



The potential of alternative fuels, bioethanol, biodiesel and bio-methane, for vehicles and their influence on emissions

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Abstract

This report compares the different lifecycles of bioethanol, biodiesel, compressed biogas, conventional gasoline and diesel on a well to wheel basis. For this analysis a model has been used for evaluating the relating energies and emissions. The model shows that any kind of renewable fuel that has been evaluated in this study has the potential to reduce oil use and greenhouse gases. The fuel that had the most benefits is compressed biogas. The reason why it has been the best fuel alternative is because its raw materials don't need energy to produce it since it is mainly organic waste that is getting decomposed by microorganisms. The least amount of energy is needed for this renewable fuel and it also releases the least amount of greenhouse gases.

Although the potentials for bioethanol and biodiesel are very high compared to the use of just conventional gas and diesel there is a disadvantage due to the high use of fertilizers and the high amounts of water that are needed for the crop growing. With the increase in using renewable fuels instead of non-renewable fuels we have the ability to save a lot of emissions and energy.

1. Problem

Transportation fuels are one of the biggest discussed issues every country has to deal with at the moment. The reason why it is that big of an issue is because the crude oil supplies are getting less, the economy and population is growing and therefore a substitute needs to be found. Transportation fuels are very important for the economies and in addition to that they are important for everybody.

At the moment more than 90 % of the energy supply is covered by fossil fuels. The reason for the high amount of fossil fuels used is that the oil based fuels have a very high energy density and the source is time independent. The production of fossil fuels has also gotten more efficient, therefore making it one of cheapest way to create an energy source.

Due to this situation the signs of climate change are getting more and more and the crude oil reserves are getting less every year. This verifies the importance of biofuels and that substitutes are needed for transportation. Biofuels were considered as high potential substitutes for crude oil and a much greener way for the transportation sector, whereas the competition with food always had a negative impact on renewable fuels.

Due to the cheaper production and governmental regulations, the production and use of biofuels is increasing rapidly. Also the developments made in the last years improved the efficiency of crop growing and the manufacturing process hugely.

However, there is a lot of energy needed for the production of either fossil- or biofuels which makes it harder to make a decision.

This study is going to show the lifecycle energies and emissions of the renewable fuels bioethanol, biodiesel and biogas and the non-renewable fuels conventional diesel and gasoline.

2. Introduction & Background

Biofuels were discussed since 1929 when Rudolph Diesel used vegetable oil for his invented engine. People knew that due to the different features of vegetable oils, such as different heating values, it can cause problems for the engines.

Biofuels are produced from organic matter such as vegetable oils, sugar containing crops and organic waste. The potential of the different biofuels is depending on their source material.

The first real large scale use was implemented in Brazil where the oil producing industry started the blending of bioethanol and normal gasoline. After this implementation more and more countries started development processes for biofuels and governments started to force the use of biofuel blends. There have been many improvements in crop growing over the last decade making the manufacturing of the biofuels much more efficient and feasible. [1]

Today the biofuels can be classified in two main divisions:

- A substitute for normal gasoline (bioethanol)
- A substitute for diesel (biodiesel)
- A substitute for natural gas (biogas)

Current global situation

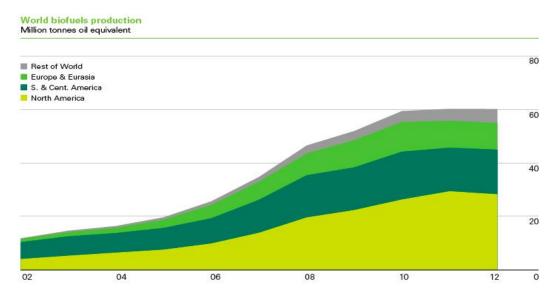


Figure 1: Current global situation of the biofuel production in million tonnes oil equivalent [15]

Currently more than 90 % of the energy mix of the U.S. and the European Union are covered by fossil fuels. There are some advantages to using fossil fuels, they are time independent and can be used the same way for individuals as well as for industries. This makes fossil fuels a unique and easy fuel. However, fossil fuels have and end they can't be produced forever that is the reason why more and more studies are done with renewable fuels.

In the year 2010 the global biofuel production was at 107 billion liters. The main producing countries are the US, Brazil and Europe. Even these countries are still producing small amounts compared to their total needs.

In the year 2010 1440 million liters of biofuels were used for transportation. That is about 3.1 per cent of the total road transport fuel. Biodiesel and bioethanol are the main fuels used as substitutes with their shares are divided into 59 per cent biodiesel and 41 per cent bioethanol. [2]

The International Energy Agency (IEA) has estimated the growth of biofuel use by a rate of 7 % annually. This means that by the year 2030 the biofuels share would be around 5 % of the total transportation fuel. The assumptions are shown in Table 1 Table 1: World estimated biofuel consumption (Mtoe) [3].

Table 1: World estimated biofuel consumption (Mtoe) [3]

| Mtoe | 2004 | 2010 | 2015 | 2030 |
|-----------------|------|------|------|------|
| OECD | 8,9 | 30,5 | 39 | 51,8 |
| North America | 7 | 15,4 | 20,5 | 24,2 |
| United States | 6,8 | 14,9 | 19,8 | 22,8 |
| Canada | 0,1 | 0,6 | 0,7 | 1,3 |
| Europe | 2 | 14,8 | 18 | 26,6 |
| Pacific | 0 | 0,3 | 0,4 | 1 |
| Transition | | | | |
| Economies | 0 | 0,1 | 0,1 | 0,3 |
| Russia | 0 | 0,1 | 0,1 | 0,3 |
| Developing | | | | |
| Countries | 6,5 | 10,9 | 15,3 | 40,4 |
| Developing Asia | 0 | 1,9 | 3,7 | 16,1 |
| China | 0 | 0,7 | 1,5 | 7,9 |
| India | 0 | 0,1 | 0,2 | 2,4 |
| Indonesia | 0 | 0,2 | 0,4 | 1,5 |
| Middle East | 0 | 0,1 | 0,1 | 0,5 |
| Africa | 0 | 0,6 | 1,1 | 3,4 |
| North Africa | 0 | 0 | 0,1 | 0,6 |
| Latin America | 6,4 | 8,4 | 10,4 | 20,3 |
| Brazil | 6,4 | 8,3 | 10,4 | 20,3 |
| World | 15,5 | 41,5 | 54,4 | 92,4 |

Europe and the U.S. can't produce enough fossil fuels for their own needs forcing them to revert to production of renewable fuels and atom energy. They are producing 48 % (EU) and 80 % (U.S.) of their needed energy, and importing the rest from other countries like Russia or Saudi Arabia.

The IEA expects that the global demand for transportation fuels will increase by over 50 % by 2030 which will have a big impact on the biofuel production. [1]

The reason for those high demands is due to the growth of population and a more immoderate usage of fuels. Also the usage of developing countries has a huge impact because there are mostly no governmental regulations to make processes more efficient and to use renewable fuels.

Due to the scarcity of crude oil and the "benefits" of biofuels, governments all around the world set regulations for the use of biofuels. Usually the regulations force the country to blend the normal gasoline by a certain percentage.

Table 2 below shows the global governmental regulations for biofuels:

Table 2: Current global governmental regulations for biofuels. [3]

| | Ethanol | Biodiesel |
|----------------|--------------|-------------|
| Angola | 10 | - |
| Argentina | 5 | 7 |
| Australia | 4 | 2 |
| Brazil | 20 | 5 |
| Canada | 5 | 2 |
| Chile | 5 | - |
| China | 10 | 0 |
| Columbia | 8 | 10 |
| Costa Rica | 7 | 20 |
| Ethiopia | 5 | - |
| European Union | 10 | 10 |
| Fiji | voluntary 10 | voluntary 5 |
| India | 5 | - |
| Indonesia | 3 | 2,5 |
| Jamaica | 10 | - |
| Kenya | 10 | - |
| Malawi | 10 | - |

| Malaysia | - | 5 |
|--------------|--------------|-------------|
| Mexico | 2 | - |
| Mozambique | 10 | - |
| Nigeria | voluntary 10 | - |
| Panama | 2 | - |
| Paraguay | 24 | 1 |
| Peru | 7,8 | 2 |
| Philippines | 10 | 2 |
| South Africa | 1 | |
| South Korea | - | 2,5 |
| Sudan | 5 | - |
| Taiwan | - | 1 |
| Thailand | - | 5 |
| USA | 10 | |
| Uruguay | voluntary 5 | 2 |
| Vietnam | 5 | - |
| Zambia | voluntary 10 | voluntary 5 |
| Zimbabwe | voluntary 10 | - |

2.1 Energy-policy situation

Both U.S. and the European Union know that the importance of renewable fuels is getting more and more. As Europe is the biggest energy importer they try to focus on the development of renewable sources. In the last couple of years the European Union made regulations which should increase the production and development of renewable fuels.

2.1.1 European Union

Currently the European Union has set goals to meet until 2020. Those aims are called 20-20-20 aims and include the following regulations:

- A 20 percent reduction of the greenhouse gases till 2020 based on the greenhouse gas levels from 1990.
- An increase of the fuel shares produced by renewable resources by 20 percent. Primarily produced by solar, wind and biomass.
- And a 20 percent increase in energy efficiency improvement. That means a reduction of the energy use by 20 percent. [4]

2.1.2 United States of America

The situation in the U.S. is very different compared to the situation in the EU. Although president Obama said that he wants to fight the climate change and increase the production of renewable resources he did not make any big changes. The reason for that is because the acceptance for renewable resources in the U.S. is not very high. His aim was to reduce the US energy consumption by 50 % in the next 20 years. In June 2013 he released the "Obamas climate action plan" which promotes the cut of greenhouse gas emissions and the increase in renewable clean energy. The aim was to increase the clean electricity by 10 % till 2015. A few months after his action plan, he signed a second memorandum to increase the share of renewable energy by 20 % until 2020. [5]

But still the U.S. is investing lots of money in the discovery of new oil and gas reserves which means oil and gas production is increasing as well.

2.2 Production of fuels

To evaluate the different potentials of fuels their production has to be observed in order to see how much emissions are released and how much energy was used.

2.2.1 Biodiesel

Biofuels are mostly derived from some kind of biomass. The materials come from plants or animals with all their byproducts. Those materials are transformed either through a chemical or biological process to create a biofuel.

For the use of plant oils there are usually two methods, either the engine gets adapted to the fuel or the fuel gets adapted to the engine. [1]

Biodiesel is the replacement for conventional diesel fuel. The oils used for the manufacturing process of biodiesel are divided into three major sections:

- Plant oils
- Recycled cooking greases
- Animal fats

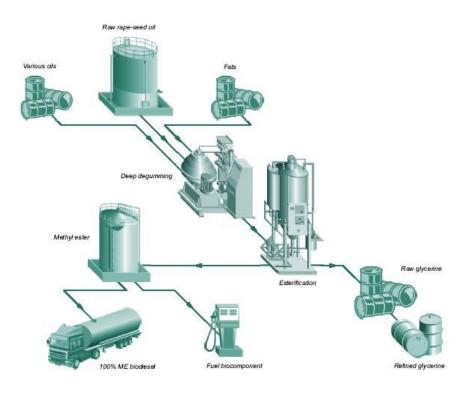


Figure 2: General scheme of the biodiesel production plant. [28]

2.2.1.1 Transesterification

During the production process of biodiesel plant or vegetable oils are transferred to Fatty Acid Methyl Ester (FAME) or biodiesel. During that process the oil gets converted, with the use of methanol and a catalyst, to biodiesel and glycerin. This process is called transesterification.

Figure 3: Transesterification process for the production of biodiesel. [29]

At the transesterification process the used oil gets blended with methanol at a mass ratio of 9:1 and after the addition of an alkali catalyst like sodium hydroxide the reaction gets started. [6]

2.2.1.2 Biodiesel conditioning

The conditioning of biodiesel is a multistage process, where the biodiesel gets washed to get rid of the reaction accrued soaps. After the washing process the biodiesel gets dried in a vaporizer. Through that process the water and methanol in the biodiesel gets removed.

The glycerin products which arise during the reactions get washed, enriched and conditioned to pharma glycerin which is sold to the pharma industries. [6]

2.2.1.3 USE

The most common use of biodiesel in the United States is the B20 blend where 20 % of biodiesel are blended with 80 % of normal diesel fuel. The big benefit with that blend is the high performance and the good material compatibility. [7]

As the blends get higher (e.g. B50, B100) the engines may need to get adapted through the assembly of special parts. The content in Table 3 shows the different features of biodiesel compared to normal diesel fuel

| Fuel | Density g/cm³ | Net Heating Value Btu/gal |
|---------------|---------------|---------------------------|
| Diesel | 0,85 | 129,5 |
| Biodiesel | 0,88 | 118,296 |
| B100 | | |
| Biodiesel B20 | 0,856 | 127,259 |
| Biodiesel B2 | 0,851 | 129,276 |

Table 3: Fuel features of biodiesel at certain blends. [7]

Conventional diesel has very high emissions in HC, CO, PM and NOx, Figure 4 below is showing how these emissions change/decrease with an increasing percentage of biodiesel.

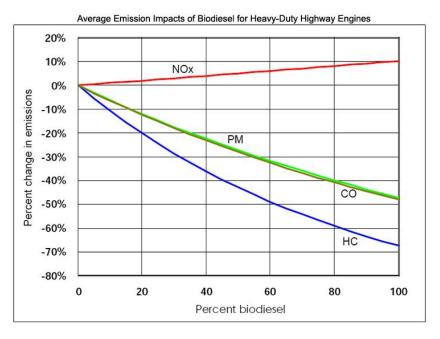


Figure 4: Percent change in pollutant emissions with biodiesel content. [30]

Figure 5 below shows the current global biodiesel production per day. The main biodiesel producers are the US and Brazil, Europe's and China's production is on an increasing pathway too.



Figure 5 : Global production of biodiesel. [25]

The world's biodiesel production has risen enormously in the past few years. In Figure 6 below the global production from 2000 to 2011 is shown. The biggest rise was in the last years due to a more efficient production method and a bigger demand.

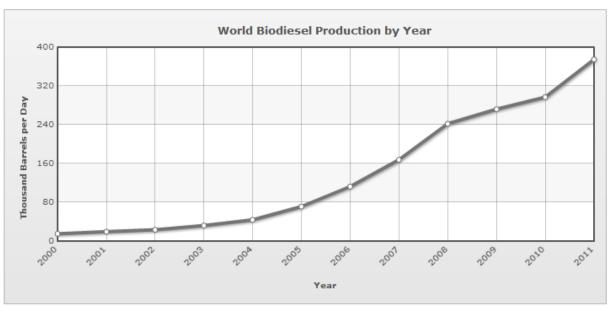


Figure 6: World's Biodiesel Production from 2000 - 2011. [25]

2.2.2 Bioethanol

Bioethanol is one of the alternatives for fossil fuels aimed at reducing carbon dioxide emissions caused by transportation. It is mainly produced from sugar or starch containing crops. Another production possibility is to use cellulose but therefore it has to be made approachable first which needs lots of energy that's why this method is still in development. The reason why bioethanol is seen as a good alternative is because the source for the production for bioethanol is grown renewably and almost everywhere around the world. [6] [8] [1]

Bioethanol is therefor available for almost everybody and due to that very important to the economy. There are statements that the use of bioethanol lowers carbon based emissions but there are also studies which are showing that the amount of fertilizers and water that is used fort the growing of the crops is enormous.

The main bioethanol producers are Brazil and the United States which are producing over 70 % of all ethanol worldwide. The United States are producing around 6500 Million gallons a year. [9] [10]

2.2.2.1 Current situation

Figure 7 shows the global fuel ethanol production in barrels per day. The main producing countries are the US, Brazil, Europe, China and Australia.



Figure 7: Global fuel ethanol production. [25]

The global fuel ethanol production has increased fivefold from the year 2001 until now and it's still growing rapidly as shown in Figure 8 below. The reason why the fuel ethanol production has increased that rapidly is because of the governmental regulation for ethanol-gasoline blends. The efficiency in the production has also increased.

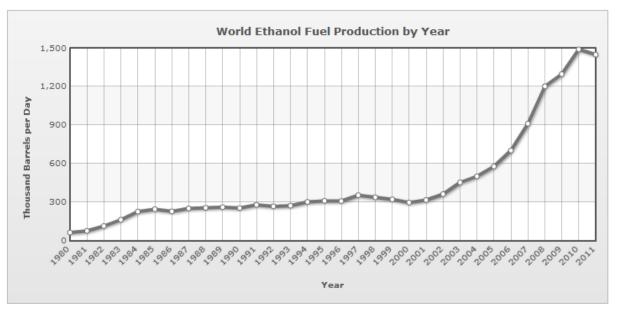


Figure 8: World fuel ethanol production from 1980 - 2011 [25]

2.2.2.2 Production Process

Feedstock for bioethanol production can be divided into 4 main categories by countries:

- In Europe it is mostly sugar beet and wheat.
- In the US the most commonly used feedstock is corn.
- And in Brazil they use mainly sugar cane.
- The lingo-cellulosic use is still in the development process to make the big industrial use affordable and efficient. [11]

Figure 9 below is showing the 3 possible ways for the production of bioethanol. Sugar is the key component that can be transferred via alcoholic fermentation to ethanol and CO₂. The easiest way to get free sugars is to take sugar containing crops and basically just extract them. For starch and cellulose containing crops the sugars have to be broken down therefore they have to undergo certain intermediate treatment steps before the usual fermentation can happen. The use of cellulose is still under development because the breaking down process is still a barrier because it is very energy consuming.

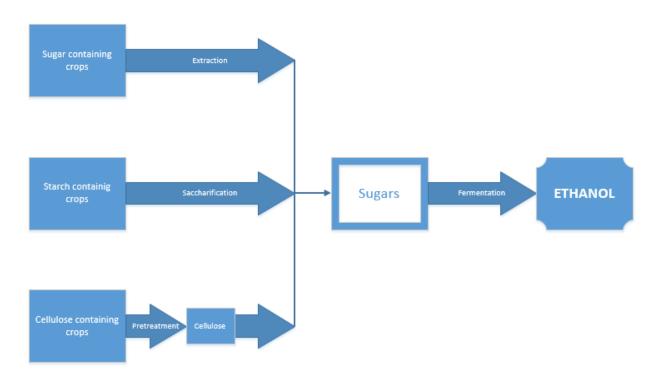


Figure 9: Bioethanol production ways.

Figure 10 below shows a schematic diagram of a fuel ethanol production plant. The basic schema starts with the milling of the grains and adding water and enzymes. This breaks the grains up into sugars and after the addition of yeast the sugar gets converted into ethanol. Because the water stays in the mixture it has to go through distillation and rectification processes. The last step is the final dehydration of the mixture to get nearly pure ethanol.

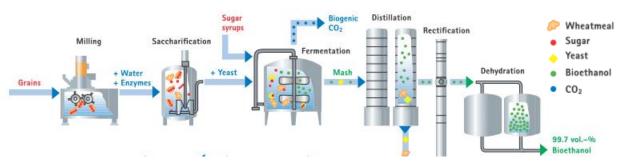


Figure 10: Scheme of a bioethanol production plant [26]

2.2.2.3 Sugar-depletion through alcoholic fermentation

The basic concept is the biochemical division of carbohydrates. This division takes place through the work of special enzymes which basically operate without oxygen. For the common use the main microorganism is yeast. The basic chemical reaction of the fermentation process is shown below:

$$C_6H_{12}O_6 + 2Pi + 2ADP \rightarrow 2 CH_3 - CH_2OH + 2 CO_2 + 2 ATP + 156 kJ$$

That equation shows that 1 mol of sugar gets converted into 2 mols of ethanol as well as energy in form of ATP and heat. [6]

2.2.2.4 Starch to Ethanol

Starch ($C_6H_{10}O_5$) is a carbohydrate that is build up out of amylose (20 %) and amylopectin. Both of the carbohydrates are made up out of glucose molecules which are linked together by glycosidic bonds. Starch needs to be converted into glucose molecules that work due to the use of special enzymes, amylases which convert starch and water, at temperatures between 60 – 70 ° C and a pH at 5 – 7.5, to glucose molecules. This process is called hydrolysis. [6]

$$(C_6H_{10}O_5)_n + n H_2O \rightarrow Amylases \rightarrow n C_6H_{12}O_6$$

2.2.2.5 Cellulose to Ethanol

Cellulose is a polysaccharide which consists of several thousand glucose molecules. It differs from starch in that the glucose molecules are joined together by beta –glycosidic bonds which means human and animals cannot break those bonds naturally. Therefore special enzymes (Cellulases) are needed to break these bonds. [6]

$$(C_6H_{10}O_5)_n + n H_2O \rightarrow Cellulases \rightarrow n C_6H_{12}O_6$$

2.2.2.6 Pretreatment

So for the fermentation process a special pretreatment is needed. The pretreatment should cover the remove of lignin, a complex polymer that hold the fibers together, and hemicellulose, a complex of sugar and sugar derivatives which form a branched network.

To perform the pretreatment there a several methods that can be used but the process is still in development because most of the methods need huge amounts of energy. [6]

Physical

<u>Milling</u>

Mechanical pretreatment methods usually try to increase the surface volume to make the biomass more available for further pretreatment steps. There are two methods used milling and grinding. [12]

Chemical Pretreatment

Liquid hot water

For this process, also known as hydrothermolysis, hot water is used to hydrolyze the biomass. Under conditions of hot water (200- 230 °C) and pressure, the biomass gets dissolved. [12]

Acid Hydrolysis

Treatment of biomass with acids is called acid hydrolysis. There are two different methods which can be used, the weak acid hydrolysis and the strong acid hydrolysis. The major difference is that for the weak acid hydrolysis the biomass gets mixed with the acid and is then heated up for a few minutes, whereas the strong acid just needs to get in contact with the biomass and following to that cuts the hydrogen bonds along the cellulose chains. [12]

Alkaline Hydrolysis

To get rid of the lignin pretreatment methods are used including different alkaline chemicals:

- Calcium or sodium hydroxide
- Ammonia
- Organic solvents

These chemicals form compounds with lignin and can therefore be removed easier. [12]

Physicochemical Pretreatment

Steam Explosion

This method uses high pressure and saturated steam which gets injected into a reactor filled with biomass. During this process the biomass gets heated up quickly and suddenly the pressure gets reduced which forces the biomass to "explode" and therefore gets degraded into their main components. [12]

AFEX

This physicochemical process uses liquid ammonia under high temperature and pressure. The principle is the same as the steam explosion where the pressure is suddenly released. [12]

CO₂ Explosion

This method uses the same principle as the steam explosion, but instead of saturated steam high pressure CO₂ is used. [12]

Biological Pretreatment

As most of the listed pretreatment methods need high amounts of energy, the more efficient way is the treatment with microorganisms such as fungi. Those microorganisms are able to degrade the cellulose by the use of special enzymes. [12]

2.2.2.7 Distillation, Rectification, Absolution

Distillation, Rectification and Absolution are processes to concentrate the ethanol to its highest possible grade.

- The raw alcohol is created by a process called distillation and reaches a concentration of 82 – 87 %. The maximum concentration which can be reached through distillation is between 95 – 96 %.
- 2. Rectification is a kind of multiple distillations where ethanol gets separated in a counter flow process. This process needs several steps in a column and can reach ethanol contents at 96 % and above.
- 3. For the use as a transportation fuel it is important that water is removed as much as possible to decrease the possibility of engine breakdowns. Because the higher the water contents the lower the efficiency and the higher the possibility for oxidation processes. Ethanol and water is an azeotrope mixture, which means water cannot be separated by simple distillation. Therefore absolution is used to reduce the water content. Thereby a chemical substance is added, a so called entrainer, which changes the boiling temperature of the mixture. With this method an ethanol content of 99.7 % can be reached. [6]

2.2.2.8 Ethanol as a fuel

Ethanol has many benefits but also some downsides. The most important fact about bioethanol is that it is renewable and easy to produce. It is also used as an oil substitute and helps therefore reducing oil related emissions like greenhouse gases. The question that still arises is the food for fuel discussion. But once the development of cellulose break down gets refined the raw materials might not be on a food basis any more. [13]

Ethanol can only be used for conventional vehicles by mixing with normal gasoline. The standard blends for that are mixed with either 5 % or 10 %. Above these concentrations the fuel can cause corrosion for the engine. But with adapting the engine by the assembly of a few special parts, cars are able to drive with nearly 100 % ethanol without damaging the engines.

Some car manufacturers are producing flex-fuel vehicles (FFVs) which are able to run ethanol-gasoline blends from 0 % ethanol up to 85 %.

The efficiency of cars running with ethanol blends is nearly the same as running them with normal gasoline. [1] [6]

2.2.3 Biogas

Biogas is a mixture of methane, carbon dioxide, water, hydrogen sulfide, oxygen, nitrogen and ammonia. Biogas accrues through anaerobic degradation of organic material through microorganisms. It is used as a substitute for natural gas in the transportation sector. Biogas can be used as it is or conditioned to natural gas quality. [1]

The main sources for the biogas production are:

- Landfills
- Aerobic digestion of organic waste
- Anaerobic digestion of organic waste

2.2.3.1 Production process

The biogas production process takes place in 4 major phases. During these phases the whole process has to be under special conditions to keep the bacteria alive/working. If the conditions vary too much the process is slowing down or even shutting down.

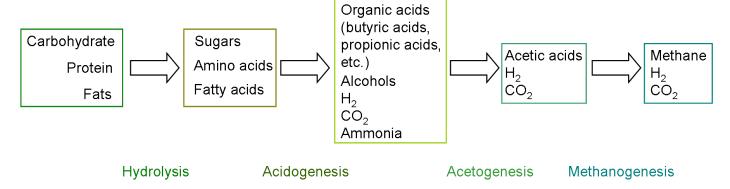


Figure 11: Production process for biogas. [27]

- Hydrolysis: large complex compounds of the starting substrate (e.g. carbohydrates, protein, fats) are decomposed in simpler organic compounds (e.g. sugars, amino acids, fatty acids). The bacteria used for this phase release special enzymes which degrade the substrate. The pH at this stage is between 4.5 -6.
- Acidogenesis: The previously built intermediate products are then further
 decomposed to low organic acids (e.g. acetic acid, propionic acid, butyric
 acid), carbon dioxide and hydrogen. The bacteria used for this stage are using
 all the remaining oxygen and therefore creating the optimum conditions for the
 methane building bacteria.
- 3. <u>Acetogenisis</u>: during this phase the organic acid (acetic acid) is formed that is an important precursor for the methane building bacteria.
- 4. <u>Methanogenesis:</u> is the stage where microorganisms produce methane. They transfer previously in the acetogenisis created products to methane. The optimum pH in this stage is at 7. The methane building bacteria are the most sensitive bacteria of the whole process. **[6]**

2.2.3.2 Temperature

The temperature used for the digestion process is usually between 35 °C and 65 °C for mesophilic and thermophilic microorganisms, therefore the organic substrate should be heated up before added to the process. A disadvantage at the high temperatures is that the microorganisms are much more sensitive to changes but the temperatures also kill harmful/toxic substances.

2.2.3.3 pH-value

The pH influences the productivity and the growth of the bacteria. The optimum pH is at 6 during the hydrolysis stage and at 7 during the acetogenisis and methanogenesis. Also the pH is dependent on the substrate this means if the components of quick decomposable substances are too high the mixture gets into the acid range to quick which inhibits the methane producing bacteria.

2.2.3.4 Biogas as a fuel

Biogas can provide heat or electricity through combustion it can be upgraded to the same grade as natural gas and therefore used as a substitute for it. Table 4 below shows the differences between biogas and natural gas. As you can see the major difference is the methane component which is the important component for combustion processes. [1] [6]

| Table 4: | Biogas | and | Natural | components. |
|----------|---------------|-----|----------------|-------------|
|----------|---------------|-----|----------------|-------------|

| Component | Biogas | Natural gas |
|------------------|-------------------------------|--------------------------|
| Methane | 55 – 70 Vol% _{dry} | >96 Vol% _{dry} |
| Carbon dioxide | 30 – 45 Vol% _{dry} | <2 Vol% _{dry} |
| Oxygen | 1 – 2 Vol% _{dry} | <0,5 Vol% _{dry} |
| Nitrogen | 0 – 2 Vol% _{dry} | <5 Vol% _{dry} |
| Hydrogen sulfide | 100 – 2000 mg/Nm ³ | <5 mg/Nm³ |
| Siloxanes | Trace | <1 ppm |
| Caloric value | 5 – 7 kWh/Nm³ | 10,7 - 12,8 kWh/Nm³ |

To upgrade the biogas there are 2 major technologies:

- Absorption: which is the transfer of one substance into another or into a another phase (water scrubbing, chemical systems)
- Adsorption: is the accumulation of a substance on an interface (pressure swing adsorption PSA, temperature swing adsorption TSA)
- Separation with membranes.

Water Scrubbing

Polar molecules like carbon dioxide have higher water solubility than methane, which means that water can be used to remove unwanted substances. The gas mixture gets pumped through water columns under high pressure. Thus the gas gets cleaned. [1] [6]

Pressure Swing Adsorption

Another efficient upgrading method is the pressure swing adsorption where an adsorbing material is used to get rid of carbon dioxide and other unwanted substances. Materials used for this process are activated carbon or zeolite. [1] [6]

Chemical Processing

This process is similar to water scrubbing except the used solvent is different.

Instead of water, chemicals are used which have higher absorption capacities than water. These chemicals can be regenerated after using it for the upgrading process.

[1] [6]

After these cleaning steps the biogas needs to be dried so that a minimum amount of water is present in the gas. When this step is finished it gets through a quality control and after a passed control it gets dosed with an odor because biomethane is odorless. After the upgrade from biogas to biomethane it can be used as a substitute for natural gas. [14]

2.2.4 Non-renewable transportation fuels

One of the most used and also needed substances in the world is crude oil. It is called crude oil when it comes out of the ground and can be used without any further treatments or upgrades. It was made from degraded plants and animals over a million years ago.

The crude oil production and mining has improved a lot during the last few years. Of course the industry is very energy consuming but due to the high demand for transportation fuels the processes to mine and produce transportation fuels have gotten increasingly more efficient and the oil companies are still investing more money in the improvement of the efficiency. By the last year the global oil production has increased by 2.2 %. [15]

Figure 12 below shows the main oil producing countries, which haven't really changed in the last few years because the oil reserves are almost fully discovered. This means that the leading countries are still the U.S., Russia, and Saudi Arabia.



Figure 12: Global oil production. [25]

Even though it was said that the oil reserves are nearly empty the oil production is not decreasing Figure 13 below. This is because of new technologies like fracking which make it possible to extract difficult to access oil. The process of fracking is under big criticism because of the environmental pollution. There are no governmental regulations yet and impact on the environment has not been fully evaluated to date. Until there are any governmental regulations the oil production will slightly increase in the next few years.

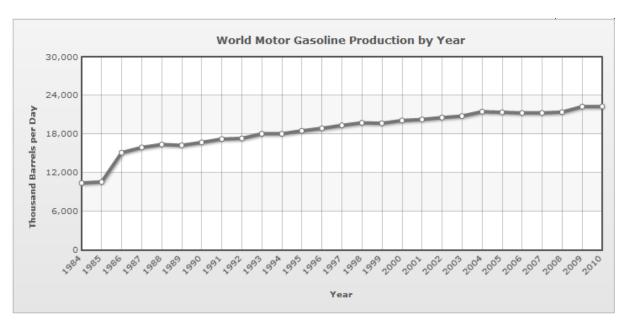


Figure 13: Production of Motor Gasoline from 1984 – 2010. [25]

2.2.4.1 Oil Production

The first step in the oil-production cycle is the mining of raw oil sand. Thereby the raw oil sand gets removed from the ground by a technology called mining. Usually this happens with big machines with attached shovels.

After an oil field is located an oil well needs to be created. That happens through drilling a hole into the earth. The extraction itself is divided into three general methods:

<u>Primary recovery</u>: For this method only natural mechanisms are used. Thereby the oil reservoir generates a pressure through the expansion of gas and forces the oil to rise to the surface.

<u>Secondary recovery</u>: For this method external energy needs to be spent by injecting fluids into the oil reservoirs to increase the pressure which then forces the oil to rise.

<u>Tertiary recovery</u>: This method uses steam, solvents or polymers by reducing the oil's viscosity. Another method which is used is the modification of the characteristics of water which changes the water-oil interaction.

Table 5 below show the general composition of crude oil after it has been extracted from the ground.

Table 5: Composition of crude oil after extraction. [16]

| Component | Percentages | |
|-----------|-------------|--|
| Carbon | 84 | |
| Hydrogen | 14 | |
| Sulfur | 1-3 | |
| Nitrogen | <1 | |
| Oxygen | <1 | |
| Metals | <1 | |
| Salts | <1 | |

After the oil is extracted from the ground it can't be used as it is, it needs to be refined. Before the refining step the oil gets tested on specific gravity and density.

Another important characteristic that is measured straight after extraction is the sulfur content. The higher the sulfur content is the worse for the refining process because of the impact it has on the used catalysts.

When the oil is analyzed it has to be transported to refineries through pipelines. If the oil has to go a long way and the way through pipelines is not cost efficient, it has to be transported with oil tankers.

2.2.4.2 Refining

The process of oil refining is based on the different densities of different oil fractions. Crude oil contains of a lot of different types of hydrocarbons which need to be separated in order to use them as fuels. Due to the different hydrocarbon chain lengths they all have different boiling points and can therefore be separated through distillation. [17]

So conventional gasoline and conventional diesel is made through the refining process. This is one of the most energy consuming processes in the non-renewable fuel production because the oil has to be heated up to over 600 °C for the distillation.

Figure 14 below is showing the different fractions at the relating temperatures that occur after the separation by distillation.

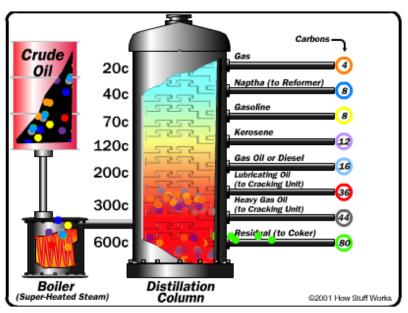


Figure 14: Crude oil separation scheme. [17]

Newer technologies use chemical processing on some of the fractions to break the hydrocarbon chains and thus creating different fractions. After the fractions are separated they need to be cleaned. This process happens by removing impurities like organic compounds, sulfur, nitrogen, oxygen or water. The fractions get cleaned through adsorption and absorption in columns and treatment with special chemicals.

[17]

3. Greet

The Greenhouse Gases, Regulated Emissions and Energy Use in Transportation Model was developed by Dr. Michael Wang, Argonne National Laboratory's Center for Transportation Research supported by the U.S. Department of Energy. It is a tool for calculating the emissions during the life cycle which includes the manufacturing process, different vehicle types and different fuel types. In this case it helped to get specific emission data of the whole lifecycle of the observed fuels. A lifecycle emission includes every emission from the growing of the crops to the production of the fuel and finally the combustion in a vehicle.

3.3 How the GREET model works

The GREET model tries to evaluate the impacts of emissions of transportation fuels and vehicle technologies from wells to wheels. The model calculates the consumption of total energy and the greenhouse gas related emissions. It includes over a 100 fuel pathways produced from different feedstock sources. Seven different vehicle systems are cover by the GREET model.

Greet includes following emissions:

- CO₂
- CH₄
- N₂O
- VOC
- CO
- NO_x

Figure 15 shows the stages that are included in the GREET simulation model for fuel life cycles. The fuel life-cycle includes feedstock, fuel and vehicle operations. It is therefore called well-to-wheel analysis. The model covers the energy that is used in these stages and also the emissions that are released during these phases.

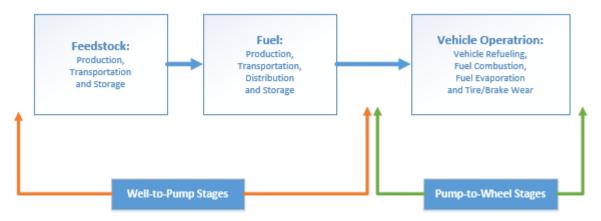


Figure 15: Scheme of the stages that are included in GREET.

Figure 16 shows the logic that is used for the calculations in the GREET model. This logic is based on a database with emissions and energy consumptions for all different kinds of plants, machines and transportation.

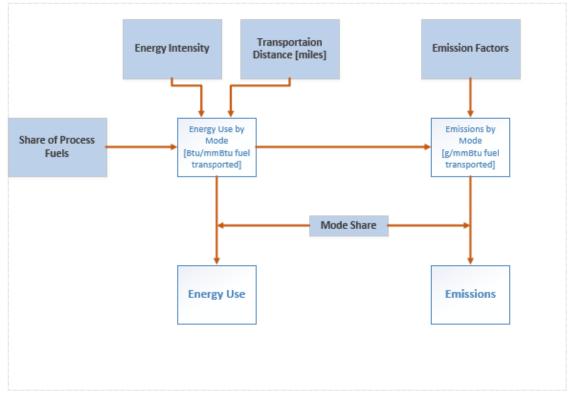


Figure 16: Calculating logic of the GREET model.

Figure 17 below shows the different input types. The desired years, fuel types and vehicle types can be adapted through this step.

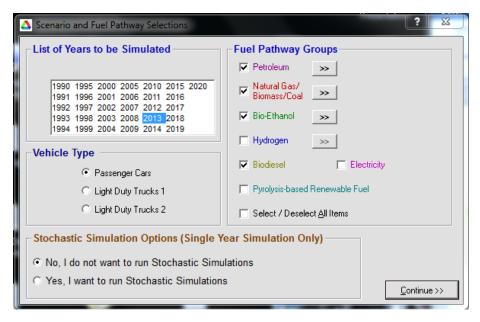


Figure 17: Fuel Pathway selection step 1.

The next step focuses on fine adjustments on volumetric shares, engine types and sulfur contents. For the calculation used in this thesis an average sulfur content of 25 ppm for normal gasoline and 12 ppm for diesel was taken. This is shown in Figure 18.

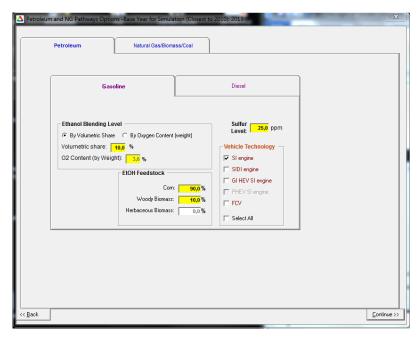


Figure 18: Blending options, fuel shares and sulfur contents.

The next step focuses on different plant types, different energy supplies and different engine models. Figure 19 shows the different ethanol production plant types which GREET sets with 88 % of dry mill production and 11 % wet mill production. The energy supply for these plants is consisting of 92 % natural gas and 8 % coal for dry mill plants and 73 % natural gas and 27 % coal for wet mill plants.

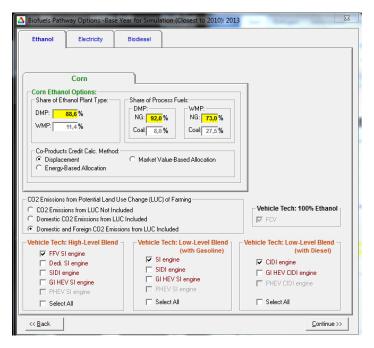


Figure 19: Production plant options and vehicle technologies.

The next step is setting up the electricity generation for the calculation model. In this case the electricity generation mix for the US was used which is shown in the Figure 20.

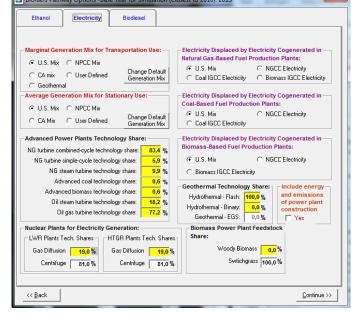


Figure 20: Electricity generation options for transportation and stationary use.

For biodiesel there are options for setting up the feedstock source, the co-product handling and the vehicle technology. For this study soybean was chosen as a feedstock source because it is the most used raw material for the biodiesel production. The vehicle technology which was chosen is a standard CIDI (Compression-Ignition Direct-Injection) engine which is used in all common diesel vehicles. The used set up is shown in the Figure 21.

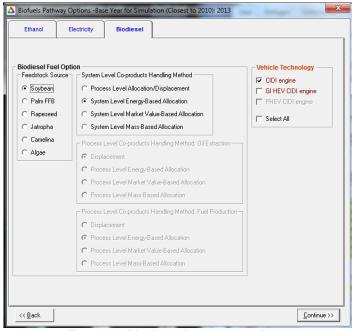


Figure 21: Biodiesel feedstock options.

The next adjustments are the different blending options for the different renewable fuels with the conventional fuels. Figure 22 below shows the blending options that were set for the calculation.

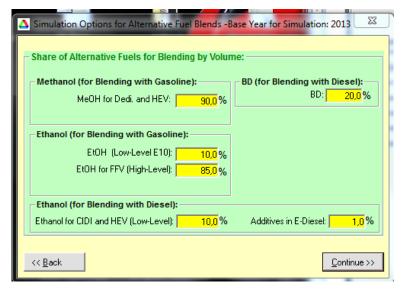


Figure 22: Blending options for bioethanol and biodiesel

The GREET model has emission rates (g/mile) and fuel economies (miles/gallon) for the different engine types. The newest data the model provides is based on 2008 vehicle models.

The used emission data is shown in the Figure 23 below.

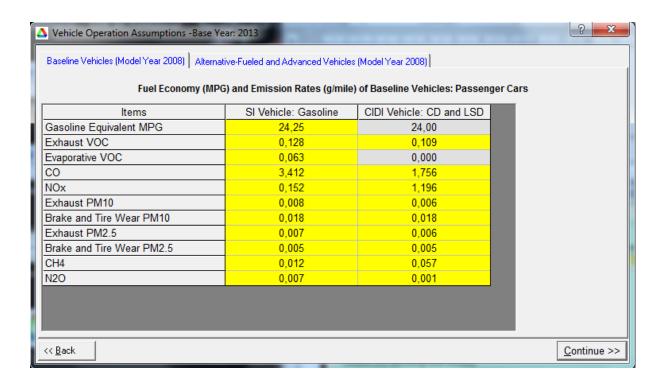


Figure 23: Vehicle related emission data.

4. Results & Discussion

Results are based on the assumptions the GREET model makes for emissions and energy use. With the used model calculations were made for a better understanding between renewable fuel and non-renewable fuels in relation to their energy use and released emissions. The model shows that renewable fuels have a large potential in saving emissions and energy. They can reduce the impact on the environment drastically if these sources are used as a substitute for oil based fuels. The calculations made for the compressed biogas are based on a ratio (30:70) between manure based raw material and landfill gas. As most of the gas in the US's is landfill gas and most of the EU's gas is made from organic waste such as sludge from water treatment plants.

4.1 Energy Use

The manufacturing processes of different fuel and biofuel types are sometimes very energy consuming. Figure 24 shows the total energy use for E10, E 85, Biodiesel, compressed biogas and conventional diesel. Total energy use is consisting of energy use for feedstock, fuel and vehicle operations. The most energy consuming fuel is E85 followed by E100. The reason that E85 is the most energy consuming is because the ethanol production needs so much energy for distillation and rectification and the blending ratio still needs another amount for the production of normal gasoline. Therefore less energy is needed to produce E100. The least amount of energy is used for the production and use of compressed biogas.

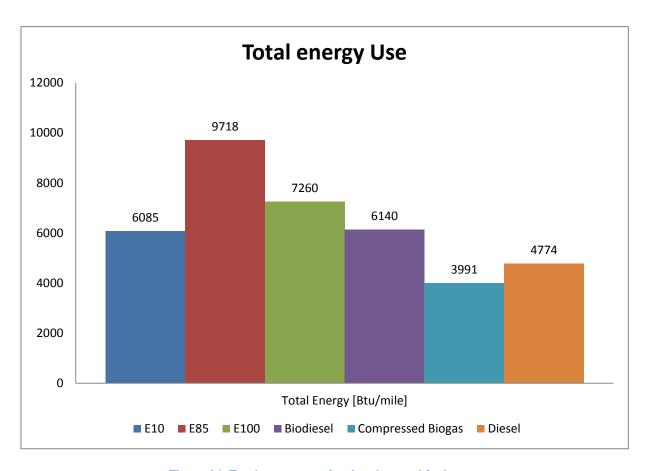


Figure 24: Total energy use for the observed fuels.

4.2 GHG Emissions

The greenhouse gas emissions are one of the most important factors for evaluating the harmfulness of processes. They are very important for the earth in case of radiation. They absorb radiation and keep the earth heated. The main GHG contributors are CO_2 , CH_4 , and N_2O .

The diagram below shows the CO_2 emissions that are released during the whole lifecycle of the observed fuels. Normal gasoline is by far the highest emitter with 428 g of CO_2 per mile followed by conventional diesel with 377 g/mile. Biodiesel is a little better than normal diesel but the real emission savers in this category are E100 and compressed biogas they are emitting the least amount of CO_2 . The compressed biogas doesn't need a lot of energy for its production and when it's used for combustion the emissions are minimal, thus, the reason why its CO_2 emissions are that low.

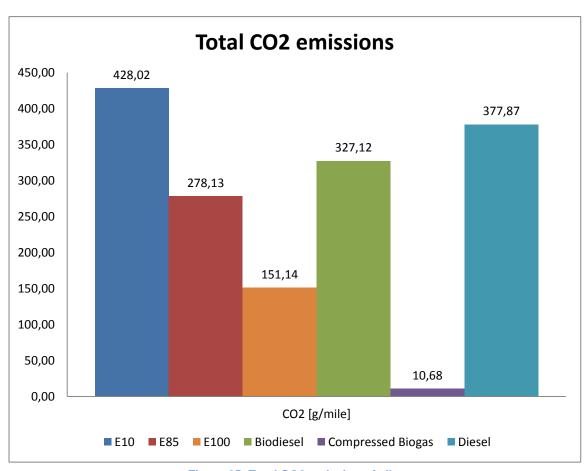


Figure 25: Total CO2 emission g/mile.

CH₄ is more than 20 times more harmful for global warming than CO₂.

For the fuels observed in this study the CH_4 emissions for compressed biogas are the highest with 2.38 grams per mile. The reason why the emissions for the compressed biogas are that high is because during the production process of biogas CH_4 is the main component that is produced which is important for the energy content of the fuel. There is a little bit of CH_4 leaking out at some point either during production or transportation.

The compressed biogas is followed by E85 (0.53 g/mile) and normal diesel fuel (0.50 g/mile) as shown in the Figure 26 below. The least CH₄ emissions are released by biodiesel (0.46 g/mile) and E100 (0.34 g/mile) production.

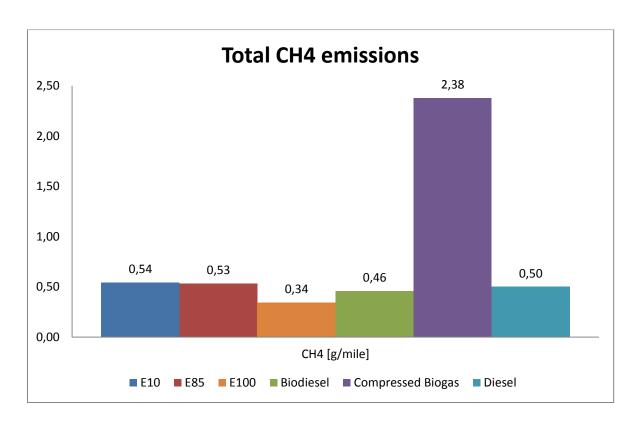


Figure 26: Total CH4 emissions g/mile.

Nitrous oxide is one of the major contributors for global warming. Its effect is more than 300 times as harmful as CO₂ and has therefore to be observed very carefully.

Figure 27 shows the different N_2O emissions for the different transportation fuels. The ethanol fuels E85 and E100 have the highest amount of N_2O emissions this is because of the nitrogen based fertilizers that are used for the growing of the biomass. The reason for the higher amount of N_2O emissions for E85 compared to E100 is because it is still blended with normal gasoline and therefore the engine technology is different. On a well to pump analysis the E85 releases less N_2O but on a well to wheel basis it is the opposite because of the different vehicle operation. The least amount is released by conventional diesel and compressed biogas with around 0 grams per mile.

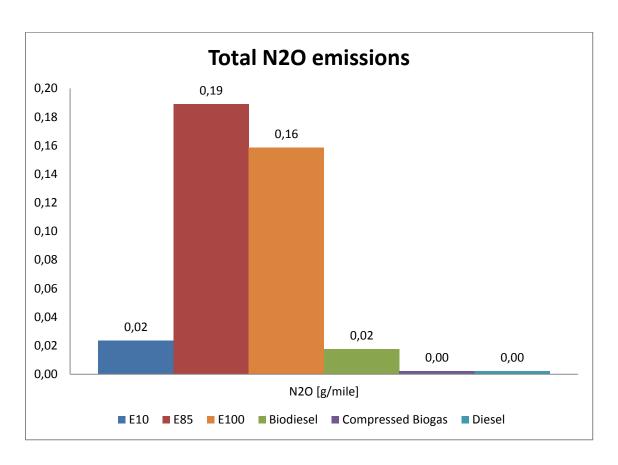


Figure 27: Total N2O emission g/mile.

4.3 Global Warming Potential Analysis

The global warming potential (GWP) is a calculation method for greenhouse gases. This method measures how much heat is trapped in the atmosphere by a greenhouse gas. The different greenhouse gases are transformed to carbon dioxide equivalents so that they can be summed up together. The global warming potential can be calculated for specific time periods, usually for 20, 100 and 500 years. A recent study updated the global warming values.

Table 6: Global warming potential values and lifetimes. [18]

| GWP values and | Lifetime (years) | GWP time horizon | |
|---------------------------------|------------------|------------------|-----------|
| lifetimes | | 20 years | 100 years |
| Methane | 12.4 | 86 | 25 |
| HFC-134a (hydrofluorocarbon) | 13.4 | 3790 | 1550 |
| CFC-11 (chlorofluorocarbon) | 45 | 7020 | 5350 |
| Nitrous oxide | 121 | 268 | 298 |

The Global warming potential is calculated after this formula:

Mass CO_2 Eq. = (mass of gas) x (GWP)

E10

| CO ₂ | CH ₄ | N_2O |
|-----------------|-----------------|--------|
| 428 | 0,54 | 0,02 |

$$428*1 + 0.54 * 25 + 0.02 * 298 = 447 g CO2 eq$$

<u>E85</u>

| CO ₂ | CH₄ | N ₂ O |
|-----------------|------|------------------|
| 278 | 0,53 | 0,19 |

E100

| CO ₂ | CH ₄ | N_2O |
|-----------------|-----------------|--------|
| 151 | 0,34 | 0,16 |

Biodiesel

| CO ₂ | CH ₄ | N ₂ O |
|-----------------|-----------------|------------------|
| 327 | 0,46 | 0,02 |

$$327 + 0.46 * 25 + 0.02 * 298 = 344 g CO_2 eq$$

<u>Diesel</u>

| CO ₂ | CH₄ | N ₂ O |
|-----------------|------|------------------|
| 377 | 0,50 | 0 |

$$377 + 0.50 * 25 + 0* 298 = 389 g CO_2 eq$$

Compressed biogas

| CO ₂ | CH₄ | N ₂ O |
|-----------------|------|------------------|
| 10,68 | 2,38 | 0 |

$$10.68 + 2.38 * 25 + 0* 298 = 70 g CO_2 eq$$

Figure 28 below is showing the greenhouse gas emissions which are released during the whole life cycle. The major greenhouse gases, CO_2 , CH_4 and N_2O , have therefore been transformed to CO_2 equivalents which is the major calculation equivalent for calculating the greenhouse gas emission impact. The highest amounts of emissions are released by E10 (447 g CO2 eq.) followed by conventional diesel (389 g CO2 equivalent). E85 (347 g CO2 eq.) and biodiesel (344 g CO2 eq.) are releasing almost the same amount of greenhouse gases during their life cycle. The fuels that are releasing the least amount of CO_2 equivalents are E100 (207 g CO2 eq.) and compressed biogas (70 g CO2 eq.).

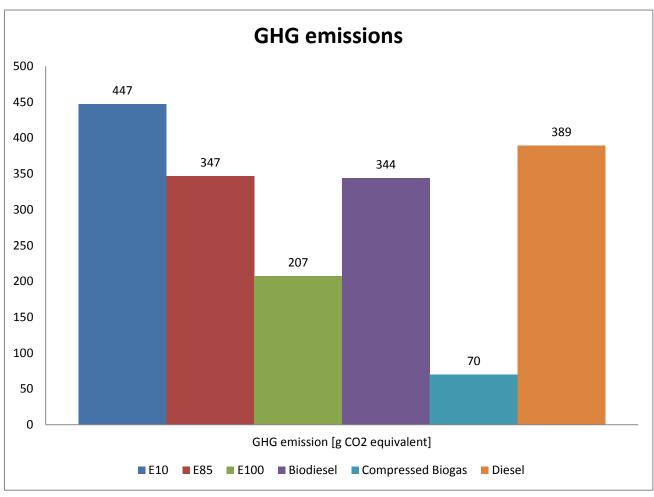


Figure 28: Sum of greenhouse gas emissions in g CO2 equivalent.

4.4 Tropospheric ozone formation compounds

Tropospheric ozone is formed by the reaction of mono-nitrogen oxides, carbon monoxide and volatile organic compounds with the influence of UV radiation from sunlight. This kind of ozone is formed on the ground by the presence of these chemicals by different combustion and production processes. It does not have the same benefits as the ozone in the stratosphere because it's formed on the ground it is very harmful for the health of humans and animals.

Volatile organic compounds are compounds that have a very low boiling point which results in an evaporation at low temperatures. These compounds have sometimes a large long term impact on the health therefore it is important to look at their related emissions. Figure 29 shows that E85 (0.41 g/mile) and E10 (0.32 g/mile) are emitting the most amount of VOCs. The biggest emission savers in this category are biodiesel (0.19 g/mile) and compressed biogas (0.14 g/mile).

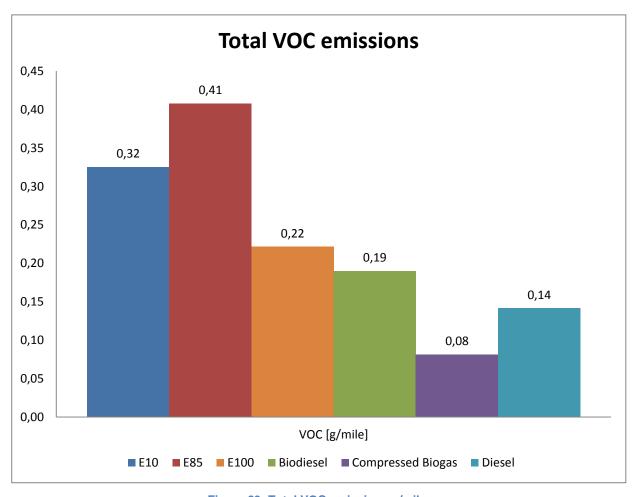


Figure 29: Total VOC emissions g/mile.

Mono-nitrogen oxides are chemicals that are formed out of nitrogen and oxygen during combustion processes at high temperatures. It is a main contributor in the ozone forming process on the ground and the destruction of the ozone in the stratosphere. The NOx emissions released from ethanol fuels and biogas are very low they range between 0.61 g/mile to 0.1 g/mile shown in the figure below. The big emitters of NOx are the diesel fuels both conventional diesel and biodiesel are emitting around 1196 g of NOx per mile.

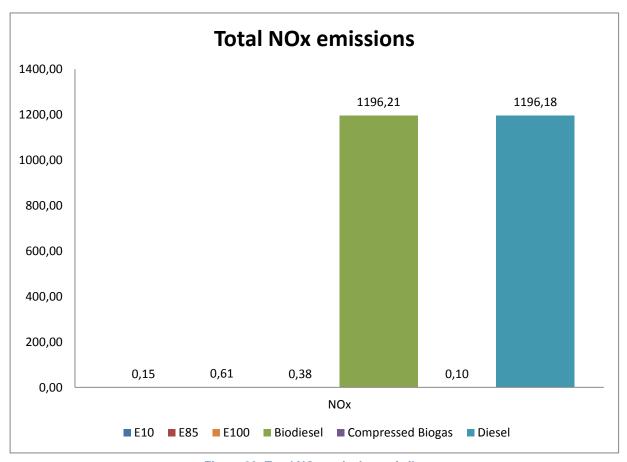


Figure 30: Total NOx emissions g/mile.

Carbon monoxide is a gas that is formed during the combustion process when not enough oxygen is present to form carbon dioxide. It is very dangerous for the human health. The big problem is that it is toxic as well as odorless and tasteless which makes it even more dangerous. The highest CO emissions are released from E10, and compressed biogas. The reason that the values are the same is because GREET has slightly different emission factors for feedstock and fuel production but the main part the vehicle operation has almost the same emissions for each fuel.

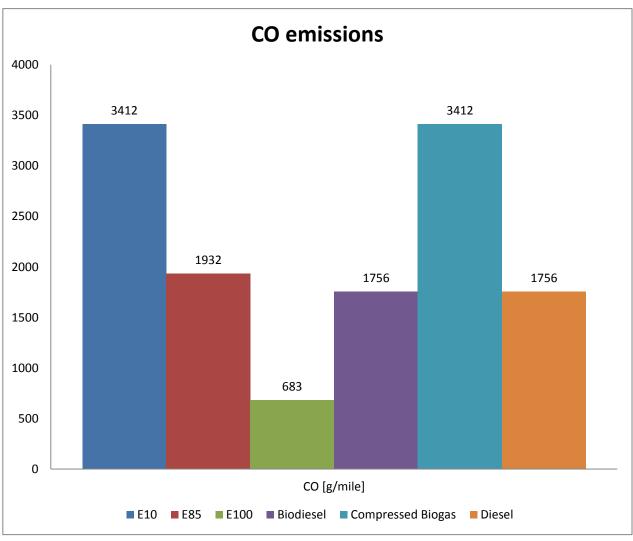


Figure 31: Total CO emissions g/mile.

5. Conclusion

minimized.

There are a lot of different reports on the energy consumption as well as greenhouse gas emissions of renewable fuels in literature. These vary in a wide range, as there are a lot of different assumptions possible, concerning for instance the usage of byproducts, the origin of electricity for the production processes, type and transport distances of raw materials, and many more. This has to be kept in mind, when comparing the values from different studies.

The GREET lifecycle analysis shows that any type of renewable fuel can help to reduce oil use and greenhouse gas emissions. There are still disadvantages for using them such as high use of production energy use or feedstock problems including using food for the production of fuels.

In general the potential of biofuels vary a lot depending on their production and use as well as their blending options. The calculations show that the most efficient and emission saving fuel is by far biogas. Even if its CH_4 emissions are very high its general greenhouse gas balance (70 g CO_2 eq.) looks very good. It therefore has the least impact on the environment. The reason for that is that there is not a lot of energy needed for the production of biogas other than just for heating and some mechanical operations and after that for the cleaning of the gas. There is almost zero energy needed for the production of the feedstock because biogas can be made out of almost everything organic which can be degraded by microorganisms. But also bioethanol and biodiesel have potential to save emissions. If more of the oil based fuels would get substituted with bio based fuels it would save a lot of emissions and the greenhouse gases would get reduced. The big disadvantage with food based biofuel is that the crop growing process needs huge amounts of fertilizers and also lots of water. Those have big impacts on land and water resources. Therefore the gap between food containing biofuels and oil based fuels is getting

The results shown in this report are partly overlapping with previous results shown in other research papers. The results shown in the report of the "Umweltbundesamt – Ökobilanzen ausgewählter Biotreibstoffe" are varying by a factor around two. The only major difference is the emission of biodiesel.

Table 7: Results of the Umweltbundesamt

| GHG-emissions | g CO₂ eq |
|---------------|----------|
| Biodiesel | 80 |
| Bioethanol | 150 |
| Biogas | 40 |
| Diesel | 200 |
| Gasoline | 250 |

The reason for the varying results is because of the big range of different assumptions, usage of by-products and the usage of the fuels. The report of the Umweltbundesamt for example is using rape for the biodiesel production which is different in the growing process, fertilization and energy content than soybean and palm oil.

This is the biggest issue for the evaluation of biofuels because the range of different assumptions is huge for example the different raw materials that are used have different yields and energy contents where rape has 2.99 t/ha*a and an energy content of 24.6 MJ/kg [19] whereas the yield of soybean is 1.20 t/ha*a [20] and the energy content is 16.8 MJ/kg [21] .

Another point is the difference in the usage of co-products where different studies give the co-product an energy value and subtract it from the energy use at the production whereas GREET uses the exact numbers and emissions based on the substitutions the co-products are used for.

In addition there are many other influencing factors which have a big impact on the evaluation process, there are differences in the energy mixes, the production plants and transportation distances.

In conclusion, the evaluation of biofuels is very sensitive based on different assumptions which all have impact on emissions. This is the reason why it is difficult to find a general solution which applies for everybody.

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