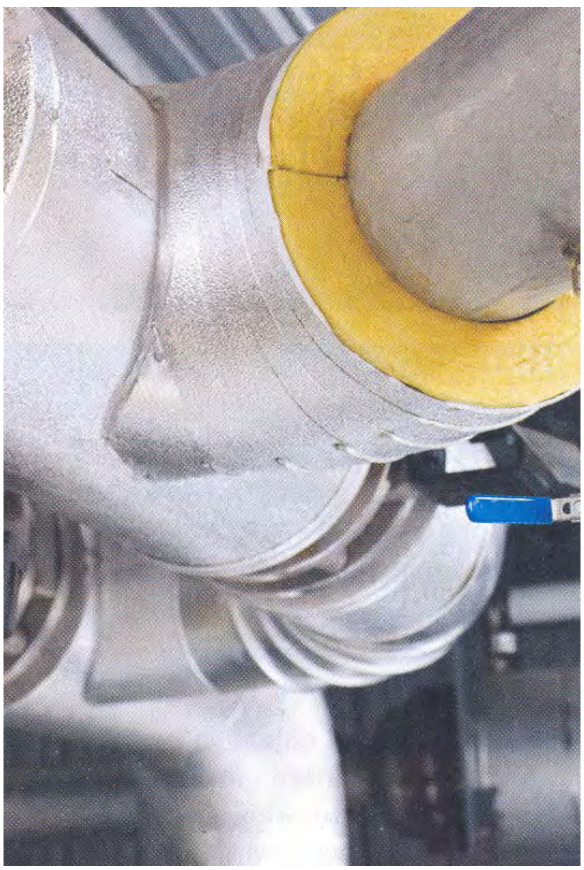

Fig. 23 Closer view of the insulated piping

4 2507 Superduplex used in the production of Biodiesel Reactor Tanks and Vessels

Biodiesel is the name of a fuel alternative to the conventional, petroleum based diesel engine fuel, which is manufactured from vegetable oils or animal fats by catalytically reacting these with a short-chain aliphatic alcohol (methanol or ethanol), typically using a process called transesterification, or alcoholysis.

These biodiesel plants consist of several storage and reaction tanks, but only a couple are made from RA2507 superduplex material. One of the tanks that use RA2507 is called a decanter tank or a separation column where all the ingredients are combined and reacted with to make the biodiesel fuel. These are roughly 36 inches in diameter and 114 inches in height.

RA2507 was chosen as a replacement to higher nickel alloys such as 904L due to its high strength, great corrosion resistance, and cost effective price.

Figure 24 depicts the basic technology for biodiesel production. [7]

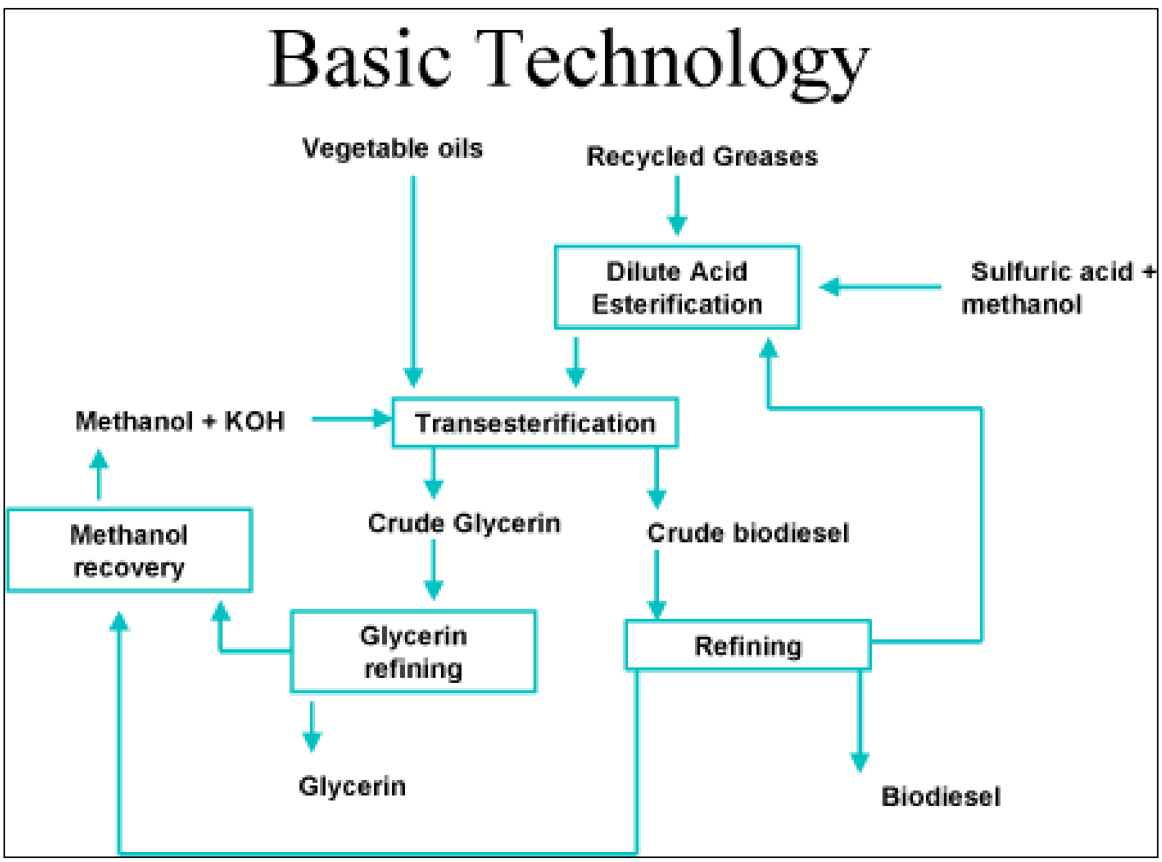

Fig. 24 Basic process for biodiesel production

Fig. 25 Schematic of a biodiesel process facility. The vertical tanks on the second level have been fabricated from 2507 superduplex.

Fig. 26 Biodiesel reactor vessel fabricated from 2507 super duplex stainless

Fig. 27 2507 super duplex vessels used in the biodiesel production

5 The Future of Cellulosic Ethanol and where Duplex Stainless Steel would fit in

Cellulosic ethanol technologies are being developed to assist in lowering the cost to produce a gallon of fuel grade ethanol. As discussed, the price of crops has increased with the demand for use in ethanol manufacturing. The use of wastes such as Cellulosic ethanol (also called lignocellulosic ethanol/ ceetoh and ceetol) is a biofuel produced from wood, grasses, or the non-edible parts of plants. Corn stover, switchgrass, miscanthus and woodchips are some of the more popular cellulosic materials for ethanol production. Cellulosic ethanol is chemically identical to ethanol from other sources, such as corn starch or sugar, but has the advantage that the lignocellulose raw material is highly abundant and diverse. However, it differs in that it requires a greater amount of processing to make the sugar monomers available to the microorganisms that are typically used to produce ethanol by fermentation.

There are several technologies for producing cellulosic ethanol currently being developed and tested in mostly pilot facilities. In the Hydrolysis process, the cellulose molecules are composed of long chains of beta-glucose molecules. These chains are broken down to sugar before feeding it to a fermenter for alcohol production. [8]

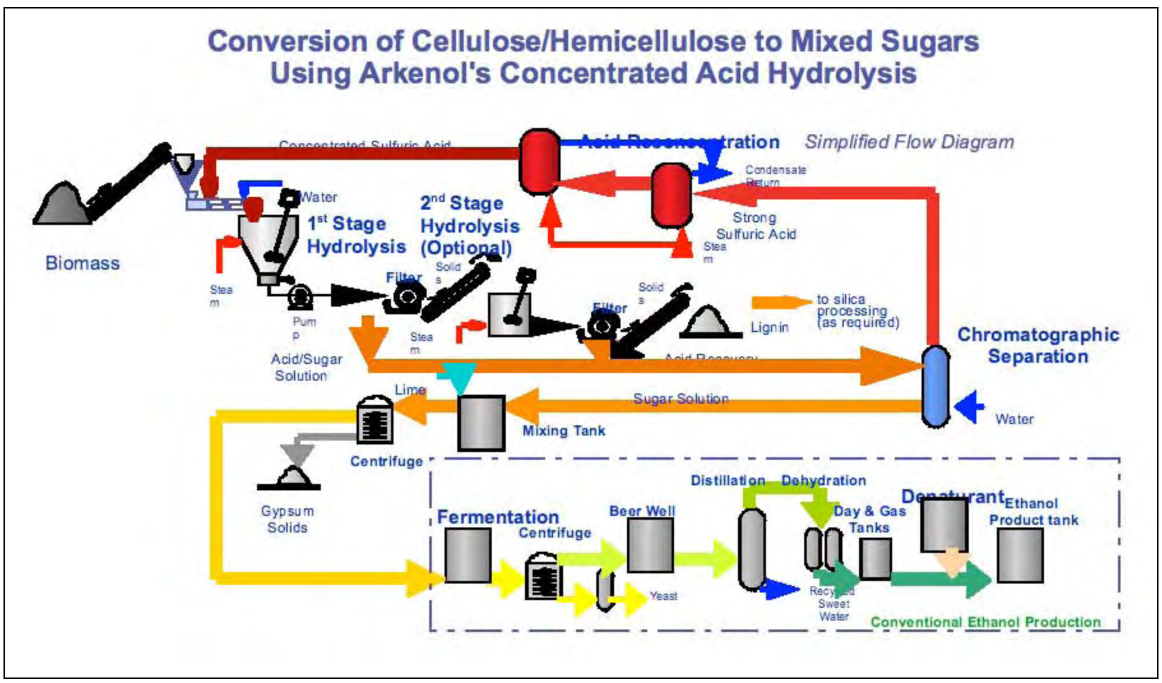

Fig. 28 Schematic of the Hydrolysis Cellulosic Ethanol process

In the gasification process, the carbon in the raw material is converted into carbon monoxide using feedstock from partial combustion. The carbon monoxide is then fed into a fermenter and a bacteria Clostridium ljungdahl will digest the carbon monoxide into ethanol, hydrogen and water. The gasification process does not require a chemical composition of the cellulose chain. The heat generated by gasification is also used to co-generate electricity.

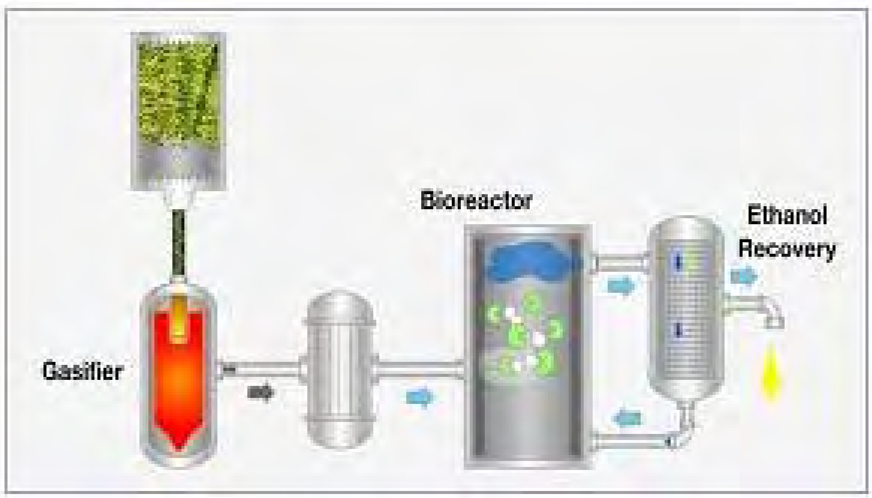

Fig. 29 Gasification Cellulosic Ethanol process

Many companies have been given grants to develop their technology to full-scale production. Full-scale production is thought to be several years down the road before this will turn into a reality. Due to the corrosivity of the two main cellulosic ethanol processes, more corrosion resistance alloys will need to be used to combat corrosion. Depending on the concentration of the sulfuric acid in the hydrolysis process and temperatures in the gasification process, duplex stainless steels will have a role in the future manufacturing of cellulosic ethanol.

6 Conclusion

Duplex stainless steels offer a cost advantage to high nickel bearing stainless steels in today's market with rising raw nickel prices. Due to rising oil prices, the increasing production of biofuels will continually grow in the U.S. Duplex stainless steels will continue to offer many advantages going forward in these numerous processes and offer superior properties and benefits to typically used stainless steels.

Acknowledgments

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