

Multi-Criteria Lifecycle Evaluation of Transportation Fuels Derived from Biomass Gasification
by
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B.S. Mathematics, B.A. Chemistry
University of Iowa, 2007

Submitted to the Engineering Systems Division and
the Department of Mechanical Engineering
in partial fulfillment of the requirements for the degrees of

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and
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ABSTRACT

The development of a domestic biofuel industry has been a major policy thrust of the United States federal government in the first decade of the 21st century. Cellulosic biofuels have been identified as the primary candidate for meeting long term sustainability and energy security goals. In this thesis potential cellulosic biofuels produced via thermochemical processing are analyzed. Thermochemical processing utilizes well established chemical synthesis technology and allows for both feedstock and product flexibility relative to traditional enzymatic biofuel production routes. In this thesis both Spark Ignition Engine fuels (Methanol, Ethanol, Mixed Alcohols, and Methanol-to-Gasoline Synthetic Gasoline) and Compression Ignition Engine fuels (Dimethyl Ether and Fischer-Tröpsch Diesel).

The abovementioned fuels are analyzed on a lifecycle basis with respect to identified criteria affecting each fuels adoptability including: (1) energy efficiency, (2) cost of production and shipping, (3) integrability into the current distribution infrastructure and (4) compatibility with regulatory and policy landscape. A primary conclusion from this analysis is that no one fuel is optimal with respect to all metrics. Instead, it is likely that a variety of fuels should be employed for different applications.

The US biofuel policy landscape is also analyzed in this thesis. It is found that the criteria above are not currently weighed in fuel adoption policies and instead parochial interests have carried more weight in the development of the US biofuel industry in which ethanol is the de facto fuel of choice. Therefore, it is likely to be difficult for a non-ethanol cellulosic biofuel industry to develop without major policy changes.

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TABLE OF CONTENTS

Table of Tables	6
Table of Figures	8
Chapter 1: Introduction	9
Chapter 2: Methodology	15
Life Cycle Energy Efficiency Analyses	15
Integrability of Fuels into Distribution Infrastructure	18
Life Cycle Economic Assessment	19
Compatibility with Regulatory and Policy Landscape	19
Other Systemic Considerations	19
Summary	20
Chapter 3: Biomass Gasification fuel system description	21
Spark Ignition Engine Fuels	22
Compression Ignition Engine Fuels	27
Biomass to Liquid Fuel Production System	30
Distribution	50
End Use	51
Chapter 4: Biomass Gasification Fuel System Analysis	53
Production Efficiency	53
Production Economics	66
Distribution Integrability	71
Distribution Efficiency	74
Distribution Economics	76
End Use Efficiency	78
End Use Economics	86
End Use Regulation and Policy	86
Systemic Environmental and Toxicological Considerations	90
Chapter 5: Results and Discussion	99
Summary of System Analysis	99
Policy Challenges: The Entrenchment of Ethanol	109
Chapter 6: Conclusions and Policy Recommendations	115
Conclusions from System Analysis	115
Policy Recommendations	119
Supporting Innovation without Picking Winners	119
Addressing Oxygenate Standards	121
Addressing Ethanol's Subsidized Feedstock	122
References	125
Table of Appendices	135
Appendix A: Acronyms	136
Appendix B: Tag cloud	137

TABLE OF TABLES

Table 1 - Physical and chemical properties of spark ignition engine fuels analyzed in this thesis.	27
Table 2 - Critical Constants of Dimethyl Ether, Propane, and n-Butane (adapted from Perry's Handbook 7th Edition 2007).....	28
Table 3 - Summary of physical and chemical properties of compression ignition engine fuels considered in this thesis.	30
Table 4 - Theoretic optimum H ₂ :CO ratios for synthesis.....	36
Table 5 - Miscibility and heating value of fuels (Perry and Green 1997).	51
Table 6 - Characteristics of biomass gasifiers adapted from (Williams et al. 1995, 18).....	58
Table 7 – Biomass to methanol production characteristics, adapted from (Williams et al. 1995, 18).	61
Table 8 - Summary of syngas to fuel production efficiencies of different fuels as taken from literature.	65
Table 9- Biomass to fuel conversion efficiencies, assuming a biomass gasification efficiency of 80%.	66
Table 10 - Natural gas to fuel conversion efficiency assuming a natural gas gasification efficiency of 90%.	66
Table 11 - Summary of costs of production in 2007 dollars.....	70
Table 12 - Celanese Canada methanol shipment analysis, adapted from (Short 1994, 215).....	71
Table 13 - Energy efficiency of transportation per 1000km.....	75
Table 14 - Half lives of common fuel components, adapted from (Howard 1991).....	94
Table 15 - Half-life of MTBE in various environmental media.	96
Table 16 - Vapor pressure change from pure gasoline for alcohol-gasoline mixtures. Adapted from (Pumphrey, Brand, and Scheller 2000, 1405-1411).....	98
Table 17 – Biomass-to-Wheel utilization efficiency of fuels plus or minus 3 standard deviations utilizing different distribution systems. These efficiencies are resultant from the consideration of current end-use technology. The highlighted efficiency values indicate that these values are unattainable due to current integrability limitations.	100
Table 18 – Biomass-to-Tank utilization efficiency of fuels plus or minus 3 standard deviations. The highlighted efficiency values indicate that these values are unattainable due to current integrability limitations.	101
Table 19 - The cost of production for fuels given in 2007 dollars per gigajoule. ¹ Katofsky 1993, ² Spath and Dayton 2003, ³ Kumabe et al. 2008, ⁴ Phillips et al. 2007, ⁵ Lynd 1996, ⁶ estimated from Sugiyama 1994, ⁷ Hamelinck and Faaij 2008.....	103
Table 20 - The cost of production for fuels given in 2007 dollars per liter. ¹ Katofsky 1993, ² Spath and Dayton 2003, ³ Kumabe et al. 2008, ⁴ Phillips et al. 2007, ⁵ Lynd 1996, ⁶ estimated from Sugiyama 1994, ⁷ Hamelinck and Faaij 2008.....	104
Table 21 - The cost of production for fuels given in 2007 dollars per gallon. ¹ Katofsky 1993, ² Spath and Dayton 2003, ³ Kumabe et al. 2008, ⁴ Phillips et al. 2007, ⁵ Lynd 1996, ⁶ estimated from Sugiyama 1994, ⁷ Hamelinck and Faaij 2008.....	104
Table 22 - Cost of shipping fuel 1000km via the most economically viable method. Alcohols and DME are calculated using rail; MTG and FTD are calculated for pipeline. These data are extrapolated from (Morrow, Griffin, and Matthews 2006, 2877-2886)	105

Table 23 – Summary of fuel integrability for different distribution infrastructures. Y indicates it is, N indicates that the fuel is not, and Y/N indicates ambiguity..... 106
Table 24 - Summary of emissions properties relative to petroleum derived counterpart (gasoline or diesel)..... 107
Table 25 - Tabulation of health and environmental risks associated with fuels considered in this thesis. 108

TABLE OF FIGURES

Figure 1 - Planned Cellulosic Biofuel Production Capacity compared to the RFS mandate in EISA adapted from (McAulay 2009)..... 11

Figure 2 - Flow diagram of the transportation fuels consisting of three main energy conversion steps: (1)Fuel Production, (2) Fuel Distribution and (3) End-Use..... 16

Figure 3 - A generalized flow diagram of thermochemical biofuel production, each of the process steps are part of three main steps 1) Pre-processing 2)syn-gas production, and 3)Fuel Production. 31

Figure 4 - Mixed alcohol product distribution of different production schemes. The data is adapted from (Phillips et al. 2007)..... 42

Figure 5 - Mixed alcohol product distribution of different production schemes (molar basis), adapted from (Phillips et al. 2007)..... 43

Figure 6 - Weibull distributions fit to the molar product distributions..... 44

Figure 7 - Mixed alcohol product distribution in an energy basis. 45

Figure 8 - ASF Model of FT Synthesis Products, adapted from (Probstein and Hicks 1982)..... 48

Figure 9 - Energy efficiency of transporting fuel 1000km by mode. 74

Figure 10 - Distribution costs adapted from (Takeshita, Yamaji, and Fujii 2006, 285; Takeshita and Yamaji 2008, 2773-2784; Vallentin 2008, 3198-3211). 77

Figure 11 - Dependence of AKI (Octane Number) on the oxygen content of 10% mixed-alcohol/gasoline blended fuel adapted from (Gautam and Martin II 2000, 497-511). 82

Figure 12 - Dependence of AKI (ON) on average alcohol carbon chain length of mixed alcohol in a 10% mixed-alcohol/gasoline blended fuel adapted from (Gautam and Martin II 2000, 497-511). 83

Figure 13 - Oral LD50 values of fuels and common substances. 92

Figure 14 - Inhalation LD50 values of fuels and common substances. 92

Figure 15 - Dermal LD50 values of fuels and common substances. 93

Figure 16 - Half lives of common fuel components in certain media. 95

Figure 17 - Plot of the Biomass-to-Wheel results in Table 17. The averages and standard deviations resultant from Monte Carlo analyses are used to generate normal distributions for plotting. 100

Figure 18 - The Biomass to Tank utilization efficiencies are plotted as normal distributions utilizing the averages and standard deviations derived from Monte Carlo analysis..... 102

CHAPTER 1: INTRODUCTION

On January 23rd, 2007 former President George W. Bush called for the United States (US) Congress to enact legislation requiring the United States of America to decrease its consumption of gasoline by 20 percent within ten years (Bush 2007). In December 2007, the Congress passed the Energy Independence and Security Act (EISA) requiring an annual production of 36 billion gallons of renewable fuel in 2022, with production ramping up to this level over the interim years (Rahall 2007, 110-140). At this time, the average daily consumption of gasoline in the US was 390 million gallons, totaling to more than 142 billion gallons per year (EIA 2009, 1-1). The yearly production of alternative fuels (approximately 98% ethanol) was estimated to be a little more than 9 billion gallons in 2008 (Dinneen 2008), which displaced only 6 billion gallons of gasoline (approximately 4% of yearly gasoline consumption) due to ethanol's lower energy density. For this 4% displacement of gasoline consumption, more than 4 billion bushels of corn is required to produce the requisite ethanol. With a total production of 14 billion bushels of corn in 2008; this is nearly 30% of US corn production.

If all 14 billion bushels of annual corn production were used to produce ethanol with today's conversion technology, only 32 billion gallons of ethanol (22 billion gallons of gasoline equivalent (GGE)) could be produced annually. This would only displace 14% of today's gasoline consumption, and not meet the 36 billion gallon annual production goal set forth by the EISA. Due to the limited amount of corn available for alternative fuel production, and the concern of increasing food costs, the need for alternative feedstocks is apparent. In order to address these concerns, Congress mandated in the EISA that in 2022, 21 billion gallons of the mandated 36 billion gallons of biofuel production must come from non-corn feedstocks, and of this amount, 16 billion gallons must come from ligno-cellulosic feedstocks. In order to meet this production goal, cellulosic biofuel production must begin in the near term and ramp up to the 2022 goal.

It is important to note that meeting this goal is not limited by the availability of biomass. If we use the USDA/DOE "Billion Ton Study" (Perlack et al. 2005) and take 1 billion tons dry as a reasonable estimate of the biomass resource in the US, then we can estimate the volumetric production of a fuel using the following formula.

$$V_{fuel} \approx \frac{\eta_{production}}{LHV_{fuel} \rho_{fuel}} \times LHV_{biomass} \times m_{biomass} \quad \text{Eq. (1)}$$

Where V_{fuel} is the total volume of annual fuel production, $\eta_{production}$ is the thermodynamic efficiency of fuel production, LHV_{fuel} is the lower heating value of the fuel, ρ_{fuel} is the density of the fuel, $LHV_{biomass}$ is the lower heating value of the biomass, and $m_{biomass}$ is the total mass of the annual biomass harvest. Using an estimate of 1 billion tons of biomass with a lower heating value of approximately 18MJ/kg, overall estimates of scope can be estimated for different fuels. If we assume a conversion efficiency of approximately 45% to ethanol (density of 0.785 kg/L, and LHV of ~27) via thermochemical production we find that the scope of potential production is 92 billion gallons of ethanol per year, much larger than the target level of 36 billion gallons per year. The efficiency of production for fuels is considered in depth in Chapter 4.

Even though there has been much focus on the development and deployment of biologically produced cellulosic biofuels, as shown in Figure 1, there is little hope that the US will meet the Renewable Fuel Standard (RFS) mandate put forth in the EISA for cellulosic biofuel production. Figure 1 shows the mandated cellulosic biofuel production goal plotted against time. Additionally the current pilot production and (ambitiously) projected full scale-up potential of production between the years 2015 and 2016 still show that the industry will fall short of the mandate in the coming decade (McAulay 2009).

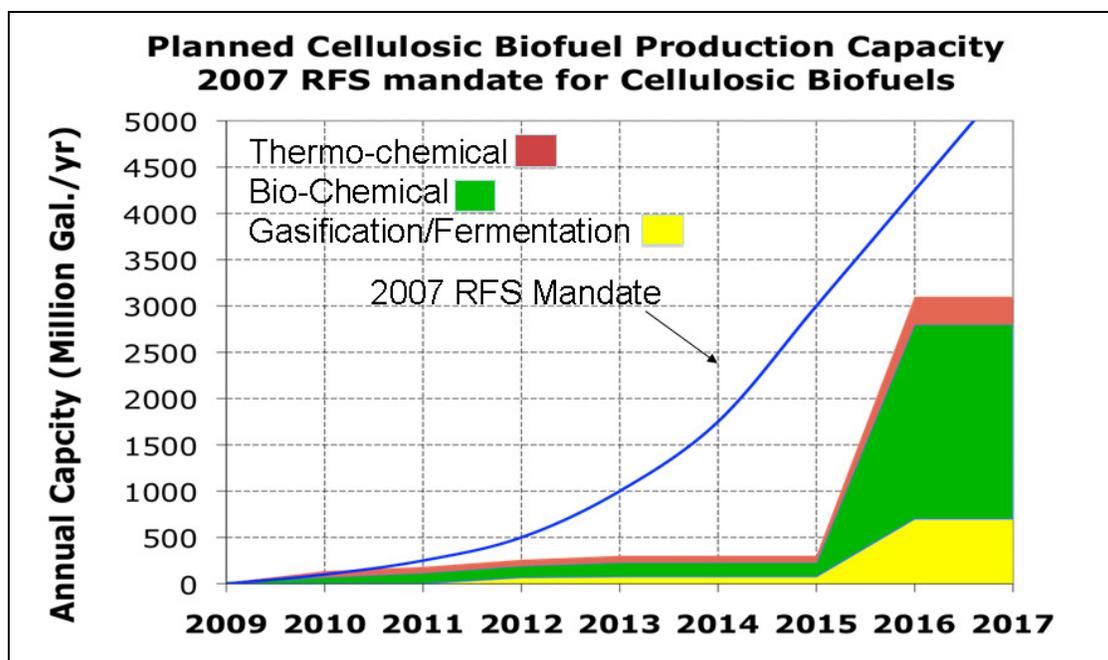


Figure 1 - Planned Cellulosic Biofuel Production Capacity compared to the RFS mandate in EISA adapted from (McAulay 2009).

Currently, the United State’s alternative fuel industry is dominated by ethanol. This is due, in no small part, to the ethanol industries successful procurement of advantageous policies which not only prop up its economic viability but also create barriers to entry for other non-ethanol fuels. The incentives driving ethanol production, largely the Volumetric Ethanol Excise Tax Credit (VEETC) also known as the Blenders’ Tax Credit, have also created additional incentive for Research and Development (R&D) into ways to produce ethanol from cellulosic materials instead of more general R&D into other possible fuels such as Fischer-Tröpsch Diesel which do not enjoy the same governmental policy support.

The largest and most noticeable effort to produce cellulosic fuels is currently in the realm of biological processing. Under this paradigm, it is envisioned that specialized microbes will be developed to break down each of the specific plant materials that make up ligno-cellulosic feedstocks (cellulose, hemicellulose, and lignin). This, however, is proving to be challenging and limited by what specialized microbes can digest (Brown 2007, 947-956). Currently, there are no microbes or enzymes which efficiently break down lignin, thus the lignin cannot be processed into useable products. Further, the use of this production method could ultimately depress the

economic viability of biofuel producers because they would be limited to certain feedstocks for which a specific biological process is designed.

Another approach being considered for biofuel production is based on thermochemical processing methods. In this approach, gasification technology is used to produce a homogenous intermediate 'syn-gas' (a mixture of carbon monoxide (CO) and hydrogen (H₂)) which is then used to produce a range of chemicals via catalytic conversions. This method offers the distinct advantage of being indiscriminant to feedstock; in particular lignin, which cannot be utilized by biological conversion methods, can be converted into fuels greatly increasing the amount of usable biomass energy. Though the ratio of CO to H₂ may vary depending on feedstock, there is a well defined technology (the water-gas shift) commonly used to adjust this ratio in downstream processing steps.

There is work currently devoted to the development of ethanol production in this manner. The Department of Energy, through the National Renewable Energy Laboratory (NREL), has performed a study of the feasibility of thermochemical ethanol production (Phillips et al. 2007). Range Fuels, a private company, announced in 2008, plans to build a large scale thermochemical ethanol plant in Georgia, USA using woody biomass wastes.

In order to produce ethanol from syngas, a modified Fischer-Tröpsch (FT) catalyst is used to produce a mixture of straight-chain aliphatic alcohols (C₁-C₅+; i.e. methanol, ethanol, propanol, butanol, pentanol, etc.). This product is then separated; the methanol is recycled into the reactor in order to boost higher alcohol production, ethanol is sold into a fuel market, and the higher alcohols are sold as byproducts. In the NREL model, ethanol only accounts for approximately 70% by weight of the product stream. Thus, due to the need of separation and processing steps, and the existence of byproducts, a significant fraction of the available energy content of the biomass is not utilized as a fuel.

There are other fuels, however, each with different physical and chemical properties that may be taken advantage of. Two such fuels are methanol and dimethyl ether. Due to their molecular simplicity, their production is much simpler than that of ethanol, and involves fewer byproducts and higher selectivity. Other possible fuels are higher mixed alcohols, Fischer-Tröpsch Diesel

(FTD), and synthetic gasoline as typified by Mobil methanol-to-gasoline (MTG) fuel, also known as Mobile-M product.

As will be further discussed in this thesis, it is largely the technology specific biofuel policies in the US which are driving over-investment and R&D into ethanol production routes and under-investment into alternatives. An illustration of this is the comparison of the two most advanced and promising thermochemical biofuel production facilities Range Fuels, based in the US, and Choren, based in Germany. Range Fuels is attempting to produce ethanol via mixed alcohol production, and Choren is planning to produce Fischer-Tröpsch Diesel (Osterreichische BauernZeitung 2009). It is likely that the choice of fuel at each of these facilities is dictated more by the energy policies and tax incentives in each of the countries and less by the systemic performance characteristics of each fuel.

Ideally, the choice of alternative transportation fuels would be made by consideration of the technological aspects along with the other systemic performance characteristics, and the economics would be made viable by taxing lesser desired petroleum derived fuel. In this thesis a life cycle system analysis methodology is developed and applied to consider thermochemical biofuel production and utilization. In Chapter 2 the methodology used to analyze potential thermochemically produced biofuels is introduced along with the criteria which will be used to compare their systematic characteristics. In Chapter 3 the potential fuels are described along with the characteristics of their production, distribution and end use. In Chapter 4 the fuel systems are analyzed per the methodology introduced in Chapter 2. The results are summarized and discussed in Chapter 5 along with the major policy challenges which new fuels face. Finally in Chapter 6 conclusions are summarized and policy recommendations are drawn.

CHAPTER 2: METHODOLOGY

For an alternative fuel to be accepted into the current transportation fuel infrastructure, it must meet a number of criteria including 1) high energy conversion efficiencies, 2) integrability into the current fuel distribution infrastructure, 3) economic competitiveness, and 4) compatibility with current regulation and policy. As such, each of the criteria must be weighed in determining the likely-hood of an alternative fuel being adopted. The analytical approaches used in this thesis to assess each of these criteria are detailed in this chapter.

Life Cycle Energy Efficiency Analyses

In order to evaluate the relative energetic efficiencies of potential fuels, this thesis employs a thermodynamic life cycle analysis. The first law of thermodynamics is the formalization of the principle of conservation of energy stating that energy cannot be created or destroyed. This principle can be applied to individual energy conversion steps to account for energy flows and to determine the efficiency of an energy conversion. Additionally, the first law can be generalized and applied to a system of multiple energy conversion steps to yield the overall system efficiency. The first law efficiency of an energy conversion is defined as the ratio of energy in the desired product over the energy input into the conversion. The life cycle analysis is performed by treating each of the major steps (fuel production, fuel distribution, automotive end use) as individual energy conversion steps and integrating the first law efficiencies of each. The first law analyses for each step of a given fuel's life are drawn from data for the major energy conversion steps such as gasification, fuel synthesis, and use in an internal combustion engine. In order to best capture the efficiency of each step in the fuel chain, the analysis will consider useful energy out to include only the targeted product (i.e. in the case of fuel production, the energetic content of byproducts will not be considered as an energetic output, but as a loss). The energy in, however, encompasses all of the energy inputs (i.e. for fuel production, in addition to the biomass feedstock being processed, additional heat and electricity inputs purchased from local utilities are considered). The ancillary energetic costs of constructing the plant and other peripheral activities are not included since these activities are required regardless of the fuel

considered. Below is a generalized flow diagram of the fuel cycles considered (see Figure 2). The methods for the analysis of each of these energy conversion steps are discussed below.

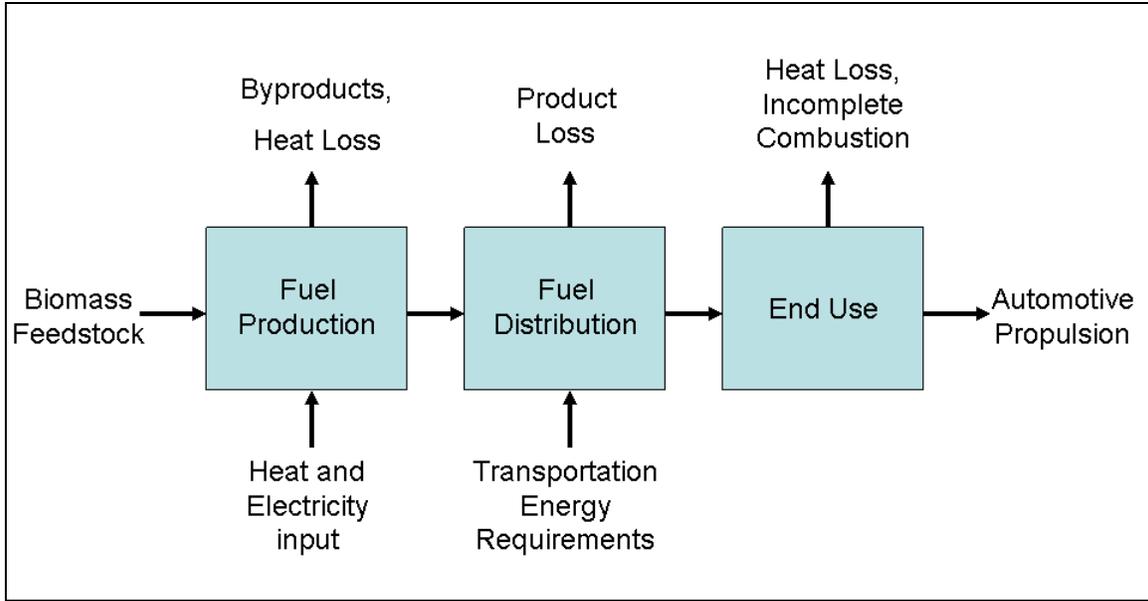


Figure 2 - Flow diagram of the transportation fuels consisting of three main energy conversion steps: (1) Fuel Production, (2) Fuel Distribution and (3) End-Use.

Energetic Analysis of Fuel Production

The major energy inputs for industrial fuel production via biomass gasification are the biomass feedstock, heat (in the form of steam) and electricity. The major energy outputs are the fuel being produced, heat-loss due to inefficiencies and the enthalpy content of by-products. Upon application of an energy balance to determine the first law efficiency of the production step a formulation for the first law conversion efficiency is derived.

$$\eta_{1, fuel_production} = \frac{(m_{out} LHV_{fuel})_{product}}{m_{in} LHV_{biomass} + Elec_{in} + Q_{steam_in}} \quad \text{Eq. (2)}$$

Where $(m_{out} LHV_{fuel})_{product}$ is the energy content of the fuel produced, $m_{in} LHV_{biomass}$ is the energy content of the biomass processed, $Elec_{in}$ is the electric energy consumed in production, and Q_{steam_in} is the energy content consumed as steam. The first law conversion efficiencies for fuel

production along with material and energy balances have been made available for a number of fuel production technologies.

Energetic Analysis of Fuel Distribution

The transport of a given quantity of fuel from some geographic location to another can be considered to be an energy conversion, even though there is no chemical change. The physical state of the fuel, its geographic location, is converted. The first law analysis for this conversion is simple. The first law efficiency is given to be:

$$\eta_{I_distribution} = \frac{(m_{fuel} LHV_{fuel})_{delivered}}{(m_{fuel} LHV_{fuel})_{shipped} + W_{in}} \quad \text{Eq. (3)}$$

Where $(m_{fuel} LHV_{fuel})_{delivered}$ is the energy content of the fuel delivered, $(m_{fuel} LHV_{fuel})_{shipped}$ is the energy content of the fuel shipped, and W_{in} is the work expended to ship the fuel. Research has been conducted on the requisite energy to ship fuels along with the percent fuel loss over a given distance (Morrow, Griffin, and Matthews 2006, 2877-2886; Takeshita, Yamaji, and Fujii 2006, 285; Takeshita and Yamaji 2008, 2773-2784). Research has indicated that the requisite energy along with the fuel loss are primarily functions of the fuels state (gaseous or liquid), density, and miscibility with water.

Energetic Analysis of Automotive End Use

The final energy conversion step in the fuel's life-cycle is its combustion in an engine. The first law analysis of this process is well understood and has been widely utilized. This first law efficiency is given to be:

$$\eta_I = \frac{P_{out_drivetrain}}{\dot{m}_{fuel} LHV_{fuel}} \quad \text{Eq. (4)}$$

Where $P_{out_drivetrain}$ is the power delivered to the drive-train, \dot{m}_{fuel} is the mass-flow rate of the fuel, and LHV_{fuel} is the energy content of the fuel. While this efficiency is largely a function of the mechanical efficiency inherent to the engine design, efficiencies have been shown to be functions of the fuel utilized (Heywood 1988). Additionally, much research has shown that the first law efficiency of internal combustion engines can be optimized to different fuels by harnessing their different physical and chemical characteristics.

Computation of Lifecycle Efficiency

While the relative conversion efficiency of each of the individual energy conversion steps are important in order to compare different transportation fuels the overall lifecycle efficiency of the fuels must be considered. This is the case because while a certain fuel might have a high efficiency of production it might have a poor end-use conversion efficiency making its overall conversion lower than its production efficiency would lead one to believe.

A Monte Carlo Analysis (MCA) method is used to calculate the overall lifecycle efficiencies in order to propagate uncertainty in each of the conversion steps into an overall uncertainty of the life cycle efficiency. The majority of reported production efficiencies are given as ranges. Additionally, there is uncertainty in the average distance that an amount of fuel must be shipped in order to arrive at the pump. In order to utilize MCA, a probability distribution function is prescribed to describe the distribution of values. Since there is no information about the functional form of these distributions, this thesis utilizes a triangle distribution, which is the norm for such distributions. The MCA then generates a distribution of values for the system efficiency from which the expected (average) value and standard deviation of the efficiency are calculated.

Integrability of Fuels into Distribution Infrastructure

The evaluation of integrability of fuels into the current fuel distribution infrastructure is determined primarily by their miscibility with water, their compatibility with materials employed in the distribution infrastructure and the physical state at standard conditions (either liquid or gaseous). Additionally, industrial preference and inertia have a major influence on the

acceptance of fuels into the infrastructure. These properties, along with the volumetric energy density (e.g. MJ/L) dictate the cost of distribution for a given fuel.

Life Cycle Economic Assessment

An economic metric is also used to characterize the fuels analyzed in this thesis. In order to assess the economics of a fuel, this thesis considers both the cost of production and the cost of shipping/distribution of each fuel. This data then gives an indication on the overall attractiveness of a specific fuel with regards to its ability to compete with its petroleum derived counterpart in a free, unregulated fuel market.

The costs of production of fuels are taken from literature values and self reported technology assessments of pilot plants and previous full scale deployments of similar fossil technologies. Distribution cost data is well documented for different modes of transport on a volumetric basis in the yearly Transportation Energy Data Book from the Oakridge National Laboratory (Davis and Diegel 2007). These data can then be used to estimate the cost of shipping different fuels on an energy basis utilizing their volumetric energy density.

Compatibility with Regulatory and Policy Landscape

A fourth dimension of this analysis, which has implications for each of the major steps in the life cycle, is the determination of the compatibility of the potential fuels with the current regulatory and policy landscape. Two of the most pertinent areas where policy influences dominate are the Clean Air Act's (CAA) regulation of vehicular emissions, and the VEETC for ethanol (Baucus 1990, 549). A fuel's chemical make-up and combustion characteristics influence its ability to comply with the CAA, and therefore influence how it can be implemented. Whether a fuel is eligible for the VEETC may influence its economic viability.

Other Systemic Considerations

Beyond the abovementioned criteria there are other aspects which greatly influence the adaptability of a transportation fuel at scale, and in some cases can totally trump the criteria

discussed hitherto. Of these the primary issues are a given fuels health and environmental characteristics. Furthermore the public perception of these characteristics, which is not necessarily reflective of fact, can play an even stronger role in a fuels adoption. In this thesis, health concerns are compared by analyzing the LD₅₀ values of these fuels, along with other measures of morbidity risks. The LD₅₀ value of a chemical is the standard measure used to assess mortality risk due to exposure to the given chemical, and will be described in further detail in Chapter 4.

The risk of environmental damage due to fuel spillage on the every order from small scale pipeline leakage to a catastrophe such as the Exxon Valdez spill is a concern. Each fuel considered in this thesis has different chemical and physical properties which dictate its ability to cause environmental damage, naturally decay, or persist in the environment.

Summary

The integration of an alternative transportation fuel at scale is a challenge wrought with complexity, and as such there is no single metric to assess the viability of a specific fuel. Each of the criteria introduced above must, to some extent, be satisfied (or at the very least, not severely violated) for a fuel to be adopted at scale. Even if all of the criteria are satisfied a fuel could still not be adopted due to another unforeseen challenge, or more likely due to perverse policy incentives created by legislation to protect sub-optimal fuels which may be parochial interests to legislatures. In Chapter 4, each of the fuels considered in this thesis are analyzed through the lenses of each of these criteria and further systemic and policy challenges are discussed.

CHAPTER 3: BIOMASS GASIFICATION FUEL SYSTEM DESCRIPTION

The lifecycles of each of the fuels analyzed in this thesis are qualitatively very similar. Each fuel, for example, is produced utilizing similar production steps. Also the fuels analyzed in this thesis can be transported using current fuel distribution infrastructures, though some are better suited than others. For example, Fischer-Tröpsch Diesel can be distributed in today's diesel infrastructure, while Dimethyl Ether (DME) must be distributed in a manner similar to liquefied propane gas (LPG). Each of the fuels considered in this thesis can be used in the existing automotive fleet with minimal adjustments such as improved onboard storage technology and optimized engine timing. In this chapter, the general systematic characteristics of thermochemical biofuel production, distribution and utilization are introduced and discussed.

First, each of the fuels which are analyzed are introduced and their general properties and historical use as a transportation fuel is discussed. The fuels considered in this thesis fall under two general classes, spark ignition engine (SI) fuels and compression ignition engine (CI) fuels; these general classifications are derived from the engine technology with which the fuel is utilized. Also, the general characteristics of thermochemical biofuel production utilizing biomass gasification are discussed. Most of the process steps are shared by each of the fuels, while the differences manifest themselves in varying production efficiencies and production costs. These differences will be further explored and analyzed in Chapter 4.

Next, the fuel distribution infrastructure is introduced. In this thesis three modes of transportation are analyzed- truck, train and rail. Depending on the chemical and physical properties of a specific fuel there exists a certain amount of either industrial push-back or acceptance as to whether the fuel will be shipped via a certain method.

Lastly, the engine technologies utilized for each fuel are considered. As with each of the other steps, the resultant efficiency and economics of utilization are functions of the type of fuel utilized along with the technology employed for its combustion. Additionally, this step is where external regulatory structures have the strongest influence on the choice of fuel through the Clean Air Act's emissions regulations.

Spark Ignition Engine Fuels

There are two broad classes of fuels used for transportation depending on the engine technology that is used. The first of these is Spark Ignition Engine Fuels, or gasoline-like fuels. These fuels are characterized by their ability to resist auto ignition. Auto ignition occurs in engines when temperatures and pressures reach a level at which there is enough thermal energy contained in the fuel-air mixture to overcome the chemical activation energy and thus sustain combustion. In a spark ignition engine this auto ignition is commonly referred to as knock and is known to cause damage to the engine hardware. A fuel's ability to resist auto ignition is traditionally measured by its Anti Knock Index (AKI) or Octane Number (ON). There exist two standard measures of this property, the Research Octane Number (RON) and the Motor Octane Number (MON).¹ When a driver goes to a pump to refill, the octane number she/he is traditionally confronted with is the Road Octane Number (RdON), which is commonly defined as the arithmetic mean of the RON and MON.

In this section the major candidates for use as alternative SI fuels are introduced and discussed. The SI fuels considered in this thesis are methanol, ethanol and synthetic gasoline. There are other fuels being studied for use as alternative spark ignition fuels such as higher alcohols like butanol. However as will be discussed later in this chapter, the route to producing these fuels- via thermochemical means- is characterized by the production of a large fraction of co-products which must be dealt with in order for the fuel to be marketable under the clean air act regulatory regime.

Methanol

Methanol, like other aliphatic alcohols, has many properties that make it an ideal fuel for spark ignition (SI) engines. Methanol has a high latent heat of vaporization, which can be leveraged as a knock suppressing characteristic in spark ignition engines (Bromberg and Cohn 2008). Additionally, methanol is an oxygenated fuel (it contains an oxygen molecule), and has been used as a gasoline additive to decrease carbon monoxide (CO) emissions and improve local air

¹ The experimental parameters of each of these measurements are well defined and are described in detail in (Heywood 1988).

quality (NSTC 1997). As apparent in the above properties, methanol's physical and chemical characteristics make it more desirable than gasoline as a spark ignition engine fuel. Additionally, these characteristics make methanol an ideal alcoholic transportation fuel. Methanol's latent heat of vaporization is 1.16 MJ/kg compared to ethanol and gasoline's 0.91 and 0.30 MJ/kg respectively. Thus, at stoichiometric operation it has been determined that the charge in the cylinder experiences a temperature change of -246K for methanol, -138K for ethanol, and -28K for gasoline (Hunwartz 1982, 1-6). A lower initial charge temperature has a positive effect on the overall engine efficiency through two mechanisms. First, with a decrease in temperature the charge density is increased and more fuel and air can be introduced per cycle thus increasing the volumetric efficiency (Heywood 1988). Secondly, because of the decreased initial temperature there is a lower temperature after compression, thus a higher compression ratio can be utilized without experiencing knock increasing the efficiency. This increased knock limit is also a product of the higher RdON of methanol, 119, versus that experienced with retail gasoline which is on the order of 90. The effective octane number of methanol is both a product of its high latent heat of vaporization and its thermochemical properties, and when both of these properties are taken advantage of a higher octane is experienced (Bromberg and Cohn 2008). Finally, due to methanol's higher oxygen to carbon ratio (1:1 versus ethanol's 1:2); a smaller amount of methanol needs to be used to achieve the equivalent amount of CO emission reduction benefit in a blended fuel. Because of these superior qualities, methanol has been previously heralded as the transportation fuel of the future (Marsden 1983, 333-354; Sperling and DeLuchi 1989, 469-482).

Despite its appreciable qualities, methanol has been rejected as a transportation fuel. Concern about methanol's safety is often cited as leading to the public's reluctance to accept the ubiquitous chemical as a transportation fuel. The predominant concern is with methanol's morbidity risks - its ability to cause non-fatal health damages. These issues will be further discussed in Chapter 4. The assessment in Chapter 4 indicates that the overall health and environmental risks of methanol are similar to gasoline. In fact, methanol offers a great decrease in the risks of fuel fire deaths compared to gasoline. For M100 a 90 percent reduction in fuel related automotive fires is projected, while a smaller reduction of 40 percent is projected for M85 (Machiele 1990).

Another set of concerns having to do with the wide scale application of methanol is its poor cold start properties and low energy density. Methanol's poor cold start ability is due to its low vapor pressure and its high latent heat of vaporization (Hu et al. 2007, 171-175). Cold start is an issue which can be addressed with the addition of hydrocarbon fuels and is not an issue for blended fuels like M85. As is seen with ethanol fuel, using blended fuels is the norm rather than the exception when employing alcoholic fuels. Methanol, which has a Lower Heating Value (LHV) of 20.0MJ/kg (15.84 MJ/l), has the lowest energy density of the liquid fuels considered in this study. Because of this, larger onboard storage would be required to maintain comparable range and therefore design constraints would be put on the automobiles design. This drawback is partially negated by the increased end use efficiency achievable with ethanol hence, decreasing the total amount of fuel needed to travel a specific distance.

Ethanol

Ethanol currently makes up more than 95% of the total biofuel use in the United States and the majority of the alternative transportation fuel market, totaling more than 5 billion gallons produced in 2006. Even at this production level, however, 25% of US corn production displaces little more than 2% of total petroleum demand. The USDA has recently released projections demonstrating that the US is reaching capacity for corn production and room for growth in the corn ethanol industry will be limited. While the growth for corn ethanol production may be limited, the production of cellulosic ethanol is seen as a promising, and indeed necessary, fuel production route by the policy and scientific community.

Ethanol, like methanol, possesses many properties that make it a good candidate for adoption as an alternative SI fuel. As discussed in the section on methanol, ethanol has a high latent heat of vaporization and is an oxygenated fuel. Thus, the use of ethanol as a spark ignition engine fuel leads to reduced emissions and the possibility of increased efficiency. While each of these characteristics is less prevalent in ethanol than methanol, ethanol has other characteristics which when used as the sole metric make it more appealing for use as a fuel than methanol. First, ethanol has a higher volumetric energy density than methanol, however it is still the case that ethanol's energy density is lower than that of gasoline. Additionally, while it is less oxygenated than methanol, this also leads to it being less corrosive than methanol. Therefore, there exists less

concern of major material damage with ethanol than with methanol. In practice however, ethanol is viewed as a corrosive fuel and there still exists major regulatory and industrial pushback against the integration of ethanol into the current infrastructure because of this, along with other, properties.

One particularly important property that ethanol has is the public (miss) perception of its toxicity. While ethanol's measured LD50 values are slightly lower than those of methanol, it is generally regarded as a much safer chemical. This is most likely due to the customary consumption of ethanol in the form of fermented beverages. However in today's fuel industry, in order for ethanol to be used excise tax-free it must be denatured with gasoline (usually blended to E85) which effectively increases its toxicity substantially. Thus, while methanol may be less likely to lead to mortality than fuel ethanol, public perception will continue to play a very large role in their respective adoption.

Higher and Mixed-Alcohols

Like methanol and ethanol, the following short-chain aliphatic alcohols have similar properties which make them attractive candidates for adoption as alternative spark ignition fuels. The fuel most often discussed is butanol. Butanol is being considered as an alternative fuel due to the confluence of its desirable properties as a co-blending agent for ethanol along with the fact that it can be biologically co-produced with ethanol. Via a thermochemical route no alcohol, other than methanol, can be produced purely. This is due to the fact that higher alcohol synthesis takes place over a modified Fischer-Tröpsch catalyst and is therefore based on a polymerization mechanism, and the chain length cannot be directly controlled. Because of this major production limitation, it is convenient to consider mixed alcohols as a possible alternative fuel, not neat higher alcohols.

Mixed alcohols do not have concrete physical and chemical properties since, like gasoline, is the product of a number of constituents. This, however, means that mixed alcohols could be quite advantageous when used as a gasoline substitute. When alcohols are mixed, one can benefit from the high octane of methanol and ethanol while capitalizing on the higher energy densities and lower water miscibilities of the longer chain alcohols. In order for these properties to be fully

utilized, more work needs to be done in order to understand the dependence of a mixed fuel's properties on the specific fractions of individual components and how to optimize component ratios.

Propanol is the first of the aliphatic alcohols to have structural isomers, propan-1-ol (n-propanol) and propan-2-ol (isopropanol). Of the short chain aliphatic alcohols, propanol has been considered the least as an alternative transportation fuel. This is due to the fact that propanol is not a major constituent of any metabolic pathway, and therefore there is no efficient natural way to produce propanol in a biological manner. Propanol can be produced through thermochemical methods, however catalytic production of propanol is not very selective and separation from other aliphatic alcohols is necessary if a neat product is desired. Propanol's energy density is higher than methanol and ethanol; additionally it is less miscible with water and less corrosive. However, due to its lower oxygen to carbon ratio it has a lower effective octane number. Additionally, it is more toxic than shorter alcohols.

Butanol is a four carbon alcohol. It is currently being investigated by a number of companies and independent groups for use as an alternative transportation fuel. Butanol has been cited as having a number of advantages over the short aliphatic alcohols methanol and ethanol: it has a lower vapor pressure, it is much less miscible with water and will not separate from gasoline; therefore it is expected to allow for a higher blending limit in contemporary SI engines. However, butanol is more toxic than methanol and ethanol, and is currently more expensive to produce. Much attention is being paid to biological conversions coupled with current ethanol production because butanol and ethanol can be produced from the same feedstocks utilizing one common microbe. Butanol is more toxic than the shorter alcohols, and has a lower octane number. It does, however, have a much better energy density and is less corrosive.

Methanol-to-Gasoline (MTG) Product

Synthetic hydrocarbons are fuels produced from non-petroleum feedstocks which are designed to have similar chemical and physical properties to hydrocarbons derived from petroleum. The production of synthetic hydrocarbons could be very important in the short term due to the fact that the country's automotive transportation infrastructure has been designed around

hydrocarbon fuels. Today, the most prevalent commercial synthetic hydrocarbons are produced via the Fischer-Tröpsch method and are primarily used as compression ignition engine fuels due to their chemical and physical properties. Another possible route to synthetic gasoline is via the Mobile-M, Methanol-to-Gasoline route. This production method was utilized (at an economic loss) at the commercial scale from natural gas in the 1970s in New Zealand (Sugiyama 1994). The MTG product consists of highly unsaturated hydrocarbons and a large fraction of aromatic compounds. Due to the high degree of saturation this fuel exhibits properties very similar to that of gasoline. Unlike petroleum derived gasoline MTG doesn't contain sulfur or other contaminants, thus while it is unoxxygenated, it exhibits marginally better emissions characteristics as compared to petroleum derived gasoline. Recently, there has been a rebirth in interest in MTG for new coal-to-liquids (CTL) projects. DKRW Advanced Fuels has planned major CTL plant capable of producing 20,000 barrels per day of MTG product in Medicine Bow, Wyoming using the ExxonMobil MTG process (Green Car Congress 2007a). Further, there are a number of MTG projects being considered in China.

Summary of Spark Ignition Fuel Properties

In the below table a selection of relevant chemical and physical properties of fuels considered in this thesis are compiled. These are the chemical formula, the molecular weight (given in grams per mol), the density, the lower heating value and the heat of vaporization.

Fuel	Formula	Molecular Weight	Density (g/cm ³)	Lower Heating Value (MJ/kg)	Heat of Vaporization (KJ/kg)
Methanol	CH ₃ OH	32.04	0.792	20	1103
Ethanol	CH ₃ CH ₂ OH	46.07	0.785	26.9	840
Propanol	CH ₃ (CH ₂) ₂ OH	60.1	0.8	30.5	790
Butanol	CH ₃ (CH ₂) ₃ OH	74.14	0.81	33	580
MTG Gasoline	CH _{1.85}	~110	0.75	44	350

Table 1 - Physical and chemical properties of spark ignition engine fuels analyzed in this thesis.

Compression Ignition Engine Fuels

Where spark ignition engine fuels are valued for their ability to resist auto ignition, compression ignition engine fuels are characterized by their ability to auto-ignite. Compression ignition

engines are designed to combust fuels by compressing the fuel-air mixture to a sufficiently high temperature and pressure for the mixture to ignite at a specified timing. This automotive design has certain properties which allow for, in general, higher energy conversion efficiency over spark ignition engines (Heywood 1988). Additionally, CI engines can be designed at a much larger scale, allowing for more power intensive applications such as semis, stationary power generation and ship engines.

A CI fuel's ability to auto-ignite is measured by its Cetane Number (CN). Like the octane number measure used for spark ignition engines this is a purely empirical number that is experimentally derived. See *Heywood* for a more detailed discussion of the experimental method utilized to determine a fuels cetane number (Heywood 1988).

Below the major candidates being considered as substitute fuels for compression ignition engines are introduced: Fischer-Tröpsch Diesel and dimethyl ether. As with the spark ignition fuels each of these fuels have certain characteristics which make them promising candidates, while each also have their own drawbacks.

Dimethyl Ether (DME)

Dimethyl ether is the simplest ether with two methyl groups connected by an oxygen atom. DME, unlike the other fuels being considered, is gaseous at ambient conditions. DME's physical properties are much like that of propane and n-butane (Table 2), thus dimethyl ether can easily conform to the current liquid propane gas (LPG) and compressed natural gas (CNG) infrastructures.

Critical Constants	Tc (K)	Pc (MPa)	Vc (cubic meters/Kmol)	Zc	Acentric Factor
Dimethyl Ether	400.1	5.27	0.171	0.271	0.192
Propane	369.83	4.21	0.2	0.273	0.149
n-Butane	425.12	3.77	0.255	0.272	0.197

Table 2 - Critical Constants of Dimethyl Ether, Propane, and n-Butane (adapted from Perry's Handbook 7th Edition 2007)

Beyond its adaptability to today's LPG and CNG infrastructure, dimethyl ether also exhibits properties which make it an excellent candidate for use as an alternative compression ignition fuel. Whereas alcohols, such as methanol, offer superior properties for use in spark ignition engines, ethers are optimal for use in compression ignition engines. Dimethyl ether has a low auto ignition temperature and a high cetane number on the order of 55-60, compared to diesel's which is on the order of 40-55 making it an excellent substitute for diesel (Semelsberger, Borup, and Greene 2006, 497-511). Due to dimethyl ether's simple molecular structure devoid of C-C bonds, and high oxygen content, as well as its latent heat of vaporization dimethyl ether exhibits low NO_x and particulate matter emissions (Wang et al. 2000, 101-106).

The biggest limitation to large scale implementation of dimethyl ether is the fact that dimethyl ether is a gas at room temperature; thus pressurized storage and a special injection system needs to be employed. Further, DME has an energy density which is significantly less than that of diesel fuel (28.4 vs. 43 MJ/kg), this coupled with the fact that DME's liquid phase density is less than that of diesel (0.668 vs. 0.84 g/cm³) means that significantly more onboard storage is required for the same range of travel.

Fischer-Tröpsch Diesel

Of all of the possible alternative fuels considered in this thesis, Fischer-Tröpsch Diesel (FTD) has the longest history of being utilized on a commercial scale. FTD synthesis has been known since the early 20th century. During World War II, Nazi Germany employed this technology to produce diesel fuel from coal since they had little access to petroleum derived fuels. Additionally, during the Apartheid, South Africa further developed this technology due to limited availability of petroleum resources and large domestic reserves of coal. Even today, South Africa is able to supply a large portion of their domestic transportation fuel need via FTD production from coal.

Fischer-Tröpsch Diesel is a mixture of synthetic hydrocarbons. It consists primarily of straight chain saturated hydrocarbons. And, like MTG, has certain characteristics that make it superior to its petroleum derived equivalent. One important characteristic of FTD is the absence of sulfur in the fuel, this leads to major reductions in particulate matter emissions. Additionally, there are

virtually no aromatic/unsaturated compounds produced, thus decreasing NO_x and particulate emissions as well. Fischer-Tröpsch Diesel's energy density is nearly equivalent to that of petroleum derived diesel and does not face any serious challenges in order to be introduced at a large scale.

Summary of Compression Ignition Fuel Properties

As above for spark ignition fuels, a selection of relevant physical and chemical properties are tabulated below for the compression ignition fuels.

Fuel	Formula	Molecular Weight	Density (g/cm ³)	Lower Heating Value (MJ/kg)	Heat of Vaporization (KJ/kg)
DME	CH ₃ OCH ₃	46.07	0.668	28.7	467
Fischer-Tröpsch Diesel	CH _{1.8}	170	0.8	43	270

Table 3 - Summary of physical and chemical properties of compression ignition engine fuels considered in this thesis.

Biomass to Liquid Fuel Production System

The production of fuels via biomass gasification consists of a few major steps which are shared by each of the fuels' production schemes. In order to produce a fuel the biomass must undergo preprocessing steps (drying and mechanical pulverization), gasification and gas clean-up/conditioning. After these steps each fuel is synthesized in one step (with one notable exception, MTG which requires a second synthesis step after methanol is produced). The crude product then undergoes clean-up and separation in order to be made into a marketable fuel.

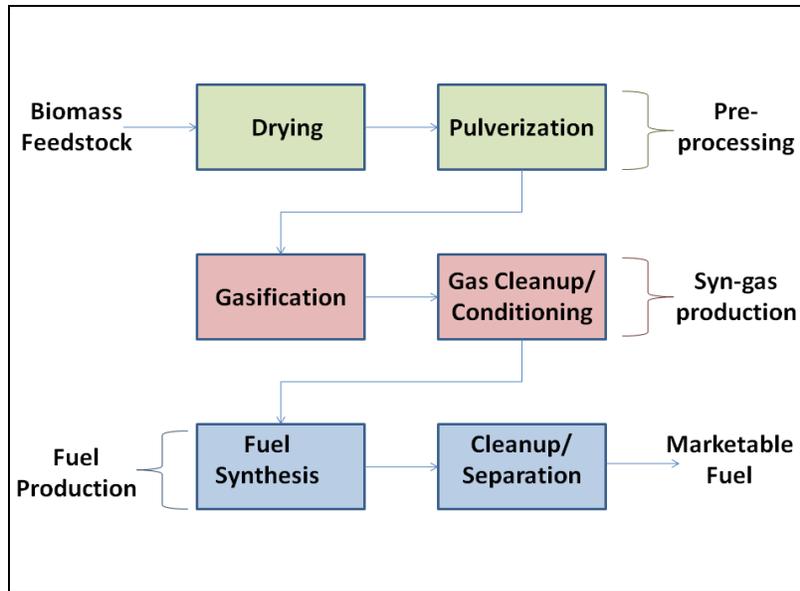


Figure 3 - A generalized flow diagram of thermochemical biofuel production, each of the process steps are part of three main steps 1) Pre-processing 2) syn-gas production, and 3) Fuel Production.

Below the general characteristics of the production steps are introduced and discussed. Additionally, the specifics for each fuel are explored.

Feedstock Handling/Drying

As is the case for current biofuel production facilities based on cereal grain and oil seed, there is a need for short term on-site storage to allow for continuous operation of the plant. This is due to the fact that biomass is produced seasonally in the US. Depending on the feedstocks energy density per volume this would need to be sized differently to allow for a sufficient feedstock stockpile.

When the feedstock is processed it is moved from the stockpile by conveyer. This feedstock is sent through a magnetic separator in order to remove any metal contaminants and is screened in order to separate large biomass particles from the smaller ready-to-process feedstock. These large particles are then reprocessed to an acceptable size. This biomass is then transported to the dryers. In their studies on biomass to hydrogen and biomass to ethanol processes, NREL proposed that the biomass can be dried with a flow of hot flue gas from the char combustor as a

way to utilize otherwise unused heat (Phillips et al. 2007; Spath et al. 2005). After the moisture content of the feedstock is reduced to approximately 5%wt the feedstock is then conveyed to the gasifier.

Gasification

Gasification is the process that converts a mixture of feedstock and an oxidizing agent into syngas, a mixture of carbon monoxide (CO) and hydrogen (H₂) along with other contaminants such as carbon dioxide (CO₂), water (H₂O) and short chain alkanes (predominantly methane CH₄). This conversion is achieved by controlling the amount of oxidizing agent present so the overall oxidation is incomplete. There are three main categories of gasification technologies being considered for biomass gasification: fixed-bed gasification, fluidized-bed gasification, and entrained-flow gasification. While gasification has found application for coal utilization, biomass gasification offers the challenge of increased slaging due to higher ash content, as such the technology must be able to minimize slaging (Higman and van der Burgt 2003). For their analysis, NREL chose to use a low-pressure indirectly-heated fluidized-bed gasifier. In the fluidized-bed reactor, the ash that begins to agglomerate will defluidize and fall to the bottom, making it easy to remove; it is because of this that fluidized bed gasifiers are being strongly considered for application to biomass feedstocks whereas direct oxidation is the technology generally employed in coal gasification.

In the gasification step, not all of the organic matter is gasified; the remainder is converted to a solid fuel mass called char. After the gasification step, often there is a char combustor, where the resultant char (mostly carbon) is combusted completely (to CO₂ and H₂O) in order to supply heat to the system. The char combustor can supply heat to the gasifier, the plant's steam system, as well as the feedstock driers. The char combustor is a necessary piece for an energy self-sufficient plant. Otherwise there plant would need to purchase natural gas, coal, or steam to power the heat/steam system (Phillips et al. 2007).

The gasification technology which will ultimately be employed for biomass gasification is uncertain. One characteristic of current pilot thermochemical biofuel systems is that each company trying to develop a system uses a different, often patented, gasification technology.

Choren, a German company who is attempting to produce Fischer-Tröpsch Diesel from various biomass feedstocks, employs a dual gasification system in which the biomass is first pyrolyzed, and then the pyrolysis gas is gasified in their so-called Carbo-V-Gasifier, which is directly heated with the char from the initial pyrolysis (Kiener 2008). Range Fuels, an American company whose goal is to thermochemically produce ethanol from cellulosic feedstocks, is using a single step gasification technology (Range Fuels 2008). Addressing the challenges associated with biomass gasification will be one of the major challenges that must be overcome in order for thermochemical biofuel production to be adopted and yet, it is unclear which gasification technology will emerge as the technological winner.

Gas Cleanup

In order to be used in fuel synthesis, the syngas produced via gasification first needs to be in a condition sufficient for catalytic conversion. Contaminants must be removed, the hydrogen to carbon monoxide ratio must be adjusted, and the syngas must be compressed to the synthesis reactors operating condition. The primary contaminants contained in raw syngas are tars, acid gases and particulates.

The term tar is used to generally describe any hydrocarbon contaminants (methane, ethane, benzene, etc) and ammonia. The removal of these contaminants is critical because they can deactivate the catalyst and decrease the fuel production efficiency over the remaining life of the catalyst. A catalytic tar reformer is used to convert these compounds into carbon dioxide, nitrogen and hydrogen. The tar reformer is based on a nickel catalyst and operated at a temperature of 900°C (Patel 2004).

Acid gases refer to the compounds hydrogen sulfide (H₂S) and CO₂. Depending on the synthesis catalysts being used there are different thresholds below which these gases must be in order to avoid deactivating the catalyst. These contaminants are removed in an acid gas scrubber where an amine solution selectively absorbs H₂S and CO₂. The acid gases are then stripped from the amine into a separate unit where elemental sulfur and CO₂ are produced. This technology is already in widespread use in power plant applications to remove sulfur from the exhaust stacks.

Particulates must also be removed to avoid decreasing available catalyst area. The cooled syngas undergoes water scrubbing to remove particulates and to further cool the syngas prior to the synthesis reactor.

Gas Preparation

To perform an efficient conversion process, the hydrogen to carbon monoxide ratio must be adjusted to the proper ratio depending on the desired product. For this a water-gas shift reactor is used. To illustrate, the optimum hydrogen to carbon monoxide ratio is 2:1 for methanol production, whereas for direct dimethyl ether synthesis a ratio of 1:1 is best. For biomass gasification it has been found that the resultant hydrogen to carbon monoxide ratio is on average 1:1 (Melgar et al. 2007, 59-67). Thus, a shift reaction is required for methanol production; whereas it may not be needed for dimethyl ether synthesis. Each neat-fuel production system has its own optimal carbon monoxide to hydrogen ratio. For mixed-fuel production, the ratio will influence the resulting ratios of products. The shift reaction from carbon monoxide to hydrogen is slightly exothermic, thus some enthalpy of the syngas mixture is lost as heat and the overall first law efficiency of the plant is reduced. Also, the added reaction step increases the capital cost and required operation and maintenance.

Product Synthesis

The synthesis step is where the majority of differences between each fuel production system is manifest. However, there are similarities between some fuel syntheses, such as methanol and dimethyl ether, where dimethyl ether is a byproduct of methanol synthesis. Additionally, ethanol and Fischer-Tröpsch synthesis are similar due to fact that ethanol is produced via a mixed-alcohol synthesis which is based on a modified Fischer-Tröpsch reaction. The differences between each of these production systems are discussed below.

Crude Product Separation and Clean-up

In all cases, the product stream is contaminated with a number of substances, primarily water with small amounts of oxygenated and unoxygenated hydrocarbons. In order for the products to be fuel grade their makeup must meet EPA fuel standards and these contaminants must be

removed. Due to the physical properties of short chain aliphatic alcohols compared to dimethyl ether and synthetic hydrocarbons additional separation is required. This is primarily because of the fact that at ambient conditions alcohols are hydrophilic liquids, whereas dimethyl ether and hydrocarbons are hydrophobic. Therefore, alcohols have to be separated via a many step distillation followed by molecular sieves, as is the case for fuel ethanol production today, whereas a simple flash distillation separation would allow the gaseous dimethyl ether to separate easily, additionally synthetic hydrocarbons would naturally separate as well.

Production System Discussion

Though the production systems share many common steps and characteristics, it is the differences which dominate the relative thermal efficiencies of the respective biomass conversions. The main differences are the required hydrogen to carbon monoxide ratio and the product separation and clean-up requirements.

Hydrogen to Carbon Monoxide Ratio

One important difference between syntheses is the required hydrogen to carbon monoxide ratio. This is significant due to the fact that different feedstocks provide different H₂:CO ratios. For stoichiometric methane reformation the resultant H₂:CO ratio is 2:1 so is ideally suited for methanol production (LeBlanc, Schneider, and Strait 1994, 51). However, via biomass gasification the H₂:CO ratio is on the order of 1:1, so a water-gas shift reactor is required for a biomass to methanol system. The addition of this step to production is detrimental to the overall system efficiency. The water-gas shift is exothermic and chemical energy stored in the syngas is lost as heat, and cannot be transferred to the resulting liquid fuel. Also since the unit cannot operate ideally the additional step increases second law losses. Finally, with another added step to the production system the overall capital costs are increased which increases the overall cost of production.

The 1:1 ratio from biomass gasification is suited to direct DME synthesis, and as such, a water-gas shift reactor is not likely needed. Therefore, given a biomass feedstock dimethyl ether may be an ideal product to produce in order to minimize the syngas processing steps.

The product mixtures of Fischer-Tröpsch synthesis along with mixed alcohol synthesis are dependent on a number of operating conditions including the H₂:CO ratio. This relation is rather complex and is discussed in the sections on their production. However, it is clear that a hydrogen to carbon monoxide ratio less than 1 is desirable since a fuel with an ultimate carbon to hydrogen ratio of ~1:1.8 is produced. In reality a hydrogen/carbon monoxide ratio of 2 is often used due to the high amount of water rejection in the process (Probstein and Hicks 1982). MTG synthesis is uninfluenced by the H₂:CO ratio since it is a synthesis that takes place in a secondary step where methanol is converted to MTG. Thus, the optimal ratio here is 2:1 since methanol must first be produced.

Fuel	Theoretically Optimum H ₂ :CO ratio
Alcohols	2
MTG	2
DME-2 step production	2
DME-1 step production	1
Fischer Tröpsch	<1

Table 4 - Theoretic optimum H₂:CO ratios for synthesis.

Product Separation and Clean-up Requirements

The separation of a mixture of compounds is heavily dependent on what compounds are contained in the mixture. Separating methanol from water is a very energy and capital intensive process because both compounds are polar and contribute to hydrogen bonding. Additionally, alcohols form azeotropes with water and cannot be completely separated via distillation. Molecular sieves must be used to dehydrate alcohols, which increase the overall processing cost.

Dimethyl ether on the other hand is gaseous at standard conditions and does not form an azeotrope with water, hence a simple low temperature distillation is all that is needed to separate dimethyl ether from water and other liquid contaminants. Thus, dimethyl ether is an ideal product in order to minimize the required product separation and clean-up steps. Similarly synthetic hydrocarbons have physical properties which make their separation and clean-up easier than alcohols. Synthetic hydrocarbons are generally hydrophobic compounds and can be separated with minimal energetic input.

Methanol Production

Currently, the catalytic conversion of syngas from natural gas accounts for 90% of the world methanol production of 32 million tons (9.7 billion gallons, 4.82 billion GGE) (Olah, Goepfert, and Prakash 2006). Where natural gas is not available, other feedstocks are used for methanol production such as coal and light petroleum products. The same processing principles used for natural gas derived syngas can be applied to syngas from biomass, coal or any other primary carbon and hydrogen source. The process is dictated by the following chemical reactions:



The yield and selectivity of methanol is dependent on the $H_2/(CO + CO_2)$ ratio as well as the CO/CO_2 ratio as shown by Yin et al. (Yin et al. 2005, 305-310). Theoretically, the most efficient/complete conversion will happen when the syngas ratios are at $H_2/(CO + CO_2) = 2$ and $CO/CO_2 = \infty$. This is due to the fact that with CO_2 in the mix equation two will compete with equation 4 for space on the catalyst decreasing yield while equations 5 and 6 will create water which both decreases the selectivity as well as deactivates the catalyst decreasing per pass yields.

As demonstrated by Melgar et al., syngas produced from biomass generally has a $H_2/(CO + CO_2)$ ratio nearer to one, and often contains a large amount of CO_2 . Though it is theoretically possible to adjust gasification parameters to produce an optimal syngas, it may not be economically optimal for commercial production. Therefore, downstream syngas conditioning may be attractive to increase methanol yield and selectivity by performing equation 6, the water-gas shift reaction with excess water removal in order to increase the $H_2/(CO + CO_2)$ ratio as well as decrease the CO/CO_2 ratio.

In methanol synthesis, contaminant substances are produced such as methyl formate, dimethyl ether, glycerine and dimethyl carbonate (Kumabe et al. 2008, 1422-1427). Also, the one pass conversion efficiency is often low and dominated by the volumetric amount of catalyst used. As

a result, methanol producers must strike a balance between desired one pass efficiency and the cost of a larger, and more expensive, catalytic reactor. A synthesis recycling loop is usually used in which part of the product stream is recycled into the reactor vessel. In this way, an overall methanol conversion efficiency on the order of 95% on a carbon basis is achieved (Kumabe et al. 2008, 1422-1427; Katofsky 1993).

Methanol Catalyst

Methanol was first produced at an industrial scale over a zinc oxide-chromium oxide (ZnO-Cr₂O₃) catalyst at high pressures and temperatures, 35 MPa and 450°C, respectively (LeBlanc, Schneider, and Strait 1994, 51). There were three major problems with this catalyst. First, this catalyst tended to promote a methanation reaction which led to overheating of the reactor. Second, the cost of syngas compression to 35 MPa is quite high. Finally, high pressure synthesis led to lower selectivity.

With the development of low-pressure synthesis catalyst technology plants utilizing the high-pressure ZnO-Cr₂O₃ catalyst were driven out of the market because they were rendered economically uncompetitive. This new low-pressure synthesis was based on a copper oxide-zinc oxide-alumina (Cu/Zn/Al₂O₃) catalyst technology developed by ICI of England. This new catalyst was extremely active and since it ran at lower pressures and temperatures, more selective. The catalyst system operates from 5-10 MPa and 200-280°C, with modern applications on the lower end of these operating conditions.

Generally these catalysts are prepared in tablet form with cylinder sizes ranging between 5.5 x 3.5 to 6 x 6 mm. They are shipped in their fully oxidized form and must be activated/reduced in situ by passing H₂/N₂ (1 mol% H₂) over the catalyst bed. This must be carefully controlled at low temperature to preserve crystalline structure and physical integrity to ensure optimal performance.

The copper based catalyst system is a much less robust system and is susceptible to poisoning and deactivation. The catalyst is particularly sensitive to chlorine and sulfur. With sulfur levels below 0.025 ppmv and chlorine levels below 0.0125 ppmv a catalyst life of two to four years can

be expected. Cleanup to this level is not uncommon or difficult. Methanol yields of 99.5% (relative to other organic byproducts when water production is not accounted for) of converted CO + CO₂ can be expected.

Ethanol Production

The National Renewable Energy Laboratory (NREL) has performed a comprehensive technology survey of ethanol production via gasification of ligno-cellulosic biomass (Phillips et al. 2007). This report concludes that production via this method is both economically and technically feasible. Thermochemical production of ethanol from ligno-cellulosic feedstock offers a number of advantages over enzymatic conversion. First, gasification technology has been proven for many carbon containing feedstocks including coal, natural gas, oil and biomass. Enzymatic conversion of ligno-cellulosic materials is still in a research and development phase, and faces significant hurdles. Further, many of the catalytic processing steps for the gasification product (syngas) are well understood and have been applied to fuel production in the past. This is the primary production method of industrial methanol from natural gas. Lastly, gasification will allow for the complete utilization of ligno-cellulosic materials, whereas enzymatic processing is unable to digest the lignin in the biomass.

The primary disadvantage of this technology is the fact that it cannot produce ethanol without a significant byproduct stream. The product stream is composed of mixed methanol, ethanol, propanol, butanol and other higher alcohols. In the scheme proposed by the study, the higher alcohols (propanol and up) are to be separated off and sold as commodity chemicals and methanol is to be recycled along with unreacted syngas into the synthesis unit to be reprocessed into higher alcohols. This injection of methanol is to shift the equilibrium towards ethanol production.

Hybrid Thermochemical/Enzymatic Ethanol Production, Syngas Fermentation

Another promising route to ethanol from ligno-cellulosic biomass is via biomass gasification followed by the enzymatic conversion of syngas to ethanol. This cellulosic ethanol production method has garnered interest because it avoids the currently inefficient pretreatment and cellulase production steps necessary for biological processing (Lynd 1996, 403-465).

This production method has a number of potential advantages over catalytic ethanol production. First, whereas most catalysts used in the petrochemical industry are easily poisoned by sulfur containing gases, syngas-consuming anaerobes have been found to be sulfur tolerant (Brown 2007, 947-956). Second, the conversion performance is not adversely affected by variable CO/H₂ ratios as well as CO₂ levels, whereas the conversion efficiency of catalytic systems are highly dependent on these ratios (Huber, Iborra, and Corma 2006, 4044-4098). Finally, unlike catalytic conversions where high temperatures and pressures are required, biological conversion takes place at near ambient conditions.

There are major shortcomings that must be addressed for this nascent technology to become commercially viable. This process utilizes anaerobic fermentation which is traditionally difficult to maintain at an industrial scale (Brown 2007, 947-956). Additionally, one of the leading microorganism considered for this purpose, *Clostridium ljungdahlii* has a relatively low rate of growth and production. Despite the challenges associated with this approach, there are pilot scale plants currently attempting this method as a viable ethanol production route (McAulay 2009).

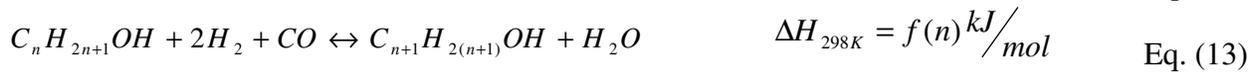
Mixed Alcohol Production

For the production of any alcohol longer than methanol, mixed alcohols must first be produced, then if a neat fuel is desired it must be separated. Here the synthesis characteristics of mixed alcohols are discussed, along with schemes being explored to boost production of specific products.

The production of mixed alcohols is achieved by the use of a modified Fischer-Tröpsch catalyst in either a modified Fischer-Tröpsch reactor or a methanol synthesis reactor. The catalyst is a molybdenum-disulfide-based (MoS₂) catalyst, such as that supplied by Dow/United Catalyst Company (UCC). This catalyst is a high surface area MoS₂ with alkali metal salt and cobalt sulfide promoters. The promoters are used to shift the products from Fischer-Tröpsch hydrocarbons to alcohols. The active parts are supported on alumina or activated carbon.

With the current state of technology, as reported by NREL, the operating conditions are as follows: Temperature approximately 300C, Pressure 1500-2000 psia, H₂/CO ratio 1.0-1.2, CO₂

concentration 0-7 mol%, and Sulfur concentration 500-1000 ppmv. The following system of reactions, along with equations (5)-(7), describe the synthetic route for production of alcohols synthetically:



Equations (13) and (14) are the general equations that can be continued with $n \rightarrow \infty$, however it impractical to model past an n of 8.

The state of the technology, as reported by NREL gives the following parameters for reaction performance: Total CO Conversion (per pass) 10%-40%, Total Alcohol Selectivity 70-80%, Gas Space Velocity (hr^{-1}) 1600-12000, Catalyst Alcohol Productivity ($\text{g}/(\text{kg-catalyst hr})$) 150-350.² Figure 4 shows the weight percent distribution of the alcohols in the product stream. Note that the NREL result includes recycling methanol with unreacted syngas in order to increase the output of ethanol.

Unlike the production of neat fuels, there would be no need for complicated separations at the end of the production (except for the removal of water, acetates, and other contaminants) which should increase the conversion efficiency.

² This is based on an assumed catalyst density of 64 lb/ft³.

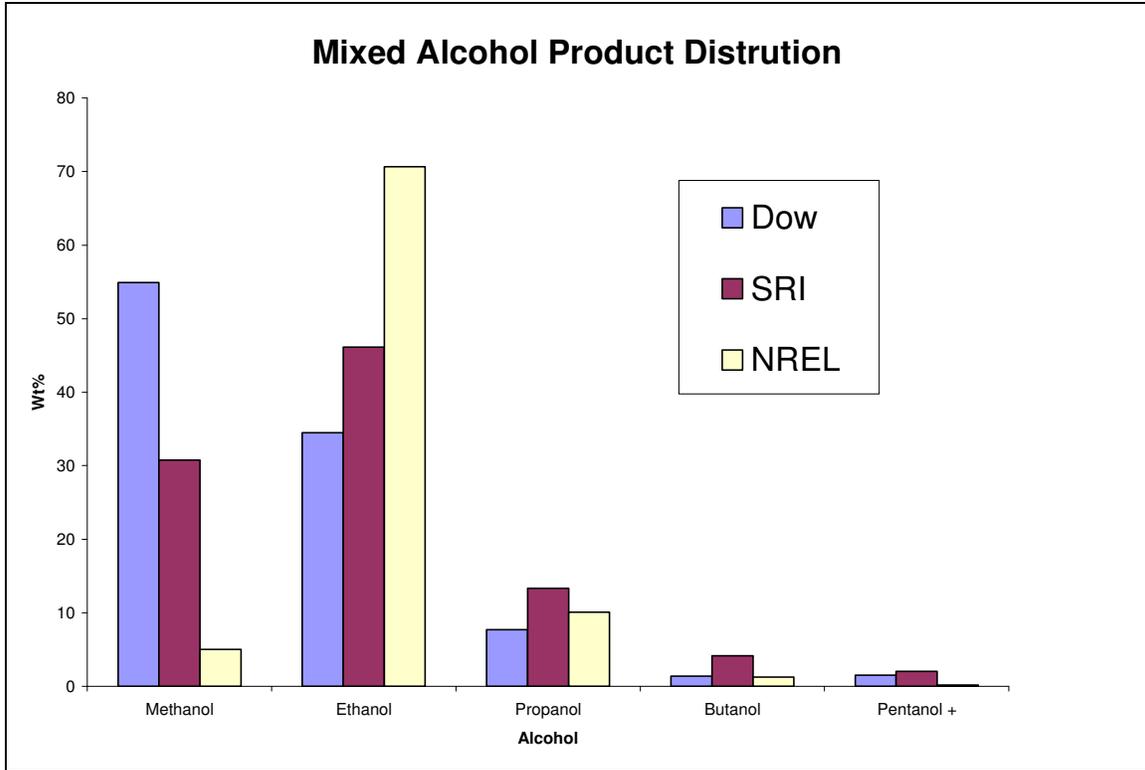


Figure 4 - Mixed alcohol product distribution of different production schemes. The data is adapted from (Phillips et al. 2007).

In Figure 4, the distribution of products is plotted as weight percent for three production schemes. The Dow process distribution is representative of the one-pass conversion, where unreacted syngas is separated from the product stream and recycled. In this process, methanol is the dominant product with the percentage of higher alcohols decreasing with length. This is resultant from kinetic limits. The reaction rate for the general reaction defined by equation nine is:

$$\frac{d[C_{n+1}H_{2(n+1)}OH]}{dt} = k[C_nH_{2n+1}OH][H_2]^2[CO] \quad \text{Eq. (15)}$$

The amount of an n-alcohol produced during a period of time is proportional to the amount of the (n-1)-alcohol produced in the same period of time. In order for propanol to be produced in a one pass reactor there must first be an appreciable amount of ethanol produced, before which an appreciable amount of methanol must first be produced. This trend is more starkly apparent in

Figure 5, where the molar basis is used to illustrate the distribution, these are the numbers that are related to the process kinetics.

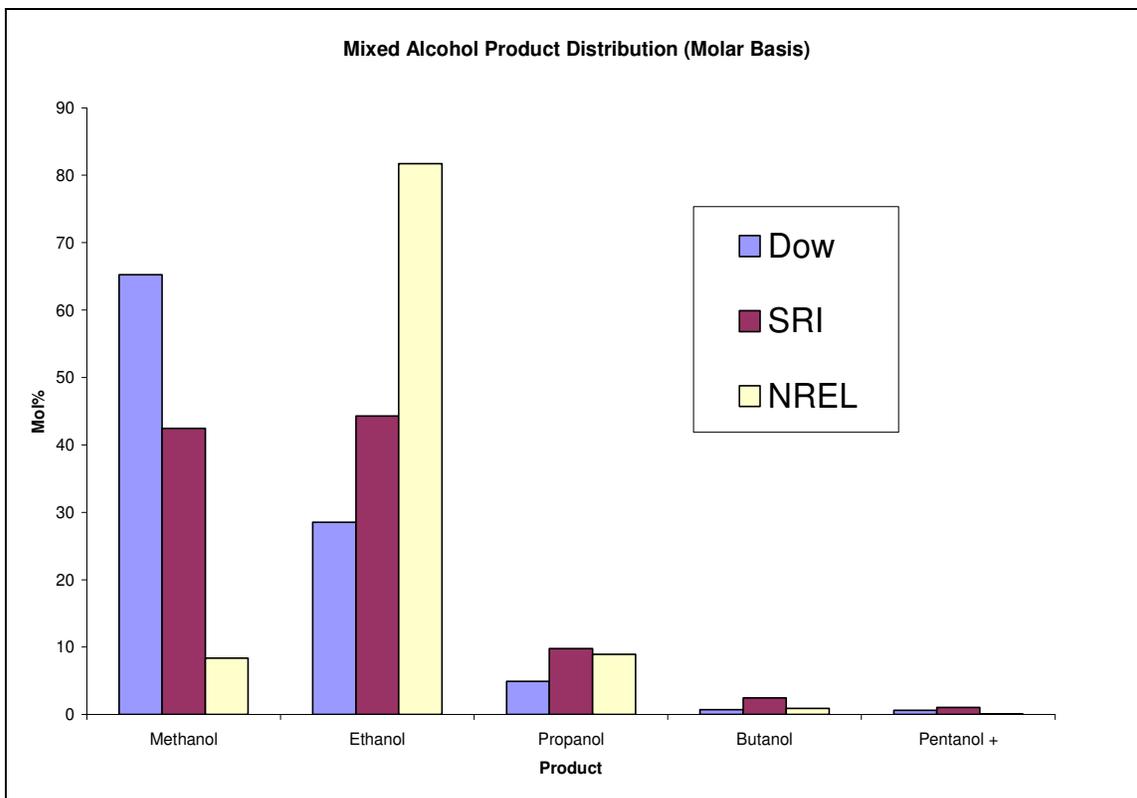


Figure 5 - Mixed alcohol product distribution of different production schemes (molar basis), adapted from (Phillips et al. 2007).

Since the relative production is related to the chemical kinetics, this can be shifted by increasing or decreasing the residence time of the reacting mixture in the catalytic reactor. For their results SRI assumed that the reaction was allowed to continue long enough to have a resultant mass percentage of 30.70% methanol. This lengthened residence time both increased the mean alcohol length (from 1.43 carbons to 1.75 carbons in a molar basis) but also increased the variance of the products (from $\sigma^2 = 0.464$ to 0.65).

NREL, however, incorporated methanol recycling into their techno-economic study of the system. In this manner instead of increasing the residence of the entire reacting mixture, which increases the overall variance and the proportion of higher alcohols (propanol+), they increased the residence of methanol relative to the other products, as a result increasing the proportion of

ethanol produced (mean carbon length of 2.03) while decreasing the overall variance of products to 0.217 (See Figure 6).

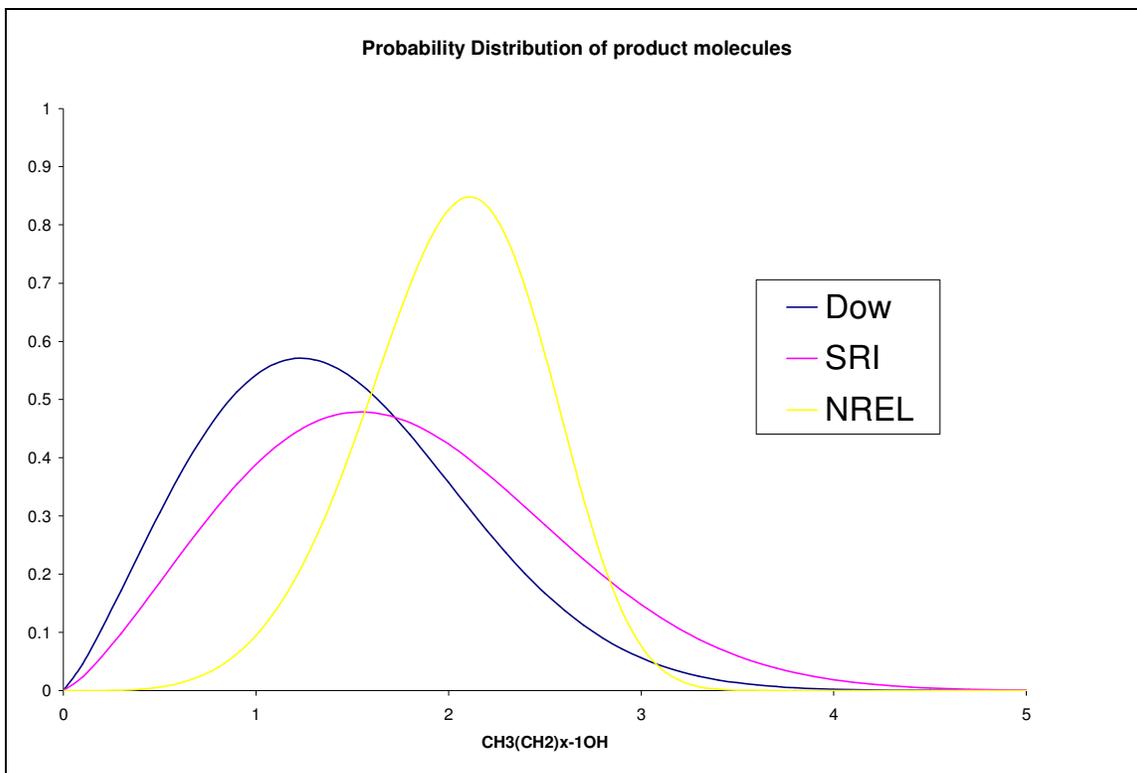


Figure 6 - Weibull distributions fit to the molar product distributions.

Since the resulting product is a fuel, another useful way to visualize this product distribution is by using an energy basis. In Figure 7, the lower heating value (LHV) of these fuels are used to show in which chemicals the useful energy is stored. It can be seen, for example, that with the NREL system that if ethanol is the only desired product only 82% of the maximum conversion efficiency is utilized; the rest of the energy is diverted into the side products which are not currently used to an appreciable amount as fuels.

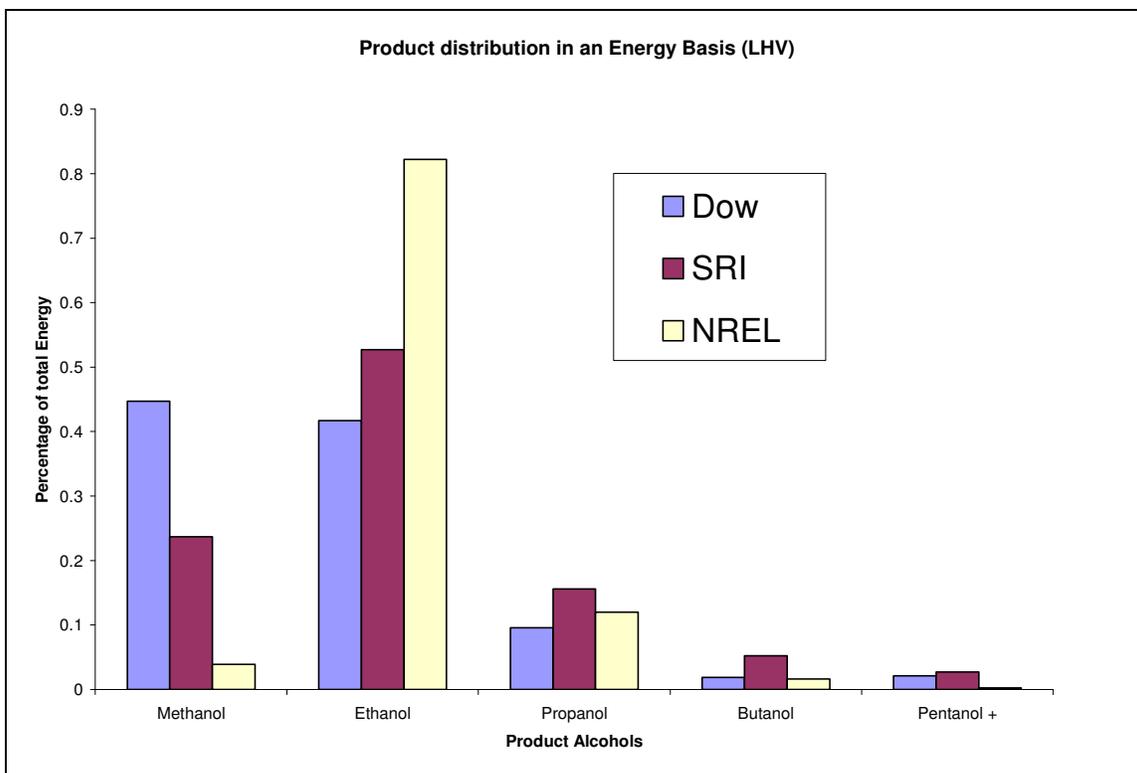


Figure 7 - Mixed alcohol product distribution in an energy basis.

Dimethyl Ether Production

Dimethyl ether is the dehydrated product of two molecules of methanol.



Industrially, DME can be produced directly from syngas to avoid the cost of an additional dehydration reactor. The reactions that govern this process are a combination of equations (5), (6), and (16). Today most DME is produced via the combination of equations (5) and (16) yielding the overall reaction:



A group in Japan (JFE Co. formerly NKK) has been developing a one-step process which in addition to reactions (5) and (16), reaction (6) occurs concurrently, yielding the overall reaction:



It is evident from the stoichiometries of reactions (17) and (18) that a H₂/CO ratio of 2 and 1 is desirable respectively (Ogawa et al. 2003, 219). The latter H₂/CO ratio, is better suited for use with syngas from biomass.

Dimethyl Ether Catalyst

In a linear production scheme, where methanol is first produced then used as the feedstock for DME production, the catalyst system used for dehydration is a γ -Al₂O₃ based catalyst which is modified with phosphates or titanates. The latter two materials are used as promoters. Additional research has been done on the use of zeolites, silica aluminas, mixed metal oxides, as well as palladium based catalysts (Kung and Smith , 175). The alumina based catalyst system requires the reaction temperature to be below 300°C to maintain high catalyst activity.

Systems such as that of JFE/NKK are aimed at creating a ‘direct DME’ synthesis from syngas. In these cases dehydration promoting catalysts are mixed with the methanol promoting catalysts in the same reaction vessel. This reaction scheme is favored by the thermodynamic equilibrium, because the dehydration creates more water which can be used to shift excess carbon monoxide to hydrogen to create more methanol, which then via Le Chatelier’s principle promotes increased dimethyl ether production.

Fischer-Tröpsch Synthesis

Fischer-Tröpsch synthesis (FTS) was the first process used to convert syngas into liquid fuels on an industrial scale and is currently one of the biggest consumers of syngas, after the production of industrial hydrogen and methanol (Wender 1996, 189-297). Today’s largest commercial FTS plants, SASOL I, II & III, are designed to produce more than 17.25 million liters (4.5 million gallons) of FT products daily (Probstein and Hicks 1982).

The first work describing the catalytic hydrogenation of carbon monoxide to methane was performed by Sabatier and Senderens in 1902. In 1913, BASF was issued patents on the synthesis of hydrocarbons and oxygenates via carbon monoxide oxygenation over oxide

catalysts. In 1923, Fischer and Tröpsch produced synthol (Wender 1996, 189-297). The production of synthol, composed mainly of straight chain alkanes from C1 to C50, takes place over cobalt, iron or ruthenium based catalysts. The distribution of products is governed by the Anderson-Schulz-Flory (ASF) polymerization model (Huber, Iborra, and Corma 2006, 4044-4098):

$$W_n = n(1 - \alpha)^2 \alpha^{n-1} \quad \text{Eq. (19)}$$

Where W_n is the selectivity of the n -carbon chain and α is the probability of chain growth. The probability of chain growth cannot be directly controlled. It must be indirectly controlled by changing the temperature, pressure, and most importantly, the species residence time in the reactor. In Figure 6, the ASF model is used to plot the selectivities of alkane product groups of interest, methane (C1), ethane through butane (C2-C4, LPG), gasoline/light distillates (C5-C10), diesel fuel (C11-C22) and higher waxes (C23+). It is apparent from this distribution that FT synthesis has a low selectivity of desired products. If the residence time is too short, the products are dominated by methane and LPG. If the residence time is too long, the products are quickly dominated by long waxes. In order to combat this problem, SASOL employs short chain gas (C1-C4) recycling which boosts the overall conversion efficiency to gasoline/diesel ranged hydrocarbons, however it decreases the overall production efficiency since the production of syngas from methane is only 70% efficient due to the exothermic nature of the reaction and second law losses (Probstein and Hicks 1982).

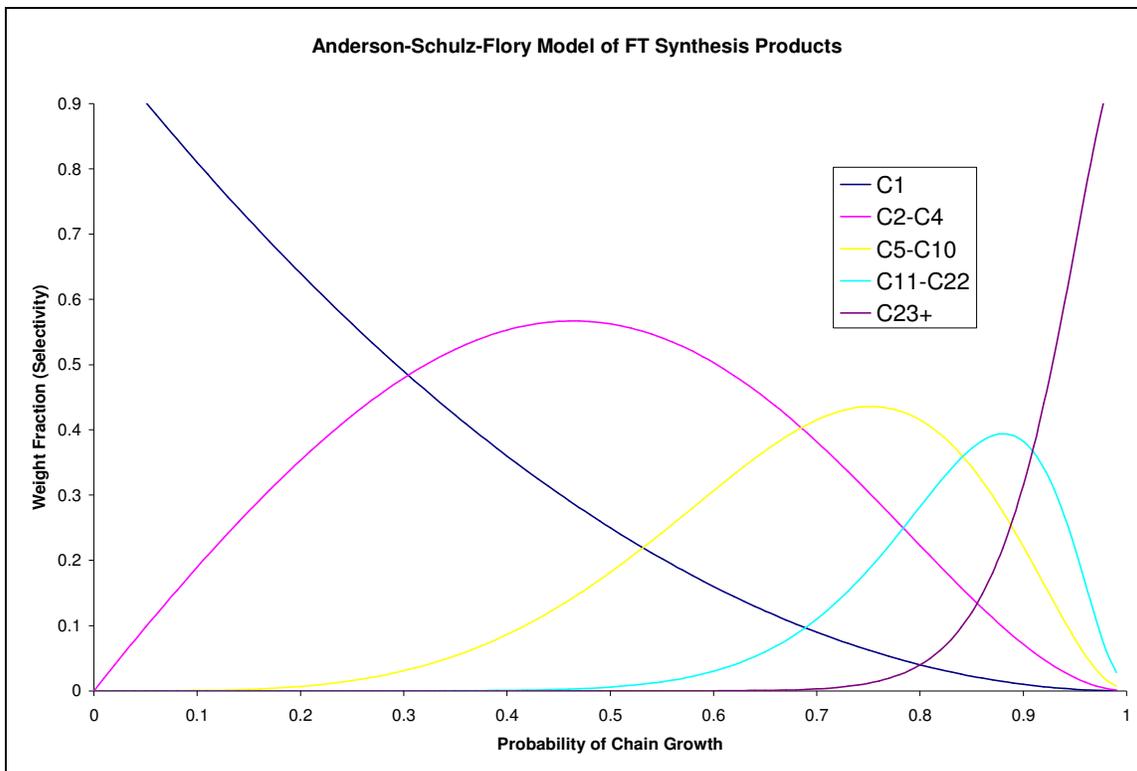


Figure 8 - ASF Model of FT Synthesis Products, adapted from (Probstein and Hicks 1982).

SASOL achieves an overall conversion efficiency of approximately 40% for the production of motor fuels from coal (Wender 1996, 189-297). It has been argued that if gas recycling was abandoned and synthetic natural gas and LPG were instead sold as co-products an overall efficiency as high as 58% could be achieved (Probstein and Hicks 1982). This is more feasible in FT plants in the US where there already exists dedicated natural gas and LPG infrastructure, which was not the case in South Africa when SASOL was built in the 1950s.

Beyond using coal as a feedstock natural gas has been used extensively in so called Gas-to-Liquids (GTL) applications where one of the primary products is Fischer-Tröpsch Diesel is one of the primary products (Fleisch, Sills, and Briscoe 2002, 1-14). The primary advantage of using natural gas as a feedstock is the improved gasification efficiency and ease of processing. As of 2002, there was only about 35,000 barrels per day of GTL production; however more than 1 million barrels per day of GTL capacity was in the pipeline or under construction(Fleisch, Sills, and Briscoe 2002, 1-14).

Though Fischer-Tröpsch fuel production is a well established fuel production technology dating back to the turn of the 20th century, there is a renewed interest in improving the technology with modern engineering methods. A US based company, Velosys, is working on advanced technology development to improve the heat and mass transfer characteristics of the catalytic FT production step (and thus the conversion efficiency) by using a micro-channel technology (Kratochwill, Glatzer, and Farrell 2008; Tonkovich et al. 2008).

Mobile Methanol-to-Gasoline (MTG) Synthesis

The Mobile Methanol-to-Gasoline (MTG) process (also known as the Mobile-M process) is a catalytic synthesis route to produce high octane gasoline from methanol over a zeolite catalyst ZSM-5. The reaction is highly exothermic with a heat of reaction of approximately 1.74 MJ per kg of methanol reacted. The reaction takes place nearly stoichiometrically producing gasoline and water (Dwyer, Hanson, and Schwartz ; Keil 1999, 49-66). Because of the high heat of reaction, a large amount of enthalpy is lost in the fuel decreasing the overall energy conversion efficiency.

The gasoline produces is a high octane product, with a RON ranging from 93-96.8. Its components have been reported to be 60-67% paraffins, 6-8% Olefins and 27-32% aromatics (Csicsery 1986, 841). The product of the New Zealand test plant was 40% aromatics (Huber et al. 2006). This high fraction of aromatics could cause for low acceptance in the United States due to its possible non-compliance with the Clean Air Act which stipulates that the aromatic hydrocarbon content of reformulated gasoline shall not exceed 25% by volume (Baucus 1990, 549). This fuel would have to be mixed with non-aromatic gasoline, such as short chain FT products in order to be marketable in the US. This fuel production method had been employed commercially in New Zealand from 1985 to the mid nineties. A test plant ran from 1981 to 1984 producing 14500 bbl/day at an efficiency of approximately 36% (Huber, Iborra, and Corma 2006, 4044-4098; Keil 1999, 49-66).

The conversion of methanol to MTG is nearly complete (~93% carbon conversion efficiency) (Fleisch 2006). With continued work towards integrated heat management in an integrated coal

(or biomass) to methanol to MTG facility it is estimated that efficiencies could be improved to higher than 40% for coal to liquids facilities (Heinritz-Adrian et al. 2007).

Distribution

One of the major challenges that must be overcome for any alternative fuel to have a meaningful impact on current petroleum based technologies is the fuel's adaptability to the current distribution infrastructure. Today's fuel distribution infrastructure is truly global, spanning all of the inhabited continents from remote energy producing locals to densely populated energy consuming centers. This fuel distribution system employs water based transport (barges and trans-oceanic super tankers), land transport (trucks and rail), as well as pipelines. Because of the vastness of this system and the variety of modes of transportation used, determining which alternative fuel best can integrate into our current infrastructure is challenging. In this thesis the three methods of transport considered are truck, rail and pipeline. The analysis performed in this thesis considers strictly domestic production and consumption³, as such there is no need for tanker utilization.

Due to their high energy density, and physical similarity to the current fuels of choice (oil, diesel and gasoline) liquid fuels would be most easily integrated into the current fuel distribution infrastructure. Further, on a volumetric basis, the cost of shipping any fuel grade liquid would be comparable to that of crude oil (Short 1994, 215). Unlike shifting to a gaseous fuel, which would require a major overhaul of refueling stations, shifting to liquid fuels would be more easily accepted by consumers, since they are familiar with handling liquid fuels at the pump (Olah, Goepfert, and Prakash 2006).

The two characteristics of a given fuel which are of interest when considering integrability of fuels into a distribution system are miscibility with water and the energy density in a volumetric basis due to the reasons cited above. These are tabulated below.

³ This thesis considers only domestic production because energy security, and as such domestic production, is one of the primary thrusts in much of the recent (and proposed) federal energy policies. Additionally, even without provisions for domestic production in federal policy, it would likely be the case that increased economically competitive biofuel production in the US would be used for domestic consumption since we are largely an energy importing nation.

Fuel	Miscibility with water (mL/mL)	LHV (MJ/L)
<i>Methanol</i>	1	15.7861
<i>Ethanol</i>	1	22.7745
<i>Propanol</i>	1	24.6483
<i>Butanol</i>	0.091	26.7841
<i>Diesel</i>	0	36.12
<i>Gasoline</i>	0	33

Table 5 - Miscibility and heating value of fuels (Perry and Green 1997).

Traditionally, gaseous fuels have not been used to power the transportation sector, and their distribution infrastructure does not integrate all the points necessary for the full distribution of fuels for transport. Because of this, the integration of gaseous fuels into the transportation fuel infrastructure has more hurdles to overcome.

Because of these fuels' physical properties, different handling and refueling systems must be employed at refueling stations. Thus, a transition to gaseous fuels may meet more public resistance, as well as industry resistance.

End Use

The last major energy conversion step in the current transportation fuel life cycle is the combustion of the fuel in an Internal Combustion Engine (ICE). Even though the ICE has been the dominant automotive propulsion technology for nearly a century, it is a rather inefficient step in the transportation fuel life cycle. The two dominant technologies today are Spark Ignition (SI) engine technology and Compression Ignition (CI) engine technology. In general, CI engines are more energy efficient than SI engines (Heywood 1988). Each of these technologies are optimized for certain fuel characteristics.

Vehicular Emissions

Just as each fuel's physical and chemical properties influence their energy conversion characteristics in an internal combustion engine, so too do these properties influence the emissions characteristics of a given fuel.

Emissions of automobiles are measured by a standardized metric, *specific emissions*, which is the mass flow rate of the pollutant per unit power output:

$$sX = \frac{\dot{m}_X}{P} (g / kW \cdot h) \quad \text{Eq. (20)}$$

Where X is the chemical species of interest (nitrogen oxides (NO_x), carbon monoxide (CO), hydrocarbons (HC) or particulate matter (PM)); \dot{m} is the mass flow rate of the given species, and P is the output power of the engine. The US government exercises its ability to regulate fuels primarily through the Clean Air Act (CAA), which spells out the allowed emissions for automotive transportation technology. Additionally, the CAA dictates the chemical make-up of fuels, such as limits on aromatic compounds, and limits on the amount of ethanol that can be mixed with fuels. Because of this existing regulatory framework, care must be taken to characterize an alternative fuels emissions characteristics and chemical make-up as compared to the fuel it is proposed to replace.

CHAPTER 4: BIOMASS GASIFICATION FUEL SYSTEM ANALYSIS

In this chapter, each fuel is analyzed using the criteria introduced in Chapter 2. Each fuel's lifecycle consist of three major steps: fuel production, product distribution and automotive end-use. The analytic criteria, as outlined in Chapter 2, are used to assess each of these major steps of the fuel lifecycle. Additionally, other system wide challenges, such as health and environmental hazards, are discussed in broader context. The results from these analyses are summarized and further discussed in Chapter 5, along with the policy challenges that thermochemically produced biofuels must overcome.

Production Efficiency

The first law efficiency of the conversion process is defined as the ratio of the usable energy out to the total amount of energy put into the process:

$$\eta_i = \frac{\text{Energy}_{fuel_produced}}{\text{Energy}_{feedstock}} \quad \text{Eq. (21)}$$

In a normal control volume system, such as a gasifier or chemical reaction vessel, the first law Energy Balance is written as:

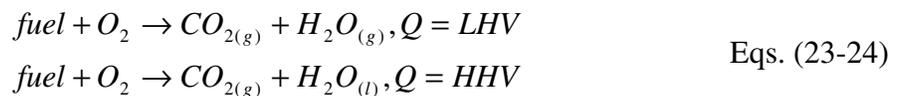
$$0 = \sum_i \dot{m}_i \hat{E}_i - \sum_o \dot{m}_o \hat{E}_o + Q_i - Q_o + W_i - W_o \quad \text{Eq. (22)}$$

Where \dot{m}_i is the mass flow into the control volume, \dot{m}_o is the mass flow out of the control volume, Q_i is the heat transfer into the control volume, Q_o is the heat transfer out of the control volume, W_i is the work done to the control volume, and W_o is the work done by the control volume. The terms \hat{E}_i and \hat{E}_o refer to the total energy carried by one unit mass of the material in the control volume; generally this is defined as the sum of the individual forms of energy:

$$\hat{E}_i = \hat{H}_i + PE_i + KE_i + Elec_i + \dots + \quad \text{Eq. (23)}$$

Where \hat{H}_i is the enthalpy per unit mass of the material, PE_i is the potential energy, KE_i is the kinetic energy, and $Elec_i$ is the electrical energy. The ellipsis indicates that this list could contain many more terms. Depending on the energy conversion system being evaluated, different terms will dominate where the others turn out to be insignificant. For example, in the conversion of wind energy to electricity the only energetic term of concern is the kinetic energy whereas for hydropower, potential energy is the most important.

For alternative fuel systems, the energy form which must be accounted for is the thermal energy contained in the chemical bonds of the fuel(s) being used and fuel(s) being produced. This form of energy is contained in the enthalpy term. This term, however, does not only account for chemical energy (measured by the standard enthalpy of formation, \hat{H}_f^o), it also accounts for thermal energy of the material as well, or the sensible enthalpy, \hat{H}_s . While the use of the standard enthalpy of formation for energy accounting in this system would be sufficient, it is not convenient. Since all of the fuels considered for automotive transportation are combusted in oxygen to release their energy, the more commonly used energy measure heat of combustion is used. The heat of combustion is defined as the enthalpy of reaction of the complete oxidation of any hydrocarbon fuel to carbon dioxide and water at standard temperature and pressure. There are two common measurements for this, the higher heating value (HHV) and the lower heating value (LHV), where for the former the water produced is assumed to be liquid and for the later the water is assumed to be gaseous. In this study the majority of reactions take place at high temperatures above 100°C and, when possible, LHV will be used as a more realistic measure of chemical energy. Equations 23-24 illustrate the general chemical reactions from which LHV and HHV are derived.



For different systems, authors will often use different accounting methods to track different energy streams. For example, in the production of fuels, there is often a need to use electricity in the process either bought from the grid or produced on-site. In the case that the electricity is

produced on-site from the combustion of some portion of the biomass used for fuel production, then the energy would be accounted for by the LHV of the biomass used for electricity production. In the case where no electricity is produced onsite, the electricity bought from the grid would either be accounted for in the work in term W_i . The more general statement of the first law efficiency of the systems of interest is thus:

$$\eta_l = \frac{\dot{m}_{prod} LHV_{prod}}{\sum_i \dot{m}_i LHV_i + W_i + Q_i} \quad \text{Eq. (26)}$$

where the numerator of the fraction accounts for the total energy of the desired product, and the denominator accounts for the energy put into the system. In this formulation, the energy content of by-products is neglected. Take for example a plant which is designed to produce ethanol thermochemically via mixed alcohol production. While methanol, propanol, butanol and other higher alcohols make up a substantial amount of byproducts, these co-products may not be produced in substantial enough numbers to justify the sale of these fuels into fuel markets as well. Additionally, this formulation neglects work out, W_o , and heat transferred out Q_o . This is justified by the same reasoning as above. Additionally for heat transferred out, this heat is very difficult to harness into usable form due to entropic losses.

In this thesis, it is assumed that all the requisite work and heat is produced from the feedstock input for the process. In the case of fuel production, it is assumed that a part of the cellulosic feedstock is used to produce the requisite shaft work, heat and electricity. For fuel distribution it is assumed that the fuel itself is used to power the pipeline infrastructure, the trains, and the trucks. This later assumption is probably further from realistic than the assumption on production because in the event that a new fuel is introduced it would not make up a significant percentage of the national fuel mix, however since this same approximation is used for each fuel it should provide a neutral metric to compare each fuel.

For linear production systems, the process efficiencies are the product of the efficiencies of their parts. The main parts of a fuel production system based on biomass gasification are the

gasification, gas clean-up and preparation, product synthesis, and product separation/clean-up. Thus the process efficiency, $\eta_{I,process}$, can be defined as follows:

$$\eta_{I,process} = \eta_g \eta_{cp} \eta_{syn} \eta_{sep} \quad \text{Eq. (27)}$$

Where η_g is the gasification efficiency, η_{cp} is the gas clean-up and preparation efficiency, η_{syn} is the product synthesis efficiency, and η_{sep} is the efficiency of product separation and clean-up. In the literature, the efficiency most often published is the overall process efficiency and the gasification efficiency. In the systems being analyzed, the step which is common to each is the gasification step. Each of the processes differ for their requirements of gas clean-up, synthesis, and product separation. Thus, the above equation can be simplified to:

$$\eta_{I,process} = \eta_g \eta_{prod,i} \quad \text{Eq. (28)}$$

where

$$\eta_{prod,i} = \eta_{cp} \eta_{syn} \eta_{sep} \quad \text{Eq. (29)}$$

Where the subscript i denotes the different produced fuels: methanol, ethanol, et cetera. Since the process efficiency and the gasification efficiencies are often known for the processes, $\eta_{prod,i}$ can be calculated for each of the fuels. This can then be used with a common gasification efficiency to estimate the relative overall process efficiencies of fuel production for each of the fuels.

Gasification

Gasification is the first major energy conversion performed in the production of transportation fuels and, as such, dictates the maximum achievable conversion efficiency for the overall process. As such, there is currently much research being performed on gasification systems in order to achieve higher energy efficiencies and more robust operation. There are two major classifications of gasifiers: directly-heated and indirectly-heated. Directly heated gasifiers derive their necessary energy from combustion inside the gasifier itself, whereas indirectly heated

gasifiers derive their energy from external sources, either from heated steam or an inert heated substrate such as sand. Indirect gasifiers generally operate at lower temperatures and pressures compared to directly heated gasifiers. While this may be ideal for applications employing syngas fermentation, it may prove disadvantageous for catalytic chemical synthesis applications where high temperatures and pressures are needed for the synthesis step which would require additional gas compression and heating.

In their study of methanol and hydrogen production via biomass gasification, Williams et al. investigated a number of gasifiers - two directly heated gasifiers, the Institute of Gas Technology (IGT) bubbling fluid-bed gasifier and the entrained-bed gasifier from Shell, and two indirectly heated gasifiers, the fluid bed gasifier by Manufacturing and Technology Conversions International (MTCI) and the fluidized bed developed for the Battelle-Columbus Laboratory (BCL). The relevant operating characteristics of the gasifiers are tabulated in Table 6.

Additional studies have been performed on biomass gasification which also report cold gas efficiencies which range from the mid seventieth percentiles to the mid eighties. In their thermochemical equilibrium study of entrained flow biomass gasification of pine bark, Melgar et al. established a cold gas efficiency ranging from 79-85% in the typical operating conditions (Melgar et al. 2007, 59-67).

Gasifier Design	Bubbling Fluid Bed (IGT)	Indirectly-heated Fluid Bed (MTCI)	Indirect-Heat Fast Fluidized-Bed (BCL)	Entrained-Bed (Shell)	Entrained Bed (Shell) COAL
Feedstock composition	CH _{1.52} O _{0.68}	CH _{1.63} O _{0.66}	CH _{1.54} O _{0.65}	CH _{1.52} O _{0.68}	CH _{0.91} O _{0.11}
Feedstock HHV (GJ/dry ton)	19.28	19.40	19.46	19.28	29.69
Gasifier Steam (kg/ kg dry feed)	0.3	1.37	0.019	0.03	0.03
Gasifier Oxygen (kg/kg dry feed)	0.3	0	0	0.45	0.8
Combustor air (kg/kg dry feed)	0	2.52	2.06	0	0
Exit Temp (°C)	982	697	863	1085	1371
Pressure (Bar)	34.5	1.01	1.01	24.3	24.3
Yield (kmol/tonne dry feed)	82.0	146.8	45.8	79.3	92.4
SynGas Molecular Weight (kg/kmol)	22.27	17.65	21.64	20.08	20.49
HHV Syngas (MJ/kg raw gas)	8.68	9.55	15.73	10.32	12.61
H ₂ O	31.8	49.5	19.9	18.4	2.1
H ₂	20.8	25.3	16.7	30.7	31.8
CO	15.0	11.2	37.1	39.0	64.3
CO ₂	23.9	9.9	8.90	11.8	1.7
CH ₄	8.2	4.0	12.6	0.1	0
C ₂ +	0.3	0.2	4.8	0	0
Net Carbon Efficiency	96.2	67.2	75.2	100	99
Cold Gas Efficiency	82.1	90.0	80.1	85.2	80.3

Table 6 - Characteristics of biomass gasifiers adapted from (Williams et al. 1995, 18).

For gasification, the efficiency most often reported is the Cold Gas Efficiency (CGE) which is the measure of the ratio of purely chemical energy contained in the exit and entrance. This is achieved by assuming no temperature change, therefore no purely thermal energy term. Therefore, the CGE is defined as

$$CGE = \frac{(\dot{m}_o LHV_o)_{T=T_o}}{(\dot{m}_i LHV_i)_{T=T_o}} \quad \text{Eq. (30)}$$

Gasification of Natural Gas: Steam Reforming

As with biomass and coal gasification technologies, there are also a number of approaches to producing syngas from natural gas.

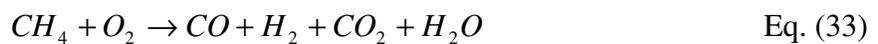
One process of gasifying natural gas is known as steam methane reforming (SMR). It is a much less complex process than the gasification of a solid fuel due to the molecular simplicity of methane. Steam reforming can be described by the following set of chemical reactions:



The steam-methane reformation, coupled with the water gas reaction. These reactions yield an higher hydrogen to carbon monoxide ratio than the gasification of solid fuels (3:1 versus 1:1). This makes methane an optimal feedstock for the production of hydrogen and other fuels which require higher hydrogen to carbon monoxide ratios (such as methanol which requires slightly above a 2:1 ratio). Steam reforming relies on the injection of superheated steam to provide the necessary activation energy to complete the reaction, and so is an indirect gasification method.

Beyond offering higher hydrogen to carbon monoxide ratios, steam reforming of methane is also a more efficient process than solid gasification. This is due to the fact that the process is dominated by two optimizable reactions (above) whereas the gasification of solid fuels undergoes a number of surface and chemical reactions which cannot be simultaneously optimized. The CGE of steam reforming of methane has been reported to be 89.9% (Simpson and Lutz 2007, 4811-4820).

Partial Oxidation (POX) reactors are also occasionally used to produce syngas. This is a non-catalytic process in which the fuel is combusted in a sub-stoichiometric amount of oxygen yielding a mixture of carbon monoxide, hydrogen, water and carbon dioxide (which is dictated by the reaction temperature via the water gas shift reaction). For natural gas the chemical reaction which describes this process is:



The final ratios are dictated by the reactor temperature, residence time and the water-gas shift kinetics (Rice and Mann 2007, 1-50).

Autothermal reformation (ATR) uses a mixture of oxygen, carbon dioxide and/or oxygen and steam to produce a syngas with variable hydrogen to carbon monoxide ratio (Rice and Mann 2007, 1-50). Since both partial oxidation and steam reformation is occurring simultaneously and can be controlled which is the dominant reaction a large range of hydrogen/carbon monoxide ratios can be achieved allowing for more flexibility in downstream use (Rice and Mann 2007, 1-50).

Methanol

Modern natural gas to methanol facilities are characterized by methanol selectivities above 99% and first law process efficiencies above 70% (Olah, Goepfert, and Prakash 2006). The use of biomass and coal as the feedstock decreases the overall efficiency to the range of 50-60%. This is due, in part, to the lower hydrogen to carbon ratio of biomass and coal, which requires additional syngas conditioning prior to methanol synthesis, along with the added gasification complications due to ash content of these feedstocks.

In a 1993 report by the Organization for Economic Co-Operation and Development (OECD), a conversion efficiency of 56.5% from woody biomass was reported. This value is in contrast with efficiencies of 64.9% from natural gas and 55.5% from coal reported in the same study (OECD 1993). Incorporating this production efficiency from woody biomass an overall well-to-station efficiency of 52% has been estimated (Ofner, Gill, and Krotscheck 1998).

More recently woody biomass to methanol conversion efficiencies have been estimated to be on the order of 60% (Azar, Lindgren, and Andersson 2003, 961-976). These estimates are based largely on the work of Williams et al. where an in-depth techno-economic study of methanol and hydrogen from biomass was performed. In the study, the group calculated thermal efficiencies of 53.9%, 56.8%, 57.6% and 61.0% with IGT, MTCI, BCL and Shell biomass gasifiers respectively, for further details see Table 7.

Gasifier Design	Bubbling Fluidized Bed (IGT)	Indirectly-heated fluid bed (MTCI)	Indirectly-heated fast fluidized-bed (BCL)	Entrained bed (Shell)	Entrained-Bed (Shell) Coal
Dry, ash free composition	CH _{1.52} O _{0.68}	CH _{1.63} O _{0.66}	CH _{1.54} O _{0.65}	CH _{1.52} O _{0.68}	CH _{0.91} O _{0.11}
HHV (GJ/dry ton)	19.28	19.4	19.46	19.28	29.69
Initial moisture (%)	45	45	45	45	5
Moisture after Drying	15	20	10	11	5
Energy Ratio	.566	.615	.606	.677	.649
Thermal Efficiency	53.9%	56.8%	57.6%	61.0%	61.3%
Prod Eff ($\eta_{prod,i}$)	65.7%	63.1%	71.9%	71.5%	76.3%

Table 7 – Biomass to methanol production characteristics, adapted from (Williams et al. 1995, 18).

Additionally, there has been work to estimate future conversion efficiencies using the assumption that technological innovation will continue to make the processes more efficient as the technology becomes more widely adapted. Using averages from contemporary studies, a short term conversion efficiency of 55% was assumed, increasing to 57-60% in the future (Faaij 2006, 335-367; Hamelinck and Faaij 2006, 3268-3283).

The production of methanol from natural gas experiences higher production efficiencies on average compared to conversion from biomass. Low estimates of 64% for first law efficiency have been made by Methanex Corporation, with high estimates on the order of 72% for an overall conversion efficiency (Allard 2000). Taken directly from operational data, Berggren calculated a first law efficiency of 69.3% (Berggren 1997). From these numbers syngas to methanol conversion efficiencies of 71.2%, 80.1% and 77.1% are obtained respectively.

Ethanol

Enzymatic Corn Ethanol Production

The conversion efficiency of enzymatic ethanol production from corn has been estimated by the USDA. Modern wet mill plants have been found to require approximately 23.3 lb of corn, 35,150 Btu of thermal energy and 2.134 kwh of electricity per gallon of ethanol produced. These values, once converted to a common energy basis, can then be used in the above equation and an efficiency of approximately 35.8% is found. Dry mill plants require 37,000 Btu of thermal energy, 1.2 kwh of electricity, and a similar amount of corn, yielding a conversion efficiency of 36% (Shapouri, Duffield, and Graboski 1995).

Thermochemical Production

Thermochemically, ethanol can be produced in two ways. First, ethanol can be produced by first making a mixed alcohol product and then separating the constituents to yield ethanol and other alcoholic byproducts, such as the system being studied by NREL and that which Range fuels is attempting to commercialize. Second, ethanol can be produced via syngas fermentation. In this process, specially engineered microbes are used to ferment syngas in much the same way that sugars are fermented to produce ethanol today. Ethanol produced via thermochemical mixed alcohol production from biomass has been reported to be 46% efficient (Phillips et al. 2007). This techno-economic assessment employed an indirect biomass gasification with methanol recycling in order to boost higher alcohol (predominately ethanol) production in a mixed alcohol synthesis unit. The gasifier unit was taken to have a 76.1% cold gas efficiency in an LHV basis and a 76.6% efficiency in an HHV basis. The syngas composition had a H₂:CO ratio of 0.60 and a CO:CO₂ ratio of 3.4. Given the overall efficiency of 46% in an LHV basis and a gasifier efficiency of 76.1% this implies that $\eta_{prod,EtOH_thermal} = 60.4\%$.

There have been some studies of theoretical conversion efficiency for a hybrid thermochemical/enzymatic ethanol production facility. Assuming an overall gasification efficiency of 75%, Huber et al. proposed overall conversion efficiency on the order of 35% from biomass to ethanol. In a ballpark estimate of the technology performed by NREL, an overall conversion efficiency of approximately 40% was found assuming a cold gas efficiency for gasification of 70% (Spath and Dayton 2003). Using these two numbers a ballpark estimate of

$\eta_{prod,EtOH_syn_ferm}$ can be found to be 46.7% - 57.1%. Due to the unproven nature of this conversion technology, these numbers have a high degree of uncertainty.

Mixed alcohol production

From the NREL analysis of thermochemical ethanol production one can get a first order estimate on the overall conversion efficiency for mixed alcohol production. In Phillips et al. the overall efficiency of ethanol production is 46% with approximately 9.6% of the energy contained in the higher alcohol co-products. Thus, an overall conversion efficiency of approximately 55.6% would be attainable if the mixture was marketed as a fuel. From this $\eta_{prod,mixedOH}$ can be estimated to be approximately 73% efficient (Phillips et al. 2007). The approximate composition of this mixed alcohol product is 5.7% MeOH, 81% EtOH, 11.5% PrOH, 1.4% BuOH, and 0.1% PeOH.

Dimethyl Ether

Dimethyl ether, being the dehydrated product of methanol, follows a similar chemical conversion process. As such, the conversion efficiency of this process is found to be on the same order as methanol. In older systems which employed a linear process where methanol was first produced then dehydrated in a separate unit operation, efficiencies were lower than that to methanol because of the additional inefficiency inherent to adding an additional unit operation. Modern production methods, however, employ a combined methanol synthesis and dimethyl ether reaction in one step. This method enjoys a boost in efficiency due to the synergy created by having dehydration and synthesis in the same step. Ogawa et al. reports a system efficiency of 66.3% from natural gas for the production of DME which is increased to 71.4% if the coproduced methanol is included as a product (Ogawa et al. 2003, 219). Natural gas steam reforming is a much more efficient process than biomass gasification with cold gas efficiencies on the order of 90%. Thus $\eta_{prod,DME}$ from this study can be estimated to be approximately 73%.

Additionally, DME production from natural gas has been calculated by Wang and Huang, along with Hansen et al. to be 68.8% efficient excluding electricity co-product and 71.7% efficient including electricity production (Wang and Huang 1999; Hansen et al. 1995). This yields

$\eta_{prod,DME}$ equal to 76.5% where a first law efficiency of 89.9 is assumed for the steam reformation of methane.

Fischer-Tröpsch Diesel

An efficiency of conversion for biomass to Fischer-Tröpsch (FT) liquids has been estimated to be 40%, similar to that of coal, assuming a cold gas efficiency of approximately 70% for biomass gasification (Wender 1996, 189-297). The efficiency of production, $\eta_{prod,FT}$, can be estimated from these numbers to be approximately 57.1%. Additional studies have put the efficiency at 45%, with future efficiency of 55% to be attainable where 10% is electricity coproduced and sold on the market (Faaij 2006, 335-367; Hamelinck and Faaij 2006, 3268-3283). These studies, however, appear to be overly optimistic in their future efficiency gains for such an old technology.

The production of FT diesel from natural gas has also been studied. In a study performed by Argonne National Laboratory conversion efficiencies of 49% for syntroleum conversion technology and 57% for shell technology were calculated resulting in conversion efficiencies from syngas to FTD of 54.5% and 63.4% respectively (Wang and Huang 1999). Additionally, further study of the shell design has been performed for both small and large implementation showing increased efficiencies with increased scale from 46% efficiency in a plant processing 100 million scf/d, to 57% for a plant processing 410 million scf/d (Choi et al. 1997, 667; Choi et al. 1997). These studies yield efficiencies of conversion from syngas to FTD of 51.1% and 63.4% respectively.

MTG Product

The Mobil-M fuel production method has been employed commercially in New Zealand in the 1980's. A test plant ran from 1981 to 1984 producing 14500 bbl/day at an efficiency of approximately 36% (Huber, Iborra, and Corma 2006, 4044-4098; Keil 1999, 49-66). This yields a 60% process efficiency, $\eta_{prod,MTG}$, for methanol to gasoline. From this, the conversion efficiency from syngas to MTG product can be estimated to be 39.6 – 43.2%. It has been estimated that this process could yield overall system efficiencies as high as 48% for coal to

gasoline (Probstein and Hicks 1982). This estimate seems overly optimistic when compared to the achieved efficiency where natural gas is the feedstock.

Production Efficiency Summary

While fuel production systems are often non-linear and many steps are connected together with in non-sequential ways, a good estimate of unit process efficiencies can be made as shown above. From the estimates made above one can more easily compare the efficiencies of production for different fuels from the gasification of a common feedstock. These syngas to fuel production efficiencies are tabulated below.

Fuel	Biomass/Coal Feedstock	Natural Gas Feedstock
Methanol	63-72%	71-80%
Ethanol via syngas fermentation	46-57%	-
Ethanol via catalytic mixed alcohol production	60%	-
Mixed alcohol production	70-73%	-
DME	-	73-76.5%
FT Diesel	57%	51-63.4%
MTG Gasoline	-	40-43%

Table 8 - Summary of syngas to fuel production efficiencies of different fuels as taken from literature.

The first law conversion efficiencies of syngas to fuel step are summarized in Table 8. The majority of losses take place in this step of fuel production. This is primarily due to irreversibilities created from heat loss across the reactor boundaries due to the need for multiple passes of the reaction gases over the catalysts. Likely, there exists room for improvement in this synthesis step and there is work being done to improve heat management and conversion efficiencies of syngas to fuels. By avoiding excess heat loss in these processes, for example by using waste heat to dry the biomass, overall systemic conversion efficiency can be improved.

In Table 9, the overall biomass to fuel conversion efficiency is calculated assuming a biomass to syngas cold gas efficiency of 80%. Since there is only one data point for catalytic ethanol production it is assumed that this is a 'best case' estimate and as such no low end efficiency can be estimated for the process.

	Methanol	Ethanol, syngas fermentation	Ethanol, catalytic	Mixed alcohol	DME	FTD	MTG
<i>Syngas to Fuel Efficiency</i>							
High	72	57	60	73	73	63.4	43.2
Low	63	46	?	70	64	51	39.6
<i>Overall Efficiency</i>							
High	60	43.6	48.3	58.4	58.4	50.7	34.5
Low	50	36.8	?	56	51.2	40.8	31.6

Table 9- Biomass to fuel conversion efficiencies, assuming a biomass gasification efficiency of 80%.

As above, Table 10 summarizes the conversion efficiency of natural gas to fuel assuming a natural gas to syngas cold gas efficiency of 90%. Again, no lower bound is estimated for the catalytic ethanol production.

	Methanol	Ethanol, syngas fermentation	Ethanol, catalytic	Mixed alcohol	DME	FTD	MTG
<i>Syngas to Fuel Efficiency</i>							
High	80	57	60	73	76.5	63.4	43.2
Low	71	46	?	70	73	51	39.6
<i>Overall Efficiency</i>							
High	72	51	54.3	65.7	69	57	38.8
Low	64	41.4	?	63	65.7	45.9	35.6

Table 10 - Natural gas to fuel conversion efficiency assuming a natural gas gasification efficiency of 90%.

Production Economics

In order to decide between alternative fuels, one of the most important parameters is the cost of production. There are many variables that affect the cost of production for a given fuel including the overall conversion efficiency, the capital investment required for the process equipment, and the investors required rate of return. Since syngas production from biomass gasification has not been implemented at large scale, many of the reported costs published in studies have been first order estimates with errors of $\pm 30\%$. Therefore, while these costs may offer a loose guideline of

the economic viability of these fuels, more data is needed from pilot scale plants in the production of these fuels. In this thesis all monetary values have been converted to 2007 US dollars and are listed by the original value from the literature source to allow for easier comparison. At the end of this section is a summary which has all prices quoted in 2007 dollars using a common energy and volume measurement.

Methanol

Methanol synthesis from syngas is the most energy efficient conversion to a liquid fuel. Additionally, the synthesis of methanol from syngas is one of the most well established industrial chemical processes, as such its production costs are relatively well known for processes which use natural gas and coal as a feedstock. The production of methanol from biomass is more cost intensive due to complications with biomass gasification which leads to lower energy conversion efficiency and the need for further gas cleanup and reactor slag controls increasing the capital intensity of a biomass to methanol plant. These problems are shared by all biomass to fuel plants which employ gasification.

Many techno-economic studies have been performed on the biomass to methanol conversion process yielding different estimates of the cost of production. In one of the first techno-economic assessments of this technology performed in the 1990s, the minimum selling price for methanol from biomass was estimated to be $_{1991}\$12-14.5$ ($_{2007}\$18.05-21.81$) per gigajoule of methanol where a cost of $_{1991}\$2.5$ ($_{2007}\$3.76$) per gigajoule of delivered biomass was assumed (Williams et al. 1995, 18).

In 2003, further assessment of this system was performed by the National Renewable Energy Laboratory (NREL). A minimum selling price of $_{2003}\$13-14$ ($_{2007}\$14.63-15.76$) per gigajoule methanol was estimated where the cost per metric ton of delivered biomass was taken to be $_{2003}\$33$ ($_{2007}\$37.14$) (Spath and Dayton 2003).

Most recently, an estimate of the minimum selling price for methanol from biomass in Europe was estimated to be $10-15\text{€}_{2006}$ ($_{2007}\$10.28-15.42$) per gigajoule in the short term evolving to 6-

8€₂₀₀₆ (2007\$6.17-8.22) in the long term due to improved technology as more production facilities employing biomass gasification are built and operated (Faaij 2006, 335-367).

Ethanol

Due to ethanol's favored status among policymakers and its favorable economic subsidies, there has been much more work dedicated to the production of ethanol from ligno-cellulosic feedstocks. As such, the current estimates of ethanol produced via biomass gasification appear to be more optimistic in part both to techno-optimism of policymakers and engineers, and due to the advanced development of these systems due to larger amounts of research moneys that have been dedicated to their study.

In the same techno-economic study which NREL performed on methanol production via biomass gasification (see above), an estimate was also made of the minimum selling price for ethanol produced via syngas fermentation. This estimate was 2003\$14 (2007\$15.76) per gigajoule again assuming 2003\$33 (2007\$37.14) per dry metric ton of biomass (Spath and Dayton 2003). The authors acknowledge, however, that this is a rough ballpark estimate based on predictions from scientists on the conversion efficiencies which could be achievable with the technology in the future. In my opinion, this estimate suffers from a heavy dose of techno-optimism for ethanol production to replace imported oil.

In a later techno-economic study exclusively focused on catalytic ethanol production via biomass gasification a minimum selling price of 2005\$1.01 (2007\$1.07) per gallon of ethanol was estimated (2007\$11.55 per gigajoule). This estimate assumes that all of the produced co-products propanol and butanol can be sold into commodity chemical markets at 60% their current market prices. Additionally, this study assumes a price of 2005\$35 (2007\$36.88) per delivered dry US-ton biomass as based on recent target prices published by the Idaho National Laboratory (Phillips et al. 2007).

A techno-economic study of ethanol produced via enzymatic conversion of ligno-cellulosic biomass put the minimum selling price at 1996\$1.18 per gallon (or 2007\$16.76 per gigajoule) (Lynd 1996, 403-465).

Dimethyl Ether

There have been no techno-economic estimates of the cost of production of dimethyl ether from biomass, however the cost of production from natural gas has been established. From these determined costs, a cost for the production from biomass can be estimated by looking at the percentage change in production costs for other fuels for which biomass has been used instead of natural gas as a feedstock.

The minimum gate selling price for dimethyl ether produced from natural gas has been established to be 2003\$4 per MMBtu (2007\$4.50 per gigajoule) with a natural gas price assumed to be 2003\$1.5 per MMBtu (2007\$1.60 per GJ) (Ogawa et al. 2003, 219). In the study on methanol production from biomass performed by Williams et al. the increase in minimum selling price of methanol from biomass versus natural gas is 240% higher when normalized against feedstock cost. As such, if the cost per MMBtu delivered dry biomass was taken to be 2003\$2 (2007\$2.13 per MMBtu), then the minimum selling price of dimethyl ether would be on the order of 2007\$14.63 per GJ.

Fischer-Tröpsch Diesel

Fischer-Tröpsch products have been employed commercially over the past century and as such their cost of production has been well established for natural gas and coal as feedstocks. Due to their complete compatibility with today's compression ignition engine technology there has been increasing interest in developing production routes from biomass as well in order to produce high volume amounts of bio-derived diesel products.

The minimum selling price of Fischer-Tröpsch products produced from biomass has been estimated to be 2003\$19-25 per gigajoule (2007\$21.38-28.13) (Huber, Iborra, and Corma 2006, 4044-4098; Spath and Dayton 2003) While much higher than other synthetic fuels, this price is competitive with today's diesel prices in a per gallon basis.

The minimum selling price of Fischer-Tröpsch products has also been estimated in Europe where an estimate of 12-17€₂₀₀₆ per gigajoule (2007\$12.34-17.48) in the short term evolving to 7-9€₂₀₀₆ per gigajoule (2007\$7.20-9.25) in the long term (Hamelinck and Faaij 2006, 3268-3283).

MTG Gasoline

Recently there has been much renewed interest in the Mobile-M methanol-to-gasoline process. There have not been any techno-economic studies of this fuel produced from biomass, however there has been analysis of data collected from the application of this technology in New Zealand in the early 1980's employing natural gas as a feedstock.

A minimum selling price of 1990\$1.55 per gallon (2007\$18.44 per GJ) of MTG gasoline has been reported assuming a full investment return of 10% and natural gas price of 1990\$1.25 per gigajoule (2007\$2 per GJ Natural Gas) (Sugiyama 1994). If the same first order estimate technique employed for dimethyl ether is used here (see above) the cost per gallon of MTG gasoline from biomass would be 2007\$43.90 assuming \$1.25 per gigajoule of delivered dry biomass.

Production Economics Summary

The production costs summarized above come from a variety of studies conducted assuming different base years and costs of inputs. In order for these numbers to be used today they have been normalized to a base year of 2007 dollars, and all of the prices have been set to an energy basis of one gigajoule of fuel.

	Low (\$/GJ)	High (\$/GJ)	cost of biomass (\$/GJ)	Year of study	biomass unit in study
methanol	\$18.05	\$21.81	\$3.76	1991	Gigajoule
	\$14.63	\$15.76	\$37.14	2003	metric ton
	\$10.28	\$15.42		2006	N/A
Ethanol	\$15.76	?	\$37.15	2003	metric ton
	\$11.55	?	\$36.88	2005	US-ton
	\$16.76	?		1996	N/A
MTG	\$18.44	?	\$1.96	1990	gigajoule(NG)
	\$43.90	?	\$1.96	1990	Gigajoule
FTD	\$21.38	\$28.13	\$37.13	2003	metric ton
	\$12.34	\$17.48		2006	N/A
DME	\$4.50	?	\$1.60	2003	MMBtu (NG)
	\$14.63	?	\$2.13	2003	MMBtu

Table 11 - Summary of costs of production in 2007 dollars.

Distribution Integrability

In order for a fuel to be adopted at scale, it must be able to be shipped via the current fuel distribution infrastructure. The current fuel shipping infrastructure consists of pipelines, rail shipment and truck transport. The fuel pipeline infrastructure in the United States was designed to ship hydrocarbon fuels (petroleum derived and natural gas) which are hydrophobic and generally non-corrosive. As such, pipeline operators have been reluctant to ship quantities of alcohols or other hydrophilic/corrosive fuels for fear that they could damage the pipelines or render delivered fuels unsellable due to increased water content. Rail and truck shipment, on the other hand, has been utilized by the growing ethanol industry to ship product nationwide though at a higher energetic and monetary cost. Due to the different physical and chemical properties of the fuels analyzed in this thesis, the optimal shipment method for each of these fuels is constrained both by physical limitations and also reluctance on behalf of a large industry. In the following sections the integration of each of the fuels into the current distribution infrastructure is analyzed.

Alcohol Distribution Infrastructure

Methanol is corrosive (as is the case for short chain aliphatic alcohols) and completely miscible in water; because of these characteristics many pipeline operators are reluctant to ship methanol in the established petro-fuel infrastructure. Taking necessary precautions, however, Celanese Canada successfully moved 4000 tons of methanol 750 miles from Edmonton to Vancouver in the mid 1980s (Mills and Ecklund 1987, 47-80). This shipment was deemed to be very successful with only minor changes in the shipments composition from Edmonton to Vancouver (see Table 12).

	Leaving Edmonton, Alberta	Arriving Burnaby, British Columbia
Methanol Content %	99.99	99.68
Hydrocarbon Content%	0	0.29
Water Content%	0.01	0.02
Non-volatiles %	0	0.01

Table 12 - Celanese Canada methanol shipment analysis, adapted from (Short 1994, 215).

The current growth of the ethanol industry has allowed for a large scale ‘proof of concept’ for alcohol fuel distribution and utilization. Currently much of the fuel grade ethanol is shipped by truck and rail, however, more petrol companies are accepting shipments of ethanol in their pipeline infrastructure (Dinneen 2008). Additionally, the 2007 Energy Independence and Security Act has extended and expanded tax credits for fueling stations to install alcohol ready fuel tanks and pumps (Rahall 2007, 110-140). In the late 1980s, a network of approximately 100 methanol refueling stations were built in California (Olah, Goeppert, and Prakash 2006). Currently there are 1,646 E85 retailers in 42 states in the United States, with calls to increase this number 10 times (NEVC 2008). For ¼ of the nearly 180,000 refueling stations in the US to install an alcohol refueling pump, the cost has estimated to be less than \$3 billion dollars one fourth of the \$12 billion dollars spent to introduce reformulated gasoline to US stations (Olah, Goeppert, and Prakash 2006). This continued expansion of alcoholic fuels should allow for an easier introduction of fuel alcohols into the mix.

Another major challenge for the integration of alcohol fuels is economics. As cited above, the cost of shipping liquid fuels is roughly the same on a volumetric basis (Short 1994, 215). However, on a volumetric basis alcoholic fuels contain less energy than the more energy dense hydrocarbons. Therefore, the cost of shipping alcoholic fuels would be more expensive than shipping an energy equivalent amount of hydrocarbon fuel.

The integration of higher alcohols into the current distribution infrastructure faces the same challenges that the integration of methanol and ethanol do. The challenges for higher alcohols are somewhat lessened, however, due to the decreasing miscibility with water and increasing energy density as the aliphatic chain is increased.

Synthetic Hydrocarbon Distribution Infrastructure

Whereas alcoholic fuels have faced hurdles in being accepted into the fuel distribution infrastructure, Fischer-Tröpsch products should garner little resistance. Compared to other synthetic fuels, Fischer-Tröpsch products have a high energy density, on par with oil, leading to a lower cost of distribution (Takeshita and Yamaji 2008, 2773-2784). Further, because of their chemical similarity to currently used hydrocarbon fuels, they can be easily integrated into the

current fuel distribution system, thus avoiding the so-called “chicken-or-egg problem” faced by more radical fuel technology shifts to gases and even alcohols.

As with FT Diesel, MTG Gasoline faces few challenges compared to alcohols when it comes to integrability in the current fuel distribution infrastructure.

Dimethyl Ether and Hydrogen

Hydrogen, due to its extremely low density, incurs very high shipping and storage costs. In order to increase the energy density per volume, one must either pressurize, or liquefy hydrogen. However this consumes a great amount of both energy and capital, greatly increasing shipping costs. As such, it is assumed that in a future transition to a hydrogen based transportation sector, local generation of hydrogen would be required. Further, because of the small size of hydrogen molecules, a much greater occurrence of fuel leakage occurs. For gaseous hydrogen shipped via pipeline a loss of approximately 3.5% occurs per 1000 km compared to 2.3% for liquid fuels over the same distance (Takeshita, Yamaji, and Fujii 2006, 285).

Unlike hydrogen, dimethyl ether is easily liquefied, allowing for better integration. Dimethyl ether, because of the similarities between its physical properties and LPG, can be easily integrated into the current LPG fuel distribution system. With minor modifications to valves, pumps and gaskets, all of the LPG distribution technologies including ocean tankers, receiving stations, train tankers and trucks can easily accommodate dimethyl ether (Semelsberger, Borup, and Greene 2006, 497-511). This distribution infrastructure, however is dedicated primarily to LPG fuel for domestic heating and cooking use. LPG refueling systems would have to be built at automotive refueling stations across the nation.

For large scale implementation of dimethyl ether fuel, the capital investment for production plants and infrastructure upgrade was estimated to be US\$4 billion, compared to US\$18 billion for hydrogen, US\$4 billion for methanol and US\$5 billion for ethanol (Semelsberger, Borup, and Greene 2006, 497-511).

Distribution Efficiency

The US fuel distribution system employs three primary modes of transport: truck, train and pipeline. As previously discussed, due to their varying chemical and physical properties each certain fuels have met resistance to being transported by certain means. As such, each of these distribution methods are analyzed in this thesis to get the best estimate of distribution efficiencies and costs for each fuel.

In order to assess the efficiency of transport via each method, it is assumed that all of the energy to transport the fuel comes from the fuel itself, thus the equation for the efficiency of transport is:

$$\eta_{I_distribution} = \frac{(m_{fuel} LHV_{fuel})_{delivered}}{(m_{fuel} LHV_{fuel})_{shipped}} = \frac{(m_{fuel} LHV_{fuel})_{delivered} - (m_f LHV_{fuel})_{lost} - W_{transport}}{(m_{fuel} LHV_{fuel})_{shipped}} \quad \text{eq. (34)}$$

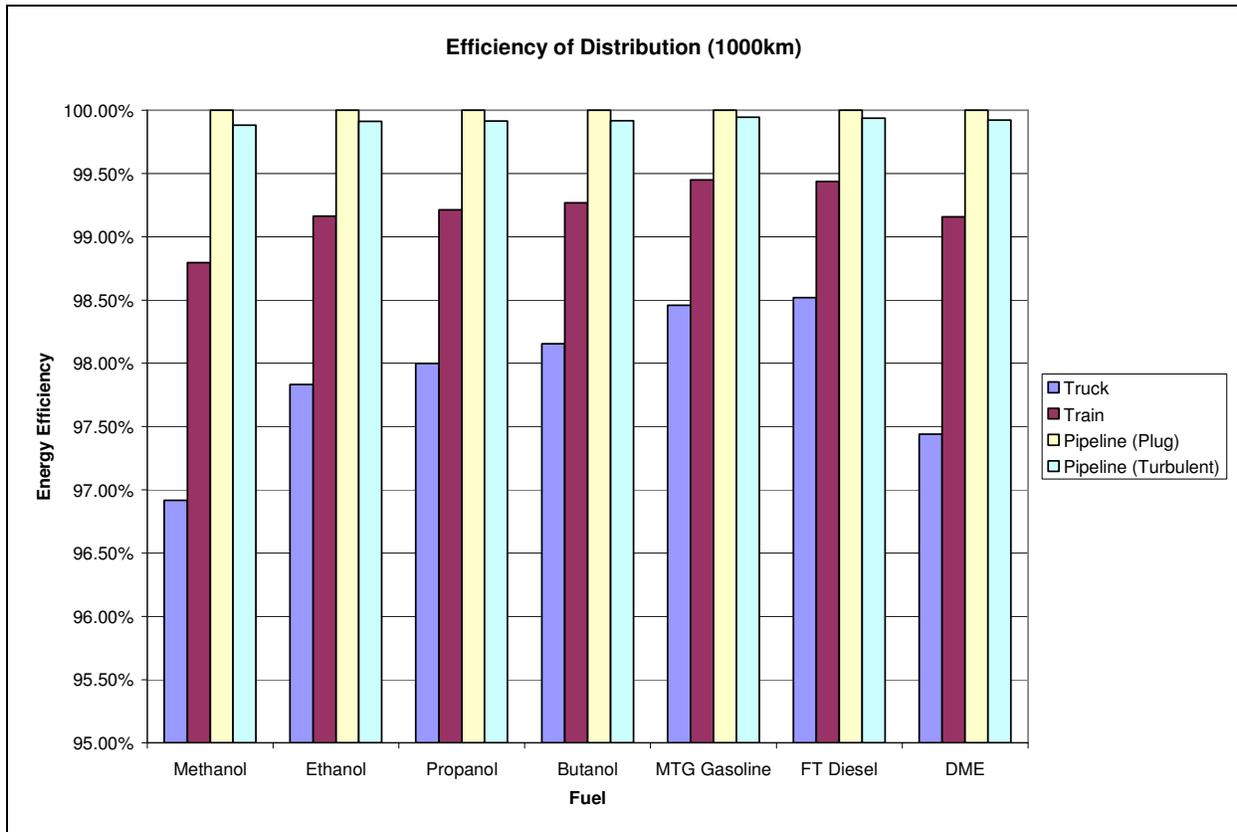


Figure 9 - Energy efficiency of transporting fuel 1000km by mode.

In Figure 9, the resultant efficiencies of each of the transportation modes are reported for shipping each fuel 1000km. The truck and rail transportation numbers were calculated using data reported for average energetic cost of shipping per mode in the Transportation Energy Data Book (Davis and Diegel 2007). The efficiency of pipeline transport was calculated assuming both plug and turbulent flow regimes and very little sensitivity relative to differing Reynolds numbers was observed (Perry and Green 1997). In Table 13, these efficiencies of distribution are tabulated.

	Truck	Train	Pipeline (Plug)	Pipeline (Turbulent)
Methanol	97.2%	98.9%	100.0%	99.90%
Ethanol	98.0%	99.3%	100.0%	99.92%
Propanol	98.2%	99.3%	100.0%	99.92%
Butanol	98.3%	99.3%	100.0%	99.93%
MTG	98.6%	99.5%	100.0%	99.98%
FT Diesel	98.7%	99.5%	100.0%	99.98%
DME	97.7%	99.2%	100.0%	99.90%

Table 13 - Energy efficiency of transportation per 1000km

The efficiencies reported above are given per 1000km of shipping distance, however there is uncertainty as to exactly how far the average biofuel will travel when it is deployed at scale. In their 2006 study, Morrow et al. reported a probable range for the average distance a cellulosic fuel will travel as 980 to 1040 km (Morrow, Griffin, and Matthews 2006, 2877-2886). In this study a symmetric triangle distribution is prescribed to this range in order to perform the MCA to compute the likely system efficiency.

The overall efficiency of distribution for a given distance is thus:

$$\eta_{xkm, fuelA} = \left(\eta_{1000km, fuelA} \right)^{x/1000} \quad \text{Eq. (34)}$$

where x is the distance the unit of fuel is shipped. This is not an obvious formulation, however it can be deduced by considering the shipment of a fuel as a series of *n* 1000km shipments plus one fractional shipment. Consider a shipment of 2351km, then this would be equivalent to shipping a fuel 1000km twice in a row then 351km; and since the efficiency of serial energy conversion steps multiply we get:

$$\begin{aligned}
\eta_{2351km, fuelA} &= \eta_{1000km, fuelA} \eta_{1000km, fuelA} \eta_{351km, fuelA} \\
&= \eta_{1000km, fuelA} \eta_{1000km, fuelA} \left(\eta_{1000km, fuelA} \right)^{351/1000} \\
&= \left(\eta_{1000km, fuelA} \right)^{2351/1000}
\end{aligned} \tag{35}$$

and the general case can be easily deduced.

Distribution Economics

The cost of distribution contributes a small fraction of the cost of a fuel at the pump, but it is variable between the fuels considered in this study. The cost of shipping liquid fuels is proportional to the volume which is shipped, i.e.

$$TotalCost_{distribution} = P \times V \tag{36}$$

Where P is the price in dollars per volume, and V is the volume. Since each of the fuels analyzed in this study have different volumetric densities and energy densities, the price of shipping fuels is not equal on an energy basis. The price of shipping a certain energetic amount of fuel is inversely proportional to the volumetric and energy density

$$P \left(\frac{\$}{E} \right) \propto \rho^{-1} E_{density}^{-1} \tag{37}$$

Where ρ is the density in units mass over volume, and $E_{density}$ is the energy density in units energy over mass. Thus, the cost of shipping an energetically equivalent amount of a fuel which is not very dense (i.e. small ρ) such as hydrogen, which has a high energy density (by mass), costs more than the equivalent amount of diesel fuel, which is both energetically and massively dense. Due to this proportionality, on an energy basis, it is more expensive to ship alcohols and ethers as compared to synthetic hydrocarbons. Further, shorter chain alcohols are more expensive yet due to their even smaller energy density. In Figure 10, the cost of shipping a number of fuels

is plotted as 2007 dollars per gigajoule versus the distance in kilometers. The influence of the above proportionality is immediate in terms of the relative cost of shipping different fuels.

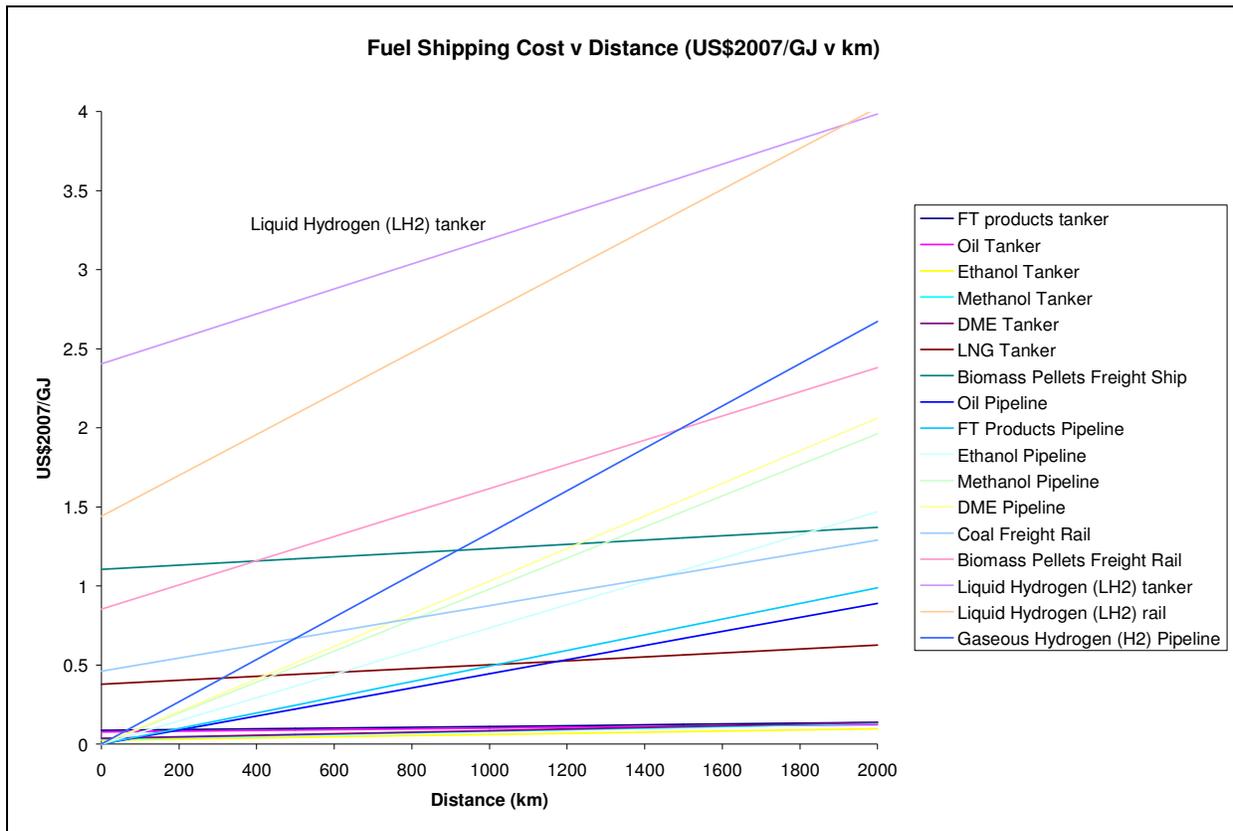


Figure 10 - Distribution costs adapted from (Takeshita, Yamaji, and Fujii 2006, 285; Takeshita and Yamaji 2008, 2773-2784; Vallentin 2008, 3198-3211).

In their study of likely distribution infrastructure for a cellulosic ethanol industry, Morrow et al. also estimated the cost of shipping cellulosic ethanol via rail and truck as well. In this thesis the reported shipping costs are extrapolated using the proportionality derived above to estimate the cost of shipping other alcohols and DME via truck and rail. Morrow et al. have reported a cost of ~\$0.05 per liter for a fuel shipped 1000km outside of the pipeline infrastructure. Additionally, the cost of shipping hydrocarbons via pipeline is reported by Morrow et al. as \$0.003 per liter shipped 1000km; this number is used to estimate the costs of MTG and FTD shipments.

End Use Efficiency

The most common measure of the efficiency of fuel use in an engine is the Brake Specific Fuel Consumption (BSFC) which is given by the equation:

$$BSFC = \frac{\dot{m}_f}{P} \quad \text{Eq. (38)}$$

where \dot{m}_f is the mass-flow rate of fuel delivered to the engine and P is the power output to the drive train. This measure of fuel efficiency does not take into account the difference in energy content of fuels, and in order to evaluate the first law conversion efficiency, one must include the energy density of the fuel. It is standard to use the lower heating value (LHV) fuel. The overall tank-to-crank first law energy efficiency is then given by the expression:

$$\eta_{I,T-to-K} = \frac{P}{\dot{m}_f LHV_f} = \frac{1}{LHV_f \cdot BSFC} \quad \text{Eq. (39)}$$

where

$$\eta_{I,T-to-K} = \eta_f \eta_m = \eta_c \eta_t \eta_m \quad \text{Eq. (40)}$$

where η_f is the fuel conversion efficiency, η_c is the combustion efficiency, η_t is the thermal conversion efficiency, and η_m is the mechanical efficiency. The fuel conversion efficiency is the overall thermodynamic efficiency of power delivered to the piston per amount of fuel consumed. The combustion efficiency is defined as the fraction of the energy contained in the fuel which is released in the combustion process, the remainder of the energy is released as unburned hydrocarbon emissions and carbon monoxide/hydrogen emissions. The thermal conversion efficiency is the ratio of actual power delivered to the piston to the energy released in the combustion process. Finally, the mechanical efficiency is the ratio of the power delivered to the crank-shaft to the power delivered to the piston, this measure of efficiency accounts for friction losses inherent in engines.

Each of the fuels examined in this study have their own specific chemical and physical properties which affect the combustion characteristics of the fuel and in-turn influence the BSFC and overall first law conversion efficiency. These characteristics are examined below and their influences on conversion efficiencies are discussed.

Methanol Use in a Spark Ignition Engine

Due to the fact that methanol is a liquid at standard conditions, current onboard fuel system can be adapted to accept methanol with minimal material changes to avoid corrosion. Also, the great increase in flexible fuel vehicles for ethanol usage has increased interest in vehicles which can accept alcohol fuels. Though these vehicles are specified for ethanol and gasoline, the technology is applicable to methanol-gasoline blends as well as methanol-ethanol-gasoline blends requiring only minimal storage and fuel delivery modification (Nichols 2003, 97).

Because of its superb chemical and physical properties, methanol has been used as a high performance spark ignition engine fuel. Methanol was the official fuel of the Indy-Car series from 1964 until 2006, when a consortium of ethanol producers influenced the series to change to an E98 blend (Green Car Congress 2007b). Neat methanol's use in spark ignition (SI) engines offers a higher knock limit allowing for the use of a higher compression ratio which in turn increases the energy conversion efficiency and power density of the engine. Additionally, methanol's high latent heat of vaporization provides for a large amount of charge cooling; thus, allowing for further compression. Because of methanol's charge cooling property the combustion temperature in the cylinder is lower than with gasoline, as such NO_x formation is lower due to its high temperature dependence (Heywood 1988). This favorable property somewhat relaxes the efficiency- NO_x tradeoff inherent in SI engines allowing methanol engines to operate at conditions not available to gasoline engines.

Methanol can be used as both a blending agent with gasoline or as a neat fuel. Often when short chain aliphatic alcohols are considered as transportation fuels there are seen as performance enhancing blending components for gasoline rather than as neat fuels; and indeed this is the most likely way that alcohols will be used in the near term. As a blending agent, methanol increases

the overall fuel mixtures octane rating as well as increases the oxygen content of the fuel, thus helping to decreasing the subsequent CO emissions.

There has been work into radically different alcohol fuel use, as a ‘booster’ for gasoline engines (Cohn, Bromberg, and Heywood 2005; Bromberg, Cohn, and Heywood 2006). In this scheme the engine regularly runs with a standard gasoline based fuel, which could be blended (E10, M10, etc), while methanol or ethanol is supplied via a separate fuel delivery system and a small amount is directly injected into the engine under high torque conditions to prevent knock. This allows for an increased fuel and carbon efficiency while decreasing the amount of alcohol needed.

Ethanol Use in a Spark Ignition Engine

Ethanol is a high performance fuel like methanol, due to its high octane number, high latent heat of vaporization and good combustion characteristics (Brusstar and Bakenhus 2005). While these characteristics are not as pronounced as that of methanol, ethanol has gained the lion’s share of the alternative fuel market for reasons other than its favorable physical and chemical properties. Ethanol is currently used as a one-to-one gasoline substitute in engines optimized for gasoline combustion; and as such, its full potential as an automotive fuel is not being fully realized.

There is currently much interest in utilizing ethanol more efficiently by taking advantage of its unique physical properties. When ethanol is utilized in a port injection spark ignition engine, ethanol’s RON and MON have been recorded to be 108.6 and 89.7 respectively, yielding an octane number of 99.2 (Hunwartz 1982, 1-6). Because of this high octane number, the compression ratio of an engine using ethanol can be increased, thus improving the energy conversion efficiency. This has been confirmed by a number of studies in particular by Brusstar and Bakenhus (Brusstar and Bakenhus 2005). In their study, Brusstar and Bakenhus find that by utilizing through the increase of compression ratio, the higher octane number of ethanol (and methanol) one can achieve thermal efficiencies of 40% using high blends of alcohol with gasoline in a port injected engine.

The beneficial properties of ethanol are better utilized by injecting the fuel directly into the engine. By using direct injection the high latent heat of vaporization allows for a large drop in the initial temperature, thus decreasing the peak pressure and temperature allowing for increased compression ratio and increased thermal efficiency. This effect has been demonstrated by Marriott et al. on a spark ignition direct injection (SIDI) engine using ethanol/gasoline mixtures from 0%-85% ethanol. Their findings suggest that 3-6% thermal efficiency improvements are possible over the optimized gasoline baseline, along with a 13% – 15% increase in specific output (Power/Volume of displacement) (Marriott et al. 2008).

As with methanol, the concept of using a boosted engine can also be achieved with ethanol. Cohn et al., has reported efficiency gains of 30% over a gasoline fueled engine using a direct injected engine with ethanol boosting capability (Cohn, Bromberg, and Heywood 2005). Additionally, utilizing a singly fuel turbo-charged direct injection engine fuel with methanol or ethanol, an overall efficiency gain of 30-35% has been reported by Bromberg et al. over a port injected gasoline engine. Further, it was reported that with the on-board reformation of methanol to hydrogen an additional efficiency gain of 10% is possible at low load operation (Bromberg and Cohn 2008).

Mixed Alcohol Use in a Spark Ignition Engine

Higher alcohols also have high octane numbers and heats of vaporization; however these properties decrease as the size of the alcohol grows. This trend has been demonstrated in a study by Gautam and Martin (Gautam and Martin II 2000, 497-511). In their study, Gautam and Martin assessed the octane number of different alcohol gasoline blends. For 10% mixed-alcohol/gasoline blends, the ratios of alcohols were adjusted and the combustion properties and octane numbers were determined.

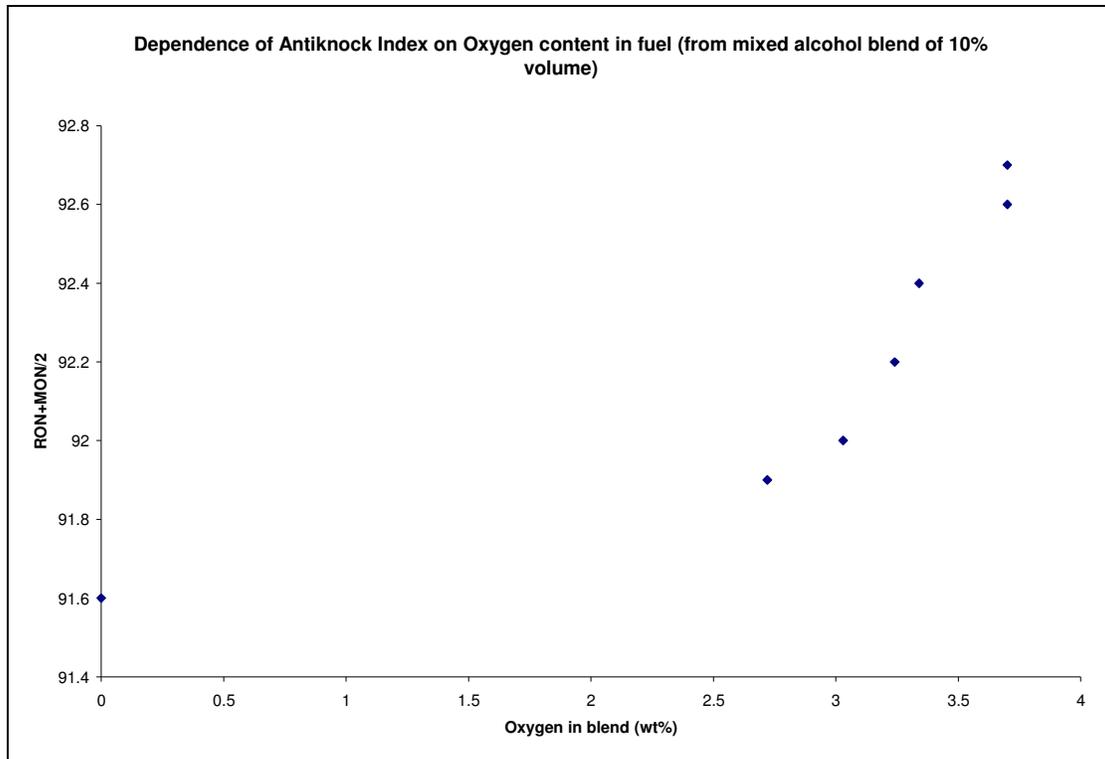


Figure 11 - Dependence of AKI (Octane Number) on the oxygen content of 10% mixed-alcohol/gasoline blended fuel adapted from (Gautam and Martin II 2000, 497-511).

It can be seen in Figure 11 and Figure 12 that the octane number of the fuels depends on the total oxygen content. As such, it is a function of both the total amount of alcohol and the oxygen content of the mixed-alcohol blended with the fuel. From the second figure, it is apparent that as the average size of the blending alcohol decreases toward methanol the octane number increases, as expected.

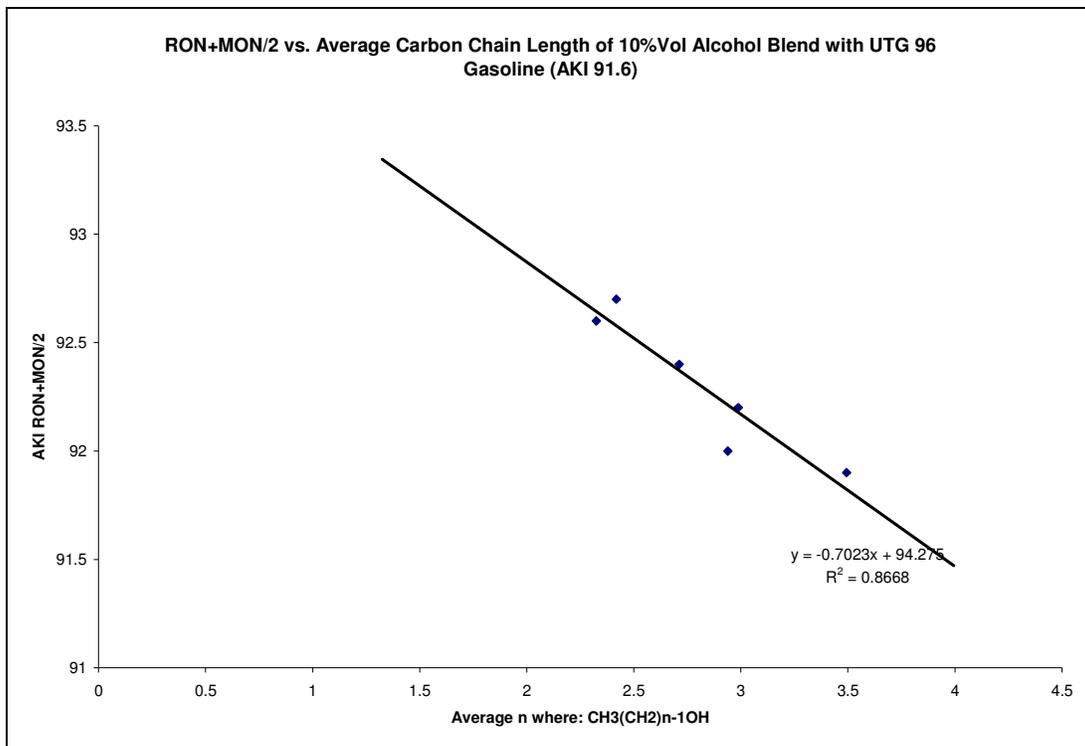


Figure 12 - Dependence of AKI (ON) on average alcohol carbon chain length of mixed alcohol in a 10% mixed-alcohol/gasoline blended fuel adapted from (Gautam and Martin II 2000, 497-511).

While the favorable characteristics inherent in short chain alcohols decrease as the size increases (to propanol, butanol, pentanol, et cetera); other favorable properties emerge which shed a more favorable light on the use of higher alcohols for transportation. Unlike methanol and ethanol which are totally miscible with water and are highly corrosive relative to petroleum products, higher alcohols are less miscible with water and are less polar, therefore decreasing their corrosive nature. Thus, higher alcohol fuels (propanol and higher) could be easily adapted for onboard storage and use with little or no modification. Additionally, higher alcohols act as a co-solvent decreasing the likelihood of phase separation of the shorter alcohols from hydrocarbons in wet conditions. Thus, while the combustion characteristics of higher alcohols are more comparable to that of gasoline, their use can enable further adaptation of methanol and ethanol in engines allowing for further capitalization on their positive properties.

MTG Gasoline Use in a Spark Ignition Engine

MTG gasoline can be considered a one-to-one substitute for today's high-grade unleaded gasoline. The MTG synthetic gasoline product can be blended at any proportion with petroleum derived gasoline with no need effect on engine performance. The thermal efficiency of MTG utilization has been shown to be equivalent to that of unleaded gasoline in a port injected engine (Freeman, Roby, and Chui 1982, 89-100; Fitch and Lee 1981, 341-355). Because of its high octane number of >92, it could more efficiently be utilized in a direct injected turbo-charged engine as described for the use of ethanol and methanol (Heinritz-Adrian et al. 2007).

Fischer-Tröpsch Diesel Use in a Compression Ignition Engine

Fischer-Tröpsch Diesel is perhaps the most studied and fully developed alternative fuel because of the number of properties which make it an excellent fuel for compression ignition engines. Fischer-Tröpsch diesel, due to its synthesis method, is composed primarily of strait-chain alkanes and contains virtually no sulfur. As such, it is a clean burning fuel that is optimal for compression ignition. Fischer-Tröpsch diesel's cetane number depends on the method of production, but ranges from 64-75 compared to 40-48 for that of EPA 2-D certification Diesel fuel (Stavinoha et al. 2000). Due to the low sulfur and aromatic content Fischer-Tröpsch diesel is a cleaner burning fuel than petroleum derived diesel's which allows for a more efficient utilization of the fuel because less energy is required to run after-treatment of the fuel.

In engine testing, Fischer-Tröpsch Diesel has been shown to allow for modest thermal efficiency gains. In a one cylinder CFR compression ignition engine operating under high load conditions Cowart et al. found that Fischer-Tröpsch Diesel showed modest efficiency gains at early injection timing (25 deg BTC) however at normal injection timing the efficiency gain was nominal (Cowart et al. 2008). Huang et al., on the other hand found an average thermal efficiency increase of 4.5 over diesel fuel at all of their test conditions (Huang, Wang, and Zhou 2008, 261-267). Huang et al. explained their results as resulting from the improved combustion process inherent to Fischer-Tröpsch Diesel due to its composition and lower boiling point. The discrepancy between these two results can probably be explained by the fact that Cowart et al. were testing only high-load conditions, while Huang et al. considered many mid to low load conditions.

Dimethyl Ether Use in a Compression Ignition Engine

Currently, there is not a large fleet of vehicles able to absorb DME fuel into the market. Due to dimethyl ether's physical properties on board high pressure storage technology and advanced engine technology is required. This technology currently exists and is used in fleet applications for CNG, LPG and LNG vehicles. These vehicles do not have widespread use, however. In the fiscal year 2006, of the 348,959 thousand GGE of fuel consumed by federal government fleets, CNG, LPG and LNG accounted for only 807, 105 and 90 thousand GGE respectively (Davis and Diegel 2007).

Dimethyl ether has been studied as an alternative fuel for use in compression ignition engines due to its excellent auto-combustion properties. Dimethyl ether has a higher cetane number than diesel which has been found to result in a faster ignition, thus allowing for retarded injection timing. Also, dimethyl ether fueled engines have been found to have a higher indicated mean effective pressure (IMEP) than diesel signifying higher thermal efficiency (Kim et al. 2008, 2779-2786).

Dimethyl ether/biodiesel blends have also been investigated. It has been found that increased biodiesel proportion increases the power density of the engine. Additionally, a high proportion of dimethyl ether allows for better cold start characteristics in a compression ignition engine (Ying and Longbao 2007, 1454-1458).

The combustion of dimethyl ether in compression ignition engines has been found to provide a moderate thermal efficiency gain over petroleum derived diesel fuel. In a single cylinder 11 kW engine with a compression ratio of 18.4, Wang et al. demonstrated that DME provided a 3% higher thermal efficiency than that of diesel fuel under comparable conditions (Wang et al. 2000, 101-106). Also, Longbao et al. showed a 3% thermal efficiency increase over that of diesel fuel in their study of DME use in a direct-injection light-duty compression ignition engine (Longbao et al. 1999).

Summary of Spark Ignition Versus Compression Ignition Fuels

Using today's fuels and engine technology, Compression Ignition engines offer an efficiency improvement of 15-30 percent over Spark Ignition engines (Heywood 1988). However, using advanced engine technologies, with alcohol fuels, spark ignition engines can approach diesel engine efficiencies (Bromberg and Cohn 2009). Further, these engines can be operated at stoichiometric, thus allowing the use of the 3-way catalyst, eliminating the need for expensive after treatment technologies.

End Use Economics

Each of the fuels considered in this thesis can utilize today's automotive technology with only minor adjustments being required. In order for alcoholic fuels to be accommodated for use in an automobile, only minor material changes are required to prevent corrosive degradation due to the presence of alcohol in the fuel system. Today, the marginal cost of producing a flex-fuel capable vehicle is on the order of \$100 per vehicle. Additionally further efficiency optimization, such as increasing the compression ratio, can be performed at minimal cost.

End Use Regulation and Policy

Perhaps the point at which policy most strongly influences the adoption of a new fuel is through the regulation of local air pollutants via the Clean Air Act. The Clean Air Act influences both automotive pollution control technologies and the make-up of transportation fuels sold in the US. If an alternative transportation fuel being considered performs worse than the petroleum derived fuel which it is proposed to displace, then its adoption is highly unlikely since there already exist many technological challenges to bringing petroleum derived fuels into compliance. In this section the emissions characteristics of each of the fuels considered in this thesis are analyzed through the lens of their performance with regards to the criteria pollutants: NO_x, CO₂, and particulates.

Methanol and Ethanol Emissions

One of the reasons methanol and ethanol have been considered as an alternative transportation fuel are their low emissions of criteria pollutants compared to gasoline. Early studies indicated that due to methanol's charge cooling properties, simple structure and high oxygen content its emissions of CO and NO_x were much lower than gasoline, as well as nearly nonexistent aromatic emissions for neat methanol (Yanju et al. 2008, 1254-1259). These studies, however, raised the concern of other hazardous emissions in the form of unburned methanol (UBM) and formaldehyde. It has been found that these emissions are controlled by kinetic factors and are readily reduced by running the engine on the lean side (which is possible due to methanol's decreased NO_x formation) (Sperling and DeLuchi 1989, 469-482; Okada, Koda, and Akita 1985). Similarly, ethanol also decreases CO and NO_x emissions drastically as compared to gasoline yet there are concerns about unburned ethanol (UBE) and acetaldehyde emissions (He et al. 2003, 949-957).

The effect of methanol's use as a blend component has also been studied recently. It has been found that blending methanol in gasoline decreased CO emissions proportionally with methanol ratio reaching a 30% reduction at and 85% methanol blend (M85) where the air to fuel ratio was constant. Also NO_x emissions were reduced by 80% with M85, while showing no significant reduction for lower blends (M10, M20) (Yanju et al. 2008, 1254-1259). Since this experiment did not adjust the air to fuel ratio to maintain a stoichiometric combustion the NO_x emissions reductions are probably less than they would be in an engine optimized for the blended fuel combustion. As a blending component, ethanol also has been shown to reduce CO emissions by ~30% and NO_x emissions by 33%; however other unregulated emissions such as acetaldehyde have been shown to be increased by more than 3 times at a 30% ethanol blend by volume (He et al. 2003, 949-957).

Mixed Alcohol Emissions

Similarly to the decreasing performance and efficiency effects of alcohols as their chain length is increased, the emissions characteristics similarly fall off as chain length is increased. As such, low NO_x reductions that characterize methanol and ethanol use are much less apparent with higher alcohols since there is less charge cooling and therefore less of a reduction of peak

pressure and temperature. Also, higher carbon monoxide emissions occur, since higher alcohols have lower oxygen content by mass. Therefore, in mixed alcohols the emissions reductions will be characterized primarily by the methanol and ethanol content of the fuel, while the content of propanol+ will be marginal (Gautam and Martin II 2000, 497-511).

The one major exception to this trend is the decrease in volatile organic compound emissions due to the lower vapor pressure of higher alcohols dissolved in gasoline. As such the use of higher alcohols as a co-solvent for the short chain methanol and ethanol can help to decrease the unwanted emissions associated with methanol and ethanol.

MTG Gasoline Emissions

MTG gasoline has been engineered to perform nearly equivalently to petroleum derived gasoline. As such, its chemical and physical properties are such that its emissions are nearly equivalent to that of petroleum derived gasoline with marginal differences. The one major difference between MTG gasoline and petroleum derived gasoline is the higher volumetric aromatic content of MTG gasoline of 25% - 35% (Fitch and Lee 1981, 341-355). While this content leads to increased octane number and improved combustion properties, it also allows for increased unburned hydrocarbon emissions along with marginally higher NO_x emissions (Freeman, Roby, and Chui 1982, 89-100). However, for all practical purposes the tank-to-crank performance and emissions of MTG are nearly equivalent to that of petroleum derived gasoline.

Fischer-Tröpsch Diesel Emissions

Due to its chemical and physical properties Fischer-Tröpsch Diesel is a clean burning substitute for petroleum derived diesel fuel. The three properties which are of primary benefit are: (1) near zero sulfur content, (2) near zero aromatic content, (3) high cetane number.

The catalysts used to produce Fischer-Tröpsch Diesel are susceptible to poisoning and degradation due to the sulfur content of feedstocks used for the production of syngas. As such, the sulfur is necessarily removed from the syngas before the catalytic fuel production (Probstein and Hicks 1982). Because of this requirement the sulfur content of Fischer-Tröpsch Diesel is virtually zero (Stavinoha et al. 2000). A number of studies have correlated the presence of sulfur

in diesel fuel with increased particulate emissions overall operating conditions. In a compression ignition engine fueled with Fischer-Tröpsch Diesel, specific emissions of particulate matter have been found to be reduced by 30% - 60% at low and medium load utilizing stock timing and EGR (Acar 2005). By optimizing timing, the specific emission of particulate matter has been shown to be 60% - 90% less than that of EPA 2-D certification diesel (Coward et al. 2008).

The second beneficial artifact of the nature of the Fischer-Tröpsch Catalyst is the fact that the fuel produced is mostly highly saturated alkanes with no aromatic content. The presence of aromatics has been shown to lead to increased NO_x emissions and a decreased H/C ratio which increases the tank-to-crank CO₂ emissions (Coward et al. 2008). It has been argued that the primary reason for aromatic content influence on NO_x emissions is the decreased local adiabatic temperature during combustion (Huang, Wang, and Zhou 2008, 261-267). At low load utilizing stock timing and EGR NO_x emissions were reduced by approximately 20% by using Fischer-Tröpsch Diesel (Acar 2005). At high-load conditions Coward et al. recorded No_x reduction on the order of 50% - 60% of EPA 2-D certification diesel (Coward et al. 2008).

Finally, because of Fischer-Tröpsch Diesel's chemical make-up, its cetane number has been demonstrated to be much higher than that of petroleum-derived diesel fuel. The cetane number of Fischer-Tröpsch Diesel is on the order of 64-65 versus 40-48 for EPA 2-D certification diesel. High cetane numbers have been shown to lead to lower NO_x emissions (Heywood 1988).

In addition to PM and NO_x emission reductions, the emission of carbon monoxide (CO) and carbon dioxide (CO₂) have also been demonstrated to be less on a tank-to-crank basis for engines utilizing Fischer-Tröpsch Diesel. These reductions are due to the highly-saturated nature of the Fischer-Tröpsch fuel which minimizes carbon-carbon bonds and maximizes the H/C ratio. Thus, there is less carbon consumed per unit of energy produced thus decreasing the overall carbon-based emissions. Huang et al. recorded CO emissions reductions of 40% - 60% at high load conditions, while marginal improvements at all other operation conditions were observed (Huang, Wang, and Zhou 2008, 261-267). Specific CO₂ emissions have been found to be 10% - 20% less than that of EPA 2-D certification diesel (Coward et al. 2008).

DME Emissions

Due to dimethyl ether's simple molecular structure it exhibits no particulate matter and low carbon monoxide emissions. Additionally, dimethyl ether can achieve lower overall NO_x emissions compared to diesel due to its shorter ignition delay (Kim et al. 2008, 2779-2786). Unburned dimethyl ether emissions are of little concern, because dimethyl ether is easily broken down in the environment (Semelsberger, Borup, and Greene 2006, 497-511).

Dimethyl ether/biodiesel blends have been found to have reduced emissions compared to neat biodiesel. With blends of less than 6% biodiesel, virtually no smoke emission is recorded. Additionally, the blended dimethyl ether has been shown to decrease CO and NO_x emissions.

Systemic Environmental and Toxicological Considerations

Beyond the efficiency, integrability, economics and end-use emissions of the fuels there also exists other concerns associated with each of the fuels discussed. One issue which can influence the adoption of a fuel is the toxicological properties of the fuel along with the risk associated with a catastrophic spill into the environment. Below these issues are summarized and the further challenge of public perception of these risks is discussed.

Toxicological Concerns

When considering the acceptability of an alternative transportation fuel, toxicity is a primary criterion that the fuel must meet in order to be considered for large scale use (Short 1994, 215). Since gasoline and diesel are currently used worldwide as the standard transportation fuel, alternative fuels should have toxicity comparable to or better than these two fuels.

The most common measurement of toxicity is the median lethal dose, LD₅₀. The median lethal dose is defined as the dose at which 50% of the test population is killed. For most substances there are three primary methods of dosing: oral consumption, inhalation and dermal application. In oral testing, populations of test animals (commonly mice and rats) ingest the chemical and are observed over the subsequent days for physiological effects. To investigate the inhalation effects populations of test animals (again mice and rats) are exposed to mixed air and vapor of the

compound over a specific time period. Similarly for dermal effects, the animal, most commonly a rabbit, is exposed to a certain concentration of the compound over a specific time period. Often different times of exposures are often used by different research groups; however, according to Haber's Law, if $C_1t_1=C_2t_2$, where t is the time of exposure and C is the concentration then the two dose schemes are equivalent. Haber's Law can be used to normalize different results for different fuels tested at different concentrations and times.

It can be inferred from Figure 13 that the oral toxicity of methanol and ethanol and propanol are comparable to gasoline and diesel with methanol and ethanol being less toxic. Only butanol is found to be more toxic. Another metric to compare these fuels to is NaCl (table salt), which the FDA has labeled as a safe food additive, along with sugar. Note that all of the alcoholic fuels as well as gasoline and diesel are at parity with, or less toxic than, table salt.

Methanol has hit major resistance, more than most fuels, due to claims that it is unsafe for public utilization due to toxicological concerns. The issue of toxicity is often overstated, however, since methanol's toxicity is on the same order as other fuels being considered as gasoline and diesel substitutes. Further, methanol has been widely used as windshield wiper fluid without any major concern. One must be careful, however, to note the difference between mortality effects and morbidity effects of fuels. The morbidity effects of a compound are the non-lethal negative health effects caused by exposure, inhalation or injection of the compound. The LD50 values of fuels measure the mortality effects, while morbidity is harder to quantify in a standardized way since morbidity is not an absolute like mortality. Methanol, for example, can cause blindness when a relatively small amount is ingested, while much more is needed to cause death. There are also high morbidity risks associated with gasoline and its components due to the carcinogenic nature of aromatic hydrocarbons, however, due to the long latency periods associated with cancer the public perception is somewhat lessened.

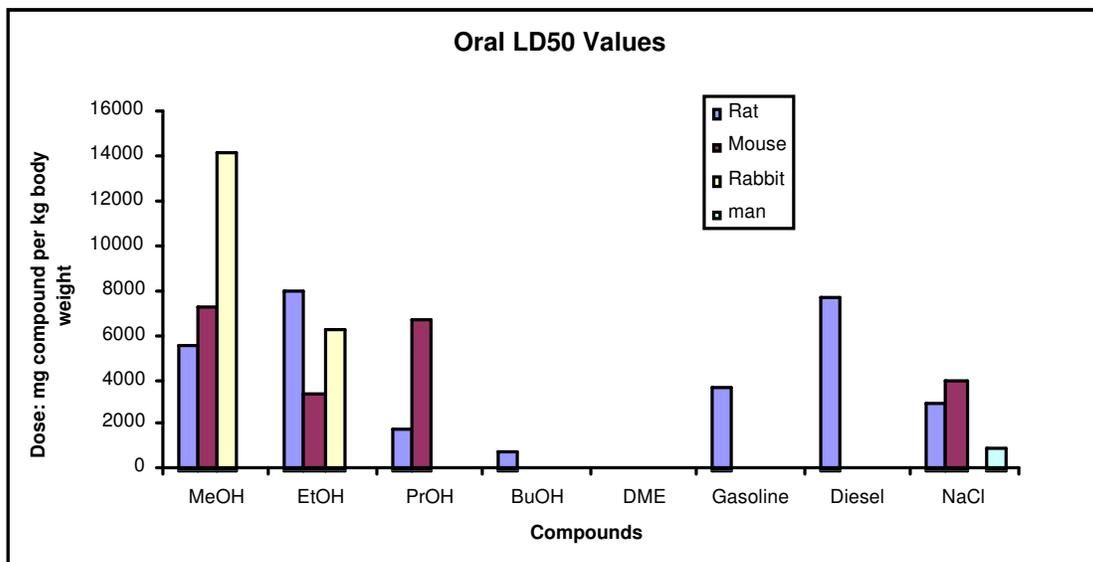


Figure 13 - Oral LD50 values of fuels and common substances.

One of the major safety concerns with fuels is the possibility of consumers inhaling vapors that are released during refueling. Methanol, ethanol and propanol all have a much higher inhalation LD₅₀ than gasoline (see Figure 14). DME is at parity with gasoline.

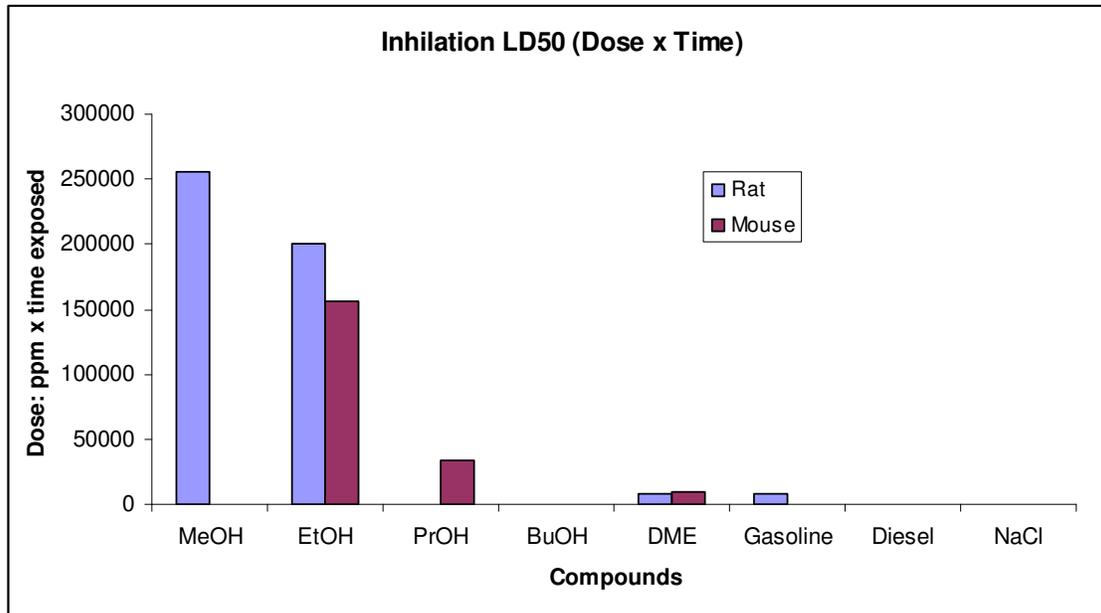


Figure 14 - Inhalation LD50 values of fuels and common substances.

Dermal absorption of a fuel is a concern because of the chance of people spilling fuel onto one's person while refueling. Again, the alternative fuels are at parity with, or less toxic than, gasoline and diesel fuel, with DME this would not be a concern due to its gaseous state.

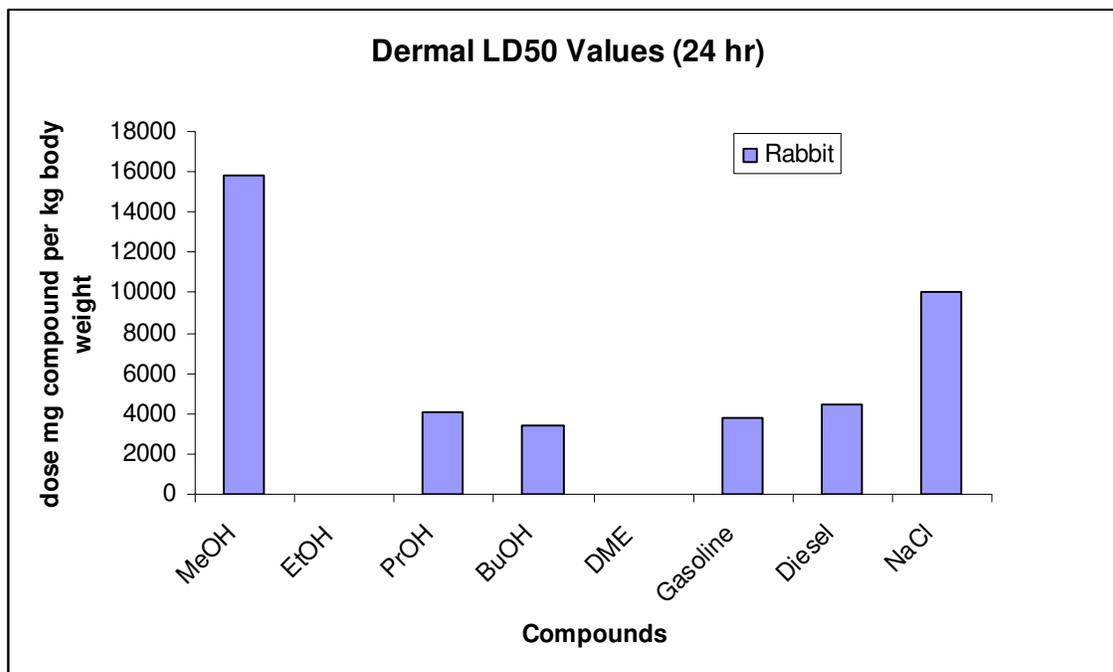


Figure 15 - Dermal LD50 values of fuels and common substances.

The toxicological hazards associated with synthetic hydrocarbons are very similar to their petroleum derived counterparts due to the fact that the goal of producing these fuels is to make a similar compound to what is currently used. MTG is slightly more toxic than its petroleum derived counterpart due to its increased aromatic content (Fitch and Lee 1981, 341-355; Chang 1994, 133). Additionally, the toxicity of Fischer-Tröpsch Diesel is somewhat less as compared to petrol-diesel due to its lower amount of aromatic content. (Probstein and Hicks 1982; Hunt 1983).

Ecological Effects

One reason that alcoholic fuels like methanol and ethanol are much more environmentally benign than gasoline is because of the lifetimes of the fuels in the environment. Unlike the alcohols which are easily used as growth substrate by micro organisms, gasoline is composed of

a whole host of compounds including some highly-toxic long-lived compounds such as benzene, toluene and trimethylbenzene.

In Table 14 the half lives of some common fuel components are tabulated. These are adapted from the “Handbook of Environmental Degradation Rates” where the half lives are estimated from predominant reaction rates in different media, from bio-degradation in the soil to photo-degradation in the air (Howard 1991). In Figure 16 the average half lives of the fuels are plotted by medium.

	Methanol	Ethanol	1-Butanol	Benzene	Toluene	Trimethylbenzene
Soil	1-7 days	2.6-24 hrs	1-7 days	5-16 days	4-22 days	7-28 days
Air	3-30 days	.5-5.1 days	.4-3.7 days	2-21 days	0.4-4.3 days	1.6-16 hrs
Surface Water	1-7 days	6.5-26 hrs	1-7 days	5-16 days	4-22 days	7-28 days
Ground Water	1-7 days	.5-2.2 days	2-54 days	10-720 days	7-28 days	14-56 day

Table 14 - Half lives of common fuel components, adapted from (Howard 1991).

Compared to crude oil and gasoline methanol is much more ecologically benign and is unlikely to cause a major environmental catastrophe in the event of a large scale spill; this is due to methanol’s miscibility with water and many micro organisms’ ability to metabolize methanol. Since methanol is totally miscible in water it will quickly dissipate when spilled and reach a concentration where organisms can begin to naturally digest the fuel. Models indicate that if 10,000 tons of methanol were spilled into open sea it would take just one hour for the methanol concentration to drop below 0.36%, at which point biodegradation can occur (Olah, Goeppert, and Prakash 2006).

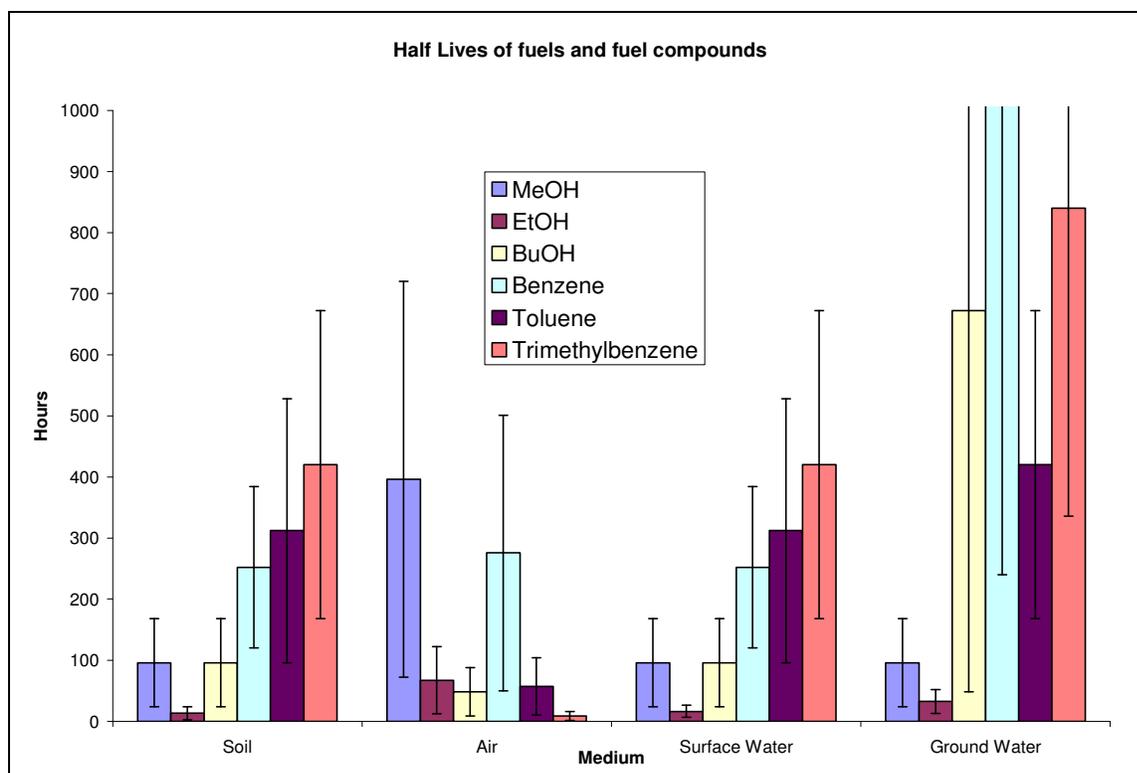


Figure 16 - Half lives of common fuel components in certain media.

Currently, the EPA regulates methanol through its inclusion in the Community Right to Know list and the TSCA Inventory. It is recommended that fuel methanol, as with all other fuels, should be stored in double walled underground tanks in order to avoid spillage into the environment or drinking water sources.

Compared to gasoline, methanol is of relatively low toxicity to aquatic and terrestrial organisms and environmental exposure is not likely to be of serious consequence under normal circumstances (Olah, Goepfert, and Prakash 2006). According to the International Programme on Chemical Safety of the World Health Organization (WHO) the LC50 values in aquatic organisms range from 1300 to 15900 mg/liter for invertebrates (over 48 and 96 hr exposures), and 13000 to 29000 mg/liter for fish (over 96 hour exposure) (WHO 1997). Even in the event of a large scale spill these times of exposure are unlikely to occur due to the rate at which methanol dissipates.

Methanol, due to its simple molecular structure and high energy content, is readily used by microorganisms as a growth substrate in both aerobic and anaerobic conditions, and is used as a process accelerator for anaerobic bacteria in waste water treatment. In the event of a major methanol spill, the micro organisms in the immediate area would be greatly affected due to a spike in concentration of the alcohol. However within a very short time span bacteria and fungi would return in order to degrade the residual alcohol with higher organisms following shortly thereafter (Mills and Ecklund 1987, 47-80).

When MTBE was banned as a fuel additive, concerns for both the environment and public health effects were cited as reasons (EIA 2006). The main concern with MTBE is its ability to infiltrate ground water sources used for drinking. In a 1997 interagency governmental study, it was reported that of 1,516 drinking water wells in 33 states 5% contained a detectable amount of MTBE (NSTC 1997). Of the 76 wells in which MTBE was detected, only 7 had concentrations that exceeded 10 µg/L. The draft drinking-water lifetime health advisory range for MTBE is 20 µg/L - 200 µg/L. Even though MTBE is rarely found in concentrations which can cause a significant health risk, there is large public awareness and opposition to it due its strong odor and taste, which falls in the lifetime health advisory range. Odor thresholds of 95 µg/L and 45 µg/L for MTBE have been reported by Ventrano, 1993 and TRC Environmental Corporation, 1994 respectively. Taste thresholds for MTBE of 30 µg/L and 134 µg/L were reported as well (TRC Environmental Corporation 1994; Ventrano 1993).

Due to MTBE's physical and chemical characteristics, it persists in the environment much longer than alcohols, and travels much further from spill sites than long lived species in gasoline such as benzene. MTBE travels further than benzene because it is much more soluble in water and can easily travel in this manner. Additionally, because of MTBE's solubility and inability to biodegrade it is much harder and more costly to clean up after a spill.

	MTBE
Soil	4 weeks - 6 months
Air	20.7 hours - 11 days
Surface Water	4 weeks - 6 months
Ground Water	8 weeks - 12 months

Table 15 - Half-life of MTBE in various environmental media.

Unlike Methanol, which is highly miscible with water and is in the liquid phase at standard conditions, dimethyl ether quickly dissipates into the atmosphere when introduced into the environment. Thus, there is little concern for adverse ecological effects in the event of a large scale DME spill. Further, whereas in the event of a CNG spill where again there would be little immediate ecological effects due to quick dissipation into the atmosphere, because of methane's high greenhouse gas equivalence to CO₂ could pose a greater ecological effect than DME released into the atmosphere. Where releasing 10,000 GGE of CNG would be equivalent releasing 625 metric tons of CO₂ into the environment, releasing the equivalent amount of DME would result in only of 84 metric tons of CO₂. This is due to the fact that methane is a more potent greenhouse gas than carbon dioxide by a factor of 25 over a 100 year time and has a lifespan of 8.4 year life in the atmosphere before decaying into carbon dioxide and water (IPCC 2001). Dimethyl ether, on the other hand is not a greenhouse gas and decays quickly into carbon dioxide and water.

Vapor Pressure and Volatile Organic Compounds

When the environmental impacts of oxygenated fuels are discussed, often concern about increased vapor pressure and volatile organic compound release at the pump and from fuel tanks is cited as a concern. While this is true for low concentration mixtures of alcohols in reformulated gasoline such as M10 or E20, higher alcohol concentrations actually decrease the overall volatility of the mixture. In binary gasoline/alcohol mixtures, the addition of a small amount of short chain aliphatic alcohols (i.e. methanol and ethanol) greatly increases the volatility of the mixture, which can increase the amount of organic compounds released at the pump on hot days. The vapor pressure reaches a maximum, for these systems, and actually decreases below the vapor pressure of the pure reformulated gasoline at a certain concentration of alcohol. Thus, for fuels such as E85 or M100, there is actually less concern for VOC release from fueling stations.

The vapor pressure behavior of the binary gasoline/alcohol mixtures have been verified theoretically and experimentally. It has been found that the maximum vapor pressure increase occurred at 10% volume for each methanol, ethanol and propanol with vapor pressure increases of 22.1, 7, and 3.7 kPa respectively. The corresponding mole fractions are listed in table 3. The

point at which the mixtures vapor pressure was equivalent to that of pure gasoline varied for each fuel, 82.4% for methanol, 46.5% for ethanol and 29.3% for propanol. Butanol was measured in a mass basis because it is solid at room temperature, and thus neat fuel could not be analyzed (Pumphrey, Brand, and Scheller 2000, 1405-1411).

Fuel		Vapor Pressure change from gasoline (kPa)	Alcohol Concentration Mol %
Methanol	Maximum	22.07	27.37
	Equivalence	0.00	94.06
	Neat	-28.21	100.00
Ethanol	Maximum	6.97	20.61
	Equivalence	0.00	66.92
	Neat	-44.35	100.00
i-Propanol	Maximum	3.72	16.53
	Equivalence	0.00	42.44
	Neat	-43.32	100.00
t-Butanol	Maximum	1.59	11.63
	Equivalence	0.00	23.60
	Neat	N/A	N/A

Table 16 - Vapor pressure change from pure gasoline for alcohol-gasoline mixtures. Adapted from (Pumphrey, Brand, and Scheller 2000, 1405-1411).

One option for decreasing the vapor pressure of gasoline-methanol and gasoline-ethanol mixtures is the use of a cosolvent such as butanol. Butanol (and other longer alcohols) has the distinct advantage of having a larger non-polar chain attached to an alcohol group. Thus, it can emulate an emulsifier by giving methanol and ethanol a more polar medium (the alcohol group) as a solvent, while the non-polar chain blends with the non-polar gasoline components. Beyond decreasing the vapor pressure of the mixture, the use of a cosolvent also decreases the likelihood of phase separation and thus decreasing the amount of water leeching due to polar fuels like methanol and ethanol.

CHAPTER 5: RESULTS AND DISCUSSION

In Chapter 4 the systematic analysis of thermo-chemically processed cellulosic biofuels was detailed. In this chapter the results are summarized and discussed. Additionally, the current policy landscape affecting the introduction of alternative transportation fuels is analyzed.

Summary of System Analysis

The system analysis performed in Chapter 4 consisted of primarily of a first law analysis of the energy conversion steps along with an evaluation of the economics of production and distribution of these fuels. Further, other systemic considerations were analyzed including the integrability of the fuels into the current distribution infrastructure, the end-use emissions characteristics of the fuels, and the toxicity and environmental risk associated with their adoption. Below these results are summarized and discussed.

It is immediately noticeable that no fuel is the top performer when each criterion is considered, thus thermochemical biofuel production does not have a clear “*silver bullet*” fuel. As such, there exist many technical and political trade-offs associated with the large scale adoption of one fuel over another. However it is clear that the adoption of thermochemical production of biofuels provides more fuel options and potential trade-offs versus the current trajectory in the biofuel industry where enzymatic production of biofuels is given preference both explicitly and implicitly through governmental policies.

System Efficiency

In Chapter 4 the first law thermodynamic efficiency of each of the predominant energy conversion steps for thermochemical cellulosic biofuel utilization were analyzed. Additionally, Monte Carlo analysis has been used to arrive at an estimate of both Biomass-to-Wheels (BtW) and Biomass-to-Tank (BtT) utilization efficiencies. In Table 17 the resulting BtW utilization efficiencies are summarized for each fuel utilizing different distribution methods.

	Truck	Rail	Pipeline
Methanol	19.6 ± 1.8%	19.9 ± 1.8%	20.1 ± 1.8%
Ethanol	14.6 ± 3.3%	14.8 ± 1.4%	14.9 ± 3.3%
Mixed Alcohol	17.4 ± 0.6%	17.6 ± 0.6%	17.7 ± 0.6%
MTG	9.8 ± 0.5%	9.8 ± 0.5%	9.9 ± 0.6%
DME	23.0 ± 1.8%	23.4 ± 1.8%	23.5 ± 1.8%
FT Diesel	18.0 ± 2.4%	18.2 ± 2.4%	18.3 ± 2.4%

Table 17 – Biomass-to-Wheel utilization efficiency of fuels plus or minus 3 standard deviations utilizing different distribution systems. These efficiencies are resultant from the consideration of current end-use technology. The highlighted efficiency values indicate that these values are unattainable due to current integrability limitations.

In Table 17 each of the average system efficiency is given plus or minus three times the resultant standard deviation (i.e. $\bar{x} \pm 3\sigma$). While it is apparent that for each of the fuels the most efficient way to transport them is via pipeline, it is not feasible to do so as will be discussed in the section on integrability below.

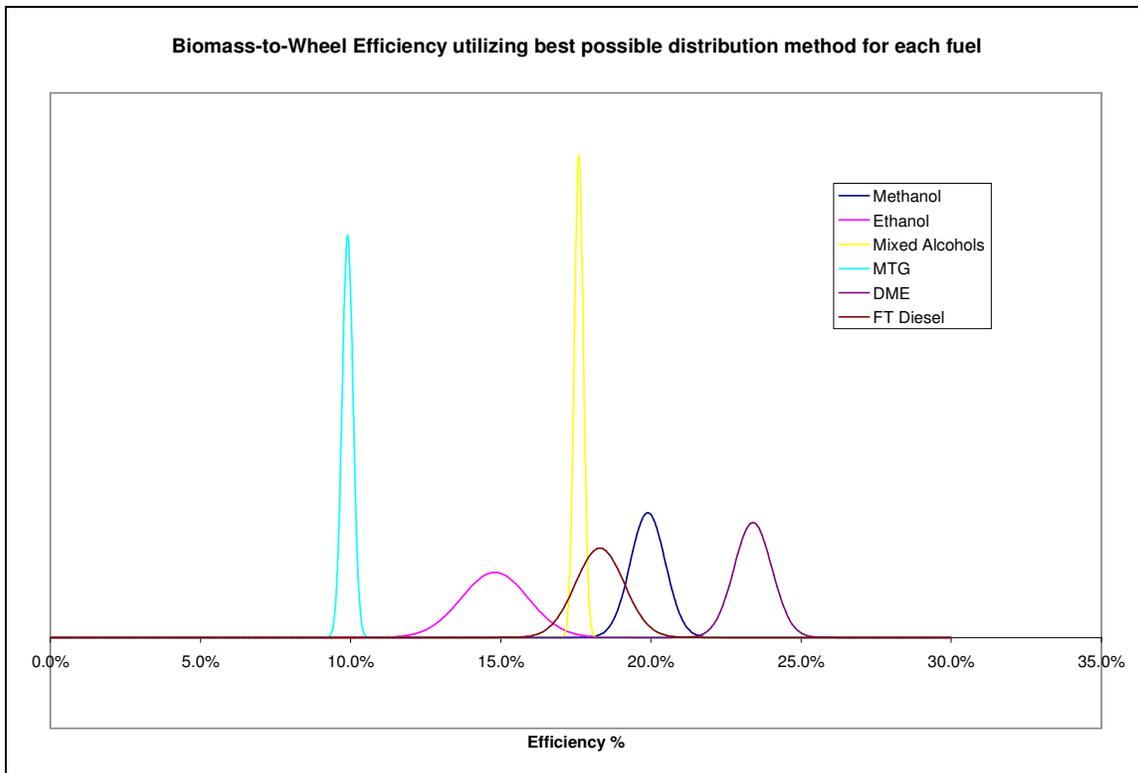


Figure 17 - Plot of the Biomass-to-Wheel results in Table 17. The averages and standard deviations resultant from Monte Carlo analyses are used to generate normal distributions for plotting.

In Figure 17 the BtW efficiencies are plotted using normal distributions generated from the resultant averages and standard deviations from the Monte Carlo Analyses. It is apparent in this

plot that, while each fuel has a distinct average efficiency, due to the uncertainty inherent in this assessment (due to the fact that there are currently no full scale plants selling fuels into the market) one cannot generate a definitive ranking of these fuel’s likely system efficiencies. For example, it cannot be determined whether mixed alcohols will be more or less efficiently utilized than Fischer-Tröpsch diesel, nor can one say for certain whether methanol will be more efficiently used than both of these. From this plot we can derive the more general ranking that DME is most likely to be the most efficiently utilized fuel followed by Fischer-Tröpsch Diesel, methanol, and mixed alcohols, then ethanol, and finally MTG synthetic gasoline.

	Truck	Rail	Pipeline
Methanol	54.4 ± 4.8%	55.4 ± 4.9%	55.9 ± 4.9%
Ethanol	44.3 ± 10.2%	44.9 ± 10.2%	45.1 ± 10.3%
Mixed Alcohol	56.1 ± 1.5%	56.8 ± 1.5%	57.2 ± 1.5%
MTG	32.6 ± 1.8%	32.9 ± 1.8%	33.1 ± 1.8%
DME	53.5 ± 4.2%	54.4 ± 4.5%	54.8 ± 4.5%
FT Diesel	45.1 ± 6.0%	45.5 ± 6.0%	45.7 ± 6.1%

Table 18 – Biomass-to-Tank utilization efficiency of fuels plus or minus 3 standard deviations. The highlighted efficiency values indicate that these values are unattainable due to current integrability limitations.

In Table 18 the BtT utilization efficiency of each of the fuels is summarized as in Table 17. Here only the production and distribution efficiencies are taken into consideration. The most noticeable difference in results is the downward shift in the system efficiencies of the CI fuels relative to the SI fuels. This happens because the end-use efficiency, for which CI fuels have an advantage, is not included in the system efficiency calculation. While this system calculation is incomplete since it doesn’t include the end-use efficiency, the ‘end’ of this system calculation more accurately reflects the information used in today’s transportation fuel market. This system efficiency reflects the efficiency that is implicitly used to calculate the at-the-pump price for fuels, and as such is what is used by consumers to decide what fuel to purchase. Transportation fuels are sold today to consumers who make their purchase under imperfect information, consumers over-value the at-the-pump price of the fuel and generally don’t calculate the impact that the end-use efficiency will have on their total fuel-costs. As such, the BtT utilization efficiency is a valuable metric to use to compare fuels since currently it is their at-the-pump price which matters most to consumers.

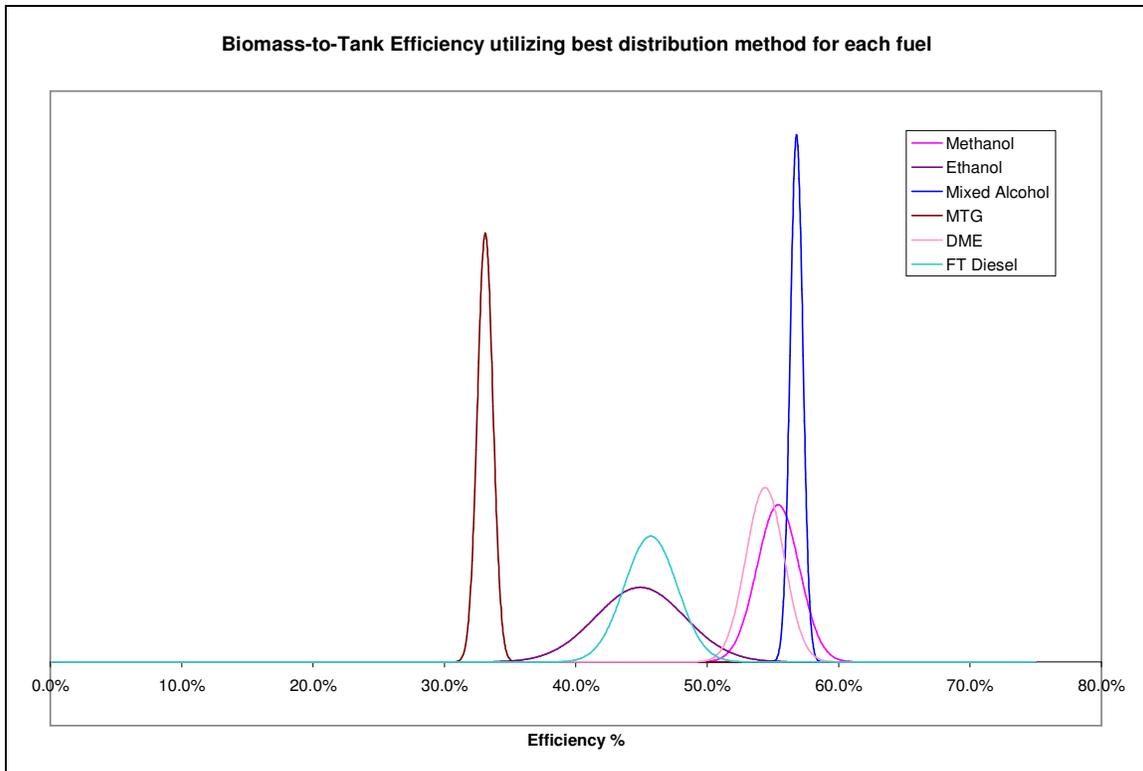


Figure 18 - The Biomass to Tank utilization efficiencies are plotted as normal distributions utilizing the averages and standard deviations derived from Monte Carlo analysis.

In Figure 18 the BtT efficiencies of the fuels are plotted as normal distributions. As above with the BtW utilization efficiencies, it is readily noticeable in this plot that, due to uncertainty, we cannot accurately predict whether certain fuels will be produced and distributed more efficiently than others. For example the higher average efficiency of DME versus methanol is statistically insignificant. Whether DME would be more efficiently brought to the pump than methanol is unknown until plants are actually built. A general trend that can be drawn from this plot, however is that Mixed Alcohols, DME and Methanol are most likely to be the most efficient, followed by Ethanol and Fischer-Tröpsch Diesel, and lastly MTG is the least efficient.

Economics

Under the current policy scenario the most important metric by which a fuel's viability is decided is by its economics. In the case of transportation fuels, the costs of greatest importance are the cost of production and delivery to the pump. This is the case since these are the costs that directly influence the price at the pump, and hence the fuels ability to compete with petroleum

derived fuels. The cost of production is by far the larger component of the total cost of delivered fuel, and as such, is the key to a fuel's viability. In Table 19 estimates of the cost of production of fuels on an energy basis are summarized from a number of studies that have been performed over the past two decades of fuels produced via gasification. Each of the prices quoted are given in 2007 dollars (₂₀₀₇\$). While many of the studies provided a range for their cost estimates there were an equal number that merely gave point estimates, these are quoted below with a question mark in the high column. Likely it is the case that these point estimates are low ball estimates since many persons working on such studies may have a bias for the particular fuel that they are studying.

Cost of Production (\$/GJ)			
fuel	low	High	Year
methanol	\$18.05	\$21.81	1991 ¹
	\$14.63	\$15.76	2003 ²
	\$10.28	\$15.42	2006 ³
ethanol	\$16.76	?	1996 ⁵
	\$15.76	?	2003 ³
	\$11.55	?	2005 ⁴
MTG	>\$30.00	?	1990 ⁶
FTD	\$21.38	\$28.13	2003 ²
	\$12.34	\$17.48	2006 ⁷
DME	\$14.63	?	2003 ²

Table 19 - The cost of production for fuels given in 2007 dollars per gigajoule. ¹Katofsky 1993, ²Spath and Dayton 2003, ³Kumabe et al. 2008, ⁴Phillips et al. 2007, ⁵Lynd 1996, ⁶estimated from Sugiyama 1994, ⁷Hamelinck and Faaij 2008.

Due to the uncertainty inherent in these estimates one cannot definitively conclude which fuel is most cost effective on an energy basis. However general trends can be noticed that alcohols, particularly methanol, are most likely to be produced cheaply. On the other end MTG synthetic gasoline, appears to be prohibitively expensive as compared to the other fuels. While the cost of production utilizing a per energy basis is of academic interest, it is not the way that consumers price and compare fuels; instead fuels are priced per volume at the pump. As such, the costs of production on a per volume basis is a more important metric to use in assessing these fuels. Table 20 lists the costs of production of these fuels when they are converted to a dollars per liter basis. Additionally, in Table 21 the costs of production are given in a dollar per gallon basis, the price most relevant in the US.

Cost of Production (\$/liter)			
fuel	Low	high	Year
methanol	\$0.29	\$0.35	1991 ¹
	\$0.23	\$0.25	2003 ²
	\$0.16	\$0.25	2006 ³
ethanol	\$0.38	?	1996 ⁵
	\$0.36	?	2003 ³
	\$0.26	?	2005 ⁴
MTG	>\$1.25	?	1990 ⁶
FTD	\$0.75	\$0.99	2003 ²
	\$0.43	\$0.62	2006 ⁷
DME	\$0.28	?	2003 ²

Table 20 - The cost of production for fuels given in 2007 dollars per liter. ¹Katofsky 1993, ²Spath and Dayton 2003, ³Kumabe et al. 2008, ⁴Phillips et al. 2007, ⁵Lynd 1996, ⁶estimated from Sugiyama 1994, ⁷Hamelinck and Faaij 2008.

These per volume production costs more accurately reflect the ordering of prices that consumers will face at the pump. Note, however, that the relative cost of production on an energy basis and the relative cost of production on a volumetric basis are not proportional. For example the cost of production of methanol on a volumetric basis is lower than that of ethanol, while using an energetic basis they are comparable. The relatively high cost of MTG production is further exacerbated on a volumetric basis versus alcohols since MTG has a higher energy density.

Cost of Production (\$/gallon)			
fuel	Low	high	Year
methanol	\$1.09	\$1.31	1991 ¹
	\$0.88	\$0.95	2003 ²
	\$0.62	\$0.93	2006 ³
ethanol	\$1.45	?	1996 ⁵
	\$1.37	?	2003 ³
	\$1.00	?	2005 ⁴
MTG	>\$4.00	?	1990 ⁶
FTD	\$2.85	\$3.75	2003 ²
	\$1.64	\$2.33	2006 ⁷
DME	\$1.06	?	2003 ²

Table 21 - The cost of production for fuels given in 2007 dollars per gallon. ¹Katofsky 1993, ²Spath and Dayton 2003, ³Kumabe et al. 2008, ⁴Phillips et al. 2007, ⁵Lynd 1996, ⁶estimated from Sugiyama 1994, ⁷Hamelinck and Faaij 2008.

In Table 22 the cost of shipping fuels 1000km is given in a volumetric (liter) and energy (GJ) basis. These costs are computed for the most economically and viable method. So for alcohols and DME this reflects train shipment, and for synthetic hydrocarbons this pricing is based on pipeline utilization. It is immediately noticeable that in both an energy and volumetric basis the cost of shipping a fuel via pipeline is cheaper by an order of magnitude. While this comparative advantage is large for synthetic hydrocarbon fuels its effect is dampened by the fact that shipping costs are a minor factor in the delivered fuel cost as compared to production cost.

	cost of shipping per liter 1000km	cost of shipping per GJ 1000km
methanol	\$0.050	\$3.141
ethanol	\$0.050	\$2.185
MTG	\$0.003	\$0.101
FTD	\$0.003	\$0.095
DME	\$0.060	\$3.130

Table 22 - Cost of shipping fuel 1000km via the most economically viable method. Alcohols and DME are calculated using rail; MTG and FTD are calculated for pipeline. These data are extrapolated from (Morrow, Griffin, and Matthews 2006, 2877-2886)

Other Systemic Considerations

While energy efficiency and economics are two important metrics with which to judge a potential transportation fuel, they are by no means the only important factor. Further these other factors influence the efficiency and cost of delivered fuels. For example, the integrability of a fuel into certain distribution infrastructures greatly dictates the delivered cost of the fuel and to a lesser extent its achievable system efficiency. Here these other systemic issues, fuel integrability, end-use emissions characteristics, and toxicity and environmental safety, are summarized and discussed.

Fuel Distribution Integrability

In Table 23 the modes by which different fuels can be shipped are summarized. As is discussed in Chapter 4, pipeline operators are reluctant to ship alcohols due to their corrosivity and hydrophilic nature. Pipeline operators are concerned that their infrastructure, which was designed for hydrocarbons, would be damaged by alcohols and the delivered product would be damaged

as well due to water accumulation. The integrability of a fuel into existing distribution infrastructure influences its overall acceptability through a number of factors.

Fuel	Truck	Rail	Pipeline
Methanol	Y	Y	N
Ethanol	Y	Y	N
Mixed Alcohol	Y	Y	N
MTG Synthetic Gasoline	Y	Y	Y
FT Diesel	Y	Y	Y
DME	Y	Y	Y/N

Table 23 – Summary of fuel integrability for different distribution infrastructures. Y indicates it is, N indicates that the fuel is not, and Y/N indicates ambiguity.

Firstly, and perhaps most importantly, it influences a fuel's ability to be delivered to the market place. If a fuel is restricted in the means that it can be transported it is less likely to reach each of the sale points utilized for transportation fuels. This issue has been manifested in the challenge of bringing sufficient amounts of ethanol to the east and west coasts to meet the mandated demand for oxygenates in reformulated gasoline (Dinneen 2008). Since pipeline operators do not currently accept alcohols in their pipeline infrastructure ethanol must be shipped via train and truck to the coasts which has limited its integration into retail fuel.

Secondly, the integrability of a fuel influences its delivered cost. As was shown above the cost of delivery for a fuel is an order of magnitude lower when pipeline is utilized as compared to train or truck. For alcohols, since they are not currently accepted in the pipeline infrastructure, this exclusion implies higher costs making them less competitive at the pump than they could be.

Finally, integrability of a fuel influences its overall achievable thermodynamic efficiency. Much like the cost of shipment, the efficiency of shipping a fuel is the best when pipeline infrastructure is utilized and worst when trucks are utilized. As such, if a fuel is excluded from the pipeline infrastructure it cannot achieve its best possible lifecycle efficiency.

End-Use Emissions

One way in which current regulation influences alternative fuel adoption is through end-use emissions regulation. Today there exist regulations limiting the amount of three major local pollutants (Carbon Monoxide (CO), Nitrogen Oxides (NO_x) and particulates) which will also

regulate any alternative fuel which is adapted as a substitute for today’s petroleum derived fuels. In SI engines the primary concern is with CO and NO_x since particulates are not produced as readily as with CI engines. In Table 24 the emissions characteristics of the fuels being analyzed are tabulated relative to their petroleum derived counterpart (gasoline and diesel fuel).

	CO	NO _x	Particulates
methanol	Slight reduction	Significant reduction	N/A
ethanol	Slight reduction	Significant reduction	N/A
mixed alcohol	Slight reduction	Slight reduction	N/A
MTG synthetic gasoline	No change	Slight increase	N/A
FT Diesel	Moderate reduction	Moderate reduction	Moderate reduction
DME	No change	Moderate reduction	Significant Reduction

Table 24 - Summary of emissions properties relative to petroleum derived counterpart (gasoline or diesel).

It is apparent that these alternative fuels perform better than petroleum derived fuels with respect to emissions - with the notable exception of MTG synthetic gasoline. This under performance is due to the fuels increased aromatic content which is resultant form the method of synthesis. In the United States and Europe there continues to be a trend of increasingly stricter limits on these pollutants, and the poor performance of MTG gasoline could seriously hamper its deployment. On the other hand, the improvement in emissions characteristics of the other fuels creates an incentive for their adoption in states striving to achieve stricter emission limiting goals. Indeed the superior emissions characteristics of alcohols have been major drivers for their previous adoption through mandatory oxygenate requirements in reformulated gasoline.

Both Europe and the United States (in particular California) are moving towards ever stricter emissions regulation which is becoming increasingly difficult for current CI engine technology to meet without the utilization of expensive after treatment systems (Teng and McCandless 2006). While alternative fuels have been utilized to address emissions concerns with SI engines there has been no mandate imposed on CI fuels. However, due to their improved emissions characteristics both FT Diesel and DME could potentially be used to meet heightened regulation. In particular DME produces practically no particulate matter, completely avoiding the tradeoff which exists for today’s diesel combustion between particulate matter and NO_x production.

Toxicity and Environmental Safety

On average, the synthetic fuels analyzed in this thesis are less hazardous to human and environmental health than their petroleum derived counterparts. In Table 25 the results from the toxicity analysis in Chapter 4 are summarized. Methanol and ethanol both have lower mortality and morbidity risks as compared to gasoline, and both would pose little threat to the environment in the event of spillage. Higher alcohols on the other hand do have higher health risks associated with them. Butanol, for example, has a lower oral LD₅₀ value than gasoline. Higher alcohols are, however more environmentally benign than gasoline and can be naturally metabolized by microbes. DME, the one ether considered, is in general of lower risk than the other compounds due to the fact that it is a vapor and the risk of concentrated exposure to it is low. Additionally, DME can decay quickly in the environment due to its sensitivity to solar irradiation and thus poses little threat in the event of leakage.

	Toxicity	Environmental Safety	Other
Methanol	low relative mortality risk, moderate morbidity risk	low environmental hazard risk	public perception of risk is high
Ethanol	low relative mortality risk, low morbidity risk	low environmental hazard risk	public perception of risk is low
Mixed Alcohol	moderate mortality risk with higher alcohols, moderate morbidity risk	increased environmental hazard with increased higher alcohols	low vapor pressure
MTG	moderate mortality risk, high morbidity risk (aromatics)	high environmental hazard (aromatics)	comparable to today's fuel
FTD	low risk relative to petrol-diesel	lower risk due lower aromatic content	
DME	low mortality risk, low morbidity risk	low environmental hazard risk	high vapor pressure, quickly disperses

Table 25 - Tabulation of health and environmental risks associated with fuels considered in this thesis.

MTG synthetic gasoline, on the other hand, may pose increased health risks as compared to its petroleum derived counterpart due to the higher aromatic content in this fuel. Also because of the long life of aromatic compounds in the environment, and their immiscibility with water, the environmental risk associated with MTG is high. Finally, Fischer-Tröpsch diesel has lower

health and environmental risk relative to its petroleum derived counterpart due to its lower aromatic content.

Policy Challenges: The Entrenchment of Ethanol

In order for alternative fuels to be adopted a favorable (or minimally, non-negative) policy climate is essential. In the United States there currently exists a strong policy and regulatory regime designed to foster and support the domestic biofuel industry, which is focused primarily on ethanol production. Ironically, it is these policies which may have erected the greatest barriers to entry for other non-ethanol biofuels into the transportation fuel market. In this section these historic policies are discussed and the challenge which they mount against further innovation in transportation fuels is analyzed.

The ethanol industry of today is a product of more than 25 years of Stiglerian regulatory capture on behalf of the special interests of the firms that make up the ethanol industry. Regulatory capture refers to a situation where a government agency, instead of acting on behalf of the public good, creates regulations favorable to the industry it is supposed to regulate. The theory states that this is due to the industries' ability to focus resources towards lobbying the agency whereas the disinterested public does not organize to oppose such action (Stigler 1971, 3-21).

There are four principal cases where the ethanol industry successfully procured favorable subsidies and regulations which dominate the market landscape today. The first case is the use of a historically subsidized feedstock, corn, to produce fuel ethanol. The second case is the successful creation of the federal Volumetric Ethanol Excise Tax Credit (VEETC) commonly called the Blender Tax Credit. Through effective lobbying, the ethanol industry was able to increase their market share of the alternative transportation fuel market by ushering through federal Renewable Oxygenate Requirements (ROR). Finally, with the passage of the 2007 Energy Independence and Security Act the biofuel industry procured guaranteed demand through federal mandates on the amount of biofuels which must be included in the national fuel mix.

Proactive Agricultural Policy

The US biofuel industry consists primarily of ethanol produced enzymatically from starchy feedstocks (primarily corn along with other cereal grains) as has been done for thousands of years for the production of fermented alcoholic beverages. As such the ethanol industry positioned itself to reap the benefits of a long history of national agricultural policy directed at price stabilization of corn (along with other commodity crops) via proactive agricultural policies (Kennedy and Visser 1990, 27-46).

The first major agricultural policy employed by the United States was a strategy of limiting production of commodity crops in order to avoid surpluses and prop up prices at the market. This was achieved through voluntary reductions in land production for which the government would partially reimburse the farmer. This policy was enacted in 1933 via passage of the Agricultural Adjustment Act (Bowers, Rasmussen, and Baker 1985). Besides times of ramped up agricultural production to meet national need in time of war, the strategy of supply management became the major thrust of national agricultural policy through the early seventies (Gardner 2002). In 1973, national agricultural policy changed from a policy of supply control to surplus creation paired with direct subsidies and guaranteed prices in response to global grain shortages. In order to keep prices competitive for farmers the federal government would buy excess grain in order to keep grain prices at an inflation adjusted goal price and donate the grain to famished markets (Bowers, Rasmussen, and Baker 1985).

It was during the late seventies when the corn ethanol industry first began to develop. During this time global shortages were becoming less severe and in turn national surpluses were beginning to depress grain prices. To address this challenge, federal agricultural policy makers sought to create additional non-food markets to absorb record breaking corn production levels (Gardner 2002). Because of these conditions, the ethanol industry was able to build upon a feedstock which through a long history of proactive agricultural policy, was being produced at levels higher than traditional demand could meet and was being supported through direct subsidy to farmers; thus, guaranteeing sub-optimal selling prices at the grain terminal (Schmitz, Furtan, and Baylis 2002). This subsidy structure continues to result in an economic transfer from tax-payers to the corn consuming ethanol industry.

Volumetric Ethanol Excise Tax Credit

While the use of a subsidized feedstock sweetened the economics of fuel ethanol production from corn, ethanol was not yet cost competitive with petroleum derived gasoline during the mid 1970s. In 1978, the longtime CEO of Archer Daniels Midland (ADM), Dwayne Orville Andreas used his influence with influential law makers, including then Senate Majority Leader Bob Dole (R-KS), to usher through the federal VEETC legislation (Barrionuevo 2007). This legislation provided an effective 51¢ per gallon subsidy for fuel ethanol. This was achieved through the exemption of the volumetric amount of ethanol blended with fuel gasoline from the federal gasoline excise tax. This subsidy, still in existence today, is equivalent to approximately \$30 per barrel of oil equivalent (boe) of ethanol.⁴

This achievement appears to be due, in part, to ADM's success in capitalizing on the political will and public sentiment towards combating high oil prices and dependence on volatile energy sources in the aftermath of the first energy crisis. With the passage of this act, the ethanol industry was now not only able to capitalize on a subsidized feedstock, but now their primary product stream was subsidized as well. Through the late seventies the ethanol industry experienced its first major boom due to the second energy crisis and ethanol's new found ability to compete economically with petroleum derived fuels.

Renewable Oxygenate Requirement and the Banning of MTBE

With the enactment of the blender tax credits in 1978 and the fuel market conditions due to the two energy crises, the market for fuel ethanol seemed assured. However, due to the 1980 recession triggered in response to the high inflation in the wake of these two energy crises, the demand for oil dropped dramatically, and the real price of oil dropped to the point at which ethanol could no longer be assumed economically competitive in the long run. Therefore, it was no longer possible to justify great capital expenditures on the deployment of large scale ethanol plants. After economic conditions returned to normal, OPEC had agreed to increase petroleum production, and thus maintain low oil prices for the foreseeable future, which continued to render

⁴ This subsidy has been somewhat variable over the years ranging from upper 40's to lower 50's cents per gallon. In 2009 the credit was 45 cents per gallon.

ethanol uncompetitive. These unfavorable conditions were faced by the ethanol industry through the late 1980s (Weiss 1990).

In 1990, the US Congress passed a major set of amendments to the Clean Air Act (Baucus 1990, 549). One of the major amendments contained in this act established the Reformulated Gasoline (RFG) program, which was aimed to combat air pollution in the nine worst affected metropolitan areas. One major aim of this program was to decrease the overall automotive emission of toxic Carbon Monoxide (CO), by requiring the addition of oxygenates which facilitate a more complete combustion to Carbon Dioxide (CO₂) (NSTC 1997). In this implementation of this oxygenate requirement, there was further stipulation by the Environmental Protection Agency's rule making that 30% of the requisite oxygenates must be derived from a renewable source. This ruling turned out to be a very controversial decision. Many interest groups questioned the scientific basis on which the requirement of the use of oxygenates was based and whether or not their use did improve local air quality (Barrionuevo 2007). The renewable oxygenate requirement turned out to be even more controversial (Brown 1997, 1299-1328). This rule was controversial due to the fact that at the time the EPA had no statutory authority to establish and enforce a requirement to use renewable fuels. Since the EPA's stated authority is to protect human health, and in the case of combustible fuels this would be done by mandating fuels which decrease harmful pollution. While it has been shown that the use of oxygenates decrease the emissions of carbon monoxide, the existence of further benefits from the use of renewable oxygenates (ethanol and ETBE over MTBE) is questionable and in some cases has been shown to produce more dangerous emissions such as increased volatile organic compounds (VOCs) (NSTC 1997). The primary fuel oxygenates used at the time of this rule making were three chemicals; methyl-tertiary butyl ether (MTBE), ethyl-tertiary butyl ether (ETBE) and ethanol. Because of the EPA's renewable oxygenate mandate 30% of the oxygenates must have then been either ethanol or ETBE which is derived from ethanol, MTBE, which was derived primarily from natural gas, could not be used to meet this mandate. As is detailed in Brown, this case is a clear example of the government giving into the concentrated interests of the ethanol and farmers lobbies. In the published history of EPA's rule making on renewable oxygenate requirements, it was even cited that the use of ethanol caused more emissions than that of MTBE. Although the

renewable oxygenate requirement was eventually struck down in the Court of Appeals for the D.C. Circuit (Brown 1997, 1299-1328), the oxygenate requirement remained.

Not long after the rejection of the renewable oxygenate requirements MTBE, which was used in reformulated gasoline outside of the Midwest, began showing up in drinking water aquifers in California and was soon banned in several states due to the possible public health risks associated with its use. Because of this, along with a concentrated effort on behalf of the EPA under the Clinton/Gore administration in 2000 to support the ethanol industry, ethanol was once again a mandated additive in reformulated gasoline (though now in an indirect manner) (EPA 2000).

Renewable Fuel Standards

Between 2000 and 2007, the ethanol industry underwent a massive expansionary period due to the confluence of the above mentioned agricultural and energy policies along with high oil prices and low corn prices. Not only did this situation create increased demand for ethanol, it also created an atmosphere on Capitol Hill ripe for policies directed at foster 'energy independence'. As oil prices continued to climb through 2007 the Congress passed the 2007 Energy Independence and Security Act which contained many energy provisions, however most notably it created an explicit mandate for biofuel production in the US.

CHAPTER 6: CONCLUSIONS AND POLICY RECOMMENDATIONS

In this thesis six potential thermochemical biofuels were analyzed: Methanol, Ethanol, Mixed Alcohols, Mobile-M synthetic gasoline (MTG), Fischer-Tröpsch Diesel and Dimethyl Ether (DME). This analysis considered each of these fuels systematically from delivered biomass to wheel. Their performance with respect to different criteria, including lifecycle energy efficiency, cost of production and distribution, integrability into infrastructure, and health and environmental risks, was considered as well. In this chapter, conclusions drawn from these results are discussed and policy recommendations are offered.

Conclusions from System Analysis

The analysis detailed in Chapter 4 produced a great amount of results, but these data alone do not say much beyond how each fuel performs relative to one another with respect to each criterion. However, when these results are taken in context of the policy landscape and how the US biofuel industry is developing certain conclusions can be drawn. Here five main conclusions are enumerated and discussed; in the next section, policy recommendations are provided to address the limitations of the US biofuel industry.

1. No one fuel analyzed in this thesis stands out as a so-called “silver bullet” solution.

Upon considering the relative performance of each of the fuels considered in this thesis one finds quickly that no single fuel is the best choice with respect to each criterion. Dimethyl ether, for example, has the potential to be produced relatively cheaply and utilized most efficiently, however because of integrability limitations and its physical properties it is unlikely to be adapted outside of small fleet deployment.

Of course, one should not necessarily expect that it would be possible to find a clear technology winner in such a complex system as that of transportation fuels. Instead, outside of the influence of technology specific policy, one would find that a number of firms would attempt to enter the market with any number of possible fuels and the market would theoretically sort out the viable technologies. This is not likely to be the case in the transportation fuel sector, however, due to the necessarily high capital expenditures and resultant financial risk of a failed technology

deployment (see hydrogen in California). Governmental support and favorable policies will be necessary for the adoption of alternative fuels. Additionally, centralized investment in a modern distribution infrastructure which can accept non-hydrocarbon fuels will be essential.

- 2. Technology specific support policies have a poor track record at efficiently addressing energy dependence, and do not necessarily allow the most effective technology to prevail.*

Although governmental support is crucial to the adoption of alternative fuels, government's records in this arena has suffered due to the utilization of technology specific policies which are often used to support the favorite parochial industries of the day. The most notorious example of this is corn ethanol in the United States. Through policy interventions (detailed in Chapter 5), the US government has created an incredibly well supported industry based on one technology whose merits have been called into question. These policies have not only created a large incentive for the continued expansion of corn ethanol, but has also created an incentive for expanded R&D into the production of ethanol from other feedstocks instead of considering other potential fuels. Another example of government ineffectually picking a technology winner in the realm of transportation fuels is the governmental support of MTG production in New Zealand from natural gas. This program ended up costing the government large sums of money over many years due to the high cost of the MTG fuels.

Since there is no clear 'silver-bullet' cellulosic fuel as this thesis has shown, it is difficult for a technology based policy to be used to support the adoption of cellulosic biofuels. Instead, policies should be designed which are technology neutral, such as taxing petroleum-derived fuels if it is the goal of a government to displace their use or at the very least providing level playing field subsidies to all replacement options that meet certain basic criteria. Such a policy puts each potential replacement technology on the same footing without incentivizing a specific technology and running the risk of a large governmental technology-welfare program.

- 3. While all of the fuels considered in this thesis have health risks comparable to or less than their petroleum derived counterparts, the public misconception of a fuels toxicity may disqualify an otherwise promising fuel.*

The health risks associated with a fuel do not directly influence its economic bottom line, but rather indirectly. If the fuel is regarded to be hazardous it is unlikely to be adopted at scale. While it is important for each consumer to be fully aware of the risks associated with fuels, a misunderstanding of a fuel's risk could have an unnecessarily harmful effect on its potential adoption, further the public's sensitivity to health risks could be potentially exploited by rival technologies to create a public misconception of a rival technology. This was the case in the battle between ethanol and other oxygenating fuels during the 1990's where a strong campaign was mounted against MTBE and to associate methanol with MTBE in order to make ethanol the default oxygenate additive (Brown 1997, 1299-1328; Libecap 2003, 89-106).

Methanol for example could be utilized as a superior gasoline substitute were it not for the public misconception of the health risks associated with its use. Further, it is highly probable that the public underestimates the health risks associated with fuel ethanol relative to other replacement fuels.

Outside of potential fuels which are listed by the EPA as being significant risks to public health, all other fuels should be considered equally as potential replacements for their petroleum derived counterparts which, in most cases, is the most hazardous option.

4. Under the current biofuel policies, it is unlikely that any non-ethanol biofuel will gain market share in the US.

Because of the ethanol-friendly transportation fuel policies in the US, it is unlikely that other fuels will be able to gain a significant hold in the US market. In the analysis performed in this thesis ethanol was not the highest ranked fuel when any criterion was considered. However because of the parochial interest of supporting farmers ethanol has found its way into being the alternative fuel of choice in America. While the policies to support ethanol were designed to support ethanol derived from corn versus petroleum derived fuels, now such policies are creating incentives for firms to focus their R&D expenditures on producing cellulosic ethanol, without seriously considering other fuels derived from cellulose.

Technology neutral fuel policies must be adopted in order for other transportation fuels to be considered seriously when compared to ethanol, otherwise another inefficient ethanol market (based on cellulose instead of corn) will be created.

5. Due to the complex interdependencies of the thermochemical biofuel value-chain, system analysis and thinking is necessary in order to approach an optimal outcome.

As with any complex system with many influences up- and downstream, using a siloed approach in which each step is optimized independently from one another will not yield a globally optimal solution. For example, by considering this problem solely with regards to the systematic energy efficiency, one would conclude that DME is the best fuel to be produced and used, however this fuel is not a good fit to the current distribution infrastructure in the US. Indeed, analyzing the problem from the distribution lens alone would lead to the identification of synthetic hydrocarbons as optimal solutions, where these fuels are more expensive to produce than the other options.

Even when fuels are considered through just one lens, a global optimum may not be reached if the different steps are considered independently. If just the energy efficiency is considered, one studying the production side might decide that mixed alcohols would be the best fuel to produce and ship based solely on the Biomass-to-Tank efficiency, however one studying the end use of the fuels may conclude that using dimethyl ether in a compression ignition engine would be the optimal choice. Though dimethyl ether has the highest average biomass to wheel efficiency, it is clear that by just analyzing the production side the global optimum was not identified.

Instead it is necessary to consider such large interconnected systems in a more holistic manner, as this thesis has done. A choice made at any one point in the system has consequences with regards to the overall system performance. Of course this result does not need to be seen as a limitation, but rather an invitation for innovation in both the technical and policy spheres.

Policy Recommendations

Today the ethanol industry is thriving as it has never been able to do before, and it is ironically the policies which were put in place to support ethanol's growth which may most likely impede the adoption of other non-ethanol biofuels. The ethanol industry has successfully erected barriers to entry into the alternative fuel industry through the procurement of subsidies on its product (blender tax credits), through the benefit of subsidies aimed at corn and through the capture of federal environmental regulation in the form of oxygenate standards for reformulated gasoline and the banning of MTBE. The ethanol industry achieved these results through the influence of ADM's long time chief executive Dwayne O. Andreas and strategic partnership with the very influential Farmer's Lobby (Weiss 1990). The result of this is a lack of innovation in the United States in the realm of alternative transportation fuels. While there is research being undertaken towards the development of advanced biofuels, the vast majority of research is towards new ways to make ethanol from a broader array of feedstocks. This drive is dictated by many firms' beliefs that the only way to be economically competitive they must 1) be able to sell into the already established and propped up ethanol market, and 2) be able to qualify for the VEETC by producing ethanol. Therefore, there is very little R&D taking place on other fuels which experience better production energy efficiencies (e.g. methanol & dimethyl ether), better integrability into the current fuel distribution structure (e.g. Fischer-Tröpsch Diesel & MTG synthetic gasoline), or some other yet to be discovered synthetic transportation fuel.

In order to address these market failures which has resulted due to ethanol's self erected boundaries to entry into the alternative fuel market and to support increased innovation in the alternative transportation fuel sector, policies must be employed which are explicitly technology and product neutral which still are aimed at making alternative transportation fuels cost-competitive with petroleum based fuels. Additionally the market structure which the ethanol industry benefits from in the form of a subsidized feedstock must also be addressed.

Supporting Innovation without Picking Winners

One major policy thrust of any attempt at resolving this market failure must be to avoid employing policies which specifically support a certain technology or fuel. So, in order to

incentivize investment in alternative non-petroleum transportation fuels, instead of directing tax credits at specific fuels, an equivalent tax should be levied against fuels derived from petroleum. In this way there is no incentive created to direct future research on fuels which have been shown to historically receive the tax credit, and thus stifle innovation and research towards fuels which may not have yet been deployed. Therefore, a better alternative policy to the per-gallon VEETC, would be the enactment of a per gallon tax on fuels derived from petroleum. This policy would have the additional benefit of being indifferent of the alternative fuel's energy density since this incentivization structure does not rely on subsidization on a volumetric basis, which in effect incentivizes the use of fuels which have a lower energy density and which will not offset as much petroleum derived fuel⁵.

While the aforementioned policy proposal would most efficiently address the need to remove incentive to invest in a small set of specific fuels, and instead to incentivize investment in all non-petrol based fuels, the feasibility of passing such legislation is unlikely. Another approach to addressing this policy goal has been advocated for by Sen. Richard Lugar of Indiana. In this approach instead of a volumetric tax levied against oil, a price floor of \$35-45 per barrel would be applied to petroleum in order to decrease the future risk that alternative fuels could be priced out of the market by petroleum derived fuels (Lugar 2006a; Lugar 2006b). By applying a price floor to petroleum as long as petroleum prices remain above the floor there would not be a tax applied to consumers and this in turn would have a negligible effect on gasoline prices (especially at current petroleum prices). Because the tax would likely not be felt by consumers, the political feasibility of this approach is greater than a volumetric tax which is levied at all prices.

The second approach, while more feasible politically, could lead to further market failure in the case that the global market price for oil is priced below the floor price. When oil is priced below the United States' floor price oil purchasers will be facing a price equal to the floor price and are

⁵ This benefit can be easily understood by considering the alternative approach of, instead of taxing petroleum based fuels, providing the 51¢ per gallon tax credit to all alternative transportation fuels. In this case ethanol which has an approximate energy density of 76,100 BTUs per gallon would receive a tax credit of \$6.70 per million BTUs of petroleum based fuels displaced, whereas synthetic gasoline derived from biomass with an energy density equivalent to regular gasoline of 114,100 BTUs per gallon would receive a tax credit of only \$4.47 per million BTUs of petroleum based fuels displaced.

indifferent to whether it goes to the Federal Coffers or the oil importers. In this case oil exporting countries and companies would be incentivized to sell oil at the floor price above the market price (Donohoo et al. 2008).

While this second approach is more politically feasible than the approach of taxing petroleum at all price levels taxes as policy tools find much less support in America than directed subsidies as policy tools. Of course utilizing a policy of direct subsidies to non-petroleum based fuels has drawbacks. Firstly, unlike taxing petroleum subsidizing alternatives will cost the federal government substantial amounts of money and would not be a revenue neutral policy less a revenue stream is matched with it. Secondly, the design of such a system of subsidies would run the risk of being a set of technology specific policies, and as reasoned above technology specific policies have a poor track record. Subsidies would have to be designed to be based on energy content not volumetric as to avoid the perverse incentives created by the VEETC to move towards fuels with low relative energy density.

Addressing Oxygenate Standards

As the federally mandated oxygenate requirement in reformulated gasoline now stands it is an indirect mandate for the use of ethanol in reformulated gasoline. As such this policy is in effect picking a certain technical approach in addressing carbon monoxide emissions, thus this policy is unlikely to yield the most cost effective solution to carbon monoxide pollution. A first order approach to achieve the same end in a more technology neutral manner would be for the federal government to mandate a cap on carbon monoxide emissions. This would allow for the most cost effective solution to emerge whether it is an improvement in automotive technology, improved exhaust clean-up, or continuation of the use of oxygenates in fuels. Since the oxygenate standard is a policy specifically designed to address air quality issues in very explicit geographic locations, solutions which are achieved through automotive technology may not completely address the goal since automotive sales cannot be targeted toward specific locations. As such a modified approach to oxygenate standards may be the only approach to address local carbon monoxide standards.

Oxygenate standards could still continue to be employed under the scenario where ethanol is no longer subject to the per-gallon VEETC tax exemption, but instead petroleum derived fuels are levied an additional per gallon tax of the same magnitude as the VEETC (see above section). In this case EPA reformulated gasoline regulations should be rewritten to reflect no favoritism to any possible oxygenates to be employed. Under these conditions there would be no specific incentivization towards the use of ethanol since all non-petroleum based oxygenate fuels (e.g. methanol, ethanol, ETBE, butanol, etc) would face the same economic landscape. Therefore, current oxygenate standards could continue to be employed in specific geographic locations so long as the requirements do not impose any favoritism toward specific fuels.

Addressing Ethanol's Subsidized Feedstock

One of the most important (and certainly most difficult) policy fixes required is to address the subsidized feedstock on which today's ethanol production depends. It is important not to incentivize any certain feedstock over another when searching for alternative transportation fuels since this will limit the different solutions and technologies considered significantly. However the removal of corn's governmental support will be no easy feat. The primary aim of the United States' national agricultural policy over the last 75 years has been aimed primarily at guaranteeing profitable markets and decrease financial risks for farmers in order to guarantee continued agricultural production in the long run. This had been achieved originally through supply control, however now it is achieved through a combined approach of price supports, guaranteed loans, and federal crop insurance which has been shown to support over-production and sub-optimal prices at the market. Attempting to remove the long standing subsidy structures from the American agricultural sector would be beyond the scope of addressing the boundaries to entry to the alternative transportation fuel market, and would probably be revealed as being politically unviable.

One way in address this issue of subsidization of agricultural products favoring certain production methods is providing a subsidy for non-grain production such as providing a guaranteed market price for cellulosic material in the short to mid-term (5-15 years) such that switchgrass or woody biomass is price-competitive with corn on an acre-planted basis. This type

of program allows for the development of a cellulosic fuel production industry. Once this market has been established then such a policy could be phased out as farmers are then able to achieve a guaranteed revenue stream for this new energy crop. While this approach does allow for rent collection on behalf of the concentrated interest (farmers) if it is passed with a clear sunset clause, it could be more a politically viable way addressing corn-ethanol's capitalization on a subsidized feedstock. Additionally, if such a program is designed to be only temporary, when the program phases out farmers would necessarily resort comparing growing an unsubsidized cellulosic feedstock versus a subsidized commodity grain. Thus in parallel to such a program either a continued subsidy structure would be needed to support cellulosic feedstock producers, or (ideally and more unlikely) grain subsidies would be phased out concurrently.

In the 2008 Farm Bill, the Biomass Crop Assistance Program was created which a very similar type of policy to the one is proposed above, however this policy does not phase out the subsidization of cereal grains. Further legislative action is needed in order to fully level the playing field in the biofuel feedstock market.

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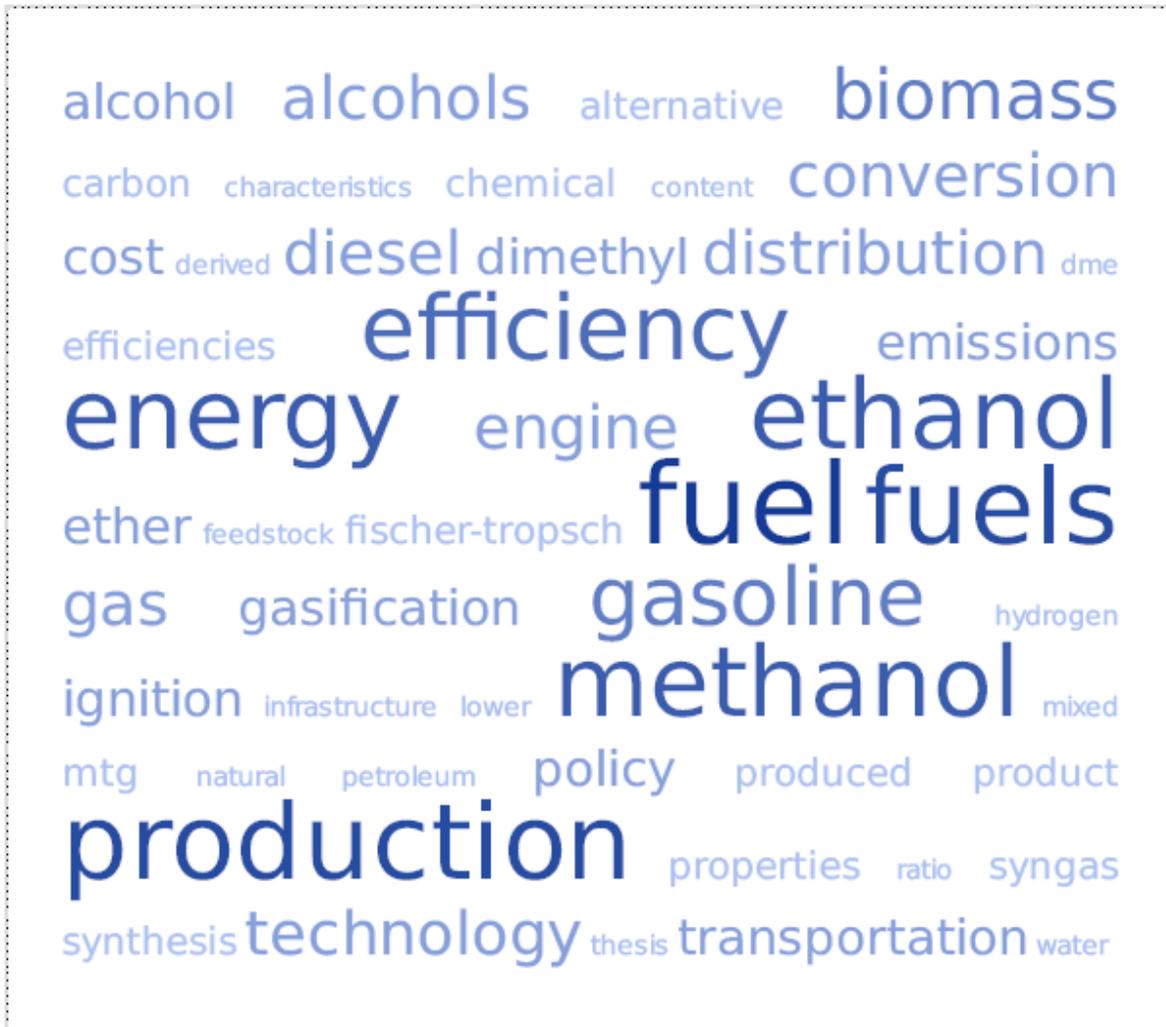
TABLE OF APPENDICES

Appendix A: Acronyms 136
Appendix B: Tag cloud 137

Appendix A: Acronyms

<u>Acronym</u>	<u>Phrase or Name</u>
2D (D2)	EPA test diesel
AKI	Anti Knock Index
ASF	Anderson-Schulz-Flory
BSFC	Brake Specific Fuel Consumption
CI	Compression Ignition
CNG	Compressed Natural Gas
DME	Dimethyl Ether
E##	Gasoline Ethanol Blend ##% Ethanol
EISA	Energy Independence and Security Act
EPA	Environmental Protection Agency
FTD	Fischer-Tröpsch Diesel
FTS	Fischer-Tröpsch Synthesis
GGE	Gallon Gasoline Equivalent
HC	Hydrocarbon
HHV	Higher Heating Value
ICE	Internal Combustion Engine
IMEP	Indicated Mean Effective Pressure
LHV	Lower Heating Value
LNG	Liquefied Natural Gas
LPG	Liquefied Petroleum Gas
M##	Gasoline Methanol Blend ##% Methanol
MON	Motor Octane Number
MTG	Methanol-to-Gasoline
NREL	National Renewable Energy Laboratory
PM	Particulate Matter
RdON	Road Octane Number
RON	Research Octane Number
SASOL	South African Synthetic Fuel Company
SI	Spark Ignition
SIDI	Spark Ignition Direct Injection
UBM	Unburned Methanol

Appendix B: Tag cloud



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