



Bachelors Chemical Engineering Research Project

Can Nitric Acid be produced in a Combustion Engine using Ammonia as a Fuel?

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Abstract

By comparison of a diesel engine and a nitric acid plant, a new process was modeled, in which a downscaled nitric acid process was incorporated in a diesel engine. Here, the properties of the raw materials were compared, and it was concluded that the project is possible if a catalyst can be found which allows for a satisfactory reaction rate and conversion for ammonia to NO_2 under the harsh conditions it would be subjected to. In order to implement this system into a moving vehicle, more attention would have to be spent to energy recovery techniques as the energy content of ammonia is significantly lower than that of diesel.

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Introduction

In a world with a constant increasing population, the demand for food is as high as ever. To face this challenge, farmers throughout the world explore all means to improve their crop quality and growth efficiency. The use of fertilizers to replenish the nutrients absorbed by the crops they cultivate is thus essential to maintain or improve production without exhausting the soil.

Fertilizers are substances added to the soil to improve plant growth and health. Fertilizers can be categorized in two different groups; Organic and inorganic fertilizers. Organic fertilizers are the result of composting organic matter, being plant or animal. Inorganic fertilizers are composed of synthesized chemicals/minerals.

The most important nutrients in fertilizers are nitrogen, phosphorous, potassium and sulphur containing salts which are consumed in large quantities by plants.

In this report, the focus will be on nitric acid, a nitrogen containing compound which is used in the production of fertilizers.

The demand for nitrogen containing fertilizers is among the highest. The consumption of the main consumers of nitrogen based fertilizers are summarized in Table 1.

Country	Share of total N consumption (%)	Absolute amount (Mt/year)
USA	51	4697
China	16	2998
France	52	1317
Germany	62	1247
Canada	55	897
UK	70	887
Brazil	40	678
Spain	42	481
Mexico	20	263
Turkey	17	262
Argentina	29	126

Table 1 - Top users of N-based Fertilizers (Steinfeld, Gerber, Wassenaar, Castel, Rosales, & de Haan, 2004)

In the production of nitrogen containing ingredients, ammonia is used as the main source of the nitrogen containing raw material. The majority of the ammonia produced worldwide is used in the production of nitrogen rich fertilizers such as urea, ammonium nitrate, ammonium phosphates, nitric acid and ammonium sulphate (Kramer, 2005). Once the nitric acid is produced, ammonium nitrate can be synthesized through the reaction of nitric acid with ammonia as shown in reaction below:



Ammonium Nitrate is a high nitrogen containing compound making it an extremely effective and valuable fertilizer.

Currently, the nitric acid plants are few in numbers, extremely large and are only growing in capacity to accommodate the ever increasing demand. Each factory acts as a supplier of fertilizers for a radius which can be in the magnitude of the thousands of kilometres, if not more, when dealing with international exports. Being dependent on supply chains which are expensive and inefficient, the fertilizers must transported over great distances, further adding to the costs of production.

The aim of this project is to make an attempt at redesigning and down-scaling the current process so that it can take place on site, relieving the need for giant plants and large transport networks. Here, the possibilities of using a diesel engine to produce the nitric acid will be explored. Engines are very complicated reactors that may be bought for relatively cheap (when compared to an entire plant), and may even give mechanical energy in return. Engines also show a high potential in being able to mimic certain aspects of the current nitric acid process. This might allow nitric acid to be more accessible those who require it, in this case, the farmers.

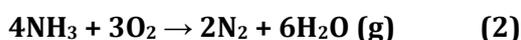
This research will handle the question: Can nitric acid be produced in a combustion engine using diesel or ammonia as a fuel?



Industrial Nitric Acid Synthesis

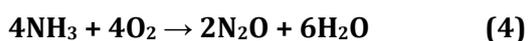
The current method of producing nitric acid uses the Ostwald process. This utilizes a catalyst to promote the production of NO when ammonia reacts with oxygen. The NO then further reacts with oxygen, giving NO₂. Nitric acid is then obtained by reacting NO₂ with water. The industrial synthesis of nitric acid from ammonia is summarized in the Process Flow Diagram (PFD) shown in Figure 1.

The reactants required are ammonia, air and water. Each reactant is pre-treated; the air is filtered of dust and compressed to 8 bar and the ammonia is vaporized at 8 bar. A portion of the compressed air and the entire ammonia flow are then combined just before or inside the reactor. The reactor contains platinum/rhodium gauze (90 wt% Platinum 10 wt% Rhodium), which acts as the catalyst. The function of the rhodium is to strengthen the gauze and to reduce the amount of platinum lost during the conversion of ammonia. If the volume %NH₃ in the air is greater than 10% then an explosive mixture will be made and the ammonia will combust^(Cresswell, 1991) according to reaction (2).



This reaction is extremely exothermic, roughly half that of the combustion of diesel, however it results in the production of nitrogen gas which is rather inert and thus unwanted.

In order to favour the production of the desired product, the catalyst is heated to 650-1000°C^(Gillespie, 1972) to favour reaction (3) over reactions (2) and (4). The following reactions may take place in the reactor:

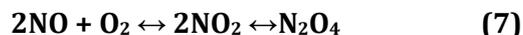


In this section the NO yield is dependent on the pressure and the temperature as shown in the Table 2:

P (bar)	T (K)	NO yield (%)
Below 1.7	1083-1123	97
1.7-6.5	1123-1173	96
Above 6.5	1173-1213	95

Table 2 - NO Yield at Respective Operation Environments^(Perez-Ramirez, 2002)

In the plant described in Figure 1, the working pressure is 8 bar, resulting in an NO yield of 95%. Due to the fact that all reactions are exothermic, the temperatures in the reactor can reach 1180°C. Due to these high temperatures the reactor is equipped with cooling coils outside the catalyst area. Due to these high temperatures small amounts of platinum from the catalyst evaporates in the form of PtO₂. From here, the gases will be cooled in order to stimulate the oxidation of NO to NO₂ and to allow for 60 to 80% recovery of Platinum^(Perez-Ramirez, 2002) by the scrubber F - 601 as shown in figure 1. The NO₂ produced will be in equilibrium with N₂O₄ as shown in equation (7).



By keeping the temperatures low and the pressure high, using a heat exchanger, the production of NO₂ is highly favoured. The temperature is reduced to around 234°C, keeping water from condensing¹. From here, the gaseous mixture flows through a scrubber, removing the PtO₂.

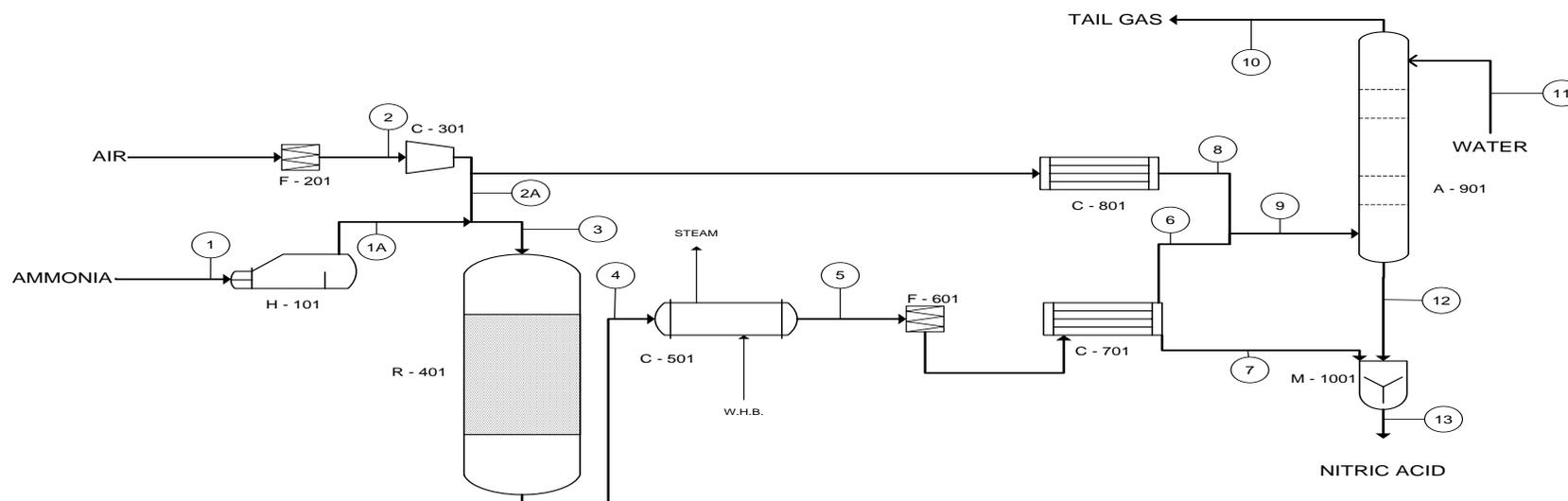
Once scrubbed, the gas is further cooled, allowing the condensation of water to take place, where small amounts of NO₂ and N₂O₄ promptly dissolve, further reacting to HNO₃ according to reaction (8). This reaction takes place in the condenser labelled C-701.



¹ See Appendix 1 – Vapour Pressure of Water



Flow sheet – Simplified Nitric Acid Process



Line No. Stream	1	1A	2	2A	3	4	5	6	7	8	9	10	11	12	13
Component	Ammonia Feed	Ammonia Vapour	Filtered Air	Oxidiser Air	Oxidiser Feed	Oxidiser Outlet	W.H.B. Outlet	Condenser Gas	Condenser Acid	Condenser Air	Absorber Feed	Tail Gas	Water Feed	Absorber Acid	Product Acid
NH ₃	731	731	—	—	731	NIL	—	—	—	—	—	—	—	—	—
O ₂	—	—	3036,9	2628,2	2628,2	935,7	935,7	275,2	TRACE	408,7	683,9	371,5	—	TRACE	TRACE
N ₂	—	—	9990,8	8644,7	8644,7	8668,8	8668,8	8668,8	TRACE	1346,1	10014,7	10014,7	—	TRACE	TRACE
NO	—	—	—	—	—	1238,4	1238,4	202,5	—	—	202,5	21,9	—	TRACE	TRACE
NO ₂	—	—	—	—	—	TRACE	—	967,2	—	—	967,2	TRACE	—	TRACE	TRACE
HNO ₃	—	—	—	—	—	NIL	NIL	—	850,6	—	—	—	—	1704	2554,6
H ₂ O	—	—	TRACE	TRACE	—	1161	1161,1	29,4	1010,1	—	29,4	26,3	1376,9	1136	2146
Total	731	731	13027,7	11272,9	12003,9	12003,9	12003,9	10143,1	1860,7	1754,8	11897,7	10434,4	1376,9	2840	4700,6
Pressure (bar)	8	8	1	8	8	8	8	8	1	8	8	1	8	1	1
Temperature (C)	15	20	15	230	204	907	234	40	40	40	40	25	25	40	43

Figure 1 - PFD Nitric Acid mono-pressure Factory (flows in kg/h) (towler, 2009)

The reaction which took place in the reactor does not produce enough of the required water for a complete absorption of NO_2 to take place. The remaining gasses are thus fed from the condenser into an absorber, where additional water is streamed in. The many reactions involved in an absorber are quite complex and therefore only the most important reactions will be covered. The reactions can either take place in the gas phase or in the liquid phase. Reactions in the gas phase will take place in the spaces between the trays, as shown in figure 2.

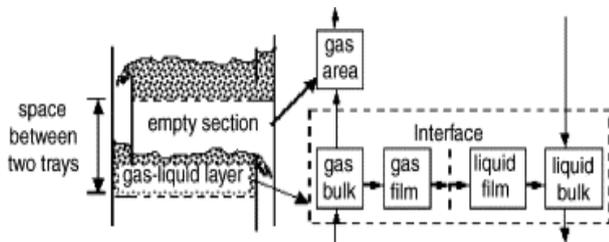
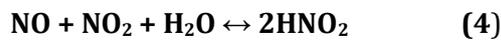


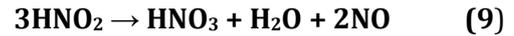
Figure 2– Absorption Tray (Bernhard Hüpen, 2005)

Once the substances have been absorbed into the water, a series of further reactions can occur. The reactions that take place in the absorber are summarized below (Bernhard Hüpen, 2005).

Gas phase reactions



Liquid phase reactions



When nitrogen monoxide NO is produced from reaction (17), it is immediately expelled into the gas phase as it is highly insoluble in water. The concentrations of N_2O_3 and HNO_2 in the gas phases are minute as their absorption into the water is extremely fast. It can be assumed that reactions 15 and 17 are extremely fast, keeping the amounts of N_2O_3 and HNO_2 in the liquid phase negligible. The overall reaction which takes place in the trays is exothermic. Therefore cooling of the trays is required to keep the temperatures low, facilitating the absorption of the gases.

These absorption columns can be quite large. The following table describes the various behaviours in the interior of such an absorption column which operates at 8 bar. It should be noted that this process does not fully absorb all the NO_x 's present, as 2.18vol% of NO_x 's are still present at the gas outlet.

N	$\text{NO} + \text{NO}_2$ (Vol%)	H_2O (Vol%)	Height (m)	% HNO_3	Temp (°C)	Amount of acid produced, %.
Gas arriving at plate n.			Acid arriving at plate n			
1	8.56	14.5	-	40.7	30	20.4
2	8.44	13.3	0.28	40.7	115	23.5
3	7.87	9.9	0.38	43.3	108	34.8
4	7.15	6.7	0.46	45.8	98	46.8
5	6.42	4.4	0.48	48.2	88.5	57.1
6	5.55	2.3	0.64	50.6	73.5	68.2
7	4.84	1.4	1.26	52.9	64	76.3
8	4.21	1.0	1.98	54.9	57.5	83.0
9	3.71	0.7	2.42	56.5	52	88.3
10	3.33	0.55	1.84	57.5	47	92.2
11	3.02	0.35	1.56	58.3	40	95.4
12	2.77	0.25	1.48	58.9	34	97.9
Gas leaving last plate (Total H)			Acid leaving the last plate			
	2.18	0.2	12.78	59.5	28	100
h=height in m between plates n and n+1.						
Time the gas remains between plates n and n+1						
H=total height (m)						

Table 3 – Behaviour in an Absorption Column (Aguinet, Manoury, & Martin., 1972)

The nitric acid streams from the condenser and the absorber are then mixed giving a nitric acid solution of $\approx 50\text{-}65$ wt% which can then be used further processed. From this step onwards, in order to meet specifications on NO_x content in the acid, the acid is degassed and sometimes bleached.

In order to compare this process to that of a diesel engine, it is required to have a good



understanding of how the diesel engine works; its chemistry, thermodynamics and to have a working model.

The Diesel Engine

The Fundamentals of a Diesel Engine

Diesel Engines are internal combustion engines. They make use of highly compressed hot air to ignite fuel which is injected into the combustion chamber when the pressure is above 40 bar and above the auto-ignition temperature. Making use of big compression ratios (between 1:14 and 1:26) high thermal efficiencies exceeding 50% can be obtained. Due to the high temperature of the air in the combustion chambers, diesel engines do not require spark plugs to ignite the fuel which is required in gasoline internal combustion engines.

An illustration of a two stroke engine can be seen in figure 3. A four stroke engine works in a similar way, however it has an extra cycle in which no fuel is injected and thus no combustion takes place. This extra cycle allows for the exhaust gases to fully exit the combustion chamber, allowing for the ignition to take place in an oxygen rich environment further increasing efficiency.

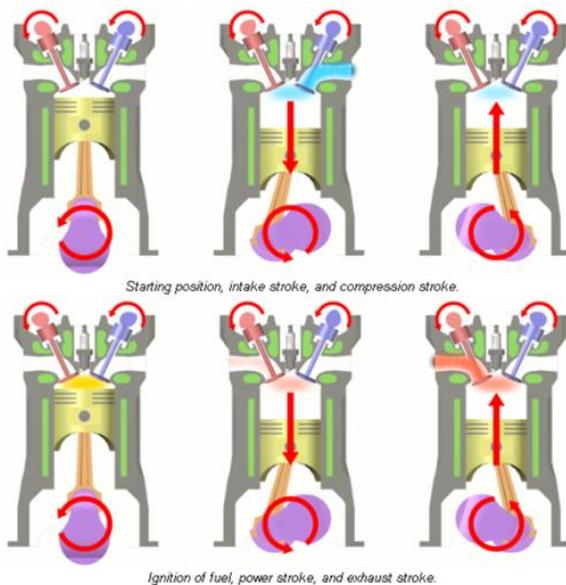


Figure 3 – Two Stroke Engine

A brief description of each stage follows, from left to right.

1. Initial position of the piston, no fuel and little air present in combustion chamber.
2. Air mixture is sucked into the engine due to the downwards movement of the piston which creates a lower pressure environment.
3. Upwards motion of piston compresses gases to high pressures, resulting temperature rises.
4. At maximum compression level, fuel is injected into the cylinder, which promptly combusts at the high temperatures present.
5. Expansion due to increase in number of molecules and in temperature forcing a downward motion of the piston.
6. Upward motion of piston forces combusted gases to exit the combustion cylinder, allowing a new cycle to begin.

The cycles can be thermodynamically described using the pressure-volume diagram as seen in figure 4, which clearly depicts the respective p-V conditions at each stage of the cycle in a 4-stroke diesel engine.

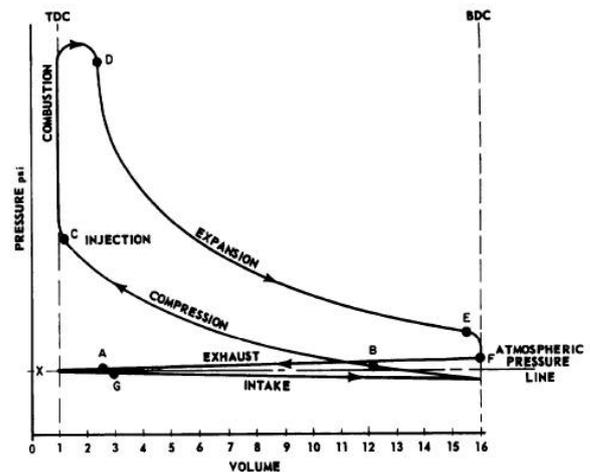


Figure 4 - Pressure-Volume Diagram of a 4-Stroke Cycle Diesel Engine (Actual Combustion Cycles)

By applying this example to an actual case of a ship engine, the pressure at the inlet is already at a higher pressure, thus above the atmospheric pressure. This enables the engine to obtain higher pressures with the same compression ratio. In figure 4, a compression ratio of 1:16 is used. Fuel injection and



combustion often takes place when the pressure is around 42 bar and temperatures above the auto-ignition point. The combustion results in a dramatic temperature increase in a very short time, and increasing the pressure to values reaching 200 bar ^(Leduc). The excess in pressure is exerted on the crown of the piston pushing it down which is converted to mechanical energy by the crank-shaft.

Having multiple cylinders running at different phases, allows for the constant supply of mechanical energy required to compress the gases to the desired pressure and temperature. Two stroke or 4 stroke diesel engines are currently used according to the application required.

High RPM engines make use of diesel fuel with a low viscosity and operate in a 4-stroke engine. These engines are used for low power/high speed applications such as cars, trucks, small boats, compressors and pumps. These engines will run above 1000 RPM.

Medium RPM engines can make use of 2 or 4 stroke engines and are often used in larger facilities such as electrical generation, large compressors and pumps. They work in a range between 300 and 1000 RPM.

Low RPM engines are primarily used to power large ships. Making use of highly viscous fuels also known as low grade heavy fuel which are cheaply available as by-product of the petrol industry, these extremely large engines operate at 2-strokes can produce up to 114 000 hp (85MW²) and run in a range between 60 and 300 RPM.

The Combustion of Diesel – The Chemistry

Diesel engines, through the injection of fuel into the cylinder at high pressures and temperatures, can make use of a variety of fuels;

² Data taken from the Wärtsilä-Sulzer RTA96-C turbocharged two-stroke diesel engine, the most powerful engine in the world, weighing 2300 tons and consuming up to 6.2m³ of fuel per hour (Wärtsilä).

from natural gas to vegetable oils, although different distillates of crude oil are the most commonly used.

For this reason, the composition of diesel is not fixed but varies with the source and specific additives required. Extensive regulations force constant quality tests to which the fuel has to comply. Impurities, such as heavy metals and sulphur-content, have to be kept below certain levels in order for the fuel to meet regulations to be marketed.

A general assumption for the composition can be made for the masses of carbon to hydrogen, at 86 wt% C to 13 wt% H with 1 wt% being other components, mainly sulphur. The table below compares different fuels and the energy content.

Fuel	Density (kg/m ³)	Chemical Comp.		Boiling Point (°C)	Energy (MJ/kg)	Auto-ignition temp (°C)	Minimum air needed for complete comb. (kg)
		C wt%	H wt%				
Normal	720 - 750	86	14	25-210	42.7	300	14.8
Super	730-780	86	14	25-210	43.5	400	14.7
Diesel	810-850	86	13	150-360	42.5	250	14.5
LPG	540 (liq) 2.25 (gas)	82.5	17.5	-30	46.1	400	15.5

Table 4 – Fuel Energy Content

Engines make use of a higher than required oxygen to fuel ratio, allowing for an almost complete combustion of all hydrocarbons, minimizing emissions of CO and other compounds as a result of the incomplete combustion of the fuel. This however is not the case with older engines or in the start up phase, when the engine, while still cold, allows for the fuel to not be fully combusted, producing several undesirable compounds.

Due to the high temperatures at which the combustion takes place and the highly compressed oxygen and nitrogen present in the combustion chamber, the production of undesirable NO_x and N₂O takes place resulting in concentrations of NO and NO₂, which can be up to the thousands ppm. NO_x reduction is a well debated problem with regulations forcing strict tolerable emissions. Developments, such as Selective Catalytic Reduction (SCR), make use of



N-containing reducers such as NH_3 to actively lower NO_x emissions.

The emissions from large diesel engines are often related to the power output of the engine, the efficiency of the engine and the ratio between emissions as a result of incomplete combustion of hydrocarbons and the formation of NO_x 's. These quantities are often expressed in g/kWh or in ppm.

Air	Fuel	Lubricant	Exhaust
3500 g/kWh	175g/kWh	1 g/kWh	
O_2 – 21%	HC – 97%	HC – 97%	O_2 –13%
N_2 – 78%	S – 3%	Ca – 2.5%	N_2 –75.8%
Other – 1%		S – 0.5%	CO_2 –5.2%
			H_2O –5.35%
% = wt%			Other – 1%

Table 5 – Inlet and exhaust composition (CIMAC, 2000)

Pollutant	Medium Speed engines (g/kWh)	Low Speed engines (g/kWh)	Low Speed engines (ppm)
NO_x	12.0	17.0	1500
CO	1.6	1.6	60
HC	0.5	0.5	180
CO_2	600	600	600
SO_2	3.6x%S	3.6x%S	—

Table 6 – Undesirable emissions of exhaust gasses (CIMAC, 2000).

These emissions are often controlled by strict legislation such as the MARPOL Annex VI (IMO, 1993) legislation which limits the Sulphur content of heavy fuels and NO_x emissions among other greenhouse gases. Different regulations apply for different uses and applications. Ships designed to sail in rivers and lakes have stricter regulations than those sailing in open waters. Figure 5 represents the limit on emissions imposed. Tier 1 is currently in place since 2000, Tier 2 will take place from 2011 and Tier 3 from 2016 within specific borders and limits. These regulations are strongly taken into consideration by manufacturing companies which must abide by them.

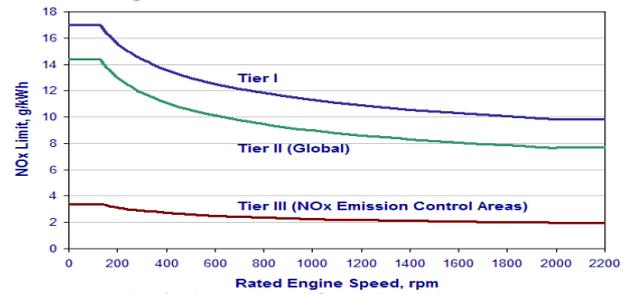


Figure 4 – MARPOL Annex VI Legislation (IMO, 1993)

Marine engines are currently being adapted to satisfy the demands at hand, by making use of technology which has been available for decades for similar land based processes. Additional utilities can be added to different stages of the engine allowing for an effective removal of particulate matter and other green house gases.

Emission Control

The aim to reduce emissions of harmful gases into the atmosphere forces shipping companies and engine manufacturers to find effective methods for the reduction of nitrogen oxides, carbon monoxides, sulphur oxides, unburned hydrocarbons and particles.

There are different methods currently applied. These range from pre-treatment where the fuel or the inlet gas is tampered with or by adding water to the mixture thus reducing the temperature of combustion. Internal measures, by modifying the conditions within the cylinder such as the shape of the injectors and the timing of the injection and post-treatment where the exhaust gases are subjected to further treatment before being released into the atmosphere. The following table shows the effectiveness of some of the many methods³.

³ -Visit Cimac's website for a complete overview of the many different techniques used and their respective properties. (CIMAC, 2000)

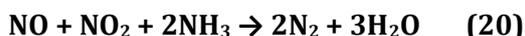
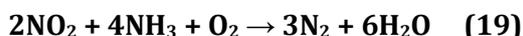
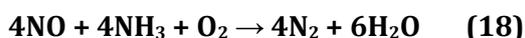


Technique Applied	Effective Reduction of Emissions (%)
Basic internal engine modifications	20%
Exhaust gas recirculation	35%
Direct water injection	50%
Humid air motor (HAM)	70%
Selective catalytic reduction (SCR)	95%

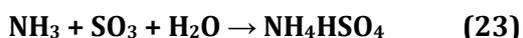
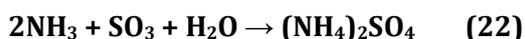
Table 7 – Techniques used to Reduce Emissions (CIMAC, 2000).

Selective catalytic reduction (SCR) makes use of ammonia or a urea solution. Since the process at hand also makes use of ammonia, a better insight of this stage may prove valuable. An ammonia or urea solution is injected into the exhaust flow of the engine. The urea is readily converted into the needed ammonia which, once entering the SCR reactor, reacts with nitrogen oxides and sulphur oxides to form nitrogen, water and ammonium bisulphates according to the following reactions:

Reactions which reduce NO_x's:



Reactions which reduce SO_x's:



The catalysts used are usually oxides of base metals, zeolites and precious metals, each with their respective advantages and disadvantages, such as thermal durability and reaction speed. The catalysts are often coated homogeneously on a ceramic backbone, whose design also varies according to fouling properties, pressure drop and costs. Here, designs such as honeycomb and plate catalyst are the most used.

The catalysts also have an optimal temperature range and therefore as a result the SCR reactor can prove itself to be ineffective during initial stages of the process. The

following figure shows the different stages which were added to a diesel engine in a ship.

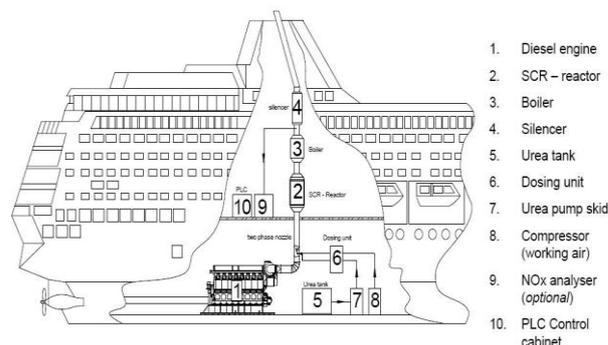


Figure 5 – SCR implemented in a boat.

The Ammonia fuelled Engine

The objective of this investigation is to combine the knowledge obtained from the nitric acid process and the diesel engine to evaluate, step by step, the potential of producing nitric acid in a diesel engine when using ammonia as the fuel. Certain changes may be required in order for the process to take place in such a way as to mimic the current industrial process conditions, as well as the desired end results obtained in a factory. This insight will determine if diesel engines are realistic candidates for a downscaling of a nitric acid plant and if further research and testing into this topic is meaningful.

A parallel analysis of both the nitric acid process and the diesel engine was performed with the objective of finding key points which might become problematic for the process to take place. A critical analysis of the problems at hand will attempt at finding ways of overcoming problems, either by assumptions when the information is not readily available or by introducing new steps or components into the engine, so that the process can, in the end, run smoothly.

To facilitate comparisons, two models in aspen were used, one for the diesel process and one for the new ammonia engine. These models can be seen in appendix 4. The same amounts of



diesel and ammonia⁴ were used for a better comparison of the process, while other factors such as pressures and volumes of air were kept as close as possible to those obtained from the literature. For a detailed explanation of each model, an explanation is included with each schematic, including mass and energy balances in Appendix 4.

The Engine Fuel

The first key difference between the two processes is the raw materials required or fuel. The energy content of the reactions at hand is important, since we are making use of a diesel engine to run a process. The ammonia will have to mimic the properties of diesel.

	Ammonia (liquid)	Diesel (liquid)
Pressure requirements	17 bar (or 1 bar @ $T \leq -33^\circ\text{C}$)	Stable at ambient pressure
Temperature requirements	Ambient ($T \leq -33^\circ\text{C}$ at 1 bar)	Stable at ambient temperature
Viscosity	$245 \cdot 10^6 \text{ Pa/m}^2$ @ -23°C	Varies from fluid to highly viscous
Corrosiveness	dissolves alkali metals and barium, calcium, and strontium, Al under presence of moisture	—
Other meaningful things	Contact with liquid may cause burns	Keep away from ignition sources

Table 8 – Fuel Properties [See Appendix 2]

Containment and transport

Diesel tanks - require special attention due to their flammability. The diesel tank should be kept away from direct sun light, in a cool and well ventilated area. Special attention must be paid to removal of all ignition sources and oxidizing materials. In the case of low grade diesel fuel, the high viscosity of the fuel requires heating to increase fluidity and improve handling. Tanks made from stainless steel or special plastic are often used.



Figure 6 – High Pressure Anhydrous Ammonia Storage Tank (Web02)

Ammonia storage tanks - are made of stainless steel to minimize the effects of long term corrosion from the ammonia. The ammonia should be in liquid form, which can be achieved in two ways. The ammonia can be refrigerated to under its melting point (-33°C) at ambient pressure or it can be kept under high pressure (17 bar) at ambient temperature. The high pressure bullet tanks can be seen above in Figure 6. Storage tanks are designed to have 85% usable capacity (liquid) and 15% vapour space to allow for expansion (Tanner Industries Inc.).

The new tank - It is cheaper and easier to maintain a fuel tank at an increased pressure then it is to maintain it at a cold temperature, especially in countries with warmer climates. The usual pressure of 17 bar is safe until a maximum temperature of 42.5°C is reached, in which case the liquid will begin to boil and cause problems. Higher pressures are required for such cases⁵. Consequently a standard ammonia tank will be used, but will have to be downsized to fit to the scale required. Piping required for transport between equipment must be made of either heavy duty carbon steel or standard carbon steel.

Air supply - For both processes, air is used as a source of oxygen required for the desired reactions to take place. The preliminary treatment of the air performed by the diesel engine can be used to supply the required pressures at the inlet of the cylinder for the new nitric acid process. The basic steps are thus,

⁴ 73.1 kg/h were used, which was taken as 10% of amounts used in figure 1

⁵ See Appendix 1 – Vapour pressure of ammonia.



filtration of dust and other impurities, compression and cooling.

The Reactor/Combustion Chamber

The diesel combustion cylinder -The cylinder of a diesel engine is designed to withstand large pressure and temperature differences over a very short period of time. It also needs to be highly resistive to frictional forces caused by the piston and also to generate different outputs of mechanical energy on request, which is a result of varying the amount of fuel injected. The process is consequently very far from a steady state process which is favoured in industrial processes and as such, hard to model and predict its theoretical behaviour.

The diesel which may be preheated is injected into the cylinder when the air is at the maximum compression point, at which point the combustion of the diesel takes place. As a result, a drastic increase in temperature and, according to laws of thermodynamics, an increase in pressure takes place. The temperature difference can therefore be close to 2000 degrees for a single cycle, as the inlet air being let in at 60-150°C and the maximum heat prior to the decrease in pressure by the piston at 1300-2000°C. Pressures also vary from a few bar at the inlet to near 200 bar just before the piston starts increasing the volume of the cylinder as seen in figure 4.

Addition of lubricant to the cylinder is also required to reduce the wear of the piston and other moving parts.

Ammonia Industrial Reactor - In the industrial reaction of NH₃ with O₂, the air and the vaporised ammonia are either mixed before or in the reactor. Once the gas is in the reactor, the mixture flows across a series of heated catalyst gauze, where the initial oxidation to NO takes place. This highly exothermic process takes place at 8 bar and is maintained at a constant temperature through cooling. The exit gases of the reactor enter a heat exchanger where they are cooled allowing the 2nd stage oxidation to take place, from NO to NO₂ shown by reaction 7.

Ammonia in a Diesel Engine Cylinder - When comparing both the diesel engine and the ammonia reactor, many differences become obvious. To start, the oxidation of ammonia to NO makes use of a catalyst and the reaction takes place at constant temperatures and pressures which are designed for optimal conversion. On the other hand, the diesel engine makes use of large fluctuations of temperatures and pressures by the combustion of the fuel, from which it obtains the desired mechanical energy.

To tackle the problem of the catalyst, which will have to be implemented in the cylinder, an adaptation of the piston seems like a reliable option. The catalyst, being attached to a mesh or a foam, at the crown of the piston, would allow for the reaction to take place. This technique, however, comes at a cost of the compression ratio, as the piston at the highest point will not have compressed the air as much as it would without the catalytic mesh. It is also vital that there is enough surface area present in this catalyst to allow the near complete conversion of ammonia in such a small amount

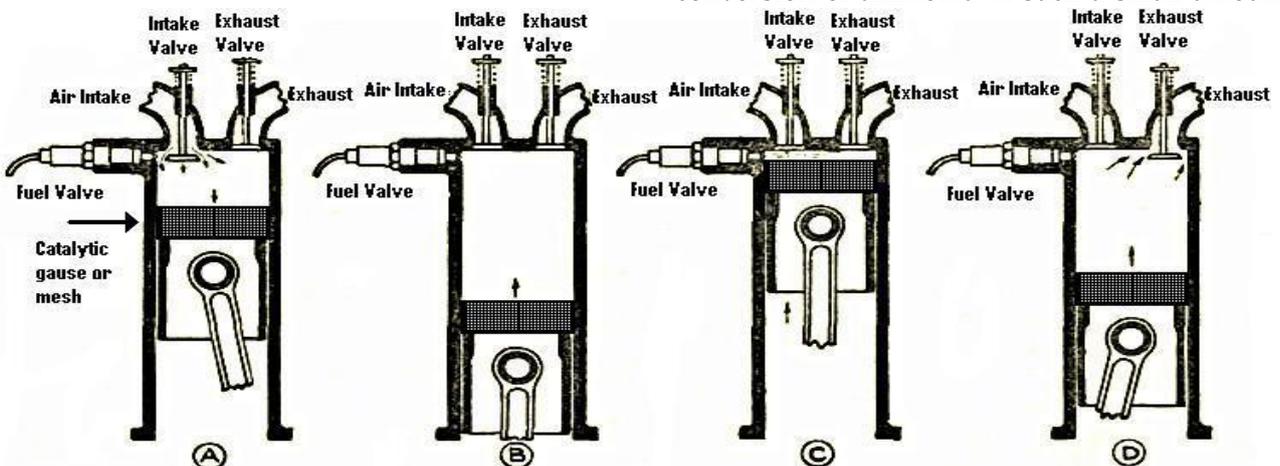
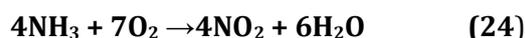


Figure 7 – Cylinder Fitted with Catalyst



of time which would result in the required increase of temperature. This can be seen in figure 7.

A further assumption was used regarding the catalyst. Assuming that a catalyst is able to withstand the various stresses imposed by the varying temperatures, pressures and mechanical motion, use was made of a catalyst which facilitates the highly exothermic reaction between ammonia and oxygen to render nitrogen dioxide according to reaction 24:



The existence of this catalyst is not based on any literature background and it is assumed that the workings of such catalyst are able to assist reaction 24 at a rate close to that of combustion of diesel.

Here, special attention will have to be made regarding the extent of the reaction. Since an incomplete reaction can result in insufficient thermal energy being released, resulting in the engine stalling. If this proves not to be an issue, unreacted NH_3 will be readily absorbed by water later in the process. A question remains to whether this is acceptable.

An aspen model was made which showed a surplus of 17% energy after compression of the inlet gases. This however was done by assuming 100% efficiency for all utilities, components and reactions (100% conversions), not taking friction and other factors into consideration. If this value is compared to that obtained from the model for the diesel engine, 60% energy is available to be used after the required air compressions took place.

Regarding the RPM of the new engine, seeing as the ammonia will have to go from liquid, to gas, and then from gas to the interface of the catalyst within a very short period of time, the lower the RPM's of the new engine, the more efficient the process can be. More insight might be needed in very low RPM engines, in the range 5-30 RPM.

The Absorber

An absorber is required for the final stage of the process. In chemical plants, similar absorbers are run under temperatures ranging from 20°C to 130°C ⁶ and pressures ranging from 4 to 8 bar, which promotes the absorption of NO_2 and the condensation of water.

In the new process, no condenser is used, in an attempt to reduce process utilities. The absorber employed will serve as both a condenser and an absorber. As such, additional attention will have to be paid to the cooling of the absorption column as incoming gas temperatures will be much greater.

Here, water obtained from the reaction between ammonia and oxygen plus water added at the top of the column is used to absorb and react with NO_2 to form nitric acid according to reaction 13.

The product obtained at the bottom of the column is composed of nitric acid and water, which according to the model in aspen results in 55 wt% nitric acid in water. After absorption, the nitric acid solution will be bleached in order to remove any dissolved NO.

The tail gas of the absorber will require further treatment for the removal of N_2O , and other NO_x gases in order to meet local legislation. This can be done by a variety of methods, one of which is catalytic scrubbing. The details of the emission treatment, will not be handled in this project, but can be assumed to be very similar to that used in nitric acid plants.

Diesel to Ammonia to Nitric Acid

The process mentioned above makes use of ammonia as a fuel and raw material. The current industrial production of ammonia and that of nitric acid, take place in large plants which supply large areas, hence being

⁶ See Table 3

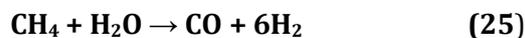


dependent on a complex and expensive logistics system. Allowing the production of HNO_3 to take place on a small scale still makes the process dependent on the supply of ammonia. The production of nitric acid on a small scale therefore only shifts the problem.

A possible solution to this problem may be to incorporate an additional stage to the new engine described earlier. This additional stage would produce, on a small scale, the ammonia required.

Ammonia is currently produced on a very large scale (130 million tonnes per year) using the Haber-Bosch process, where hydrocarbons are reacted together with the nitrogen present in air to produce ammonia. Were such a system incorporated into the process, farmers could make use of readily available diesel to produce their own fertilizers.

The Haber-Bosch process makes use of methane, LPG or petroleum naphtha which undergoes catalytic steam reduction, Hydrogen gas is produced in a process which takes place between 25 and 35 bar according to reactions 25 and 26.



The newly obtained hydrogen gas is then mixed with nitrogen from the air at high temperatures and pressures which produces the ammonia required in an exothermic reaction according to reaction 26.

(26)

The high temperatures has a negative effect on the reaction, resulting in lower yields, however the temperature must be high enough in order for the catalyst to work. Higher pressures have a positive effect on the conversion as seen if figure 8.

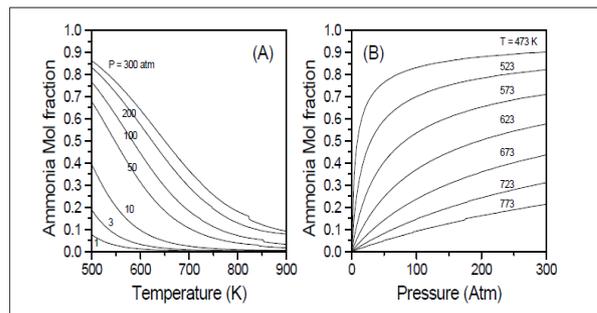


Figure 8 - Mole fraction of ammonia at equilibrium from an initial mixture of 1:3 N_2/H_2 gas at (A) at different temperatures for fixed value of pressure (B) at different pressures at fixed value of temperature. (Modak, 2002)

Since the diesel engine is designed to deliver high pressures which are close to the range shown in figure 8 at similar temperatures, it may be worth considering the possibility of producing ammonia in a modified diesel engine. Again the catalysts will be required for the reactions to take place. This must be strongly taken into account, as the incorporation of the catalyst in the pistons is required.

Conclusion

The goal of this report was to analyze the possibility of downscaling the current nitric acid process by using a diesel engine. Here, properties of the diesel engine and the current process for the nitric acid were compared in order to conceive a new theoretical and possible alternative to the current process.

Through research, important overlaps between the properties of diesel and ammonia became apparent which could make this project feasible. The energy content of ammonia is, despite being lower than that of diesel, still proved to be enough to run the models used but with a lower energy output. 17% mechanical energy output for ammonia were obtained compared to 60% of diesel. These values however, do not include the possibility of using other means for energy recovery from the exhaust gases such as heat recovery which offers potential to increase these efficiencies.

Essential changes include alterations to the piston used, where a catalyst is incorporated in the form of a gauze or mesh to the crown of the piston facilitating the reaction of ammonia to NO_2 . Additional research into the catalyst is required, as the literature studies resulted in no



evidence of such a catalyst. Furthermore, boat engines were considered as the best option for the task at hand, as they are able to run efficiently at lower RPMs, in ranges between 60 and 300, which would allow for longer residence times needed for the reaction.

Additional changes would have to be implemented in order to absorb the NO_2 in water allowing it to be converted into the desired nitric acid. Here an absorption column can be used, although due to its inconvenient large size, alternative techniques should be explored. After this unit, the exit gas is pre-treated before being released to the environment. This is done to tackle the strong regulations imposed on exhaust gases such as NO_x 's and N_2O .

An additional stage for this process would be to incorporate the production of ammonia from diesel, as ammonia is currently produced by catalytic steam reduction of hydrocarbons. Were such a step be successfully implemented in the process, then the process shows the potential to produce nitric acid using diesel as a raw material, being independent of the supply of ammonia.



Appendix

Appendix 1 – Vapour Pressure Curves

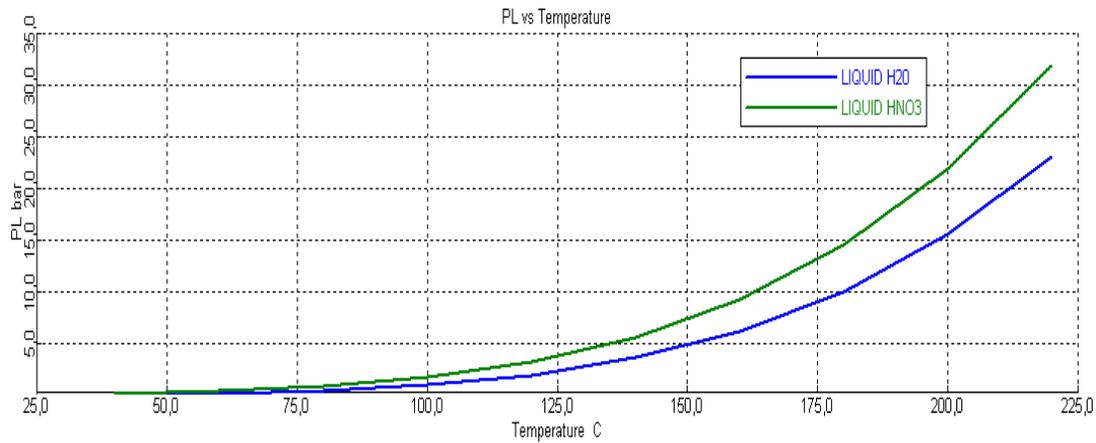


Figure 5 - Vapour pressure of Water (blue) and Nitric Acid (Green)

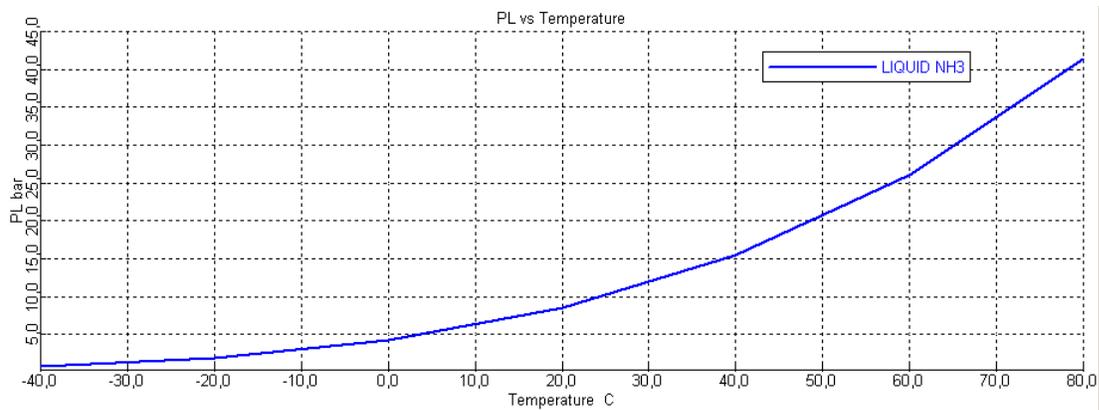


Figure 6 – Vapour Pressure of Ammonia



Appendix 2 – MSDS

Component	Formula	M (g/mol)	M.P. (°C)	B.P. (°C)	Critical Temperature (°C)	Critical Pressure (kPa)	Solubility in water at 40°C (wt%)	ρ (kg/m ³)
Ammonia	NH ₃	17.03	-77.7	-33.35	133	11425	23.4	730.000
Oxygen	O ₂	32	-218.8	-182.9	-118.57	5043	0.0231	1327
Carbon Monoxide	CO	28.011	- 205.06	-191.5	-140.25	3496	slight	1250.1
Carbon Dioxide	CO ₂	44.01	Sublimes at -78.5		31.1	7383	slight	1145
Diesel	C _n H _{2n+2}			180-390	—	—	—	820-845
Nitrogen	N ₂	14	-209.9	195.8			very slight	1161
Dinitrogen Monoxide	N ₂ O	44.013	-90.8	-88.5	36.4	7245	very slight	1977
Dinitrogen trioxide	N ₂ O ₃	76.01	-100.1	3			very soluble	1783
Dinitrogen tetraoxide	N ₂ O ₄	92.011	-11.2	21.1	158		reacts	1443
Nitrogen Monoxide	NO	30.006	-163.6	-151.7	-93		7.4ml/100ml	1340.2
Nitrogen Dioxide	NO ₂	46.005 5	-11.2	21.1	158		reacts	1443
Nitrous Acid	HNO ₂	47.013	Only in Solution		—	—	—	1540
Nitric Acid 100%	HNO ₃	63.012	-42	83 (azeotrope, 68% sol. @ 120.5)	—	—	Completely miscible	1512.9
water	H ₂ O	18.015	0	100	380-386	22100		1000
Conditions								(1.013 bar at 15 °C)



Component	Formula	Flash Point (°C)	Auto Ignition Temperature (°C)	Flammable Limits % by volume in Air	Cp (J/mol.K)	enthalpy of formation (kJ/mol)	enthalpy of vaporization (kJ/mol)	enthalpy of fusion (kJ/mol)	Corrosive?
Ammonia	NH ₃	11	650	16-25	35.1	-45.9	23.35	28.93	
Oxygen	O ₂	—	—	—	29.4	0	6.82	0.444	
Carbon Monoxide	CO		608.85	12.5-74.2	29.1	-110.53	6.042	0.837	
Carbon Dioxide	CO ₂	—	—	—	37.1	-393.5			
Diesel	C _n H _{2n+2}	closed cup >55	260	6 - 13.5%*		—			
Nitrogen	N ₂	—	—	—	29.1	0			
Dinitrogen Monoxide	N ₂ O	—	—	—	38.6	81.6	376.14kJ/kg	148.53kJ/kg	
Dinitrogen trioxide	N ₂ O ₃	—	—	—	72.7	86.6			
Dinitrogen tetraoxide	N ₂ O ₄	—	—	—	79.2	11.1			
Nitrogen Monoxide	NO	—	—	—	29.9	91.3			
Nitrogen Dioxide	NO ₂	—	—	—	37.2	33.2			
Nitrous Acid	HN O ₂	—	—	—	45.6	-79.5	—	—	—
Nitric Acid 100%	HN O ₃	—	—	—	(Liq. 109.9) gas 54.1	-133.9	39.04	10.48	EXTE MELY !
water	H ₂ O				(liq. 75.3) gas 33.6	-241.8	40.65	333.35 kJ/kg	
Conditions					298.15 K	for gas state	at BP	at MP	



Terra Industries Inc.
 Terra Centre – 600 Fourth Street
 Sioux City, Iowa 51101

Material Safety Data Sheet

Anhydrous Ammonia

MSDS Number 2001 (Revised April 23, 2008)

10 Pages

1. CHEMICAL PRODUCT and EMERGENCY TELEPHONE CONTACT

Product Name:..... Anhydrous Ammonia
 Chemical Family:..... Inorganic Nitrogen Compound
 Synonyms:..... Ammonia, Liquid Ammonia, Nitro-Sil, Spirit
 of Hartshorn, NH₃
 Formula:..... NH₃
 Product Use:..... Fertilizers; Fibers and Plastics; Explosives;
 Animal Feed; SCR NO_x Control

EMERGENCY TELEPHONE NUMBER

CHEMTREC (U.S.):..... 800-424-9300
 CANUTEC (Canada):..... 613-996-6666

2. COMPOSITION/INFORMATION ON INGREDIENTS

Ingredient Name/CAS Number	Concentration	Exposure Limits
Ammonia #7664-41-7	99-100%	25 ppm TWA 35 ppm STEL 50 ppm PEL 300 ppm IDLH

3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW

Colorless gas and liquid (liquid under pressure). Vapor is toxic and irritating to eyes, nose, throat and skin. Liquid will burn skin and eyes and cause frostbite. Vapor is flammable under limited conditions. Use water to control fire and disperse vapors. Do not put water on liquid ammonia.

NFPA Hazard Classification	Health Hazard (Blue)	3
	Flammability (Red)	1
	Reactivity (Yellow)	0



POTENTIAL HEALTH EFFECTS

Primary Routes of Entry: Inhalation, skin contact/absorption and eye contact.

General Acute Exposure: Anhydrous ammonia reacts with moisture in mucosal surfaces (eyes, skin, and respiratory tract) to produce ammonium hydroxide, which may cause caustic injury. The severity of injury depends upon the concentration and duration of exposure. The extent of injury ranges from mild cough to laryngeal edema and life-threatening pulmonary edema.

Inhalation:

Acute Exposure: Ammonia is toxic and a severe irritant of the respiratory tract. It may cause a running nose, coughing, chest pain, cessation of respiration and death. It may cause severe breathing difficulties, which may be delayed in onset. **ADDITIONAL MEDICAL INFORMATION:** Bronchospasm, laryngitis, tracheitis, wheezing, dyspnea, and laryngeal stridor may be noted. Mucosal burns to the tracheobronchial tree, Pulmonary Edema, and associated hypoxemia frequently occur following exposure to concentrated ammonia.

Skin:

Acute Contact: Ammonia is a severe irritant of the skin. Skin exposure to high concentrations of the gas may cause burning and blistering. Contact with liquid may cause severe skin burns. **ADDITIONAL MEDICAL INFORMATION:** Concentrated ammonia may produce liquefaction necrosis and deep penetrating burns.

Eye:

Acute Contact: Exposure to the eyes (>700 ppm) may cause temporary or permanent blindness. **ADDITIONAL MEDICAL INFORMATION:** Eye exposure may result in conjunctivitis, lacrimation and/or corneal irritation. Total corneal epithelial loss may occur.

Neurologic:

Acute Exposure: An altered mental status (coma) may be seen, but is not characteristic unless hypoxemia occurs.

Gastrointestinal:

Acute Exposure: Nausea and vomiting occurs frequently following ingestion. Swelling of the lips, mouth, and larynx, and oral or esophageal burns may occur if concentrated ammonia solutions are ingested.

Genitourinary:

Acute Exposure: Urinary retention may occur.

Note to the Physician: Pneumonitis should be anticipated after inhalation or ingestion. If severe exposure is suspected, observe for 48-72 hours for delayed pulmonary edema.

Carcinogenicity:

NTP:	Not Listed
IARC:	Not Listed
OSHA:	Not Regulated

Medical Conditions Aggravated by Exposure: Chronic respiratory or skin disease



4. FIRST AID MEASURES

First Aid for Eyes: Immediately flush eyes with copious amounts of tepid water for at least 15 minutes. If irritation, pain, swelling, excessive tearing, or light sensitivity persists, the patient should be seen in a health care facility and referral to an ophthalmologist considered.

First Aid for Skin: Immediately flush exposed area with copious amounts of tepid water for at least 15 minutes followed by washing area thoroughly with soap and water. The patient should be seen in a health care facility if irritation or pain persists.

First Aid for Inhalation: Move patient to fresh air. Monitor for respiratory distress. If cough or difficulty in breathing develops, evaluate for respiratory tract irritation, bronchitis, or pneumonitis. If trained to do so administer supplemental oxygen with assisted ventilation as required. Administer artificial respiration if patient is not breathing.

First Aid for Ingestion: Call a physician. If conscious, give the patient 4 to 8 ounces of milk or water to drink immediately. Do not induce vomiting.

Caution: Clothing frozen to the skin should be thawed before being removed.

5. FIRE FIGHTING MEASURES

Flash Point: Not Applicable
Lower Flammable Limit: 15.5 % Volume in Air
Upper Flammable Limit: 27.0 % Volume in Air
Autoignition Temperature 1204° F (651° C)

Extinguishing Media: Stopping the flow of gas rather than extinguishing the fire is usually the best procedure to follow when escaping gas is burning.

Small Fire: Dry chemical or CO₂
Large Fire: Water spray, fog or foam

Special Fire Fighting Procedures:

- Do not get water inside container.
- Move container from fire area if you can do it without risk.
- Apply cooling water to sides of containers that are exposed to flames until well after fire is out. Stay away from ends of tanks due to exploding potential when tanks are involved in a fire.
- Isolate area until gas has dispersed.
- Use water spray or foam to control vapors.
- Positive pressure self-contained breathing apparatus (SCBA) should be used when there is a potential for inhalation of vapors and/or fumes.
- Chemical protective clothing that is safe for use with ammonia involved in a fire should be worn.



CAUTION:

- a. With proper training, structural fire fighter's protective clothing and SCBA used in conjunction with water spray will provide limited protection for short-term exposure to ammonia vapors.
- b. Liquid ammonia may cause protective equipment to become brittle.
- c. Use of welding or flame cutting equipment on or in ammonia container is not recommended unless all ammonia has been purged, rinsed with water, and any oil residue removed.

Runoff from fire control or dilution water may cause pollution.

6. ACCIDENTAL RELEASE MEASURES

Spill or Leak Measures: Stop leak if you can do so without risk. Keep unnecessary people away, isolate hazard area and deny entry. Stay upwind, out of low areas, and ventilate closed spaces before entering. Evaluate the affected area to determine whether to evacuate or shelter-in-place by taping windows and doors, shutting off outside air intakes (attic fans, etc.), and placing a wet towel or cloth over the face (if needed). With proper training, self-contained breathing apparatus (SCBA) and structural firefighter's protective clothing used in conjunction with water spray will provide limited protection in outdoor releases for short-term exposure. Fully encapsulating, vapor-protective clothing should be worn for spills and leaks with no fire. Use water spray or foam to control vapors. Mixing of water and liquid ammonia will increase vaporization rate. Do not put water on liquid ammonia unless more than 100 volumes of water are available for each volume of liquid ammonia.

CAUTION:

- a. Personal protective clothing may become brittle when exposed to liquid ammonia.
- b. Runoff from vapor control or dilution may cause pollution.

Determining Spill Size: Generally, a small spill is one that involves a single, small container (55-gallon capacity or less), or a small (non-continuing) leak from a larger tank or vessel.

Small Spill:

- a. Flush area with flooding amounts of water.
- b. First isolate 100 feet in all directions and then protect persons downwind 0.1 miles during daylight and 0.1 miles at night.

Large Spill:

- a. Dike far ahead of liquid spill for later disposal.
- b. Follow local emergency protocol for handling.
- c. First isolate 200 feet in all directions, then protect persons downwind 0.4 miles during daylight and 1.4 miles at night.



7. HANDLING AND STORAGE

Follow the current ANSI-K61.1 Standard, "Safety Requirements for the Storage and Handling of Anhydrous Ammonia", or applicable Ammonia Manufacturing Industry Standards. (See Section 15 for information on Equipment, Pressure Vessels and Testing).

Handling Precautions: Use proper personal protective equipment when working with or around ammonia. See Section 8.

8. EXPOSURE CONTROLS, PERSONAL PROTECTION

Respiratory Protection Requirements:

<25 ppm:	No protection required.
25 to 35 ppm:	Protection required if the daily TWA is exceeded.
35 to 50 ppm:	Protection required if exposed for more than 15 minutes.
50 to 250 ppm:	Minimum of an air-purifying respirator equipped with ammonia canister(s) or cartridge(s).
250 to 300 ppm:	Minimum of a full-face air-purifying respirator equipped with ammonia canister(s) or cartridge(s).
>300 ppm:	A fresh air supply system must be used (i.e. positive pressure self contained breathing apparatus).

Skin Protection Requirements: Skin protection is required for exposure to liquid, mist, and > 1000 ppm of ammonia gas or vapors. Neoprene or rubber gauntlet-type gloves, ammonia resistant clothing (overalls, jacket, and boots) or vapor suit, as required.

Eye Protection Requirements: Use chemical (indirectly vented) goggles when there is a potential for contact with liquid or mist. A full-face shield is recommended in addition to goggles for added protection.

Other Protective Equipment: Safety shower and eyewash fountain should be provided in the ammonia handling area. In agricultural distribution, provide easily accessible shower and/or at least 100 gallons of clean water in open top container (check regulations). When transporting, provide at least 5 gallons of readily accessible, clean water and personal protective equipment.

Engineering Controls: Maintain adequate ventilation to keep ammonia concentrations below applicable standards when possible.

NOTE: See Section 2 for regulatory exposure limits.



9. PHYSICAL AND CHEMICAL PROPERTIES

Physical Form:	Gas (liquid under pressure)
Color:	Colorless gas and liquid, forms white vapor in contact with moisture
Odor:	Strong pungent penetrating odor, ammonia.
Boiling Point:	-28.1° F (-33° C) at 1 atm
Melting point:	-107.9° F (-78° C)
Ph:	Approximately 12.0 (neat)
Solubility:	510 - 530 g/L @ 20° C
Specific Gravity:	0.6818 @ -33.35° C and 1 atm
Vapor Density:	0.597 @ 0° C (0.60 @ 60° F)
Vapor Pressure:	7,600 mm Hg @ 25° C (93 psig @ 60° F)
% Volatile by Volume:	100
Molecular Weight:	17.03
Density:	0.696 g/L @ 20° C (5.14 lb./gal. @ 60° F)
Critical Temperature:	271° F (133° C)
Critical Pressure:	1636 psia

10. REACTIVITY

Stability: This is a stable material.
Hazardous Polymerization: Will not occur.

Decomposition: Hydrogen is released on heating above 850° F (454° C). The decomposition temperature may be lowered to 575° F (300° C) by contact with certain metals such as nickel. At 1290° F (690° C) or in the presence of an electric spark, ammonia decomposes into nitrogen and hydrogen gases, which may form a flammable mixture in the air.

Incompatibilities:

- Ammonia has potentially explosive or violent reactions with interhalogens, strong oxidizers, Nitric Acid, Fluorine, and Nitrogen Oxide.
- Ammonia forms sensitive explosive mixtures with air and hydrocarbons, Ethanol and Silver Nitrate, and Chlorine; and explosive products are formed by the reaction of ammonia with Silver Chloride, Silver Oxide, Bromine, Iodine, Gold, Mercury, and Tellurium Halides.
- Ammonia is incompatible or has potentially hazardous reactions with Silver, Acetaldehyde, Acrolein, Boron, Halogens, Perchlorate, Chloric Acid, Chlorine Monoxide, Chlorites, Nitrogen Tetroxide, Tin, and Sulfur.

NOTE: The incompatibilities above are a partial list taken from two books by Sax & Lewis: "Dangerous Properties of Industrial Materials", 7th. ed., 1989 and "Hawley's Condensed Chemical Dictionary", 11th. ed. 1987, both published by Van Nostrand Reinhold Company, New York. It is recommend that if additional information is required, the reader refer to these and other published information.



11. TOXICOLOGICAL INFORMATION

Toxicity

Acute Inhalation Toxicity

LC₅₀ Rat, mouse:..... 4,200 - 19,060 mg NH₃/m³ (1 hr)

Acute Toxicity, Other Routes

LC₅₀ Rat, mouse:..... 45.5 - 195.1 mg NH₃/kg bw (I hr intravenous)

Corrosiveness / Irritation

Skin Irritation / Corrosion:..... Corrosive to skin

Eye Irritation / Corrosion:..... Subacute and chronic exposure to 200 – 1,000 ppm produced eye damage. 100 – 200 ppm produced moderate to severe irritation.

Repeated Dose Toxicity

Rats, guinea pigs, rabbits, etc:..... No mortality (Inhalation up to 770 mg/m³)

Genetic Toxicity *in vitro*

Salmonella typhimurium, etc:..... Negative (Bacterial gene mutation assay)

Chick fibroblasts:..... Induced chromosomal clumping, polyploidy, and arrested spindle formation. No data showing that ammonia is mutagenic in mammals. (Cytogenetic assay)

Genetic Toxicity *in vivo*

Drosophila melanogaster:..... No evidence for mutagenicity

Carcinogenicity

All:..... No carcinogenic effects

Toxicity to Reproduction

Pig:..... Temporarily depressed mean daily gain (MDG) at 35 mg/kg in gilts (One generation study)

Human Experience

Inhalation, human volunteers:..... Nasal and pulmonary irritation at concentrations of about 100 ppm and higher.

Ecotoxicity

Acute Toxicity to Fish

LC₅₀ Many species:..... 0.09 – 3.51 mg un-ionized NH₃/L (96 hr)

Acute Toxicity to Aquatic Invertebrates

LC₅₀ *Daphnia magna*:..... 2.94 mg un-ionized NH₃-N/L (48 hr)

Toxicity to Aquatic Plants

LOEC Benthic diatoms:..... 0.5 – 1.0 mg N/L (Up to 25 days)

LOEC *Chlorella vulgaris*:..... 500 mg N/L (21 days)

Toxicity to Bacteria

EC₅₀ *Photobacterium phosphoreum*:..... 1.49 mg un-ionized NH₃/L (5 min)



Chronic Toxicity to Fish

NOEC Many species: 0.025 – 1.2 mg un-ionized NH₃/L (Varied 12 days – 5 years)

Chronic Toxicity to Aquatic Invertebrates

NOEC *Daphnia magna* and others: 0.163 – 0.42 mg un-ionized NH₃/L (Varied 21 days – 76 weeks)

Toxicity to Terrestrial Plants

LOEC Many species 3 – 250 ppm (Varied 4 min – 16 hrs)

Toxicity to Other Non-Mammalian Terrestrial Species

LD₅₀ *G. Domesticus*: 2.72 mM (1 hr injections)

Source: TFI Product Testing Program April 2003

12. ECOLOGICAL INFORMATION

- a. Ammonia is harmful to aquatic life in very low concentrations and may be hazardous if it enters water intakes.
- b. Local health and wildlife authorities, as well as operators of water intakes in the vicinity, should be notified of water releases.
- c. Waterfowl toxicity may occur at elevated concentrations.
- d. Ammonia does not concentrate in the food chain.
- e. The conversion of ammonia to nitrites/nitrates by bacteria in aquatic systems can reduce the concentration of dissolved oxygen (referred to as nitrogenous oxygen demand).

Effect on water treatment process: Chlorination will produce chloramines, which are more readily detected by taste and odor.

Note: See Ecotoxicity information in section 11.

13. DISPOSAL CONSIDERATIONS

Reclaim as fertilizer if possible. Waste must be disposed of in accordance with federal, state, and local environmental control regulations.

14. TRANSPORTATION INFORMATION

U.S. DOT and Canadian TGD Act

Shipping Name: Ammonia, anhydrous

Shipping Class/Division: 2.2 (U.S.); 2.3 (8) (Canada)

Hazard Class: Non-Flammable Gas (U.S.); Toxic Gas (Canada)

Product Identification Number (PIN): UN1005

DOT Placard: Non-Flammable Gas 2.2, color: green (U.S.); Class 2.3 or UN1005, color: white (Canada)

DOT Special Provision: 13, "Inhalation Hazard"

OSHA Label Required: Yes

RQ (Reportable Quantity): 100 pounds

STCC Number: 4904210



15. REGULATORY INFORMATION

Controlled Products Regulations Classification: A: Compressed Gas; E: Corrosive

OSHA: This product is considered a hazardous material under criteria of the Federal OSHA Hazard Communication Standard 29 CFR 1910.1200 (Toxic; Corrosive), and is listed as a Highly Hazardous Chemical subject to the requirements of the Process Safety Management Standard 29 CFR 1910.119.

CAA Chemical Accident Prevention: Ammonia is considered a regulated substance subject to the Chemical Accident Prevention provisions of 40 CFR Part 68. The threshold quantity for this substance is 10,000 lbs.

SARA TITLE III:

- a. EHS (Extremely Hazardous Substances) List: Listed (EPA, 1992a)
- b. SARA RQ (Reportable Quantity): 100 pounds
- c. TPQ (Threshold Planning Quantity): 500 pounds
- d. Regulation: "Emergency Planning and Notification" - 40 CFR Part 355 (Appendices A and B).
- e. Section 313: "Specific Toxic Chemical Listings" - 40 CFR Part 372
Ammonia is subject to the reporting requirements of Section 313 "Specific Toxic Chemical Listings" 40 CFR Part 372. Terra is required by 40 CFR 372.45 to notify certain customers as to which of its mixture or trade name products contain those chemicals. The purpose of that notification is to ensure that facilities that may be subject to the reporting requirements of Section 313 and that use products of unknown formulation will have knowledge that they are receiving products that contain chemicals subject to those reporting requirements.

CERCLA Hazardous Substances List:

- a. CERCLA RQ (Reportable Quantity): 100 pounds
- b. Regulation: "Designation, Reportable Quantities, Notification" - 40 CFR 302

TSCA Inventory: Listed (RTECS)

Chemical Facility Anti-Terrorism Standard (CFATS) / 6 CFR Part 27:

Ammonia (anhydrous) is listed in Appendix A as a Chemical of Interest (COI) due to threat of "Release"

Screening Threshold Quantity (STQ): 10,000 pounds

Equipment, Pressure Vessels, Testing, Etc.: All equipment used to handle, store, transfer or apply anhydrous ammonia must be properly engineered, constructed and maintained in compliance with all applicable regulations and standards. Pressure vessels, piping and appurtenances should be regularly inspected and tested using methods designed to reveal external and internal deterioration or defects that may impair the integrity of the equipment such that an unintended release of anhydrous ammonia may result. Consult with your State Department of Agriculture and other experts, as applicable, concerning the methods that would be most appropriate given the particular circumstances. Refer to 29 CFR 1910.111, *Storage and Handling of Anhydrous Ammonia*; 29 CFR 1910.119, *Process Safety Management of Highly Hazardous Materials*; and the current ANSI standard K61.1, *Safety Requirements for the Storage and Handling of Anhydrous Ammonia*, for additional information.



16. OTHER INFORMATION

- Dec. 18, 1995: The MSDS was rewritten to comply with ANSI Standard Z400.1-1993.
July 1, 2003: Added toxicity information from the TFI Product Testing Program April 2003.
October 4, 2006: Added NFPA hazard classification information and updated isolation / protective action distances per ERG 2004.
Dec. 19, 2006: Added Equipment, Pressure Vessel and Testing Information.
August 24, 2007: Reviewed and revised.
January 2, 2008: Revised 15. Regulatory Information to add CFATS requirements
April 23, 2008: Revised 14. Transportation Information to change Canadian TDG requirements

The information and recommendations herein are taken from data contained in independent, industry-recognized references including but not limited to NIOSH, OSHA, ANSI, NFPA, DOT ERG, the TFI Product Testing Program, Global Engineering Documents, MEDITEXT, HAZARDTEXT, SARATEXT, CHRIS, OHM/TADS, and IRIS. Terra Industries Inc. makes no guarantee, warranty or other representation concerning this substance, since conditions of its use are beyond the control of the company. Terra Industries Inc. disclaims any liability for loss or damage incurred in connection with the use of this substance.



Conforms to Regulation (EC) No. 1907/2006 (REACH), Annex II - United Kingdom (UK)

SAFETY DATA SHEET

Greenergy Ultra Low Sulphur Diesel

1. IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND OF THE COMPANY/UNDERTAKINGIdentification of the substance or preparation

Product name : Greenergy Ultra Low Sulphur Diesel
Product type : Liquid.
Date of issue/Date of revision : 08/10/2008.

Use of the substance/preparation : Transport Fuel to BS EN590.
Fuel for compression ignition diesel engines used to power vehicles on the public highway Low Emission Automotive Diesel Fuel, DERV, Diesel Fuel including up to 5% FAME (Fatty acid methyl ester).

Company/undertaking identification

Distributor : Greenergy Fuels Limited
198 High Holborn
London WC1V 7BD

e-mail address of person responsible for this SDS : msds-info@greenergy.com

Emergency telephone number (with hours of operation) : 020 7404 7700 (24 hrs)

2. HAZARDS IDENTIFICATION

The product is classified as dangerous according to Directive 1999/45/EC and its amendments.

Classification : Carc. Cat. 3; R40
Xn; R65
R66
N; R51/53

Human health hazards : Limited evidence of a carcinogenic effect. Harmful: may cause lung damage if swallowed. Repeated exposure may cause skin dryness or cracking.

Environmental hazards : Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

See section 11 for more detailed information on health effects and symptoms.

3. COMPOSITION/INFORMATION ON INGREDIENTS

Substance/preparation : Preparation
Transport Fuel to BS EN590

Ingredient name	CAS number	%	Number	Classification
fuels, diesel	68334-30-5	75 - 100	269-822-7	Carc. Cat. 3; [1] R40 Xn; R65 R66 N; R51/53
See section 16 for the full text of the R-phrases declared above				

There are no additional ingredients present which, within the current knowledge of the supplier and in the concentrations applicable, are classified as hazardous to health or the environment and hence require reporting in this section.

[1] Substance classified with a health or environmental hazard

[2] Substance with a workplace exposure limit

[3] PBT-substance

[4] vPvB-substance

Occupational exposure limits, if available, are listed in section 8.



Greenergy Ultra Low Sulphur Diesel

4. FIRST AID MEASURES

First-aid measures

- Inhalation** : Move exposed person to fresh air. Keep person warm and at rest. If not breathing, if breathing is irregular or if respiratory arrest occurs, provide artificial respiration or oxygen by trained personnel. It may be dangerous to the person providing aid to give mouth-to-mouth resuscitation. Get medical attention. If unconscious, place in recovery position and get medical attention immediately. Maintain an open airway. Loosen tight clothing such as a collar, tie, belt or waistband.
- Ingestion** : Wash out mouth with water. Remove dentures if any. Move exposed person to fresh air. Keep person warm and at rest. If material has been swallowed and the exposed person is conscious, give small quantities of water to drink. Stop if the exposed person feels sick as vomiting may be dangerous. Aspiration hazard if swallowed. Can enter lungs and cause damage. Do not induce vomiting. If vomiting occurs, the head should be kept low so that vomit does not enter the lungs. Get medical attention. Never give anything by mouth to an unconscious person. If unconscious, place in recovery position and get medical attention immediately. Maintain an open airway. Loosen tight clothing such as a collar, tie, belt or waistband.
- Skin contact** : Wash skin thoroughly with soap and water or use recognised skin cleanser. Remove contaminated clothing and shoes. Continue to rinse for at least 10 minutes. Obtain medical attention if symptoms occur. Wash clothing before reuse. Clean shoes thoroughly before reuse.
- Eye contact** : Immediately flush eyes with plenty of water, occasionally lifting the upper and lower eyelids. Check for and remove any contact lenses. Continue to rinse for at least 10 minutes. Get medical attention.
- Protection of first-aiders** : No action shall be taken involving any personal risk or without suitable training. It may be dangerous to the person providing aid to give mouth-to-mouth resuscitation.
- Notes to physician** : No specific treatment. Treat symptomatically. Contact poison treatment specialist immediately if large quantities have been ingested or inhaled.

See section 11 for more detailed information on health effects and symptoms.

5. FIRE-FIGHTING MEASURES

Extinguishing media

- Suitable** : Use dry chemical, CO₂, water spray (fog) or foam.
- Not suitable** : Do not use water jet.
- Special exposure hazards** : Combustible liquid. In a fire or if heated, a pressure increase will occur and the container may burst, with the risk of a subsequent explosion.
Promptly isolate the scene by removing all persons from the vicinity of the incident if there is a fire. No action shall be taken involving any personal risk or without suitable training. Move containers from fire area if this can be done without risk. Use water spray to keep fire-exposed containers cool. This material is toxic to aquatic organisms. Fire water contaminated with this material must be contained and prevented from being discharged to any waterway, sewer or drain.
- Hazardous thermal decomposition products** : No specific data.
- Special protective equipment for fire-fighters** : Fire-fighters should wear appropriate protective equipment and self-contained breathing apparatus (SCBA) with a full face-piece operated in positive pressure mode.

6. ACCIDENTAL RELEASE MEASURES

- Personal precautions** : No action shall be taken involving any personal risk or without suitable training. Evacuate surrounding areas. Keep unnecessary and unprotected personnel from entering. Do not touch or walk through spilt material. Shut off all ignition sources. No flares, smoking or flames in hazard area. Avoid breathing vapour or mist. Provide adequate ventilation. Wear appropriate respirator when ventilation is inadequate. Put on appropriate personal protective equipment (see section 8).
- Environmental precautions** : Avoid dispersal of spilt material and runoff and contact with soil, waterways, drains and sewers. Inform the relevant authorities if the product has caused environmental pollution (sewers, waterways, soil or air). Water polluting material. May be harmful to the environment if released in large quantities.

Methods for cleaning up

Date of issue/Date of revision : 08/10/2008.

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Greenergy Ultra Low Sulphur Diesel

6. ACCIDENTAL RELEASE MEASURES

- Small spill** : Stop leak if without risk. Move containers from spill area. Dilute with water and mop up if water-soluble or absorb with an inert dry material and place in an appropriate waste disposal container. Use spark-proof tools and explosion-proof equipment. Dispose of via a licensed waste disposal contractor.
- Large spill** : Stop leak if without risk. Move containers from spill area. Approach the release from upwind. Prevent entry into sewers, water courses, basements or confined areas. Wash spillages into an effluent treatment plant or proceed as follows. Contain and collect spillage with non-combustible, absorbent material e.g. sand, earth, vermiculite or diatomaceous earth and place in container for disposal according to local regulations (see section 13). Use spark-proof tools and explosion-proof equipment. Dispose of via a licensed waste disposal contractor. Contaminated absorbent material may pose the same hazard as the spilt product. Note: see section 1 for emergency contact information and section 13 for waste disposal.

7. HANDLING AND STORAGE

- Handling** : Put on appropriate personal protective equipment (see section 8). Eating, drinking and smoking should be prohibited in areas where this material is handled, stored and processed. Workers should wash hands and face before eating, drinking and smoking. Do not get in eyes or on skin or clothing. Do not ingest. Avoid breathing vapour or mist. Avoid release to the environment. Refer to special instructions/safety data sheet. Use only with adequate ventilation. Wear appropriate respirator when ventilation is inadequate. Do not enter storage areas and confined spaces unless adequately ventilated. Keep in the original container or an approved alternative made from a compatible material, kept tightly closed when not in use. Store and use away from heat, sparks, open flame or any other ignition source. Use explosion-proof electrical (ventilating, lighting and material handling) equipment. Use non-sparking tools. Take precautionary measures against electrostatic discharges. To avoid fire or explosion, dissipate static electricity during transfer by earthing and bonding containers and equipment before transferring material. Empty containers retain product residue and can be hazardous. Do not reuse container.
- Storage** : Store in accordance with local regulations. Store in a segregated and approved area. Store in original container protected from direct sunlight in a dry, cool and well-ventilated area, away from incompatible materials (see section 10) and food and drink. Eliminate all ignition sources. Separate from oxidizing materials. Keep container tightly closed and sealed until ready for use. Containers that have been opened must be carefully resealed and kept upright to prevent leakage. Do not store in unlabelled containers. Use appropriate containment to avoid environmental contamination.
- Packaging materials**
- Recommended** : Use original container.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Exposure limit values

<u>Ingredient name</u>	<u>Occupational exposure limits</u>
No exposure limit value known.	

- Recommended monitoring procedures** : If this product contains ingredients with exposure limits, personal, workplace atmosphere or biological monitoring may be required to determine the effectiveness of the ventilation or other control measures and/or the necessity to use respiratory protective equipment. Reference should be made to European Standard EN 689 for methods for the assessment of exposure by inhalation to chemical agents and national guidance documents for methods for the determination of hazardous substances.

Exposure controls

- Occupational exposure controls** : Use only with adequate ventilation. Use process enclosures, local exhaust ventilation or other engineering controls to keep worker exposure to airborne contaminants below any recommended or statutory limits. The engineering controls also need to keep gas, vapour or dust concentrations below any lower explosive limits. Use explosion-proof ventilation equipment.

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8. EXPOSURE CONTROLS/PERSONAL PROTECTION

- Hygiene measures** : Wash hands, forearms and face thoroughly after handling chemical products, before eating, smoking and using the lavatory and at the end of the working period. Appropriate techniques should be used to remove potentially contaminated clothing. Wash contaminated clothing before reusing. Ensure that eyewash stations and safety showers are close to the workstation location.
- Respiratory protection** : Use a properly fitted, air-purifying or air-fed respirator complying with an approved standard if a risk assessment indicates this is necessary. Respirator selection must be based on known or anticipated exposure levels, the hazards of the product and the safe working limits of the selected respirator.
- Hand protection** : Chemical-resistant, impervious gloves complying with an approved standard should be worn at all times when handling chemical products if a risk assessment indicates this is necessary.
- Eye protection** : Safety eyewear complying with an approved standard should be used when a risk assessment indicates this is necessary to avoid exposure to liquid splashes, mists or dusts.
- Skin protection** : Personal protective equipment for the body should be selected based on the task being performed and the risks involved and should be approved by a specialist before handling this product.
- Environmental exposure controls** : Emissions from ventilation or work process equipment should be checked to ensure they comply with the requirements of environmental protection legislation. In some cases, fume scrubbers, filters or engineering modifications to the process equipment will be necessary to reduce emissions to acceptable levels.

9. PHYSICAL AND CHEMICAL PROPERTIES

General information

Appearance

- Physical state** : Liquid. [Clear to slightly hazy liquid.]
- Odour** : Bland.

Important health, safety and environmental information

- Boiling point** : 180 to 390°C (356 to 734°F) BS EN ISO 3405
- Flash point** : Closed cup: >55°C (>131°F) [ISO 2719]
- Density** : 0.82 to 0.845 g/cm³ [15°C (59°F)] BS EN ISO 3675
- Viscosity** : Kinematic (40°C (104°F)): 0.02 to 0.045 cm²/s (2 to 4.5 cSt) [ISO 3104/3105]

Other information

- Auto-ignition temperature** : 260°C (500°F) ASTM E659

10. STABILITY AND REACTIVITY

- Chemical stability** : The product is stable.
- Possibility of hazardous reactions** : Under normal conditions of storage and use, hazardous reactions will not occur.
- Conditions to avoid** : Avoid all possible sources of ignition (spark or flame). Do not pressurise, cut, weld, braze, solder, drill, grind or expose containers to heat or sources of ignition. Avoid release to the environment. Refer to special instructions/safety data sheet. Do not swallow.
- Materials to avoid** : Reactive or incompatible with the following materials:
oxidizing materials
- Hazardous decomposition products** : Under normal conditions of storage and use, hazardous decomposition products should not be produced.

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11. TOXICOLOGICAL INFORMATION

Toxicokinetics

- Absorption** : Not available.
Distribution : Not available.
Metabolism : Not available.
Elimination : Not available.

Potential acute health effects

- Inhalation** : No known significant effects or critical hazards.
Ingestion : Aspiration hazard if swallowed. Can enter lungs and cause damage.
Skin contact : Defatting to the skin. May cause skin dryness and irritation.
Eye contact : May cause eye irritation.

Acute toxicity

Product/ingredient name	Result	Species	Dose	Exposure
fuels, diesel	LD Dermal	Rabbit	>5 mL/kg	-
	LD50 Oral	Rat	7.5 gm/kg	-
	LD50 Oral	Rat	7500 mg/kg	-

- Conclusion/Summary** : Not available.

Potential chronic health effects

Chronic toxicity

- Conclusion/Summary** : Not available.

Irritation/Corrosion

- Conclusion/Summary** : Not available.

Sensitiser

- Conclusion/Summary** : Not available.

Carcinogenicity

- Conclusion/Summary** : Not available.

Mutagenicity

- Conclusion/Summary** : Not available.

Teratogenicity

- Conclusion/Summary** : Not available.

Reproductive toxicity

- Conclusion/Summary** : Not available.

Product name	Carcinogenic effects	Mutagenic effects	Developmental effects	Fertility effects
fuels, diesel	Carc. Cat. 3; R40	-	-	-

- Chronic effects** : Prolonged or repeated contact can defat the skin and lead to irritation, cracking and/or dermatitis.
Carcinogenicity : May cause cancer, based on animal data. Limited evidence of a carcinogenic effect. Risk of cancer depends on duration and level of exposure.
Mutagenicity : No known significant effects or critical hazards.
Teratogenicity : No known significant effects or critical hazards.
Developmental effects : No known significant effects or critical hazards.
Fertility effects : No known significant effects or critical hazards.

Over-exposure signs/symptoms

- Inhalation** : No specific data.
Ingestion : Adverse symptoms may include the following:
nausea or vomiting
Skin : Adverse symptoms may include the following:
irritation
dryness
cracking
Eyes : No specific data.

Date of issue/Date of revision : 08/10/2008.

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12. ECOLOGICAL INFORMATION

- Environmental effects** : Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
- Aquatic ecotoxicity**
- Conclusion/Summary** : Not available.
- Biodegradability**
- Conclusion/Summary** : Not available.
- Other adverse effects** : No known significant effects or critical hazards.
- PBT** : No.
P: Not available. B: Not available. T: No.
- vPvB** : Not available.

13. DISPOSAL CONSIDERATIONS

- Methods of disposal** : The generation of waste should be avoided or minimised wherever possible. Empty containers or liners may retain some product residues. This material and its container must be disposed of in a safe way. Dispose of surplus and non-recyclable products via a licensed waste disposal contractor. Disposal of this product, solutions and any by-products should at all times comply with the requirements of environmental protection and waste disposal legislation and any regional local authority requirements. Avoid dispersal of spill material and runoff and contact with soil, waterways, drains and sewers.
- Hazardous waste** : The classification of the product may meet the criteria for a hazardous waste.

14. TRANSPORT INFORMATION

International transport regulations

Regulatory information	UN number	Proper shipping name	Classes	PG*	Label	Additional information
ADR/RID Class	UN1202	GAS OIL	3	III		Hazard identification number 30 Limited quantity LQ7 CEPIC Tremcard 30S1202
ADNR Class	UN1202	GAS OIL	3	III		-
IMDG Class	UN1202	GAS OIL	3	III		Emergency schedules (EmS) F-E, S-E
IATA Class	UN1202	Gas oil	3	III		Passenger and Cargo Aircraft Quantity limitation: 60 L Packaging instructions: 309 Cargo Aircraft Only Quantity limitation: 220 L Packaging instructions: 310 Limited Quantities - Passenger Aircraft Quantity limitation: 10 L Packaging instructions: Y309

PG* : Packing group

Date of issue/Date of revision : 08/10/2008.

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15. REGULATORY INFORMATION

Chemical Safety Assessment : This product contains substances for which Chemical Safety Assessments are still required.

EU regulations

Classification and labeling have been determined according to EU Directives 67/548/EEC and 1999/45/EC (including amendments) and take into account the intended product use.

Hazard symbol or symbols :



Harmful, Dangerous for the environment

Risk phrases : R40- Limited evidence of a carcinogenic effect.
R65- Harmful: may cause lung damage if swallowed.
R66- Repeated exposure may cause skin dryness or cracking.
R51/53- Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

Safety phrases : S2- Keep out of the reach of children.
S29- Do not empty into drains.
S36/37- Wear suitable protective clothing and gloves.
S46- If swallowed, seek medical advice immediately and show this container or label.
S61- Avoid release to the environment. Refer to special instructions/safety data sheet.

Contains : fuels, diesel

Product use : Consumer applications.

Europe inventory : Not determined.

Black List Chemicals :

Priority List Chemicals :

Integrated pollution :

prevention and control list (IPPC) - Air

Integrated pollution :

prevention and control list (IPPC) - Water

Prior Informed Consent. :

List of chemicals subject to the international PIC procedure (Part I, II, III)

Other EU regulations

Containers to be fitted with child-resistant fastenings : Yes, applicable.

Tactile warning of danger : Yes, applicable.

International regulations

Chemical Weapons Convention: List Schedule I Chemicals

Chemical Weapons Convention: List Schedule II Chemicals

Chemical Weapons Convention: List Schedule III Chemicals

Date of issue/Date of revision : 08/10/2008.

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Greenergy Ultra Low Sulphur Diesel

16. OTHER INFORMATION

Full text of R-phrases referred to in sections 2 and 3 - United Kingdom (UK) : R40- Limited evidence of a carcinogenic effect.
R65- Harmful: may cause lung damage if swallowed.
R66- Repeated exposure may cause skin dryness or cracking.
R51/53- Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

Full text of classifications referred to in sections 2 and 3 - United Kingdom (UK) : Carc. Cat. 3 - Carcinogen Category 3
Xn - Harmful
N - Dangerous for the environment

Restrictions on use

Uses

None identified.

History

Date of printing : 08/10/2008.

Date of issue/ Date of revision : 08/10/2008.

Date of previous issue : No previous validation.

Version : 1

Prepared by : Not available.

☑ Indicates information that has changed from previously issued version.

Notice to reader

To the best of our knowledge, the information contained herein is accurate. However, neither the above-named supplier, nor any of its subsidiaries, assumes any liability whatsoever for the accuracy or completeness of the information contained herein.

Final determination of suitability of any material is the sole responsibility of the user. All materials may present unknown hazards and should be used with caution. Although certain hazards are described herein, we cannot guarantee that these are the only hazards that exist.

Annex



Appendix 3 – Safety Study

1.DOW FEI

DOW F&E Index	ammoniak	25/06/2010 14:51
Material Factor (MF)	4	Industrial Nitric Acid Plant
State of operation:		design
Process temperature (Tp)	200 [°C]	Temperature adjustment MF
Material Factor T corrected (MFT)	4	
1. General Process Hazards:		
	1.00	Penalty Factor
A. Exothermic Chemical Reactions:	0.50	
2d. Oxidation with oxygen		
B. Endothermic Process:	0.00	
0. No Endothermic Process		
C. Material Handling and Transfer:	0.00	
0. No Material Handling and Transport		
0. No warehouse or yard storage involved		
D. Enclosed or Indoor Process Units:	0.00	
0. No enclosed area involved.		
No mechanical ventilation present		
E. Access:	0.00	
0. Adequate access present		
F. Drainage and Spill Control:	0.00	
0. Excellent draining is present		
General Process Hazards Factor (F1):	1.50	
2. Special Process Hazards:		
	1.00	Penalty Factor
A. Toxic Material(s):	0.60	
B. Sub-Atmospheric Pressure:	0.00	
0. No Sub-Atmospheric Pressure involved.		
C. Operation In or Near Flammable Range (OINFR):	0.00	
3. Always in or near flammable range, due to absence of purge.		
0. Not applicable.		
D. Dust Explosion:	0.00	
0. No dust explosion possible; NFPAF=0 or no dust.		
0. Not applicable.		
E. Relief Pressure (RP):	0.34	
Operating Pressure (Pp):	8.1	[bar]
Relief Pressure (Pr):	9.6	[bar]
1. Flammable & Combustible liquids (FEITp>Tv or Tv<FEITo).		
2b. Pressurized flammable liquids with gas above 2 bar.		
F. Low Temperature:	0.00	
0. Not applicable due to material choice or absence of needed abnormal operating conditions.		
G. Quantity of Flammable/Unstable Material:	0.00	
Mass of material involved (Q _{hm}):	1	[ton]
Energy hold-up (Btu):	0.01	[GBtu]
Mass solid/dust hold-up (lb):	0.00	[Mlb]
1. Liquids or Gases in Process and Tv < 60°C or Tp > Tv or NFPAR > 1.		
H. Corrosion and Erosion:	0.00	
1. Corrosion rate < 0,5 mm/yr, with risk for pitting or local erosion.		
I. Leakage - Joints and Packing:	0.00	
1. Some minor leakage is likely.		
J. Use of Fired equipment:	0.00	
Distance to anticipated process unit (Df):	20	[m]
0. No fired equipment is used.		
K. Hot Oil Heat Exchange System:	0.00	
Quantity of heat exchanger system (active part)	10	[m ³]
Process temperature HO (TpHO):	264	[°C]
Flash point HO (TvHO):	260	[°C]
Boiling point HO (TbHO):	271	[°C]
1. Hot oil with Tp > Tv hot oil system.		
L. Rotating Equipment:	0.50	
3. Agitator and circulation pumps in coolant in exothermic process.		
Special Process Hazards Factor (F2):	2.4	
Process Unit Hazards Factor (F1*F2)=F3:	3.7	
Fire and Explosion Index (F3*MF=F&EI):	15	Degree of Hazard LIGHT.
	4 [m]	Radius of exposure



2.DOW CEI

Stofgegevens deel1:			NH3
naam gekozen in "1-stof":	ammoniak		ammoniak
molgewicht	17	[kg/kmol]	
atmosferisch kookpunt (Tb)	-33	[°C]	
smeltpunt (Ts)	-78	[°C]	
vlampunt (Tv)	-100	[°C]	
zelfontbrandingstemperatuur (Tz)	630	[°C]	
"exotherm start" temperatuur (Ta)	630	[°C]	
meldendheid (ZMS)	ZM		geur en/of directe lichaamsreactie bij ongevaarlijke concentratie
NFPA -code Health (NFPAH)	3		Blootstelling gedurende een korte tijd aan deze stof kan ernstig (voorbijgaand of blijvend) letsel veroorzaken, zelfs indien er onmiddellijk medische hulp gegeven is.
NFPA -code Flammability (NFPAF)	1		Stof die moet worden verhit, voordat ontsteking kan plaats hebben.
NFPA -code Reactiviteit (NFPA R)	0		Stabiele stof die, zelfs in een brand met water kan reageren.
Stofgegevens deel2:			
warmtecapaciteit vloeistof (Cp)	0	[kJ/kg.°C]	voor organische verbindingen 1-2 kJ/kg.°C
verdampingswarmte (Hv)	0	[kJ/kg]	voor organische verbindingen 300 - 400 kJ/kg
ratio Cp/Hv (CpHv)	0.0044	[1/°C]	(default 0.0044 tenzij Cp en Hv beide ingevuld.)
verbrandingswarmte (Hc)	18.6	[MJ/kg]	
dampdruk (bij 20°C) (Po)	8.5	[bar]	
richtwaarde acute toxiciteit (TOX)	720	[mg/m ³]	(volgens 190/96 V&AH 20-03-96 copie BST 3/7/98)
L.E.L waarde in lucht (LEL)	15	[vol.%]	(indien niet brandbaar 0 invullen)
U.E.L waarde in lucht (UEL)	29	[vol.%]	(indien niet brandbaar 0 invullen)
dichtheid vloeistof bij Tp (sm)	595	[kg/m ³]	voor organische verbindingen 500 - 1000 kg/m ³
Buitenlucht omstandigheden:			
buitenlucht temperatuur (To)	10	[°C]	(default 10 tenzij anders ingevuld)
Procesomstandigheden:			
proces-druk (absoluut) (Pp)	8.1	[bar]	systeem op overdruk
proces-temperatuur (Tp)	900	[°C]	gasvorming bij 1 atm
gasfase in proces	1	[-]	gasfase uitstroming
Uitstroom-scenario-info:			
openscheuren leiding	0	[-]	geen guillotine breuk aangenomen
geen flenslekkage	0	[-]	geen flenslekkage aangenomen
diameter leiding (Do)	100	[mm]	
diametergat berekening (D)	50	[mm]	
vloeistofhoogte t.o.v. uitstroomopening (h)	5	[m]	(gebruik beginhoogte)
volume vat (Vv)	100	[m ³]	(gas-inhoud beschouwd systeem/vat)
diameter leidingen (DI)	100	[mm]	(t.b.v. bepalen gas-inhoud beschouwd systeem)
lengte leidingen (LI)	20	[m]	(t.b.v. bepalen gas-inhoud beschouwd systeem)
inhoud gashouder (V)	188.8126	[Nm ³]	(inhoud achterliggend gasvolume)
nalevering van gas (Qv)	0	[Nm ³ /u]	(vloeistof welke a.g.v. de regelingen naar de uitstroomopening wordt gevoerd)
	4.95	[m]	diameter tank o.b.v. Vv en D/H=1
lengte opvangbak (Lbb)	6.00	[m]	
breedte opvangbak (Bbb)	7.00	[m]	tank past in opvangbak
diameter tank (Dt)	5.00	[m]	(dit oppervlak wordt in mindering gebracht)



Berekende uitstroom-gegevens:			
Released Quantity Rate RQR) begin (RQRo)	1.2	[kg/s]	<-- Uitgestroomde hoeveelheden:
RQR over 5 minuten (RQR5)	1.2	[kg/s]	
(RQ5)	347	[kg]	
RQR na 15 minuten (RQR15)	1.2	[kg/s]	
(RQ15)	1042	[kg]	
RQ na 1 uur (RQ60)	4170	[kg]	
Airborne Quantity Rate (AQRo) begin	1.2	[kg/s]	<-- Hoeveelheden Airborne:
AQR5 over 5 minuten	1.2	[kg/s]	
AQ5m	347	[kg]	massa van de wolk na 5 minuten.
AQR15 na 15 minuten	1.2	[kg/s]	
AQ15m	1042	[kg]	massa van de wolk na 15 minuten.
plasgrootte (Ap) na 15 minuten	0	[m^2]	<-- Hoeveelheden op de grond:
"plasgrootte" (Wp) na 15 minuten	0	[kg]	
Gevolgen van "Loss of Containment":			0

Scenario: Bij uitstroming:		gaswolk bestaande uit enkel gas	
Na uitstroming:		gas blijft in de gasfase in de gaswolk	
	5	(factor tot letale dosis o.b.v. richtw aarde acute toxiciteit)	
Hazard Distance Toxiciteit (HD)	118	[m]	#REF!
Chemical Exposure Index (CEI) Explosie en brandgevaar	2.16		(o.b.v. 5 minuten release)
Hazard Distance Explosie en brandgevaar (HD) o.b.v. L.E.L	22	[m]	
Hazard Distance Explosie en brandgevaar (HDstof)	n.v.t.	[m]	
Hazard Distance m.b.t. <u>Effect</u> van explosie en/of brand (HDex)	118	[m]	brandbare gaswolk bestaande uit enkel gas

The hazard effect distance from a fire/explosion of an ammonia tank of 100 m³ that has a rupture of 50 mm, 5 m above ground level, is 118 meters. This distance is extremely large, meaning working with tanks of this size is not favourable.



Appendix 3 –PSA

PSA – Diesel engine

	O ₂	N ₂	NO ₂	CO ₂	H ₂ O	C _n H _{2n+n}	CO	NO	NO ₃	NO _x
O ₂		R ¹				R ²		R ³		
N ₂	R ¹									
NO ₂			R ⁴		R ⁵		R ⁶			
CO ₂					R ⁷					
H ₂ O			R ⁵	R ⁷			R ⁸			
C _n H _{2n+2}	R ²									
CO			R ⁶		R ⁸					
NO	R ³									
NO ₃										
NO _x										

Nitrogen monoxide is formed at high T: $O_2 + N_2 \rightarrow 2 NO$

Combustion reaction, Auto-ignition temperature $\approx 210\text{ }^\circ\text{C}$

Slow reaction under normal atmospheric conditions: $2 NO + O_2 \rightarrow 2 NO_2$

@ $150\text{ }^\circ\text{C}$ decomposes NO_2 ($\Delta H = 114\text{ kJ/mol}$): $2 NO_2 \rightarrow 2 NO + O_2$

Hydrolysis of NO_2 : $3 NO_2 + H_2O \rightarrow NO + 2 HNO_3$

$CO + NO_2 \rightarrow NO + CO_2$ (@ $T > 327\text{ }^\circ\text{C}$)

Carbonic acid formation $H_2O + CO_2 \rightarrow H_2CO_3$

Water-Gas shift reaction: $CO + H_2O \rightarrow CO_2 + H_2$

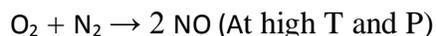
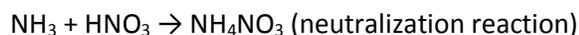
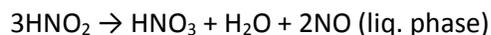
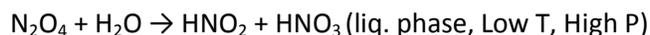
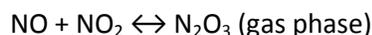
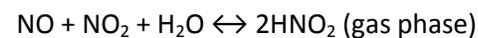
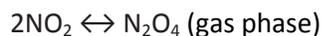
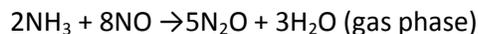
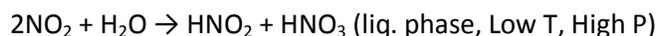
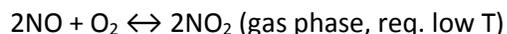
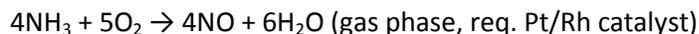
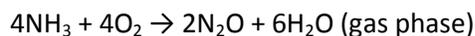


PSA - Industrial Nitric Acid Plant

Component	NH ₃	O ₂	N ₂	N ₂ O	N ₂ O ₃	N ₂ O ₄	NO	NO ₂	HNO ₂	HNO ₃	H ₂ O
NH ₃	—	1/5	—	—	—	—	4/5	—	—	12	—
O ₂	1/5	—	13	—	—	—	2/5	—	—	—	—
N ₂	—	13	—	—	—	—	—	—	—	—	—
N ₂ O	—	—	—	—	—	—	—	—	—	—	—
N ₂ O ₃	—	—	—	—	—	—	—	—	—	—	9
N ₂ O ₄	—	—	—	—	—	—	—	—	—	—	10
NO	4/5	2/5	—	—	—	—	—	7/8	—	—	—
NO ₂	—	—	—	—	—	—	7/8	6	—	—	3
HNO ₂	—	—	—	—	—	—	—	—	11	—	—
HNO ₃	12	—	—	—	—	—	—	—	—	—	—
H ₂ O	—	—	—	—	9	10	7	3/7	—	—	—

All Reactions are exothermic.

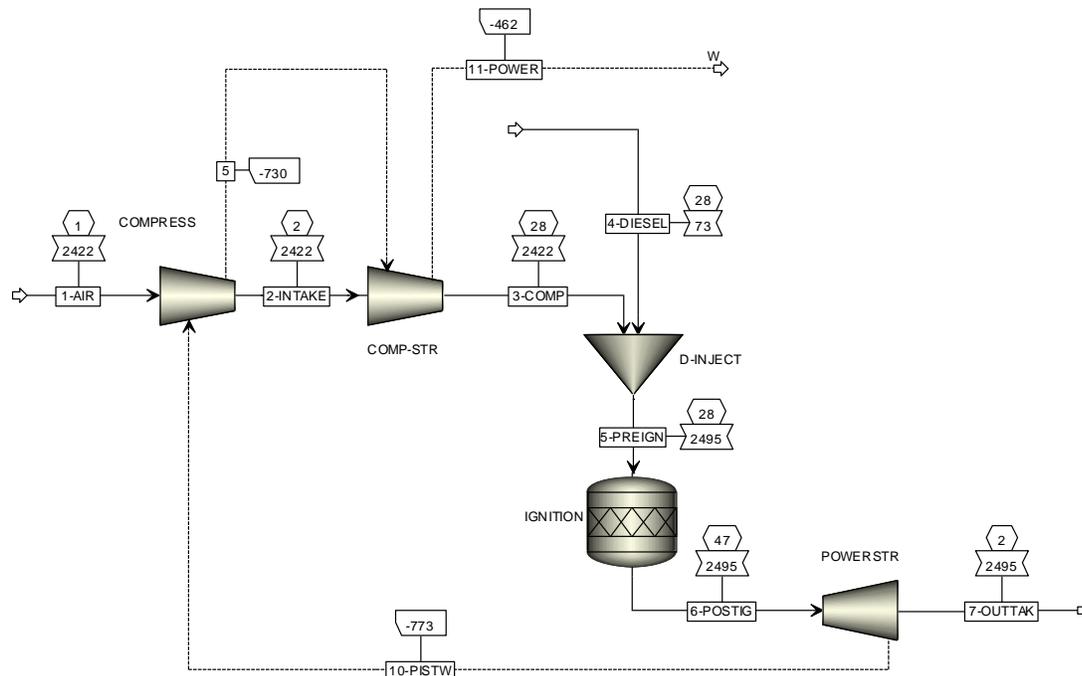
a, b are favored at lower temperatures.





Appendix 4 – The Aspen Models

1. Diesel Engine Model



		1-Air	2-intake	3-Comp	4-Diesel	5-preign	6-Postig	7-Outtak
From			compress	Comp-str		D-inject	Ignition	PowerStr
To		Compress	Comp-str	D-inject	D-inject	Ignition	PowerStr	
Phase:		Vapor	Vapor	Vapor	Liquid	Vapor	Vapor	Vapor
Mass Flow								
O2	KG/HR	508,62	508,62	508,62	0	508,62	263,21	263,21
N2	KG/HR	1913,38	1913,38	1913,38	0	1913,38	1913,38	1913,38
H2O	KG/HR	0	0	0	0	0	92,11	92,11
C6H12	KG/HR	0	0	0	70,91	70,91	0	0
H2S	KG/HR	0	0	0	2,19	2,19	0,22	0,22
CO2	KG/HR	0	0	0	0	0	222,47	222,47
SO2	KG/HR	0	0	0	0	0	3,71	3,71
Mass Flow	KG/HR	2422	2422	2422	73,1	2495,1	2495,1	2495,1
Volume Flow	CUM/HR	2015,88	1228,6	183,98	0,09	177,32	264,04	2953,03
Temperature	C	15	77,94	456,19	25	422,28	1433,96	545,14
Pressure	BAR	1	2	28	28	28	47	2
Mass Enthalpy	MJ/KG	-0,01	0,05	0,45	-1,82	0,38	0,38	-0,73
Enthalpy Flow	MJ/HR	-25,27	129,25	1092,41	-133,07	959,34	959,34	-1823,34
Mass Entropy	KJ/KG-K	0,11	0,11	0,11	-7,05	-0,06	1,03	1,03
Mass Density	KG/CUM	1,2	1,97	13,16	771,17	14,07	9,45	0,84



Model Description

Using a computer model for the diesel engine, an overview of the engine can be simplified by analyzing individual stages of the critical components of the process. In this model, the combustion of cyclohexane was used to simulate the combustion of diesel.

Cyclohexane was chosen as it has a C to H ratio close to as that of diesel as to replicate the CO₂ emissions after complete combustion, plus a very similar heat of combustion to mimic the release of energy. These two properties are critical and for the purpose of modelling, other properties were ignored.

	Diesel	Cyclohexane
Heat of combustion (Mj/kg)	44.8	43.45
Mass percentage - %C/%H	86/13	86/14

Table 1 – Combustion for Model

Table 1 – Combustion for Model

A compression ratio of 14:1 for the piston was chosen, which is the lowest ratio commonly found for diesel engines. The range can go up to 24:1. The lowest one was chosen, as the process with the ammonia will require a lower compression ratio as an allowance for the catalyst present.

Use was also made of Fig. 4 as a basis for the pressure conditions within the cylinder before and after ignition. Ignition takes thus place at 28bar which further increases the pressure to 48bar. At this point the pressure is released and making use of a turbine, work is extracted, which is used to power the initial compressors with the excess being freely available for desired applications at hand such as motion of wheels.

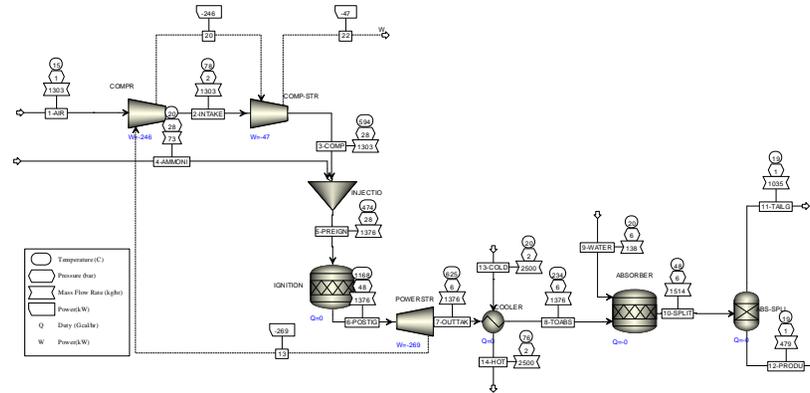
Excess air is also used as to simulate the workings of a real engine, as after complete combustion 13% of oxygen is still present in the exhaust gas.

A low content of sulphur was added to the fuel, as H₂S is present in quite significant amounts.

The production of NO_x's, CO, and un-combustible hydrocarbons were ignored as they are produced in very small amounts (PPM's, see table 4).



2. The Ammonia Engine Model



Stream		1-Air	2-intake	3-Comp	4-Diesel	5-preign	6-Postig	7-Outtak	8-Toabs	9-WATER	10-SPLIT	11-TAILG	12-PRODU
From:			compressor	Comp-str		D-inject	Ignition	PowerStr	Cooler		Absorber	Abs-spli	Abs-spli
To:		Compress	Comp-str	D-inject	D-inject	Ignition	PowerStr		Absorber	Absorber	Abs-spli		
Phase:		Vapor	Vapor	Vapor	Liquid	Vapor	Vapor	Vapor	Vapor	Liquid	Mixed	Vapor	Mixed
Mass Flow													
NH3	KG/HR	0	0	0	73,1	73,1	0	0	0	0	0	0	0
O2	KG/HR	303,69	303,69	303,69	0	303,69	63,33	63,33	63,33	0	30,27	30,26	0
N2	KG/HR	999,08	999,08	999,08	0	999,08	999,08	999,08	999,08	0	999,08	998,98	0,1
N2O	KG/HR	0	0	0	0	0	0	0	0	0	0	0	0
NO	KG/HR	0	0	0	0	0	0	0	0	0	1,59	1,59	0
NO2	KG/HR	0	0	0	0	0	197,47	197,47	197,47	0	0	0	0
HNO3	KG/HR	0	0	0	0	0	0	0	0	0	267,13	0	267,13
H2O	KG/HR	0	0	0	0	0	115,99	115,99	115,99	137,69	215,49	4,12	211,38
Mass Flow	KG/HR	1302,77	1302,77	1302,77	73,1	1375,87	1375,87	1375,87	1375,87	137,69	1513,56	1034,95	478,61
Volume Flow	CUM/HR	1081,11	658,86	117,28	0,12	110,61	121,91	603	339,78	0,14	171,94	894,52	0,49
Temperature	C	15	77,92	594,44	20	474,05	1168,28	625,06	234	20	48,19	18,67	18,67
Pressure	BAR	1	2	28	28	28	48	6	6	6	6	1	1
Vapor Fraction		1	1	1	0	1	1	1	1	0	0,73	1	0
Mass Enthalpy	KJ/KG	-10,41	53,2	603,66	-3962,13	361,08	361,08	-342,85	-801,91	-15994	-2659,65	-55,63	-8600,3
Enthalpy Flow	MJ/HR	-13,56	69,31	786,42	-289,63	496,79	496,79	-471,71	-1103,32	-2202,21	-4025,53	-57,58	-4116,2
Mass Entropy	KJ/KG-K	0,12	0,12	0,31	-11,14	-0,05	0,57	0,57	-0,1	-9,4	-2,21	0,02	-6,91



Model Description

An Aspen model of the ammonia fuelled engine was designed in such a way, that the chemical process in figure 1 was run at 10% capacity in the diesel engine. Here, all inputs were kept at a 10% level of the original process and the pressures and temperatures changed in order to adapt as close as possible to the conditions required, so that the engine would function.

Here, attention was paid so that the overall power balance (compressors and turbine) remains negative, so that there is enough power being produced to fully compress the air by the piston.

A compression ratio of 14:1 was used, together with a compression of 2:1 to reach the value of 28 bar prior to combustion.

Unlike the original process, no separate condenser was used. This choice was made, as the absorption column used in the following stage includes cooling which extracts the excess heat by the incoming flows as from the exothermic reactions taking place within it. This heat extraction should allow for the water present in the exhaust fumes to condensate and leave the absorption column together with the product. In the end a final 55% by mass of HNO₃ in water is obtained.



Appendix 5 – P&ID Nitric Acid Plant

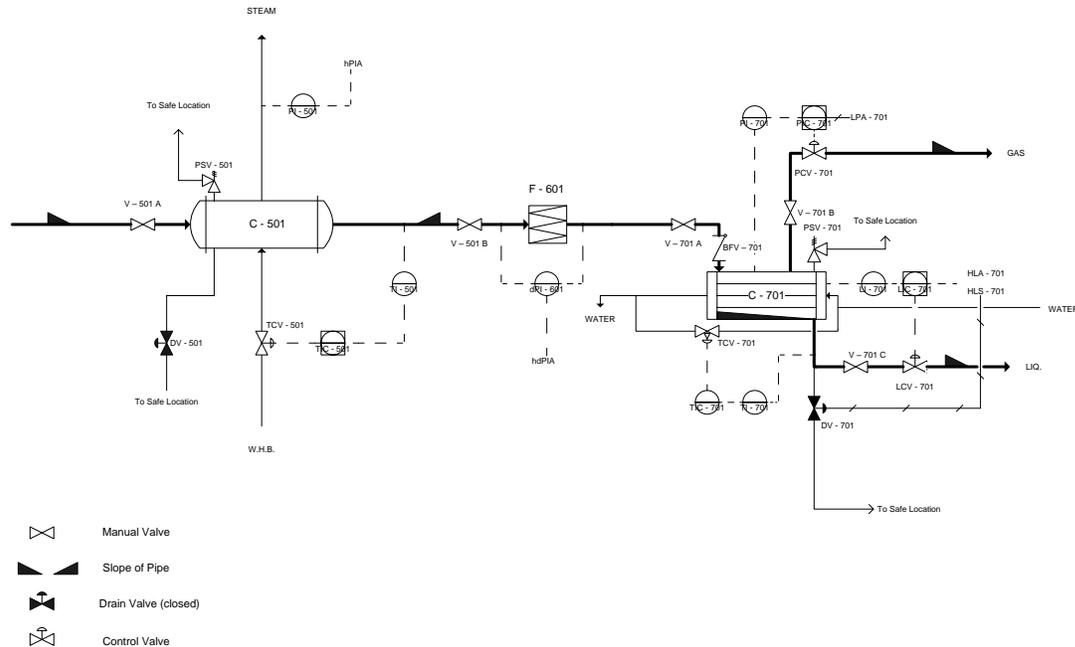


Figure 7 – P&ID Nitric Acid Plant

- V – 501, 701 are manually controlled valves to seal off the units C- 501 and C – 701
- PSV are required for high pressure relief
- PI – 501 measures the steam temperature. If Pressure is too high an alarm will alert the operator.
- Gas temperature of outlet is controlled by controlling WHB feed.
- F – 601 is used to recover evaporated Pt catalyst in form of PtO_2 by scrubbing.
- dPIA alerts operator that filter is dirty (large pressure change)
- Temperature of condenser C-701 is controlled with a bypass (TCV-701) of the cold water feed. Minimum cold water feed will always be present.
- C-701 water/acid level is controlled by adjusting the water removal stream with LCV-701
- C-701 pressure is regulated by controlling PCV-701 in the gas outlet.



HAZOP Analysis of P&ID:

Installation:						
Intention:		To cool reactor exhaust gases to just above vapor pressure				
Equipment:		C-501 (cooler)				
Nr.	Deviation	Initial failure	Sequence of consequences leading to the effect	Risk level	SHE Provisions (chain of input-devise-output)	Action / remark
1.1	Too high P in:	Burst in Cooler	Outlet blockage, higher pressures give liquid buildup	low	Pressure Safety Valve (PSV-501) to safe location	
1.2	Too low P in:	Gas inadequately cooled	Pressure drop from internal resistance before C-701	Low		
2.1	Too high T in	Inadequate cooling	Insufficient cooling system in reactor	low	Temperature measurement of outbound gas by regulating coolant flow (TI,TIC-501)	
2.2	Too low T in	Inadequate cooling	Failure cooling system in reactor	low	Temperature measurement of outbound gas by regulating coolant flow (TI,TIC-501)	
4.1	Too high flow to	Inadequate cooling	Failure cooling system in reactor	low	Temperature measurement of outbound gas by regulating coolant flow (TI,TIC-501)	
4.2	too low flow to	Inadequate cooling	Failure cooling system in reactor	low	Temperature measurement of outbound gas by regulating coolant flow (TI,TIC-501)	
4.3	Backflow from .. To..	Leakage	Leak in piping before C-501	Medium	Back Flow Valve (BFV-701)	Poisonous Gases, Avoid Contact/Inhalation

Installation						
Intention		To remove PtO ₂ from gas flow through scrubbing				
Equipment		F-601 (Filter/Scrubber)				
Nr.	Deviation	Initial failure	Sequence of consequences leading to the effect	Risk level	SHE Provisions (chain of input-devise-output)	Action / remark
1.3	Differential P over	Blocked Filter	Deposition of PtO ₂ on filter	low	High differential pressure indicating alarm (hdPIA-601)	Replace Filter
4.3	Backflow from .. To..	Leakage	Leak in piping before F-601	Medium	Back Flow Valve (BFV-701)	Poisonous Gases, Avoid Contact/Inhalation

Installation						
Intention		To cool reactor exhaust gases to just below vapor pressure point resulting in condensation of water				
Equipment		C-701 (condenser)				
Nr.	Deviation	Initial failure	Sequence of consequences leading to the effect	Risk level	SHE Provisions (chain of input-devise-output)	Action / remark
1.1	Too high P in:	Burst in Cooler	Outlet blockage, higher pressures give liquid buildup	low	Pressure Safety Valve (PSV-701) to safe location	
1.2	Too low P in:	Gas inadequately cooled	Pressure drop from internal resistance before C-701	Low		
2.1	Too high T in	Outlet liquid temperature is too high	Insufficient cooling of system in cooler C-501	low	Temperature measurement of outbound liquid by regulating coolant flow using bypass (TI,TIC -701)	
2.2	Too low T in	Inadequate cooling	Too much cooling from the condenser C-501	low	Temperature measurement of outbound liquid by regulating coolant flow using bypass (TI,TIC -701)	
3.1	Too high level in	Insufficient condensation	Insufficient out flow of liquid phase	medium	Level of tanks is controlled by regulation of the liquid outbound valve (LI,LIC-701)	n/a
3.2	Too low level in	Insufficient condensation, Insufficient cooling	Valve of outlet liquid flow too open, Insufficient cooling	low	Level of tanks is controlled by regulation of the liquid outbound valve (LI,LIC-701)	n/a
4.3	Backflow from .. To..	Leakage	Leak in piping before C-701	Medium	Back Flow Valve (BFV-701)	Poisonous Gases, Avoid Contact/Inhalation



Appendix 6: Bibliography

Actual Combustion Cycles. (n.d.). Retrieved from Integrated Publishing: <http://www.tpub.com/engine3/en3-15.htm>

Aguinet, G., Manoury, J., & Martin., E. (1972). *Patent No. 3658472*. France.

Bernhard Hüpen, E. K. (2005). *Rigorous modelling of NOx absorption in tray and packed columns*. Dortmund, Germany: ELSEVIER.

CIMAC. (2000). *BAE SYSTEMS*. Retrieved from Guide to Exhaust Emission Control Options: http://www.cimac.com/workinggroups/wg5WebDocument/DieselEmissions_31Mar00.htm

Cresswell, D. (1991). *Patent No. 5,041,276*. United States of America.

Gillespie, G. R. (1972). *Patent No. 3,660,024*. United States of America.

IMO. (1993). *International Maritime Organization - MARPOL Annex VI*.

Kramer, D. A. (2005, January). U.S. Geological Survey, Mineral Commodity Summaries. *Nitrogen (FIXED) - Ammonia* , p. 116.

Leduc, M. (n.d.). *The marine Diesel engine*. Retrieved from Dieselduck: http://www.dieselduck.net/machine/01%20prime%20movers/diesel_engine/diesel_engine.01.htm

Modak, J. M. (2002, August). Haber Process for Ammonia Synthesis. *RESONANCE* , pp. 69-77.

Perez-Ramirez, J. (2002). *Catalyzed N2O Activation - Promising (New) Catalyst for Abatement and Utilization*. Delft: Ponsen & Looijin BV.

Steinfeld, H., Gerber, P., Wassenaar, T., Castel, V., Rosales, M., & de Haan, C. (2004). *Livestock's long shadow*. Rome: Food and agriculture organization of the United Nations.

Tanner Industries Inc. (n.d.). Retrieved from <http://www.tannerind.com/PDF/blue-anhy-amm.pdf>

towler, g. &. (2009). *Chemical Engineering and Design*. Butterworth - Heinemann Inc.

Wärtsilä. (n.d.). *WÄRTSILÄ RT-flex96C AND WÄRTSILÄ RTA96C TECHNOLOGY REVIEW*. Retrieved from http://www.wartsila.com/Wartsila/global/docs/en/ship_power/media_publications/brochures/product_engines/low_speed/wartsila-RTA96C-engine-technology-review.pdf

Web02. (n.d.). Retrieved from <http://www.croplife.com/articles/image/2009-02/ammoniatank.jpg>