

Economic Issues Related to Continuous Supercritical Biodiesel Production

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Introduction

Commercially, the most common method of biodiesel production is alkali-catalyzed transesterification (Freedman et al, 1984, 1986). In this process a feedstock is reacted with alcohol in the presence of an alkali catalyst to yield biodiesel and glycerol. Virgin soybean oil is the most common feedstock used in commercial biodiesel production in the U.S. as it lends itself well to transesterification, is the largest source of vegetable oil, and allows for fast reaction times (Knothe, Jurgens and Van Gerpen, 2005; Ginder and Paulson, 2006). Alkali-catalyzed transesterification, however, requires expensive, refined feedstocks composed mainly of triglycerides and with low free fatty acid (FFA) content. This is because FFAs react with the alkali catalyst to form soaps that make it difficult to separate the biodiesel from the glycerol. The cost of virgin, low FFA feedstocks has limited the competitiveness of biodiesel, compared to petro-diesel, and is a barrier to its commercialization.

Alternate production methods that use less expensive feedstocks, such as waste vegetable oil and low grade poultry fat, have been explored (Canakci and Van Gerpen, 1999, 2001; Mattingly, 2005; Mattingly et al., 2004; Schulte, 2007). These studies have led to consideration of: i) a two-step process of hydrolysis followed by esterification with an acid catalyst; and ii) a similar two-step process under supercritical (i.e. high temperature, high pressure) conditions without catalyst (Kusdiana and Saka, 2004; Schulte, 2007). It is possible to use feedstocks that are high in FFA content with these alternate production methods without the interference of soap formation as the first hydrolysis step separates glycerin from the feedstock. Studies have compared alkali-catalyzed transesterification to acid-catalyzed processes (Zhang et al., 2003). These studies found acid-catalyzed esterification to be slower than alkali-catalyzed processes. This is mainly a function of the acid-catalyzed process generating water which impedes forward progress of the reaction and hence requires separation. Yet Zhang et al. suggests that acid-catalyzed biodiesel production using waste vegetable oil (aka yellow grease) is potentially an economically competitive alternative to alkali-catalyzed transesterification as higher FFA content in the feedstock would lower overall production cost given the lower feedstock cost generally observed (see Figure 1).

This study focuses on the cost-effectiveness and price risk effects of the latter processing technology -- supercritical methanol biodiesel production. By using supercritical conditions (temperatures of $\geq 240^{\circ}\text{C}$ (464°F) and pressure of $\geq 1,140$ psia (Kusdiana

and Saka, 2004; Schulte, 2007), the feedstock and methanol form a single phase that allows more significant mixing and hence no catalyst is required to speed the reaction (Chiu, Goff and Suppes, 2005). An added benefit is that the presence of water in the feedstock methanol mixture does not impede the reaction. The tradeoff is the added expense of additional heating and high-pressure equipment.

A bench-scale experimental reactor built at the University of Arkansas has demonstrated that continuous supercritical methanol production with conversion rates ranging from 60 to 85 percent is possible with feedstocks ranging from 100 percent FFA to 100 percent triglycerides (Magie et al. 2009). The objectives of this study were i) to scale up from these bench-scale estimates to a full-scale production facility; ii) to estimate biodiesel production costs for a variety of feedstocks with different FFA contents - brown grease (50 percent FFA), yellow grease (15 percent FFA) and refined soybean oil (< 1 percent FFA); and iii) to show how a range of feedstocks might mitigate associated price risk.

Process Description - The Continuous Bench-Scale Supercritical Methanol Reactor

Students at the University of Arkansas designed and built a bench-scale continuous supercritical methanol reactor using commercially available components (see Figure 2 below). The reactor produces biodiesel at a rate of 16mL/minute. The experimental reactor consisted of three sections: the pre-treatment section, the reaction section, and the cooling section.

In the pre-treatment section of the process, two feed vessels are used to hold the reactants. One vessel contains methanol at room temperature and the other contains oil heated and insulated with heat tape. Each fluid is filtered and pressurized to 2000 psi and mixed before entering the reaction section of the process under supercritical conditions with a residence time of several minutes. A cooling process is required to collect the reaction products consisting of two immiscible layers.

Depending on the initial feedstock employed these two immiscible layers are different. For the case of pure FFA feedstock, the top layer is a methanol water mixture saturated with oil (that can be fed back to the reactor without complications) and the bottom layer is a biodiesel layer saturated with methanol. The bottom layer is removed using a separatory funnel and subsequently heated to 70° C to vaporize and recover the methanol, leaving the biodiesel product.

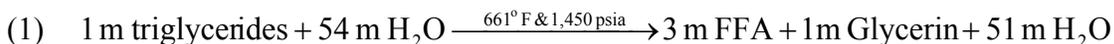
To produce methyl-esters from triglycerides, water was added to the system to break the FFA from the glycerin backbone. Per molecule of triglyceride, one glycerin molecule and three FFA molecules are now mixed with the methanol in the biodiesel reactor in a hydrolysis, esterification and transesterification reaction. The three FFA molecules convert to methyl-esters by means of esterification as in the process described above. The glycerin and water pass through. Now the two immiscible layers contain water, glycerin and excess methanol in the top half and primarily biodiesel and unreacted oil and methanol in the bottom half. The top half can be separated by vaporizing and recovering the excess methanol at 70° C and subsequently raising the temperature to drive off the

water from the glycerin. The bottom half is impure and requires several steps to clean. Results of conversion efficiencies of this process are described in Table 1.

Given the above complications associated with cleaning the biodiesel, unreacted oil and methanol mixture with the triglyceride feedstock, a separate first-step hydrolysis reaction to remove glycerin was proposed for a scaled up version of a supercritical biodiesel production process as highlighted in Figure 3.

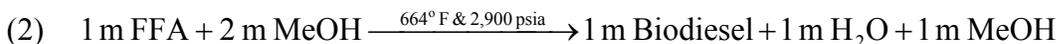
Proposed Commercial Scale Continuous Flow Supercritical Production

The process begins with feedstock filtration to remove impurities. A hydrolysis reaction follows in a continuous flow pipeline reactor creating plug flow and converts the triglycerides in the feed to FFA and glycerin with subcritical water using a 54:1 water to fat molar ratio. The reactor operates at 661°F and 1,450 psia. It has fully developed turbulent flow and results in 100% conversion of feed to free fatty acids.



Not included in this reaction is the pass through of FFA. Following triglyceride conversion to FFA, the resultant mixture is cooled to 590°F and enters a gravity separator to separate the FFA from the glycerol/water mixture formed during the hydrolysis reaction. Glycerol recovered from the gravity separation is depressurized and cooled further for eventual use as an offset to natural gas heat requirements for the steam required in the hydrolysis reaction (necessary glycerol distillation column and tube cooling bank not shown in Figure 3). For each mole of triglyceride entering the hydrolysis reaction, 0.5 moles of glycerol is recovered with the remaining 0.5 moles of glycerol leaving the system in waste water (Griffin, Lewis and Mengarelli, 2008). Hence varying the FFA content of the initial feedstock leads to varying amounts of glycerol recovery and thereby the amount of natural gas for steam heating in the hydrolysis reaction varies by FFA content of the feedstock.

The resultant stream of FFA leaving the hydrolysis reaction is reheated to 664°F and the pressure is doubled from 1,450 psia to 2,900 psia. Methanol is added to the FFA (molar ratio of 1:2) at similar pressure and heat for the esterification reaction under supercritical conditions in the absence of catalyst. The increased pressure above the critical pressure is for the purposes of increased reaction rates.



Gravity separation after cool down and release of pressure results in biodiesel ready for product drying as well as recovery of methanol. It is assumed that some portion of initial feedstock by weight would leave the system with water as unreacted feedstock during the biodiesel drying and methanol recovery operations.

All storage tanks were designed to run at 85% capacity for surge protection and a targeted 1.5 days of storage for disruptions built into the system. Where possible, heat

recovery from cooling operations was performed. Filtration of fat impurities resulted in a loss of 395 lbs per 7,000 gal tanker truck delivery or 0.75% by weight. An average biodiesel density of 7.25 lb/gal was used regardless of feedstock and an average feedstock density of 7.5 lb/gal based on poultry fat and yellow grease as reported by Goodrum et al, 2002. Molar weights of FFA and hence biodiesel are not constant across feedstocks as fat composition is different. Molar weight changes are marginal, however and hence average values, as reported, were used.

To model a system that is capable of handling feedstock with varying FFA content, Roberts and Braud ran ProII chemical process design software to develop design specifications for equipment for a 20 million gallon per year biodiesel facility using the above process.

The output from the analysis allows determination of energy requirements for the system. Capital investment varies if the design is optimized for feedstocks with different FFA contents as varying amounts of FFA lead to different product stream rates (see Table 2). Glycerol production, labor and energy requirements as well as waste water flows were monitored across the two different designs. The two data points for yellow and brown grease at expected FFA contents of 15% and 50% were then used to extrapolate to other FFA content feedstock with reasonable accuracy.

Table 2 shows the capital investment information associated with the flow diagram illustrated in Figure 3. Equipment installation charges, labor and maintenance charges were estimated using parameters from Peters, Timmerhaus and West, 2003. Industrial electricity cost, and natural gas charges were averaged from February, 2005¹ through latest available data (September, 2009 at time of writing) using purchased price series from the Jacobsen Publishing Company, Energy Information Administration as well as a chemical price reporting service for methanol. Price series were deflated using appropriate monthly producer price index information available from the Bureau of Labor Statistics. A labor charge of \$25.58 per hour including benefits was assumed. Capital ownership charges were calculated using a 10% capital recovery rate and 1% charge for taxes and insurance assuming a 20 year useful life and zero salvage value for capital investments. Land charges were excluded from the analysis.

In the absence of performing additional design analyses for specific fats, the above information was used to extrapolate the natural gas and electricity use rates for different FFA while keeping the ownership charges, labor and water use rates constant at the average observed across both design values.

This results in the following FFA dependent processing charges:

$$(3) \quad pc_x = \frac{(2,311,139 + 8,050x) \cdot p_e + (107,686 + 555x) \cdot p_{ng}}{CAP}$$

¹ The data starting point was dictated by available biodiesel price information.

where pc_x are processing charges per gallon of biodiesel produced, x is the FFA content by weight for the feedstock processed, p_e and p_{ng} are the 2005 to 2009 monthly, deflated average costs for electricity and natural gas and CAP is the targeted 20 mm gallon annual plant capacity.

Adding, FFA independent charges

$$(4) \quad pc = pc_x + \frac{L + W + CR + CAP \cdot (1 + r_x + d_x) \cdot p_f}{CAP}$$

where pc are total per gallon processing and feedstock costs, L are the annual labor charges, W are annual water charges estimated at \$4 per thousand gallon, CR are annual capital recovery charges on equipment and buildings including insurance and taxes only but excluding land since it does not depreciate. To account for changes in FFA content, r_x -- a standard weight conversion factor² and d_x -- a factor accounting for the likely increase in processing losses due to impurities ranging from 2.75% for yellow grease to 5% for brown grease, were applied to the initial feedstock cost, p_f . In turn, p_f is the 2005 to 2009 monthly, deflated cost for feedstock that changes from 20.5 ¢ for yellow grease to 9.8 ¢ for brown grease. Subtracting pc from the biodiesel price p_{bio} leads to an estimate of profitability per gallon of annual output to management and land. Changes in non-feedstock costs are highlighted in Figure 5.

Note that natural gas costs increase with increasing FFA content as less glycerol becomes available for heating. Other costs are nearly identical.

In essence, this turns the attention of the cost analysis to the initial feedstock prices for fats and oils as well as input prices for electricity, water, natural gas and methanol. Price histories of these feedstocks and inputs are presented in Figure 4. Water charges were held constant at \$4 per thousand gallons.

Feedstock Price Relationships

As shown in Figure 4, fats and oil prices tend to move in the same direction over time. This is a function of the final value for use of these varying fat and oil sources as well as supply conditions. That is, vegetable oil is used for food and feed and the food value for soybean oil is higher than for non-edible brown grease, for example. This difference in value would persist over time unless changes to the system occur – i.e. a technology is found to convert brown grease to something more valuable and hence its price increases relative to the other fats and oil prices.

² Using molar weights of 858.07, 273.32, 287.32, 92.11, 32 and 18 for triglycerides, FFA, biodiesel, glycerin, methanol and water, respectively, the ratio of feedstock weight to final biodiesel weight varies by FFA content as follows: $r_x = 0.99549 - 0.00044 x$.

To test for this co-movement in prices the price histories for soybean oil, poultry fat and beef tallow were evaluated to see if price changes indeed show a historical relationship. To do this, the monthly price observations were tested for stationarity using an Augmented Dickey Fuller test (Gujarati, 1995). All series proved to be integrated of the same order and hence were regressed against each other to see if the price series were co-integrated (Enders, 1995). This is a common procedure used to test for the law of one price – the price differential is accounted for by a consistent factor like transport cost, for example, such that traders would bid prices between two markets for the same commodity to be the transport cost between the two markets. Otherwise traders purchase the product in one market and move it to the other to make a profit.

Testing for similar reactions in fats and oils prices to shocks to the system (i.e. the startup of biodiesel production) allows decision makers to see if the price series react in the same way as perhaps the leading price series, in this case, soybean oil, the most abundant vegetable oil produced in the U.S. Since futures markets exist for soybean oil, biodiesel processors have the opportunity to hedge price risk. A logical extension of the above co-integration or law of one price test is that soybean oil futures may be suitable for other fats and oils in the system if the price series are co-integrated.

Return Expectations for SCM Biodiesel Using Different Feedstock Sources

The above price information and processing charges were also subjected to Monte-Carlo type risk analyses. In essence cost parameter uncertainty was simulated such that return risk to biodiesel production using different feedstock sources could be employed. Risk parameters included the price of water, electricity, natural gas, methanol, feedstock price, biodiesel price and processing losses. Table 3 summarizes these aspects for soybean oil, poultry fat, beef tallow, yellow and brown grease. A range of estimates for the water cost and the processing losses are authors' estimates and modeled using a triangular distribution. The remaining information pertains to observed historical price information illustrated in Figure 4.

Results

Applying equations 3 and 4 with a constant feedstock cost of \$0.25 per lb regardless of FFA content resulted in a product cost differential favoring yellow grease by 0.81 ¢ per gallon or ~\$163,000 per year. This is mainly a result of natural gas and electricity cost savings as well as changes in biodiesel yield due to impurities. Applying the average historical feedstock costs observed, however, leads to a 77.53 ¢ per gallon savings for brown grease or ~\$15.5 million per year as the feedstock cost is half the amount for brown grease when compared to yellow grease. The reader is cautioned, however, that these profit differences would likely disappear with the above technology as the price of brown grease would be bid up until profitability from biodiesel production would be the same as for yellow grease. Additionally, excess supply of yellow grease and tight supplies of brown grease would also narrow the gap observed above. Since that has not been observed, our model results may be underestimating yield losses due to higher

impurities in brown grease or any discounting for final biodiesel product color or cold flow properties.

Nonetheless, the model results suggest, from a processing cost perspective, that FFA content does not alter non-feedstock cost of production significantly. This is a significant advantage over traditional alkali-catalyzed transesterification in the sense that a biodiesel producer has the ability to source fats and oils with a wide range of FFA characteristics without suffering significant yield losses due to soap formation. In fact, higher FFA content allowed for lower feedstock cost as long as supplies are available.

Prior to biodiesel blenders tax credits and other fuel taxes, Table 3 showed both expected returns and their associated risk as estimated from the uncertain parameter estimates related to water, electricity, methanol, natural gas, processing loss as well as input and output price risk. Soybean oil yields the most expensive and most risky solution. This is likely a function of elevated price risk and price level for this edible vegetable oil as well as the large amount of glycerin byproduct generated and used for heating in this analysis. All the non-virgin feedstock sources provided positive returns even in light of greater yield loss potential due to impurities. In general, higher FFA content resulted in better results (both higher returns and lower risk), but these feedstocks are generally less available in the market place than soybean oil. Not considered in the analysis are cold flow properties and energy ratio, both of which would be expected to decline with increasing FFA and grease based feedstock leading to a potential price discount for the biodiesel end product unless blending is performed..

The law of one price results shown in Table 4, suggest that soybean oil futures could indeed be used to cross hedge beef tallow and brown grease prices but not poultry or yellow grease prices -- a finding similar to Graf, McKenzie and Popp (2008) at least in the case of poultry fat.

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Table 1. Supercritical Methanol Reaction Experimental Results

Feed Composition		Biodiesel	Biodiesel	Percent	Residence	Water
Trigly- cerides (%)	Free Fatty Acids (%)	Viscosity (cSt)	Specific Gravity (g/ml)	Conversion (mole basis)	Time (min)	Added
0	100	3.48	0.854	78%	10	no
0	100	4.50	0.884	80%	10	no
0	100	3.20	0.885	75%	6	no
50	50	15.20*	0.902	60%	10	no
50	50	7.20	0.885	84%	10	yes
100	0	--	--	0%	10	no
100	0	--	0.920	68%	10	yes

*Sample was not visually homogeneous and was probably not pure biodiesel.

Table 2. Capital Cost, Energy, Labor and Cooling Water Assumptions. Dollar Values are in constant 2009 Dollars.

	Yellow Grease	Brown Grease	Install Factor ^a
Equipment			
Heat Exchangers	82,196	81,184	4.8
Pumps	38,143	31,407	7.7
Separators	48,624	48,624	4
Storage Vessels	560,173	560,173	4
Supercritical Methanol Reactor	77,181	77,181	4.8
Steam Generator	128,202	128,202	4
Purification Column	215,271	215,271	4
Total Equipment	1,149,790	1,142,042	
Buildings (50% of Total Equipment)	574,895	571,021	
Total Installed Fixed Cost	5,442,684	5,382,087	
kWh used	2,431,886	2,713,629	
Natural Gas (1000's of ft ³)	116,018	135,459	
Water use in millions of gallons	90.0	90.0	
Labor Force	19	19	
Energy Ratio^b	9.46	8.81	
Processing Cost per Gallon^c	\$ 0.31	\$ 0.32	

Notes:

- ^a Equipment cost data was multiplied by the install cost factor to arrive at the Total Installed Fixed Cost excluding Land.
- ^b The energy ratio is calculated as ratio of biodiesel Btu generated divided by the sum total of Btu from electricity, methanol and natural gas consumed and excludes transportation energy charges for inputs and output. The following Btu contents were used: 3,412 Btu/kWh, 1,000 Btu per ft³ of natural gas, 56,800 Btu per gal of methanol and 129,500 Btu per gal of biodiesel.
- ^c The processing costs per gallon of final biodiesel sold are calculated using an average cost of \$1.07/gal of methanol using 0.13154 gal of methanol / gal of biodiesel, \$4 / thousand gal of water, and a 10% capital recovery rate assuming 20 year useful life and zero salvage value on Total Installed Fixed Cost (FCI), direct labor charges of \$25.58 per hour at 52 weeks per year and 40 hours of work per week, annual labor maintenance charges of 7% of FCI, 1% of FCI for taxes and insurance, an average natural gas price of \$6.89 / thousand ft³ and an industrial average electricity price of \$0.104/kWh. Capital equipment charges are based on 2002 prices and were converted to 2009 using the machinery and equipment producer price index as published by the Bureau of Labor Statistics. Using nominal prices for operating inputs changed the processing cost per gallon to \$0.37 and \$0.38 per gal for yellow and brown grease, respectively.

Table 3. Summary of Average and Standard Deviation of Profitability Factors for Supercritical Methanol Production. Prices are in constant 2009 Dollars.

	SBO	Poultry	Tallow	Yellow	Brown
Input Costs					
Water (\$/000 gal)			4.00 (2.00, 6.00)		
Electricity (¢ / kWh)			10.359 (0.245)		
Natural Gas (\$/000 ft ³)			6.886 (1.748)		
Methanol (\$/gal)			1.070 (0.370)		
Feedstock (¢ / lb)	32.631 (6.420)	21.458 (4.634)	23.676 (5.621)	20.468 (4.666)	9.769 (2.821)
Output Price					
Biodiesel (\$/gal)			2.606 (.330)		
Processing Losses					
(% of Feedstock wt)	0.5 (0.5,1.5)	3.0 (1.0,5.0)	3.0 (1.0, 5.0)	2.75 (0.75, 5.0)	5.0 (0.75, 10.0)
Expected FFA content					
	0.5	4	4	15	50
Biodiesel Profit (¢ / gal)					
	-8.1 (57.8)	70.4 (48.0)	53.9 (52.5)	78.5 (47.6)	155.9 (39.9)

Notes:

Numbers in columns entitled SBO (soybean oil), Poultry (stabilized poultry fat), Tallow (fancy bleachable beef tallow), Yellow (yellow grease) and Brown (brown grease) are average and standard deviation or minimum and maximum reported in parentheses depending on normal or triangular distributions. All numbers refer to available monthly data available from February 2005 to September 2009. Processing losses are a result of impurities filtered out prior to processing as well as conversion losses due to impurities that can't be filtered.

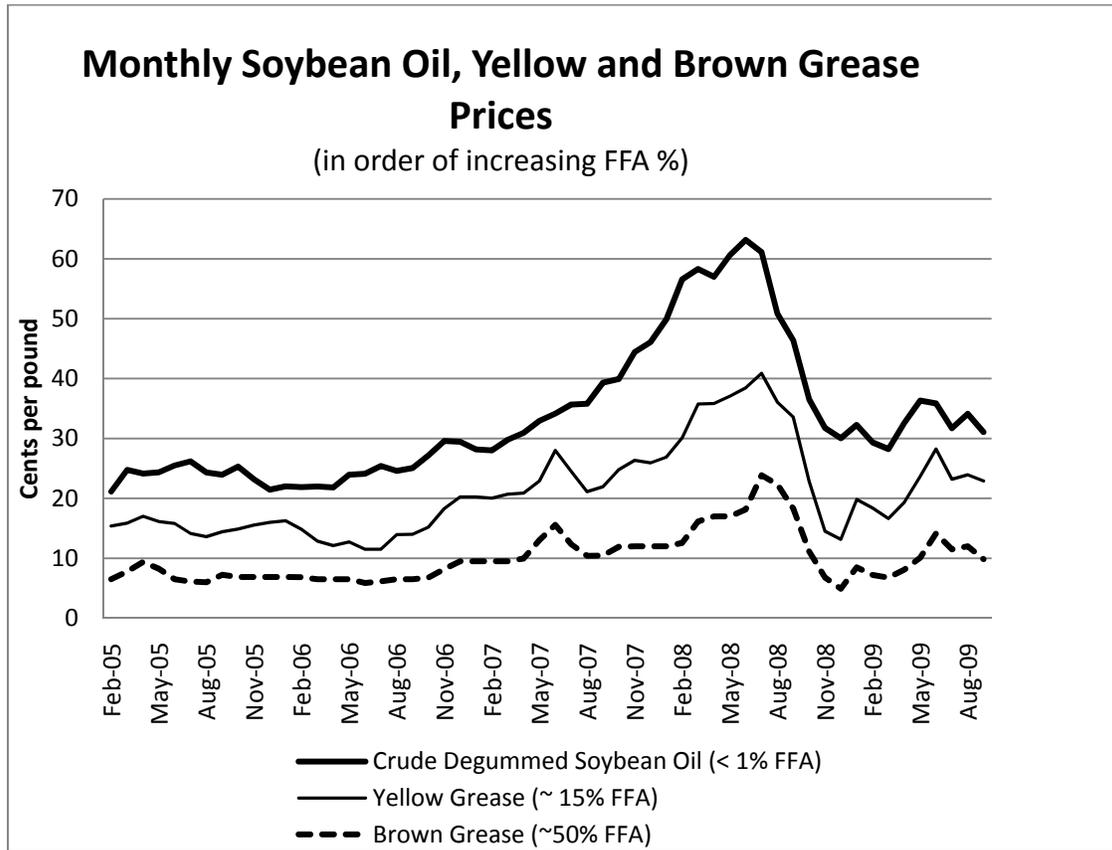
Table 4. Law of One Price Results for Soybean Oil, Beef Tallow, Poultry Fat, Yellow Grease and Brown Grease.

Price Series		β_I	S.E.	Residual stationarity t-stat	β_{II}	S.E.	Residual stationarity t-stat	R^2	Loop Holds
lnsbo	lnpoultry	0.868	0.060	-3.100	0.944	0.065	-3.407	0.816	No
	lntallow	0.846	0.053	-4.095	1.003	0.062	-4.386	0.845	Yes
	lnyellow	0.806	0.056	-2.922	1.013	0.071	-3.624	0.813	No
	lnbrown	0.740	0.059	-4.237	1.042	0.084	-4.976	0.766	Yes
lnpoultry	lntallow	0.890	0.052	-2.985	0.971	0.057	-3.016	0.861	No
	lnyellow	0.901	0.034	-3.575	1.041	0.040	-3.547	0.937	Yes
	lnbrown	0.828	0.043	-3.975	1.072	0.056	-4.497	0.885	Yes
lntallow	lnyellow	0.947	0.032	-3.469	1.004	0.033	-3.451	0.950	No
	lnbrown	0.885	0.036	-4.186	1.051	0.042	-4.165	0.929	Yes
lnyellow	lnbrown	0.917	0.034	-3.340	1.027	0.038	-3.354	0.940	No

Notes:

Price series entitled lnsbo, ln poultry, lntallow, lnyellow and ln brown are the natural logarithm of monthly soybean oil, poultry fat, beef tallow, yellow and brown grease prices, respectively. All price series were stationary of the same order and hence could be regressed against each other. The $\beta_{I/II}$ values are cross price elasticities indicating by what percentage the price of the oil or fat in the second/first column were to change with a one percent change in the oil or fat in the first/second column.

Figure 1. The Relationship between FFA content and Price for Ag Derived Fats and Oils, Central U.S. Markets.



Source: The Jacobsen Publishing Company.

Figure 2. Process Flow Diagram for Experimental Reactor

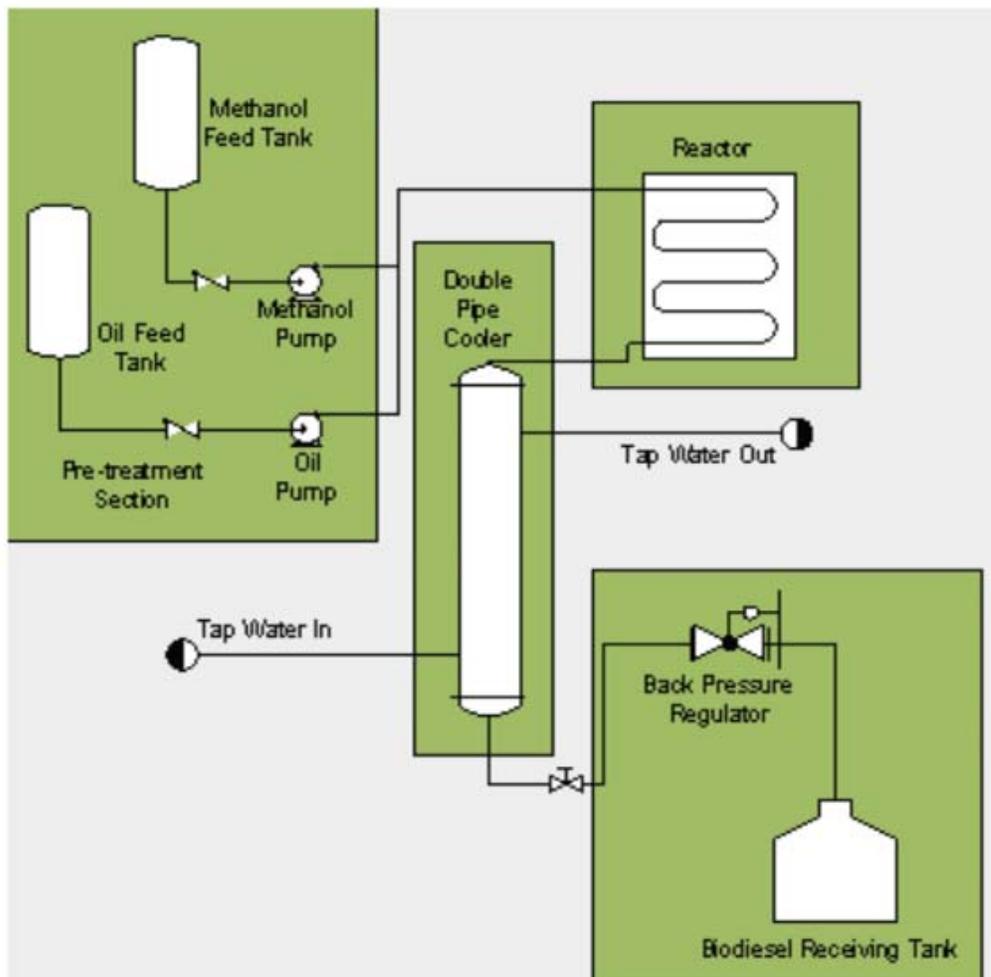


Figure 3. Proposed Scale Up of Continuous Flow Supercritical Biodiesel Production.

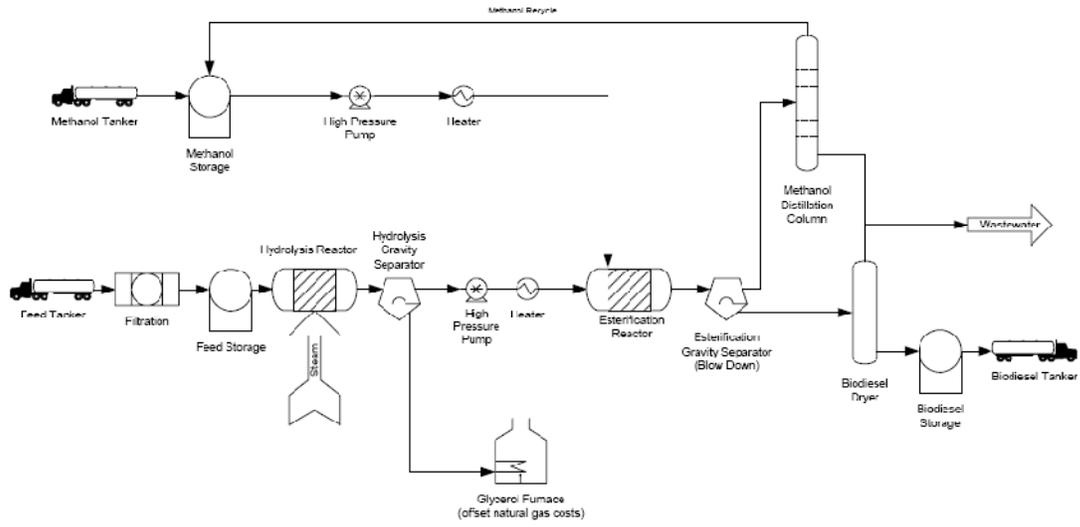
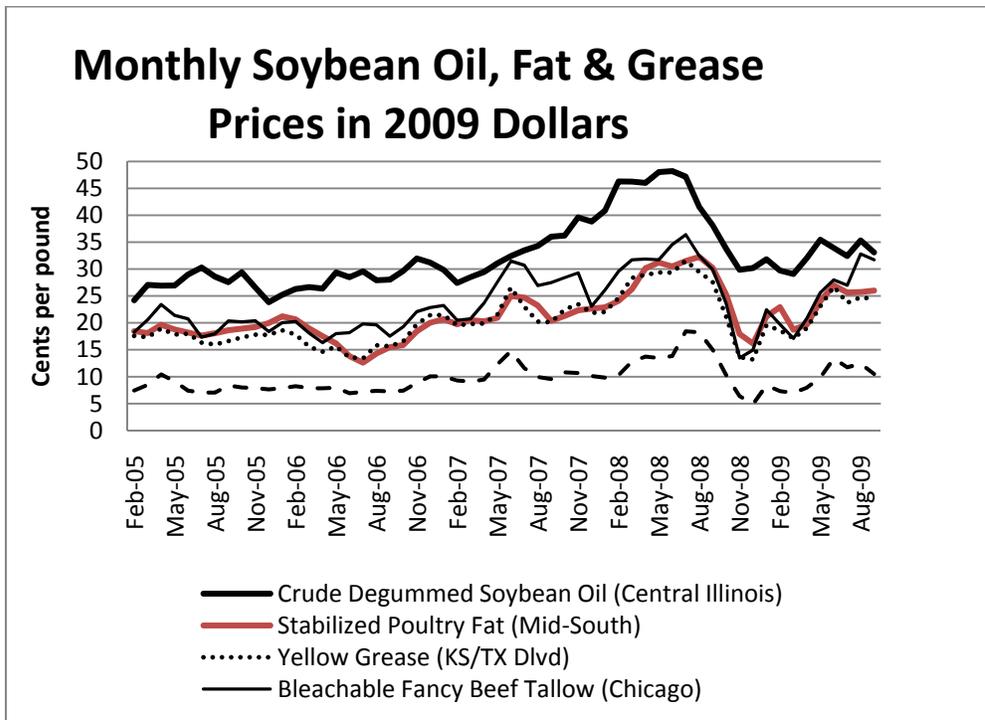
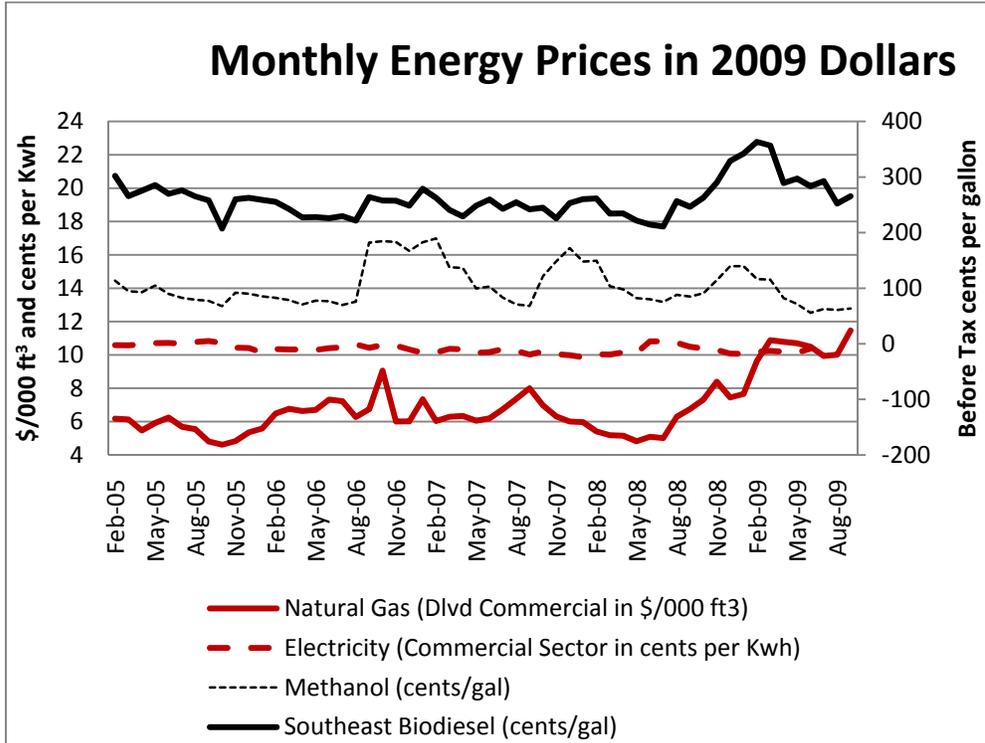


Figure 4. Historical Input and Output Prices.



Sources: The Jacobsen Publishing Company, U.S. Energy Information Administration, and Purchasing Data.com.

Figure 5. Breakdown of Estimated Non-Feedstock Input Costs in \$/gal of Biodiesel in 2009 Dollars using Monthly Averages of 2005 to 2009 Natural Gas, Methanol and Electricity Prices.

