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Life-Cycle Assessment of Energy and Greenhouse Gas Effects of Soybean-Derived Biodiesel and Renewable Fuels

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Life-Cycle Assessment of Energy and Greenhouse Gas Effects of Soybean-Derived Biodiesel and Renewable Fuels

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Notation

Acronyms and Abbreviations

BFW	boiler feed water
BP	British Petroleum
CETC	CANMET Energy Technology Centre
CH_4	methane
CIDI	compression-ignition, direct-injection
CO	carbon monoxide
CO_2	carbon dioxide
CSO	clarified slurry oil
$DeCO_2$	decarboxylation
DOE	U.S. Department of Energy
ERS	Economic Research Service (USDA)
FCC	fluidized catalytic cracker
GHG	greenhouse gas
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation
HDO	hydrodeoxygenation
IPCC	Intergovernmental Panel on Climate Change
K	potassium
LCA	life-cycle analysis
LCO	light-cycle oil
LHV	lower heating value
LPG	liquefied petroleum gas
LSD	low-sulfur diesel
N	nitrogen
N_2O	nitrous oxide
NaOH	sodium hydroxide
NG	natural gas
NO_x	nitrogen oxide
NRCan	Natural Resources Canada
NREL	National Renewable Energy Laboratory
P	phosphorus
PM_{10}	particulate matter with a diameter of 10 micrometers or less
$PM_{2.5}$	particulate matter with a diameter of 2.5 micrometers or less
PTW	pump-to-wheels
RFG	reformulated gasoline
SI	spark-ignition
SMR	steam methane reforming
SO_x	sulfur oxides
USDA	U.S. Department of Agriculture
VGO	vacuum gas oil
VOC	volatile organic compound
WTP	well-to-pump

WTW	well-to-wheels
WWT	wastewater treatment

Units of Measure

bpd	barrel(s) per day
Btu	British thermal unit(s)
bu	bushel(s)
°C	degree(s) Celsius
°F	degree(s) Fahrenheit
ft^3	cubic foot (feet)
g	gram(s)
gal	gallon(s)
h	hour(s)
ha	hectare(s)
kW	kilowatt(s)
kWh	kilowatt-hour(s)
L	liter(s)
lb	pound(s)
mmBTU	million Btu
ppm	part(s) per million
psia	pound(s) per square inch absolute
psig	pound(s) per square inch gauge
scf	standard cubic foot (feet)
USD	U.S. dollar(s)
yr	year(s)

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Abstract

We assessed the life-cycle energy and greenhouse gas (GHG) emission impacts of the following three soybean-derived fuels by expanding, updating, and using Argonne National Laboratory's Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model: (1) biodiesel produced from soy oil transesterification, (2) renewable diesel produced from hydrogenation of soy oil by using two processes (renewable diesel I and II), and (3) renewable gasoline produced from catalytic cracking of soy oil. We used four allocation approaches to address the co-products: a displacement approach; two allocation methods, one based on energy value and one based on market value; and a hybrid approach that integrates both the displacement and allocation methods. Each of the four allocation approaches generates different results. The displacement method shows a 6–25% reduction in total energy use for the soybean-based fuels compared with petroleum fuels, except for renewable diesel II. The allocation and hybrid approaches show a 13–31% increase in total energy use. All soybean-derived fuels achieve a significant reduction (52–107%) in fossil energy use and in petroleum use (more than 85%). With the displacement approach, all four soybean-based fuels achieve modest to significant reductions (64–174%) in well-to-wheels GHG emissions. With the allocation and hybrid approaches, the fuels achieve a modest reduction in GHG emissions (57–74%). These results demonstrate the importance of the methods that are used in dealing with co-product issues for these renewable fuels.

1 Introduction

There has long been a desire to find alternative liquid fuel replacements for petroleum-based transportation fuels. Biodiesel, produced from seed oils or animal fats via the transesterification process, has been the focus of biofuel production because of its potential environmental benefits and because it is made from renewable biomass resources. Biodiesel can be derived from various biological sources such as seed oils (e.g., soybeans, rapeseeds, sunflower seeds, palm oil, jatropha seeds, waste cooking oil) and animal fats. In the United States, a majority of biodiesel is produced from soybean oil. In Europe (especially in Germany), biodiesel is produced primarily from rapeseeds. Biodiesel can be blended with conventional diesel fuel in any proportion and used in diesel engines without significant engine modifications (Keller et al. 2007). In recent years, the sales volume for biodiesel in the United States has increased dramatically: from about 2 million gallons in 2000, to 75 million gallons in 2005, to 250 million gallons in 2006 (National Biodiesel Board 2007).

Transesterification of seed oils and animal fats has been the major technology for biodiesel production to date. New process technologies based on hydrogenation to convert seed oils and animal fats to diesel fuel and gasoline have recently emerged. The CANMET Energy Technology Centre (CETC) of Natural Resources Canada (NRCan) has developed a technology to convert seed oils and animal fats into a high-cetane, low-sulfur diesel fuel blending stock called "SuperCetane" [$(S\&T)^2$ Consultants Inc. 2004]. UOP developed conversion processes based on conventional hydroprocessing technologies that are already widely deployed in petroleum refineries. The hydro-generation technologies utilize seed oils or animal fats to produce an isoparaffin-rich diesel substitute referred to as "green diesel" (Kalnes et al. 2007). UOP also proposed a technology that can produce "green gasoline" by cracking seed oils and grease in a fluidized catalytic cracker (FCC) unit (UOP 2005). The diesel and gasoline produced from these processes are often referred to as renewable diesel and gasoline.

In this report, we present a life-cycle analysis of the energy and GHG emission impacts of biodiesel, renewable diesel, and renewable gasoline relative to those of petroleum diesel and gasoline. In the United States, soybeans are the major feedstock for biodiesel production now and, potentially, for renewable diesel and gasoline production in the future. In our study, we evaluated production of biodiesel, renewable diesel, and renewable gasoline from soybeans.

For this study, we expanded and updated the GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation) model (see http://www.transportation.anl.gov/software/GREET/index.html). In 1995, with funding from the U.S. Department of Energy (DOE), Argonne National Laboratory's Center for Transportation Research developed the GREET model for use in estimating the full fuel-cycle energy and emissions impacts of alternative transportation fuels and advanced vehicle technologies. Since that time, the model has been updated to include new fuels and transportation technologies. The latest version — GREET 1.8a — is capable of analyzing more than 100 transportation fuel pathways.

For a given vehicle and fuel system, GREET evaluates total energy use, fossil fuels, natural gas (NG) use, coal use, and petroleum use; emissions of carbon dioxide (CO_2)-equivalent greenhouse gases (GHGs) including CO_2, methane (CH_4), and nitrous oxide (N_2O); and emissions of six criteria pollutants — volatile organic compounds (VOCs), carbon monoxide (CO), nitrogen oxides (NO_x), particulate matter with a diameter of 10 micrometers or less (PM_{10}) and 2.5 micrometers or less ($PM_{2.5}$), and sulfur oxides (SO_x). These criteria pollutant emissions are further separated into total and urban emissions to reflect human exposure to air pollution caused by emissions of the six criteria pollutants.

Our analysis in this study includes the following six fuel pathways:

(1) Conventional petroleum-based reformulated gasoline (RFG);

(2) Conventional petroleum-based low-sulfur diesel (LSD) with 15 parts per million (ppm) sulfur content;

(3) Soybean-based biodiesel produced by using the transesterification process;

(4) Soybean-based renewable diesel I (“SuperCetane”) produced by using the hydrogenation process;

(5) Soybean-based renewable diesel II (“green diesel”) produced by using the hydrogenation process; and

(6) Renewable gasoline (“green gasoline”) produced by using catalytic cracking.

We used petroleum gasoline and diesel as the baseline fuels; our analysis was conducted for year 2010. We estimated consumption of total energy, fossil energy, and petroleum oil and emissions of GHGs (CO_2, N_2O, and CH_4) for each of the six pathways. Figure 1-1 illustrates the system boundary for the six fuel pathways. The four soybean-based pathways consist of six stages: (1) farming activities, including manufacture of fertilizer and other chemicals, soybean farming, and soybean harvest; (2) soybean transportation from farms to processing plants; (3) soy oil extraction in processing plants; (4) production of biodiesel or other renewable fuels in plants; (5) fuel transportation and distribution from plants to refueling stations; and (6) fuel use during vehicle operation. As shown, the four soybean-based fuel pathways have three common stages: soybean farming, soybean transportation, and soy oil extraction. The four paths differ in terms of their fuel production processes and vehicle operations.

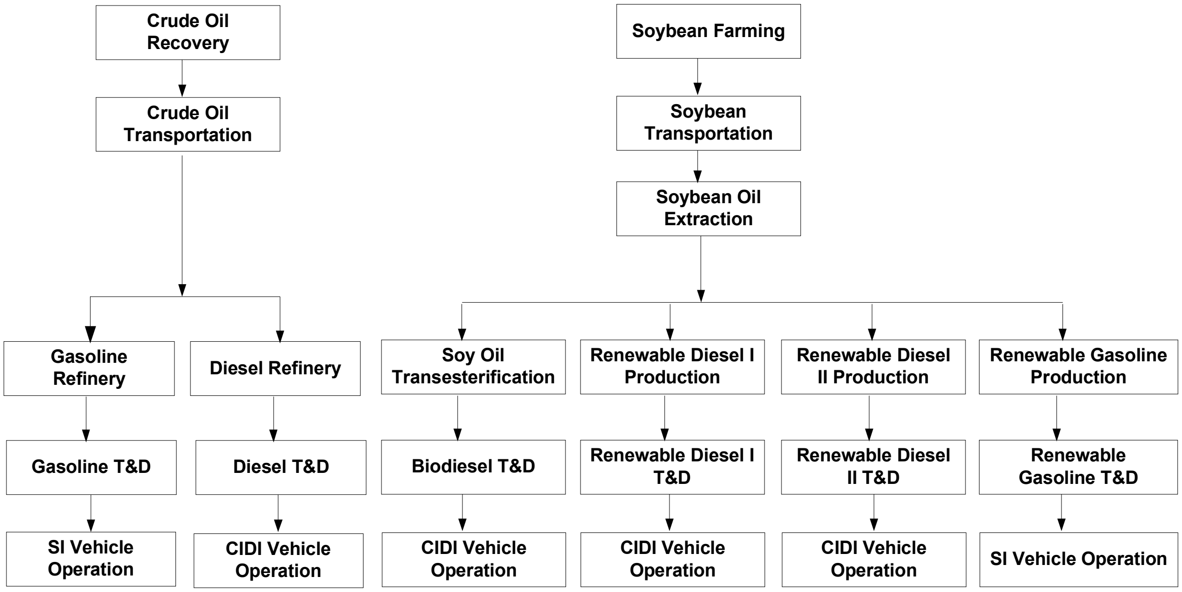


Figure 1-1 System Boundaries for Life-Cycle Analysis of Petroleum Gasoline and Diesel Fuels and Soybean-Based Biodiesel and Renewable Fuels

The pathways for petroleum gasoline, petroleum diesel, and soybean-based biodiesel had been incorporated into the GREET model before this study. However, for this study, we updated soybean farming simulations in GREET with the latest U.S. Department of Agriculture data on energy and fertilizer use associated with soybean farming (USDA 2007a, b). We updated N_2O emission simulations for soybean fields by using newly released data from the Intergovernmental Panel on Climate Change (IPCC 2006). Moreover, we expanded GREET to include pathways for soybean-based renewable diesel and gasoline.

Process energy and mass balance data for the four soybean-based fuels are from our evaluation of available literature and process simulations by the National Renewable Energy Laboratory (NREL) using the ASPEN model. The processing of energy and mass balance data is described in Section 2. Section 3 presents the key issues regarding life-cycle simulations, gives GREET input assumptions, and compares the different production processes and fuel properties of soybean-derived fuels. Section 4 presents the approaches used to address co-product credits. Section 5 provides an analysis and comparison of the life-cycle (or well-to-wheels [WTW]) energy and emission results for the six pathways examined in this study. Section 6 presents our conclusions. Finally, Appendices 1 and 2 present ASPEN simulations by NREL.

Note that this study does not consider potential land use changes. Increased CO_2 emissions from potential land use changes are an input option in GREET, but it was not used in the current analysis since reliable data on potential land use changes induced by soybean-based fuel production are not available. Furthermore, the main objective of this study is to concentrate on the process-related issues described above.

2 Production Processes of Soybean-Based Renewable Fuels

This section describes the three basic processes that have been proposed for renewable diesel and gasoline production: two for renewable diesel fuel and one for renewable gasoline. It also presents the results of the process modeling work undertaken by NREL to characterize the mass and energy balances associated with the three processes. The NREL-simulated results were inputs to the life-cycle analysis (LCA) described in Sections 3 and 4.

Table 2-1 provides a list of current and planned renewable energy diesel facilities. For example, ConocoPhillips is currently operating a 1,000-barrel-per-day (bpd) facility in Ireland using soybean and other vegetable oils; the company entered into a partnership with Tyson foods in April 2007 to produce up to 12,000 bpd from animal fat generated in the United States.

Refinery-based biofuels have received strong support from vehicle manufacturers, both in the United States and abroad, because their physical and chemical properties are similar to conventional petroleum-based fuels. Refinery-based biofuels have also been supported by major international oil companies because they can be delivered by using the existing fuel delivery infrastructure with no modifications.

Table 2-1 Current and Planned Renewable Diesel Facilities

Company	Size (bpd)	Location	Online Date
ConocoPhillips	1,000	Ireland	2006
ConocoPhillips	12,000	United States	To be determined
British Petroleum (BP)	1,900	Australia	2007
Neste	3,400	Finland	2007
Neste	3,400	Finland	2009
Petrobras	4 × 4,000	Brazil	2007
UOP/Eni	6,500	Italy	2009

Feedstocks that can be used in biofuel production processes include seed oils (e.g., soy, corn, canola, or palm oil), recycled oils (e.g., yellow grease or brown [trap] grease), and animal fats (e.g., tallow, lard, or fish oil). Table 2-2 lists current estimates of these oils, which amount to about 100,000 bpd (UOP 2005). Vegetable oils, particularly soybean-derived oils, are of particular interest in this study because (1) soy oil is the principal feedstock used in the United States for production of biodiesel via the transesterification process and (2) soy oil is a currently modeled pathway in GREET.

Table 2-2 Feedstock Availability for Renewable Diesel Production in the United States (UOP 2005)

Feedstock	Feedstock	Total U.S. Production (bpd)	Available for Conversion to Fuels (bpd)
Vegetable oils	Soybeans, corn, canola, palm	194,000	33,500
Recycled products	Yellow grease, brown (trap) grease	51,700	33,800
Animal fats	Tallow, lard, fish oil	71,000	32,500

Because crude oil and bio-feedstocks are derived from the same sources (i.e., crude oil owes its existence to plants and animals that have decomposed over 600 million years), the question arises: Why not add the bio-feedstocks directly to the feeds for conventional refineries? The answer is that the molecular structures of all of the bio-feedstocks listed in Table 2-2 contain significant amounts of oxygen that must be removed prior to their processing with other petroleum-based feedstocks. The two standard processes to remove oxygen from hydrocarbon feeds are hydrodeoxygenation (HDO) and decarboxylation ($DeCO_2$). Under the proper conditions and with the addition of hydrogen, the HDO reaction, given in Equation 2-1, converts the oxygen in the product feed into plain water.

$$C_nCOOH + 3H_2 \rightarrow C_{n+1} + 2H_2O \qquad (2\text{-}1)$$

In the $DeCO_2$ reaction, shown in Equation 2-2, the oxygen in the feed is removed as simple CO_2 in a lead/hydrogen catalytic reaction.

$$C_nCOOH \xrightarrow{Pb/H} C_n + CO_2 \qquad (2\text{-}2)$$

In reality, it is difficult to have a processing vessel where only one process occurs; in all the current renewable diesel design schemes, both reactions take place. The particular operating designs and conditions determine which process is favored. A basic tradeoff is that, in order to optimize the HDO reaction shown in Equation 2-1, additional hydrogen is required; production of the hydrogen can be expensive and can result in environmental impacts. On the other hand, the only byproduct of the HDO process (Equation 2-1) is water, while the principal by-product of the $DeCO_2$-process (Equation 2-2) is CO_2 — a GHG that is of concern in life-cycle modeling. However, the CO_2 from this process is the CO_2 uptaken during soybean growth.

2.1 Renewable Diesel Production Based on SuperCetane

The first renewable diesel production pathway, renewable diesel I, was modeled after a process called SuperCetane that was originally developed in the 1980s at the Saskatchewan Research Council and is now being developed by NRCan's CETC.

The SupereCetane process is based on adapting a conventional hydrotreating process so it can operate under proprietary operating conditions. Figure 2-1 shows a general process schematic for the SuperCetane process. A number of reactions occur in the process, including hydrocracking, hydrotreating, and hydrogenation. The hydrocracking process breaks apart large molecules; the hydrotreating removes oxygen. The process uses a conventional commercial refinery hydrotreating catalyst and hydrogen to produce a hydrocarbon liquid. This liquid can be distilled into three basic fractions: naphtha, middle distillate (or SuperCetane), and waxy residues. The principal product, the middle distillate, can be produced at yields of 70–80%. Because of the high cetane number (around 100), CETC believes that SuperCetane may prove most valuable as a blending agent for lower-quality diesels (CETC undated).

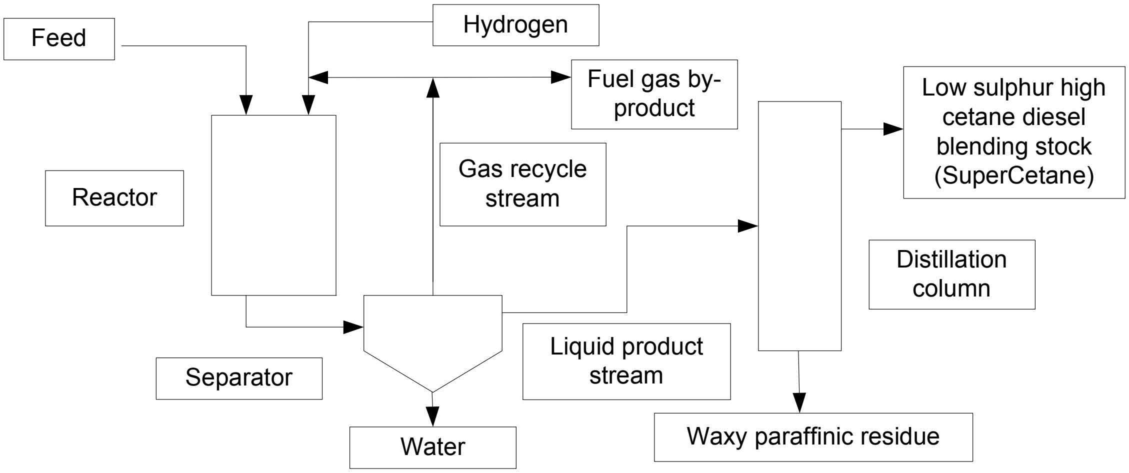


Figure 2-1 SuperCetane Process Flow
(NRCan 2003)

The process has been used successfully in a 1-bpd pilot reactor. Feedstocks used in the pilot process include canola oil, soy oil, yellow grease, animal tallow, and tall oil (a by-product of the kraft pulping process). An important characteristic of this processing scheme is that internally generated fuel gas is combusted on site to meet facility steam requirements. Thus, all energy demands except electricity are met on site.

2.2 Renewable Diesel Production Based on UOP Hydrogenation Technology

The second renewable diesel production pathway, renewable diesel II, was modeled on a hydrogenation process developed by UOP, a leading supplier and licensor of process technology, catalysts, adsorbents, process plants, and consulting services to the petroleum refining, petrochemical, and gas processing industries. UOP, located in Des Plaines, Illinois, is a wholly owned subsidiary of Honeywell International. In 2005, UOP conducted a study for DOE entitled *Opportunities for Biorenewables in Oil Refineries* (UOP 2005). In November 2006, UOP announced the formation of a new Renewable Energy and Chemicals business unit focused on using the company's refinery skills to develop profitable and efficient ways to enable refineries to convert bio-feedstocks (e.g., vegetable oils and greases) into valuable fuels and chemicals.

UOP took another major step in June 2007, when the company announced that it had entered into an agreement with Eni S.p.A, a large European refiner, to build a 6,500-bpd renewable diesel unit in Livorno, Italy. The facility, which will process soy, rapeseed, palm, and other oils, is expected to come online in 2009. Facility operations will be based on a newly branded UOP process called Ecofining^{TM}. UOP has also announced that the technology that it developed in partnership with Eni integrates seamlessly into existing refinery operations and is currently available for licensing. The most recent license was granted to Galp Energia, Portugal's largest refiner, to develop a 6,500-bpd facility in Sines, Portugal (Reuters News 2007).

In its study for DOE, UOP examined two potential approaches for renewable diesel production. The first involved co-processing the bio-feedstock in an existing hydroprocessing unit; the second involved processing the bio-feedstock in a standalone processing unit. In order to design a process comparable to the CETC process modeled for renewable diesel I, the UOP standalone process scheme was characterized for this project by using ASPEN modeling. Figure 2-2 shows the basic production scheme for the UOP process in standalone mode.

In the standalone process, the bio-feedstock is fed into a diesel hydrotreater, where hydrogen and steam are added. An advantage of the UOP operating scheme is that, although the principal product is renewable diesel, the by-product is a valuable propane fuel mix. UOP reports that its resultant renewable diesel has a cetane value in the 70–90 range, offering significant blending benefits for existing refinery operations. UOP notes that when the standalone process is used, additional pretreatment is required to remove contaminants such as water, alkali metals,

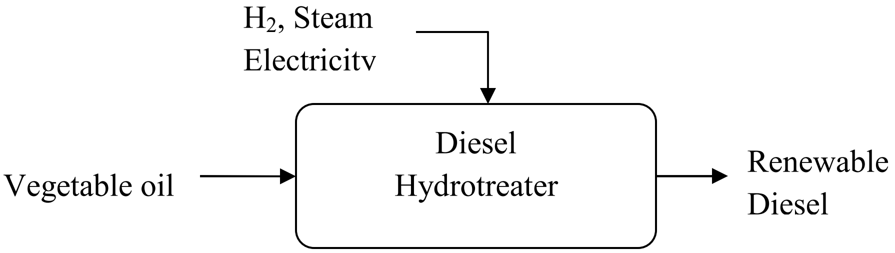


Figure 2-2 UOP-Proposed Standalone Renewable Diesel Production (UOP 2005)

phosphorous, and ash. These would be removed by using a combination of existing equipment, such as hydrocyclones, desalting, acid washing, ion exchange, or fixed-guard bed catalyst systems (UOP 2005).

2.3 Renewable Gasoline Production Based on UOP FCC Technology

As mentioned earlier, because bio-feedstocks are basically chains of carbon and hydrogen with added oxygen, standard refinery vessels could be modified to produce gasoline from these feedstocks. UOP has proposed such a scheme based on the use of an FCC unit (UOP 2005). (It should be noted that renewable gasoline is not nearly as far along the commercialization path as the renewable diesel processes discussed in Sections 2.2 and 2.3.) Figure 2-3 shows the general flow of the system proposed by UOP. As in the case of renewable diesel, the first step is pretreatment of the bio-feedstock; in this case, primarily to remove metals like calcium and potassium that would poison the FCC catalyst. Pretreatment also prevents metallurgy issues in the feed system, especially when processing greases. The pretreated oil is fed into the FCC unit along with the vacuum gas oil (VGO) stream. It should be noted that in the ASPEN modeling runs used to characterize renewable gasoline in Table 2-3, the FCC unit was characterized with only soybean oil feedstock. Although the standalone production of green gasoline would probably not be as economical as dual processing with VGO, it does allow for comparable life-cycle analysis, which is the principal thrust of this study. One of the differences between the renewable gasoline and the renewable diesel processes is that additional hydrogen is not required for the gasoline process. Another difference is that a significant portion of the energy value of the feedstock is contained in process by-products rather than the desired end product: renewable gasoline. The other principal product streams include light ends, light-cycle oil (LCO), and clarified slurry oil (CSO).

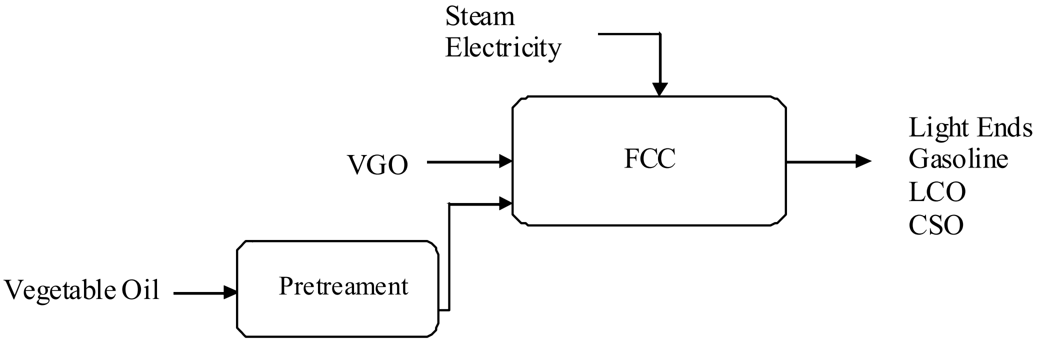


Figure 2-3 UOP Proposed Renewable Gasoline Production (UOP 2005)

2.4 ASPEN Model Results

A specific goal of the GREET WTW modeling has been to compare various transport fuels on a consistent basis. Consistency is achieved by basing model calculations on process mass and energy balances that are validated by using data from commercial operating facilities. Modeling of new renewable energy fuels thus presents a problem because facility mass and energy balances are either unavailable or available only from limited pilot plant operations that may not reflect mature commercial operating conditions.

For the three new fuels characterized in this report (pathways 4 through 6), NREL developed initial mass and energy balances by using the ASPEN process simulation model. The NREL-modeled mass and energy balances for the three fuels are listed in Table 2-3. Details of NREL's ASPEN simulations are presented in Appendices 1 and 2. Note that all data have been normalized to the basis of one pound of final fuel product. This adjustment allows the data to be incorporated into GREET on a consistent basis with existing fuel paths. The emissions presented in the table were estimated by using standard AP-42 emission factors.

To conduct the GREET analysis by using the three new renewable fuel pathways, additional component energy data are needed. The values used in the simulation were provided by NREL and are listed in Table 2-4. As data from commercial facility operations become available, the information will need to be updated to reflect any changes that might occur as the technologies mature.

The ASPEN simulations showed the mass and energy flow differences that were expected from proposed technology design schemes. For example, when renewable diesel I and renewable diesel II are compared, differences in hydrogen requirements, as well as the resultant CO_2 emissions, demonstrate the extent to which the HDO or $DeCO_2$ reaction was favored by the

Table 2-3 NREL-Simulated Renewable Fuels Mass and Energy Balances

	Fuel		
Inputs and Outputs	**Renewable Diesel I (SuperCetane)**	**Renewable Diesel II (UOP-HDO)**	**Renewable Gasoline**
Inputs (lb per lb of final fuel product)			
Soybean oil	1.510	1.174	2.2313
Hydrogen	0.030	0.032	
Steam		0.0329	0.0286
Air	0.9588		1.6782
Boiler feed water (BFW)			1.47
Outputs (lb/lb soybean oil)			
Renewable diesel	1.000	1.000	
Renewable gasoline			1.000
Fuel gas	0.253		
Product gas			0.3447
Heavies	0.175		
Water vapor	0.200		0.0287
Propane fuel mix		0.059	
CO_2[a]	0.049	0.082	0.4103
LCO			0.2454
CSO			0.2914
Water-to-wastewater treatment (WWT)	0.0663	0.0971	0.2599
Return BFW/steam			1.47
O_2	0.0201		0.0593
N_2	0.7355		1.2675
Energy Inputs (unit per lb of final fuel product)			
Steam (Btu)	Process is self-sufficient in energy	84.05	−1,237
Electricity (kWh)	0.0394	0.0275	0.0544
CW (lb/h)	65.06	27.11	50.3

[a]: This is the amount of CO_2 from feedstock oil, which is eventually from the air during soybean growth

process design. Another difference is that all facility energy demands (except electricity) are met by recycling process-generated fuel gas in the renewable diesel I scheme. This process characteristic increases facility emissions and reduces facility energy by-products. These types of tradeoffs are central to the use of GREET in linking the new fuels to the existing fuel pathways in order to assess their life-cycle energy and GHG emission impacts.

Table 2-4 NREL-Provided Base Energy Values of Renewable Fuel Components

Component	Lower Heating Value (Btu/lb)
Soybean oil	16,000
H_2[a]	52,226
Renewable diesel I – SuperCetane	18,746
Renewable diesel II – UOP	18,925
Renewable gasoline	18,679
Fuel gas	27,999
Product gas	18,316
Heavies	20,617
Propane fuel mix	18,568
LCO	19,305
CSO	18,738

[a] Simulation of hydrogen production is done inside GREET. In this analysis, we assumed that hydrogen would be produced from natural gas via steam methane reforming.

3 Data Sources and Assumptions for GREET Simulations

3.1 Soybean Farming

3.1.1 Yield

Soybean yield (in bushels per acre or bu/acre) is a key factor in life-cycle analysis because it will affect energy use and fertilizer use per bushel of soybeans harvested. Soybeans were ranked the second-leading U.S. crop in terms of both harvested acreage (74.6 million acres) and revenue (19.7 billion U.S. dollars [USD]) in 2006 (USDA 2007a). Over the past several decades, both harvested acreage and soybean yield per harvested acre have experienced enormous growth, leading to total soybean production increases of 4% annually. Table 3-1 lists planted and harvested acreage and yield over the past five decades in the United States. Figure 3-1 shows the 3-year moving average of soybean yield in the United States. The soybean yield has been increasing at an annual rate of 1.2%, and this trend is expected to continue in the near future.

Table 3-1 U.S. Historical Soybean Acreage and Yields (USDA 2007a)

	Acreage (10^6 acres)		**Total Production (10^6 bu)**	**Yield (bu/acre)**		**3-Year Moving Average Yield (bu/acre)**	
Year	**Planted**	**Harvested**		**Planted Acres**	**Harvested Acres**	**Planted Acres**	**Harvested Acres**
1950	15.0	13.8	299.2	19.9	21.7	19.5	21.8
1960	24.4	23.7	555.1	22.7	23.5	22.9	23.7
1970	43.1	42.2	1127.1	26.2	26.7	26.3	26.9
1980	69.9	67.8	1797.5	25.7	26.5	28.8	29.3
1990	57.8	56.5	1925.9	33.3	34.1	30.4	31.1
1991	59.2	58.0	1986.5	33.6	34.2	32.8	33.5
1992	59.2	58.2	2190.4	37.0	37.6	34.6	35.3
1993	60.1	57.3	1869.7	31.1	32.6	33.9	34.8
1994	61.6	60.8	2514.9	40.8	41.4	36.3	37.2
1995	62.5	61.5	2174.3	34.8	35.3	35.6	36.4
1996	64.2	63.3	2380.3	37.1	37.6	37.6	38.1
1997	70.0	69.1	2688.8	38.4	38.9	36.8	37.3
1998	72.0	70.4	2741.0	38.1	38.9	37.9	38.5
1999	73.7	72.4	2653.8	36.0	36.6	37.5	38.2
2000	74.3	72.4	2757.8	37.1	38.1	37.1	37.9
2001	74.1	73.0	2890.7	39.0	39.6	37.4	38.1
2002	74.0	72.5	2756.1	37.3	38.0	37.8	38.6
2003	73.4	72.5	2453.7	33.4	33.9	36.6	37.2
2004	75.2	74.0	3123.7	41.5	42.2	37.4	38.0
2005	72.0	71.3	3063.2	42.5	43.0	39.2	39.7
2006	75.5	74.6	3188.2	42.2	42.7	42.1	42.7

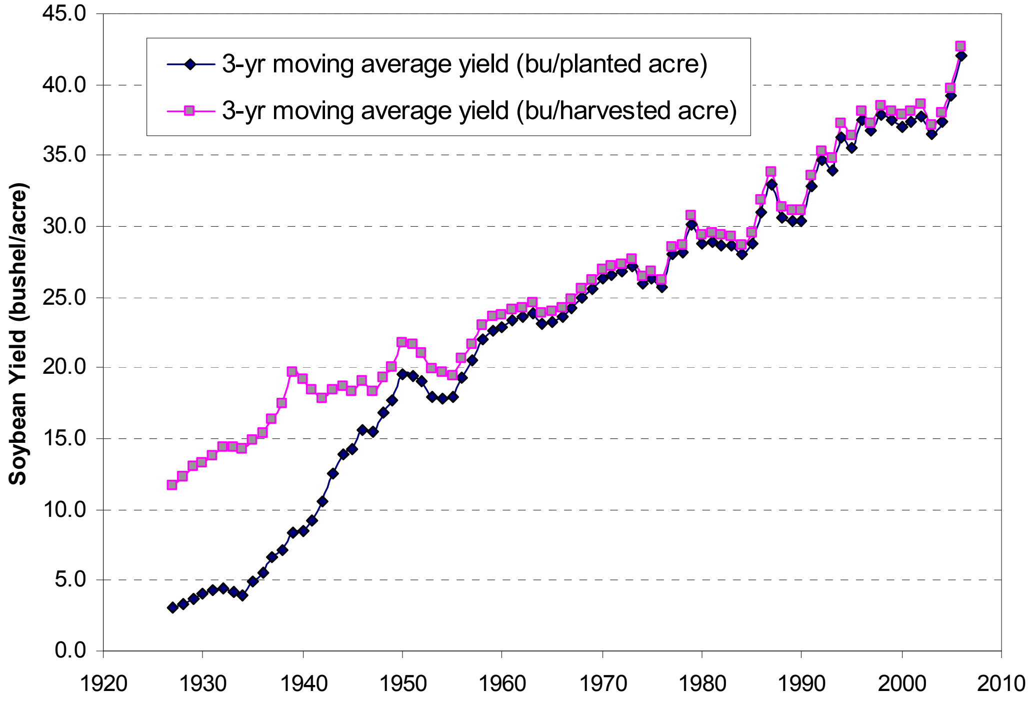


Figure 3-1 Three-Year Moving Average of Soybean Yield in the United States (USDA 2007a)

3.1.2 Energy Use

The USDA's Economic Research Service (ERS) survey data provides U.S. energy use values for soybean farming (on a per-acre basis) in 2002 (USDA 2007b); these values are listed in Table 3-2. On the basis of these energy use values and the average yields for soybeans, we estimated the energy use (by type) per bushel of soybeans harvested. We converted the values listed in Table 3-2 to Btu-based values by using the lower heating values (LHVs) of fuels in GREET: 128,450 Btu/gal for diesel; 116,090 Btu/gal for gasoline; 84,950 Btu/gal for liquefied petroleum gas (LPG); 3,412 Btu/kWh for electricity (energy loss for electricity generation is simulated separately in GREET); and 983 Btu/ft^3 for natural gas. The total energy use is estimated to be 22,084 Btu/bu: 64% diesel, 18% gasoline, 8% LPG, 7% natural gas, and 3% electricity. In comparison, Hill et al. (2006) reported 23,474 Btu/bu and 34,625 Btu/bu when custom-work-related diesel use and farm-related transportation and personal commuting energy use are taken into account. Pimentel and Patzek (2005) reported 20,447 Btu/bu of energy use for soybean production when labor, machinery, and fertilizer were taken into account. Table 3-3 provides a detailed comparison of the energy use for soybean farming across these references.

Table 3-2 Energy Use for Soybean Farming in the United States (USDA 2007b)

State	Diesel (gal/acre)	Gasoline (gal/acre)	LPG (gal/acre)	Electricity (kWh/acre)	Natural Gas (ft^3/acre)
Arkansas	9.9	1.3	L[a]	11.2	L
Illinois	2.5	0.9	0.0	L	0.0
Indiana	2.3	1.6	L	1.3	L
Iowa	3.4	1.1	0.0	0.0	0.0
Kansas	2.9	1.1	1.8	9.1	349.2
Kentucky	2.1	1.4	L	4.5	0.0
Louisiana	6.5	1.1	L	L	L
Maryland	2.9	2.1	L	0.8	0.0
Michigan	4.0	1.5	L	L	0.0
Minnesota	4.0	1.1	L	L	0.0
Mississippi	4.3	1.2	L	3.8	0.0
Missouri	4.3	1.4	L	L	0.0
Nebraska	12.9	1.3	4.4	39.4	586.4
North Carolina	2.4	1.5	L	0.6	0.0
North Dakota	3.2	1.4	L	0.8	0.0
Ohio	2.0	1.3	L	0.0	0.0
South Dakota	2.8	1.4	0.0	L	0.0
Tennessee	2.2	1.3	L	1.0	0.0
Virginia	1.9	1.2	L	L	0.0
Wisconsin	5.2	2.4	0.0	L	0.0
Average of all states	4.1	1.3	0.4	7.8	52.5
Energy use (Btu/bu)	14,221.8	3,934.1	1676.9	634.7	1619.9
Total energy use (Btu/bu)					22,087.4

[a] L = insufficient data for legal disclosure.

Table 3-3 Comparison of Energy Use for Soybean Farming Taken from Three Data Sources

	Source		
Parameter	USDA 2007b	Hill et al. 2006	Pimentel and Patzek 2005
Year	2002	2002	Not available
Energy use (Btu/bu)	22,087	23,474/34,625[a]	20,447[b]
Percentage			
Diesel	64.4	61.7	57.7
Gasoline	17.8	17.2	35.2
LP gas	7.6	4.1	3.3
Electricity	2.9	11.0	3.8
Natural gas	7.3	6.1	0

[a] The 34,625 value includes diesel use of 6.6 L/ha for custom work and farm-related transportation and personal commuting energy use equal to those values associated with corn farming.

[b] Including energy input for labor, machinery, and fertilizer.

3.1.3 Fertilizer Use

We updated fertilizer use values for soybean farming in GREET by using the newly released USDA ERS data (USDA 2007c) (see Table 3-4). We used soybean yield per planted acre to calculate the fertilizer use per bushel of soybeans. Figure 3-2 shows the fertilizer use for soybean farming over the past 15 years. The amount of fertilizer used (nitrogen [N], phosphorous [P], and potassium [K], in grams) per bushel of soybeans did not change significantly. In fact, the usage patterns for each fertilizer type follow a similar time trend. For year 2010 (as our target year for this study), the following amounts were used: nitrogen at 61.2 g/bu, phosphorus at 186.1 g/bu, and potassium at 325.5 g/bu. The energy use and emissions for fertilizer manufacturing are simulated separately in GREET. On the basis of GREET simulations, the total energy use values per gram of fertilizer produced are 45.9 Btu/g N, 13.29 Btu/g P, and 8.42 Btu/g K.

Table 3-4 Fertilizer Use for Soybean Farming (USDA 2007c)

Year	Percent Acreage Receiving Nitrogen Fertilizer	Nitrogen Application Rate (lb/received acre)	Percent Acreage Receiving Phosphorus Fertilizer	Phosphorus Application Rate (lb/received acre)	Percent Acreage Receiving Potassium Fertilizer	Potassium Application Rate (lb/received acre)
1988	16	22	26	48	31	79
1989	17	18	28	46	32	74
1990	17	24	24	47	29	81
1991	16	25	22	47	23	76
1992	15	22	22	47	25	75
1993	14	21	21	46	25	79
1994	13	25	20	47	25	82
1995	17	29	22	54	25	85
1996	15	24	25	49	27	85
1997	20	25	28	50	33	88
1998	17	23	24	48	27	81
1999	18	21	26	46	28	78
2000	18	24	24	48	27	76
2001	NA[a]	24	NA	49	NA	84
2002	20	21	26	49	29	89
2003	NA	NA	NA	NA	NA	NA
2004	21	28	26	69	23	121
2005	NA	NA	NA	NA	NA	NA

[a] NA = not available.

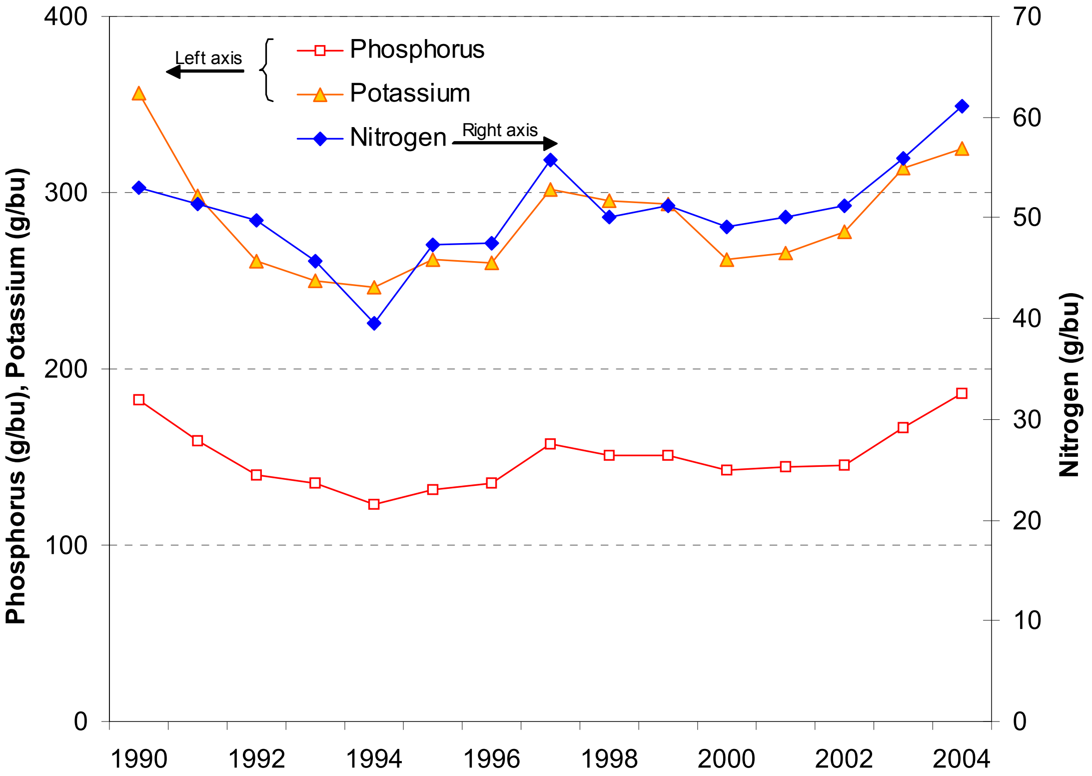


Figure 3-2 Fertilizer Use for Soybean Farming in the United States

3.1.4 N_2O Emissions

N_2O, a potent GHG, is produced from nitrogen in the soil through nitrification and denitrification processes (direct N_2O emissions). N_2O can also be produced through volatilization of nitrate from the soil to the air and through leaching and runoff of nitrate into water streams (indirect N_2O emissions).

Estimation of direct and indirect N_2O emissions from crop farming requires two important parameters: (1) the amount of nitrogen applied to soil and (2) rates for converting nitrogen into N_2O. The application of nitrogen fertilizer is the key to crop farming. For legume crops, such as soybeans, nitrogen fixation is another major nitrogen input. In 1996, IPCC considered nitrogen input to soil from biological nitrogen fixation by legume crops in estimating N_2O emissions from soil. However, in 2006, IPCC elected not to consider this nitrogen input because of a lack of evidence of significant emissions from the nitrogen fixed by legumes.

Even without considering the nitrogen that results from the biological fixation process, two sources of nitrogen inputs to soil for crop farming remain: nitrogen from fertilizer application and nitrogen in the aboveground biomass left in the field after harvest and in the belowground biomass (i.e., roots). For crops such as corn, nitrogen in the aboveground and belowground biomass is from nitrogen fertilizers. For crops such as soybeans, nitrogen in the aboveground and belowground biomass is eventually from nitrogen fertilizers and the biological nitrogen fixation process. GREET 1.8 takes into account the nitrogen in nitrogen fertilizers and the nitrogen in aboveground and belowground biomass in estimating N_2O emissions from crop farming.

For corn, IPCC (2006) estimates that aboveground biomass is 87% of corn yield (on a dry-matter basis). Aboveground biomass has a nitrogen content of 0.6%. Belowground biomass is about 22% of aboveground biomass, with a nitrogen content of 0.7%. The total amount of nitrogen in corn biomass that is left in corn fields per bushel of corn harvested is calculated as shown in Equation 3-1:

$$56 \text{ lb/bul} \times 85\% \text{ (dry matter content of corn)} \times (87\% \times 0.6\% + 87\% \times 22\% \times 0.7\%) = 0.312 \text{ lb N/bu} = 141.6 \text{ g/bu} \tag{3-1}$$

To estimate N_2O emissions from corn farming, 141.6 g of N are added to nitrogen fertilizer inputs for corn farming (which are about 420 g of N per bushel).

For soybeans, IPCC (2006) states that aboveground biomass is about 91% of soybean yield (on a dry-matter basis). Aboveground biomass has a nitrogen content of 0.8%. Belowground biomass is about 19% of aboveground biomass, with a nitrogen content of 0.8%. The total amount of nitrogen in soybean biomass that is left in soybean fields per bushel of soybean harvested is calculated as shown in Equation 3-2:

$$60 \text{ lb/bu} \times 85\% \text{ (dry matter content of soybeans)} \times (91\% \times 0.8\% + 91\% \times 19\% \times 0.8\%) = 0.442 \text{ lb N/bu} = 200.7 \text{ g/bu} \tag{3-2}$$

To estimate N_2O emissions from soybean farming, 200.7 g of N are added to nitrogen fertilizer inputs for soybean farming (which are about 62 g of N per bushel). The rates for converting the nitrogen in soil and water streams to N_2O emissions to the air are subject to great uncertainties (Wang et al. 2003; Crutzen et al. 2007). IPCC (2006) presents a conversion rate of 1% for direct N_2O emissions from soil (compared with 1.25% in IPCC [1996]), with a range of 0.3–3%.

Indirect N_2O emissions include those from volatilization of nitrate from the soil to the air and leaching and runoff of nitrate into water streams where N_2O emissions occur. IPCC (2006) estimates a volatilization rate for soil nitrogen of 10%, with a range of 3–30%. The conversion rate of volatilized nitrogen to N in N_2O emissions is 1%, with a range of 0.2–5%. The leaching and runoff rate of soil nitrogen is estimated to be 30%, with a range of 10–80%. The conversion rate of leached and runoff nitrogen to N in N_2O emissions is 0.75%, with a range of 0.05–2.5%.

Thus, the conversion rate for direct and indirect N_2O emissions is 1.325% (1% + 10% × 1% + 30% × 0.75%). This conversion rate was used in GREET 1.8. In contrast, Crutzen et al. (2007) estimated a conversion rate of 3–5% on the basis of the global N_2O balance. While the top-down approach adopted in Crutzen et al. is a sound approach, especially for checking and verifying results against the bottom-up approach used by the IPCC and others, data for the top-down approach needs to be closely examined in order to generate reliable N_2O conversion factors. In particular, Crutzen et al. adopted the global N_2O emission balance from a 2001 study but adopted the nitrogen inputs from a separate 2004 study for deriving N_2O conversion factors. Furthermore, Crutzen et al. did not get into agricultural subsystems (such as crop farming, animal waste management, and crop residual burning), which are required for generating N_2O conversion rates for the nitrogen inputs into crop farming. Their allocation of aggregate N_2O emissions (even after subtracting N_2O emissions from industrial sources) to the aggregate agricultural system could result in overestimation of N_2O conversion rates from nitrogen inputs into crop farming systems. Nonetheless, N_2O conversion rates, which are subject to great uncertainties, need to be reconciled between the bottom-up and the top-down approach.

3.2 Soy Oil Extraction

At soybean processing plants, soybean seeds are crushed, soy oil is extracted from the crushed seeds, and crude soy oil is refined. Soybeans contain 18–20% oil by weight. To maximize soy oil production, organic solvents are used during oil extraction. The solvent extraction process is a widely used and well-established technology. The standard solvent extraction process uses n-hexane that is produced from petroleum. Most of the n-hexane used in oil extraction is recovered and recycled, with some inevitable loss. Table 3-5 presents the inputs and outputs from oil extraction plants. In calculating emissions and energy use, we assumed that steam is generated from natural gas. N-hexane is a straight-chain hydrocarbon. Commercial hexane is manufactured by distillation of straight-run gasoline produced from crude oil or natural gas liquids. In GREET, hexane is assumed to be produced from crude oil, and its upstream production energy use and emissions are adopted from energy use and emissions calculated for production of LPG from crude oil. Because hexane is volatile, the amount of hexane lost during soy oil extraction is assumed to be in the form of VOC emissions to the atmosphere. For more details, see Wang (1999).

Table 3-5 Inputs and Outputs of Soybean Oil Extraction Plants

Inputs and Outputs	GREET Value[a]
Input	
Soybeans (lb)	5.7
Steam (Btu)	2,900 (44.5%)
NG (Btu)	2,800 (43.0%)
Electricity (Btu)	614 (9.4%)
N-hexane (Btu)	205 (3.1%)
Total energy (Btu)	6,519 (100%)
Output	
Soy oil (lb)	1
Soy meal (lb)	4.48

[a] From previous GREET assumptions. We assumed in GREET that steam is produced from natural gas with an efficiency of 80%. The Btu value for steam is the natural gas Btu used to generate the needed steam. Values in parentheses are percentage shares of process fuels.

3.3 Production of Soybean-Derived Fuels

Figure 3-3 illustrates the fuel production processes for the four soybean-derived fuels.

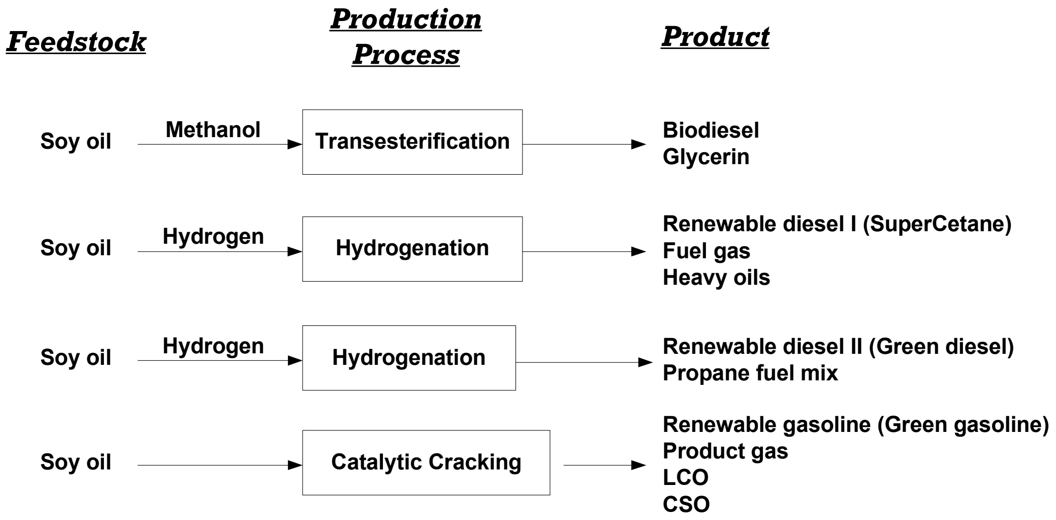
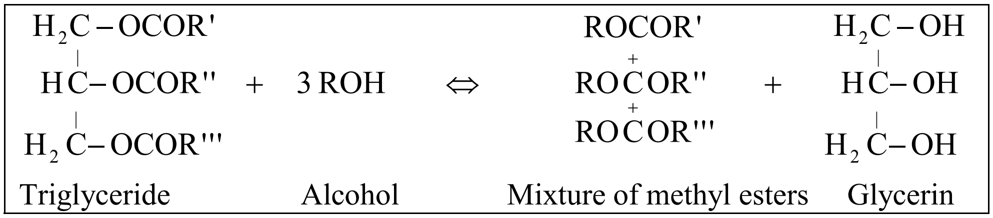


Figure 3-3 Fuel Production Processes for the Four Soybean-Derived Fuels

3.3.1 Biodiesel

Biodiesel is produced through the so-called transesterification process, in which soy oil is combined with alcohol (ethanol or methanol) in the presence of a catalyst (sodium hydroxide [NaOH] in this case) to form ethyl or methyl ester, as illustrated in Figure 3-4. The transesterification process requires steam and electricity as energy inputs and produces both biodiesel and glycerin.

For this study, we updated GREET biodiesel production simulations on the basis of data in Haas et al. (2006). Table 3-6 presents the inputs and outputs of biodiesel plants per pound of biodiesel produced. To apply the values specified in Table 3-6 to GREET, we assumed that (1) steam is generated from natural gas with an energy conversion efficiency of 80% and (2) the energy embedded in the three chemical compounds is half oil and half natural gas.



$$\begin{matrix} H_2C-OCOR' & & & ROCOR' & & H_2C-OH \\ | & & & \overset{+}{} & & | \\ HC-OCOR'' & + \; 3\,ROH & \Leftrightarrow & RO\overset{+}{C}OR'' & + & HC-OH \\ | & & & & & | \\ H_2C-OCOR''' & & & RO\overset{+}{C}OR''' & & H_2C-OH \end{matrix}$$

Figure 3-4 Transesterification of Soy Oil to Biodiesel

Table 3-6 Inputs and Outputs of Biodiesel Plants (lb or Btu/lb biodiesel)

Inputs and Outputs	Haas et al. 2006	Sheehan 1998	GREET Value
Inputs			
Soy oil (lb)	1.001	1.050	1.001
Methanol (lb)	0.1001	0.0900	0.1001
Sodium hydroxide (lb)	0.0050	0.0023	0.0050
Sodium methoxide (lb)	0.0125	0.0244	0.0125
Hydrochloric acid (lb)	0.0071	0.0077	0.0071
NG (Btu)	888	789	888
Electricity (Btu)	46	45	46
Outputs			
Biodiesel (lb)	1	1	1
Glycerin (lb)	0.116	0.213	0.213

3.3.2 Renewable Diesel I

The production of renewable diesel I comprises a series of reactions, including those involved in hydrocracking (breaking apart of large triglyceride molecules), hydrotreating (removal of oxygen), and hydrogenation (saturation of double bonds). Besides soy oil, hydrogen is needed as input. Some steam is also needed; ASPEN simulations conducted by NREL assumed that the required steam would be generated with the fuel gas and/or heavy oils that are co-produced from the plant. The output of this process is high-cetane diesel (with fuel gas and heavy oils as co-products). Table 3-7 lists the inputs and outputs of renewable diesel I plants. Note that the output values for fuel gas and heavy oils are net amounts (i.e., after steam generation for internal use). In GREET, hydrogen used in renewable diesel plants is assumed to be produced from natural gas via steam methane reforming (SMR).

Table 3-7 Inputs and Outputs of Renewable Diesel I Plants (lb or Btu per lb of renewable diesel I)

Inputs and Outputs	ASPEN Simulation Results as GREET Input
Inputs	
Soy oil (lb)	1.510
Hydrogen (lb)	0.030
Electricity (Btu)	134.4
Outputs	
Renewable diesel I (lb)	1
Fuel gas (Btu)	7083.7
Heavy oils (Btu)	3608.0

3.3.3 Renewable Diesel II

For the production of renewable diesel II, soy oil is combined with hydrogen in a catalytic reactor and then converted by a hydrogenation reaction to a high-cetane renewable diesel. This process requires electricity and thermal energy as inputs; the outputs are renewable diesel and a small amount of propane fuel mix. We assumed that thermal energy is generated from natural gas with an energy conversion efficiency of 80% and that hydrogen is produced from natural gas via SMR. Table 3-8 presents the inputs and outputs of renewable diesel plants per pound of renewable diesel II produced.

Table 3-8 Inputs and Outputs of Renewable Diesel II Plants (lb or Btu per lb of renewable diesel II)

Inputs and Outputs	ASPEN Simulation Results as GREET Input
Inputs	
Soy oil (lb)	1.174
Hydrogen (lb)	0.032
Natural gas (Btu)	84.05
Electricity (Btu)	93.83
Outputs	
Renewable diesel II (lb)	1
Propane fuel mix (Btu)	1095.5

3.3.4 Renewable Gasoline

The production of renewable gasoline takes place in an FCC unit. This process requires electricity and steam. The steam is assumed to be generated by combusting the by-product and product gas mix that results from the cracking process. The process also generates extra steam for export. The outputs are renewable diesel, product gas, LCO, and CSO. Table 3-9 presents the inputs and outputs from renewable gasoline plants per lb of renewable gasoline produced.

Table 3-9 Inputs and Outputs of Renewable Gasoline Plants (lb or Btu per lb of renewable gasoline)

Inputs and Outputs	Aspen Simulation Results as GREET Input
Inputs	
Soy oil (lb)	2.231
Electricity (Btu)	185.6
Outputs	
Renewable gasoline (lb)	1
Product gas (Btu)	6313.5
LCO (Btu)	4737.4
CSO (Btu)	5460.3

3.3.5 Comparison of the Four Soybean-Derived Fuels

On the basis of the analysis and assumptions outlined in Sections 3.3.1 through 3.3.4, Table 3-10 summarizes the energy use and amounts of product and co-product that can be produced from 1 ton of soybeans. According to Table 3-10, the transesterification process can generate a much larger amount of diesel product and co-products from 1 ton of soybeans than the other processes; however, it requires a lot more energy and chemical inputs than do the other processes. The hydrogenation process (used to produce renewable diesel II) has the best yield (in terms of energy content from 1 ton of soybeans) of the three new fuels, while it generate less energy co-product than the other processes. Because all of the processes produce other products (besides the target fuel), the energy value or market value of the co-products of these processes is an important factor in evaluating the energy and emission benefits of each soybean-based fuel. The co-product issue is discussed in Section 4. The production processes for the two renewable diesel options require hydrogen. Because hydrogen production is energy intensive, so determining which process is more energy intensive simply on the basis of inputs and outputs would not lead to a proper conclusion. The fuel cycles of hydrogen and other types of energy inputs must be taken into consideration, emphasizing the importance of a complete life-cycle analysis like the one conducted for this study.

Table 3-10 Energy Use and Amount of Fuel Product and Co-Products from One Ton of Soybeans

	Fuel			
Inputs and Outputs	**Biodiesel**	**Renewable Diesel I**	**Renewable Diesel II**	**Renewable Gasoline**
Outputs				
Product				
lb	351	232	299	157
mmBtu	5.66	4.36	5.66	2.94
Co-products				
Soy meal (lb)	1572	1572	1572	1572
Glycerin (lb)	75			
Energy co-product (mmBtu)		2.48	0.33	2.60
Inputs				
Natural gas (mmBtu)				
I. Soy oil extraction	1.80		1.80	
II. Fuel production	0.31		0.03	
Electricity (mmBtu)				
I. Soy oil extraction	0.194	0.194	0.194	0.194
II. Fuel production	0.016	0.031	0.028	0.029
Other inputs				
Methanol (mmBtu)	0.303			
Hydrogen (mmBtu)		0.36	0.49	

3.4 Fuel Properties

Table 3-11 presents the properties of the soybean-based fuels examined in this study. Compared with conventional diesel and biodiesel, renewable diesel fuels have much higher cetane numbers and lower density. Cetane number is one measure of the quality of a diesel fuel — a high number is a valuable feature for renewable diesel as a diesel blending component and a cetane enhancer.

3.5 Fuel Use in Vehicles

For our life-cycle analysis, we assumed that soybean-derived diesel fuels are used in 100% pure form in compression-ignition, direct-injection (CIDI) engine vehicles, and renewable gasoline is used in 100% pure form in spark-ignition (SI) engine vehicles. Since there were no testing data, we assumed that the fuel economy and CH_4 and N_2O emissions for CIDI vehicles are the same for all three diesel types. Likewise, we assumed that the fuel economy and CH_4 and N_2O emissions for SI vehicles are the same for the two gasoline types.

Table 3-11 Properties of the Four Soybean-Based Fuels

Fuel	Lower Heating Value (Btu/gal)	Density (lb/gal)	Carbon Content (%)[e]	Oxygen Content (%)	Cetane Value
Petroleum gasoline[a]	113,602	6.23	84.0	NA[f]	NA
Petroleum diesel[a]	129,488	7.06	87.1	0.0	40
Biodiesel[a]	119,550	7.40	77.6	11.0	50–65
Renewable diesel I[b]	117,059	6.24	87.1	0.0	100
Renewable diesel II[c]	122,887	6.49	87.1	0.0	70–90
Renewable gasoline[d]	115,983	6.21	84.0	NA	NA

[a] From the GREET model.

[b] From $(S\&T)^2$ Consultants Inc. (2004).

[c] From Kalnes et al. (2007).

[d] From UOP (2005).

[e] Because of a lack of data, the carbon content of renewable diesel fuels is assumed to be the same as that for petroleum-based diesel; the carbon content of renewable gasoline is assumed to be the same as that of petroleum-based gasoline.

F NA = not applicable.

4 Co-Product Credits for Biofuels

4.1 Methods for Addressing Co-Product Credits

The objective of calculating the credit allotted for co-products in life-cycle analysis is to fairly address the energy and emission burdens of the primary product, especially when the co-products have value in the marketplace. Two methods that are commonly used are the displacement method and the allocation method.

With the displacement method, a conventional product is assumed to be displaced by a new product. The life-cycle energy that would have been used and the emissions that would have been generated during production of the displaced product are counted as credits for the new product that is co-produced from the fuel pathway under evaluation. These credits are subtracted from the total energy use and emissions associated with the fuel pathway under evaluation. The difficulties with the displacement method involve accurately determining the displaced products and identifying the approach to obtain their life-cycle energy use and emissions. Also, if the amounts of co-products are relatively large compared with the amount of primary product from a given process (as is the case for renewable diesel I and renewable gasoline, see Table 3-10), the displacement method results — which are WTW analysis results that are mathematically normalized to production of a unit of the primary product — can generate distorted results for the primary product.

The allocation method allocates the feedstock use, energy use, and emissions between the primary product and co-products on the basis of mass, energy content, or economic revenue. This method is easier to implement in life-cycle analyses than the displacement method. However, it could result in inaccurate results if the values of product and co-products cannot be simply measured on a single basis (such as mass or energy content).

In this study, various co-products are produced during the production of soybean-based fuels, including protein products such as soy meal; solvents such as glycerin; and energy products such as propane fuel mix and heavy oils (see Table 3-10), which makes addressing their credit very difficult. If the displacement method is used, it is time-consuming to identify a displaced product for each of the co-products and obtain the life-cycle energy use and emissions of the identified products. Besides, the co-products almost have Btu values equivalent to those of their primary products (e.g., renewable diesel I and renewable gasoline), which makes the displacement method not a preferable approach. On the other hand, because these co-products have different values (for instance, the primary products and most of the co-products have Btu values and can be treated as energy products; some of the co-products, however — such as soy meal and glycerin — have nonenergy values), the Btu-based allocation method would not be able to fairly treat the co-products that have low energy contents but are valuable in other ways. The market value-based allocation method is subject to the variation in price of the co-products.

On the basis of these considerations, four approaches were employed to address the co-product issues: (1) the displacement approach, (2) an energy-based allocation method, (3) an allocation method based on the market values of the primary products and co-products, and (4) a hybrid approach that employs both the displacement and the allocation methods, in which the displacement method is used for soy meal and glycerin, and the allocation method is used for other energy co-products. For biodiesel, the hybrid approach is the same as the displacement approach. Table 4-1 summarizes the four approaches.

Table 4-1 Approaches to Address Co-Products of Soybean-Based Fuels

Fuel Product	**Process**	**Approach 1 (Displacement)**	**Approach 2 (Energy-Value-Based Allocation)**	**Approach 3 (Market Value-Based Allocation)**	**Approach 4 (Hybrid)**
Biodiesel production	Soy oil extraction	Displacement	Allocation	Allocation	Displacement
	Transesterification	Displacement	Allocation	Allocation	Displacement
Renewable diesel I production	Soy oil extraction	Displacement	Allocation	Allocation	Displacement
	Hydrogenation	Displacement	Allocation	Allocation	Allocation
Renewable diesel II production	Soy oil extraction	Displacement	Allocation	Allocation	Displacement
	Hydrogenation	Displacement	Allocation	Allocation	Allocation
Renewable gasoline production	Soy oil extraction	Displacement	Allocation	Allocation	Displacement
	Catalytic cracking	Displacement	Allocation	Allocation	Allocation

4.2 Displacement Approach

The first step in using the displacement method is to determine an equivalent product replaced by each co-product. Soy meal, which is primarily used as a livestock feed in the United States, is assumed in this study to replace soybeans. Soybean-based glycerin is assumed to replace petroleum-based glycerin. Other energy co-products are assumed to replace similar energy forms on the basis of their energy value; for example, fuel gas is assumed to replace equivalent-Btu natural gas for industrial use, heavy oil is assumed to replace equivalent-Btu residual oil. Table 4-2 lists the products that are to be displaced by the co-products from soybean-based fuel production.

Table 4-2 Products to Be Displaced by Co-Products

Product	Product to Be Displaced
Soy meal	Soybeans
Glycerin	Petroleum-based glycerin
Fuel gas	Natural gas
Heavy oil	Residual oil
Propane fuel mix	LPG
Product gas	Natural gas
LCO	Diesel fuel
CSO	Residual oil

The energy use and emissions resulting from production of one million Btu of natural gas, residual oil, LPG, and diesel fuel are already simulated in GREET and can be readily used. Also, GREET has addressed life-cycle energy use and emissions for obtaining soybeans, including soybean farming and fertilizer manufacturing, and these results are also readily used.

However, the displacement ratio between soy meal and soybeans for the purpose of feeding animals is yet to be determined in our study. Moreover, life-cycle analysis for petroleum-based glycerin is not included in GREET and thus needs further examination in this study.

4.2.1 Soy Meal

The displacement ratio of soy meal to soybeans is determined by protein content. Literature reports a protein content of 44–50% in soybean meal and 35–40% in soybeans (Ahmed et al. 1994; Maier et al. 1998; Britzman 2000). In this study, we assumed that soy meal contains 48% protein and soybeans contain 40%. On the basis of that assumption, we estimated that 1 lb of soy meal can replace 1.2 lb of soybeans.

4.2.2 Glycerin

Glycerin produced from petrochemical sources is called synthetic glycerin; natural glycerin is produced from plant oils and animal fats. Petroleum-based glycerin uses propylene, chlorine, and sodium hydroxide as raw materials. The theoretical raw material input to produce 1 lb of glycerin can be calculated according to the mass balance of the chemical reactions. In practice, there are some differences between theoretical mass balance and actual plant mass balance. Table 4-3 shows the amount of raw material needed to produce 1 lb of synthetic glycerin.

Table 4-3 Raw Material Input for One Pound of Synthetic Glycerin (lb/lb glycerin)

	Theoretical Input[a]	Industry Input[b]
Propylene	0.46	0.62
Chlorine	1.54	2.00
Sodium compounds	0.87	0.90

[a] Based on Chemical Economics Handbook (Greiner et al. 2005; Malveda et al. 2005).

[b] From Ahmed et al. (1994).

Production of synthetic glycerin requires little energy, so this energy is not addressed in our analysis. The energy use and emissions embedded in the raw material are the key issues in determining the life-cycle energy use and emissions of synthetic glycerin.

In this study, the production data for propylene, chlorine, and sodium hydroxide were taken from the Eco-Profile life-cycle inventory (Association of European Plastic Industry 2005). The Eco-Profile reports average industry data in detail for various petrochemical processes, including the amount of petroleum and natural gas used as feedstocks to produce each type of chemical, and the amount of petroleum, natural gas, electricity, and other fuels used as process fuels. We use the GREET model to generate the upstream energy use and emissions for the fuel (e.g., petroleum, natural gas, and electricity) used in producing propylene, chlorine, and sodium hydroxide. Table 4-4 compares the total energy embedded in raw material per pound of glycerin between our study and the study conducted by Ahmed et al. Some European studies report 30,000 to 90,000 Btu of total or fossil energy (Scharmer and Gosse 1996; Malça and Freire 2006).

Table 4-4 Total Btu in Raw Material per Pound of Glycerin

Study	Propylene	Chlorine	Sodium Hydroxide	Total
Our study	9,373	12,267	10,128	39,460
Ahmed et al. (1994)	8,577	5,319	11,275	21,296

4.3 Allocation Approach

Two different allocation approaches are applied in this study: energy-value-based and market-value-based. Generally, the allocation method is easier to implement than the displacement method in terms of data requirements. With the energy-value-based allocation method, the energy contents of the primary product and co-products are used to split the burden of energy input, feedstock input, and pollutant emissions. With the market-value-based allocation method, the market value of the products becomes the determining factor in splitting the burden.

4.3.1 Allocation at the System Level and Subsystem Level

The process of producing soybean-based fuels from soybeans involves two stages: soy oil extraction and fuel production. Both stages generate co-products, resulting in two different ways of allocating co-product credit: system level and subsystem level. As Figure 4-1 shows, system-level allocation takes soy oil extraction and fuel production processes as a whole system, with soybeans and the required energy and chemicals as inputs and fuel, soy meal, and other co-products as outputs. With the whole system level, the effect of soy oil is eliminated. Subsystem-level allocation includes two subsystems. In the first, soybeans are the inputs, and soy oil and soy meal are the outputs; in the second, soy oil is the input.

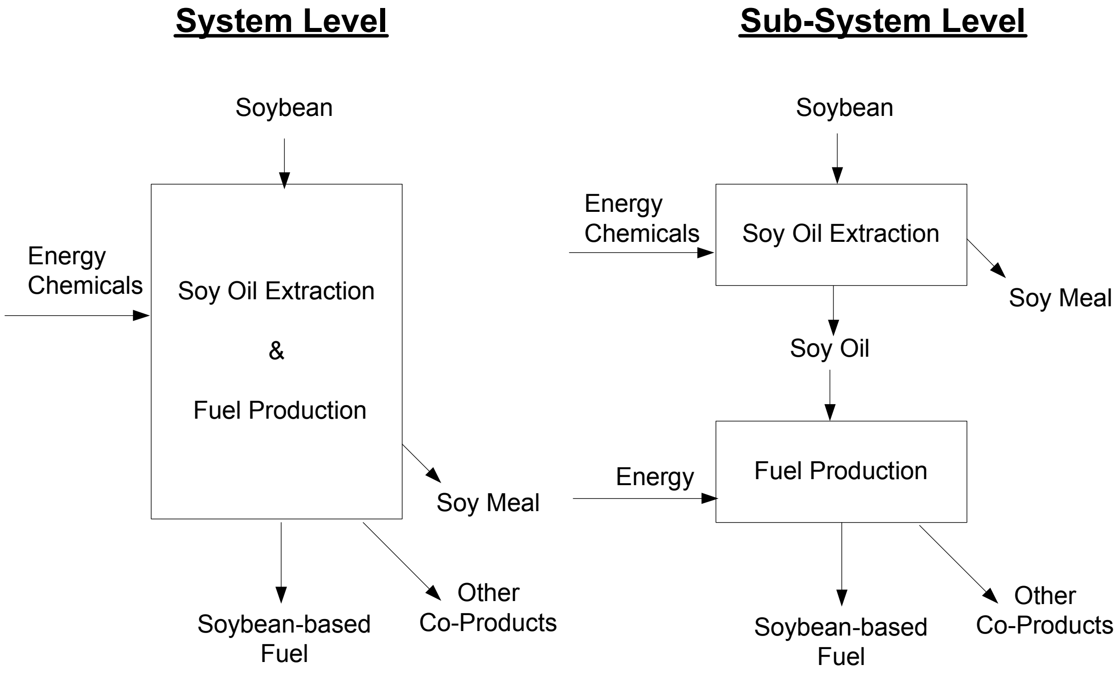


Figure 4-1 Two System Levels of Soybean-Based Fuel Production in the Allocation Approach

The displacement method will give the same final results no matter which system level is considered, but the allocation method will not. Because the allocation ratio is determined by the energy value or market value of the primary product and co-products, the variation in market value of soy oil could obviously affect the allocation results of the first subsystem level but not affect the result of the second subsystem level, which means that it could affect the final results. However, in the soybean-to-biodiesel/renewable fuels case, soy oil is only a transitional product, which is produced and then consumed, so there is no reason that its market value or other value could affect the final results. On the basis of this consideration, we selected the whole-system level for the allocation approach.

4.3.2 Energy Value and Market Value

As mentioned, the energy value and market value of the primary product and co-products are the major determining factors for splitting energy and emissions among these products by using the allocation method. The energy value of soy meal was obtained from the Soybean Meal Info Center (http://www.soymeal.org). Note that soy meal is an animal food rather than a fuel, so its energy value is measured as the energy released when it is digested. The energy content of renewable fuels and their co-products were obtained on the basis of ASPEN simulation results (see Section 2.4).

Unlike the energy content value — which is stable and will not change — the market value of products could vary over time and by region. For soy meal, we used the average growth rate of the state-average market price during the last decade (1997–2007) to project market prices in 2010 (Ash and Dohlman 2007).

The glycerin market is heavily oversupplied worldwide (Malveda et al. 2005), so the price for glycerin is not expected to rise in the near future; in fact, extensive biodiesel production could even lower glycerin's market price. We assumed a price of \$0.15/lb for glycerin, as provided in the Haas et al. (2006) study.

Because of the high cost of feedstock, the production cost of biodiesel is higher than that of conventional petroleum diesel. A wealth of research has been conducted to examine the cost for producing biodiesel at different industry scales (Haas et al. 2006; Bender 1999). These researchers estimate a production cost of \$2.00–\$2.30 per gallon of pure biodiesel, taking credits for soy meal and glycerin into consideration. The cost of biodiesel could vary significantly as a result of soybean and soy meal price variations. The United States has recently begun providing incentives to make biodiesel production costs competitive with those of petroleum-based diesel. Also, as biodiesel use increases and the infrastructure is established, the price of biodiesel could decrease. In this study, we used the biodiesel price before incentives.

For renewable diesel and gasoline fuels that are not yet on the market, we assumed the same market value as that of biodiesel fuel (on a per-million-Btu basis). Because the co-products of renewable diesel and gasoline production all have energy value and can be used in industry, we assumed the same prices per million Btu as their corresponding fuel (natural gas, residual oil, diesel, and LPG), determined as in Table 4-2. DOE's Energy Information Administration (EIA) *Annual Energy Outlook 2007* (EIA 2007a) projected the prices of natural gas, residual oil, diesel, and LPG in the industrial sector in 2010; these projected prices are used in our study.

Table 4-5 summarizes the energy content and market value of all products involved in this study. Note that prices in Table 4-5 are normalized to 2005 U.S. dollars (2005$) on the basis of an implicit U.S. price deflator from 1997 to 2006, as reported in the EIA *Annual Energy Review* (EIA 2007b).

Table 4-5 Energy Content and Market Value of Primary Products and Co-Products

Product or Co-Product	Energy Content (Btu/lb)	Market Value ($ 2005/lb)
Biodiesel	16,149	0.490
Renewable diesel I	18,746	0.569
Renewable diesel II	18,925	0.574
Renewable gasoline	18,679	0.567
Soy meal	4,246	0.274
Glycerin	7,979	0.150
Fuel gas	27,999	0.174
Heavy oils	20,617	0.195
Propane fuel mix	18,568	0.301
Product gas	18,316	0.114
LCO	19,305	0.248
CSO	18,738	0.177

4.3.3 Allocation Ratios

Table 4-6 presents the allocation ratios for the energy and emission burdens between primary products and co-products for the four soybean pathways. As indicated in Table 4-6, the allocation ratios of primary products based on energy value are a little lower than those based on market value.

4.4 Hybrid Approach

There are some shortcomings to both the displacement and allocation approaches. First, the production processes for renewable diesel I and renewable gasoline generate a large amount of

Table 4-6 Allocation Ratios of Total Energy and Emission Burdens between Primary Products and Co-Products from Using the Allocation Approach (shown as %)

Product or Co-Product	Biodiesel	Renewable Diesel I	Renewable Diesel II	Renewable Gasoline
Energy-value-based allocation				
Primary fuel (biodiesel, renewable fuels)	42.9	32.2	44.7	24.1
Co-products (soy meal, glycerin, and others)	57.1	67.8	55.3	75.9
Market-value-based allocation				
Primary fuel (biodiesel, renewable fuels)	45.7	39.4	47.4	29.9
Co-products (soy meal, glycerin, and others)	54.3	60.6	52.6	70.1

co-products, resulting in overestimation of credits for those products if the displacement method is used. In fact, using this method can even result in negative energy input and emissions. On the other hand, in the energy-based allocation method, soy meal and glycerin have values not because they have energy content but for their other applications. Soy meal, particularly, has low energy value but high protein content and is thus valuable in the animal feed market; if soy meal is treated as fuel (like other energy co-products), its credit could be greatly underestimated. The market-value-based allocation method is subject to variations in the product prices, which may lead to numerous uncertainties.

To overcome these shortcomings, we introduced a hybrid approach, in which the displacement method is used for soy meal and glycerin, and the energy-based allocation method is used for other energy co-products. For biodiesel, the hybrid approach is the same as the displacement approach. Unlike the allocation approach, which considers the production processes from soybean to fuel as a whole system, the hybrid approach separates the production system into two subsystems because each subsystem is addressed by using different allocation methods. Table 4-7 presents the allocation ratio between primary products and co-products of the second subsystem that results from using the hybrid approach.

Table 4-7 Allocation Ratios of Total Energy and Emission Burdens between Primary Products and Co-Products of the Second Subsystem from Using the Hybrid Approach (%)

Parameter	Renewable Diesel I	Renewable Diesel II	Renewable Gasoline
Primary fuel (renewable fuels)	63.7	94.5	53.1
Co-products (heavy oil, etc)	36.3	5.5	46.9

5 Life-Cycle Energy and GHG Emission Results for Soybean-Derived Fuels

On the basis of the data and key assumptions presented in Section 3 and Section 4, we used GREET to conduct life-cycle simulations of energy use and GHG emissions for the six pathways examined in this study. GHG emissions are the sum of emissions of three gases — CO_2, CH_4, and N_2O — weighted by their global warming potentials. According to IPCC, the global warming potentials of CO_2, CH_4, and N_2O are 1, 25, and 298, respectively.

Figure 5-1 shows the GREET WTW modeling boundary. Results of a WTW analysis are separated into two stages: well-to-pump (WTP) and pump-to-wheels (PTW). Well-to-pump stages start with fuel feedstock recovery and end with fuels available at refueling stations. Pump-to-wheels stages cover vehicle operation activities. For example, for gasoline, the simulated stages include crude recovery; transportation of crude oil from oil fields to central storage terminals; crude oil storage at terminals; crude oil transportation from terminals to petroleum refineries; crude oil storage at refineries; crude refining to gasoline; transportation, storage, and distribution of gasoline; and combustion of gasoline in vehicles.

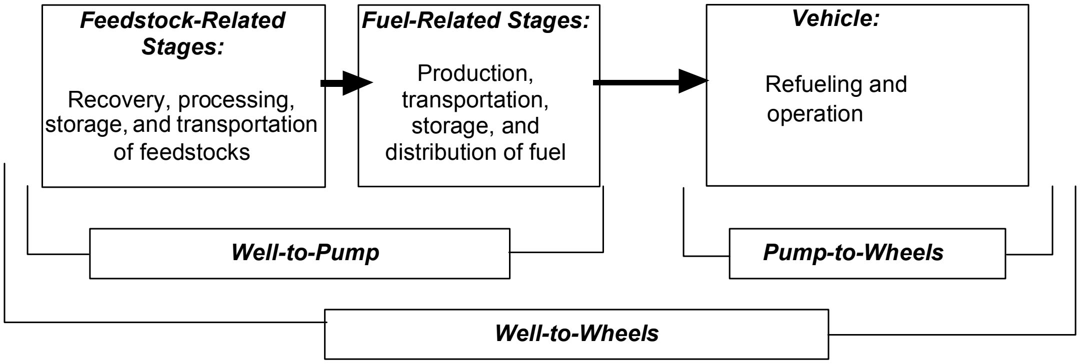


Figure 5-1 GREET Well-to-Pump and Pump-to-Wheels Stages

In the following sections, petroleum-based RFG is the baseline for soybean-based renewable gasoline, and petroleum-based LSD is the baseline for soybean-based biodiesel and renewable diesel fuels.

5.1 Total Energy Use

Figure 5-2 presents WTW total energy use for 1 million Btu of fuel produced and used. Total energy use comprises all energy sources, including fossil energy and renewable energy (excluding energy embedded in soybeans, which is eventually from solar energy).

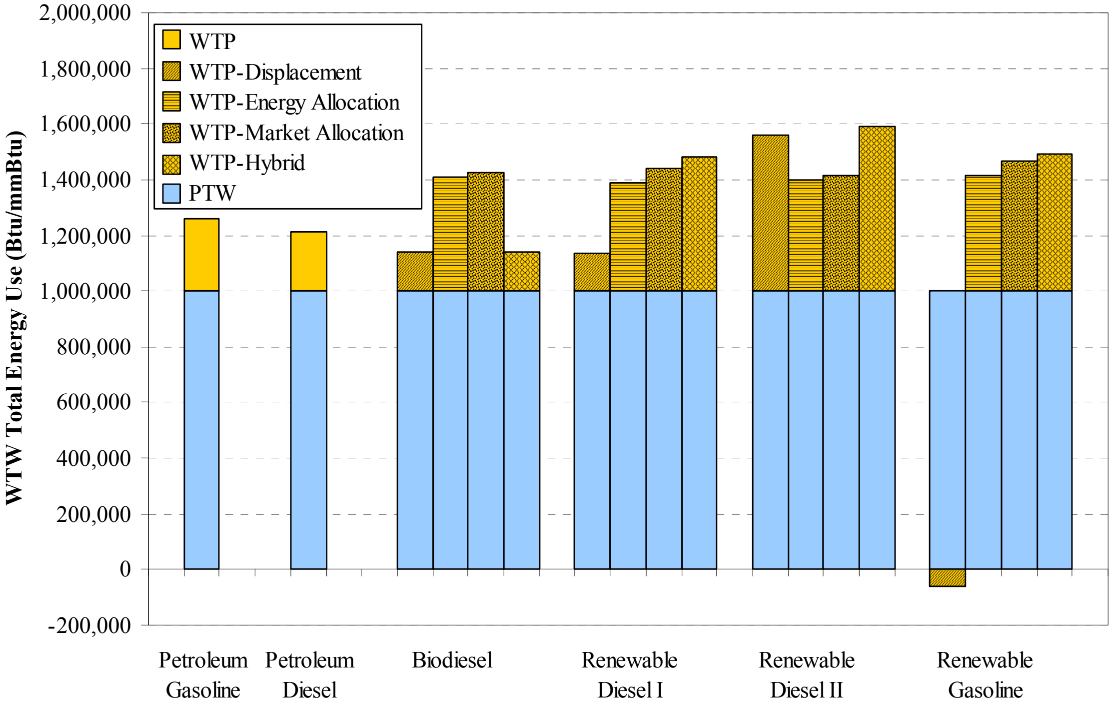


Figure 5-2 Well-to-Wheels Total Energy Use of Six Fuel Types

Figure 5-2 shows that different allocation approaches provide different results. The displacement approach gives the lowest total energy use among the four allocation approaches except in the case of renewable diesel II, whose production process generates a much smaller amount of co-product than the others. With the displacement approach, soybean-based fuels offer 6–25% lower total energy use than petroleum diesel or gasoline per million Btu, again except in the case of renewable diesel II, for which WTW total energy increases by 29% relative to LSD.

The two allocation approaches — energy-based allocation and market-based allocation — show good agreement with each other, with very similar results (1–4% difference). With the two allocation approaches, soybean-based fuels have 13–18% higher total energy use than petroleum diesel or gasoline.

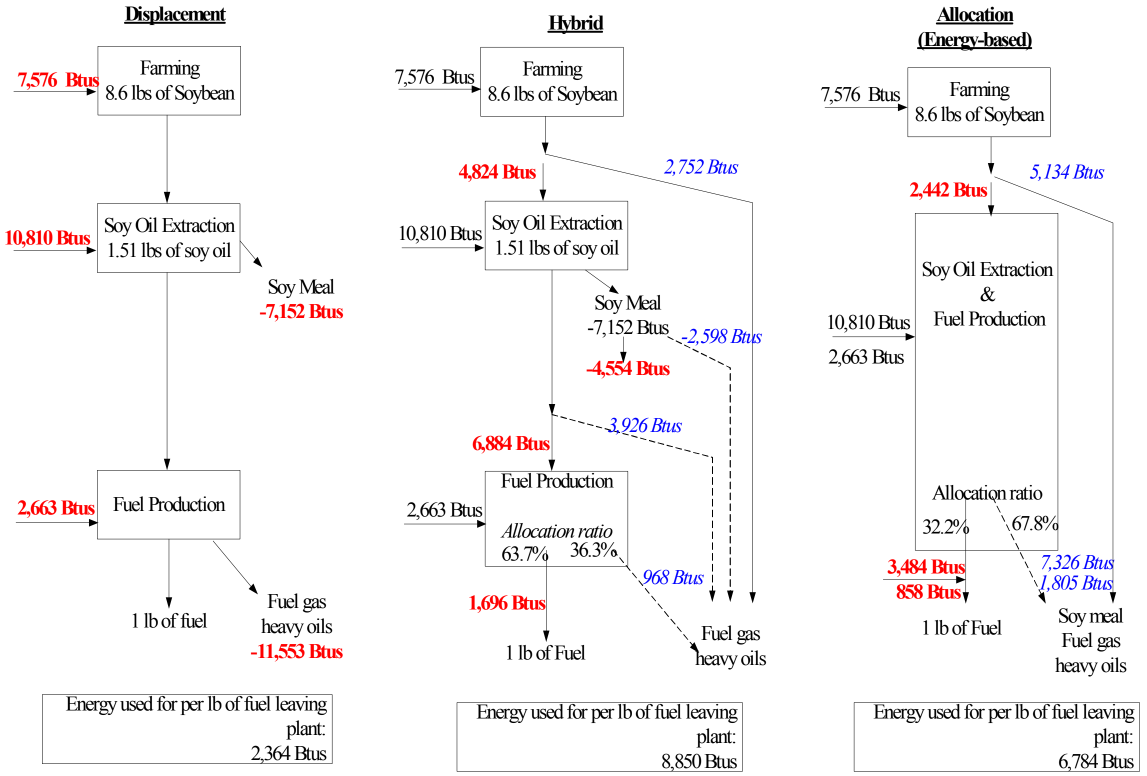


Figure 5-3 Comparison of Total Energy Use among Three Allocation Approaches for Renewable Diesel I
(Note: Red indicates energy values allocated to primary product; blue values and dashed lines indicate energy values allocated to co-products.)

The hybrid approach gives the highest total energy use results for the renewable diesel and gasoline, 19–31% higher than their conventional counterparts. Biodiesel is an exception because the hybrid approach is exactly the same as the displacement approach for biodiesel. It is interesting that the hybrid approach provides higher energy use results than the displacement and allocation approaches, because the hybrid approach is derived from the integration of the both of the latter methods. To explore the reason, Figure 5-3 compares the allocation of energy use per pound of fuel leaving the plant for the three allocation approaches, taking renewable diesel I as an example. Note that the energy use in Figure 5-3 includes farming, transportation of feedstock, and production in the plant only, not over the whole life cycle. The higher energy use of the hybrid approach compared with the displacement approach is attributable to two factors. First, the farming and production energy use allocated to the final co-products (fuel gas and heavy oil) is much lower than their displacement credit (2,752 + 3,926 + 968 for the hybrid method versus 11,533 for the displacement method). Second, part of the credit for soy meal (–2,598) is allocated to the co-product (fuel gas and heavy oil), while all soy meal credit belongs to the primary product with the displacement approach. The reason that energy use is higher for the hybrid approach than the allocation approach is because the allocation approach allocates more energy to the co-products (5,134 + 7,326 + 1,805 for the allocation method versus 2,752 + 3,926

+ 968 for the hybrid method) because the allocation ratio for co-products is much higher with the soy meal included (67.8% allocation versus 36.3% hybrid), and the difference between them (6,619) is larger than the soy meal credit earned in the hybrid approach (–4,554).

Renewable diesel II has fewer co-products; thus, its co-products and the method used to address them have a smaller effect on the results, which is apparent from the very similar energy use results among the four allocation approaches for this fuel.

5.2 Fossil Energy Use

Figure 5-4 presents the WTW fossil energy use of the six fuel options on the basis of 1 million Btu of fuel produced and used. Fossil energy use includes petroleum, natural gas, and coal.

Figure 5-4 reveals that all soybean-derived fuels offer significant reductions (52–107%) in fossil energy use. These reductions result from the fact that soybeans, as the feedstock for the four renewable fuel options, are a nonfossil feedstock. Soybean-based fuels, even with a certain amount of fossil energy input when they are used as process fuels during soybean farming and fuel production processes, can still achieve substantial reductions in fossil energy use.

Like the results for total energy use, the results for fossil energy use vary on the basis of the allocation method applied. With the displacement method, renewable gasoline can reduce WTW fossil energy use by 107% compared with petroleum gasoline. This large reduction in fossil energy use results from the large amount of co-products produced with renewable gasoline; these products were assumed to displace fossil energy (product gas to replace natural gas, LCO to replace diesel fuel, and CSO to replace residual oil), which helps renewable gasoline earn a large credit in fossil energy saving. Biodiesel, renewable diesel I, and renewable diesel II can achieve WTW fossil energy reductions of 84%, 90%, and 55%, respectively. With the allocation approach, the reduction ratios are around 63–71%. The hybrid approach shows a 52–61% reduction in fossil energy use for soybean-based renewable fuels compared with conventional fuels.

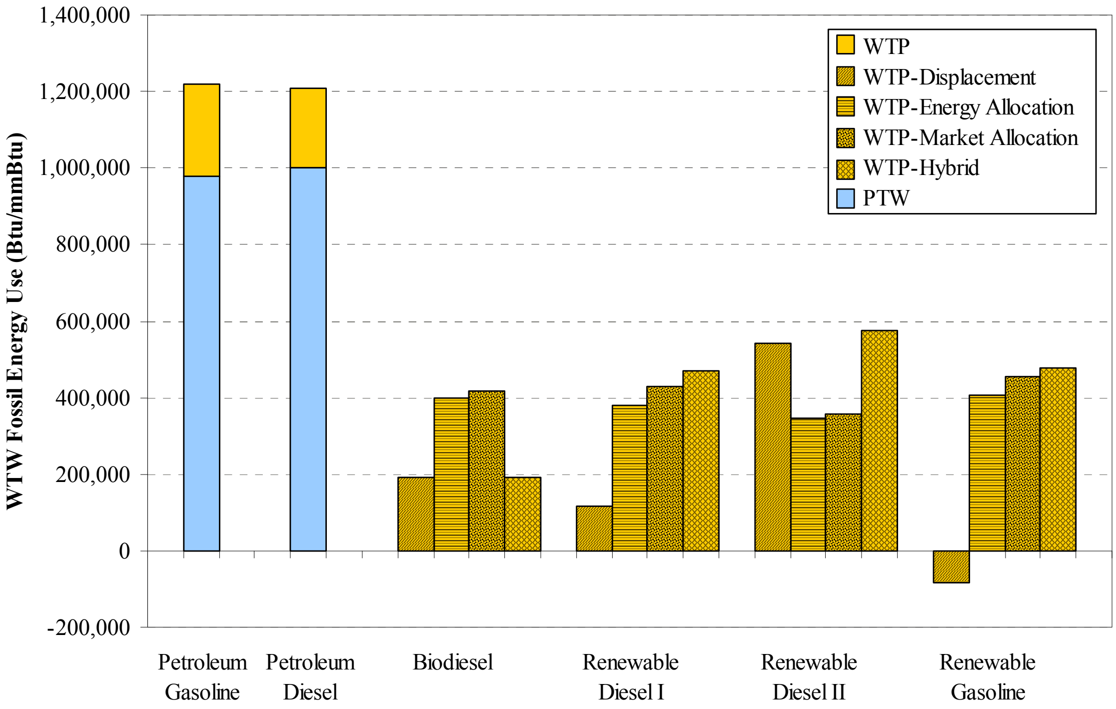


Figure 5-4 Well-to-Wheels Fossil Energy Use of the Six Fuel Types

5.3 Petroleum Use

Figure 5-5 presents the WTW petroleum energy use for the six fuel options. Soybean-derived fuels offer significant oil savings. Petroleum energy used in the soybean-based fuel cycle is entirely from the WTP stage, primarily from diesel use for farming equipment and for the trucks and locomotives needed to transport feedstock and fuel. For soybean-based fuels, PTW fuel use is zero.

All of the four soybean-derived fuels can save more than 85% of petroleum use. With the displacement approach, for each million Btu of fuel produced and used, renewable gasoline reduces petroleum use by 148% compared with petroleum gasoline, and soybean-based diesel fuels reduce petroleum use by 99–106% relative to petroleum diesel. Like fossil energy use, the petroleum use associated with renewable gasoline is low because its production process generates large quantities of co-products (product gas, LCO, and CSO) in terms of Btu, and the co-products (LCO and CSO) are assumed to replace petroleum fuels (diesel and residual oil), providing large petroleum savings credits.

With the allocation approach, petroleum use among the four soybean-based fuels is very similar; use by all is about 88–92% lower than that of conventional petroleum fuels.

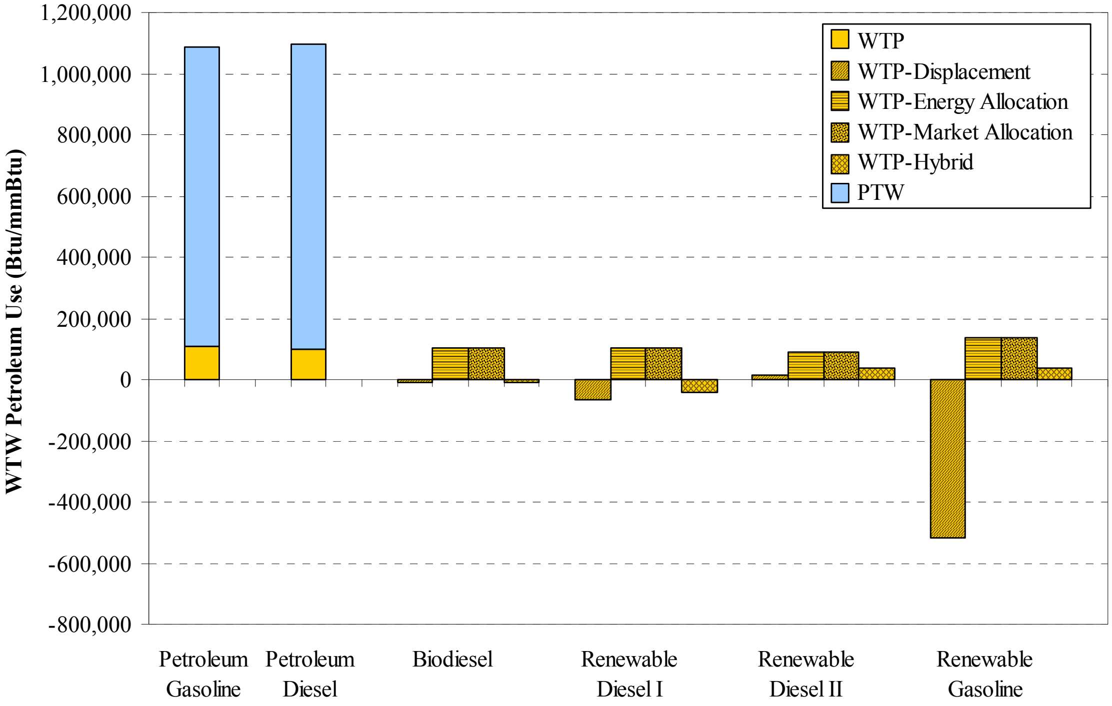


Figure 5-5 Well-to-Wheels Petroleum Energy Use of the Six Fuel Types

With the hybrid approach, soybean-based fuels reduce WTW petroleum use by 97–104% relative to petroleum fuels. Unlike total energy use and fossil energy use results, WTW petroleum use for the hybrid approach is lower than that for the allocation approach for the three renewable fuels. This is because the production process for renewable fuels uses very little petroleum, so petroleum use allocated to the co-products is very small. On the other hand, farming of soybeans, assigned to be displaced by soy meal, consumes large amounts of diesel and gasoline, and makes the hybrid approach result in lower petroleum use because of the petroleum credit from soy meal.

5.4 GHG Emissions

Figure 5-6 presents WTW CO_2-equivalent grams of GHGs (including CO_2, CH_4, and N_2O) for the six fuel pathways studied. To clearly show the GHG reduction benefit of different soybean-based fuels, Figure 5-7 presents the changes in GHG emissions of the soybean-based fuels relative to their petroleum counterparts.

The emission results for the two renewable diesel fuels depend on the allocation approach used. Of the four allocation approaches, the displacement approach offers the best GHG reduction benefit, except for renewable diesel II. When this approach is used, all four soybean-based fuels can achieve a modest to significant reduction in WTW GHG emissions (64–174%) compared

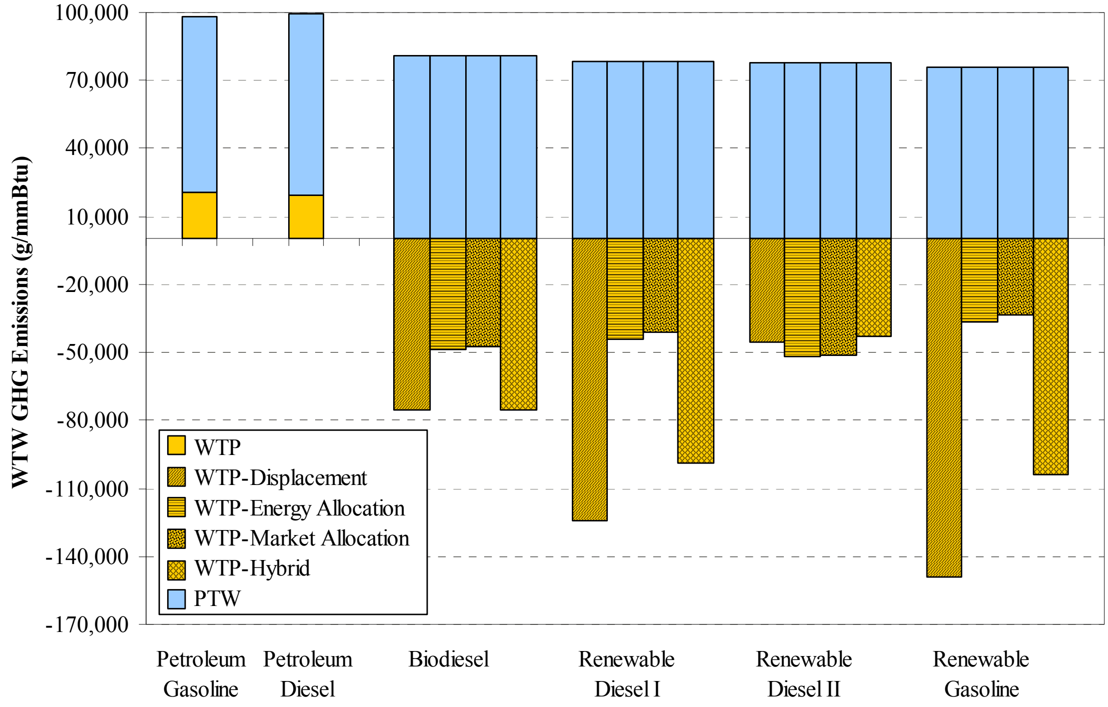


Figure 5-6 Well-to-Wheels GHG Emissions of the Six Fuel Types

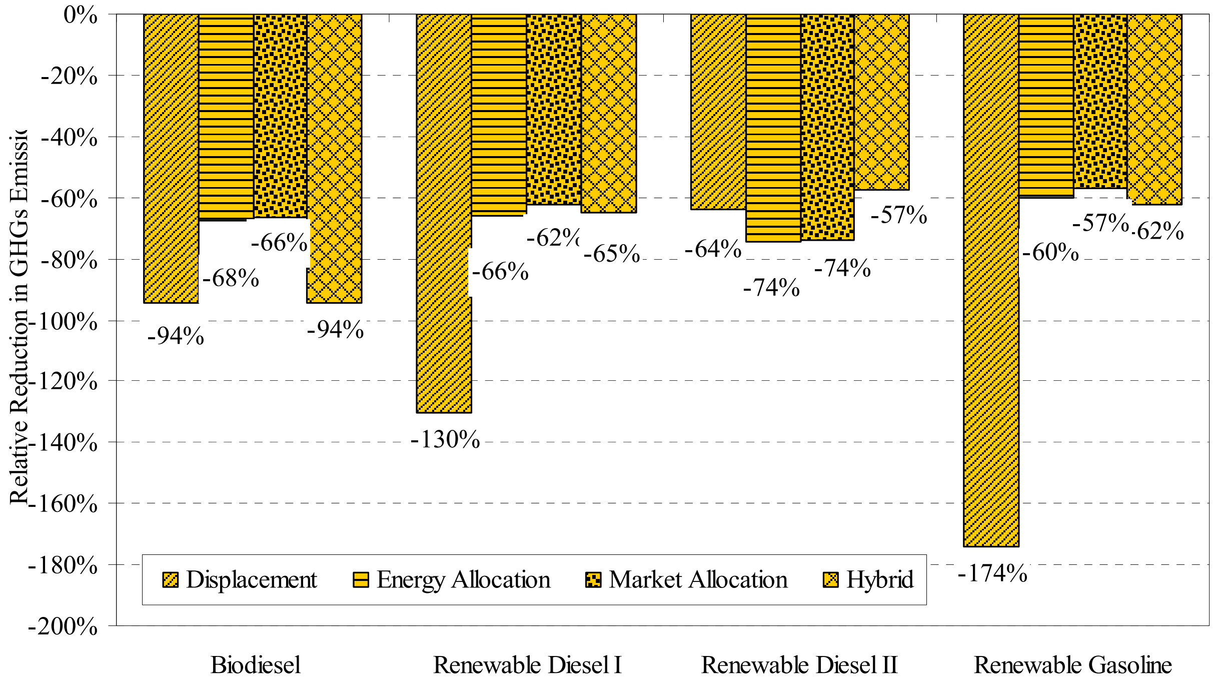


Figure 5-7 Well-to-Wheels GHG Emission Reductions for Soybean-Derived Fuels Compared with Petroleum Gasoline or Diesel

with petroleum-based fuels. The reason that renewable diesel I and renewable gasoline can achieve a much larger GHG emission reduction (-130% and –174%) is because they have a significant amount of co-products (fuel gas and heavy oil; product gas, LCO, and CSO) and because the production and combustion of the replaced fuels (natural gas, diesel fuel, and residual oil) could release lots of GHGs.

With the allocation approach, soybean-based fuels achieve a modest reduction in GHG emissions (57–74%). The results from using the hybrid approach are similar to the results obtained from using the allocation approach.

These results are based on 1 million Btu of fuel produced and used. While we do not expect significant engine efficiency differences between the two gasoline types in SI engines and among the four diesel types in CIDI engines, it is well known that CIDI engines are more efficient than SI engines. Fuel consumption in CIDI engines could be 15–20% less than that of SI engines per distance traveled. To compare WTW results on a per-mile basis among the six options, researchers could reduce energy use and GHG emissions for the four diesel fuel options as presented in Figure 5-6.

6 Conclusions

We assessed the life-cycle energy and GHG emission impacts of soybean-derived biodiesel and soybean-derived renewable diesel and gasoline fuels by expanding, updating, and using the GREET model. Soybean-derived renewable diesel is produced from hydrogenation of soy oil, and renewable gasoline is produced from catalytic cracking of soy oil.

The method applied to determine energy and emission credits for co-products is a key issue in life-cycle analysis. The production processes of the four soybean-based fuels generate various kinds of co-products, which could lead to very different results depending on the method that is used to address the co-products. We used four different allocation approaches in this study: displacement, energy-based allocation, market-value-based allocation, and a hybrid approach (integrating the displacement and allocation methods). The four allocation approaches generate considerably different results.

For WTW total energy use, the displacement approach gives the lowest total energy use for the four bio-based fuels — showing a 6–25% reduction in total energy use for the biofuels (except for renewable diesel II) compared with petroleum fuels. The two allocation approaches show good agreement with each other, providing very similar results. The hybrid approach gives the highest total energy use results. Both the allocation and hybrid approaches show a 13–31% increase in total energy use compared with petroleum fuels.

All soybean-derived fuels achieve a significant reduction (52–107%) in fossil energy use. The displacement approach offers the best benefit in fossil energy use, with a reduction of 55–107%. With the allocation approach, the reduction ratios are around 63–71%. The hybrid approach shows a 52–61% reduction in fossil energy use for soybean-based renewable fuels compared with conventional fuels.

All four of the soybean-derived fuels can save more than 85% of petroleum use. With the displacement approach, renewable gasoline reduces petroleum use by 148% compared with petroleum gasoline because its production process generates a large amount of energy co-products. Soybean-based diesel fuels reduce petroleum use by 99–106% relative to petroleum diesel. With the allocation approach, the use of petroleum by the four soybean-based fuels is about 88–92% lower than its use by conventional petroleum fuels. With the hybrid approach, soybean-based fuels reduce WTW petroleum use by 97–104% relative to petroleum fuels.

With the displacement approach, all four soybean-based fuels can achieve a modest to significant reduction in WTW GHG emissions (64–174%) compared with petroleum-based fuels. While with the allocation approach, soybean-based fuels achieve a modest reduction in GHG emissions (57–74%).

7 References

Ahmed, I., J. Decker, and D. Morris, 1994, *How Much Energy Does It Take to Make a Gallon of Soydiesel?* prepared for the National SoyDiesel Development Board.

Ash, M., and Dohlman, E., 2007, *Oil Crops Outlook: Prices Strengthen as Outlook for U.S. Soybean Supply Tightens,* U.S. Department of Agriculture, Oct. 15, available at http://usda.mannlib.cornell.edu/usda/ers/OCS//2000s/2007/OCS-10-15-2007.pdf, accessed Nov. 2007.

Association of European Plastic Industry, 2005, *Eco-Profiles of the European Plastic Industry: Propylene, Chlorine, and Sodium Hydroxide*, available at http://lca.plasticseurope.org/index.htm, accessed Nov. 2007

Bender, M., 1999, "Economic Feasibility Review for Community-Scale Farmer Cooperatives," *Bioresource Technology*, 70: 81–87.

Britzman, D.G., 2000, *Soybean Meal — An Excellent Protein Source for Poultry Feeds*, American Soybean Association Technical Bulletin, available at http://www.asaim-europe.org/pdf/Britzman.pdf, accessed Nov. 2007.

CETC (CANMET Energy Technology Centre), undated, *SuperCetane Technology*, available at http://canren.gc.ca/app/filerepository/381B2685235D4C6E924E0665F0A84344.pdf, accessed Nov. 2007.

Crutzen, P.J., A.R. Mosier, K.A. Smith, and W. Miniwarter, 2007, "N_2O Release from Agro-Biofuel Production Negates Global Warming Reduction by Replacing Fossil Fuels," *Atmospheric Chemistry and Physics*, 7: 11191–11205.

Greiner, E., T. Kalin, and M. Yoneyama, 2005, "Epichlorohydrin," in *Chemical Economics Handbook 2004*, Report #642.3000A, SRI Consulting, Menlo Park, Calif.

EIA (Energy Information Administration), 2007a, *Annual Energy Outlook 2007*, U.S. Department of Energy, available at http://www.eia.doe.gov/oiaf/aeo/, accessed Nov. 2007.

EIA, 2007b, *Annual Energy Review 2007*, U.S. Department of Energy, available at http://www.eia.doe.gov/emeu/aer/contents.html, accessed Nov. 2007.

Haas, M.J., A.J. McAloon, W.C. Yee, et al., 2006, “A Process Model to Estimate Biodiesel Production Costs,” *Bioresource Technology,* 97: 671–678.

Hill, J., E. Nelson, D. Tilman, et al., 2006, “Environmental, Economic, and Energetic Costs and Benefits of Biodiesel and Ethanol Biofuels,” in *Proceedings of the National Academy of Sciences of the United States of America*, doi:10.1073/pnas.0604600103.

Intergovernmental Panel on Climate Change (IPCC), 2006, “N_2O Emissions from Managed Soils, and CO_2 Emissions from Lime and Urea Application,” in *2006 IPCC Guidelines for National Greenhouse Gas Inventories*, Volume 4, Chapter 11, available at http://www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/4_Volume4/V4_11_Ch11_N2O&CO2.pdf, accessed Nov. 2007.

IPCC, 1996, *Revised IPCC Guidelines for National Greenhouse Gas Inventories: Workbook*, London, U.K., 2.15–2.16.

Kalnes, T., T. Marker, and D.R. Shonnard, 2007, “Green Diesel: A Second Generation Biofuel,” *International Journal of Chemical Reactor Engineering*, 5, A48.

Keller, G., M. Mintz, C. Saricks, M. Wang, and H. Ng, 2007, *Acceptance of Biodiesel as a Clean-Burning Fuel: A Draft Report in Response to Section 1823 of the Energy Policy Act of 2005,* Center for Transportation Research, Argonne National Laboratory, prepared for Office of FreedomCAR and Vehicle Technologies, U.S. Department of Energy, Oct.

Maier, D., J. Reising, J. Briggs, K. Day, and E.P. Christmas, 1998, *High-Value Soybean Composition*, Fact Sheet #39, Grain Quality Task Force, Purdue University, available at http://www.ces.purdue.edu/extmedia/GQ/GQ-39.html, accessed Nov. 2007.

Malça, J., and F. Freire, 2006, *A Comparative Assessment of Rapeseed Oil and Biodiesel (RME) to Replace Petroleum Diesel Use in Transportation,* presented at Bioenergy I: From Concept to Commercial Processes, Tomar, Portugal, March 5–10, available at http://services.bepress.com/cgi/viewcontent.cgi?article=1029&context=eci/bioenergy_i, accessed Nov. 2007.

Malveda, M., M. Blagoev, R. Gubler, and K. Yagi, 2005, “Glycerin,” in *Chemical Economics Handbook 2004*, Report #662.5000A, SRI Consulting, Menlo Park, Calif.

National Biodiesel Board, 2007, *FAQs: How Much Biodiesel Has Been Sold in the U.S.?* available at http://www.biodiesel.org/resources/faqs/, accessed Nov. 2007.

NRCan (Natural Resources Canada), 2003, *Technologies and Applications: The CETC SuperCetane Technology*, last updated Aug. 11, available at http://www.canren.gc.ca/tech_appl/index.asp?CaID=2&PgId=1083, accessed Nov. 2007.

Pimentel, D., and T.W. Patzek, 2005, "Ethanol Production Using Corn, Switchgrass, and Wood; Biomass Production Using Soybean and Sunflower," *Natural Resources Research*, 14(1): 65–75.

Reuters News, 2007, *Galp Energia Selects UOP/Eni Ecofining^{TM} Technology to Produce Green Diesel Fuel*, available at http://www.reuters.com/article/pressRelease/idUS44541+28-Nov-2007+BW20071128, accessed Nov. 2007

Scharmer, K., and G. Gosse, 1996, "Ecological Impact of Biodiesel Production and Use in Europe," *The Liquid Biofuels Newsletter*-7, available at http://www.blt.bmlf.gv.at/vero/liquid_biofuels_newsletter/Liquid_biofuels_Newsletter-07_e.pdf, accessed Nov. 2007.

(S&T)^2 Consultants Inc., 2004, *The Addition of NRCan's Supercetane and ROBYS^{TM} Processes to GHGenius*, prepared for Natural Resources Canada.

Sheehan, J., V. Camobreco, J. Duffield, et al., 1998, *Life-Cycle Inventory of Biodiesel and Petroleum Diesel for Use in an Urban Bus*, prepared for U.S. Department of Energy, Office of Fuels Development.

UOP, 2005, *Opportunities for Biorenewables in Oil Refineries*, Final Technical Report, prepared for U.S. Department of Energy.

USDA (U.S. Department of Agriculture), 2007a, *Quick Stats: Agricultural Statistics Data Base*, available at http://www.nass.usda.gov/QuickStats/, accessed Nov. 2007.

USDA, 2007b, *Data Sets: Commodity Costs and Returns*, available at http://www.ers.usda.gov/Data/CostsAndReturns/Fuelbystate.xls, accessed Nov. 2007.

USDA, 2007c, *Data Sets: U.S. Fertilizer Use and Price,* available at http://www.ers.usda.gov/Data/FertilizerUse/, accessed Nov. 2007.

Wang, M.Q., 1999, *GREET 1.5 — Transportation Fuel-Cycle Model, Volume 1: Methodology, Development, Use, and Results, Volume 1*, ANL/ESD-39, Center for Transportation Research, Argonne National Laboratory, Argonne, Ill., Aug.

Wang, M., C. Saricks, and H. Lee, 2003, *Fuel-Cycle Energy and Emission Impacts of Ethanol-Diesel Blends in Urban Buses and Farming Tractors*, prepared for Illinois Department of Commerce and Economic Opportunities, by Center for Transportation Research, Argonne National Laboratory, Argonne, Ill., July.

Appendix 1: ASPEN Simulation Process of Renewable Diesel I (Super Cetane)

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Center for Transportation Technologies and Systems
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A1-1 Introduction

A preliminary analysis was conducted for a hydrogenation-derived renewable diesel (HDRD) facility on the basis of the Natural Resources Canada (NRCan) process [(S&T)^2 Consultants 2004]. NRCan has named its renewable diesel “SuperCetane.” Material and energy balances were developed by using ASPEN Plus® 12.1 (super_cetane2.inp). The overall goal of the study was to confirm the preliminary overall material and energy balances provided by NRCan [(S&T)^2 Consultants 2004] and to provide input for a life-cycle analysis (LCA). The following report summarizes the basis for the analysis and its results.

A1-2 Design Basis and Process Description

HDRD is made from reacting hydrogen with oil or grease in a refinery-hydrotreating process. Several reactions occur in the conversion including hydrocracking, hydrotreating, and hydrogenation [(S&T)^2 Consultants 2004]. A commercial refinery catalyst is used to facilitate conversion.

For this analysis, the production of HDRD is based on the NRCan process, which involves hydrogen production, hydrogenation, water separation, distillation gas recycle, and steam generation. All of the unit operations were modeled except hydrogen production. It is assumed that hydrogen is supplied by an off-site hydrogen plant. Figure A1-1 is a block flow diagram of the NRCan process.

One of the important characteristics of the process is that energy demands, except electricity, are met on site. That is, a portion of the fuel gas product is combusted on site to generate steam for the process. The remaining fuel gas as well as the heavy waxy fraction are sent off site and assumed to be used for fuel. For this process configuration, the LCA will determine the emissions from the off-site fuel gas and heavies combustion as well as the electricity generation

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and will apportion it appropriately to the main process. This analysis will estimate the emissions from the fuel gas combusted on site.

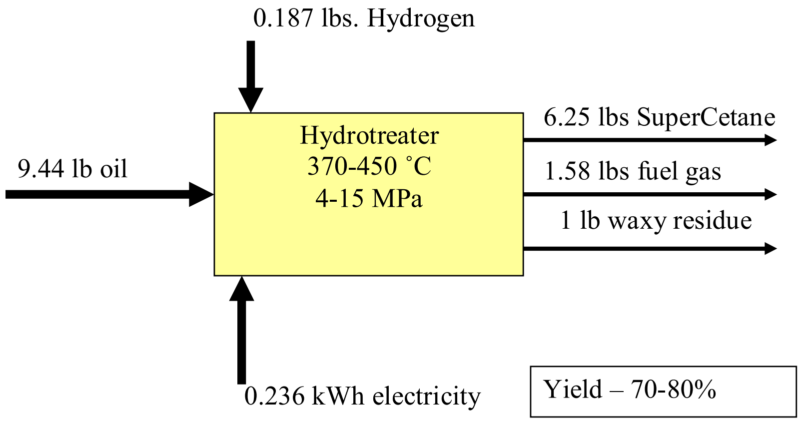

Figure A1-1 HDRD (SuperCetane) Block Flow Diagram

The renewable diesel process was modeled by using numerous assumptions and data sources. Table A1-1 summarizes the key design parameters and their sources.

Table A-1 Design Basis

Parameter	Value	Source
Feedstock		
Type	Soybean oil	Most common oil in U.S. for biodiesel
Throughput	100 lb/h	For LCA analysis
Feedstock fatty acid composition (wt fraction)		
Linolenic acid	0.075	
Palmitic acid	0.11	
Stearic acid	0.041	
Oleic acid	0.22	
Linoleic acid	0.54	
Arachidic acid	0.014	
Hydrogenation design		
Temperature	325 ºC	
Pressure	500 psia	
Yields (per pound inlet feed)		
SuperCetane		Derived from published yields [(S&T)^2 Consultants 2004]
Water	64.9%	
CO_2	5.0%	
Propane	8.2%	
Hydrogen	8.2%	
Naphtha	10.4%	
	0.35	

Several of these assumptions, particularly the feedstock choice and facility size, require further explanation. The feedstock selected was soybean oil, even though many of the feedstocks in the literature were rapeseed oil or other oils, because it is the most prevalent oil in fuels production (i.e., biodiesel), and one of the purposes of the study was to compare the environmental impacts of HDRD to biodiesel, and the most thorough LCA of biodiesel (Sheehan et al. 1998) was based on soybean oil. The facility size of 100 lb/h was selected as an easy, round number for the LCA. The results of most LCAs are shown on a pound of feed or product basis since the impacts are directly scalable to throughput. Therefore, this simple number was selected, even though this would not be a typical facility size.

A1-3 Model Description

An ASPEN Plus® model (super_cetane) was developed for the NRCan SuperCetane process, based largely on the $(S\&T)^2$ report [$(S\&T)^2$ 2004]. ASPEN Plus® is a steady-state process simulator, and Appendix A1-6 contains the input file for the model.

The ASPEN Plus® HDRD model has one flowsheet to model the four major process areas: hydrogenation, sour water separation, stripping, and pressure swing adsorption (PSA)/gas recycle. Each of these areas is briefly discussed, and the flow diagram from ASPEN Plus® is presented. The flow diagram shows only those unit operations modeled in ASPEN Plus®. Equipment used for operations such as conveyance, size reduction, and storage is generally not included in the model. The power requirements of this equipment, however, are included and are modeled as work streams.

ASPEN Plus® is composed of physical property and unit operation models that are combined into a process model. The simulation can be broken into three major sections: components (i.e., chemical species), physical property option sets (e.g., what set of physical property models to use), and the flowsheet (i.e., the series of unit operations). Each of these sections is described in more detail below.

Components

Fourteen components were modeled in the simulation; all were modeled as conventional (e.g., water) components in the mixed substream. The following is a list of the components in the simulation:

- Hydrogen – H_2
- Linolenic acid – $C_{18}H_{30}O_2$
- Palmitic acid – $C_{16}H_{32}O_2$

- Stearic acid – $C_{18}H_{36}O_2$
- Linoleic acid – $C_{18}H_{32}O_2$
- Arachidic acid – $C_{20}H_{40}O_2$
- Oleic acid – $C_{18}H_{34}O_2$
- Green Diesel – $C_{18}H_{38}$
- Water – H_2O
- Hydrogen Sulfide – H_2S
- Ammonia – NH_3
- Propane – C_3H_8
- Naphtha
- Oxygen – O_2
- Nitrogen – N_2
- Wax – $C_{26}H_{54}$
- Carbon dioxide – CO_2

Green diesel is not a specific compound but is a complex mixture of hydrocarbons; however, for simplicity, it was modeled as a single component, $C_{18}H_{38}$, which is within the range of diesel hydrocarbons. Green diesel was specified with a specific gravity of 0.78 (Marker, T. 2007) and a MW of 254. Naphtha was specified with a specific gravity of 0.7 and a MW of 100.

As noted earlier, the vegetable oil feed was modeled as a mixture of six fatty acids: linolenic acid, palmitic acid, stearic acid, linoleic acid, arachidic acid, and oleic acid. All of these components are available in the ASPEN Plus® databanks. Table A1-2 shows the molecular formula, the component name in the model, and the weight fraction in the feed of each fatty acid.

Table A1-2 Organic Acid Composition of Bio-Oil

Organic Fatty Acid	Composition	Component Name	Weight Fraction
Linolenic	$C_{18}H_{30}O_2$	LINOL3	0.075
Palmitic	$C_{16}H_{32}O_2$	PALM	0.11
Stearic	$C_{18}H_{36}O_2$	STEARIC	0.041
Oleic	$C_{18}H_{34}O_2$	OLEIC	0.22
Linoleic	$C_{18}H_{32}O_2$	LINOL2	0.54
Arachidic	$C_{20}H_{40}O_2$	ARACHID	0.014

One Henry component, CO_2, was specified. The Henry's constants were obtained from ASPEN Plus®.

Physical Property Option Sets

The physical property set selected was POLYUF with properties estimated by using the POLYNRTL method. Physical property databanks used in the simulation were PURE13, AQUEOUS, SOLIDS AND INORGANIC.

Flowsheet

One flowsheet was developed for the process: (A1000). The flowsheet is briefly discussed, and flow diagrams from ASPEN Plus® are presented. The flow diagrams (Figure A1-2) show only those unit operations modeled in ASPEN Plus®. Equipment used for operations such as conveyance and storage are generally not included in the model and are thus not shown. Similarly, certain complex unit operations (e.g., gas turbine) require several ASPEN Plus® models (e.g., compressors, reactors, heat exchangers).

Bio-oil is introduced into the process in stream 101. It is assumed to be at ambient conditions (i.e., 68°F and 14.7 psia) with a flow rate of a nominal 100 lb/h. The 100 lb/h value was selected as it would be easily scaled to any other value; since the model was developed to be the basis for an LCA, any flow rate would be reasonable.

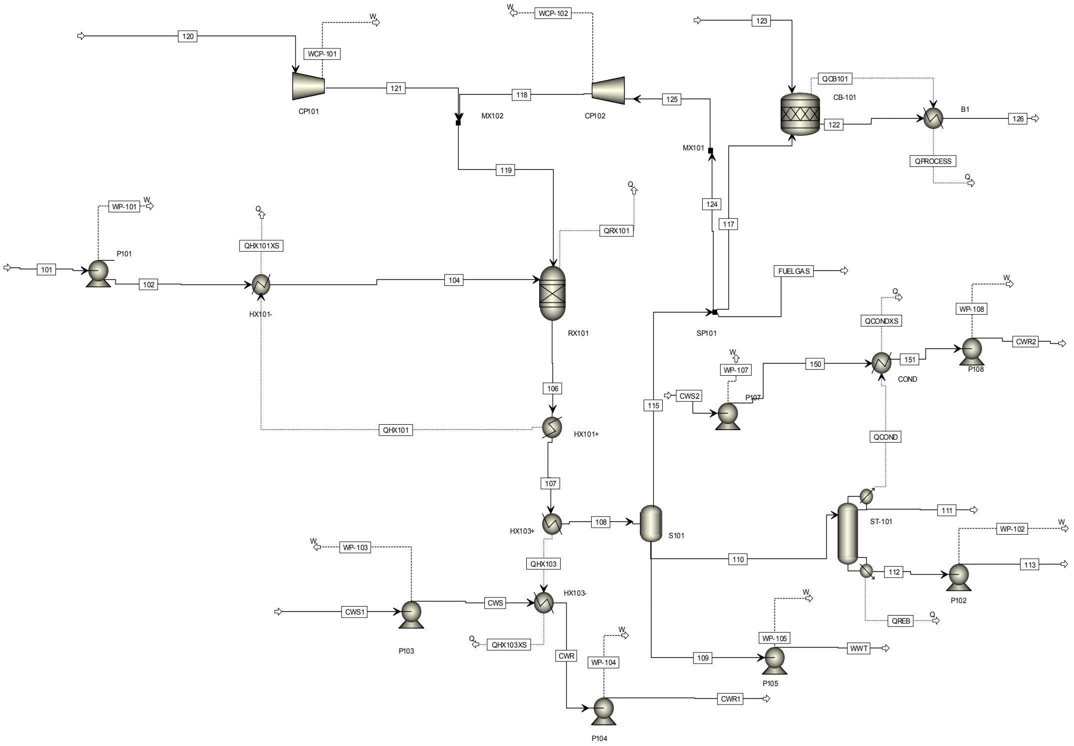

Figure A1-2 ASPEN Simulation Process Flowcharts for Renewable Diesel I (SuperCetane)

Hydrogenation

As shown in Figure A1-2, the soybean oil feed (Stream 101) is pumped to 500 psia (P-101) and then mixed with recycle oil (Stream 110C) from the splitter, SP-101, following the sour water separator (S101). This stream is then heated to 290°F by exchange with hydrogenator effluent (Stream 106) in HX101+ and HX101−. The next stage of the process is the hydrogenator, where the oil stream is combined with the inlet hydrogen (Stream 120) and recycle fuel gas (Stream 118) and reacted.

The hydrogenator (RX101) is modeled as an RYIELD reactor. All of the incoming oil is converted to gas (e.g., CO_2, H_2, propane), water, green diesel (GDSL), waxes, and a small amount of naphtha. As noted in the design basis, the yield of green diesel is estimated at 64.5% of the total inlet feed streams on a mass basis. The hydrogenation reactions are exothermic, and there is excess heat (QRX101) after the reactor is brought to reaction temperature (325°C).

After the oil feed is preheated, the hydrogenator effluent (Stream 107) is cooled with cooling water (Stream CWS1) to 100°F in HX103. The cooled reactor products are then sent to the sour water separation, S101.

Sour Water Separation

In sour water separation, the gases (Stream 115) are flashed off and sent to a splitter (SP101) for recycle, combustion, and product recovery. The aqueous stream is decanted and sent to wastewater treatment (Stream 109). After the separator, the organic stream (110) is sent to a distillation column (ST-101) for product recovery.

Product Recovery

The product recovery area consists of a distillation column where the SuperCetane (Stream 111) with a small amount of naphtha is separated from the heavies (Stream 112). The distillation column is modeled as a RADFRAC column with eight stages with both a condenser and a reboiler. The system is operated at 100 psi (stage 1). The feed is introduced on stage 5, while SuperCetane is recovered on stage 1, and the heavies are taken off on stage 8.

Gas Recycle

As noted earlier, the off-gas from the water separator, S101, is sent to a splitter where it is separated for gas recycle (124), combustion (117), and product (FUELGAS). The amount of product is controlled by overall process yields, while the amount sent to combustion is specified so that the system's energy demand is satisfied.

Heat Generation

The last major section of the flowsheet is steam generation. Here, some of the fuel gas is combusted (CB-101), which is operated at 1700°F. Heat is recovered from the off-gases in a HEATER block, B1. The amount of heat recovery is compared to the process heat demands [e.g., the reboiler (QREB)] to ensure that enough heat is available. A more rigorous model could be developed that would generate steam and meet the specific heat demands of each unit operation. For this analysis, this gross heat balance was deemed sufficient.

A1-4 Results and Discussion

This effort was aimed at confirming the material and energy balances summarized for the NRCan process. As shown in the table below, the ASPEN Plus® model shows good agreement with the published literature. All of the yields and utility requirements are similar between the model and the literature. Table A1-3 compares the results of this modeling effort and the values from the $(S\&T)^2$ Consultants (2004).

Table A1-3 Comparison of Overall Mass and Energy Balances

Feedstock	NRCan Yield per 100 lb oil	Current Analysis per 100 lb Oil
Oil	100	100
H_2	1.98	1.98
Air		63.47
Products		
Fuel Gas	16.74	16.74
HDRD	66.21	66.2
Naphtha	0.36	
Heavies (113)	11.60	11.6
Waste water		4.39
Flue Gas (lb/h)		66.52
Flue Gas (126) (scf)		24.2
Utilities		
Electricity (kWh)	2.50	2.61
Cooling water (lb/h)		4307

Besides SuperCetane, this process generates three other products: fuel gas, naphtha, and heavies. The amount of naphtha is very small and is included in the SuperCetane product. Table A1-4 summarizes the calculated compositions of the other products.

Table A1-4 Product Compositions

Product	Composition
Fuel gas	
Propane	25.45
Carbon dioxide	27.96
Water	2.33
Hydrogen	43.68
Naphtha	0.58
LHV (Btu/lb)	27,999
Heavies	
Wax	80
Naphtha	20
LHV (Btu/lb)	20,617

In addition to the material and energy balance, the analysis projected the air emissions from the process. As noted earlier, it is assumed that a portion of the fuel gas, which is primarily propane, is combusted to make steam to meet the energy demand of the process. Air emissions of criteria pollutants were estimated on the basis of the U.S. Environmental Protection Agency's AP-42 emission factors. The fuel gas is a mix of several gases, but for this analysis, the emissions were assumed to be equivalent to natural gas combustion. Table A1-5 summarizes the emission factors and the emission rate of each pollutant.

Table A1-5 Air Emission Factors

Pollutant	Emission Factors (lb/MM scf fuel)	Emissions (lb/100 lb product)
CO	84	3.07E-03
NO_x	32	1.17E-03
PM	7.6	2.78E-04
VOCs	5.5	2.01E-04

The NRCan process uses hydrogenation to convert bio-oils like soybean oil into a diesel substitute. Several companies are looking into this process. This analysis developed an ASPEN Plus® model of the process and compared its results with published results by $(S\&T)^2$ Consultants (2004). Good agreement was obtained between the two studies. These results will be used to develop an LCA for this process.

A1-5 References

Sheehan, J., V. Camobreco, J. Duffield, M. Graboski, H. Shapouri. 1998, *An Overview of Biodiesel and Petroleum Diesel Life Cycles*, joint study sponsored by U.S. Department of Agriculture and U.S. Department of Energy, NREL/TP-580-24772.

(S&T)^2 Consultants Inc., 2004. *The Addition of NRCan's SuperCetane and ROBYS ^{TM} Processes to GHGenius*, prepared for Natural Resources Canada, March 30.

A1-6 ASPEN Plus® Input File: Super_Cetane2.inp

```
;
;Input Summary created by Aspen Plus Rel. 20.0 at 16:58:40 Sun Oct 21, 2007
;Directory E:\HDRD  Filename E:\HDRD\super_cetane2.inp
;



TITLE ‘Super Cetane’

IN-UNITS ENG DENSITY=‘lb/gal’ POWER=kW VOLUME=gal  &
    MOLE-DENSITY=‘lbmol/gal’ MASS-DENSITY=‘lb/gal’

DEF-STREAMS CONVEN ALL

DATABANKS PURE13  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
    NOASPENPCD

PROP-SOURCES PURE13  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
  H2 H2 /
  LINOL3 C18H30O2 /
  PALM C16H32O2 /
  STEARIC C18H36O2 /
  OLEIC C18H34O2 /
  LINOL2 C18H32O2 /
  ARACHID C20H40O2 /
  GDSL C18H38 /
```

```
   H2O H2O /
   H2S H2S /
   NH3 H3N /
   PROPANE C3H8 /
   NAPTHA /
   CO2 CO2 /
   WAX C26H54 /
   O2 O2 /
   N2 N2

PC-USER
   IN-UNITS ENG
   PC-DEF ASPEN GDSL GRAV=0.749 MW=254.
   PC-DEF ASPEN NAPTHA GRAV=0.7 MW=72.

ADA-SETUP
   ADA-SETUP PROCEDURE=REL9

HENRY-COMPS HC-1 CO2

FLOWSHEET
   BLOCK RX101 IN=119 104 OUT=106 QRX101
   BLOCK S101 IN=108 OUT=115 110 109
   BLOCK P101 IN=101 OUT=102 WP-101
   BLOCK P102 IN=112 OUT=113 WP-102
   BLOCK CP102 IN=125 OUT=118 WCP-102
   BLOCK CP101 IN=120 OUT=121 WCP-101
   BLOCK HX101+ IN=106 OUT=107 QHX101
   BLOCK HX101- IN=102 QHX101 OUT=104 QHX101XS
   BLOCK MX102 IN=118 121 OUT=119
   BLOCK ST-101 IN=110 OUT=111 112 QCOND QREB
   BLOCK HX103+ IN=107 OUT=108 QHX103
   BLOCK HX103- IN=CWS QHX103 OUT=CWR QHX103XS
   BLOCK P105 IN=109 OUT=WWT WP-105
   BLOCK P103 IN=CWS1 OUT=CWS WP-103
   BLOCK P104 IN=CWR OUT=CWR1 WP-104
   BLOCK SP101 IN=115 OUT=117 FUELGAS 124
   BLOCK CB-101 IN=117 123 OUT=122 QCB101
   BLOCK MX101 IN=124 OUT=125
   BLOCK COND IN=150 QCOND OUT=151 QCONDXS
```

```
    BLOCK P107 IN=CWS2 OUT=150 WP-107
    BLOCK P108 IN=151 OUT=CWR2 WP-108
    BLOCK B1 IN=122 QCB101 OUT=126 QPROCESS

PROPERTIES POLYUF HENRY-COMPS=HC-1
    PROPERTIES POLYNRTL

PROP-DATA HENRY-1
    IN-UNITS ENG
    PROP-LIST HENRY
    BPVAL CO2 H2O 175.2762325 -15734.78987 -21.66900000  &
        6.12550005E-4 31.73000375 175.7300026 0.0

STREAM 101
    IN-UNITS ENG
    SUBSTREAM MIXED TEMP=68. PRES=14.7 MASS-FLOW=100.
    MASS-FRAC LINOL3 0.075 / PALM 0.11 / STEARIC 0.041 /  &
        OLEIC 0.22 / LINOL2 0.54 / ARACHID 0.014

STREAM 117
    IN-UNITS ENG
    SUBSTREAM MIXED TEMP=68. PRES=14.7 MASS-FLOW=1.
    MASS-FRAC H2 1.

STREAM 120
    IN-UNITS ENG
    SUBSTREAM MIXED TEMP=68. PRES=14.7 MASS-FLOW=100.
    MASS-FRAC H2 1.

STREAM 123
    SUBSTREAM MIXED TEMP=68. PRES=14.7 MASS-FLOW=67.
    MOLE-FRAC O2 0.21 / N2 0.79

STREAM 125
    SUBSTREAM MIXED TEMP=68. PRES=14.7 MASS-FLOW=10.
    MASS-FRAC H2 1.

STREAM CWS
    IN-UNITS ENG
    SUBSTREAM MIXED TEMP=35. <C> PRES=500. MASS-FLOW=100.
```

```
    MASS-FRAC H2O 1.

STREAM CWS1
    IN-UNITS ENG
    SUBSTREAM MIXED TEMP=35. <C> PRES=14.7 MASS-FLOW=100.
    MASS-FRAC H2O 1.

STREAM CWS2
    SUBSTREAM MIXED TEMP=35. <C> PRES=14.7 MASS-FLOW=100.
    MASS-FRAC H2O 1.

DEF-STREAMS HEAT QCB101

DEF-STREAMS HEAT QCOND

DEF-STREAMS HEAT QCONDXS

DEF-STREAMS HEAT QHX101

DEF-STREAMS HEAT QHX101XS

DEF-STREAMS HEAT QHX103

DEF-STREAMS HEAT QHX103XS

DEF-STREAMS HEAT QPROCESS

DEF-STREAMS HEAT QREB

DEF-STREAMS HEAT QRX101

DEF-STREAMS WORK WCP-101

DEF-STREAMS WORK WCP-102

DEF-STREAMS WORK WP-101

DEF-STREAMS WORK WP-102

DEF-STREAMS WORK WP-103
```

```
DEF-STREAMS WORK WP-104

DEF-STREAMS WORK WP-105

DEF-STREAMS WORK WP-107

DEF-STREAMS WORK WP-108

BLOCK MX101 MIXER

BLOCK MX102 MIXER
   IN-UNITS ENG

BLOCK SP101 FSPLIT
   FRAC FUELGAS 0.5
   MASS-FLOW 124 10.

BLOCK B1 HEATER
   PARAM TEMP=100. PRES=14.7

BLOCK COND HEATER
   PARAM PRES=14.7 DELT=15.

BLOCK HX101+ HEATER
   IN-UNITS ENG
   PARAM TEMP=110. PRES=500.

BLOCK HX101- HEATER
   IN-UNITS ENG
   PARAM TEMP=567. PRES=500.

BLOCK HX103+ HEATER
   IN-UNITS ENG
   PARAM TEMP=100. PRES=500.

BLOCK HX103- HEATER
   IN-UNITS ENG
   PARAM PRES=500. DELT=15.
```

```
BLOCK S101 FLASH2
   IN-UNITS ENG
   PARAM TEMP=100. PRES=175.
   BLOCK-OPTION FREE-WATER=YES

BLOCK ST-101 RADFRAC
   IN-UNITS ENG
   PARAM NSTAGE=8
   COL-CONFIG CONDENSER=TOTAL REBOILER=KETTLE
   FEEDS 110 5
   PRODUCTS 111 1 L / 112 8 L
   PRODUCTS QREB 8 / QCOND 1
   P-SPEC 1 100.
   COL-SPECS DP-STAGE=1. MASS-D=66.2 MOLE-RR=0.1

BLOCK CB-101 RSTOIC
   PARAM TEMP=1700. PRES=0. COMBUSTION=YES PROD-NOX=NO2
   STOIC 1 MIXED H2 -1. / O2 -0.5 / H2O 1.
   STOIC 2 MIXED PROPANE -1. / O2 -5. / CO2 3. / H2O 4.
   STOIC 3 MIXED NAPTHA -1. / O2 -8. / CO2 5. / H2O 6.
   CONV 1 MIXED H2 1.
   CONV 2 MIXED PROPANE 1.
   CONV 3 MIXED NAPTHA 1.

BLOCK RX101 RYIELD
   IN-UNITS ENG
   PARAM TEMP=325. <C> PRES=500.
   MASS-YIELD MIXED GDSL 0.8415 / H2O 0.02125 / CO2  &
      0.10625 / PROPANE 0.029 / H2 0.001 / NAPTHA 0.01 /  &
      WAX 0.104

BLOCK P101 PUMP
   IN-UNITS ENG
   PARAM PRES=500.

BLOCK P102 PUMP
   IN-UNITS ENG
   PARAM DELP=10.
```

```
BLOCK P103 PUMP
   IN-UNITS ENG
   PARAM PRES=500. PUMP-TYPE=TURBINE

BLOCK P104 PUMP
   IN-UNITS ENG
   PARAM DELP=10.

BLOCK P105 PUMP
   IN-UNITS ENG
   PARAM DELP=10.

BLOCK P107 PUMP
   PARAM DELP=10.

BLOCK P108 PUMP
   PARAM DELP=10.

BLOCK CP101 COMPR
   IN-UNITS ENG
   PARAM TYPE=ISENTROPIC PRES=500. MODEL-TYPE=TURBINE

BLOCK CP102 COMPR
   IN-UNITS ENG
   PARAM TYPE=ISENTROPIC PRES=500. MODEL-TYPE=TURBINE

DESIGN-SPEC COMBAIR
   DEFINE O2OUT MASS-FLOW STREAM=122 SUBSTREAM=MIXED  &
      COMPONENT=O2
   DEFINE O2IN MASS-FLOW STREAM=123 SUBSTREAM=MIXED  &
      COMPONENT=O2
   SPEC “O2IN” TO “11*O2OUT”
   TOL-SPEC “1”
   VARY STREAM-VAR STREAM=123 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   LIMITS “50” “150”

DESIGN-SPEC DS-FGAS
   DEFINE SPLT BLOCK-VAR BLOCK=SP101 SENTENCE=FRAC  &
      VARIABLE=FRAC ID1=FUELGAS
```

```
   DEFINE FGAS STREAM-VAR STREAM=FUELGAS SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   SPEC “FGAS” TO “16.74”
   TOL-SPEC “0.05”
   VARY BLOCK-VAR BLOCK=SP101 SENTENCE=FRAC VARIABLE=FRAC  &
      ID1=FUELGAS
   LIMITS “0.05” “0.95”

DESIGN-SPEC DS-HX101
   IN-UNITS ENG
   DEFINE QXS INFO-VAR INFO=HEAT VARIABLE=DUTY  &
      STREAM=QHX101XS
   SPEC “QXS” TO “0.0”
   TOL-SPEC “0.1”
   VARY BLOCK-VAR BLOCK=HX101+ VARIABLE=TEMP SENTENCE=PARAM
   LIMITS “100” “617”

DESIGN-SPEC DS-HX103
   IN-UNITS ENG
   DEFINE CWIN STREAM-VAR STREAM=CWS1 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE QXS INFO-VAR INFO=HEAT VARIABLE=DUTY  &
      STREAM=QHX103XS
   SPEC “QXS” TO “0”
   TOL-SPEC “0.1”
   VARY STREAM-VAR STREAM=CWS1 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   LIMITS “100” “10000”

DESIGN-SPEC DS-QCOND
   DEFINE QXS INFO-VAR INFO=HEAT VARIABLE=DUTY STREAM=QCONDXS
   DEFINE CWIN STREAM-VAR STREAM=CWS2 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   SPEC “QXS” TO “0”
   TOL-SPEC “0.1”
   VARY STREAM-VAR STREAM=CWS2 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   LIMITS “5” “5000”

EO-CONV-OPTI
```

```
CALCULATOR H2IN
   IN-UNITS ENG
   DEFINE H2IN STREAM-VAR STREAM=120 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE OILIN STREAM-VAR STREAM=101 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
F       H2IN = 0.0198*OILIN
   READ-VARS OILIN

CALCULATOR HYDCRK
   IN-UNITS ENG
   DEFINE FEED STREAM-VAR STREAM=101 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE GDYLD BLOCK-VAR BLOCK=RX101 VARIABLE=YIELD  &
      SENTENCE=MASS-YIELD ID1=MIXED ID2=GDSL
   DEFINE PROYLD BLOCK-VAR BLOCK=RX101 VARIABLE=YIELD  &
      SENTENCE=MASS-YIELD ID1=MIXED ID2=PROPANE
   DEFINE CO2YLD BLOCK-VAR BLOCK=RX101 VARIABLE=YIELD  &
      SENTENCE=MASS-YIELD ID1=MIXED ID2=CO2
   DEFINE H2OYLD BLOCK-VAR BLOCK=RX101 VARIABLE=YIELD  &
      SENTENCE=MASS-YIELD ID1=MIXED ID2=H2O
   DEFINE FD105 STREAM-VAR STREAM=104 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE FD119 STREAM-VAR STREAM=119 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE H2IN STREAM-VAR STREAM=120 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE H2YLD BLOCK-VAR BLOCK=RX101 VARIABLE=YIELD  &
      SENTENCE=MASS-YIELD ID1=MIXED ID2=H2
   DEFINE NPYLD BLOCK-VAR BLOCK=RX101 VARIABLE=YIELD  &
      SENTENCE=MASS-YIELD ID1=MIXED ID2=NAPTHA
   DEFINE FGAS STREAM-VAR STREAM=FUELGAS SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE WXYLD BLOCK-VAR BLOCK=RX101 VARIABLE=YIELD  &
      SENTENCE=MASS-YIELD ID1=MIXED ID2=WAX
F      TTLFD = FD105+FD119
F      GDYLD = 0.649*(FEED+H2IN)/TTLFD
F      PROYLD = 0.082*(FEED+H2IN)/TTLFD
F      CO2YLD = 0.082*(FEED+H2IN)/TTLFD
F      H2OYLD = 0.050*(FEED+H2IN)/TTLFD
```

```
F      NPYLD = 0.0035*(FEED+H2IN)/TTLFD
F      WXYLD = 0.104*(FEED+H2IN)/TTLFD
F      SUM = GDYLD+PROYLD+CO2YLD+H2OYLD+NPYLD+WXYLD
F      DIFF = TTLFD - (SUM*TTLFD)
F       H2YLD = DIFF/TTLFD
F      WRITE(NHSTRY,*)SUM,DIFF,H2YLD
    READ-VARS FEED FD105 FD119 H2IN FGAS
    WRITE-VARS GDYLD PROYLD CO2YLD H2OYLD H2YLD NPYLD WXYLD
    BLOCK-OPTION SIM-LEVEL=4

STREAM-REPOR NOMOLEFLOW MASSFLOW

PROPERTY-REP NOPARAM-PLUS
;
```

Appendix 2: ASPEN Simulation Process of Renewable Diesel II (Hydrogenation-Derived Renewable Diesel)

Victoria Putsche
Center for Transportation Technologies and Systems
National Renewable Energy Laboratory[2]

A2-1 Introduction

A preliminary analysis was conducted for a hydrogenation-derived renewable diesel (HDRD) facility on the basis of the UOP process (UOP 2006). Material and energy balances were developed by using ASPEN Plus® 12.1 (uop_hdrd.inp). The overall goal of the study was to confirm the preliminary overall material and energy balances provided by UOP (UOP 2006; Markel 2006) and to provide input for a life-cycle analysis (LCA). The following report summarizes the basis for the analysis and its results.

A2-2 Design Basis and Process Description

HDRD is made from reacting hydrogen with oil or grease in a refinery-hydrotreating process. Two primary reactions occur in the conversion: hydrodeoxygenation and decarboxylation (UOP 2006)

Hydrodeoxygenation:

C_nCOOH (bio-oil) + $3\ H_2 \rightarrow C_{n+1}$ (HDRD) + $2\ H_2O$

Decarboxylation:

C_nCOOH (bio-oil) $\rightarrow C_n$ (HDRD) + CO_2

The selectivity of the reactions depends on the processing conditions.

For this analysis, the production of HDRD is based on the UOP process, which is composed of hydrogen production, hydrogenation, separation, distillation, and pressure swing adsorption (PSA). All of the unit operations were modeled except hydrogen production. It is assumed that

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hydrogen is supplied by a hydrogen plant. Figure A2-1 is a block flow diagram of the HDRD process.

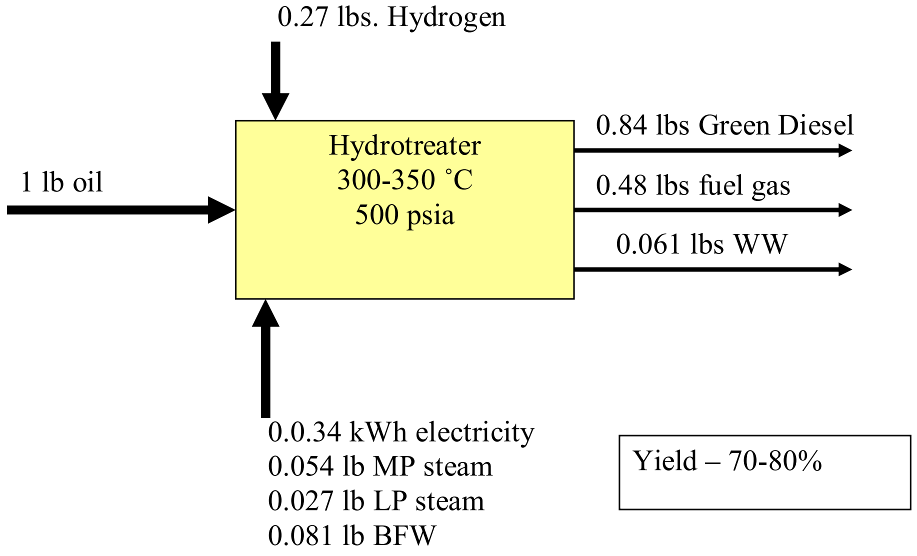

Figure A2-1 HDRD Block Flow Diagram

One of the important characteristics of the process is that energy demands are met off site. That is, the fuel gas product is not combusted on site to generate steam for the process; it is assumed that steam is sent to the process from an off-site source. Similarly, the process also generates a fuel gas, which is also sent off site and used for fuel. For this process configuration, the LCA will determine the emissions from the fuel gas combustion as well as the steam and electricity generation and will apportion it appropriately to the main process.

The renewable diesel process was modeled by using numerous assumptions and data sources. Table A2-1 summarizes the key design parameters and their sources.

Several of these assumptions, particularly the feedstock choice and facility size, require further explanation. The feedstock selected was soybean oil, even though many of the feedstocks in the literature were rapeseed oil or other oils, because it is the most prevalent oil in fuels production (i.e., biodiesel) and because one of the purposes of the study was to compare the environmental impacts of HDRD to biodiesel, and the most thorough LCA of biodiesel (Sheehan et al. 1998) was based on soybean oil. The facility size of 100 lb/h was selected as an easy, round number for the LCA. The results of most LCAs are shown on a pound of feed or product basis, since the impacts are directly scalable to throughput. Therefore, this simple number was selected, even though this would not be a typical facility size.

Table A2-1 Design Basis

Parameter	Value	Source
Feedstock		
Type	Soybean oil	Most common oil in US for biodiesel
Throughput	100 lb/h	For LCA analysis
Feedstock fatty acid composition (wt fraction)		
Linolenic acid		
Palmitic acid	0.075	
Stearic acid	0.11	
Oleic acid	0.041	
Linoleic acid	0.22	
Arachidic acid	0.54	
	0.014	
Hydrogenation design		
Temperature	325°C	UOP 2006
Pressure	500 psia	UOP 2006
Yields (per pound inlet feed)		
HDRD		UOP 2006
Water	84.15%	
CO_2	2.125%	
Propane	10.625%	
Hydrogen	2.9%	
	0.1%	

A2-3 Model Description

An ASPEN Plus® model (uop_hdrd) was developed for the pyrolysis process, largely on the basis of the UOP report (UOP 2006). ASPEN Plus® is a steady-state process simulator. Appendix A2-6 contains the input file for the model.

The ASPEN Plus® HDRD model has one flowsheet to model the four major process areas: hydrogenation, sour water separation, stripping, and pressure swing adsorption (PSA)/gas recycle. Each of these areas is briefly discussed, and the flow diagram from ASPEN Plus® is presented. The flow diagram shows only those unit operations modeled in ASPEN Plus®. Equipment used for operations such as conveyance, size reduction, and storage us generally not included in the model. The power requirements of this equipment, however, are included and are modeled as work streams.

ASPEN Plus® is composed of physical property and unit operation models that are combined into a process model. The simulation can be broken into three major sections: components (i.e., chemical species), physical property option sets (e.g., what set of physical property models to use), and the flowsheet (i.e., the series of unit operations). Each of these sections is described in more detail below.

Components

Fourteen components were modeled in the simulation; all were modeled as conventional (e.g., water) components in the mixed substream. The following is a list of the components in the simulation:

- Hydrogen – H_2
- Linolenic acid – $C_{18}H_{30}O_2$
- Palmitic acid – $C_{16}H_{32}O_2$
- Stearic acid – $C_{18}H_{36}O_2$
- Linoleic acid – $C_{18}H_{32}O_2$
- Arachidic acid – $C_{20}H_{40}O_2$
- Oleic acid – $C_{18}H_{34}O_2$
- Green Diesel – $C_{18}H_{38}$
- Water – H_2O
- Hydrogen Sulfide – H_2S
- Ammonia – NH_3
- Propane – C_3H_8
- Naptha
- Carbon dioxide – CO_2

Green diesel is not a specific compound but is a complex mixture of hydrocarbons; however, for simplicity, it was modeled as a single component, $C_{18}H_{38}$, which is within the range of diesel hydrocarbons. Green diesel was specified with a specific gravity of 0.78 (Marker, T. 2007) and a MW of 254. Naphtha was specified with a specific gravity of 0.7 and a MW of 100.

As noted earlier, the vegetable oil feed was modeled as a mixture of six fatty acids: linolenic acid, palmitic acid, stearic acid, linoleic acid, arachidic acid, and oleic acid. All of these components are available in the ASPEN Plus® databanks. Table A2-2 shows the molecular formula, the component name in the model, and the weight fraction in the feed of each fatty acid.

One Henry component, CO_2, was specified. The Henry's constants were obtained from ASPEN Plus®.

Table A2-2 Organic Acid Composition of Bio-Oil

Organic Fatty Acid	Composition	Component Name	Weight Fraction
Linolenic	$C_{18}H_{30}O_2$	LINOL3	0.075
Palmitic	$C_{16}H_{32}O_2$	PALM	0.11
Stearic	$C_{18}H_{36}O_2$	STEARIC	0.041
Oleic	$C_{18}H_{34}O_2$	OLEIC	0.22
Linoleic	$C_{18}H_{32}O_2$	LINOL2	0.54
Arachidic	$C_{20}H_{40}O_2$	ARACHID	0.014

Physical Property Option Sets

The physical property set selected was POLYUF with properties estimated by using the POLYNRTL method. Physical property databanks used in the simulation were PURE13, AQUEOUS, SOLIDS AND INORGANIC.

Flowsheet

One flowsheet was developed for the process: (A1000). The flowsheet is briefly discussed, and flow diagrams from ASPEN Plus® are presented. The flow diagrams (Figure A2-2) show only those unit operations modeled in ASPEN Plus®. Equipment used for operations such as conveyance and storage are generally not included in the model and are thus not shown. Similarly, certain complex unit operations (e.g., gas turbine) require several ASPEN Plus® models (e.g., compressors, reactors, heat exchangers).

Bio-oil is introduced into the process in stream 101. It is assumed to be at ambient conditions (i.e., 68°F and 14.7 psia) with a flow rate of a nominal 100 lb/h. The 100-lb/h value was selected as it would be easily scaled to any other value; since the model was developed to be the basis for an LCA, any flow rate would be reasonable.

Hydrogenation

As shown in Figure A2-2, the soybean oil feed (Stream 101) is pumped to 500 psia (P-101) and then mixed with recycle oil (Stream 110C) from the splitter, SP-101, following the sour water separator (S101). This stream is then heated to 290°F by exchange with hydrogenator effluent (Stream 106) in HX101+ and HX101−. It is then further heated to 370°F with medium-pressure steam, MPSS (150 psig). The next stage of the process is the hydrogenator, where the oil stream is combined with the inlet hydrogen (Stream 119) and reacted.

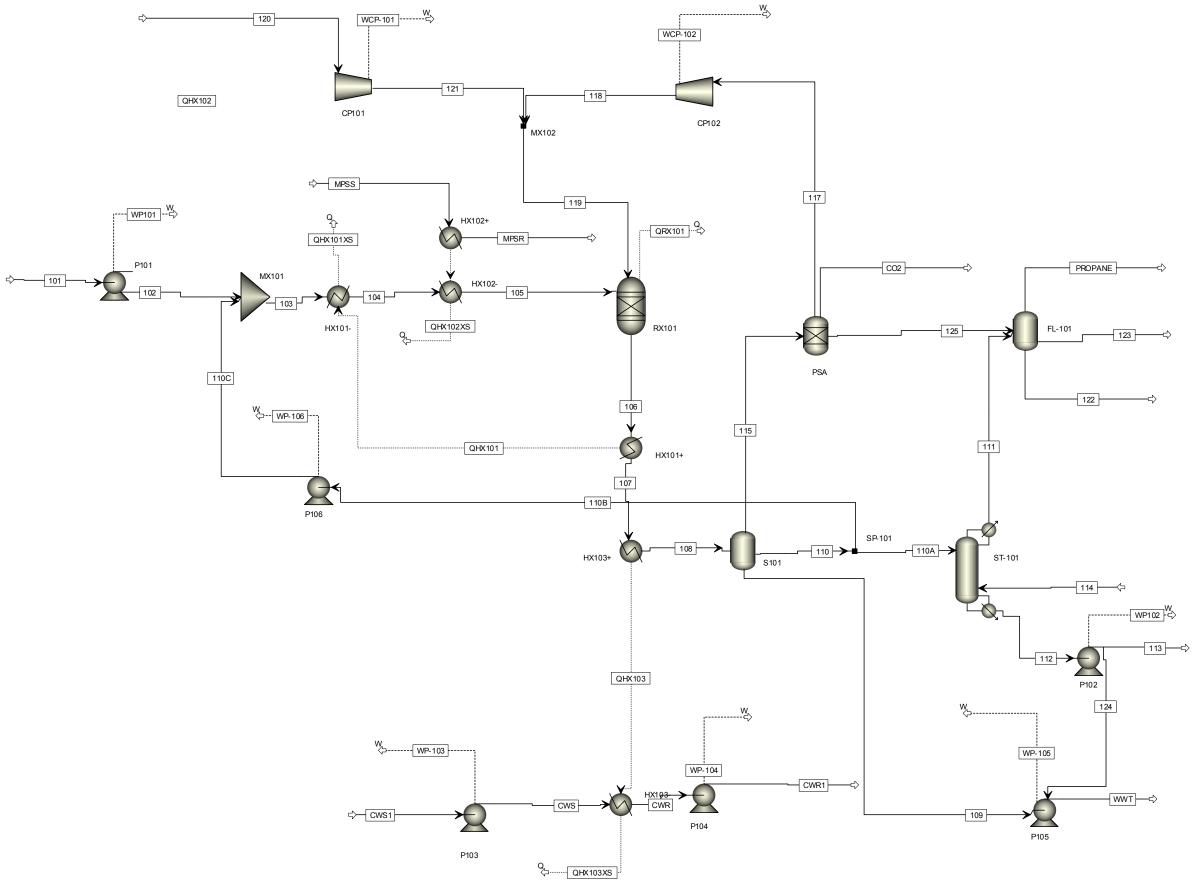

Figure A2-2 ASPEN Simulation Process Flowcharts FOR Renewable Diesel II

The hydrogenator (RX101) is modeled as an RYIELD reactor. All of the incoming oil is converted to gas (e.g., CO2, H2, propane), water, and green diesel (GDSL). As noted in the design basis, the yield of green diesel is estimated at 84.15% of the inlet feed streams on a mass basis. The hydrogenation reactions are exothermic, and there is excess heat (QRX101) after the reactor is brought to reaction temperature (325°C).

After the oil feed is preheated the hydrogenator effluent (Stream 107) is cooled with cooling water (Stream CWS1) to 100°F in HX103. The cooled reactor products are then sent to the sour water separation, S101.

Sour Water Separation

In sour water separation, the gases (Stream 115) are flashed off and sent to the PSA for recovery, and the aqueous stream is decanted and sent to wastewater treatment (Stream 109). After the separator, a portion of the organic stream (110B) is recycled to the hydrogenator inlet. The remainder (Stream 110A) is sent to a stripping column (ST-101) for product recovery.

Product Recovery

The product recovery area consists of a stripping column where LP (50 psig) steam (Stream 114) is used to remove the light ends from the green diesel product (112). The stripping column is modeled as a RADFRAC column with eight stages without a condenser or reboiler under atmospheric pressure.

The overheads are sent to the flash unit of the PSA system, FL-101. The product stream is taken from the bottom of the column (Stream 112).

Pressure Swing Adsorption (PSA)

The PSA system is a complex batch unit operation that was treated basically as a black box for this simulation. It is modeled as two unit operations in series, a separator block (PSA) followed by a flash block (FL-101). The separator block is assumed to remove all of the hydrogen in the overhead stream (111). The recovered hydrogen is then compressed (CP102) to 500 psia before introduction into the hydrogenator.

In addition to hydrogen, the PSA unit operation has two other outlet streams: CO_2 and Stream 125. The CO_2 stream contains all of the carbon dioxide from the operation and is released to the atmosphere. Stream 125 contains a mixture of water, propane, and other organics. These are separated in FL-101 modeled as a FLASH2. As shown in the diagram, FL-101 has two inlets (Streams 111 and 125) and three outlets: PROPANE and Streams 122 and 123. Stream 111 is the overheads from the stripping column, ST-101. PROPANE is a fuel gas, composed primarily of propane (93%) with small amounts of green diesel and CO_2.

A2-4 Results and Discussion

This effort was aimed at confirming the material and energy balances summarized for the UOP HDRD process as found in UOP (2006) and Markel (2006). As shown in Table A2-3, the ASPEN Plus® model shows good agreement with the published literature. All of the yields and utility requirements are similar between the model and the literature except cooling water. The uop_hdrd.bkp model predicts a much higher cooling water load than projected by UOP. This discrepancy can be due to many factors, including improved equipment design and heat integration in the UOP process and differing cooling water specifications (e.g., allowable temperature rise). The discrepancy was not explored further since cooling water is a very small

Table A2-3 Comparison of Overall Mass and Energy Balances

Feedstock	UOP Yield per 100 lb of feed	Current Analysis Yield per 100 lb of feed
Oil	100.00	100.00
H_2	2.72	2.72
LP steam	2.72	2.80
Products		
Propane mix gas	4.75	5.02
HDRD	84.19	85.23
CO_2		7.01
Waste water	6.11	8.27
Utilities		
Electricity (kWh)	3.39	2.34
LP Steam (into process)	2.72	2.80
MP steam	5.43	5.37
Cooling water	1,356	2,310
Boiler feed water	8.15	8.17
Total steam (Btu)		7,161

contributor to the impacts in an LCA. Table 3 compares the results of this modeling effort and the values from the UOP report (2006). Carbon dioxide was not reported in the UOP study.

The propane mix gas is composed of 93.3% propane, 5.7% CO_2, and 1% water. The lower heating value (LHV) of the mix is estimated at 18,568 Btu/lb. The entire mass balance for the simulation is contained in Appendix A2-6.

In addition to the material and energy balance, the analysis projected the air emissions from the process. As noted earlier, it is assumed that the fuel gas, which is primarily propane, is combusted with make-up natural gas in order to meet the energy demand of the process. Thus, it was assumed that there were minimal air emissions from the main process. The LCA analysis will provide the emissions from the combustion of the fuel gas and any other fuel needed to generate the necessary steam and electricity. This assessment is outside the process lines for this process configuration.

The UOP HDRD process uses hydrogenation to convert bio-oils like soybean oil into a diesel substitute. Several companies are looking into this process. This analysis developed an ASPEN Plus® model of the process and compared its results with published results by UOP and NREL (UOP 2006). Good agreement was obtained between the two studies. These results will be used to develop an LCA for this process.

A2-5 References

Marker, T., 2006, Email to V. Putsche with cc to C. Johnson of NREL, "Follow-up on Green Diesel and Green Gasoline LCA Requests," Aug. 15.

Sheehan, J., V. Camobreco, J. Duffield, M. Graboski, H. Shapouri, 1998, *An Overview of Biodiesel and Petroleum Diesel Life Cycles*, joint study sponsored by U.S. Department of Agriculture and U.S. Department of Energy, NREL/TP-580-24772.

UOP, 2006, *Opportunities for Biorenewables in Oil Refineries*, Final Technical Report, DOE Award Number DE-FG36-05GO15085, contributors were Terry Marker, John Petri, Tom Kalnes, Micke McCall, Dave Mackowiak, Bob Jerosky, Bill Reagan, Lazlo Nemeth, Mark Krawczyk (UOP); Stefan Czernik (NREL); Doug Elliott (PNNL); David Shonnard (Michigan Technological University).

A2-6 ASPEN Plus® Input File: UOP_HDRD.inp

```
;
;Input Summary created by Aspen Plus Rel. 13.1 at 18:15:55 Fri Sep 22, 2006
;Directory C:\AspenTech\Aspen Plus 2004  Filename C:\AspenTech\Aspen Plus 2004\uop_hdrd.inp
;



TITLE 'HDRD - UOP'

IN-UNITS ENG DENSITY='lb/gal' POWER=kW VOLUME=gal  &
     MOLE-DENSITY='lbmol/gal' MASS-DENSITY='lb/gal'

DEF-STREAMS CONVEN ALL

DATABANKS PURE13  / AQUEOUS  / SOLIDS  / INORGANIC  /  &
     NOASPENPCD

PROP-SOURCES PURE13  / AQUEOUS  / SOLIDS  / INORGANIC

COMPONENTS
  H2 H2 /
  LINOL3 C18H30O2 /
```

```
    PALM C16H32O2 /
    STEARIC C18H36O2 /
    OLEIC C18H34O2 /
    LINOL2 C18H32O2 /
    ARACHID C20H40O2 /
    GDSL C18H38 /
    H2O H2O /
    H2S H2S /
    NH3 H3N /
    PROPANE C3H8 /
    NAPTHA /
    CO2 CO2

PC-USER
    IN-UNITS ENG
    PC-DEF ASPEN GDSL GRAV=0.78 MW=254.
    PC-DEF ASPEN NAPTHA GRAV=0.7 MW=100.

ADA-SETUP
    ADA-SETUP PROCEDURE=REL9

HENRY-COMPS HC-1 CO2

FLOWSHEET
    BLOCK RX101 IN=105 119 OUT=106 QRX101
    BLOCK S101 IN=108 OUT=115 110 109
    BLOCK P101 IN=101 OUT=102 WP101
    BLOCK P102 IN=112 OUT=113 19 WP102
    BLOCK CP102 IN=117 OUT=118 WCP-102
    BLOCK CP101 IN=120 OUT=121 WCP-101
    BLOCK HX101+ IN=106 20 OUT=107 QHX101
    BLOCK HX101- IN=103 QHX101 OUT=104 QHX101XS
    BLOCK HX102- IN=104 QHX102 OUT=105 QHX102XS
    BLOCK MX101 IN=102 OUT=103
    BLOCK MX102 IN=118 121 OUT=119
    BLOCK PSA IN=115 OUT=117 CO2 125
    BLOCK ST-101 IN=114 110A OUT=111 112
    BLOCK HX103+ IN=107 OUT=108 QHX103
    BLOCK HX103- IN=CWS QHX103 OUT=CWR QHX103XS
    BLOCK HX102+ IN=MPSS OUT=MPSR QHX102
```

```
    BLOCK SP-101 IN=110 OUT=110A 110B
    BLOCK P105 IN=109 18 OUT=WWT WP-105
    BLOCK P106 IN=110B OUT=110C WP-106
    BLOCK P103 IN=CWS1 OUT=CWS WP-103
    BLOCK P104 IN=CWR OUT=CWR1 WP-104
    BLOCK FL-101 IN=125 111 OUT=PROPANE 17 16
    BLOCK B8 IN=19 OUT=18
    BLOCK B9 IN=QRX101 OUT=20 21

PROPERTIES POLYUF HENRY-COMPS=HC-1
    PROPERTIES POLYNRTL

PROP-DATA HENRY-1
    IN-UNITS ENG
    PROP-LIST HENRY
    BPVAL CO2 H2O 175.2762325 -15734.78987 -21.66900000  &
        6.12550005E-4 31.73000375 175.7300026 0.0

STREAM 101
    IN-UNITS ENG
    SUBSTREAM MIXED TEMP=68. PRES=14.7 MASS-FLOW=100.
    MASS-FRAC LINOL3 0.075 / PALM 0.11 / STEARIC 0.041 /  &
        OLEIC 0.22 / LINOL2 0.54 / ARACHID 0.014

STREAM 114
    IN-UNITS ENG
    SUBSTREAM MIXED TEMP=400. PRES=50. MASS-FLOW=2.8
    MASS-FRAC H2O 1.

STREAM 117
    IN-UNITS ENG
    SUBSTREAM MIXED TEMP=68. PRES=14.7 MASS-FLOW=1.
    MASS-FRAC H2 1.

STREAM 120
    IN-UNITS ENG
    SUBSTREAM MIXED TEMP=68. PRES=14.7 MASS-FLOW=100.
    MASS-FRAC H2 1.
```

```
STREAM CWS
    IN-UNITS ENG
    SUBSTREAM MIXED TEMP=35. <C> PRES=500. MASS-FLOW=100.
    MASS-FRAC H2O 1.

STREAM CWS1
    IN-UNITS ENG
    SUBSTREAM MIXED TEMP=35. <C> PRES=14.7 MASS-FLOW=100.
    MASS-FRAC H2O 1.

STREAM MPSS
    IN-UNITS ENG
    SUBSTREAM MIXED TEMP=667. PRES=150. MASS-FLOW=100.
    MASS-FRAC H2O 1.

DEF-STREAMS HEAT 20

DEF-STREAMS HEAT 21

DEF-STREAMS HEAT QHX101

DEF-STREAMS HEAT QHX101XS

DEF-STREAMS HEAT QHX102

DEF-STREAMS HEAT QHX102XS

DEF-STREAMS HEAT QHX103

DEF-STREAMS HEAT QHX103XS

DEF-STREAMS HEAT QRX101

DEF-STREAMS WORK WCP-101

DEF-STREAMS WORK WCP-102

DEF-STREAMS WORK WP-103

DEF-STREAMS WORK WP-104
```

```
DEF-STREAMS WORK WP-105

DEF-STREAMS WORK WP-106

DEF-STREAMS WORK WP101

DEF-STREAMS WORK WP102

BLOCK B8 MIXER

BLOCK MX101 MIXER
  IN-UNITS ENG

BLOCK MX102 MIXER
  IN-UNITS ENG

BLOCK B9 FSPLIT
  FRAC 20 0.15

BLOCK SP-101 FSPLIT
  IN-UNITS ENG
  FRAC 110A 0.99

BLOCK PSA SEP
  IN-UNITS ENG
  PARAM
  FRAC STREAM=117 SUBSTREAM=MIXED COMPS=H2 H2O PROPANE CO2  &
    FRACS=1. 0. 0. 0.
  FRAC STREAM=CO2 SUBSTREAM=MIXED COMPS=PROPANE CO2 FRACS= &
    0. 1.

BLOCK HX101+ HEATER
  IN-UNITS ENG
  PARAM TEMP=100. <C> PRES=500.

BLOCK HX101- HEATER
  IN-UNITS ENG
  PARAM TEMP=290. <C> PRES=500.
```

```
BLOCK HX102+ HEATER
   IN-UNITS ENG
   PARAM PRES=500. VFRAC=0.

BLOCK HX102- HEATER
   IN-UNITS ENG
   PARAM TEMP=325. <C> PRES=500.

BLOCK HX103+ HEATER
   IN-UNITS ENG
   PARAM TEMP=100. PRES=500.

BLOCK HX103- HEATER
   IN-UNITS ENG
   PARAM PRES=500. DELT=15.

BLOCK FL-101 FLASH2
   PARAM TEMP=68. PRES=14.7
   BLOCK-OPTION FREE-WATER=YES

BLOCK S101 FLASH2
   IN-UNITS ENG
   PARAM TEMP=100. PRES=175.
   BLOCK-OPTION FREE-WATER=YES

BLOCK ST-101 RADFRAC
   IN-UNITS ENG
   PARAM NSTAGE=8
   COL-CONFIG CONDENSER=NONE REBOILER=NONE
   FEEDS 114 9 / 110A 1
   PRODUCTS 111 1 V / 112 8 L
   P-SPEC 1 14.7
   COL-SPECS DP-STAGE=1.

BLOCK RX101 RYIELD
   IN-UNITS ENG
   PARAM TEMP=325. <C> PRES=500.
   MASS-YIELD MIXED GDSL 0.8415 / H2O 0.02125 / CO2  &
      0.10625 / PROPANE 0.029 / H2 0.001
```

```
BLOCK P101 PUMP
    IN-UNITS ENG
    PARAM PRES=500.

BLOCK P102 PUMP
    IN-UNITS ENG
    PARAM DELP=10.
    BLOCK-OPTION FREE-WATER=YES

BLOCK P103 PUMP
    IN-UNITS ENG
    PARAM PRES=500. PUMP-TYPE=TURBINE

BLOCK P104 PUMP
    IN-UNITS ENG
    PARAM DELP=10.

BLOCK P105 PUMP
    IN-UNITS ENG
    PARAM DELP=10.

BLOCK P106 PUMP
    IN-UNITS ENG
    PARAM DELP=10. PUMP-TYPE=PUMP

BLOCK CP101 COMPR
    IN-UNITS ENG
    PARAM TYPE=ISENTROPIC PRES=500. MODEL-TYPE=TURBINE

BLOCK CP102 COMPR
    IN-UNITS ENG
    PARAM TYPE=ISENTROPIC PRES=500. MODEL-TYPE=TURBINE

DESIGN-SPEC DS-HX101
    IN-UNITS ENG
    DEFINE QXS INFO-VAR INFO=HEAT VARIABLE=DUTY  &
        STREAM=QHX101XS
    SPEC “QXS” TO “0.0”
    TOL-SPEC “0.1”
    VARY BLOCK-VAR BLOCK=HX101+ VARIABLE=TEMP SENTENCE=PARAM
```

```
   LIMITS “100” “617”

DESIGN-SPEC DS-HX102
   IN-UNITS ENG
   DEFINE STMIN STREAM-VAR STREAM=MPSS SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE QXS INFO-VAR INFO=HEAT VARIABLE=DUTY  &
      STREAM=QHX102XS
   SPEC “QXS” TO “0”
   TOL-SPEC “0.1”
   VARY STREAM-VAR STREAM=MPSS SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   LIMITS “0” “10000”

DESIGN-SPEC DS-HX103
   IN-UNITS ENG
   DEFINE CWIN STREAM-VAR STREAM=CWS1 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE QXS INFO-VAR INFO=HEAT VARIABLE=DUTY  &
      STREAM=QHX103XS
   SPEC “QXS” TO “0”
   TOL-SPEC “0.1”
   VARY STREAM-VAR STREAM=CWS1 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   LIMITS “100” “10000”

EO-CONV-OPTI

CALCULATOR H2IN
   IN-UNITS ENG
   DEFINE H2IN STREAM-VAR STREAM=120 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE OILIN STREAM-VAR STREAM=101 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
F       H2IN = 0.0272*OILIN
   READ-VARS OILIN

CALCULATOR HYDCRK
   IN-UNITS ENG
   DEFINE FEED STREAM-VAR STREAM=101 SUBSTREAM=MIXED  &
```

```
      VARIABLE=MASS-FLOW
   DEFINE GDYLD BLOCK-VAR BLOCK=RX101 VARIABLE=YIELD  &
      SENTENCE=MASS-YIELD ID1=MIXED ID2=GDSL
   DEFINE PROYLD BLOCK-VAR BLOCK=RX101 VARIABLE=YIELD  &
      SENTENCE=MASS-YIELD ID1=MIXED ID2=PROPANE
   DEFINE CO2YLD BLOCK-VAR BLOCK=RX101 VARIABLE=YIELD  &
      SENTENCE=MASS-YIELD ID1=MIXED ID2=CO2
   DEFINE H2OYLD BLOCK-VAR BLOCK=RX101 VARIABLE=YIELD  &
      SENTENCE=MASS-YIELD ID1=MIXED ID2=H2O
   DEFINE FD105 STREAM-VAR STREAM=105 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE FD119 STREAM-VAR STREAM=119 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE H2IN STREAM-VAR STREAM=120 SUBSTREAM=MIXED  &
      VARIABLE=MASS-FLOW
   DEFINE H2YLD BLOCK-VAR BLOCK=RX101 VARIABLE=YIELD  &
      SENTENCE=MASS-YIELD ID1=MIXED ID2=H2
F      TTLFD = FD105+FD119
F      GDYLD = 0.828*(FEED+H2IN)/TTLFD
F      PROYLD = 0.047*(FEED+H2IN)/TTLFD
F      CO2YLD = 0.075*(FEED+H2IN)/TTLFD
F      H2OYLD = 0.050*(FEED+H2IN)/TTLFD
F      SUM = GDYLD+PROYLD+CO2YLD+H2OYLD
F      DIFF = TTLFD - (SUM*TTLFD)
F       H2YLD = DIFF/TTLFD
F      WRITE(NHSTRY,*)SUM,DIFF,H2YLD
   READ-VARS FEED FD105 FD119 H2IN
   WRITE-VARS GDYLD PROYLD CO2YLD H2OYLD H2YLD
   BLOCK-OPTION SIM-LEVEL=4

TEAR
   TEAR 117

STREAM-REPOR NOMOLEFLOW MASSFLOW
```

PROPERTY-REP NOPARAM-PLUS

	101	102	103	104	105	106	107	108	109	110
	P101	MX101	HX101-	HX102-	RX101	4□	;□	S101	P105	SP-101
		P101	MX101	HX101-	HX102-	RX101	4□	4□	S101	S101
	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	MIXED	MIXED	MIXED	LIQUID	LIQUID
Substream: MIXED										
Mass Flow lb/hr										
H2	0	0	0	0	0	1.084999	1.084999	1.084999	0	2.04E-07
LINOL3	7.5	7.5	7.5	7.5	7.5	0	0	0	0	0
PALM	11	11	11	11	11	0	0	0	0	0
STEARIC	4.1	4.1	4.1	4.1	4.1	0	0	0	0	0
OLEIC	22	22	22	22	22	0	0	0	0	0
LINOL2	54	54	54	54	54	0	0	0	0	0
ARACHID	1.4	1.4	1.4	1.4	1.4	0	0	0	0	0
GDSL	0	0	0	0	0	85.05216	85.05216	85.05216	0	85.052
H2O	0	0	0	0	0	5.54688	5.54688	5.54688	5.445815	0.0218078
H2S	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	0	0	0	0	0	0	0
PROPANE	0	0	0	0	0	4.82784	4.82784	4.82784	0	2.468692
NAPTHA	0	0	0	0	0	0	0	0	0	0
CO2	0	0	0	0	0	7.29312	7.29312	7.29312	0	0.2876933
Total Flow lbmol/hr	0.3591571	0.3591571	0.3591571	0.3591571	0.3591571	1.456175	1.456175	1.456175	0.3022887	0.3985819
Total Flow lb/hr	100	100	100	100	100	103.805	103.805	103.805	5.445815	87.8302
Total Flow cuft/hr	1.786671	1.795957	1.795957	1.975812	2.061152	29.28627	25.1053	10.49892	0.0877934	1.907063
Temperature F	68	80.58947	80.58948	290	370	617	507.6096	100	100	100
Pressure psi	14.7	500	500	500	500	500	500	500	175	175
Vapor Frac	0	0	0	0	0	0.8408124	0.7704222	0.4824463	0	0
Liquid Frac	1	1	1	1	1	0.1591876	0.2295778	0.5175537	1	1

PROPERTY-REP NOPARAM-PLUS (Cont.)

	101	102	103	104	105	106	107	108	109	110
	P101	MX101	HX101-	HX102-	RX101	4□	;□	S101	P105	SP-101
		P101	MX101	HX101-	HX102-	RX101	4□	4□	S101	S101
	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	MIXED	MIXED	MIXED	LIQUID	LIQUID
Solid Frac	0	0	0	0	0	0	0	0	0	0
Enthalpy Btu/lbmol	-3.14E+05	-3.12E+05	-3.12E+05	-2.83E+05	-2.71E+05	-70801.07	-77885.8	-1.00E+05	-1.22E+05	-1.99E+05
Enthalpy Btu/lb	-1126.343	-1120.916	-1120.916	-1017.751	-971.6202	-993.1961	-1092.581	-1406.734	-6797.624	-903.7778
Enthalpy Btu/hr	-1.13E+05	-1.12E+05	-1.12E+05	-1.02E+05	-97162.02	-1.03E+05	-1.13E+05	-1.46E+05	-37018.6	-79378.98
Entropy Btu/lbmol-R	-415.036	-412.2374	-412.2374	-367.7857	-351.4557	-80.66001	-87.58823	-118.2502	-38.21506	-382.6785
Entropy Btu/lb-R	-1.490631	-1.48058	-1.48058	-1.320929	-1.262278	-1.131497	-1.228686	-1.658812	-2.121258	-1.736632
Density lbmol/gal	0.0268725	0.0267335	0.0267335	0.0243	0.0232939	6.65E-03	7.75E-03	0.0185411	0.4602862	0.0279396
Density lb/gal	7.482102	7.443416	7.443416	6.765855	6.485721	0.4738298	0.5527402	1.321727	8.292184	6.156685
Average MW	278.4297	278.4297	278.4297	278.4297	278.4297	71.28609	71.28609	71.28609	18.01528	220.3567
Liq Vol 60F cuft/hr	1.803603	1.803603	1.803603	1.803603	1.803603	2.596039	2.596039	2.596039	0.0874017	1.834368

	110A	110B	110C	111	112	113	114	115	117	118
	ST-101	P106	MX101	FL-101	P102		ST-101	PSA	CP102	MX102
	SP-101	SP-101	P106	ST-101	ST-101	P102		S101	PSA	CP102
	LIQUID	MISSING	MISSING	VAPOR	LIQUID	LIQUID	VAPOR	VAPOR	VAPOR	VAPOR
Substream: MIXED										
Mass Flow lb/hr										
H2	2.04E-07	0	0	2.04E-07	4.05E-35	4.05E-35	0	1.084998	1.084999	1.084999
LINOL3	0	0	0	0	0	0	0	0	0	0
PALM	0	0	0	0	0	0	0	0	0	0
STEARIC	0	0	0	0	0	0	0	0	0	0
OLEIC	0	0	0	0	0	0	0	0	0	0
LINOL2	0	0	0	0	0	0	0	0	0	0

PROPERTY-REP NOPARAM-PLUS (Cont.)

	101	102	103	104	105	106	107	108	109	110
	P101	MX101	HX101-	HX102-	RX101	4□	;□	S101	P105	SP-101
		P101	MX101	HX101-	HX102-	RX101	4□	4□	S101	S101
	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	MIXED	MIXED	MIXED	LIQUID	LIQUID
ARACHID	0	0	0	0	0	0	0	0	0	0
GDSL	85.052	0	0	1.60E-04	85.05184	85.05184	0	1.58E-04	0	0
H2O	0.0218078	0	0	0.4588025	2.363005	0.029885	2.8	0.0792568	0	0
H2S	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	0	0	0	0	0	0	0
PROPANE	2.468692	0	0	2.321827	0.1468655	0.1468655	0	2.359148	0	0
NAPTHA	0	0	0	0	0	0	0	0	0	0
CO2	0.2876933	0	0	0.2876933	4.45E-12	4.45E-12	0	7.005427	0	0
Total Flow lbmol/hr	0.3985819	0	0	0.0846584	0.469347	0.3398392	0.1554236	0.7553041	0.5382258	0.5382258
Total Flow lb/hr	87.8302	0	0	3.068483	87.56171	85.22859	2.8	10.52899	1.084999	1.084999
Total Flow cuft/hr	1.907065	0	0	34.10666	1.85258	1.832826	19.0754	25.87814	18.60182	8.231991
Temperature F	100.002			98.90795	143.0657	149.9646	297.7949	100	99.97435	240.933
Pressure psi	175		500	14.7	21.7	31.7	64.7	175	175	500
Vapor Frac	0			1	0	0	1	1	1	1
Liquid Frac	1			0	1	1	0	0	0	0
Solid Frac	0			0	0	0	0	0	0	0
Enthalpy Btu/lbmol	-1.99E+05			-72054.6	-1.90E+05	-2.16E+05	-1.02E+05	-39284.66	163.5656	1154.758
Enthalpy Btu/lb	-903.7778			-1987.963	-1018.401	-861.4131	-5676.514	-2818.112	81.13857	572.831
Enthalpy Btu/hr	-79378.98			-6100.031	-89172.93	-73417.02	-15894.24	-29671.86	88.03524	621.5208
Entropy Btu/lbmol-R	-382.6781			-40.91684	-319.5699	-425.8229	-10.82218	-7.527309	-4.635141	-5.164754
Entropy Btu/lb-R	-1.73663			-1.128883	-1.712954	-1.69792	-0.6007222	-0.5399766	-2.299314	-2.562034
Density lbmol/gal	0.0279396			3.32E-04	0.0338676	0.0247868	1.09E-03	3.90E-03	3.87E-03	8.74E-03
Density lb/gal	6.156679			0.0120268	6.318376	6.216305	0.0196224	0.0543903	7.80E-03	0.0176194

PROPERTY-REP NOPARAM-PLUS (Cont.)

	101	102	103	104	105	106	107	108	109	110
	P101	MX101	HX101-	HX102-	RX101	4□	;□	S101	P105	SP-101
		P101	MX101	HX101-	HX102-	RX101	4□	4□	S101	S101
	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID	MIXED	MIXED	MIXED	LIQUID	LIQUID
Average MW	220.3567			36.24543	186.5607	250.7909	18.01528	13.94006	2.01588	2.01588
Liq Vol 60F cuft/hr	1.834368	0	0	0.0864746	1.792832	1.755387	0.0449381	0.6742691	0.4617512	0.4617512

	119	120	121	122	123	124	125	CO2	CWR	CWR1
	RX101	CP101	MX102			P105	FL-101		P104	
	MX102		CP101	FL-101	FL-101	P102	PSA	PSA	HX103-	P104
	VAPOR	VAPOR	VAPOR	LIQUID	LIQUID	LIQUID	MIXED	VAPOR	LIQUID	LIQUID
Substream: MIXED										
Mass Flow lb/hr										
H2	3.804999	2.72	2.72	0	0	0	0	0	0	0
LINOL3	0	0	0	0	0	0	0	0	0	0
PALM	0	0	0	0	0	0	0	0	0	0
STEARIC	0	0	0	0	0	0	0	0	0	0
OLEIC	0	0	0	0	0	0	0	0	0	0
LINOL2	0	0	0	0	0	0	0	0	0	0
ARACHID	0	0	0	0	0	0	0	0	0	0
GDSL	0	0	0	2.84E-04	0	0	1.58E-04	0	0	0
H2O	0	0	0	4.63E-08	0.4894927	2.33312	0.0792568	0	2309.68	2309.68
H2S	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	0	0	0	0	0	0	0
PROPANE	0	0	0	1.48E-05	0	0	2.359148	0	0	0
NAPTHA	0	0	0	0	0	0	0	0	0	0

PROPERTY-REP NOPARAM-PLUS (Cont.)

	101 P101 LIQUID	102 MX101 P101 LIQUID	103 HX101- MX101 LIQUID	104 HX102- HX101- LIQUID	105 RX101 HX102- LIQUID	106 4□ RX101 MIXED	107 ;□ 4□ MIXED	108 S101 4□ MIXED	109 P105 S101 LIQUID	110 SP-101 S101 LIQUID
CO2	0	0	0	3.64E-08	0	0	0	7.005427	0	0
Total Flow lbmol/hr	1.887512	1.349287	1.349287	1.46E-06	0.0271709	0.1295079	0.0578996	0.1591788	128.2067	128.2067
Total Flow lb/hr	3.804999	2.72	2.72	2.99E-04	0.4894927	2.33312	2.438563	7.005427	2309.68	2309.68
Total Flow cuft/hr	42.90768	520.0834	34.66854	6.53E-06	7.85E-03	0.0381251	1.507645	5.167461	37.93036	37.93266
Temperature F	586.7733	68	724.6138	68	68	149.9646	99.97435	99.97435	110.4626	110.571
Pressure psi	500	14.7	500	14.7	14.7	31.7	175	175	500	510
Vapor Frac	1	1	1	0	0	0	0.9295689	1	0	0
Liquid Frac	0	0	0	1	1	1	0.070431	0	1	1
Solid Frac	0	0	0	0	0	0	0	0	0	0
Enthalpy Btu/lbmol	3577.495	-61.40031	4543.916	-1.88E+05	-1.23E+05	-1.22E+05	-50942.12	-1.69E+05	-1.22E+05	-1.22E+05
Enthalpy Btu/lb	1774.657	-30.45832	2254.061	-914.9968	-6829.944	-6748.178	-1209.537	-3843.429	-6786.474	-6786.371
Enthalpy Btu/hr	6752.566	-82.84663	6131.045	-0.2738398	-3343.207	-15744.31	-2949.533	-26924.86	-1.57E+07	-1.57E+07
Entropy Btu/lbmol-R	-2.354373	-0.1171418	-1.486812	-363.1769	-39.26957	-36.67663	-66.63749	-4.062922	-37.84993	-37.8467
Entropy Btu/lb-R	-1.167913	-0.0581095	-0.7375498	-1.771269	-2.179792	-2.035862	-1.582198	-0.0923185	-2.10099	-2.100811
Density lbmol/gal	5.88E-03	3.47E-04	5.20E-03	0.02986	0.4624672	0.4541016	5.13E-03	4.12E-03	0.4518477	0.4518203
Density lb/gal	0.0118546	6.99E-04	0.0104882	6.122437	8.331475	8.180767	0.2162236	0.1812281	8.140163	8.139668
Average MW	2.01588	2.01588	2.01588	205.0377	18.01528	18.01528	42.11703	44.0098	18.01528	18.01528
Liq Vol 60F cuft/hr	1.619323	1.157571	1.157571	6.32E-06	7.86E-03	0.037445	0.0759562	0.1365617	37.06883	37.06883

	CWS	CWS1	MPSR	MPSS	PROPANE	WWT
	HX103-	P103		4□		
	P103		4□		FL-101	P105
	LIQUID	LIQUID	LIQUID	VAPOR	VAPOR	LIQUID
Substream: MIXED						
Mass Flow lb/hr						
H2	0	0	0	0	2.04E-07	0
LINOL3	0	0	0	0	0	0
PALM	0	0	0	0	0	0
STEARIC	0	0	0	0	0	0
OLEIC	0	0	0	0	0	0
LINOL2	0	0	0	0	0	0
ARACHID	0	0	0	0	0	0
GDSL	0	0	0	0	3.35E-05	0
H2O	2309.68	2309.68	5.372242	5.372242	0.0485666	7.778936
H2S	0	0	0	0	0	0
NH3	0	0	0	0	0	0
PROPANE	0	0	0	0	4.68096	0
NAPTHA	0	0	0	0	0	0
CO2	0	0	0	0	0.2876933	0
Total Flow lbmol/hr	128.2067	128.2067	0.2982047	0.2982047	0.1153857	0.4317965
Total Flow lb/hr	2309.68	2309.68	5.372242	5.372242	5.017253	7.778936
Total Flow cuft/hr	37.61554	37.60596	0.1048887	15.27979	43.78178	0.1280346
Temperature F	95.46259	95	366.04	366.0404	68	114.4461
Pressure psi	500	14.7	164.7	164.7	14.7	41.7
Vapor Frac	0	0	0	1	1	0
Liquid Frac	1	1	1	0	0	1
Solid Frac	0	0	0	0	0	0
Enthalpy Btu/lbmol	-1.23E+05	-1.23E+05	-1.17E+05	-1.02E+05	-53610.59	-1.22E+05
Enthalpy Btu/lb	-6800.593	-6801.025	-6510.467	-5651.786	-1232.925	-6782.69
Enthalpy Btu/hr	-1.57E+07	-1.57E+07	-34975.8	-30362.76	-6185.896	-52762.11
Entropy Btu/lbmol-R	-38.29923	-38.31317	-30.87826	-12.05098	-59.06788	-37.73145
Entropy Btu/lb-R	-2.125931	-2.126704	-1.714004	-0.6689311	-1.35843	-2.094414
Density lbmol/gal	0.4556294	0.4557454	0.3800617	2.61E-03	3.52E-04	0.4508374
Density lb/gal	8.208291	8.210381	6.846918	0.0470009	0.0153193	8.121961
Average MW	18.01528	18.01528	18.01528	18.01528	43.48245	18.01528
Liq Vol 60F cuft/hr	37.06883	37.06883	0.0862209	0.0862209	0.1545686	0.1248467

Energy Systems Division
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