

Characterizing the Greenhouse Gas Footprints of Aviation Fuels from Fischer-Tropsch Processing

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EXECUTIVE SUMMARY

The US Air Force is currently assessing the use of Fischer-Tropsch (FT) fuels, blended with conventional jet fuel, as aircraft fuel. However, a potential barrier to the use of FT fuels is the greenhouse gas emissions associated with their manufacture. Emerging guidelines for procurement of fuels place limits on the life cycle greenhouse gas emissions for fuels purchased by the US federal government. Using methodologies recommended by an Aviation Fuel Life Cycle Assessment Working Group, assembled by the US Air Force, this report describes estimates of life cycle greenhouse gas emissions for FT aviation fuels made from three types of processes:

- 1) Steam methane reforming followed by FT wax production (cobalt catalyst) and upgrading (US average natural gas as a feed)
- 2) Coal (Kittanning #6 coal) gasification followed by FT wax production (cobalt catalyst) and upgrading
- 3) Coal/biomass (mixtures of switchgrass and Kittanning #6 coal) gasification followed by FT wax production (cobalt catalyst) and upgrading

These greenhouse gas emission estimates were compared to a petroleum baseline fuel. The results, for greenhouse gas emissions that can be attributed directly to the fuel life cycle, are summarized in Table ES-1.

Table ES-1. Global warming potentials (GWPs), expressed as equivalent CO₂ emissions per megajoule of lower heating value (g CO₂e/MJ LHV), for Fischer-Tropsch fuels

	<i>Life cycle stage</i>		
	<i>Pre-combustion</i>	<i>Combustion</i>	<i>Total</i>
Petroleum baseline	14.3±4	73.2±1	87.5
Natural Gas feedstock	84±10	70±1	154
Coal feedstock	117±10	70±1	187
93% Coal 7% switchgrass	111±15	67±1	178
85% Coal 15% switchgrass	101±15	64±1	165
75% Coal 25% switchgrass	85±20	59±1	144

The results summarized in Table ES-1 indicate that the greenhouse gas footprints of natural gas-derived FT fuels are approximately 80% larger than the petroleum baseline; coal-derived FT fuels have greenhouse gas footprints that are 110% larger than the petroleum baseline. These estimates assume no carbon dioxide capture and sequestration. Mixing biomass with coal has a moderate impact on the greenhouse gas footprint directly attributed to fuel production, decreasing the footprint by about 1% for each 1% of biomass added to the feed. The emission estimates are reduced further if indirect effects are considered.

It has become increasingly common to include indirect (consequential) greenhouse gas emissions associated with production of biomass in life cycle greenhouse gas assessments of fuels. For a variety of reasons, there are very large uncertainties associated with these emissions. A recent estimate for indirect impacts associated with switchgrass production was provided in the US EPA's Draft Regulatory Impact Assessment for the Renewable Fuel Standard. If these indirect effects are included in the assessment, then the greenhouse gas footprint of mixed biomass/coal

derived fuels decreases by up to 15% (for 25% biomass feed). This value is highly uncertain, however, and other assessments have used much larger values for this credit.

Overall, the greatest process uncertainties associated with the greenhouse gas footprints of FT derived fuels are the yield of syngas in gasification and the yield of liquid hydrocarbons from the FT synthesis. With coal/biomass as a feed, more than one mole of CO₂ is produced in the gasification process for every mole of carbon converted into CO in the syngas. In the FT synthesis, additional carbon in syngas is converted to CO₂, making the carbon efficiency of the overall process (conversion of carbon in the feed into carbon in liquid fuel) less than 50%. This fundamental limitation is the primary factor causing the footprint of coal-based FT fuels (without carbon dioxide capture and sequestration) to be greater than the footprint of petroleum-based fuels. With natural gas as a feedstock, much less CO₂ is generated in syngas production and so an overall carbon efficiency of 75-80% can be achieved, resulting in a lower greenhouse gas footprint than for coal-based FT fuels.

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CHAPTER 1: INTRODUCTION

1.1 Background

The US Air Force is currently assessing the use of Fischer-Tropsch (FT) fuels, blended with conventional jet fuel, in a variety of aircraft. However, a potential barrier to the use of FT fuels is the greenhouse gas emissions associated with their manufacture. The Energy Independence and Security Act of 2007 (EISA 2007) prohibits the federal government from purchasing alternative fuels for transportation that have greater greenhouse gas footprints than fuels produced from conventional petroleum sources. Specifically, Section 526 of the Energy Independence and Security Act (EISA) of 2007 provides that:

No Federal agency shall enter into a contract for procurement of an alternative or synthetic fuel, including a fuel produced from nonconventional petroleum sources, for any mobility-related use, other than for research or testing, unless the contract specifies that the lifecycle greenhouse gas emissions associated with the production and combustion of the fuel supplied under the contract must, on an ongoing basis, be less than or equal to such emissions from the equivalent conventional fuel produced from conventional petroleum sources.

As shown in Figure 1-1, assessments performed by the US Environmental Protection Agency (EPA) on a wide range of fuels indicate a range of greenhouse gas performances. The three process configurations considered by the EPA for the production of FT fuels have total greenhouse gas emissions greater than that of conventional petroleum (US EPA, 2007, 2009). The EPA analyses indicate that FT transportation fuels that are generated from synthesis gas made from the gasification of coal (labeled Coal to Liquids without carbon capture and sequestration in the Figure) have greenhouse gas emissions that are 118% greater than conventional petroleum. However, these analyses have considered a limited number of process and feedstock configurations, and have not been performed specifically for aviation fuels.

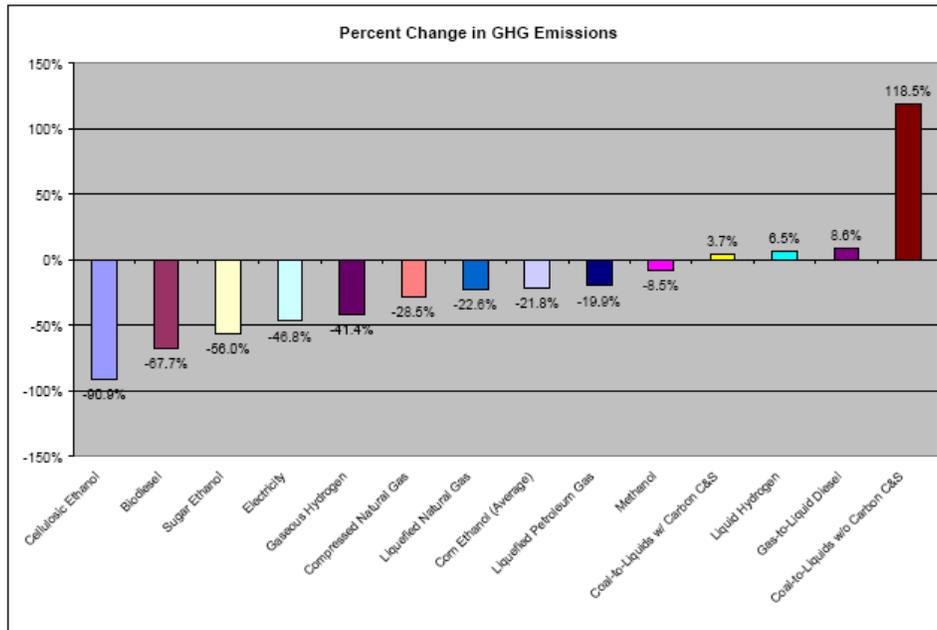


Figure 1-1. Greenhouse gas emissions associated with the production and use of transportation fuels, relative to a base case of petroleum gasoline (US EPA, 2009a,b)

The goal of this project is to evaluate, using the most current information available, the greenhouse gas footprints of jet fuel produced using synthesis gas, derived from multiple sources, followed by Fischer-Tropsch synthesis. As described in this report, the project team reviewed base case greenhouse gas emissions for a standard aviation fuel from conventional petroleum and estimated greenhouse gas emissions for three FT fuel production scenarios. The petroleum base case was used to provide a baseline for comparison, as suggested by Section 526 of EISA. The three FT scenarios involve the production of FT waxes that are subsequently upgraded to produce aviation fuels along with other fuel co-products. The three feedstock scenarios are natural gas, coal and coal/biomass blends. The specific feedstock scenarios are described in the next section.

1.2 Fuels Selected and Functional Unit

The life cycle performance of FT fuels made from three types of feedstocks is assessed in this report:

- 1) Natural Gas (US average production, as described in Chapter 3)
- 2) Coal (Kittanning #6 coal, as described in Chapter 3)
- 3) Coal/Biomass mixture involving three different feed ratios (Mixtures of switchgrass and Kittanning #6 coal, as described in Chapter 3).

These will be compared to greenhouse gas emission estimates for a petroleum baseline fuel developed by the US Department of Energy (Skone and Gerdes, 2008). When comparing life cycle performance between multiple products performing the same function, a reference unit related to the product's function, called a functional unit, is selected as the basis for comparison. Since the function of an aviation fuel is to propel an aircraft, the functional unit for an aviation fuel could be either the energy released when the fuel is combusted (energy made available for propelling the aircraft), or the distance that a reference aircraft, over a reference path, is propelled. In this work, the functional unit will be the energy released when the fuel is combusted, specifically the mega-joules of the lower heating value (MJ LHV) of fuel. The lower heating value is used since water in the exhaust from the aircraft is in vapor form.

This choice of functional unit is consistent with the functional unit used by the Environmental Protection Agency (US EPA, 2007, 2009), the Department of Energy (Skone and Gerdes, 2008) and the State of California (CARB, 2009) in assessing life cycle performance of transportation fuels, however, this functional unit does not capture all of the functions of an aviation fuel. For example, the fuel energy density (MJ/kg or MJ/L) affects the range and efficiency of an aircraft; fuel characteristics such as low temperature fluidity, heat transfer properties, or the ability of fuels to provide engine lubrication, are all important in aircraft operation. FT aviation fuels are in general paraffinic, containing straight and branched alkanes with carbon numbers ranging from roughly 8 to 18 (kerosene range, discussed in more detail in Chapter 7). Consequently, these mixtures are often referred to as synthetic paraffinic kerosene (SPK), and that term will be used to refer to FT fuels in this report. Testing done by the Air Force has indicated that when SPK meeting specifications is blended 50/50 with conventional jet fuels, the resulting fuel meets

necessary performance standards (US DoD, 2008). Therefore, it will be assumed that the LHV of the fuel captures the primary function of the fuel, providing energy for propelling the aircraft, and that other fuel specifications will be met when SPK is blended 50/50 with petroleum-derived jet fuel.

1.3 Performance Criterion: Greenhouse Gas Emissions

The life cycle performance of the fuels will be assessed using a single performance criterion, weighted greenhouse gas emissions. The contributions of three greenhouse gases, carbon dioxide, methane and nitrous oxide, to global warming emissions will be quantified over the life cycles of the fuels. While emissions of each gas will be reported, the emissions weighted by Global Warming Potentials (GWPs), summed for the three compounds, will be the primary reporting metric. GWPs express the potency of each pollutant, as global warming gases, in units of kg of equivalent emissions of carbon dioxide per kg emitted, for global warming over a 100-year time horizon. GWPs are reported by the Intergovernmental Panel on Climate Change. This report will use the GWPs for CO₂ (1), methane (25) and nitrous oxide (298) from the 2007 IPCC assessment (IPCC, 2007). Global warming impacts over the life cycle will be reported as g CO_{2e}/MJ LHV fuel combusted.

1.4 Life Cycle Assessments

A variety of terminology, standards and practices exist for life cycle assessments (LCAs). The most widely accepted LCA terminology has been established by the International Organization for Standardization (ISO 14000 series of standards) and international groups assembled by the Society for Environmental Toxicology and Chemistry (SETAC) (see, for example, Consoli et al. 1993; Allen et al. 1997). Terminology used by these organizations will be used. Definitions of common terms are provided in a Glossary available in Allen et al. (2009).

The assumptions, methods, standards and practices used in performing LCAs of aviation fuels are rapidly evolving as this report is being prepared. Because standards and practices may evolve over time, the primary goal in this report will be to follow current practices suggested by a work group established by the US Air Force, while being as transparent as possible in the documentation of methods and assumptions. A detailed description of the work group, and the methodology it has suggested, is provided in Chapter 2 of this report.

Briefly, the Air Force workgroup recommended conducting four steps in estimating life cycle greenhouse gas emissions of aviation fuels. These four steps are consistent with ISO recommendations (ISO 2006a, ISO 2006b), and are:

1. Describe the goal and scope of the assessment
2. Develop an inventory
3. Assess the impacts
4. Interpret the results

The goal and scope of the assessments performed in this work are described below. The remaining steps are briefly described in this introduction, and are reported on in more detail in subsequent chapters.

Step 1: Determine the goal and scope of the assessment.

ISO 14044: 2006(E) (2006b) requires the goal and scope of a study to be clearly defined and consistent with the intended use of the study results. ISO guidelines and the Air Force Workgroup recommend addressing the following questions, related to the study goals:

What is the intended application of the study? The purpose of this study is to develop life cycle greenhouse gas emission estimates for Fischer-Tropsch aviation fuels. The study was designed as a response to a Request for Proposals (RFP) from the University of Dayton Research Institute (SC419 in support of government Cooperative Agreement No. F33615-03-2-2347, January 9, 2009). The RFP stated that the purpose of the study is to “improve understanding of greenhouse gas footprints of FT fuels”.

Who is the intended audience? The sponsor of the study is the University of Dayton Research Institute (UDRI), which is funding the work in support of Cooperative Agreement No. F33615-03-2-2347 with the US Air Force. The expected audience for the report is therefore both UDRI and the Air Force. It is anticipated that the Air Force, through UDRI, may wish to make the report public.

Will comparative assertions be made? The RFP calls for life cycle greenhouse gas emission estimates for both a base case petroleum-based fuel and a series of FT fuels. Therefore, it can be anticipated that comparative assertions may be made based on the report. In support of these anticipated comparisons, the study will be transparent in describing modeling approaches and data sources, and will use publicly available data to the extent practicable.

Table 1-1 provides a summary of the study goals.

Table 1-1. Definition of Life Cycle Goal for Transportation Fuel LCAs

General Question	Specific Goal
Intended application	Improve understanding of greenhouse gas footprints of FT fuels
Intended audience	Primary audiences are the University of Dayton Research Institute and the US Air Force
Intended level of detail: Comparative assessment status	Comparative assertions may be made, therefore the data quality objectives are to have publically available data and full transparency in modeling approach and data sources

The scope statements for the life cycle assessments of greenhouse gas emissions, as called for in the ISO standards and the US Air Force Workgroup guidelines, are provided in Tables 1-2 through 1-5. Specifications define the fuel produced, the processes used (including geographic and temporal representation of the processes selected), the impacts, the reporting methods and the data quality objectives.

Table 1-2. Baseline Fuel Life Cycle Study Design for Jet Fuel from Petroleum

Life Cycle Boundary for the primary fuel production chain	Well-to-Wake (Raw Material Acquisition thru Fuel Use)
Temporal Representation	2005
Technological Representation	Average U.S.
Geographical Representation	Jet fuel sold in the United States
Transportation Fuel Life Cycles Modeled	Petroleum-Based jet fuel
Impact Categories (Impact Assessment Methodology)	Global Warming Potential (IPCC 2007, 100-year time-frame Non-CO ₂ combustion emissions not included)
Reporting Metric	g CO ₂ e per MJ LHV of Fuel Consumed
Data Quality Objectives	Publicly Available Data; Full Transparency of Modeling Approach and Data Sources; Accounting for a targeted uncertainty in Mass and Energy; Process-based (“Bottom-up”) Modeling Approach

Table 1-3. Fuel Life Cycle Study Design for SPK from Natural Gas

Life Cycle Boundary for the primary fuel production chain	Well-to-Wake (Raw Material Acquisition thru Fuel Use)
Temporal Representation	2005
Technological Representation	Average U.S. Natural Gas Production; steam methane reforming to produce synthesis gas; FT and fuel upgrading technology based on anticipated 50,000 – 100,000 bpd SPK facility
Geographical Representation	Jet fuel sold in the United States
Transportation Fuel Life Cycles Modeled	SPK from natural gas
Impact Categories (Impact Assessment Methodology)	Global Warming Potential (IPCC 2007, 100-year time-frame Non-CO ₂ combustion emissions not included)
Reporting Metric	g CO ₂ e per MJ LHV of Fuel Consumed
Data Quality Objectives	Publicly Available Data; Full Transparency of Modeling Approach and Data Sources; Accounting for a targeted uncertainty in Mass and Energy; Process-based (“Bottom-up”) Modeling Approach

Table 1-4. Fuel Life Cycle Study Design for SPK from Coal

Life Cycle Boundary for the primary fuel production chain	Mine-to-Wake (Raw Material Acquisition thru Fuel Use)
Temporal Representation	Year procured
Technological Representation	Kittanning #6 coal; Shell Gasifier; FT and fuel upgrading technology based on anticipated 50,000 – 100,000 SPK bpd facility
Geographical Representation	Jet fuel sold in the United States
Transportation Fuel Life Cycles Modeled	SPK from gasified coal
Impact Categories (Impact Assessment Methodology)	Global Warming Potential (IPCC 2007, 100-year time-frame Non-CO ₂ combustion emissions not included)
Reporting Metric	g CO ₂ e per MJ LHV of Fuel Consumed
Data Quality Objectives	Publicly Available Data; Full Transparency of Modeling Approach and Data Sources; Accounting for a targeted uncertainty in Mass and Energy; Process-based (“Bottom-up”) Modeling Approach

Table 1-5. Fuel Life Cycle Study Design for SPK from Coal/Biomass mixtures

Life Cycle Boundary for the primary fuel production chain	Mine and field-to-Wake (Raw Material Acquisition thru Fuel Use)
Temporal Representation	Year procured
Technological Representation	Kittanning #6 and switchgrass; Shell Gasifier; FT and fuel upgrading technology based on anticipated 50,000 – 100,000 SPK bpd facility
Geographical Representation	Jet fuel sold in the United States
Transportation Fuel Life Cycles Modeled	SPK from gasified coal/biomass mixtures; various coal to biomass blending ratios evaluated
Impact Categories (Impact Assessment Methodology)	Global Warming Potential (IPCC 2007, 100-year time-frame Non-CO ₂ combustion emissions not included)
Reporting Metric	g CO ₂ e per MJ LHV of Fuel Consumed
Data Quality Objectives	Publicly Available Data; Full Transparency of Modeling Approach and Data Sources; Accounting for a targeted uncertainty in Mass and Energy; Process-based (“Bottom-up”) Modeling Approach

Step 2: Develop an inventory of the life cycle greenhouse gas emissions for the fuel systems.

In an LCA, the inputs and outputs of the fuel production systems are assembled into an inventory. The life cycle inventories begin with descriptions of process flow models for the life cycles of each fuel up to the point of use. The process steps include feedstock production, raw material acquisition, agricultural activities (if applicable), allocation of by-products, transportation to a processing facility, the technologies required to convert the feedstocks into desirable fuels for powering aircraft, the means for delivering the fuels, and the combustion of the fuels.

The process flow models are then populated with an accounting of mass balances, energy balances, and emissions of the processes up to the point of use. The system boundaries of this analysis include conversion of feedstock into fuel, the transportation and distribution of the fuels into aircraft for use, and the combustion of the fuels. Combustion emissions are reported separately.

Step 3: Assess the impacts of the emissions In this study, life cycle inventory information will be used to estimate weighted greenhouse gas emissions. Atmospheric emissions of carbon dioxide, methane and nitrous oxide, and the emissions weighted by Global Warming Potentials (GWPs) summed for the three compounds will be reported in units of g CO₂e/MJ LHV fuel combusted. GWPs for CO₂ (1), methane (25) and nitrous oxide (298) with a 100 year time horizon, from the 2007 IPCC assessment (IPCC, 2007), will be used.

Step 4: Interpretation of the LCA results The life cycle GWP weighted global warming gas emissions will be compared per MJ LHV of fuel consumed. Uncertainties in the estimates will be discussed.

1.5 Organization of the Report

Chapter 2 provides a detailed description of the methodologies that will be used in the report. Chapters 3-8 describe the life cycle inventories for the major life cycle stages: raw material acquisition (petroleum, coal, natural gas and biomass, Chapter 3), synthesis gas manufacture (via gasification and steam methane reforming, Chapter 4), synthesis gas clean-up (Chapter 5), Fischer-Tropsch processing to produce waxes (Chapter 6); wax upgrading to produce SPK (Chapter 7) and combustion (Chapter 8). Chapter 9 reports on the aggregation of the life cycle inventory data into weighted greenhouse gas emission estimates for each of the fuels and Chapter 10 summarizes the report and makes suggestions for future work.

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CHAPTER 2: METHODOLOGY FOR ESTIMATING LIFE CYCLE GREENHOUSE GAS EMISSIONS FROM AVIATION FUELS

2.1 Background

The steps used in the estimating the life cycle greenhouse gas emissions (referred to as Greenhouse Gas Life Cycle Assessments (GHG LCA)) of aviation fuels are:

- *Step 1*: Determine the goal and scope of the assessment.
- *Step 2*: Develop an inventory of the life cycle greenhouse gas emissions for the aviation fuel systems
- *Step 3*: Assess the impacts of the emissions, using global warming potentials
- *Step 4*: Interpretation of the GHG LCA results.

Chapter 1 defined the goal and scope of the GHG LCAs performed in this study. This Chapter will outline the methods used to develop inventories of greenhouse gas emissions and the global warming potentials used in impact assessment.

Although the general methodologies used to develop life cycle inventories have been codified in a variety of publications (ISO 2006a; ISO 2006b; Consoli et al. 1993; Allen et al. 1997), in practice, variations in the assumptions, methodological choices, strategies for filling data gaps, and other factors can have a significant impact on the results of the life cycle analyses. Accepted practices can vary among life cycle assessment practitioners, and for regulatory applications, methods are still undergoing refinement. In order to ensure that the results of this study are as widely accepted as possible, the study team helped organize, then participated in, a work group that developed a framework and guidance document for performing life cycle assessments of greenhouse gas emissions of liquid aviation fuels. The work group included representatives from federal agencies, universities, consultancies and the private sector. A list of the participants is provided in Table 2-1. The work group produced a document (Allen et al., 2009) that provided detailed guidance on methodologies, data documentation and reporting. The remainder of this Chapter will highlight key features of the framework and guidance and how they are applied in this report. Details of the framework and guidance are available in the working group report.

Table 2-1. Participants in Working Group on Life Cycle Assessments of Transportation Fuels

David Allen	University of Texas at Austin
Charles Allport	Universal Technology Corporation
Kristopher Atkins	The Boeing Company
Joyce Cooper	University of Washington
Robert Dilmore	National Energy Technology Laboratory
Laura Drauker	Science Applications International Corporation
Ken Eickmann	University of Texas at Austin
Jeffrey Gillen	U.S. Air Force Fellow at Argonne National Laboratory
Warren Gillette	Federal Aviation Administration
Michael Griffin	Carnegie Mellon University
William Harrison III	US Air Force Research Laboratory
James Hileman	Massachusetts Institute of Technology
John Ingham	URS Corporation
Fred Kimler III	US Air Force Research Laboratory
Aaron Levy	Environmental Protection Agency
Cynthia Murphy	University of Texas at Austin
Michael O'Donnell	University of Texas at Austin
David Pamplin	Defense Logistics Agency
Greg Schivley	Franklin Associates, A Division of ERG
Timothy Skone	National Energy Technology Laboratory
Shannon Strank	University of Texas at Austin
Russell Stratton	Massachusetts Institute of Technology
Philip Taylor	University of Dayton Research Institute
Valerie Thomas	Georgia Institute of Technology
Michael Wang	Argonne National Laboratory
Michael Webber	University of Texas at Austin
Thomas Zidow	URS Corporation

2.2 Types of LCAs

As described in the Framework and Guidance document (Allen et al., 2009), life cycle assessments can be done on an average or marginal basis, and can be attributional or consequential. An LCA that considers the energy and material flows over a broad enough spatial or temporal range so that conditions are considered generally representative would be considered an “average” LCA. For example, this study will compare greenhouse gas emissions for Fischer-Tropsch aviation fuels to an average LCA for aviation fuels in the United States, largely based on data for the year 2005. This spatial scale (the United States) and time frame (the calendar year 2005) for petroleum based aviation fuels represent a relatively broad range of conditions, including the use of crude oil derived from multiple countries and the operation of refineries during both peak gasoline production (summer) and peak heating oil production (winter).

In contrast, a marginal LCA considers product produced at the margin, generally under very specific conditions. For example, this study considers the production of fuels produced from Fischer-Tropsch (FT) processes. Although FT technology has been known for decades, only a few commercial scale FT fuel facilities operate globally, and much of the data available for these facilities is based on processes that produce a spectrum of fuels, rather than being optimized for aviation fuel production. So, the data for FT fuels presented in this study will be marginal, rather than average.

Since this study will report both marginal and average LCA data, it is important to distinguish between these types of LCA data. Marginal and average LCA inventory data for petroleum based fuels are quite different, and it should be noted that comparisons between marginal LCAs of emerging aviation fuels and petroleum based fuels may lead to different conclusions depending on whether a marginal or average LCA is employed for the comparison. Nevertheless, this study will compare an average LCA of petroleum based fuels to marginal LCAs of FT fuels, since that comparison is called for in EISA (see Chapter 1).

LCAs are also categorized as to whether they are attributional or consequential. Attributional LCAs examine a single product system and determine the material and energy flows that are attributed to that product. In contrast, consequential LCAs examine systems of products and services. In the context of the LCAs examined in this work, a consequential LCA would examine fuel systems, including both petroleum and FT fuels. In such a consequential LCA, increased FT fuel use would impact the demand for, and consequent impacts of, petroleum fuels. A more transparent example of a consequential LCA is provided by biofuels. If a food crop is used to make a biofuel, the market for food is impacted and a consequential LCA would examine the entire food-fuel system.

The analyses presented in this report will be attributional, rather than consequential. There is, however, one increasingly reported component of fuel life cycles that is consequential in nature. That life cycle element is indirect land use, and is associated primarily with biomass derived fuels. Indirect land use refers to the increased use of land that is required to maintain food crop production when fuel crops are added to agricultural operations. As has been reported in a number of recent publications (Fargione et al., 2008; Searchinger et al., 2008), the changes in carbon stored in soils can change dramatically when lands are converted to agricultural operations. Thus, including indirect land use in greenhouse gas emission estimates for biomass derived fuels (such as FT fuels derived from the gasification of switchgrass) has a significant impact on overall life cycle greenhouse gas emissions, and recent reports from the EPA on estimating greenhouse gas emissions for biofuels have included indirect land use (US EPA, 2009a,b). Because of these precedents, estimates of indirect land use impacts will be cited in this report (Chapters 3 and 9). However, they will be reported separately from the attributional LCA data that are the main topic of the report.

2.3 Life-Cycle Stages

Five life cycle stages will be used in reporting of life cycle inventory and assessment results. The definitions and boundaries for these life cycle stages are consistent with those recommended by Allen et al. (2009).

- Raw Material Acquisition
- Raw Material Transport and Storage
- Liquid Fuels Production
- Product Transport and Fueling (considered small and identical between FT and petroleum-based fuels in this report)
- Vehicle Operation

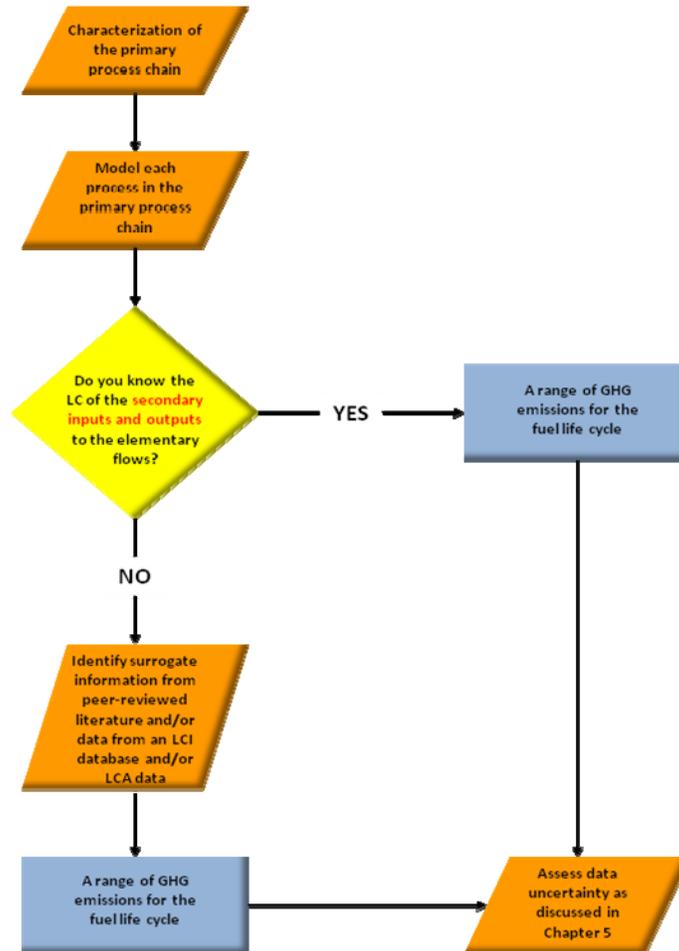
End of Life impacts are not considered in this report since the product is consumed in the vehicle operation stage. The primary focus in this report will be on the liquid fuels production step. Greenhouse gas emissions will be reported for the other life cycle stages, but these emission estimates will be drawn from previously reported work.

2.4 System Boundaries

A comprehensive LCA accounts for all material and energy flows, from both primary and secondary processes. For aviation fuel LCAs, the primary process is the production and use of the fuel, while an example of a secondary process would be the production of fertilizers used as an input in the production of biofuels. The secondary processes also have inputs (which in this report will also be referred to as secondary, rather than tertiary or higher level processes) that should be accounted for. For example, the production processes for nitrogen fertilizers use ammonia as an input, and the ammonia production processes have energy and material flows that need to be accounted for in the life cycle assessment. The ammonia production process, in turn, requires hydrogen and the production of hydrogen involves material and energy flows that need to be accounted for in the LCA.

In principle, a life cycle assessment includes the primary and all of the secondary flows of materials, but in practice, some secondary flows are difficult to quantify and may not be significant in estimating life cycle impacts. For example, while for many biofuels, fertilizer inputs will be significant, it is not necessarily clear whether inputs such as the steel required to build fertilizer production facilities needs to be accounted for. Generally, some material and energy flows are categorically excluded from consideration. In this report, flows that will be categorically excluded (based on the guidance provided in Allen et al., 2009) are low frequency, non-predictable catastrophic events, such as large spills, and human activities (e.g. workers' lunch breaks and commuting activities). Beyond categorically excluded flows, the methods for determining whether a material or energy flow should be included in an LCA have generally been left to the expert judgment of the LCA practitioner. However, in recent guidance (Allen et al., 2009), this process has been systematized. To the extent practicable, this report will follow the system outlined in the decision tree shown as Figure 2-1 (Figure 3-1 in the Framework and Guidance document (Allen et al., 2009)).

Figure 2-1. System boundary decision flow (Allen et al., 2009).



The decision tree in Figure 2-1 contains a series of steps. The first of these steps is to characterize the primary process chain. Section 2.3 briefly outlines the life cycle stages to be considered in characterizing the primary process chain. The methods used to characterize the primary processes (second step in the decision tree) are described in detail in subsequent chapters. The next step in the decision tree is to determine whether the life cycles of secondary material and energy flows are well known. For flows that are not well known, the guidance suggests methods for developing surrogates for the unknown information.

Specifically, two sources of surrogate data are recommended. These are:

- “peer reviewed documentation of the life cycle of surrogate processes in archival literature, in a project report, or in a LCI [Life Cycle Inventory] database. Although striving to achieve the closest match to the system at hand, these data may not match geographic, temporal, technological, or other specific characteristics of the higher order process of interest” (Allen et al., 2009).
- “EIOLCA data for the life cycle of the sector in which the higher order flow is produced” (Allen et al., 2009). The EIOLCA method is a systems level model of material and energy flows in regional or national economies (www.eiolca.net). It can provide data on average material and energy flows in broad sectors of the economy (e.g.,

the flows associated with the construction and operation of industrial buildings are averaged in a sector named “manufacturing and industrial buildings”). As described in the guidance, the EIOLCA model can be applied, and an uncertainty range can be assigned to those data.

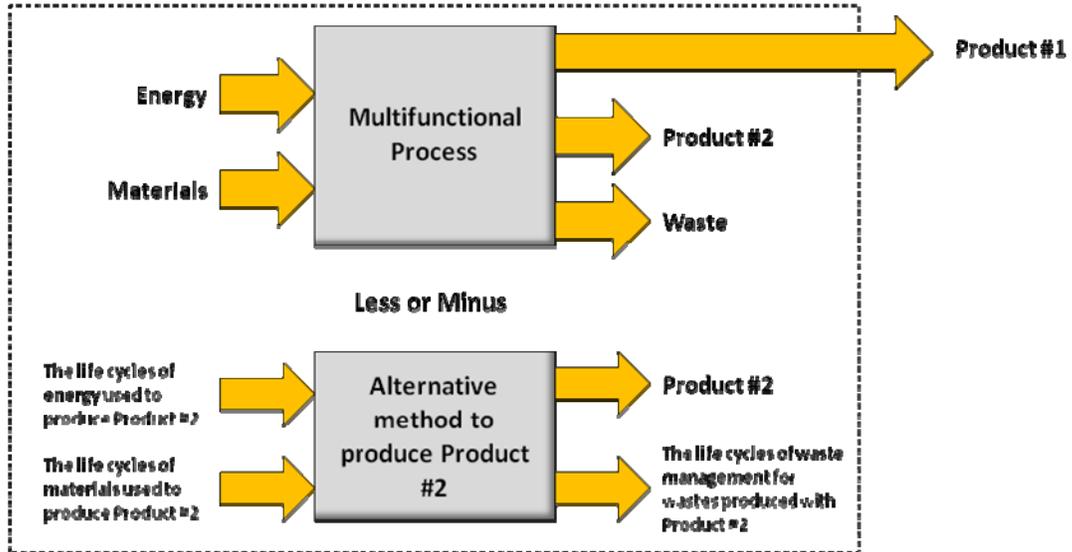
Life cycle information from these two types of datasets are used to create bounds for the contribution of less well defined secondary flows, and the resulting uncertainties are reported, as outlined in later sections of this chapter.

2.5 Disaggregation, System Expansion, and Allocation

An issue that commonly arises in developing LCA data is how to distribute material and energy flows associated with processes that produce more than one product. For example, in a petroleum refinery, if energy use data are only available at the scale of the full refinery, then that energy flow must be distributed between the refinery gases, gasoline, diesel, aviation fuel, heating oil, lubricating oils, asphalt, coke, and other products produced by the refinery. Similarly, if a FT process leads to a variety of fuel types (light gases, gasoline, diesel, aviation fuel) then the greenhouse gas emissions of the FT process would be allocated among those fuels.

As noted in Allen et al. (2009) the preferred method for performing co-product allocation is process disaggregation, defined as further dividing the process so that inputs and outputs can be assigned to individual products. In this work, for some of the most significant co-product allocations, where product disaggregation will not be possible, displacement will be used as the method for allocating emissions. Displacement methods are described in Allen et al. (2009). To summarize, as shown in Figure 2.2 (Figure 4-3 in Allen et al., 2009), displacement allows the primary process to take credit for avoided greenhouse gas emissions associated with co-products. For example, if a FT process produces light gases and naphtha as co-products in aviation fuel production, then the aviation fuel greenhouse gas burden due to the FT process is calculated as the total FT process greenhouse gas emissions minus a co-product credit. That co-product credit is the amount of greenhouse gas emissions that would normally be required to produce naphtha and light gases from petroleum. The rationale for using this approach is that the small amounts of light gases and naphtha produced by FT processes will not significantly impact the large markets for these products. Therefore, the co-products would displace products that would normally be derived from petroleum.

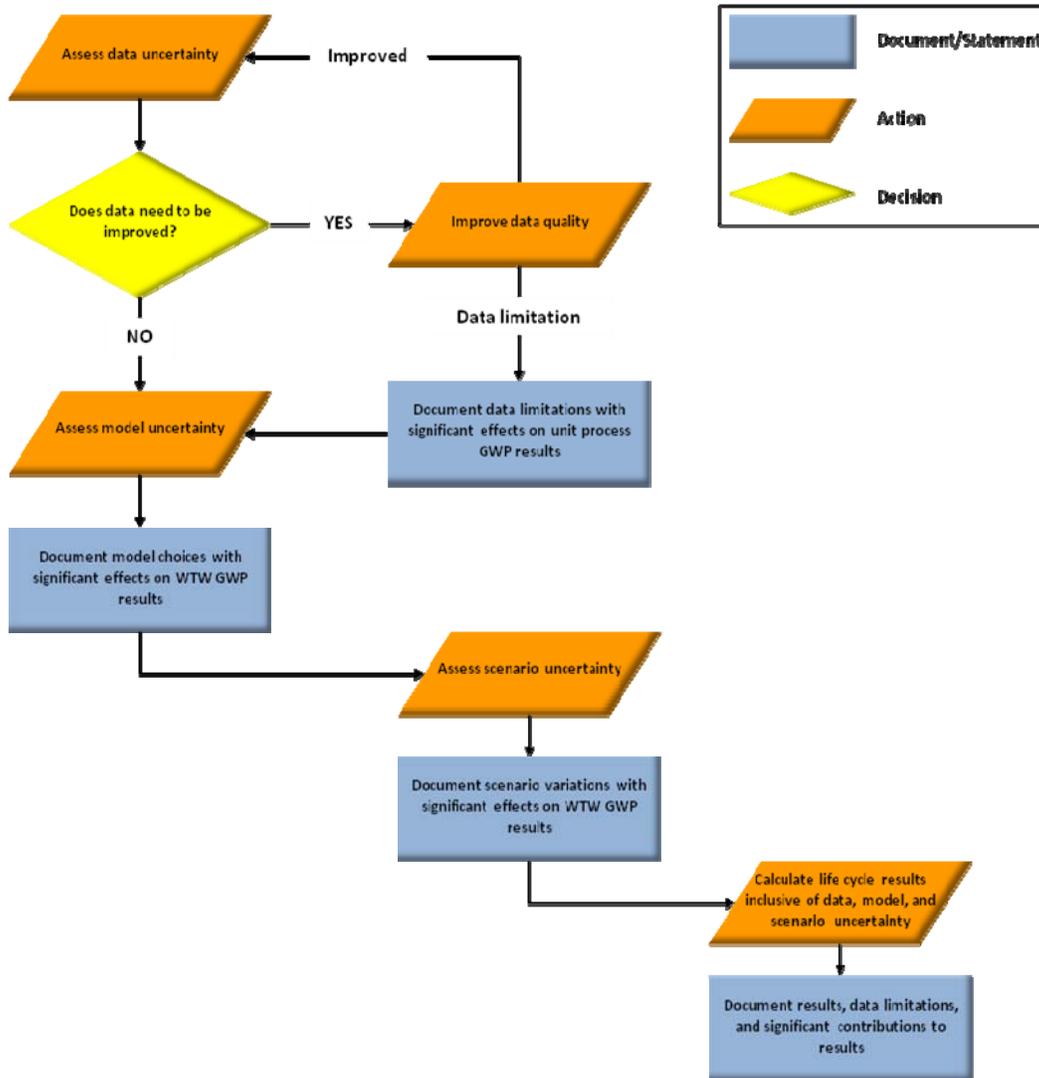
Figure 2-2. An alternate process that produces primarily product #2 can be used to determine a displacement credit for a multifunctional process that produces product #2 as a co-product. (Figure 4-3 from Allen et al., 2009)



2.6 Data Quality

The quality of the data used in life cycle analyses inevitably affects the results of GHG-LCAs. Recommended methods for documenting data quality and performing sensitivity/uncertainty analyses are provided by Allen et al. (2009, Chapter 5), and are summarized in the flow chart shown in Figure 2-3 (Figure 5-1 from Allen et al., 2009). The process notes the need to characterize data, model and scenario uncertainties.

Figure 2-3. Process for assessing and documenting uncertainty in LCA.



2.7 Impact Assessment

The life cycle impacts of the fuels will be assessed using a single performance criterion, weighted greenhouse gas emissions. The contributions of three greenhouse gases, carbon dioxide, methane and nitrous oxide, to global warming emissions will be quantified over the life cycles of the fuels. The emissions weighted by Global Warming Potentials (GWPs), summed for the three compounds, will be the reporting metric. GWPs express the potency of each pollutant, as global warming gases, in units of kg of equivalent emissions of carbon dioxide per kg emitted, for global warming over a 100-year time horizon. GWPs are reported by the Intergovernmental Panel on Climate Change. This report will use the GWPs for CO₂ (1), methane (25) and nitrous oxide (298) from the 2007 IPCC assessment (IPCC, 2007). Global warming impacts over the life cycle will be reported as g CO₂e/MJ LHV fuel combusted.

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CHAPTER 3: RAW MATERIAL ACQUISITION

3.1 Feedstock Selection

This report compares the life cycle greenhouse gas emissions of a petroleum baseline fuel to FT fuels made from three types of feedstocks:

- 1) Natural Gas (US average production)
- 2) Coal (Kittanning #6 coal)
- 3) Coal/Biomass mixture involving three different feed ratios (Mixtures of switchgrass and Kittanning #6 coal).

This Chapter examines the greenhouse gas emissions for the raw material acquisition steps for each of these fuels. The primary sources of data for this stage of the life cycle are the U.S. Life Cycle Inventory database (US LCI), maintained by the National Renewable Energy Laboratory (NREL, 2009), and data reported by the National Energy Technology Laboratory (NETL; Skone and Gerdes, 2008).

3.2 Petroleum

The baseline fuel for comparison will be an aviation fuel based on US average petroleum feedstocks from 2005. This baseline fuel and analogous baselines for gasoline, diesel, and other refined products have been characterized in Department of Energy (DoE) reports (Skone and Gerdes, 2008). The goals and scope for the DoE study were designed to meet the EISA definition of “baseline lifecycle greenhouse gas emissions”, so the results of the DoE study represent a valid point of comparison for this study. Details of these baseline greenhouse gas emission assessments are reported in the NETL reports, so the presentation of these assessments will be limited to the comparisons reported in Chapter 9.

The only difference between the petroleum baseline reported by Skone and Gerdes (2008) and the baseline used in this report is that, in this report, the greenhouse gas footprint for combustion emissions will be limited to CO₂. This is based on recommendations in the Framework and Guidance document prepared by the Aviation Fuel Life Cycle Assessment Working Group of the US Air Force (Allen et al., 2009). This issue is discussed in more detail in Chapter 8.

For the extraction of petroleum, the central estimate of the global warming potential of the greenhouse gas emissions that will be used in this report is 6.8 ± 3 kg CO₂e /MMBTU LHV [$6.4 \text{ g} \pm 3 \text{ g CO}_2\text{e/MJ}$]. The variability reported in this result is due to differences in the practices used in extracting petroleum from different sources, particularly the assumed value of methane releases, depending on the source of the petroleum (see Chapter 9; Skone and Gerdes, 2008).

3.3 Natural Gas

Data on the greenhouse gas emissions associated with natural gas extraction and processing, from the US LCI (NREL, 2009) are provided in Tables 3-1 and 3-2. The data are based on US averages of natural gas produced on-shore and off-shore, and includes natural gas co-produced with oil as well as from reservoirs that contain only natural gas. The basis of the reporting in the

US LCI is 1000 standard cubic feet. This is converted to emissions per kg in the tables. These data will be compared to data from the NETL assessments in Chapter 4.

Table 3-1. Greenhouse Gas Footprints of Natural Gas Extraction (NREL, 2009)

Process Fuels

	Value per 1000 scf	Value per kg**	Units	GWP equivalents kg CO ₂ e per kg*
Distillate fuel oil	0.0071	3.56×10 ⁻⁴	gallons	0.004
Electricity	0.81	0.041	kWh	0.031
Gasoline	0.0038	1.91×10 ⁻⁴	gallons	0.002
Natural Gas	24.1	1.21	cu ft	0.064
Residual fuel oil	0.0044	2.21×10 ⁻⁴	gallons	0.002
Air Emissions				
Methane	0.55	0.028	lb	0.318
Total				0.42

* life cycle greenhouse gas emissions for fuels are based on data from Skone and Gerdes (2008)

- Distillate fuel oil = 0.116 MM BTU LHV/gal ; 96.3 kg CO₂e/MMBtu LHV
Residual fuel oil = 100 kg CO₂e/MMBtu/LHV
Natural gas = 53.3 kg CO₂e/MMBtu HHV; 0.0224 MM BTU HHV/lb
(Derived from emission factors in Tables 4-9 to 4-11 citing Table 4-1 of API's 2004 "Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry" and energy content from Table 4-3 citing EIA's "Petroleum Navigator," accessed in 2008.)
- Electricity = 0.763 kg CO₂e/kWh (2004 US grid average; Skone and Gerdes, 2008, Table B-1)
- Gasoline = 0.116 MM BTU LHV/gal ; 96.3 kg CO₂e/MMBtu LHV from Executive summary, Skone and Gerdes, 2008

**1000 scf = 19.92 kg

Table 3-2. Greenhouse Gas Footprints of Natural Gas Processing (NREL, 2009)

Process Fuels

	Value per 1000 scf	Value per kg**	Units	GWP equivalents kg CO ₂ e per kg*
Distillate fuel oil	0.0003	0.15×10 ⁻⁴	gallons	0.0017
Electricity	0.44	0.022	kWh	0.017
Gasoline	0.0003	0.15×10 ⁻⁴	gallons	0.0017
Natural Gas	25.5	1.28	cu ft	0.067
Residual fuel oil	0.0003	0.15×10 ⁻⁴	gallons	0.0017
Air Emissions				
Methane	0.086	0.0043	lb	0.049
Total				0.138

* life cycle greenhouse gas emissions for fuels are based on data from Skone and Gerdes (2008)

- Distillate fuel oil = 0.116 MM BTU LHV/gal ; 96.3 kg CO₂e/MMBtu LHV
Residual fuel oil = 100 kg CO₂e/MMBtu/LHV
Natural gas = 53.3 kg CO₂e/MMBtu HHV; 0.0224 MM BTU HHV/lb
(Derived from emission factors in Tables 4-9 to 4-11 citing Table 4-1 of API's 2004 "Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry" and energy content from Table 4-3 citing EIA's "Petroleum Navigator," accessed in 2008.)
- Electricity = 0.763 kg CO₂e/kWh (2004 US grid average; Skone and Gerdes, 2008, Table B-1)
- Gasoline = 0.116 MM BTU LHV/gal ; 96.3 kg CO₂e/MMBtu LHV from Executive summary, Skone and Gerdes, 2008

**1000 scf = 19.92 kg

3.4 Coal

Coal is the most plentiful fossil fuel on earth, with 27% of the coal reserves in the world being located in the United States (BP, 2007). The United States has recoverable coal reserves totaling 247,000 million tons and an annual coal production ranging from 1,000 to 1,100 million tons. At current production rates, the recoverable reserves are sufficient to power the United States for the next 200 years (BP, 2007). The energy contained in the United States coal reserves is greater than all recoverable oil in the world (US DoE, 2009).

The abundance and availability of coal makes it an attractive choice as a feedstock for the production of liquid transportation fuels, however, there is substantial variability in the nature of coal reserves, the methods used in the extraction of coal, and the greenhouse gas emissions associated with the extraction. The two primary categories of coal extraction are surface and sub-surface extraction. Table 3-3 shows some of the differences in energy use and emissions associated with surface and underground mining (US LCI; NREL, 2009). Underground mining uses less inputs, except for coal, than surface mining and the associated global warming potential for greenhouse gas emissions is less for underground coal extraction. In contrast, however, methane emissions are estimated to be 8.68 and 0.854 lb methane per 1000 lb coal for underground and surface mines, respectively (NREL, 2009). This translates to 98.6 and 9.7 kg CO₂e per 1000 lb coal. This wide range of methane emission estimates is a source of considerable uncertainty in the life cycle greenhouse gas emission estimates for coal-derived FT fuels.

Table 3-3. Surface and Underground mining energy requirements (NREL, 2009)

	Surface	Underground	Units per 1000 lb coal produced	Global warming potential of emissions (eastern underground) kg CO ₂ e/1000 lb coal
Percent of mining type	58%	42%		
Fuels/Electricity Consumed				
Residual	0.17	0.0072	Gal	0.08
Distillate	1.79	0.033	Gal	0.36
Gasoline	0.17	0.0048	Gal	0.05
Natural gas	4.03	0.59	Cu. Ft	0.03
Coal	0.36	0.53	lbs	0.8
Electricity	24.18	8.39	kWh	6.4

* life cycle greenhouse gas emissions for fuels are based on data from Skone and Gerdes (2008)

- Distillate fuel oil = 0.116 MM BTU LHV/gal ; 96.3 kg CO₂e/MMBtu LHV
Residual fuel oil = 100 kg CO₂e/MMBtu/LHV
Natural gas = 53.3 kg CO₂e/MMBtu HHV; 0.0224 MM BTU HHV/lb
(Derived from emission factors in Tables 4-9 to 4-11 citing Table 4-1 of API's 2004 "Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry" and energy content from Table 4-3 citing EIA's "Petroleum Navigator," accessed in 2008.)
- Electricity = 0.763 kg CO₂e/kWh (2004 US grid average; Skone and Gerdes, 2008, Table B-1)
- Gasoline = 0.116 MM BTU LHV/gal ; 96.3 kg CO₂e/MMBtu LHV from Executive summary, Skone and Gerdes, 2008

This report will assume that the coal being used for fuel production is an eastern coal produced using underground mining. This type of coal was selected based on the location of the US Air Force Assured Aerospace Fuels Research Facility (AAFRF) in Ohio. An Ohio coal, Kittanning #6 coal, was chosen. A typical composition for this coal is compared to that of a widely studied alternative coal, Illinois #6, in Table 3-4.

Table 3-4. Coal Composition (Mass %) (Akhtar et al., 1974; Gray et al., 2007)

	Kittanning #6	Illinois #6
C	71.0	63.8
H	5.2	4.5
N	1.3	1.3
O	7.3	6.9
S	3.0	2.5
Cl	0.4	0.3
Moisture	2.4	11.1
Ash	9.4	9.7

The composition of the Kittanning #6 coal is similar to that of Illinois #6 coal. If the Illinois #6 coal is dried to a similar moisture level as Kittanning #6 (the drying of coal to a lower moisture level is common prior to gasification), then the carbon content of Illinois #6 would be 69.9% by mass at 2.4% moisture, compared to 71.0% for Kittanning #6. Based on the similarity of composition between the coals it will be assumed that the Kittanning #6 can be processed using the same gasifier technologies as for Illinois #6. The gasifier will be discussed in more detail in the Chapter 4.

Table 3-5 summarizes the global warming potential of the greenhouse gas emissions associated with coal mining that will be used in this report (106. kg CO₂e per 1000 lb coal). The data are for an eastern bituminous coal extracted from an underground mine.

Table 3-5. Greenhouse Gas Footprints of Coal Mining Process Fuels

	Value per 1000 lb	Units	GWP equivalents kg CO ₂ e per 1000 lb*
Distillate fuel oil	0.033	Gallons	0.36
Electricity	8.39	kWh	6.4
Gasoline	0.0048	Gallons	0.05
Natural Gas	0.59	cu ft	0.03
Residual fuel oil	0.0072	Gallons	0.08
Coal	0.53	lb	0.8
Air Emissions			
Methane	8.68	lb	98.6
Total			106.3

* life cycle greenhouse gas emissions for fuels are based on data from Skone and Gerdes (2008)

- Distillate fuel oil = 0.116 MM BTU LHV/gal ; 96.3 kg CO₂e/MMBtu LHV
Residual fuel oil = 100 kg CO₂e/MMBtu/LHV
Natural gas = 53.3 kg CO₂e/MMBtu HHV; 0.0224 MM BTU HHV/lb
(Derived from emission factors in Tables 4-9 to 4-11 citing Table 4-1 of API's 2004 "Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry" and energy content from Table 4-3 citing EIA's "Petroleum Navigator," accessed in 2008.)
- Electricity = 0.763 kg CO₂e/kWh (2004 US grid average; Skone and Gerdes, 2008, Table B-1)
- Gasoline = 0.116 MM BTU LHV/gal ; 96.3 kg CO₂e/MMBtu LHV from Executive summary, Skone and Gerdes, 2008

3.5 Switchgrass

Corn, poplar trees, switchgrass, algae and other dedicated energy crops are being studied to determine their ability to meet demand, suitability for conversion to liquid transportation fuels and economic feasibility. Switchgrass is the biomass feedstock that has been chosen for evaluation in this study. The choice of switchgrass was largely based on (1) analyses made by the US Environmental Protection Agency as part of the review of the Renewable Fuel Standard (US EPA 2009a,b), which indicated that switchgrass has one of the smallest net greenhouse gas footprints of the biomass feedstocks that have been examined extensively for their use in fuels, and (2) the geographical extent of the regions in which switchgrass can be grown.

The natural range for switchgrass, shown in Figure 3-1, covers 46 states and major areas in Canada (USDA, 2009). Switchgrass can be grown on marginal and degraded lands that cannot be used for cultivation of food crops. Figure 3-2 shows an estimate of land available for switchgrass production when the price of switchgrass is \$44/metric ton. A greater price would result in an increase in available land for switchgrass production. Reported yields range from 16-22 metric tons/hectare on crop lands (McLaughlin et al., 2002, 2004) and from 5.2-11.1 tons/hectare on marginal lands (Schmer et al., 2008).

The primary inputs for switchgrass production, reported in Table 3-6, have been summarized from Farrell et al. (2006), and these are the values used in the National Research Council analysis of coal and biomass feeds for liquid fuels (NRC, 2009).

Table 3-6. GWP of greenhouse gas emissions for Switchgrass production (Farrell et al., 2006, as cited in NRC, 2009)

	GWP of emissions kg CO ₂ e/hectare
Nitrogen fertilizer	547
Phosphorous	3.4
Herbicide	2.4
Insecticide	10.4
Transport	3
Diesel	341
Electricity	42
Farm machinery	21
Total	971 (400 kg CO ₂ e/acre) 100 kg CO ₂ e/ton at 4 tons/ac)

These inputs are relatively straightforward to document and estimate. A source of considerable uncertainty, however, in the assessment of GHG emissions associated with switchgrass production is related to the ability of switchgrass to perform nitrogen fixing, which in turn determines its requirements for nitrogen-based fertilizer. In their life cycle studies associated with the Reformulated Fuel Standard (US EPA 2009a,b), the EPA estimated a net 2 million tons of CO₂e credit for a scenario involving 3.2 billion gallons of switchgrass derived ethanol production (US EPA, 2009c). This is equivalent to a credit of 50 kg CO₂e per ton of switchgrass, at a yield of 80 gal/ton (NRC, 2009). This makes the net direct emissions associated with switchgrass production **50 kg CO₂e/ton**

Figure 3-1. Natural Switchgrass Distribution (USDA, 2009)

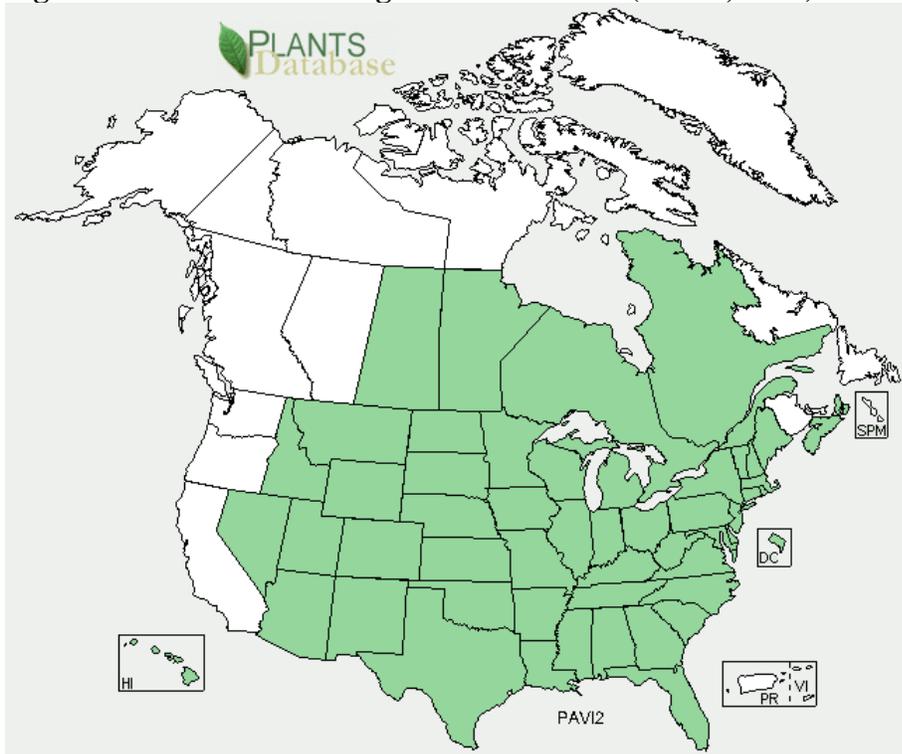
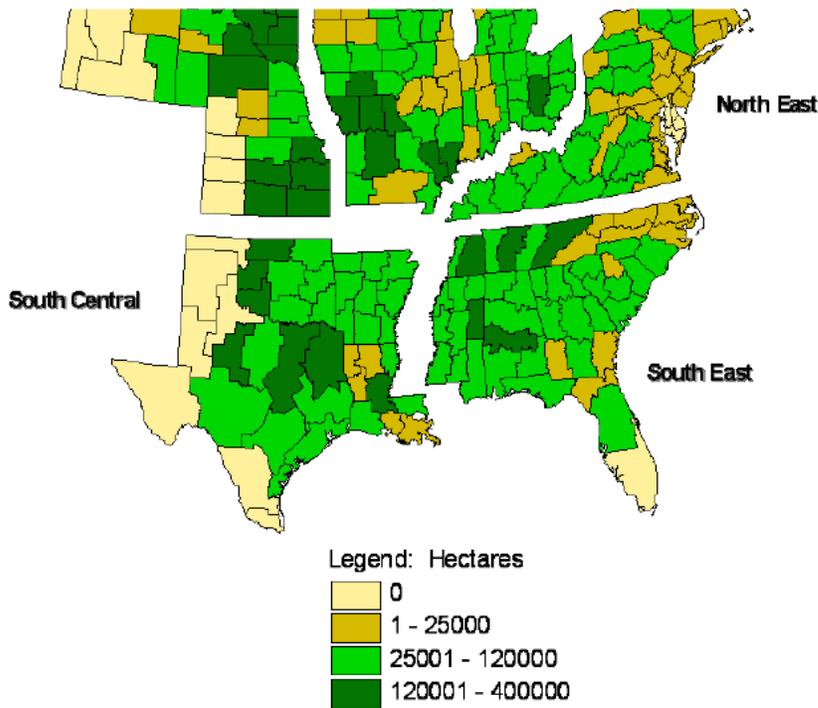


Figure 3-2. Land Area Available for Switchgrass Production



Far more difficult to estimate are the impacts on land, including impacts on other types of crop production. If large tracts of land are converted from conservation lands or from the production of other crops to produce switchgrass, the amount of carbon stored in the land and the ability of land to take up carbon is changed. In addition, changes in diesel use, electricity use, nitrous oxide emissions, and other sources of greenhouse gas emissions occur as land is converted from one type of crop to another (e.g., if producing switchgrass causes less corn to be produced and if switchgrass uses less nitrogen fertilizer than corn, then there is a net decrease in the use of nitrogen fertilizer). For the purposes of this report, these land use changes and consequential impacts are not included in the primary analyses.

There are several reasons for not including land use changes and consequential impacts on other crops in the analyses presented in this report. First, the methods for estimating the greenhouse gas emissions associated with both direct and indirect land use changes are just emerging, and are subject to considerable uncertainty. Second, as noted in Chapter 2, inclusion of indirect land use and other consequential impacts makes a life cycle assessment consequential, rather than attributional. The analyses presented in this report are attributional, therefore including just this single type of consequential impact is difficult to justify (e.g., if growing switchgrass requires electricity, why not include all of the consequences of increases in electricity demand?). A more detailed examination of this issue of consistent treatment of consequential emissions is provided in a recent National Research Council report (NRC, 2009b).

On the other hand, greenhouse gas emissions associated with indirect land use changes have been estimated to be large, and they have been included in EPA analyses (US EPA 2009a,b). The EPA analyses include not only changes due to the carbon storage of soils of new land converted to agriculture, but also changes in diesel use, electricity use, nitrous oxide emissions, and other factors, as land is converted from one type of crop to another. In this report, the US EPA estimates of greenhouse gas emissions from land use changes will be cited, but will be reported separately from all of the attributional greenhouse gas impacts.

Table 3-7 reports the global warming potential of greenhouse gas emissions due to land use change and other consequential analyses for switchgrass production, reported by the US EPA in their draft Regulatory Impact Analysis for the Renewable Fuel Standard (US EPA 2009d). Interested readers are referred to the EPA report for analyses. For the purposes of this report, it is merely noted that these impacts lead to a significant impact on the greenhouse gas footprint of switchgrass. To assess this sensitivity, we will examine the impact of **assuming two values of the GWP of greenhouse gas emissions associated with switchgrass: 50 kg CO₂e/ton (attributional only), and -600 kg CO₂e per ton of switchgrass (similar to the EPA central estimate)**

Table 3-7. Consequential impacts of switchgrass production

Parameter	Central estimate	Assumptions
Net greenhouse gas benefit from consequential analyses	Approx. -100% of petroleum baseline; -600 kg CO ₂ e per ton of switchgrass	92.9 kg CO ₂ e per million BTU of fuel (US EPA RFS pg. 281, Fig 2.1-2; 80 gallons (NRC, 2009) of ethanol per ton of switchgrass; 75,700 BTU/gal lower heating value of fuel

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US EPA, 2009a, EPA Lifecycle Analysis of Greenhouse Gas Emissions from Renewable Fuels, EPA-420-F-09-024, May 2009, available at: <http://epa.gov/otaq/renewablefuels/420f09024.htm> , accessed July 31, 2009.

US EPA, 2009b, Greenhouse Gas Impacts of Expanded Renewable and Alternative Fuels Use, EPA-420-F-07-035, May 2009, available at: <http://www.epa.gov/otaq/renewablefuels/420f07035.pdf> accessed August 9, 2009.

US EPA, 2009c, Draft Regulatory Impact Analysis: Changes to the Renewable Fuel Standard Program, EPA-420-D-09-001, May 2009, available at: <http://www.epa.gov/otaq/renewablefuels/420d09001.pdf> accessed November 30, 2009, page 334, Table 2.6-8

US EPA, 2009d, Draft Regulatory Impact Analysis: Changes to the Renewable Fuel Standard Program, EPA-420-D-09-001, May 2009, available at: <http://www.epa.gov/otaq/renewablefuels/420d09001.pdf> accessed November 30, 2009, page 281, Table 2.1-2

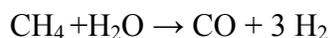
CHAPTER 4: SYNTHESIS GAS MANUFACTURE

4.1 Introduction

For the aviation fuel systems considered in this report, there are two methods of generating synthesis gas feed for the Fischer-Tropsch (FT) reactors. With natural gas, steam methane reforming is used. With a coal or mixed coal/biomass feedstock, a partial oxidation (gasification) process is used. This Chapter describes the processing steps and greenhouse gas emissions associated with each of these technologies.

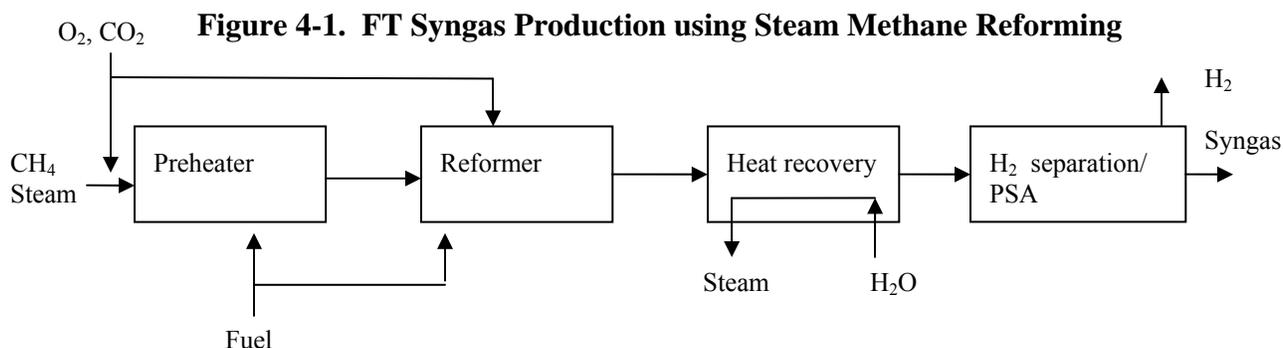
4.2 Steam-Methane Reforming (SMR)

In SMR, equimolar amounts of methane and water react to form CO and H₂ with the overall stoichiometry:

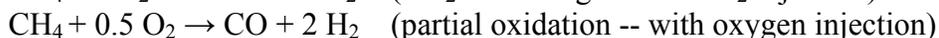
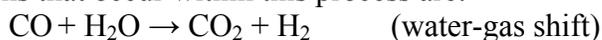


The reaction is endothermic (49 kcal/mol of methane), (Kirk-Othmer, 2004) so heat must be provided to preheat reactants and sustain the desired reaction temperature in the reformer. There are two ways to provide this heat: 1) using an externally fired heater fueled by methane, a portion of the product syngas, or fuel gas produced in the FT product purification section, or 2) autothermally by introducing a small quantity of oxygen into the reactor such that the heat of reaction is provided by partial oxidation of the reacting gases.

SMR is a very flexible process. In addition to different heat sources, different reactant gas mixtures, operating temperatures and pressures can be used to generate syngases containing H₂/CO molar ratios ranging from 1:1 to 3:1, depending on the requirements of downstream processes. In a typical gas-to-FT liquids production facility, the SMR process would be configured as shown in Figure 4-1, and would operate at a pressure of 30 atm and a reformer temperature of 950°F (Molburg and Doctor, 2003).



Important side reactions that occur within this process are:



By adjusting the operating temperatures, pressures and feed gas rates, this process can produce a synthesis gas having a molar H₂/CO ratio ranging from 2.1, which is the correct proportion for

feed to a slurry bed FT reactor using a cobalt catalyst, to approximately 3:1. With approximately equimolar feed of steam and methane, and using external fuel sources, the product syngas will contain mostly H₂ and CO, at about a 3:1 ratio, together with small quantities of H₂O, CO₂ and unreacted methane. Under this scenario, approximately a third of the H₂ in the raw syngas would be recovered in the pressure swing adsorption (PSA) section for use in FT wax upgrading.

The best available data for SMR is from hydrogen production, rather than syngas production. Therefore, the greenhouse gas emissions for SMR syngas production were estimated by adjusting data from SMR for hydrogen production. When SMR is used in a conventional configuration to produce H₂ (with no CO), the CO that remains after H₂ separation is normally used as fuel in the preheat/reforming furnace(s). In an FT syngas facility, the CO is needed as a reactant, so an alternate fuel must be used to generate this heat. For the purposes of this report, it will be assumed that CO in SMR is produced in a 1:3 ratio, relative to hydrogen (0.33 scf CO per SCF H₂) and that the heat provided by CO is replaced by methane. Thus, the net greenhouse gas emissions GWP assigned to synthesis gas (with a 3:1 H₂/CO ratio) produced from methane (cradle to gate) is:

GWP per 1.33 scf synthesis gas from CH₄ (3:1 H₂/CO molar ratio) = GWP per scf hydrogen + GWP for methane used to replace the heat from 0.33 scf CO

Since the desired molar ratio of hydrogen to carbon monoxide in the FT processes is 2.1:1 (see Chapter 6), there is an excess of hydrogen produced. This hydrogen could be used in subsequent upgrading of the FT waxes (see Chapter 7), however, for the purposes of this report, it will be assumed that the excess hydrogen is a co-product and a displacement credit for this hydrogen will be included in the greenhouse gas calculation. Thus the net greenhouse gas emissions GWP assigned to synthesis gas (with a 2.1:1 H₂/CO ratio, where there is 0.69 scf H₂ produced with 0.33 scf CO for a total of 1.02 scf synthesis gas) produced from methane (cradle to gate) is:

GWP per 1.02 scf synthesis gas from CH₄ (2.1:1 H₂/CO ratio) = GWP per scf hydrogen + GWP for methane used to replace the heat from 0.33 scf CO – co-product credit for 0.31 scf hydrogen production

The most current and detailed analysis done to date for the GWP of hydrogen from SMR is that presented by Skone and Gerdes (2008), which estimates 0.0212 kg CO₂e/scf H₂. These data and data for methane production are summarized in Table 4-1, which also reports the net GWP for synthesis gas with a 2.1:1 H₂/CO ratio.

Table 4-1. Greenhouse gas emissions for SMR (cradle to gate)

GWP (kg CO ₂ e/scf H ₂)	0.0212
scf natural gas required to replace 0.33 scf CO, based on HHVs for natural gas and CO of 1089 and 320 BTU/ft ³ respectively*	0.097
GWP for 0.097 scf natural gas; GWP for natural gas of 53.3 kg CO ₂ e per MM BTU HHV, HHV of 0.0224 MM BTU HHV/lb, and density of 19.92 kg/1000 scf apply to natural gas	0.0051
GWP credit for .31 scf H ₂ hydrogen available after adjusting synthesis gas to 2.1:1 H ₂ /CO (0.0212 kg CO ₂ e/scf H ₂)	0.0065
GWP per scf synthesis gas from CH ₄ (2.1:1 H ₂ /CO ratio)	0.020
GWP per kg synthesis gas at 0.0125 kg per scf	1.6 kg CO ₂ e per kg syngas

*From GREET model, Argonne National Laboratory

Density of natural gas assumed to be 19.92 kg per 1000 scf

Since this is a cradle to gate inventory of greenhouse gas GWP, a comparison of the methane extraction and processing greenhouse gas provides an indication of the net GWP of the SMR process. The value from Chapter 3 for natural gas extraction and processing is 0.56 kg CO₂e per kg. Since 0.5 kg of methane is required to produce 1 kg of synthesis gas at a 2.1 molar ratio of H₂ to CO, the burden associated with methane production is roughly 0.3 kg CO₂e per kg syngas. Thus, roughly a quarter of the burden for the synthesis gas production from methane is from the raw material extraction and initial processing.

4.3 Gasification

For the four FT fuel production scenarios involving coal and biomass feedstocks, gasification is the route used to produce synthesis gas.

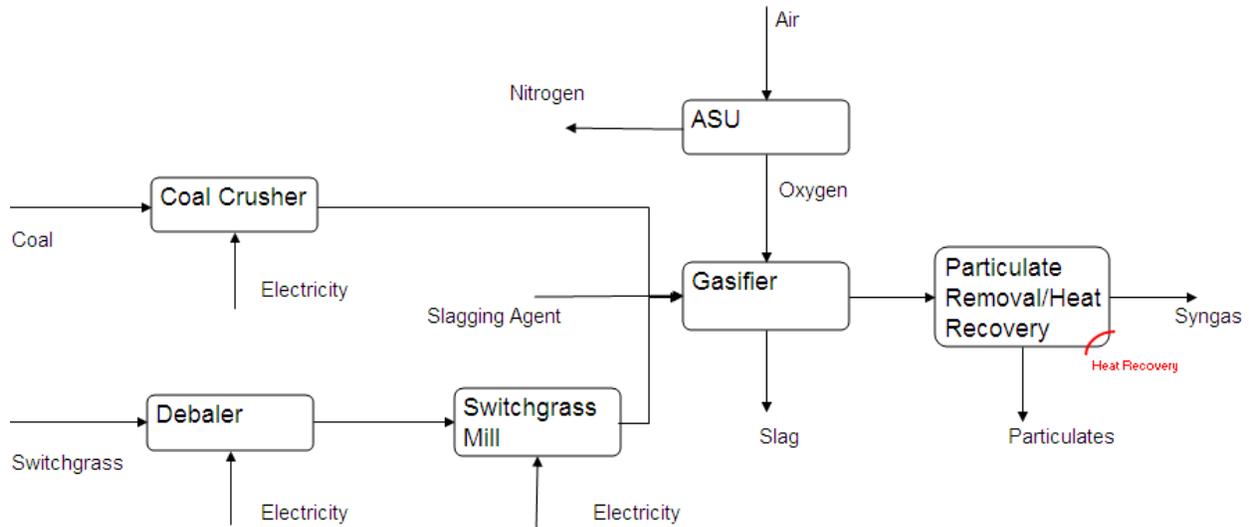
4.3.1 Background

Coal and biomass have been burned as a heat source since the early days of human history. Coal gasification dates to the early 1800's when coal was gasified to produce "town gas" or low BTU fuel gas for heating and lighting. In contrast, gasification of biomass is a relatively new concept. Gasification of biomass can be performed in a low temperature, low pressure, air blown gasifier but the products of this process include tars and lighter hydrocarbons, which make the syngas produced less suitable for FT liquid fuel production than that produced in a higher temperature, higher pressure process (NRC, 2009). Co-gasification of coal and biomass is also a relatively new concept. When gasified together, coal and biomass create a number of synergies including decreasing emissions and increasing supply security/flexibility while still producing a quality syngas. Co-gasification also allows a greater scale of production, compared to biomass gasification. While the size of a biomass-only gasification unit will be limited by the supply of biomass available in an area, by gasifying the biomass with coal, larger gasifier sizes can be employed and economies of scale can be achieved that cannot be achieved with biomass alone. Another advantage of co-gasification, compared to biomass-only gasification, is stability of supply. Poor weather, disease and other factors can cause fluctuations in the available supply and quality of biomass (Ciferno, 2002). Coal can be used to level the fluctuations in the feedstock supply, allowing full utilization of a liquid fuels production facility (Tarka, 2009). These factors motivated the choices of gasification processes, coal and combined biomass/coal feedstocks, presented in this report.

4.3.2 Gasification Process Flows

Figure 4-2 presents a process flow diagram for the gasification process used in the analysis. Each of the process blocks are described below.

Figure 4-2. Gasification Process Flow Diagram (ASU is air separation unit)



Coal Preparation Coal is delivered to the plant via rail from the mine (a 100 mi. transport distance is assumed in this analysis, leading to a greenhouse gas footprint of 2 kg CO₂e per ton of coal based on data in the NREL US LCI, 2009) and is stored until needed. From the storage area, coal is fed into a commercially available coal crusher and is crushed to a size less than 200 mesh (Gray et al., 2007). If coal drying is necessary, that process would most likely be integrated mechanically with the crushing operation, using nitrogen from the air separation unit heated with recovered process heat, however, drying is not needed for Kittanning coal used in this analysis. The crushed coal is fed into a lock hopper, where it is pressurized with CO₂ and fed to the gasifier with a screw feeder. The electricity requirement for coal preparation, exclusive of augers and conveyers, is estimated to be 0.006 kWh electricity per pound of coal (0.005 kg CO₂e/lb coal), based on published data for coal crushed in a rod mill (Van Bibber et al., 2007). In this analysis, the energy burdens for conveyers, augers and initial handling of the coal upon receiving are assumed to be equivalent to the handling burden for the crushing and milling operation (0.005 kg CO₂e/lb coal).

Switchgrass Preparation It is assumed that the switchgrass has been field dried to 15% moisture and baled prior to delivery and that the switchgrass is stored at the production site and delivered to the gasifier on demand (Tarka, 2009). The switchgrass is assumed to be delivered to the plant by truck (assuming a delivery distance of 50 km). This results in a greenhouse gas impact of 10 kg CO₂e/ton switchgrass (assuming 3400 BTU/ton-mile for truck transport). The switchgrass is unloaded into a separate mass storage area from the coal, and from the storage area the switchgrass is sent to a debaler. The debaler removes the twine from the bales and starts to break apart the compressed switchgrass in the bale. The switchgrass is then sent to a commercial mill such as a collision mill or knife mill and processed to size of approximately 2 inches for

gasification. Feeding of biomass into gasifiers is known to be problematic, with frequent plugging of biomass feed systems. While milling to smaller sizes (~1 mm) may improve the reliability of the feed system (Tarka, 2009), the electricity requirements for knife mills are not readily available. To be conservative, the electricity burden was calculated using the electricity burden for an equivalent amount of coal (0.005 kg CO₂e/lb coal). As with the coal preparation, the mill is operated under negative pressure to eliminate dust. From the mill, the switchgrass is fed into a lock hopper and pressurized with CO₂ (recovered later in the process). From the lock hopper, the biomass is fed to the gasifier with a screw feeder. The burden was assumed to be the same as for an equivalent mass of coal (0.005 kg CO₂e/lb coal). The coal and biomass are fed to the gasifier through separate feed systems. This allows the gasifier to continue to operate on coal should the biomass feed system become plugged (Gray et al., 2007).

Air Separation Unit (ASU) Oxygen is supplied to the gasifier from a standard cryogenic ASU. The oxygen supplied is assumed to be 95% pure by volume. This is the same design assumption made in several of the NETL studies upon which the FT yield model and greenhouse gas emissions burden calculations in this report are based. The nitrogen stream generated in the ASU, which contains 98.7% N₂ and 1.3% O by volume, can be used to provide inert gas to other areas of the plant as needed (Gray et al., 2007). The electricity burden for the ASU is based on the mass flow rate of air required (described in the gasifier section), and is listed for the five feed scenarios in Table 4-2. This electricity burden is based on an electricity demand of 0.0474 kWh/lb air fed to the ASU (Van Bibber et al., 2007). Oxygen from the ASU is also needed by the Autothermal Reformer (ATR) in the FT synthesis process as discussed in Section 6.2. Although SMR of natural gas does not require cryogenic oxygen to produce a syngas suitable for a FT reactor, the ATR in the FT synthesis section does require cryogenic oxygen from an ASU.

Table 4-2. Electricity demands of air separation unit

Feed Ratio	100% Coal By Mass	93% Coal by Mass	85% Coal by Mass	75% Coal by Mass	Natural Gas
Mass Air In (lb/hr)	10,670,000	10,590,000	10,310,000	9,967,000	385,400
Mass O ₂ Out (lb/hr)	2,495,000	2,475,000	2,410,000	2,331,000	90,120
Mass O ₂ Out (lb/hr) to Gasifier ¹	2,405,000	2,385,000	2,320,000	2,240,000	not applicable
Mass O ₂ Out (lb/hr) to ATR ¹	90,120	90,120	90,120	90,120	90,120
Mass N ₂ Out (lb/hr) ²	8,174,000	8,111,000	7,897,000	7,636,000	295,300
Total Electric Demand (kW)	505,900	502,000	488,700	472,600	18,270
kWh per lb of Gasifier/SMR Feedstock	0.20	0.19	0.18	0.17	0.0046
kWh per lb of Gasifier/SMR Carbon Input	0.28	0.28	0.28	0.28	0.0062
GWP (kg CO ₂) per pound Feedstock ³	0.15	0.15	0.14	0.13	0.0035
GWP (kg CO ₂) per pound Carbon Input ³	0.21	0.21	0.21	0.21	0.0047

¹This stream is 95% oxygen.

²This stream is 1.3% oxygen.

³Electricity = 0.763 kg CO₂e/kWh (2004 US grid average)

Gasifier Selection. The Shell Gasifier was selected for this study because of its proven ability to handle a wide range of coal/biomass feedstocks of varying compositions. The Shell Gasifier is a high temperature, high pressure, entrained-flow gasifier that operates at approximately 2500° F and 450 psia. Under these conditions, no tar is produced and the slag from the gasifier is a fused/inert material. The product is a high quality syngas, which has CO and H₂ mole fractions of .65 and .26, respectively. Virtually no methane or higher hydrocarbons are produced. Shell Gasifiers have very high carbon conversions, typically in the range of 98%-99% (Gray et al., 2007) and have proven their ability to operate continuously with biomass (demolition wood) feeds of up to 30% by mass (van Haperen and de Kler, 2007). Table 4-3 reports typical compositions of syngases from Shell Gasifiers.

As shown in Table 4-3, the raw syngas from a Shell gasifier contains significant amounts of H₂S and has a H₂ to CO molar ratio of about 0.4:1. As described in Section 6, the FT reactors used in this study, require a sulfur-free syngas with a H₂ to CO molar ratio of about 2.1:1. This requirement means that the raw Shell gasifier syngas stream must undergo significant purification and conditioning, as described in the water-gas shift section of this chapter and in Chapter 5 (Synthesis Gas Cleanup).

Table 4-3. Shell Gasifier Syngas (Tarka, 2009; Ciferno, 2002; DeVan, et Al., 1997)

	2002 NETL	2009 NETL	Lockheed 1997
H ₂ O	0.03	0.025	0.002
CO ₂	0.04	0.017	0.013
O ₂	0	0	0
N ₂	0.01	0.02	0.044
CH ₄	0.0002	0	0.00035
CO	0.67	0.657	0.629
COS	0	0.001	0
H ₂	0.24	0.27	0.308
H ₂ S	0.01	0.009	0.004
HCl	0	0.001	0
Total	1.0002	1	1.00035

4.3.3 Gasification Results and Products

Gasification of coal and coal/biomass mixtures at three different feed ratios was evaluated. Since Shell Gasifiers have been used commercially to process coal/biomass mixtures containing up to 30% biomass by mass, a biomass feed of 25% was used as a practical upper limit for the feed streams considered in this report. The 2009 NETL Report modeled a Shell gasifier using feedstocks of both coal (Illinois #6, which is similar in composition to Kittanning #6) and biomass (switchgrass, the same as used for analysis in this report). The NETL Report contains data, including syngas compositions and gasification conditions for feeds of 100% coal and 85% coal/15% switchgrass by mass. For this report, feed rates of 100% coal, 93% coal/7% switchgrass, 85% coal/15% switchgrass and 75% coal/25% switchgrass (by mass) were considered. There are no commercial data available for gasifier operating conditions and syngas compositions for the 93% coal and 75% coal feed ratios, so these conditions were interpolated and extrapolated from the data for 100% coal and 85% coal/15% switchgrass feeds. The gasifier mass and energy balances presented below are based on a clean, conditioned syngas output necessary to produce 50,000 bpd of SPK.

Gasification Feed: 100% Coal To produce 50,000 bpd of SPK, 1,269 tons of coal/hour must be gasified. The mass and energy balance data for this case are provided in Table 4-4. Note that the syngas and oxygen leaving the gasifier contain 3500 MMBtu/hour of useable thermal energy, which can be recovered as the exit stream from the gasifier is cooled to the feed temperature for the subsequent Water-Gas Shift Reactor.

Table 4-4. Mass and Energy Balance: 100% Coal Feed by Mass

	Coal	Switchgrass	Oxygen	Syngas	Slag
Temp (F)	77		201	2,662	2,600
Pressure (psi)	15		665	615	15
Composition	lb/hr	lb/hr	lb/hr	lb/hr	lb/hr
C	1,802,000	0	0		36,050
H	132,000	0	0		2,640
O	185,300	0	2,299,000		3,706
N	33,000	0	105,900		660
S	76,150	0	0		6,303
Cl	10,150	0	0		2,430
Ash	238,600	0	0		238,600
H ₂ O	60,920	0	0	121,700	0
CO ₂				201,400	
O ₂				0	
N ₂				138,300	
CH ₄				0	
CO				3,985,000	
COS				13,090	
H ₂				118,400	
H ₂ S				66,830	
HCl				7,944	
Total	2,538,000	0	2,405,000	4,653,000	290,400
Available Energy (btu/lb)	12,050	6,228	0	5,741	0
Available Energy (btu/hr)	30,590,000,000	0	0	26,710,000,000	0
Sensible Heat (MMbtu/Hr)	0	0	223	3,304	145

Gasification Feed: 93% Coal and 7% Switchgrass To produce 50,000 bpd of SPK, 1,220 tons per hour of coal and 92 tons per hour of switchgrass must be gasified. This feed ratio corresponds to a coal feed of 96% by energy content. The mass and energy balance data is provided in Table 4-5. Note that the syngas and oxygen leaving the gasifier contain 3500 MMBtu/hour of useable thermal energy, which can be recovered.

Table 4-5. Mass and Energy Balance: 93 % Coal, 7% Switchgrass

	Coal	Switchgrass	Oxygen	Syngas	Slag
Temp (F)	77	77	201	2,612	2,600
Pressure (psi)	15	15	665	615	15
Composition	lb/hr	lb/hr	lb/hr	lb/hr	lb/hr
C	1,732,000	73,270	0		36,100
H	126,800	8,925	0		2,715
O	178,000	62,690	2,280,000		4,815
N	31,700	1,342	105,100		661
S	73,160	140	0		3,986
Cl	9,755	0	0		2,489
Ash	229,200	9,658	0		238,900
H ₂ O	58,530	27,540	0	161,300	0
CO ₂				258,000	
O ₂				0	
N ₂				137,400	
CH ₄				672	
CO				3,954,000	
COS				13,240	
H ₂				120,300	
H ₂ S				66,180	
HCl				7,473	
Total	2,439,000	183,600	2,385,000	4,718,000	289,700
Available Energy (btu/lb)	12,050	6,228	0	5,651	0
Available Energy (btu/hr)	29,390,000,000	1,143,000,000	0	26,660,000,000	0
Sensible Heat (MMbtu/Hr)	0	0	221	3,267	145

Gasification Feed: 85% Coal and 15% Switchgrass To produce 50,000 bpd of SPK, 1,150 tons per hour of coal and 203 tons per hour of switchgrass must be gasified. This feed ratio corresponds to a coal feed of 91% by energy content. The mass and energy balance data is provided in Table 4-6. Note that the syngas and oxygen contain 3400 MMBtu/hour of useable thermal energy leaving the gasifier, which can be recovered.

Table 4-6. Mass and Energy Balance: 85% Coal, 15% Switchgrass

	Coal	Switchgrass	Oxygen	Syngas	Slag
Temp (F)	77	77	201	2,556	2,600
Pressure (psi)	15	15	665	615	15
Composition	lb/hr	lb/hr	lb/hr	lb/hr	lb/hr
C	1,632,000	161,900	0		35,890
H	119,600	19,730	0		2,786
O	167,800	138,600	2,218,000		6,128
N	29,890	2,966	102,200		657
S	68,970	310	0		4,045
Cl	9,196	0	0		1,181
Ash	216,100	21,350	0		237,500
H ₂ O	55,180	60,860	0	183,300	0
CO ₂				328,400	
O ₂				0	
N ₂				134,400	
CH ₄				3,629	
CO				3,879,000	
COS				13,580	
H ₂				124,200	
H ₂ S				61,640	
HCl				8,243	
Total	2,299,000	405,700	2,320,000	4,737,000	288,100
Available Energy (btu/lb)	12,050	6,228	0	5,603	0
Available Energy (btu/hr)	27,700,000,000	2,527,000,000	0	26,540,000,000	0
Sensible Heat (MMbtu/Hr)	0	0	215	3,184	144

Gasification Feed: 75% Coal and 25% Switchgrass To produce 50,000 bpd of SPK, 1,057 tons per hour of coal and 352 tons per hour of switchgrass must be gasified. This feed ratio corresponds to a coal feed of 85% by energy content. A carbon conversion of 99% was assumed. The mass and energy balance data is provided in Table 4-7. Note that the syngas and oxygen contain 3300 MMBtu/hour of useable thermal energy leaving the gasifier, which can be recovered.

Table 4-7. Mass and Energy Balance: 75% Coal, 25% Switchgrass

	Coal	Switchgrass	Oxygen	Syngas	Slag
Temp (F)	77	77	201	2,485	2,600
Pressure (psi)	15	15	665	615	15
Composition	lb/hr	lb/hr	lb/hr	lb/hr	lb/hr
C	1,501,000	281,300	0		35,650
H	110,000	34,270	0		2,884
O	154,400	240,700	2,142,000		7,901
N	27,490	5,152	98,680		653
S	63,430	539	0		3,419
Cl	8,458	0	0		2,584
Ash	198,800	37,080	0		235,800
H ₂ O	50,750	105,700	0	226,100	0
CO ₂				398,600	
O ₂				0	
N ₂				130,700	
CH ₄				5,141	
CO				3,805,000	
COS				13,270	
H ₂				128,700	
H ₂ S				56,840	
HCl				6,041	
Total	2,114,000	704,800	2,240,000	4,771,000	288,900
Available Energy (btu/lb)	12,050	6,228	0	5,539	0
Available Energy (btu/hr)	25,480,000,000	4,390,000,000	0	26,420,000,000	0
Sensible Heat (MMbtu/Hr)	0	0	208	3,087	144

Table 4-8 provides a summary of the greenhouse gas emissions associated with gasifying enough coal and switchgrass to make 50,000 bpd of SPK for each of the four gasifier feed stream cases. A credit for sensible heat produced is taken at 96 kg CO₂e/MMBTU (Tables 4-5 to 4-7 in Skone and Gerdes, 2008).

Table 4-8. Summary of greenhouse gas emission estimates for synthesis gas from gasification

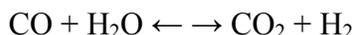
Parameter	Feed ratio, by mass			
	100% Coal	93% Coal	85% Coal	75% Coal
CO produced in syngas, lb/hr	3,985,000	3,954,000	3,879,000	3,805,000
H ₂ produced in syngas, lb/hr	118,400	120,300	124,200	128,700
Coal required, tons/hr	1,269	1,220	1,150	1,057
GWP for coal transport, kg CO ₂ e/hr	2,538	2,439	2,299	2,114
GWP for coal extraction, kg CO ₂ e/hr	269,800	259,300	244,400	224,700
GWP for coal prep., kg CO ₂ e/hr	12,690	12,200	11,500	10,570
GWP for coal receiving, kg CO ₂ e/hr	12,690	12,200	11,500	10,570
GWP for air separation, kg CO ₂ e/hr	385,900	356,200	316,900	270,400
Switchgrass required, tons/hr	0	92	203	352
GWP for switchgrass transport, kg CO ₂ e/hr	0	918	2,029	3,524
GWP for switchgrass prep, kg CO ₂ e/hr	0	918	2,029	3,524
GWP for switchgrass receiving, kg CO ₂ e/hr	0	918	2,029	3,524
GWP for switchgrass extraction (attributional), kg CO ₂ e/hr	0	4,590	10,140	17,620

Total GWP (attributional, no sensible heat credit), kg CO ₂ e/hr	683,600	649,700	602,800	546,500
Sensible heat credit, MMBtu/hr	3,527	3,488	3,399	3,295
GWP credit for sensible heat, kg CO ₂ e/hr	338,600	334,800	326,300	316,300
Net after sensible heat credit, kg CO ₂ e/hr	345,000	314,800	276,500	230,200
Consequential credit for switchgrass, kg CO ₂ e/hr	0	55,080	121,700	211,400
Net after sensible heat and switchgrass consequential credit, kg CO ₂ e/hr	345,000	259,700	154,800	18,780

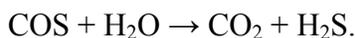
4.4 Water Gas Shift (WGS) and COS Removal

The syngas exiting the gasifier has a H₂:CO molar ratio that ranges from 0.42:1 to 0.47:1. The cobalt catalyst used in the FT reactor requires a H₂:CO ratio of 2.1:1. Some of the hydrogen supplied in FT synthesis comes from unreacted hydrogen that is recycled to the FT reactors (in the gasifier-fed cases) and some comes from hydrogen generated during autothermal reforming of light ends formed in the FT reactors, so the required H₂:CO molar ratio of the syngas fed to the FT reactor is slightly less than 2.1:1.

To achieve the required ratio, a portion of each syngas stream is split and sent to a water gas shift (WGS) reactor to undergo the water gas shift reaction:



This is a slightly exothermic reaction and the heat produced can be used to generate steam. In this process any COS present is hydrolyzed to CO₂ and H₂S:



Any COS in the portion of the raw syngas that does not go to the WGS reactor is also assumed to be hydrolyzed, as shown in Figure 4-3. Following WGS and COS hydrolysis, the syngas streams are combined and enter the syngas cleanup section. In an actual FT liquids production facility, the amount of CO and H₂O reacted to produce H₂ and CO₂ in the WGS reactor would be limited by the WGS equilibrium. To get higher conversion rates, more gas would be fed to the WGS reactor. In this simulation, an actual WGS reactor was not modeled; instead, the amount of CO and steam that would need to react in the WGS reactor in order to yield a blended FT feed gas stream containing H₂:CO at the necessary molar ratio was determined.

The WGS reactor step does not have a significant GWP footprint since it is a net producer of heat. In this analysis, the GWP reduction benefit of this recovered heat (typically about 1.5 MMBTU per ton of gasifier feed) was assumed to offset the GWP burden of WGS and COS hydrolysis catalyst manufacture and the thermal and electrical energy loads of other syngas production process equipment.

Tables 4-9 through 4-12 display the results for the output of the WGS, and Tables 4-13 through 4-16 summarize the combined syngas stream (the output of the gasifier that is not sent to WGS but that does undergo COS hydrolysis combined with the output of the WGS process) that goes on to gas cleanup.

Figure 4-3. Water Gas Shift (WGS) Process Flow Diagram

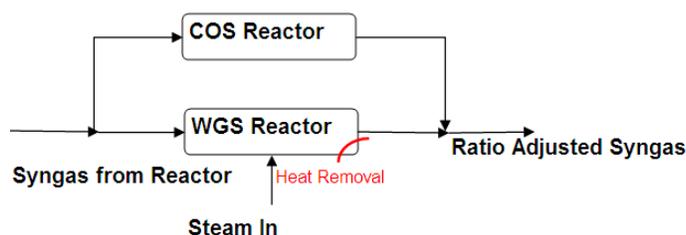


Table 4-9. Mass balance for Water Gas Shift (WGS)for syngas from gasifier fed with 100% coal

	Syngas Input to WGS			Water Injected to WGS		
	Mole Frac	Mole Flow, lb-mol/hr	Mass Flow, lb/hr	Mole Frac	Mole Flow, lb-mol/hr	Mass Flow, lb/hr
H ₂ O	0.03077	3,419	61,610	1	68,710	1,237,000
CO ₂	0.02084	2,316	101,900	0	0	0
O ₂	0	0	0	0	0	0
N ₂	0.02248	2,498	69,970	0	0	0
CH ₄	0	0	0	0	0	0
CO	0.6481	72,010	2,017,000	0	0	0
COS	0.000925	110	6,625	0	0	0
H ₂	0.2669	29,660	59,910	0	0	0
H ₂ S	0.008932	993	33,830	0	0	0
HCl	0.000925	110	4,021	0	0	0
Total	1	111,100	2,355,000	1	68,710	1,237,000
Output of WGS						
	Mole Fraction	Flow Rate, lb-mol/hr				
H ₂ O	0	0				
CO ₂	0.4140	74,440				
O ₂	0	0				
N ₂	0.01389	2,498				
CH ₄	0	0				
CO	0	0				
COS	0	0				
H ₂	0.5654	101,700				
H ₂ S	0.006133	1,103				
HCl	0.0006133	110				
Total	1	179,800				

There are 2907 MMBTU/hr of recoverable thermal energy created in the WGS reaction.

Table 4-10. Mass balance for Water Gas Shift (WGS)for syngas from gasifier fed with 93% coal, 7% switchgrass

	Syngas Input to WGS			Water Injected to WGS		
	Mole Frac	Mole Flow lb mol/hr	Mass Flow lb/hr	Mole Frac	Mole Flow lb mol/hr	Mass Flow lb/hr
H ₂ O	0.04016	4,497	81,040	1	66,550	1,198,000
CO ₂	0.02631	2,946	129,700	0	0	0
O ₂	0	0	0	0	0	0
N ₂	0.02202	2,466	69,070	0	0	0
CH ₄	0	21	338	0	0	0
CO	0.6334	70,930	1,987,000	0	0	0
COS	0.0009891	111	6,654	0	0	0
H ₂	0.2673	29,930	60,460	0	0	0
H ₂ S	0.008714	976	33,260	0	0	0
HCl	0.0009199	103	3,756	0	0	0
Total	1	112,000	2,371,000	1	66,550	1,198,000
	Output of WGS					
	Mole Frac	Mole Flow lb mol/hr				
H ₂ O	0	0				
CO ₂	0.4144	73,990				
O ₂	0	0				
N ₂	0.01381	2,466				
CH ₄	0.0001179	21				
CO	0	0				
COS	0	0				
H ₂	0.5650	100,900				
H ₂ S	0.006086	1,087				
HCl	0.0005770	103				
Total	1	178,500				

There are 2863 MMBTU/hr of recoverable thermal energy created in the WGS reaction.

Table 4-11. Mass balance for Water Gas Shift (WGS) for syngas from gasifier fed with 85% coal, 15% switchgrass

	Syngas Input to WGS			Water Injected to WGS		
	Mole Frac	Mole Flow lb mol/hr	Mass Flow lb/hr	Mole Frac	Mole Flow lb mol/hr	Mass Flow lb/hr
H ₂ O	0.04524	5,031	90,660	1	63,560	1,144,000
CO ₂	0.0332	3,689	162,400	0	0	0
O ₂	0	0	0	0	0	0
N ₂	0.0213	2,372	66,450	0	0	0
CH ₄	0	112	1,794	0	0	0
CO	0.616	68,480	1,918,000	0	0	0
COS	0.001005	112	6,716	0	0	0
H ₂	0.273	30,390	61,390	0	0	0
H ₂ S	0.00804	894	30,480	0	0	0
HCl	0.001005	112	4,076	0	0	0
Total	1	111,200	2,342,000	1	63,560	1,144,000
WGS Output						
	Mole Frac	Mole Flow lb mol/hr				
H ₂ O	0	0				
CO ₂	0.4136	72,280				
O ₂	0	0				
N ₂	0.01357	2,372				
CH ₄	0.0006397	112				
CO	0	0				
COS	0	0				
H ₂	0.5658	98,870				
H ₂ S	0.005757	1,006				
HCl	0.0006397	112				
Total	1	174,800				

There are 2764 MMBTU/hr of recoverable thermal energy created in the WGS reaction.

Table 4-12. Mass balance for Water Gas Shift (WGS) for syngas from gasifier fed with 75% coal, 25% switchgrass

	Syngas Input to WGS			Water Injected to WGS		
	Mole Frac	Mole Flow lb mol/hr	Mass Flow lb/hr	Mole Frac	Mole Flow lb mol/hr	Mass Flow lb/hr
H ₂ O	0.05498	6,091	109,800	1	59,970	1,079,000
CO ₂	0.0397	4,397	193,500	0	0	0
O ₂	0	0	0	0	0	0
N ₂	0.0204	2,264	63,430	0	0	0
CH ₄	0	155	2,494	0	0	0
CO	0.595	65,950	1,847,000	0	0	0
COS	0.000968	107	6,442	0	0	0
H ₂	0.279	30,930	62,470	0	0	0
H ₂ S	0.00731	810	27,590	0	0	0
HCl	0.000726	80	2,932	0	0	0
Total	1	110,800	2,316,000	1	59,970	1,079,000
Output of WGS						
	Mole Frac	Mole Flow lb mol/hr				
H ₂ O	0	0				
CO ₂	0.4126	70,450				
O ₂	0	0				
N ₂	0.01326	2,264				
CH ₄	0.0009106	155				
CO	0	0				
COS	0	0				
H ₂	0.5674	96,880				
H ₂ S	0.005370	917				
HCl	0.0004710	80				
Total	1	170,700				

There are 2662 MMBTU/hr of recoverable thermal energy created in the WGS reaction.

Table 4-13. Combined syngas stream after WGS and COS hydrolysis for 100% coal case.

species	flow rates, lb/hr				combined syngas stream after WGS and COS hydrolysis
	gasifier output sent to WGS	water injected to WGS	output of WGS	gasifier output sent to COS hydrolysis	
H ₂ O	61,610	1,237,000	0	60,100	58,170
CO ₂	101,900	0	3,276,000	99,440	3,380,000
O ₂	0	0	0	0	0
N ₂	69,970	0	69,970	68,270	138,200
CH ₄	0	0	0	0	0
CO	2,017,000	0	0	1,968,000	1,968,000
COS	6,625	0	0	6,463	0
H ₂	59,910	0	205,400	58,450	263,800
H ₂ S	33,830	0	37,580	33,000	74,250
HCl	4,021	0	4,021	3,923	7,944
Total	2,355,000	1,237,000	3,593,000	2,298,000	5,891,000

Table 4-14. Combined syngas stream after WGS and COS hydrolysis for 93% coal case.

species	flow rates, lb/hr				combined syngas stream after WGS and COS hydrolysis
	gasifier output sent to WGS	water injected to WGS	output of WGS	gasifier output sent to COS hydrolysis	
H ₂ O	81,040	1,198,000	0	80,210	78,240
CO ₂	129,700	0	3,256,000	128,400	3,389,000
O ₂	0	0	0	0	0
N ₂	69,070	0	69,070	68,370	137,400
CH ₄	338	0	338	334	672
CO	1,987,000	0	0	1,967,000	1,967,000
COS	6,654	0	0	6,586	0
H ₂	60,460	0	203,700	59,840	263,600
H ₂ S	33,260	0	37,030	32,920	73,690
HCl	3,756	0	3,756	3,718	7,474
Total	2,371,000	1,198,000	3,570,000	2,347,000	5,917,000

Table 4-15. Combined syngas stream after WGS and COS hydrolysis for 85% coal case.

species	flow rates, lb/hr				combined syngas stream after WGS and COS hydrolysis
	gasifier output sent to WGS	water injected to WGS	output of WGS	gasifier output sent to COS hydrolysis	
H ₂ O	90,660	1,144,000	0	92,680	90,620
CO ₂	162,400	0	3,181,000	166,000	3,352,000
O ₂	0	0	0	0	0
N ₂	66,450	0	66,450	67,930	134,400
CH ₄	1,794	0	1,794	1,834	3,627
CO	1,918,000	0	0	1,961,000	1,961,000
COS	6,716	0	0	6,866	0
H ₂	61,390	0	199,700	62,760	262,500
H ₂ S	30,480	0	34,290	31,160	69,350
HCl	4,076	0	4,076	4,167	8,244
Total	2,342,000	1,144,000	3,488,000	2,394,000	5,882,000

Table 4-16. Combined syngas stream after WGS and COS hydrolysis for 75% coal case.

species	flow rates, lb/hr				
	gasifier output sent to WGS	water injected to WGS	output of WGS	gasifier output sent to COS hydrolysis	combined syngas stream after WGS and COS hydrolysis
H ₂ O	109,800	1,079,000	0	116,300	114,300
CO ₂	193,500	0	3,101,000	205,100	3,311,000
O ₂	0	0	0	0	0
N ₂	63,430	0	63,430	67,230	130,700
CH ₄	2,496	0	2,496	2,645	5,141
CO	1,847,000	0	0	1,958,000	1,958,000
COS	6,442	0	0	6,828	0
H ₂	62,470	0	195,700	66,220	261,900
H ₂ S	27,590	0	31,250	29,250	64,370
HCl	2,932	0	2,932	3,108	6,041
Total	2,316,000	1,079,000	3,396,000	2,455,000	5,851,000

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CHAPTER 5: SYNTHESIS GAS CLEANUP

5.1 Background

After exiting the gasifier, the raw synthesis gas must have sulfur impurities removed before it can be fed to the Fischer-Tropsch unit. In addition, capture of carbon dioxide for sequestration would occur at this stage, if carbon capture and sequestration (CCS) is planned. In this work it was assumed that CCS would not be implemented. Typically two processes would be used to remove sulfur prior to feeding syngas to an FT process with a cobalt catalyst: a bulk sulfur removal step and a polishing step. In this work, it will be assumed that the bulk sulfur removal is an adsorption system and the polishing step utilizes a ZnO adsorbent.

5.2 Sulfur removal via the Rectisol® process

The Rectisol® process is one means of removing sulfur from the syngas. According to a licensee of this process, Rectisol® is used to purify 75% of the world's syngas produced from oil residue, coal, and wastes (Lurgi, not dated). It can be used to remove sulfur to less than 0.1 ppm by volume and CO₂ to 2 ppm by volume, but in the application modeled in this report, CO₂ removal in the range of 95-99% is adequate to satisfy process requirements. A removal rate of 96% for carbon dioxide was assumed.

In the Rectisol® process, refrigerated methanol is used as a solvent to capture unwanted contaminants, and then regenerated. This process requires cooling, followed by reheating of the syngas for FT processing. The primary greenhouse gas burden estimated for the process will be the utility usage for the Rectisol® process.

The estimates of GHG emissions rely on estimates of utility usage for a process designed to desulfurize and remove carbon dioxide from a syngas for producing 2000 kg/d of methanol. Values were scaled to reflect the ratio of carbon in the finished methanol product to carbon in the modeled gasifier output. Each of the gasifier scenarios has approximately the same output of carbon in carbon dioxide and carbon monoxide to produce equivalent amounts of SPK, so the Rectisol® estimates are the same for all scenarios. The flow diagram for the methanol syngas process is shown in Figure 5-1. Assuming that this process is a good parallel for the process that would be required for syngas cleanup from biomass and coal in order to produce SPK from an FT column introduces considerable uncertainty in the greenhouse gas emission estimates, but no other source of utility demands for the Rectisol® process could be found, and the utility demands for the methanol case were represented as being “typical” (Lurgi, not dated). Table 5-1 provides the flow rates used to estimate the GHG emissions.

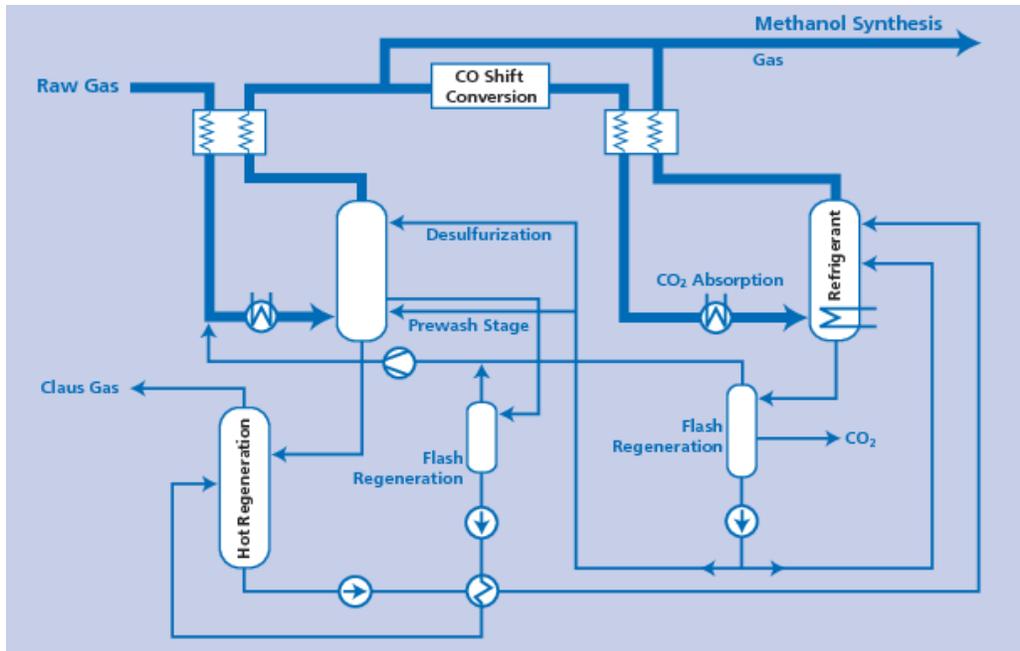


Figure 5-1. Selective desulfurization and CO₂ removal to produce methanol synthesis gas (Lurgi, not dated).

Table 5-1. Flow rates used to estimate greenhouse gas emissions from the Rectisol[®] gas cleanup process for gasifiers described in Chapter 4.

Parameter	Value	unit	Source
electricity demand for methanol plant (not inc. refrigeration)	1600	kW	Lurgi literature
low pressure steam demand for methanol plant	5500	kg/h	Lurgi literature
cooling water for methanol plant	130	m ³ /hr	Lurgi literature
refrigeration duty for methanol plant	4200	kW(th)	Lurgi literature
output of methanol at methanol plant	2000	tonnes/d	Lurgi literature
output of methanol at methanol plant	2,000,000	kg/d	unit conversion
output of carbon in methanol production process	750,000	kg/d	based on output of methanol and weight fraction of carbon in methanol
output of carbon from gasifier after WGS	1,800,000	lb/hr	based on output of gasifier and WGS
output of carbon from gasifier after WGS	19,00,000	kg/d	based on output of gasifier and WGS
estimated electricity demand not inc. refrigeration	41,000	kW	calculation based on scaleup around carbon content of gasifier stream after WGS vs. methanol
estimated low pressure steam demand	140,000	kg/h	calculation based on scaleup around carbon content of gasifier stream after WGS vs. methanol
estimated cooling water	3,300	m ³ /hr	calculation based on scaleup around carbon content of gasifier stream after WGS vs. methanol
estimated refrigeration duty	110,000	kW(th)	calculation based on scaleup around carbon content of gasifier stream after WGS vs. methanol
est. electricity draw for refrigeration	44,000	kW	calculation based on scaleup around carbon content of gasifier stream after WGS vs. methanol

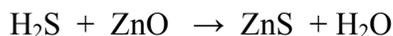
It was assumed that the utility demands and greenhouse gas emissions from cooling water for the Rectisol® process would be negligible. A greenhouse gas emission factor of 96 kg CO₂e/MMBtu HHV (Tables 4-5 to 4-7 in Skone and Gerdes, 2008) for purchased steam was applied, with an energy content of steam of 1200 Btu HHV/lb (Table 4-3 in Skone and Gerdes, 2008). This emission factor is for steam in general and not low pressure steam, which is required for the Rectisol® process. The nonrefrigeration-associated electricity demand was reported separately from the refrigeration duty, and a coefficient of performance of 2.5 was assumed for refrigeration in order to convert the refrigeration duty to electrical demand for refrigeration. The CO₂e emission factor for purchased electricity, representing an estimate of the GHG emissions due to electricity production for the national grid average, is 0.763 kg CO₂e/kWh. The GHG emission estimates and the scaled up utility estimates are shown in Table 5-2.

Table 5-2. Greenhouse gas emissions for sulfur removal using the Rectisol® process

	100% Coal	93% Coal, 7% Switchgrass	85% Coal, 15% Switchgrass	75% Coal, 25% Switchgrass
Electricity required (refrig. and non-refrig)	86,000 kW	86,000 kW	86,000 kW	86,000 kW
GWP of greenhouse gas emissions associated with electricity	64,000 kg CO ₂ e/hr			
GWP of steam	36,000 kg CO ₂ e/hr			
GWP for 99.97% sulfur removal	100,000 kg CO ₂ e/hr			

5.3 Sulfur removal via zinc oxide polishing

A supplemental means of removing sulfur in the syngas is to contact the syngas with zinc oxide (ZnO). This process can remove the sulfur in the syngas that is in the form of H₂S. Sulfur in the form of hydrogen sulfide (H₂S) is removed using ZnO pellets in the following slightly exothermic (approximately -70 kJ/mol) reaction



For the purposes of this analysis, all residual sulfur in the form of H₂S is assumed to be removed from the syngas, and the ZnO pellets are assumed to have a maximum loading of 50% of stoichiometric. The molecular mass of ZnO is 81.408 and the atomic mass of sulfur is 32.065, thus 5.0 kg of ZnO is required for every kg of sulfur to be removed.

Zinc oxide is made by vaporizing zinc and reacting it with ambient oxygen. Zinc does not occur as a native metal and must be obtained by processing ore that contains zinc. A simplified process flow diagram is shown in Figure 5-2.

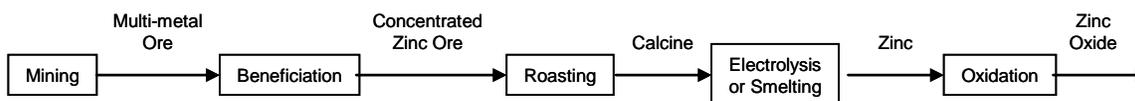


Figure 5-2. Process flow for zinc oxide

High purity oxide is produced using the indirect, or French, process. It requires nearly pure zinc as a starting material and thus often utilizes recycled zinc as a source material. The resulting zinc oxide is employed in the manufacture of rubber, pharmaceuticals, and nanomaterials. Lower grade zinc oxide is used as paint pigment and is produced using the direct, or American, process. It can be generated with lower grade starting material, including small amounts of ore and zinc processing residues. In this analysis, it is assumed that lower grade zinc oxide would be adequate for sulfur removal.

Zinc is primarily obtained from ferrous zinc sulfide (sphalerite) taken from underground mines in China and Canada, where it occurs as a mixed metal ore, typically in combination with lead or copper. The zinc content of these ores typically ranges from 2 to 5% although occurrences as high as 20% are found. It is estimated that Canadian mines require between 1.4 and 13.7 GJ of energy per ton of zinc ultimately produced to remove and concentrate the ore (Fthenakis et al., 2009). These authors recommended a typical value for use in life cycle assessment of 10.2 GJ/ton; 4.2 GJ (1167 kWh) is assumed to be provided by electricity and 6.0 GJ is from fuel oil. Using data from NETL (Skone and Gerdes 2008), this would result in emissions of 890.2 kg CO₂e due to electricity and 568.7 kg CO₂e due to fuel oil, for a total of 1458.9 kg CO₂e per ton (1000 kg) of zinc produced.

The amount of energy used to refine the concentrated zinc ore into pure zinc is very dependent on the method used. Until recently, most zinc was produced via smelting (also referred to as pyrometallurgy). During the past 10 to 15 years, however, the industry has been converting to

electrolysis or hydrometallurgy, which in addition to have lower emissions, also has a smaller energy footprint. The ecoinvent database reports values for both types of metal refining systems based on facilities in China (Classen et al., 2007), but the data are from only one source and the authors suggest that the data may not be very reliable. The data suggest that smelting is three times as energy intensive as electrolysis, but the ecoinvent inventory assumes that only 20% of zinc is obtained in this manner. Fthenakis et al. (2009) give data for the electrolysis (hydrometallurgy) process based on Canadian facilities. Of the four operations considered, three range between 20 and 25 GJ/kg of pure metal. The fourth facility ranged from 35 to 45 GJ/kg in the years 1994 to 2003; however, the authors note that this site conducts multiple operations, including ones that are more energy intensive than zinc refining. The final recommended number for use in life cycle inventories made by Fthenakis et al. (2009) is 19.2 GJ/1000 kg of zinc, which is at the bottom of the observed range, as the trend is heading in this direction.

Table 5-3. Zinc refining process greenhouse gas emissions

	Minimum for Electrolysis (Hydrometallurgical) Process ¹		Estimate of Smelting (Pyrometallurgical) Process ⁶	Value used: 80% Electrolysis and 20% Smelting	
Fuel	GJ per 1000 kg Zn	Equivalents	CO ₂ e per 1000 kg Zn	CO ₂ e per 1000 kg Zn	
Electricity	6.3	1750 kWh	1335 ³	4005	1869
Coal	3.2	114.2 kg ²			
Mining			27 ⁴	80	37
Combustion			282 ⁵	846	395
Natural Gas	8.4		424 ³	1273	594
Fuel Oil	1.3		123 ³	370	173
Total	19.2		2191	6574	3068

¹ Fthenakis et al., 2009, Table 5: Canadian facilities, electrolysis

² This report, Section 4.3.3.1: coal = 12050 Btu/lb LHV; 28.0 MJ/kg LHV

³ Skone and Gerdes, 2008, based on data from or as reported in

Electricity = 0.763 kg CO₂e/kWh (2004 US grid average, Table B-1)

Residual fuel oil = 100 kg CO₂e/MMBtu/LHV; 94.78 kg CO₂e/GJ/LHV

Natural gas = 53.3 kg CO₂e/MMBtu HHV; 0.0224 MM BTU HHV/lb; 50.5 kg CO₂e/GJ HHV

⁴ This report, Table 3-5, Greenhouse Gas Footprints of Coal Mining = 105.5 kg CO₂ per 1000 lb coal; 232.6 kg CO₂ per 1000 kg coal

⁵ Hong and Slatick, 1994, US average for bituminous coal of 205 lbs of CO₂ per MMBtu; 88.1 kg CO₂ per GJ

⁶ As indicated by data in Classen et al., 2007, where smelting of Zn requires three times the energy of electrolysis

The final step in producing zinc oxide is to oxidize zinc vapor in coal-fired burners using air as a source of oxygen. The coal (typically damp anthracite) provides heat to first melt and then vaporize zinc metal; it also produces CO that creates a reducing environment. The size and shape of the zinc oxide particle is determined by controlling the concentration and flow of air and zinc vapor. The process is initiated when hot kilns are fed with a mixture of 35% anthracite and 65% zinc. The exiting solid residue is water quenched (Goodwin, 2006). Although the formation of ZnO produces heat (356 kJ/mol) it does not appear that this energy is utilized.

Exact calculation of the coal required per unit of ZnO is complicated by the fact that in the American or direct process, the feed does not have to be pure zinc. Thermodynamic estimates of the energy required for vaporizing zinc can be made. However, given that the coal is damp, the

mixture is not pure zinc, and the temperature of the heated gases are likely to be a mixture, 200°C above the 907°C vaporization temperature of zinc, the theoretical value is likely to be significantly lower than the actual. For the sake of simplicity, the calculations performed here will assume that all of the source material is pure zinc and all of the coal is consumed in the process. This means that 0.54 kg of coal is required for every kg of zinc. It is estimated that anthracite coal releases 227.4 lbs of CO₂ per MMBtu (97.8 kg CO₂ per GJ) upon combustion (Hong and Slatick, 1994). The EIA reports an energy content between 29 and 33 MJ/kg LHV for anthracite; as the coal is damp, a value of 30 will be used here. This equates to 2.9 kg of CO₂e per kg of coal or 0.54×2.9 = 1.58 kg of CO₂e per kg of Zn.

The total CO₂e emissions associated with ZnO production is estimated to be 6.11 kg CO₂e per kg of Zn (Table 5-4). As stated earlier, the molar ratio of sulfur to zinc is presumed to be 0.5:1. The mass ratio is 32.07/2 (S) to 65.37 (Zn) or 0.25 (0.20 S/ZnO mass ratio). This is equivalent to a mass ratio of 25 CO₂e emissions to sulfur content in the gas when zinc oxide is used to remove sulfur. Table 5-5 summarizes the greenhouse gas emissions associated with removing all the sulfur from the synthesis gas streams described in Chapter 4.

Table 5-4. Summary of life cycle CO₂e emissions associated with ZnO production

Process Step	kg CO ₂ e per kg of Zn
Mining and beneficiation of zinc ore	1.46
Roasting and refining of zinc ore to produce zinc metal	3.07
Production of zinc oxide	1.58
Total	6.11
Total per kg ZnO	4.91

Table 5-5. Greenhouse gas emissions for sulfur removal using the zinc oxide process

	100% Coal	93% Coal, 7% Switchgrass	85% Coal, 15% Switchgrass	75% Coal, 25% Switchgrass
S in syngas that is H ₂ S	70,000 lb/hr	69,000 lb/hr	65,000 lb/hr	61,000 lb/hr
ZnO required to remove S (50% utilization)	350,000 lb/hr	350,000 lb/hr	330,000 lb/hr	300,000 lb/hr
GWP for sulfur removal	780,000 kg CO ₂ e/hr	770,000 kg CO ₂ e/hr	730,000 kg CO ₂ e/hr	680,000 kg CO ₂ e/hr

These results indicate that removing sulfur via the Rectisol® process produces seven to eight times less GWP than sulfur removal via ZnO. In addition, the sulfur remaining in the syngas after ZnO absorption would be expected to range from 340 to 370 ppmv. If the ZnO is used only as a polishing step, removing the last 0.001%-0.1% of the sulfur, then the greenhouse gas burdens would be in the range of 10-1000 kg CO₂e/hr. Since this is less than 1% of the GWP of the syngas clean-up, the total GWP burden associated with the clean-up will be assumed to be due to the Rectisol® process (100,000 kg CO₂e/hr).

5.4 References

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CHAPTER 6: FISCHER-TROPSCH PROCESSING

6.1 Reactor Selection

An iron-based catalyst is typically used for Fischer-Tropsch (FT) synthesis when syngas is produced by gasification, as compared to a cobalt-based catalyst which is typically used in applications which generate syngas by steam-methane reforming. The iron-based catalyst is often used in preference to cobalt because it is less sensitive to sulfur poisoning, because it is less expensive, and because it promotes the Water-Gas Shift reaction, enabling a lower H₂:CO ratio in the feed to the reactor. However, the iron catalyst also produces a distribution of relatively light products, while the cobalt catalyst produces a higher yield of waxes that can be selectively upgraded to the desired products (see Chapter 7).

For this report, a bubble slurry reactor using a cobalt catalyst has been chosen. This type of reactor was selected because it is the type of reactor used in most new commercial FT facilities, as well as in the US Air Force Assured Aerospace Fuels Research Facility (AAFRRF). Bubble slurry reactors have very favorable heat transfer properties, and can operate with high single pass conversions, due to the large surface area of catalyst available for reaction. Also, since a slurry reactor is liquid filled, an internal heat exchanger removes the excess heat from the exothermic FT reaction, which helps to keep the temperature of the reactor in the ideal operating range.

6.2 Fischer-Tropsch Hydrocarbon Synthesis

The syngas stream leaving the gas purification section will be mainly H₂ and CO, will be free of sulfur and chloride species, and will have some residual CO₂. Calculations in this section are based on the assumption that 96% of the CO₂ in the syngas exiting the WGS and COS hydrolysis processes for the coal cases is removed during syngas cleanup. Steam methane reforming (SMR) outlet gases (for the natural gas case) have low concentrations of CO₂, and sulfur species, so no CO₂ or sulfur removal upstream of the FT synthesis reactors is required for the SMR case.

A simplified flow diagram of the FT reaction and product separation section is shown in Figure 6-1. This simplified flow diagram shows the streams that were modeled for this report.

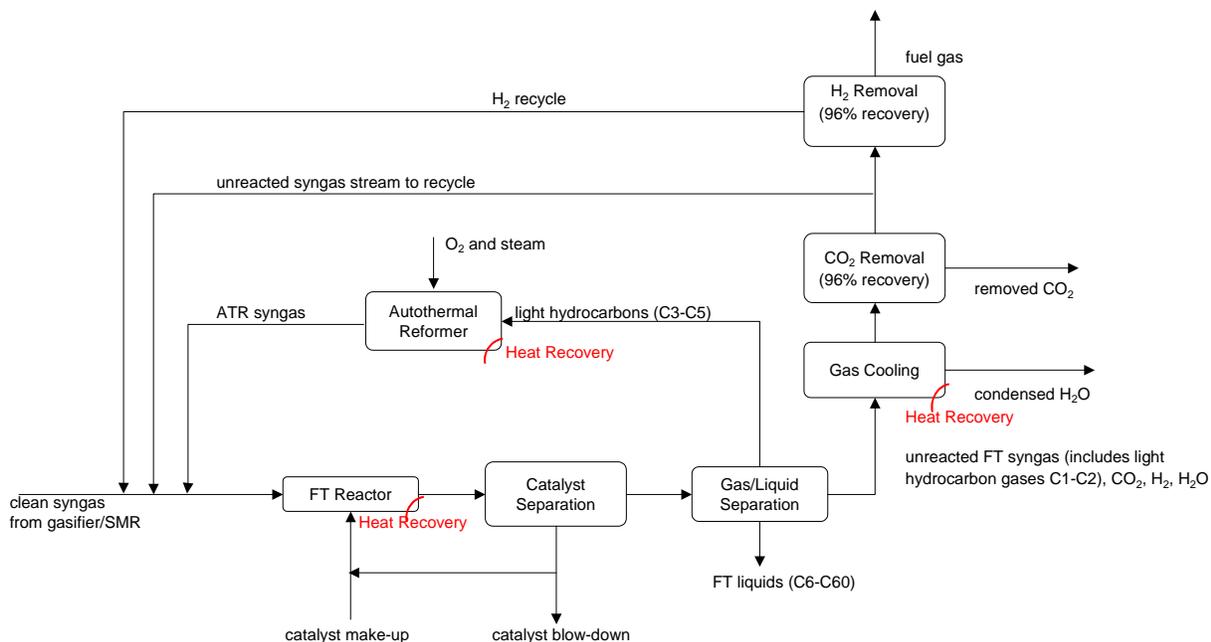
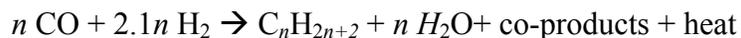


Figure 6-1. Process flow diagram for FT processing

In the FT reaction section, clean syngas is mixed with recycled gases and fed to the FT reactors, which operate at 30 atm pressure and 450-480°F. In the FT reaction, H₂ and CO react over a cobalt catalyst to form a series of mostly aliphatic saturated hydrocarbons ranging from methane to heavy waxes (C50+). The main FT reaction is



A number of parallel reactions that produce carbon dioxide, oxygenated hydrocarbons (alcohols, aldehydes) and unsaturated hydrocarbons as co-products can also occur. For this work, these reactions, except for carbon dioxide production, will be assumed to be negligible since many of these co-products will be hydrotreated to yield aliphatic SPK components in the FT liquid product upgrading section.

For modeling purposes it was assumed that all hydrocarbons produced in the FT reactions are paraffins. A sensitivity analysis was performed and it was determined that this assumption had less than a 1% impact on the reactor carbon footprint. All FT products leave the FT reactor along with the suspended catalyst. These products enter the catalyst separation section. No energy requirements for catalyst separation or catalyst makeup are included in this analysis. After separating and recovering/recycling the catalyst, the products of FT synthesis are separated into three streams: 1) a wax stream that is sent to the FT liquid product upgrading section (discussed in the next chapter), 2) a stream containing C3 to C5 hydrocarbons, and 3) a stream containing unreacted syngas along with methane, ethane, water, carbon dioxide, and hydrogen.

The stream containing hydrocarbons in the 3-5 carbon number range is sent to a catalytic autothermal reformer (ATR) where the hydrocarbons react with oxygen and steam to produce

additional syngas that is recycled to the FT reactor. Carbon dioxide as well as CO and H₂ are produced during autothermal reforming. For these calculations, 65% of the carbons that enter autothermal reforming are assumed to be converted to CO and the remainder are assumed to be converted to CO₂. All of the hydrogen in the steam and in the hydrocarbons that enter autothermal reforming are converted to molecular hydrogen. Oxygen is fed at a rate of 0.55 mol O₂/mol of carbon atom input and the amount of steam provided to the ATR (at 30 atm and 464°F) is 0.25 mol steam/mol of carbon atom inputs. Catalytic ATR is exothermic and the syngas leaving the process is at a higher temperature than the temperature of the FT reactor. This stream undergoes a heat recovery step to reduce the temperature from ATR reaction temperature to FT reaction temperature.

The stream containing unreacted syngas is cooled and treated to remove water (a major FT reaction product) and CO₂. This report assumes that 96% of the CO₂ is removed from the stream in the CO₂ removal process. Half of the unreacted syngas stream, containing mainly CO, H₂, methane, ethane, residual CO₂ and inerts such as nitrogen, is recycled back to the FT reactor. The amount of unreacted syngas that is recycled is a variable that should be studied for process optimization. The rest of the unreacted syngas is treated to recover H₂ before being burned as a plant fuel gas. Nearly all (96%) of the H₂ in this stream is assumed to be recovered during this step and returned to the FT synthesis process. Utility requirements internal to the FT reactor section (e.g., for liquid product pumping or recycle gas compression) have not been included in this carbon footprint analysis.

There is limited product yield and distribution data available for cobalt catalyzed Fischer-Tropsch reactors, mainly due to the highly proprietary nature of many of the catalysts and processes involved. To estimate conversions for this reactor, data on hydrocarbon yields from an iron catalyst slurry reactor were used (Tarka, 2009). Specifically, a single pass conversion of 87% for CO was assumed. Tarka reported a 36% conversion of CO to CO₂, but for this analysis a value of two percent conversion to CO₂ was used because there is no CO₂-producing water-gas shift reaction in a cobalt-based catalyst FT reactor such as there is with an iron-based catalyst reactor. The remaining carbon monoxide that is fed to the reactor (85%) is assumed to be converted to hydrocarbons ranging from methane to C₆₀. Of these hydrocarbons, 0.56 mole fraction is assumed to consist of C₆₊ FT liquid products, or wax, and the remaining 0.44 mole fraction consists of C₁ to C₆ hydrocarbons (these are the mole fractions reported for the hydrocarbon products in Case 5 of Tarka, 2009, which describes a reactor fed with a mix of biomass and coal).

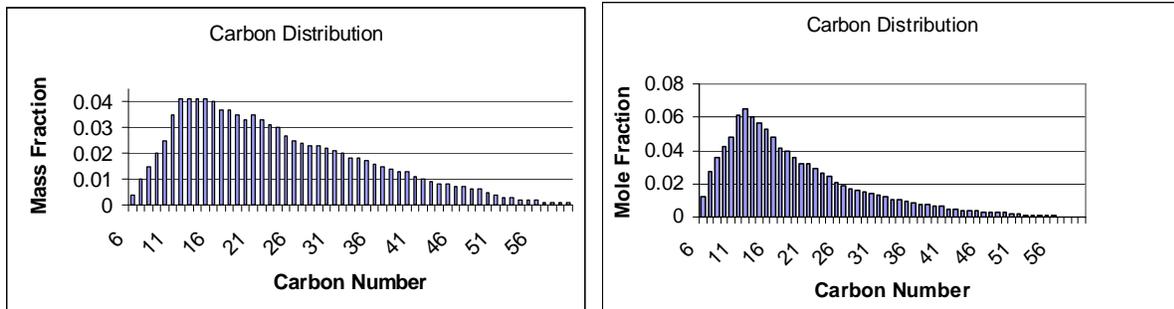
For this analysis, the total yield of methane was set at 12% because it is known that the range of reasonable values is 10% to 15%. In all, 50.5% of the C₁-C₅ light ends were assumed to be C₁-C₂ and the remainder C₃-C₅ (on a molar basis). As discussed earlier, the C₃ to C₅ portion of the C₁-C₅ light ends is routed to the ATR, converted to syngas, and fed back into the synthesis process. The C₁ to C₂ portion of the C₁-C₅ light ends is entrained in the unreacted syngas stream, half of which is recycled to the FT reactor and half of which exits the process in the fuel gas output stream.

The FT liquids were assumed to fit the carbon distribution profile for a cobalt catalyst shown in Figure 6-2 (Vessia et al., 2005). There are reports that cobalt catalyst will have a higher

conversion to Fischer-Tropsch products than an iron catalyst, but without specific conversion percentages for a cobalt catalyst, the iron catalyst conversion rate was assumed. It was also assumed that half of the unreacted syngas would be recycled to the reactor, however, so the impact of the assumed value for overall single pass conversion should be small.

The degree of hydrogen recovery and CO₂ removal, the portion of light ends that are routed to ATR, and the portion of the unreacted syngas stream that is sent to recycle are all variables that could be optimized for reduction of GHG footprint.

Figure 6-2. Assumed product distribution of wax from FT reactor



6.3 Results

SMR Feed: Natural Gas

Table 6-1 shows the mass and energy balance for the natural gas feedstock. For the 984,000 lb per hour of natural gas initially fed to the SMR unit, 864,600 pounds of wax per hour are formed.

Table 6-1. FT reactor data for natural gas feedstock

Inputs:

Clean Syngas

	Moles, lbmol/hr	Mass, lb/hr
H ₂ O	0	0
CO ₂	0	0
O ₂	0	0
N ₂	0	0
CH ₄	0	0
CO	70,260	1,968,000
COS	0	0
H ₂	143,800	290,500
H ₂ S	0	0
HCl	0	0
Total	214,100	2,258,000

ATR

ATR O₂

	Mole Frac	Lbmol/ hr	lb/hr		Mole Frac	Lbmol/hr	lb/hr
O ₂	0			O ₂	0.95	2,692	86,150
N ₂	0			N ₂	0.05	142	3,970
H ₂ O	1	1,196	21,560	H ₂ O			
Total	1	1,196	21,560	Total	1	2,834	90,120

Internal Streams:

ATR Feed Stream				ATR Output		
	Mole Frac	Flow, lbmol/hr	Flow, lb/hr	Mole Frac	Flow, lbmol/hr	Flow, lb/hr
O ₂	0	0	0	0	0	0
N ₂	0	0	0	0.01148	142	3,970
H ₂ O	0	0	0	0	0	0
C ₃	0.3945	494	21,810	0	0	0
C ₄	0.3211	402	23,390	0	0	0
C ₅	0.2844	356	25,720	0	0	0
CO	0	0	0	0.2568	3,168	88,749
H ₂	0	0	0	0.5935	7,323	14,793
CO ₂	0	0	0	0.1383	1,706	75,090
Total	1	1,253	70,920	1	12,340	182,600

Unreacted Syngas Stream to Recycle			
	Mole Frac	Flow, lbmol/hr	Flow, lb/hr
H ₂ O	0	0	0
CO ₂	0.003235	63	2,760
O ₂	0	0	0
N ₂	0.007373	143	4,004
CH ₄	0	0	0
CO	0.2628	5,094	142,700
COS	0	0	0
H ₂	0.7088	13,740	27,750
H ₂ S	0	0	0
HCl	0	0	0
C ₁	0.01779	345	5,536
C ₂	0.01512	293	8,818
Total	1	19,380	191,600

Outputs:

Liquid FT Products (wax)				Condensed H₂O	65,600	lbmol/hr
	Mole Frac	lbmol/hr	lb/hr		1,182,000	lb/hr
C6-C15	0.460	1,481	238,400	H₂ Out (for credit)	13,190	lbmol/hr
C16-C29	0.394	1,269	378,200		26,640	lb/hr
C30+	0.146	469	248,000	CO₂ Removed	3,010	lbmol/hr
Total	1	3,219	864,600		132,500	lb/hr

Fuel Gas

	Mole Frac	lbmol/hr	lb/hr
H ₂ O	0	0	0
CO ₂	0.01012	63	2,760
O ₂	0	0	0
N ₂	0.02307	143	4,004
CH ₄	0	0	0
CO	0.8224	5,094	142,700
COS	0	0	0
H ₂	0.08873	550	1,110
H ₂ S	0	0	0
HCl	0	0	0
C1	0.05568	345	5,536
C2	0.04733	293	8,818
Total	1	6,194	156,100

Energy:

Steam Energy into ATR

Steam T	464°F
Steam P	30 atm
Btu/Lb	1,205
lb steam/hr	21,560
Btu/hr	25,970,000
MMBtu/hr	26

Reactor

Energy Balance	Reactor Inputs	FT Products	Extracted Thermal Energy
Available Energy, Btu/Hr	28,580,000,000	23,630,000,000	4,955,000,000
Available Energy, MMBtu/Hr	28,580	23,630	4,955

*An average value of 20,000 Btu/lb was used for the hydrocarbon products.

Cooler

Cooling	Start Temp (°F)	464
	End Temp (°F)	100
Input	Mass Flow	Extracted Heat MMBtu/hr
H ₂ O	1,182,000	1,147
CO ₂	138,000	11
O ₂	0	0
N ₂	8,009	1
CH ₄	0	0
CO	285,400	25
COS	0	0
H ₂	55,510	69
H ₂ S	0	0
HCl	0	0
C1	11,070	2
C2	17,640	3
Total	1,680,000	1,257

Recovered Heat After ATR

Sensible Heat Btu/Hr	88,660,000
Sensible Heat MMBtu/hr	89

Gasifier Feed: 100% Coal

Table 6-2 shows the mass and energy balance for the 100% coal feedstock. For the 1,269 tons per hour of coal initially fed to the gasification unit, 864,600 pounds per hour of wax are formed.

Table 6-2. FT reactor data for 100% coal feedstock

Inputs:

Clean Syngas			
	Mole Frac	Moles	Mass
H ₂ O	0.01522	3,228	58,170
CO ₂	0.01448	3,072	135,200
O ₂	0	0	0
N ₂	0.02327	4,935	138,900
CH ₄	0	0	0
CO	0.3312	70,260	1,968,000
COS	0	0	0
H ₂	0.6158	130,600	263,800
H ₂ S	0	0	0
HCl	0	0	0
Total	1	212,100	2,564,000

ATR Steam

ATR O₂

	Mole Frac	Lbmol/hr	lb/hr		Mole Frac	Lbmol/hr	lb/hr
O ₂	0	0	0	O ₂	0.95	2,692	86,150
N ₂	0	0	0	N ₂	0.05	142	3,969
H ₂ O	1	1,196	21,560	H ₂ O	0	0	0
Total	1	1,196	21,560	Total	1	2,834	90,120

Internal Streams:

ATR Feed Stream				ATR Output		
	Mole Frac	Flow, lbmol/hr	Flow, lb/hr	Mole Frac	Flow, lbmol/hr	Flow, lb/hr
O ₂	0	0	0	0	0	0
N ₂	0	0	0	0.01148	142	3,969
H ₂ O	0	0	0	0	0	0
C ₃	0.3945	494	21,810	0	0	0
C ₄	0.3211	402	23,390	0	0	0
C ₅	0.2844	356	25,720	0	0	0
CO	0	0	0	0.2568	3,168	88,750
H ₂	0	0	0	0.5935	7,323	14,790
CO ₂	0	0	0	0.1383	1,706	75,090
Total	1	1,253	70,920	1	12,340	182,600

Unreacted Syngas Stream to Recycle			
	Mole Frac	Flow, lbmol/hr	Flow, lb/hr
H ₂ O	0	0	0
CO ₂	0.005075	125	5,519
O ₂	0	0	0
N ₂	0.206269	5,097	142,800
CH ₄	0	0	0
CO	0.206152	5,094	142,700
COS	0	0	0
H ₂	0.556681	13,760	27,790
H ₂ S	0	0	0
HCl	0	0	0
C ₁	0.013958	345	5,536
C ₂	0.011864	293	8,818
Total	1	24,710	333,100

Outputs:

Liquid FT Products						
	Mole Frac	lbmol/hr	lb/hr			
C6-C15	0.460	1,481	238,400	Condensed H₂O	68,830	lbmol/hr
					1,240,000	lb/hr
C16-C29	0.394	1,269	378,200	H₂ Returned to FT Synthesis	13,210	lbmol/hr
					26,670	lb/hr
C30+	0.146	468	248,000	CO₂ Removed	6,020	lbmol/hr
Total	1	3,218	864,600		264,900	lb/hr

Fuel Gas

	Mole Frac	lbmol/hr	lb/hr
H ₂ O	0	0	0
CO ₂	0.010901	125	5,519
O ₂	0	0	0
N ₂	0.443032	5,097	142,800
CH ₄	0	0	0
CO	0.442779	5,094	142,700
COS	0	0	0
H ₂	0.047826	550	1,111
H ₂ S	0	0	0
HCl	0	0	0
C1	0.029979	345	5,536
C2	0.025482	293	8,818
Total	1	11,500	306,500

Energy:**Steam Energy Into ATR**

Steam P	464 F
Steam T	30 atm
Btu/Lb	1,205
lb steam/hr	21,560
Btu/hr	25,970,000
MMBtu/hr	26

Reactor

Energy Balance	Reactor Inputs	FT Products	Extracted Heat
Available Energy Btu/Hr	28,590,000,000	23,630,000,000	4,955,000,000
Available Energy MMBtu/Hr	28,590	23,630	4,955

*An average value of 20000 Btu/lb was used for the hydrocarbon products.

Cooler

Cooling	Start Temp (F)	464
	End Temp (F)	100
Input	Mass Flow	Extracted Heat MMBtu/hr
H ₂ O	1,240,000	1,204
CO ₂	276,000	21
O ₂	0	0
N ₂	285,600	26
CH ₄	0	0
CO	285,400	25
COS	0	0
H ₂	55,570	69
H ₂ S	0	0
HCl	0	0
C1	11,070	2
C2	17,640	3
Total	2,154,000	1,350

Recovered Heat After ATR

Sensible Heat Btu/Hr	94,870,000
Sensible Heat MMBtu/hr	95

93% Coal, 7% Switchgrass

Table 6-3 shows the mass and energy balance for the 93% coal feedstock. For the 1,220 tons per hour of coal and 92 tons per hour of switchgrass initially fed to the gasification unit, 864,600 pounds of wax per hour are formed.

Table 6-3. FT reactor data for 93% coal feedstock

Inputs:

Clean Syngas

	Mole Frac	Moles	Mass
H ₂ O	0.02038	4,342	78,240
CO ₂	0.01446	3,081	135,600
O ₂	0	0	0
N ₂	0.02303	4,906	137,500
CH ₄	0.0001965	42	672
CO	0.3295	70,210	1,967,000
COS	0	0	0
H ₂	0.6124	130,500	263,600
H ₂ S	0	0	0
HCl	0	0	0
Total	1	213,100	2,582,000

ATR Steam

ATR O₂

	Mole Frac	Lbmol/hr	lb/hr		Mole Frac	Lbmol/hr	lb/hr
O ₂	0	0	0	O ₂	0.95	2,692	86,150
N ₂	0	0	0	N ₂	0.05	142	3,970
H ₂ O	1	1,196	21,560	H ₂ O	0	0	0
Total	1	1,196	21,560	Total	1	2,834	90,120

Internal Streams:

	ATR Feed Stream			ATR Output		
	Mole Frac	Flow, lbmol/hr	Flow, lb/hr	Mole Frac	Flow, lbmol/hr	Flow, lb/hr
O ₂	0	0	0	0	0	0
N ₂	0	0	0	0.01148	142	3,969
H ₂ O	0	0	0	0	0	0
C ₃	0.3945	494	21,810	0	0	0
C ₄	0.3211	402	23,390	0	0	0
C ₅	0.2844	356	25,720	0	0	0
CO	0	0	0	0.2568	3,168	88,750
H ₂	0	0	0	0.5935	7,323	14,790
CO ₂	0	0	0	0.1383	1,706	75,090
Total	1	1,253	70,920	1	12,340	182,600

Unreacted Syngas Stream to Recycle			
	Mole Frac	Flow, lbmol/hr	Flow, lb/hr
H ₂ O	0	0	0
CO ₂	0.005081	126	5,526
O ₂	0	0	0
N ₂	0.2060	5,092	142,700
CH ₄	0	0	0
CO	0.2060	5,091	142,600
COS	0	0	0
H ₂	0.5571	13,770	27,810
H ₂ S	0	0	0
HCl	0	0	0
C ₁	0.01396	345	5,536
C ₂	0.01186	293	8,818
Total	0	24,710	333,000

Outputs:

Liquid FT Products						
	Mole Frac	lbmol/hr	lb/hr			
C6-C15	0.460	1,481	238,400	Condensed H₂O	69,900	lbmol/hr
					1,260,000	lb/hr
C16-C29	0.394	1,269	378,200	H₂ Returned to FT Synthesis	13,220	lbmol/hr
C30+	0.146	469	248,000		26,700	lb/hr
Total	1	3,219	864,600	CO₂ Removed	6,027	lbmol/hr
					265,300	lb/hr

Fuel Gas

	Mole Frac	lbmol/hr	lb/hr
H ₂ O	0	0	0
CO ₂	0.010921	126	5,526
O ₂	0	0	0
N ₂	0.4429	5,092	142,700
CH ₄	0	0	0
CO	0.4428	5,091	142,600
COS	0	0	0
H ₂	0.04790	551	1,112
H ₂ S	0	0	0
HCl	0	0	0
C1	0.03000	345	5,536
C2	0.02550	293	8,818
Total	1	11,500	306,300

Energy:

Steam Energy Into ATR

Steam P	464 F
Steam T	30 atm
Btu/Lb	1,205
lb steam/hr	21,560
Btu/hr	25,980,000
MMBtu/hr	26

Reactor

Energy Balance	Reactor Inputs	FT Products	Extracted Heat
Available Energy Btu/Hr	28,570,000,000	23,630,000,000	4,936,000,000
Available Energy MMBtu/Hr	28,570	23,630	4,936

*An average value of 20000 Btu/lb was used for the hydrocarbon products.

Cooler

Cooling	Start Temp (F)	464
	End Temp (F)	100
Input	Mass Flow	Extracted Heat MMBtu/hr
H ₂ O	1,260,000	1,222
CO ₂	276,300	21
O ₂	0	0
N ₂	285,400	26
CH ₄	0	0
CO	285,200	25
COS	0	0
H ₂	55,620	69
H ₂ S	0	0
HCl	0	0
C1	11,070	2
C2	17,640	3
Total	2,191,000	1,369

Recovered Heat After ATR

Sensible Heat Btu/Hr	94,870,000
Sensible Heat MMBtu/hr	95

85% Coal, 15% Switchgrass

Table 6-4 shows the mass and energy balance for the 85% coal feedstock. For the 1,150 tons per hour of coal and 203 tons per hour of switchgrass initially fed to the gasification unit, 864,600 pounds of wax per hour are formed.

Table 6-4. FT reactor data for 85% coal feedstock

Inputs:

Clean Syngas

	Mole Frac	Moles	Mass
H ₂ O	0.02360	5,029	90,620
CO ₂	0.01430	3,047	134,100
O ₂	0	0	0
N ₂	0.02251	4,797	135,000
CH ₄	0.001061	226	3,629
CO	0.3286	70,010	1,961,000
COS	0	0	0
H ₂	0.6099	129,900	262,500
H ₂ S	0	0	0
HCl	0	0	0
Total	1	213,100	2,587,000

ATR Steam

ATR O₂

	Mole Frac	Lbmol/hr	lb/hr		Mole Frac	Lbmol/hr	lb/hr
O ₂	0	0	0	O ₂	0.95	2,692	86,150
N ₂	0	0	0	N ₂	0.05	142	3,970
H ₂ O	1	1,196	21,560	H ₂ O	0	0	0
Total	1	1,196	21,560	Total	1	2,834	90,120

Internal Streams:

	ATR Feed Stream			ATR Output		
	Mole Frac	Flow, lbmol/hr	Flow, lb/hr	Mole Frac	Flow, lbmol/hr	Flow, lb/hr
O ₂	0	0	0	0	0	0
N ₂	0	0	0	0.01148	142	3,969
H ₂ O	0	0	0	0	0	0
C ₃	0.3945	494	21,810	0	0	0
C ₄	0.3211	402	23,390	0	0	0
C ₅	0.2844	356	25,720	0	0	0
CO	0	0	0	0.2568	3,168	88,750
H ₂	0	0	0	0.5935	7,323	14,790
CO ₂	0	0	0	0.1383	1,706	75,090
Total	1	1,253	70,920	1	12,340	182,600

Unreacted Syngas Stream to Recycle			
	Mole Frac	Flow, lbmol/hr	Flow, lb/hr
H ₂ O	0	0	0
CO ₂	0.005066	125	5,492
O ₂	0	0	0
N ₂	0.2022	4,981	139,600
CH ₄	0	0	0
CO	0.328615	5,077	142,200
COS	0	0	0
H ₂	0.5608	13,810	27,910
H ₂ S	0	0	0
HCl	0	0	0
C ₁	0.01400	345	5,536
C ₂	0.01190	293	8,819
Total	1	24,640	329,500

Outputs:

Liquid Products	Mole Frac	lbmol/hr	lb/hr	Condensed H ₂ O	70,410	lbmol/hr
					1,269,000	lb/hr
C6-C15	0.460	1,481	238,400	H ₂ Returned to FT Synthesis	13,260	lbmol/hr
C16-C29	0.394	1,269	378,200		26,790	lb/hr
C30+	0.146	469	248,000	CO ₂ Removed	5,990	lbmol/hr
Total	1	3,219	864,600		263,600	lb/hr

Fuel Gas

	Mole Frac	lbmol/hr	lb/hr
H ₂ O	0	0	0
CO ₂	0.01097	125	5,492
O ₂	0	0	0
N ₂	0.4379	4,981	139,600
CH ₄	0	0	0
CO	0.4464	5,077	142,200
COS	0	0	0
H ₂	0.04859	553	1,116
H ₂ S	0	0	0
HCl	0	0	0
C1	0.03033	345	5,536
C2	0.02578	293	8,819
Total	1	11,370	302,700

Energy:

Steam Energy Into ATR

Steam P	464 F
Steam T	30 atm
Btu/Lb	1,205
lb steam/hr	21,560
Btu/hr	25,980,000
MMBtu/hr	26

Reactor

Energy Balance	Reactor Inputs	FT Products	Extracted Heat
Available Energy Btu/Hr	28,490,000,000	23,640,000,000	4,852,000,000
Available Energy MMBtu/Hr	28,490	23,640	4,852

*An average value of 20000 Btu/lb was used for the hydrocarbon products.

Cooler

Cooling	Start Temp (F)	464
	End Temp (F)	100
Input	Mass Flow	
H ₂ O	1,269,000	1,231
CO ₂	274,600	21
O ₂	0	0
N ₂	279,100	25
CH ₄	0	0
CO	284,400	25
COS	0	0
H ₂	55,810	69
H ₂ S	0	0
HCl	0	0
C1	11,070	2
C2	17,640	3
Total	2,191,000	1,377

Recovered Heat After ATR

Sensible Heat Btu/Hr	94,870,000
Sensible Heat MMBtu/hr	95

75% Coal, 25% Switchgrass

Table 6-5 shows the mass and energy balance for the 75% coal feedstock. For the 1,057 ton per hour of coal and 352 tons per hour of switchgrass initially fed to the gasification unit, 864,600 pounds of wax per hour are formed.

Table 6-5. FT reactor data for 75% coal feedstock

Inputs:

Clean Syngas	Mole Frac	Moles	Mass
H ₂ O	0.02965	6,343	114,300
CO ₂	0.01407	3,009	132,400
O ₂	0	0	0
N ₂	0.02180	4,664	130,700
CH ₄	0.001497	320	5,141
CO	0.3268	69,910	1,958,000
COS	0	0	0
H ₂	0.6062	129,700	261,900
H ₂ S	0	0	0
HCl	0	0	0
Total	1	213,900	2,603,000

ATR Steam

ATR O₂

	Mole Frac	Lbmol/hr	lb/hr		Mole Frac	Lbmol/hr	lb/hr
O ₂	0	0	0	O ₂	0.95	2,692	86,150
N ₂	0	0	0	N ₂	0.05	142	3,970
H ₂ O	1	1,196	21,560	H ₂ O	0	0	0
Total	1	1,196	21,560	Total	1	2,834	90,120

Internal Streams:

ATR Feed Stream				ATR Output		
	Mole Frac	Flow, lbmol/hr	Flow, lb/hr	Mole Frac	Flow, lbmol/hr	Flow, lb/hr
O ₂	0	0	0	0	0	0
N ₂	0	0	0	0.01148	142	3,969
H ₂ O	0	0	0	0	0	0
C ₃	0.3945	494	21,810	0	0	0
C ₄	0.3211	402	23,390	0	0	0
C ₅	0.2844	356	25,720	0	0	0
CO	0	0	0	0.2568	3,168	88,750
H ₂	0	0	0	0.5935	7,323	14,790
CO ₂	0	0	0	0.1383	1,706	75,090
Total	1	1,253	70,920	1	12,340	182,600

Unreacted Syngas Stream to Recycle			
	Mole Frac	Flow, lbmol/hr	Flow, lb/hr
H ₂ O	0	0	0
CO ₂	0.005057	124	5,457
O ₂	0	0	0
N ₂	0.1977	4,847	135,800
CH ₄	0	0	0
CO	0.2068	5,070	142,000
COS	0	0	0
H ₂	0.5644	13,840	27,950
H ₂ S	0	0	0
HCl	0	0	0
C ₁	0.01407	345	5,536
C ₂	0.01196	293	8,818
Total	1	24,520	325,600

Outputs:

Liquid FT Products	Mole Frac	lbmol/hr	lb/hr	Condensed H ₂ O	71,630	lbmol/hr
					1,291,000	lb/hr
C6-C15	0.460	1,481	238,400	H ₂ Returned to FT Synthesis	13,280	lbmol/hr
C16-C29	0.394	1,269	378,200		26,840	lb/hr
C30+	0.146	469	248,000	CO ₂ Removed	5,951	lbmol/hr
Total	1	3,219	864,600		261,900	lb/hr

Fuel Gas

	Mole Frac	lbmol/hr	lb/hr
H ₂ O	0	0	0
CO ₂	0.01104	124	5,457
O ₂	0	0	0
N ₂	0.4315	4,847	135,800
CH ₄	0	0	0
CO	0.4513	5,070	142,000
COS	0	0	0
H ₂	0.04928	554	1,118
H ₂ S	0	0	0
HCl	0	0	0
C1	0.03071	345	5,536
C2	0.02610	293	8,818
Total	1	11,230	298,800

Energy:

Steam Energy Into ATR

Steam P	464 F
Steam T	30 atm
Btu/Lb	1,205
lb steam/hr	21,560
Btu/hr	25,970,000
MMBtu/hr	26

Reactor

Energy Balance	Reactor Inputs	FT Products	Extracted Heat
Available Energy Btu/Hr	28,450,000,000	23,640,000,000	4,808,000,000
Available Energy MMBtu/Hr	28,450	23,640	4,808

*An average value of 20000 Btu/lb was used for the hydrocarbon products.

Cooling	Start Temp (F)	464
	End Temp (F)	100
Input	Mass Flow	Extracted Heat MMBtu/hr
H ₂ O	1,291,000	1,253
CO ₂	272,800	21
O ₂	0	0
N ₂	271,600	25
CH ₄	0	0
CO	284,000	25
COS	0	0
H ₂	55,910	70
H ₂ S	0	0
HCl	0	0
C1	11,070	2
C2	17,640	3
Total	2,204,000	1,397

Recovered Heat After ATR

Sensible Heat Btu/Hr	94,870,000
Sensible Heat MMBtu/hr	95

Table 6-6. Summary of Cradle to Gate FT wax production (for production of 393,000 kg/hr or 9.43×10^6 kg/day of wax)

	Natural gas	100% Coal	93% Coal, 7% Switchgrass	85% Coal, 15% Switchgrass	75% Coal, 25% Switchgrass
CO ₂ removed (96%) in syngas cleanup	0 kg/hr 0 kg/day	1,475,000 kg/hr 35.4×10^6 kg/day	1,479,000 kg/hr 35.5×10^6 kg/day	1,463,000 kg/hr 35.1×10^6 kg/day	1,445,000 kg/hr 34.7×10^6 kg/day
CO ₂ removed in FT system	60,220 kg/hr 1.45×10^6 kg/day	120,420 kg/hr 2.89×10^6 kg/day	120,600 kg/hr 2.89×10^6 kg/day	119,800 kg/hr 2.88×10^6 kg/day	119,100 kg/hr 2.86×10^6 kg/day
Total CO ₂ after credit for biomass derived CO ₂	1.45×10^6 kg/day	38.3×10^6 kg/day	36.8×10^6 kg/day (3)	34.6×10^6 kg/day (4)	31.6×10^6 kg/day (5)
Thermal energy credit (1)	6,301 MMBTU/hr 14.5×10^6 kg CO ₂ e/day	6,400 MMBTU/hr 14.7×10^6 kg CO ₂ e/day	6,400 MMBTU/hr 14.7×10^6 kg CO ₂ e/day	6,323 MMBTU/hr 14.6×10^6 kg CO ₂ e/day	6,301 MMBTU/hr 14.5×10^6 kg CO ₂ e/day
Credit for hydrogen produced in FT synthesis	4,226 kg CO ₂ e/hr 0.10×10^6 kg CO ₂ e/day	no credit (100% recycled to process)			
Net GWP for FT processing	-1.4 kg CO ₂ e/kg FT wax	2.5 kg CO ₂ e/kg FT wax	2.3 kg CO ₂ e/kg FT wax	2.1 kg CO ₂ e/kg FT wax	1.8 kg CO ₂ e/kg FT wax
Feed required/hr	984,000 kg methane/hr	1,269 tons/hr coal	1,220 tons/hr coal 92 ton/hr switch	1,150 tons/hr coal 203 ton/hr switch	1,057 tons/hr coal 352 ton/hr switch
GWP of feed (2)	1,574,000 kg CO ₂ e/hr	345,000 kg CO ₂ e/hr	314,800 kg CO ₂ e/hr	276,500 kg CO ₂ e/hr	230,200 kg CO ₂ e/hr
Net GWP for syngas clean-up	0 kg CO ₂ e/kg FT wax	0.25 kg CO ₂ e/kg FT wax	0.25 kg CO ₂ e/kg FT wax	0.25 kg CO ₂ e/kg FT wax	0.25 kg CO ₂ e/kg FT wax
Net GWP for feed per kg FT wax	4.0 kg CO ₂ e/kg FT wax	1.1 kg CO ₂ e/kg FT wax	1.1 kg CO ₂ e/kg FT wax	1.0 kg CO ₂ e/kg FT wax	0.8 kg CO ₂ e/kg FT wax
Cradle to gate GWP per kg FT wax	2.6 kg CO₂e/kg FT wax	3.6 kg CO₂e/kg FT wax	3.4 kg CO₂e/kg FT wax	3.1 kg CO₂e/kg FT wax	2.6 kg CO₂e/kg FT wax
Cradle to gate GWP per kg FT wax with switchgrass credit	2.6 kg CO₂e/kg FT wax	3.6 kg CO₂e/kg FT wax	3.3 kg CO₂e/kg FT wax (3)	2.8 kg CO₂e/kg FT wax (4)	2.1 kg CO₂e/kg FT wax (5)

(1) A greenhouse gas emission factor of 96 kg CO₂e/MMBtu HHV (Tables 4-5 to 4-7 in Skone and Gerdes, 2008) for steam was applied

(2) From Tables 4-1 and 4-8

(3) From Table 4-5; 4% of the carbon is from switchgrass (4% credit)

(4) From Table 4-6; 9% of the carbon is from switchgrass (9% credit)

(5) From Table 4-7; 16% of the carbon is from switchgrass (16% credit)

6.4 References

Tarka, Thomas J. “Affordable, Low-Carbon Diesel Fuel from Domestic Coal and Biomass”, prepared for the Department of Energy, National Energy Technology Laboratory, 2009 available at: <http://www.netl.doe.gov/energy-analyses/pubs/CBTL%20Final%20Report.pdf>

Vessia, Oyvind, Finden, Per, Oyvind, Syreiberg, “Biofuels from Lignocellulosic Material”, Prepared for Norwegian University of Science and Technology, Department of Electrical Engineering, December 2005.

CHAPTER 7: WAX UPGRADING

7.1 Background

The hydrocarbon product (waxes) generated during Fischer-Tropsch processing must be upgraded to yield jet fuel. The basic process configuration, shown conceptually in Figure 7-1, was assumed to start with a feed material of FT wax at FT liquid product flash separator temperatures. Wax was heated to hydrocracking conditions, and mixed with an excess of hydrogen. Hydrocracking led to lower molecular weight and more extensively branched products. Excess hydrogen was recycled to the hydrocracker feed, and products were separated.

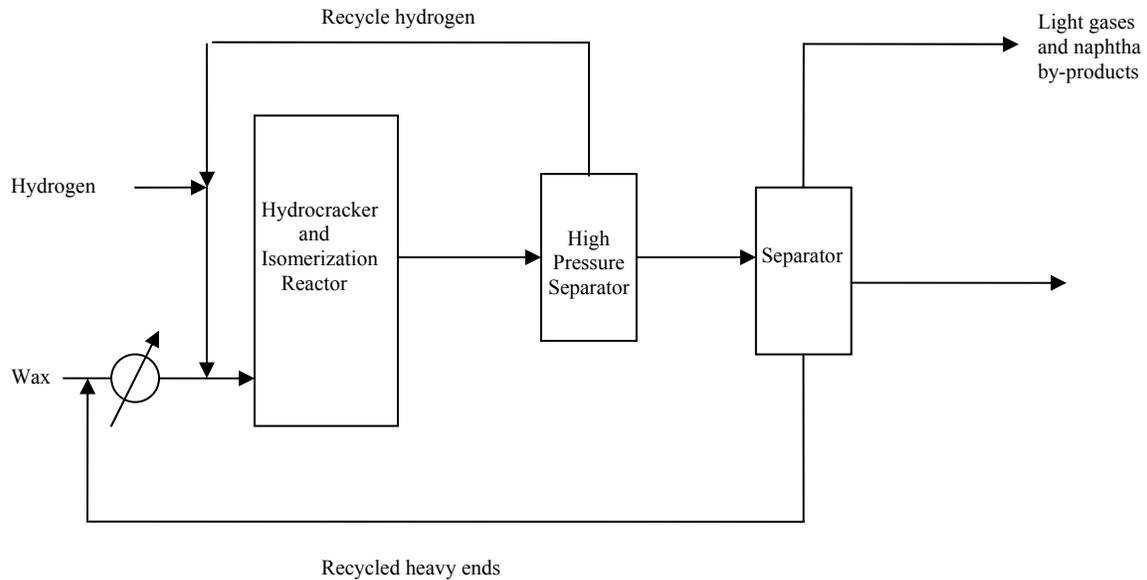


Figure 7-1. Configuration of wax upgrading unit

Five processing scenarios for the upgrading were explored, three that treat the anticipated wax (wax described in Chapter 6) and two that treat another cobalt catalyst FT wax produced by Air Products whose composition was found in literature (Shah et al., 1998). Three of the scenarios are run under recycle conditions, where the hydrocracker is operated so that approximately one third of the hydrocracker products have boiling points too high to be included in the SPK stream. These heavy products are recycled back to the hydrocracker for a combined feed ratio (CFR) (fresh feed to recycle) of 1.5. Two of the scenarios are run under no-recycle conditions, where the hydrocracker is operated so that virtually all of the hydrocracker outputs have boiling points that are in the SPK range or lower. Four of the scenarios explore introduction of the wax directly to the hydrocracker, where the fifth scenario separate out the wax components that are jet grade and lighter. This light feed fraction bypasses the reactor and is sent directly to product separation. The scenarios are:

1. Anticipated wax with recycle and no pre-separation
2. Anticipated wax without recycle and no pre-separation
3. Anticipated wax with recycle and pre-separation
4. Air Products wax with recycle and no pre-separation
5. Air Products wax without recycle and no pre-separation

Detailed calculations are presented here for the CFR=1.5 case with the anticipated wax described in Chapter 6 and no pre-separation. Results from the other scenarios are summarized for comparison. The calculations presented in this Chapter will assume a net output of 50,000 barrels per day of SPK output, or 7.0 million kg per day.

7.1 Wax feed composition

For scenarios using the anticipated wax, the wax composition from Chapter 6 was combined with values for oxygenated compounds and compounds with olefinic bonds found in literature for a wax from an FT reactor using a cobalt catalyst (Shah et al., 1988). A hydrocracking model was developed for this project and the wax that was used to test this model was based on the only available literature reports containing detailed characterization of both the feed wax and the product distributions from hydrocrackers (Shah et al., 1988). These characterizations are described in more detail later in this Chapter.

7.2 Preheat of feed to hydrocracker:

Reactor temperatures in an iron-based FT reactor are 182-275°C (DOE, 1998, page 30-31 reports 230-275°C; DOE, 2009, p 12 reports 360-480°F). The temperature of a reactor using a cobalt catalyst is 200-225°C (Dancuart and Steynberg, 2007 report that 180-200°C is slightly below the range considered of commercial interest. Literature values for FT wax hydrocracking temperatures vary from 250-440°C. Gamba et al. (2009) report 343-375°C; Möller et al. (2009) report 250-350°C; Kumar and Froment (2007) report 300-375°C; Lappas (2007) reports 350-440°C; Dancuart and Steynberg (2007) report 300-350°. Since the analysis in this report assumed a cobalt-moly FT catalyst, the feed from the FT unit would be expected to be in the 200-225°C range, and FT conditions of Chapter 6 specify a temperature of 450-480°F (230-250°C). Therefore, some preheating of the wax feed to the hydrotreater is necessary.

Preheat requirements can be calculated from the specific heat of the wax, the flow rate of the wax, the required temperature change, and the heat transfer efficiency. The specific heat of the wax was estimated by taking a weighted average of the wax components and assuming that temperature and pressure have an unimportant effect on the specific heat. Above a carbon number of ten, the specific heat of straight chain alkanes is uniform (Huang et al., 2005), and the specific heat of the wax is estimated to be 2.21 kJ/kg·K. As described later in this Chapter, the flow rate of the wax for the anticipated wax/recycle case/no preseparation case is estimated to be 9,400,000 kg/d. The average of the midpoint of the hydrocracker temperatures from literature is 340°C. This is above the initial boiling point for the wax, but values in the literature for hydrocracking of FT waxes with similar chain length ranges support this (Gamba et al., 2009; Kumar and Froment, 2007; Lappas, 2007; Dancuart and Steynberg, 2007). The FT liquid products synthesis section is assumed to deliver the wax at 240°C. The heat transfer needed is

$$\begin{aligned}
 q &= nc_p \Delta T \\
 &= \left(9,400,000 \frac{\text{kg}}{\text{d}}\right) \left(2.21 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}\right) (340 - 240) \text{K} \\
 &= 2.1 \times 10^9 \text{ kJ/d}
 \end{aligned}$$

Hydrogen would be mixed with the feed to the hydrocracker before heating; it is assumed that the heat required to raise the temperature of the hydrogen is insignificant compared to heating the wax, due to the relatively small mass flow rate of make-up hydrogen required, and since the hydrogen may be delivered, at near reaction temperature, from the FT unit. It is assumed that heat transfer would occur in a counter-current heat exchanger whose transfer fluid was heated in a furnace fueled by the fuel gas from the hydrocracker. If η_{HEX} and η_{FUR} are the efficiencies of the heat exchanger and the furnace, respectively, then the total heat transfer required is

$$\begin{aligned}
 q_{\text{TOT}} &= \frac{q}{\eta_{\text{HEX}} \eta_{\text{FUR}}} \\
 &= \frac{2.1 \times 10^6 \frac{\text{MJ}}{\text{d}}}{(0.83)(0.8)} \\
 &= 3.1 \times 10^6 \frac{\text{MJ}}{\text{d}}
 \end{aligned}$$

The recycle stream from the hydrocracker would also be combined with the wax before heating; that stream is at 272°C when it exits separation. This increases the heat transfer needs by 1.0×10^9 kJ/d and q_{TOT} to 4.2×10^6 MJ/d.

The LHV of the fuel gas is based on a weighted average of the LHVs for propane and butane, which are 46.35 and 45.75 MJ/kg, respectively. The modeled output of propane and butane in the hydrocracker product stream is 0.87 and 1.98 wt %, respectively, so the LHV for this stream is estimated to be 45.9 MJ/kg. Of the fuel gas produced by wax hydrocracking, 1.4×10^6 scfd can provide fuel needed for preheating. The GHG emissions from combustion of the fuel gas can be estimated from a carbon balance. The modeled fuel gas has an average of 3.6 carbons per molecule and an average molecular weight of 53 g/mol, so the GHG emissions from fuel gas combustion are

$$\text{CO}_2 \text{ emissions} = \frac{\left(\frac{3.6 \text{ mol C}}{\text{mol fuel gas}}\right) \left(91,000 \frac{\text{kg fuel gas}}{\text{d}}\right) \left(1 \frac{\text{mol CO}_2}{\text{mol C}}\right) \left(44 \frac{\text{g CO}_2}{\text{mol CO}_2}\right)}{\left(53 \frac{\text{g fuel gas}}{\text{mol fuel gas}}\right)}$$

$$= 270,000 \text{ kg CO}_2/\text{d}$$

This corresponds to 0.88 kg CO₂/MMBtu LHV SPK.

Note that this estimate assumes that no opportunities for heat integration/heat recovery are taken advantage of and so this estimate is conservatively high.

7.3 Heat supplied during hydrocracking:

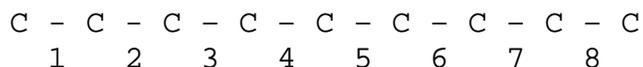
It was assumed that hydrocracking is thermally neutral and no heat was required except for heat tracing to keep wax from thickening.

7.4 Hydrocracker Model

The hydrocracker for upgrading FT wax to SPK can play a significant role in determining the overall GHG emissions of the process of making fuels from natural gas, coal and biomass because of its role in determining product slate and because of the hydrogen consumption in the reactor. Therefore, this study included efforts to understand the effect of wax feed characteristics on hydrocracker output, and to understand the impact of recycling on both product slate and hydrogen consumption. A model was developed that converts wax characterization into product characterization. The results of the model compare favorably to published data, and so the model results for heavy and light waxes with and without recycle for both diesel and jet cutoff conditions should be representative.

During hydrocracking, bonds are saturated and compounds are hydrogenated so that nearly all the products of the hydrocracker are saturated alkanes. Also, molecules are broken into smaller molecules, and straight-chain molecules are isomerized to form branched molecules.

The model developed in this work relies on well-known rules for hydrocracking (Shah et al., 1988). In a hydrocracker, the two outermost carbon-to-carbon bonds at both ends of a molecule are unable to break. If the next innermost bond is broken, propane is created. This bond has half the likelihood of all the other bonds in the molecule of breaking, and the likelihood of the other bonds breaking is all the same. For example, consider a molecule of n-nonane, which has eight carbon-to-carbon bonds:



Bonds 1, 2, 7, and 8 are unable to break. Bonds 3 and 6 have half the likelihood of breaking as bonds 4 and 5, and bonds 4 and 5 have an equal likelihood of breaking.

Detailed wax characterization data (weight percent by carbon number) for four waxes is available in a report by Shah et al.(1988). Distillation cuts resulting from hydrocracking one of

the four waxes, a heavy wax, are also reported by Shah et al.(1988). In addition to the anticipated wax described in Chapter 6, two of the waxes characterized by Shah et al. (1988) were modeled for this study: the heavy wax whose hydrocracking results were reported, and a light wax that provides another example of waxes from cobalt catalyst FT reactors. The heavy wax was used in model performance evaluation and the light wax was used in the sensitivity analyses described earlier in this Chapter.

For the model, the weight percent by carbon number was converted to mole percent, and then the number of bonds for each carbon number that are available for breaking was calculated for a given basis. Then, a user-input value for the fraction of bonds broken is used to determine the number of bonds broken for each carbon number. By assuming that each molecule breaks in half each time it is broken, an average carbon number output per carbon number input was calculated. These average carbon numbers were converted to integers and summed.

The model does not take into account loss of availability in long molecules of the bonds adjacent to breaks once they have occurred in the hydrocracker. The modeling calculations treat the process as if all the breaks occur simultaneously, not as a sequential series of breaks.

Since during hydrocracking, molecules do not break in their center, a means of distributing output around the average carbon numbers was needed. This distribution has to meet two criteria: the average carbon number of the distribution must be the same as the average carbon number calculated by the model, and no molecules longer than the original wax molecule can be produced. For the two waxes from Shah et al. (1988), both of which are heavier than the anticipated wax, meeting the second criteria was not an important limiting factor, and the distribution was chosen such that propane was the lowest carbon number compound possible no matter what the average carbon number was, and the highest carbon number created was the average carbon number plus the difference between the average carbon number and the carbon number of propane (3). For example, modeled results for the average carbon number of nine were distributed from C3 to C15. Thus, the number of carbon numbers that the average was distributed over increases by two for each increase of one in the average carbon number. It was assumed that an equal mol fraction of each carbon number in the distribution was created. For the anticipated wax of Chapter 6, which is lighter, the distribution was a hybrid of the above method at large average carbon numbers. At smaller average carbon numbers, a method that assigned propane and the molecule with three less carbons than the originating wax molecule an equal value was used. That value was one-half the value of all the molecules with carbon numbers in between. Mol fractions of output were assigned so that the average carbon number of the distribution equaled the average carbon number calculated by the model. For example, if the C9 wax input produces an output with average carbon number of 7.9 at 2.0 mol %. then C3 and C6 outputs would be assigned a mol % of 0.084, C4 and C5 outputs would be assigned a mol % of 0.17, and C9 would be assigned 1.5 mol %. Once the distributions for each average carbon number were developed, they could be summed to get the weight percent of the hydrocracker's output by carbon number.

Cracking is not the only reaction that takes place in a hydrocracker. Isomerization also occurs. Isomerization does not consume hydrogen, but it does have an affect on product slate, as boiling point decreases with increased branching. The model discussed here does not predict

isomerization, but data on the molecular compounds present in hydrocracker output was used to gain insight into how isomerization in the hydrocracker output influences distillate cuts.

As noted earlier in this Chapter, some hydrocracker output characterization is available for one of the waxes characterized in Shah et al. (1988). These data are presented by distillation cut, so in order to make the comparison between modeled and measured outputs, the carbon numbers given as the output of the model had to be assigned to distillation cuts based on their boiling point. Table 7-1 gives boiling point by carbon number and number of branches for saturated alkanes. Some of the values in this table are experimental and were obtained from property estimation software available from the US EPA (EPI Suite; US EPA 2007). In cases where boiling points were available for more than one isomer of a singly branched alkane, the values were averaged. Values for which experimental data could not be found are based on an adaptation of the Stein and Brown (1994) estimation method, as described in the documentation for EPI Suite. The equations are (T_b in K):

$$T_b \text{ (degrees K)} = 198.2 + \Sigma(n_i \times g_i)$$

$$T_b \text{ (corr)} = T_b - 94.84 + 0.5577 T_b - 0.0007705 (T_b)^2 \quad [T_b \leq 700 \text{ K}]$$

$$T_b \text{ (corr)} = T_b + 282.7 - 0.5209 T_b \quad [T_b > 700 \text{ K}]$$

boiling point coefficients:

$$-\text{CH}_3 \quad 21.98$$

$$-\text{CH}_2- \quad 24.22$$

$$-\text{CH}< \quad 11.86$$

Table 7-1. Boiling points of saturated alkanes in degrees Fahrenheit (shaded areas in indicate heavily branched compounds that are unlikely to be created during hydrocracking; yellow shading represents the diesel fraction (550°F to 700°F), dark yellow shading represents the SPK fraction (300°F to 550°F), and red-orange shading represents heavy naphtha)

carbon number	number of branches								
	0	1	2	3	4	5	6	7	8
7	209*	197*	152						
8	258*	245*	196	170					
9	303*	290*	239	214					
10	345*	332*	318*	256	231				
11	385*	373*	321	297	272				
12	421*	381	359	336	313	289			
13	456*	417	395	373	351	328			
14	488*	450	430	409	388	366	343		
15	519*	483	463	444	423	402	380		
16	548*	513	495	476	457	437	416	395	
17	576*	542	525	507	489	470	450	430	
18	601*	592*	553	537	519	501	482	463	443
19	626*	596	580	564	548	531	513	495	476
20	649*	620	605	590	575	559	542	525	507
21	674*	642	629	615	600	585	569	553	536
22	695*	663	651	638	624	610	595	580	564
23	716*	684	672	659	646	633	619	605	590
24	736*	705	693	680	667	655	642	629	615
25	755*	726	714	701	688	676	663	650	637
26	760	747	734	722	709	697	684	671	659
27	780	768	755	743	730	718	705	692	680
28	801	789	776	764	751	738	726	713	701

*from measured values in EPI Suite; other values calculated from relationship.

Shah et al. provided molecular composition data for initial boiling point to 350°F hydrocracker output (Table C.6; the particular set of hydrocracking conditions that these data describe was not provided). These data provide some information about the patterns of isomerization that are produced in a hydrocracker. Molecular composition is only given for alkanes with less than nine carbons. Table 7-2 summarizes the degree of branching for butane to octane.

Table 7-2. Fraction of branching observed in hydrocracker output (derived from Shah et al., 1988).

number of branches	number of carbons				
	4	5	6	7	8
0	1	0.455	0.394	0.340	0.289
1		0.545	0.556	0.573	0.585
2			0.0493	0.0867	0.0880
3					0.0377

The shaded areas in Table 7-1 indicate compounds that exist but that are unlikely to be created during hydrocracking. The amount of branching that can be created in a hydrocracker is limited by shape constraints, so that $>C<$ groups and adjacent $-CH<$ groups are not likely to be created. The shaded areas on the right-hand side of Table 7-1 are compounds whose degree of branching requires adjacent $-CH<$ or the creation of $>C<$ groups. The shaded areas on the left-hand side of Table 7-1 are also compounds that are unlikely to exist in hydrocracker products. Note that the total fraction of molecules that are branched in Table 7-2 have a linear increasing relationship by carbon number (total fraction of molecules that are branched = $5.5 \times 10^{-2} \times (\text{carbon number}) + 2.71 \times 10^{-1}$, $R^2 = 9.98 \times 10^{-1}$). This means that at higher carbon numbers, an unbranched molecule in the product stream is unlikely. It would be expected that for even higher carbon numbers, a molecule that is only singly branched is not likely to exit the hydrocracker, and so on.

Table 7-1 is color-coded, with yellow representing the diesel fraction (550°F to 700°F), orange representing the SPK fraction (300°F to 550°F), and red-orange representing heavy naphtha. (Shah et al. also had cuts C1-C4 and C5-C6, but those are not distributed by boiling point.) Fractions boiling above 700°F are not colored.

Table 7-1 shows that branched nonanes fall into the heavy naphtha cut, while n-nonane falls into the SPK cut. This kind of split occurs several times in the table. Therefore, a means of apportioning the fraction of each carbon number to the three splits had to be devised. The values from Table 7-3 were used.

Table 7-3. Values used to apportion to distillation cuts by carbon number.

carbon number	distillation cut		
	C7-300	jet	diesel
7	1	0	0
8	1	0	0
9	0.7687	0.2313	0
10	0	1	0
11	0.2931	0.7069	0
12	0	1	0
13	0	1	0
14	0	1	0
15	0	1	0
16	0	1	0
17	0	1	0
18	0	0.75	0.25
19	0	0.5	0.5
20	0	0.25	0.75
21	0	0	1
22	0	0	1
23	0	0	1
24	0	0	1
25	0	0	1
26	0	0	1

With this assumption, the modeled hydrocracker output can be assigned to distillation cuts and compared to measured values found in Shah et al. (1988). Shah et al. (1988) ran a heavy wax (commercial Arge wax) through their hydrocracker under differing run conditions and provided data on the resulting distillation fractions. For five of the runs, conditions were set such that the heaviest fraction produced was the diesel fraction. In order to compare modeled results to observed results, the fraction of bonds broken in the model was set so that no appreciable amount of compounds heavier than diesel were produced. Figure 7-2 shows that, under these conditions, the model is in good agreement with the distillation cut distributions observed by Shah et al. (1988). Numbers in the legend of Figure 7-2 refer to run numbers from Shah et al. (1988).

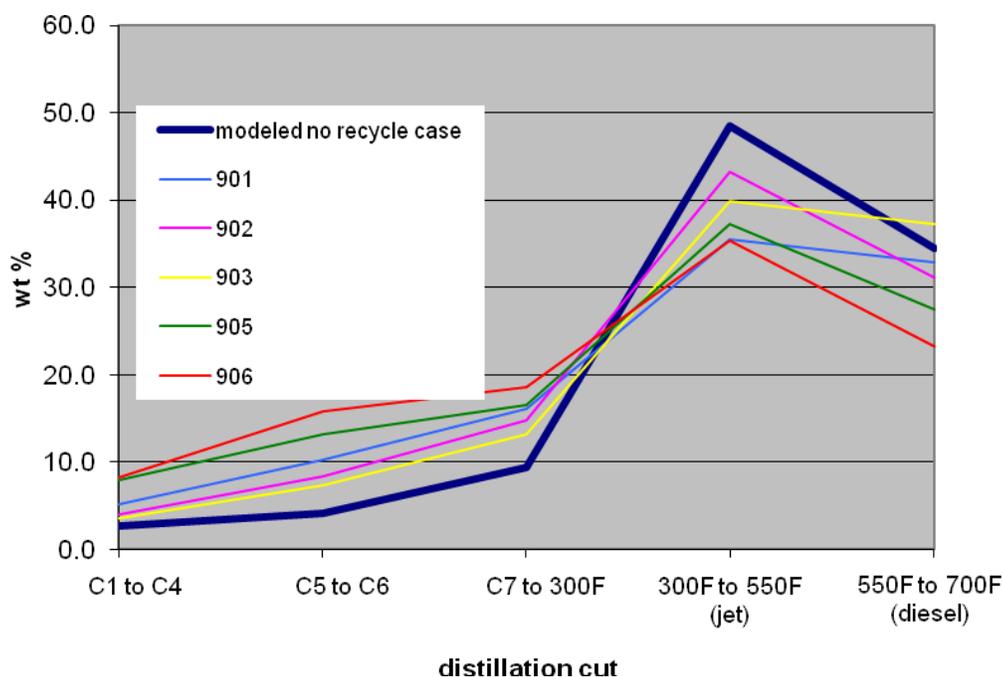


Figure 7-2. Modeled and measured distillate cut yields (heavy wax, diesel cutoff)

Shah et al. (1988) also ran the hydrocracker under the conditions of run 902, but with a combined feed ratio of 1.5, so that the heaviest third of the output was recycled. Another recycle scenario with a combined feed ratio of 2.0 was tested by Shah et al. as well (although not all the conditions matched those of run 902 for the 2.0 recycle case). Figure 7-3 shows that the model was in good agreement with measured values for the recycle runs as well as the no recycle case.

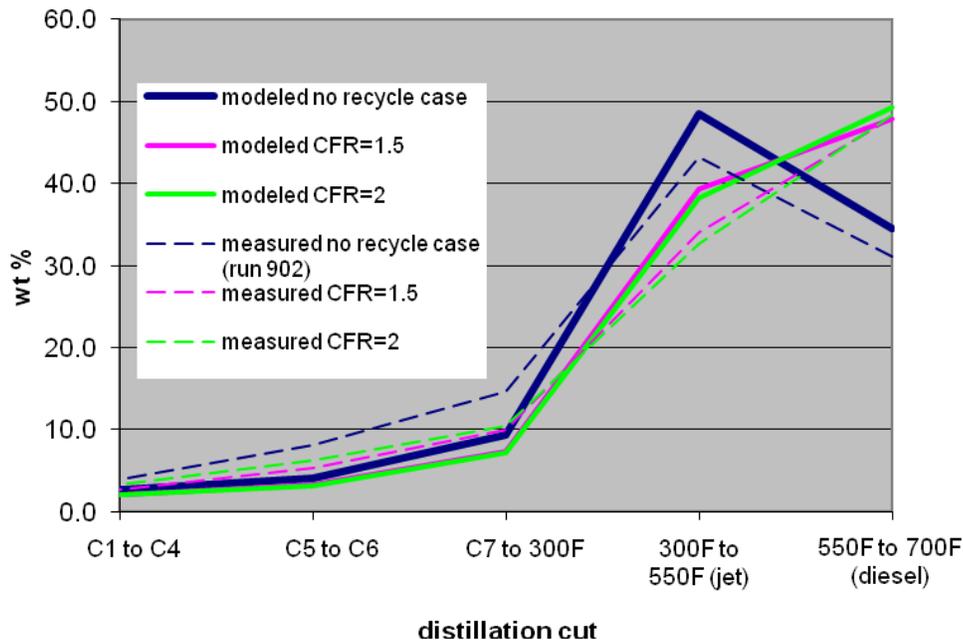


Figure 7-3. Modeled and measured distillate cut yields for recycle and no recycle cases (heavy wax, diesel cutoff).

Note that the fraction of diesel produced is higher for the recycle case than for the no recycle case, and that there was essentially no additional benefit in product slate observed when the combined feed ratio rose from 1.5 to 2.0 (Shah et al. (1988) were trying to maximize production of diesel).

Figure 7-4 shows that FT waxes vary considerably in carbon number distributions. Three of the curves in this figure were created by fitting lognormal curves to raw GPC data for FT waxes found in Shah et al. (1988). The fourth curve is for the wax described in Chapter 6, which is based on data from Vessia et al., 2005. The analyses presented to this point have been based on the Arge wax of Figure 7-4. In order to explore the effect of wax characteristics on hydrocracker output, the model was run with the Air Products wax as input for both the recycle and no recycle case. Figure 7-5 shows the results of these analyses.

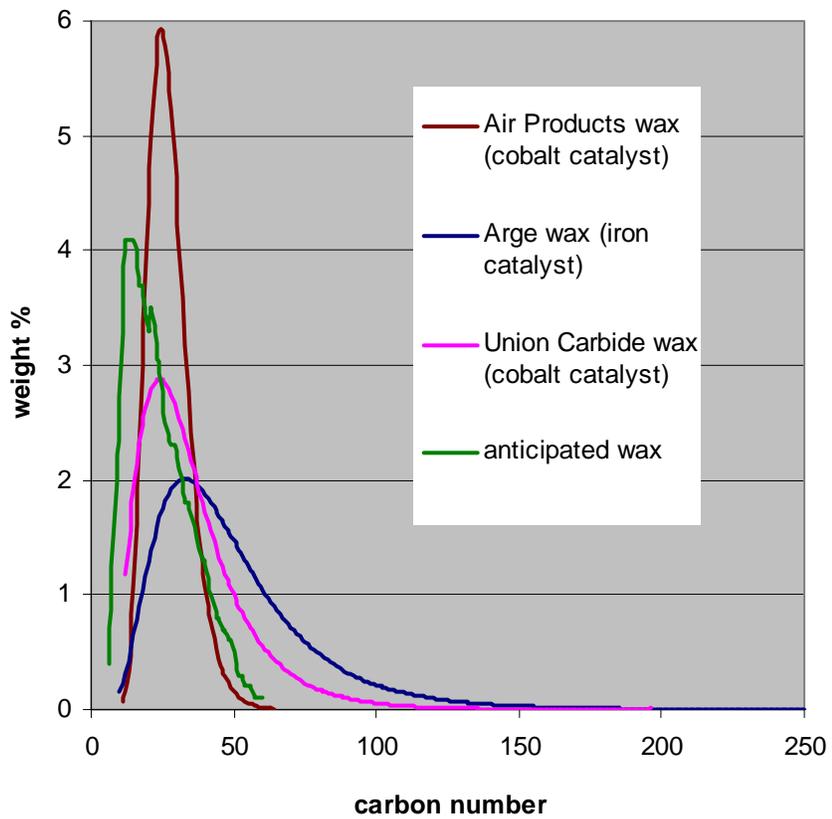


Figure 7-4. Characterization of four FT waxes.

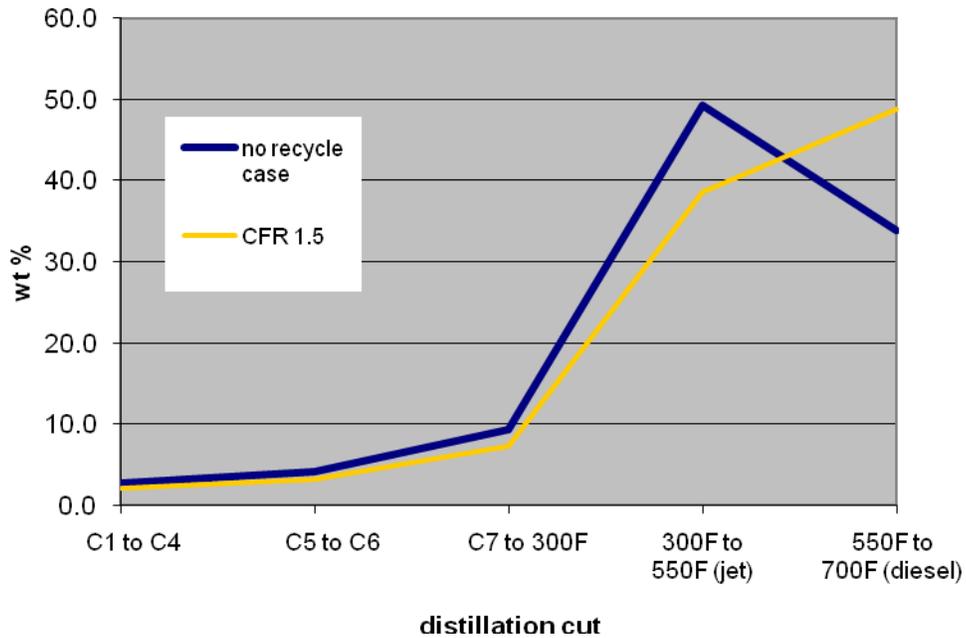


Figure 7-5. Modeled distillate cut yields for no recycle and recycle cases (light wax, diesel cutoff).

Figure 7-5 shows that the advantage of recycling heavier fractions than diesel remains for the light wax. The next question of interest is whether the advantage of recycling will exist when the hydrocracker is adjusted to produce nothing heavier than the SPK fraction. Figure 7-6 shows the results of this modeling exercise.

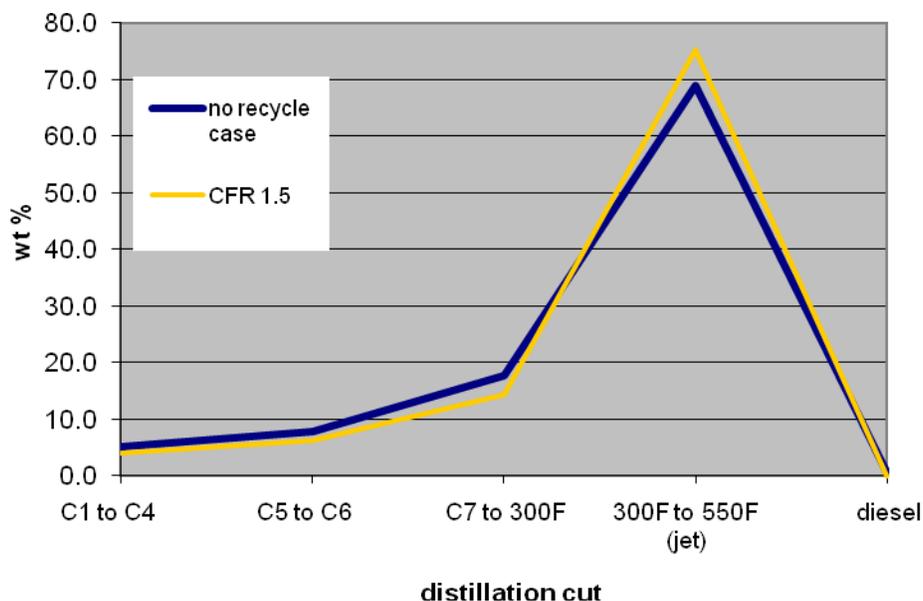


Figure 7-6. Modeled distillate cuts for recycle and no recycle cases (light wax, jet cutoff).

The modeling results shown in Figure 7-6 suggest that the product slate is no different for the recycle case than it is for the no recycle case. This may leave the impression that there would be no difference in greenhouse gas emissions for the two hydrocracker conditions. However, Figure 7-7 shows that while the distillation cuts for the two runs are nearly identical, the composition of the cuts is quite different. Since the SPK cut is mostly C10-C19, even though the carbon number distributions in Figure 7-7 are very different, the SPK yield is the same. (The discontinuities at high odd carbon numbers in the no recycle case are an artifact of the way the modeled average carbon numbers were distributed; actual output would be expected to be smooth. This discontinuity does not appear in the recycle case because the modeled average carbon numbers have a wider distribution in the recycle case.)

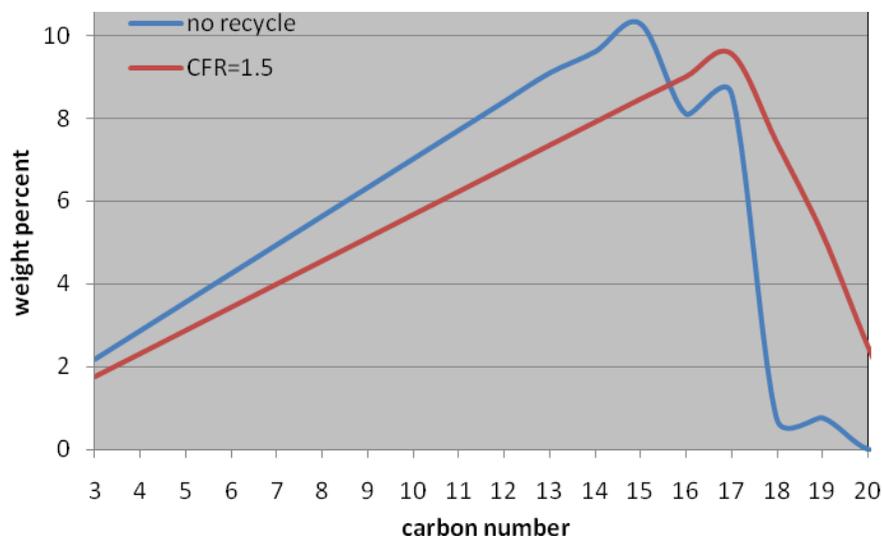


Figure 7-7. Modeled hydrocracker output characterization (light wax, jet cutoff).

7.5 Stoichiometric hydrogen demand during hydrocracking:

Up to this point, the focus in the modeling calculations has been on comparisons with the data reported by Shah et al. (1988), in order to evaluate the performance of the model. From this point forward, in this chapter, the focus will be on estimating the hydrogen consumption and greenhouse gas emissions associated with hydrocracking the FT wax produced by the reactor described in Chapter 6 and the Air Products wax from Shah et al. (1988).

Using the reactor model described in Section 7.4, a simple means of estimating hydrogen consumption in the hydrocracker is to calculate the stoichiometric hydrogen demand – the hydrogen required to saturate and hydrogenate all the molecules and to take the place of carbon when molecules are broken. Stoichiometric hydrogen demand can be estimated if the average molecular weight of the wax feed and the average molecular weight of the hydrocracker output are known, along with the concentration of olefinic bonds and oxygenated compounds. For a given feed, the smaller the molecular weight of the output, the higher the stoichiometric hydrogen demand. The fraction of oxygenated molecules and olefinic bonds in the wax are important to hydrogen consumption if they are present in significant quantities.

The average molecular weight of the hydrocracker output is calculated by the model that was developed for this project. The average molecular weight of the hydrocracker products (including those that were recycled) in the recycle case of Figure 7-7 was 182, and the average molecular weight of the hydrocracker products in the no recycle case was 139. Therefore, less hydrogen is required in the recycle case to achieve the same output of SPK.

For calculating hydrogen consumption for SPK production, the specifications for jet fuel will be based on military specifications (DoD, 2008). The military specification for the final boiling point of SPK is a maximum of 300°C, and there is no initial boiling point. Instead, military specifications allow no more than 10% of SPK to be recovered at 157°C, no more than 50% to be recovered at 168°C, and no more than 90% to be recovered at 183°C. They also require that at least 10% of SPK be recovered at 205°C, at least 50% be recovered at 229°C, and at least 90% be recovered at 262°C. Table 7-4 gives the boiling points of saturated alkanes in degrees centigrade. As with Table 7-1, the shaded areas in this table indicate compounds that exist but that are unlikely to be created during hydrocracking. The table is color-coded to show the military specifications for SPK.

Table 7-4. Boiling points of saturated alkanes in degrees centigrade with military specifications for SPK. Required cumulative SPK recovered at each temperature is given in the legend (shaded areas in indicate heavily branched compounds and minimally branched large hydrocarbons that are unlikely to be created during hydrocracking).

carbon number	number of branches								
	0	1	2	3	4	5	6	7	8
3	-42								
4	0	-12							
5	36	28							
6	69	60	41						
7	99	92	67						
8	126	118	91	77					
9	151	143	115	101					
10	174	167	159	124	110				
11	196	189	160	147	134				
12	216	194	182	169	156	143			
13	235	214	202	190	177	164			
14	254	232	221	210	198	185	173		
15	271	250	240	229	217	206	194		
16	287	267	257	247	236	225	213	202	
17	302	284	274	264	254	243	232	221	
18	316	311	290	280	271	261	250	239	228
19	330	313	305	296	287	277	267	257	247
20	343	327	319	310	302	293	283	274	264
21	357	339	332	324	316	307	299	289	280

Table 7-4 shows that triply branched and quadruply branched C20s fall into the heavier-than-SPK cut, while C20s with five or six branches fall into the SPK cut. This kind of split occurs several times in the table. Also, verifying that the modeled SPK meets the military specifications requires separating fractions over many different temperature ranges. Therefore, a means of apportioning the fraction of each carbon number to each temperature range was used. Values used in apportioning are given in Table 7-5.

Table 7-5. Values used to apportion model results to distillation temperature by carbon number.

bp, °C	Carbon number																			
	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22+
<91	1	1	1	1																
91						0.36														
92					0.66															
99					0.34															
115							0.38													
118						0.36														
126						0.29														
143							0.38													
147									0.29											
151								0.23												
159									0.41											
160										0.29										
167									0.41											
169											0.31									
174								0.18												
182											0.31									
189										0.29										
190												0.33								
194												0.31								
196									0.12											
198													0.25							
202												0.33								
210													0.25							
214													0.33							
216										0.07										
217														0.25						
221														0.25						
229															0.25					
232															0.25					
235												0.01								
236															0.25					
240														0.25						
243																0.25				
247															0.25					
250														0.25						
254																0.25				
257															0.25					
261																	0.25			
264																0.25				
267															0.25					
271																	0.25			
274																0.25				
277																	0.25			
280																	0.25			
283																		0.25		
287																		0.25		
290																0.25				
293																		0.25		
296																		0.25		
299																			0.25	
301+																	0.25	0.5	0.75	1

The molecular composition of the modeling results should not be over-interpreted, but they can provide a sense of the hydrogen demand when the modeled SPK meets the distillation temperature specifications. For the anticipated wax at a recycle ratio of 1.5 and no pre-separation, the SPK cut included compounds boiling at 130°C -272°C. Both the initial boiling

point and final boiling point were adjusted by trial and error to make the SPK portion of the output meet military specifications. Details of the hydrocracker output under these conditions are given in Table 7-6.

Table 7-6. Modeled SPK meeting military specifications for distillation temperatures at a recycle ratio of 1.5 (anticipated wax, no preseparation).

Modeled distillation temperature range (°C)	Modeled weight percent of output (not including recycle)	Modeled weight percent of SPK	Specification
SPK			
263-272	6.0		
230-262	18.5	91.9%	must be at least 90%
206-229	12.2	66.8%	must be at least 50%
184-205	14.4	50.2%	must be at least 10%
169-183	6.9	30.6%	must be less than 90%
158-168	8.8	21.2%	must be less than 50%
130-157	6.8	9.3%	must be less than 10%
Total SPK	73.6		
Naphtha (C5-129°C)	22.2		
Fuel gas (C1-C4)	4.2		

The modeled results could be used to calculate the density of the modeled SPK output, which military specifications require to be between 0.751 and 0.890 kg/L at 15°C. Values for some of the individual compound densities were available at 20°C, and these were used to develop a relationship for density by carbon number. The resulting estimate of the weighted average density of the SPK stream at this temperature is 0.756 kg/L. Therefore, the density of the modeled stream meets the milspec for density.

There are military specifications for SPK other than distillation temperatures and density. These include maximum allowed aromatics, sulfur, freezing point, viscosity, naphthalenes, thermal stability, particulate matter, and filtration time. There are also allowed ranges for flash point temperature range, API, and electrical conductivity, and minimum required values for heat of combustion and water separation. These properties were not evaluated in this study, except for heat of combustion, which is described in Chapter 8.

Modeled values were used to calculate the stoichiometric hydrogen demand in the hydrocracker and from that, an estimate of the greenhouse gas emissions from hydrogen consumed during hydrocracking. This stoichiometric hydrogen consumption is equal to the hydrogen required to crack the molecules entering the hydrocracker, the hydrogen required to consume the oxygen in the oxygenated compounds entering the hydrocracker, and the hydrogen required to saturate the olefinic bonds entering the hydrocracker.

In order to calculate the hydrogen demand, the input to the hydrocracker had to be calculated. For the recycle case, this is the wax feed plus the recycle stream. The wax feed rate was

calculated by performing a carbon balance around the hydrocracker. The required output of SPK is 50,000 bpd, and the other output flow rates (for naphtha, fuel gas, and recycle) were determined by this value and the model results. The equation for the carbon balance is
carbon in wax input = carbon in fuel gas + carbon in naphtha + carbon in SPK + carbon in residual

$$= \left(\frac{m_W}{MW_W} \right) N_W$$

$$= \left(\frac{m_F}{MW_F} \right) N_F + \left(\frac{m_N}{MW_N} \right) N_N + \left(\frac{m_S}{MW_S} \right) N_S + \left(\frac{m_R}{MW_R} \right) N_R$$

In this equation, N is the average number of carbon atoms per molecule, m is the mass flow rate, and MW is molecular weight. The subscripts W, F, N, S, and R stand for wax input, fuel gas, naphtha, SPK, and recycle, respectively. For a saturated alkane, N is equal to

$$N = \frac{(MW - 2)}{14}$$

The oxygen and olefin concentrations in the input to the hydrocracker are not large enough to change the molecular weight of the feed, so a value for the molecular weight that assumes saturated alkanes gives reasonable results. Substituting and rearranging gives

$$\text{Carbon input} = \left(\frac{m_W}{MW_W} \right) \left(\frac{MW_W - 2}{14} \right)$$

$$= \left(\frac{m_F}{MW_F} \right) \left(\frac{MW_F - 2}{14} \right) + \left(\frac{m_N}{MW_N} \right) \left(\frac{MW_N - 2}{14} \right)$$

$$+ \left(\frac{m_S}{MW_S} \right) \left(\frac{MW_S - 2}{14} \right) + \left(\frac{m_R}{MW_R} \right) \left(\frac{MW_R - 2}{14} \right)$$

$$m_W = \left(\frac{\left(\frac{m_F}{MW_F} \right) \left(\frac{MW_F - 2}{14} \right) + \left(\frac{m_N}{MW_N} \right) \left(\frac{MW_N - 2}{14} \right) + \left(\frac{m_S}{MW_S} \right) \left(\frac{MW_S - 2}{14} \right) + \left(\frac{m_R}{MW_R} \right) \left(\frac{MW_R - 2}{14} \right)}{\left(\frac{MW_W - 2}{14} \right)} \right) \times MW_W$$

Per mol of hydrocracker feed (recycle plus wax), the moles of hydrogen molecules required for cracking is equal to

$$\frac{\text{mol H}_2 \text{ for cracking}}{\text{mol input}} = 1 \text{ mol H}_2 \times \frac{\text{number of broken bonds}}{\text{mol input}} = 1 \text{ mol H}_2 \left(\frac{\frac{N_I - 1}{N_O}}{\text{mol input}} \right)$$

In this equation, N (the average number of carbons per molecule) is derived from the molecular weights of the hydrocracker input and output that were calculated by the model. The subscript O designates output (including the portion of the output that is recycled). Per mole of wax feed, the moles of hydrogen molecules required to consume the oxygen in oxygenated compounds and to saturate the bonds in the olefinic compounds is given by

$$\frac{\text{mol H}_2 \text{ to oxygenate}}{\text{mol wax}} = \frac{2 \text{ mol H}_2 \times f_{\text{oxygenated}}}{\text{mol wax}}$$

and

$$\frac{\text{mol H}_2 \text{ to saturate}}{\text{mol wax}} = \frac{2 \text{ mol H}_2 \times f_{\text{olefinic}}}{\text{mol wax}}$$

In these equations, f is the fraction of molecules in the wax feed that are olefinic or oxygenated. The values for f were taken from the characterization provided in Shah et al. (1988) for Air Products wax. Information about anticipated olefinic and oxygenated compounds was not available, and the Air Products wax had the most similar carbon number distribution to the anticipated wax. The recycle stream is assumed to be 100% saturated alkanes, so only the wax portion of the total feed to the hydrocracker has oxygenated compounds, not the recycle portion. That portion is

$$\text{mol fraction of input that is wax} = \frac{\text{mols of wax}}{\text{mols of wax} + \text{mols of recycle}}$$

Molar consumption can be converted to mass consumption by applying the molecular weights, so that

$$\begin{aligned} & \text{Stoichiometric hydrogen consumption (kg hydrogen/kg input to hydrocracker)} \\ &= \left(1 \text{ mol H}_2 \left(\frac{N_1}{N_o} - 1 \right) + \text{mol fraction of input that is wax} \times \left(2 \text{ mol H}_2 \times f_{\text{oxygenated}} + 1 \text{ mol H}_2 \times f_{\text{olefinic}} \right) \right) \frac{MW_{H_2}}{MW_1} \\ &= \left(1 \text{ mol H}_2 \left(\frac{20}{12} - 1 \right) + \frac{9,400,000 \frac{\text{kg}}{\text{d}}}{\left(268 \frac{\text{g}}{\text{mol}} \right) \left(\frac{9,400,000 \frac{\text{kg}}{\text{d}}}{268 \frac{\text{g}}{\text{mol}}} + \frac{4,600,000 \frac{\text{kg}}{\text{d}}}{297 \frac{\text{g}}{\text{mol}}} \right)} \times \left(2 \text{ mol H}_2 (0.029) + 1 \text{ mol H}_2 (0.074) \right) \right) \frac{2 \frac{\text{g}}{\text{mol}}}{277 \frac{\text{g}}{\text{mol}}} \\ &= 0.0053 \text{ kg H}_2/\text{kg input to hydrocracker} \end{aligned}$$

The estimated greenhouse gas emissions due to hydrogen demand in the hydrocracker are 620,000 kg/d (CO₂ equivalent) for a hydrocracker producing 50,000 bpd of SPK. This is 12 kg of CO₂ equivalent per barrel of SPK produced, or 2.0 kg CO₂ equivalent/MMBtu LHV of SPK. In order to obtain the latter value, the LHV of the SPK had to be estimated. This was done using the group contribution method described in Chapter 8 to estimate the LHVs by carbon number and number of branches for the individual species in the modeled SPK. A weighted average of these component values provides an estimate for the LHV of the modeled SPK of 44.6 MJ/kg.

A greenhouse gas emission factor of 0.0212 kg/SCF H₂ (CO₂ equivalents) was applied in order to estimate the greenhouse gas emissions for the modeled stoichiometric hydrogen demand. This is the combined emission factor for the values found in Table G-3 of Skone and Gerdes (2008). This value is intended to reflect average cradle-to-gate emissions from hydrogen production at refineries nationwide, and assumes hydrogen is produced at a modern steam methane reforming plant using natural gas as the feed, with subsequent hydrogen purification by pressure swing absorption. Note that an opportunity for process integration exists, as noted earlier in this report.

Tables 7-7 and 7-8 give the values used to make the hydrogen demand calculations for the case where the the anticipated wax is fed to the hydrocracker with no preseparation and the combined feed ratio is 1.5.

Table 7-7. Flow rates used to obtain GHG emissions from hydrocracking of anticipated FT wax (without separation, CFR=1.5).

parameter	value	unit	source
output of SPK	50,000	bpd	determined by contract
output of SPK	6,980,874	kg/d	unit conversion
H2 consumption per barrel of fresh feed to hydrocracker (wax+recycle)	299	scf	unit conversion
H2 consumption per kg of fresh feed to hydrocracker (wax+recycle)	0.0053	kg	stoichiometric hydrogen consumption based on modeled average number of carbons in input and output streams plus hydrogen needed to saturate oxygenates and olefins
wax input to hydrocracker	9,431,791	kg/d	from carbon balance adjusted for olefins and oxygenated compounds
wax input to hydrocracker	65,895	bpd	unit conversion
H2 consumption	73,885	kg/d	based on stoichiometric hydrogen consumption and feed rate to hydrocracker
H2 consumption	29,223,828	scfd	based on stoichiometric hydrogen consumption and feed rate to hydrocracker
H2:wax ratio	0.008	kg/kg	calculated
fraction of hydrocracker outputs to SPK by mass (not inc recycle)	0.736		from model run to meet milspecs using anticipated wax as input and CFR of 1.5
fraction of hydrocracker outputs to naphtha by mass (not inc recycle)	0.222		from model run to meet milspecs using anticipated wax as input and CFR of 1.5
fraction of hydrocracker outputs to fuel gas by mass (not inc recycle)	0.0423		from model using anticipated wax as input and CFR of 1.5
fraction of hydrocracker outputs to recycle by mass	0.3273		from model using anticipated wax as input and CFR of 1.5
fraction of hydrocracker outputs to residual by mass	0		from model -- no recycle case only; milspec requires less than 1.5% residual
naphtha output	2,105,644	kg/d	calculated based on fraction of hydrocracker outputs to naphtha by mass
naphtha output	16,779	bpd	unit conversion
fuel gas output	401,211	kg/d	calculated based on fraction of hydrocracker outputs to fuel gas by mass
fuel gas output	6,003,254	scfd	unit conversion
recycle stream flow rate	4,616,224	kg/d	calculated based on flow rates of SPK, fuel gas, and naphtha and the ratio of hydrocracker output to recycle
recycle stream flow rate	31,846	bpd	unit conversion
residual flow rate	0	kg/d	calculated based on fraction of hydrocracker outputs to residual by mass
water flow rate	18,371	kg/d	calculated based on fraction of oxygenated compounds in wax, MW of wax, MW of water, flow rate of wax
heat transfer required to preheat feed to hydrocracker	4,169,921	MJ/d	from specific heat capacity of wax, wax flow rate, temp change required, efficiencies of heat transfer
fuel gas to preheat	83,802	kg/d	from LHV of fuel gas and preheat requirement
fuel gas to preheat	1,253,913	scfd	unit conversion
fuel gas to separation	210,263	kg/d	from LHV of fuel gas and heat of separation requirement
fuel gas to separation	3,146,138	scfd	unit conversion
heat required for separation	10,462,564	MJ/d	from specific heat capacities of hydrocracker outputs and temperature change required for separation

Table 7-8. Properties used to calculate GHG emissions during hydrocracking of anticipated FT wax (without separation, CFR=1.5).

parameter	value	unit	source
initial boiling point for SPK	130	C	trial and error in model (can have 10% recovered at 157 degrees C, must have 10% recovered at 205 degrees C, etc.)
final boiling point for SPK	272	C	trial and error in model, meets milspec max of 300
density of SPK (20 degrees C)	0.755505839	kg/L	from model using anticipated wax as input and CFR of 1.5; used weighted average of densities of individual compounds; milspec is min of .751 and max of .840
density of wax input to hydrocracker	0.77453483	g/mL	wtd average for anticipated wax; for Air Products wax in Shah et al. Table 3.3 this was 0.8299 but no individual component densities are that low (do not correct for recycle stream)
density of naphtha output from hydrocracker (20 degrees C)	0.679054257	g/mL	from model using anticipated wax as input and CFR of 1.5; used weighted average of densities of individual compounds
density of recycle stream (20 degrees C)	0.784374219	g/mL	from model using anticipated wax as input and CFR of 1.5; used weighted average of densities of individual compounds; had to estimate some densities
MW of naphtha	96.69745544	g/mol	from model using anticipated wax as input and CFR of 1.5
MW of SPK	182.2717123	g/mol	from model using anticipated wax as input and CFR of 1.5
MW of recycle	296.6596132	g/mol	from model using anticipated wax as input and no recycle
MW of fuel gas	52.86749724	g/mol	from model using anticipated wax as input and CFR of 1.5
MW of hydrogen molecules	2	g/mol	periodic table of elements
ave number of carbons in hydrocracker output (three streams plus recycle)	12		calculated from average molecular weight result in model using anticipated wax as input and CFR of 1.5
ave number of carbons in wax + recycle fed to hydrocracker	20		calculated from average molecular of input to hydrocracker (wax + recycle) in model using anticipated wax as input and CFR of 1.5
% oxygenated compounds by weight in wax fed to hydrocracker	2.9		from Shah et al. table 4.9 for Air Products wax; this value was not available for the anticipated wax
% olefinic compounds by weight in wax fed to hydrocracker	7.4		from Shah et al. table 4.9 for Air Products wax (diolefinic are double counted because hydrogen consumption is doubled); this value was not available for the anticipated wax
average MW of input to hydrocracker (assumes 100% saturated alkane)	277		from model using anticipated wax as input and CFR of 1.5
average MW of output from hydrocracker	170		from model using anticipated wax as input and CFR of 1.5 (this is for three streams + recycle)
average MW of wax (before mixing with recycle stream)	268		from model using anticipated wax as input and no recycle
atomic mass of oxygen	16		periodic table of elements
MW of water	18		periodic table of elements
efficiency of furnaces for heating heat transfer fluid	0.80		from Process Heat Tip Sheet #2, U.S. Department of Energy, DOE/GO-102002-1552; assume 10% excess air and 400 degree exhaust temperature for natural gas
efficiency of heat exchangers for hydrocracker feed preheat and separation	0.83		from formula for heat exchanger effectiveness at NTU = 2.5, with the heat capacity of the transfer fluid equal to twice the heat capacity of the wax
heat capacity of wax	2.21	kJ/kg/K	from weighted average of heat capacities for components in anticipated wax; per Huang et al., the specific heat of alkanes plateaus at decane
exit temperature of wax from FT column	240	degrees C	from Vessia et al. 2005
temperature of feed to hydrocracker	340	degrees C	average of midpoint of several literature values
average number of carbon atoms per molecule of fuel gas	3.6		from the modeled molecular weight of the fuel gas
lower heating value (LHV) of fuel gas	49.76	MJ/kg	from weighted average of LHV for propane and butane, taken from NIST Chemistry Webbook
MW of carbon dioxide	44		from molecular formula

heat capacity of transfer fluid in heat exchanger	4.42	kJ/kg/K	estimate
number of transfer units in heat exchanger	2.5		estimate
LHV of SPK	44.6	MJ/kg	from weighted average of group cont method LHV for species in modeled SPK, see "chapter 8 table 1.xls"
HHV of still gas	51.0	MJ/kg	from http://cta.ornl.gov/bedb/appendix_a/Lower-Higher_Heating_Values_for_Various_Fuels.xls .
HHV of still gas	6.0	MMBtu/bbl	NETL 2008 (table 4.3)
HHV of LPG	50.2	MJ/kg	from http://cta.ornl.gov/bedb/appendix_a/Lower-Higher_Heating_Values_for_Various_Fuels.xls .
HHV of LPG	3.6	MMBtu/bbl	NETL 2008 (table 4.3)
HHV of fuel gas	49.8	MJ/kg	from weighted average of HHV for modeled fuel gas components
HHV of naphthas less than 401°F and special naphthas	5.2	MMBtu/bbl	NETL 2008 (table I-2)
HHV of naphtha	48.7	MJ/kg	from weighted average of HHV for modeled naphtha components
heat capacity of naphtha stream	2.21	kJ/kg/K	from weighted average of heat capacities for components in modeled naphtha
heat capacity of SPK	2.21	kJ/kg/K	from weighted average of heat capacities for components in modeled SPK
heat capacity of recycle stream	2.21	kJ/kg/K	this is the specific heat of decane; per Huang et al., the specific heat of alkanes plateaus at decane
temperature of naphtha, SPK, and recycle stream after flash	20.0	degrees C	estimate
temperature of SPK and recycle stream after naphtha removal	130.0	degrees C	trial and error in model

7.6 High pressure separator compression:

Energy is required to compress the hydrocracker products in order to recover the hydrogen. The greenhouse gas emissions from the power required to effect this compression are expected to be the same magnitude as the greenhouse gas emissions from producing the hydrogen needed and from separating the fuel stream (~ 2 kg CO₂/MMBtu LHV SPK).

7.7 Heat required for separation of SPK, fuel gas, naphtha, and recycle stream:

The output of the hydrocracker needs to be separated into fuel gas, naphtha, SPK, and recycle streams. This process requires heat, which is assumed to be supplied by burning fuel gas. The amount of heat required is estimated by summing the stepwise values for the amount of heat necessary to bring remaining fractions to the final boiling point of the fraction being removed. It is assumed that the C1-C4 compounds (fuel gas) can be removed by flash distillation with no heat input, and that liquids after flash are taken to ambient temperature with no heat recovery. For the recycle case, the weighted average heat capacity of the liquids that remain after fuel gas is removed is 2.21 kJ/kg/K and the mass of liquids remaining is 14×10^6 kg/d. The naphtha stream is removed by heating the liquids to 129°C, which requires heat input of 3.3×10^6 MJ/d. Heating the remaining 12×10^6 kg/d of liquids (the SPK and the recycle stream) to 272°C to remove the SPK requires 3.6×10^6 MJ/d of heat. The total estimated heating needs for separation are thus 6.9×10^6 MJ/d.

As with preheating the wax feed to the hydrocracker, it is assumed that heat transfer would occur in a counter-current heat exchanger whose transfer fluid was heated in a furnace fueled by the fuel gas from the hydrocracker. If η_{HEX} and η_{FUR} are the efficiencies of the heat exchanger and the furnace, respectively, then the total heat transfer required is

$$\begin{aligned} q_{\text{TOT}} &= \frac{q}{\eta_{\text{HEX}} \eta_{\text{FUR}}} \\ &= \frac{6.9 \times 10^6 \frac{\text{MJ}}{\text{d}}}{(0.83)(0.8)} \\ &= 10 \times 10^6 \frac{\text{MJ}}{\text{d}} \end{aligned}$$

The LHV of the fuel gas is based on a weighted average of the LHVs for propane and butane, which are 46.35 and 45.75 MJ/kg, respectively. The modeled output of propane and butane is 1.4 and 1.8 wt %, respectively, so the LHV for this stream is estimated to be 45.9 MJ/kg. Of the fuel gas produced by wax hydrocracking, 3.4×10^6 scfd can provide for this need. The GHG emissions from combustion of the fuel gas can be estimated from a carbon balance. The modeled fuel gas has an average of 3.6 carbons per molecule and an average molecular weight of 53 g/mol, so the GHG emissions from fuel gas combustion are

$$\text{CO}_2 \text{ emissions} = \frac{\left(\frac{3.6 \text{ mol C}}{\text{mol fuel gas}}\right)\left(230,000 \frac{\text{kg fuel gas}}{\text{d}}\right)\left(1 \frac{\text{mol CO}_2}{\text{mol C}}\right)\left(44 \frac{\text{g CO}_2}{\text{mol CO}_2}\right)}{\left(53 \frac{\text{g fuel gas}}{\text{mol fuel gas}}\right)}$$

$$= 690,000 \text{ kg CO}_2/\text{d}$$

This corresponds to 2.2 kg CO₂/MMBtu LHV SPK.

Note that this estimate assumes that no opportunities for heat integration are taken advantage of.

7.8 Fuel gas compression:

Energy is also required to cool and compress the fuel gas that is produced during hydrocracking. This is expected to contribute modestly to the overall greenhouse gas emissions from the process.

7.9 Credit for fuel gas produced and not burned as fuel within the process:

A credit can be given for the fuel gas produced that is not burned as fuel. This credit is equal to the cradle-to-gate greenhouse gas emissions for a stream similar to fuel gas that produced at conventional refineries (emissions are not explicitly reported for fuel gas at refineries). Light ends (LPG, still gas, special naphthas, and petrochemical feedstocks) produced by refineries are the most appropriate stand-ins for fuel gas. Allocation methods used by Skone and Gerdes (2008) result in the same emissions per barrel refined for each type of light end, but the values are different on an energy content basis. For light ends, the greenhouse gas emissions consistent with acquisition of light end fuels can be calculated by finding the CO₂ equivalent of still gas or LPG in Appendix C of Skone and Gerdes (2008) and dividing by the barrels produced. Using LPG, the equation is

$$\begin{aligned} & \text{cradle to gate emissions for light ends} \\ & = \frac{696,439 \frac{\text{kg CO}_2}{\text{d}} + \left(5,866 \frac{\text{kg CH}_4}{\text{d}}\right)\left(\frac{25 \text{ kg CO}_2 \text{ eq}}{\text{kg CH}_4}\right) + \left(15 \frac{\text{kg CH}_4}{\text{d}}\right)\left(\frac{298 \text{ kg CO}_2 \text{ eq}}{\text{kg N}_2\text{O}}\right)}{11,438 \frac{\text{bbl}}{\text{d}}} \\ & = 74 \text{ kg CO}_2 \text{ eq/bbl} \end{aligned}$$

The same result is obtained if still gas is used:

$$\begin{aligned} & \text{cradle to gate emissions for light ends} \\ & = \frac{39,740,582 \frac{\text{kg CO}_2}{\text{d}} + \left(335,879 \frac{\text{kg CH}_4}{\text{d}}\right)\left(\frac{25 \text{ kg CO}_2 \text{ eq}}{\text{kg CH}_4}\right) + \left(850 \frac{\text{kg CH}_4}{\text{d}}\right)\left(\frac{298 \text{ kg CO}_2 \text{ eq}}{\text{kg N}_2\text{O}}\right)}{652,701 \frac{\text{bbl}}{\text{d}}} \\ & = 74 \text{ kg CO}_2 \text{ eq/bbl} \end{aligned}$$

The credit assigned to fuel gas that is not consumed within the process depends on whether still gas or LPG is selected as the stand-in for fuel gas produced in the hydrocracker, because the energetic content of the LPG and the still gas are not the same. The credit will be calculated for these two fuels to gain a sense of the magnitude of the credit for fuel gas from the hydrocracker.

The HHV of the modeled fuel gas from the hydrocracker is 49.8 MJ/kg HHV. The higher heating values of still gas and LPG are 6.000 MMBtu/bbl and 3.616 MMBtu/bbl, respectively (Skone and Gerdes, 2008, Table 4-3). The equation for finding the fuel gas credit based on still gas is

$$\begin{aligned} \text{fuel gas credit via still gas} &= \frac{\left(74 \frac{\text{kg CO}_2 \text{ eq}}{\text{bbl still gas}}\right) \left(49.8 \frac{\text{MJ HHV}}{\text{kg fuel gas}}\right)}{\left(6.000 \frac{\text{MMBtu HHV}}{\text{bbl still gas}}\right) \left(1055.06 \frac{\text{MJ}}{\text{MMBtu}}\right)} \\ &= 0.58 \text{ kg CO}_2 \text{ eq/kg fuel gas} \end{aligned}$$

Based on LPG, it is

$$\begin{aligned} \text{fuel gas credit via LPG} &= \frac{\left(74 \frac{\text{kg CO}_2 \text{ eq}}{\text{bbl LPG}}\right) \left(49.8 \frac{\text{MJ HHV}}{\text{kg fuel gas}}\right)}{\left(3.616 \frac{\text{MMBtu HHV}}{\text{bbl LPG}}\right) \left(1055.06 \frac{\text{MJ}}{\text{MMBtu}}\right)} \\ &= 0.97 \text{ kg CO}_2 \text{ eq/kg fuel gas} \end{aligned}$$

These two values vary by roughly a factor of two. The upgrading section produces 1.2×10^6 scfd of fuel gas that is not burned for process heating. Applying the midpoint of the above two values results in a credit of 64,000 kg/d (CO₂ equivalent) for a hydrocracker producing 50,000 bpd of SPK. This corresponds to a credit of 0.21 kg CO₂ equivalent/MMBtu LHV SPK when an LHV of 44.6 MJ/kg (calculated based on the weighted average of the LHVs for the modeled SPK components) is applied.

7.10 Credit for naphtha production

The ASTM boiling range of light straight-run gasoline is 90-220°F (Skone and Gerdes, 2008). The naphtha produced in the hydrocracker is similar to straight run gasoline because it is paraffinic and the compounds it contains boil between 82 and 246°F. This type of naphtha is usually used as feedstock for production of olefins. A credit can be taken for the cradle-to-gate greenhouse gas emissions that would have been released due to production of this naphtha stream at a conventional refinery.

Special naphthas and petrochemical feedstocks are grouped with the "light ends" streams at a refinery, along with still gas and LPG. As discussed in the previous section, the cradle-to-gate GHG emissions of all light ends are estimated as being equal on a per barrel basis, at 74 kg CO₂ eq/bbl. For naphtha less than 401°F and special naphthas, the HHV is 5.248 MMBtu/bbl (Skone and Gerdes, 2008, Table I-2). The HHV of the modeled naphtha stream (calculated using a weighted average of the individual components) is 48.7 MJ/kg.

$$\begin{aligned} \text{naphtha credit} &= \frac{\left(74 \frac{\text{kg CO}_2 \text{ eq}}{\text{bbl naphtha}}\right) \left(48.7 \frac{\text{MJ HHV}}{\text{kg naphtha}}\right)}{\left(5.248 \frac{\text{MMBtu HHV}}{\text{bbl naphtha}}\right) \left(1055.06 \frac{\text{MJ}}{\text{MMBtu}}\right)} \\ &= 0.65 \text{ kg CO}_2 \text{ eq/kg naphtha} \end{aligned}$$

The upgrading section produces 2,100,000 kg/d of naphtha. Applying the above value results in a credit of 1,400,000 kg/d (CO₂ equivalent) for a hydrocracker producing 50,000 bpd of SPK. This corresponds to a credit of 4.4 kg CO₂ equivalent/MMBtu LHV of SPK when an LHV of 44.6 MJ/kg (calculated based on the weighted average of the LHVs for the modeled SPK components) is applied.

7.11 Comparison of upgrading section scenarios

Estimates of greenhouse gas emissions for the upgrading section were done for a recycle scenario using the anticipated wax and no pre-separation (used as the example in the above calculations), for a no-recycle scenario using the anticipated wax and no pre-separation, for a recycle scenario using the anticipated wax with pre-separation (where a light fraction of the wax is routed directly to product instead of being fed to the hydrocracker, for a recycle scenario using an Air Products cobalt catalyst FT wax and no pre-separation, and for a no-recycle scenario using the Air Products wax and no pre-separation.

Table 7-9 shows that the output streams of a scenario where only fresh wax (the anticipated wax) is fed to the hydrocracker are different from the recycle scenario. The profile of greenhouse gas emissions from the recycle scenario for producing SPK that meets the military specifications for distillation temperatures also differs from the estimate for a no recycle scenario. Figure 7-8 shows a simplified flowsheet of the FT wax upgrading process, with flow rates and GHG emission estimates, for the recycle configuration where the ratio of wax to recycle is 1:0.5. Figure 7-9 shows the flowsheet for a configuration with no recycle. Greenhouse gas emissions from hydrogen production are lower in the recycle case, but separation requires more energy and produces more greenhouse gas emissions for the recycle case than for the no-recycle case (because there is more material to heat in the recycle case). Also, in the no-recycle scenario, there is more naphtha and fuel gas produced per barrel of SPK produced, and the credit for these fuels is higher in the no-recycle case. However, while greenhouse gas emission estimates are lower in the no-recycle case, the estimated wax feed to the hydrocracker is less in the recycle scenario than in the no recycle scenario for the same amount of SPK produced (66,000 bpd vs. 75,000 bpd, and the greenhouse gas emissions associated with the reduced production of wax are lower for the recycle case than for the no-recycle case.

Table 7-9. Modeled SPK meeting military specifications for distillation temperatures with no recycle (anticipated wax, no pre-separation).

Modeled distillation temperature range (°C)	Modeled weight percent of output	Modeled weight percent of SPK	Specification
SPK			
263-291	6.4		
230-262	13.4	90.1%	must be at least 90%
206-229	10.9	69.2%	must be at least 50%
184-205	13.5	52.3%	must be at least 10%
169-183	6.7	31.3%	must be less than 90%
158-168	9.1	20.8%	must be less than 50%
145-157	4.3	6.6%	must be less than 10%
Total SPK	64.3		
Naphtha (C5-129°C)	29.4		
Fuel gas (C1-C4)	5.6		

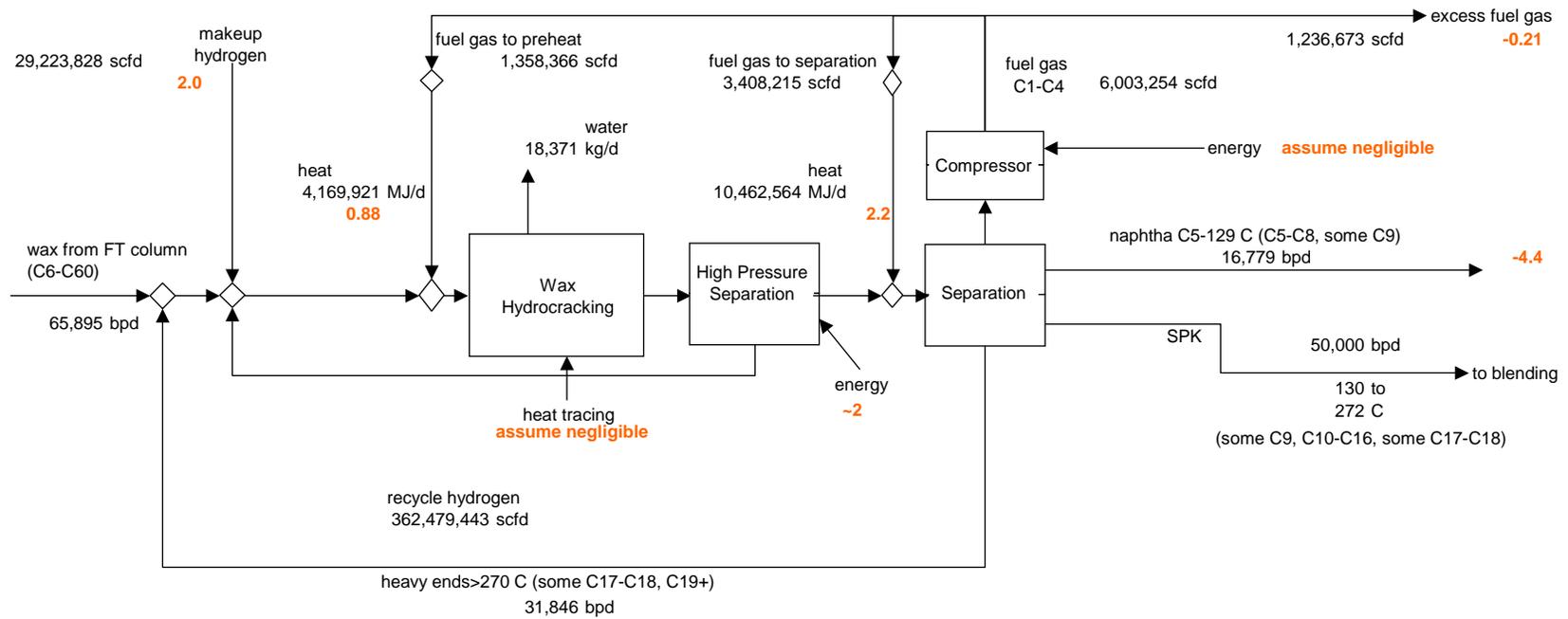


Figure 7-8. Simplified flowsheet of FT wax upgrading process for a combined feed ratio of 1.5 (recycle scenario) using the anticipated wax and no preseparation. Greenhouse gas emissions (CO₂ equivalent in g/MJ LHV SPK) are in orange.

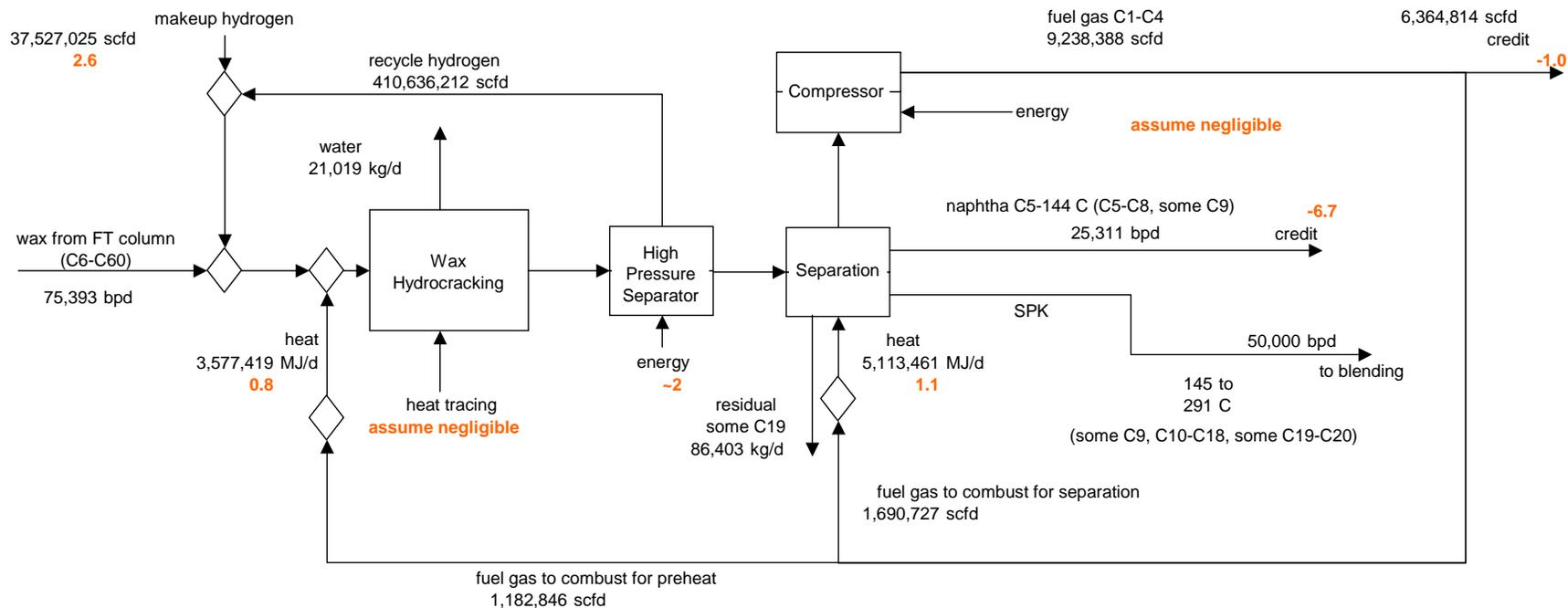


Figure 7-9. Simplified flowsheet of FT wax upgrading process for no-recycle process using the anticipated wax and no pre-separation. Greenhouse gas emissions (CO₂ equivalent in g/MJ LHV SPK) are in orange.

Table 7-10 and Figure 7.10 show the impact of pre-separating the anticipated wax prior to hydrocracking on SPK yield and greenhouse gas emissions for the recycle case. In this scenario, wax components that are SPK fraction and lighter are routed directly to the fuel separator where naphtha and SPK are separated from each other and from the recycle stream. Because less wax is fed to the hydrocracker, greenhouse gas emissions from hydrogen production and from preheat and separation are lower than for the recycle case without pre-separation. More importantly, the yield of SPK with pre-separation is higher than without pre-separation, and 62,000 bpd of wax produces 50,000 bpd of SPK. Without pre-separation, 66,000 bpd of wax are required to produce 50,000 bpd of SPK.

Table 7-10. Modeled SPK meeting military specifications for distillation temperatures for recycle case (anticipated wax, with pre-separation).

Modeled distillation temperature range (°C)	Modeled weight percent of output from hydrocracker	Modeled weight percent of total output (straight from wax and from hydrocracker)	Modeled weight percent of total SPK output	Specification
SPK				
263-269	4.9	3.8		
230-262	22.6	25.5	95.2%	must be at least 90%
206-229	13.1	14.1	62.3%	must be at least 50%
184-205	13.5	13.9	44.1%	must be at least 10%
169-183	6.4	7.4	26.3%	must be less than 90%
158-168	8.1	6.2	16.7%	must be less than 50%
130-157	6.2	6.8	8.7%	must be less than 10%
Total SPK	74.7	77.7		
Naphtha (C5-129°C)	21.0	19.0		
Fuel gas (C1-C4)	4.3	3.3		

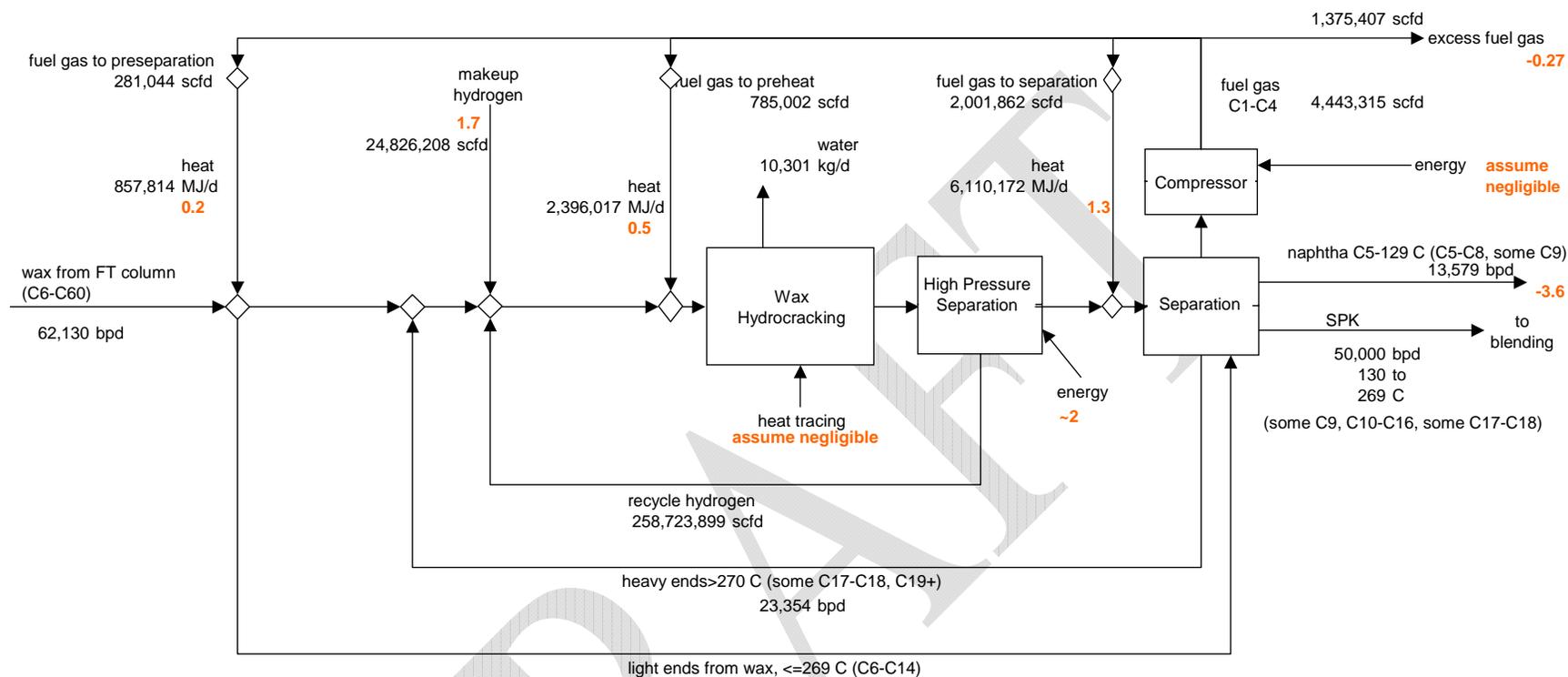


Figure 7-10. Simplified flowsheet of FT wax upgrading process for recycle process using the anticipated wax with pre-separation. Greenhouse gas emissions (CO₂ equivalent in g/MJ LHV SPK) are in orange.

Tables 7-11 to 7-12 and Figures 7-11 to 7-12 report the results of repeating the analyses provided for the recycle and no-recycle processes with no pre-separation, but for another cobalt catalyst FT wax (the Air Products wax from Shah et al., 1998). This is a heavier wax than the anticipated wax, and more hydrogen is required to produce the desired products during hydrocracking.

Table 7-11. Modeled SPK meeting military specifications for distillation temperatures, recycle case (Air Products wax, no preseparation).

Modeled distillation temperature range (°C) SPK	Modeled weight percent of output	Modeled weight percent of SPK	Specification
263-270	5.4		
230-262	23.8	92.9%	must be at least 90%
206-229	13.0	62.0%	must be at least 50%
184-205	13.6	45.1%	must be at least 10%
169-183	6.2	27.5%	must be less than 90%
158-168	7.7	19.5%	must be less than 50%
120-157	7.4	9.6%	must be less than 10%
Total SPK	77.0		
Naphtha (C5-129°C)	18.3		
Fuel gas (C1-C4)	4.8		

Table 7-12. Modeled SPK meeting military specifications for distillation temperatures, no-recycle case (Air Products wax, no preseparation).

Modeled distillation temperature range (°C) SPK	Modeled weight percent of output	Modeled weight percent of SPK	Specification
263-278	6.8		
230-262	18.1	92.9%	must be at least 90%
206-229	13.4	62.0%	must be at least 50%
184-205	14.1	45.1%	must be at least 10%
169-183	6.4	27.5%	must be less than 90%
158-168	8.0	19.5%	must be less than 50%
130-157	6.1	9.6%	must be less than 10%
Total SPK	73.0		
Naphtha (C5-129°C)	20.7		
Fuel gas (C1-C4)	5.0		

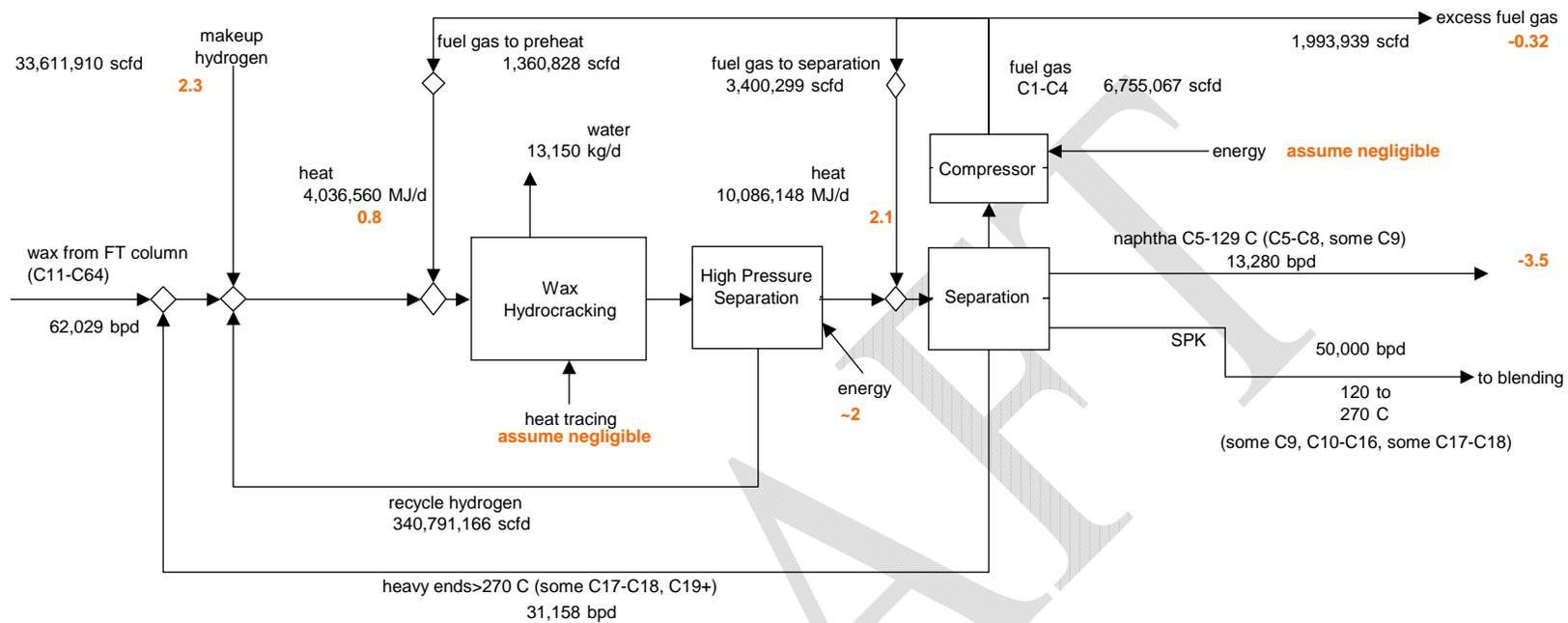


Figure 7-11. Simplified flowsheet of FT wax upgrading process for recycle process using the Air Products wax with no pre-separation. Greenhouse gas emissions (CO₂ equivalent in g/MJ LHV SPK) are in orange.

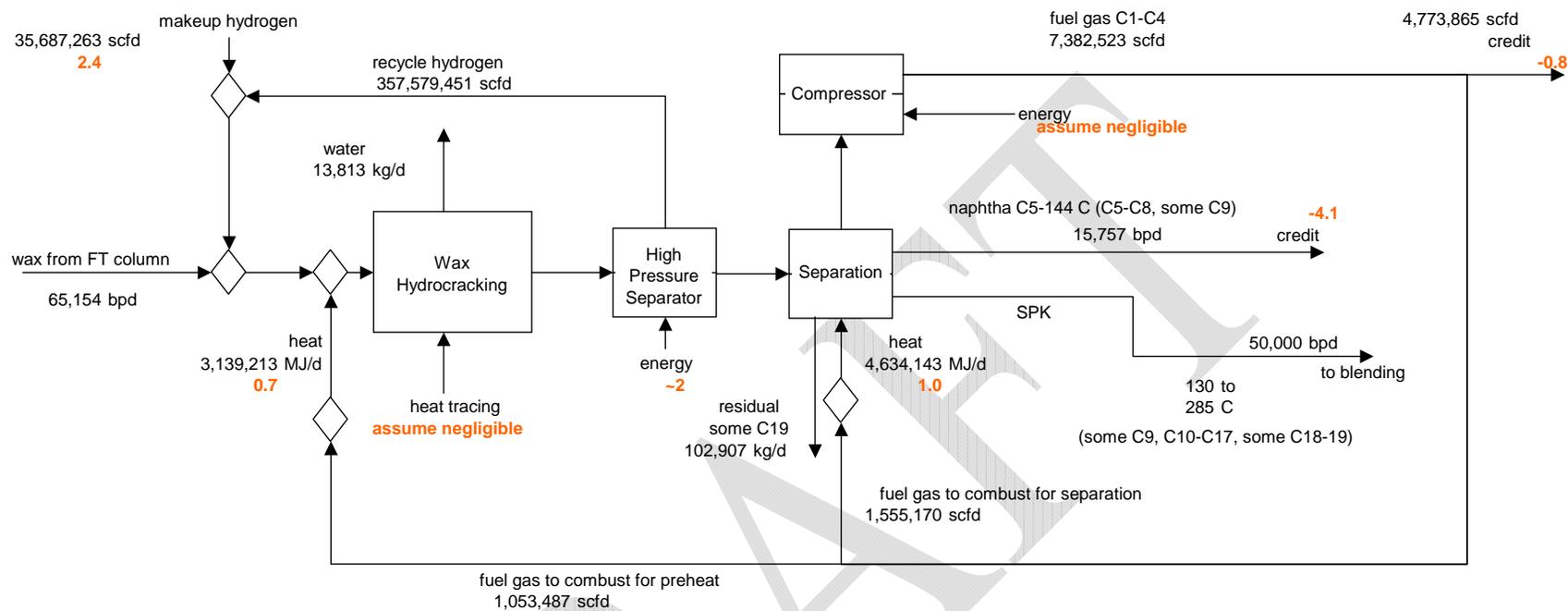


Figure 7-12. Simplified flowsheet of FT wax upgrading process for recycle process using the Air Products wax with no pre-separation. Greenhouse gas emissions (CO₂ equivalent in g/MJ LHV SPK) are in orange.

A summary of the net global warming potential of the upgrading section (per kg of SPK produced) for each of the scenarios is given in Table 7-13. Note that the no-recycle cases have a lower greenhouse gas footprint within the process than their corresponding recycle case. This is due to more co-product credits for a fixed amount of SPK production in the no recycle case. However, because there are more co-products, more feed FT wax is required in the no-recycle case, causing more upstream greenhouse gas emissions.

Table 7-13. Global warming potential associated with upgrading section (kg CO₂e per kg of SPK produced)

<i>Scenario</i>	<i>Net kg CO₂e per MMBTU LHV SPK produced</i>	<i>Net g CO₂e per MJ LHV SPK produced</i>	<i>Net g CO₂e per kg of SPK produced (at 44.6 MJ LHV/kg)</i>
Anticipated wax, no-recycle, no pre-separation	-1.4	-1.3	-59
Anticipated wax, recycle, no pre-separation	2.6	2.5	110
Anticipated wax, recycle, with pre-separation	3.7	3.5	156
Air Products wax, no-recycle, no pre-separation	1.2	1.2	51
Air Products wax, recycle, no pre-separation	3.6	3.5	154

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CHAPTER 8: COMBUSTION

8.1 Background and petroleum based fuel GHG emissions

The largest single component of the life cycle greenhouse gas emissions for most aviation fuels is combustion of the fuel to propel the aircraft. Since this combustion occurs at altitude, developing comprehensive estimates of global warming potentials associated with aircraft combustion emissions can be complicated. For example, water emitted at altitude may or may not result in the formation of contrails, which influence the atmosphere's radiative balance. Sulfur dioxide emissions from combustion of petroleum based fuels (SPK fuels are generally sulfur-free) can lead to particle formation, which can have a cooling effect. Emissions of nitrogen oxides can have a net warming impact. Substantial uncertainties exist in the global warming potentials of these non-CO₂ emissions, at altitude. In contrast, because of the long atmospheric lifetime of CO₂ in the atmosphere, the emissions of CO₂ due to combustion are essentially equivalent at ground level and at altitude.

Based on these factors, the Framework and Guidance document prepared by the Aviation Fuel Life Cycle Assessment Working Group of the US Air Force (Allen et al., 2009) recommends accounting only for CO₂ emissions associated with combustion. That recommendation will be followed in this report. Additional documentation of the rationale behind this choice is provided in Allen et al., (2009; Chapter 2)

Using this approach, the global warming potential of combustion emissions of **petroleum based jet fuels** is **73.2 g CO₂e / MJ**. This is based on the central estimate of 73.65 g CO₂e / MJ combustion emissions (77.7 kg of CO₂ equivalents per million BTUs of Lower Heating Value, LHV, fuel consumed) reported by NETL for aviation fuels (Skone and Gerdes, 2008), adjusted for non-CO₂ emissions.

8.2 SPK fuel GHG emissions

The global warming potential of combustion emissions from SPK fuels might be expected to be different than the value for petroleum based fuel due to the lack of aromatics and cyclic paraffins (naphthenes) in SPK fuels. Therefore, in this work, the global warming potential of combustion emissions from SPK fuels will be estimated by directly calculating both the heat of combustion of the SPK fuel and the total carbon emissions, based on the molecular composition of SPK fuels as reported in Chapter 7.

The heats of combustion were estimated based on group contribution methods developed by the Department of Transportation/Federal Aviation Administration (DOT/FAA, 2001). This report provides group contributions for the heats of combustion (higher heating value) for each of the three functional groups in SPK fuels:

-CH ₃	775 kJ/mol
-CH ₂ -	670 kJ/mol
-CH<	518 kJ/mol

Using this approach, a straight chain C₁₂ paraffin in an SPK fuel will have a molar heat of combustion (HHV) of 8250 kJ/mol or 48.5 kJ/g (ten -CH₂- groups and two -CH₃ groups). A

C12 paraffin with two branch points will have a molar heat of combustion (HHV) of 48.0 kJ/g (six $-CH_2-$ groups and four $-CH_3$ groups and two $-CH<$ groups). The HHV is converted to a LHV by adjusting for the heat of vaporization of water at 298 K (DOT/FAA, 2001):

$$\text{LHV (kJ/g)} = \text{HHV (kJ/g)} - 21.96 (\text{weight fraction hydrogen})$$

For the C12 straight or branched chain paraffin, the weight fraction of hydrogen is 26/170, so the LHVs are 45.17 and 44.62 kJ/g for the straight and two-branch C12 paraffins, respectively. These values can be compared to an average SPK fuel LHV of 44.1 kJ/g (MJ/kg) reported in Allen et al. (2009).

The CO_2 emissions are based on an assumption of complete combustion and are therefore 44 g CO_2 per mole combusted for each carbon atom in the molecule. For the C12 paraffins, the carbon emissions are therefore;

$$3106 \text{ g } CO_2/\text{kg fuel} = 3.106 \text{ g } CO_2/\text{g fuel} = 12 * 44/170$$

Thus the global warming potential per MJ of LHV for the straight chain and two branch C12 paraffins are:

$$\begin{aligned} \text{Straight chain C12: } & [3106 \text{ g } CO_2/\text{kg fuel}] / [45.17 \text{ MJ/kg fuel}] = 68.8 \text{ g } CO_2/\text{MJ LHV} \\ \text{Two branch C12: } & [3106 \text{ g } CO_2/\text{kg fuel}] / [44.62 \text{ MJ/kg fuel}] = 69.6 \text{ g } CO_2/\text{MJ LHV} \end{aligned}$$

These values are calculated for each of the combinations of carbon number and number of branch points listed in Table 8-1.

Global warming potentials for two representative SPK compositions from Chapter 7 were used to estimate emissions. Table 8-2 shows the modeled SPK composition by carbon number and number of branches for the case where SPK is produced by operating the hydrocracker in the wax upgrading section at a combined feed ratio (CFR, see Chapter 7 for definition) of 1.5, with the anticipated wax and no pre-separation. The weighted average of the lower heating values (derived from the group contribution method) of the individual components in this SPK is 44.60 MJ/kg. (This meets the specification for the net heating value of SPK that can be blended to make JP-8, which is a minimum of 42.8 MJ/kg; US DoD, 2008) The resulting GHG emissions are 69.70 g CO_2 /MJ LHV of SPK.

Similarly, Table 8-3 shows the modeled SPK composition by carbon number and number of branches for the case where SPK is produced by operating the hydrocracker in the wax upgrading section under no-recycle conditions (CFR=1), with the anticipated wax and no pre-separation. The weighted average of the lower heating values (derived from the above group contribution method) of the individual components in this SPK is 44.62 MJ/kg, and the resulting GHG emissions are 69.67 g CO_2 /MJ LHV of SPK.

In both cases, the global warming potential (GWP) of combustion emissions of SPK is 69.7 g CO_2e / MJ, 4.5% less than for petroleum based jet fuel. In principle, based on the calculations reported in Table 8-1, the possible range of GWPs is 67.3 - 71.5 g CO_2 /MJ LHV, but most of the

SPK components are tightly clustered around 70 g CO₂/MJ LHV. Therefore, for this report, the value of the global warming potential of combustion emissions of **SPK will be reported as 70±1 g CO₂e / MJ**. Table 8-4 reports the net greenhouse gas emissions for combustion for the 5 feedstock scenarios considered in this work. The net emissions count only fossil carbon and do not include the CO₂ emissions associated with carbon derived from switchgrass.

Table 8-1. Combustion greenhouse gas emissions (CO₂ only) for SPK fuel components (g CO₂/MJ LHV)

Carbon Number	Number of branches								
	0	1	2	3	4	5	6	7	8
6	67.3	68.1							
7	67.7	68.4							
8	68.0	68.6	69.3						
9	68.3	68.8	69.4						
10	68.5	69.0	69.5	70.0					
11	68.6	69.1	69.6	70.0					
12	68.8	69.2	69.6	70.0	70.5				
13	68.9	69.3	69.7	70.1	70.5				
14	69.0	69.3	69.7	70.1	70.5	70.8			
15	69.1	69.4	69.7	70.1	70.4	70.8			
16	69.1	69.5	69.8	70.1	70.4	70.8	71.1		
17	69.2	69.5	69.8	70.1	70.4	70.7	71.1		
18	69.3	69.5	69.8	70.1	70.4	70.7	71.0	71.3	
19	69.3	69.6	69.9	70.1	70.4	70.7	71.0	71.3	
20	69.4	69.6	69.9	70.1	70.4	70.7	70.9	71.2	71.5
21	69.4	69.6	69.9	70.1	70.4	70.6	70.9	71.2	71.4

Table 8-2. Weight fraction of branched compounds by carbon number in modeled SPK (CFR=1.5, anticipated wax, no pre-separation)

Carbon Number	Number of Branches					
	0	1	2	3	4	5
8	0	0	0	0	0	0
9	0.022103	0.036738	0	0	0	0
10	0.018213	0.042635	0.042635	0	0	0
11	0.013939	0.033849	0.033849	0.033849	0	0
12	0.007969	0.037958	0.037958	0.037958	0	0
13	0.001228	0.040116	0.040116	0.040116	0	0
14	0	0.030023	0.030023	0.030023	0.030023	0
15	0	0.029037	0.029037	0.029037	0.029037	0
16	0	0.026819	0.026819	0.026819	0.026819	0
17	0	0	0	0.026953	0.026953	0.026953
18	0	0	0	0	0.027198	0.027198

Table 8-3. Weight fraction of branched compounds by carbon number in modeled SPK (CFR=1, anticipated wax, no pre-separation)

Carbon Number	Number of Branches					
	0	1	2	3	4	5
9	0.027733	0	0	0	0	0
10	0.021972	0.051434	0.051434	0	0	0
11	0.015955	0.038745	0.038745	0.038745	0	0
12	0.008692	0.041405	0.041405	0.041405	0	0
13	0.001286	0.042014	0.042014	0.042014	0	0
14	0	0.030355	0.030355	0.030355	0.030355	0
15	0	0.028795	0.028795	0.028795	0.028795	0
16	0	0.022702	0.022702	0.022702	0.022702	0
17	0	0	0.022531	0.022531	0.022531	0.022531
18	0	0	0.006273	0.006273	0.006273	0.006273
19	0	0	0	0	0.006191	0.006191

Table 8-4. Net greenhouse gas emissions for combustion emissions

	100% Coal and 100% Natural Gas	93% Coal, 7% Switchgrass	85% Coal, 15% Switchgrass	75% Coal, 25% Switchgrass
Percentage of carbon from switchgrass	0	4.0%	9.0%	16%
GWP from combustion of SPK	70±1 g CO ₂ e / MJ	67±1 g CO ₂ e / MJ	64±1 g CO ₂ e / MJ	59±1 g CO ₂ e / MJ

8.4 References

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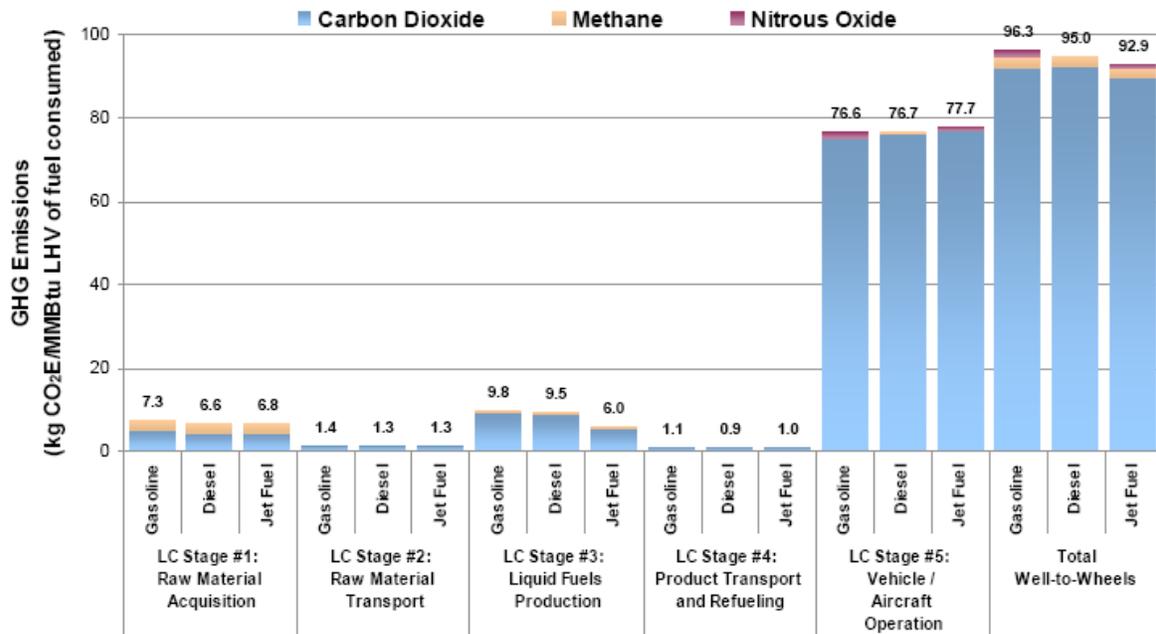
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CHAPTER 9: LIFE CYCLE PROFILES

2.1 Baseline fuel

Until recently, many analyses of aviation fuels have considered jet fuels to be similar in their greenhouse gas footprints to diesel fuels. This has been based on similarities in the lower boiling point of the two fuels. Using diesel as a basis leads to a central estimate of 95.0 kg CO₂e per million BTU of lower heating value of fuel provided [90.0 g CO₂/MJ], of which 81% (76.7 kg CO₂e/MMBTU LHV) is attributed to combustion (Skone and Gerdes, 2008). Use of the same methodology leads to a central estimate of 92.9 kg CO₂e/MMBTU LHV [88.1 g CO₂/MJ] for aviation fuel (slightly lower than diesel), of which 84% (77.7 kg CO₂e/MMBTU LHV) is attributed to combustion. The main difference between jet fuel and diesel in the NETL analysis is in the fuel refining and production stage. A summary of the NETL analyses is shown in Figure 9-1.

Figure 9-1. Summary of NETL life cycle greenhouse gas emission estimates, kg CO₂e per MMBtu LHV fuel consumed (Skone and Gerdes, 2008)



The NETL analysis of baseline jet fuel production does not include an uncertainty bound. A team led by MIT, analyzing much of the same data, arrives at a central estimate of 87.5 g CO₂e/MJ with combustion CO₂ emissions accounting for 73.2 g CO₂/MJ (84%). In characterizing the uncertainties in their estimates, for combustion emissions, the MIT team estimates that “combustion emissions for about 90 percent of Jet A falls within 1 percent of this figure.” They note “however, considerable variation in the well-to-tank estimate of 14.3 g CO₂e/MJ”. They estimate “a variation of up to 7 percent based primarily on the quality of the crude oil and how the jet fuel is refined. Specifically, the production of purely straight-run jet fuel in one extreme, and the production of jet fuel through various hydroprocessing steps in the other, will cause WTW GHG

emissions to range from a factor of 0.95 to 1.07 of those of the baseline case, respectively.” (Hileman et al., 2009)

Based on these analyses the baseline greenhouse gas emissions for jet fuel derived from petroleum will be assumed to be $87.5 \pm 5 \text{ g CO}_2/\text{MJ}$, with most of the uncertainty attributed to the sourcing of the petroleum and the emissions associated with refining the fuel.

Table 9-1. Global warming potential (GWPs), expressed as equivalent CO₂ emissions per megajoule of lower heating value (g CO₂e /MJ LHV), for the petroleum baseline fuel

	<i>Life cycle stage</i>		
	<i>Pre-combustion</i>	<i>Combustion</i>	<i>Total</i>
Petroleum baseline	14.3±4	73.2±1	87.5

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9.2 Natural gas to SPK

The synthetic paraffinic kerosene (SPK) fuel derived from natural gas resulted in a net greenhouse gas footprint approximately 80% higher than the petroleum baseline, as summarized in Table 9-2. Table 9-3 summarizes the analyses performed for the natural gas to SPK. Results are shown for the two processing scenarios outlined in Chapter 7 (Recycle and no-recycle).

Table 9-2. Global warming potential (GWPs), expressed as equivalent CO₂ emissions per megajoule of lower heating value (g CO₂e /MJ LHV), for the SPK fuel derived from natural gas

	<i>Life cycle stage</i>		
	<i>Pre-combustion</i>	<i>Combustion</i>	<i>Total</i>
Petroleum baseline	14.3±4	73.2±1	87.5
Natural Gas feedstock	84±10	70±1	154

Table 9-3. Summary of calculations of the Global warming potential (GWPs) for each stage in the fuel life cycle, for the SPK fuel derived from natural gas

RECYCLE CASE

<i>Data</i>	<i>Value</i>	<i>Calculation</i>	<i>Source</i>
LHV of SPK fuel	44.6 MJ/kg		Chapter 8
GWP SPK fuel combustion	70±1 g CO ₂ e /MJ		Chapter 8
GWP for upgrading of FT wax to produce 1 MJ (Table 7-13)	2.5 g CO ₂ e /MJ	Assumes wax described in Chapter 6, no pre-separation	Chapter 7
Cradle to gate GWP for FT wax (Table 6-6)	78 g CO ₂ e /MJ	Mass of wax required to produce 0.0224 kg SPK (1 MJ) is 0.0302 kg wax at 2.6 g CO ₂ e per g FT wax	Chapter 6
Total	150 g CO ₂ e /MJ		

NO RECYCLE CASE

<i>Data</i>	<i>Value</i>	<i>Calculation</i>	<i>Source</i>
LHV of SPK fuel	44.6 MJ/kg		Chapter 8
GWP SPK fuel combustion	70±1 g CO ₂ e /MJ		Chapter 8
GWP for upgrading of FT wax to produce 1 MJ (Table 7-13)	-1.3 g CO ₂ e /MJ	Assumes wax described in Chapter 6, no pre-separation	Chapter 7
Cradle to gate GWP for FT wax	90 g CO ₂ e /MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0346 kg wax at 2.6 g CO ₂ e per g FT wax	Chapter 6
Total	159 g CO ₂ e /MJ		

9.3 Coal to SPK

The synthetic paraffinic kerosene (SPK) fuel derived from coal resulted in a net greenhouse gas footprint approximately 180% higher than the petroleum baseline, as summarized in Table 9-4. Table 9-5 summarizes the analyses performed for the natural gas to SPK. Results are shown for the two processing scenarios outlined in Chapter 7 (Recycle and no-recycle).

Table 9-4. Global warming potential (GWPs), expressed as equivalent CO₂ emissions per megajoule of lower heating value (g CO₂e /MJ LHV), for the SPK fuel derived from coal

	<i>Life cycle stage</i>		
	<i>Pre-combustion</i>	<i>Combustion</i>	<i>Total</i>
Petroleum baseline	14.3±4	73.2±1	87.5
Coal feedstock	117±10	70±1	187

Table 9-5. Summary of calculations of the Global warming potential (GWPs) for each stage in the fuel life cycle, for the SPK fuel derived from coal

RECYCLE CASE

<i>Data</i>	<i>Value</i>	<i>Calculation</i>	<i>Source</i>
LHV of SPK fuel	44.6 MJ/kg		Chapter 8
GWP SPK fuel combustion	70±1 g CO ₂ e /MJ		Chapter 8
GWP for upgrading of FT wax to produce 1 MJ (Table 7-13)	2.5 g CO ₂ e /MJ	Assumes wax described in Chapter 6, no pre-separation	Chapter 7
Cradle to gate GWP for FT wax (Table 6-6)	109 g CO ₂ e /MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0302 kg wax at 3.6 g CO ₂ e per g FT wax	Chapter 6
Total	181 g CO ₂ e /MJ		

NO RECYCLE CASE

<i>Data</i>	<i>Value</i>	<i>Calculation</i>	<i>Source</i>
LHV of SPK fuel	44.6 MJ/kg		Chapter 8
GWP SPK fuel combustion	70±1 g CO ₂ e /MJ		Chapter 8
GWP for upgrading of FT wax to produce 1 MJ (Table 7-13)	-1.3 g CO ₂ e /MJ	Assumes wax described in Chapter 6, no pre-separation	Chapter 7
Cradle to gate GWP for FT wax (Table 6-6)	125 g CO ₂ e /MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0346 kg wax at 3.6 g CO ₂ e per g FT wax	Chapter 6
Total	193 g CO ₂ e /MJ		

9.3 Coal/Biomass mixtures to SPK

The synthetic paraffinic kerosene (SPK) fuel derived from coal/biomass mixtures resulted in a net greenhouse gas footprint approximately 100-150% higher than the petroleum baseline, as summarized in Table 9-6. Tables 9-7 to 9-9 summarize the analyses performed for the three feed mixtures. As in previous sections, results are shown for the two processing scenarios outlined in Chapter 7 (Recycle and no-recycle). However, in addition, in Tables 9-7 through 9-9, a sensitivity analysis is performed that examines the effect of introducing a greenhouse gas credit for switchgrass production, due to land use changes and other consequential impact (see discussion in Chapter 3). These credits reduce the greenhouse gas footprint of the biomass/coal mixtures. The effect scales with the fraction of biomass.

Table 9-6. Summary of calculations of the Global warming potential (GWPs) for each stage in the fuel life cycle, for the SPK fuel derived from coal/biomass mixtures (in g CO₂e/MJ LHV)

	<i>Life cycle stage</i>		
	<i>Pre-combustion</i>	<i>Combustion</i>	<i>Total</i>
Petroleum baseline	14.3±4	73.2±1	87.5
93% Coal 7% switchgrass	111±15	67±1	178
85% Coal 15% switchgrass	101±15	64±1	165
75% Coal 25% switchgrass	85±20	59±1	144

Table 9-7. Summary of calculations of the Global warming potential (GWPs) for each stage in the fuel life cycle, for the SPK fuel derived from 93% coal

**93% COAL/7% SWITCHGRASS
RECYCLE CASE**

<i>Data</i>	<i>Value</i>	<i>Calculation</i>	<i>Source</i>
LHV of SPK fuel	44.6 MJ/kg		Chapter 8
GWP SPK fuel combustion	67±1 g CO ₂ e/MJ		Chapter 8
GWP for upgrading of FT wax to produce 1 MJ (Table 7-13)	2.5 g CO ₂ e /MJ	Assumes wax described in Chapter 6, no pre-separation	Chapter 7
Cradle to gate GWP for FT wax (Table 6-6)	103 g CO ₂ e/MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0302 kg wax at 3.4 g CO ₂ e per g FT wax	Chapter 6
Total	172 g CO ₂ e/MJ		
Cradle to gate GWP for FT wax including switchgrass consequential credit	100 g CO ₂ e/MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0302 kg wax at 3.3 g CO ₂ e per g FT wax	Chapters 3,6
Total	169 g CO ₂ e/MJ		

NO RECYCLE CASE

<i>Data</i>	<i>Value</i>	<i>Calculation</i>	<i>Source</i>
LHV of SPK fuel	44.6 MJ/kg		Chapter 8
GWP SPK fuel combustion	67±1 g CO ₂ e/MJ		Chapter 8
GWP for upgrading of FT wax to produce 1 MJ (Table 7-13)	-1.3 g CO ₂ e /MJ	Assumes wax described in Chapter 6, no pre-separation	Chapter 7
Cradle to gate GWP for FT wax (Table 6-6)	118 g CO ₂ e/MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0346 kg wax at 3.4 g CO ₂ e per g FT wax	Chapter 6
Total	183 g CO ₂ e/MJ		
Cradle to gate GWP for FT wax including switchgrass consequential credit	114 g CO ₂ e/MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0346 kg wax at 3.3 g CO ₂ e per g FT wax	Chapters 3,6
Total	179 g CO ₂ e/MJ		

Table 9-8. Summary of calculations of the Global warming potential (GWPs) for each stage in the fuel life cycle, for the SPK fuel derived from 85% coal

**85% COAL/15% SWITCHGRASS
RECYCLE CASE**

<i>Data</i>	<i>Value</i>	<i>Calculation</i>	<i>Source</i>
LHV of SPK fuel	44.6 MJ/kg		Chapter 8
GWP SPK fuel combustion	64±1 g CO ₂ e/MJ		Chapter 8
GWP for upgrading of FT wax to produce 1 MJ (Table 7-13)	2.5 g CO ₂ e /MJ	Assumes wax described in Chapter 6, no pre-separation	Chapter 7
Cradle to gate GWP for FT wax (Table 6-6)	94 g CO ₂ e/MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0302 kg wax at 3.1 g CO ₂ e per g FT wax	Chapter 6
Total	160 g CO ₂ e/MJ		
Cradle to gate GWP for FT wax including switchgrass consequential credit	85 g CO ₂ e/MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0302 kg wax at 2.8 g CO ₂ e per g FT wax	Chapters 3,6
Total	151 g CO ₂ e/MJ		

NO RECYCLE CASE

<i>Data</i>	<i>Value</i>	<i>Calculation</i>	<i>Source</i>
LHV of SPK fuel	44.6 MJ/kg		Chapter 8
GWP SPK fuel combustion	64±1 g CO ₂ e/MJ		Chapter 8
GWP for upgrading of FT wax to produce 1 MJ (Table 7-13)	-1.3 g CO ₂ e /MJ	Assumes wax described in Chapter 6, no pre-separation	Chapter 7
Cradle to gate GWP for FT wax (Table 6-6)	107 g CO ₂ e/MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0346 kg wax at 3.1 g CO ₂ e per g FT wax	Chapter 6
Total	170 g CO ₂ e/MJ		
Cradle to gate GWP for FT wax including switchgrass consequential credit	97 g CO ₂ e/MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0346 kg wax at 2.8 g CO ₂ e per g FT wax	Chapters 3,6
Total	160 g CO ₂ e/MJ		

Table 9-9. Summary of calculations of the Global warming potential (GWPs) for each stage in the fuel life cycle, for the SPK fuel derived from 75% coal

**75% COAL/25% SWITCHGRASS
RECYCLE CASE**

<i>Data</i>	<i>Value</i>	<i>Calculation</i>	<i>Source</i>
LHV of SPK fuel	44.6 MJ/kg		Chapter 8
GWP SPK fuel combustion	59±1 g CO _{2e} /MJ		Chapter 8
GWP for upgrading of FT wax to produce 1 MJ (Table 7-13)	2.5 g CO _{2e} /MJ	Assumes wax described in Chapter 6, no pre-separation	Chapter 7
Cradle to gate GWP for FT wax (Table 6-6)	79 g CO _{2e} /MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0302 kg wax at 2.6 g CO _{2e} per g FT wax	Chapter 6
Total	140 g CO_{2e}/MJ		
Cradle to gate GWP for FT wax including switchgrass consequential credit	63 g CO _{2e} /MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0302 kg wax at 2.1 g CO _{2e} per g FT wax	Chapters 3,6
Total	124 g CO_{2e}/MJ		

NO RECYCLE CASE

<i>Data</i>	<i>Value</i>	<i>Calculation</i>	<i>Source</i>
LHV of SPK fuel	44.6 MJ/kg		Chapter 8
GWP SPK fuel combustion	59±1 g CO _{2e} /MJ		Chapter 8
GWP for upgrading of FT wax to produce 1 MJ (Table 7-13)	-1.3 g CO _{2e} /MJ	Assumes wax described in Chapter 6, no pre-separation	Chapter 7
Cradle to gate GWP for FT wax (Table 6-6)	90 g CO _{2e} /MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0346 kg wax at 2.6 g CO _{2e} per g FT wax	Chapter 6
Total	148 g CO_{2e}/MJ		
Cradle to gate GWP for FT wax including switchgrass consequential credit	73 g CO _{2e} /MJ	Mass of wax required to produce 0.0224 kg SPK is 0.0346 kg wax at 2.1 g CO _{2e} per g FT wax	Chapters 3,6
Total	131 g CO_{2e}/MJ		

9.4 References

Hileman, J.I., Ortiz, D.S., Bartis, J.T., Wong, S.M., Donohoo, P.E., Weiss, M.A., Waitz, I.A., Near-Term Feasibility of Alternative Jet Fuels, Technical Report by the MIT Partnership for Air Transportation Noise and Emission Reduction (PARTNER) and RAND, accessed at <http://web.mit.edu/aeroastro/partner/reports/index.html> , November 20, 2009.

DRAFT

CHAPTER 10: SUMMARY

10.1 Overview

The US Air Force is currently assessing the use of Fischer-Tropsch fuels, blended with conventional jet fuel, as aircraft fuel. However, a potential barrier to the use of Fischer-Tropsch (FT) fuels is the greenhouse gas emissions associated with their manufacture. As described in Chapter 1, emerging guidelines for procurement of fuels place limits on the life cycle greenhouse gas emissions for fuels purchased by the US federal government. Using methodologies recommended by an Aviation Fuel Life Cycle Assessment Working Group assembled by the US Air Force Aviation (Group member names are provided in Chapter 2), this report has described estimates of life cycle greenhouse gas emissions for FT aviation fuels made from three types of processes:

- 1) Steam methane reforming followed by FT wax production (cobalt catalyst) and upgrading (US average natural gas as a feed)
- 2) Coal (Kittanning #6 coal) gasification followed by FT wax production (cobalt catalyst) and upgrading
- 3) Coal/Biomass (mixtures of switchgrass and Kittanning #6 coal) gasification followed by FT wax production (cobalt catalyst) and upgrading

These greenhouse gas emission estimates were compared to a petroleum baseline fuel. The results, for greenhouse gas emissions that can be attributed directly to the fuel life cycle, are summarized in Table 10-1. The calculations leading to these assessments are provided in Chapter 9.

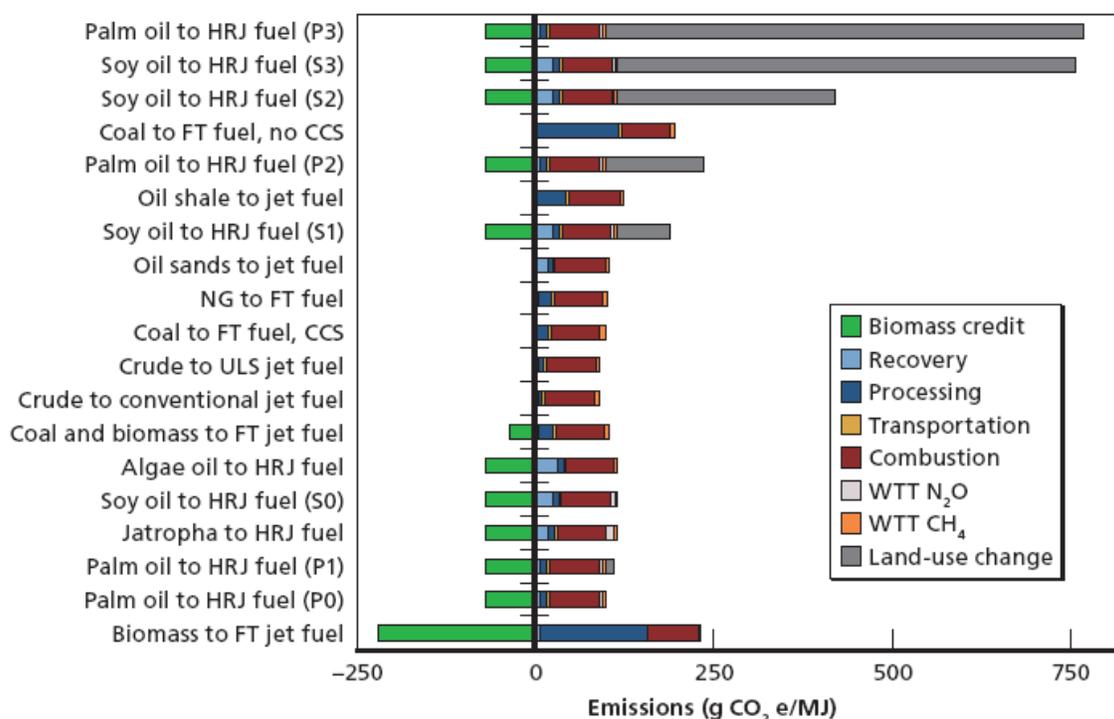
Table 10-1. Global warming potentials (GWPs), expressed as equivalent CO₂ emissions per megajoule of lower heating value (g CO₂e/MJ LHV), for each stage in the fuel life cycle, for Fischer-Tropsch fuels

	<i>Life cycle stage</i>		
	<i>Pre-combustion</i>	<i>Combustion</i>	<i>Total</i>
Petroleum baseline	14.3±4	73.2±1	87.5
Natural Gas feedstock	84±10	70±1	154
Coal feedstock	117±10	70±1	187
93% Coal 7% switchgrass	111±15	67±1	178
85% Coal 15% switchgrass	101±15	64±1	165
75% Coal 25% switchgrass	85±20	59±1	144

The results summarized in Table 10-1 indicate that the greenhouse gas footprints of natural gas derived Fischer-Tropsch fuels are approximately 80% larger than the petroleum baseline; coal derived Fischer-Tropsch fuels have greenhouse gas footprints that are 110% larger than the petroleum baseline. Mixing biomass with coal has a moderate impact on the greenhouse gas footprint directly attributed to fuel production, decreasing the footprint by about 1% for each 1% of biomass added to the feed. The emission estimates are reduced further if indirect effects are considered.

These estimates are reasonably consistent with previous analyses performed for Fischer-Tropsch processing directly yielding liquid fuels (iron catalyst). For example, Figure 1-1 showed that in its evaluation of Fischer-Tropsch fuels for the renewable Fuel standard, the US EPA estimated that coal based Fischer-Tropsch diesel fuels would have a footprint 118% larger than petroleum based diesel. As shown in Figure 10-1, an analysis from MIT produced greenhouse gas emission estimates for a range of processes that included production of jet fuel from coal using a Fischer-Tropsch synthesis. The estimates for natural gas derived FT fuels are somewhat lower footprints than calculated in this work. However, this might be due primarily to the method of taking displacement credits (rather than co-product allocation credits) for co-products in this analysis.

Figure 10-1. (Hileman et al., 2009)
Baseline Life-Cycle Greenhouse-Gas Emissions for Jet-Fuel Pathways



10.2 Uncertainties

The two largest uncertainties in the greenhouse gas emission estimates produced in this work are (1) the method of addressing indirect impacts of biomass production, and (2) the yields of SPK from the coupled Fischer-Tropsch synthesis/upgrading reactions.

It has become increasingly common to include indirect (consequential, see Chapter 2) greenhouse gas emissions associated with production of biomass in life cycle greenhouse gas assessments of fuels. There are very large uncertainties associated with these emissions, but if a recent estimate for indirect impacts associated with switchgrass production, based on data from the US EPA's Draft Regulatory Impact Assessment for the Renewable Fuel Standard, is included in the assessment, then the greenhouse gas footprint of mixed biomass/coal derived fuels decreases by up to 15% (for 25% biomass feed). This value is highly uncertain, however, and

other assessments have used much larger values for this credit. Figure 10-1, for example, shows a very large biomass credit in the MIT analysis (Hileman et al., 2009) of biomass to FT jet.

Overall, the greatest process uncertainty associated with the greenhouse gas footprint of FT derived fuels is the yield of desirable hydrocarbons from the FT synthesis. The chemistry of coal/biomass gasification, coupled with FT synthesis, produces more than one mole of CO₂ for every mole of carbon converted to a liquid fuel (see Chapter 6), making the carbon efficiency of the process (conversion of carbon in the feed into carbon in liquid fuel) less than 50%. This fundamental limitation is the primary factor causing the footprint of FT fuels to be greater than the footprint of petroleum fuels.

10.3 Recommendations

This report has provided estimates of greenhouse gas emissions associated with FT aviation fuel production. Based on the magnitudes of these estimates, and the uncertainties in the data supporting the estimates, the following future work is suggested:

- Perform detailed process modeling of the coupled FT synthesis/upgrading process, complemented to the extent possible by research unit process data. This modeling should systematically examine the impact of various light hydrocarbon, hydrogen, synthesis gas, and heavy end recycle strategies and process integration decisions on desirable product yields.
- Examine the impact of co-product allocation procedures, particularly for the co-products associated with wax upgrading; this work used displacement calculations. Mass and energy based calculations/assumptions should also be examined.
- Examine additional assumptions/sensitivity analyses for different estimates of indirect (consequential) biomass emissions.

10.4 References

Hileman, J.I., Ortiz, D.S., Bartis, J.T., Wong, S.M., Donohoo, P.E., Weiss, M.A., Waitz, I.A., Near-Term Feasibility of Alternative Jet Fuels, Technical Report by the MIT Partnership for Air Transportation Noise and Emission Reduction (PARTNER) and RAND, accessed at <http://web.mit.edu/aeroastro/partner/reports/index.html> , November 20, 2009.