DIVISION OF THERMAL POWER ENGINEERING
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MASTER THESIS IN ENGINEERING PHYSICS

Liquid Bio Fuels for Gas Turbines

Examining the possibilities of introducing
liquid bio fuels in gas turbines at E.ON Värmekraft

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Abstract

In this study the different liquid biofuels that could be used as alternative fuels in gas turbines are reviewed. The pre-conditions are biofuel in liquid state, suited for seven specific gas turbines at E.ON Värmekraft that are a part of the disturbance reserve of Svenska Kraftnät. The alternative fuels need to comply with the agreement with Svenska Kraftnät.

The most probable candidates are biooil, dimethyl ether, bio-ethanol, Fischer-Tropsch synthesized fuels, straight vegetable oils, fatty acid (m) ethyl esters (FAME, RME, bio-diesel) and hydro-treated (or -genated) vegetable oils (HVO). These fuels are studied and their different properties are listed.

Earlier works where these fuels have been used in gas turbines are studied and conclusions are drawn from this. Several issues concerning combustion and emissions with respect to gas turbines are reviewed.

The gas turbine fuel consumption regarding alternative fuels is presented and a market research of prices of the alternative fuels is performed. The specific sustainability demands of both the Swedish Energy Agency and E.ON are discussed.

An analysis is performed of the alternative fuels, of the earlier work and how this will affect the issues with combustion and emissions. Some specifics concerning the use and storage of these alternative fuels are also analyzed.

An economic analysis is performed calculating the total cost from using these alternative fuels, including cost for fuel and investments and possible subsidies.

The conclusion is that it is both technically feasible to use liquid biofuels in gas turbines, and with some requirements, there can be an economical gain in it. Though this requires large investments.

Biooil or Pyrolysis oil could, during an estimated time period of 15 years, with subsidies, cover the material investments needed for the conversion.

Disregarding economy, there is a relatively new alternative fuel on the market, HVO, that seems very good and it is in some aspects better than the current fuel. The price on this fuel is on the other hand very high due to the fact that it can substitute diesel fuel for vehicles.

Sammanfattning

I följande arbete studeras biobränslen för användning i gasturbiner. Förutsättningarna är flytande bränsle samt sju specifika gasturbiner inom E.ON Värmekraft, som ingår i Svenska Kraftnäts störningsreserv. För att vara ett tänkbart alternativ till dagens bränsle måste avtalet med Svenska Kraftnät kunna uppfyllas.

Troliga kandidater är pyrolysolja, dimetyleter, bio-etanol, Fischer-Tropsch syntetiserat bränsle, vegetabiliska oljor, fettsyrametylestrar (FAME, RME, bio-diesel) och vätebehandlade vegetabiliska oljor (HVO). Samtliga bränslen är undersökta och deras fysikaliska egenskaper redovisade.

Tidigare arbeten där dessa bränslen studerats redovisas. Slutsatser dras från dessa arbeten, där flera aspekter avseende förbränning och emissioner studeras.

Gasturbinernas bränsleförbrukning med avseende på olika energiinnehåll i bränslet undersöks och en marknadsundersökning av tillgång och priser för hållbara bränslen utförs. Specifika krav på hållbarhet som ställs inom E.ON studeras och jämförs med kraven på hållbarhet som den Svenska Energimyndigheten ställer.

I analysen sammanställs förbrukning, lagring och investeringar med priser på de alternativa bränslena. I den ekonomiska sammanställningen studeras kostnader och eventuella ekonomiska stöd.

Slutsatsen är att det finns både tekniska samt ekonomiska möjligheter att konvertera till ett biobränsle. För att kunna göra en vinst på denna konvertering krävs att bränslekostnad tillsammans med eventuella ekonomisk stöd för konvertering gör att driften blir billigare än med dagens bränsle. Detta gäller för två bränslen. Men det är bara ett bränsle som över en femtonårsperiod klarar att täcka de investeringar som krävs, nämligen pyrolysolja. För att kunna täcka investeringarna måste gasturbinerna köras ett visst minimum av timmar per år samt att bränslepris, elcertifikat samt elpris inte förändras till det sämre och att kvaliteten på bränslet kan hållas från leverantör och vid nödvändig lagring.

Bortser man från det ekonomiska perspektivet finns det ett relativt nytt alternativt bränsle på marknaden som är så likt dagens fossila bränsle att inga investeringar i material krävs. Det kallas HVO, Hydrerade vegetabiliska oljor, men genom att det kan ersätta fordonsdiesel kommer priset att vara mycket dyrare än dagens bränsle.

Acknowledgements

Contents

Nomenclature

Acronyms

ASTM	American Society for Testing and Materials
CC	Combustion chamber
CO	Carbon monoxide
DME	DiMethyl Ether
E85	Ethanol and petrol mix with 85 % ethanol
Eo1	No.2 diesel fuel, (Eldningsolja 1)
FAEE	Fatty Acid Ethyl Ester
FAME	Fatty Acid Methyl Ester
FID	Flame Ionization Detector
FTS	Fischer Tropsch Synthesis
GTL	Gas To Liquid
HGP	Hot Gas Path
HHV	Higher Heating Value
HTC	High Temperature Corrosion
HVO	Hydrogenated(-treated) Vegetable Oil
LHV	Lower Heating Value
LPG	Liquid Petroleum Gas, (gasol)
MSGC	Mass Spectroscopy Gas Chromatography
NO_x	Oxides of nitrogen
SDF	Synthetic Diesel Fraction
SEA	Swedish Energy Agency (Energimyndigheten)
SEK	Swedish Crown
SO_x	Oxides of sulfur
SVO	Straight Vegetable Oil
UHC	Unburned hydrocarbons
VO	Vegetable oil
XTL	Anything To Liquid

Chapter 1

Introduction

1.1 Background

Fossil fuel is a finite resource, biomass is not. In the view of this and the desire to decrease the emissions of greenhouse gases, it is not hard to find the motivation for this study;

to be able to use biofuels for electricity production

This specific examination deals with the possibility of using biofuels as an alternative fuel in gas turbines. Gas turbines are reliable and quick to full load and as such suitable to be used as disturbance reserve which could make way for other green technology such as wind and wave power which are more dependent on the weather.

E.ON Värmekraft's disturbance reserve consists of seven gas turbines at four locations in the southern part of Sweden. Through an agreement with Svenska Kraftnät (Swedish national grid), they are a part of the national fast disturbance reserve. They provide about 500 MW of power which could be accessed within fifteen minutes and this comprises about 40 % of Svenska Kraftnäts total disturbance reserve [1].

The disturbance reserve could be used for example in case of loss of a major power plant. They could also be utilized for black start of larger power plant, or as peak load source on extremely cold days at winter, i.e. when he electricity system is experiencing disturbance in frequency, voltage or transmission.

The gas turbines in the disturbance reserve is today used very rarely, the most efficient one runs from 10 to 50 hours at peak load per year, the rest of the gas turbines average about 2 to 50 hours per year. This is dependant on many factors e.g. availability of nuclear power, low outdoor temperature, water level in reservoirs. This is an important observation in the following thesis.

E.ON Värmekraft's disturbance reserve is today fueled with fossil fuel, Eo1 (E10 quality) [2], similar to *light heating fuel oil* or *No.2 diesel fuel*.

Due to pressure from stakeholders, i.e. market and customers (which probably will be tomorrow's requirements, e.g. The City of Malmö has a vision to be fossil free to 2030 [3]), E.ON Värmekraft strives to introduce renewable fuels in their electricity production, within a near future. This study is a part in achieving that goal.

1.1.1 Gas turbines at E.ON Värmekraft

The gas turbines in the fast disturbance reserve distributed by E.ON Värmekraft, is located in the southern part of Sweden. They will be referred to with the generator name and location. This

means that the two turbines placed in Halmstad at Halmstadverket will be referred to as HVT G11 and HVT G12. Further there are two turbines in Barsebäck at the former nuclear power plant - Barsebäcksverket - called BVT G13 and BVT G14, two turbines in Malmö located at Öresundsverket called ÖVT G24 and ÖVT G25 and there is one turbine in Karlshamn at Karlshamnsverket called KVT G13.

All the data concerning TIT (turbine inlet temperature), peak load power, fuel consumption and storage capabilities are presented in Tab. 1.1.

Table 1.1: Peak load power, fuel consumption and storage capabilities at the gas turbine locations.

Site	GT	TIT [°C]	Peak load	Fuel cons.[a]	Storage capabilities
HVT	G11	-	78 MW	24	
	G12	1050	172 MW	40	
BVT	G13	849	42 MW	14	
	G14	849	42 MW	14	8 000 - 30 000 m^3
ÖVT	G24	837	63 MW	20	
	G25	837	63 MW	20	
KVT	G13	850	37 MW	12	

[a] tons/hour with current fuel

Using the LHV of Eo1 of 42.9 MJ/kg gives the following table of energy consumption in the different turbines, Tab. 1.2

Table 1.2: Energy consumption in the gas turbines at peak load conditions with current fuel

Location		Energy cons./h [GJ]	Energy cons./year [GJ] least hours	Energy cons./year [GJ] most hours
HVT	G11	1 000	2 000	50 000
	G12	1 800	18 000	90 000
BVT	G13	600	1 200	30 000
	G14	600	1 200	30 000
ÖVT	G24	900	1 800	45 000
	G25	900	1 800	45 000
KVT	G13	500	1 000	25 000

1.2   Problem description

There are several aspects to consider when introducing a new fuel in a gas turbine. Some questions that need to be answered from the beginning are;

1. How high output power is needed?

2. Is it necessary to keep the emissions regulations?

3. Do the gas turbines need to be as reliable as they are today, running on fossil fuel?

   The answers to question one, two and three is yes. The agreement with Svenska Kraftnät stipulates the available power and the environmental regulations regulate the emissions. The agreement also specifies conditions on reliability. They have to be operating at full load within fifteen minutes from start.

4. In what way will the alternative fuels affect the gas turbines ?

5. What will a new fuel cost in terms of capital investments, maintenance, fuel price etc?

1.2.1 Gas turbine fuel

A gas turbine converts energy stored in a fuel to mechanical energy. To simplify the process, it could be described as such: Burning some amount of fuel will make an axis turn, this could be connected to a generator which will convert the mechanical energy to electrical power. For a more detailed explanation, see Appendix A.

1 MW equals 1 MJ/s. If a fuel with a LHV of 43 MJ/kg is used in the gas turbine and it combusts 100 MJ/s (1.1) gives the required mass flow of the fuel.

$$\frac{100 \ [MJ/s]}{43 \ [MJ/kg]} \approx 2.33 \ [kg/s] \tag{1.1}$$

This means that a fuel with a lower LHV will require a higher mass flow of the fuel, e.g. 15 MJ/kg, as in (1.2)

$$\frac{100 \ [MJ/s]}{15 \ [MJ/kg]} \approx 6.67 \ [kg/s] \tag{1.2}$$

This in turn means that we have to consider the LHV of any alternative fuel and the required fuel mass flow and its implications for fuel supply systems and the required fuel storage and the price of the fuel per MWh.

1.2.2 Gas turbine emissions

Since the use of a gas turbine involves the combustion of hydrocarbons, emissions of CO_2 and H_2O is expected looking at a chemical reaction equation describing complete combustion of any hydrocarbon, including some oxygen part, as (1.3)

$$C_xH_yO_z + \underbrace{(x + \frac{y}{4} - \frac{z}{2})}_{A}(O_2 + 3.76N_2) \rightarrow$$

$$x \cdot CO_2 + \frac{y}{2} \cdot H_2O + A \cdot 3.76 \cdot N_2 \tag{1.3}$$
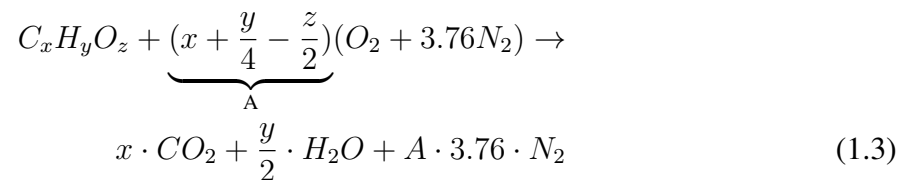
Different kind of flame types

There are mainly two different types of flames, diffusion flame and premixed flame. In a diffusion flame, the fuel and oxidizer are separated at first. They mix through diffusion and the combustion occurs in that mixing zone at stoichiometric conditions. In a premixed flame the fuel and oxidizer are mixed prior to combustion which means that the combustion can occur at the mixing ratios present which could be either rich, lean or at stoichiometry.

Combustion of liquid fuels

Liquid fuels burn in gas form. This means that the liquid first has to evaporate before the chemical reactions of combustion can occur. The finer the droplets, the faster the evaporation of the same. This in turn increases the probability to achieve complete combustion inside the combustion chamber, all else equal. Due to heat losses at various places in the combustion chamber and inadequate atomization, incomplete combustion can occur. This will lead to emissions of CO and UHC.

Emissions of NO_x

Gas turbine combustion of hydrocarbons will result in emissions of nitrogen oxides, NO_x. The reaction is exothermal, and since air contains both nitrogen and oxygen, there will be both atomic nitrogen and oxygen available, which in turn will react through several mechanisms.

Emissions of SO_x

If the fuel contains sulfur, sulfuric oxides, SO_x can be formed. From combustion it is primarily SO_2 that is formed [4].

Particulate emissions

Particulate matter emitted is mainly due to soot formation [4].

Ash

Solid species that do not participate in the combustion process, i.e. sodium, potassium, calcium, magnesium and vanadium, and other metals, form ash. The ash can either stick to the turbine parts or be emitted. If it sticks it can, depending on the temperature, either be as solid deposits or melted deposits, chemically reaction with the underlaying material.

1.2.3 Gas turbine corrosion and erosion

Another area in which the fuel properties are important are the harmful processes inside the turbine. The adiabatic flame temperature (the highest theoretical temperature a flame can produce under normal conditions) could be well above 2000°C. This kind of temperature would certainly destroy the the turbine very fast. The metals in the turbine could not withstand these kind of temperatures. So how do they still function? The combustion chambers are cooled both externally and internally with air. The hot gases are also cooled by adding more primary air than needed in the combustion and in the combustion chamber there is also space for diluting the hot gas after the reaction zone, with secondary air, called the dilution zone. But still the temperature entering the turbine usually range from 800°C up to 1200°C. At these temperatures the constituents of the gas can still pose real threat to the life span of the turbine parts. Minimal solid particles in the combustion gases can erode the material and chemical compounds can corrode the metals inside the turbine.

1.2.4 Atomization of the fuel

A good atomization of the liquid fuel is an important part of preventing incomplete combustion. Incomplete combustion will lead to both emissions of soot, UHC, CO and lowering of the efficiency. The ability to atomize a liquid fuel is highly dependant on the viscosity, surface tension of the fuel and nozzle design [5, 6]. The lower the viscosity and surface tension, the better the atomization will be inside the combustion chamber. Density of the fluid is somewhat influencing the atomization, but the influence seem quite small [5].

If the atomization is poor, some of the fuel could still be burning through the dilution zone and create hot spots damaging material in the HGP (hot gas path).

1.2.5 Storing the fuel

Some of the fuels might have physical properties that makes them problematic to store in conventional cisterns e.g. corroding or low boiling point. Some of the fuels might be suffering from ageing since it is a biological product. A low heating value means larger volumes.

1.2.6 Economy

Different fuels have different prices. The fuel price is one part of the economy, another is if the use of a fuel means that the gas turbine needs any investment in new materials or processing units. If the use of the fuel needs any investments but the fuel price is lower compared to the present fuel price, the use of the fuel could still be economically favorable.

Another consideration is the available subsidies when converting to a renewable fuel.

1.2.7 Sustainability criteria

One issue is that any biofuel considered have to meet the criterias of *Biomass Purchasing Amendment to the E.ON Responsible Procurement Policy*. This is a document issued by E.ON AG as a set of rules needed to be followed by any biomass (-fuel) purchaser within E.ON. This document dictates several conditions of the biofuel and the distributor.

1.3 Purpose

The purpose of this thesis is to examine the liquid biofuels with respect to the problem description and to evaluate them economically for use in the gas turbines.

This means that the study will try to answer question four and five in section 1.2

- In what way will the alternative fuels affect the gas turbines ?

- What will a new fuel cost in terms of capital investments, maintenance, fuel price etc?

when considering an alternative fuel, while at the same time meet the requirement on power, emissions and reliability.

1.4 Method

The methods used in this study has been:

- Literature studies

- Market research

- Interviews/Personal communication

The literature study mainly consists of scientific articles found through the Libraries at Lund University and some scientific books.

Many studies examines/reviews alternative fuels for gas turbines. In several of these, the properties and production of the specific fuel is presented, and also the effects for the gas turbine with respect to function and emissions. This has been considered an adequate way of collecting data of specific fuels.

In some occasions, internet sources are being referred to. In these cases the information gathered has either been considered relatively common and accurate or not affecting the outcome of the report.

The market research was performed by scanning the Swedish market for fuel and oil distributors. One resource was the SEA (Swedish Energy Agency, Energimyndigheten) that provides a list of companies that has received sustainability approval for certain fuel products. The use of biomass derived fuels that has attained this approval is a prerequisite for receiving the subsidy green certificate (elcertifikat) when producing electricity through combustion.

One problem with this is that the study is confined to the Swedish market and not considering companies outside Sweden. The study has been extended beyond this list in one instance when no biooil product was found in the list.

Interviews with persons of specific expertise were performed in person, over telephone and through e-mail.

1.5   Limitations

Electricity production using gas turbines fired with biofuels could be an attractive way of energy conversion from a sustainability perspective. The fuels in liquid and gaseous states derived from biomass, have the advantage over solid biomass in that they are easier to control for use in the gas turbine. The fuels in liquid state have the advantage over gas in that they are easier transported from the processing unit to the power plant [7], and the storage of a liquid fuel is easier than the storage of gaseous fuel. The scope of this study will therefore limit itself to liquid biofuels.

The currently used fuel is a liquid and if the fuel system and tanks for this fuel can be re-used by an alternative fuel, that must be seen as an advantage, both economically and environmentally.

Another limitation has been mentioned earlier, the study will begin with the companies represented in the aforementioned list provided by the SEA. These companies meet the demands of sustainability set by the SEA. If any product or company, outside this list, emerges as candidate during the study, those will be considered.

Due to the fact that the different materials and coatings in the gas turbines are several, it was decided in discussion with Fredrik Hermann, acting head of gas turbines at E.ON Värmekraft, that the study would be limited to one material and one coating with respect to corrosion, erosion and oxidation.

Chapter 2

Liquid biofuels

The word *bio* is derived from the Greek word $\beta\iota o\varsigma$, meaning *life*, and fuel is any matter that can store energy that later can be extracted to perform mechanical work. Biofuels are matter that can store energy derived from biological sources, these sources are most commonly bundled into the concept biomass.

Biomass

Biomass can be any material that once was part of a living thing: trees, branches, twigs, roots, grass, plants, sea weed, animal fat and tissue etc. It can, besides virgin products, also be waste products from various industries. These can e.g. be construction, agriculture and food production industries - any industry that dispose of large quantities of biomass [8].

Plants use the photosynthesis to store energy from the sun. They combine sunlight, carbon dioxide from the surrounding atmosphere and water from the soil to form hydrocarbons. The hydrocarbons are stored inside the plant as lignocellulosic biomass in the form of lignin, hemicellulose and cellulose. These are the building blocks of plants, see Fig. 2.1.

These *lignocellulosic* or *cellulosic* biomass materials and generally contains of

> "... 30-50 % cellulose, 20-30 % hemicellulose, and 20-30 % lignin. Some exceptions to this are cotton that contains 98 % cellulose and flax that has 80 % cellulose... " [8]

The ratio between these different building blocks vary amongst the plant species. The composition of a plants biomass building blocks determine somewhat how that plant can be used as a source for biofuel. How the biomass is used to produce biofuel is also depending on the process of conversion.
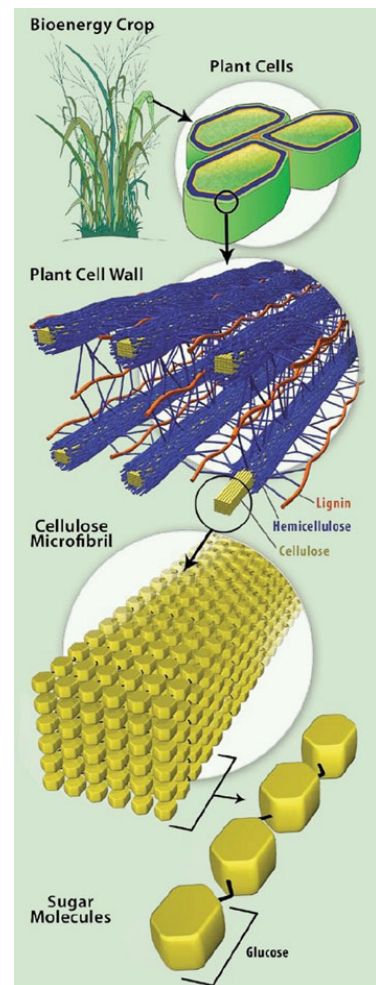
Figure 2.1: Plant cell structure [8]

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Cellulose

Cellulose is a polysaccharide consisting of several hundred to ten thousands of sugars. This is the primary feedstock for the microorganisms converting biomass to ethanol.

Hemicellulose

Hemicellulose is a material that is mostly present along cellulose in cell walls. But where cellulose form a crystalline structure which is strong and resistant to hydrolysis, hemicellulose has a random structure which leads to poor strength and it is easily hydrolysed.

Lignin

The lignin is an integral part of the secondary cell wall. The molecule is amorphic and heavily branched as opposed to cellulose which form a crystallin structure. A lignin molecule could theoretically reach all the way from the roots to the tree top. It contributes to the strength of wood.

The amount of lignin in the biomass is of no concern if the biomass is utilized in a thermal conversion process, such as the pyrolysis process to produce pyrolysis oil.

On the other hand if the biomass is to be used in a biological process through fermentation, the amount of lignin is important since the enzymatic hydrolysis of cellulose to sugars is inversely proportional to the amount of lignin present in the biomass, and a difference of a few percentages in lignin content has a large effect on the efficiency of cellulose digestion [9].

This means that herbaceous species with a higher proportion of cellulose are more well suited for the production of bio-ethanol than wood from trees which contain a higher share of lignin.

2.1 Converting biomass to fuels
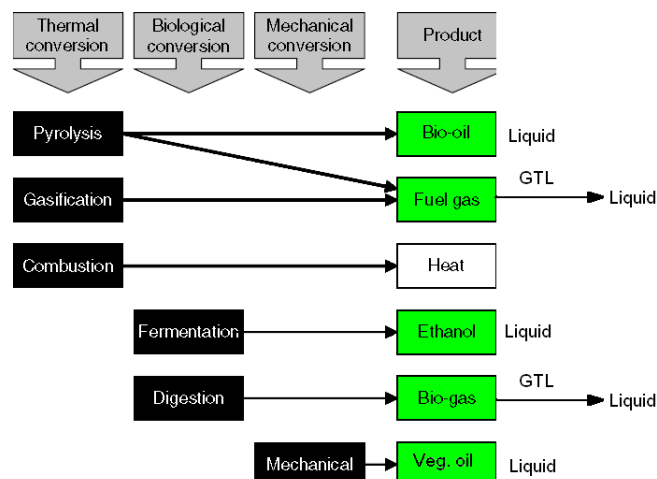
Figure 2.2: Conversion processes and products that is or could lead to liquid fuels [10]

In his paper, *Biomass For Energy* [10], Bridgewater suggests three ways of converting biomass into useful energy.

- Thermal conversion

- Biological conversion

- Mechanical conversion

Thermal conversion

The thermal conversion process could be divided into three different methods, see Fig. 2.2.

- Pyrolysis

- Gasification

- Combustion

Pyrolysis of biomass

One option of thermal conversion is pyrolysis in which the biomass is heated to about 400-600°C with a rate of 500°C/s in the absence of oxygen [11]. This causes a decomposition of the biomass. In this process the solids in biomass are separated from gaseous compounds.

The solids form charcoal and the non-condensible gaseous components, CO_2, CO, H_2 and CH_4 may either be used as gas fuel or converted into some liquid by any GTL-process.

The condensible gases are rapidly cooled to form liquid which is separated from the non-condensible gases through substantiable difference in density. Through so called fast pyrolysis up to 75 % of the weight of the biomass can be converted into a liquid that is known as biooil in english (Swedish: "pyrolysolja").

Gasification of biomass

If the pyrolysis process is performed in a higher temperature range, the product will be a gas. This process is known as gasification of biomass and the product is known as syngas or synthetic gas, consisting mainly of H_2 and CO.

When biomass is heated to approximately 800 - 900°C the organic molecules that comprise biomass rapidly decompose to syngas plus some residual char and tar.

Through custom catalyzing methods the syngas can be converted into a wide variety of other molecules, including methanol, ethanol, and DME (dimethyl ether), as well as a range of hydrocarbons and waxes that can be reformed to fuels that resemble gasoline and diesel [12]. In this thesis, the liquid fuels produced via a GTL (gas-to-liquid) process to resemble No.2 diesel fuel will be referred to as Fischer-Tropsch fuel or FT-fuel though this is just the name of one of several GTL methods.

Combustion of biomass

The combustion method has been used for thousands of years to generate heat. It is used today both for heating and electricity production, either direct heat from a stove or furnace or district heat and also for electricity production in thermal power plants.

Biological conversion

The biological conversion process could be divided into two methods

- Fermentation

- Digestion

Fermentation of biomass

The fermentation process is performed by first hydrolyzing the cellulose and hemicellulose in biomass into sugars [10].

Hydrolysis is the process where a molecule is split by adding a water molecule. Thereafter, microorganisms are added, usually some yeast which use the sugars as cellular energy and their residual product is ethanol and carbon dioxide.

There are many losses associated with the conversion of biomass to ethanol through fermentation since conventionally only cellulose is used in the conversion but successes are made converting hemicellulose which will increase efficiency. Just about half of the carbon is put to use, the rest goes to carbon dioxide. Further losses are the loss of the carbon in lignin which is not converted to ethanol, and the need to concentrate the dilute ethanol solution which is done by boiling and condensing [10].

Digestion of biomass

Digestion refers to a microbial conversion of organic materials into methane and carbon dioxide in the absence of oxygen, typically from farm digesters and landfills, which could produce gas with a methane content of up to 60 % [10].

Methanol

Ethanol is not the only alcohol that can be produced from biomass. Methanol, also known as *wood alcohol* is sometimes referred to as a biofuel and it can be made from biomass via partial oxidation reaction, but commercially, it is mostly produced by a GTL process with natural gas as main source, which is of fossil origin [13].

Mechanical conversion

Straight vegetable oil can be extracted from oil seeds by grinding ans/or pressing. These oils can be combusted as they are or converted into FAME by esterification or hydrotreated into HVO. Chemical processing is nowadays a more common procedure to extract oil from plant material since it is a more efficient method.

2.2 Summary of feasible commercial liquid biofuels and oils

Other liquid products on the market

Another biofuel is TOP (tall oil pitch). This is a rest product from the paper industry and is commonly used as a substitute for heavy fuel oil, either by the paper producer or for district

Table 2.1: Commercial liquid biofuel products and their processes

Product	Process
Biooil	Pyrolysis of biomass
FT-fuels	Any GTL-process, either utilizing syngas from the pyrolysis process or methane from the digestion process
DME	De-hydration of methanol
Ethanol	Fermentation of biomass
SVO	Mechanical or chemical extraction from plant or animal material
FAME	Transesterification of SVO
HVO	Hydrotreating of SVO

heating production. The use of TOP has dropped in recent years because of decreased availability which amongst others can be the result of increased fossil oil price and failing market for the spruce- and pine based paper industry [14].

A product derived from crude tall oil is turpentine. It has a high heating value and low viscosity which could possibly make it suitable for use in gas turbines. This is something worth further studies.

Fats and oils not derived from plants such as animal fat, and rest products e.g. frying oil are all sorted into the *Straight Vegetable Oil* category. These could be used as fuel for combustion or as base for production of biodiesel.

Another liquid fuel is methanol. But since sustainable methods of producing methanol is not yet economically viable, methanol currently is made from natural gas and hence not a biofuel [15]. Sweden has a slightly different situation than many other countries; we have an abundance of cheap wood. In Sweden projects for commercially produce methanol from wood is in its early stages. This is an area which this study does not cover and that could be well worth looking into.

2.3 Biooil from biomass

Biooil is also known as; biomass pyrolysis liquid, pyrolysis oil or bio-crude oil. Biooil is a liquid with a typical smokey odor and it is usually almost black to dark red or brown in color. [15, 16]. Biooil produced from fast pyrolysis is an emerging technology and a good option for power generation [13].

Production of biooil

Production of biooil is performed through the pyrolysis process described in section 2.1. The subject of processing could be any kind of biomass but the composition of the product is highly dependent on the properties of the feedstock, the temperature of the process and the water content of the feedstock.

Properties of biooil

The kinematic viscosity of biooils is high, compared to the fossil fuel currently used, but it varies a lot due to the above mentioned reasons. The viscosity of the pyrolytic liquids have been found as low as 11 cSt up to 115 cSt [15]. It is quite certain that the viscosity will be higher for a biooil than the standard fossil fuel used in gas turbines.

There is a standard by ASTM International which specifies the physical and chemical properties for biooil and also a set of properties as seen in Tab. 2.2. Since the characteristics are

Table 2.2: ASTM standards for pyrolysis oil [17]

Property	Value
Higher Heating Value [MJ/kg]	Minimum: 15
Solids [wt%]	Maximum: 2.5
Water [wt%]	Maximum: 30
Kinematic Viscosity 40°C [cSt]	Maximum: 125
Density 20°C [kg/dm^3]	1.1 - 1.3
Sulfur Content [wt%]	Maximum: 0.05
Ash Content [wt%]	Maximum: 0.25
Flash Point [°C]	Minimum: 45
Pour Point [°]	Maximum: -9

so varying, Wetterstrand [17] gathered data from reports and calculated an average pyrolysis oil. This strategy is also used here, Wetterstrands result have been complemented with further sources, and the result is seen in Tab. 2.3

Table 2.3: Property values of an average biooil [13, 16, 17, 18, 19, 20]

Property	Value
LHV [MJ/kg]	16.1
Density @ 15 ° C [kg/m^3]	1190
Kinematic viscosity @ 40°C [cSt(mm^2/s)]	33.31
Cloud point [°C]	-
Cold Filter Plugging Point [°C]	-
Pour point [°C]	-17.3
Flash point [°C]	50.3
Boiling point [°C]	-
Ignition temperature [°C]	580
Acidity [pH]	2.5
Max burning velocity [cm/s]	-
Flammable limits in air [%]	-
Sulfur [% wt]	0.022
Solids [% wt]	0.08
Metallic contaminants [% wt]	0.066

2.4 GTL fuels from biomass

Gas-to-liquid is a process in which gases containing light hydrocarbons are converted into liquid products by binding the short and light hydrocarbons into longer chains. The first method for achieving GTL was the FTS (Fischer Tropsch Synthesis).

Originally the FTS process was discovered by F. Fischer and K. Tropsch at the Fuel Research laboratory of the Kaiser Wilhelm Institute for Coal research in Mülheim, Germany in the 1920s [21].

The use of syngas is a vital part of GTL. Syngas itself is a mixture of carbon monoxide and hydrogen. The potential process to obtain clean liquid fuels based on FTS is shown in Fig. 2.3 [22]. The only commercially available FT-fuels at the moment are produced from fossil sources
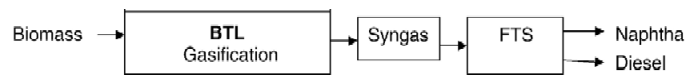
Figure 2.3: FTS process [22]

[23].

Production of GTL-fuels via FTS

Syngas can be produced through gasification of biomass. Syngas can in turn be converted into different sorts of fluid fuels through the FTS process. The main reaction, from gas-to-liquid, is performed in a flow reactor, at temperatures ranging from 180-360°C and pressures up to 45 atm. The products from this process comes in a wide range, from C_1 to C_{100} and even higher hydrocarbon chains. The reaction can also produce oxygen containing substances as alcohols, ketones and carbolic acids as well as - at higher temperatures - benzene and other cyclic hydrocarbons (aromatic compounds). Two different reactions occur at the surface of the catalyst: chain propagation which adds a monomer to the intermediate chain, and chain termination which will end the reaction and produce the final product [24]. The rate of the two reactions can be called k_1 and k_2. The molecular mass distribution of the product will be determined by these constants according to expression (2.1)

$$\alpha = \frac{k_1}{k_1 + k_2} \tag{2.1}$$

The weight fraction of a product with the carbon number n is given by the *Flory* expression (2.2)

$$p_n = n\alpha^{n-1}(1-\alpha)^2 \tag{2.2}$$

The α value can vary between 0 and 1, at low α light hydrocarbons are produced and equally heavy at high α. This restricts the amount of different fractions possible to produce in the process, only methane can be produced at 100 wt% exchange. In the range of C_5-C_{10} (gasoline fraction) can be produced at a rate of 45 wt%, and in the span of C_{11}-C_{18} (diesel fraction) 30 wt%. This can also be graphically expressed as in fig 2.4
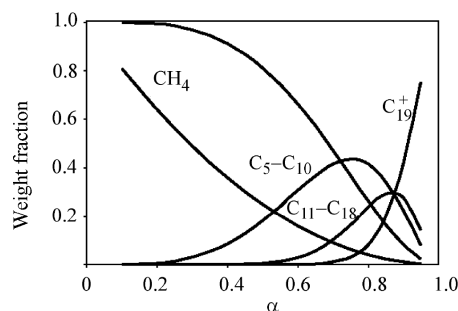
Figure 2.4: Fractional selectivity of the Fischer-Tropsch synthesis [24]

The products of the FTS vary greatly in chain length, but the controlling parameter is temperature. In low temperature the fraction of paraffin wax may be as high as 50 % and more.

13

In the high temperature synthesis, gasoline hydrocarbons is mostly produced, including 70 % olefins (petroleum industry word for alkenes, which is a hydrocarbon with at least one carbon double bond in the chain. Many countries put restrictions on the upper limit of olefin content of gasoline) [24].

The gasolines produced through FTS cannot directly be used in modern ignition engines because the contents of olefins are to high and the octane number is to low [24]. The product can be used after several additional, economically unfavourable, processes.

A more attractive way is to use the low temperature synthesis and produce diesel fractions since it possesses good performance characteristics and requires no further processing [24].

By only adding one productional step, the yield of diesel fraction is radically improved. This is done by focusing the production on paraffine waxes, which can reach 60 % selectivity. Then these waxes are mildly hydrocracked (cracking is simply put the breaking of longchained hydrocarbons into lighter ones by breaking the carbon-carbon bond. Hydrocracking is a catalytic cracking process assisted by the presence of an elevated partial pressure of hydrogen gas [25]) which forms 80 % of the diesel fraction [24].

Properties of GTL-fuels

Since GTL just is one of several processes in converting gaseous hydrocarbons into longer chains of hydrocarbons in liquid form, an exact definition of "the" GTL fuel is difficult to give. But focusing on the most effective way - FTS of syngas from gasification of biomass into SDF (synthetic diesel fraction) - there are some aspects that needs to be mentioned.

SDF has a high cetane number and excellent ecological characteristics, it represents almost pure paraffins containing very few aromatic compounds. It has a higher hydrogen content than standard diesel fuel and as a result SDF burns better and emissions of NO_x and of UHC is much lower. The reductions are 6-18 % NO_x, 18-91 % CO and 40-63 % UHC.

But without the aromatic compounds the lubricating capacity is lower and the freezing point is higher which could cause problems in cold regions. This could be dealt with to some extent using additives. It is also more sensitive to the oxygen in air which degrades the product [24].

The physical properties of SDF are presented in Tab. 2.4.

2.5   Dimethyl ether from biomass

The lightest of ethers is called DME (Dimethyl ether). The chemical formula is CH_3OCH_3. The physical properties of DME are similar to liquified petroleum gas, LPG (gasol in Swedish), in that it is a gas under atmospheric conditions, it turns into a liquid either below its boiling point, -25.1°C or at 5 bars pressure. This means that it can be transported and stored in the same system as LPG.

DME is very clean, it does not contain neither alkali metals nor sulfur or aromatic compounds [29].

Production of DME from biomass

Once again, syngas can be used which is converted into methanol. Dimethyl ether can be produced from dehydration of methanol. The methanol synthesis from syngas is expressed in (2.3) and the methanol dehydration process is expressed in (2.4) [30].

$$CO + 2H_2 \rightleftarrows CH_3OH \tag{2.3}$$

Table 2.4: Properties of average SDF from [24, 26, 27, 28]

Property	Value
LHV [MJ/kg]	44.1
Density @ 15 ° [kg/m^3]	765
Kinematic viscosity @ 40 °C [cSt (mm^2/s)]	0.96
Cloud point [°C]	-
Cold Filter Plugging Point [°C]	-
Pour point [°C]	-
Flash point [°C]	49
Boiling point [°C]	-
Ignition temperature [°C]	-
Acidity [pH]	-
Max burning velocity [cm/s]	-
Flammable limits in air [%]	-
Sulfur [wt%]	<0.004
Solids [wt%]	-
Metallic contaminants [wt%]	-

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \qquad (2.4)$$
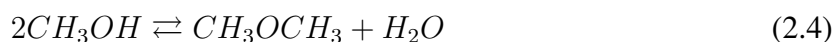
Of course methanol from biomass could be used as feedstock instead of syngas if it was available.

Properties of DME

Dimethyl ether shares many characteristics of LPG. The most prominent difference is its low heating value. Some properties of DME is presented in Tab. 2.5

Table 2.5: Physical and chemical characteristics of DME [29, 30, 31, 32]

Property	Value
LHV [MJ/kg]	28.7
Density @ 15 ° [kg/m^3]	670
Kinematic viscosity @ 40 °C [cSt (mm^2/s)]	-
Cloud point [°C]	-
Cold Filter Plugging Point [°C]	-
Pour point [°C]	-
Flash point [°C]	-
Boiling point [°C]	-25.1
Ignition temperature [°C]	-
Acidity [pH]	-
Max burning velocity [cm/s]	50
Flammable limits in air [%]	3.4-17
Sulfur [wt%]	-
Solids [wt%]	-
Metallic contaminants [wt%]	-

2.6 Ethanol from biomass

Bio-ethanol is a fuel derived from biomass; typically plants such as wheat, sugar beet, corn and sugar cane which all are high in primarily cellulose and secondary hemicellulose, and low in lignin.

Bio-ethanol is currently mostly used as a petrol additive/substitute. In the future it is possible that wood, straw and even household wastes may be economically converted to bio-ethanol. Ethanol is the most widely used liquid bio-fuel which 2009 accounted for more than 94 % of the global biofuel production [15].

Production of ethanol from biomass

Cellulose and hemicellulose are long hydrocarbon molecules in plant material, classified as polysaccharides. These polysaccharides can be converted to sugars through hydrolysis process.

Hydrolysis is a process in which the chemical bonds in molecules are ruptured by water. Through the hydrolysis process these polysaccharides are split into monosaccharides.

Fermentation of ethanol is a biological process in which sugars are converted to cellular energy and ethanol is the residual product.

The fermentation process could be performed using yeast; one enzyme in the yeast converts the disaccharide *sucrose* into the monosaccharides *glucose* and *fructose*, another enzyme converts the glucose and fructose into ethanol as in (2.5) (simplified reaction) and (2.6).

$$\underbrace{C_{12}H_{22}O_{11}}_{\text{sucrose}} \rightarrow \underbrace{C_6H_{12}O_6}_{\text{glucose}} + \underbrace{C_6H_{12}O_6}_{\text{fructose}} \qquad (2.5)$$

$$\underbrace{C_6H_{12}O_6}_{\text{glucose or fructose}} \rightarrow \underbrace{2C_2H_5OH}_{\text{ethanol}} + \underbrace{2CO_2}_{\text{carbon dioxide}} \qquad (2.6)$$
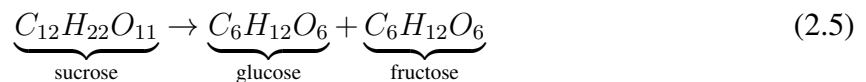
Demirbas [33] presents the following flow-chart for the production of bio ethanol, see figure 2.5. After the fermentation to ethanol, the ethanol needs to be purified and separated from the
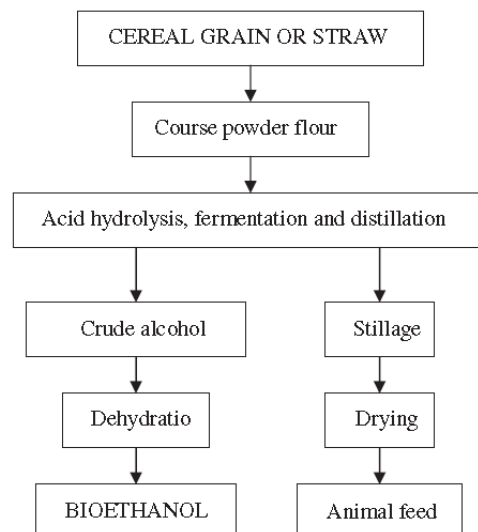
Figure 2.5: Flow chart for the production of bio-ethanol form cereal grain or straw [33]

rest of the blend, which is usually done by distillation [15].

Ethanol consists of a single type of molecule, the characteristics of pure ethanol is very defined and consistent. But since the molecule is highly water miscible, it is impossible to dehydrate ethanol completely using common distillation, the highest distillation rate of ethanol is 95 % volume. Completely dehydrated ethanol can be produced by so called azeotropic distillation with benzene, which is called *absolutioning* [34].

Properties of ethanol

Ethanol is a volatile, combustible, clear and colorless liquid in room temperature. It has a distinct and well known smell and taste. In Tab. 2.6 the properties of ethanol is presented.

Table 2.6: Properties of average ethanol [13, 18, 35, 36, 37]

Property	Value
LHV [MJ/kg]	29.2
Density @ 15 ° [kg/m^3]	799
Kinematic viscosity @ 40 °C [cSt (mm^2/s)]	1.44
Cloud point [°C]	-
Cold Filter Plugging Point [°C]	-
Pour point [°C]	-117
Flash point [°C]	13
Boiling point [°C]	-
Ignition temperature [°C]	423
Acidity [pH]	-
Max burning velocity [cm/s]	-
Flammable limits in air [%]	-
Sulfur [wt%]	0.00015
Solids [wt%]	-
Metallic contaminants [wt%]	-

2.7 Straight vegetable oils

Vegetable oils are water-insoluble and hydrophobic substances with an energy content almost like fossil diesel. They are possibly an inexhaustible source of energy but an increased use as an alternative fuel might cause shortage of vegetable oil as nourishment. Fats and oils coming from the animal kingdom are included in this category.

The shortcomings of SVO are the high viscosity, the low volatility and the high reactivity. The high reactivity comes from the unsaturated nature of the fatty acids in vegetable oil. This makes vegetable oils a perishable commodity [15].

Very early in the internal combustion engines childhood, Rudolf Diesel tried to construct an engine running on vegetable oil [38, 39]. In the 1900's world fair in Paris, Diesel demonstrated an engine running on peanut oil. Twelve years later, at a presentation at the Institution of Mechanical Engineers in Great Britain, he states:

> "The fact that oils from vegetable sources can be used may seem insignificant today, but such oils may perhaps become, in course of time, of the same importance as some natural mineral oils ... [40]

Vegetable and animal fats and oils are lipid material from plants and animals respectively [41, 42]. The exact definition of what a lipid is, is disputed, but one definition is presented by William W. Christie:

> "Lipids are fatty acids and their derivatives, and substances related biosynthetically and functionally to these components" [43]

Fats and oils are commonly separated by the state they are in at room temperature, fats being solid and oils being in liquid state. But since the components of a lipid are very heterogeneous, it is more appropriate to talk about a melting interval. There are lipid products that are modified in such a way that the interval between solid and liquid is narrow, like margarine, that is supposed to be solid at 32°C and melted at 37°C [41]. More common though, is an interval of several decades of degrees.

To the most part all commercial fast and oils comprise exclusively (90-98 %) of triacylglycerides, commonly known as, and in older literature called triglycerides [43, 44].

Lipids also comprise of mono- and diglycerides. These names are referring to whether the glycerol has one, two or three fatty acids binding to it. The triacylglyceride is a molecule that consists of a glycerol and three fatty acids connected (esterified) to it, see Fig. 2.6. A fatty
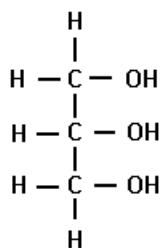
Figure 2.6: A glycerol molecule. Three carbon atoms with three hydroxyl-groups (OH) [45]

acid is a chain of hydrocarbons connected to a "head" with a carboxyl group, see Fig. 2.7, the carboxyl group is a carbon atom connected to a oxygen atom with a covalent bond and also connected to a hydroxyl group. The two most common fatty acids in plant and animal tissue is C_{16} (Palmitic acid) and C_{18} (stearic acid). These compounds can either be saturated, monoenoic or polyunsaturated fatty acids, in which there is either none, one or several double bindings in the hydrocarbon chain. When the fatty acid binds through esterification to the glycerol, one
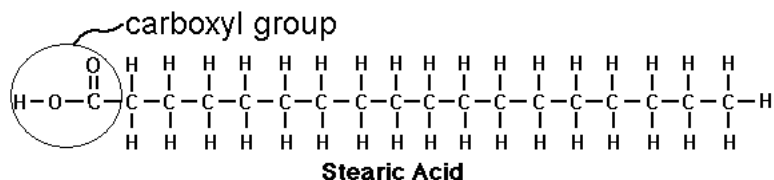
Figure 2.7: The saturated fatty acid commonly known as Stearic acid [46]

hydrogen atom from one hydroxyl group forms a water molecule together with a hydrogen atom from the other hydroxyl group, see Fig. 2.8. At time when there has been shortage in petroleum as during the Second World War and during the oil crisis in the 70's, new interest has been put into the use of vegetable oils as fuel [38, 39]. The liquid biofuels mainly used today in district heating plants in Sweden are vegetable oils (including tall oil pitch) with few exceptions [14].
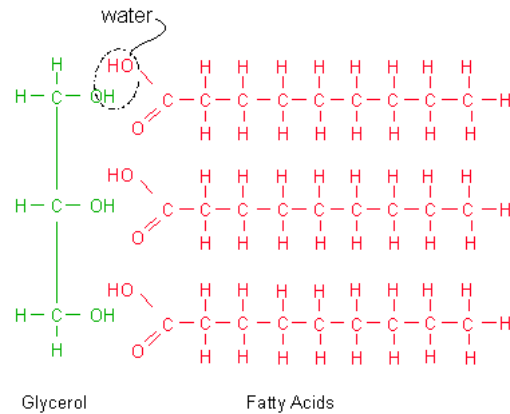
Figure 2.8: The formation of water during the esterification of triacylglycerol [47]

The SVO's follow no set standards and do not have the same given qualities as mineral oil. The terms used colloquially could give some clues about the properties of the oil as "light fuel" and "heavy fuel", acronyms are also used as "MFA" (Mixed Fatty Acids) which tells us that the product is a mixed waste product, or what origin the product has as in "PFAD" (Palm Fatty Acid Distillate). There are also examples of brand names as Bioolja V4 (waste product from the production of RME, Rapeseed Methyl Ester) [14].

Production of straight vegetable oils

Straight vegetable oils are mostly extracted from some part of the plant, usually an oily seed or kernel, through mechanical or chemical extraction [41]. Mechanical extraction of oil from plant material is done by crushing and/or pressing of the plant material. This method is mostly used for the vegetable oils used as food.

A more effective way of extraction is the chemical solvent extraction method which produces higher yields and is faster. The most used chemical solvent being petroleum-derived Hexane [41, 48].

Not all SVO's are unused and virgin. A lot of the products are reused oil mainly from industrial deep frying factories, snack food factories and fast food restaurants [41]. This makes the quality of the oil even more uncertain.

Properties of straight vegetable oils

Straight vegetable oils have comparable numbers for energy density, cetan number, heat of vaporization as well as stoichiometric air/fuel mass ratio as fossil diesel [44]. Compared to biodiesel and hydrotreated vegetable oils they are attractive thanks to lower production cost, better energy balance (less energy input to produce) and simpler production process.

Due to the high viscosity SVO's need to be treated in a viscosity decreasing manner in advance of injecting it into a gas turbine [48]. There are four ways of lowering the viscosity of SVO's [40, 44]:

1. Heating

2. Dilution/blending

3. Water emulsification

4. Transesterification

It is common knowledge that solid fat will melt in a hot frying pan. The same method can be used to lower the viscosity of vegetable oils. Put a pre-heater in the fuel system, upstream the atomizing nozzle.

A blend of liquids with different viscosities will have a viscosity somewhere in between of the components as long as they do not separate.

Water emulsification is a treatment in which water and the oil are mixed just before entering the atomizing nozzle. This leads to that droplets of water, on a macroscopic level, are covered by an oil film. Since water evaporates at 100°C and the water vapor has a much larger volume than water, the oil film covering the drop is exploded. This enhances the evaporation and in turn the combustion. [48].

Transesterification is the process where the fatty acids are separated from the glycerol by replacing glycerol with a short linear alcohol, e.g. methanol or ethanol, creating Fatty Acid (M)Ethyl Ester, more commonly known as biodiesel. This adds an extra cost to the product because the process of transesterification demands extra chemical and process heat inputs [13, 44], although this is considered the best suited method without significant long-term operational and durability issues [13, 44].

The physical and thermal properties of the most common vegetable oils and fats can be seen in Tab. 2.7.

Table 2.7: Physical and thermal properties of the four oils which constituted more than 83 % of the worlds total production of vegetable oils in 2006, and a calculated average [38, 48]

Vegetable oil	Kinematic viscosity @ 40°C	Lower heating value [MJ/kg]	Cloud point [°C]	Pour point [°C]	Flash point [°C]	Density [Kg/dm^3]	Ash [wt%]	Sulfur [wt%]
Palm	39.6	-	31	-	267	0.9180	-	-
Rapeseed	37.0	39.7[a]	-3.9	-31.7	246	0.9115	0.054	0.01
Soybean	32.6	39.6[a]	-3.9	-12.2	254	0.9138	<0.01	0.01
Sunflower	33.9	39.6[a]	7.2	-15.0	274	0.9161	<0.01	0.01
Average	35.8	39.6	7.6	-19.6	260.3	0.915	<0.025	0.01

[a] From [48]

2.7.1 Fatty acid alkyl ester

In a report from 1939 Walton writes:

> *"To get the utmost value from vegetable oils as fuel, it is academically necessary to split off the triglycerides and to run on the residual fatty acid. Practical experiments have not yet been carried out with this; the problems are likely to be much more difficult when using free fatty acids than when using the oils straight from the crushing mill. It is obvious that the glycerides have no fuel value and in addition are likely, if anything, to cause an excess of carbon in comparison with gas oil"*
> [49]

The recommendation to remove glycerol from vegetable oils and to use the fatty acids as an alternative fuel, could be considered pointing in the direction of what is commonly known as biodiesel. Already 1937 a Belgian, G. Chavanne, was granted a Belgian patent, describing the use of ethyl esters of palm oil as diesel fuel [40].

Some standards exist for biodiesel. One standard is the European norm EN14214. It defines the properties of Fatty acid methyl esters, FAME.

The expression FAME is as common as biodiesel, to describe esterified fatty acids, the M representing methyl, meaning that methanol was used in the process. Ethanol could just as well have been used which would render the expression FAEE, hardly ever used colloquially. Using the expression fatty acid alkyl ester covers the use of both ethanol and methanol [40, 50, 51].

Undiluted biodiesel is called B100. Other products on the market are B5 and B20 with 5 and 20 percent biodiesel respectively, mixed with mineral diesel.

Production of biodiesel

Biodiesel is a *Fatty Acid Alkyl Ester* which is a chemically modified triacylglycerol. The modification consists of a removal of the glycerol molecule by reacting the triacylglycerole with three mono-alcohols in which the fatty acids of the triacylglycerole are forced to be a part of an ester [40, 50]. Currently the preferred alcohol is methanol since this is the cheapest alcohol. A general ester is seen in fig: 2.9 and the process using methanol is seen in Fig. 2.10.
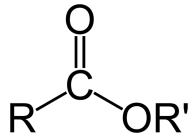
Figure 2.9: General ester, R and R' being arbitrary groups of hydrocarbons [52]
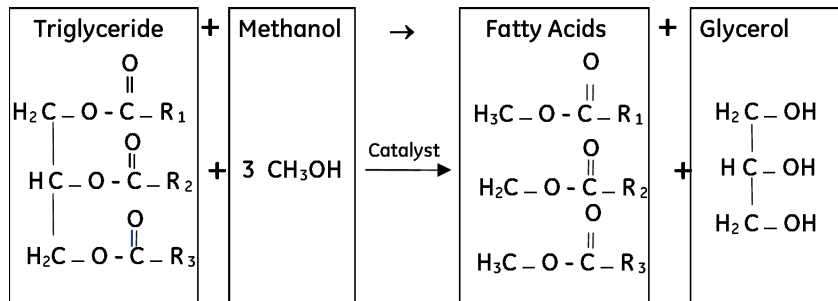
Figure 2.10: Transesterification of triacylglycerol (the same as triglyceride) into a Fatty Acid and glycerol utilizing Methanol [50]

Properties of biodiesel

The characteristics of biodiesel is very much like that of mineral diesel, although biodiesel is less in sulfur. In Tab. 2.8 is seen the properties of an average biodisel.

2.7.2 Hydrotreated vegetable oils

Hydrotreating of vegetable oils is an attractive process in that it can be integrated in the hydro processing in conventional refineries. This will lower the capital cost of the process. It also produces a fuel with characteristics more like fossil diesel than biodiesel [23].

There are today several companies producing hydrotreated triglycerides. They are marketing their processes under different names e.g. Ecofining, Bio-Synfining and H-bio, and their

Table 2.8: Properties of average biodiesel calculated from [13, 18, 53, 54]

Property	Value
LHV [MJ/kg]	38.4
Density @ 15 $^\circ$ [kg/m^3]	869
Kinematic viscosity @ 40 $^\circ$C [cSt (mm^2/s)]	4.3
Cloud point [$^\circ$C]	-9
Cold Filter Plugging Point [$^\circ$C]	-5
Pour point [$^\circ$C]	-
Flash point [$^\circ$C]	114
Boiling point [$^\circ$C]	-
Ignition temperature [$^\circ$C]	-
Acidity [pH]	-
Max burning velocity [cm/s]	-
Flammable limits in air [%]	-
Sulfur [wt%]	<0.02
Solids [wt%]	-
Metallic contaminants [wt%]	0.007

products names are also called similarly; hydrotreated vegetable oils, hydrodeoxygenated vegetable oil, hydrobiodiesel, renewable diesel and so forth [23].

Production of hydrotreated vegetable oils

One difference between producing biodiesel and HVO can be illustrated in Fig. 2.11. Instead of transesterifying the vegetable oil using methanol (or ethanol for that matter), the vegetable oil is hydrotreated with hydrogen, the hydrogen does not necessary originate from natural gas, it could e.g. come from syngas.

In this process the oxygen from the vegetable oil is removed and the triglyceride is split into intermediates such as monoglycerides, diglycerides and carboxylic acids. These intermediates are after this converted into alkanes, C_nH_{2n+2}, also known as paraffins, and the reaction is done in temperatures between 300 and 360°C at pressures between 50 and 180 bar with a zeolite catalyst [23].
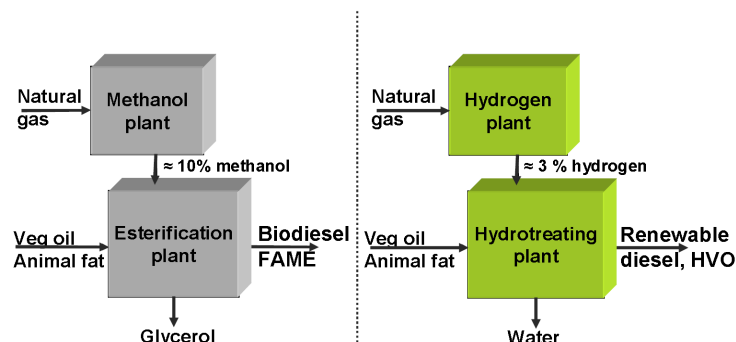
Figure 2.11: Schematic picture showing the difference between producing FAME and HVO [55]

Properties of hydrotreated vegetable oils

Table 2.9: Properties of average HVO from [23, 55, 56]

Property	Value
LHV [MJ/kg]	44
Density @ 15 ° [kg/m^3]	779
Kinematic viscosity @ 40 °C [cSt (mm^2/s)]	3.01
Cloud point [°C]	-14.1
Cold Filter Plugging Point [°C]	-
Pour point [°C]	-
Flash point [°C]	>61
Boiling point [°C]	65
Ignition temperature [°C]	-
Acidity [pH]	-
Max burning velocity [cm/s]	-
Flammable limits in air [%]	-
Sulfur [wt%]	<0.0005
Solids [wt%]	<0.001
Metallic contaminants [wt%]	<0.001

2.8   Summary of properties of liquid biofuels

In Tab. 2.10 are presented a summary of the properties from the previously tables in this chapter and of the currently used fuel in the gas turbines, Eo1 (Preem quality E10). In addition is a fuel mentioned in the coming chapter, Jet A-1.

Property	biooil	SDF	DME	ethanol	SVO	biodiesel	HVO	Eo1	Jet A-1 [57]
LHV [MJ/kg]	16.1	44.1	28.7	29.2	39	38.4	44	42.9	42.8
Density @ 15°C [kg/m^3]	1190	765	670	799	915	869	779	840	775 - 840
Kin. visc. @ 40°C [cSt (mm^2/s)]	33.31	0.96	-	1.44	35.8	4.3	3.01	3	1 - 2
Cloud point [°C]	-	-	-	-	7.6	-9	-14.1	-3	-
Cold Filter Plugging Point [°C]	-	-	-	-	-	-5	-	-15	-
Pour point [°C]	-17.3	-	-	-117	-19.6	-	-	-	-47
Flash point [°C]	50.3	49	-	13	260.3	141	>61	68	>38
Boiling point [°C]	-	-	-25.1	-	-	-	65	-	-
Ignition temperature [°C]	580	-	-	423	-	-	-	-	-
Acidity [pH]	2.5	-	-	-	-	-	-	-	-
Max burning velocity [cm/s]	-	-	50	-	-	-	-	-	-
Flammable limits in air [%]	-	-	3.4-17	-	-	-	-	-	-
Sulfur [wt%]	0.022	<0.004	-	0.00015	0.01	<0.02	<0.0005	0.410	0.3
Solids [wt%]	0.08	-	-	-	<0.025	-	<0.001	-	0.001
Metallic contaminants [wt%]	0.066	-	-	-	<0.025	0.007	<0.001	<0.001	0.001

Table 2.10: Summary of properties for liquid biofuels. If a value either is not found in the studied material or applicable for the specific material it is marked with -

Chapter 3

Earlier work

Through thorough search, only one report is found where experiments has been performed on a gas turbine running on several fuels and dealing with "all" of the aspects concerning combustion, emission and storing. It is the Orenda OGT2500 test results. Furthermore several papers are concerned with a single alternative fuel. Either neat or as a mix with the original, fossil fuel in varying ratios. These papers also tend to only deal with one or some of the aspects of running on the specific fuel, e.g: emissions, flame stability and so forth.

3.1 The Orenda OGT2500 test results
Examining Biooil, Ethanol and Biodiesel

In a paper from 2005, test result from an

> "... *on going development program aimed at determining the technical feasibility of utilizing alternative fuels such as bio-mass derived biooil, ethanol, biodiesel* ... *in a 2.5 MW GT2500 industrial gas turbine engine"* [18]

are presented. A table of the fuels listed is presented in Fig. 3.1. This development program started in 1994 at ORENDA Aerospace Corporation. The paper presents several challenges running on such fuels:

- High viscosity of biooils.

- Acidity of biooils.

- More particulate matter in alternative fuels.

- Problems with emissions.

- Deposits on the hardware in the hot gas path.

- Fuel nozzle design.

- Control system complexity.

Properties	FUEL					
	#2 Diesel Oil	Crude Oil	Ethanol	BioOil (Dynamotive)	BioOil (Ensyn)	Biodiesel
Lower heating/calorific value [MJ/kg]	42-43	35-39	25-26	15-17	16-20	32-38
Relative density @15°C/1 bar [kg/l]	0.82-0.86	0.99	0.8 - 0.82	1.2-1.3	1.2-1.3	0.87
Kinematic viscosity @40°C [cST]	3-6	2484	1.4	17-48	8-15	2-6
Flash point temperature [°C]	74	65	13	58	56-63	110 - 174
Carbon [wt%]	84-87	84.67	52.2	42.04	41-49	78
Hydrogen [wt%]	13-16	10.35	13.1	7.32	7.8	12
Nitrogen [wt%]	<0.05	0.32	-	0.06	0.08	0.03
Oxygen [wt%]	-	0.58	34.8	44.72	47	9-11
Water [wt%]	<200 [ppm]	<0.3	<6.2	15	18-22	<0.05
Sulphur [wt%]	<0.4	<4.5	-	<0.02	-	<0.03
Ash [wt%]	<0.01	<0.1	-	<0.05	<0.06	<0.02
Vanadium [ppm]	<0.01	187	-	<3	<2	-
Sodium+Potassium [ppm]	<0.2	<100	-	5	5	5
Calcium [ppm]	<2	<10	-	<13	<15	-
Nickel [ppm]	-	78.6	-	-	-	-

Figure 3.1: Different fuels tested at the Orenda test facility and their respective properties as presented in the report [18]

Viscosity

The problem of high viscosity was dealt with through several steps. The tank of the alternative fuels was heated, and upstream the fuel pump a preheater was used that could raise the temperature to 95 °C. The warmer the fuel, the lower the viscosity, but the temperature had to be kept below a critical point where the fuel otherwise would go through a deteriorating chemical change.

For even better atomization, the fuel nozzle was installed with a separate channel for externally compressed air. This air was bled from the turbine compressor and then compressed to 250 kPa in an air booster driven by an electrical motor.

The fuel nozzle was also installed with a third channel for diesel pilot fuel and the control system was designed to be able to smoothly switch from the pilot fuel, used for start-up purpose, to the alternative fuel.

Acidity

Since some of the alternative fuels tend to be acidic, the materials used needs to be chosen to withstand the corrosion caused from acidity. This was particularly important and challenging in the case of the pumps pressurizing the fuel prior to injection.

Particulate matter

Particulate matter that was higher in the alternative fuels needed to be either filtered out or ground/homogenized to a finer size, prior to use to prevent plugging of filters and for adequate atomization.

Emissions

Since bio fuels tend to be low in sulphur, SO_x emissions was going to be low but NO_x and CO still needed to be controlled and kept below acceptable limits.

Ash

Some of the alternative fuels tend to deposit ash in the HGP. This increases the risk of hot corrosion which will reduce efficiency and ultimately lead to turbine failure. One way of solving this problem is to install an on-line system for cleaning the turbine blades and vanes.

Fuel system

The control system was redesigned to cope with three channels in the nozzle and to be able to switch smoothly from one fuel to another.

Test results

Their test results are shown in Fig. 3.2. From these results can be seen that there is a slight increase in outlet temperature for crude oil and even more so for biodiesel. Some of these differences can perhaps be derived from the fact that they also differ a bit in inlet temperature, probably more important is that the three fuels with the lowest LHV need a much higher fuel flow to achieve a power output in the same vicinity as diesel oil.

Moreover of importance is that the SO_x emissions is within the same reach as, and even smaller than the SO_x emissions from the standard fuel. This is due to the low sulfur in biofuels.

The only NO_x emissions exceeding the ones from the standard fuel is the crude oil blend. The CO's are higher for all the alternative fuels and this can probably be derived from the higher viscosity and hence poorer atomization and combustion efficiency.

Parameters	FUEL					
	#2 Diesel Oil	BioOil (Dynamotive)	BioOil (Ensyn)	Ethanol	Crude Oil Blend	Bio - Diesel
Gas turbine inlet air temperature [degC]	-2.8	2.1	-10	2	5.6	11
Turbocompressor rotor speed [RPM]	13850	13850	14050	13850	13850	13850
Gas turbine exhaust gas temperature [degC]	403	417	420	415	444	467
Fuel flow [liter/h]	1071	1883	1800	1800	1055	1200
Generator electrical power [KW]	2510	2510	2650	2510	2510	2550
SO2 normalized emission [ppm]	7	2	1	2	421	1.4
NOx normalized emission [ppm]	321	57.5	60	101	326	321
CO normalized emission [ppm]	1	48.7	55	14.8	4.1	4.1

Figure 3.2: The results from the Orenda test as presented in the report [18]

3.2 GTL-fuels
Examining FT-fuels as alternative aviation fuel

The studies found on GTL-fuels in gas turbines concerns FT-fuels substituting JP-8, which is a military aviation fuel, or Jet A-1, which is a commercial flight fuel/diesel. The probable reason for this is that GTL-fuels might be too expensive to consider utilizing in any other application than aviation use.

Another point is that there is a fine line between fuels suitable for aviation and not, and that FT-fuels are within that range. An index used to define the suitability is the Wobbe index. This index takes into account the mass density and the energy density of the fuel as in Fig. 3.3. There is a minimum limit in LHV of aviation fuels of 42.8 MJ/kg and an allowed intervall in density of 775-840 kg/m^3. The two red lines illustrates a constant Wobbe index of ± 0.05 of jet fuel using (3.1)

$$I_{wobbe} = \frac{LHV}{\sqrt{SG}} \tag{3.1}$$

where SG is specific gravity. In Fig. 3.3 FTS and HVO are called "alternative-SPK", as in synthetic paraffinic kerosenes. They are marked with triangles, most of them above the energy density limit but some of them are too light due to the fact that the processes used mainly produce n- and iso-paraffins, meaning they don't have the spread of hydrocarbons seen in conventional fuels [58]. The n- and iso-prefix differentiate between the types of structure the paraffine
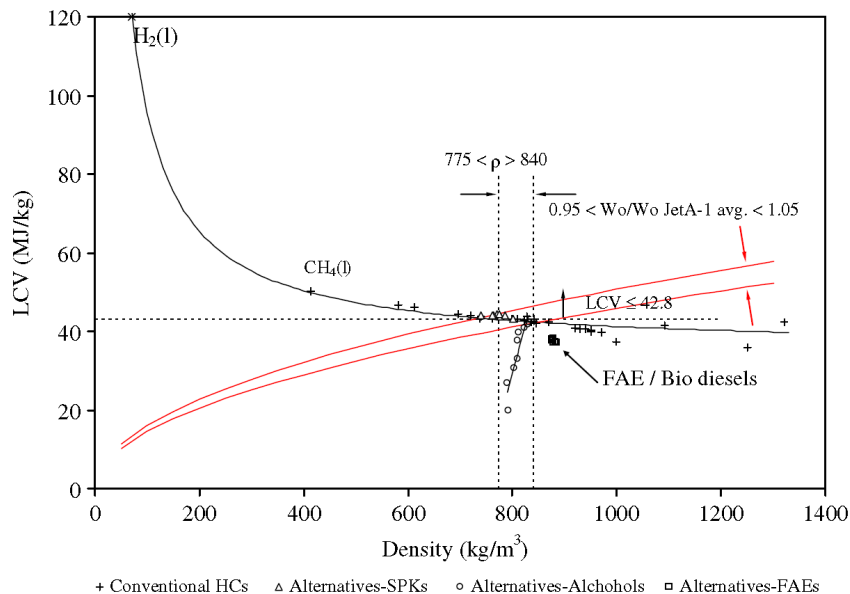
Figure 3.3: Illustrating the narrow span within which an aviation fuel is suitable [58]

is demonstrating, n-paraffins being the completely "linear" structure without any branching and iso-paraffins are also linear but with one branch, e.g. n-pentane and iso-pentane also known as pentane and 2-methylbutane, see Fig. 3.4.

The reports [28, 27, 60] study the emission characteristics, the particulate matter emissions and the ignition performance of FT-fuels.

Corporan et al. finds 90 % reduction in particulate matter with respect to mass and number and over 80 % reduction in engine smoke number, relative to the use of JP-8 and they saw a direct correlation to the concentration of FT-fuel when mixing the two.

C5H10
2-methylbutane

C5H10 Pentane
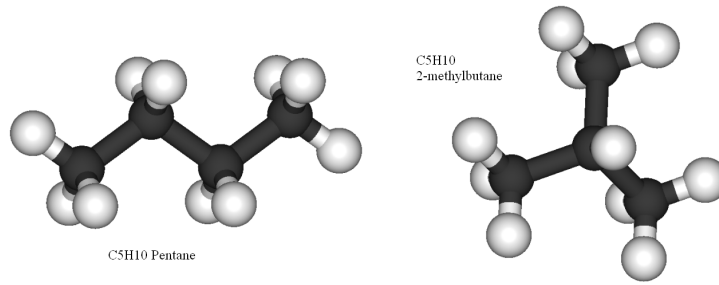
Figure 3.4: Illustrating the difference between n- and iso-paraffins. Pentane to the left and 2-methylbutane [59]

Further they experienced a decrease in sulfur oxides due to the low sulfur rate of FT-fuels. They observed no negative effects on engine performance when using the synthetic fuel. They correlate the decrease in particulate matter to the reduced aromatic content of the synthetic jet fuel [28].

Timko et al. experience the same findings as Corporan et al. adding that the emission index with respect to mass of both CO and UHC is reduced for FT-fuel relative JP-8 at idle and that NO_x is reduced between 6 % and 11 % relative JP-8, at power levels $\geq$30 % [27].

Rye and Wilson examines the influence of fuel composition on ignition performance in a gas turbine when using GTL-fuel. They use a FID (Flame Ionization Detector), to get a gas chromatogram of the GTL-fuel, a Jet A-1 fuel, a diesel fuel and standard n-alkanes, Fig. 3.6. From this picture it is clear that the fuel composition of a GTL-fuel is quite different from the composition of a the other fuels examined. It consists of a mixture of light narrow hydrocarbons.
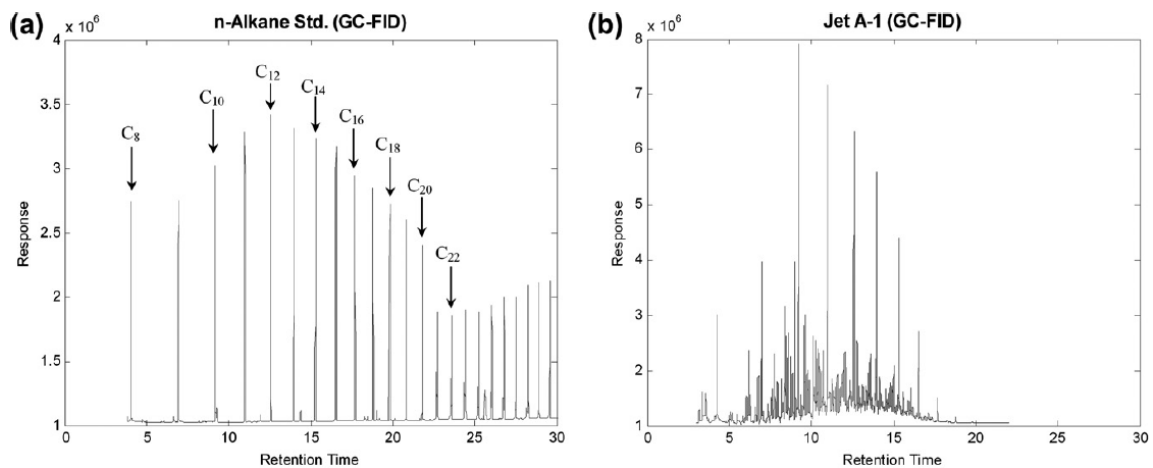
Figure 3.5: Gas chromatograms of different test fuels [60]

Despite the fact that Jet A-1 contains less quantity of lighter hydrocarbons than the GTL-fuel, the ignition probability was comparable. They conclude that it indicates that the atomization in the primary zone in the combustor was sufficiently rich. They also finds that a leaner combustion technology favor the lighter synthetic [60].
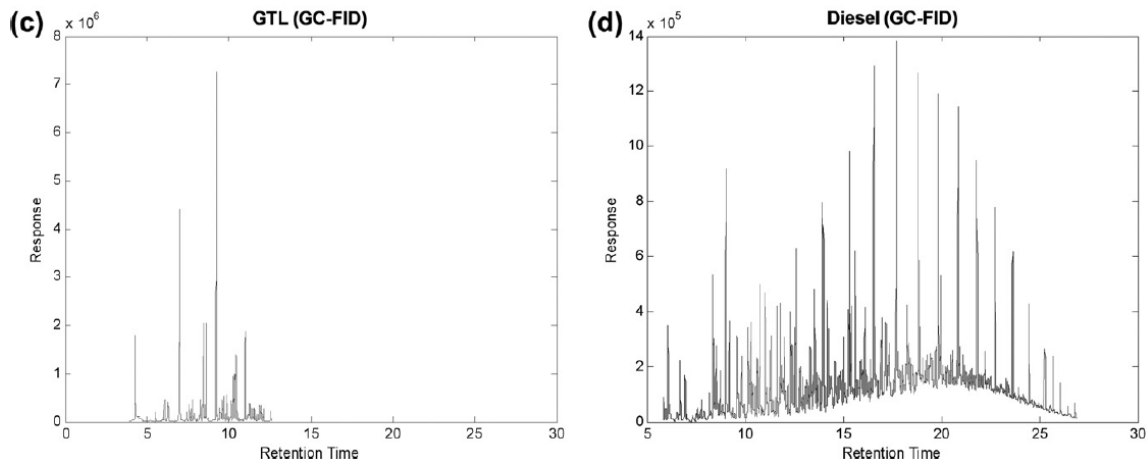
Figure 3.6: Gas chromatograms of different test fuels [60]

3.3 Dimethyl ether

A good alternative to bridge the gap between fossil fuels and hydrogen?

In a paper from 2006, Semelsberger et al. studies the possibilities of DME as an alternative fuel for vehicles [30]. They mean that since many consider hydrogen as the end-game fuel, due to the depletion of fossil fuel, a transition from petroleum to hydrogen via DME, might be a more cost-effective way than a direct switch to hydrogen. They mention some advantages of DME as a fuel and energy carrier:

- Dimethyl ether as a turbine fuel demonstrates an increase in efficiency, and decreased NO_x and CO compared to methane and liquid naptha

- Dimethyl ether is non-toxic, non-teratogenic (causing birth deficiencies), non-mutagenic, and non-carcinogenic (causing cancer)

Lee et al. [31] examines the combustion performance of DME in an atmospheric gas turbine combustor test facility of 60 kW output. They test combustion oscillations, NO_x and CO emissions with different lean equivalence ratios. In their tests they also use a bluff body in the nozzle, as seen in Fig. 3.7. With this configuration they also test NO_x, CO and exit gas temperature.

(a) Recessed C.B.   (b) Plane C.B.   (c) Protruded C.B.
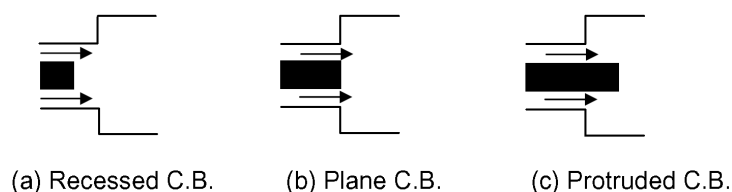
Figure 3.7: Different configurations of the center body in the nozzle

They do all tests on DME simultaneous with methane and find that DME have very good results on NO_x, with the lean combustion it never goes beyond 30 ppm. CO emissions for DME is far better than methane due to the high burning velocity of DME, and keeps well below 15 ppm.

They conclude that DME is a very good fuel for power generation because of the low NO_x and CO emissions and that DME show a very low combustion instability. One position of the

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bluff body, the recessed position a), showed increased emissions of NO_x and elevated exit gas temperature due to combustion of the gases before lean mix is achieved.

But all in all, the exit temperature for DME was low and this reduces the potential of thermal failure on the turbine blades and nozzles as long as a recessed center body in the nozzle is avoided [31].

In another paper from Lee et al. [32] they study the combustion of DME in a GE7EA gas turbine. Once again they compare the combustion results of DME with methane (which is a major component of natural gas). They find that the temperatures in the combustion chamber are lower using DME compared to methane except close to the nozzle due to the fact that DME have a different shape on the flame cone and thus burns closer to the nozzle, see Fig. 3.8.

(a) DME flame   (b) Methane flame
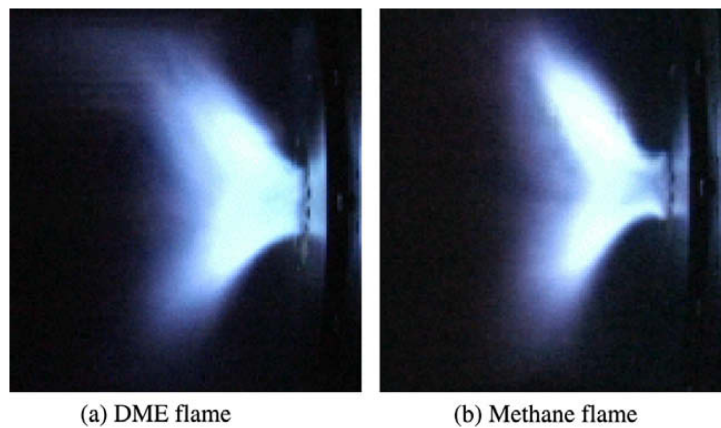
Figure 3.8: Different shape of flame cone of DME and methane [32]

They also find that the pressure oscillations for DME are higher than for methane but that it still is 2 psi lower than the regulated value of the combustion vibrations for an industrial gas turbine [32].

Further in the study they find that CO emissions are higher for DME than methane but decreases from 18 ppm at low load to 3.5 ppm at high load. On the other hand, NO_x emissions for DME keeps a bit lower than for methane, see Fig. 3.9. The conclusion is that DME is a
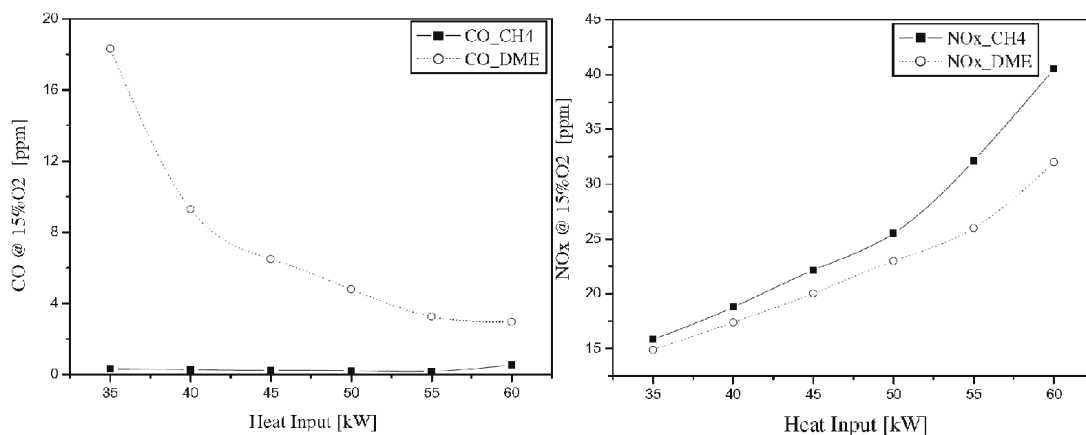
Figure 3.9: Emissions of NO_x and CO for DME and methane for different loads [32]

clean, sulfur free, good fuel for gas turbines and that the emissions can be as good as methane or even better, but the fuel nozzles need to be modified [13].

3.4 Ethanol
Gas Turbines in Alternative Fuel Applications: Bio-Ethanol Field Test

In this paper from 2009 [61], ethanol is tested as fuel in a naphtha-fueled, 6B frame, General Electric GT in Goa, India. It was important to find a naphtha-fueled GT, since this allowed a successive increasing ethanol strength in the ethanol-naphtha blend due to ethanol is hydrophilic and hygroscopic thus making it miscible with gasoline/naphtha but immiscible with gasoil (No. 2 diesel fuel). Also due to the hydrophilic character and the miscibility with water, it can carry ionic species like sodium, potassium and calcium as well as chlorides and sulfates. They find that

> "...ethanol, like all short alcohols, displays a poor lubricity and is slightly corrosive. Its corrosiveness is increased by the presence of tracks of water and dissolved salts that are potentially aggressive towards gas turbine hot gas path materials." [61]

They point out that ethanol exhibits a relatively low but not negligible electrical conductivity as compared to pure water, and that the electrical conductivity increases with the water content and especially in case of dissolved ionic species. But they also mention that such conductivity levels does not generate real electrostatic charging risks when ethanol flows inside pipes contrary to naphtha which has a typical conductivity of 0.001 nS/cm. They conclude that liquid ethanol

> "exhibits excellent general combustibility, however its physical properties essentially differ from those of petroleum fuel and its handling and combustion in gas turbines must be approached with deliberate precautions." [61]

Since ethanol has a lower LHV than the standard fuel, this will lead to higher mass flows of ethanol to keep the same energy output. On the other hand, the use of ethanol leads to NO_x that is about half of the NO_x from the use of naphtha.

Carbon monoxide and unburned hydrocarbons are both very low when ethanol is burned, at all loads. The increase in fuel flow leads to another issue, the pressure over the fuel nozzle is higher which in turn leads to an increase of pressure in the HP section. But the HP section pressure was never above the operational range of flow divider and pumps.

Emissions of CO_2 increased as the fuel consumption was higher, this can be seen in Fig. 3.10. Gupta et al. [13] conclude that it would probably be required to replace any white metal or aluminum in the system as well as some elastomers. They also states that the emissions of burning ethanol are 48 % of that of diesel; the lowest of any fuel. They further states that the change to ethanol probably would extend the gas turbines life expectancy with 100 %. The disadvantages being the low vapor pressure that leads to rapid evaporation and miscibility with water, creating handling problem [13].

3.5 Straight vegetable oils
Only tested in micro gas turbines

Campbell et al. [62] browse the alternative fuels available for gas turbines. Among others they discuss vegetable oils. They mention several features of vegetable oil that would require special attention and consideration, both transporting, storing, pumping and injecting the fuel. Some of these features are:
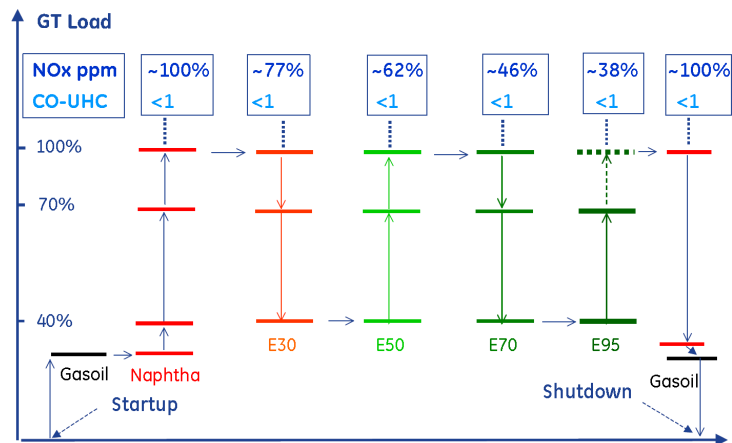
Figure 3.10: Field test result sketch [61]

- High viscosity and non-Newtonian behavior

- High hydrogen content

- Higher flash point data compared to diesel fuel

- Poor resistance to oxidation due to unsaturated and tend to harden by oxidative polymerization during storage

- Difficult cold flow properties, some being solid at ambient temperature

The exact properties of a specific SVO can only be assessed through testing due to the fact that it depends on the feedstock. To come to terms with these issues a consistent procurement strategy is required [62]. They point out that SVO's have been used in smaller gas turbines but not yet in any full scale facility and as a fuel for gas turbines it has not experienced any larger demand due to the variability described above [62].

Chiaramonti et al. have done several tests utilizing SVO's in micro gas turbines. In one of the papers [63], they study the exhaust emissions from a micro gas turbine fed with SVO. They concur that there are several issues that need to be addressed in order to adapt a MGT to use SVO as alternative fuel; it requires significant re-design and changes of standard technologies before being used [63].

Chiaramonti et al. concludes that

> "Compared to diesel . . . vegetable oil . . . showed higher levels of CO in the exhaust under the same fuel feeding conditions . . . the use of vegetable oil as fuel requires preheating at temperature of at least 120°C. Lower fuel temperatures do not allow smooth operation of the MGT" [63]

Still they point out that one of the most important findings in the study was that SVO preheated to 120°C gave CO emissions similar to that of diesel at standard conditions. The high preheat was mainly to avoid flameout due to poor atomization, in turn dependent on the high viscosity. Even at that high temperature, at idle, the MGT could not always run on SVO. They mean that to switch fuels appropriately, it should be done at high load since the combustion chamber temperature should be high enough [63].

Gupta et al. states that

"Vegetable oils and their derivatives lead to substantial reductions in emissions of sulfur oxides, carbon monoxide (CO), poly aromatic hydrocarbons (PAH), smoke and particulate matter (PM)" [13]

They also point out some important parameters to diffusion controlled gas turbine combustors, namely fuel volatility and spray cone angle, a decrease in these parameters will drastically reduce the combustion efficiency [13].

3.6 Biodiesel

Impact of Biodiesel on fuel preparation and emissions for a liquid fired gas turbine engine, 2007

Biodiesel can be used in any gas turbine without modification [13]. In this paper [64] from 2007 the authors study the differences between running a gas turbine on B99 (biodiesel 99 % and No. 2 diesel fuel 1 %) and pure No. 2 diesel fuel. Through MSGC they find that the biodiesel used - soy bean methyl ester - has a much narrower span of species, it consists of, close to 94 % of two unsaturated fatty acids as seen in Tab. 3.1. The result from the MSGC analysis can

Table 3.1: Mass composition form MSGC analysis [64]

Fatty acid composition	Species	Mass %
Linoleic (18 2)	Octadecadienoic Acid, Methyl Ester	49.49
Oleic (18 1)	Octadecenoic Acid, Methyl Ester	44.43
Palmitic (16:0)	Hexadecanoic Acid, Methyl Ester	4.35
Stearic (18 0)	Octadecanoic Acid, Methyl Ester	1.74
Other	-	<0.5
-	Total	100

be seen in Fig. 3.11. Here it is obvious how simple the composition of biodiesel is compared to fossil diesel and that it is a higher distillate than fossil diesel [64]. An MSGC of ethanol would comprise of a single peak since it is a single species. In the report the distillation curves of ethanol, biodiesel and No. 2 diesel fuel are presented as seen in Fig. 3.12. Since ethanol comprise of a single species, the whole fraction will boil at the same temperature, 78.4°C. But since both biodiesel and No. 2 diesel fuel comprise of more than one molecule, they will show a different kind of curve which is seen in Fig. 3.12. What they mention as an interesting point is the high boiling temperature of BF99 which they fear will cause problems during startup.

"The lower (high volatility) distillates of No. 2 diesel fuel help ensure the ignition of the higher (lower volatility) distillates toward the right side" [64]

They further comment this issue in the conclusion:

"It was shown in the distillation results that B99 has few volatile components. This was identified as a potential issue, especially during cold startup, although the results obtained on the engine indicated successful cold start from relatively warm conditions (15°C). Cold starting under more extreme conditions will likely prove to be a significant challenge"
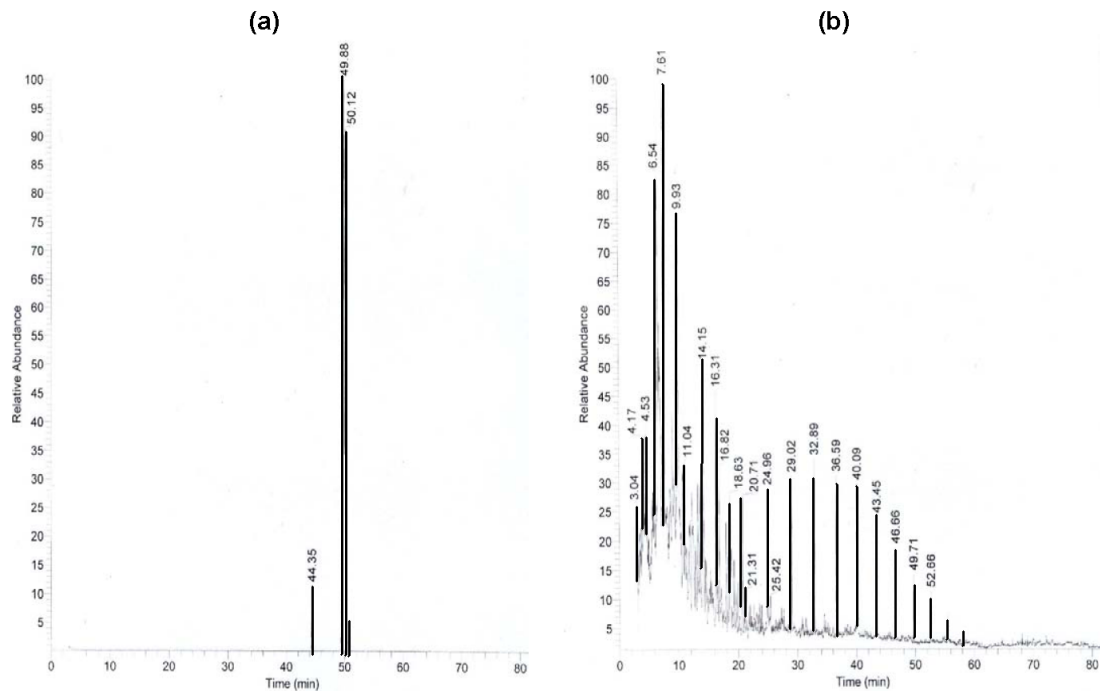
Figure 3.11: Comparison of GC spectrums for biodiesel (a) and No. 2 diesel fuel (b) (some of the lines are enhanced for this paper to increase the visibility) [64]

The authors also find, through laser diffraction experiments, that the Sauter Mean Diameter (SMD), the diameter of the droplets in the atomization spray, are larger for biodiesel than the No. 2 diesel fuel, especially at lower loads. This will inevitability lead to longer evaporation times. They also test the spray cone angle and find that it is largest for B99, and that this can lead to droplets oxidizing on the injector wall. They test the evaporation time for biodiesel and No. 2 diesel fuel both with the same initial drop size and actual drop size and find that both the lack of volatiles and the larger drop size will contribute to an increased evaporation time for the biodiesel spray. The results can be seen in Fig. **??**. It takes twice the time to prepare a biodiesel droplet for combustion than the No. 2 diesel fuel droplet [64]. Due to a 15 % difference in heating value between B99 and No. 2 diesel fuel, it is expected that the fuel flow rate was to be higher for B99, and so it was as seen in Fig. 3.14. This causes a 1 % loss in efficiency due to increase in pumping power. The authors find that especially the NO_x emissions was higher using B99 than No. 2 diesel fuel, and that this probably is linked to the larger droplet sizes and longer evaporation times. This can be seen in Fig. 3.15. Their suggestion is to modify the atomizer to improve droplet size which will reduce emissions and to employ a designer fuel, some biodiesel/ethanol mix, that will help improve ignition performance [64].

3.7 Hydrotreated vegetable oils

There are some shortcomings in the terminology concerning Hydrotreated/Hydroprocessed or Hydrogenated Vegetable Oils. When these products are considered as an alternative for jet propellants, they are called HRJ or Hydrotreated Renewable Jet. Otherwise they are known as Hydrotreated Vegetable Oils.

The studies found that are examining HVO as GT fuel, deal either with the combustion characteristics as Hui et al. [65], or in a review of alternative fuels for aviation gas turbines

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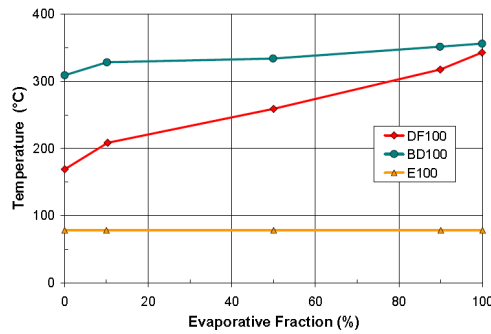
Figure 3.12: Distillation curve for biodiesel (BD100), ethanol (E100) and low sulfur No. 2 diesel fuel [64]
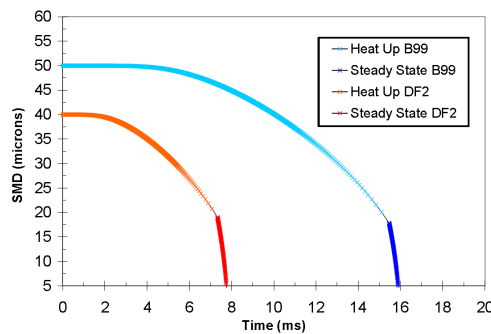
Figure 3.13: Droplet evaporation history for biodiesel and No. 2 diesel fuel for actual droplet size [64]

as Blakey et al [58]. In the first study the authors study the cetane number, the auto ignition response, the laminar flame speed and the extinction stretch rate [65]. The review by Blakey et al. first call the hydroprocessing of vegetable oils a

> *". . . technology at a lower readiness level, recently used to produce fuel for a series of test flights"* [58]

later in the text they refer to three airline companies that have performed tests flights with 50/50 blend of Jet A-1 and HRJ of either Jatropha, Camelina or algae feedstock. They state that

> *"The success of the recent test campaigns has not only highlighted gas turbine biomass product compatibility but also demonstrates the technological readiness . . . and feedstock independence of the hydro treatment process"* [58]

According to Blakey et al. several works that have studied XTL (anything-to-liquid) or HRJ has shown that the use of these fuels lead to a decrease in particle emissions and that the main reason for this is probably that these fuels have much less aromatic content [58].

Besides this, NO_x is generally reduced by up to 12 % when running on HVO, the NO_x emission being closely connected to the adiabatic flame temperature of the combustion. It has been shown that CO could be increased when running on HVO but it should be noted that CO emissions are significantly dependent on the aromatic content of the fuel [58]. The CO emissions are also very sensitive to the functions of the fuel injectors and are most significant on low load. The UHC emissions are analogous to the CO emisssion, highest emissions on low load and the emissions are closely connected to the aromatic content [58].
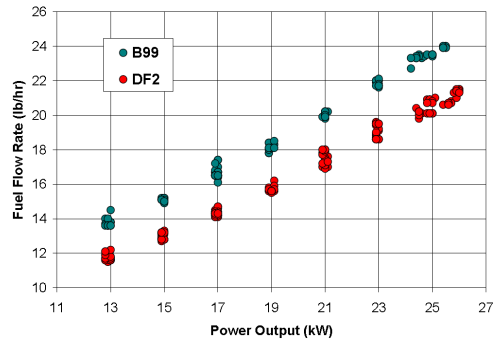
Figure 3.14: Fuel flow rate vs. electrical output [64]
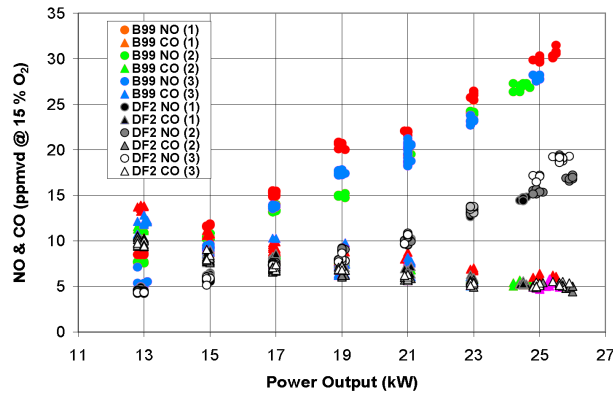
Figure 3.15: Emissions vs. load output

Chapter 4

Issues concerning combustion and emissions

Combustion is a gaseous chemical reaction. This means that if the fuel under current conditions is in solid or liquid phase, it needs to be gasified or evaporated. Consider a candle which unlit is in solid state. To make it burn, the wax or stearin first needs to be melted. The melted stearin is then evaporated from the wick and the chemical reactions comprising combustion commences. This type of flame is called diffusion flame where there is a defined boundary between fuel and oxidizer.

In a diffusion flame the fuel will always burn at stoichiometric conditions and the temperature of the flame will be the adiabatic flame temperature, which is the highest theoretically possible temperature achievable in a flame under normal conditions [66].

At the other end of the spectra there is a flame type called premixed flame. A schematic picture showing the difference between diffusion and premixed flame is shown in Fig. 4.1. As
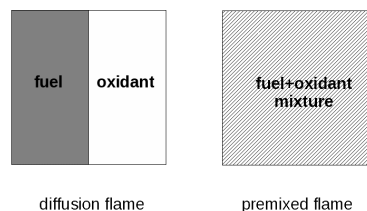
Figure 4.1: Schematic of diffusion flame and premixed flame [67]

the name states, the oxidizer and fuel in a premixed flame is mixed before combustion. With this type of flame it is possible to control the burning conditions. The flame will burn at the fuel-air ratio present in the mix. This means that it is possible to let the flame burn at slightly rich or lean conditions, which in turn will lower the flame temperature.

In a diffusion flame the reactions are more dependent on the fluid dynamics and diffusion processes while the reactions in a premixed flame are more influenced by chemical kinetics. A premixed flame can either be too lean or too rich to burn, whereas a diffusion flame is less dependent on the available air since the combustion in the reaction zone always is stoichiometric in a diffusion flame.

Therefore a diffusion flame is often more stable than a premixed flame, on the other hand it is more easy to control the emissions from a premixed flame. This has led to that diffusion flames are more often used in aircraft jet engines where safety is more important than emissions and

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that experiments with premixed flames in gas turbines more have been performed in land-based machinery.

In the primary combustion zone, the adiabatic flame temperature can be well over 1600°C, the temperature is fuel dependent, different fuels having different flame temperature. In Table 4.1, some examples of different fuels and their respective adiabatic flame temperatures, is presented.

Table 4.1: Adiabatic flame temperatures of some fuels using air as oxidizer and using atmospheric conditions (1 bar, 20°C) [4]

Fuel	T_{ad}[°C]
Methane (CH_4)	1953
Methanol (CH_3OH)	1877
Ethane (C_2H_6)	1987
Ethanol (C_2H_5OH)	1922
Acetylene (C_2H_2)	2268

4.1 Gas turbine combustion

Burning a candle there is seldom any limiting factors, but in a gas turbine there are. The flame is confined within metal surfaces in a combustion chamber. The combustion chambers far end merges into the turbine inlet. At that point, the hot gases should be at a sufficient temperature not to harm the vanes and blades of the turbine.

The Udimet 520, a common metal in GT's, has a melting range of 1260-1405°C [68] but is developed for the temperature interval 760–927°C. Since the adiabatic flame temperature of any fuel is well beyond that limit, protective measures has to be taken. Nowadays there are several ways that turbine manufacturers deal with higher gas temperatures, but the intended GT's use diluting air. This is done by adding dilute air through holes in the combustor chamber walls in the so called dilution zone, see Fig. 4.2. The extra air lower the temperature of the combustion gases. The success of lowering the temperature by dilution depends to a great extent on whether
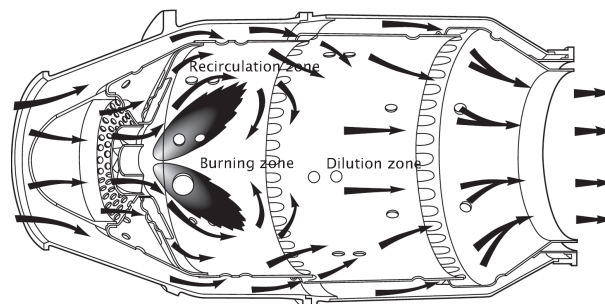
Figure 4.2: A typical diffusion combustor can with straight-through flow [69]

or not the fuel is completely combusted. If some fuel is still burning through the dilution zone, the temperature of the gases will be too high entering the turbine.

The main reason to why fuel would still be burning through the dilution zone, is that the fuel drops injected from the fuel nozzle, are too large. The evaporation takes time to achieve and to quote Arthur H. Lefebvre:

> *"The evaporation of drops in a spray involves simultaneous heat and mass transfer process in which the heat for evaporation is transferred to the drop surface by conduction and convection from the surrounding hot gas, and vapor is transferred by convection and diffusion back into the gas stream"* [5]

Evaporation is achieved when some molecules are given high enough energy to leave the liquid surface and the fastest way to evaporate a given amount of liquid, given everything else is constant (pressure, temperature and transport properties of the gas, temperature and volatility of the drops in the spray, and the velocity of the drops relative to the surrounding gas) is to first split the liquid in as small parts as possible.

> *"The overall rate of evaporation depends on . . . the diameter of the drops in the spray . . . "*[5]

By doing this, the surface between the liquid and the ambient air is increased and possible rate of heat transfer is increased. The finer the particles, the faster the evaporation rate.

One issue is that the velocity of the air flow in a gas turbine often is very high, often higher than the flame speed. To ensure complete combustion the flame is recirculated back into the fuel flow and secondary air is added. The recirculation can be done by swirling the fuel flow, giving it both an axial velocity component as well as a tangential velocity component. The fuel flow will then form in the shape of a cone increasing in diameter as it leaves the fuel nozzle. This creates a lower pressure on the inside of the cone, and by adding more air through holes with radial vanes enhancing radial motion, the flame and more air is circulated back into the primary zone [70].

The overall air/fuel ratio is between 60:1 up to 120:1 for a simple cycle gas turbine, averaging in 100:1. The stoichiometric air/fuel ratio is on the other hand about 15:1. This means that the air needs to be added with caution to avoid local cooling of the flame that might inhibit complete combustion or at least lower the reaction rate in that area [70]. Some 15-20 % of the air is added in the primary zone to enable the high temperatures needed for high reaction rates. After this ca 30 % is added in the secondary zone to help with the complete combustion and the rest is added in the dilution zone [70].

4.2   Atomization of liquid sprays

In gas turbines combusting liquid fuel, the fuel needs to be injected as a fine spray. This could be achieved through a number of ways. The tool for this is called an *atomizer* and Lefebvre lists eight main types of atomizers in his book *Atomization and sprays*; pressure, rotary, air-assist, airblast, effervescent, electrostatic, ultrasonic and whistle atomizers [5].

The process of atomization is mainly a way to overcome the surface tension of the liquid which can be achieved both by internal and external forces [71]. Without any external forces the surface tension pulls the liquid into the shape of a sphere which is the lowest state of energy regarding surface tension.

To exert the forces on the liquid, one method is to pump it with high pressure through orifices of the fuel nozzle. The higher the pressure difference over the nozzle, the larger the kinetic energy (velocity) of the liquid [5]. As mentioned, there are many types of fuel injectors which have been proven to work well for various applications. One of the more common in gas turbines is the pressure-swirl atomizer, see Fig. 4.3

One of the issues that the fuel injector needs to cope with is the variability in fuel flow due to the change in load. From (4.1), Bernoulli's equation for incompressible flow in a tube, it is
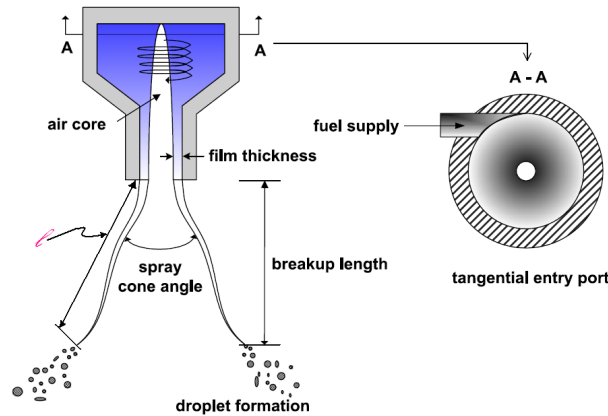
Figure 4.3: Schematics of a typical pressure-swirl nozzle [72]

seen that the flow rate varies as the square root of the injection pressure differential, if the fluid velocity is to be increased by two times, the pressure needs to be increased four times.

$$\frac{v^2}{2} + gz + \frac{p}{\rho} = constant \qquad (4.1)$$

where v is the velocity, g is the gravity, z is the height, p is the pressure and ρ is the density of the fluid.

The development of the spray goes through many stages as the pressure over the nozzle is increased from zero [71]:

1. Fuel dribbles from the orifice

2. Fuel leaves in a thin distorted pencil

3. A cone forms at the orifice, but is contracted to a bubble by surface tension

4. The bubble opens to a hollow tulip form

5. The curved surface straightens into a conical sheet

Since the size of the orifice is constant, the success of the atomization is depending on the pressure.

Consider an orifice designed to atomize a fuel at lowest mass flow. For a low viscosity fluid, the lowest injection pressure at which atomization can occur is 0.1MPa. At peak load the mass flow might increase 20 times, meaning that the pressure needs to be increased to 40MPa which could be hard achieving for most pumps [71]. If the size of the orifice would have designed to fit the flow at peak load, but then the pressure will be too low at low load.

To handle this problem an atomizer called *spill atomizer* can be used, see Fig. 4.4. In this type of nozzle the excess fuel is returned through a separate return line in the middle of the swirling chamber. This means that the fuel injector pressure can be high enough even for the lowest fuel flow rates [71]. The fuel flow rate and pressure of the fuel is constant to the swirl chamber, but the mass flow through the main outlet is controlled by opening and closing the valve to the return line. By using this high pressure it has been shown that this kind of nozzle is able to perform adequate atomization at 1 % of maximum flow rate [5].
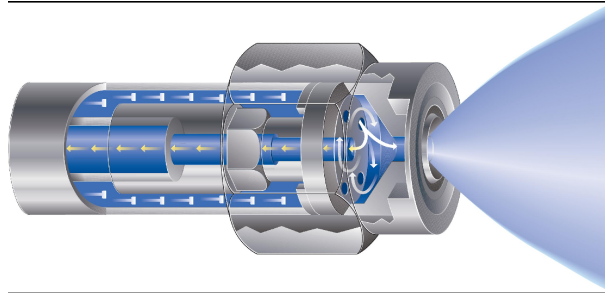
Figure 4.4: Schematic of a spill nozzle [73]

4.2.1 Impact of surface tension, viscosity and density on the atomization of sprays

The surface tension is an important factor for the outcome of atomization. Surface tension resists the formation of new surface area, which is the whole purpose of atomization [71]. When studying the relationship between drop-size and surface tension, the Weber number (4.2) is a useful dimensionless parameter.

$$We = \frac{\rho v^2 l}{\varrho} \tag{4.2}$$

where ρ is the density of the fluid, v is the velocity, l is the characteristic length and ϱ is the surface tension.

The Weber parameter is useful when there is an interface between two different fluids, e.g. liquid fuel and gaseous air. The Weber number is the ratio between the inertial forces and the surface tension. Consider a fluid surface, e.g. the spray cone from a swirl nozzle as in Fig. 4.3. The l marks the characteristic length. A long surface and high density of the fluid and high velocity of the flow will increase the Weber number and the probability of break up of the fluid surface. A high surface tension act as a resisting force.

Viscosity

Viscosity is a more important fuel property than surface tension to atomization from a practical point of view. An important parameter of any flow in a pipe is the Reynolds number 4.3

$$Re = (\frac{\rho v D_H}{\mu}) = \frac{v D_H}{\nu} \tag{4.3}$$

where ρ is the density, v is the flow velocity, the D_H is the hydraulic diameter, μ is the dynamic viscosity and the ν is the kinematic viscosity.

With higher viscosity the Reynolds number decrease and the flow inside the atomizer is less turbulent and the cone sheet produced, see Fig. 4.3, becomes thicker. A lower Reynolds number means that instabilities are developed later and the launch of atomization is delayed [71].

Density

Most fuels show very small differences in density, and the available data on the effect of liquid density on mean drop size suggests that the importance of this property for the atomization is small [5].

Sauter mean diameter, SMD

The Sauter mean diameter is the

> *"Diameter of a droplet whose surface-to-volume ratio is equal to that of the entire spray"* [5]

this makes it a representative measurement of the efficiency of the atomizer. Lefebvre [5] argues that since the atomization is such a complex process, it would be more convenient to subdivide it into two separate main stages. In the first stage the effects of the hydrodynamic and aerodynamic forces are combined which generates surface instabilities. In the second stage the surface breaks up into first ligaments and then drops. Lefebvre admits that this is an oversimplification of the problem but it allows for the expression for SMD to be expressed as (4.4)

$$SMD = SMD_1 + SMD_2 \tag{4.4}$$

Lefebvre propose the following expression (4.5) for the SMD of a pressure swirl atomizer

$$SMD = 4.52 \left(\frac{\sigma \mu_L^2}{\rho_A \Delta P_L^2} \right)^{0.25} (t \cos \theta)^{0.25} + 0.39 \left(\frac{\sigma \rho_L}{\rho_A \Delta P_L} \right)^{0.25} (t \cos \theta)^{0.75} \tag{4.5}$$

where σ is the surface tension, μ_L is the liquid dynamic viscosity, ρ_A is the density of the air, ΔP_L is the injection pressure differential across the nozzle, t is the film thicknes in the final orifice, θ is half the cone angle and the ρ_L is the density of the liquid.

4.3 Detrimental processes related to combustion

There are several problems related to the use of a gas turbine, some of them are the processes that are detrimental to the gas turbine itself. Due to the high speed rotation of the turbine axis, there are enormous forces acting on the blades of the turbine, testing the material to its stress limits. Therefore, new material with extreme strength has been developed, such as single crystal materials, super alloys and even ceramics have been tested.

To further insult to injury, the turbine and all the HGP materials needs to deal with extreme temperatures, which add to the challenge of the solid strength. But besides challenging the solidity of the materials, the extreme temperature also contributes with some chemical challenges like oxidation, corrosion and erosion. The high fluid flow can also be an issue if the fluid contains solid particles, which could erode the material, and if the fluid contains melted ash that could deposit in the HGP which could cause hot spots on the blades.

4.3.1 Oxidation

When a metal or alloy oxidizes, it means that the metal, exposed to oxygen, are converted into its oxide. If the oxide sticks to the metal surface, it can form a protective scale that prevents further oxidation. But it may also fall off exposing new metal to further oxidation. This will have a detrimental effect to the structure and the load-bearing capabilities of the original metal or alloy [74].

Metals oxidize because the reaction releases free energy. From figure 4.5 one example is the following

$$2Mg + O_2 \rightarrow 2MgO \tag{4.6}$$

will release ~ 0.99 MJ/mole of oxygen at 850°C and 1 atmosphere of pressure (red lines).
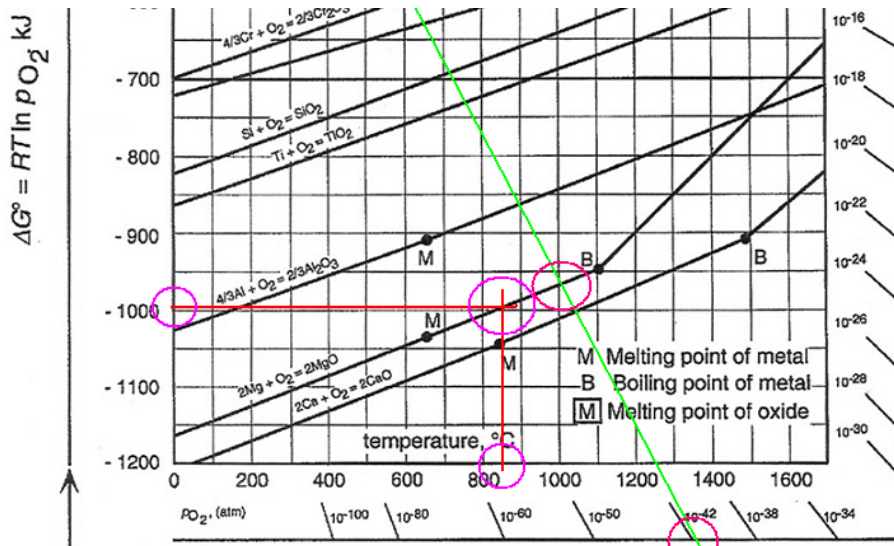
Figure 4.5: Ellingham diagram of free energy of formation of oxides as a function of temperature

Temperature effects

From figure 4.5 it is possible to see that the free energy release are reduced with increased temperature (positive slopes), for many metals. This means that most oxides become less stable at elevated temperatures [74].

Partial pressure effect

The expression for chemical equilibrium can be used to calculate the partial pressure of oxygen when the chemical reaction oxidation and reduction of oxide will be equal

$$K = \frac{[MgO]^2}{[Mg]^2 P_{O_2}} \tag{4.7}$$

where $[\dots]$ means concentration and P is the partial pressure.

At chemical equilibrium, the ratio between the metal and oxide is assumed unity. This gives $K = \frac{1}{P_{O_2}}$ and with Gibbs free energy; $\Delta G^\circ = -RT\ ln\ K$ gives us the partial pressure of oxygen $P_{O_2} = 1/exp(\frac{-\Delta G^\circ}{RT})$ with R being the universal gas constant, T the temperature. At 1000K this gives a partial pressure of $6.5 \cdot 10^{-40}$, see green line in Fig. 4.5 and the approximate compliance with the calculated value. Since the partial pressure of oxygen hardly is that low in a gas turbine, magnesium will always oxidize, but since the oxide will create a protecting layer, all magnesium is not oxidized at once.

Oxide scale protectiveness

Depending on the characteristics of the oxide scale it could either protect the underlying metal from further oxidation or allow permeation of oxygen for further oxidation. This characteristic is measured using the Pilling-Bedworth Ratio (PBR) which is defined as (4.8)

$$PBR = V_{OF}/V_{CM} \tag{4.8}$$

where V_{OF} is the volume of the oxide formed and V_{CM} is the volume of metal consumed.

The value of PBR is interpreted as follows: PBR≪1 means that the volume of the oxide scale formed is less than the volume of the metal consumed which means that in order to cover the same area, the oxide scale needs to be porous and thus permeable [74].

If on the other hand PBR≫1 this means that the oxide scales volume is larger than the volume of the metal consumed, leading to wrinkling and spall of the scale thus allowing further oxidation. Therefore the PBR needs to be in the vicinity of unity if the oxide scale will be protective against further oxidation [74].

Oxygen reactive elements

Some elements form oxide scale which are more stable and adherent than other alloy constituents in a high-temperature environment. Such elements are called oxygen reactive elements (REs) and examples of these are Yttrium (Y), Hafnium (Hf), Lanthanum (La), Scandium (Sc), Cesium (Ce) and Zirconium (Zr) [74].

Implications of water vapor on the rate of oxidation

The spalling of the oxide scales are known to increase in the presence of water vapor, thus increasing the rate of oxidation. This phenomenon is less in alloys containing reactive elements such as PWA 1487 and yttrium-containing Rene N5 (two common GT material today) because the oxide scales formed by aluminum sticks better to these alloys [74].

4.3.2 Corrosion

In *Encyclopedic Dictionary of Polymers* [75], Jan Goosh defines corrosion as

> *"The deterioration of metal . . . by chemical or electrochemical reaction resulting from exposure to . . . chemicals, or other agents in the environment in which it is placed"*

In a gas turbine, metals and alloys are subject to an oxidizing atmosphere at an elevated temperature. If the components are subject to deposits of fused salts, these deposits can have an accelerating influence on the degradation process. This process is known as high temperature corrosion or "hot" corrosion, where a

> *". . . porous non-protective oxide scale is formed at the surfaces with sulfides in the substrate, and the mechanism of attack does not include aqueous electrolyte"* [76]

The deposits of fused salt are mostly sulfates of Na, Ca, K as well as vanadates and carbonates, that comes from impurities in both the ingested air and the fuel [77].

One of the most common sulfates is Na_2SO_4, or Sodium sulfate, where the sodium and sulfur may exist as impurities in the the air and/or in the fuel. It is formed in the flame from Sodium chloride or other sodium compounds and sulfur-containing organic compounds [76]:

$$oxygen + sulfur + sodium =$$
$$sodium\ sulfate(from\ air)(from\ fuel\ and/or\ sea\ salt) \quad (4.9)$$
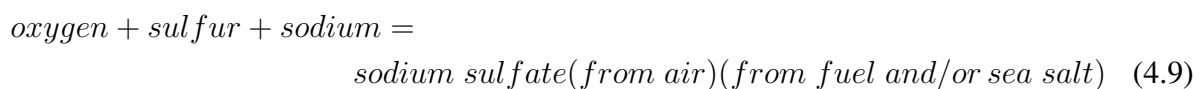
The characteristics of hot corrosion depends on several factors; the amount of deposits, the composition of the deposit, the composition of the base metal or alloy but most notably the temperature [76, 77].
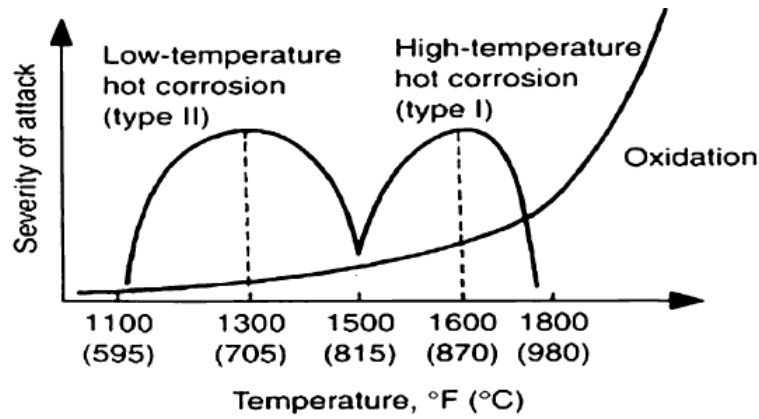
Figure 4.6: Regimes of high temperature attack; temperatures are approximate [76].

It is customary to differ between type I - high temperature hot corrosion which occurs in a higher temperature span and type II - low temperature hot corrosion which occurs in a lower temperature span as seen in figure 4.6. If the Na/V-ratio (sodium/vanadium) of the fuel is high, the melting point of the ash could be lower than the blade temperature, and the melting ash could corrode through the protective oxide layer [78]. In Fig. 4.7 is shown a damaged blade from a low-firing temperature 1970's machine. The failure occurred just after 1000 hours operation on distillate fuel containing 2 ppm sodium from sea water contamination [78].

Figure 4.7: Sulfidation failure on a 1970's low-firing temperature machine [78]

High temperature hot corrosion HTHC - type I corrosion

High temperature hot corrosion is a rapid form of corrosion that can occur when potassium- and/or sodium- sulfate is present. Other impurities from the the air or fuel can combine with these sulfates to lower the melting temperature and thus broadening the range of attack [76].

The sulfur diffuses into the metal faster than oxygen, reacting with chromium, forming chromium sulfides. As oxygen diffuses behind the sulfur, it oxides the sulfide particles that have formed because the oxides are more stable than the sulfides, this in turn releases elemental sulfur which then diffuses further into the metal and the process repeats itself.

Low temperature hot corrosion LTHC - type II corrosion

This form of hot corrosion is observed in the lower temperature regime, see Fig. 4.6. The exact temperature range is not completely established, in the figure it is possible to distinguish a lower limit of 595°C and a higher limit of 815°C. But in other reports the range is noted as 650-800°C [79], 600-730°C [80], 650-750°C [77]. This makes an average of 613-773°C.

LTHC forms typical pitting in the material and is the result of sulfur in the fuel. The corrosion is induced by melting sulfates - $NaSO_4$ and $CoSO_4$. Separately they have melting temperatures of 884°C and 735°C respectively, but together they have the eutectic melting point of 540°C. The cobalt sulfate is itself a corrosion product from the reaction of the cobalt in the surface of the blades and the SO_3 formed in the combustion gases [79].

Wortman et al presents a figure in their report that represents the threshold fuel sulfur expected to result in $NaSO_4$-$CoSO_4$ liquid formation from a solid $NaSO_4$ deposit on an alloy containing cobalt, see Fig. 4.8. They mention that similar calculations for $NaSO_4$-$NiSO_4$ shows that the levels needed for LTHC corrosion induced from this combination are at least ten times higher. Below the solid-liquid transition line in Fig. 4.8, very low corrosion rates were ob-
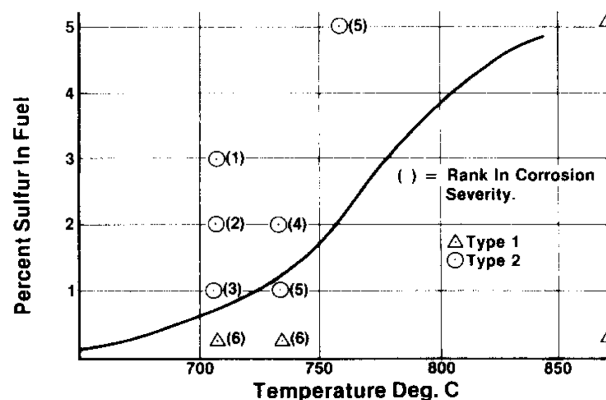
Figure 4.8: The curve defines threshold fuel sulfur levels necessary to form liquid $NaSO_4$-$CoSO_4$ [80]

served, even for tests performed during 1000h. The corrosion rates increased with an increase in sulfur levels above this curve [80].

The most severe attack was observed at 704°C at sulfur levels of 3 % in the fuel, this condition is similar to what could be expected in a gas turbine working at 10 atm with a 65:1 air-fuel ratio and 0.4 % sulfur in the fuel since the result are from a burner rig and not an actual gas turbine [80].

Particulate depositions

The gas coming from the combustion chamber and entering the turbine is not "clean" in any way, but apart from the environmentally harmful or toxic constituents such as CO_2, SO_x, NO_x, unburned hydrocarbons and polycyclic aromatic hydrocarbons, un-clean here is referring to particulate that, depending on temperature either can erode the turbine blades or deposit onto the blades and thus increase their weight and possibly cause catastrophic failure to the turbine, or hot spots melting the material.

These particles can either come from external sources such as the ingested air. The amount of particles from this source will vary due to the operating environment. Of course most cites try to clean the air from most of its particles when that is possible (which is the case with land

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based gas turbines) but due to the amounts of air needed, it is not economically justified to completely eliminate all particles from the air [81].

The particles can also come from internal sources such as products from the fuel combustion, eroded turbo-machinery components and secondary chemical reactions [81].

In their study, Crosby et al.[81], showed that particle deposition on turbine blades increased as the particle diameter increased, at a constant temperature of 1183°C and a flow speed of Mach 0.25. When they increased the particle size from 3 μm to 16 μm the particle deposition increased more than double. They also tried various temperatures and noticed that at a constant flow velocity of 170 m/s particle deposition rates decreased with decreasing gas temperature and that they reached a threshold in temperature for deposition at approximately 960°C. Below this temperature of the gas, no deposits were found.

Even though the process of deposition is a slow process, it is not to take lightly on, since the implications of its effect could be catastrophically with complete break down of the turbine.

4.3.3 Erosion

Erosion is the mechanical removal of material. In a gas turbine both compressor blades as well as turbine blades and vanes could be victims to this effect depending on the erodent which could include sand and silicates, fly ash, sea salt or pyrolytic carbon [82].

At ambient temperatures the way oxides and metals are eroded are different, as they are different in their material structure, oxides being brittle and metals being ductile. But at elevated temperatures similar impact damages in both oxides and metals are observed, but the oxide scale may modify the erosive response [82].

This means that two factors are of importance; the temperature and particle loading. The temperature is important for how fast the oxide scale is formed and the particle loading defines the time between two consecutive impacts at a given point. But it is also shown that the mass and velocity of the particle is of some importance. Both higher velocity and larger particles increase the erosion rate and surface roughness of the blades and vanes [83].

4.4 Emissions

The emissions from combustion of hydrocarbons are well known; CO and UHC due to incomplete combustion, NO_x from the oxidation of nitrogen (due to the high temperatures) which is always present in air and SO_x from the oxidation of sulfur in the fuel. Of course CO_2 and H_2O is emitted but they are not always regarded as pollutants but they both contribute to global warming and can only be reduced by burning less fuel. As for renewable fuel this is not an issue since the CO_2 and H_2O released were stored in the biomass no later than 100 years ago. The principal pollutants from gas turbines and their effect is listed in Tab. 4.2. The nature of

Table 4.2: Principal pollutants emitted by gas turbines [71]

Pollutant	Effect
Carbon monoxide (CO)	Toxic
Unburned hydrocarbons (UHC)	Toxic
Particulate matter (C)	Visible
Oxides of nitrogen (NO_x)	Toxic, precursor of chemical smog, depletion of ozone in stratosphere
Oxides of sulfur (SO_x)	Toxic, corrosive

pollutant emissions are such that CO and UHC are highest at low loads in the gas turbine but almost disappears at max power. NO_x and smoke are in the other hand modest at low load and at their highest at high power. This is illustrated by Fig. 4.9.
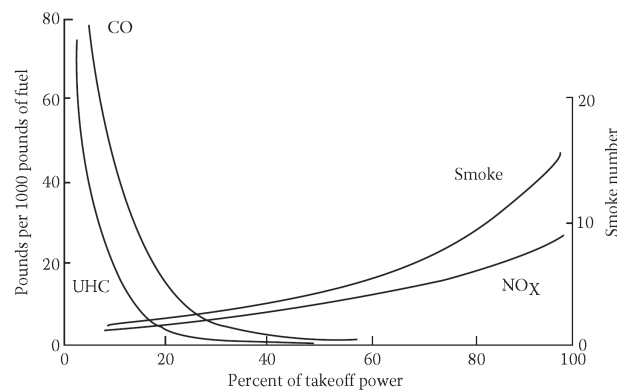
Figure 4.9: Emission characteristics of gas turbines [71]

4.4.1 Carbon monoxide

When combustion is performed rich, i.e. with less oxidizer than stoichiometric condition, large amounts of CO will be emitted due to the lack of sufficient oxidizer to complete the reaction to CO_2. If the combustion is performed at stoichiometry or slightly lean, large amounts of CO will also be emitted but now due to the dissociation of CO_2. But equilibrium rates are not enough to explain the amounts of CO emitted which are much higher than one might expect from those. Lefebvre and Ballal suggests that much of the emitted CO are the result of one or more of the following [71]:

- Inadequate burning rates in the primary zone, due to a fuel/air ratio that is too low and/or insufficient residence time

- Inadequate mixing of fuel and air, which produces some regions in which the mixture strength is too weak to support combustion, and others in which over-rich combustion yields high local concentrations of CO

- Quenching of the postflame products by entrainment into the liner wall-cooling air, especially in the primary zone

Lefebvre and Ballal also lists actions to reduce the emissions of CO:

- Keeping the equivalence ratio at 0.8, see Fig. 4.10

- Keeping a high combustion pressure, see Fig. 4.10

- High ambient temperature (valid up to 303K)

- Don't let the CO migrate towards the wall-cooling air to be entrained there

- Keep the fuel drop size small to admit for earlier combustion instead of evaporation
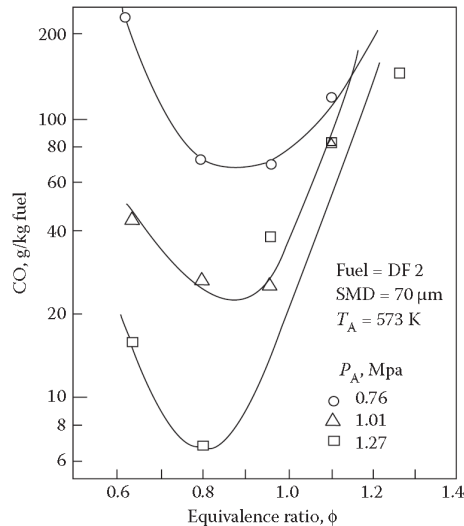
Figure 4.10: Influence of temperature and equivalence ratio on CO

4.4.2 Unburned hydrocarbons

The emissions of unburned hydrocarbons are comprised of drops and vapor from the combustor and thermally degraded hydrocarbons that are lighter than the parent fuel. UHC are mainly seen as the product of poor atomization, local cool-spots, slow burning rates or a combination of the above [71].

Lefebvre and Ballal mentions that while the formation of UHC is more complex than the formation of CO, the same factors influencing the emissions of CO is also influencing the emissions of UHC [71].

4.4.3 Smoke

Smoke from combustion are finely divided soot particles. They are produced when fuel vapor becomes trapped in zones where the oxygen is insufficient. If that happens, large amounts of soot can be produced but much of it is oxidized further downstream in more air-rich regions [71].

Lefebvre and Ballal lists some factors that they mean leads to an increase in soot formation:

- High combustion pressure (valid for combustion chambers fitted with pressure atomizers, newer airblast atomizer does not experience increase in soot formation with increase in combustion pressure)

- High concentration of aromatics in fuel. Fuels with no aromatics produce no soot

- Large spray drop diameter

4.4.4 Oxides of nitrogen

NO sooner or later oxidize into NO_2 therefore they are lumped together to the term NO_x. Four different mechanisms are proven to produce NO_x:

- Thermal NO_x

- Nitrous NO_x

- Prompt NO_x

- Fuel NO_x

Thermal NO_x

The most prominent source of NO_x from the combustion process is thermal NO_x which is highly temperature dependent. It is formed from the diatomic nitrogen and oxygen in air. At temperatures above 1600°C nitrogen and oxygen are dissociated into their atomic states and as such participate in a series of reactions called *Zeldovich mechanisms* as in (4.10) forming NO_x.

$$O + N_2 \rightleftarrows NO + N$$
$$N + O_2 \rightleftarrows NO + O$$
$$N + OH \rightleftarrows NO + H \qquad (4.10)$$

The formation of NO_x increases linearly with temperature as seen in Fig. 4.11.
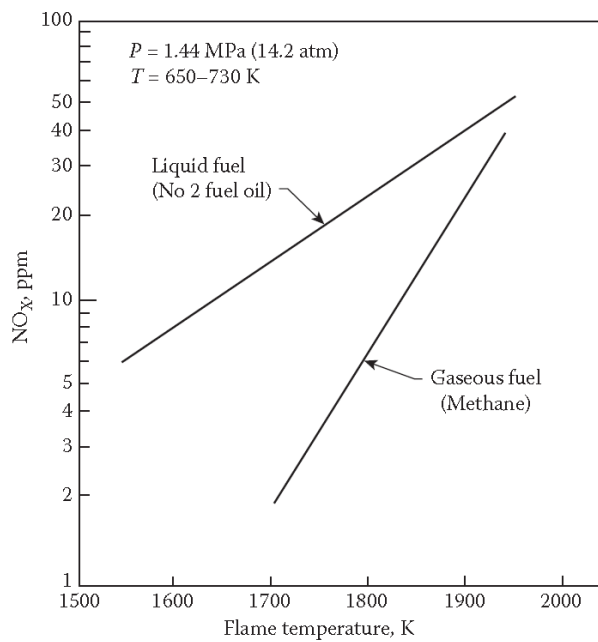
Figure 4.11: Temperature dependence for the formation of NO_x, for liquid and gaseous fuel [71]

Nitrous NO_x

The reaction series begin with the formation of nitrious oxide (N_2O) which is then oxidized into NO according to Lefebvre and Ballal [71]:

$$N_2 + O \rightleftarrows N_2O$$
$$N_2O + O \rightleftarrows NO + NO$$
$$N_2O + H \rightleftarrows NO + NH$$
$$N_2O + CO \rightleftarrows NO + NCO$$

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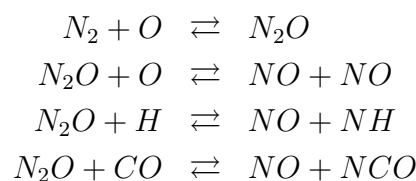
Prompt NO$_x$

This type could be found very early in the combustion process and the initiating reaction for this type of NO$_x$ is:

$$N_2 + CH \quad \rightleftarrows \quad HCN + N$$
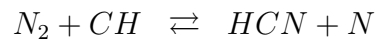
The N follows the second Zeldovich mechanism and HCN oxidizes by the following reactions:

$$HCN \rightarrow CN \rightarrow NCO \rightarrow NO$$
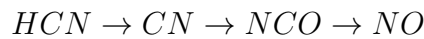
Fuel NO$_x$

Many fuels contains organically bound nitrogen. Some of this nitrogen can react with oxygen during combustion to form fuel NO$_x$.

Ratio between NO$_x$ forming mechanisms

The contributions to the total amount of NO$_x$ varies with temperature and equivalence ratio. In a paper, where the authors studied the combustion of methane (no fuel nitrogen) where the temperature was 1900K and the equivalence ratio 0.8 the contributions were: 60 % Thermal NO$_x$, 10 % nitrous NO$_x$ and 30 % prompt NO$_x$. When the temperature were reduced to 1500K and the equivalence ratio were reduced to 0.6, the distribution had changed: 5 % thermal NO$_x$, 30 % nitrous NO$_x$ and 65 % prompt NO$_x$ [71].

4.4.5   Oxides of sulfur

Almost all sulfur in the fuel is oxidized into mainly SO$_2$ and SO$_3$, also known as SO$_x$. It is toxic and corrosive and lead to the formation of sulfuric acid in the atmosphere. The only reasonable strategy to lower the emissions of SO$_x$ when combusting fuel is to remove the sulfur from the fuel or to use fuel with very small amounts of sulfur [71].

Chapter 5

Sustainability criteria

To govern their actions, both internal and external, most organizations use rules and regulations. To regulate the purchasing of biomass, E.ON uses a regulatory document called *Biomass Purchasing Amendment to the E.ON Responsible Procurement Policy* [84]. In it is stipulated the objectives, scope and context and purchasing conditions when buying biomass and its derivatives.

The SEA has also set up criterias for sustainability. Further more they publish a list of companies and their fuels that already have passed the regulations and are approved for sustainability.

There are four documents governing the decision whether a company gains sustainability approval:

1. *Law of sustainability criteria for bio propellants and liquid bio fuels* (Swedish: "Lag om hållbarhetskriterier för biodrivmedel och flytande biobränslen") SFS 2010:598 [85]

2. *The regulation of sustainability criteria for bio propellants and liquid biofuels* (Swedish: "Förordning om hållbarhetskriterier för biodrivmedel och flytande biobränslen") SFS 2011:1088 [86]

3. *The energy agencies direction of sustainability critieria for bio propellants and liquid biofuels* (Swedish: "Statens energimyndighets föreskrift om hållbarhetskriterier för biodrivmedel och flytande biobränslen") STEMFS 2011:2 [87]

4. *Guidance to the regulations of sustainability criteria for bio propellants and liquid biofuels* (Swedish: "Vägledning till regelverket om hållbarhetskriterier för biodrivmedel och flytande biobränslen") ER 2011:23 [88]

These documents all emanate from the EU Directive: *Directive 2009/28 EC of the European parliament and of the council*. All the EU countries have to adapt to this directive, eventually. If these laws, regulations and directives meet with the E.ON purchasing amendment, the SEA list of companies can be used as basis for this study.

One solution to the problem of comparing the purchasing policy with the laws and regulations, is given during a conversation with Tobias Norin at E.ON Värme. They have already purchased biofuels in the form of SVO. They have already considered the *Biomass Purchasing Amendment to the E.ON Responsible Procurement Policy* and they found that the SEA criteria of sustainability with one addition was enough to comply with the E.ON policy. The addition was that the feedstock for the biofuel had to be palm oil free [89]. If it is good enough for E.ON Värme, then it will most likely apply for E.ON Värmekraft.

Chapter 6

Market research

The definition of what a bio fuel is, is by no meaning a clear concept. Svebio's Lena Dahlman made a distinction between bio fuels and bio oils, where she meant that bio fuels implied a propellant for vehicles and bio oil meant fuel for heating [90]. This definition gives only two biofuels: E85 and biodiesel. But if biofuels is defined as in chapter 2 - *a matter that can store energy* - there are many more options.

The Swedish Energy Agency presents a list with the "operators" in Sweden that have attained sustainability approval for the use of biofuel for commercial purpose [91]. May that be for heating, processing, electricity production or distribution.

Examining the liquid biofuels listed, shows that all fuels from the list in chapter 2, except Fischer-Tropsch synthetic fuels, are offered. Why no Fischer-Tropsch fuel is on this list is something not studied. It probably means that no such fuel is sold in Sweden, and the reasons for that could be many, but these are just speculations.

Many operators are offering "bioolja". According to the department of sustainable fuels at SEA [92], "bioolja" could mean just about anything, or at least tall oil, leaf oil and vegetable oil, both virgin and recycled vegetable oil.

6.1   Liquid biofuels available on the Swedish market

The main goal of examining the Swedish market has been to gather information about the liquid biofuels offered concerning specifications and price.

When contacting companies that have gas stations and also offering bio fuels, it was discovered that three companies on the Swedish market had their own production and that the rest of the companies bought their products from them. The companies with production are Preem, Statiol and ST1. This means that logically, the lowest prices of the biofuels offered from this sector would be achieved from these three companies.

In addition to these companies - vehicle propellant distributors - there are several companies on the list offering liquid biofuels as substitute to the fuels used in boilers for district heating or additives to e.g. paint, food or other chemical industries.

Further more there are some companies importing liquid biofuels that could be used as propellants and as such challenging the three big ones. These companies does not seem to distribute directly to consumers, but rather as wholesalers.

A questionnaire was constructed, see Appendix B based on the criteria in the fuel specification used at E.ON Värmekraft and sent to the relevant companies. Many answered that they did not have any fuel that would live up to these standards. A new method developed which focused more on what they actually could offer, not too concerned if what they could offer didn't live

up to the high demands of the fuel specification. How they differed and what this would mean would have to be a later question.

The result from the examination of the fuels offered on the market is that the properties of these fuels are in high correspondence with the properties presented in 2.10.

6.2   Prices of available biofuels on the Swedish market

Getting prices for the fuels has not been as straightforward as one might have imagined. Some companies have willingly given price offerings of both quantities and qualities, some have been more reluctant and referred to official price statistics publicly available on internet. A common saying has been that

> "...the most common use of a fuel determines the price of that fuel, if a fuel is sold as a substitute for diesel, then it will be priced as diesel ..." [93, 94]

Sören Ericsson at Preem argues - and the above quote implies - that, to get the price for biodiesel that an electricity producing company would have to pay, the official price of diesel (the price you would pay at the gas station filling up your car) could be used as a starting point.

From this price, Sören Ericsson continues

> " if you deduce the VAT, energy and excite taxes and a margin of 70-90 öre per litre, this will put you in the right district" [93]

The same arrangement goes for fuels like e.g. DME.

Sören Ericsson further means that if a company distributing a fuel that could be used to substitute vehicle fuels e.g. DME, and the choice stands between selling it as a substitute for heating oil or as a substitute for a vehicle fuel, every distributor would choose the latter since those prices are much higher.

This gives the producer of the fuel a better way to cover the (probably) larger production costs of a fuel that fulfilles the requirements for use in a vehicle, due to higher standards [93].

6.2.1   The price of biooil

According to Andreas Kannesten at SEA, none of the registered biooils are pyrolysis liquid. This means that there is no company to contact, on the basis of the SEA list, to get a price estimate on pyrolysis oil. Another strategy was used for this estimate. At the webpage of the Dutch company BTG-BTL [95] a graph showing a rough price indication for biooil, is presented, see Fig. 6.1. Assuming an average price of the biomass of €30/ton, and assuming an average value of moisture content and the price of steam, the black lines can be drawn in the Fig. 6.1.

Then a price estimate for the pyrolysis oil would be €12.35/GJ. This gives 106.3 SEK/GJ (€1=8.61 SEK per 2012-11-02) which is ∼383 SEK/MWh.

6.2.2   The price of DME

In the list from SEA there are two companies (Biofuel Express AB and Chemrec Kraftliner AB) that have attained sustainability approval distributing DME. When asked, they can not deliver this product at the quantities needed. But to get a rough price estimate, the above mentioned model can be applied. According to Patrik Löwnertz at Chemrec [94], DME will probably be sold as a substitute for diesel fuel which will give it the same price per energy content as diesel. This means that DME will cost about 1 140 SEK/MWh.
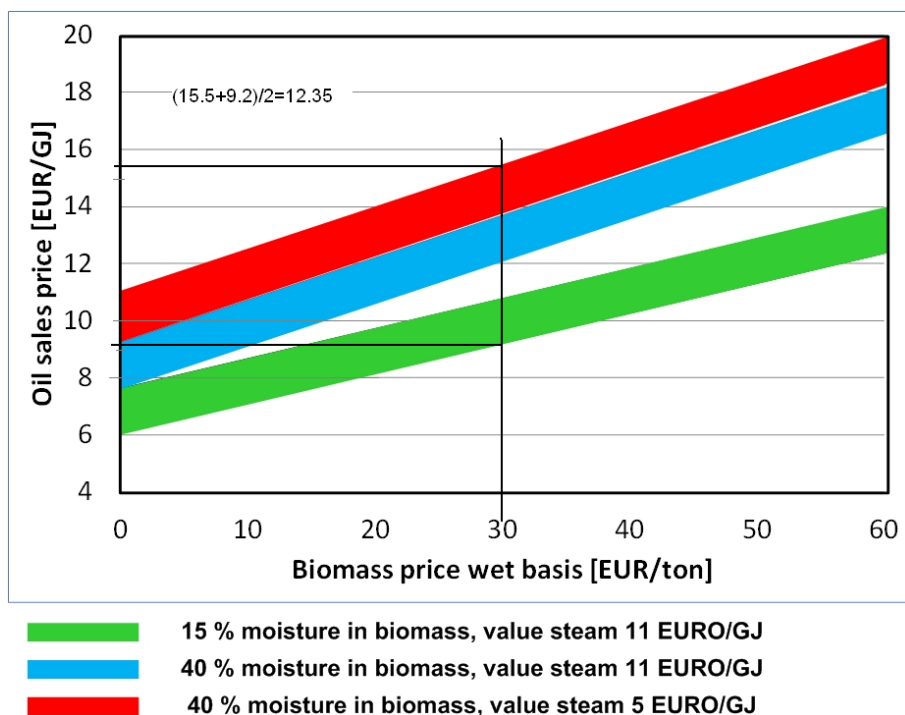
Figure 6.1: Graph showing the expected price range of biooil as a function of both moisture in biomass and price of biomass [95]

6.2.3 The price of E85

In the case of E85 there is the price statistics that can be used [96]. This gives an average of 10.13 SEK/litre. Deducing VAT and the margin of 70 öre per litre gives 7.40 SEK/l. Since 15% of E85 is petrol, the energy and excite taxes for this can be deduced; 0.15*5.65 SEK/l≈0.85 SEK/l which gives a price per litre of 6.55 SEK. This in turn gives a price per MWh of ∼1010 SEK.

6.2.4 Summary fuel prices

For vegetable oil, biodiesel and HVO (NExBTL), there has been given price indications from various companies [97, 98]. The price for biooil, E85 and DME has been calculated as shown above. FT-fuels are not listed below since no FT-fuel is listed by SEA.

Table 6.1: Summary of fuel prices in SEK

	Biooil	DME	E85	VO	FAME	HVO	Eo1 [a]
Price per MWh	383	1 140	1 010	552	937	990	527
Price per ton	1 713	9 088	8 192	5 980	10 147	12 105	6 300

[a] From Ola Olsson, fuel development, E.ON Värmekraft [2]

6.3 Subsidies available on the Swedish energy market

To increase the production of electricity from renewable sources (wind, sun, wave, geothermic, bio and hydro) Sweden has introduced a subsidy *green certificate* (elcertifikat). It is a sum of

money given to the electricity producer for every produced MWh of electricity from renewable sources. Since it is supposed to be an incentive to increase this production by expansion of new plants, it is not granted without conditions.

First the fuel must come from the SEA list [91]. But if the plant is taken into production before 1st of May 2003 (applies to all of the concerned gas turbines) just changing to renewable fuel will not suffice, it will get this subsidy for an increase in electricity production with renewables if it can show that the increase in electricity production from renewables is due to

> *". . . a consistent and substantive investment . . . "* [99]

All the regulations are noted in *STEMFS 2011:4* [100]. For different plants the amount of conversion needed to be granted green certificate is specified. Gas turbine plants for electricity production is not mentioned. From conversations with Martin Johansson at SEA, it is stated that, to get green certificate for electricity production from these gas turbines, a change of fuel is not enough. There has to be some kind of investment in the plant. This could be e.g. change of fuel system, nozzles or something else. This means that if an alternative fuel is used that does not require any material investment, green certificate will not be granted.

The mean value of the subsidy between September 2011 and October 2012 has been 198.5 SEK/MWh.

Chapter 7

Analysis

In chapter 2 different liquid fuels were listed that could be used as fuel in a gas turbine. The properties of the different fuels varies and so does their respective suitability as fuel in this specific application.

7.1 Heating value

As seen in chapter 5, the difference in LHV makes the fuel mass flow very varying, from the low LHV of biooil to the high LHV of HVO, which is even higher than the LHV of the current fuel.

To keep the same output power, the needed fuel mass flow of biooil is almost three times higher than that of the current fuel. Neither piping nor gas turbine nozzles will cope with this increase in flow. According to Fredrik Hermann, these systems could withstand an increase of 10-15 %. A difference in mass flow larger than this means that the whole fuel system need to be replaced; piping, pipe fittings, control valves, quick closing valves etc. These are investments in "the size of millions per site" [6].

In addition to this comes the cost for an operational manager from the manufacturer/service provider that adjusts the different parameters in the turbine to the new conditions. Perhaps even the fuel nozzles have to be replaced, which of curse is only viable if suitable nozzles are available on the market.

In Tab. 7.1 is presented the difference in heating value between the alternative fuels and the current fuel and how much higher mass flow of fuel that is needed to keep the power output. From Tab. 7.1 it is seen that to keep the same energy output from the turbines using biooil, it

Table 7.1: Difference in heating value between alternative fuels and current fuel and the increase in mass flow needed to keep the power output by using the alternative fuel

	Biooil	DME	E85	SVO	biodiesel	HVO
Heating value compared to current fuel	37 %	67 %	68 %	91 %	88 %	102 %
Times higher mass flow needed	2.67	1.50	1.47	1.10	1.13	0.98

would demand a mass flow almost three times higher than the current mass flow, DME and E85 about 50 % higher, vegetable oil and biodiesel about 10 % higher. This means that if biooil, DME or E85 were to be used, it would demand a substantial investment, between a half to one million € per turbine in changed fuel supply system. If the nozzles need to be replaced it will cost about one million € per turbine [6].

7.1.1 Estimated yearly consumption of fuels

The estimated yearly consumption of both current and alternative fuels are presented in the following diagrams and tables. The estimations are made on the proposed number of hours of operation per year, the energy consumption in Tab. 1.2 and the LHV's of the alternative fuels. The data are presented for the lower end of the interval and the high end of the interval.

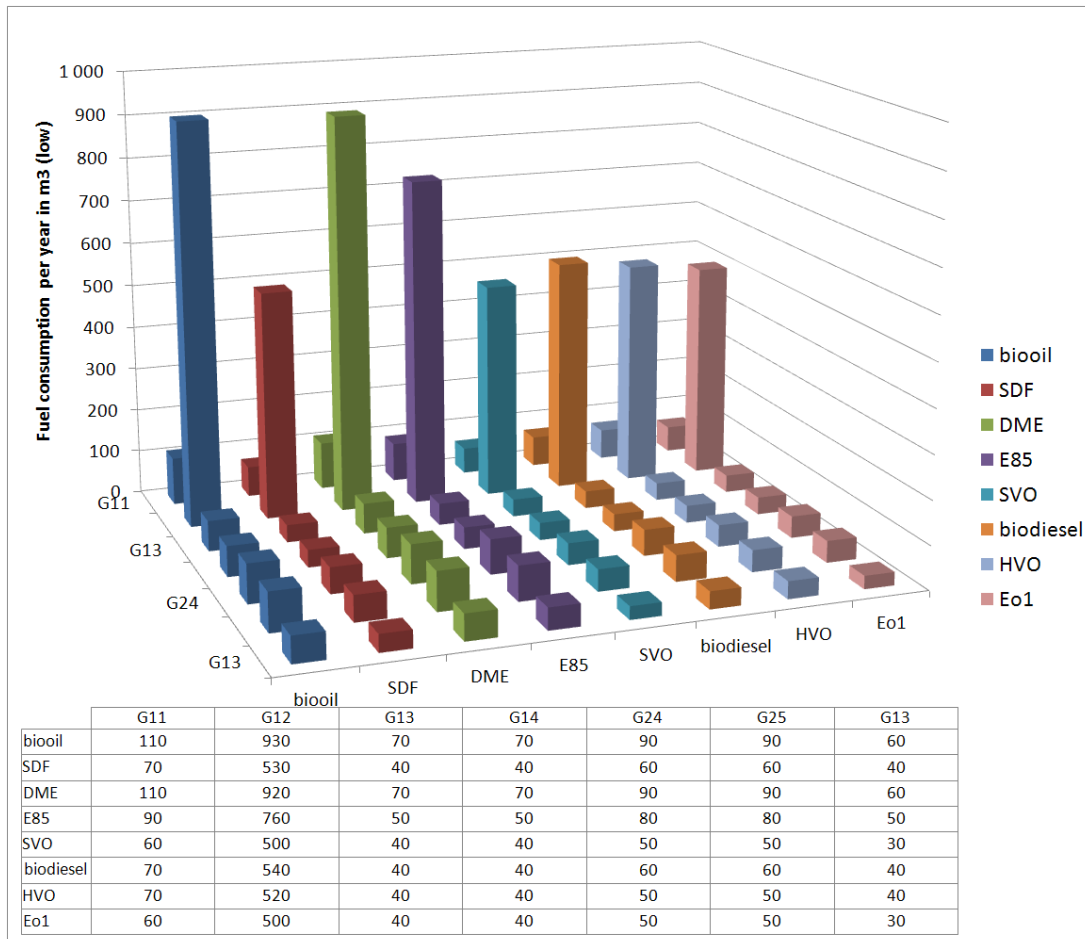|	G11	G12	G13	G14	G24	G25	G13
biooil	110	930	70	70	90	90	60
SDF	70	530	40	40	60	60	40
DME	110	920	70	70	90	90	60
E85	90	760	50	50	80	80	50
SVO	60	500	40	40	50	50	30
biodiesel	70	540	40	40	60	60	40
HVO	70	520	40	40	50	50	40
Eo1	60	500	40	40	50	50	30

Figure 7.1: Estimated fuel consumption per year at the different gas turbines for the various fuels. Lower end of the consumption interval

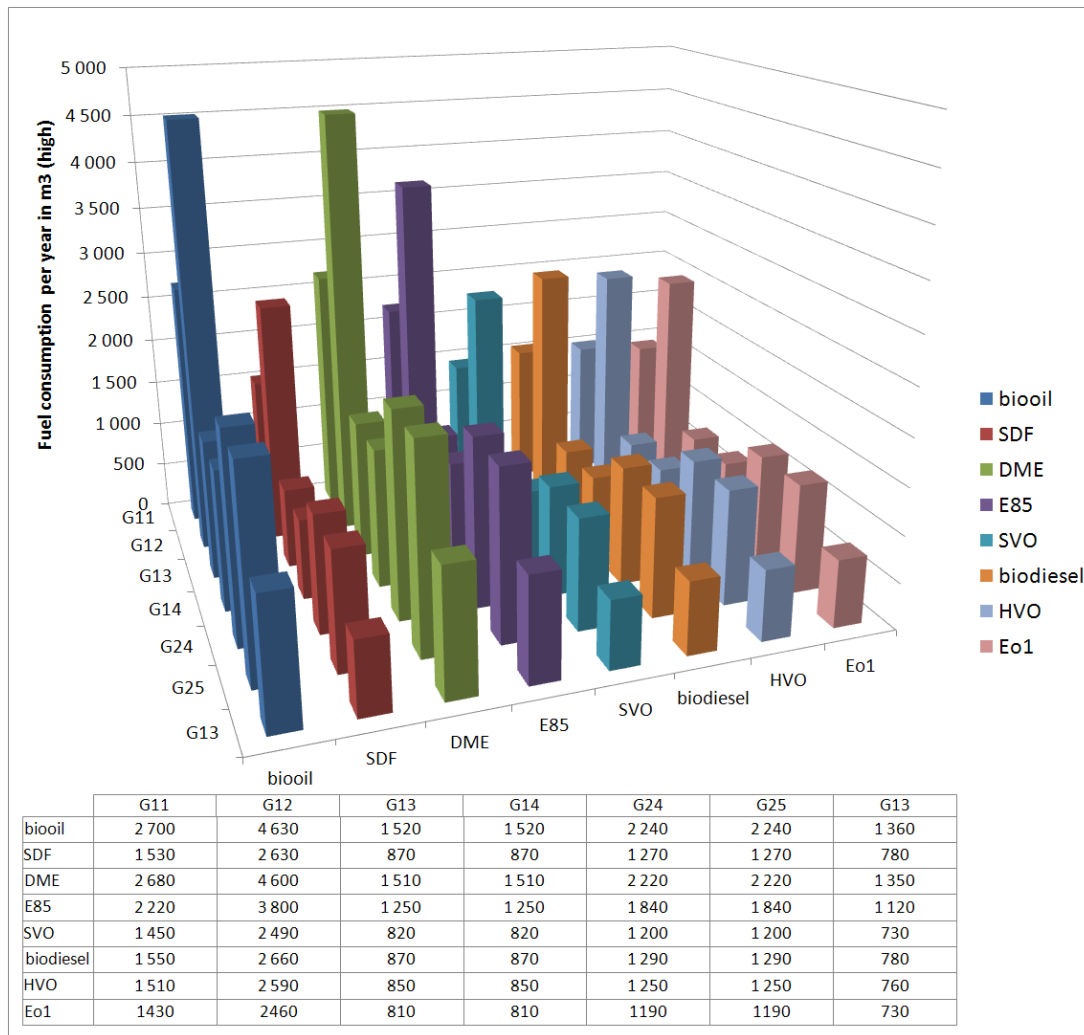|	G11	G12	G13	G14	G24	G25	G13
biooil	2 700	4 630	1 520	1 520	2 240	2 240	1 360
SDF	1 530	2 630	870	870	1 270	1 270	780
DME	2 680	4 600	1 510	1 510	2 220	2 220	1 350
E85	2 220	3 800	1 250	1 250	1 840	1 840	1 120
SVO	1 450	2 490	820	820	1 200	1 200	730
biodiesel	1 550	2 660	870	870	1 290	1 290	780
HVO	1 510	2 590	850	850	1 250	1 250	760
Eo1	1 430	2 460	810	810	1 190	1 190	730

Figure 7.2: Estimated fuel consumption per year at the different gas turbines for the various fuels. Higher end of the consumption interval

7.2 Viscosity

As seen in chapter 4, to be able to perform a suitable combustion process in the combustion chamber in a gas turbine, proper atomization is essential. Also shown in chapter 4, is the importance of viscosity for the ability to properly atomize the fuel. A high viscosity could result in improper atomization and it is shown in chapter 3 that preheating of the fuel could be utilized to deal with this.

Two of the fuels show very high values of viscosity; biooil and straight vegetable oil. The viscosity of biodiesel is just above the limit, see appendix B, # 3g. Storing biodiesel at a bit higher temperature could be enough to lower the viscosity below the limit. The other two, biooil and SVO would have to be heated using a preheater, upstream the atomizer.

According to chapter 3, biooil could be pre-heated to 95°C without starting to deteriorate, and SVO has been heated to 120°C in a MGT test. This would require preheaters that can handle these volumes and the energy amounts needed. Besides the investment cost of preheaters, the energy used in the preheaters will also add a cost, when in operation.

To calculate the cost of the pre-heating energy, the mass flow in kg/s of the fuels are needed. This is presented as tons per hour in chapter 5, those number need to be divided by 3.6 as in

Tab. 7.2 Also the substances specific heat capacity is needed. According to an internet source

Table 7.2: Mass flow at max load. biooil and vegetable oil as fuel

Location		Mass flow in kg/s	
		Biooil	Vegetable oil
Halmstad	G11	17.8	7.4
	G12	30.6	12.6
Barsebäck	G13	10.0	4.1
	G14	10.0	4.1
Malmö	G24	14.8	6.1
	G25	14.8	6.1
Karlshamn	G13	9.0	3.7

- *engineeringtoolbox* [101] - vegetable oil has a specific heat capacity of 1.67 kJ/(kg·K). Since biooil contains a lot more water, between 15-30 %, and that water has a specific heat capacity close to 4, a fair guess would be that the heat capacity for biooil would be somewhere between 1.67 and 4. According to Anil Goteti, a mean value of the specific heat capacity of biooil would be 2.4 (with a standard deviation of 0.8 using a model and 1 million iterations) [102].

The number of degrees needed to pre-heat depends on what temperature the fuel has entering the preheater. Assuming well isolated piping, the temperature of the fuel entering the preheater would be similar to the temperature of the fuel inside the tank. This needs to be at least 20 degrees above CFPP not to run into problems with filters plugging [103].

The pour points of biooil and vegetable oil respectively, are, -17.3°C and -19.6°C. There is no data of the respective CFPP, but the cloud point of vegetable oil is 7.6°C, which is the temperature when precipitations of waxes are starting to show in the liquid. At that temperature any abberation like local cold areas due e.g. to the pressure difference over a filter could cause precipitation of waxes. That in turn means that the temperature in the tanks has to be kept well above that limit.

André Norberg at E.ON Värme mentions that they keep a temperature of 40°C in their tanks with vegetable oil. E.ON Värme uses a vegetable oil as substitute for Eo5, which means that it can have properties a bit cruder than fuels substituting Eo1. That in turn means that the cold flow properties could be a bit worse. If the vegetable oil is stored at 30°C, the needed pre-heating energy will hopefully not be underestimated.

In the case of the biooil it is important to keep the storing temperature low due to increased rate of aging with temperature. In Anton Wetterstrands work he calculates that the preheater capacity should be "T_{in}=10°C and T_{out}=60°C" [17]. This probably means that he considers 10°C to be an acceptable storing temperature.

The expression for the needed power in the preheaters is (7.1)

$$W_{ph} = \dot{m} \cdot c_p \cdot \Delta T [\frac{kg}{s} \frac{kJ}{kg \cdot K} K = kW]$$ (7.1)

where W_ph is the power needed in the preheater, $\dot{m}$ is the mass flow of fuel in the preheater, c_p is the specific heat capacity of the fuel and ΔT is the temperature difference between the inlet temperature and the outlet temperature of the fuel, in Kelvin. Using the above expression the energy needed in the respective preheaters are calculated and presented in Tab. 7.3

Table 7.3: Assumed power needed in preheaters using biooil and vegetable oil at the different sites at full load

Location		Power needed in preheater [kW]	
		Biooil	Vegetable oil
Halmstad	G11	3 700	1 200
	G12	6 300	1 900
Barsebäck	G13	2 100	700
	G14	2 100	700
Malmö	G24	3 100	1 000
	G25	3 100	1 000
Karlshamn	G13	1 900	600

7.3 Storability

Biooil is corrosive and so are both biodiesel and vegetable oil [103]. This means that they have to be stored in tanks constructed in such a way that they will not corrode. High corrosion resistance would be achieved with a tank in stainless steel. The prices of tanks in this material is on the other hand much higher than tanks made of standard metal. According to André Norberg at E.ON Värmekraft, they have had success storing vegetable oil in standard material tanks that were painted inside with corrosive resistant paint, and adds that at a life expectancy of 10-15 years, these kind of tanks are more affordable [103].

Norberg mentions, that one other important factor is to avoid any condensation inside the tanks, because this would increase the rate of the corrosion. To avoid condensation, good isolation of the mantle of the tank was applied to prevent any cold surfaces allowing condensation [103].

A reasonable volume of fuel to store at each turbine would be the upper limit of operating hours, perhaps with some buffert. This is on the other hand a financial risk. Several of the fuels have problems with aging. Biooil, vegetable oil and biodiesel show signs of aging already after a year (some distributors will not guarantee more than six month), deterioration in values of: viscosity, heating value and polymerization. This means that if fuel for fifty hours is stored, and the turbines only run for the very few hours that are in the lower end of the interval i.e. ten hours for G12 and two hours for the rest, large volumes of fuels have to be disposed of in some way.

One solution is to sell the redundant fuel to some energy company with access to a thermal power plant in which they can utilize the now degraded fuel in the boiler furnace. In that way, a fuel can be used with a higher efficiency than single cycle gas turbines, and they are not that picky about the fuel quality. This requires an agreement and arrangements for transportation and that the plant have storage space for this particular fuel. This type of arrangement creates a complexity in the system. An easier but probably less efficient way, and a solution that at the time for this writing is possible to examine financially, is to assume that at the date for fuel replacement, combust any redundant fuel in the gas turbines. Best scenario would be at a time with high electricity price and low fuel price

Dual fuel system

What if a dual-fuel system was applied? Both fossil fuel and alternative fuel at each site? The volume stored of alternative fuels would only have to apply to the lower number of hours per

year. If the turbines would have to run for more than this, they could be switched to run on fossil fuel. Separate tanks for fossil and biofuels would have to be used. The latter could be quite small, storing fuel needed for between two to ten hours of operation.

Again the LHV of the fuel would put restrictions on the biofuel used, since the gas turbines can only handle a change of mass flow of 10-15 %. Beyond this the gas turbines would have to be re-adjusted to the new conditions. This know-how is not kept in-house, external experts would have to be consulted, resulting in that the requirement of reliability would not be upheld. The procedure with two fuels could not be used with biooil, since the difference in mass flow is too large, but with both vegetable oil and biodiesel since they are close enough in LHV to Eo1.

If this approach is to be used, separate tanks for the alternative fuels are needed, although smaller in size than they would have been otherwise. Also separate fuel systems including pipes, valves, pumps and filters are needed.

Boiling point

One of the fuels, DME, is not a liquid under normal conditions. It must either be cooled below its boiling point or kept under pressure, 6.1 bars at room temperature. Small volumes (up to 400 m^3) are commonly stored under pressure, larger volumes are cooled.

Acidity

One of the fuels, biooil, is acidic. This means that it is corrosive at all temperatures in its liquid state. This in turns means that all material coming into contact with this liquid has to be corrosion resistant: tanks, pipes, filters, pump, valves etc. If the acidity adds to the total corrosiveness inside the HGP has not been studied.

7.4 Fuel contaminants

Sulfur

An increased sulfur content compared to Eo1 could lead to an increase in emissions of SO_x. But since the quality currently used has a typical value of sulfur of 410 ppm, which is the same as 0.041 %wt, this is more than any of the alternative fuels studied, see Tab. 2.10. This means that there is a low risk of increasing the emissions of SO_x combusting any of the alternative fuels.

Ash

If any of the fuels contain levels of ash higher than the current fuel, this could lead to an increased corrosion process in the HGP. The current fuel specification specifies that the amount of ash in the fuel shall be less than 10ppm. Four fuels make that limit; FT-fuels, DME, E85 and HVO. The use of these fuels in gas turbines will most likely not lead to either increased corrosion or an increase in other damages in the HGP.

Biodiesel comes relatively close to the upper limit of metallic contaminants, just seven (!) times higher. Both biooil and vegetable oil are relatively brimming with metallic contaminants (66 and 25 times more respectively) and the use of these as fuel in the gas turbines could lead to trouble as seen in chapter 4. This kind of failure is of course absolutely necessary to avoid. If any of these "high-risk"-fuels are used, there is a need to increase the rate of inspection and/or maintenance.

7.5 Summary of the fuels and their respective problems and suggested actions

Table 7.4: Compilation of liquid bio fuels and their different problems and suggested solutions

Fuel	Problematic property	Causing problems where?	Possible solution
Biooil	1.Low LHV	1.Fuel distribution	1.Increase size of piping and change fuel nozzles to cope with 3 times higher fuel flow
	2.Viscosity	2.Pumping and atomization	2.Heated tank and preheater in front of CC
	3.Acidity/Corrosivity	3.Storing	3.Stainless/corrosion protected material in cistern, piping, gaskets
	4.High ash content	4.Combustion chamber and turbine	4.Filtering ash, shorter inspection/maintenence interval
	5.Storage stability	5.Degrading fuel properties	5.Keep cistern cold and combust all heated fuel, high turn-over rate
Synthetic Diesel Fuel	None	-	-
Dimethyl ether	1.Low LHV	1.Fuel distribution	1.Increase size of piping and change fuel nozzles to cope with 50% higher fuel flow
	2.Low boiling point	2.Storing	2.Cooled storage cisterns or large pressure vessels
Ethanol	1.Low LHV	1.Fuel distribution	1.Increase size of piping and change fuel nozzles to cope with 50% higher fuel flow
Straight Vegetable Oil	1. Low LHV	1.Fuel distribution	1.Increase size of piping and change fuel nozzles to cope with 16% higher fuel flow
	2. Viscosity	3.Pumping and atomization	2.Heated tank and preheater in front of CC
	3.Corrosivity	2.Storing	3.Stainless/corrosion protected material in cistern, piping, gaskets
	4.High ash content	4.Combustion chamber and turbine	4.Filtering ash, shorter inspection/maintenence interval
	5.Storage stability	5.Degrading fuel properties	5.Keep cistern cold and combust all heated fuel, high turn-over rate
Biodiesel	1.Low LHV	1.Fuel distribution	1.Increase size of piping and change fuel nozzles to cope with 16% higher fuel flow
	2.Storage stability	2.Degrading fuel properties	2.Keep cistern cold and combust all heated fuel, high turn-over rate
Hydrogenated Vegetable Oil	None	-	-

Chapter 8

Economical calculations

The profit of a company is highly correlated to its costs. Therefore it is important to examine the financial aspects of changes in the company's operations. The outlook of this chapter is to examine the presumed costs related to a possible change to any of the renewable fuels discussed in earlier chapters.

Due to the various properties of the fuels, some of them require investments in material. This could be:

- storage tanks

- fuel systems (including piping, valves, pumps and filters)

- nozzles

- preheaters

Some of the fuels does not require any investments to be used. As explained earlier, SEA require some sort of material investment to grant green certificate, which means that changing to a fuel and not making any kind of investment in material is a procedure that would deny a subsidy like e.g. green certificate, to be issued.

The fuels come at various prices and due to the different LHV they are needed in various amounts at the sites. This could mean differences in locked up money in stored fuel. This also means a risk when it comes to the fuels that are suffering from changing properties due to ageing. These fuels needs to be renewed at least every year (some distributors only guarantee six month for unchanged properties, but in this examination is assumed stability of properties over a full year). This means losses whether the fuel is combusted in the turbines and the electricity is sold or whether the fuel is sold to another consumer.

Some of the fuels needs pre-heating before injected in the combustor. This could be solved using electrical preheaters. Such require electricity and this also adds a cost.

When switching to a sustainable fuel listed by SEA, the electricity could be granted a subsidy for as long as fifteen years. This means an income for every produced MWh.

8.1 Investments

There are several investments that are needed in order to use some of the fuels.

1. Biooil:

    (a) Corrosion resistive tanks

(b) Corrosion resistive fuel systems

(c) Nozzles

(d) Preheaters

2. DME:

(a) Either double hulled, cooled tanks or large pressure vessels

(b) Correctly sized fuel system

3. Vegetable oil:

(a) Corrosion resistive tanks

(b) Corrosion resistive fuel systems

(c) Preheaters

4. E85:

(a) Correctly sized fuel system

5. Biodiesel:

(a) Corrosion resistive tanks

Since it is stated above that three fuels suffer from ageing (biooil, vegetable oil and biodiesel), these fuels could possibly be stored for up to a year. To make calculations equal, all tank volumes are calculated considering one year of consumption in the higher end of operating hours per turbine, i.e. fifty hours.

Dimethylether needs to be stored in specialized tanks due to its low boiling point, either tanks that can cope with the pressure of DME in gas form or tanks that can keep DME at temperatures below its boiling point. Either way, these tanks are more expensive than standard fuel tanks, and since the cost of a tank is proportional to the size of the tank, it is preferred if the tanks could be made as small as possible. This means that the tank sizes are considered for fifty hours of operation, i.e. one year of operation in the higher end of the operation span.

8.1.1 Fuel tanks

Table 8.1: Storage volumes of fuels that needs separate tanks

Location	Biooil 50h [m^3]	DME 50h [m^3]	SVO 50h [m^3]	Biodiesel 50h [m^3]
Halmstad	7 300	7 300	3 940	4 210
Barsebäck	3 000	3 000	1 640	1 740
Malmö	4 500	4 500	2 400	2 580
Karlshamn	1 350	1 350	730	780

Biooil, straight vegetable oil and biodiesel need corrosion resistive tanks. Corrosion resistance can be achieved using stainless steel with the quality EN 1.4301/ASTM 304. Using [104] (the prices are from 2007 and quoted in $ and converted to SEK by the average dollar price of 2007), price estimate for a vertical tank with cone roof and flat bottoms is received. The prices

are compiled in Fig. 8.1. A red line in Fig. 8.1 marks the estimation made by Anton Wetterstrand [17] of a 8 000 m³ stainless steel tanks. It is obvious that the estimation is quite accurate.
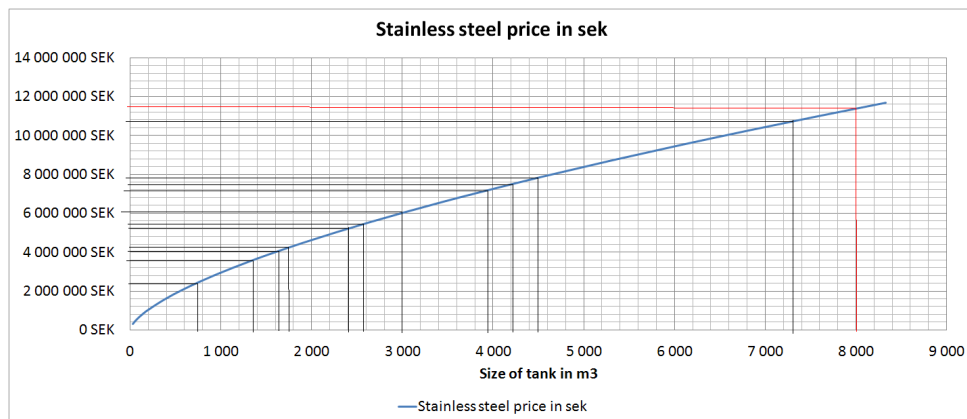

Figure 8.1: Price estimate of storage tanks in stainless steel quality 304

Corrosion resistance can also be achieved with carbon steel and some corrosion resistive lining on the inside of the tank. This was suggested by André Norberg at E.ON Värme. He has been involved in converting heat plants to bio fuels [103]. According to him a 150 m³ tank with corrosion resistive painting inside could be achieved for about 500 000 SEK. Using [104], there is no such tank to be considered. But there are price estimates for carbon steel tanks with anti-corrosion lining. André Norberg's price estimate fits right in between the price estimates of carbon steel tanks with lead and rubber lining. An average of these estimates were calculated as seen in Fig. 8.2. Dimethyl ether could be stored in double hulled, cooled tanks or in pressure
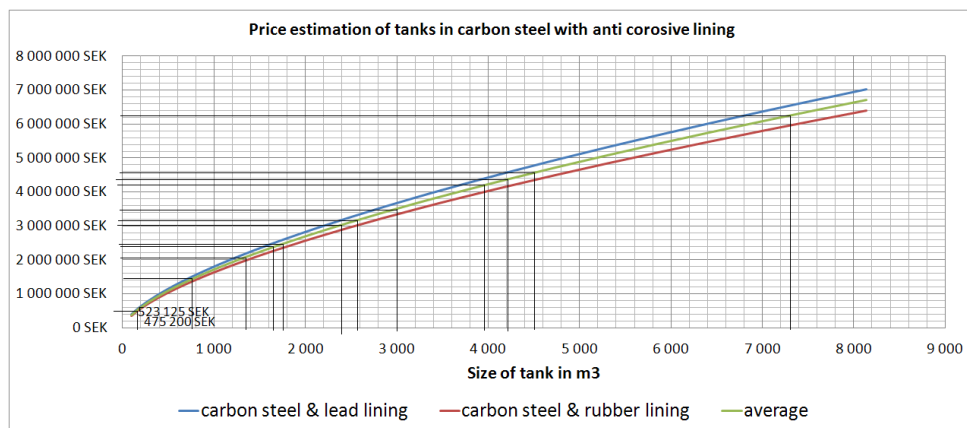

Figure 8.2: Price estimate of carbon steel tanks with corrosion resistive lining

vessels. According to Pär Hedendahl at Rodoverken [105] they recently built a cooled tank for Ethylene. It was a double hull, isolated 30 000 m³ tank and the price was about 80 million SEK. He guesses that a tank half that size would cost about 50 million SEK. With the same reasoning - half the size cost 5/8 of the price - would render a development as in Fig. 8.3. From Fig. 8.3 it is obvious that investing in a cooled tank will be very expensive.

Using [104] a price estimate for pressure vessels can be achieved. The mass of the vessel is calculated using (8.1) [106]

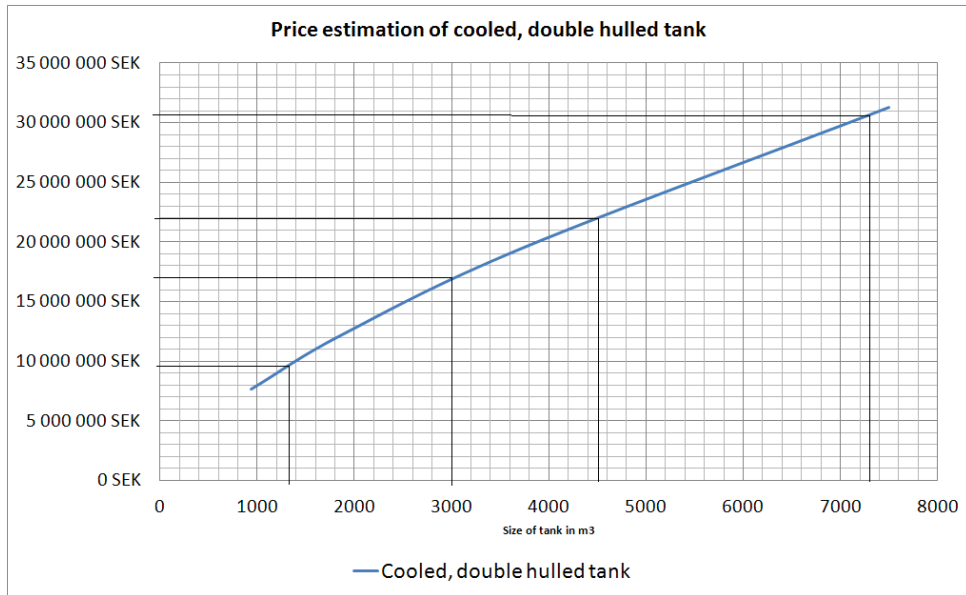$$M = \frac{3}{2} P V \frac{\rho}{\sigma} \tag{8.1}$$

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Figure 8.3: An estimate of costs of double hulled, cooled tanks for liquified gases
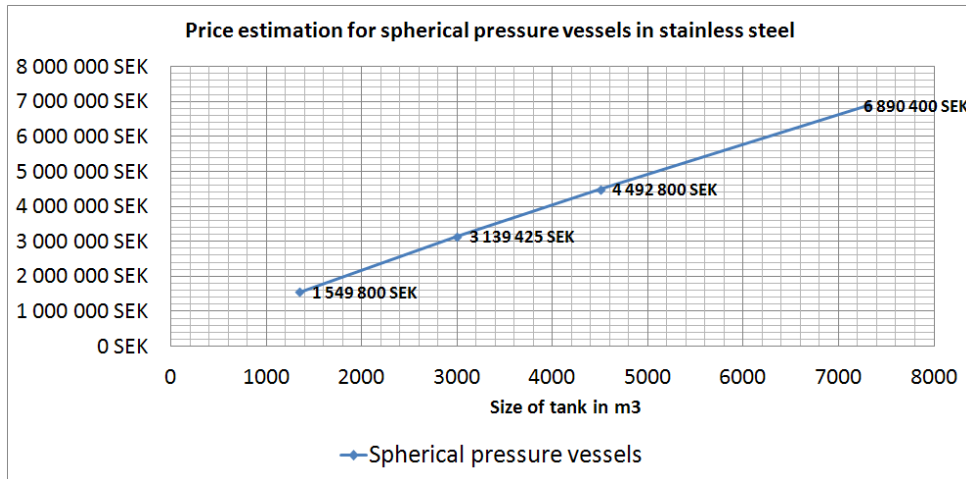

Figure 8.4: Price estimate of spherical pressure vessels in stainless steel

where M is the mass of the vessel, P is the pressure inside, V is the volume, ρ is the density of the material and σ is the maximal working stress that material can tolerate. To calculate the mass a density of 7 850 kg/m^3 was used and a maximum working stress of 400 MPa [107, 108]. From these data a price estimate was calculated and can be seen in Fig. 8.4

8.1.2 Fuel system

According to Fredrik Hermann a new fuel system with piping, pipe fitting, valves, filters and pumps would cost about seven hundred thousand €, roughly six million SEK for G12. In the case of G24 and G25 in Malmö this cost will be about four million SEK.

8.1.3 Nozzles

According to Fredrik Hermann new nozzles would cost about one million €, roughly eight million SEK per turbine.

8.1.4 Preheaters

Anton Wetterstrand assumed a price of a 1.5 MW preheater to 1 million SEK. Assuming a linear relationship between size/effect and the price, the price of a 6.3 MW preheater would be 4.2 million SEK, Tab. 8.2

Table 8.2: Estimated investment cost of preheaters in kSEK

Location		Biooil	Vegetable oil
Halmstad	G11	2 500	800
	G12	4 200	1 300
Barsebäck	G13	1 400	500
	G14	1 400	500
Malmö	G24	2 100	700
	G25	2 100	700
Karlshamn	G13	1 300	400

8.2 Possible losses due to ageing of fuels

The ageing of some of the fuels could also mean an economical loss. For example, if fuel for forty hours of operation is left at G12 when it is time to change the fuel and assuming that the leftover fuel is combusted in the GT.

Forty hours of operation means an output of electricity of $40 \cdot 172 \ MW = 6 \ 880 \ MWh$. The mean price (weekly spot notations [109]) per MWh from 2011 was 403.57 SEK. This gives a revenue of $\sim 2\ 780\ 000$ SEK. If biooil was used, forty hours of operation means 3 704 m³, which in turn means 4 445 tons. The price of that amount of fuel will be roughly 7.6 MSEK and a total economical loss of about 4.8 MSEK.

8.3 Electricity cost preheaters

The price of electricity is determined on a spot market, *Nordpool*. The price varies from day to day. To get a rough estimate of the price on electricity in the future, a mean value of historic prices are used.

The mean price (weekly spot notations [109]) per MWh from 2011 was 403.57 SEK. This gives 0.404 SEK/KWh. This gives the costs for pre-heating as presented in Tab. 8.3

8.4 Possible subsidies

In Tab. 8.4 is listed the possible revenue from the green certificate system. Since biooil, SVO and biodiesel all needs to be completely renewed after every year, these fuels receive the same amount of subsidy regardless of contracted production. Ethanol, which is only renewable to

Table 8.3: Estimated cost of the energy used in pre-heating in MSEK

	Biooil	SVO
Halmstad	0.2	0.06
Barsebäck	0.08	0.03
Malmö	0.12	0.04
Karlshamn	0.04	0.01

85 % will only get 85 % of the subsidy. HVO does not receive green certificate since no investments are needed for this to be used and we assume that no investment is made ??unnecessarily.

Table 8.4: Estimated revenue from subsidies for using renewable fuel for electricity production in MSEK

		Biooil	DME	Ethanol	SVO	Biodiesel	HVO
Halmstad	Min	2.48	0.37	0.32	2.48	2.48	
	Max	2.48	2.48	2.11	2.48	2.48	
Barsebäck	Min	0.83	0.03	0.03	0.83	0.83	
	Max	0.83	0.83	0.71	0.83	0.83	
Malmö	Min	1.25	0.05	0.04	1.25	1.25	
	Max	1.25	1.25	1.06	1.25	1.25	
Karlshamn	Min	0.37	0.01	0.01	0.37	0.37	
	Max	0.37	0.37	0.31	0.37	0.37	

8.5   Case study: Halmstadverket, HVT

This section will deal with just a single turbine site and lay out the economical consequences when using the different fuels discussed. The turbine site chosen is Halmstadverket. This is the site with the turbine with most operating hours per year and the two turbines with highest electricity output. It has the highest fuel consumption per year and as such, if a fuel is to be making any kind of cost reduction, this is where it will happen.

We assume that, the fuel stored per site, at least has to cover the maximum operating hours per year, i.e. fifty hours and that the fuels that suffers from ageing need to be renewed after a year. We further assume that, any leftover fuel at the date for replacing the stock, is combusted in the gas turbines and that the produced electricity is sold on the spot market to the previously assumed average price.

First is listed the kind of investments needed for the various fuels and the estimated cost of those, in Tab. 8.5

Table 8.5: Summary of investments for various fuels and their respective costs in MSEK

	Biooil	DME	Ethanol	SVO	Biodiesel	HVO
Tank	6.1	6.9	-	4.2	4.4	-
Fuel system	12	12	12	12	12	-
Nozzles	16	16	-	-	-	-
Preheaters	6.7	-	-	2.1	-	-
Total cost investment	40.8	34.9	12	18.3	16.4	0

To this comes the cost of energy for pre-heating. From Tab. 8.6 it is obvious that this cost is marginal. The pre-heating is only a subject for biooil and straight vegetable oil.

Table 8.6: Cost of pre-heating per year in MSEK

Biooil	DME	Ethanol	SVO	Biodiesel	HVO
0.200	-	-	0.062	-	

Now we come upon a paradox - the fuel cost. If the turbines run for maximum hours according to contract with Svenska Kraftnät, E.ON can save money using a cheaper fuel. But if the turbines run for minimum contracted hours per year, there is an increased cost of using the fuels that suffers from ageing because these fuels needs to be consumed after a year, whether it is by Svenska Kraftnät or not. This can be seen in Tab. 8.7.

Table 8.7: Cost of fuels compared to using current fuel in MSEK

	Biooil	DME	Ethanol	SVO	Biodiesel	HVO
Max hours of operation	-5.7	23.7	18.8	1.0	16.5	18.1
Min hours of operation	12.0	3.3	2.6	18.7	34.2	2.5

If the fuels are consumed in the turbines as a result of the fact that they are ageing and as such need to be renewed after a year, they of course generate some electricity. This electricity can be sold on the spot market. The price of electricity is 403.57 SEK/MWh as accounted for above. The result of this generates an income as listed in Tab. 8.8 where we are assuming worst case, i.e. lowest contracted production (two hours in G11 and ten hours in G12, resulting in fuel for 48 hours of production in G11 and 40 hours of production in G12 left for use by E.ON).

Table 8.8: Income from production using leftover fuels of worst case scenario in contracted production in MSEK

Biooil	DME	Ethanol	SVO	Biodiesel	HVO
4.3	-	-	4.3	4.3	-

When producing electricity with renewable fuels SEA can grant green certificate. The value of this is 198.5 SEK/MWh as accounted for above. If no investment is done, no certificate is issued, as is the case for HVO. Ethanol will only get 85% since it is only renewable to 85%. The fuels that suffer from ageing are not affected by the number of contracted hours. The result is presented in Tab. 8.9 Combining fuel cost, pre-heating cost, income from electricity

Table 8.9: Income from green certificate in MSEK

	Biooil	DME	Ethanol	SVO	Biodiesel	HVO
Max	2.5	2.5	2.2	2.5	2.5	-
Min	2.5	0.38	0.32	2.5	2.5	-

production when not running by contract and income from green certificate the resulting figures are presented in Tab. 8.10

Table 8.10: Combined fuel cost, pre-heating cost, income from production of electricity outside contract and green certificate in MSEK

	Biooil	DME	Ethanol	SVO	Biodiesel	HVO
Max hours of operation	-7.9	21.3	16.7	-1.4	14.1	18.1
Min hours of operation	5.5	3.0	2.3	12.0	27.5	2.5

Economically there are two fuels that have the potential of lowering the cost annually, biooil and straight vegetable oils. On the other hand, they both suffer from ageing and as such need to be renewed in stock after a year. This means that in worst case scenario, there are a lot of fuel that needs to be combusted in the turbines at great economical loss. For biooil this loss can reach 5.5 MSEK per year and in the case of SVO 12 MSEK per year. These numbers includes income from green certificate and selling produced electricity.

Assuming best case scenario, will the reduced cost cover for the investments of 40.8 MSEK and 18.3 MSEK respectively? Using the economical model of *Net Present Value*, NPV, a life-time expectancy of 15 years (the green certificate is only granted for 15 years, after this new investments are needed), a discount rate of 6 % and 12 % (just to get some alternatives) and maximum of cost reduction for biooil and SVO, the result can be seen in Tab. 8.11

Table 8.11: Net present value of estimated incomes from best case scenario in MSEK (rounding errors creating inconsistencies)

Year	Biooil	SVO	Year	Biooil	SVO
	6 %			12 %	
1	7.9	1.4	1	7.9	1.4
2	15.4	2.8	2	15.0	2.7
3	22.5	4.1	3	21.4	3.9
4	29.2	5.3	4	27.0	4.9
5	35.5	6.4	5	32.1	5.8
6	41.4	7.5	6	36.6	6.6
7	47.0	8.5	7	40.6	7.3
8	52.3	9.4	8	44.2	8.0
9	57.3	10.3	9	47.4	8.6
10	62.0	11.2	10	50.3	9.1
11	66.4	12.0	11	52.9	9.5
12	70.6	12.7	12	55.1	10.0
13	74.6	13.5	13	57.2	10.3
14	78.3	14.1	14	59.0	10.7
15	81.8	14.8	15	60.6	10.9

As seen in Tab. 8.11, biooil has the potential to pay for the investments made after just six years with a discount rate of 6 % and seven years with a discount rate of 12 %. Straight vegetable oils will not pay back the investments made within 15 years, and since the green certificate only lasts for 15 years, using SVO after this increases the costs by a million SEK per year.

This is putting the focus on biooil. How many hours per year must the turbines at Halmstad-verket run according to contract for the investments to be paid within 15 years? When getting a cost reduction of 3.96 and 5.35 MSEK respectively every year the calculations look like Tab. 8.12. How many hours must the turbines at Halmstadverket run by contract to generate a cost

Table 8.12: Net present value using an average cost reduction every year by 3.96 and 5.35 MSEK respectively for 6 and 12 % discount rate

year	3.96 MSEK, 6 %	5.35 MSEK, 12 %
1	4.0	5.4
2	7.7	10.1
3	11.2	14.4
4	14.5	18.2
5	17.7	21.6
6	20.6	24.6
7	23.4	27.3
8	26.1	29.8
9	28.6	31.9
10	30.9	33.9
11	33.1	35.6
12	35.2	37.1
13	37.2	38.5
14	39.0	39.7
15	40.8	40.8

reduction of 3.96 and 5.35 MSEK per year is listed in Tab. 8.13. It is seen in Tab. 8.13 that both turbines need to run at least 38 hours per year (with a discount rate of 6 %) or 42 hours per year (with a discount rate of 12 %) for the cost reductions to cover the investments made in tanks, fuel system, nozzles and preheaters.

Table 8.13: Estimating number of hours per year both turbines at Halmstadverket must run in order to reach a cost reduction of 3.96 MSEK and 5.35 MSEK respectively, per year

hours	Cost of biooil	Cost of Eo1	Income from produced electricity	Income from green certificate	Cost of energy in pre-heaters	Cost diff from running on Eo1
10	14.9	4.1	4.0	2.5	0.2	4.50
11	14.9	4.5	3.9	2.5	0.2	4.19
12	14.9	4.9	3.8	2.5	0.2	3.88
13	14.9	5.4	3.7	2.5	0.2	3.57
14	14.9	5.8	3.6	2.5	0.2	3.25
15	14.9	6.2	3.5	2.5	0.2	2.94
16	14.9	6.6	3.4	2.5	0.2	2.63
17	14.9	7.0	3.3	2.5	0.2	2.32
18	14.9	7.4	3.2	2.5	0.2	2.01
19	14.9	7.8	3.1	2.5	0.2	1.70
20	14.9	8.2	3.0	2.5	0.2	1.39
21	14.9	8.7	2.9	2.5	0.2	1.08
22	14.9	9.1	2.8	2.5	0.2	0.76
23	14.9	9.5	2.7	2.5	0.2	0.45
24	14.9	9.9	2.6	2.5	0.2	0.14
25	14.9	10.3	2.5	2.5	0.2	-0.17
26	14.9	10.7	2.4	2.5	0.2	-0.48
27	14.9	11.1	2.3	2.5	0.2	-0.79
28	14.9	11.5	2.2	2.5	0.2	-1.10
29	14.9	11.9	2.1	2.5	0.2	-1.41
30	14.9	12.4	2.0	2.5	0.2	-1.72
31	14.9	12.8	1.9	2.5	0.2	-2.04
32	14.9	13.2	1.8	2.5	0.2	-2.35
33	14.9	13.6	1.7	2.5	0.2	-2.66
34	14.9	14.0	1.6	2.5	0.2	-2.97
35	14.9	14.4	1.5	2.5	0.2	-3.28
36	14.9	14.8	1.4	2.5	0.2	-3.59
37	14.9	15.2	1.3	2.5	0.2	-3.90
38	14.9	15.7	1.2	2.5	0.2	-4.21
39	14.9	16.1	1.1	2.5	0.2	-4.53
40	14.9	16.5	1.0	2.5	0.2	-4.84
41	14.9	16.9	0.9	2.5	0.2	-5.15
42	14.9	17.3	0.8	2.5	0.2	-5.46

Chapter 9

Results

Biooil

Even though biooil has the problems with high viscosity, low LHV, ageing, acidity, and high ash content it can technically be used in gas turbines. At Halmstadverket, investments and cost reductions will break even over a 15 year time period if the turbines run for at least 38 (42) hours per year according to contract with Svenska Kraftnät. Then the machines would have been in production with biooil for 570 (630) hours, and this many hours would probably not lead to any major issues inside the turbines, considering corrosiveness. And perhaps some inspection within these 15 years could straighten any question marks about the health of the turbines.

The biggest doubts lies in the assumptions that the fuel will keep its properties for 12 month. What will actually happen with the fuel when stored and can distributors actually guarantee quality over time.

And right now there are no biooil approved by SEA for green certificate which adds a problem.

Fischer-Tropsch fuel

Fischer-Tropsch fuels would probably be a good alternative to use in the gas turbines, in all aspects, according to section 3.2. Using this sort of fuel would probably lower emissions of PM, CO, UHC, NO_x and sulfur oxides. There was no evidence of ignition problems either. The only problem with this fuel seems to be that it is not available on the Swedish market and that no company has applied for approval of sustainability for any such fuel.

Another aspect is that E.ON Värmekraft probably could choose to import this type of fuel from an external (with respect to Sweden) distributor and apply for sustainability approval for this fuel. By doing this, this type of fuel would have been made available and comply with the purchasing amendment.

Dimethyl ether

Dimethyl ether has in studies shown to be a appropriate fuel for gas turbines, but probably as a substitute for natural gas rather than liquid fuel. Its emission characteristics seems to be decent.

The problem is with the material investments due to the low boiling point of DME. It can either be stored in small volumes in pressure vessels, or cooled to a liquid in isolated, double hulled cooling tanks, and it is the latter that is quite economically demanding. Using pressure

vessels, the investments needed is about the same size as SVO, but due to the high price of DME, it will never be economically viable.

Ethanol

Bio-ethanol is distributed in Sweden as a substitute for petrol and goes by the name of E85, 85 % ethanol and 15 % petrol. This means that if it were used as fuel to produce electricity and that the production would be granted the subsidy green certificate, it would only be for 85 % of the production. The studies in chapter 3 show very good emission characteristics for ethanol but it can be tricky to store, partly because of its miscibility with water and the electrical conductivity, partly because of the low flash point temperature which is $13°C$. Economically it is the second most expensive fuel in this study, the high price mainly due to its main use as alternative vehicle fuel.

Straight vegetable oil

Vegetable oils suffers from the same issues as biooil, except that it has a similar LHV as current fuel. It to, as biooil, suffers from high viscosity and degradation due to ageing. Due to the price it it lowers the operational costs but over a 15 year time period it does not break even with investments made, at least not at Halmstadverket.

Biodiesel

Another fuel suffering from ageing is biodiesel. This means that if used, the leftover fuel has to be replaced every year, which leads to economical losses. It is also on the high limit of viscosity which could prevent proper evaporation, already proven to be an issue due to the lack of volatiles in biodiesel, as seen in chapter 3. The lack of volatiles can also be a problem at cold startup. It was shown to work fine at $15°C$, but questions were raised about the ignition ability. As the disturbance reserve is supposed to work all year, especially at the coldest days of the year, this could be a problem in the case where the combustion is spark ignited. Economically it is a bit more expensive than SVO and the cost and investments needed makes it unfit for use.

Hydrotreated vegetable oil

Hydrotreated vegetable oils are not suffering from the problems afflicting the other fuels. It is low in viscosity, it has a high LHV, and the sulfur and other contaminants are also within limits. It can be used in the current tanks and even blended with the current fuel. It is stated not to suffer from ageing, although it has only been tested for about four years. The emissions from the studies in chapter 3 are good and the only question is the price. It is already the most expensive fuel and it is quite new on the market.

Chapter 10

Discussion

In the case study it is proven that biooil can be an economically feasible fuel. But there are large investments to be covered by the decrease in cost that biooil can produce. There are many assumptions and requirements for that calculation to be valid.

If investments in the order of tenth of million SEK is discouraging, there is only two fuels; FT-fuels and HVO's. But since no FT-fuel is approved for sustainability, only HVO's are relevant. HVO's have proven to be a competitive fuel in jet applications, but very expensive. If oil from algae is ever industrialized (the oil revenue from algae is tenfold that of the best oil crop) we might see a true opening for liquid biofuels as an alternative to fossil fuel.

There are many assumptions made in this report, one of the more crucial is the production hours per year which the whole cost analysis is based on. If this fails, the results fails to. Another assumption is the upholding of the agreement with Svenska Kraftnät. If this agreement is ever ended, biooil could again be a feasible fuel.

Another issue based on the production hours is the absence of discussion about corrosion in the turbine. Based on the very few hours of production per year, a time span of 15 years with the most corrosive fuels one could find would not pose a problem.

Chapter 11

Recommendations

Since Biooil is the only liquid biofuel that is making any cost reduction that can cover for the probable investments made, the main focus in the economical calculations is put on this fuel. It is a fuel with many property difficulties, that technology can make up for. This is of course costly and the investments can be profitable under certain circumstances. These circumstances are quite unlikely. For example the number of hours per year that the GT's will have to run, 38 of the maximal 50. Therefore will my recommendations be, due to the assumptions made in this study, that no conversion to any biofuel should be made in the gas turbines studied.

There can be other aspects that possibly could make up for the financial risks, i.e. good will and media coverage. But the possible effects of these aspects were never the aim of this study, therefore I will leave it at that.

Appendices

Appendix A

Introduction to gas turbines

A picture of a so called Brayton cycle can be seen in Figure A.1.
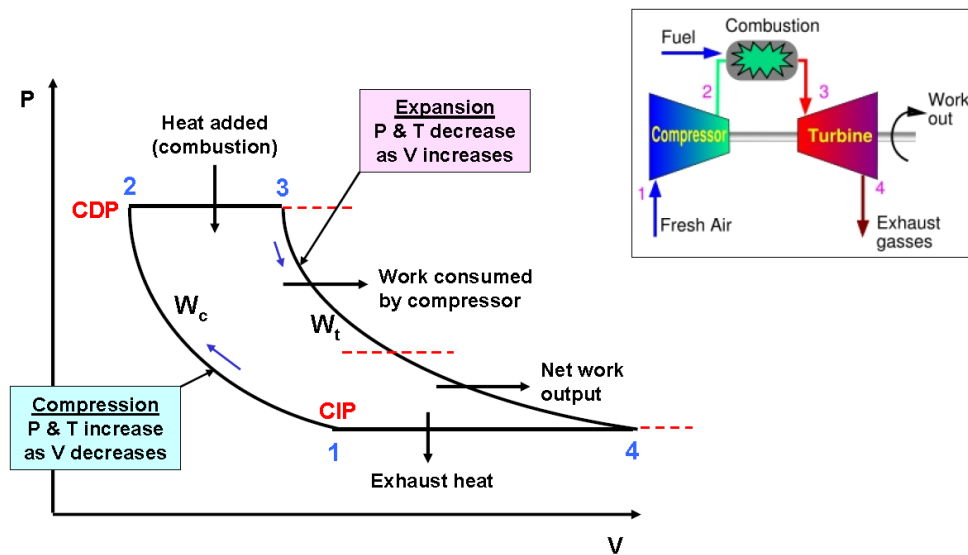
Figure A.1: Brayton simple cycle [78]

At point 1 in Figure A.1, ambient air is sucked into the compressor which increases the pressure of the air from point 1 to point 2. Energy is added in form of heat in the combustor by burning a fuel. This increases the volume of the compressed air, now combustion gases, from point 2 to point 3. The hot gases is expanded over the turbine from 3 to 4. This energy is used to power the compressor via the horizontal axis. What is left of the energy in the combustion gases are work out.

The electric energy output will not be the same amount as the input of heat energy by the fuel. Depending on various losses here and there and the efficiency of the various parts the total efficiency will vary from 25 % to 35 % (common values for gas turbines from the 60s to early 90s), i.e. if the gas turbine combusts fuel of 100 MW, the power output will be 25 MW to 35 MW depending on the efficiency.

Appendix B

Questionnaire to companies

Based on the requirements to the supplier statued by E.ON Värmkekraft, a questionnaire was constructed to be sent to suppliers of alternative fuels. The questionnaire was formulated in Swedish and presented here in a non-translated form.

1. Vilka flytande biobränslen för ni?

2. Vilka av ovan nämnda bränslen kan ni leverera minst 10,000 (tiotusen) ton per år av?

3. Vilka av ovan nämnda bränslen klarar uppfylla följande krav:

    (a) Askans vidhäftningstemperatur (°C) >900

    (b) Metallinnehåll (mg/kg)

        - Kalium < 0.1
        - Kalcium < 0.1
        - Bly< 0.1
        - Zink < 0.1
        - Nickel < 0.5
        - Koppar < 0.02
        - Litium < 0.1
        - Natrium < 0.1
        - Vanadin < 0.1

    (c) Askhalt (mg/kg) < 10

    (d) Svavelinnehåll (mass%) <0.05

    (e) Flampunkt (°C) > 56

    (f) Grumlingspunkt (°C) < 0

    (g) Viskositet(@ 40°C, cSt) 1.5 - 3.5

    (h) Densitet (@ 15°C, g/cm^3) 0.81 - 0.86

    (i) Oxidationsstabilitet (g/m^3) < 2.5

    (j) Organiska klorföreningar (mg/kg) < 2

    (k) Bromtal < 5

4. Om avvikelse från ovan angiven specifikation, vad och hur mycket?

5. Vilket värmevärde har ovan nämnda bränslen (MJ/kg)?

6. Ungefärligt dagspris per ton, på ovan angivna bränslen?

7. Hur uppfyller ovan angivna bränslen hållbarhetskriterier uppställda från energimyndigheten?

8. Vilka garantier för lagerhållning över tid lämnar ni för nämnda bränslen? Vilka förändringar kan man räkna med vid längre lagerhållning?

9. Hur bör bränslet lagras för att minimera förändringar och finns det några andra aspekter att tänka på vid lagerhållning och hantering?

Appendix C

General pricing estimation

The average price of diesel the last year, according to the official statistics available on the homepage of Statiol, has been 14.75 SEK/litre. Companies does not pay VAT which means that this could be deduced from the price. The VAT is a supplement charge of 25 % on the price to private end users. This means that the price is down to 11.80 SEK/litre.

Then deducing a margin of 70 öre per litre gives 11.10 SEK/litre. This means that the price per energy content, using data from Preem (product information, Diesel mk1), ρ=0.818 and LHV=42.9MJ/kg, 1 140 SEK/MWh, see (C.1).

$$\frac{11.10 \text{ SEK}/l}{0.818 \ kg/l} = 13.57 \text{ SEK}/kg$$

$$\frac{3600}{42.9} \cdot 13.57 \approx 1 \ 140 \text{ SEK}/MWh \tag{C.1}$$

C.1 Conversion from price per volume or mass to price per MWh

One MWh is the same as 3600 MJ (C.2)

$$1MWh = 1\frac{MJ}{s} \cdot 3600s = 3600MJ \tag{C.2}$$

The the fuels LHV is used lets say it is 42.9 MJ/kg (C.3)

$$\frac{3600MJ}{42.9MJ/kg} = 83.96kg \tag{C.3}$$

that is, 83.96 kg of this fuel contains equal energy of 1 MWh. If the price per mass were known this could be multiplied with the required amount (83.96 kg) and we would have the price per MWh. If the price is defined per volume, e.g. 6.43 sek/litre we need utilizing the fuels density, lets say it is 0.82 kg/litre, then (C.4) gives the price per mass (kg).

$$\frac{6.43 \ sek/l}{0.82 \ kg/l} \approx 7.84 \ sek/kg \tag{C.4}$$

this in turn gives the price of $\approx$658 sek/MWh.

Bibliography

[1] E.ON. 2010. Pressmeddelanden. *E.ONs gasturbiner kan rycka ut vid akut brist på el i Sverige.*
http://www.eon.se/om-eon/Press/Pressmeddelanden/Pressmeddelanden-2010/EONs-gasturbiner-kan-rycka-in-vid-akut-brist-pa-el-i-Sverige/(Retrieved 2012-04-12).

[2] Olsson, O. Fuel development manager, Project & Development, E.ON Värmekraft Sverige AB. Private communication 2012-02-06.

[3] *Energistrategi För Malmö.* Approved by the municipal council 2009-12-17.

[4] Glassman, I. Yetter, R. A. *Combustion (Fourth Edition).* Elsevier Inc., 2008.

[5] Lefebvre, A. H. *Atomization and Sprays.* Taylor & Francis, 1989.

[6] Hermann, F. Acting head of Gas Turbines. E.ON Värmekraft. Private communication. 2012.

[7] Juste López, G. Salva Monfort, J. J. *Preliminary Test on Combustion of Wood Derived Fast Pyrolysis Oils in a Gas Turbine Combustor.* Biomass and Bioenergy 19 (2000) 119-128.

[8] Ghosh, T. K. Prelas, M. A. *Energy Resources and Systems.* Springer, 2011.

[9] Chen, F. Dixon, R. A. *Lignin Modification Improves Fermentable Sugar Yields for Biofuel Production.* Natural Biotechnology 25 (2007) 759-761.

[10] Bridgewater, T. *Review: Biomass for Energy.* Journal of the Science for Food and Agriculture 86 (2006) 1755-1768.

[11] Carroll, A. Sommerville, C. *Cellulosic Biofuels.* Annual Review of Plant Biology 60 (2009) 165-182.

[12] Huber, G. W. Iborra, S. Corma, A. *Synthesis of Transportation Fuels from Biomass:Chemistry, Catalysts and Engineering.* Chemical Review 106 (2006) 4044-4098.

[13] Gupta, K.K. Rehman, A. Sarviya, R.M. *Bio-fuels for the Gas Turbine: A review.* Renewable and Sustainable Energy Reviews 14 (2010) 2946-2955.

[14] Strömberg, B. Herstad Svärd, S. *Handbook of Fuels 2012[Bränslehandboken 2012].* Värmeforsk, 2012.

[15] Demirbas, A. *Biofuels - Securing the Planet's Future Energy Needs.* Springer, 2009.

[16] Czernik, S. Bridgewater, A. V. *Overview of Applications of Biomass Fast Pyrolysis Oil.* Energy & Fuels 18 (2004) 590-598.

[17] Wetterstrand, A. *Introducing Pyrolysis Oil as Fuel in Karlshamn Power Station.* Master Thesis. Lund University, 2010.

[18] Lupandin, V. Thamburaj, R. Nikolayev, A. *Test Results of the OGT2005 Gas Turbine Engine Running on Alternative Fuels: Biooil, Ethanol, Biodiesel and Crude oil.* Proceedings of GT2005, ASME Turboexpo 2005.

[19] Chiaramonti, D. Oasmaa, A. Solantausta, Y. *Power Generation using Fast Pyrolysis Liquids from Biomass.* Renewable & Sustainable Energy Reviews (2007) 1056-1086.

[20] Boucher, M. E. Chaala, A. Roy, C. *Bio-oils obtained by vacuum pytolysis of softwood bark as a liquid fuel for gas turbines. Part I: Properties of bio-oil and its blends with methanol and a pyrolytic aqueous phase.* Biomass and Bioenergy (2000) 337-350.

[21] Wikipedia. 2012. *http://en.wikipedia.org/wiki/Fischer%E2%80%93Tropsch_process (Retrieved 2012-09-10).*

[22] Keshav, T. R. Basu, S. *Gas-to-liquid technologies: India's perspective.* Fuel Processing Technology 88 (2007) 493-500.

[23] Lapuerta et al. *Key properties and blending strategies of hydrotreated vegetable oil as biofuel for diesel engines.* Fuel Processing Technology 92 (2011) 2406-2411.

[24] Eliseev, O. L. *Gas-to-Liquid Technologies.* Russian Journal of General Chemistry 79 (2009) 2509-2519.

[25] Wikipedia. 2012. *http://en.wikipedia.org/wiki/Cracking_(chemistry) (Retrieved 2012-09-11).*

[26] Kalnes et al. *A tedhnoeconomic and environmental life cycle comparison of green diesel to biodiesel and syndiesel.* Environmental Progress & Sustainable Energy Vol.28, No.1 (2009) 111-120.

[27] Timko et al. *Particulate emissions of a gas turbine engine combustion of a Fischer-Tropsch synthetic fuel.* Energy & Fuels 24 (2010) 5883-5896.

[28] Corporan et al. *Emissions characteristics of a turbine engine and research combustor burning a Fischer-Tropsch jet fuel.* Energy & Fuels 21 (2007) 2615-2626.

[29] Cocco, D. Tola, V. Cau, G. *Performance evaluation of chemically recuperated gas turbine (CRGT) power plants fuelled by di-methyl-ether (DME).* Energy 31 (2006) 1446-1458.

[30] Semelsberger, T. A. Borup, R. L. Greene, H. L. *Dimethyl ether (DME) as an alternative fuel.* Journal of Power Sources 156 (2006) 497-511.

[31] Min Chul Lee et al. *Combustion performance test of a new fuel DME to adapt to a gas turbine for power generation.* Fuel 87 (2008) 2162-2167.

[32] Min Chul Lee et al. *Industrial gas turbine combustion performance test of DME to use as an alternative fuel for power generation.* Fuel 88 (2009) 657-662.

[33] Demirbas, A. *Progress and recent Trends in Biofuels*. Progress in energy and combustion science 33 (2007) 1-18.

[34] KemI. Kemikalieinspektionen. 2006. *http://apps.kemi.se/flodessok/floden/kemamne/etanol.htm(Retrieved 2012-08-10)*.

[35] Molière et al. *Gas turbines in alternative fuel applications: bio-ethanol field test*. Proceedings of ASME Turbo Expo 2009. GT2009-59047.

[36] Thomas, G. *Overview of storage development DOE hydrogen program (Retrieved 2012-10-08)*. Livermore, CA. Sandia National Laboratories. Hydrogen Program Review. 2000.

[37] Preem. 2012. *E85 Data sheet (Retrieved 2012-10-08)*.

[38] Mondal, P. Basu, M. Balasubramanian, N. *Direct use of Vegetable Oil and Animal Fat as Alternative Fuel in Internal Combustion Engine*. Biofuels, Biorpoducts and Biorefining 2 (2008) 155-174.

[39] Wikipedia. 2012. *http://en.wikipedia.org/wiki/Straight_vegetable_oil (Retrieved 2012-08-16)*.

[40] Knothe, G. *Historical Perspective on Vegetable oil-based Diesel Fuels (Retrieved 2012-08-16)*. Lipidlibrary, American Oil Chemists Society. http://lipidlibrary.aocs.org/history/Diesel/index.htm. First publication: Inform 12 (2001) 1103-1107.

[41] Wikipedia. 2012. *http://en.wikipedia.org/wiki/Vegetable_fats_and_oils (Retrieved 2012-08-16)*.

[42] Wikipedia. 2012. *http://en.wikipedia.org/wiki/Animal_fat (Retrieved 2012-08-16)*.

[43] Lipidlibrary, American Oil Chemists Society. Christie, W. W. *What is a Lipid (Retrieved 2012-08-16)*.

[44] Agarwal, D. Agarwal, A. K. *Performance and emissions characteristics of Jatropha oil (preheated and blends) in a direct injection compression ignition engine*. Applied Thermal Engineering 27 (2007) 2314-2323.

[45] *http://www.monashscientific.com.au/GlycerolMolecule.htm (retrievd 2012-08-20)*.

[46] *http://www.raw-milk-facts.com/fatty_acids_T3.html (Retrieved 2012-08-20)*.

[47] *http://schools.nashua.edu/myclass/marshalll/anatomy/Pictures/Forms/DispForm.aspx?ID=39 (Retrieved 2012-08-20)*.

[48] Carzavere et al. *Fuelling Micro Gas Turbines with Vegetable Oils. Part I: Straight and Blended Oil Properties*. Proceedings of ASME Turbo Expo 2012. GT2012-68238.

[49] Walton, J. *The Fuel Possibilites of Vegetable Oils*. Gas Oil Power 33 (1938) 167-168.

[50] Campbell et al. *Heavy Duty gas Turbines Fuel Flexibility*. Proceedings of ASME Turbo Expo 2008. GT2008-51368.

[51] Editors: Knothe, G. Van Gerpen, J. Krahl, J. *The Biodiesel Handbook*. AOCS Press, 2004.

[52] Wikipedia. 2012. *http://en.wikipedia.org/wiki/Ester(Retrieved 2012-08-21).*

[53] Preem. 2012. *Product information. Alternative fuels. Biodiesel 100. 100% RME. http://www.preem.se/templates/ProductInformation9526.aspx.Retreived 2012-10-15.*

[54] Liu et al. *Biodiesel as an alternative fuel in Siemens DLE combustors: atmospheric and high pressure rig testing.* Proceedings of ASME Turbo Expo 2009. GT2009-59065.

[55] Neste Oil Oy. *The HVO handbook.* 2012. *http://www.nesteoil.com/default.asp ?path=1,41,11991,12243,12335. Retrieved 2012-09-19.*

[56] Arvidsson et al. *Life cycle asessment of hydrotreated vegetable oil from rape, oil palm and Jatropha.* Journal of Cleaner Production 19 (2011) 129-137.

[57] Exxonmobile. 2005. *World jet fuel specifications (Retrieved 2012-11-27).*

[58] Blakey, S. Rye, L. Wilson, C. W. *Aviation gas turbine alternative fuels: A review.* Proceedings of the combustion institute 33 (2011) 2863-2885.

[59] Wikipedia. 2012. *http://en.wikipedia.org/wiki/Alkane. Retreived 2012-10-16.*

[60] Rye, L. Wilson, C. *The influence of alternative composition on gas turbine ignition performance.* Fuel 96 (2012) 277-283.

[61] Moliere et al. *Gas Turbines in Alternative Fuel Applications: Bio-Ethanol Field Test* Proceedings of ASME Turbo Expo 2009. GT2009-59047.

[62] Campbell et al. *Heavy duty gas turbines fuel flexibility.* Proceedings of ASME Turbo Expo 2008. GT2008-51368.

[63] Chiaramonti et al. *Exhaust emissions from liquid fuel micro gas turbine fed with diesel oil, biodiesel and vegetable oil.* Appl Energy (2012), doi: 10.1016/j.apenergy.2012.01.066.

[64] Bolszo, C. McDonell, V. Samuelsen, S. *Impact of Biodiesel on Fuel Preparation and Emissions for a Liquid Fired Gas Turbine.* Proceedings of GT2007-27652, ASME Turbo Expo 2007.

[65] Hui et al. *Experimental studies on the combustion characteristics of alternative fuels.* Fuel 98 (2012) 176-182.

[66] Glaude et al. *Adiabatic flame temperature from biofuels and fossil fuels and derived effect on NOx emissions.* Fuel Processing Technology 91 (2010) 229–235.

[67] Maidhof. 2012. *http://www.maidhof.com/glossary/glossary.html (Retrieved 2012-10-03).*

[68] Specialmetals. 2008. udimet alloy 520. Technical bulletin. *http://www.specialmetals.com/products/udimetalloy520.php (Retrieved 2012-11-18)*

[69] Boyce, M. P. *Gas Turbine Engineering Handbook.* Butterworth-Heinemann, 2012.

[70] Saravannamuttoo et al. *Gas Turbine Theory.* Pearson Education Limited, 2009.

[71] Lefebvre, A. H. Ballal, D. R. *Gas turbine combustion: alternative fuels and emissions* Taylor and Francis Group, 2010.

[72] Lee et al *Measuring air core characteristics of a pressure-swirl atomizer via a transparent acrylic nozzle at various Reynolds numbers*. Experimental Thermal and Fluid Science 34 (2010) 1475–1483.

[73] Lechler. 2012. *http://www.lechler.de/Products/Environmental-Technologies/ Gas-Conditioning/Overview-Nozzles/Spillback-Nozzles/. Retreived 2012-10-23*.

[74] Bose, S. *High Temperature Coatings*. Butterworth-Heinemann, 2007.

[75] Goosh, J. *Encyclopedic Dictionary of Polymers*. Springer, 2007.

[76] Kosieniak et al. *Corrosion Failures in Gas Turbine Hot Components*. Journal of failure analysis and prevention, 2011.

[77] Pettit, F. *Hot Corrosion of Metal and Alloys*. Oxidation of Metals, 2011.

[78] Bromley, A. F. *Tutorial: introduction to gas turbines*. ASME Gas turbine users symposium 2010.

[79] Eliaz et al. *Hot corrosion in gas turbine components*. Engineering Failure Analysis 9 (2002) 31-43.

[80] Wortman et al. *Mechanism of low temperature hot corrosion: burner rig studies*. Thin Solid Films 64 (1979) 281-288.

[81] Crosby et al. *Effects of Temperature and Particle Size on Deposition in Land Based Turbines*. Journal of Engineering for Gas Turbines and Power, 2008.

[82] Stephenson, D. J. *Predicting the high temperature erosion behaviour of materials used in gas turbines*. Corrosion Science 29 (1989) 647-656.

[83] Hamed et al *Turbine blade surface detorioration by erosion*. Journal of Turbomachinery 127 (2005) 445-452.

[84] E.ON AG. Department Corporate Sustainability. 2010. *Biomass Purchasing Amendment to the E.ON Responsible Procurement Policy*.

[85] Svensk Författningssamling. *Lag om hållbarhetskriterier för biodrivmedel och flytande biobränslen*. SFS 2010:598.

[86] Svensk Författningssamling. *Förordning om hållbarhetskriterier för biodrivmedel och flytande biobränslen*. SFS 2011:1088.

[87] Statens energimyndighets författningssamling. *Statens energimyndighets föreskrifter om hållbarhetskriterier för biodrivmedel och flytande biobränslen*. STEMFS 2011:2.

[88] Statens energimyndighet. *Vägledning till regelverket om hållbarhetskriterier för biodrivmedel och flytande biobränslen*. ER 2011:23.

[89] Norin, T. E.ON Värme. Private communication 2012.

[90] Dahlman, L. SVEBIO, Svenska Bioenergiföreningen. Private communication 2012-03-27.

[91] Swedish Energy Agency. 2012. *Lista med aktörer som meddelats hållbarhetsbesked . Retreived 2012-10-10.*

[92] Kannesten, A. Swedish Energy Agency. Private communication. 2012.

[93] Ericsson, S. Refinery Development, Preem. Private communication. 2012.

[94] Löwnertz, P. VP Sales and Marketing, Chemrec AB. Private communication. 2012.

[95] BTG-BTL. 2012. *http://www.btg-btl.com. Retreived 2012-10-12.*

[96] Statoil. 2012. *https://www.statoil.se/file_archive/produktinformation/Prisutv_2012_ftg.xls.*

[97] Nydahl, S. Vegoil. Private communication 2012.

[98] Rasmussen, C. CEO Biofuel Express AB. Private communication. 2012.

[99] Johansson, M. Energimyndigheten. Private communication. 2012.

[100] Statens Energimyndighets Författningssamling. 2011. *Föreskifter och allmänna råd om elcertifikat. STEMFS 2011:4.* 2011-12-29.

[101] Engineeringtoolbox. *http://www.engineeringtoolbox.com/specific-heat-fluids-d_151.html (Retrieved 2012-11-05).*

[102] Goteti, A. *Experimental investigation and systems modeling of fractional catalytic pyrolysis of pine.* A thesis. Georgia institute of technology. 2010.

[103] Norberg, A. E.ON Värme. Private communication. 2012.

[104] Matche. 2007. *http://www.matche.com. (Retrieved 2012-12-22).*

[105] Hedendahl, P. Tankar & Tryckkärl. Rodoverken. Private communication. 2012-10-30.

[106] Wikipedia. 2012. *http://en.wikipedia.org/wiki/Pressure_vessel (Retrieved 2013-01-05).*

[107] Wikipedia. 2013. *http://en.wikipedia.org/wiki/Steel (Retrieved 2013-01-25).*

[108] Wikipedia. 2013. *http://en.wikipedia.org/wiki/Ultimate_tensile_strength (Retrieved 2013-01-25).*

[109] Nordpoolspot. 2012. *http://www.nordpoolspot.com/ (Retrieved 2012-11-06).*