**Why Algae?**
Algae photosynthesize hundreds of times faster than terrestrial crops. It also remediates toxic wastewater and agricultural runoff.

**Corn Soy Canola Algae**
32% 12% 36% 0.9%

Fraction of US required to satisfy domestic transportation demand with biodiesel.

**Experimental Methods**
Biodiesel synthesis was conducted in two steps. The esterification energy barrier is lower than the transesterification energy barrier, so algae paste was simmered for twenty hours to ensure that all triglycerides were hydrolyzed. The dried product was loaded into the supercritical reactor with known ethanol and water weights. A 2x2 design of experiment was conducted to determine the effects of ethanol lipid excess and ethanol/water excess on conversion from free fatty acids to biodiesel.

**Analytical Methods**
Gas chromatography is the analytical benchmark for esters because triglycerides can only be distinguished from biodiesel by retention times. GC is robust, but it’s costly, finicky and time consuming. Infrared Spectroscopy is faster, easier and cheaper, but it can only identify analytes from chemical bonds. The supercritical esterification product, however, is suited for spectroscopy because lipids are hydrolyzed before the reaction—the only esters in the product are biodiesel.

**The Scaled-Up Concept**
Supercritical esterification researchers in the past have conducted reactions at 350 °C for short durations, but steel anneals at 300 °C, making laboratory results unscaleable in steel reactors. These trials deal with steady-state outcomes at 250 °C, conditions suitable for scale-up. The by-product of the in-situ process is hydrolyzed algal cellulose, free of lignin. These degraded sugars can be fermented internally regenerate ethanol for biodiesel production. A hypothetical process flow diagram is inset.

**In-situ Supercritical Biodiesel Production from Algae**
Dan Golden · James Gunadi · Nathan Rooney

**PARR 23 mL Supercritical Reactor, 250 C 120, atmospheres**
Separation of water and ethanol is too costly for base catalyzed ethyl esterification to be viable. Distillation from 180 to 190 proof consumes 350 times more energy than heating a supercritical reactor to 250 °C.

**Why Supercritical Esterification?**
Conventional biodiesel synthesis relies on a strong base (NaOH) to bypass the reaction energy barrier, so the presence of water catalyzes the formation of soap instead of biodiesel. Supercritical ethanol does not require a catalyst to esterify with triglycerides, so the reaction is more tolerant of moisture.

**Hydrolysis of Triglycerides**
1. Centrifuged Algae paste is hydrolyzed & dried
2. Hydrolyzed biomass is reacted at 250 °C and 120 atmospheres for 12 hours

**Hydrolysis**

**Ethanol**

**Soap (Undesired)**

**Ethyl Esters (Biodiesel)**

**Concentration Energy Distribution Energy**

Ethanol in Product (wt. %)

85 90 95

15 10 5

**Fourier Transform Infrared Spectrometer**
1. Spectra of prepared standards from the same feedstock
2. Model of absorbance vs. FAEE concentration
3. Spectra of supercritical product samples
4. Characterization of samples from model