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## Biofuels, Duplex Stainless Steel and Molybdenum

A number of countries, including the US, Brazil, China and India, are putting more emphasis on biofuels, as crude oil prices remain high worldwide

New molybdenum supply will be required as a consequence of the production of biofuels.

This article reviews the current status of the two primary biofuels: ethanol and biodiesel, and then outlines the molybdenum connection which is through new so-called "lean duplex" stainless steels.

Interest in renewable fuels certainly is growing, although the market is still quite small. Global ethanol production currently equals approximately 0.6 percent of the world's crude oil consumption. Biodiesel accounts for less than 0.1 percent of global oil demand.

Nevertheless, energy consultancy Poyry estimates that the biofuels industry worldwide, including ethanol and biodiesel, will be worth \$40.5 billion this year against \$13.6 billion in 2002.

Here are a couple of definitions:

At its most basic, ethanol is grain alcohol, produced from crops such as corn, sorghum, potatoes, wheat, or sugarcane, for example, although there are other raw materials like wood fibre from which it can also be produced. Brazil and the United States account for 90 percent of global ethanol production. The primary ethanol feedstock is corn in the United States, and sugarcane in Brazil.

At the moment, ethanol production is rising faster in the United States than in Brazil. It has very strong policy support here because of concerns about oil prices and national security. Brazilian officials say their ethanol industry would develop even faster if the U.S. did not levy a tax of 15 cents a litre on all imports of Brazilian cane-based ethanol.

2006 global crop-based ethanol production was 51 billion liters. Of that, the United States produced 18 billion liters, Brazil; 17 billion liters and EU states; 3 billion liters.

According to the Organisation for Economic Co-operation and Development (OECD), U.S. ethanol production is expected to double between 2006 and 2016. Brazil, the world's second largest producer of ethanol, expects its production to reach 44 billion litres by 2016.

Pure, 100 percent ethanol is not generally used as a motor fuel; instead, a percentage of ethanol is combined with unleaded gasoline. Any amount of ethanol can be combined with gasoline, but the most common blends are: E10, which is 10 percent ethanol and 90 percent unleaded gasoline, and E85 – 85 percent ethanol and 15 percent unleaded gasoline.

E10 is approved for use in any make or model of vehicle sold in the United States. About half the gasoline formulated in the U.S. today contains some ethanol, most as the E10 blend.

E85 is an alternative fuel for use in flexible fuel vehicles (FFVs). There are currently about 6 million FFVs on America's roads today, and automakers, particularly GM, are rolling out more each year. These FFVs can operate on straight gasoline or any ethanol blend up to 85 percent.

Brazil was the pioneer in the use of flexible fuel vehicles and today over 80 percent of the cars sold in Brazil are FFVs. Largely thanks to ethanol use, last year the country became self-sufficient in energy. In a recent interview, Expedito Parente, the Brazilian engineer who invented biodiesel in the 1970s, said: "We have 80 million hectares of the Amazon that will be converted into the Saudi Arabia of biofuels."

According to the OECD: "Some 5 percent to 10 percent of all vehicles worldwide could be FFVs by 2030. "If extremely aggressive carbon dioxide limits are established, the penetration of biofuels could rise to between 20 percent and 25 percent by 2030."

Biodiesel is typically produced by a reaction of a vegetable oil or animal fat with an alcohol such as methanol or ethanol in the presence of a catalyst (lye). The process yields mono-alkyl esters (the biodiesel) and glycerin, which is removed.

(This glycerine supply is driving a whole new industry: glycol produced from byproduct glycerine, which has proven big enough to attract the likes of Cargill, Davy – now, a Johnson Matthey company – and Ashland Chemical, but an analysis is beyond the scope of this paper.)

Biodiesel can be used in any concentration with petroleum-based diesel in existing diesel engines with little or no modification, but it seems likely that most nations will follow the blending model used by France and the United States for B2, B5, and, most commonly, B20 – the numbers indicating the percentage blended in. It burns substantially cleaner than petroleum-based fuel, releasing 78 percent less carbon dioxide, according to a joint study by the Department of Energy and the USDA.

Biodiesel has many sources: the oil of seed plants like soy or canola, palm trees, used cooking oil (including french-fry grease, although this is much smaller than commonly thought), and animal fat.

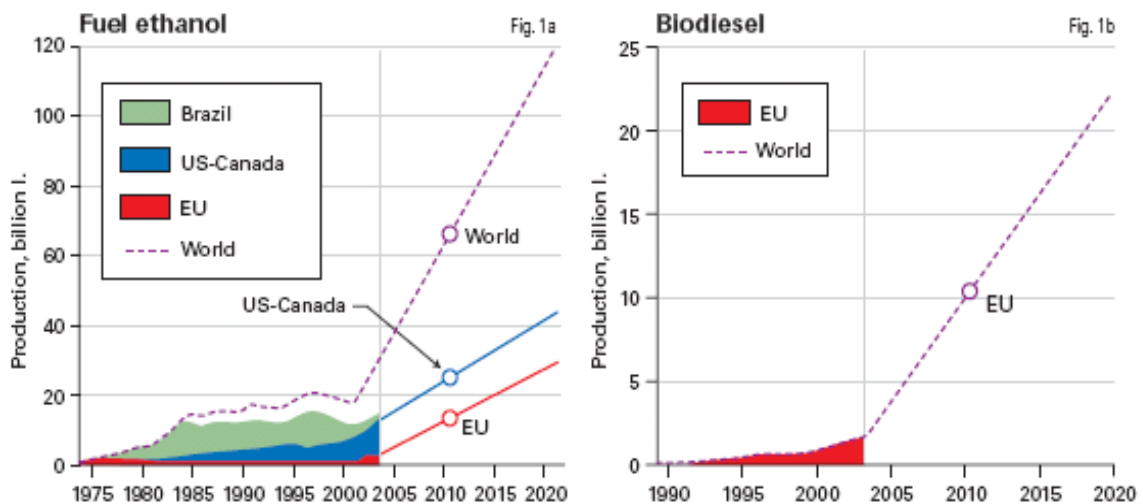
Solazyme, a San Francisco biotechnology firm, has even started making biodiesel from genetically modified algae.

Biodiesel is 30 percent more fuel-efficient than regular unleaded gasoline, which in turn is 30 percent more efficient than ethanol.

Biodiesel production and consumption in the U.S. is in its infancy, compared with ethanol, and is generally used in state and federal fleet vehicles to comply with federal alternative-fuel requirements. Biodiesel use outside of the U.S., particularly in Europe, is more advanced due to the greater penetration of diesel engines in the consumer marketplace.

The International Energy Agency (IEA) forecasts a tripling of ethanol and biodiesel production through 2020. (See charts below.)

## BIOETHANOL, BIODIESEL PRODUCTION TO 2020



Source: International Energy Agency (<http://www.worldenergyoutlook.org/graphs/Slide12.gif>)

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The ethanol business is very topical. At the time of writing, plant construction in the United States has been so aggressive that prospects of a temporary glut loom. According to consultants Friedman, Billings, Ramsey and Co., 2007, capacity next year could be as much as 1.8 times demand.

The ethanol boom was largely ignited by Congress in 2005 when it enacted an energy law that included a national mandate for the use of renewable fuels in gasoline, obliging the U.S. market to consume 7.5 billion gallons of renewable fuels a year by 2012.

Called the Renewable Fuels Supply mandate or RFS, ethanol would account for the majority of it. Hart Energy Consulting, however, predicts that before the present Congressional session ends in October 2008, the current RFS will be revised up to 12 billion annual gallons in 2012, and then increased again to 10 percent of total gasoline supplies by 2015, creating an annual demand for 15 to 16 billion gallons of ethanol. Within 10 years, they say, the commercialization of cellulosic ethanol production could drive that number to between 35 and 60 billion gallons per year, or, in other words, from 25 percent to 43 percent of the gasoline supply.

To correct the current dislocation, it looks like wider availability of E85 is needed in the retail marketplace:

The fact is that of the 179,000 pumps at U.S. gas stations, only about 1,000 dispense E85. Almost none are at oil-company-owned stations, and if an independent station that operates under, say, the ExxonMobil or Shell brand wants one, it can cost around \$200,000 to install a separate pump after all corporate restrictions are met. ExxonMobil bars branded independents from buying fuel from anyone but them and ConocoPhillips has a similar policy.

The Consumer Federation of America recently characterized the situation as "Big Oil's war on ethanol." The industry, they write, "reacted aggressively against the expansion of ethanol production, suggesting that it perceives the growth of biofuels as an independent, competitive threat to its market power in refining and gasoline marketing."

In response, the American Petroleum Institute (API), the chief trade group for oil and natural-gas companies says: "We think [ethanol] makes an effective additive to gasoline but that it doesn't work well as an alternative fuel. And we don't think the marketplace wants E85." The API says its research shows that many consumers fill up once, and not again, after they experience the 25 percent loss in fuel economy that comes with E85. There remains as well a large variation in pricing: While some states near ethanol plants, like Indiana, sell E85 as much as 33 percent cheaper than gasoline; in others, like New York, E85 actually costs more!

Infrastructure problems are behind much of the oil companies' resistance to E85. It adds "too much complexity and cost," according to Shell, since it requires separate pumps, trucks, and storage tanks.

The industry's stance angers consumers and carmakers as well, who have about 6 million flex-fuel vehicles on the road. General Motors, Ford, and Chrysler all pledge that half of their vehicle sales should be flex-fuel by 2012 but are waiting for bigger commitments to the E85 pumps. "Big Oil is at the top of the list for blocking the spread of ethanol acceptance by consumers and the marketplace," says Loren Beard, senior manager for energy planning and policy at Chrysler, referring to the struggle to get E85 pumps installed.

We'll see what happens.

The global biodiesel industry also has grown rapidly over the past decade. Some of the main drivers behind this tremendous growth are

- reduced dependence on imported oil,
- environmentally friendly alternative to diesel,
- Kyoto protocol: for reducing greenhouse gasses (GHG),
- easy blending with little or no engine modification
- compatibility with existing fuel distribution infrastructure.

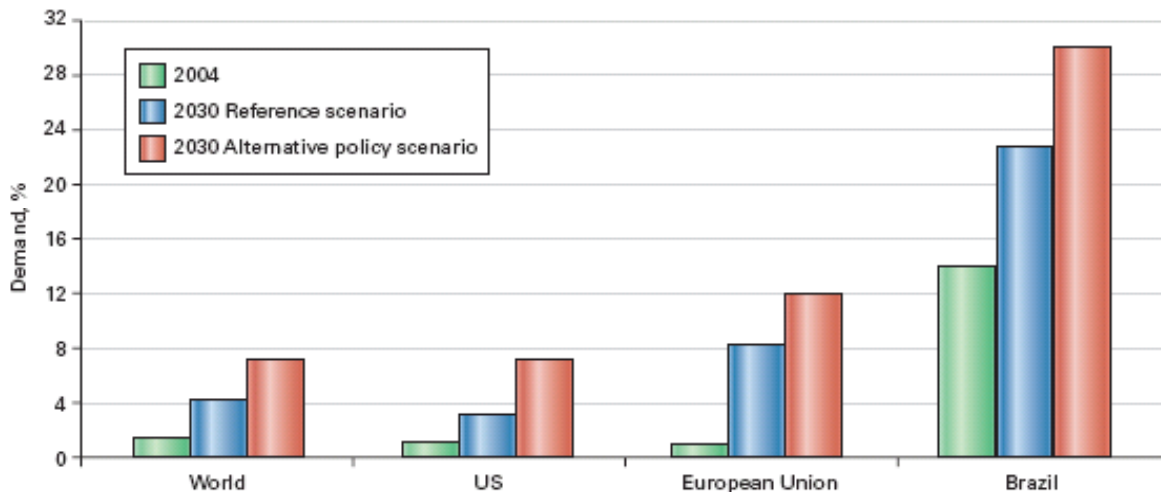
The global biodiesel market is estimated to reach 37 billion gallons by 2016 growing at an average annual growth of 42 percent (forty-two percent - not a typo). Europe will continue as the major biodiesel market for the next decade or so. The European market accounts for 80 percent of the biodiesel supply and demand, because 60 percent of all new cars sold in Europe have diesel engines. Biodiesel demand is also expected to grow briskly in China and India.

Sales of biodiesel in the U.S. jumped tenfold from 2004 to an estimated 250 million gallons last year, according to the National Biodiesel Board, which represents researchers, agro producers, processors and distributors. Production of biodiesel in the U.S. is expected to reach 1 billion gallons by 2010 and nearly 1.5 billion gallons by 2015.

International Energy Agency forecasts for the share of biofuels in road-transport are shown in the chart, below.

### SHARE OF BIOFUELS IN ROAD-TRANSPORT FUEL CONSUMPTION

Fig. 2



Source: International Energy Agency (<http://www.worldenergyoutlook.org/graphs/Slide12.gif>)

What does it all mean to molybdenum?

In the first instance, we note the agricultural equipment market is on the cusp of a major turnaround, driven by strong agri-commodity prices which are due in large part to burgeoning demand for biofuels.

Strong agri-commodity prices translate to increased farm income, increased investment in farm equipment and thus increased demand for steel in castings, sheet and structurals to make the equipment, and for cast iron used for diesel engines. Molybdenum is increasingly seen in newer steels and cast irons in these applications.

We can illustrate molybdenum demand in biofuels production, by looking at a typical plant. A typical biofuels facility will include:

- reactors
- cooling towers
- steam boilers for heat tracing (especially in cold climates due to the viscosity of the feedstock and finished product)
- natural gas thermal oil boilers for processes that require more heat than can be produced by steam.
- process pipe
- process and utility pumps
- storage tanks and
- heat exchange coils inside the finished storage tanks



General view of an ethanol plant. (Source: Agroetanol AB, Sweden)

Here's where it gets really interesting:

Ethanol processes largely take place in stainless steel vessels and pipes – typically grade 304 stainless (no molybdenum). But very recently, a low molybdenum, low-nickel, duplex stainless steel called “lean duplex” is entering the equation. It contains nominally 0.3 percent molybdenum.

To get an idea of the tonnage of stainless steel involved in a typical plant we can look at a 2007 plant expansion in Europe: The first phase of an expansion to the Agroetanol AB ethanol plant near Norrköping, Sweden will begin this Fall and increase capacity from 55 million to 210 million liters. The material shopping list includes these items, of which about 70 weight percent has been specified in lean duplex stainless steel:

- Sheet : 600 tonnes, 4-8mm thick (2101 duplex stainless)
- Plate: 80 tonnes, 8-25mm thick (2101 duplex stainless)
- Pipe, fittings: 300 tonnes, 33.7-914mm OD (304L stainless)

These biofuels-sponsored changes to the molybdenum demand curve are very recent: The first known use of duplex stainless steels in a biofuels reactor was at Perstorp Oxo AB's biodiesel facility: Their two reactors were made from a lean duplex stainless steel 2304 (also 0.3% Mo), and the facility was completed only last year.

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In a June 2006 Chemical Week article on this project, company engineers were quoted as saying the duplex 2304 grade demonstrated 55 percent higher strength and superior corrosion resistance against type 304 stainless. This allowed the reactor vessel wall thickness to be reduced by 30 percent compared to the original design wall thickness of 75 mm (nominally 3 inches) in type 304 stainless. As a result, the plant investment cost was "considerably lower".

The biofuels transport equation also contains molybdenum.

In the case of pipelines, ethanol would have to be in a dedicated service. Unlike gas and oil, ethanol can't be sent down a pipeline separated by a plug of water, since it absorbs water. Plus there are some additional corrosion considerations at any ethanol blend over 10 percent. Our experience is that newer pipelines contain higher levels of molybdenum.

The potential for dedicated biofuel pipelines is being discussed. For instance, Senator Tom Harkin (D-IA) has proposed legislation that would award funds to study the feasibility of dedicated ethanol pipelines: "These pipelines could link high-density ethanol areas such as Iowa and Minnesota with the large East Coast markets."  
(Bulk Transporter, August 2007)

Pipeline shipments would cost slightly more than two cents a gallon. Truck transportation costs around 20 cents a gallon.

In the absence of pipelines, however, 7.5 billion gallons in the U.S. by 2012 means a million truckloads a year!

And the use of lean duplex stainless steel is growing in this sector as well, given the higher net weights that can be hauled when the tare weight of the truck is reduced.

Brenner Tank was the first to introduce a next generation tank compliant with DOT 407 regulations, utilizing duplex stainless steels, and thereby substantially reducing the weight and total cost of their new bulk tank trailers. They received a variance from the DOT in January of this year. At the time of writing, a second company has just received a similar variance. Change is coming.

Brenner Tank told the writer that robust demand for stainless steel, partially fueled by the booming ethanol industry, has seen the price of the most common stainless steel tank trailers almost double in the last four years. The company decided on "lean duplex" as the primary solution. Interestingly, they also note that while nickel surcharges were the initial driver, it is the strength:weight ratio that will bring them back to lean duplex stainless, even as the nickel part of the equation seems to have gone.

This change in biofuels production- and transportation materials not only represents a cost breakthrough for the biofuels business, but also a breakthrough for molybdenum which has traditionally been absent from the largest portion of the stainless market: Molybdenum stainlesses have historically represented something in the order of just 10 percent of the overall tonnage of stainless steels sold. Finding a molybdenum-bearing stainless substitute for 304 represents a significant structural change.

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The story of duplex stainless steels goes beyond biofuels, representing a subclass of stainlesses growing even faster than standard stainless grades.

Annual growth in duplex stainless demand is estimated to be over 20 percent. The high strength of the material enables the use of thinner gages in a variety of applications such as tanks, pressure vessels, piping, transportation, civil engineering and structures, thus bringing considerable savings in the total cost of ownership.

In anticipation of this market taking off, Outokumpu, the largest producer of duplex stainless steels, announced plans this year to increase their capacity by the year 2010 from the current 250,000 tonnes to 650,000 tonnes.

As well, in 2007 they've licensed their lean duplex stainless technology to two other producers in Europe and Asia.

A listing of the common duplex stainless steels and their molybdenum content is reproduced, below.

COMPOSITION OF COMMON DUPLEX STAINLESS STEELS										
UNS Number Duplex Grades	Type	C	Mn	P	S	Si	Cr	Ni	Mo	Other
S32101	2101	0.03	5	0.040	0.030	1.00	21	1.5	0.3	
S31200		0.030	2.00	0.045	0.030	1.00	24.0-26.0	5.5-6.5	1.20-2.00	
S31260		0.03	1.00	0.030	0.030	0.75	24.0-26.0	5.5-7.5	2.5-3.5	W 0.10-0.20
S31803	2205	0.030	2.00	0.030	0.020	1.00	21.0-23.0	4.5-6.5	2.5-3.5	
S32001		0.030	4.0-6.0	0.040	0.030	1.00	19.5-21.5	1.00-3.00	0.60	
S32205	2205	0.030	2.00	0.030	0.020	1.00	22.0-23.0	4.5-6.5	3.0-3.5	*
S32304	2304	0.030	2.50	0.040	0.030	1.00	21.5-24.5	3.0-5.5	0.3	
S32520		0.030	1.50	0.035	0.020	0.80	24.0-26.0	5.5-8.0	3.0-4.0	
S32550	255	0.04	1.50	0.040	0.030	1.00	24.0-27.0	4.5-6.5	2.9-3.9	
S32750	2507	0.030	1.20	0.035	0.020	0.80	24.0-26.0	6.0-8.0	3.0-5.0	
S32760		0.030	1.00	0.030	0.010	1.00	24.0-26.0	6.0-8.0	3.0-4.0	W 0.50-1.00
S32900	329	0.06	1.00	0.040	0.030	0.75	23.0-28.0	2.5-5.5	1.0-2.0	

Weight percent. "Type" is the common name, not a trademark. 329 is an AISI designation. Highlighted are very common.  
 \*S31803 can be used in most cases. **304 stainless = 0% Mo, 10% Ni** **316 stainless = 2-2.5% Mo, 10-14% Ni**

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