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Technical Report

Environmental Life Cycle Implications of Fuel Oxygenate Production from California Biomass - Technical Report

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1 PROJECT OVERVIEW

1.1 BACKGROUND

1.1.1 Purpose of the Study

Historically, a large portion (>90%) of the excess agricultural residue produced in California (approximately 10 million dry metric tons per year) has been disposed of through the use of open-field burning. Because of concerns over the amount of air pollutants released through this practice, federal, state, and local air quality agencies have been tightening regulations related to the burning of agricultural biomass. In looking at the alternatives to burning, a California Legislative Committee determined that the production of ethanol from the excess biomass was a viable option.

A related concern is the growing volume of dead/diseased trees, underbrush, and small diameter green trees in California that are creating a severe forest management problem. With the state government's concern about burning as a management option, some of this forest biomass is available for ethanol production.

Besides the above two sources of feedstock, chaparral or brush can be another source of biomass that, if not removed, can eventually be consumed by wildfires in California. Although little commercial use is made of chaparral, the brush lands surrounding a considerable number of California's homes in the wildland areas could be a major source of biomass for an ethanol facility. In fact, the existence of these homes could justify greater investments to mechanically remove the chaparral and transport it to an ethanol facility. The local, state, and federal entities responsible for wildland fire protection would also be supportive of assessing the potential conversion of chaparral to ethanol since it is one of their major fuel loading problems.

One of the uses of biomass-derived ethanol is as a fuel oxygenate. The Clean Air Act Amendments of 1990 mandated the sale of oxygenated fuels in ambient air quality nonattainment areas;[1] so there has been a sharp increase in the demand for these products. The two main oxygenates sold in the United States are methyl tertiary-butyl ether (MTBE) and ethanol. However, MTBE is currently the oxygenate of choice in California for reasons explained below.

The California Cleaner-Burning Gasoline regulations specify a summertime Reid vapor pressure (RVP) standard,[2] which limits the evaporation of volatile organic compounds, and oxygen content limits, which apply equally regardless of the oxygenate used (typically MTBE).

Until the start of the Cleaner-Burning Gasoline program, state law allowed blends of gasoline with 10% ethanol (3.5 wt.% oxygen) an exemption from the RVP standard. However, in the Cleaner-Burning Gasoline program, the California Air Resources Board (CARB) established comprehensive gasoline specifications that apply to all fuels, including ethanol blends. This effectively eliminated the RVP waiver previously available to ethanol blends. In essence, ethanol blends do not qualify for the RVP exemption because the oxygen content limits preclude the use of greater than 2.7% oxygen to avoid NO_x increases.

Hence, the direct replacement of MTBE with ethyl tertiary butyl ether (ETBE) is the focus of this study; however, the E10 option is also analyzed as part of the sensitivity analysis. Although the benefits of utilizing these three feedstocks for ETBE production are qualitatively evident, the environmental aspects of the biomass disposal options (burning or ETBE production) have not been comprehensively assessed. In fact, the full set of environmental aspects associated with a product such as a fuel additive is very broad, both in terms of the environmental media or issues involved and in terms of the scope of industrial processes involved.

[1] Geographical areas whose air quality does not meet federal air quality standards (for CO, ozone, and particulate matter) designed to protect public health.

[2] The State of California limits the RVP for summertime gasoline to 7.0 psi.

The purpose of the present study is to quantify and compare the comprehensive sets of flows to and from the environment (raw material and energy use, wastes, emissions, etc.) associated with the disposal options for California biomass over their life cycles.

1.1.2 Project Partners

This project was being conducted by the National Renewable Energy Laboratory (NREL) and the State of California through CARB, the California Energy Commission (CEC), and California Department of Forestry and Fire Protection (CDF). TSS Consultants, Inc. of Rancho Cordova, California, and Ecobalance, Inc. of Rockville, Maryland, served as consultants on this project.

1.1.3 Related Research

Biomass-derived ethanol has recently been the subject of life cycle analyses (LCAs) from both environmental and economic perspectives. In 1993 three of the U.S. Department of Energy's (DOE) laboratories completed a life cycle comparison of biomass ethanol and reformulated gasoline [1,2,3]. There has also been a series of studies estimating the life cycle energy balance of ethanol derived from corn [4,5]. The most recent of these studies, by researchers with the U.S. Department of Agriculture's Economic Research Service, includes a review of this literature and summarizes the factors contributing to variability in published results and conclusions on this issue. There are also a few reports that have focused on the state of California:

- Craig, Unnasch, and Lowell, The Effect of Fuel Cycle Energy Efficiency and Transportation Efficiency on Greenhouse Gas Emissions, March 1991
- Unnasch, Moyer, Lowell, and Jackson, Comparing the Impacts of Different Transportation Fuels on Greenhouse Effect, April 1989
- Darrow, Comparison of Fuel Cycle Emissions for Electric Vehicle and Ultralow Emissions Natural Gas Vehicle, May 1994; Darrow, Light Duty Vehicle Full Fuel Cycle Emissions Analysis; April 1994.

The objective of the current study goes beyond these past projects by quantifying and comparing the comprehensive sets of flows associated with the disposal options for California biomass, including air emissions, water effluents, solid waste, and the consumption/depletion of resources. However, the analysis does not include an examination of toxicological effects, since that is beyond the capacity of the LCA tool. All of these flows are examined over the product life cycle, from production and extraction of raw materials, through intermediate conversion processes, transportation, distribution, and use. Net life cycle energy consumption ("energy balance") is one component of the more comprehensive scope of an LCA such as undertaken in this study. Life Cycle Cost assessment is outside the scope of the present study.

1.1.4 Stakeholder Involvement

For several reasons, a key ingredient of this project is the involvement of a broad group of interested stakeholders. Firstly, the results of a life cycle study such as this are strongly influenced by decisions made at the study outset, related to scoping, modeling, and methodology. Objectivity as well as acceptance of the results depends upon widespread critique and feedback from stakeholders on tentative scoping, modeling, and methodological decisions.

Secondly, the quality and utility of the study's results depend upon the use of data characterizing processes throughout the life cycles of biomass disposal alternatives that are comprehensive, accurate, validly comparable, and up-to-date.

For both reasons, the formative and early stages of this project allowed for input and comment on the approach from all stakeholders. These stakeholders included government agencies (federal, state, and local), the petroleum industry, ethanol producers, ethanol trade associations, timber industry companies, the biomass electricity industry, the biomass collection industry, agriculture groups, environmental groups, consumer groups, and fuel users.

1.2 PROJECT PHASES

The project was divided into three tasks, which corresponded to the three project phases:

- **TASK I**: ESTABLISH APPROACH TO LIFE CYCLE ANALYSIS
  - Step 1: Establish Draft Scoping Document
  - Step 2: Present and Discuss Draft Scoping Document with Key Stakeholders
  - Step 3: Prepare Final Scoping Document
- **TASK II**: DEVELOP DATABASE FOR LIFE CYCLE ANALYSIS
  - Step 1: Obtain Data on Resource Production, Collection and Distribution
  - Step 2: Obtain Data on Existing Biomass Disposal Method
  - Step 3: Obtain Data on ETBE Production
  - Step 4: Obtain Data on MTBE Production
  - Step 5: Input Data into the LCA Database
  - Step 6: Report on the LCA Database
- **TASK III**: CONDUCT LIFE CYCLE ANALYSIS
  - Step 1: Develop Models for ETBE and MTBE Production
  - Step 2: Generate Final Report

2 LIFE CYCLE ASSESSMENT PRINCIPLES

2.1 OVERVIEW

Life cycle assessment is a technique for assessing the environmental aspects and potential impacts associated with a product, by

- Compiling an inventory of relevant inputs and outputs of a system (life cycle inventory [LCI])
- Evaluating the potential environmental impacts associated with those inputs and outputs
- Interpreting the results of the inventory and impact phases in relation to the objectives of the study.

Life cycle assessment studies the environmental aspects and potential impacts throughout a product's life (i.e., cradle-to-grave) from raw material acquisition through production, use, and disposal. The general principle for extending the system boundaries is illustrated in Figure 1, although the boundaries may not all be relevant to the LCA of a transportation fuel.

In the most straightforward and transparent approach to LCI interpretation, the inventory results may be used as-is to help identify and prioritize opportunities for pollution prevention or increases in material and energy efficiency for processes within the life cycle. A particular advantage of LCI applied in this way is its comprehensiveness. LCAs help detect the shifting of environmental burdens from one life cycle stage to another (e.g., lower energy consumption during use, achieved at the cost of much higher manufacturing energy consumption), or from one medium to another (e.g., lower air emissions at the cost of increased solid waste).

Because the number of flows calculated during an LCI analysis is often very large, subsets of the flows are sometimes consolidated or aggregated to facilitate interpretation, especially when two or more products or processes are being compared using LCA. This consolidation/aggregation of flows has been given the (perhaps misleading) name of Life Cycle Impact Assessment (LCIA). In fact, it is not the impacts of the environmental flows in the inventory that are estimated using LCIA. Instead, the inventory flows are consolidated and aggregated using information about their relative potential strength of influence with respect to separate categories of potential environmental impact, thereby generating indicators. The results within each LCIA impact category are useful for comparison of one product or process versus another, but have little meaning in an absolute sense (i.e., relative to estimating the actual environmental impacts of a product or process).

Because the results of an LCI and an LCIA are influenced by a significant number of assumptions and uncertainties, the interpretation phase includes some sensitivity analyses. This allows an assessment of the robustness of the baseline results, project assumptions, methodological choices, future scenarios, and uncertainties. In this study, data quality was assessed for its 1) precision, 2) completeness, 3) representativeness, 4) consistency, and 5) the origin of the data (measured, calculated, estimated).

Principal aspects of LCI and LCIA are discussed briefly in the sections that follow. Further information about LCA methodology is provided in a number of publications from the Society of Environmental Toxicology and Chemistry [1,2,3,4], the U.S. EPA [5,6,7], the International Organization for Standardization (ISO) [8,9], as well as a few European sources [10,11].

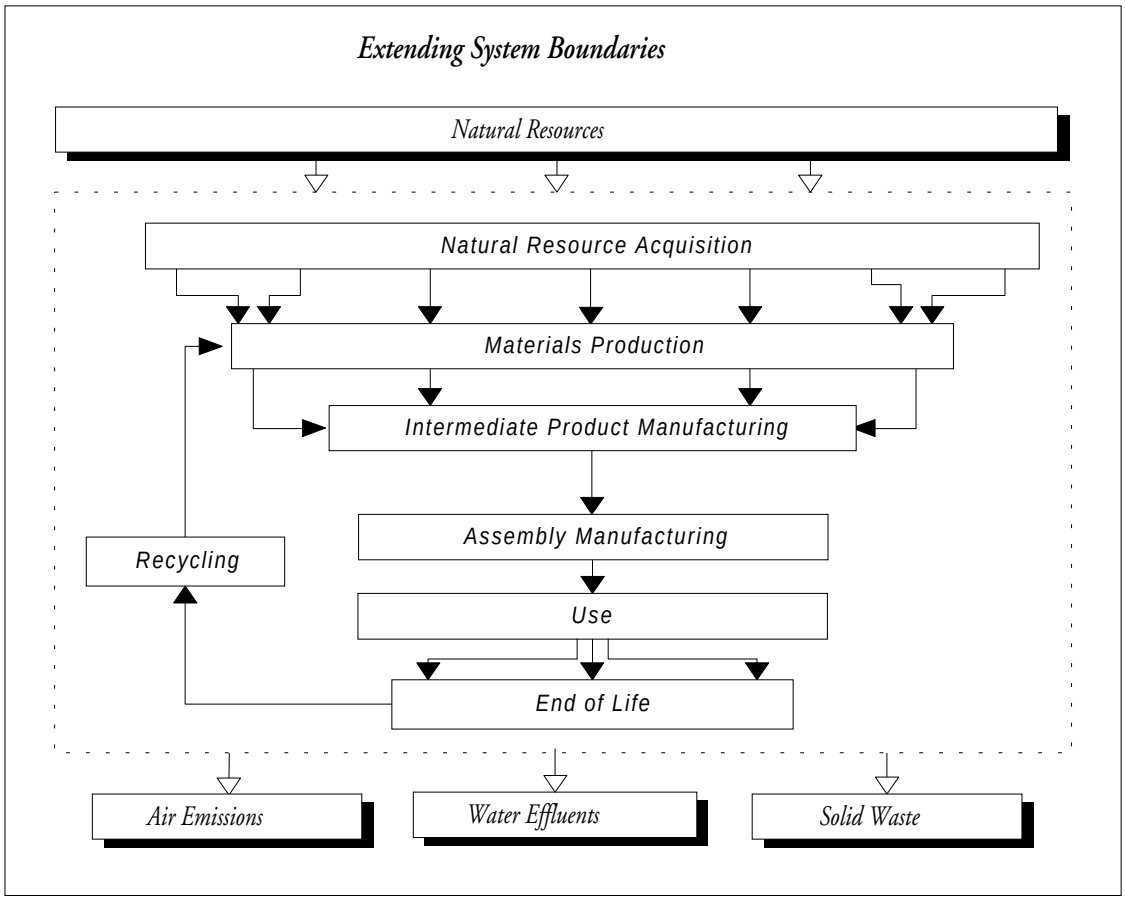


Figure 1: Life Cycle Analysis Principles

2.2 METHODOLOGY

2.2.1 Functional Unit

The comparison of different industrial systems can only be achieved if they perform the same function. Once this shared function is defined a unit has to be chosen in order to compare the systems on the same quantitative basis. All the energy and mass flows in the inventory are normalized to this functional unit. Examples of how this is done are presented below:

- The comparison of different indoor paints (solvent-borne, water-borne, etc.) would be made on the following basis:
  - Function: covering a surface,
  - Functional unit: the quantity of paint required to cover 10 square feet of wall (this function could be further refined to take into account secondary functions like opacity, washability, durability and lifetime, etc.).
- The comparison of different gasoline additives could be made on the following basis:
  - Function: addition of oxygen to fuel,
  - Functional unit: the quantity of additive required to achieve an oxygen content of 2%.

2.2.2 Definition of the System Boundaries

For each option being compared on a life cycle basis, the corresponding systems are then determined (i.e., relevant processes to be included in the system are selected). The three main issues to address, for each of the systems, are:

1) Exhaustivity of the systems. The LCA theoretical principle implies that *each* material and constituent be studied and traced *back* to natural resources, and *forward* through final disposal. The strict application of this principle would lead to the study of almost every industrial process, as all industrial operations work within a complex network.
   In order to focus LCA projects on the main operations, quantitative rules are applied to exclude the constituents and ancillary materials whose impacts are estimated to be negligible compared to those of the overall studied system. Any systems that are excluded and the reasons for their exclusion will be provided in the presentation of the project.
2) Identification of steps/operations that are different from one system to another. As the project focuses on a comparison, steps that are functionally equivalent for the compared products could be excluded from both systems. On the other hand, steps or operations that are not functionally equivalent for the compared products should be taken into account, i.e., included in the system boundaries. Any excluded steps will be indicated in the project presentation.
3) Identification of coproducts and determination of the appropriate partitioning parameter. This facilitates proper allocation to a defined product its share of the total pollution, energy consumption and material flows for which the process is responsible.

2.2.3 Interpretation: Life Cycle Impact Assessment

In this section of the LCA, after the inventory has been prepared, there are two further steps that need to be considered:

1) Whether and how to aggregate/consolidate the inventory data using information about each flow's relative potential strength of influence with respect to separate categories of potential environmental impact; and
2) Whether and how to aggregate the results of the step mentioned above, across the impact categories considered.

Note that the first of these two steps is pursued in addition to the LCIA, not as a replacement for it.

Those attempting to develop a final "score" for comparing products or processes only use the second of these two aggregation steps. It was not used in this project because it is fraught with numerous problems whose discussion is beyond the scope of this document.

Uncertainties associated with input parameters were examined through sensitivity analysis, which includes an examination of data quality and its influence on the final report.

3 PROJECT SCOPING OPTIONS AND DECISIONS

This section presents the various parameters that should be considered in order to define precisely the scope of the project. These parameters can be addressed sequentially, as indicated in Figure 2. We begin by first considering "project" level parameters that involve high-level choices that can have a profound impact on the general orientation and outcome of the project. These choices involve geographic, temporal, technical, and environmental aspects of the life cycle scenarios considered. Next, we need to consider more specific product parameters, including the exact nature and form of the products studied and the type of application in which they are used. The third group of parameters involves the production processes used to make the product. The types of choices made for high-level project parameters influence both product- and process-related parameters. Finally, there is a group of parameters that must be defined regarding the methodology of the LCA itself.

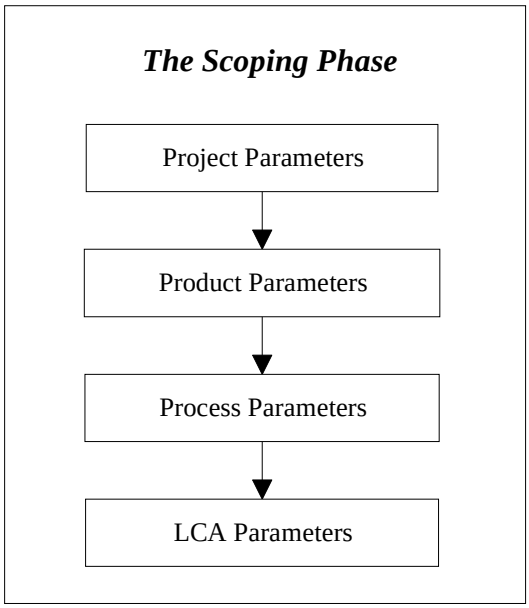


Figure 2: Elements of the Scoping Phase for Life Cycle Analysis

Subsequent sections address the separate scoping elements in turn, as follows:

Project Parameters	⇒	Section 3.1
Product Parameters	⇒	Section 3.2
Process Parameters	⇒	Section 3.3
LCA-Specific Parameters	⇒	Section 3.4

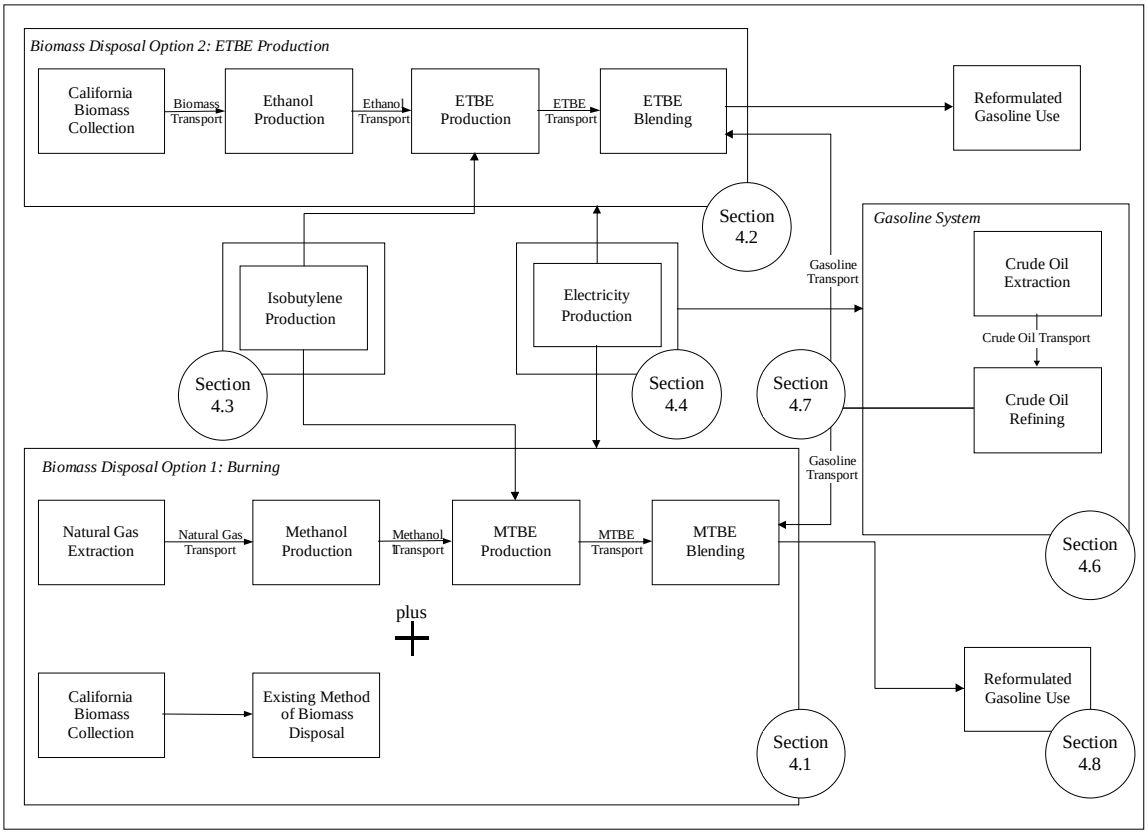
The key criteria that have been accounted for in selecting an option for each parameter are:

- Relevance to the project's goals
- Availability of data, and
- Time and cost constraints

3.1 PROJECT PARAMETERS

3.1.1 General System Boundaries

Figure 3 shows the general system boundaries considered in this study of the use of ETBE derived from California biomass versus use of MTBE derived from natural gas in reformulated gasoline.



NOTE: Section numbers refer to section numbers in this report.

Figure 3: General System Boundaries for the Comparison of ETBE and MTBE Use in RFG

It should be noted that this project is not a simple comparison of ETBE versus MTBE use in reformulated gasoline but rather a comparison of two different methods for California biomass disposal. In one option, the biomass is collected and converted into ETBE and used in reformulated gasoline. In the other option the biomass is collected and disposed of via burning. However, the second option also involves the use of MTBE to satisfy the oxygenate requirements of the reformulated gasoline as the ETBE would not be available.

This affects the choice of the functional unit of comparison (Section 3.2.2), as it is linked not only to the use of reformulated gasoline but also, and primarily, to the disposal amounts for California biomass.

3.1.2 Environmental Issues Considered

The LCA methodology traditionally calls for the establishment of complete mass and energy balances for each process, including: energy consumption, raw material consumption, air emissions, water effluents, and solid waste. This comprehensive compilation exercise results in a quantification of all existing flows into the environment. However, this scheme has become increasingly questionable, due to:

- **Practical Reasons**: an ever-expanding number of parameters can be tracked within an inventory, reflecting more comprehensive data measurements. For instance, including U.S. Toxic Release Inventory (TRI) data would result in a list of approximately 200 pollutants being released during gasoline production. Similarly, including radionucleide emissions from electricity production would result in tracking more than 150 specific flows. Managing such a large inventory list adds to the complexity of carrying out (since these additional flows should be collected for all sources within the system for the sake of consistency) as well as interpreting the LCA.
- **More Fundamental Reasons:** by restricting the inventory data collection to the data actually needed in a subsequent decision analysis, a more focused LCA can be carried out, which ensures that the issues at stake receive the highest priority and data quality. Some studies even restrict their data collection to pollutants contributing a single effect (e.g., greenhouse gases).

Therefore, it is important to understand the issues or impacts that are of greatest concern to the users (or decision-makers) of the LCA and then tailor the data collection to meet their needs. It should be noted that an inventory number (e.g., quantity of lead) is only an indication of a potential impact. Additional data such as ambient concentration, pathways to human and ecological toxicity, and the existence of thresholds would be needed to assess the actual impact of this emission. These additional data are of the type required in risk assessment, in which exposure data are collected for a few emissions at a single site. An actual LCA would need to gather these additional data for all inventory flows and for all sites included in the system boundaries (generally well over a hundred). This type of actual impact assessment is as difficult (as the limits of inventories are well known) as impractical.[3]

Life cycle assessment should consequently be considered as providing an indication of potential environmental impact, complementary to actual impacts evaluated by other tools. The following sections detail the most well known approaches for determination of these potential environmental impacts through the use of LCI results.

The following steps were used to facilitate interpretation of the inventory results through impact assessment:

- **CLASSIFICATION:** The organization of inventory data into environmental impact and resource consumption categories, such as global warming potential, acidification potential, eutrophication potential, natural resource depletion, etc.
- **CHARACTERIZATION:** Weighted summing of inventory data within each environmental impact category, based upon each flow's relative strength of potential influence upon the identified environmental impact or effect.[4]

The characterization step takes explicit account of the latest scientific assessments of the uncertainty inherent in the equivalency factors, such as global warming potentials. In addition, the discussion accompanying the characterization results clearly states that the results of a characterization analysis serve strictly to normalize the multiple flows within the LCI with respect to a particular environmental issue in terms of their relative strength of potential contribution to that issue. Characterization is not in any way intended to estimate the actual impact of the emissions upon environmental issues.

Furthermore, some of the inventory flows themselves may be highly uncertain, with an estimable magnitude of uncertainty. This uncertainty was appropriately combined with the uncertainty inherent in the equivalency factors used in the characterization step.

Table 5 indicates the environmental inventory flows and their corresponding impact assessment categories considered in this study:

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[3] For instance, the Tellus Institute conducted such a comprehensive impact assessment for a single type of site (power plant) in a limited area (New York State). The study lasted for about two years and cost several hundreds of thousands of dollars.

[4] Further details concerning the characterization step, for many of the most commonly-studied environmental impact categories, are provided in chapters 3 and 4 of Heijungs, R., et al., eds., *Environmental Life Cycle Assessment of Products*.

Table 5: Environmental Inventory Flows Considered

Environmental Flows Considered	*Associated Impact Category*
Natural Resources	
Oil	Natural resources depletion
Coal	Natural resources depletion
Natural Gas	Natural resources depletion
Other Significant Resources Depending on Decision Rules	Natural resources depletion[5]
Water Effluents	
COD	Eutrophication potential
BOD	Eutrophication potential
Nitrates	Eutrophication potential
Phosphates	Eutrophication potential
Total Suspended Solids	Direct Use
Metals	Direct Use
Air Emissions	
CO_2	Greenhouse effect potential
CH_4	Greenhouse effect potential
N_2O	Greenhouse effect potential
NO_x	Acidification potential
SO_x	Acidification potential
Particulate	Direct Use
Hydrocarbons	Direct Use
CO	Direct Use
Solid Waste	
Nonhazardous	Direct Use
Hazardous	Direct Use
Energy Use	
Total Primary Energy	Direct Use
Fossil Fuel Energy	Direct Use

Some of these environmental flows can potentially have impacts on the environment that go beyond the effects caused by just the flow itself. For this study, the potential impacts of the life cycle flows have been assessed for four impact assessment indicators: *greenhouse effect potential, eutrophication potential, acidification potential*, and *natural resource depletion*.

To calculate the impact indicators, each flow that is determined to be a contributor to one of these categories is weighted according to its impact in comparison to a set baseline, e.g., for greenhouse effect potential indicator the baseline is gram of CO_2 equivalent. The value for the flow is multiplied by this weighting factor to give an impact score for the particular flow. The impact scores for all contributing flows are then summed to give an overall impact score for potential impact. The weighting of the environmental flows is based upon the best available scientific

[5] Inflows such as sand, limestone, etc. could be used in the natural resources depletion index although their impact is zero because of their abundance in nature.

knowledge; however, the score should be interpreted as potential impacts, not actual impacts. The exact methodology is discussed in more detail in Appendix B.

3.1.3 Geographical Scope

The focus of the project is the disposal of California biomass and the use of ETBE and MTBE in reformulated gasoline in California. However, the geographic scope of particular data items pertains to whatever locations are dictated by actual plant locations, feedstock origins, sources of electricity, etc.

ETBE System

The biomass used for ETBE production is of California origin. Hence, data on biomass collection, distribution, and alternative uses were California based. The production of ethanol and ETBE was assumed to occur in California. However, data on ancillary materials needed for the conversion of the biomass to ETBE may be based on a U.S. average situation.

MTBE System

MTBE is produced both in and out of California, so the system was examined based solely on MTBE production in California. The natural gas feedstock necessary for MTBE production was regionalized.

Reformulated Gasoline System

The production of gasoline was based on Ecobalance data and data provided by CEC. The combustion of the reformulated gasoline was assumed to occur in California.

3.1.4 Temporal Scope

The issue here is whether to study a current situation or to model a future situation or to model both current and future scenarios. Current and future scenarios could be quite different. For example, current scenarios would be limited to existing ethanol production technology as well as existing transportation vehicle scenarios and biomass availability scenarios. Future scenarios could be limited in the alternatives for biomass disposal as open-field burning is being phased out as an option.

One reason for studying a mid- to long-term time frame, is that a widespread use of biomass derived ETBE in the very near-term is not probable. However, the results of this study are data-driven, and the use of forecast or modeled (rather than current, empirically based) production, conversion, and end-use technology parameters would greatly increase the uncertainty in the final results.

For this study, the early part of the next decade has been selected as the production period. Empirical data still provide the most logical starting point for future projections or extrapolations.

3.2 PRODUCT PARAMETERS

3.2.1 Scenarios

As was mentioned, the feedstock for producing ETBE was California biomass. However, there are a number of possibilities within this broad category. Different types of biomass are available in different parts of the state and during different seasons. Furthermore, the different types of biomass require distinct methods of collection and possible disposal alternatives. The three types of California biomass selected are as follows:

- Rice Straw
- Forest Residue and Thinnings
- Chaparral

The analysie of other agricultural residues such as wheat straw, orchard trimmings, and safflower stalks were not considered for this project.

This project involves the study of two separate ethanol production processes for the three biomass types: an enzyme-based process and a concentrated acid-based process.

The alternative disposal method could be different for each type of biomass. These methods could include incorporation into building materials, use in commercial products, use as mulch or burning. In order to simplify the system under study, only one existing alternative for each biomass scenario was considered. Since one of the motivations behind the study is the mandate to reduce open-field burning and fires, prescribed burning is assumed to be the major disposal alternative for all three biomass types.

3.2.2 Functional Unit

The functional unit of this study is the disposal of a defined amount of California biomass. Two disposal options were examined: the production and use of ETBE from the biomass and the existing disposal method. The use of ETBE substitutes for the use of MTBE in reformulated gasoline since both of these compounds add oxygen content to reformulated gasoline. Therefore, ETBE and MTBE use is compared based on their oxygen contents. Additionally, the function of the reformulated gasoline is to provide energy as a transportation fuel. Therefore, the comparison of ETBE and MTBE in reformulated gasoline is also linked to the heating value of the fuels.

Table 6 shows the comparison of ETBE versus MTBE use in reformulated gasoline from a functional unit perspective (the base wt % oxygen is mandated at 2%):

Table 6: Comparison of ETBE versus MTBE Use in Reformulated Gasoline

	Gasoline	*MTBE*	*ETBE*	*MTBE RFG*	*ETBE RFG*
Heating Value (MJ/l):	34.8	26.1	27.0	33.9	33.8
wt % Oxygen:	0%	18.2%	15.7%	2.0%	2.0%
Density (kg/l):	0.739	0.743	0.745	0.739	0.739
			wt % MTBE:	11.0%	
			wt % ETBE:		12.7%
			wt % Gasoline:	89.0%	87.3%
			MTBE (kg/l of RFG):	0.081	
			ETBE (kg/l of RFG):		0.094
			Gasoline (kg/l of RFG):	0.658	0.645
			Difference in Gasoline Use (kg):	0.014	
				1 kg ETBE is equivalent to:	
				0.86 kg MTBE + 0.14 kg Gasoline	

It can be seen from Table 6 that slightly more ETBE is needed per gallon of reformulated gasoline (as compared to MTBE) to provide the same amount of oxygen content. However, this additional amount of ETBE provides additional heating value as well. It is assumed that the two gallons of reformulated gasoline (one with ETBE and one with MTBE) are equal in terms of heating value.[6] Therefore, the comparison of one gallon of reformulated gasoline with ETBE versus one gallon of reformulated gasoline with MTBE would entail comparing 1 kg of ETBE with 0.86 of MTBE plus 0.14 of gasoline.

[6] There is actually a 0.09 % difference (33.87 vs. 33.84) in heating value. However, this is felt to be negligible given the possible variation in heating values of the individual fuels.

3.3 PROCESS PARAMETERS

Process parameters are strongly affected by the choices made on the previous project-related and product-related parameters. For example, the assumption of technology bases using the early part of the next decade for all processes leads to a number of conclusions about fuel production and feedstock supplies.

MTBE is produced via the selective reaction of isobutylene and methanol over an acidic ion-exchange resin catalyst, in the liquid phase. The resin typically consists of sulfonated styrene cross-linked with divinylbenzene. Reaction conditions are usually mild, with temperatures ranging from 30°C to 100°C and pressures between 7 and 14 atmospheres (100-200 psig). For MTBE to be economically competitive as an octane enhancer in gasoline, a low-cost isobutylene source is necessary. For this study it is assumed that methanol is produced from natural gas since a majority of methanol commercially made in the United States is derived from natural gas.

The process for ETBE production from ethanol is similar to the process used for MTBE, where ethanol reacts with isobutylene over an acidic ion exchange catalyst under similar conditions. However, there are a number of different processes available to convert biomass to ethanol. The conversion to ethanol through dilute acid pretreatment followed by simultaneous saccharification and fermentation (SSF) and distillation were used in the analysis of rice straw, forest residue, and chaparral. An alternative process, concentrated-acid hydrolysis followed by fermentation and distillation, was also examined.

Feedstock for gasoline is crude oil produced domestically and imported from foreign countries. Data characterizing the split between foreign and domestic crude oil supplies to fuel production were used, with regional differences taken into account.

3.4 LCA-SPECIFIC PARAMETERS

3.4.1 Allocation Rules

The production of both ethanol and natural gas-based fuel generates other products, which are recovered and used in other product systems. They are considered as coproducts. The problem is the apportioning or allocating of energy resources, raw materials, pollutants, etc. from the common production steps to the product studied (fuels) and the coproducts. Inputs and outputs of the common steps can be partitioned across the coproducts on various bases, including (for example):

- Mass
- Dry mass
- Energy content
- Energy content

For this analysis, there were three main processes that required allocation. Natural gas production used throughout the life cycle of both systems (but predominantly for methanol) produces sulfur as a coproduct. The emissions and energy use for the production of natural gas and sulfur were allocated on a mass basis (see Section 4.1.1.). Crude oil refining produces a number of petroleum products. This study was mainly interested in one of those products, namely gasoline. Allocation of the refinery energy use and emissions was done based on the process energy requirements of the different products (see Section 4.6.4.). Another process that required allocation was ethanol production. The production of ethanol also produces lignin as a coproduct, which can be used as an energy source. The allocation technique used in the study was to expand the system boundaries to include the use of the lignin residue either for on-site cogeneration or off-site electricity production. In this way the emissions from an alternate energy production method were offset by the use of the lignin. These offset emissions were accounted for as negative values in the life cycle.

3.4.2 Modeling Biomass-Based CO_2 Emissions

All of the content in carbon (C) of the biomass portion of the ethanol is derived from the CO_2 absorbed by plants while growing (photosynthesis). These carbon atoms are released at the end of life of the products, predominantly in the form of CO_2, but also in the form of CO, hydrocarbons or methane (CH_4) molecules. These carbon releases are offset (while not all at the same rate) by the CO_2 uptake or sequestering during plant growth. A distinction was made between net carbon emissions from the production and subsequent combustion of biomass products and carbon emissions from the combustion of fossil fuels. The carbon uptake by plants was accounted for as a credit.

3.5 SUMMARY OF SCOPING DECISIONS AND APPROACHES

Table 7 summarizes the scoping decisions and approaches to be used in this project, which were described in the previous sections 3.1 through 3.4.

Table 7: Summary of Scoping Decisions and Approaches

Element	*Parameter Type*	*Decision or Approach*
Project	Spatial	• Biomass: California • Fuel Production: Worldwide • Fuel use: California
	Temporal	Early part of the 2001 decade
Product	Biomass Scenarios	• Agricultural Residue: Rice Straw • Forest Residue: Thinnings • Brush Growth: Chaparral
	Disposal Alternatives	• Agricultural Residue: Open Field Burning • Forest Residue: Controlled Burning • Brush Growth: Controlled Burning
	Functional Unit	Disposal of a defined quantity of California biomass through the production of fuel oxygenate.
Process	ETBE	• Ethanol: dilute acid pretreatment, followed by SSF • Ethanol: concentrated acid treatment followed by fermentation • ETBE: isobutylene reaction
	MTBE	• Methanol: natural gas feedstock • MTBE: isobutylene reaction
	Gasoline	• Feedstock: domestic plus imports • Refining: Early part of the 2001 decade
LCA	Coproduct Allocation	Mass-based w/ sensitivity analysis; energy based for petroleum products
	Interpretation	Classification and characterization Perform sensitivity analysis on uncertain or variable input parameters

4 MODELING

4.1 OPTION 1: MTBE PRODUCTION + BIOMASS BURNING

The first system (Figure 4) that was modeled consists of a combination of two elements: one liter of oxygenated fuel containing MTBE plus the environmental burdens from the open burning of one metric bone dry ton (MBDT) of biomass. The various components of this system are detailed in the sections below.

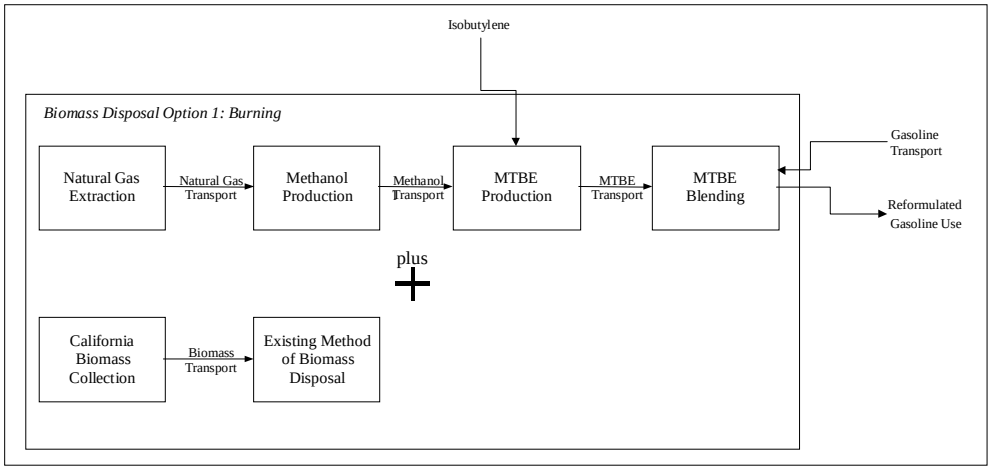


Figure 4: Option 1 Systems

The model for the production of MTBE consists of the production of natural gas, the conversion of the natural gas to methanol, the reaction of the methanol with isobutylene to produce MTBE, and finally the blending of MTBE with gasoline. Isobutylene and gasoline production, as well as the use of the oxygenated fuels, are modeled outside this system.

4.1.1 Natural Gas Production

Raw natural gas is a mixture of hydrocarbons, N_2, CO_2, sulfur compounds, and water. It may have any range of compounds from mostly methane to inert gases, such as nitrogen, carbon dioxide, and helium, and smaller amounts of ethane, propane, and butane. Natural gas may be extracted onshore, offshore, and in conjunction with petroleum extraction processes. The production model is based on data for U.S. production, which were adjusted to represent its use in California to produce methanol. Although some natural gas could be imported into California, foreign production was not studied because of lack of data. The U.S. model is used as a surrogate for foreign production as well. The adjustments for California use entailed modifying the transportation distance of the natural gas and the sweetening of the gas. The methodology, as it is explained below, details the modeling of U.S. average natural gas production.

Natural Gas Extraction

The process energy used to extract natural gas is apportioned among petroleum, natural gas, and natural gas liquids based on the following assumptions [1]:

- Almost all of the natural gas used for fuel goes toward field operations—natural gas lifting and reinjecting. The data in this section correspond with data provided by the Energy Information Administration (EIA). Any energy used to reinject natural gas into wells is excluded from the natural gas precombustion processes, since reinjection is mainly used in oil wells.

- The amount of electricity used for field equipment and processing plants is little relative to the amount of gas they produce. Therefore, all capital equipment is excluded from the study boundaries.

Thus, energy in this model excludes gas reinjection energy requirements. Plant fuel is estimated at 3% of gas input to processing plants [1].

Carbon Dioxide

Carbon dioxide is vented into the atmosphere from the ground during natural gas extraction. The total amount of all non-hydrocarbon gases (CO, CO_2, etc.) removed from raw natural gas is 4.4% of gas production, one-half of which consists of CO_2 (2.2%). Approximately 85% of the CO_2 escapes into the atmosphere.

Other Air Emissions

Other air emissions associated with natural gas extraction are assumed to come from the combustion of diesel oil, crude oil, residual fuel oil, and natural gas in miscellaneous machinery. Emission factors for diesel powered equipment come from AP-42 [2]. Emission data on combustion of the other fuels come from AP-42 and Ecobalance's database.

Natural Gas Venting

The quantity of fugitive methane and methane from venting was accounted for as one module in the model.[7] The following table (Table 8) presents the source of methane and its percentage of gross production:

Table 8: Natural Gas Venting Methane Emissions

Source	***% of total NG produced***
Fugitive Emissions: Equipment Leaks	
---Compressor stations	0.31%
---Production facilities	0.08%
---Gas plants	0.11%
---Metering and pressure-regulating stations	0.14%
---Customer meter sets	0.03%
Fugitive Emissions: Underground pipeline leaks	0.22%
Vented Emissions:	
---Pneumatics	0.21%
---Blow and purge	0.14%
---Dehydrator glycol pumps	0.05%
---Dehydrator vents	0.02%
---Chemical injection pumps	0.01%
TOTAL	1.30%

Glycol Dehydration

Glycol dehydration units are commonly used in natural gas operations to remove water from natural gas streams to prevent corrosion and the formation of hydrates in pipelines. This model takes into account the quantity of triethylene glycol consumed in the process as well as the vented methane emissions from dehydrator glycol pumps.

[7] All vented and fugitive methane emissions are based on a gross natural gas production of 22,130 billion scf in 1992.

Triethylene glycol is used (circulated) for the dehydration process. The amount "consumed" is much less than the circulation rate. More specifically, typical losses of triethylene glycol are normally on the order of 16 kg triethylene glycol/million scm. It should be noted that most of this loss comes from carryover of the triethylene glycol from the glycol dehydrator and into the natural gas pipeline.

Natural Gas Sweetening

Gas sweetening, or the amine process, removes and recovers H_2S. The recovered hydrogen sulfide gas is vented, flared in waste gas flares or modern smokeless flares, incinerated, or utilized for the production of elemental sulfur or sulfuric acid. Emissions due to only venting the gas into the environment are covered in the model. Vented gas is usually passed to a tail gas incinerator in which the H_2S is oxidized to SO_2 and is then passed to the atmosphere out through a stack. Emissions are mostly SO_2 due to the 100% conversion of H_2S to SO_2. Very little particulate and NO_x emissions are generated from this process, so we assume these emissions to be zero. For this model, 10% of total H_2S is vented. The remaining 90% is allocated by mass to the production of a sulfur-bearing coproduct such as sulfuric acid or liquid sulfur dioxide.

In terms of the question of what gas produced goes through the sweetening process, it is assumed that all gas is sweetened. Natural gas is considered "sour" if hydrogen sulfide is present in amounts greater than 0.065 g/sm^3 natural gas [2]. Hydrogen sulfide content was based on California production.

Transportation

Natural gas is transported by way of high-pressure transmission lines. Compressors along these lines may be powered from different sources: gas-fueled reciprocating engines and gas turbines, and electric motors. Emissions are all different due to the different sources of power in the compressors.

Gas turbines and compressor engines are modeled in this study, but electric motors are neglected from the model for the following reason [1]. Averaging out the percentage horsepower for each type of power source for the pipeline, it was found that:

Turbines:	24.2%
Engines:	73.4%
Electric:	2.5%

Since electric power is so little relative to the other compressors (2.5%), it is included in the turbine and engine values.

The quantity of natural gas consumed to transmit the natural gas product is assumed to be, on average, 4% of the product. This percentage was obtained by dividing "pipeline fuel" by "total delivered [natural gas] to customers" for several states [3]. The total fuel consumed for transport as a U.S. average comes from taking 4% of the total U.S. Interstate movements [3].

The criteria pollutant emission factors were obtained and averaged together from AP-42 and GRI-95/0270.1 [4]. AP-42 presents emission factors for each of four technologies: gas turbines, 2-cycle lean-burn engines, and 4-cycle lean- and rich-burn engines. The GRI-95/0270.1 report, in its description of host sites for data collection, describes the market share of the engines in the gas transmission service. As a result, the emission factors from AP-42 were incorporated with GRI-95/0270.1 and recorded as a weighted average of the technologies according to the following market share breakdown:

- Gas Turbine: 10%
- 2-Cycle Lean Burn: 48% (53% * 90%)
- 4-Cycle Lean Burn: 21% (47% * 90% divided by 2)
- 4-Cycle Rich Burn: 21% (47% * 90% divided by 2)

There were no available data regarding what percentage of these technologies had pollution control equipment, so emission factors for controlled and uncontrolled technologies for CO_2, NO_x, CO, total non-methane organic

compounds, CH_4, and PM-10 are averaged together where data are available. The technologies with pollution controls were averaged without a weighting factor.

4.1.2 Methanol Production

Methanol is produced via the reforming of natural gas, through a series of four steps: reforming, compression, synthesis, and purification. At the beginning of the process, the influx of raw natural gas is mixed with gas that has recycled through the system. This mixture passes first through a centrifugal compressor, and then, if necessary, through a steam turbine. As it exits, the pressurized gas is preheated through heat exchange with the reactor effluent, and then the stream is split into two flows.

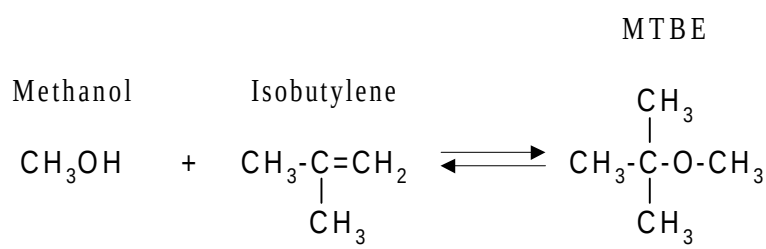
When leaving the reactor, the gas flow is initially cooled by a heat exchange with the gas entering the reactor and the water used for the high pressure steam generators, and then by passing through a condenser where the methanol and water condense. This condensate moves on to a pressurized chamber, where the gas and liquid constituents are separated. The gas fraction is mostly recycled, and the raw methanol has the gas removed and is then distilled. In order to reach the level of purity required for MTBE production, the raw methanol passes through two separation columns to remove the lighter elements (gas, ethers, ketones...), the heavier alcohols, and the water. The emissions resulting from the production of methanol are limited, mainly some traces of alcohol (about 0.5% of the overall finished product) in the wastewater. The inputs for methanol production are shown in Table 9.

Table 9: Inputs for Methanol Production

	Input *(per Kilogram Methanol)*
natural gas -	
fuel (kg)	0.36
raw material (kg)	0.55
electricity (MJ)	0.16

4.1.3 MTBE Production

Methyl tertiary-butyl ether is produced through a catalytic reaction between methanol and isobutylene over an acidic ion exchange resin:



The process also leads to side reactions,

Isobutylene + water ⟷ Tertiary Butyl Alcohol (TBA)

Methanol +methanol ⟷ water + Dimethyl Ether (DME)

Isobutylene + isobutylene ⟷ Di-isobutylene (DIB)

but conditions are controlled so that the selectivity of isobutylene and methanol to MTBE is very high. TBA, DME and DIB make up only a total of 0.6% of the outflow by weight. The presence of these coproducts has no adverse effect on the quality of the MTBE, since they are also acceptable octane gasoline components.

Even though most of the MTBE used in the California is actually produced out of state, it is assumed that the ETBE that is produced from biomass is only replacing the MTBE produced in California (15% of total demand). This is because the infrastructure for producing the remaining ETBE has not been determined. An analysis of the factors that would affect an increase in production capacity is beyond the scope of this study. Therefore, the baseline model only reflects MTBE produced in state, and oxygenate transport from non-local refineries is not included. (The case of producing 100% of total oxygenate demand is analyzed as a separate case in the sensitivity analysis.) California MTBE production is defined as a blend of two separate processes that differ mainly by the type of finishing reaction.

The first process (Figure 5) consists of an expanded bed front reactor and a fixed bed finishing reactor [5]. Most of the conversion occurs in the main reactor, which contains the catalyst. Unconverted methanol is recycled via a final methanol recovery step that consists of washing of the outflow to remove the methanol from the C_4 raffinate, followed by a fractionation of the methanol/water mixture.

The second process (Figure 6) consists of an expanded bed front reactor with catalytic distillation as the finishing reaction. As with the first process, most of the conversion of isobutylene occurs in the main reactor.

As shown in Table 10, both of these reactions consume similar amounts of electricity, steam, and cooling water; their difference is more apparent in the rate at which they convert isobutylene to MTBE.

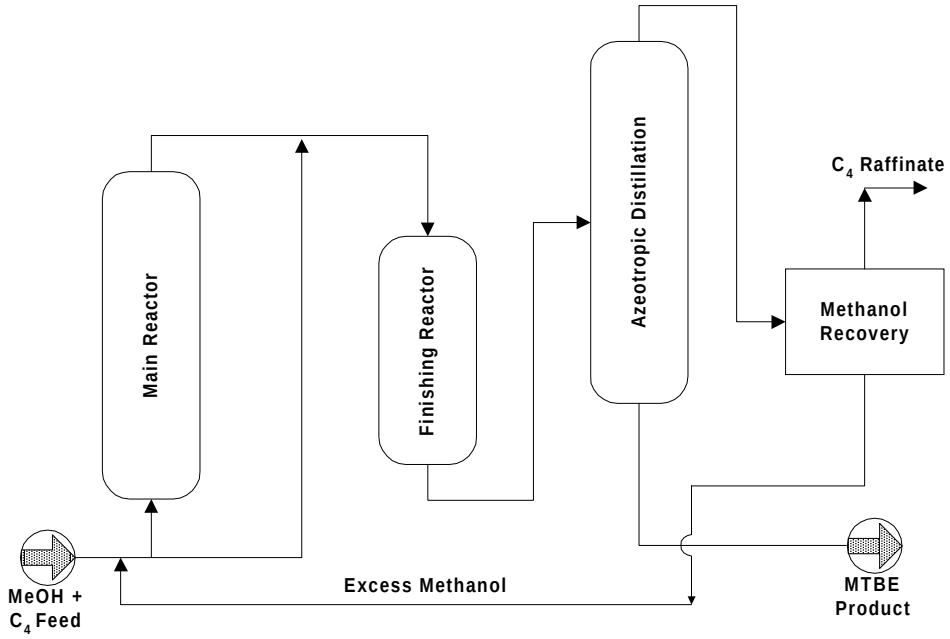


Figure 5: Fixed Bed Finishing Reactor

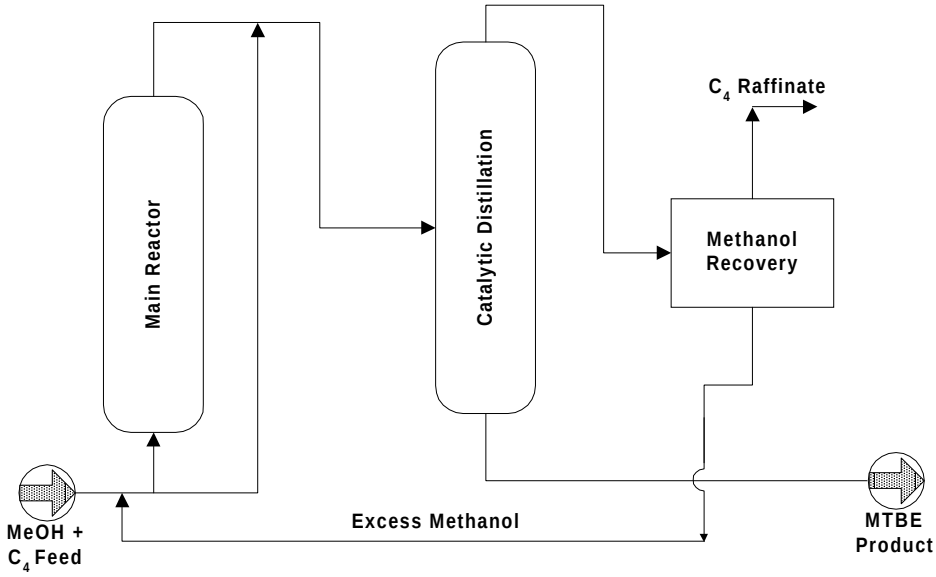


Figure 6: Catalytic Distillation Finishing Reactor

Table 10: Inputs for MTBE Production

Input	*Fixed bed finishing reactor*	*Catalytic distillation finishing reactor*
Isobutylene conversion	97 %	98 %
Electricity	234 MJ/h	234 MJ/h
Steam	5.5 t/h	5.5 t/h
Cooling water	300 m^3/h	300 m^3/h

Values are given for a rate of 40,000 metric tons of MTBE produced per year.

4.1.4 MTBE Blending

It is assumed that the MTBE is matched with the gasoline it is blended with to produce the appropriate oxygenated fuel. No emissions are assumed from blending.

4.1.5 Biomass Burning

The standard disposal option for the three biomass types being examined (rice straw, forest residue, and chaparral) was determined to be burning. The type of burning depends on the actual biomass type: open-field burning for rice straw and prescribed burning for forest residue and chaparral. The pollutant emissions for each scenario were calculated using emission factors provided by the U.S. EPA and CARB. Carbon dioxide emissions for each scenario were based on the estimated carbon contents of the biomass types.

Forest Residue Burning

Prescribed burning is a land treatment, used under controlled conditions, to accomplish natural resource management objectives. Prescribed fire is a cost-effective and ecologically sound tool for forest management. Its use reduces the potential for destructive wildfires. The major concern derives from the smoke produced, which is a mixture of carbon, tars, liquids, and different gases. This open burning produces particles of widely ranging sizes, depending to some extent on the rate of energy release of the fire.

In order to model the open burning of forest residues, emission factors from the U.S. EPA's AP-42 [2] were used.[8] Wildfire emission factors were used as a good representation of the emissions from prescribed burning.[9] Emissions from the harvesting of the forest residue were also included in the model. The emission factors gave data for emissions specific to California forests (Table 11). While the feedstock for the production of ethanol is set as a mix of 30% ponderosa pine and 70% white fir by weight, it is assumed that the emissions are independent of the type of tree that is burned.

Table 11: Emission Factors for Forest Residue Burning

Geographic Area	***Wildfire Fuel Consumption*** (MBDT/hectare)	***Emission Factors*** (kg/MBDT)			
		Particulates	***CO***	***VOCs***	***NO_x***
California	44	9.5	77.8	13.3	2.2

Rice Straw Burning

The emissions from the open burning of rice straw were the driving concern behind this study, therefore open-field burning is set as the disposal option. The practice has been studied extensively, and emission factors have been calculated by CARB (Table 12), based upon a standard field density of 6.7 metric tons of rice straw per hectare [6]. No harvesting of the rice straw was assumed to take place, so emissions come only from the open burning of the material.

Table 12: Emission Factors for Rice Straw Burning

	PM 10	***VOC***	***NO_X***	***SO_X***	***CO***
Emission Factors (kg/hectare)	23.3	5.8	19	4.1	211
Emission Factors (kg/MBDT)	3.7	1.0	3.1	0.7	34.7

Chaparral Burning

The burning of chaparral is assumed to include the cutting and piling of the biomass prior to open burning. The emissions for open burning only were modeled using emission factors given by the U.S. EPA [2].[10] Data on emissions for the harvesting of chaparral (diesel chainsaw use, for example) were included in the model. The following table (Table 13) outlines the emission factors that were used for chaparral open burning:

Table 13: Emission Factors for Chaparral Burning

	Pollutant (kg/MBDT)					
	Particulate Matter			***Carbon Monoxide***	***Volatile Organics***	
Fuel Configuration	***PM- 2.5***	***PM- 10***	***Total***		***Methane***	***Nonmethane***
Chaparral shrub	11	12	23	111	5.0	13.8

[8] Wildfire and prescribed burning emission factors were used.

[9] Many large wildfires occur when there is low humidity and dry fuel, and they are wind driven with lots of oxygen (less smoke per fuel unit) during hot weather and deep mixing, with very hot burn temperature causing a high venting height. Frequently the emissions are transported far over the heads of people into higher levels of the atmosphere.

[10] Wildfire and prescribed burning emission factors were used.

4.2 OPTION 2: ETBE PRODUCTION FROM BIOMASS

The second disposal option (Figure 7) assumes that rather than disposing of the biomass, it is converted to ethanol and subsequently to ETBE, which is blended with gasoline. The use of ETBE as an oxygenate is assumed to replace the use of MTBE in gasoline.

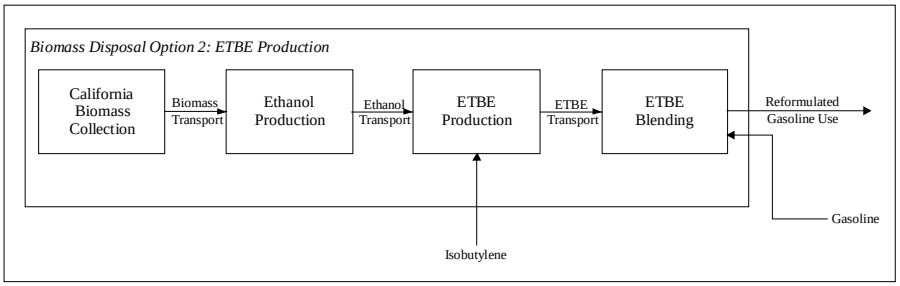


Figure 7: Option 2 Systems

4.2.1 Biomass Harvesting

Biomass harvesting is defined in the model as the fuel (energy) use and emissions from the gathering of the biomass and its transport to an ethanol production plant. Emissions data for diesel equipment were taken from the Ecobalance database and emissions from gasoline equipment were modeled using the AP-42 emission factors for light-duty truck use at low altitude. Detailed maps outlining the distribution of biomass throughout the state of California are provided in Appendix C.

Forest Residue Harvesting

The area where forest residue is harvested was modeled as a 35-mile radius circle around the site of the ethanol plant, and transportation emissions were calculated for 1 vehicle round trip. The collection data are assumed to be representative of the Quincy area (Northeast Plateau on the map). The equipment (and source of emissions) consists of two feller-bunchers, two grapple skidders, one whole tree chipper, and associated support equipment for road maintenance, equipment maintenance, moving equipment, and transportation of processed forest residue (chips). The average production rate was calculated to be nine loads per day at approximately 11.8 MBDT per load, yielding 106.3 MBDT per day.

Rice Straw Harvesting

The rice fields are assumed to be 20 miles from the ethanol production plant, and transportation emissions were modeled for one vehicle round trip. The data for rice straw are representative of the Sacramento area. The equipment that is used during harvesting includes one tractor with rake, one tractor with big bale baler, one loader and associated support equipment for equipment maintenance, and transportation of baled rice straw. According to the data, on average, 9.1 MBDT of rice straw are baled per hour, amounting to 127.3 MBDT per day.

Chaparral Harvesting

The chaparral data are assumed to come from the South Coast Air Basin. Transportation emissions were modeled for 1 vehicle round trip assuming that the ethanol production plant is located 30 miles from the chaparral growth area. The data cover the clearing of a 40.5-hectare plot, yielding 1,181.2 MBDT of chaparral. The clearing of chaparral requires a 16-man crew with 4 chainsaws, 1 chipper, 1 front-end loader, and associated support equipment for moving equipment, equipment maintenance, and transportation of the processed chaparral residue (chips). About 0.2 hectares is cleared per day, with a yield of about 5.9 MBDT of chaparral per day.

Table 14: Summary of Fuel Consumption for Biomass Harvesting

Biomass Harvested	***Fuel Consumption*** (liters/day)	***Biomass Harvested*** (MBDT/day)	***Specific Fuel Consumption*** (liters/MBDT)
Rice Straw	769.9	127.3	6.0
Forest Residue	1,910.3	106.3	17.9
Chaparral	163.8	5.9	27.8

The MBDT/day values in Table 14 were used to generate data on a unit MBDT basis and do not reflect total possible production rates.

4.2.2 Ethanol Production

Ethanol production from corn is a well-established technology with several plants located in the Midwestern United States. Using lignocellulosic biomass as a substrate to make ethanol is also a promising approach. Many sources of lignocellulosic biomass, such as agricultural residues, forestry residues, pulp and paper waste streams, and municipal solid waste, are abundant and underutilized resources, which can be converted to ethanol. Woody and herbaceous energy crops such as hybrid poplar and switchgrass can also be used as renewable resources for ethanol production.

The three biomass types chosen for this study are all lignocellulosic feedstocks, their primary organic components being cellulose, hemicellulose, and lignin. Figure 8 through Figure 10 show the approximate distribution of these components in these types of biomass. The detailed compositional analyses of these feedstocks are shown in Table 15, Table 16, and Table 17. It should be added that rice straw and forest residue have been studied as possible feedstocks for ethanol production, whereas chaparral has not been. Furthermore, the low sugar contents, combined with high lignin and extractives contents, make chaparral a technically challenging feedstock.

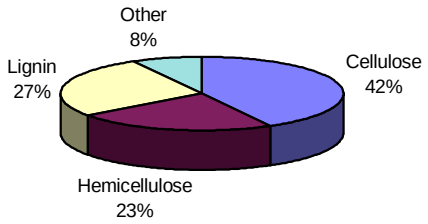


Figure 8: Composition of Forest Residue Feedstock

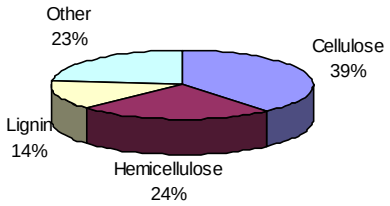


Figure 9: Composition of Rice Straw Feedstock

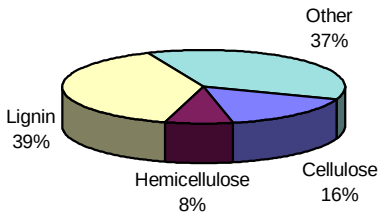


Figure 10: Composition of Chaparral Feedstock

Table 15: Forest Residue/Thinnings Composition—Whole Tree Chips

Feedstock Component	***White Fir*** (dry wt %)	***Ponderosa Pine*** (dry wt %)	***70/30 Mixed Feedstock*** (dry wt %)
Glucan	43	38	40.5
Mannan	11	10	10.5
Galactan	3	5	4.0
Xylan	6	6	6.0
Arabinan	2	4	3.0
Lignin	28	25	26.5
Extractives	5	10	7.5
Ash	2	2	2.0
Total	*100*	*100*	*100*

Table 16: Rice Straw Composition

Feedstock Component	***Dry wt %***
Glucan	39.0
Galactan	0.5
Mannan	0.0
Xylan	20.5
Arabinan	3.4
Lignin	13.6
Extractives & other	5.0
Ash	18.0
Total	*100*

Table 17: Chaparral Composition—Whole Tree

Feedstock Component	***Chemise*** (dry wt %)	***Hoaryleaf Ceanothus*** (dry wt %)	***Scrub Oak*** (dry wt %)	***Black Sage*** (dry wt %)	***50/25/20/5 Mixed Feedstock*** (dry wt %)
Glucan	16.8	9.7	14.2	12.0	12.5
Mannan	2.8	2.0	5.9	3.0	2.9
Galactan	0.0	1.5	2.1	0.6	0.8
Xylan	8.6	1.7	4.4	6.1	5.4
Arabinan	2.9	1.6	2.8	1.9	2.1
Lignin	36.2	40.7	29.7	40.2	39.0
Extractives	19.2	29.4	21.2	21.6	23.1
Ash	3.0	2.8	8.1	3.5	3.5
Other	10.6	10.5	11.5	10.9	10.8
Total	*100*	*100*	*100*	*100*	*100*

The production of ethanol from biomass requires the following basic steps: pretreatment to hydrolyze the hemicellulose, hydrolysis of cellulose to produce glucose, fermentation of sugars to ethanol, and ethanol recovery. There are different process configurations, both enzyme based and non-enzyme based, that can be used to achieve the overall goal. In the non-enzyme based approach, acid is used for both hemicellulose and cellulose hydrolysis, and the mode is separate hydrolysis and cofermentation (SHCF); cofermentation refers to the fermentation of both six-carbon (hexoses, i.e., glucose, mannose, and galactose) and five-carbon (pentoses, i.e., xylose and arabinose) sugars to ethanol. In the enzymatic approach, dilute-acid pretreatment is used to hydrolyze the hemicellulose portion. The saccharification (hydrolysis) of cellulose to cellobiose and eventually to glucose is catalyzed by the synergistic action of cellulase and β-glucosidase enzymes. The mode of operation used is simultaneous saccharification and cofermentation (SSCF). In this study the following different biomass-to-ethanol conversion technologies are used:

- Concentrated sulfuric acid process
- Enzyme-based process.

The flow diagrams for the two technology options are shown in Figure 11 and Figure 12, and process descriptions are provided below.

Concentrated Acid Process

Arkenol, Inc. of Mission Viejo, California, has developed an improved version of the concentrated acid hydrolysis technology. The acid-based technology presented in this report is similar to the Arkenol technology. However, the process was independently modeled by NREL using the Aspen® simulator, and the estimates for inputs and outputs presented in this report may not necessarily reflect those that would be developed by Arkenol.

The concentrated acid process consists of four basic unit operations:

1) Hydrolysis
2) Separation of the acid and sugars
3) Ethanol fermentation
4) Product purification

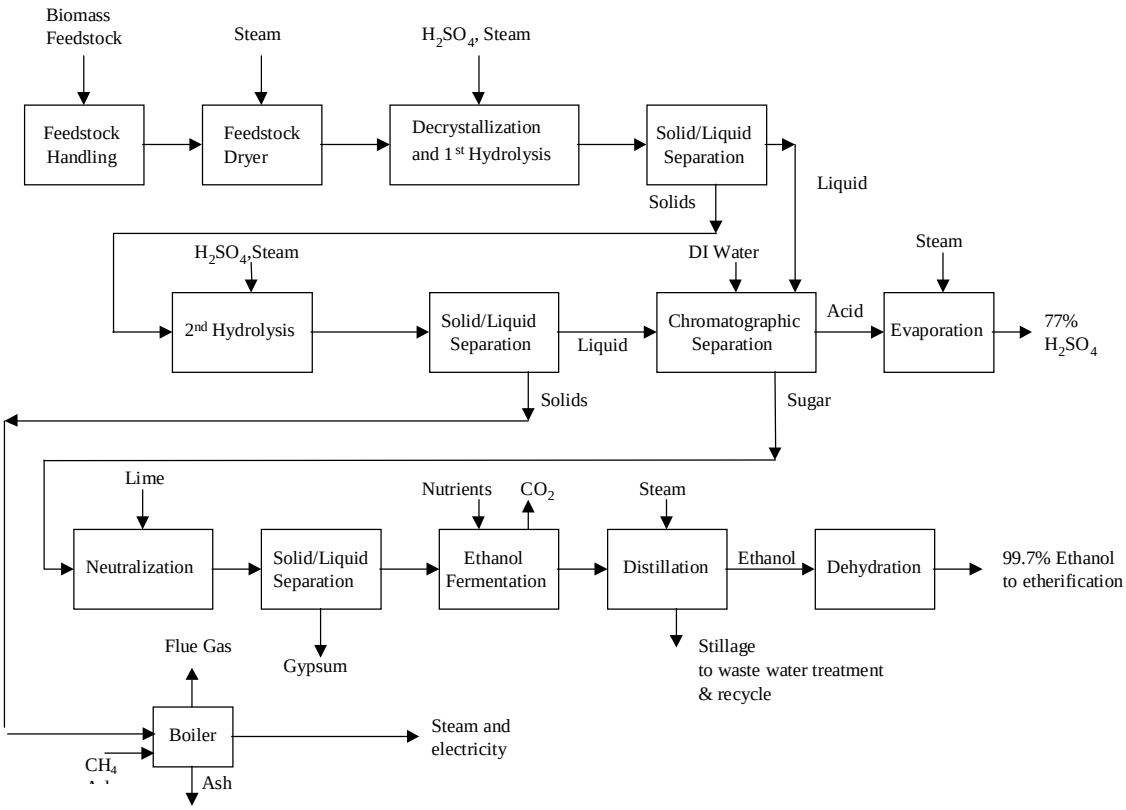


Figure 11: Concentrated Acid Process Flow Diagram

Decrystallization and First Hydrolysis

Prior to acid hydrolysis, the biomass is dried to a moisture content of approximately 10% and milled to an average size of 15 mm. The feedstock is mixed with concentrated sulfuric acid at a concentration of 70%-77%. The sulfuric acid to C+H ratio is 1.25 to 1. This step results in the disruption of the bonds between the crystalline cellulose chains, making the long chain cellulose accessible for hydrolysis. The resulting acid concentration is 30%. The decrystallization is performed at temperatures in the range of 30° to 50°C. The addition of acid to the biomass results in the formation of a thick gel. In the first hydrolysis, the mixture of acid and biomass is heated to 100°C for 60 minutes to hydrolyze the cellulose. The resulting gel is pressed to obtain an acid-sugar stream (approximately 17% sugar and 35% acid, depending on feedstock composition).

Second Hydrolysis

The solids remaining after the first hydrolysis and solid/liquid separation are mixed with concentrated sulfuric acid until a concentration of 30% acid is again reached. The second hydrolysis step is very similar to the first hydrolysis step. The mixture is heated for 50 minutes at 100°C to effect further cellulose hydrolysis. The resulting gel is pressed to obtain a second acid-sugar stream (approximately 18% sugar and 30% acid, depending on feedstock composition), and the streams from the two hydrolysis steps are combined. The remaining lignin-rich solids are collected and optionally pelletized for fuel.

Chromatographic Separation of Acid and Sugar

The acid-sugar stream is further processed through a chromatographic separation column packed with a strong-acid polystyrene-divinylbenzene resin. Water is used as an eluant. As a result of this chromatographic separation process,

two streams are collected: the 25% concentrated acid stream and the 12%-15% concentrated sugar stream. The sugar recovery is 95% whereas the acid recovery is 98%. The acid stream is concentrated and recycled. The sugar stream, which contains no more than 1% acid, can then be fermented after the pH has been adjusted. Residual acid in the sugar stream is neutralized by adding lime, which forms a gypsum precipitate. Gypsum is removed in a solid/liquid separation step. This neutralization has the added benefit of precipitating unwanted metal hydroxides and other fermentation inhibitors.

Concentration and Recycling of Acid

The acid solution recovered from the separation unit can be concentrated and recycled to the earlier stages of the process. Concentration of the acid to 70%-77% is achieved through the use of a triple effect evaporator.

Fermentation

A recombinant *Zymomonas mobilis* can be used to ferment both six-carbon and five-carbon sugars. However, *Z. mobilis* is not suitable for softwood conversion, as this bacterium does not ferment mannose and galactose, two major hemicellulosic sugars prevalent in softwoods. A recombinant xylose-fermenting yeast can be used in the case of forest residue or thinnings. Recombinant *E. coli* and *Klebsiella oxytoca* are also possible choices.

An appropriate ethanologen is mixed with nutrients and added to the sugar solution where it efficiently converts both six-carbon and five-carbon sugars to ethanol and carbon dioxide.

The SHCF is carried out in continuous, anaerobic, fermenters. The flow of fermentation broth between fermenters is facilitated by gravity. Fermentation off gases, containing mostly carbon dioxide and ethanol vapor, are sent to the vent scrubber for ethanol recovery. The fermentation broth is sent to the distillation section for ethanol recovery.

Distillation and Ethanol Dehydration

Ethanol is separated from the fermentation beer by conventional distillation technology and dehydrated with conventional molecular sieve technology. The 99.7% ethanol is sent to the ETBE section. The stillage from the distillation column is sent to wastewater treatment and recycle.

Ligneous Residue

The ligneous residue, containing mostly lignin and cellulose, removed after the second hydrolysis step is pH adjusted and burned on-site to cogenerate steam and electricity that can be used by the process. A supplemental fuel is needed to generate steam needed by the process. The net electricity produced for this process is zero for all the three feedstocks. Alternatively, the residue can be sold as fuel to a nearby biomass-power plant. This option was studied as part of the sensitivity analysis.

Data Summary for Concentrated Acid Process

The estimates of inputs and outputs for the process were developed using an Aspen®-based model and are shown in Table 18. The plant capacity was assumed to be 800 metric tons/d of dry feedstock.

Enzymatic Process

A generalized process was modeled based on *Trichoderma reesei*-derived cellulases for cellulose hydrolysis and an appropriate recombinant ethanologen for cofermentation of six-carbon and five-carbon sugars to ethanol. The enzyme-based process consists of four basic unit operations:

1) Pretreatment
2) Cellulase production
3) Ethanol production
4) Product purification.

Table 18: Data Summary for Concentrated Acid Process

Environmental Flows	***Rice straw*** kg/kg biomass	***Softwood*** kg/kg biomass	***Chaparral*** kg/kg biomass
Inputs			
Biomass	1.000	1.000	1.000
Lime	0.025	0.025	0.025
Water	5.892	5.139	4.975
NH_3	0.001	0.001	0.000
Diesel	0.003	0.003	0.001
CSL	0.035	0.034	0.034
H_2SO_4	0.051	0.045	0.047
Natural gas	0.279	0.187	0.119
Outputs			
Ethanol	0.223	0.222	0.083
Gypsum	0.059	0.058	0.058
Ash	0.176	0.020	0.034
Ligneous Residue	0.383	0.345	0.494
Wastewater	4.544	4.400	4.653
CO_2	1.776	1.878	1.772

Feedstock Preparation and Pretreatment

The biomass is milled to an average size of 15 mm. A screw feeder conveys the biomass from the storage bunker to the acid impregnator. Dilute sulfuric acid and low-pressure steam are also fed to the acid impregnator. The acidic slurry is discharged from the acid impregnator into the pretreatment reactor. High-pressure steam and additional dilute sulfuric acid are fed to the reactor where hemicellulosic sugars are hydrolyzed to their respective monomers/oligomers (temperature = 160°–180°C, liquid phase acid concentration = 0.7%–1.0% wt.).

The hydrolyzed mash is discharged from the acid hydrolysis reactor into the lower-pressure flash drum where cooling quenches the reactions. The hydrolyzate is separated from the solids in a solid/liquid separation step. The hydrolyzate is then pumped to the neutralization and detoxification section. This involves continuous ion exchange using a weak-base anion resin followed by overliming. The process primarily removes acetic acid and other species that could be toxic to the microorganisms used.

Lime is used to neutralize the detoxified hydrolyzate; the neutralization reaction produces calcium sulfate, which is removed in a solid/liquid separation step. The neutralized hydrolyzate is pumped through a heat exchanger where it is cooled using cooling tower water to fermentation temperature. The hydrolyzate and solids from the solid/liquid separation step are then pumped to the ethanol fermentation section.

Cellulase Production

Cellulase production is by *T. reesei* using a slipstream of pretreated biomass as a carbon source. The fermentation is conducted in a fed-batch mode at 28°C and pH 5. Corn steep liquor is used as a source of nitrogen and micro-nutrients. For a low-cost product such as ethanol, the enzyme need not be processed to any great extent to be useful. Whole broth from cellulase fermentation is actually more effective for the SSCF process. In this process, the whole fermentation broth is used as a source of cellulase enzyme. Because enzyme production is via the fed-batch mode and the SSCF is a continuous process, a surge storage tank is necessary. It is assumed that cellulase production using pretreated forest thinnings, rice straw, and chaparral as substrates is feasible.

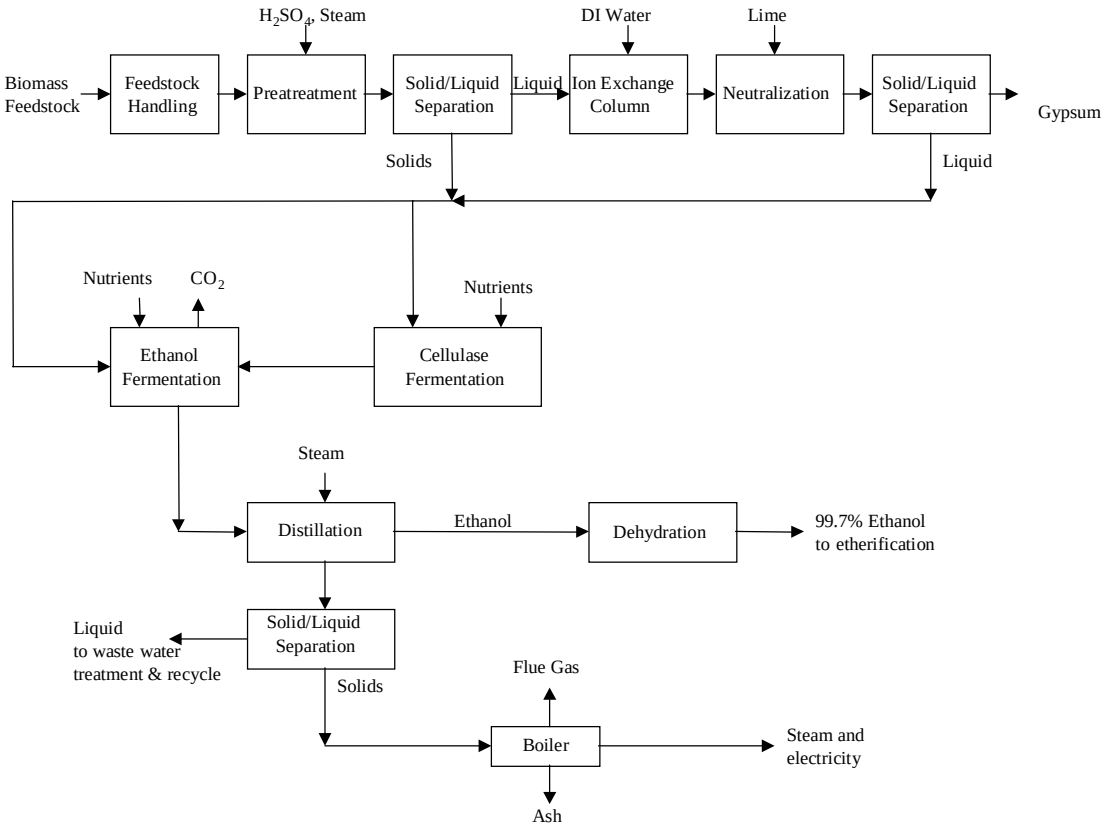


Figure 12: Enzymatic Process Flow Diagram

Ethanol Production

The simultaneous saccharification and cofermentation process converts cellulose and five-carbon sugars to ethanol and carbon dioxide. Cellulase catalyzes the hydrolysis of cellulose to glucose. A recombinant *Z. mobilis* can be used to ferment both six-carbon and five-carbon sugars for rice straw and chaparral, and recombinant xylose-fermenting yeast (or rDNA *E. coli* or *K. oxytoca*) can be used with forest thinnings.

The SSCF operation takes place in continuous anaerobic fermenters. Gravity drives the flow of fermentation broth between fermenters. Fermentation exhaust gases consisting of carbon dioxide and ethanol vapor are sent to the vent scrubber for ethanol recovery. The SSCF broth is pumped to the distillation section for the recovery of ethanol.

Distillation and Ethanol Dehydration

The fermentation broth is sent to the distillation section. Ethanol is separated from the fermentation beer by conventional distillation technology and dehydrated using conventional molecular sieve technology. The still bottoms are collected and the 99.7% ethanol is sent to the ETBE section. The lignin residue is further dewatered in a solid/liquid separation step. The liquid stream is sent to wastewater treatment and recycle.

Ligneous Residue

The dewatered ligneous residue is burned on-site to cogenerate steam and electricity that can be used by the process. With most feedstocks, excess electricity is generated, which can be sold. (Due to its high ash and low lignin contents, rice straw needs a supplemental fuel to generate steam needed by the process.) As in the acid process, the residue can alternatively be sold as fuel to a nearby biomass-power plant. This option was considered in the sensitivity analysis.

Data Summary for Enzymatic Process

The estimates of inputs and outputs for the process were developed using NREL's Aspen®-based model, with technology targets established for the early part of the next decade (see Table 19). The plant capacity was assumed to be 800 metric tons/d of dry feedstock.

Ligneous Residue

The ligneous residue recovered is burned on-site to cogenerate steam and electricity, which is used by the process. In some cases, the excess electricity can be sold. As an option, this residue can be sold as fuel to an existing biomass-power plant in the vicinity. Table 20 provides a list of some of the waste-to-energy plants in California, with information on the MW of power generated and the county where the plant is located. This alternative was examined as part of the sensitivity analysis. If this residue is sold, the electricity and steam required by the process will need to be imported.

Sulfuric Acid

The production of sulfuric acid (H_2SO_4) was modeled based on the contact process according to the following reactions:

$$2\ SO_2 + O_2 \rightarrow 2\ SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Emissions information is based on data collected from a number of production plants worldwide, as well as engineering calculations.

Table 19: Data Summary for Enzymatic Process

Environmental Flows	***Rice straw*** kg/kg biomass	***Forest Residue*** kg/kg biomass	***Chaparral*** kg/kg biomass
Inputs			
Biomass	1.000	1.000	1.000
Lime	0.002	0.002	0.001
Water	4.522	3.753	5.254
NH_3	0.003	0.004	0.001
Diesel	0.006	0.006	0.002
CSL	0.018	0.019	0.019
H_2SO_4	0.000	0.000	0.000
Natural gas	0.041	0.000	0.000
Outputs			
Ethanol	0.248	0.272	0.093
Gypsum	0.004	0.004	0.003
Ash	0.178	0.021	0.035
Ligneous Residue	0.453	0.435	0.578
Wastewater	2.024	2.033	2.078
CO_2	1.236	1.373	2.492
	MJ/kg biomass	MJ/kg biomass	MJ/kg biomass
Net electricity	0.67	0.00	3.54

Table 20: Waste-to-Energy Plant Locations in California

Plant Name	*Fuel Source (Cogen)*	*Online* (MW)	*County*
Wheelebrator-Shasta	Biomass	50	Anderson
Georgia Pacific (Martell)	Biomass - Woodwaste	9.0	Amador
Martell Cogeneration	Biomass - Woodwaste (Cogen)	18.0	Amador
Pacific Oroville Power	Biomass - Ag. & Woodwaste	18.0	Butte
Koppers Industries	Biomass - Woodwaste (Cogen)	6.0	Butte
Waldham Energy	Biomass - Ag. Waste	26.5	Colusa
Western Rock Products	Biomass	0.250	San Bernardino
Big Valley Lumber	Biomass - Woodwaste (Cogen)	5.0	Lassen
Honey Lake Power	Biomass - Woodwaste (Cogen)	30.0	Lassen
Mt. Lassen Power	Biomass - Woodwaste (Cogen)	10.5	Lassen
Sierra Pacific Industries (Susanville)	Biomass - Woodwaste (Cogen)	15.0	Lassen
Lincoln Cogeneration	Biomass - Woodwaste (Cogen)	7.5	Placer
Rio Bravo Rocklin	Biomass - Woodwaste	25.0	Placer
Collins Pine	Biomass - Woodwaste (Cogen)	12.0	Plumas
Sierra Pacific Industries (Quincy)	Biomass - Woodwaste (Cogen)	20.0	Plumas
Mecca Plant	Biomass - Ag. & Woodwaste	49.9	Riverside
Sierra Pacific Industries (Loyalton)	Biomass - Woodwaste (Cogen)	20.0	Sierra
Woodland Biomass	Biomass - Ag. & Woodwaste	25.0	Yolo

Corn Steep Liquor

Corn steep liquor production involves the steeping of harvested corn for a period of from 24 to 48 hours in a light sulfurous acid solution. The burdens from the production of corn were allocated according to the mass of corn matter that stays in the steeping liquor after the corn is removed. Other allocation methods could be used including allocation based on the economic value of the coproducts. Different allocation methods could effect the results of the study in terms of nitrate emissions. Most of the nitrate emissions for the overall study are due to growing the corn necessary to produce the CSL.

The production of sulfurous acid was assumed to be negligible. The only emissions from the steeping process consist of SO_x emissions from the steeping tanks. Emission factors from the U.S. EPA AP-42 were used.

Lime

The production process for lime was modeled to include the following steps:

- Limestone extraction
- Limestone crushing
- Limestone calcination: $CaCO_3 \rightarrow CaO + CO_2$

The transport of limestone to the calcination facility was not taken into account, since it was assumed to be inconsequential. Limestone crushing yields 50% in mass of small pieces (coproducts) which are sold. Electricity consumption for crushing was allocated on a mass basis. Emission data were gathered from a major European lime producer.

Ammonia

The production of synthetic anhydrous ammonia is modeled as using a natural gas reforming process, in which natural gas used as feedstock (and fuel). It was assumed that the natural gas consumption consists of:

- 60% feedstock (the feedstock value of the ammonia = 23.61 MJ)
- 40% fuel

There is no CO_2 recovery from the reforming process. Energy requirements for the process are based on Fertilizer Institute data [7]. Air emissions were modeled using AP-42: process emissions plus emissions from a Natural Gas industrial boiler.

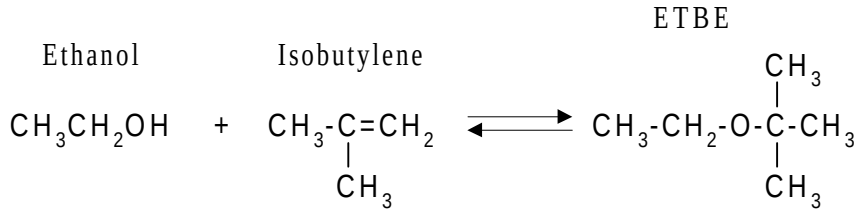
4.2.3 ETBE Production

As was explained in the section on MTBE modeling (section 3.1.7), the production capacity of ETBE in the state of California is limited to 15% of California's oxygenate demand, namely due to the limited availability of isobutylene and the small number of facilities. Therefore, even if there is sufficient biomass to produce enough ETBE to completely replace the MTBE that is consumed, there is currently no way of producing more than 15% of the total demand in state. For the production of the remaining 85% of demand, there are a number of options:

1) The remaining ETBE would be produced out of state, requiring shipping the ethanol to Texas, and subsequent shipping of the ETBE back to California.
2) The construction of additional plants in California to meet the remaining 85% of demand, which would also require the importation of sufficient isobutylene.
3) The construction of new plants that have a combined paraffin isomerization/etherification process, such as the STeam Active Reforming—or the "STAR"—process and the High Conversion Etherification Process patented by Phillips Petroleum [8]. The process allows for the conversion of California sources of butane to isobutylene for use during the ETBE production process.

Since these decisions have an economic basis, the best decision is beyond the scope of this study, and it is assumed that the model only reflects the production of enough ETBE to replace the MTBE produced in California. This is consistent with the near-term scope of this study.

Since thermodynamics do not favor the production of ETBE, there is a less efficient use of isobutylene in the model. The reaction for producing ETBE is as modeled below:



As with the production of MTBE, this process leads to side reactions,

Isobutylene + water	$\longleftrightarrow$	Tertiary Butyl Alcohol (TBA)
Ethanol +Ethanol	$\longleftrightarrow$	water + Diethyl Ether (DEE)
Isobutylene + isobutylene	$\longleftrightarrow$	Di-isobutylene (DIB)

but conditions are controlled so that the selectivity of isobutylene and ethanol to ETBE is very high. TBA, DEE and DIB make up less than 1% of the outflow by weight. The presence of these coproducts has no adverse effect on the quality of the ETBE, since they are also acceptable octane gasoline components.

The azeotropic properties of ethanol with C_4 compounds widely differ from those of methanol. The excess ethanol feeding the reaction is therefore mostly recovered with the ETBE product. Ethanol free ETBE is produced by the addition of an ethanol separation step: distillation, adsorption, and extraction. Removal of ethanol from the C_4 raffinate is achieved via an ethanol recovery section similar to that used in the MTBE model. The inputs for ETBE production are given in Table 21.

Table 21: Inputs for ETBE Production

Input	*Fixed bed finishing reactor*	*Catalytic distillation finishing reactor*
Isobutylene conversion	92 %	95 %
Electricity	234 MJ/h	234 MJ/h
Steam	5.5 t/h	5.5 t/h
Cooling water	300 m^3/h	300 m^3/h

Values are given for a rate of 40,000 metric tons of ETBE produced per year.

4.2.4 ETBE Blending

It is assumed that the ETBE is matched with the gasoline it is blended with to produce the appropriate oxygenated fuel. No emissions are assumed from blending.

4.3 ISOBUTYLENE PRODUCTION

Isobutylene is normally obtained from a C_4 fraction that results from the cracking of petroleum fractions and natural gas. This fraction contains a mixture of butylenes and butanes. Generally speaking, there are two commercially important processes for producing isobutylene: steam cracking of saturated hydrocarbons derived from natural gas or crude oil (yielding 40%-50% isobutylene), and catalytic cracking of high boiling petroleum fractions (yielding 15%-20% isobutylene). The latter process is the process that is used predominantly in the United States. An approximate composition of this feed is given in Table 22.

Table 22: C4 Fraction Composition

Composition	*Weight %*
Propane	0.1
Isobutane	34.6
n butane	11.0
Isobutylene	**15.0**
1 butene	12.8
t2 butene	15.8
C2 butene	9.6
Butadiene	0.1
C5	1.0

The model for the production of the C_4 fraction follows the petroleum refining model that is detailed in section 4.6.

4.4 ELECTRICITY PRODUCTION

The electricity grid model includes the following:

- Pre-combustion processes: coal mining (surface and underground) and transportation, natural gas extraction and transportation, crude oil extraction (off-shore and on-shore) refining, and transportation, production of nuclear fuel (UF_6, accumulation and fuel rod manufacturing), and hydroelectric power production
- Combustion in power plants
- Distribution (losses: 7.7%)

4.4.1 Natural Gas

The approach to modeling natural gas production is covered at the beginning of section 4.1.1 above.

4.4.2 Natural Gas Combustion

Natural gas is combusted in gas boilers. Emissions from the combustion of natural gas (except for NO_x) are mainly due to improper operating conditions, such as inefficient mixing of fuel and air in the boiler, or an insufficient amount of air, etc. Emissions vary by the type and size of combustor and operating conditions.

Emissions factors for gas boilers were obtained from AP-42 for NO_x, CO, SO_x, particulate matter, CO, and VOCs. Emissions factors modeled are uncontrolled emissions.

4.4.3 Coal

The processes that make up coal production include extraction of coal, cleaning and preparation of coal for use at utility plants, and transportation to the utilities.

Coal Mining

Materials and energy consumed in mining and cleaning of coal comes from Delucchi [1]. These energy data are modeled in conjunction with the quantity of coal produced in 1987 reported by EIA [9].

Emissions due to mining coal are those from the combustion of diesel oil of mining equipment, and methane, released directly from the mine. Emissions factors for the diesel oil combustion come from AP-42. While mining data from 1987 are used, the quantity of methane released from the mines comes from a later year [10]. These data give the value for methane releases from total coal production as 0.6% to 0.9% (averaged to 0.75%).

Waste from mining is generated from activities such as portal construction and mine ventilation, and is assumed to be 32% of underground mined coal produced. Eastern surface mining waste totals 27% of mined output and western surface mining produces waste equaling 10% of mined output [11].

Coal mining is regionalized by taking into account a weighted average of surface mining (eastern and western surface mining modeled as the same process) and underground mining [9].

Coal Cleaning

Coal cleaning removes impurities, such as sulfur, ash, and rock, from the mined coal. The processes included are initial preparation, fine and coarse coal processing, and final preparation of coal. Emission factors are modeled for mechanical, as opposed to chemical, separation processes.

The quantity of coal used in cleaning was derived from average mining/cleaning data [1]. The coal component is assumed to be the energy source for cleaning and preparation. Therefore, the quantity of coal used in the model as energy for cleaning was found by taking the ratio of coal consumed to coal produced. This number was found to be 0.05% of total coal consumed (4.1×10^5 tons consumed to clean and prepare 8.3×10^8 tons of coal).

Transportation from Site of Extraction to Power Plant

Coal may be transported by different transportation means, including rail, road, pipeline, and river. The expression used to describe the energy intensity of transporting coal (or any other material) is joules per ton-kilometer. It is safe to assume that for the most part, the carrier returns empty. For example, 91% of the unit train cars that carry coal return empty to the mine, and trucks return empty unless they can find a similar product to transport back [1]. Therefore, all transportation data assume a one-way haul.

Rail

The 1987 national average length of haul for coal by means of rail is 788 kilometers [1,9]. This distance may be applied to the U.S. Northeast since bituminous coal may travel from states such as Kentucky and Tennessee to the most Northeastern states of the United States, and coal may also come from closer sources, such as West Virginia. It is assumed that diesel fuel is used for rail transportation [1]. The energy consumed is averaged out to be 4.2×10^5 joules per ton-kilometer.

Truck

The average haul distance for coal delivery is 97 kilometers for a round trip [1,12]. It is assumed that diesel fuel is used for truck transportation. The energy consumed is averaged out to be 1.7×10^6 joules per ton-kilometer [1].

Ship

The national average length of haul for coal by means of water is 724 kilometers although DOE estimates one-way transportation for eastern barges to be 306 kilometers [11]. It is assumed that ships use residual fuel oil. Since the former source of data is most recent but the latter is more specific to eastern bituminous coal, the two figures are averaged out to 515 kilometers. The energy consumed is averaged 3.9×10^5 joules per ton-kilometer.

Slurry Pipeline

Data for energy consumed in coal transportation by slurry pipeline gives an average energy consumed for this mode of transport of 5.2×10^5 joules per ton-kilometer [1]. Included in this average is energy used for slurry preparation, pipeline pumping, dewatering facilities, and specifically, energy used in the Black Mesa Pipeline, which runs 439 kilometers from the Black Mesa Coal Mine in Arizona to the Mohave Power Plant in Laughlin, Nevada. The estimated average length of haul for a pipeline is 483 kilometers, including the pipeline itself, tramway transportation, and conveyor belts.

4.4.4 Coal Combustion

Energy consumed and emissions associated with combustion of coal in utility boilers come from a variety of sources. Emissions and total coal burned were obtained from the 1994 Interim Inventory based on the Form EIA-767 data.[11] Emissions factors for pollutants not provided in the Interim Inventory are obtained from AP-42.

Emissions are presented for each individual firing configuration. Because firing configurations have varying combustion requirements (coal combustion temperatures, firing methods, and emissions control equipment, etc.), they emit varying amounts of pollutants.

The firing configurations included in the model are:

- Pulverized coal fired, dry bottom and wall fired;
- Pulverized coal fired, dry bottom and tangentially-fired;
- Pulverized coal-fired and wet bottom;
- Spreader stoker;

[11] Database provided by the U.S. EPA.

- Fluidized bed combustor; and
- Cyclone furnace.

The Interim Inventory provides actual air emissions (VOCs, NO_x, CO, SO_x, and PM-10) by specific type of coal (bituminous, subbituminous, and lignite) and by furnace type. The firing types provided are also identified by a Source Classification Code (SCC). Each firing type was placed into a broader category of firing configurations using SCC numbers.

The following table (Table 23) presents the firing types and how they were placed in the firing configuration category, based on SCC numbers. Firing types were grouped together so that a weighted percentage of boilers and amount of specific coal fed into the boilers would be obtained since different firing configurations emit differing quantities of pollutants.

Table 23: Coal Firing Configurations/Firing Types

Firing Configuration (AP-42)	*Firing Types (Interim Inventory)*
Pulverized coal fired, dry bottom, wall fired	Front Furnace
	Arch Furnace (50%)[12]
	Rear Furnace
	Spreader Stoker (80%)[13]
	Opposed Furnace
	Vertical Furnace
Pulverized coal fired, dry bottom and tangentially-fired	Tangential Furnace
Pulverized coal-fired, wet bottom	Arch Furnace (50%)
Spreader stoker	Spreader Stoker (20%)
Fluidized bed combustor	Fluidized Bed
Cyclone furnace	Cyclone

Several steps were made to obtain actual emissions in pounds per ton of bituminous coal. The tonnage for each emission was summed for each firing configuration. This figure was divided by the total amount of bituminous coal consumed for each firing configuration, to obtain actual emissions per firing configuration. The results of this calculation are presented in Table 24.

Where actual emissions data were not available, such as for N_2O, methane, and trace elements, emissions factors were obtained from AP-42 (Table 25).

The model also takes into account all carbon dioxide emissions, which are calculated by multiplying the fuel carbon concentration by the ratio of molecular/atomic weights of CO_2 and C [13]. The fixed carbon content and the CO_2 emissions factor (in g/kg coal) are presented in Table 26.

Finally, the model takes the weighted average of each of the firing configurations for each type of coal. For example, the emissions from the spreader stoker for bituminous coal combustion are omitted from the model, since bituminous coal combusted in the spreader stoker is a negligible representation of all of the bituminous coal fed into the firing configurations.

[12] About half of the arch furnace boilers had SCC numbers for dry-bottom wall-fired units and the other half for wet-bottom units.

[13] An estimated 80% of the spreader stoker boilers had SCC numbers for dry-bottom wall-fired units and the other 20% belonged in the spreader stoker category of firing configurations.

Table 24: Bituminous Coal Combustion Emissions (kg/ton of coal burned)[14]

Firing Configuration	*VOC's*[15]	*NO_x*	*CO*	*SO_x*	*PM-10*
Pulverized Coal-Fired, Dry Bottom, Wall Fired	0.03	9.0	0.27	19.8	0.33
Pulverized Coal-Fired, Dry Bottom, Tangentially-Fired	0.03	6.8	0.27	21.4	0.44
Pulverized Coal-Fired, Wet Bottom	0.04	12.5	0.27	13.7	11.2
Spreader Stoker	0.03	9.1	0.55	19.4	0.20
Fluidized Bed Combustor	0.03	4.4	0.00	6.4	0.21
Cyclone Burner	0.03	16.8	0.27	37.9	0.04

Table 25: Bituminous Coal Combustion Emissions Factors

Boiler Type	*N_2O* (kg/ton of coal burned)
Pulverized Coal-Fired, Dry Bottom, Wall Fired	0.04
Pulverized Coal-Fired, Dry Bottom, Tangentially-Fired	0.01
Pulverized Coal-Fired, Wet Bottom	0.04
Spreader Stoker[16]	0.04
Fluidized Bed Combustor[17]	2.6
Cyclone Furnace	0.04

Table 26: Coal Fixed Carbon Content

	Fixed Carbon Content (%)	*CO_2 Emissions Factor* (g/kg)
Bituminous Coal	85	3116

Emissions Control Technology

Because there are actual plant data for VOCs, NO_x, CO, SO_2, and particulate matter, emission control technologies for some of the major pollutants of concern, such as NO_x and SO_x, are already taken into account.

Lime and limestone, used for flue gas desulfurization (FGD), are modeled. Coal utility plants use different methods for scrubbing, such as limestone slurries and dry spraying, and use lime and limestone as the primary FGD materials. Quantities of lime and limestone vary, depending on the type of coal, the molar ratio needed to scrub the SO_x, and the percentage of SO_x (by weight) in the coal. FGD for bituminous coal is modeled according to the general scrubbing material for that type of coal and based on its percentage by weight of SO_x.[18]

[14] Interim Inventory provides emissions on a 1000 tons per year basis.

[15] Includes methane and non-methane VOCs.

[16] Emissions factors averaged over spreader stoker, spreader stoker with multiple cyclones and reinjection, and spreader stoker with multiple cyclones, without reinjection.

[17] Emissions factors averaged over fluidized bed combustor: bubbling bed and circulating bed.

[18] Data collected from a source at a coal utility plant in North America (1996), a source at American Electric Power Company (1997) and from the Electric Power Annual 1994.

4.4.5 Coal Post-Combustion

The coal combustion process produces waste that must be disposed of off-site, including coal ash (resulting from coal combustion) and sludge (resulting from FGD). In 1984, 69 x 10^6 tons and 16 x 10^6 tons of coal ash and sludge, respectively, were generated from electrical facilities [1]. Energy and emissions to remove coal ash and sludge are modeled. Since the quantity of sludge is approximately 25% of the amount of coal ash, all energy and emissions to remove and dispose of sludge are considered to be about 25% of those found for the disposal of coal ash.

Energy to transport and place sludge and coal ash from the plant to the respective storage locations is modeled. The moisture content of coal ash (in % weight of ash) at the point it is removed from the silo is assumed to be approximately 17%.[19] The distance from the power plant to the coal ash and FGD sludge landfills is assumed to be one mile.

The trucks used to transport the materials are tandem trucks, filled based on weight of the material. The tandem truck carries an actual payload of about 25 metric tons, and consumes 0.14 liters of diesel fuel per metric ton of material per trip.

4.4.6 Heavy Fuel Oil

Fuel oil pre-combustion is outlined below.

AP-42 contains emissions factors for the combustion of residual fuel oil nos. 4, 5, and 6, for normal and tangential firing configurations at utilities. Emissions factors of NO_x, SO_2, SO_3, CO, total organic compounds, non-methane total organic compounds, and methane are provided.

Emissions controls include combustion and post-combustion NO_x and SO_x technologies. These control technologies were incorporated into the NO_x and SO_x emissions so that emissions data are more representative of actual emissions, as opposed to uncontrolled emissions alone.

SO_x is scrubbed from fuel oil burners the same way it is for coal combustion. Lime and limestone are used as the FGD material. Fuel oil boilers use about 50% lime and 50% limestone as FGD material. The quantity of SO_x scrubbed is about 90% of total SO_x for fuel oil [2]. The quantity of lime and limestone that is used is calculated by assuming that the SO_2 is the remaining 10% of SO_2 that was not scrubbed. Therefore, 90% of the total SO_2 is found, and is multiplied by the grams of a mole of CaO and $CaCO_3$ that is needed to scrub a mole of SO_2 (0.88 and 1.56, respectively).

4.4.7 Nuclear Power Production

Uranium contains two different isotopes—^{238}U and ^{235}U; ^{235}U is used as a fuel for nuclear reactors because it is fissionable, so the atoms can be split, releasing large amounts of heat. However, natural uranium consists of more than 99% ^{238}U and less than 1% ^{235}U. To be used as a fuel, its ^{235}U content must be enriched to 3%-5%.

The data included in the upstream portion of nuclear energy production are uranium hexafluoride (UF6) manufacturing, enrichment of ^{235}U, and fuel rods manufacturing [14,15].

4.4.8 Hydroelectric Power Production

Hydroelectric power generation refers to water used to generate electricity at plants in which turbine generators are driven by falling water.

The emissions due to hydroelectric power production are primarily the greenhouse gases CO_2 and CH_4, generated because of the decomposing flooded biomass in the reservoir, and emissions from capital equipment and construction of the facility: steel and concrete production, transportation to the reservoir, and construction energy. However, capital equipment and construction are not included in this model, for the same reasons that are outlined in the next section.

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[19] Moisture content may be anywhere from 8% to 25%. Data from an American power plant (confidential client of Ecobalance Inc.), 1996.

Therefore, the remaining part of hydroelectricity that is modeled is the greenhouse gas emissions (CO_2 and CH_4) from operation of the plant. Chamberland [16][20] provides life cycle data on few hydroelectric power sites in northern Canada, and the Federal Energy Regulatory Commission[21] provides U.S. hydroelectric plant information such as average annual generation, plant capacity, and reservoir area and depth.

The data obtained on greenhouse gases emissions do not distinguish flooded biomass decomposition from new biomass decomposition and are assumed to refer only to flooded biomass.

4.4.9 Capital Equipment Exclusion

In LCA, one might include capital equipment, or production and transportation of concrete and steel, as well as construction burdens, in the system boundaries. However, for this electricity generation comparison, capital equipment has been excluded for the following reasons:

- It may be assumed that most electricity production facilities are made up of comparable quantities of concrete and steel. Therefore, the burdens due to capital equipment are the same for all sources, so any quantities that are capital equipment-related may be subtracted out of both sides of the results in each comparison.
- Dr. Ian Boustead in *Eco-balance—Methodology for Commodity Thermoplastics* [17] states: "…although the inventory flows associated with the construction of capital plant and buildings are high, their effect upon the products they produce is usually negligible because of the large total throughput that is usually achieved in their lifetime."
- The energy used in the construction of large energy facilities and other equipment used in fuel cycles (including electric power plants, oil wells, oil tankers and hydroelectric plants) is negligible (less than 1%) compared with the energy produced or carried by that equipment over its useful life [1].

4.4.10 Electricity Grids

The following tables (Table 27 and Table 28) show the electricity *production* percentages for the different North American Electric Reliability Council (NERC) regions in the North America [18].

Note that the percentages are given for the U.S. portion of the region listed. Some regions are split between Canada and the United States (WSCC for example), however, the electricity production percentages are given for only the U.S. portion. The different NERC regions are described in Figure 13.

The electricity model was tailored to the specific NERC region from which the modeled material is derived. Data were gathered for the production of renewable energy in California, based on information obtained from CEC and AP-42. In order to model the use of electricity in California for specific systems, the following distribution of fuel types was used [19].

4.5 STEAM PRODUCTION

The energy necessary to convert water to steam is based on the enthalpy of the steam (2.6 MJ/kg at approximately 150 psi and 350°F) and a boiler efficiency of 80%. Steam is assumed to be produced by combusting fuel in industrial boilers. The fuel can consist of coal, natural gas or heavy fuel oil.

[20] Chamberland's life cycle study is based on a group of facilities in northern Canada whose average lifespan is 100 years and produces annually 62,200 GWh of electricity.

[21] FERC database, 1996.

Table 27: Electricity Production by NERC Region

	NERC Region				
Fuel Type	***NPCC***	***ECAR***	***WSCC***	***ERCOT***	***SERC***
HFO*	10.7 %	0.3 %	0.1 %	0.1 %	3.4 %
Hydro	15.4 %	0.5 %	40.6 %	0.3 %	4.6 %
Natural gas	18.3 %	0.5 %	10.2 %	37.4 %	5.9 %
Nuclear	35.1 %	10.4 %	12.8 %	17.1 %	29.5 %
Coal	20.5 %	88.3 %	36.3 %	45.2 %	56.6 %

	NERC Region				
Fuel Type	***MAAC***	***MAPP***	***MAIN***	***SPP***	***U.S. Average***
HFO*	3.1 %	0.5 %	0.5 %	0.3 %	2 %
Hydro	0.8 %	8.4 %	1.4 %	2.9 %	9.8 %
Natural gas	5.3 %	0.9 %	1.7 %	28.3 %	10.2 %
Nuclear	40.8 %	15.9 %	42.4 %	15.7 %	23 %
Coal	50 %	74.3 %	54 %	52.8 %	55 %

* Heavy Fuel Oil

Table 28: California Net System Power

Fuel Type	***Net System Power***
Coal	17%
Large Hydroelectric	24%
Natural Gas	35%
Nuclear	14%
Eligible Renewables	11%
Total:	**100%**

The assumed heating values of the three fuels are as follows:

- Natural Gas – 52 MJ/kg
- Heavy Fuel Oil – 42 MJ/kg
- Coal – 29.3 MJ/kg

The emission factors for industrial boilers were obtained from AP-42. These numbers were compared with a study done by the Argonne National Laboratory [20], to verify and expand on the U.S. EPA emission factors.

All the factors reported are for uncontrolled emissions. If control technologies are used, the emission factors should be reduced by the efficiencies of the control devices.

Heavy fuel oil production emission factors are shown in section 4.4.6, and natural gas production emissions are outlined above in section 4.1.1.

Figure 13: **Map of the NERC regions in the United States and in Canada**

4.6 GASOLINE SYSTEM

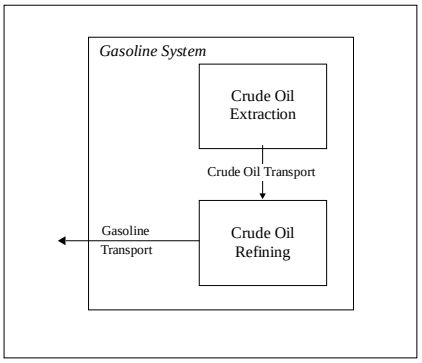

Figure 14: Gasoline Production Systems

This section includes pre-combustion data for gasoline. The pre-combustion steps includes extraction of crude oil from the ground, transportation of the crude oil to a refinery, and refining the crude oil into finished refinery products (Figure 14). Transportation of the finished refinery products to the point of use is also included at this stage. The model was regionalized to California whenever possible. For a full description of petroleum products modeling see Appendix D.

4.6.1 Geographical Boundaries

The modeling of refined petroleum products production includes worldwide crude oil extraction and U.S. refinery operations. Foreign crude oil extraction and transportation to the United States is modeled because half of the U.S. supply of crude oil is imported. The transport of finished refinery products into the United States is not studied because foreign refinery products only accounts for a small percentage of the total finished refinery products used in the United States in 1994 [21], and may be accounted for under domestic refinery production. In addition, domestic refinery data are more accurate and reliable.

4.6.2 Crude Oil Extraction

There are three separate methods for crude oil extraction and recovery: onshore production, offshore production, and thermal enhanced recovery, which entails the underground injection of carbon dioxide or steam produced by natural gas boilers.[22] All of these methods were modeled.

Heater treater separators are used to separate the crude oil, natural gas, and water mixture that is extracted. As natural gas is produced as a coproduct of crude oil production, emissions were allocated between gross natural gas and crude oil production on a mass-based method. The emissions associated with the venting and flaring of some of the natural gas extracted from the well was also accounted for.

The inflows associated with the three different methods of crude oil extraction include electricity used in pumping, and natural gas used as fuel to run the heater treater systems. Outflows include air emissions, water effluents, and solid waste.

4.6.3 Transportation

The United States is broken up into Petroleum Administration for Defense Districts (PADDs) in order to ensure that each region or PADD is supplied with enough petroleum for strategic defense reasons. The transportation distances used in this report were based on the PADD in which California is located. The amount of foreign and domestic crude oil transported into each PADD was estimated from refinery receipts of crude oil that is known for each PADD [22][23]. The mix of foreign and domestic crude oil shipped to the PADD in which California is located was also used in this model.

Distances used to model transportation of are based on national averages, obtained from the following types of data and methods of calculation:

Domestic Tanker and Domestic Barge [12]: Report lists tons and ton-miles of crude oil transported by tanker and barge on all U.S. waterways. Average miles are calculated by dividing total ton-miles traveled by total tons transported. This is done separately for both tanker and barge.

Domestic Pipeline [22]: Association of Oil Pipelines lists total ton-miles of crude oil carried in domestic pipelines. Average miles are calculated by dividing total ton-miles of crude oil, carried in domestic pipelines, by tons of crude oil received at refineries via pipeline. Foreign pipeline distance is calculated the same way.

Domestic Rail [23]: Association of Oil Pipelines lists total ton-miles of crude oil carried by rail in the United States. Average miles are calculated by dividing total ton-miles of crude oil, carried by rail, by tons of crude oil received at refineries via railroad tank cars.

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[22] Shares of each production type were obtained from the Oil & Gas Journal Database, using numbers obtained in 1994. Note that the Other Enhanced/Advanced category includes all advanced crude oil extraction techniques except water flooding. It was assumed that the emissions associated with thermal advanced recovery as listed by Tyson et al. (November 1993, Fuel Cycle evaluations of Biomass-Ethanol and Reformulated Gasoline) applied to the percentage of wells operating with the other Enhanced/Advanced techniques obtained from the Oil & Gas Journal Database.

[23] 1993 data were used because that was the latest year for which information used to calculate transportation distances could be found (see Section 3.3.2).

Domestic Truck [24]: Association of Oil Pipelines lists estimated total ton-miles of crude oil transported by motor carriers in the United States. Average miles are calculated by dividing total ton-miles of crude oil, transported by motor carriers, by tons of crude oil received at refineries via truck.

Foreign Tanker [1,21]: The Petroleum Supply Annual lists imports of crude oil by country for each PADD (in barrels). PADD I crude oil is assumed to all arrive at New York. PADD II and III oil is assumed to arrive at Houston. PADD V oil is assumed to arrive at Los Angeles. PADD IV does not receive any foreign oil other than from Canada.

Nautical miles between ports of origin and U.S. ports (New York, Houston, and Los Angeles) are given in Delucchi's study, based on information from the Defense Mapping Agency [25]. From this information a weighted average is calculated, for each PADD, by multiplying barrels imported from each country by the distance from that country to the specified U.S. port of entry. These results, in barrel-miles for each PADD, are added together and then divided by the total number of barrels imported to get an average distance in miles traveled by the foreign tankers.

4.6.4 Crude Oil Refining

The inflows associated with refining include crude oil, natural gas, liquefied petroleum gas, steam, electricity, and coal [21]. Outflows for this process include air emissions [2], water effluents, and solid waste. The California electricity grid was used to model refinery electricity use.

Allocation of refining processes must be addressed. Petroleum refineries produce a number of different products from the amount of crude oil that they receive. Additional complexity is introduced by the fact that the refinery product mix is variable, both among refineries and even with time for a given integrated refinery.

The simplest allocation procedure would be to allocate total refinery releases (and consumption) among the products on a mass output basis. The following table (Table 29) outlines how this would be done, based on the output of a generic U.S. refinery:

Table 29: Production of an Average U.S. Refinery

Refinery Flow	***Mass*** (kg/yr)	***Mass*** (%)
Diesel Oil (< 0.05% Sulfur, kg):	9.30×10^{10}	12.8%
Diesel Oil (> 0.05% Sulfur, kg):	6.76×10^{10}	9.33%
Gasoline:	3.08×10^{11}	42.5%
Heavy Fuel Oil:	4.52×10^{10}	6.24%
Jet Fuel (kg):	6.53×10^{10}	9.01%
Kerosene (kg):	2.74×10^{9}	0.38%
Misc. Refinery Products (U.S., kg):	2.19×10^{9}	0.30%
Petroleum Coke (kg):	4.12×10^{10}	5.69%
LP Gas:	1.92×10^{10}	2.66%
Asphalt (kg):	2.72×10^{10}	3.75%
Lubricants (kg):	8.87×10^{9}	1.22%
Petrochemical Feedstocks (kg):	4.04×10^{10}	5.57%
Petroleum Waxes (kg):	9.71×10^{8}	0.13%
Naphthas (kg):	2.35×10^{9}	0.33%
Total:	7.24×10^{11}	

However, this would result in the same LCI profile for every kg or refinery product regardless of its characteristics (e.g., one kg of diesel fuel would have the same profile as one kg of gasoline).

An objection to the mass allocation approach, which is based on output share, is that a kilogram of different refinery products requires different amounts of processing, thus requiring different amounts of energy input and leading to different amounts of releases.

An alternative allocation method would be one based on the share of the total process energy required to produce the refinery product.

This method of allocating refinery flows based on process energy requirements is outlined in the following steps:

- Calculate the percentage of total refinery energy used by each different process within the refinery.
- Calculate a specific refinery product's share of each process' energy consumption.
- Multiply the two results in order to get the percentage of total refinery energy allocated to a single refinery product production for each process. Adding the results of each process gives the percentage of **total** refinery energy allocated to a **total** single refinery product.
- Allocate emissions and energy use based on the percentage of total refinery energy allocated to a **total** single refinery product. (From step 3 above)

Many different studies have been done in the past in order to estimate total refinery energy allocation to the different processes within a refinery [1]. These studies, however, were predominantly done in the late 1970s and early 1980s and their relevance to today's refinery processes is not fully known. This is complicated by the fact that refinery energy requirements are considered proprietary information so it is difficult to confirm the past studies findings.

For this project, an additional study done by White et al. [26][24] was used with two studies listed by Delucchi [1] to help estimate refinery process energy allocation. This study may not be completely applicable, for the reasons outlined above, but it was found to be the most comprehensive and descriptive of what had been done.

The three refinery models list energy consumption for different refinery processes. This information is used to calculate the percentage of total refinery energy used by each different process within the refinery.[25] **Error! Not a valid bookmark self-reference.** lists the results.

For this study, the average values for fraction of total refinery energy used by each process were used. Averaging the values from the three studies is thought to help compensate for the differences in refinery configurations and size.

An individual refinery product's share of each process' energy consumption can be calculated from information provided in a recent DOE study [1] and information on refinery production [21]. The DOE study allocates energy use in different refinery process areas to gasoline, total distillates and residual fuel in proportion to process energy output of the different products.[26] Table 31 shows the results. The values in Table 31 can be multiplied by the average fraction of total refinery energy used by each process to determine the total process energy required to produce each of the four different types of refinery fuels shown above. The results of this are shown in Table 32.

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[24] The authors were, at the time of the study, all members of Mobil Research and Development Corp., Princeton and Paulsboro, NJ.

[25] Note: White et al. do not take into account increased energy requirements for producing low sulfur diesel fuel. Therefore, energy values from White et al. for hydrogen manufacture and hydrodesulfurizer have been increased to account for removal of more sulfur. The increase is based on assuming that the energy consumption given in White et al. represented removal of 1.25% of the sulfur in the incoming crude (crude oil = 1.5% sulfur, diesel fuel = 0.25% sulfur). Then a linear increase is assumed in energy consumption based on removing 1.45% of the sulfur (low sulfur diesel fuel = 0.05% sulfur).

[26] Allocation is based on the energy output of the three different products from each of the different refinery processes. For example alkylation, reforming, and isomerization produce only high-octane gasoline components. Therefore, the process energy associated with alkylation, reforming, and isomerization is allocated entirely to gasoline production.

Table 30: Fraction of Total Refinery Energy Used by Each Process

	Fraction of Total Refinery Energy			
Refinery Process	***Lawerence***	***Haynes***	***White et al.***	***Average***
Crude distillation	0.276	0.364	0.266	0.302
Catalytic cracking	0.314	0.065	0.124	0.168
Thermal cracking	0	0.033	0	0.011
Hydrocracking	0	0.044	0	0.015
Desulfurization	0.02	0	0.046	0.022
Hydrotreating	0	0.085	0.068	0.051
Alkylation	0.065	0.069	0.040	0.058
Reforming	0.191	0.225	0.140	0.185
Coking	0.038	0.032	0.077	0.049
Visbreaking	0	0.007	0	0.002
Propylene concentration	0.05	0	0	0.017
Isomerization	0.042	0.002	0	0.015
Hydrogen	0	0.025	0.070	0.032
Depentanizer	0	0	0.0167	0.006
Naphtha Pretreater	0	0	0.054	0.018
Saturated gas plant	0	0	0.035	0.012
Unsaturated gas plant	0	0	0.064	0.021
Finishing and other	0.003	0.055	0	0.019
Total:	0.999	1.006	1.000	1.002

Table 31: Fraction of Refinery Process Energy Used by Types of Refinery Products

	Fraction of Process Energy			
Refinery Process	***Gasoline***	***Distillate***	***Residual***	***Other***
Crude distillation	0.454	0.302	0.07	0.174
Catalytic cracking	0.55	0.365	0.085	0
Thermal cracking	0.454	0.302	0.07	0.174
Hydrocracking	0.541	0.359	0	0.1
Desulfurization	0.454	0.302	0.07	0.174
Hydrotreating	0.541	0.359	0	0.1
Alkylation	1	0	0	0
Reforming	1	0	0	0
Coking	0.541	0.359	0	0.1
Visbreaking	0	1	0	0
Propylene concentration	0	0	0	1
Isomerization	1	0	0	0
Hydrogen	0.541	0.359	0	0.1
Depentanizer	1	0	0	0
Naphtha Pretreater	0.994	0	0	0.006
Saturated gas plant	0.89	0	0	0.11
Unsaturated gas plant	0.89	0	0	0.11
Finishing and other	0.454	0.302	0.07	0.174

Table 32: Fraction of Total Refinery Energy Used by Category of Refined Product

	Fraction of Total Refinery Energy			
Refinery Process	***Gasoline***	***Distillate***	***Residual***	***Other***
Crude distillation	0.14	0.091	0.021	0.053
Catalytic cracking	0.09	0.061	0.014	0
Thermal cracking	0.0050	0.0033	0.0008	0.0019
Hydrocracking	0.008	0.0053	0	0.0015
Desulfurization	0.0100	0.0066	0.00154	0.0038
Hydrotreating	0.028	0.018	0	0.0051
Alkylation	0.058	0	0	0
Reforming	0.19	0	0	0
Coking	0.026	0.018	0	0.0049
Visbreaking	0	0.0023	0	0
Propylene concentration	0	0	0	0.0167
Isomerization	0.0147	0	0	0
Hydrogen	0.0171	0.0113	0	0.0032
Depentanizer	0.0056	0	0	0
Naphtha Pretreater	0.0178	0	0	0.0001
Saturated gas plant	0.0105	0	0	0.0013
Unsaturated gas plant	0.0189	0	0	0.0023
Finishing and other	0.009	0.0058	0.0014	0.0034
Total:	0.6429	0.2230	0.0390	0.0967

An example of how this allocation procedure is used to determine the allocation percentage for diesel fuel is shown below.

The results of Table 32 state that 22.3% of the total refinery energy is needed to produce distillate fuels. However, total distillates, as described in the DOE study, include diesel fuel, jet fuel, kerosene, and residual fuel. The fraction of total distillates taken up by diesel fuel is shown in the following table (Table 33).

Table 33: Diesel Fuel's Share of Total Distillates

Distillates	***Mass*** (kg/yr)	***Mass*** (%)
Diesel Fuel:	1.61×10^{11}	59%
Heavy Fuel Oil:	4.52×10^{10}	17%
Jet Fuel (kg):	6.53×10^{10}	24%
Kerosene (kg):	2.74×10^{9}	1%
Total:	2.74×10^{11}	

It is found that diesel fuel makes up 59% of total distillate production on a mass basis. This result can be combined with the energy fraction needed to produce total distillates to give diesel fuel's share of refinery energy consumption as follows:

$$22.3\% x 59\% = 13.2\%$$

The same method is used to calculate the allocation percentage for the other refinery products used in this study. For gasoline an allocation of 64.3% is used directly from Table 32.

4.7 GASOLINE TRANSPORT

The transport modeling of gasoline to the point of use location is shown in Figure 15.

4.7.1 Modes of Transport and Distance Transported

It is assumed that a fraction of gasoline produced at the refinery is shipped to local point of use locations an average distance of 100 miles. The remaining fraction is shipped via pipeline to a tank farm where it is in turn shipped by truck 100 miles to a point of use location.

The fraction of gasoline shipped via pipeline is based on Association of Oil Pipelines, using data from Annual Report (Form 6) of oil pipeline companies to the Federal Energy Regulatory Commission. The report lists the percentage of total finished petroleum products that is shipped by pipelines, water carriers, motor carries, and railroads. The report states that 59% of the finished petroleum products are shipped via pipeline. The remaining 41% is assumed to be transported by truck. The Association of Oil Pipelines report also lists total ton-miles of finished petroleum products carried in domestic pipelines. Average pipeline transportation miles are calculated by dividing total ton-miles of petroleum products, carried in domestic pipelines, by tons of petroleum products shipped via pipeline. The result is 595 miles of pipeline transport.

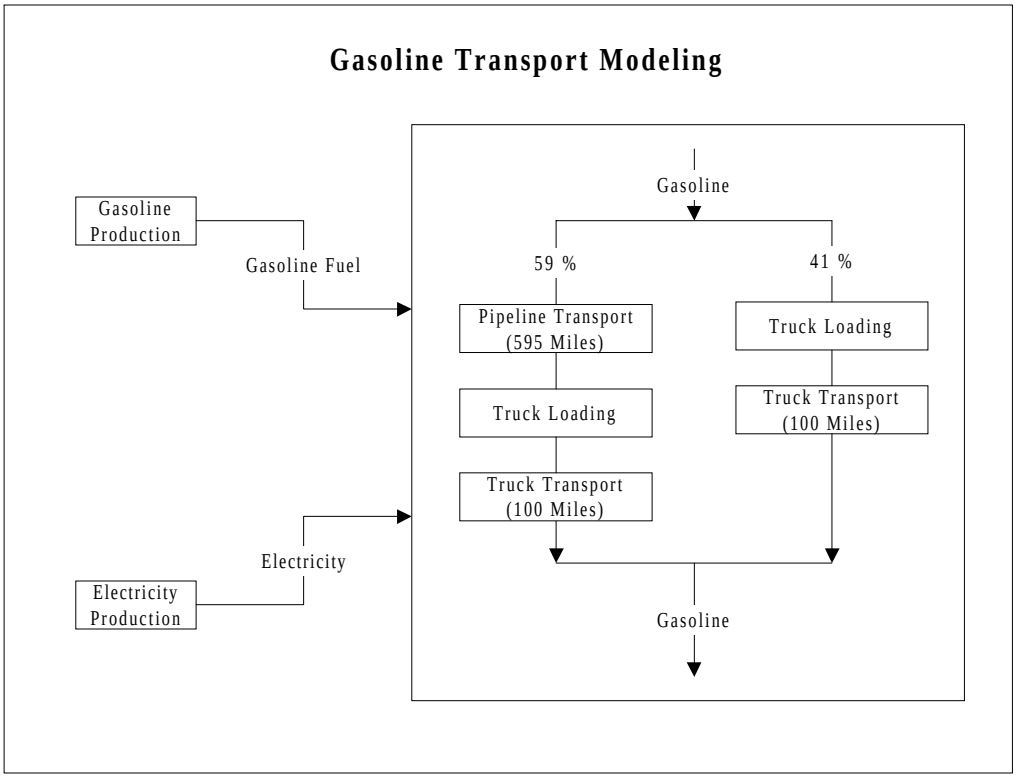

Figure 15: Gasoline Transportation Modeling

4.7.2 Energy and Fugitive Emissions from Storage and Handling

In addition to the energy requirements and subsequent emissions from the actual modes of transportation (e.g., truck diesel use and emissions, pipeline electricity requirements, and emissions from electricity production, etc.), there are also energy and emissions due to loading and unloading of the gasoline. The pumping requirements for gasoline are calculated by the same method as that for crude oil pumping (outlined in Section 4.6). The fugitive emissions from

the loading, unloading and transportation of the gasoline are calculated using the same formulas as for the crude oil fugitive emissions (described in Section 4.6). The formulas are modified based on the gasoline properties (true vapor pressure, molecular weight of the vapors, etc.) as outlined in AP-42.

Note that fugitive tank emissions from the storage of gasoline at the refinery are accounted for in the refinery model. Also, fugitive tank emissions from the storage of gasoline at refueling locations are assumed to be negligible. Figure 16 represents how the emissions from gasoline transportation are modeled in this project.

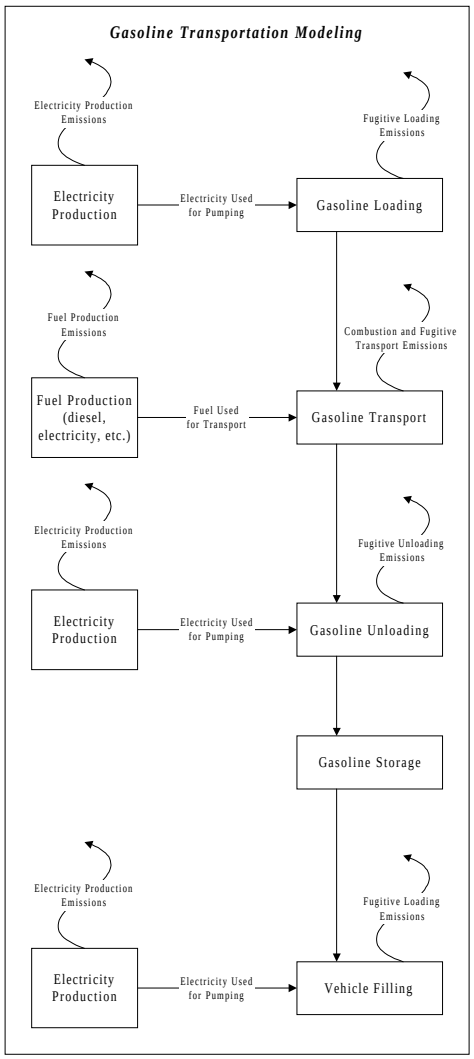

Figure 16: Gasoline Transportation Emissions Modeling

4.8 OXYGENATED GASOLINE FUEL COMBUSTION

The modeling of oxygenated gasoline combustion is based on emissions from the use of equivalent amounts of ETBE and MTBE. The base is assumed to be the amount of ETBE that is produced from the conversion of one MBDT of biomass. Since the study assumes that the ETBE is a direct replacement for MTBE, and ETBE displaces slightly more gasoline than does MTBE (see Table 6), the combustion emissions were equal to the emissions from excess number of liters of MTBE oxygenated fuel.

4.8.1 Tailpipe Emissions

The baseline emissions from the tailpipe of the vehicle modeled is based on emission standards from the U.S. EPA AP-42 for light-duty gasoline powered vehicles (Table 34).

Carbon dioxide emissions are based on converting 100% of the carbon in the gasoline to CO_2, adjusting the value for the CO that is produced. The carbon content of the fuel is assumed to be 86% by weight.

These emissions are then converted using the percentage benefits from reformulated gasoline use for the year 2000, provided by CARB (Table 35).

Table 34: Vehicle Emission Factors

Pollutant	***Emission Factors*** (g/mile)
Total VOC	0.56
Carbon Monoxide	6.65
Nitrogen Oxides	0.81

Table 35: Reformulated Gasoline Benefits: Year 2000

Pollutant	***Reduction*** (%)
Total VOC (exhaust + evap.)	18%
Carbon Monoxide	9%
Nitrogen Oxides	9%

Carbon dioxide reductions were calculated using the carbon content of the fuel. There are no reductions in total CO_2 emissions that are modeled.

4.8.2 Fuel Efficiency

To give the emissions in terms of fuel consumed, a default fuel efficiency value was calculated to give the number of liters of gasoline used per mile. This value was based on a calculated average of data provided by DOE for 1997 mid-sized vehicles [27]. Average fuel consumption values are listed in Table 36.

Table 36: Average Fuel Consumption Values

City	***Highway***
20 miles per gallon / 5.3 miles per liter	28 miles per gallon / 7.4 miles per liter

The fuel consumption for the vehicle was calculated as the inverse of the average fuel economy using the following equation, which was determined based on information published by DOE [27]:

$$F = 0.45/C + 0.55/H$$

where,

C = City fuel economy (miles/liter)

H = Highway fuel economy (miles/liter)

4.8.3 Biomass versus Fossil Fuel Carbon Dioxide

A portion of the CO_2 that is generated from the combustion of the oxygenated fuel containing ETBE comes from biomass. The amount of CO_2 that comes from biomass was calculated based on the non-isobutylene carbon content of the oxygenate. Biomass and fossil CO_2 were reported separately in the model and results. CO_2 sequestered in the biomass is carried through the LCA as CO_2 (biomass) versus CO_2 (fossil) which results from the combustion of petroleum resources.

The net biomass CO_2 produced by the system is assumed to be zero. The positive values for biomass CO_2 reported in the results are assumed to be offset by biomass CO_2 uptake by the biomass during its growth. Plants use solar energy to fix carbon from carbon dioxide during photosynthesis. For this project, it will be assumed that CO_2 uptake by the biomass will be released back to the environment through decomposition of plant residue, left in the field after harvesting, through the burning of the biomass itself, or through the burning of ETBE made from the biomass. Thus the net CO_2 balance for growing and disposal of biomass is zero. Therefore, the CO_2 (biomass) results are <u>not</u> used in the impact assessment phase to calculate greenhouse gas potential.

5 DATA QUALITY AND SOURCES

For an LCA, there are two different types of data: primary and secondary [1]. Primary data are obtained directly from individual production plants or companies. Secondary data are published sources such as databases, industry or government publications, journals, or books. Another kind of secondary data also includes "educated guesses," or data coming from experts based on their knowledge in the field, but not published.

In general, the goals for data collection, quality, and utilization are to use the most recent data available that are representative of an industry or practice. The goals specifically for this study were to obtain data on the processes leading to MTBE production from natural gas, the disposal of biomass, the conversion of biomass into ETBE, and the use of MTBE and ETBE in oxygenated fuels.

5.1 DATA QUALITY

Data in an LCA should have indicators for reliability and completeness. The "reliability indicator" pertains to how data were obtained and verified, independent of the data quality goals outlined in the study. The "completeness indicator" pertains to how representative the data samples are, i.e., do the data represent an adequate sample size, and do the data cover an adequate period such that normal fluctuations are evened out. The completeness indicator is also treated as independent of the data quality goals outlined in the study. Presently, actual data indicators have not been established in LCA guidelines. Instead, a table is generally provided to indicate the type of data in each life cycle sector and the reliability and completeness for each.

Table 37 outlines the general data categories in this study and provides a description of each, the sources and whether they are primary or secondary, a "checklist" of the reliability criteria, including the geographical and temporal extent of the data, and limitations.

Table 37: Data Quality

Data Category	*Description*	*Primary or secondary; Source and date*	*Geographic and temporal representation*	*Reliability and Completeness*
Natural Gas Production	materials, energy, emissions	Primary and secondary; Gas Research Institute (1997)	U.S. 1990s	Reliable and complete
Methanol Production	materials, energy, emissions	Secondary; Petrochemical Processes (1995)	U.S., World 1980s, 1990s	Reliable but incomplete
MTBE Production	materials, energy	Secondary; French Petroleum Institute (1994)	World 1980s, 1990s	Reliable but incomplete since there is no data regarding process emissions
MTBE Blending	materials, emissions	Secondary; U.S. AP-42 (1995)	U.S., California 1990s	Complete and somewhat reliable
Biomass Burning	materials, emissions	Secondary/Primary; U.S. EPA AP-42 / CARB (1997)	U.S., California 1990s	Reliable but incomplete since the emissions do not take into account the effect of burning conditions
Biomass Harvesting	materials, energy, emissions	Primary; TSS Consultants (1997)	California 1990s	Reliable and complete
Ethanol Production	materials, energy, emissions	Primary; NREL (1998)	U.S. 1990s	Reliable and complete
ETBE Production	materials, energy	Secondary; French Petroleum Institute (1994)	World, California 1980s, 1990s	Reliable but somewhat incomplete since there is no data regarding process emissions
ETBE BLENDING	materials, emissions	Secondary; U.S. AP-42 (1997)	U.S., California 1990s	Complete and somewhat reliable
Isobutylene Production	materials, energy, emissions	Secondary; Petrochemical Processes (1995)	California 1980s, 1990s	Somewhat reliable and incomplete
Electricity Production	materials, energy, emissions	Secondary; see references in Section 4.4	U.S., California 1980s, 1990s	Reliable and complete
Steam Production	materials, energy, emissions	Secondary; U.S. EPA AP-42 (1997)	United States 1980s, 1990s	Reliable and complete
Gasoline Production	materials, energy, emissions	Secondary; see references in Section 4.6	U.S., California, World 1980s, 1990s	Reliable and complete
Reformulated Gasoline Use	materials, emissions	Secondary; CARB / U.S. EPA AP-42 (1997)	California 1990s	Reliable and complete

6 RESULTS AND DISCUSSION

6.1 PRESENTATION OF RESULTS

The results are presented here for six different scenarios modeled from three different biomass feedstocks and two methods of ethanol production. These scenarios follow the base case assumption that all of the lignin generated during the production of ethanol is used for on-site cogeneration (which produces steam and electricity used at the ethanol facility). An additional six scenarios were modeled following the assumption that the lignin is shipped to a biomass power plant (which produces electricity). The detailed results from these additional scenarios are presented in Appendix A.

The three biomass feedstocks are rice straw, forest residue, and chaparral, each of which was modeled using an enzyme process and a concentrated acid process to produce ethanol. The exact nature of these scenarios is described in more detail in Section 4. The six scenarios are summarized in the following table (Table 38).

Table 38: Description of Scenarios Studied

Scenario	*Biomass Type*	*Ethanol Production Method*
1	Rice Straw	Enzyme
2	Rice Straw	Concentrated Acid
3	Forest Residue	Enzyme
4	Forest Residue	Concentrated Acid
5	Chaparral	Enzyme
6	Chaparral	Concentrated Acid

The results presentation is organized first by biomass type and then by ethanol production method. Each scenario has a table with values for the environmental flows that were deemed significant during the scoping phase. The results for each disposal option are presented as totals based on the functional unit of the study. As described in Section 3.2.2, the functional unit is disposal of one MBDT of biomass, and the conversion of the equivalent amount of biomass into a fuel oxygenate to produce a reformulated gasoline with 2% oxygen content. This functional unit results in differing quantities of ethanol, ETBE, and MTBE as shown in Table 39.

Table 39: Ethanol and ETBE Yield by Biomass Type

Biomass Source	*Ethanol Production Method*	*Ethanol Produced* (liters)	*ETBE Produced* (liters)	*Equivalent in MTBE plus Gasoline*	
One metric bone dry ton (1000 kg)				**MTBE** (liters)	**Gasoline** (liters)
Rice Straw	Enzyme	314.1	738.3	635.9	104.3
	Acid	283.2	665.7	573.4	94.0
Forest Residue	Enzyme	344.7	810.3	698.1	114.2
	Acid	280.1	658.4	567.2	92.9
Chaparral	Enzyme	117.8	277.0	238.6	39.0
	Acid	105.7	248.4	213.9	35.1

There are some negative values in the results tables, which arise from the electricity offset of the ethanol biomass disposal option. These values are supplemented with a percentage difference, which indicates the degree to which the values for the ETBE scenario were different from those for the MTBE scenario, i.e., 100x(MTBE value – ETBE value)/MTBE value. A positive value indicates the percentage by which the values for the ETBE scenario were lower than those for the MTBE scenario, and vice versa. It should be noted that the percentages presented cannot be used to compare any other option for disposing of biomass to the conversion of biomass to ETBE, since the emissions would not be normalized to the same basis.

Table 40 demonstrates the meaning of negative values in the following results tables.

Table 40: Explanation of Negative Values in Summary Tables

	Flow	Negative Value in the Totals for Each Option	Negative Value in the % Difference Column
Inflows	All Raw Material Inflows	Indicates an offset that is greater than the use of materials for the option. Primarily due to electricity offset of energy related materials.	Indicates that the ETBE option has higher raw material inflows than the MTBE option. **(Unfavorable)**
Outflows	All Air Emissions, Water Effluents, and Solid Waste	Indicates that electricity offset is greater than the emission of the pollutant for the option resulting in a net negative value.	Indicates that the ETBE option has higher emissions than the MTBE option. **(Unfavorable)**
Energy	Nonrenewable Energy	Indicates that electricity offset is greater than the energy use of the option resulting in a net negative value.	Indicates that the ETBE option has higher nonrenewable energy use than the MTBE option. **(Unfavorable)**
	Renewable Energy		Indicates that the ETBE option has higher renewable energy use than the MTBE option. **(Favorable)**
	Total Primary Energy		Indicates that the ETBE option has higher total energy use than the MTBE option. **(Unfavorable)**

These tables are supplemented with figures that present criteria pollutant emissions for each disposal option, in terms of the functional unit. In situations where the criteria pollutant emissions for Option 2 are higher than those for Option 1, pie graphs are provided to show the life cycle stages that are the source of the emission. More detailed results, showing the percentage contribution of each life cycle stage to the total environmental flow, are provided in the Appendix A.

Note on the summary tables: The impact of a hydrocarbon emission is dependent on, among other things, its point of release and its composition. Since these data are not available, the impact from individual speciated emissions cannot be accurately assessed. Therefore all speciated non-methane hydrocarbon flows (see Table 41) have been aggregated to give a value for the net hydrocarbon emissions.

Table 41 : Speciated Sources of Non-Methane Hydrocarbon Emissions

Non-Methane Hydrocarbon Sources
Volatile Organic Compounds (VOC)
Ethanol (air emissions)
Furfural
Hydroxymethyl Furfural (HMF)
Aldehydes
Formaldehyde
Benzene
Hydrocarbons (except methane)

It should be noted that this report shows the life cycle emissions of the two options meaning that the results are summarized over different locations and different time frames. Therefore, it does not take into account the fact that open burning results in a pulse of emissions at one time and location versus ETBE combustion in a vehicle that takes place over a period of time and at different locations. This report only shows the difference in the total emissions of the two options and does not account for concentrations of pollutants at a given time.

6.2 LIFE CYCLE ENERGY BALANCE

LCIs provide an opportunity to quantify both the total energy demands and the overall energy efficiencies of processes and products. In this study, we track several different types of energy flows through each life cycle. For clarity, each of these energy flows is defined below.

- *Total Primary Energy*. All raw materials extracted from the environment can contain[27] energy. In estimating the total primary energy inputs to each life cycle, we consider the cumulative energy content of all resources extracted from the environment.
- *Feedstock Energy*. Energy contained in raw materials that end up directly in the final product is termed "feedstock energy." For ethanol production, feedstock energy includes the energy contained in the biomass. Likewise, the natural gas converted to methanol contains primary energy that is considered a feedstock energy input for MTBE. Feedstock energy is a subset of the primary energy inputs.
- *Process Energy*. The second major subset of primary energy is "process energy." This is limited to energy inputs in the life cycle exclusive of the energy contained in the feedstock (as defined in the previous bullet). It is the energy contained in raw materials extracted from the environment that does not contribute to the energy of the product itself, but is needed in the processing of feedstock energy into its final product form. Process energy consists primarily of coal, natural gas, uranium, and hydroelectric power sources consumed directly or indirectly in the product life cycle.
- *Fossil Energy*. Because we are concerned about the renewable nature of ethanol/ETBE, we also track the primary energy that comes from fossil sources specifically (coal, oil and natural gas). All three of the previously defined energy flows can be categorized as fossil or nonfossil energy.
- *Renewable Energy*. Renewable energy refers to energy obtained from biomass sources, as is the case for ethanol production in this study. Renewable energy also refers to electricity production from renewable sources such as biomass and hydroelectricity.

The energy use of the different options studied is a good measure of the overall environmental performance of the option. The energy obtained from burning biomass and ethanol is considered renewable energy. Energy obtained from fossil fuels is considered nonrenewable. ETBE has both renewable and nonrenewable components as its synthesis requires isobutylene, which is derived from fossil fuel.

In the results tables the following energy values are reported: 1) fossil or nonrenewable energy, 2) renewable energy, 3) process energy, 4) feedstock energy, and 5) total primary energy. Criteria air pollutants are linked to the use of both nonrenewable and renewable energy, whereas natural resource depletion[28] and fossil CO_2 emissions are only linked to nonrenewable sources. Renewable energy use by the MTBE system is due to electricity use produced from renewable resources. Process energy indicates the net energy input to the process and can be useful in comparing process options. Feedstock energy describes the energy contained in the final product, which is available to do work in an engine. All other things being equal, feedstock energy is a function of the energy densities of each of the fuel oxygenates.

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[27] The energy "contained" in a raw material is the amount of energy that would be released by the complete combustion of that raw material. This "heat of combustion" can be measured in two different ways: as a higher heating value or a lower heating value. Combustion results in the formation of carbon dioxide and water. Higher heating values consider the amount of energy released when the final combustion products are gaseous carbon dioxide and liquid water. Lower heating values take into account the loss of energy associated with the vaporization of the liquid water combustion product. Our energy content is based on the lower heating values for each material.

[28] Soil erosion is not included in the calculation of natural resource depletion since data were not available. The effects of biomass harvesting on soil erosion is more difficult to quantify than the removal of other natural resources, e.g., as coal and oil.

6.3 MASS FLOWCHART

In addition to the results tables and graphs for each scenario, there is a mass flow diagram that outlines the system flows associated with each scenario. Once again, the value chosen for the comparison of the two different biomass disposal options is ***One MBDT*** of biomass. The example in Figure 17 shows the system flows associated with the two disposal options for rice straw:

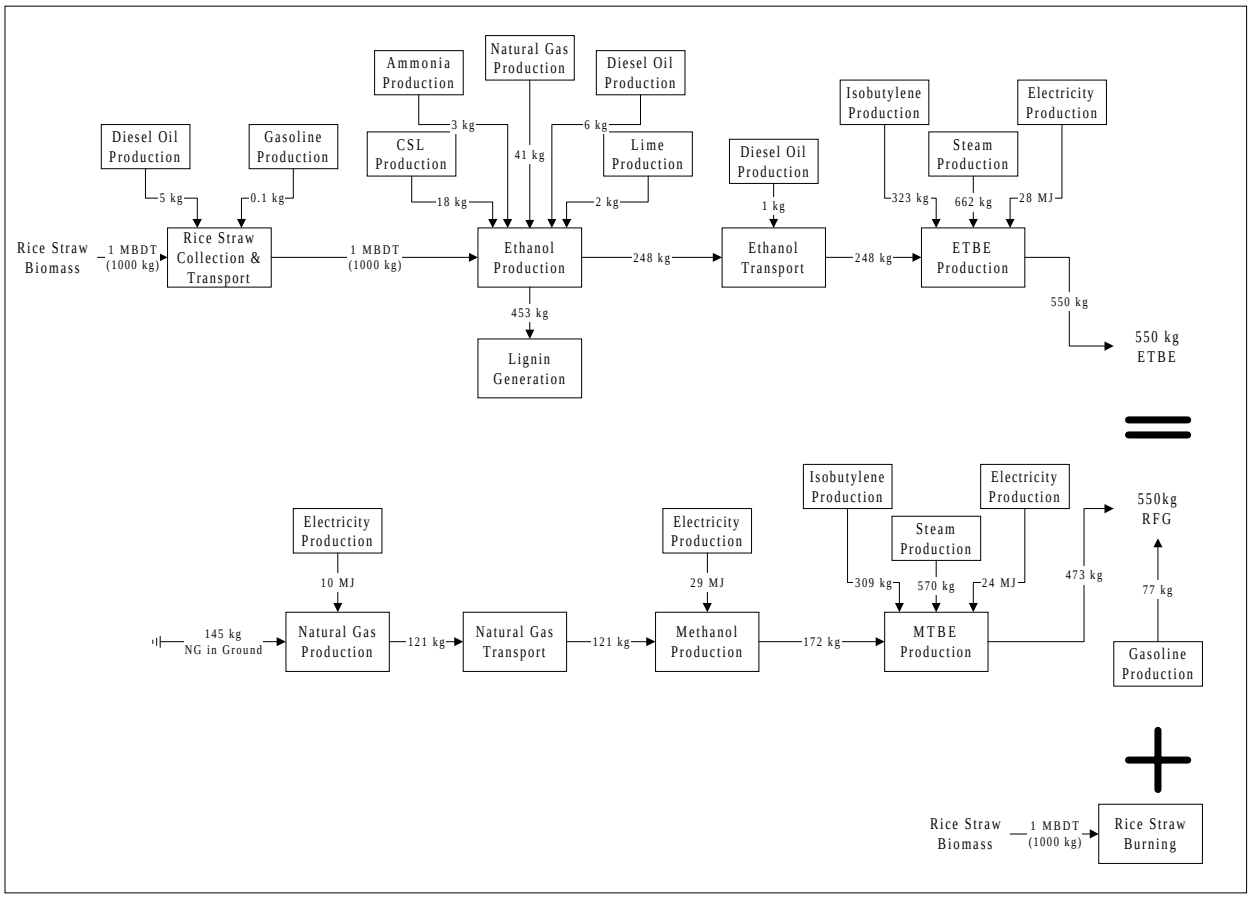

Figure 17: Mass Flow Diagram for Rice Straw with the Enzyme Process

How to Read the Mass Flow Diagram: The example in Figure 17 shows that the amount of MTBE used in the biomass burning option is dependent on the amount of ETBE produced from disposing one MBDT of biomass through ethanol production. As stated in Section 1.2, this study focused on the amount of oxygenates needed to perform the same function in reformulated gasoline. Based on Table 6, more ETBE is needed to produce the same amount of oxygen as MTBE but MTBE requires some additional gasoline to have the same heating value as the ETBE. This study looks at only the differences between ETBE and MTBE reformulated gasoline. Therefore, Figure 17 shows that 550 kg of ETBE effectively replaces 473 kg of MTBE and 77 kg of gasoline in reformulated gasoline production.

The different feedstocks and different ethanol production methods lead to different amounts of ethanol (and therefore, ETBE) that are produced. This is due to the fact that one MBDT of biomass yields different amounts of ethanol depending on the type of biomass and method of ethanol production. Different quantities of ETBE imply that different amounts of MTBE (and gasoline) need to be produced. Therefore, the life cycle results vary accordingly, as shown in the overall results.

6.4 BASELINE SCENARIO RESULTS AND DISCUSSION

6.4.1 Rice Straw Feedstock—Enzyme Process

Table 42: Results Summary for Rice Straw Feedstock—Enzyme Process

	Flow	Units	**OPTION 1:** MTBE Production/Use + Biomass Burning	**OPTION 2:** ETBE Production/Use	Change from **OPTION 1** to **OPTION 2**
Inflows	Coal	kg	314	7	98%
	Natural Gas	kg	434	290	33%
	Oil	kg	383	277	28%
Outflows	Carbon Dioxide (CO_2, biomass)	g	1,521,110	1,606,570	**-6%**
	Carbon Dioxide (CO_2, fossil)	g	2,929,590	1,406,330	52%
	Carbon Monoxide (CO)	g	32,121	1,037	97%
	Hydrocarbons (except methane)	g	10,204	3,990	61%
	Methane (CH_4)	g	3,452	1,317	62%
	Nitrogen Oxides (NO_x)	g	8,449	2,586	69%
	Nitrous Oxide (N_2O)	g	57	9	84%
	Particulates (unspecified)	g	7,281	788	89%
	Sulfur Oxides (SO_x)	g	7,447	1,183	84%
	COD	g	761	118	84%
	Nitrates (NO_3-)	g	4	13	**-204%**
	Waste (total)	kg	512	190	63%
Energy	Nonrenewable Energy	MJ	40,525	20,688	49%
	Renewable Energy	MJ	74	13,455	**-18203%**
	Process Energy	MJ	20,628	13,133	36%
	Feedstock Energy	MJ	19,970	21,009	**-5%**
	Total Primary Energy	MJ	40,598	34,143	16%

For this scenario, Option 2 leads to a decrease from Option 1 for almost all of the environmental flows (Table 42). The exceptions are nitrates and renewable energy (an increase in renewable energy consumption is more desirable than a decrease). The higher values for these two parameters originate from the ethanol production step. The difference between the two options for biomass CO_2 is not considered to be statistically significant.

Criteria Pollutants

Carbon monoxide emissions are lower for Option 2 by a factor of about 30, which is a significant advantage for Option 2. Similarly, particulate emissions are lower for Option 2 by a factor of ten, again a significant reduction for an important criteria pollutant. Particulate emissions from burning of rice straw are especially important since it contains high amounts of silica, although silica emissions are not regulated. It should be noted that most of the carbon monoxide and a lot of the particulate emissions are from biomass burning in Option 1. The SO_x emissions for Option 2 are lower by a factor of about seven, while the NO_x and non-methane hydrocarbon emissions for Option 2 are lower by a factor of about three. These emissions are higher for Option 1 primarily because of higher emissions for MTBE production when compared to ETBE production.

Energy Consumption and CO_2

The total primary energy is less for Option 2 by 16%, and the renewable portions of the total energy are 0.2% and 40% for Options 1 and 2, respectively. Process energy required is less for Option 2 by 36%; this is despite the need for supplemental natural gas to generate the steam needed by the ethanol production step. The need for supplemental natural gas arises from the high ash and low lignin contents of rice straw. The ethanol yield per dry ton of rice straw is similar to those for forest residue and chaparral. Hence, the steam needed by the ethanol production step is about the same as well. However, the ligneous residue has a much lower heating value due to its higher ash and lower lignin contents, thereby requiring supplemental natural gas. The fossil-derived CO_2 is still lower for Option 2 by 52%, which is a substantial reduction in the emissions of CO_2.

Water Emissions

Nitrates are significantly higher for Option 2 mainly because of the use of CSL during ethanol fermentation. CSL is a by-product of corn wet-milling, and agricultural operations lead to water run-offs containing fertilizer-derived nitrates. If this is perceived as a negative attribute of Option 2, alternatives to CSL need to be considered. However, as explained in the Impact Assessment section, the eutrophication potential is still lower for Option 2.

Graphical Representation of Key Results

The mass flow diagram for this system is shown in Section 0 (Figure 17). The following graphs show the comparative emissions for five criteria pollutants—carbon monoxide (Figure 18), nitrogen oxides (Figure 19), particulates (Figure 20), sulfur oxides (Figure 21), and nonmethane hydrocarbons (Figure 22 through Figure 24)—as well as energy consumption (Figure 25 and Figure 26). The first column represents values for Option 1, split out as values from MTBE production and biomass burning. The second column shows the flows for Option 2, ETBE production. The scales are kept the same throughout the entire results section, in order to facilitate comparison among the different biomass feedstocks and ethanol production methods.

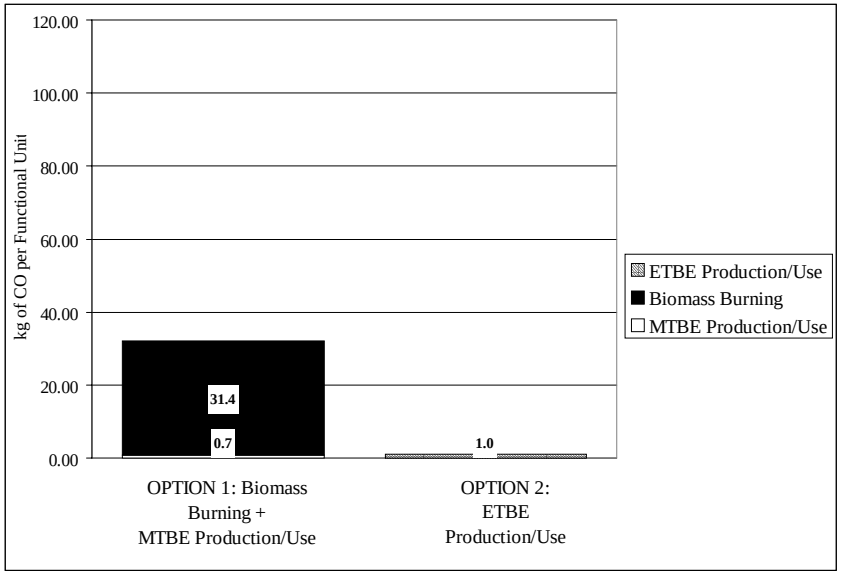

Figure 18: Rice Straw (Enzyme Process) Carbon Monoxide Emissions

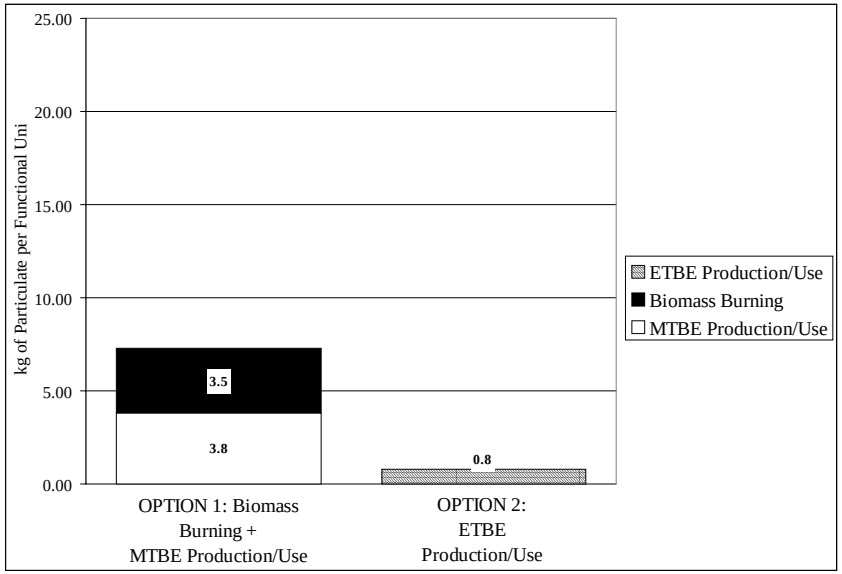

Figure 20: Rice Straw (Enzyme Process) Particulate Emissions

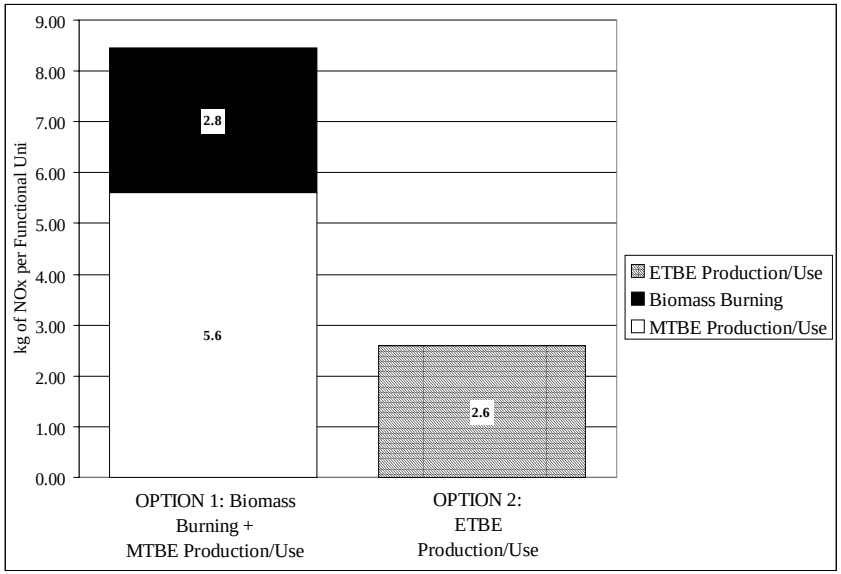

Figure 19: Rice Straw (Enzyme Process) NO_x Emissions

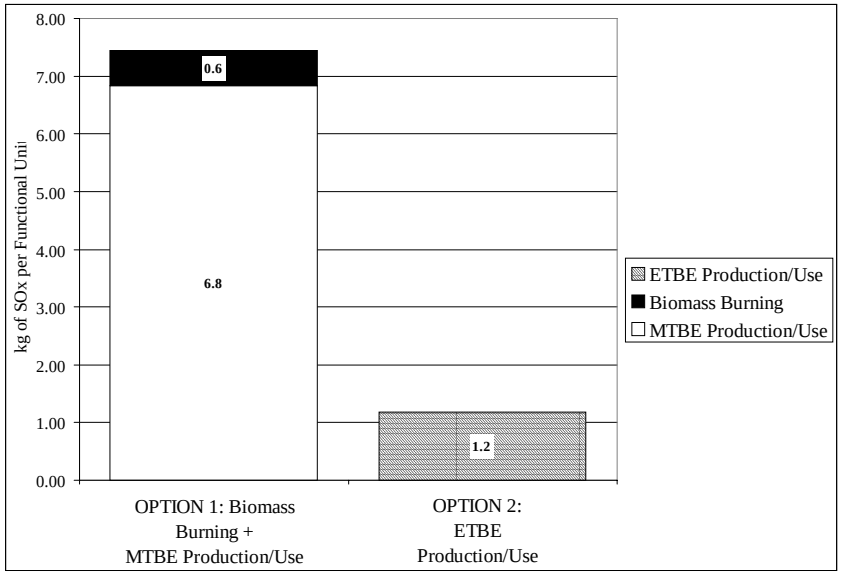

Figure 21: Rice Straw (Enzyme Process) SO_x Emissions

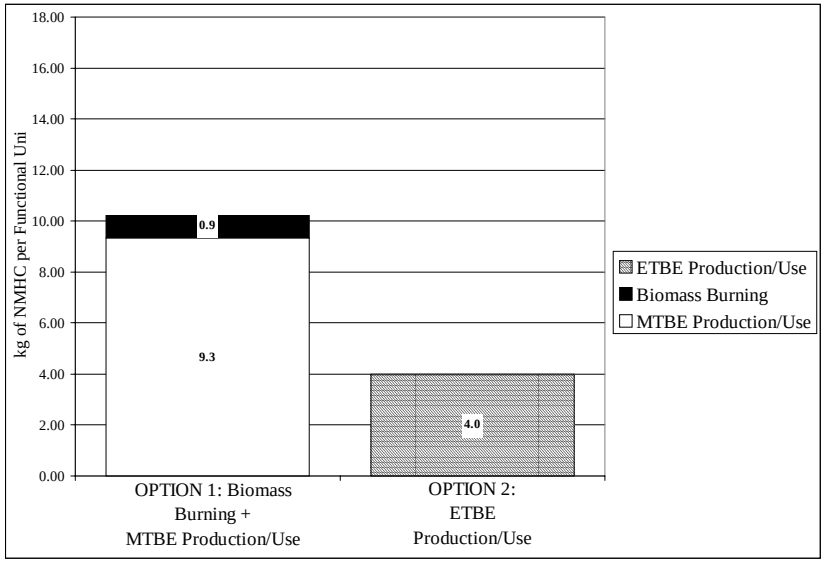

Figure 22: Rice Straw (Enzyme Process) Non-Methane Hydrocarbon Emissions

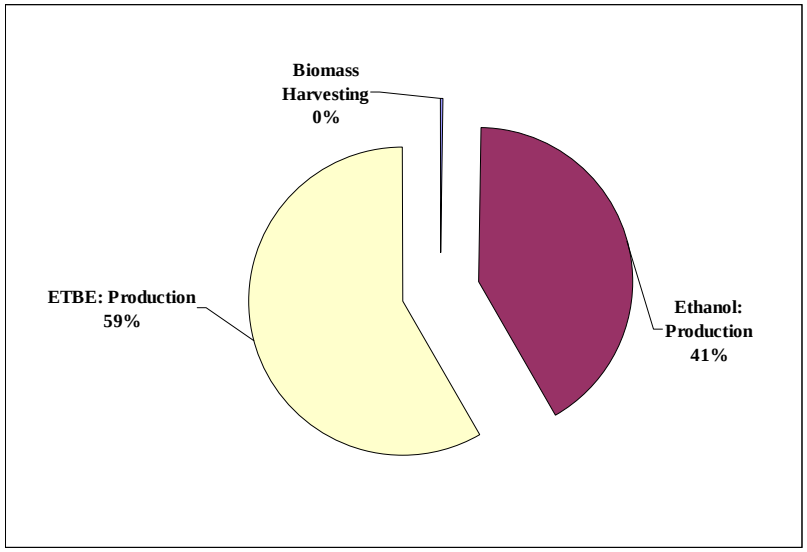

Figure 23: Rice Straw (Enzyme Process) Non-Methane Hydrocarbon Emissions for Option 2 by Source

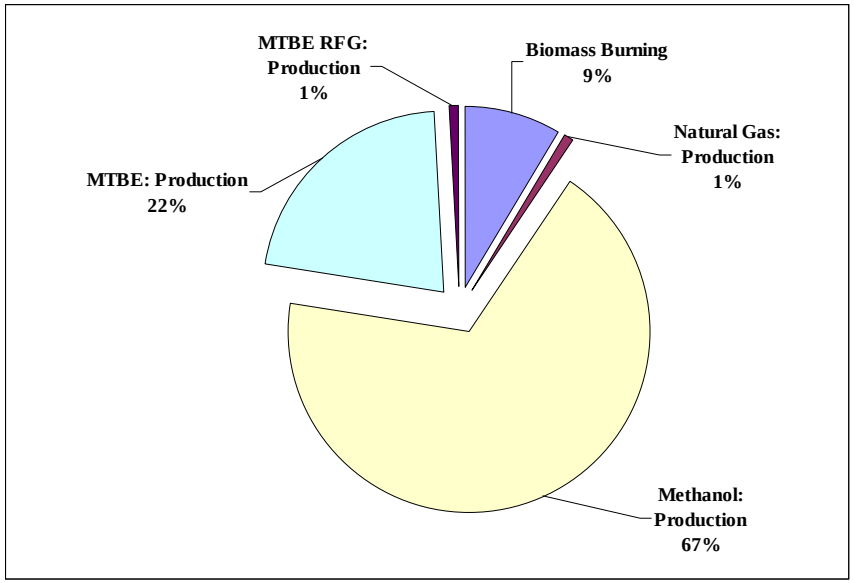

Figure 24: Rice Straw (Enzyme Process) Non-Methane Hydrocarbon Emissions for Option 1 bySource

The two pie charts (Figure 23, Figure 24) show which life cycle stages contributed to the total value for the non-methane hydrocarbon emissions in Figure 22. Figure 23 shows that the value for Option 2, while smaller than the total value for Option 1, is higher than that for the biomass burning portion of Option 1. Figure 23 also shows that these emissions are derived from the ETBE and ethanol production stage, where natural gas is used in the process. Figure 24 highlights the information that the main source of non-methane hydrocarbons for Option 1 is the MTBE and methanol production.

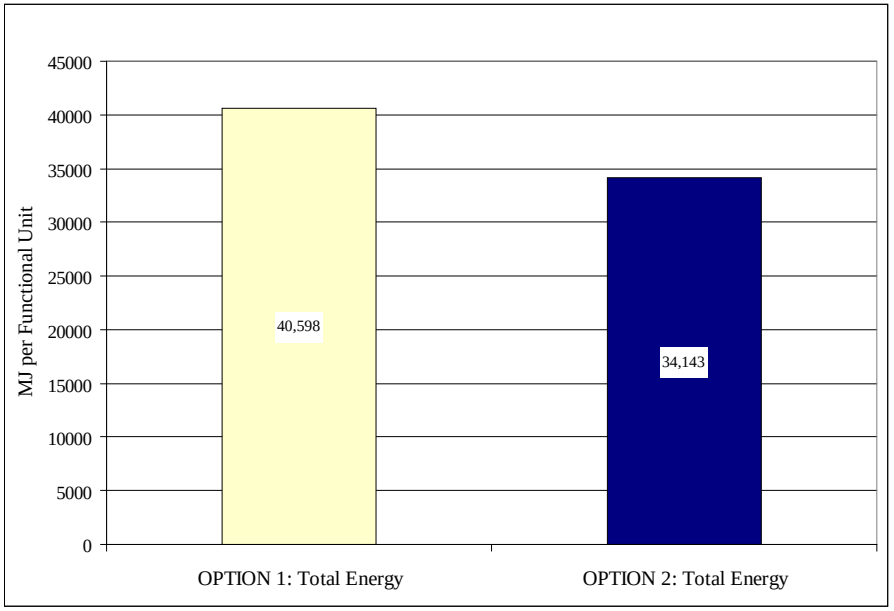

Figure 25: Rice Straw (Enzyme Process) Total Energy Consumption

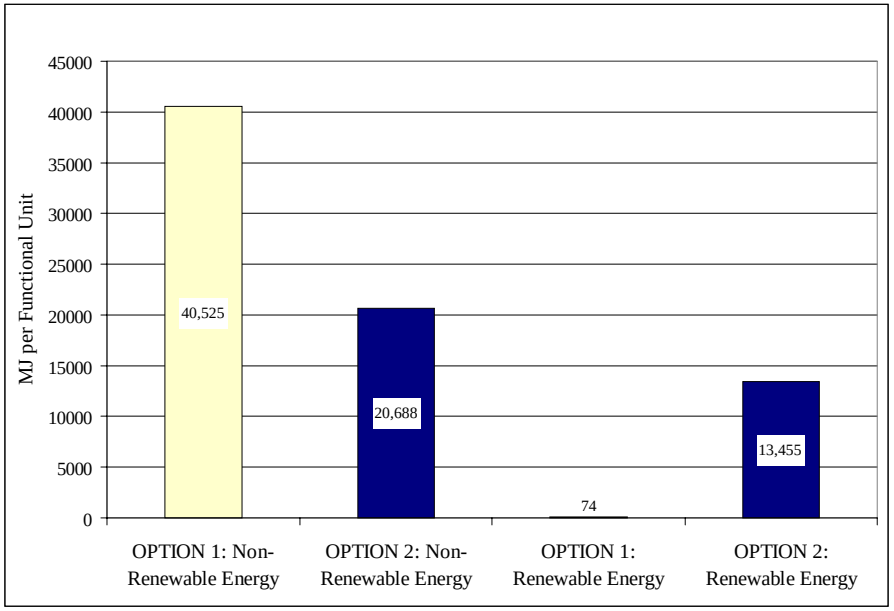

Figure 26: Rice Straw (Enzyme Process) Nonrenewable and Renewable Energy Consumption

6.4.2 Rice Straw Feedstock—Concentrated Acid Process

Table 43: Results Summary for Rice Straw Feedstock—Acid Process

	Flow	Units	**OPTION 1:** MTBE Production/Use + Biomass Burning	**OPTION 2:** ETBE Production/Use	Change from **OPTION 1** to **OPTION 2**
Inflows	Coal	kg	282	8	97%
	Natural Gas	kg	391	567	**-45%**
	Oil	kg	345	249	28%
Outflows	Carbon Dioxide (CO_2, biomass)	g	1,521,110	1,354,290	11%
	Carbon Dioxide (CO_2, fossil)	g	2,637,810	1,979,070	25%
	Carbon Monoxide (CO)	g	32,049	1,449	95%
	Hydrocarbons (except methane)	g	9,274	3,362	64%
	Methane (CH_4)	g	3,108	4,968	**-60%**
	Nitrogen Oxides (NO_x)	g	7,890	3,407	57%
	Nitrous Oxide (N_2O)	g	51	16	69%
	Particulates (unspecified)	g	6,902	3,846	44%
	Sulfur Oxides (SO_x)	g	6,767	1,294	81%
	COD	g	685	94	86%
	Nitrates (NO_3-)	g	4	22	**-466%**
	Waste (total)	kg	461	253	45%
Energy	Nonrenewable Energy	MJ	36,489	34,153	6%
	Renewable Energy	MJ	66	11,774	**-17688%**
	Process Energy	MJ	18,574	27,010	**-45%**
	Feedstock Energy	MJ	17,981	18,917	**-5%**
	Total Primary Energy	MJ	36,555	45,926	**-26%**

The relative performance of Option 1 versus Option 2 with a concentrated acid process is mostly similar to that with an enzyme process, natural gas and primary energy consumption being major exceptions (Table 43). In terms of the criteria pollutants, the acid process is generally higher than the enzyme process for all of the emissions. The use of additional natural gas in the concentrated acid process leads to higher values for depletion of natural resources and greenhouse gas potential indicators. Methane emissions are also higher because of the additional natural gas that is required to run the acid process.

For a given feedstock, the concentrated acid process demands more energy than the enzymatic process. This is due to the thermal energy required in concentrating the diluted acid stream, obtained after chromatographic separation of acid and sugars, back to the concentration of 70%-77%. The enzymatic process does not have this step or the concomitant energy needs. For these reasons, the relative performance of Option 2 with the concentrated acid process is lower for nonrenewable energy consumption, primary energy consumption, fossil CO_2, SO_x, NO_x, non-methane hydrocarbons and particulate emissions.

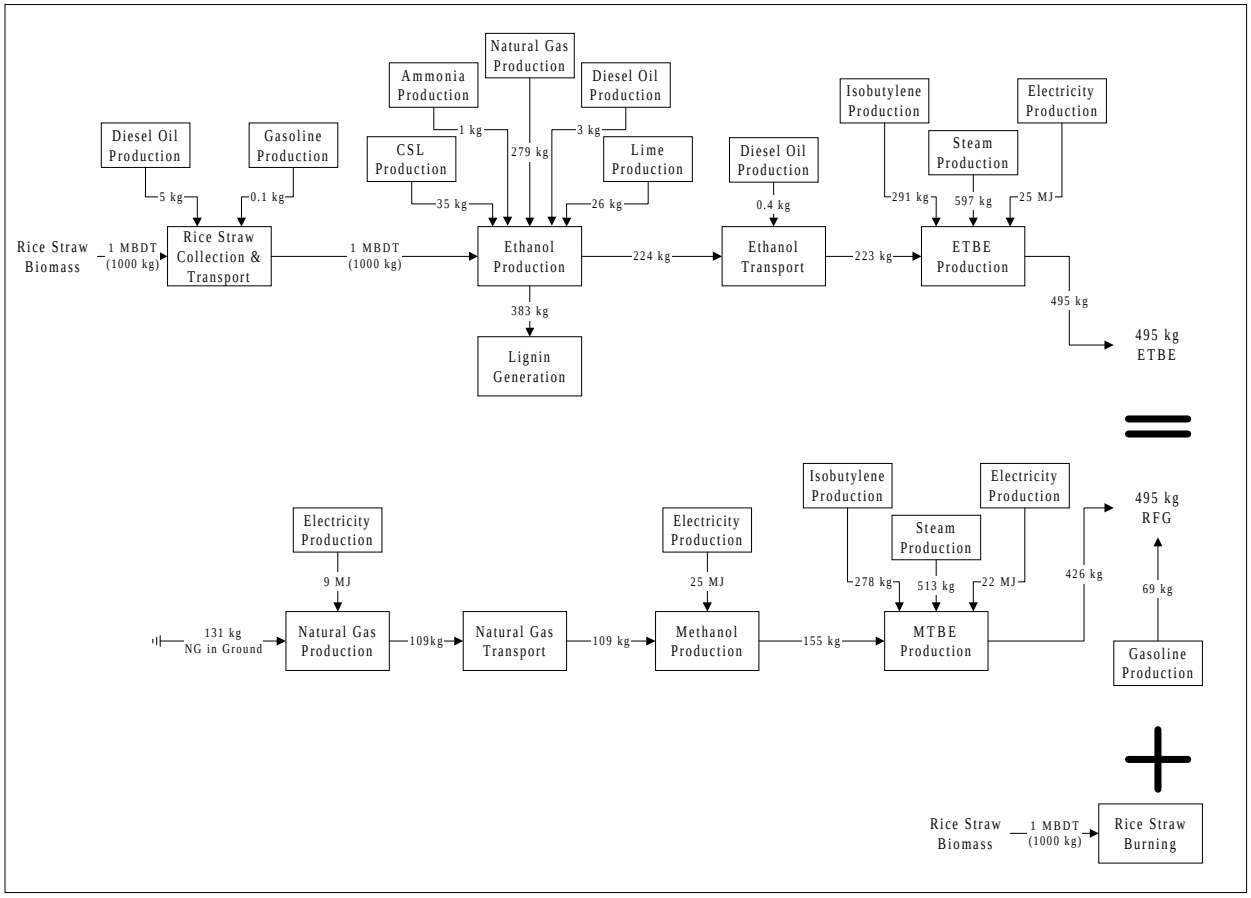

Figure 27: Mass Flow Diagram for Rice Straw—Acid Process

Graphical Representation of Key Results

The mass flow diagram for this system is shown in Figure 27. The following graphs show the comparative emissions for five criteria pollutants—carbon monoxide (Figure 28), nitrogen oxides (Figure 29), non-methane hydrocarbons (Figure 30), sulfur oxides (Figure 31), and particulates (Figure 32 through Figure 34)—as well as energy consumption (Figure 35 and Figure 36). The first column represents values for Option 1, split out as values from MTBE production and biomass burning. The second column shows the flows for Option 2, ETBE production. The scales are kept the same throughout the entire results section, in order to facilitate comparison among the different biomass feedstocks and ethanol production methods.

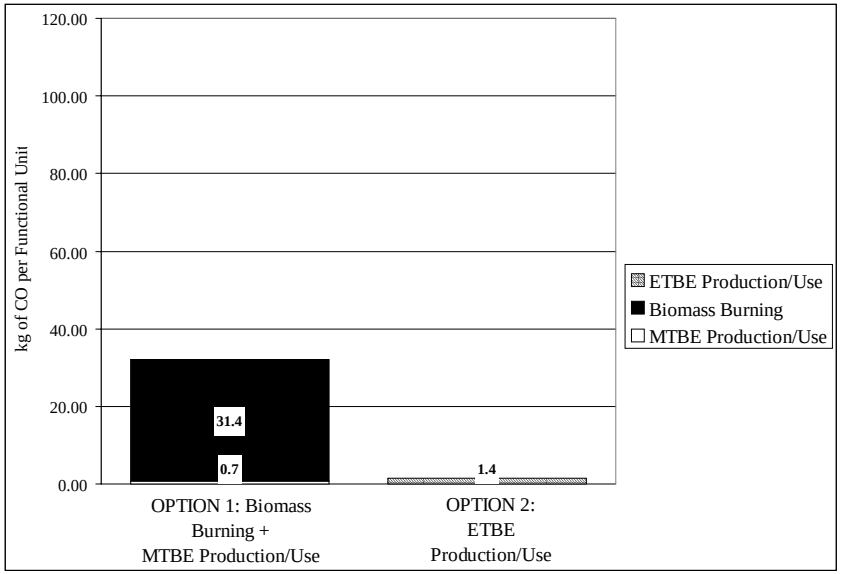

Figure 28: Rice Straw (Acid Process) Carbon Monoxide Emissions

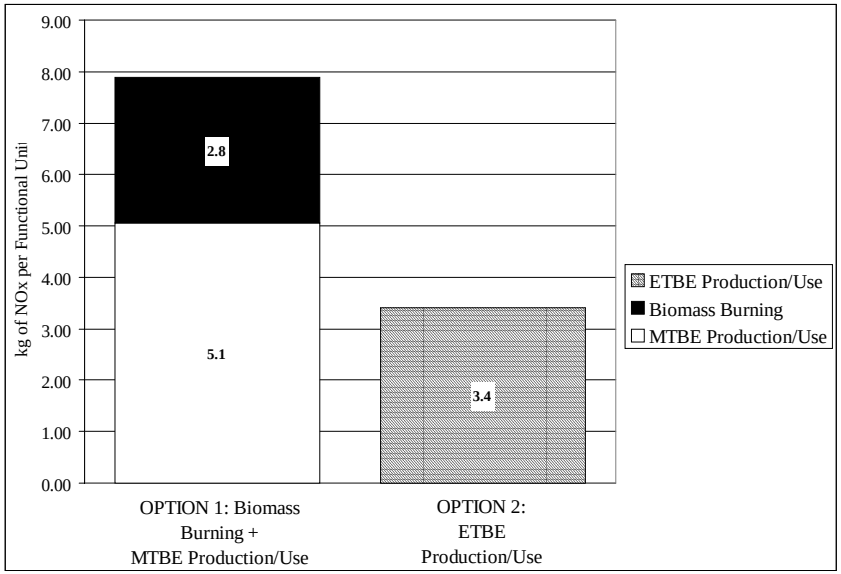

Figure 29: Rice Straw (Acid Process) NO_x Emissions

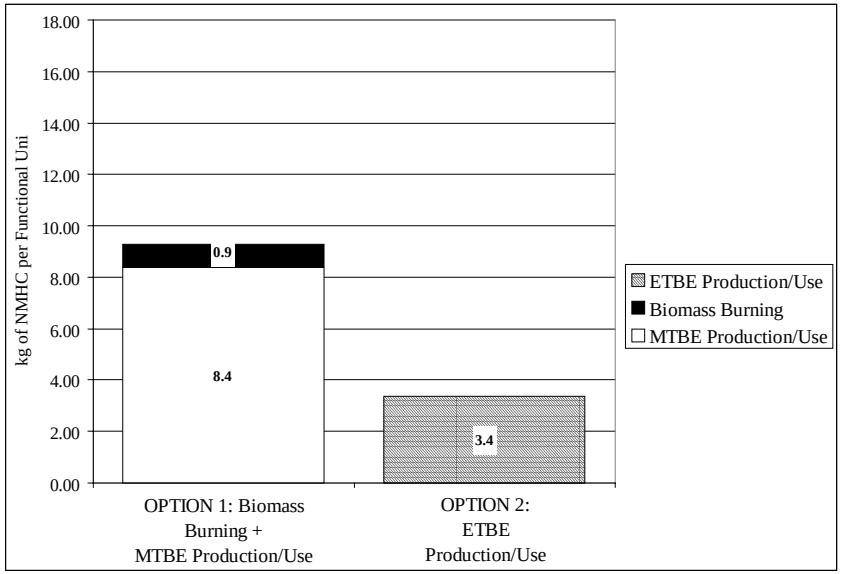

Figure 30: Rice Straw (Acid Process) Non-Methane Hydrocarbon Emissions

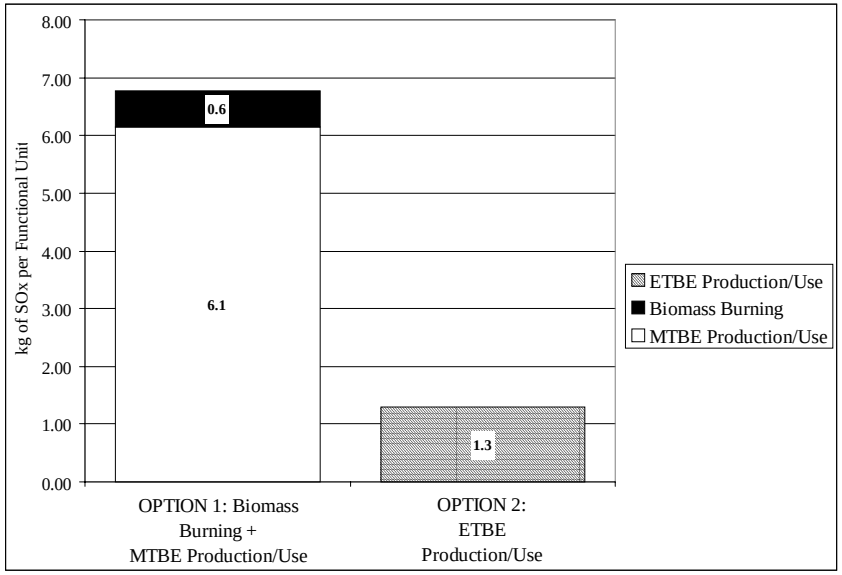

Figure 31: Rice Straw (Acid Process) SO_x Emissions

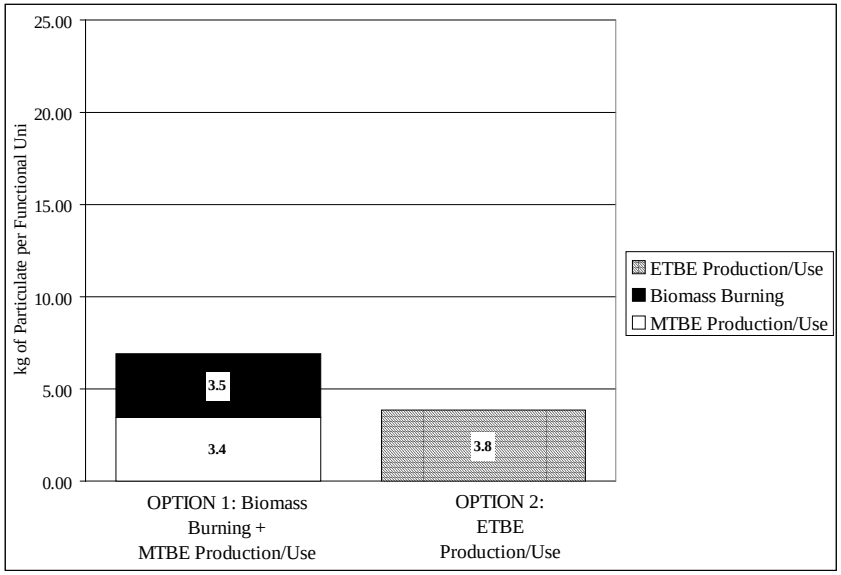

Figure 32: Rice Straw (Acid Process) Particulate Emissions

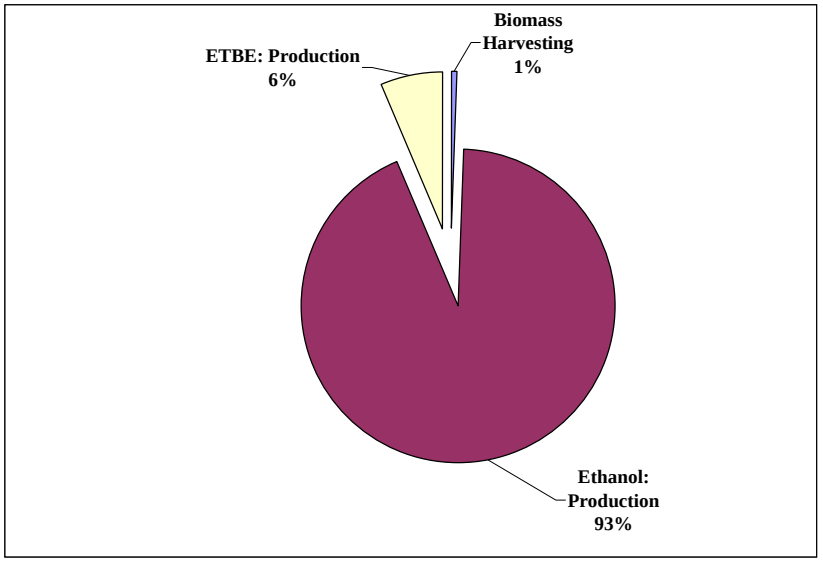

Figure 33: Rice Straw (Acid Process) Particulate Emissions for Option 2 by Source

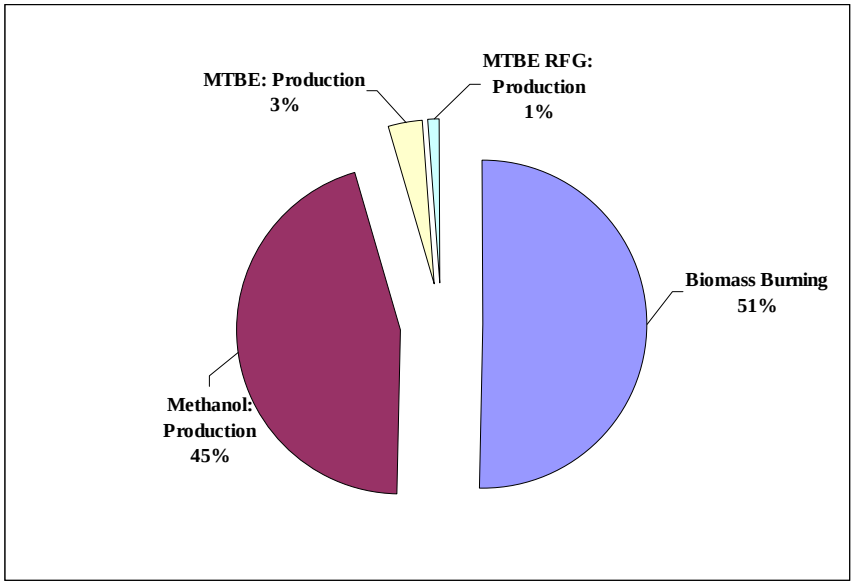

Figure 34: Rice Straw (Acid Process) Particulate Emissions for Option 1 by Source

The two pie charts (Figure 33, Figure 34) show which life cycle stages contributed to the total value for the particulate emissions in Figure 32. Figure 33 shows that the value for Option 2, while smaller than the total value for Option 1, is higher than that for MTBE production portion of Option 1. Figure 33 also shows that these emissions are derived from the ethanol production stage, where natural gas is used in the process. Figure 34 highlights the information that the main source of particulates for Option 1 is the burning of biomass and methanol production.

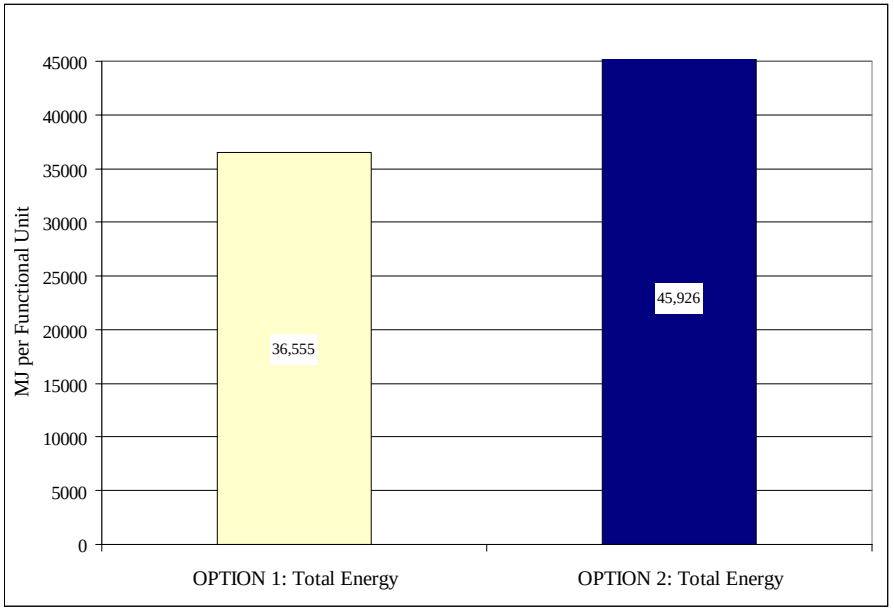

Figure 35: Rice Straw (Acid Process) Total Energy Consumption

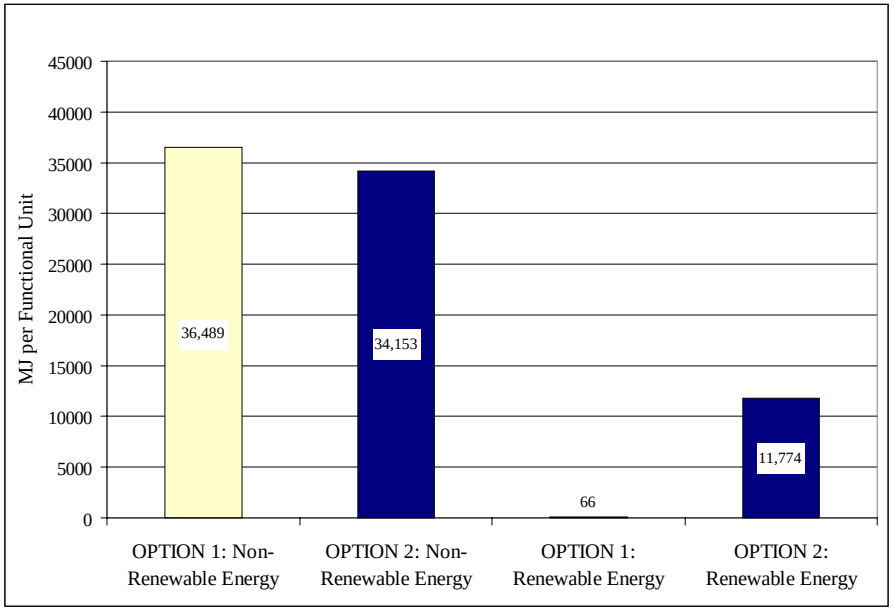

Figure 36: Rice Straw (Acid Process) Nonrenewable and Renewable Energy Consumption

6.4.3 Rice Straw Feedstock Summary

The production of ETBE from a rice straw feedstock leads to a reduction in environmental flows over the burning of the rice straw and the production of MTBE. The production of ethanol in general has greater negative impacts on water effluents (e.g., nitrates); however, in terms of other criteria pollutants, the production of ETBE from rice straw leads to lower net emissions.

6.4.4 Forest Residue Feedstock—Enzyme Process

Table 44: Results Summary for Forest Residue Feedstock—Enzyme Process

	Flow	Units	**OPTION 1:** MTBE Production/Use + Biomass Burning	**OPTION 2:** ETBE Production/Use	Change from **OPTION 1** to **OPTION 2**
Inflows	Coal	kg	344	-9	103%
	Natural Gas	kg	477	247	48%
	Oil	kg	427	314	27%
Outflows	Carbon Dioxide (CO_2, biomass)	g	1,887,770	1,925,160	**-2%**
	Carbon Dioxide (CO_2, fossil)	g	3,237,431	1,361,190	58%
	Carbon Monoxide (CO)	g	71,698	1,275	98%
	Hydrocarbons (except methane)	g	10,263	4,382	57%
	Methane (CH_4)	g	15,931	564	96%
	Nitrogen Oxides (NO_x)	g	8,340	2,561	69%
	Nitrous Oxide (N_2O)	g	65	7	89%
	Particulates (unspecified)	g	12,783	891	93%
	Sulfur Oxides (SO_x)	g	7,515	982	87%
	COD	g	867	163	81%
	Nitrates (NO_3-)	g	5	14	**-196%**
	Waste (total)	kg	562	15	97%
Energy	Nonrenewable Energy	MJ	44,842	18,748	58%
	Renewable Energy	MJ	81	15,708	**-19282%**
	Process Energy	MJ	23,012	11,405	50%
	Feedstock Energy	MJ	21,910	23,051	**-5%**
	Total Primary Energy	MJ	44,923	34,456	23%

For forest residue, Option 2 leads to a decrease from Option 1 for almost all of the environmental flows (Table 44). The exceptions are nitrates and renewable energy. As with rice straw, the higher values from these flows ensue from the ethanol production stage. The biomass CO_2 values for the two options are statistically similar.

Criteria Pollutants

Carbon monoxide emissions are lower for Option 2 by a factor of about 60; this decrease is substantial and is twice that observed with rice straw. The difference is due to the differing burning-emissions profiles for forest residue and rice straw (see Table 11 and Table 12). Particulate emissions are lower for Option 2 by a factor of about 15, a significant decline. Again, most of the carbon monoxide and a lot of the particulate emissions in Option 1 accrue from biomass burning. The SO_x emissions for Option 2 are lower by a factor of about eight, while NO_x and non-methane hydrocarbons emissions are lower for Option 2 are by a factor of about 3–4. As in the case of rice straw, these emissions are higher for Option 1 essentially because MTBE production is responsible for higher emissions when compared to ETBE production.

Energy Consumption and CO_2

The total primary energy is less for Option 2 by 23%. The renewable portions of the total energy are 0.2% and 46% for Options 1 and 2, respectively. This is due to the excess electricity that is generated during the ethanol production stage. Process energy requirement is lower for Option 2 by 50%; this reduction is higher than that for rice straw. Unlike rice straw, forest residue produces enough ligneous fuel to satisfy process steam and electricity needs, and excess electricity is treated as a credit. The fossil-derived CO_2 is lower for Option 2 by 58%, a sizable mitigation of CO_2 emissions.

Water Emissions

As is the case with rice straw, Option 2 results in considerably higher nitrates that are attributable to the use of CSL during ethanol fermentation. However, as explained in the Impact Assessment section, the eutrophication potential is still lower for Option 2.

Graphical Representation of Key Results

The mass flow diagram for this system is shown in Figure 37. The graphs that follow show the comparative emissions for five criteria pollutants—carbon monoxide (Figure 38), nitrogen oxides (Figure 39), particulates (Figure 40), sulfur oxides (Figure 41), and non-methane hydrocarbons (Figure 42 through Figure 44)—as well as energy consumption (Figure 45 and Figure 46). The first column represents values for Option 1, split out as values from MTBE production and biomass burning. The second column shows the flows for Option 2, ETBE production. The scales are kept the same throughout the entire results section, in order to facilitate comparison among the different biomass feedstocks and ethanol production methods.

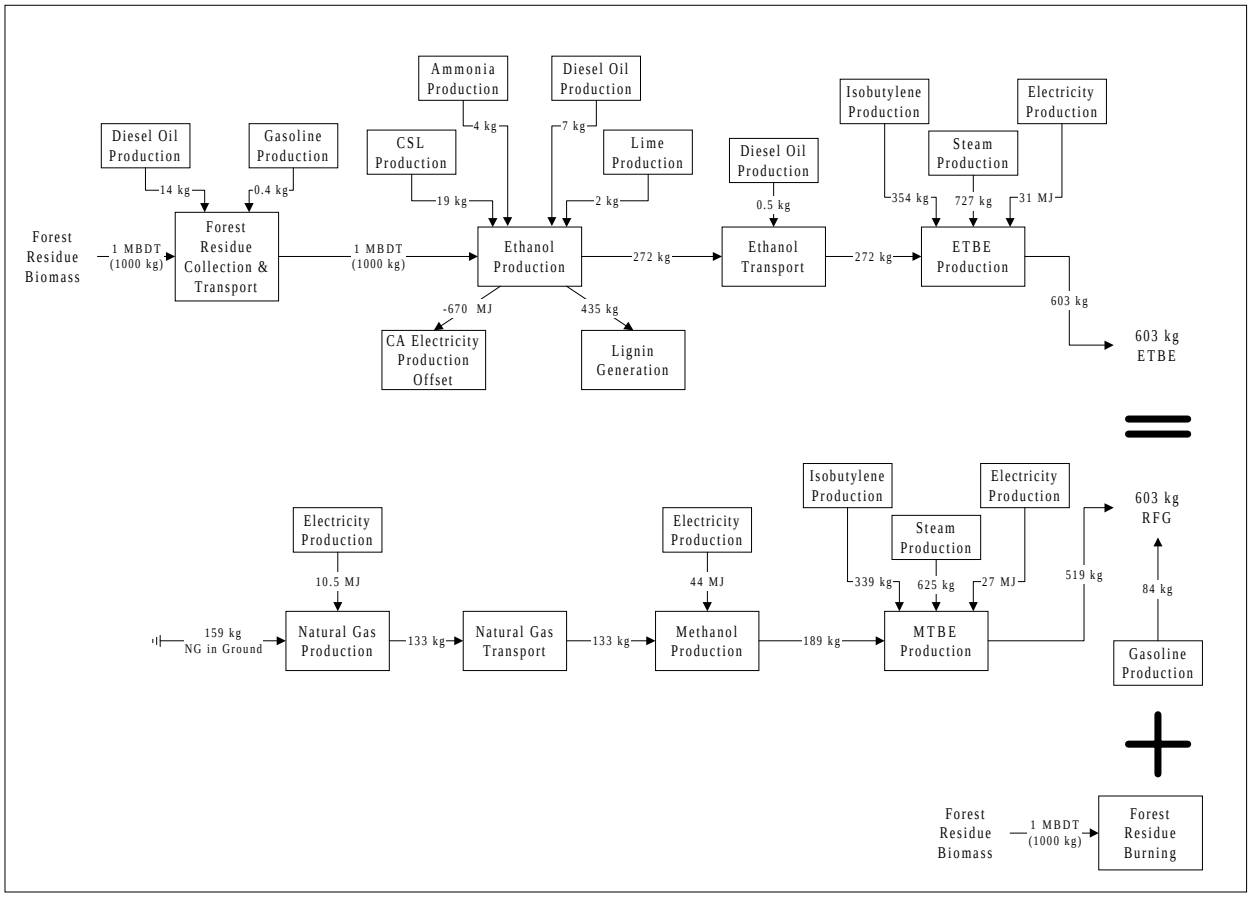

Figure 37: Mass Flow Diagram for Forest Residue—Enzyme Process

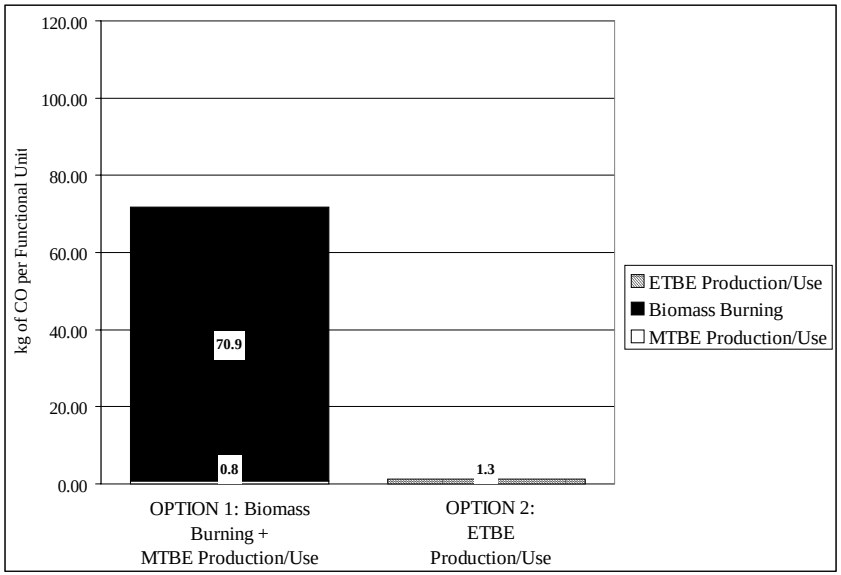

Figure 38: Forest Residue (Enzyme Process) Carbon Monoxide Emissions

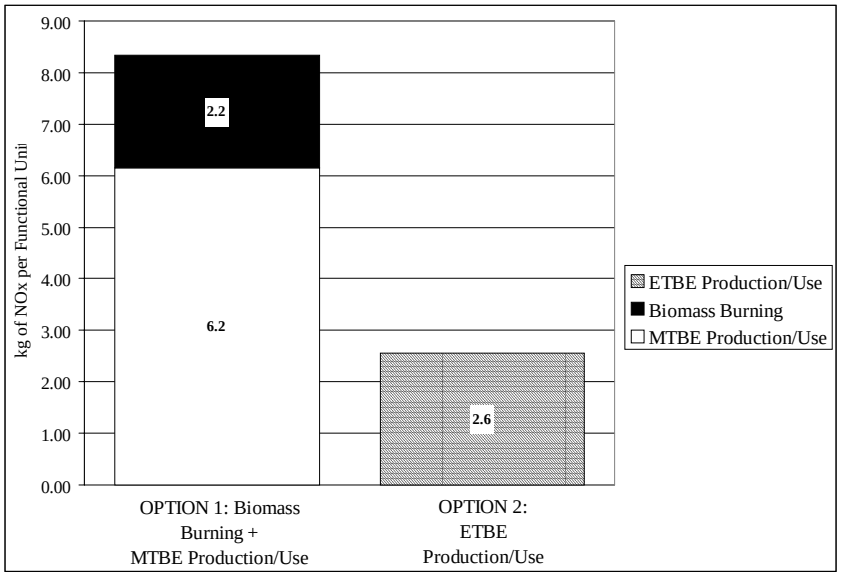

Figure 39: Forest Residue (Enzyme Process) NO_x Emissions

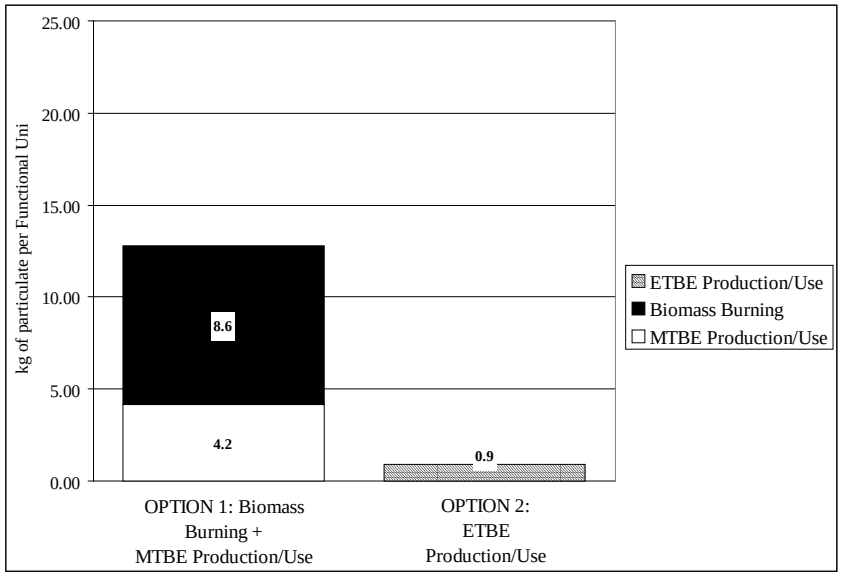

Figure 40: Forest Residue (Enzyme Process) Particulate Emissions

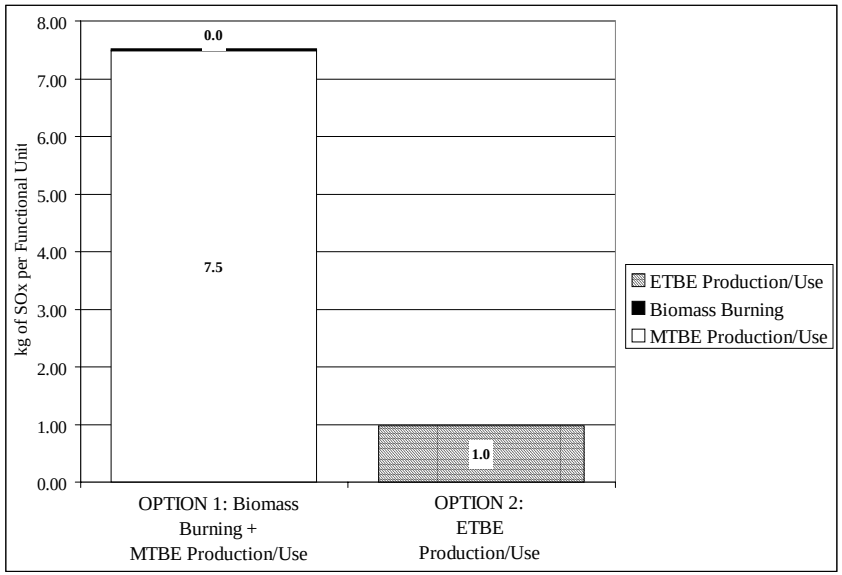

Figure 41: Forest Residue (Enzyme Process) SO_x Emissions

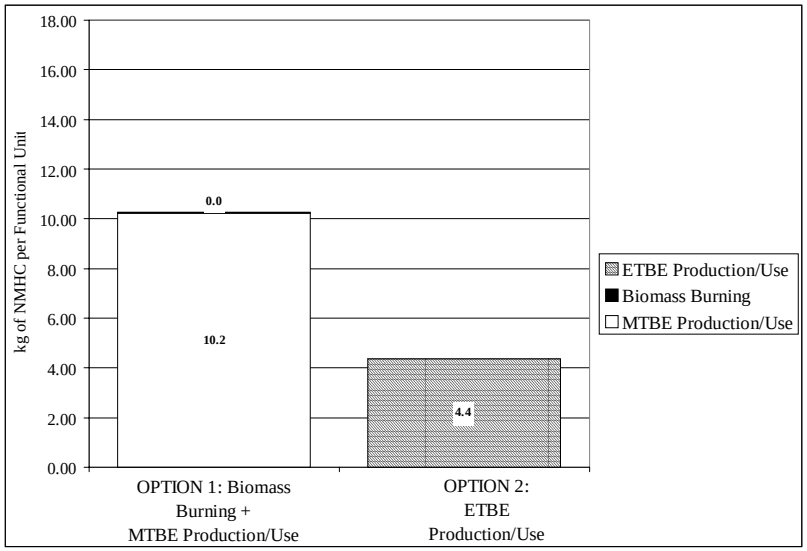

Figure 42: Forest Residue (Enzyme Process) Non-Methane Hydrocarbon Emissions

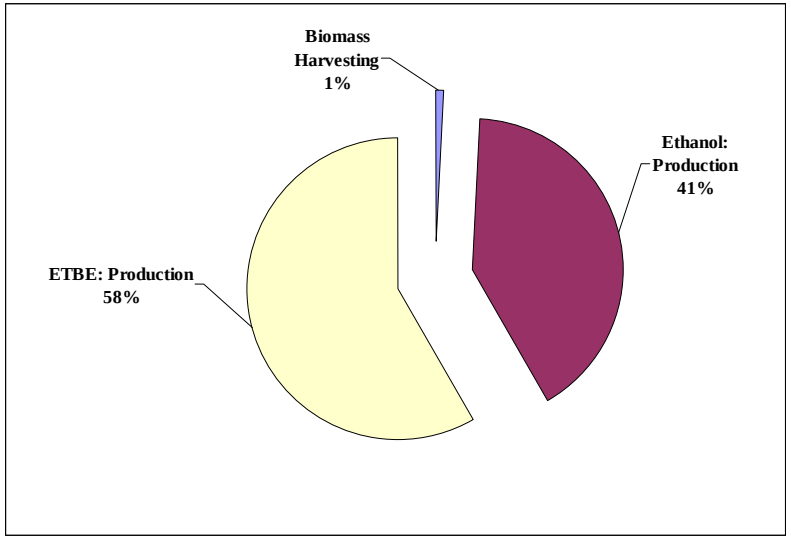

Figure 43: Forest Residue (Enzyme Process) Non-Methane Hydrocarbon Emissions for Option 2 by Source

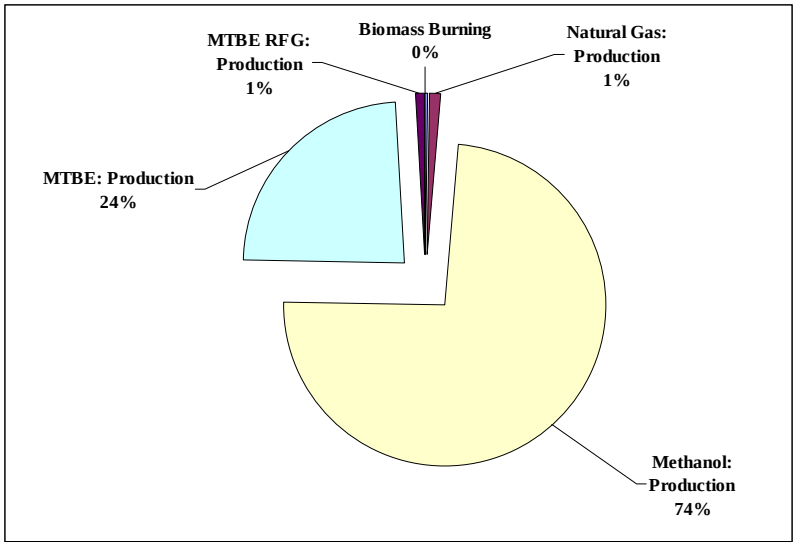

Figure 44: Forest Residue (Enzyme Process) Non-Methane Hydrocarbon Emissions for Option 1 by Source

The two pie charts (Figure 43, Figure 44) show which life cycle stages contributed to the total value for the non-methane hydrocarbon emissions in Figure 42. Figure 43 shows that the value for Option 2, while smaller than the total value for Option 1, is higher than that for the biomass burning portion of Option 1. Figure 43 also shows that these emissions are derived from the ethanol and ETBE production stages, where natural gas is used in the process. Figure 44 highlights the information that the main source of non-methane hydrocarbons for Option 1 is the MTBE and methanol production.

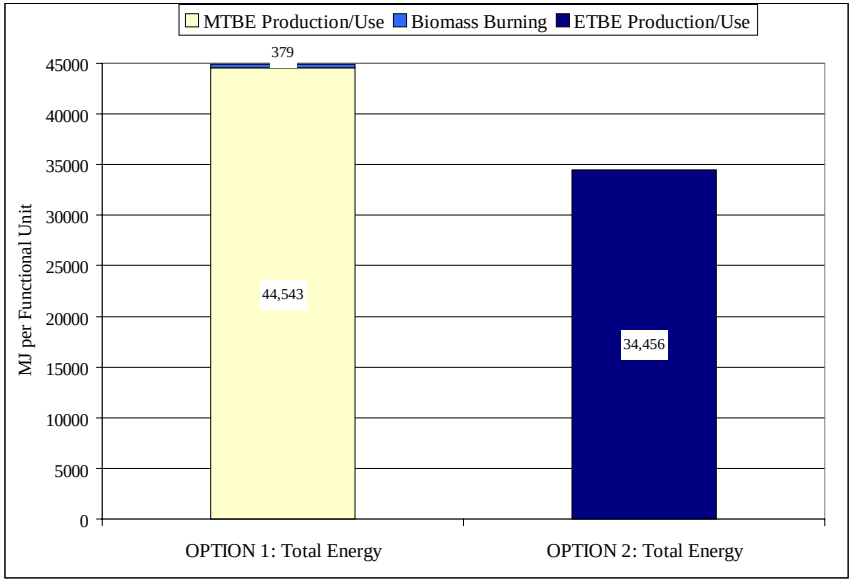

Figure 45: Forest Residue (Enzyme Process) Total Energy Consumption

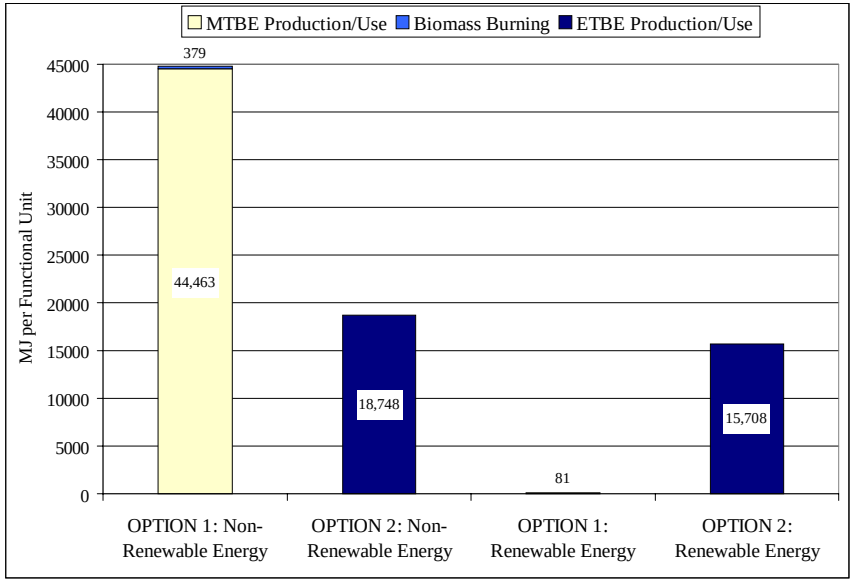

Figure 46: Forest Residue (Enzyme Process) Nonrenewable and Renewable Energy Consumption

6.4.5 Forest Residue Feedstock—Concentrated Acid Process

Table 45: Results Summary for Forest Residue Feedstock—Acid Process

	Flow	Units	**OPTION 1:** MTBE Production/Use + Biomass Burning	**OPTION 2:** ETBE Production/Use	Change from **OPTION 1** to **OPTION 2**
Inflows	Coal	kg	281	8	97%
	Natural Gas	kg	390	455	**-17%**
	Oil	kg	350	258	26%
Outflows	Carbon Dioxide (CO_2, biomass)	g	1,887,770	1,658,260	12%
	Carbon Dioxide (CO_2, fossil)	g	2,647,971	1,742,200	34%
	Carbon Monoxide (CO)	g	71,550	1,567	98%
	Hydrocarbons (except methane)	g	8,385	3,259	61%
	Methane (CH_4)	g	15,236	3,593	76%
	Nitrogen Oxides (NO_x)	g	7,211	3,327	54%
	Nitrous Oxide (N_2O)	g	53	16	69%
	Particulates (unspecified)	g	12,017	3,852	68%
	Sulfur Oxides (SO_x)	g	6,141	1,299	79%
	COD	g	714	130	82%
	Nitrates (NO_3-)	g	4	21	**-458%**
	Waste (total)	kg	459	94	79%
Energy	Nonrenewable Energy	MJ	36,688	28,881	21%
	Renewable Energy	MJ	66	13,295	**-19967%**
	Process Energy	MJ	18,862	23,352	**-24%**
	Feedstock Energy	MJ	17,892	18,824	**-5%**
	Total Primary Energy	MJ	36,754	42,176	**-15%**

As with rice straw, the relative performance of Option 1 versus Option 2 with a concentrated acid process is mostly similar to that with an enzyme process, with the main exception of natural gas and energy use (Table 45). The acid process is generally responsible for higher emissions of the criteria pollutants than is the enzyme process. The need for auxiliary natural gas in the concentrated acid process results in higher values for depletion of natural resources and greenhouse gas potential indicators. This also yields higher methane emissions.

As the concentrated acid process requires more energy than the enzymatic process, the relative performance of Option 2 with the concentrated acid process is lower for nonrenewable energy consumption, primary energy consumption, fossil CO_2, SO_x, NO_x, non-methane hydrocarbons, and particulate emissions.

Graphical Representation of Key Results

The mass flow diagram for this system is shown in Figure 47. The graphs that follow show the comparative emissions for five criteria pollutants—carbon monoxide (Figure 48), particulates (Figure 49), non-methane hydrocarbons (Figure 50), sulfur oxides (Figure 51), and nitrogen oxides (Figure 52 through Figure 54)—as well as energy consumption (Figure 55 and Figure 56). The first column represents values for Option 1, split out as values from MTBE production and biomass burning. The second column shows the flows for Option 2, ETBE production. The scales are kept the same throughout the entire results section, in order to facilitate comparison among the different biomass feedstocks and ethanol production methods.

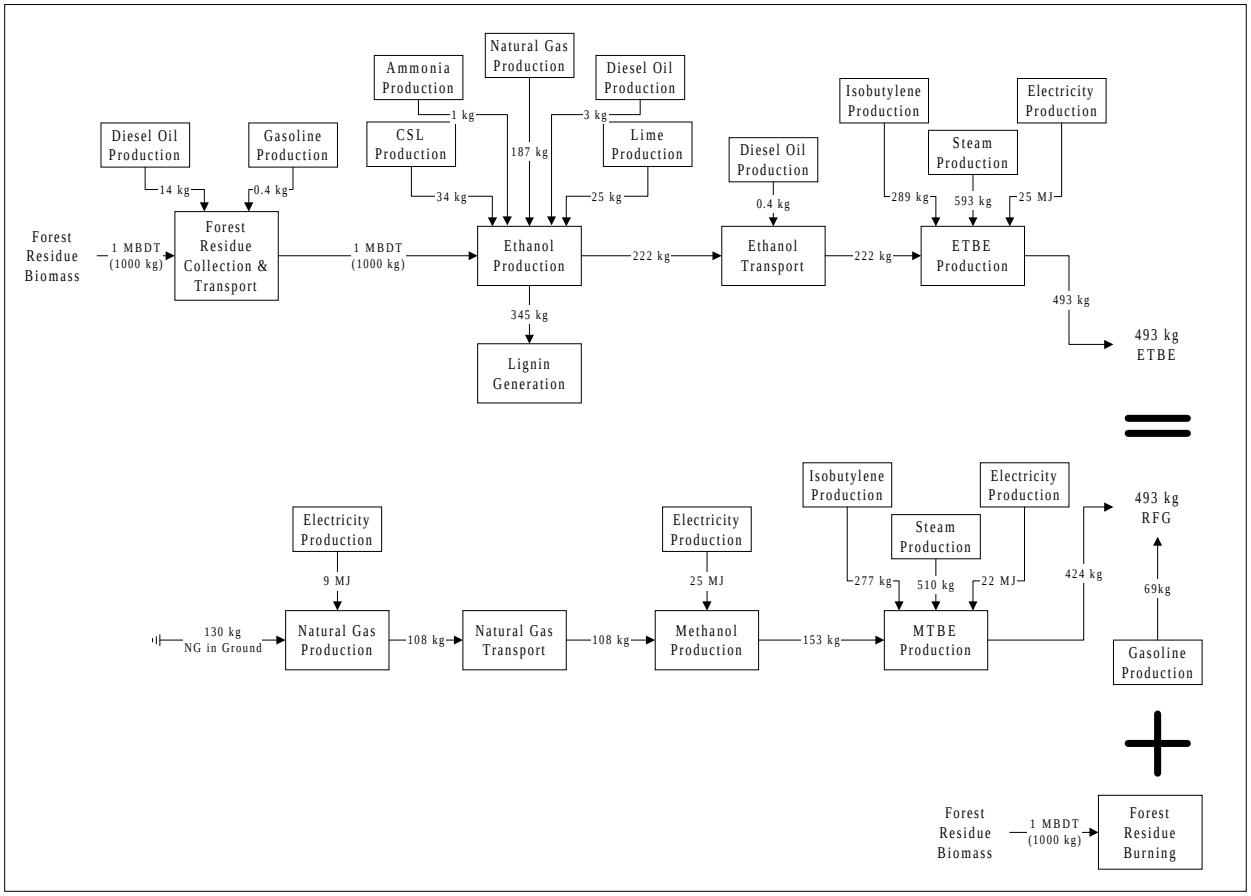

Figure 47: Mass Flow Diagram for Forest Residue—Acid Process

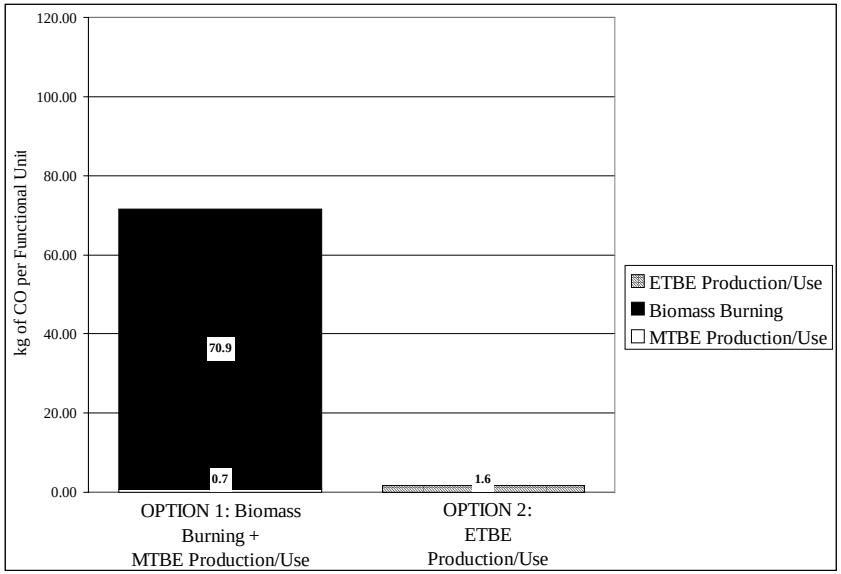

Figure 48: Forest Residue (Acid Process) Carbon Monoxide Emissions

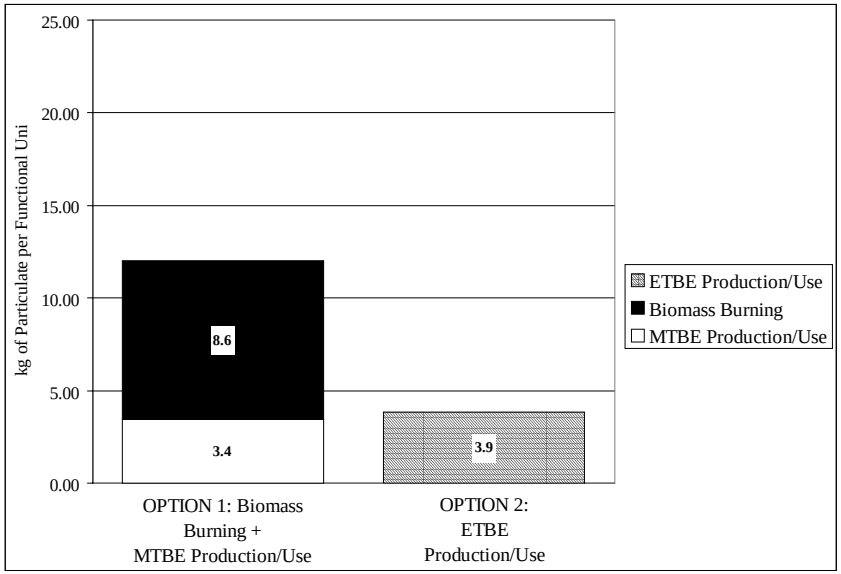

Figure 49: Forest Residue (Acid Process) Particulate Emissions

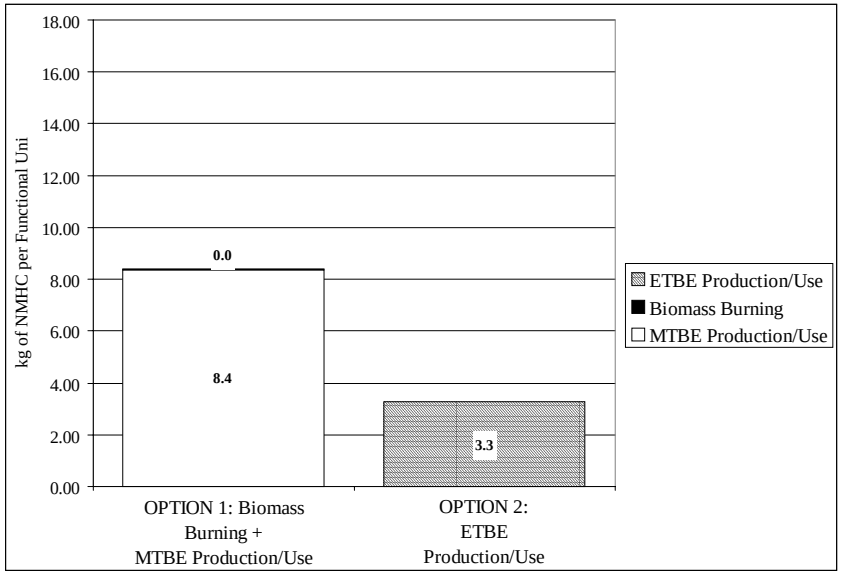

Figure 50: Forest Residue (Acid Process) Non-methane Hydrocarbon Emissions

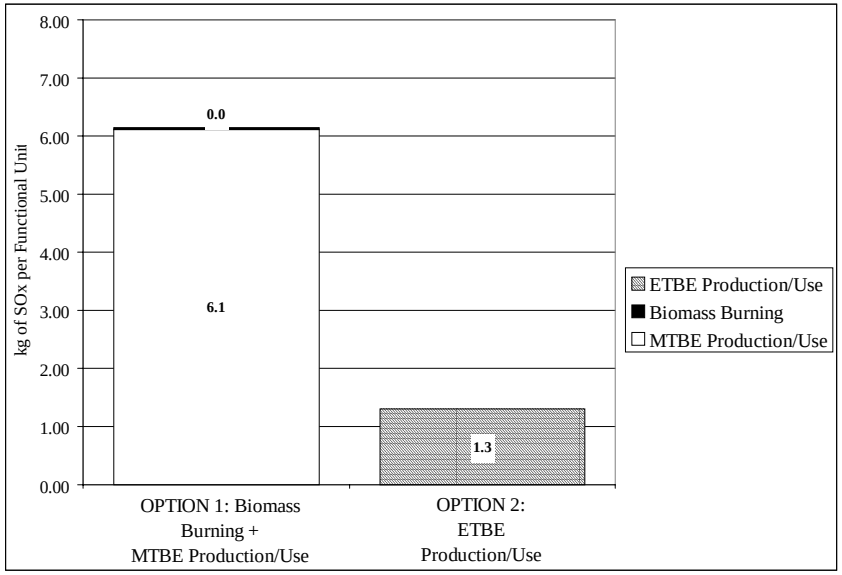

Figure 51: Forest Residue (Acid Process) SO_x Emissions

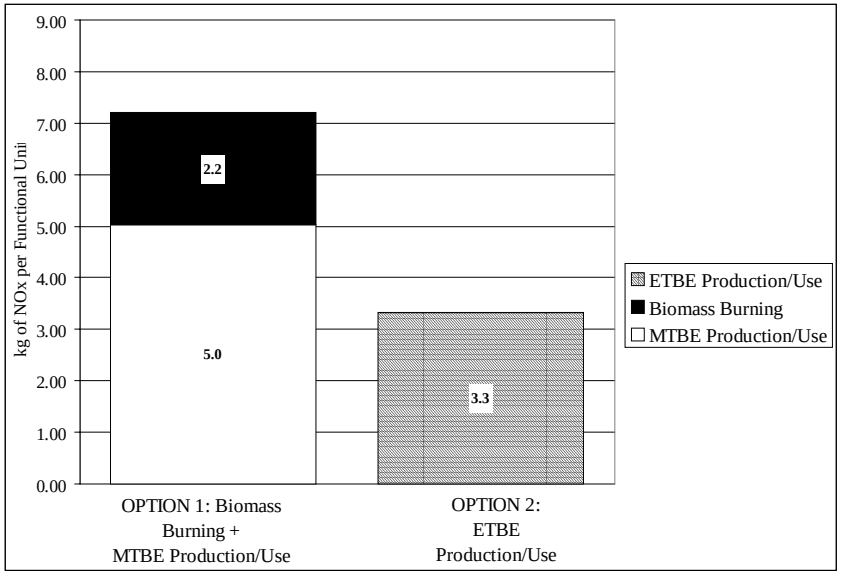

Figure 52: Forest Residue (Acid Process) NO_x Emissions

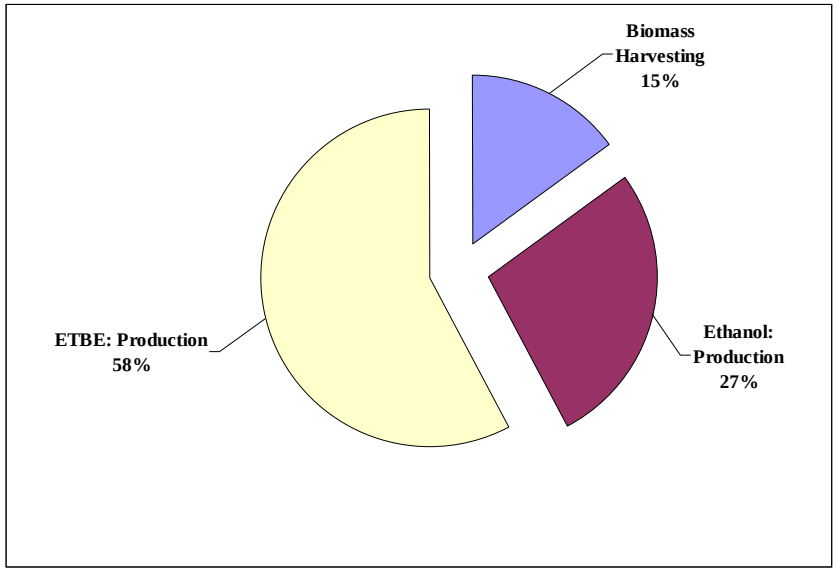

Figure 53: Forest Residue (Acid Process) NOx Emissions for Option 2 by Source

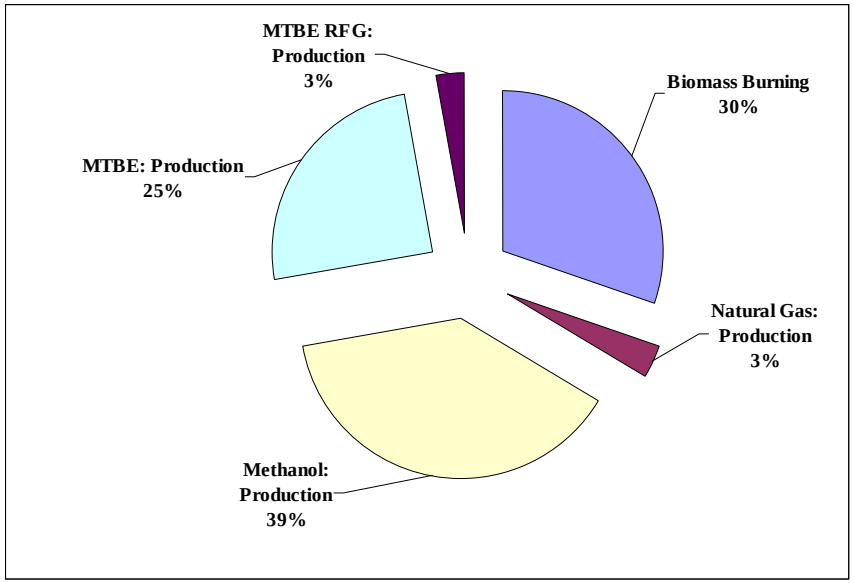

Figure 54: Forest Residue (Acid Process) NOx Emissions for Option 1 by Source

The two pie charts (Figure 53, Figure 54) show which life cycle stages contributed to the total value for the NOx emissions in Figure 52. Figure 53 shows that the value for Option 2, while smaller than the total value for Option 1, is higher than that for biomass burning portion of Option 1. Figure 53 also shows that these emissions are primarily derived from the ETBE production stage. Figure 54 highlights that the main sources of NO_x for Option 1 are the burning of biomass, MTBE and methanol production.

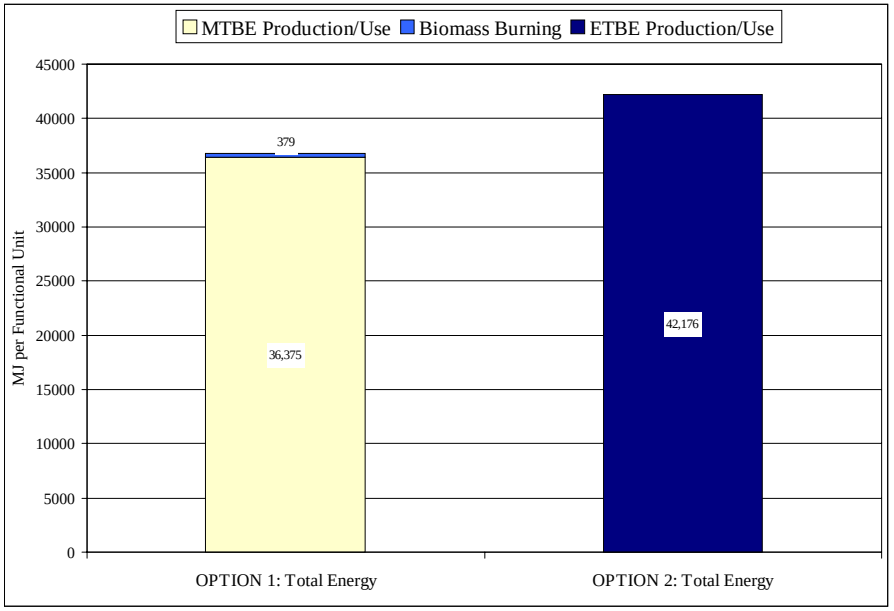

Figure 55: Forest Residue (Acid Process) Total Energy Consumption

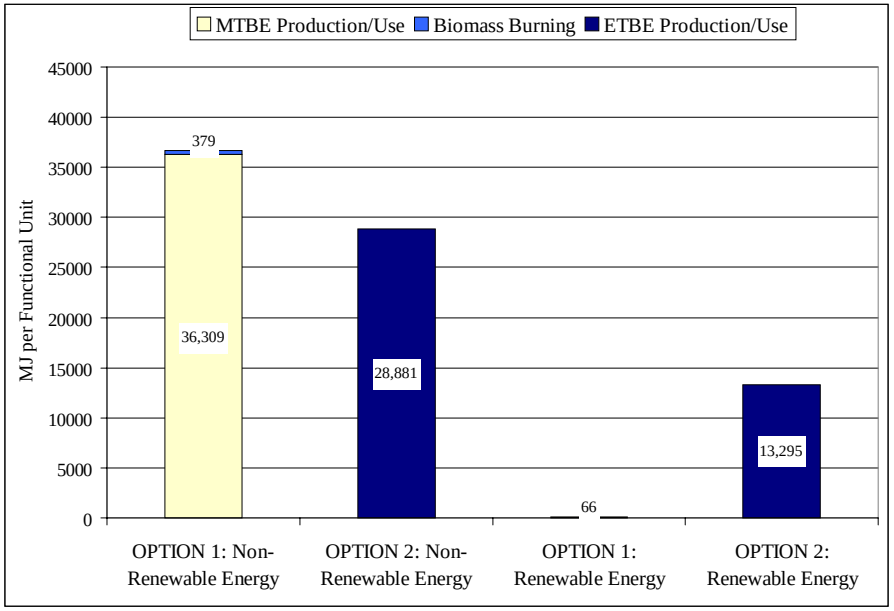

Figure 56: Forest Residue (Acid Process) Nonrenewable and Renewable Energy Consumption

6.4.6 Forest Residue Feedstock Summary

The production of ETBE from a forest residue feedstock leads to a net reduction in environmental flows over producing of MTBE and allowing for the burning of forest biomass. For all of these scenarios, the production of ethanol has greater negative impacts on water effluents (e.g. nitrates). However, in the case of forest residue, all of the criteria pollutant emission values for ETBE production are lower than those values for MTBE production and biomass burning combined.

6.4.7 Chaparral Feedstock—Enzyme Process

Table 46: Results Summary for Chaparral Feedstock—Enzyme Process

	Article	Units	**OPTION 1:** MTBE Production + Biomass Burning	**OPTION 2:** ETBE Production	Change from **OPTION 1** to **OPTION 2**
Inflows	Coal	kg	118	-84	171%
	Natural Gas	kg	165	6	96%
	Oil	kg	160	203	**-27%**
Outflows	Carbon Dioxide (CO_2, biomass)	g	1,931,340	1,914,160	1%
	Carbon Dioxide (CO_2, fossil)	g	1,148,478	366,154	68%
	Carbon Monoxide (CO)	g	101,738	2,672	97%
	Hydrocarbons (except methane)	g	16,049	428	97%
	Methane (CH_4)	g	5,839	-714	112%
	Nitrogen Oxides (NO_x)	g	2,404	1,841	23%
	Nitrous Oxide (N_2O)	g	25	10	62%
	Particulates (unspecified)	g	21,483	930	96%
	Sulfur Oxides (SO_x)	g	2,610	439	83%
	COD	g	375	401	**-7%**
	Nitrates (NO_3-)	g	2	11	**-615%**
	Waste (total)	kg	193	-57	130%
Energy	Nonrenewable Energy	MJ	16,081	2,895	82%
	Renewable Energy	MJ	29	12,197	**-42685%**
	Process Energy	MJ	8,629	7,222	16%
	Feedstock Energy	MJ	7,481	7,870	**-5%**
	Total Primary Energy	MJ	16,110	15,092	6%

Using chaparral as a feedstock, Option 2 leads to a decrease from Option 1 for almost all of the environmental flows; nitrates and renewable energy are again the two major exceptions (Table 46). As with rice straw and forest residue, these exceptions stem from the ethanol production stage. The difference between the two options for COD values is not regarded as statistically significant.

Criteria Pollutants

Carbon monoxide emissions are lower for Option 2 by a factor of about 40; this decrease is smaller than that observed with forest residue but is higher than that for rice straw. These differences are ascribed to the differing burning-emissions profiles of the three feedstocks (see Table 11 through Table 13). Particulate emissions are lower for Option 2 by a factor of 23, indicating an appreciable decrease. As with rice straw and forest residue, biomass burning in Option 1 is the source of most of the carbon monoxide and a lot of the particulate emissions. The SO_x emissions for Option 2 are lower by a factor of about seven, while NO_x and non-methane hydrocarbons emissions are lower for Option 2 by a factor of about 1.3 and 38, respectively. As in the case of rice straw, the SO_x and NO_x

emissions are higher for Option 1, essentially because MTBE production is responsible for higher emissions in comparison to ETBE production. Unlike with rice straw and forest residue, however, the majority of the non-methane hydrocarbons emissions are also from biomass burning in Option 1. This is due to the very high extractives content of chaparral. As chaparral burning is eliminated in Option 2, the decrease in non-methane hydrocarbons emissions is dramatic.

Energy Consumption and CO_2

The total primary energy consumption is less for Option 2 by 6%, which is not statistically significant. Process energy needed is less for Option 2 by 16%; this reduction is lower than that for either rice straw or forest residue. This is mainly due to the energy expended during chaparral collection, which is more energy intensive than either rice straw or forest residue collection. Another reason is that, due to chaparral's low sugar content, the ethanol stream fed to the distillation step is more dilute, requiring more energy per unit weight of ethanol.

The renewable contributions of the total energy are 0.2% and 80% for Options 1 and 2, respectively. The fossil-derived CO_2 is lower for Option 2 by 68%, a large abatement of CO_2 emissions. The higher values for renewable energy and CO_2 mitigation are due to the excess electricity that is generated during the ethanol production stage. Compared to rice straw or forest residue, chaparral contains a relatively high amount of lignin. This leads to lower SO_x, NO_x, and fossil CO_2 emissions because of the correspondingly high electricity offset credits. Furthermore, chaparral is also high in extractives, which are converted to biogas during wastewater treatment, and the methane-rich biogas is also used as fuel. This likewise provides similar offset credits.

Water Emissions

As is the case with the other two feedstocks, considerably higher nitrates ensue from Option 2, which again are associated with the use of CSL during ethanol fermentation. However, as explained in the Impact Assessment section, the eutrophication potential is still lower for Option 2.

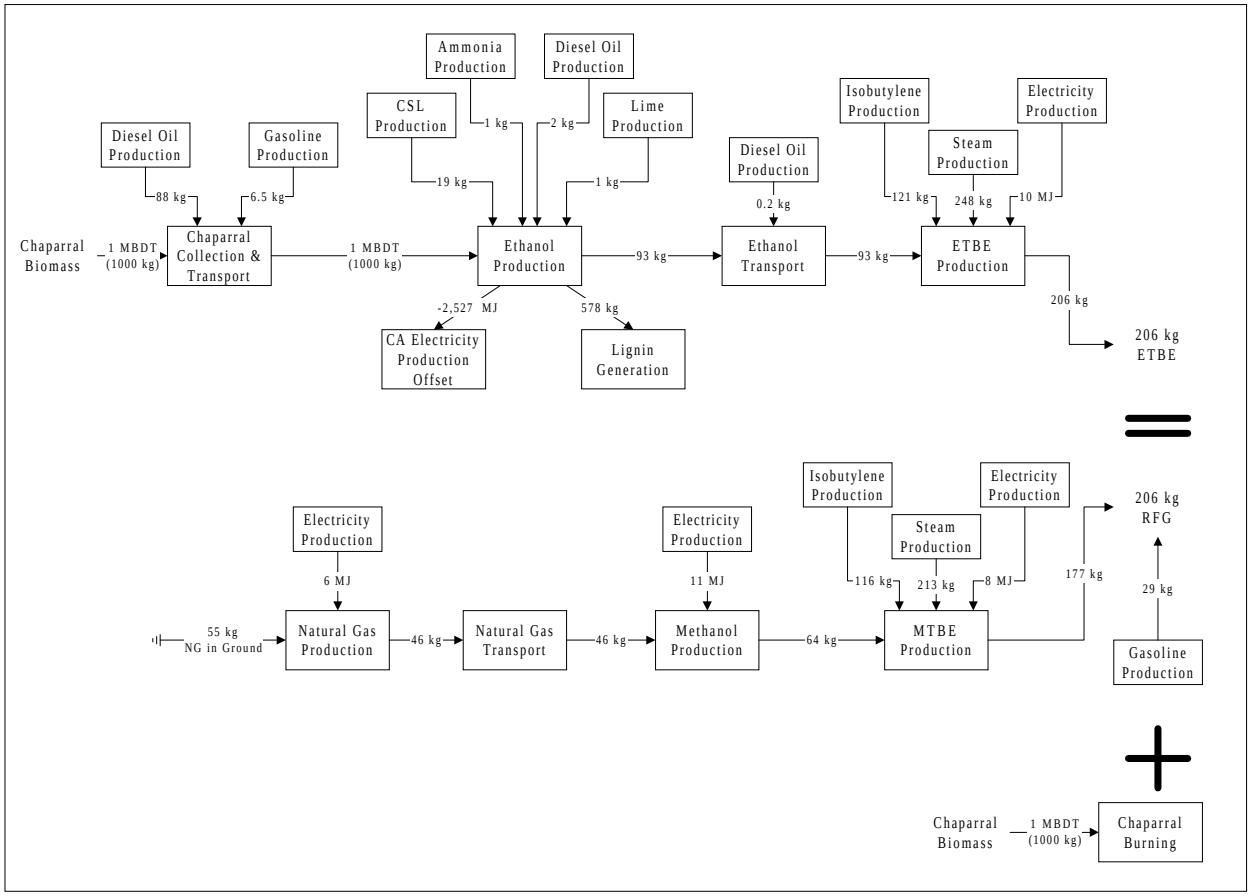

Figure 57: Mass Flow Diagram for Chaparral—Enzyme Process

Graphical Representation of Key Results

The mass flow diagram for this system is shown in Figure 57. The graphs that follow show the comparative emissions for five criteria pollutants—carbon monoxide (Figure 58), particulates (Figure 59), non-methane hydrocarbons (Figure 60), sulfur oxides (Figure 61), and nitrogen oxides (Figure 62 through Figure 64)—as well as energy consumption (Figure 65 and Figure 66). The first column represents values for Option 1, split out as values from MTBE production and biomass burning. The second column shows the flows for Option 2, ETBE production. The scales are kept the same throughout the entire results section, in order to facilitate comparison among the different biomass feedstocks and ethanol production methods.

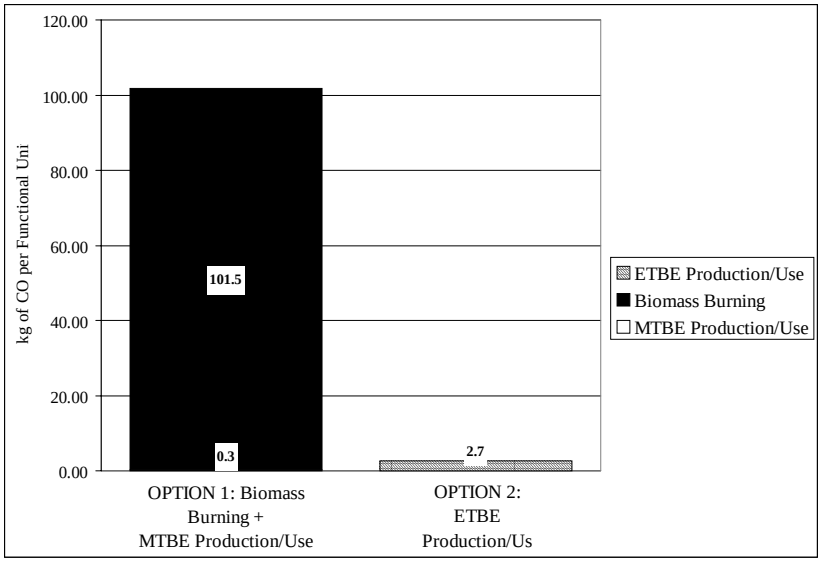

Figure 58: Chaparral (Enzyme Process) Carbon Monoxide Emissions

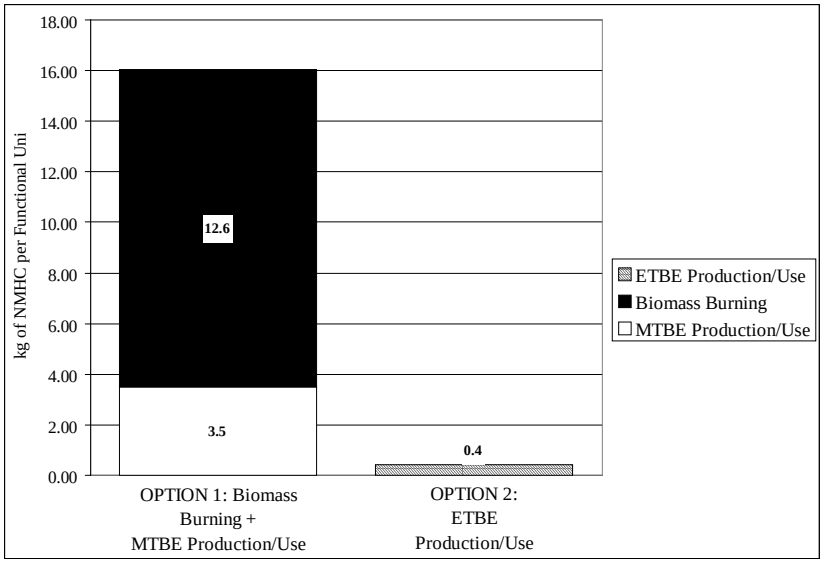

Figure 60: Chaparral (Enzyme Process) Non-methane Hydrocarbon Emissions

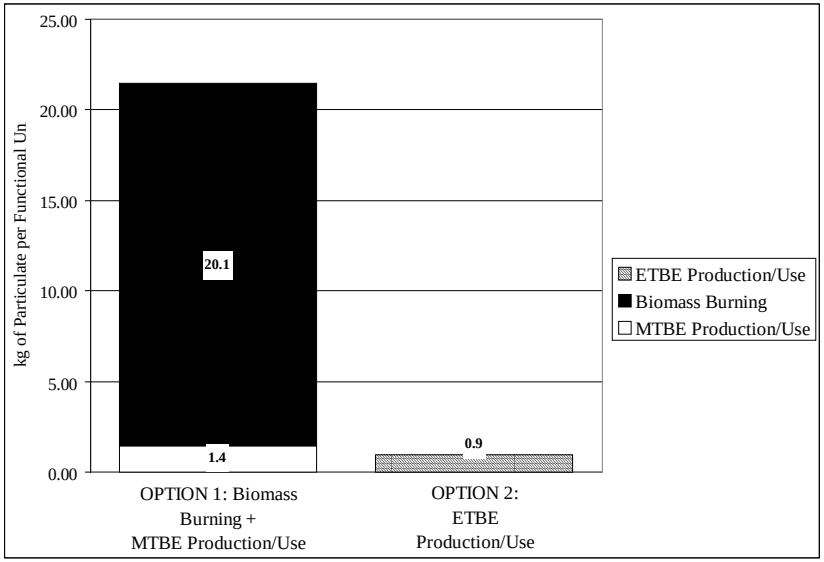

Figure 59: Chaparral (Enzyme Process) Particulate Emissions

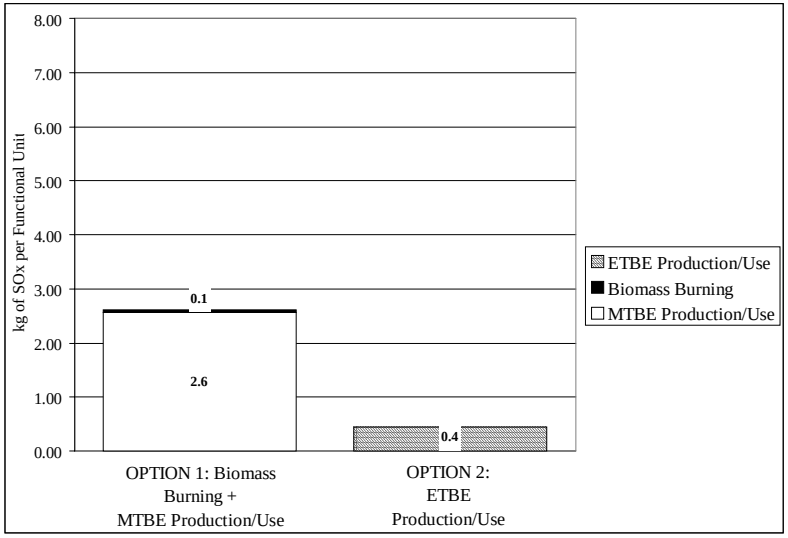

Figure 61: Chaparral (Enzyme Process) SO_x Emission

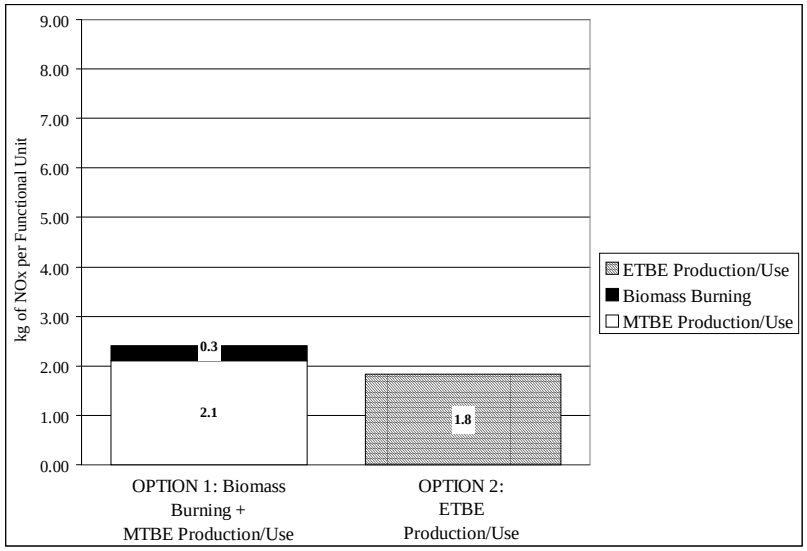

Figure 62: Chaparral (Enzyme Process) NO_x Emissions

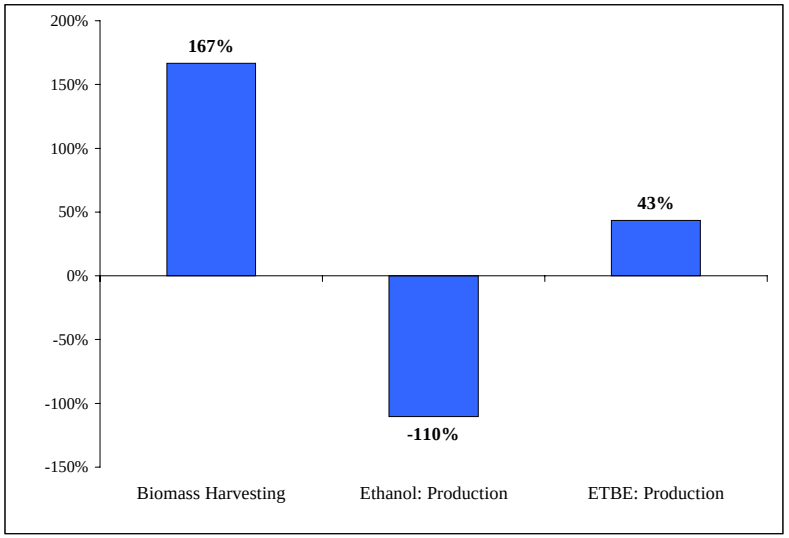

Figure 63: Chaparral (Enzyme Process) NO_x Emissions for Option 2 by Source

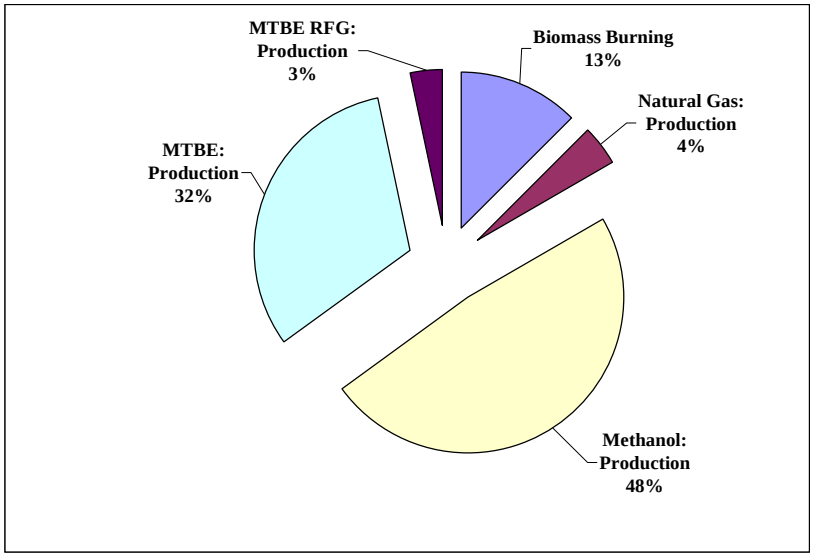

Figure 64: Chaparral (Enzyme Process) NO_x Emissions for Option 1 by Source

The bar graph (Figure 63) and the pie chart (Figure 64) indicate which life cycle stages contributed to the total value for the nitrogen oxide emissions in Figure 62. The first chart (Figure 63) shows that the ethanol production stage has a negative NO_x emission, where the excess lignin is burned to generate electricity. This electricity generation provides an offset of NO_x emissions from the biomass collection and etherification steps. For Option 1, the main source of NO_x emissions is the production of methanol (Figure 64).

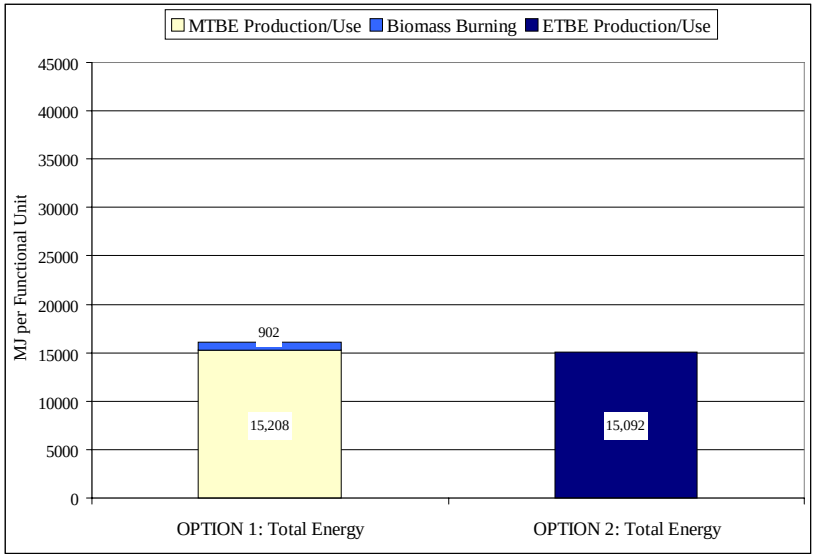

Figure 65: Chaparral (Enzyme Process) Total Energy Consumption

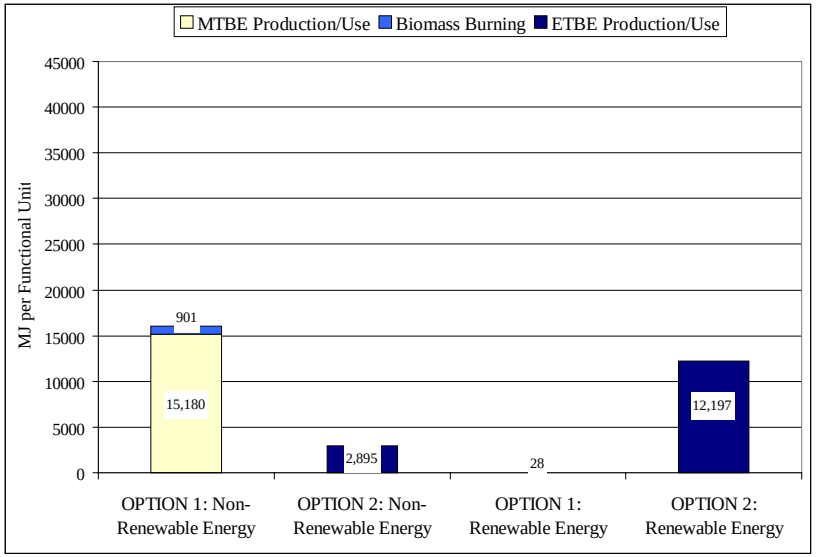

Figure 66: Chaparral (Enzyme Process) Nonrenewable and Renewable Energy Consumption

6.4.8 Chaparral Feedstock—Concentrated Acid Process

Table 47: Results Summary for Chaparral Feedstock—Acid Process

	Article	Units	**OPTION 1:** MTBE Production + Biomass Burning	**OPTION 2:** ETBE Production	Change from **OPTION 1** to **OPTION 2**
Inflows	Coal	kg	106	7	93%
	Natural Gas	kg	149	253	**-70%**
	Oil	kg	146	195	**-34%**
Outflows	Carbon Dioxide (CO_2, biomass)	g	1,931,340	1,814,130	6%
	Carbon Dioxide (CO_2, fossil)	g	1,036,259	1,129,100	**-9%**
	Carbon Monoxide (CO)	g	101,710	4,187	96%
	Hydrocarbons (except methane)	g	15,692	1,717	89%
	Methane (CH_4)	g	5,707	2,413	58%
	Nitrogen Oxides (NO_x)	g	2,189	4,428	**-102%**
	Nitrous Oxide (N_2O)	g	23	39	**-67%**
	Particulates (unspecified)	g	21,337	4,128	81%
	Sulfur Oxides (SO_x)	g	2,349	979	58%
	COD	g	346	393	**-14%**
	Nitrates (NO_3-)	g	1	20	**-1268%**
	Waste (total)	kg	173	109	37%
Energy	Nonrenewable Energy	MJ	14,529	19,220	**-32%**
	Renewable Energy	MJ	26	12,013	**-46655%**
	Process Energy	MJ	7,839	24,168	**-208%**
	Feedstock Energy	MJ	6,716	7,065	**-5%**
	Total Primary Energy	MJ	14,555	31,233	**-115%**

The relative performance of Option 1 versus Option 2 with a concentrated acid process is generally similar to that with an enzyme process, and as with rice straw and forest residue, there are the principal exceptions of natural gas and energy demand (Table 47). Higher energy is expended during chaparral collection; the fuel consumption per dry ton of chaparral collected is about twice that for forest residue and about four times that for rice straw. Also, the ethanol distillation step requires more energy per unit weight of ethanol. The enzyme case has a net energy output, whereas the acid case is a net consumer of energy and does not have electricity offset credits. The chaparral-enzyme process scenario has enough offset credits to have lower NO_x, N_2O and COD emissions (Table 46). However, for this particular chaparral-acid process scenario, NO_x, N_2O and COD emissions end up higher for Option 2 compared to those for Option 1.

The use of additional natural gas in the concentrated acid process also results in higher values for depletion of natural resources and greenhouse gas potential indicators (besides CO_2 generation during its combustion, higher methane use also results in correspondingly higher fugitive methane emissions during its production).

The higher energy requirements for the concentrated acid process, as compared to the enzymatic process, renders the relative performance of Option 2 with the concentrated acid process to be lower for nonrenewable energy, primary energy, fossil CO_2, SO_x, NO_x, non-methane hydrocarbons, and particulate emissions.

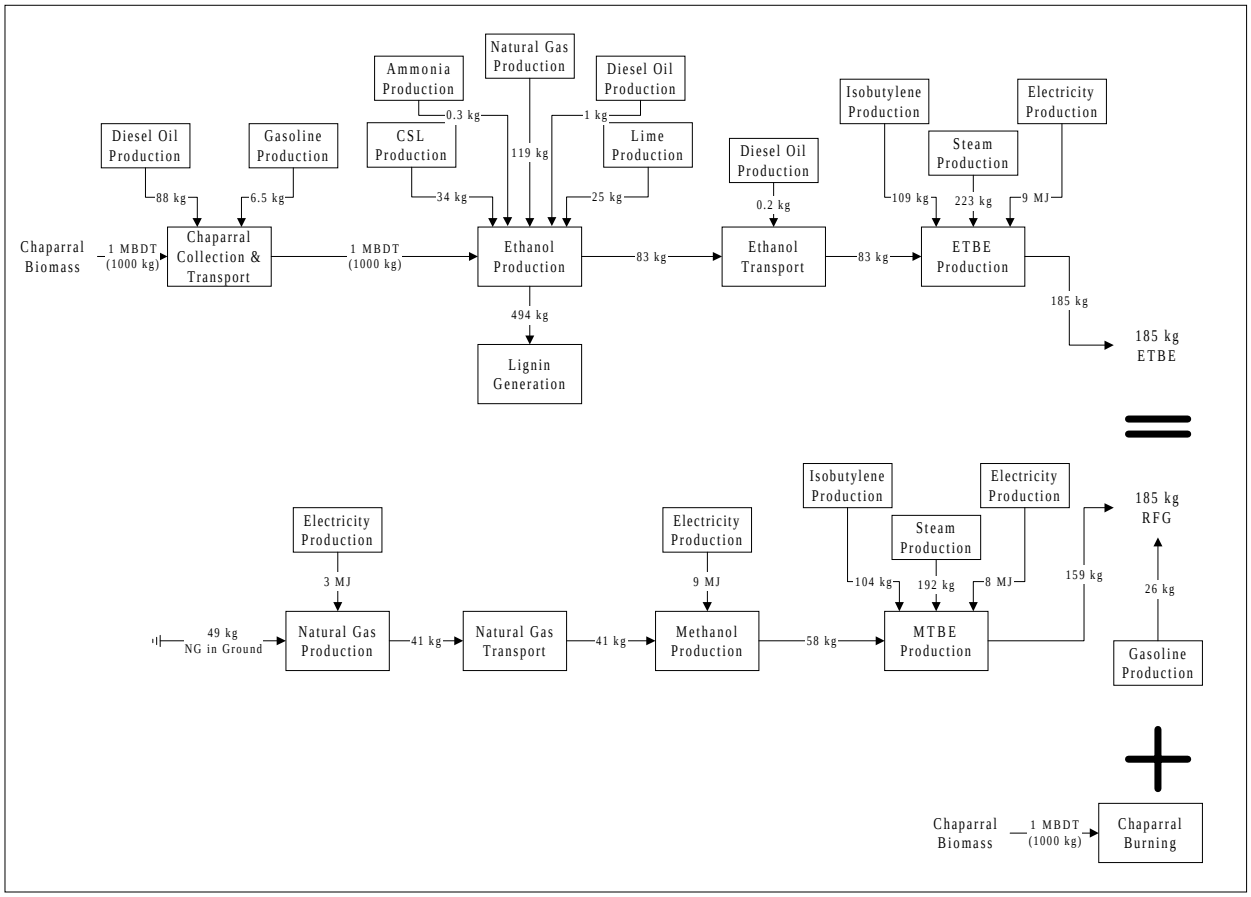

Figure 67: Mass Flow Diagram for Chaparral—Acid Process

Graphical Representation of Key Results

The mass flow diagram for this system is shown in Figure 67. The following graphs show the comparative emissions for five criteria pollutants—carbon monoxide (Figure 68), non-methane hydrocarbons (Figure 69), sulfur oxides (Figure 70), particulates (Figure 71), and nitrogen oxides (Figure 72 through Figure 74)—as well as energy consumption (Figure 75 and Figure 76). The first column represents values for Option 1, split out as values from MTBE production and biomass burning. The second column shows the flows for Option 2, ETBE production. The scales are kept the same throughout the entire results section, in order to facilitate comparison among the different biomass feedstocks and ethanol production methods.

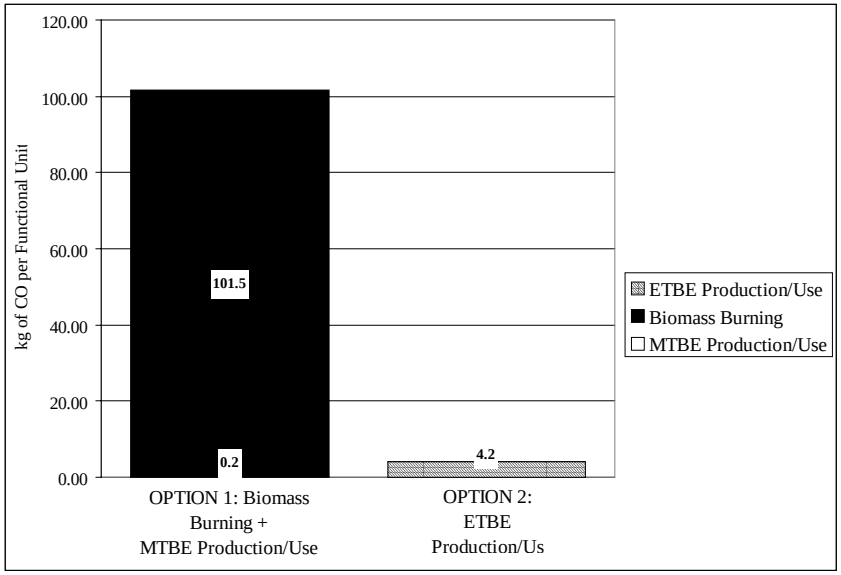

Figure 68: Chaparral (Acid Process) Carbon Monoxide Emissions

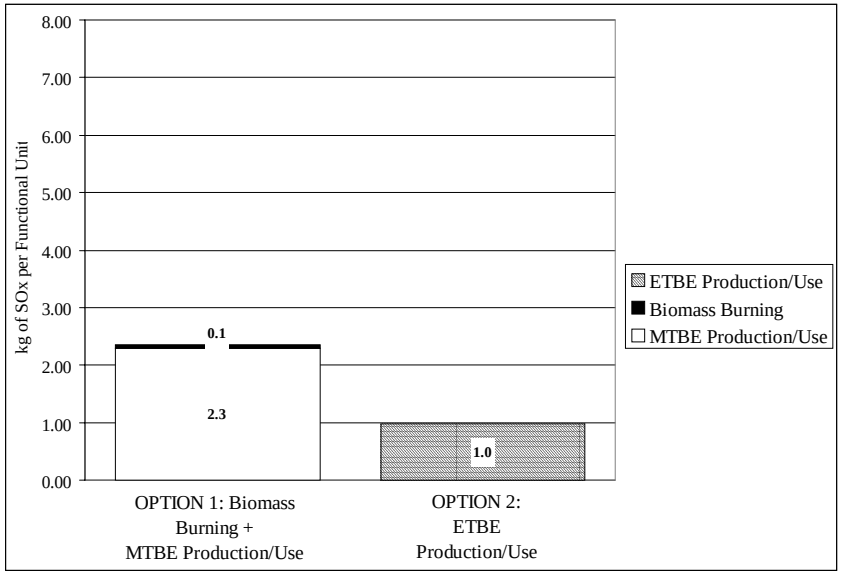

Figure 70: Chaparral (Acid Process) SO_x Emissions

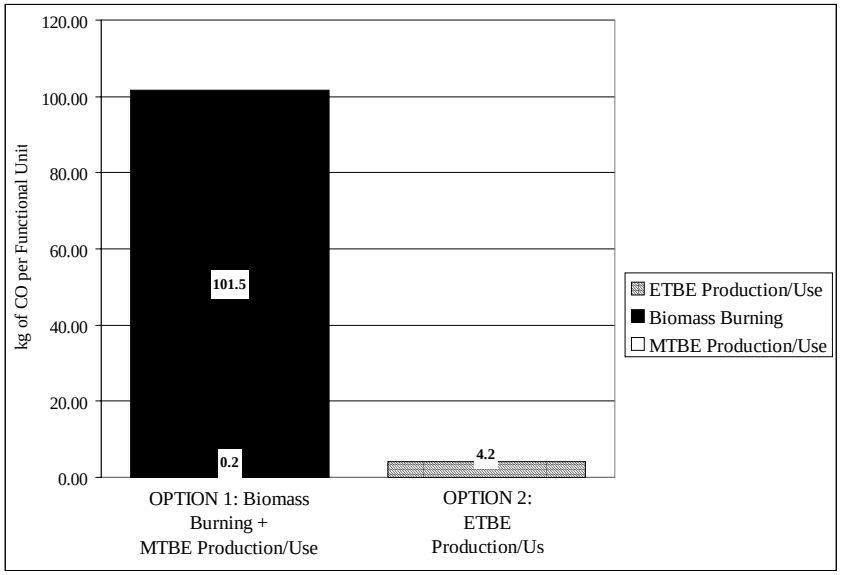

Figure 69: Chaparral (Acid Process) Non-methane Hydrocarbon Emissions

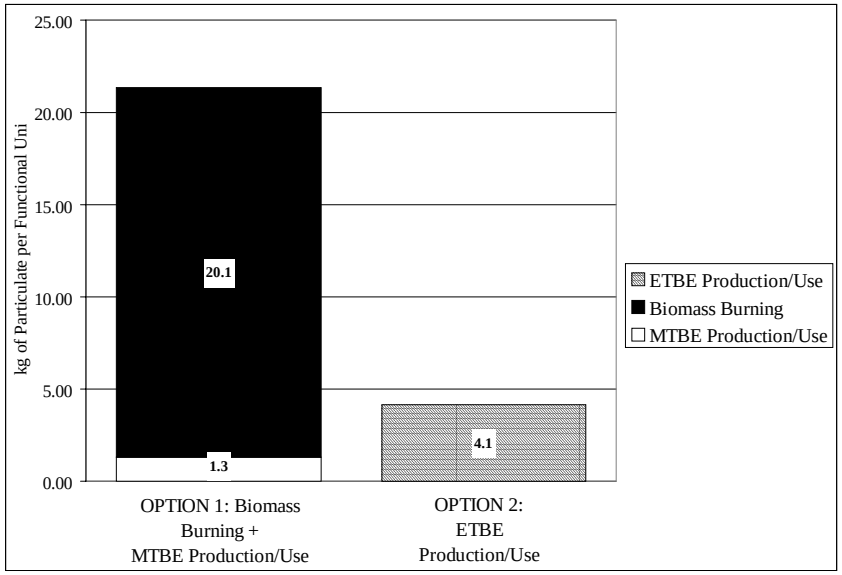

Figure 71: Chaparral (Acid Process) Particulate Emissions

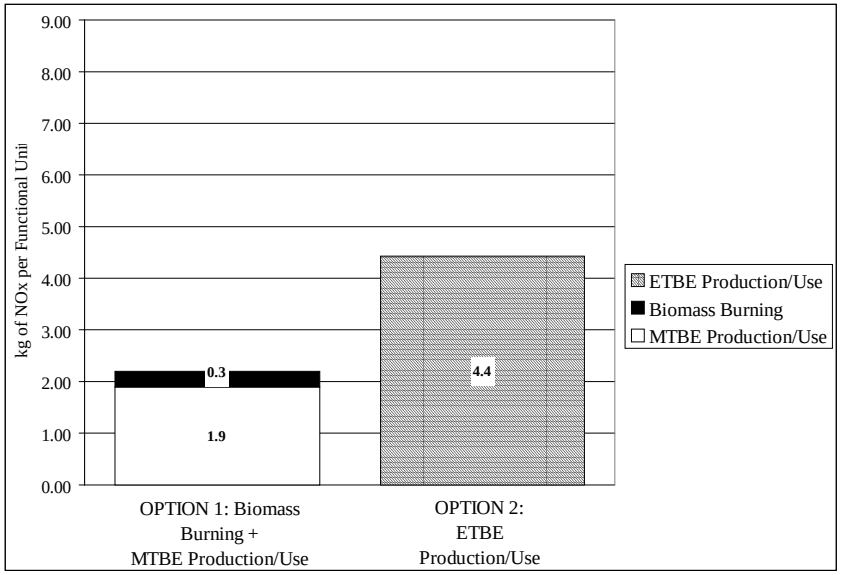

Figure 72: Chaparral (Acid Process) NO_x Emissions

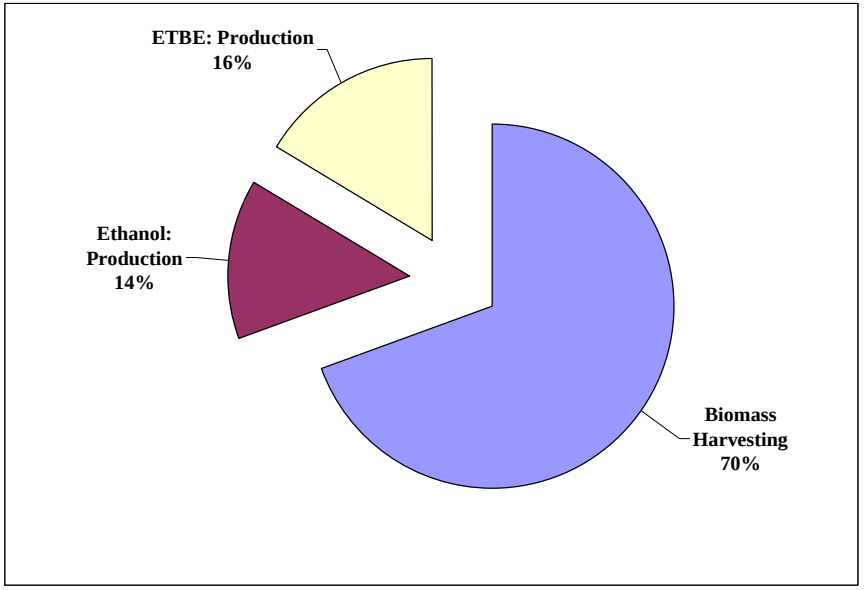

Figure 73: Chaparral (Acid Process) NO_x Emissions for Option 2 by Source

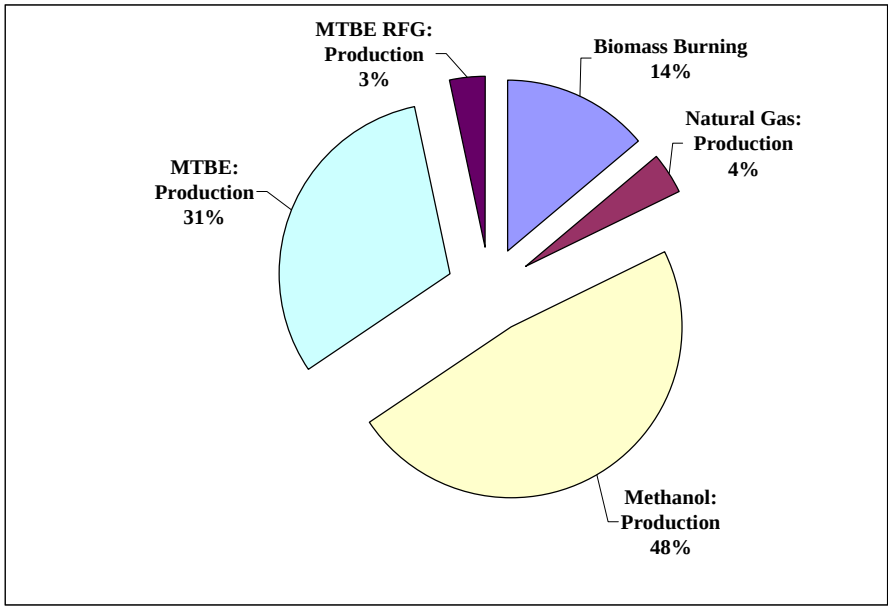

Figure 74: Chaparral (Acid Process) NO_x Emissions for Option 1 by Source

The two pie charts (Figure 73, Figure 74) indicate which life cycle stages contributed to the total value for the nitrogen oxide emissions in Figure 72. Figure 73 shows that the main source of NO_x emissions for Option 2 is from biomass harvesting. Harvesting for chaparral is energy intensive compared to collection of other feedstocks. For Option 1, the main source of NO_x emissions is the production of methanol (Figure 74).

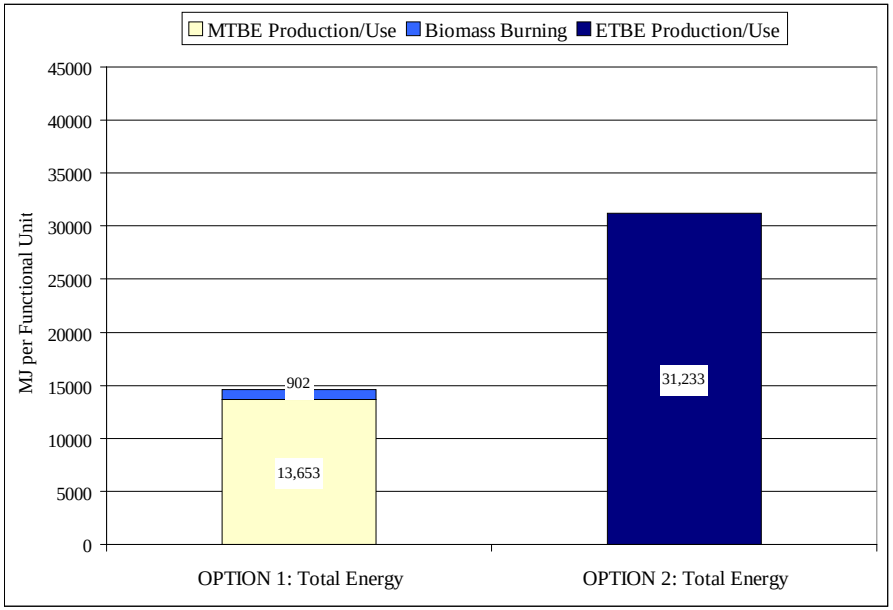

Figure 75: Chaparral (Acid Process) Total Energy Consumption

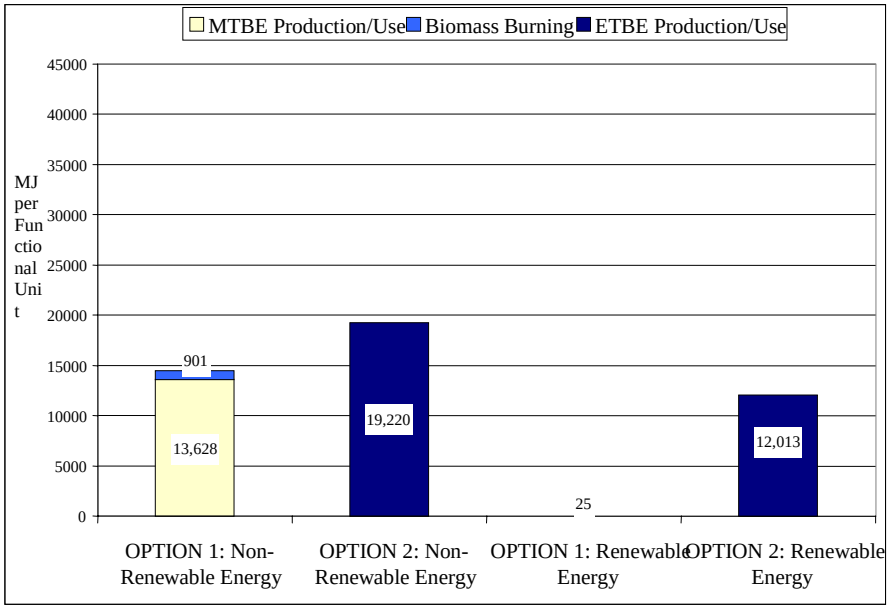

Figure 76: Chaparral (Acid Process) Nonrenewable and Renewable Energy Consumption

6.4.9 Chaparral Feedstock Summary

The production of ETBE from chaparral feedstock through the enzymatic route leads to a net reduction in environmental flows over MTBE production and allowing for the burning of chaparral. However, if an acid-based ethanol process is used for chaparral, the ETBE option shows higher emissions of NO_x, N_2O, and fossil CO_2. For both of these scenarios, the production of ethanol has greater negative impacts on water effluents (e.g., nitrates); however, the eutrophication potential is still lower for Option 2.

6.5 COMPARISON OF BASELINE SCENARIOS

Table 48 shows the summary of results for all of the baseline scenarios.

Table 48: Summary Data for Baseline Scenarios

		Difference between Option 2 (ETBE Production) and Option 1 (Biomass Burning + MTBE Production)					
		Rice Straw		***Forest Residue***		***Chaparral***	
	Flow	***Acid***	***Enzyme***	***Acid***	***Enzyme***	***Acid***	***Enzyme***
Inflow	Coal	97%	98%	97%	103%	93%	171%
	Natural Gas	**-45%**	33%	**-17%**	48%	**-70%**	96%
	Oil	28%	28%	26%	27%	**-34%**	**-27%**
Outflow	Carbon Dioxide (CO_2, biomass)	11%	**-6%**	12%	**-2%**	6%	1%
	Carbon Dioxide (CO_2, fossil)	25%	52%	34%	58%	**-9%**	68%
	Carbon Monoxide (CO)	95%	97%	98%	98%	96%	97%
	Hydrocarbons (except methane)	64%	61%	61%	57%	89%	97%
	Methane (CH_4)	**-60%**	62%	76%	96%	58%	112%
	Nitrogen Oxides (NO_x as NO_2)	57%	69%	54%	69%	**-102%**	23%
	Nitrous Oxide (N_2O)	69%	84%	69%	89%	**-67%**	62%
	Particulates (unspecified)	44%	89%	68%	93%	81%	96%
	Sulfur Oxides (SO_x as SO_2)	81%	84%	79%	87%	58%	83%
	COD (Chemical Oxygen Demand)	86%	84%	82%	81%	**-14%**	**-7%**
	Nitrates (NO_3^-)	**-466%**	**-204%**	**-458%**	**-196%**	**-1268%**	**-615%**
	Waste (total)	45%	63%	79%	97%	37%	130%
Energy	Nonrenewable Energy	6%	49%	21%	58%	**-32%**	82%
	Renewable Energy	**-17688%**	**-18203%**	**-19967%**	**-19282%**	**-46655%**	**-42685%**
	Process Energy	**-45%**	36%	**-24%**	50%	**-208%**	16%
	Feedstock Energy	**-5%**	**-5%**	**-5%**	**-5%**	**-5%**	**-5%**
	Total Primary Energy	**-26%**	16%	**-15%**	23%	**-115%**	6%

Positive values in the above table represent that Option 2 (biomass conversion to ethanol and ETBE reformulated gasoline) has lower environmental emissions compared to Option 1 (biomass burning and MTBE reformulated gasoline). Negative values indicate that Option 2 has higher emissions.

6.6 CALIFORNIA SPECIFIC EMISSIONS

One of the key issues for the decision makers faced with two alternative disposal biomass options is the amount of emissions that are occurring within California and those occurring out of state. Currently the comparison is based on ETBE replacing MTBE that is produced within the state. This implies that all the emissions from ETBE and MTBE production occur within California.

The only emissions occurring outside the state are associated with foreign[29] crude oil extraction for producing the fuels used by both biomass disposal options, and production of the ancillary materials used for ethanol production.[30] It should be noted that the nitrates emission in run-offs occurs where corn is grown, i.e., outside of California.

Section 6.9.1 outlines how the overall results would be affected if the ETBE and MTBE were produced out of state.

6.7 CARBON BALANCE

During the conversion of biomass into ETBE, biomass and fossil carbon flows through the system, as is illustrated in the following diagram (Figure 77). The feedstocks—rice straw, forest residue, or chaparral—photosynthetically absorb CO_2, which is stored in the biomass in the form of carbon-bearing compounds. This carbon is converted to ETBE and eventually burned and returned to the atmosphere again as CO_2.

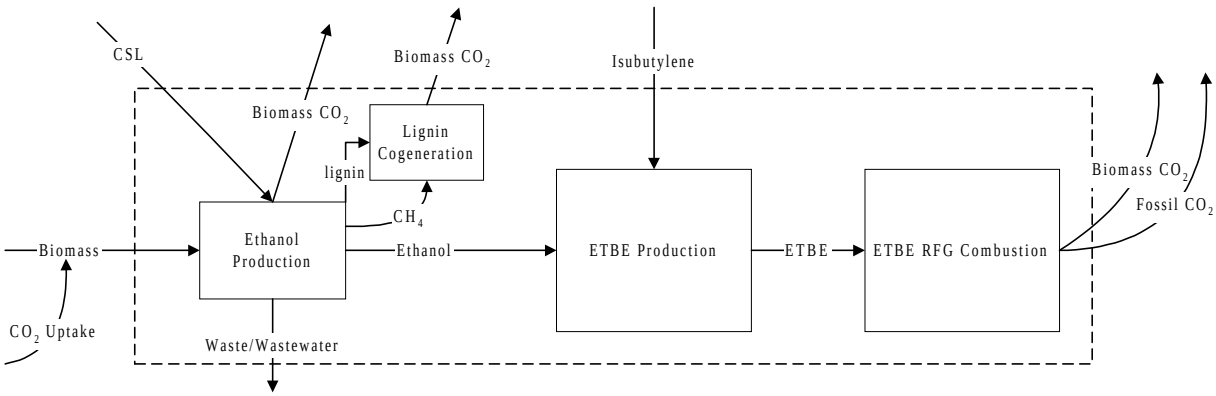

Figure 77: Overview of Carbon Balance

The box with the dashed line in Figure 77 indicates the system boundaries for the disposal Option 2. The flows that cross the system boundaries indicate carbon inflows into and outflows from the system. Overall, the outflows of carbon (biomass CO_2 and carbon-containing waste) equal the net inflow of carbon (the inflow of biomass). The biomass carbon outflows for this system consist of CO_2 from ethanol production (from fermentation and from the combustion of biomass-derived CH_4), CO_2 from the combustion of excess lignin during cogeneration, carbon-containing solid waste from ethanol production, and CO_2 from the combustion of the biomass-derived portion of ETBE. Fossil CO_2 values come from the combustion of the isobutylene-derived portion of ETBE. Although external methane is also needed for some of the scenarios during ethanol/ETBE production, it is considered as energy input and, hence, is not included in the carbon balance.

The following tables (Table 49 through Table 54) indicate the contribution of each of these inflows and outflows for the system shown above. The flows are given in terms of an inflow of 1 metric ton of biomass. The possible sources of errors in this exercise are: compositional analyses of biomass and lignin, assumptions regarding the fate of various carbon-bearing compounds in modeling the ETBE process, and common experimental/analytical inaccuracies and variabilities. Given these uncertainties, the carbon balance closure is generally reasonable, i.e., within ±5%.

[29] Foreign refers to both overseas and domestic extraction that is occurring in other states.

[30] Actually the production of ancillary materials could occur within California as well.

Table 49: Carbon Balance for Rice Straw Feedstock—Enzyme Process

	Mass (kg)	***Carbon Content***	***Total Carbon*** (kg)	***Contribution to Inflow/Outflow*** (%)
Inflow				
Biomass	1,000.0	0.4187	418.7	59.9%
CSL	8.8	0.4500	4.0	0.6%
Isobutylene	323.0	0.8571	276.9	39.6%
Outflow				
CO_2 from Ethanol	237.2	0.2727	64.7	8.7%
CO_2 from Cellulase	22.8	0.2727	6.2	0.8%
Fuel Residue	453.2	0.3807	172.5	23.2%
CO_2 from ETBE	1,569.5	0.2727	428.0	57.6%
Methane	26.0	0.7500	19.5	2.6%
CO_2 from Biogas	26.0	0.2727	7.1	1.0%
Waste water (solids)	3.4	0.4000	1.3	0.2%
Gypsum stream (soluble)	10.8	0.4850	5.2	0.7%
Aerobic treatment CO_2	142.5	0.2727	38.9	5.2%
Inflow Carbon Accounted For: 105%				

Table 50: Carbon Balance for Forest Residue Feedstock—Enzyme Process

	Mass (kg)	***Carbon Content***	***Total Carbon*** (kg)	***Contribution to Inflow/Outflow*** (%)
Inflow				
Biomass	1,000.0	0.5201	520.1	62.8%
CSL	9.5	0.4500	4.3	0.5%
Isobutylene	354.0	0.8571	303.4	36.7%
Outflow				
CO_2 from Ethanol	260.4	0.2727	71.0	8.7%
CO_2 from Cellulase	33.7	0.2727	9.2	1.1%
Fuel Residue	435.3	0.5951	259.0	31.7%
CO_2 from ETBE	1,560.7	0.2727	425.6	52.0%
Methane	19.4	0.7500	14.6	1.8%
CO_2 from Biogas	19.4	0.2727	5.3	0.6%
Waste water (solids)	5.6	0.4000	2.3	0.3%
Gypsum stream (soluble)	13.8	0.4810	6.7	0.8%
Aerobic treatment CO_2	89.1	0.2727	24.3	3.0%
Inflow Carbon Accounted For: 99%				

Table 51: Carbon Balance for Chaparral Feedstock—Enzyme Process

	Mass (kg)	***Carbon Content***	***Total Carbon*** (kg)	***Contribution to Inflow/Outflow*** (%)
Inflow				
Biomass	1,000.0	0.5320	532.0	83.2%
CSL	8.8	0.4500	4.0	0.6%
Isobutylene	121.0	0.8571	103.7	16.2%
Outflow				
CO_2 from Ethanol	88.9	0.2727	24.2	4.0%
CO_2 from Cellulase	8.9	0.2727	2.4	0.4%
Fuel Residue	577.7	0.5882	339.8	53.9%
CO_2 from ETBE	533.2	0.2727	145.4	23.1%
Methane	62.7	0.7500	47.0	7.7%
CO_2 from Biogas	62.7	0.2727	17.1	2.8%
Waste water (solids)	4.7	0.4000	1.9	0.3%
Gypsum stream (soluble)	14.5	0.6370	9.2	1.5%
Aerobic treatment CO_2	157.1	0.2727	42.8	6.8%

Inflow Carbon Accounted For: 99%

Table 52: Carbon Balance for Rice Straw Feedstock—Acid Process

	Mass (kg)	***Carbon Content***	***Total Carbon*** (kg)	***Contribution to Inflow/Outflow*** (%)
Inflow				
Biomass	1,000.0	0.4187	418.7	61.9%
CSL	19.1	0.4500	8.6	1.3%
Isobutylene	291.0	0.8571	249.4	36.9%
Outflow				
CO_2 from Ethanol	213.8	0.2727	58.3	9.1%
CO_2 from Cellulase	0.0	0.2727	0.0	0.0%
Fuel Residue	383.0	0.3457	132.4	20.6%
CO_2 from ETBE	1,283.8	0.2727	350.1	54.5%
Methane	32.9	0.7500	24.6	3.8%
CO_2 from Biogas	32.9	0.2727	9.0	1.4%
Waste water (solids)	32.4	0.4000	13.0	2.0%
Gypsum stream (soluble)	27.8	0.4550	12.6	2.0%
Acid stream (sugars etc.)	33.5	0.4003	13.5	2.1%
Aerobic treatment CO_2	104.9	0.2727	28.6	4.5%

Inflow Carbon Accounted For: 95%

Table 53: Carbon Balance for Forest Residue Feedstock—Acid Process

	Mass (kg)	***Carbon Content***	***Total Carbon*** (kg)	***Contribution to Inflow/Outflow*** (%)
Inflow				
Biomass	1,000.0	0.5201	520.1	67.1%
CSL	17.1	0.4500	7.7	1.0%
Isobutylene	289.0	0.8571	247.7	31.9%
Outflow				
CO_2 from Ethanol	212.5	0.2727	58.0	7.9%
CO_2 from Cellulase	0.0	0.2727	0.0	0.0%
Fuel Residue	344.8	0.6080	209.7	28.6%
CO_2 from ETBE	1,283.8	0.2727	350.1	47.7%
Methane	37.9	0.7500	28.4	3.9%
CO_2 from Biogas	37.9	0.2727	10.3	1.4%
Waste water (solids)	43.9	0.4000	17.6	2.4%
Gypsum stream (soluble)	32.8	0.4830	15.9	2.2%
Acid stream (sugars etc.)	35.5	0.4003	14.2	1.9%
Aerobic treatment CO_2	110.3	0.2727	30.1	4.1%

Inflow Carbon Accounted For: 95%

Table 54: Carbon Balance for Chaparral Feedstock—Acid Process

	Mass (kg)	***Carbon Content***	***Total Carbon*** (kg)	***Contribution to Inflow/Outflow*** (%)
Inflow				
Biomass	1,000.0	0.5320	532.0	84.0%
CSL	17.9	0.4500	8.1	1.3%
Isobutylene	109.0	0.8571	93.4	14.7%
Outflow				
CO_2 from Ethanol	79.8	0.2727	21.8	3.5%
CO_2 from Cellulase	0.0	0.2727	0.0	0.0%
Fuel Residue	494.3	0.6178	305.4	49.8%
CO_2 from ETBE	478.8	0.2727	130.6	21.3%
Methane	73.1	0.7500	54.8	8.9%
CO_2 from Biogas	73.1	0.2727	19.9	3.2%
Waste water (solids)	6.5	0.4000	2.6	0.4%
Gypsum stream (soluble)	28.5	0.6240	17.8	2.9%
Acid stream (sugars etc.)	28.6	0.4003	11.5	1.9%
Aerobic treatment CO_2	180.9	0.2727	49.3	8.0%

Inflow Carbon Accounted For: 97%

6.8 IMPACT ASSESSMENT AND BIOMASS DISPOSAL OPTIONS

In addition to the environmental flows that were analyzed for these six scenarios, impact indicator values were also calculated. These values give a sense of the ***potential*** impacts of some of the emissions from these scenarios. The four indices that were calculated are the greenhouse potential, acidification potential, eutrophication potential, and natural resources depletion. The method of calculation for each of these indicators is explained in more detail in Appendix B. It should be emphasized that only fossil CO_2 was taken into account in calculating greenhouse potential.

These environmental impact indicators are used to give a broader insight into the environmental impacts of these six scenarios, by examining the *potential* impacts beyond the initial release. The following table (Table 55) gives the overall values for these impact indicators. The meaning of these values is addressed in the discussion following Table 55. The one thing that is evident from this table is that for most of the indicators, Burning + MTBE production (Option 1) is worse than ETBE production (Option 2) using either of the ethanol production methods.

Table 55: Impact Assessment Summary

Biomass Source and Ethanol Production Method		***Option***	***Greenhouse Potential***	***Acidification Potential***	***Eutrophication Potential***	***Natural Resource Depletion***
			gram equivalent of CO_2	gram equivalent of H^+	gram equivalent of PO^{4-}	reserve x 10^{15}/year
Rice Straw	*enzyme*	Burning + MTBE	3,019,698	422	24	72
		ETBE	1,436,798	93	6	49
	acid	Burning + MTBE	2,718,943	388	21	65
		ETBE	2,088,355	115	6	80
Forest Residue	*enzyme*	Burning + MTBE	3,592,002	422	27	80
		ETBE	1,375,204	87	7	46
	acid	Burning + MTBE	2,984,411	354	22	65
		ETBE	1,822,680	113	7	68
Chaparral	*enzyme*	Burning + MTBE	1,278,970	136	12	28
		ETBE	354,155	54	13	11
	acid	Burning + MTBE	1,163,299	123	11	26
		ETBE	1,191,771	127	14	40

The following figures illustrate the differences among the different feedstock and ethanol production methods. The darker colored bars indicate the values for Burning + MTBE (Option 1), and the lighter colored bars indicate the ETBE Production (Option 2) values for both the enzyme and concentrated acid processes. The values for the two options for a particular biomass type and ethanol production method can be compared, simply by comparing the height of the lighter colored bar with that of the darker colored bar to its left.

6.8.1 Greenhouse Potential

The greenhouse potential values for Option 1 (Burning + MTBE) are predominantly larger than the values for Option 2 (Figure 78). The reason behind this is that there are more emissions from the combustion of the MTBE reformulated gasoline than from the combustion of the ETBE. This comes from the extra gasoline that is consumed in the MTBE reformulated gasoline.

The main driver for the greenhouse potential values for Option 2 comes from the combustion of the ETBE in the reformulated gasoline, which generates fossil CO_2 corresponding to the amount of isobutylene in ETBE. The impact indicator value is also driven somewhat by the production of ETBE and the emissions from ethanol production. The

difference between the two methods of producing ethanol (enzyme and acid) is due to the higher fossil energy requirements for the concentrated acid process (i.e. more energy use leads to higher CO_2 emissions).

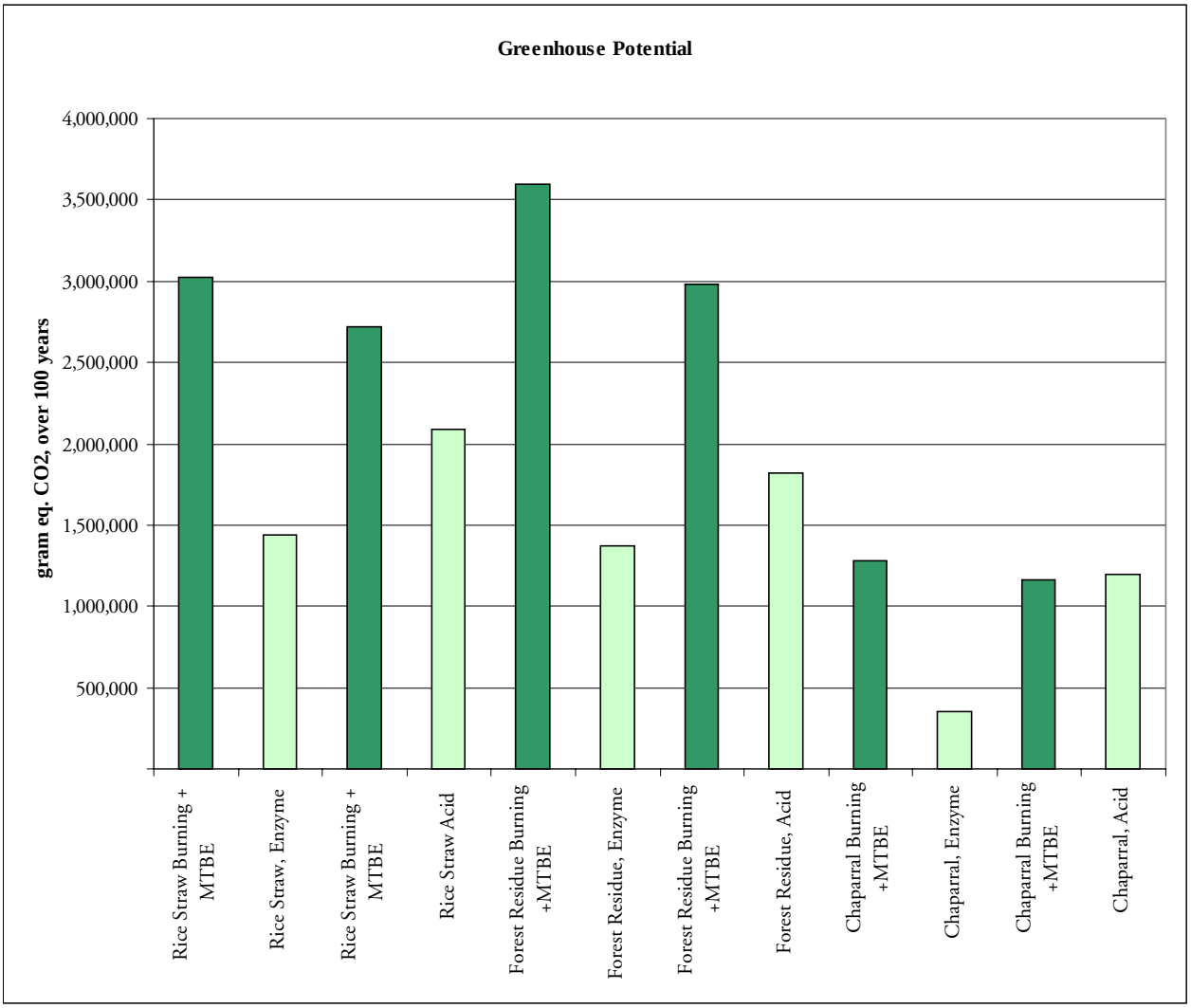

Figure 78: Greenhouse Effect Impact Potential

6.8.2 Air Acidification Potential

In Figure 79, the darker columns indicate that Option 1 generates more of an acidification impact than the comparative ETBE production scenarios. For Option 1, the use of electricity in the MTBE production process generates most of the emissions that contribute to the acidification values. The burning of the biomass itself also contributes to this impact value.

Similar to the Greenhouse Potential, the Air Acidification indicator values are affected by the electricity offset from lignin-based cogeneration. This is because electrical plants generate a large amount of NO_x and SO_x. For Option 2, the emissions that contribute most to this impact value are generated mostly during the production of ETBE.

6.8.3 Eutrophication Impact Potential

As shown in Figure 80, the eutrophication impact values are also higher for Option 1 than for Option 2. While all of the scenarios in Option 2 had high nitrate emissions than Option 1, the emissions of other water effluents drove the overall eutrophication impact values higher. The production of the fuel used to produce the reformulated gasoline as well as that used during the collection of the biomass were the main contributors to this value. The eutrophication impact values for chaparral are higher than those for forest residue or rice straw, since chaparral collection involves higher diesel consumption, which heavily contributes to the eutrophication potential. Unlike in the case of air-related impacts, the eutrophication potential is not greatly affected by the higher electricity offset credits.

The eutrophication values for all of the scenarios for Option 2 are driven by the water emissions from ethanol production. However, it is not the actual process that is the driver, but rather the upstream emissions from the production of raw materials used in the process (e.g., corn steep liquor, sulfuric acid, lime, etc.). These inputs are usually higher for the acid process than for the enzyme process, which explains why this impact value is generally higher for the acid process.

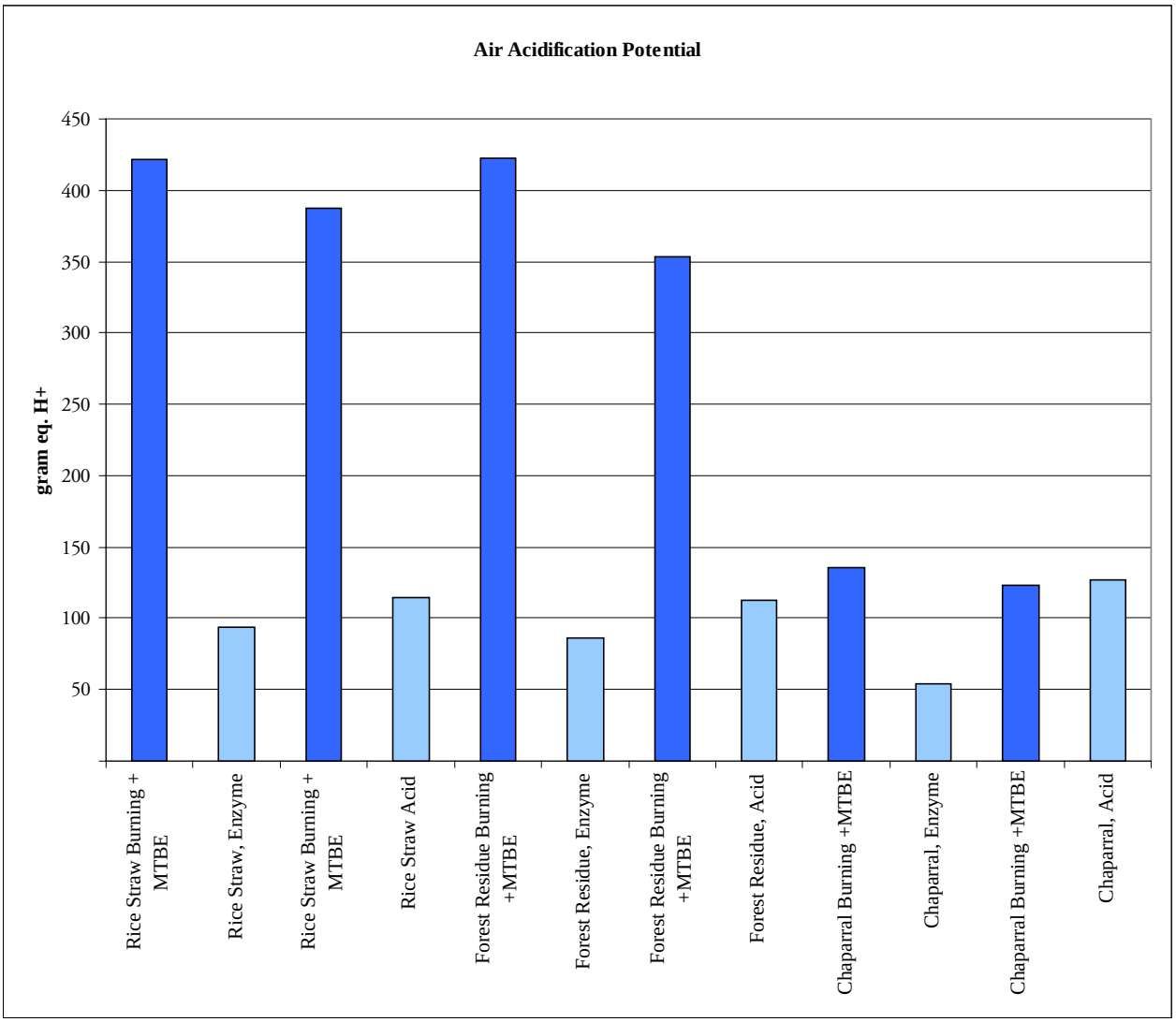

Figure 79: Air Acidification Impact Potential

6.8.4 Natural Resource Depletion Potential

Figure 81 shows Natural Resource Depletion Potential for all the baseline scenarios. The natural resource values are driven to a large degree by how much of a designated natural resource the system consumes (e.g. coal, oil, phosphate, natural gas, uranium, bauxite, and iron). Natural gas consumption has the largest impact on the overall depletion potential, which leads to high impact values for many of the scenarios. The natural resource depletion values for Option 1 are driven by the production of the gasoline used in the reformulated gasoline and the production of the MTBE (which requires relatively large amounts of electricity and natural gas).

These values are higher than those for their comparative ETBE production scenarios, except in the case of the acid-based ethanol production scenarios. This is due to the amount of natural gas that is consumed during the production of the ethanol. For all of the scenarios, most of the natural gas consumption comes during the ETBE production process, where a substantial amount of electricity is consumed. For the concentrated acid process, there is also some natural gas consumed during the production of ethanol that leads to the values higher than those for the enzyme process. Once again, the amount of lignin that is produced by the chaparral leads to an electricity offset, which results in a reduction in natural gas, oil and coal consumption. The chaparral values (enzyme process) are not zero, however, because of the electricity consumption during the ETBE production step.

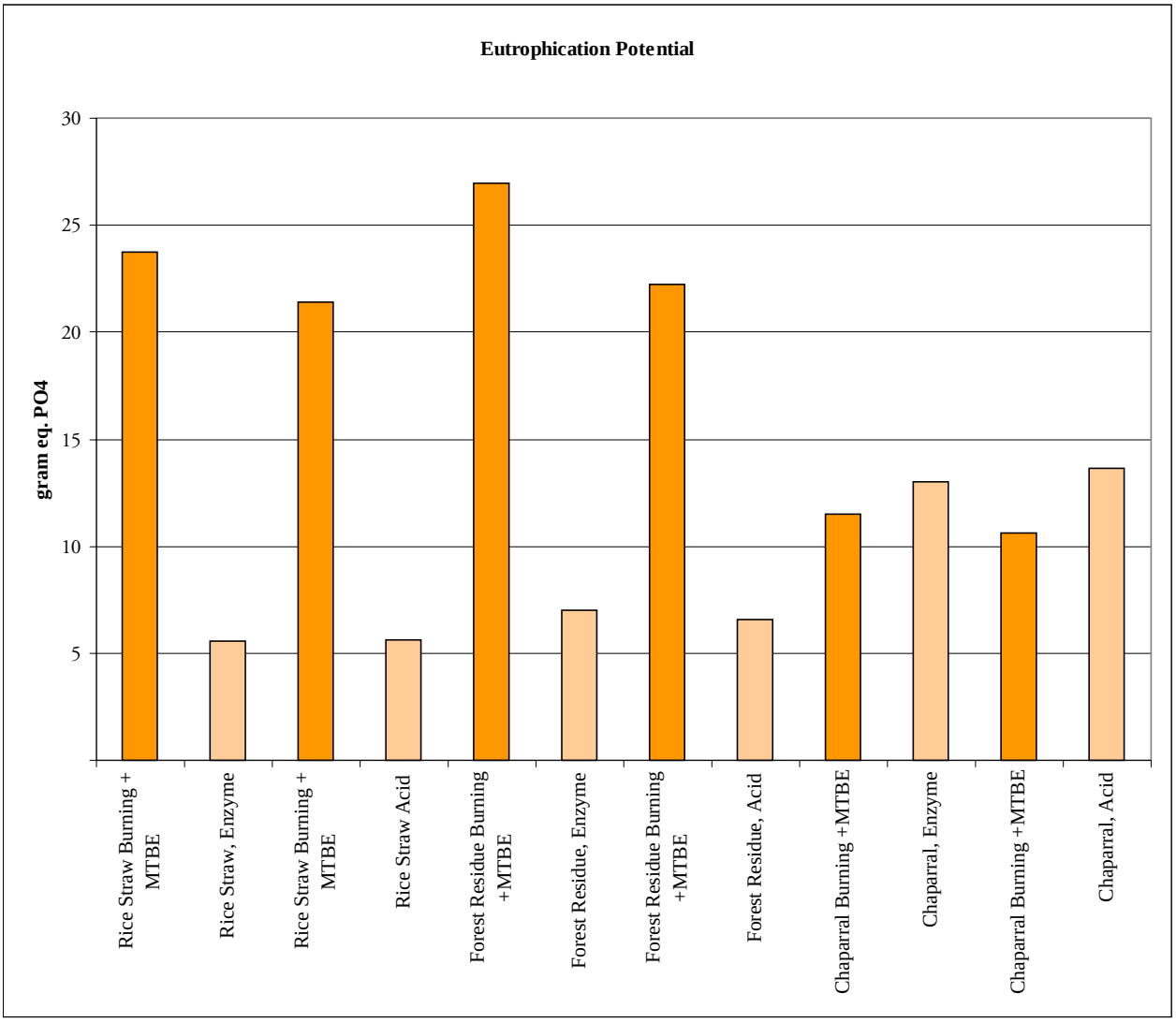

Figure 80: Eutrophication Impact Potential

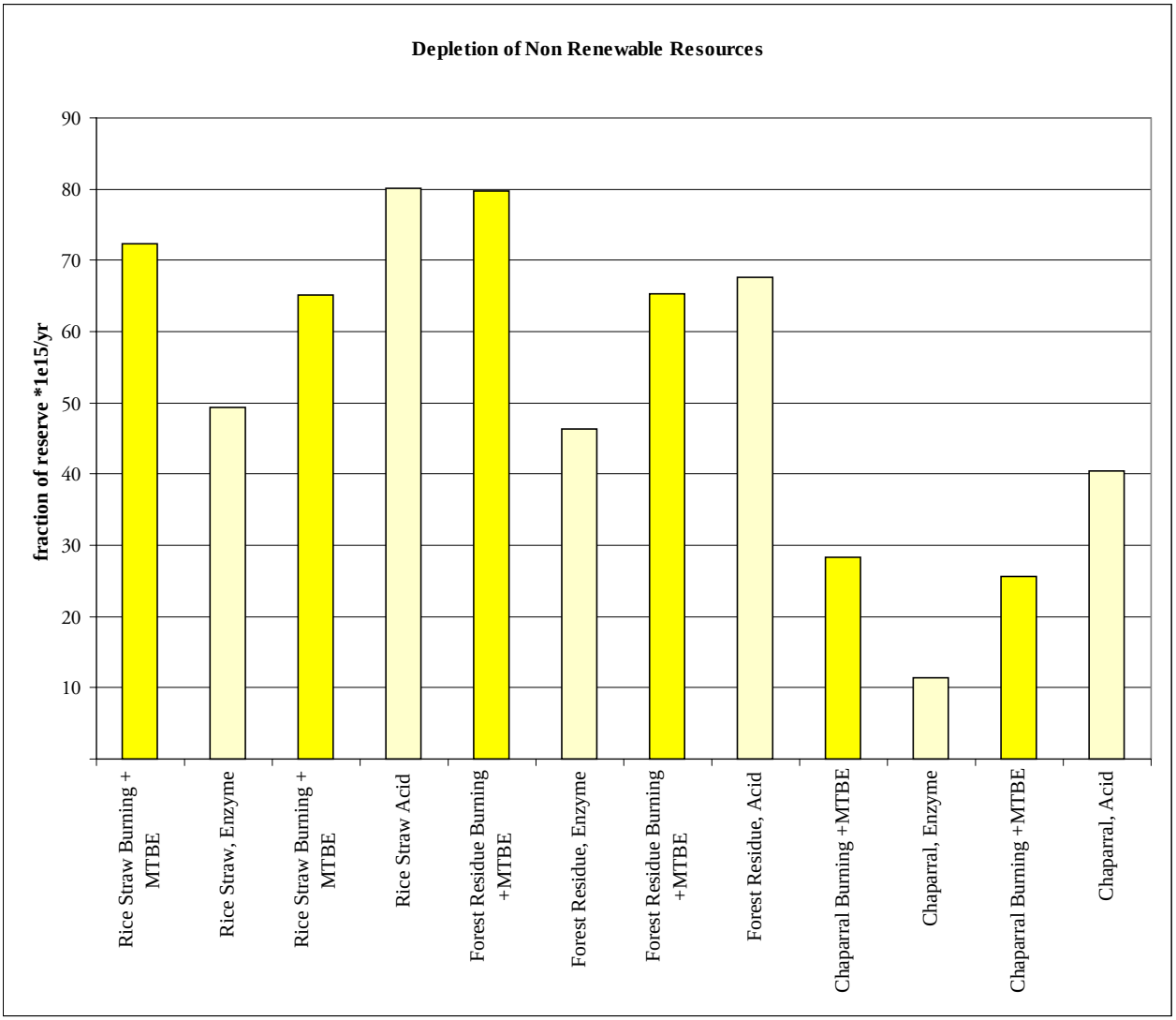

Figure 81: Natural Resource Depletion Potential

6.8.5 Impact Potential for Chaparral

Among the feedstocks, chaparral (enzyme process) exhibits the lowest potential values for greenhouse effect, air acidification, and natural resource depletion. This is related to the ETBE and electricity outputs of chaparral. Chaparral is low in sugar and high in lignin and extractives. This results in much less ETBE being generated from chaparral than from the other sources, as well as a greater output of lignin and biogas from the ethanol production process. The larger output of renewable energy leads to a lower natural resource depletion potential, and the lower amount of ETBE leads to smaller amounts of CO_2 and SO_x emitted from combustion. Additionally, the high electricity offset from cogeneration further decreases the greenhouse effect value. This is a key observation and brings up an interesting point: if low ethanol/ETBE yields per ton of biomass are good in terms of greenhouse effect, air acidification, and natural resource depletion potential, would a zero ethanol/ETBE yield be better, i.e., can we burn the biomass just to produce electricity? This would be tantamount to comparing biomass burning in the field versus in a biomass power plant. However, the biomass power industry in California has been suffering due to low electricity prices, and this may not be a feasible alternative, especially in light of the recent legislation on utility deregulation. Also, steam is cogenerated with electricity in the current scheme, and the ethanol plant uses this steam. Consequently, there would not be a steam host on site for the above scenario.

Hence, considering these non-LCA factors and constraints, ethanol production and power generation need to coexist, since these two operations are synergistic and improve each other's economic performance. This can be accomplished in two ways. The turbo-generation section of the ethanol plant resembles a biomass power plant with cogeneration. Thus, the base-case scenario is similar to co-locating the ethanol plant with a biomass power plant. Shipping distance for fuel residue is zero for this co-location scenario. Another case would be to ship the fuel residue off-site to an existing biomass power plant; this option was considered in the sensitivity analysis.

6.9 SENSITIVITY ANALYSIS

6.9.1 Total Replacement of MTBE with ETBE

The baseline results of this study assume that the ETBE produced from biomass ethanol would be produced in the state of California. It is also assumed that it would be produced at the same facilities that are currently producing MTBE. In this way the ETBE is replacing MTBE production in California.

However, the current California MTBE capacity only covers 15% of the total MTBE used in California. The remaining 85% is assumed to be produced in Texas and shipped to California. This limited capacity is due to limitations in the ability to produce isobutylene in California. If the total amount of California biomass were utilized for ethanol (and ETBE) production it would exceed the 15% in state production. Therefore, it would also replace out-of-state production of MTBE.

Table 56 outlines the differences in modeling California production of MTBE and ETBE versus modeling out-of-state production. Only the changes in the modeling are shown in the table. It should be reiterated that the proposed scenario is a hypothetical one and may not be feasible from economic or marketing perspectives. It is presented to illustrate that even with the burden of transporting ethanol out of and ETBE into the state, the ETBE scenario shows lower values for key environmental flows when compared to the MTBE scenario.

Table 57 shows the comparison of the overall life cycle results for both biomass disposal options for forest residue biomass, Enzyme-based ethanol production and lignin cogeneration. For Option 1, the total results are presented for California and out-of-state production of MTBE. For Option 2, the total results are presented for California and out-of-state production of ETBE. This table also presents the difference between California and out-of-state production. A value of 100% means the two locations are equal for that inventory flow. A value less than 100% means that the California production has lower emissions.

Table 56: Difference in Modeling Out-of-State MTBE/ETBE Production

Life Cycle Phase	*15% California Production*	*85% Outside California Production*
Ethanol Transport	From assumed ethanol production facility locations to California refineries by truck.	From assumed ethanol production facility locations to Texas refineries by train.
ETBE Production	Using California electricity grid.	Using Texas electricity grid.
ETBE Transport	None, assumed to be blended on site.	From refineries in Texas to California by train.
Methanol Production	Using California electricity grid.	Using Texas electricity grid.
MTBE Production	Using California electricity grid.	Using Texas electricity grid.
MTBE Transport	None, assumed to be blended on site.	From refineries in Texas to California by train.

Table 57: Comparison of California and Out-of-State ETBE/MTBE Production

	Flows	Unit	**OPTION 1:** MTBE Production /Use + Biomass Burning			**OPTION 2:** ETBE Production/Use		
			California	**Out of State**	**Calif./Out of State**	**California**	**Out of State**	**Calif./Out of State**
Inflows	Coal	kg	344	348	99%	-9	-7	129%
	Natural Gas	kg	477	478	100%	247	249	100%
	Oil	kg	427	434	99%	314	324	97%
Outflows	Carbon Dioxide (CO_2, biomass)	g	1,887,770	1,887,770	100%	1,925,160	1,925,900	100%
	Carbon Dioxide (CO_2, fossil)	g	3,237,431	3,265,651	99%	1,361,190	1,398,500	97%
	Carbon Monoxide (CO)	g	71,698	71,761	100%	1,275	1,374	93%
	Hydrocarbons (except methane)	g	10,263	10,256	100%	4,382	4,404	99%
	Methane (CH_4)	g	15,931	15,973	100%	564	602	94%
	Nitrogen Oxides (NO_x as NO_2)	g	8,340	8,614	97%	2,561	2,998	85%
	Nitrous Oxide (N_2O)	g	65	65	99%	7	8	86%
	Particulates (unspecified)	g	12,783	12,842	100%	891	938	95%
	Sulfur Oxides (SO_x as SO_2)	g	7,515	7,580	99%	982	1,047	94%
	COD (Chemical Oxygen Demand)	g	867	887	98%	163	196	83%
	Nitrates (NO_3^-)	g	5	5	100%	14	14	100%
	Waste (total)	kg	276	277	100%	20	21	96%
Energy	Nonrenewable Energy	MJ	44,842	45,233	99%	18,748	19,299	97%
	Renewable Energy	MJ	81	58	140%	15,708	15,696	100%
	Process Energy	MJ	23,012	23,381	98%	11,405	11,944	95%
	Feedstock Energy	MJ	21,910	21,910	100%	23,051	23,051	100%
	Total Primary Energy	MJ	44,923	45,291	99%	34,456	34,995	98%

Table 58 also shows the comparison of the overall life cycle results for both biomass disposal options for forest residue biomass, enzyme-based ethanol production and lignin-based cogeneration. However, Table 57 compares the results for the same option (relative performance of in-state versus out-of-state production for a given option), while Table 58 compares the results for the different options (relative performance of Option 1 versus Option 2 for in-state versus out-of-state production). Both California and out-of-state production of MTBE and ETBE are shown, and they differ in the ratios that are derived from the base information.

The percentages in the table represent the differences between both options. A value greater than 100% indicates that Option 1 is higher by that amount. A value less than 100% indicates that Option 1 is less than Option 2. An exception to this is negative numbers. A negative number is due to the negative values associated with electricity offset in the ethanol production system.

The results of Table 58 indicate that the out of state sensitivity analysis changes the results but does not change the conclusion regarding which option produces lower emissions.

6.9.2 E10 Scenario

A sensitivity analysis was also performed on using ethanol as a direct fuel additive as opposed to transforming it first into ETBE before being added to gasoline. As noted in the above sensitivity case, replacing 85% of the imported MTBE with ETBE is not a straightforward situation. Ethanol, however, can satisfy all of the oxygenate demand, i.e., it can substitute MTBE that is produced in the state as well as that is imported. This implies that the emissions will all be in-state emissions for 100% replacement of MTBE with ethanol. As mentioned in Section 6.9.1, the only emissions occurring outside the state are associated with foreign crude oil extraction for producing the fuels needed by both biomass disposal

options, and production of the ancillary raw materials required during ethanol production. Again, the nitrate emissions in run-offs materialize where corn is grown, and hence, are outside of California.

A blend of 10% by volume of ethanol with gasoline (referred to as E10) was used as it represents a fairly standard blend of ethanol with gasoline and has similar properties as MTBE reformulated gasoline. It is possible to create a blend of reformulated gasoline with ethanol based on a 2% oxygen content (less than 10% volume of ethanol). However, this option was not studied because of the lack of data on the emissions of the fuel when burned and also on the gasoline used for this blend.

The functional unit of comparison for the study is different when ethanol is used instead of ETBE. Table 59 shows the new functional unit of comparison.

Table 58: Comparison of the Two Biomass Disposal Options

			California Comparison			Out of State Comparison		
	Flows	**Unit**	**Option 1**	**Option 2**	**Option 1 / Option 2**	**Option 1**	**Option 2**	**Option 1 / Option 2**
Inflows	Coal	kg	344	-9	-3,754%	348	-7	-4,873%
	Natural Gas	kg	477	247	193%	478	249	192%
	Oil	kg	427	314	136%	434	324	134%
Outflows	Carbon Dioxide (CO_2, biomass)	g	1,887,770	1,925,160	98%	1,887,770	1,925,900	98%
	Carbon Dioxide (CO_2, fossil)	g	3,237,431	1,361,190	238%	3,265,651	1,398,500	234%
	Carbon Monoxide (CO)	g	71,698	1,275	5,623%	71,761	1,374	5,222%
	Hydrocarbons (except methane)	g	10,263	4,382	234%	10,256	4,404	233%
	Methane (CH_4)	g	15,931	564	2,826%	15,973	602	2,651%
	Nitrogen Oxides (NO_x as NO_2)	g	8,340	2,561	326%	8,614	2,998	287%
	Nitrous Oxide (N_2O)	g	65	7	920%	65	8	799%
	Particulates (unspecified)	g	12,783	891	1,435%	12,842	938	1,369%
	Sulfur Oxides (SO_x as SO_2)	g	7,515	982	765%	7,580	1,047	724%
	COD (Chemical Oxygen Demand)	g	867	163	531%	887	196	453%
	Nitrates (NO_3^-)	g	5	14	34%	5	14	34%
	Waste (total)	kg	276	20	1,357%	277	21	1,312%
Energy	Nonrenewable Energy	MJ	44,842	18,748	239%	45,233	19,299	234%
	Renewable Energy	MJ	81	15,708	1%	58	15,696	0%
	Process Energy	MJ	23,012	11,405	202%	23,381	11944	196%
	Feedstock Energy	MJ	21,910	23,051	95%	21,910	23051	95%
	Total Primary Energy	MJ	44,923	34,456	130%	45,291	34,995	129%

The difference in heating values (~1%) of the two fuels is assumed to be negligible compared to the inherent uncertainties in the calculations. Therefore, the use of 1 kg of ethanol and 0.09 kg of gasoline is equivalent to the use of 1.02 kg of MTBE.

As opposed to the baseline model, there was a difference in the emissions from the combustion of E10 reformulated gasoline versus MTBE reformulated gasoline. The difference in the composition of the fuels causes differences in the tailpipe emissions of vehicles using the fuels. Therefore, the emissions from the combustion of the fuels were taken into account in the comparison. Also, the E10 blended fuel has higher evaporative emissions than MTBE blended fuel. Therefore, evaporative emissions were also taken into account.

Table 59: Comparison of E10 versus MTBE Use in Reformulated Gasoline

	Gasoline	*MTBE*	*Ethanol*	*MTBE RFG*	*E10 RFG*
Heating Value (Mbtu/gal):	125	93.5	76	121.6	120.1
wt % Oxygen:	0%	18.2%	33%	2.0%	3.5%
Density (lb/gal):	6.15	6.19	6.6	6.15	6.20
			wt % MTBE:	11.0%	
			wt % Ethanol:		10.7%
			wt % Gasoline:	89.0%	89.3%
			MTBE (kg/gal):	0.31	
			Ethanol (kg/gal):		0.30
			Gasoline (kg/gal):	2.48	2.51
			Difference in Gasoline Use (kg):		0.03
				1 kg Ethanol + 0.09 kg gasoline are equivalent to:	
				1.02 kg MTBE	

The following table (Table 60) summarizes the tailpipe emissions for the two fuels studied[31]:

Table 60: Tailpipe Emissions Factors in Grams/Gallon of Fuel Burned

Emission Category	*Oxygenate*	
	MTBE	*Ethanol as E10*
CH_4	0.67	0.77
NMHC	3.7	4.1
CO	67	68
CO_2	8,742	8,556
NO_x	6.4	7.4
MTBE	0.14	0.0033
Ethanol	1.7×10^{-4}	0.22
Benzene	0.15	0.17
Formaldehyde	0.065	0.058

The following two tables (Table 61 and Table 62) show the evaporative emissions of the two fuels studied:

Table 61: Hotsoak Evaporative Emissions Factors

Emission Category	*Oxygenate*	
	MTBE (g)	*Ethanol as E10* (g)
NMHC	0.13	0.19
MTBE	0.016	0.0041
Ethanol	0.0028	0.076

[31] Based on CARB data.

Table 62: Diurnal (0-24hr) Evaporative Emissions Factors

Emission Category	*Oxygenate*	
	MTBE (g)	*Ethanol as E10* (g)
CH_4	0.0071	4.7×10^{-4}
NMHC	3.9	6.3
MTBE	0.408	0.129
Ethanol	0.011	0.846

Both hotsoak and diurnal (0-24hr) evaporative emissions were taken into account. However, running evaporative emissions were not known and, therefore, not used in the comparison.

Table 63 shows the percentage difference between Option 2A (biomass conversion to ethanol and E10 reformulated gasoline) and Option 1 (biomass burning and MTBE reformulated gasoline). Positive values in Table 63 represent that Option 2A (biomass conversion to ethanol and E10 reformulated gasoline) has lower environmental emissions compared to Option 1 (biomass burning and MTBE reformulated gasoline). Negative values indicate that Option 2 has higher emissions.

Table 63: Summary Data for E10 Sensitivity Analysis

		Difference between Option 2A (Ethanol Production) and Option 1 (Biomass Burning + MTBE Production)					
		Rice Straw		*Forest Residue*		*Chaparral*	
	Flow	*Acid*	*Enzyme*	*Acid*	*Enzyme*	*Acid*	*Enzyme*
Inflow	Coal	97%	99%	98%	108%	90%	236%
	Natural Gas	**-79%**	74%	**-24%**	103%	**-126%**	194%
	Oil	77%	77%	71%	72%	**-62%**	**-48%**
Outflow	Carbon Dioxide (CO_2, biomass)	-2%	**-20%**	1%	**-15%**	2%	**-4%**
	Carbon Dioxide (CO_2, fossil)	32%	83%	50%	94%	**-30%**	110%
	Carbon Monoxide (CO)	82%	82%	91%	90%	94%	95%
	Hydrocarbons (except methane)	53%	48%	47%	41%	89%	98%
	Methane (CH_4)	**-186%**	53%	77%	100%	56%	117%
	Nitrogen Oxides (NO_x as NO_2)	64%	81%	61%	83%	**-170%**	18%
	Nitrous Oxide (N_2O)	40%	70%	43%	81%	**-182%**	36%
	Particulates (unspecified)	31%	90%	65%	94%	80%	96%
	Sulfur Oxides (SO_x as SO_2)	87%	93%	85%	100%	45%	93%
	COD (Chemical Oxygen Demand)	**-578%**	**-615%**	**-293%**	**-339%**	**-331%**	**-338%**
	Nitrates (NO_3^-)	**-815%**	**-325%**	**-802%**	**-310%**	**-2315%**	**-1095%**
	Waste (total)	**-102%**	**-38%**	30%	88%	**-121%**	121%
Energy	Nonrenewable Energy	**-15%**	75%	16%	94%	**-89%**	138%
	Renewable Energy	**-36008%**	**-37055%**	**-40397%**	**-39055%**	**-91359%**	**-83899%**
	Process Energy	**-430%**	**-25%**	**-98%**	48%	**-145%**	20%
	Feedstock Energy	**-12%**	**-12%**	**-12%**	**-12%**	**-12%**	**-12%**
	Total Primary Energy	**-83%**	5%	**-59%**	21%	**-253%**	**-13%**

It can be seen from Table 63 that the E10 Option, in comparison to the MTBE Option 1, results in a decrease in many of the environmental flows. The obvious exceptions are nitrates, COD, and renewable energy; in some particular scenarios NO_x, N_2O, and solid waste emissions are also greater. As with the ETBE scenarios, the higher values are related to ethanol production, and the nitrates and COD values stem from upstream emissions. For a given kg of MTBE, 0.52 kg of ethanol is used in the ETBE Option versus 0.98 kg ethanol in the E10 Option. This means that ethanol usage is almost doubled in the E10 Option compared to the ETBE Option, i.e., Option 2, and the ethanol-related emissions therefore are magnified. For example, nitrates are higher because CSL usage is proportionately elevated to satisfy the larger ethanol requirement. More biomass is also needed to make the requisite amount of ethanol for the E10 Option. The greater COD and solid waste values are from the increased energy consumption during biomass collection and supplementary methane usage, when applicable.

The higher N_2O values for chaparral are related to the harvesting operation. The fuel used per dry ton of chaparral collected is about twice that for forest residue and about four times that for rice straw; this results in large emissions in general. This combined with the need for additional methane consumption makes the NO_x and N_2O emissions much bigger for the chaparral-acid process scenario compared to the MTBE scenario. The methane emissions are higher for rice straw-acid process because this scenario consumes the most methane of all the scenarios. This is again due to the low lignin and high ash contents of rice straw, characteristics which result in a lower heating value of the ligneous residue. This effect is amplified in the E10 Option.

Although the E10 Option does not have isobutylene production, it needs to burn extra gasoline due to the lower heating value of ethanol (see Table 6) to achieve the same energy content as the MTBE Option. Conversely, in the comparison of ETBE Option versus MTBE Option, the latter has to burn extra gasoline (the ETBE Option then has “negative” gasoline consumption, see Table 6).

It also bears repeating that the E10 RFG has a higher oxygen content than the baseline reformulated gasolines containing ETBE or MTBE. Hence, the comparison of E10 Option versus MTBE Option is different from the comparison of ETBE Option versus MTBE Option. These factors further explain the differences in environmental flows for the two options.

In terms of impact indicators, the total greenhouse gas potential is substantially lower for the E10 Option versus the MTBE Option (except for chaparral-acid process) due to lower fossil-based CO_2, and so are the acidification, eutrophication, and natural resources depletion potentials (results not shown). Thus, it can be concluded that the production of ethanol from the forest residue and rice straw feedstock generally results in overall lower emissions than the burning of biomass and the production of MTBE, and especially in terms of criteria pollutants.

7 CONCLUSIONS

It is likely that agricultural burning and forestry residue disposal will be problematic issues in California for the foreseeable future. This study provides specific quantitative data on biomass disposal options in California and environmental implications of oxygenates for gasoline. While the study does not include information on the current concern over MTBE groundwater contamination, it does provide data on true environmental costs of fuel systems that may be useful for public policy makers now confronting the difficult choices of oxygenate use.

The LCA performed in this study demonstrates the potentially significant benefits of using ETBE derived from California biomass. Overall the results show that there is a significant difference between Options 1 and 2 (MTBE scenario and ETBE scenario, respectively); the magnitude of this difference varies with the types of biomass feedstocks and ethanol production processes. However, in all cases, the comparison of the ETBE scenario with the MTBE scenario revealed a fundamental difference in energy derived from renewable sources, and the concomitant benefits of reduced greenhouse gas emissions. This difference can be significant when aiming to shift fuel choices to renewable sources.

Important advantages are also found with the ETBE scenario with regard to emissions reductions. The ETBE scenarios have lower net energy consumption and carbon dioxide emissions, which—although not regulated or mandated by state or federal laws—are desirable attributes. Specifically, the prevailing trends observed for the ETBE scenarios were lower net values for:

- Carbon monoxide
- SO_x and NO_x
- Particulates
- Carbon dioxide
- Fossil energy consumption

Hence, implementation of the ETBE scenario would facilitate the improvement of air quality. Emissions of nitrates in water run-offs, however, were somewhat higher for ETBE production. This is due to the use of CSL during ethanol fermentation. CSL is a by-product of corn wet-milling and agricultural operations lead to water run-offs containing fertilizer-derived nitrates. It is not mandatory that CSL be used during ethanol fermentation, and non-agricultural based alternatives are possible. It should be noted that the nitrate emissions occur at the geographical site where corn is grown, i.e., near the farm.

The four impact assessment categories—eutrophication potential, depletion of natural resources, greenhouse gas potential, and air acidification potential—show lower values for the ETBE scenario than for the MTBE scenario. Thus, despite higher nitrates values, the ETBE scenario shows a lower eutrophication potential. Hence, the ETBE scenario is shown to commonly exhibit lower values than the MTBE scenario for key environmental criteria, both regulated and unregulated. The same can be said when the E10 scenario is compared with the MTBE scenario if we exclude the case of the chaparral-acid process.

Finally, this effort is part of a larger picture for transportation fuels. This work may be used as a stepping stone for future studies to develop additional fuel LCIs, such as those for ethanol/gasoline blends (e.g., 10% ethanol using a low RVP gasoline), neat ethanol blends (e.g., E85—85% ethanol, 15% gasoline blend), and others.