## Wolan Story

They might not be spinning straw into gold in the Department of Chemical \& Biomedical Engineering, but it's close. In the fairy tale, a little man does all the work at night in a dark basement. Now, a little bench scale reactor, in a bright, state-of-the-art laboratory takes the gas produced from the straw and transforms it into clean diesel and jet fuel. While you might prefer gold, fuel is much more valuable, just ask any historian or modern industrial country dependent on foreign fossil fuels.

The non-fairy tale description for this serious research is "thermo-chemical conversion of lignocellulosic biomass to liquid hydrocarbon fuels." Technically speaking, you don't spin the straw, but dry it out a bit and burn it in an oxygen-reduced atmosphere to create synthesis gas. This syngas, which is mostly carbon monoxide and hydrogen, is then heated in our pressurized little reactor and forced through a one-inch pipe containing a catalyst made from cobalt and silica pellets. From the bottom of this pipe, which can get a bit warm and is hardly more than a foot long, comes precious drops of liquid fuel. While this is a rather simple retelling of the tale, the patented process is referred to as Fischer-Tropsch (FT) synthesis. And don't try this at home.

Both Rumpelstiltskin and the FT synthesis originated in Germany. Like many wartime projects that advance technology at warp speed, the FT conversion of carbon monoxide and hydrogen into liquid hydrocarbons was discovered by Franz Fischer and Hans Tropsch in the 1920's. Their process used coal, not biomass, as the feedstock. Iron served as the catalyst. Petroleum-poor Germany recognized the need for synthetic fuels and by the beginning of WWII had produced over 600,000 tons of liquid hydrocarbons using the FT process. When war was declared, Germany was importing about $60 \%$ of its fuel from foreign countries. The FT plants couldn't keep up with government production demands, and the decision was made to invade Russia in order to control its oil refineries and coal reserves. Many historians point to the Eastern Front as the primary reason for Germany's defeat. How history might have been changed if all of the FT plants went on line as planned. While it's mind-boggling that you could start a war on half the fuel you need, keep in mind that today the U.S. military gets $50 \%$ of its fuel from foreign fossil sources.

These lessons of history are not lost on Professor John T. Wolan. Along with graduate student Ali Gardezi, these chemical engineers keep their tabletop Fischer-Tropsch reactor humming with biomass consisting of pine sawdust and pine chips. Florida has more biomass waste than any other state. Pine chips, along with sugarcane bagasse, citrus pulp, grass, and municipal solid waste constitute just some of the available biomass feedstock for the new generation of FT syntheses. Even barnyard waste can fuel this process. Basically anything that is rich in lignin or cellulose can be used.
"We don't have to use corn, which people eat," explains Wolan. "We can use the dried corn stalks and corn grass." Unlike the fermentation process that creates ethanol from the sugar in the corn, the liquid hydrocarbon fuels created with FT synthesis are chemical rearrangements of the carbon found in the grassy parts of the corn plant. "Like making beer
or wine, fermentation is a tricky process, best done in small batches. It is not easily scalable to a large refinery," he explains.

If the FT process works on both coal and biomass, why don't we have them all over the country? "That," says Professor Wolan, "is a good question, but there are many reasons. The plant itself is costly, a lot of capital is necessary to get started. And of course, investors want to know what their return will be. The break-even point is estimated when a barrel of oil reaches one hundred dollars." It would be possible, he continues, to build a plant expecting to make fuel valued at $\$ 100$ a barrel, and then the price of crude drops to $\$ 35$. Since 2000, prices have ranged from $\$ 17$ to $\$ 147$ per barrel, so it has been difficult to predict what an investor can sell his biomass-based fuel for. "Remember the scare in the 70's, when a lot of research on these non-fossil fuel technologies started?" he asks. "The price of crude dropped. I don't think that was a coincidence."

Fraud is also involved when there is a potential for vast profits. "I have had to go so far as to have my fuel carbon-dated," he says with amazement. "People go to the gas station and get diesel and claim they made it from a biomass source. Investors want to see that the carbon is from a modern-day source, and not fossil based."
"The FT process works on coal, natural gas or biomass," explains Wolan, "but it is not necessarily interchangeable. Coal and natural gas are homogenous. Biomass is diverse, so you have to have a system that allows for that flexibility. For example, municipal solid waste (MSW) like cut grass or landscape waste here in the South contains a lot of sand. The sand particles will turn to glass at high temperatures. Also, you have to make both coal and biomass into smaller particles before gasification, which is not trivial."

At the core of the FT process is the type of catalyst used. This is where Wolan and Gardezi spend much of their testing and analyzing the precious liquid fuel that is produced. In simple terms, small silica pellets, about the size of a lentil, are impregnated with cobalt to a specific depth. Any deeper and you would be wasting both the cobalt and the gasses that come in contact with the pellet. Called an eggshell catalyst, the USF team is furthering the work started by Enrique Iglesia at the University of California, Berkeley. Within the small bench scale reactor, the pipe containing the pellets can reach undesired high temperatures, something which must be addressed when building a full-scale pilot reactor. However, heat produced by the catalyst coming in contact with the syngas can be harvested for other processes such as heating water to create steam to drive a turbine, or can help in the initial heating of the biomass.

So how much biomass does it take to produce fuel? "For every four tons of biomass, we produce 1 ton of fuel. The only byproduct we have is water and a small amount of high quality ash that is used in the cement industry," explains Wolan. "We can make a very high quality diesel fuel that is so low in sulfur that you have to add a substance to provide lubrication for diesel engines. We also make jet fuel, called JP-8." Because the formulation of diesel and JP-8 are very similar, the future of military fuel may be consolidated into a one fuel operation. In other words, jets, tanks, jeeps and more will all burn the exact same fuel which makes sense strategically.

Professor Wolan, graduate students Ali Gardezi and Jaideep Rajput of USF's Division of Patents and Licensing were among the finalists in the Global Venture Challenge 2010. It was sponsored by the U.S. Department of Energy and international venture capital organizations. Funding has been provided by several sources including the Florida Energy Systems Consortium (FESC). The FESC Principal Investigator at USF is the very distinguished Dr. Yogi Goswami. The FESC was established and funded by the Florida Legislature in 2009 and is comprised of faculty from many different disciplines at 11 public universities here in Florida. Funding is also being provided by The Bill Hinkley Center for Solid and Hazardous Waste Management. The Bill Hinkley Center is a state-wide research center created by the Florida Legislature in 1988. (Bill Hinkley is a remarkable man who worked for the Florida Department of Environmental Protection for almost 30 years who was the architect of the way we recycle and manage waste here in Florida. Mr. Hinkley was deceased in 2005.) The Hinkley Center provides funding for waste management research to professors at 7 public and 2 private universities here in Florida. A tiny bit of the cost of buying a tire or a car battery here in Florida goes to fund this very important research of turning waste into a valuable resource. The Hinkley Center is hosted by the University of Florida College of Engineering and is the only center of its kind in the United States. The ultimate goal is to build a large pilot plant based on the small bench scale reactor and the analysis it provides.

