Sustainable Production and Deployment of Biodiesel in Texas

Final Report

Submitted to the Shell Center for Sustainability
Rice University

Project Team:
Daniel Cohan
Kyriacos Zygourakis
Ramon Gonzalez

Student Assistants:
Wei Zhou
Venetia Rigou
Seoyeon Hong

May 2009

Overview

Biodiesel production increased rapidly in recent years as producers sought a renewable alternative to petroleum diesel fuel. At some point, biodiesel production in the Houston region encompassed ten facilities with a combined capacity of 380 million gallons per year. Produced by the trans-esterification of vegetable oils and animal fats, biodiesel has similar density, flash point, viscosity, oxidation stability to petroleum diesel. These similarities enable biodiesel blends to be used in conventional diesel engines without significant modifications.

Even if production continues to increase, limitations in the availability of soybeans and other potential feedstocks will likely limit biodiesel to replacing only a modest percentage of diesel fuel use. How this limited resource is produced and deployed will shape its potential impact on the environment, fossil fuel use, and cost. The large range of feedstocks, scale, and chemical processes by which biodiesel can be manufactured may provide opportunities to identify cost-effective and environmentally sustainable approaches. Likewise, the range of blending percentages, vehicle types, and locations in which biodiesel can be deployed may provide opportunities to target deployment for optimal air quality impacts. The work conducted for this Shell Center grant has begun to explore the implications of alternative approaches to biodiesel production and deployment.

2. Production of Biodiesel

Biodiesel is produced by transesterifying vegetable oils (canola, soybean etc.), waste cooking oil or other fats. The overall reaction may be written as follows:

$$
\begin{array}{lcccccc}
CH_2-OOC-R_1 & & & & R_1-OOC-R' & & CH_2-OH \\
| & & & & | & & | \\
CH_2-OOC-R_2 & + & 3R'OH & \xrightleftharpoons{\text{Catalyst}} & R_2-OOC-R' & + & CH_2-OH \\
| & & & & | & & | \\
CH_2-OOC-R_3 & & & & R_3-OOC-R' & & CH_2-OH
\end{array}
$$

The detailed reaction scheme involves a sequence of reversible reactions that transform the triglycerides to diglycerides, monoglycerids and, finally, to alkyl-esters. We used triolein ($C_{57}H_{104}O_6$), a triglyceride formed from oleic acid, to represent canola oil was used in our simulations. Methanol was the alcohol chosen because of its low cost and favorable kinetics. Thus, methyl oleate was the main product of the transesterification reaction, which we will dente here by FAME for fatty acid methyl esters.

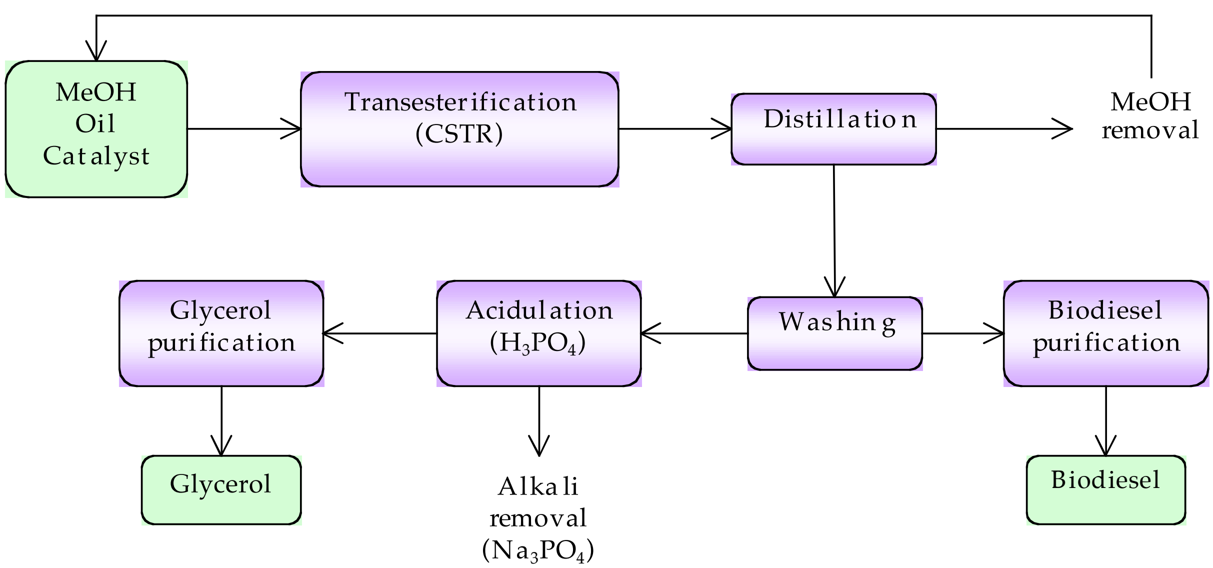

Figure 2.1: Basic steps of alkali-catalyzed process for biodiesel production.

Figure 2.1 depicts the basic steps of biodiesel production, for the alkali-catalyzed process. The vegetable oil is mixed with the methanol and NaOH (that acts as a catalyst) and pumped into the continuous stirred tank reactor. The product mixture goes to the first distillation column where most of the methanol is separated and recycled back to the reactor to minimize costs. The remaining mixture is washed and goes though a gravity separator. The top layer contains most of the product (FAME) that is purified to biodiesel fuel specification in another distillation column.

The bottom layer from the gravity separator is neutralized with phosphoric acid to remove the KOH and is then pumped into another distillation column that purifies the glycerol byproduct.

2.1 Development of Process Simulator

The biodiesel industry lists 137 plants in the United States as operating, under construction or planned. Their capacities range from a maximum of 105 million down to 1 million gallons per year (MMgy). Figure 2.2 shows a histogram of the capacities of the US biodiesel plants. The average plant capacity is about 16.8 MMgy and the median capacity is 9.5 MMgy. Since our objective was to study the operation of plants with capacities more appropriate for for distributed production and distribution of biodiesel, we chose to simulate plants with capacities ranging from 0.25 to 2.6 MMgy.

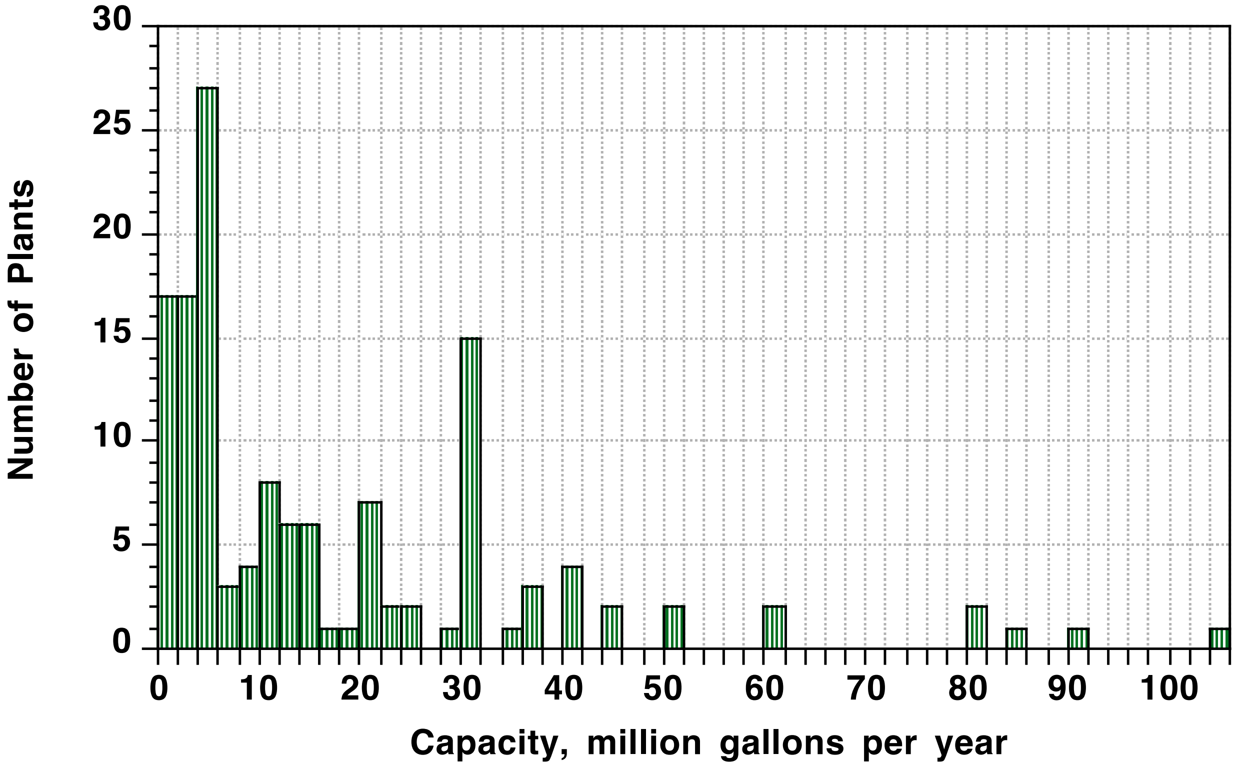

Figure 2.2: Histogram of the production capacities of US biodiesel plants.

The flowsheet for the final simulation is depicted in Figure 2.3. The canola oil stream is mixed with the methoxide (methanol and NaOH) stream and pumped into the CSTR reactor (R-101) where the transesterification reactions take place at 60^{o}C and 2 bar pressure. For simplicity, transesterification has been considered as a single-step reaction with 95% conversion. Since we have used excess methanol to speed up the reaction rate, the product stream from R-101 goes to the first distillation column T-201 where most of the excess methanol is separated and recycled back to the reactor.

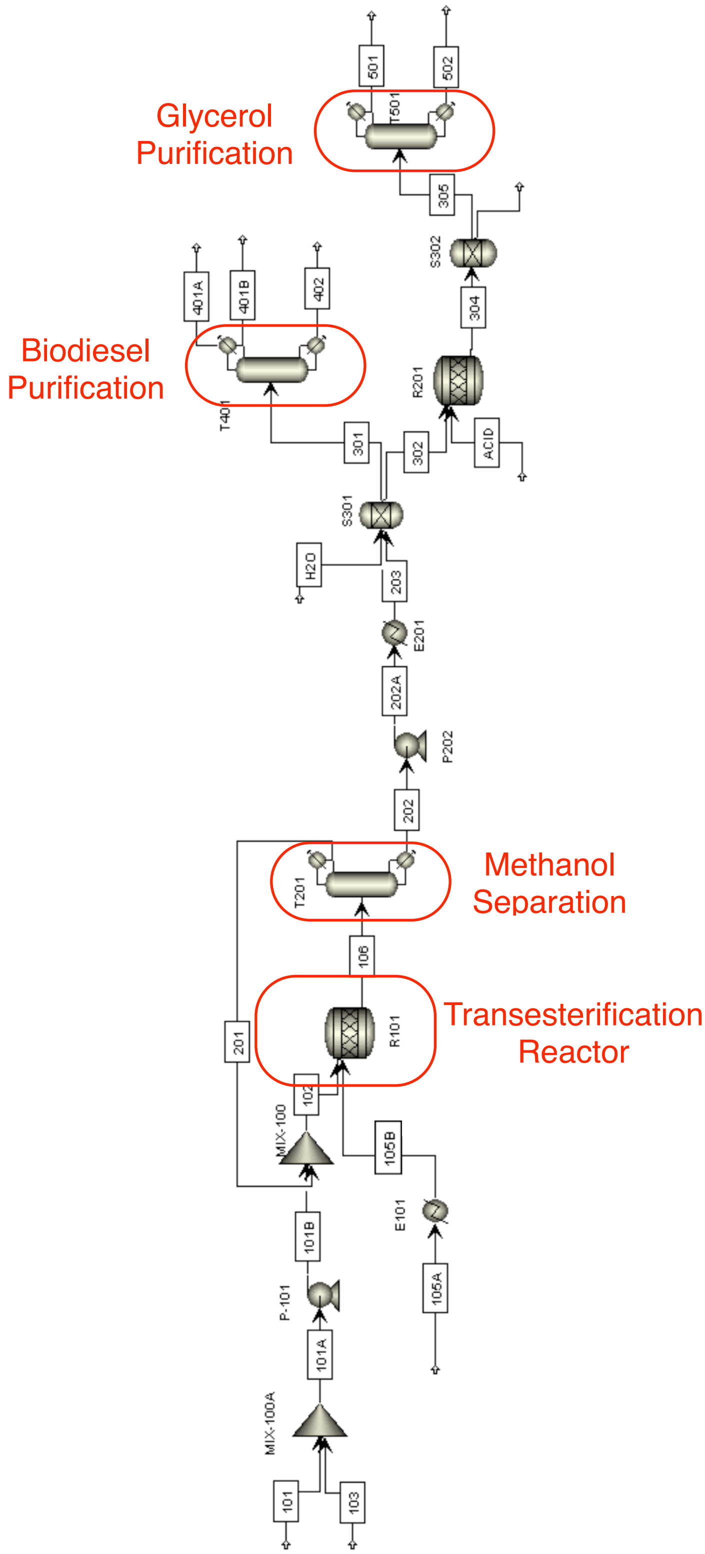

Figure 2.3: Simplified flow chart diagram showing the main processing units of the the alkali-catalyzed process for biodiesel production.

The remaining products go into a mixer-settler separation unit (S-301) where they are first washed with water before they are allowed to flow into the settler unit where the lighter FAME-rich phase separates (with the help of gravity) from the heavier glycerol-water phase. The FAME-rich stream is pumped to a distillation column (T-401) in order to obtain high-purity biodiesel (stream 401B) that meets ASTM fuel specifications for low water, methanol and oil content.

The glycerol-rich stream is first neutralized with H_3PO_4 in an acidulation unit to remove the NaOH catalyst. The salt (Na_3PO_4) formed during this step is removed in a gravity separator (S-302). Finally, the salt-free stream enters the distillation column T-501 where the glycerol is purified and exits from the bottom of the column.

Tables 2.1 and 2.2 give the flow rates and compositions for the reactant and product streams, as well for some of the key intermediate streams. The stream designations are given in Figure 2.3 and the flow rates are for the plant with the 2.6 MMgy capacity.

Table 2.1: Reactant and Key Intermediate Stream Compositions

Stream Name	**101**	**103**	**105B**	**106**	**202**	**301**	**302**
Mass flow (kg/h)	117.2	10.00	1050.00	1288.4	1177.20	1058.03	219.17
Component Mass Fraction							
MeOH	1.000	--	--	0.093	0.008	0.003	0.024
Oil	--	--	1.000	0.041	0.045	0.048	0.007
FAME	--	--	--	0.778	0.851	0.947	--
Glycerol	--	--	--	0.081	0.088	--	0.473
NaOH	--	1.000	--	0.008	0.008	--	0.046
H_2O	--	--	--	--	--	0.001	0.449
H_3PO_4	--	--	--	--	--	--	--
Na_3PO_4	--	--	--	--	--	--	--

Table 2.2: Product Stream Compositions

Stream Name	**401A**	**401B**	**402**	**501**	**502**
Mass flow (kg/h)	4.29	**980.71**	73.03	85.00	**127.1**
Component Mass Fraction					
MeOH	0.353	0.002	Trace	0.063	48 ppb
Oil	0.001	55 ppm	0.697	--	--
FAME	0.506	**0.998**	0.303	--	--
Glycerol	--	--	--	1 ppb	**0.816**
NaOH	--	--	--	--	--
H_2O	0.139	831 ppm	Trace	0.937	0.184
H_3PO_4	--	--	--	--	--
Na_3PO_4	--	--	--	--	--

2.2 Discussion of Results and Conclusions

The summary results presented in Table 2.3 demonstrate that the plant we designed is very efficient in converting the reactant (vegetable oil) into biodiesel. More than 95% of the oil is converted into biodiesel. The biodiesel recovery is even higher and exceeds 97%. Only two small output streams (401A and 402) have significant FAME concentrations. Finally, the the recycling of methanol reduces the losses of this reactant to a level below 8%.

Table 2.3: Overall Conversion and Methanol Utilization

Fraction of vegetable oil converted to biodiesel	95.1%
Fraction of produced biodiesel recovered in high purity (ASTM spec)	97.6%
Fraction of methanol utilized in the reaction	92.5%

Table 2.4 presents the heat duties calculated for the various units of our process. Clearly, the three distillation units account for the vast majority of energy requirements demonstrating, once more, that the separation steps are the most energy-intensive part of the process. Thus, the recovery of methanol and the purification of FAME and glycerol will add significantly to the overall cost of the produced biodiesel.

Table 2.4: Energy requirements

Process Unit	Heat duty (MJ/hr)
Heating of inlet stream (E-101)	51.3
Cooling of intermediate stream (E-201)	-396.7
Transesterification Reactor (R-101)	-96.7
MeOH removal (T-201) - Condenser	-350.7
MeOH removal (T-201)- Reboiler	757.3
Water washing (S-301)	0.83
FAME purification (T-401) - Condenser	-1,539.2
FAME purification (T-401) - Reboiler	2,009.58
Acidulation (R-201)	-84.5
Na_3PO_4 removal (S-302)	0.03
Glycerol purification (T-501) - Condenser	-551.4
Glycerol Purification (T-501) - Reboiler	616.2
Pumps (Electric)	0.052

Our simulations have shown that the heat duties of the various units scale linearly with production. Of course, the capital costs and (as we will see later) the options for meeting the heating and cooling requirements of our process will vary significantly with the plant production capacity.

An important metric that is commonly used to measure the sustainability of biofuels is its net energy ratio NER that is defined as follows:

$$\text{NER}=\frac{\begin{bmatrix}\text{Energy Content}\\ \text{of Biofuel}\end{bmatrix}+\begin{bmatrix}\text{Energy Content}\\ \text{of Coproduct}\end{bmatrix}}{\begin{bmatrix}\text{Energy Used in}\\ \text{Agricultural Phase}\end{bmatrix}+\begin{bmatrix}\text{Energy Used in}\\ \text{Production Phase}\end{bmatrix}}=\frac{E_{biofuel}+E_{coproduct}}{E_{agri}+E_{prod}} \qquad (2.1)$$

The main objective of this study is the calculation of E_{prod}, the energy used in the biodiesel production phase. The total heating requirements for our plant are **3.52 MJ/kg** or **11.7 MJ/gallon of biodiesel**. However, the total primary energy needed to meet these needs depends on how we heat or cool the units of our process.

A large plant will have its own boiler system that uses natural gas to generate high- and medium-pressure steam for the distillation column reboilers and the other heat exchangers. Such a system, however, may not be economical for a smaller plant that may meet its heating needs with electrical heaters. As a result, a small, all-electric plant will be less efficient in utilizing its primary energy source (usually coal) than a large plant that uses gas-fired steam boilers. Table 2.5 summarizes the results for the two scenarios. Note that electric pumps will be used in both cases.

TABLE 2.4: Primary Energy Requirements for Heating

	Primary Energy, MJ/gallon
Reboilers/heat exchangers: Steam - Pumps: Electric	18.0
All electric plant	39.0

With an end-user price of $0.12 per kWh (typical Reliant price for large customers), meeting the heating requirements in an all-electric plant will add $0.39 to the cost of a gallon of biodiesel.

Similar considerations apply to the cooling requirements. A large plant located close to a river or the sea can use water to meet its cooling needs and only incur the small cost of pumping the water and (perhaps) of chilling down the used water in a cooling tower. A smaller plant, however, may have to use more expensive city water or meet its cooling needs with expensive electric refrigeration units. The latter case will add up to **45.6 MJ/gal** of primary energy (depending on the efficiency of the refrigeration system) to the total. Electric refrigeration will add $0.52 to the cost of each gallon of biodiesel.

Our E_{prod} calculations for a steam plant are in good agreement with those presented by Hill and coworkers[1]. These values, however, are lower than those used by Pimentel and Patzek[2]. This may be due to the fact that the latter investigators assumed a different operatingmode for their biodiesel plant.

Clearly, different operating modes for the biodiesel plant can lead to large differences in the calculated values for E_{prod} and NER. From equation (1):

$$\frac{1}{\text{NER}} = \left[\frac{E_{prod}}{E_{biofuel} + E_{coproduct}}\right] + \left[\frac{E_{agri}}{E_{biofuel} + E_{coproduct}}\right] \tag{2.2}$$

Since our plant produces 7.4 gallons of glycerol for every 100 gallons of biodiesel, the contribution of the first term of equation (2) becomes:

$$\boxed{\frac{E_{prod}}{E_{biofuel} + E_{coproduct}} = \frac{18.0}{131.1} \text{ to } \frac{84.6}{131.1} = 0.14 \text{ to } 0.64}$$

The lower value is for a biodiesel plant that uses steam from a gas-fired boiler to meet its heating requirements and has access to free cooling water. On the other hand, smaller biodiesel plants that use electric power to meet all their cooling and heating needs may spend up to half of the energy in the biofuel and the coproduct (glycerol) in the production phase. Such wide variations may explain the significant differences in the NER values reported by the various literature studies[1-2].

---

[1] Hill, J., E. Nelson, et al. (2006). "Environmental, economic, and energetic costs and benefits of biodiesel and ethanol biofuels." PNAS 103(30): 1206 –11210.

[2] Pimentel, D. and T. W. Patzek (2005). "Ethanol Production Using Corn, Switchgrass, and Wood; Biodiesel Production Using Soybean and Sunflower." Natural Resources Research 14(1): 65-76.

3. Deploying Biodiesel to Optimize Air Quality Impacts

3.1 Background

This part of the report examines the potential air quality impacts of substituting biodiesel for petroleum diesel in the Houston region. While our research to date focuses on how biodiesel would impact ambient concentration of ozone, it should be acknowledged that biodiesel's impacts on particulate matter could be significant and will be the subject of future research. Atmospheric chemical formation of ozone is a strongly nonlinear function of its precursor emissions – nitrogen oxides (NO_x) and volatile organic compounds (VOCs). Thus, depending on atmospheric conditions, adding more NO_x emission to the atmosphere may increase or decrease ozone concentrations. Therefore, it is crucial to investigate whether the ambient ozone concentration will increase or decrease when deploying biodiesel in a region with high ozone concentrations. Houston-Galveston-Brazoria (HGB) has a long history of high ozone concentrations and continues to violate federal standards for ozone, even as those standards are in the process of being tightened.

Our examination of the potential air quality impact of biodiesel use in Houston is composed of three steps. First, the change of air pollutants emission when switching from diesel to biodiesel will be quantified based on available literature. Then, we apply an emission model to create air quality model input files representing alternative biodiesel scenarios. Finally, a regional air quality model is applied to simulate the air quality impacts of the hypothetical scenarios of biodiesel use. The objective of this research is to explore how biodiesel could be targeted to optimize its impacts on local air quality.

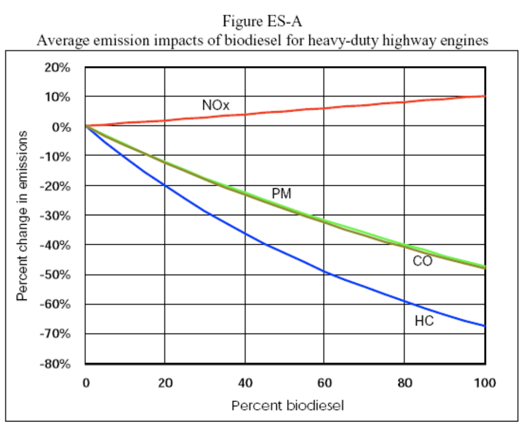

Figure 3.1: EPA estimates of average emission impacts of biodiesel for heavy-duty highway engines.

Numerous studies have reported that substituting biodiesel for petroleum diesel can reduce the emission of VOC, CO, and particulate matter, but they differ as to whether biodiesel increases NO_x emissions. A landmark study by the U.S. Environmental Protection Agency concluded that pure biodiesel (B100) increases NO_x emissions by 10% whereas PM (-48%), CO (-48%), and VOC (-57%) are significantly reduced (Figure 3.1).

3.2 Methods

The EPA study primarily relied on data from 1997 or earlier heavy-duty highway vehicle engines. Thus, we conducted a literature review to examine the emissions impacts indicated by more recent studies and by studies that examined other vehicle types (Table 3.1). These studies used a wide range of feedstock such as soybean, rapeseed and animal fat, covering various testing scenarios of biodiesel use, such as laboratory test and on-road test. Averaging across these studies suggests that biodiesel increases NOx emissions by 13.5% relative to petroleum diesel.

We apply this value in emission modeling of NOx, and the EPA estimate for VOC.
For air quality modeling, NOx and VOC emission files are generated from the Emission Processing System (EPS) model. We then employ the Comprehensive Air Quality Model with Extension (CAMx) to study the air quality impacts of deployment of biodiesel in the Houston region. CAMx is a three-dimensional photochemical dispersion model that has been used to inform development of the State Implementation Plan (SIP) for ozone attainment in Texas. Specifically, an air pollution episode over Texas and Houston in June 2006 has been chosen as our base scenario of air quality modeling. Our CAMx modeling is conducted on four nested domains, ranging from a coarse domain covering the East U.S. to a 2-km resolution fine domain covering the Houston-Galveston region.

Table 3.1 Emission test of using biodiesel in diesel engines.

Fuel	Feedstock	Engine Type	NOx Impact
B100	yellow grease	2004 Model A2	-3.0%
B100	yellow grease	2004 Model A2	-2.0%
B100	yellow grease	2004 Model A2	-2.0%
B100	yellow grease	2004 Model A2	0
B100	yellow grease	1992 Ford F9000	41.0%
B100	yellow grease	2000 250kW Generator	8.0%
B100	-	four-stroke diesel outboard engine	8.0%
B100	raw cottonseed	40kW generator cylinder John Deere engine	11.0%
B100	raw cottonseed	40kW generator cylinder John Deere engine	16.0%
Average			13.5%

Meteorology and emissions inputs for the episode were obtained from TCEQ. TCEQ has made improvements in meteorology modeling by updating the land surface of Texas and Houston region and merging large amounts of meteorological observation data, and emission modeling by merging the highly reactive VOC emissions from the Houston Ship Channel. These enhancements make the episode a good reference for our study.

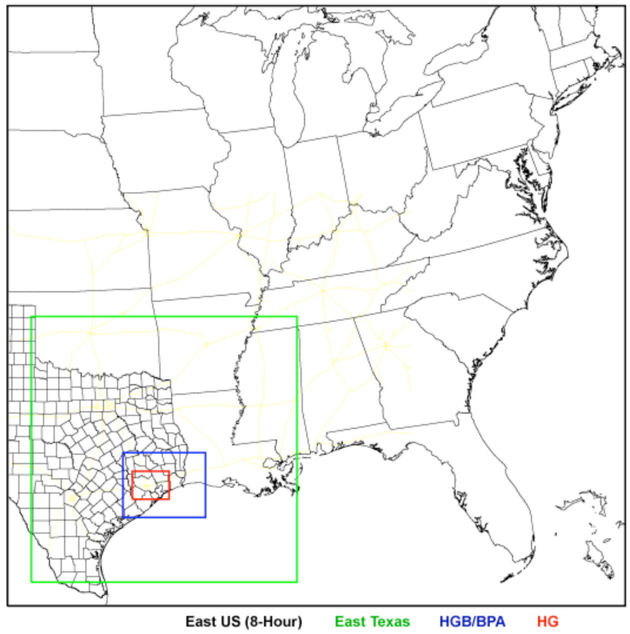

Figure 3.2: The modeling domains for air quality study.

Our base modeling scenario simulates air quality under standard emission conditions, including those from the actual petroleum diesel-related sources. Additional scenarios are then simulated in which biodiesel is used in place of petroleum diesel in one or more vehicle types and/or regions. On-road diesel vehicles, non-road diesel engines, and ship diesel engines in Houston ship channel are the dominant consumers of diesel fuel. They are also the targets for deploying biodiesel.

Figure 3.3 shows the sources of NOx and VOC emissions in the HGB region. Diesel engines in the HGB region emit 158 tons/day of NOx but only 8 tons/day of VOC are emitted. On-road diesel vehicles include heavy duty diesel vehicles (HDDV), light duty diesel vehicles (LDDV), school buses, and other on-road diesel vehicles. Non-road diesel engines are composed of recreation vehicles, construction equipment, lawn-garden equipment, and agricultural equipment. Ship diesel engines include bulk cargo vessels, ferries, towboats, and other marine vessels.

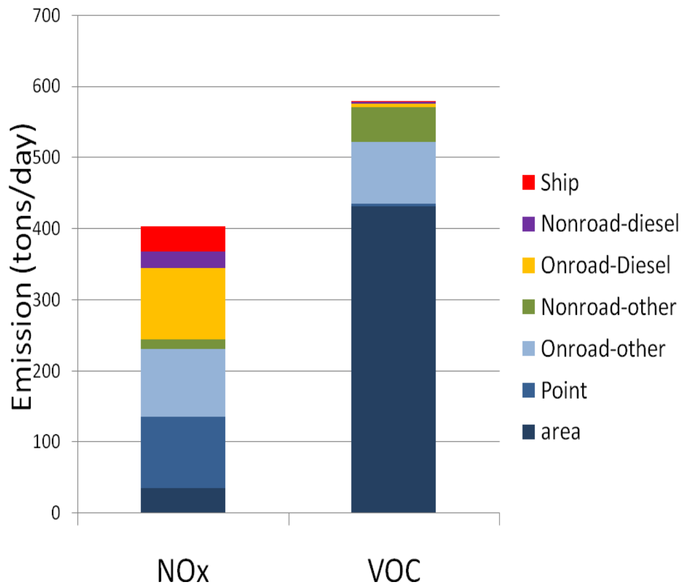

Figure 3.3: NOx and VOC emissions from various source categories.

In designing where to deploy biodiesel, the spatial pattern of NOx emissions is also considered. As shown in figures 3.4 and 3.5, NOx emitted from on-road diesel vehicles in Harris County concentrates in the urban center of Harris County. On the other hand, NOx emission from on-road diesel vehicles in 7 counties can be mostly found along highways.

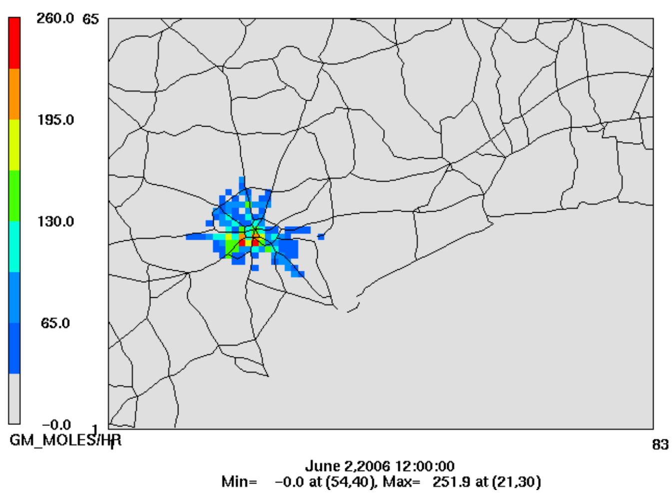

Figure 3.4: On-road diesel vehicle NOx emissions in Harris County.

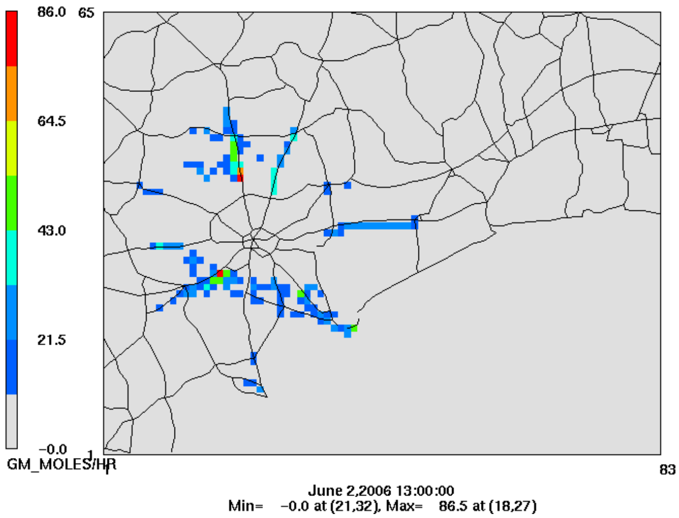

Figure 3.5: On-road diesel vehicle NOx emissions in 7 counties.

In consideration of both the regional pattern of diesel-fuel emission and emission categories, five scenarios of biodiesel replacing petroleum diesel have been designated. These biodiesel scenarios include biodiesel used in Harris County and the seven counties surrounding Harris, biodiesel used in different types of diesel engines.

Table 3.2: Biodiesel Scenarios.

Region	Biodiesel Type	Emission Category	Diesel Consumption	Emission Change
Harris	B100	On-road diesel vehicles	1.00	NOx:+13% VOC:-47%
7 Counties	B100	On-road diesel vehicles	0.414	NOx:+13% VOC:-47%
Harris	B100	Non-road diesel engines	0.150	NOx:+13% VOC:-47%
7 Counties	B100	Non-road diesel engines	0.089	NOx:+13% VOC:-47%
Ship	B50	Ship diesel engines	0.143	NOx:-14.6% VOC:-48.8%

Table 3.2 shows the five biodiesel scenarios and includes the regions, biodiesel types, emission categories, and the factors of emission change. Ozone concentration simulated from biodiesel scenario is compared to ozone concentration of base case. The difference between the two scenarios represents the ozone impact of using biodiesel to replace petroleum diesel. It should be noted that substituting biodiesel for petroleum diesel in ship diesel engines decreases both NOx and VOC emission because ships traditionally use relatively high-emitting fuels.

3.3 Results

Figure 3.6 compares ozone between the on-road Harris scenario and the base. It shows that ozone concentration in Harris County decreases and the ozone concentration in the surrounding counties increases. The maximum decrease of O3 in Harris County is 1.5ppb, but the maximum increase is just 0.3ppb. That is because the urban core already experiences NOx-saturated (VOC-limited) ozone formation, so higher levels of NO_x from biodiesel can reduce ambient O3 concentrations. O3 in NOx-limited surrounding counties, however, can increase.

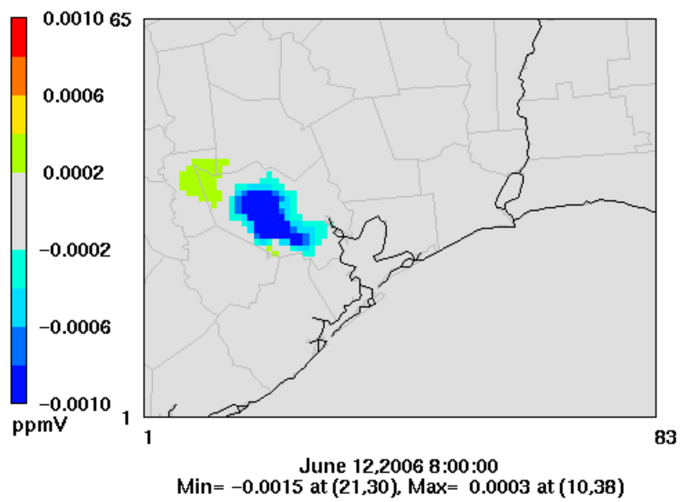

Figure 3.6: ΔO3 (Onroad Harris - Base)

Figure 3.7 is the comparison of ozone between the on-road 7 counties scenario and the base. In this scenario, ozone in the surrounding counties increases and there is no visible change of ozone in Harris County.

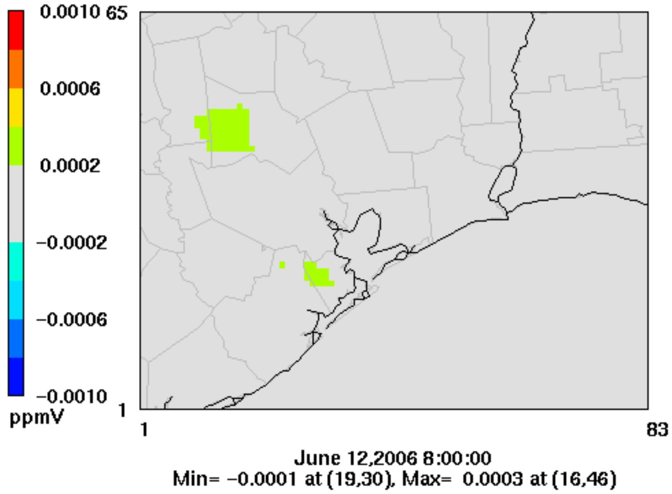

Figure 3.7: ΔO3 (Onroad 7 Counties - Base)

Figure 3.8 is the comparison of ozone between the non-road Harris County scenario and the base. It shows that ozone concentration in Harris County decreases and the ozone concentration in the surrounding counties increases. The reason for these is more NOx emission from using biodiesel in NOx-saturated urban region can reduce the ambient O3 concentration. As the increase of NOx from non-road biodiesel is smaller than the NOx increase of on-road Harris County biodiesel scenario, the ozone reduction is less than that of on-road Harris County biodiesel scenario. There is no visible change of ozone in surrounding 7 counties for non-road Harris County scenario.

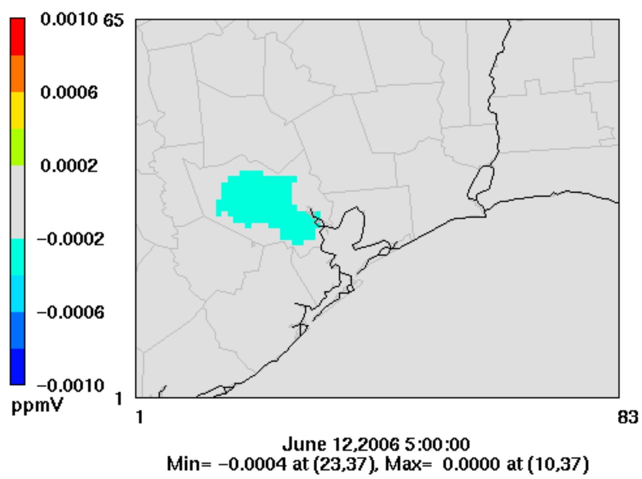

Figure 3.8: ΔO3 (Nonroad Harris - Base)

Figure 3.9 is the comparison of ozone between the non-road 7 counties biodiesel scenario and the base. Visible ozone change could be only found in the surrounding 7 counties. The result is very similar to the on-road 7 counties biodiesel scenario.

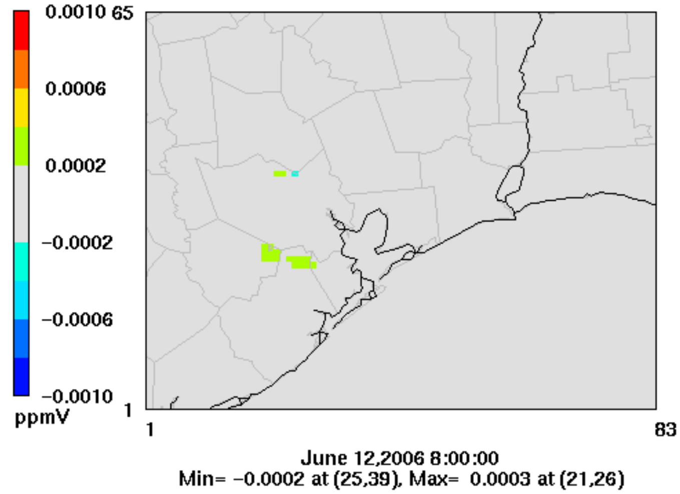

Figure 3.9: ΔO3 (Nonroad 7 Counties - Base)

Figure 3.10 shows the NOx emitted from ship diesel engines in HGB, most of which occurs in Galveston Bay and the Houston Ship Channel. If biodiesel is used in ship diesel engines, both NOx and VOC emissions are reduced. Therefore, less NOx emission in ship biodiesel scenario compared to the base scenario increase the NO-saturated Harris County, as shown in Figure 3.11. Then the ozone in the downwind Galveston Bay decreases as less NOx could be transported there. The maximum increase of O3 in Harris County is 0.8 ppb.

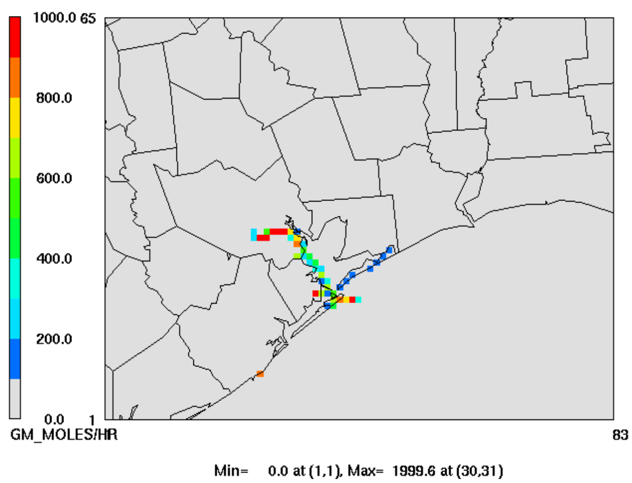

Figure 3.10: NOx emitted from ships diesel engines

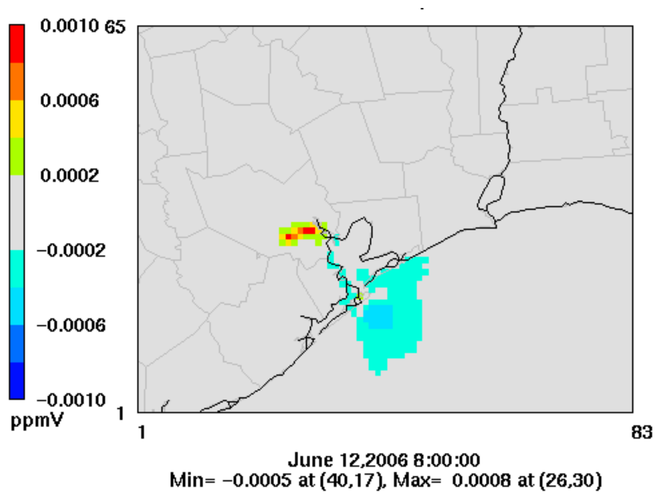

Figure 3.11: ΔOzone (ship diesel engines - base)

3.4 Conclusions

The analysis of modeled ozone from both the biodiesel scenarios and base scenario suggests that the air quality impacts of deploying biodiesel are very complicated. The NO_x increase from deploying biodiesel in Harris County could actually decrease ozone concentrations in the already NO_x-rich urban center. On the contrary, deploying biodiesel in the surrounding 7 counties can increase O_3 concentration over the most of the modeling regions. Deploying biodiesel in ship diesel engines would likely reduce their NO_x and VOC emissions, but this could actually increase O_3 concentrations in the already NO_x-rich urban center. It must be noted that all of the O_3 impacts that have been found in this research are relatively small changes, even for widespread deployment of biodiesel. However this research points to the potential for targeting biodiesel in ways that account for its varied air quality impacts.