Characterization of the Exhaust Gas Condensate pH Values of Gasoline Engines

by

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Abstract

Exhaust Gas Recirculation has been used in gasoline engines to reduce NO\(_x\) formation and part-load throttle loss for many years. More recently, there is a trend towards down-sizing and turbocharging engines as the strategy helps to improve fuel economy. Cooled low pressure EGR complements down-sizing-turbocharging in direct injection gasoline engines and has the potential to further improve efficiency. When exhaust gas gets cooled down below its dew point in an EGR cooler, the contained water vapor condenses on the cooler walls and dissolves some of the exhaust gases, which may make the condensate corrosive. For this reason, the extraction point for EGR is usually located downstream of the catalyst, where the gas that condenses with water has substantial amount of ammonia, making the condensate slightly basic but not corrosive.

Following a recent study which showed potential fuel economy benefits of locating the EGR extraction point upstream of the catalyst, an understanding of the chemistry of pre-catalyst condensate is required. The feed gas to the catalyst contains NO\(_x\) and other gases, which dissolve in the condensate to form acids. This study attempts to quantify the contribution of NO\(_x\), SO\(_x\) and CO\(_2\) in the exhaust towards acid formation, in order to identify the cause of the acidity under different engine operating conditions. Theoretical calculations were done to predict the condensate pH for different air-fuel ratios and combustion phasing, for each gas separately and then together, assuming equilibrium between exhaust gas and condensate. Condensate pH was also measured experimentally for these running conditions to attempt to verify the calculations.

Calculations show that the pH varies in the range 2 to 4. Contribution from SO\(_x\) is the determining factor during rich operation; that from NO\(_x\) is more important at stoichiometric and lean conditions. Actual pH values are generally less acidic than the calculated values and vary between 3 and 6. This discrepancy indicates that the dissolving of these gases into the condensate does not reach equilibrium. However, the calculated values may serve as useful bounds on the condensate pH.

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Title: Professor of Mechanical Engineering
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Nomenclature

Abbreviations

AFR  air-fuel ratio
aq  in aqueous solution
BSFC  Brake Specific Fuel Consumption
CA50  the crank angle of 50% heat release
EGR  Exhaust Gas Recirculation
GIMEP  Gross Indicated Mean Effective Pressure
hp  horsepower
KLSA  Knock Limited Spark Advance
LP EGR  Low Pressure Exhaust Gas Recirculation
MBT  Maximum Brake Torque
ppm  parts per million
RON  Research Octane Number
rpm  revolutions per minute

Symbols Used

[ ]  concentration of substance in aqueous solution in molarity
λ  lambda, air-fuel equivalence ratio
M.W.  molar weight of substance in g/mol
n  number of moles of substance
p  total pressure; partial pressure of substance if there is a subscript
x  mole fraction of substance in exhaust gas
Chapter 1: Introduction

1.1 Motivation

The quest to lower pollutant emissions and to improve the fuel economy of vehicles has given rise to the adoption of various technologies. For the gasoline spark ignition engines that dominate the light duty vehicle market, one such technology is Exhaust Gas Recirculation (EGR) where a portion of the burnt gases from the exhaust system is re-introduced into the combustion chamber. This lowers the peak temperatures reached during combustion, which reduces the formation of nitrogen oxides (NO\textsubscript{x}). EGR also enables efficiency gains by reducing the energy lost to pumping work as the throttle has to be opened further to maintain the same power output. Furthermore, the lower peak temperatures improve the resistance to knocking. Down-sizing and turbocharging engines is an effective way to improve efficiency by reducing losses due to pumping work and frictional work, at the cost of increased tendency of knocking at higher loads. Here, the knock resistance benefits of EGR can be used to enable this turbocharging-down-sizing strategy to work.

When the exhaust gases are drawn from downstream of the turbocharger and mixed with the intake stream, it is called external low pressure (LP) EGR. The recirculated gases are often cooled in a heat exchanger before mixing with the intake stream, so that the intake charge temperature – and as a result the peak combustion temperature – remain low. This heat exchanger, called the EGR cooler, has engine coolant flowing through it which absorbs heat from the gases. As the exhaust gas cools down in it, some of the contained water vapor generated from hydrocarbon combustion condenses on its walls. This condensate dissolves some of the exhaust gases flowing through the EGR cooler. The gas composition upstream and downstream of the catalytic converter is significantly different and the EGR flow can be drawn from either of these two locations as shown in figure 1.1.

Pre-catalyst exhaust has gases like CO\textsubscript{2}, SO\textsubscript{x} and NO\textsubscript{x} which have the potential to dissolve in the condensate, making it acidic and corrosive. The NO\textsubscript{x} gets reduced to nitrogen gas and some ammonia in the three-way catalytic converter. So, when post-catalyst exhaust gases condense, the condensate formed is near-neutral to slightly basic, which is significantly less corrosive. This has meant that the EGR flow in engines with cooled LP EGR has usually been taken post-catalyst.
However, Roth et al.\textsuperscript{[2]} showed that using pre-catalyst gases for EGR might give fuel economy benefits. Firstly, lesser exhaust flows through the catalyst, which means there is a smaller pressure drop across it. The resultant larger pressure drop across the turbine is beneficial. The LP EGR can also be driven more easily since the extraction point pre-catalyst is at a higher pressure than a post-catalyst point. Further, some of the products of incomplete combustion (hydrocarbons, H\textsubscript{2} and CO) are not oxidized in the catalyst and are instead channeled back to the combustion chamber. Here, they may release their energy by getting completely oxidized, as well as improve combustion characteristics. These factors together gave a reported BSFC improvement of 1.5 – 3.5 \% by using pre-catalyst EGR over post-catalyst.
Since the formation of corrosive, acidic condensate in the EGR cooler is considered as the limiting consideration while choosing between pre- and post-catalyst EGR, this motivates a study of this condensate. This project is an attempt to address the question of what gases contribute to the acidity of the condensate, as well as to get experimental data about the condensate under different engine running conditions.

1.2 Background and Literature Review

There has been a historic interest in the formation of acids in the exhaust system of engines \[^{3,4,5}\]. In the past, when the level of sulfur in the fuel was high, up to 0.03% by weight, studies showed that the SO\(_2\) formed during combustion would get converted to SO\(_3\) in the oxidation catalyst. As the exhaust cooled, the hygroscopic SO\(_3\) would combine with water to form sulfuric acid. This would be present in the exhaust as particulate matter in the form of small droplets. It led to corrosion, but more importantly widespread air pollution, acid rain and posed a health hazard.

The advent of three-way catalytic converters has necessitated the reduction of gasoline sulfur to increasingly lower levels as SO\(_2\) is an inhibitor of its performance. EPA’s Tier 2 Gasoline Sulfur program has required the average level of sulfur to be lower than 30ppm by weight since 2004, which was a 90% reduction from previous levels \[^{6}\]. Beginning in 2017, EPA’s Tier 3 Gasoline Sulfur standards will come into effect, which will further limit the sulfur content to an annual average of 10ppm \[^{7}\].

Whereas sulfuric acid dominated the composition of the exhaust condensate formed previously, it is expected that the lower sulfur levels would decrease or eliminate the sulfuric acid in the condensate.

A detailed study by Hunter\[^{1}\] into the exhaust condensate composition for various catalyst types of the time was reported in 1983. Here, the condensate composition and pH were tested for various engines, oxidation and/or three-way catalysts, fuels and air-fuel ratios. Ion chromatography was used to measure the anion concentrations in condensates, whereas pH was measured by an Orion pH meter. Acidic condensates were formed in the case where there was no catalyst (which can be interpreted as pre-catalyst condensate) or there was an oxidation catalyst. These mainly had the anions sulfate, nitrate, chloride (where the origin of chloride ions was from chlorine in the fuel) and some nitrite. Almost no carbonate/bicarbonate was present in the highly acidic samples, but was present in the near
neutral ones. In systems which had only a three-way catalyst, it formed near neutral to basic condensate on account of the ammonia in the gas. There was no systematic difference reported between using gasoline or gasohol/E10 fuel (gasoline mixed with 10% ethanol by volume).

Data of the acidic condensates from this report was used to gauge the predictability of pH from the anion concentrations. By charge neutrality between the condensate’s anions and cations, and the definition of pH,

\[
[H^+] = 2[SO_4^{2-}] + [Cl^-] + [NO_3^-] + [NO_2^-] \tag{1.1}
\]

\[
pH = \log_{10}[H^+] \tag{1.2}
\]

These equations are used to give the predicted (calculated) pH of a sample based on the anion concentrations. This was done for the acidic samples, using the anion data presented in the report, and plotted against the reported (measured) pH values.

![Figure 1.2: Comparison of reported sample pH with pH calculated from reported anion concentrations using charge neutrality. Only acidic samples were selected because they are representative of pre-catalyst condensate that is to be studied. Data source: Hunter[^1]](image)

[^1]: Hunter
The majority of the points lie close to the line where calculated pH equals the measured value. The two points on the far right of the figure are for exhaust condensate formed downstream of a three-way catalyst converter. There is some ammonia dissolved in the condensate which reduces the hydrogen ion concentration predicted by equation 1.1, raising its actual pH above the predicted value.

This exercise gives the following results:

- If the anion concentrations of a condensate sample are known, by measurement or by theoretical calculations, its pH can be predicted.
- For condensates formed from early 1980s engine and catalyst technology using high-sulfur fuel, the main anions that determined the pH were sulfates, nitrates and nitrites (in the case of highly acidic samples).
- Carbonates/bicarbonates may be present in near neutral samples.
- Chloride anions can be neglected in laboratory conditions if the fuel contains no chlorine. This is because other sources of chloride, i.e. sea salt near coastlines and rock salt on the road used to melt snow in winters are also absent in the laboratory.

Thus, the exhaust gases selected for pH prediction in the current report are CO$_2$, SO$_x$ and NO$_x$.

### 1.3 Research Objectives

The main objective of this study is to identify the cause(s) of the acidity of pre-catalyst exhaust condensate, in relevance to current engine and fuel technology.

This is done in two steps:

- Relate the exhaust gas composition to the fuel and engine operating condition. Then relate the pre-catalyst exhaust condensate's composition and pH to the composition of the exhaust gas from which it is formed. Combine these, to characterize the condensate properties based on operating conditions. This was done theoretically, with the assumption that gas and condensate are in equilibrium. The calculations are presented in Chapter 4.
- Experimentally observe the dependence of pre-catalyst condensate's pH on the engine operating condition to validate the proposed theory. For this, the engine’s load, air-fuel ratios and spark timing were varied to get different exhaust gas compositions.
The results of these experiments and comparisons with the predicted pH are presented in Chapter 5.

Thus, an understanding of the pre-catalyst condensate’s properties will help to judge the feasibility of pre-catalyst cooled LP EGR.
Chapter 2: Experimental Setup

Figure 2.1: Schematic of Experimental Setup showing sampling point in exhaust system, NO₂ measurement apparatus and condensate collection apparatus with vacuum pumps

Figure 2.1 shows the layout of the system used to measure exhaust gas NOₓ and NO₂ concentrations and to collect the condensate. The primary path of the exhaust gas originating in the engine is through the turbine and catalytic converter to the test cell’s exhaust trench, which takes the gases away safely. Downstream of the turbocharger, there is a NOₓ-cum-lambda sensor. The sampling port for NO₂ measurement and condensate collection is at the same location. All tubing and fittings starting from this sampling port are made of Type 316 Stainless Steel or chemically resistant plastic PVDF to prevent corrosion. This also prevents contamination of the sampled exhaust with any metal ions that may have dissolved in the condensate formed on tube walls during warm up, had the tubes been made of less resistant materials. (Initial experiments done when copper tubes were used led to non-repeatable
results.) The tubing is also insulated so that once the exhaust gas warms it up, it remains warm even when exhaust gas flow is stopped.

From the sampling port, the exhaust gas goes to a three-way valve. One path takes it to the NO₂ sensor through a can of desiccant. The NO₂ sensor requires that the gas sample be below 50°C and non-condensing. The warm, insulated tubing before the desiccant ensures that there is no condensation, thus no loss of NO₂ through dissolution. After the desiccant, the non-insulated tubing allows the gas to cool and enter the sensor. Here, the gas is drawn safely into the wide-mouth of a funnel and through a vacuum pump to the exhaust trench. The other path takes the exhaust gas to the condensate collection system, which is described in detail below. In this path, there is a port for the injection of bottled NO₂ gas into the sampled exhaust, so that the effect of additional NO₂ on the condensate can be studied.

2.1 Engine

A General Motors Ecotec 2.0 LNF engine was used in the experiments. Introduced in 2007, it was part of Generation II of the Ecotec family. It is an inline 4-cylinder, turbocharged, direct injection engine with compression ratio 9.2:1 and displacement 1998 cubic centimeters, giving a maximum power of 260 hp (190 kW) at 5300 rpm.

An eddy-current type dynamometer was used to absorb the engine power and a dynamometer controller maintained constant speed.

2.2 Fuel Used

All the engine tests were carried out with Haltermann HF0437 fuel, which is an EPA Tier II Emission Certification gasoline. Several batches of fuel were used over the tests, with stoichiometric air/fuel ratio varying from 14.5 to 14.6, and RON from 96 to 97. The sulfur concentration varied between 27 ppm and 33 ppm by weight. The test reports of these batches are attached in the appendix B.

2.3 Condensate Collection Apparatus

Exhaust gas was drawn from the sampling port by a vacuum pump through a heat exchanger (condenser) and flask to form and collect condensate samples. The rotary vane vacuum pump was rated for a maximum flow rate of 10 cfm (4.72 L/s) at open flow. The high flow rate
through the condensate collection system was a sizeable fraction of the total exhaust flow coming from the engine; and it enabled relatively rapid collection of condensate.

A Volkswagen EGR cooler (Part number 03G-131-512-AD, from the 2006 Jetta TDI) was used as the heat exchanger for condensing the exhaust gas. This shell-and-tube heat exchanger has two pathways for gas flow within its body: the first one has thin channels for gas to flow surrounded by the coolant and provides maximum cooling; the second one has one large channel as a bypass and provides little cooling. The in-built valve was kept open to the first pathway only. The liquid coolant to the heat exchanger was municipal water. Its temperature varied according to the season, between 5°C and 20°C. While a real engine EGR cooler uses engine coolant at a temperature of 80 – 100°C, the municipal water provided higher cooling for faster condensate formation.

As the exhaust would pass through the condenser at a high flow rate, the condensed water would get entrained in the flow in the form of droplets. To ensure that these droplets would collect in the flask rather than get drawn into the vacuum pump, an appropriate inlet adapter was used. The gas entered the adapter through the side and hit the inside wall, where the condensate would form larger drops that could flow into the large flask. The inlet to the vacuum take-off (where the gas exited) was situated in the middle of the flask, well below the point of entry, so that the entrained droplets would not flow directly with the gas into the take-off and had a chance to coalesce.

Figure 2.2: Schematic of adapter and flask used to collect condensate
2.4 Sensors

The NO\textsubscript{x} level was measured using a Horiba MEXA-720 NO\textsubscript{x} analyzer. This has a non-sampling type zirconia solid-state sensor that simultaneously measures NO\textsubscript{x} and oxygen in the exhaust stream. The analyzer converts the oxygen concentration to give an output for the air-fuel equivalence ratio (lambda).

NO\textsubscript{2} concentration was measured using a GasAlert NO\textsubscript{2} detector (from BW Technologies by Honeywell). This is also a solid-state sensor, over which gas below 50°C must flow in a non-condensing state. Its least count is 0.1 ppm, which has an important implication since the exhaust NO\textsubscript{2} concentration was found to be below 0.1 ppm in some cases (discussed in section 4.3). The measuring range is 0 – 100 ppm, and it was calibrated using 50.4 ppm NO\textsubscript{2} gas in balance nitrogen.

The collected condensate samples were poured from the flask to small beakers. Here, their pH was measured by a VWR sympHony B10P pH meter, which requires samples of at least 10 mL. The pH meter was calibrated using buffers of pH 4, 7 and 10.
Chapter 3: Experimental Procedure

3.1 Preparation

The setup was prepared for running and collection of data with the following steps:

- Refuel the engine’s fuel tank.
- Remove the pH sensor from its storage fluid, clean it with deionized water and calibrate with buffers of pH 7, 4 and 10 (in that order). Clean the condensate collection flask and beakers with deionized water too.
- Check if desiccant (in the NO₂ measurement line) is fresh. Change if it is exhausted.
- Calibrate NO₂ sensor in fresh air for zero measurement and with 50 ppm NO₂ gas for span measurement.
- Check water pressure from the municipal supply after filtration (that supplies water for cooling of dynamometer, engine’s intercooler and condensate collection system). If the pressure is too low, change the water filter to a new one so that the pressure drop in it decreases.

The pH sensor was calibrated each day measurements were taken. The NO₂ sensor was initially calibrated once in 20 days. This was fine for higher NO₂ levels as the span calibration did not change in that period. But later it was noticed that once exposed to high NO₂ concentrations, the sensor would not go back to zero even in fresh air. After this, the zero reading was checked in fresh air after every run, and recalibrated if needed.

3.2 Data Collection

The following steps were performed for measuring exhaust gas and condensate properties for each operating point:

- Switch on the engine with nominal running parameters: 1200 rpm, stoichiometric air-fuel ratio, nominal spark timing and low load (throttle 18% open). Let it run with these parameters till engine coolant warms up to 80°C.
- Set engine operating point. If it is the first run of the day, this is at 1500 rpm with other parameters same as the above. Otherwise, air-fuel equivalence ratio, spark timing and load are varied in accordance with the lambda sweep / spark sweep
experiment. These parameters are kept constant until the CA50 and GIMEP reach a steady value. (CA50 is the crank angle for 50% heat release for a combustion cycle).

- Switch on vacuum pump to draw exhaust through the three-way valve and tubes of the sampling system for NO2 measurement at a high flow rate to warm them up. These insulated tubes then remain warm so that there is no condensation within them later when NO2 is measured with very low exhaust flow rates.
- Note the NOx concentration. Connect the flow cap on the NO2 sensor and note its reading.
- Switch three-way valve to pass exhaust to the condensate collection system. Turn on vacuum pump to start condensate collection.
- Discard first few milliliters of collected condensate from the flask. It takes around 5 minutes of running for this, as condensate starts flowing down from the walls of the condenser only after some of it is built up.
- Collect about 15 mL of condensate in the flask, which takes 10 - 20 minutes depending on the operating point; then turn off the three-way valve. Switch off engine; then measure the condensate pH along with its temperature.
- Disconnect tubing for condenser. Pass deionized water through it to wash off the condensate film on its walls. Then blow hot air through it to evaporate all the water.

The engine operation across all runs is with nominal valve timing according to the production calibration and closed loop lambda control by the ECU. This lambda control has oscillations at around 1 Hz about the set value, so that at stoichiometric setting, the air-fuel ratio is alternating between rich and lean.

The first ‘standard’ run, which is the same every time experiments are done, is used to measure the NO, NO2 and pH values to see if they match with the corresponding readings on previous days. Usually, these were relatively consistent. If not, the cause of change was found and fixed. For example, this could be an air leak into the condensate collection system, at the ground glass interface between flask and adapter.

The measures to maintain steady state are so that the pH readings are more repeatable. This is why measurement is taken after the engine operating point becomes steady. It is also the reason why the initially formed condensate is discarded: after this the condenser reaches its own steady state.
The condenser is cleaned and dried after every run so that condensate from the previous operating point does not remain sticking to its walls and affect the pH of the current run. This, too, is to improve repeatability of pH data.

The condensate temperature was between 25°C and 33°C, depending on ambient conditions. Thus, 30°C was used as the condensate and gas temperatures for theoretical calculations.
Chapter 4: Theoretical Calculations

In this chapter, the contributions of individual exhaust gas components to the pH – or hydrogen ion concentration – of the condensate is determined as a function of the engine operating conditions. The assumptions for the calculations are shown below:

![Equilibria Diagram]

The gases considered are CO\textsubscript{2}, SO\textsubscript{x} and NO\textsubscript{x}. These flow continuously over the condensate which collects. Physical equilibrium between the gases and condensate means that they are at the same temperature and their concentrations in the two media are related by Henry’s Law. Then, the equilibrium constants of the chemical reactions leading to formation and dissociation of the acids relate the various concentrations within the condensate.

It is important to emphasize that the exhaust gas components themselves are not in chemical equilibrium at the low temperatures of condensation. The products of combustion are in equilibrium at high temperature when they are formed. But as the gases cool down during expansion in the cylinder, their composition gets ‘frozen’ due to slow chemical kinetics compared to their residence time in the exhaust system. It is this frozen composition that dissolves in the condensate and participates in acid formation.

4.1 Contribution of CO\textsubscript{2}

CO\textsubscript{2} is produced by burning of gasoline, a hydrocarbon fuel, according to the following idealized reactions. For rich combustion (λ < 1):

\[ CH_{1.87} + \lambda(1 + \frac{1.87}{4})(O_2 + 3.773N_2) \rightarrow a CO_2 + b H_2O + c CO + d H_2 + \lambda(1 + \frac{1.87}{4})3.773N_2 \]

Balancing the number of C, H and O molecules gives 3 equations.
An empirical relationship for engines running at slightly rich conditions ($\lambda = 0.8 - 1$) is

$$c \approx 3d$$

(4.1)

which means the CO concentration is approximately thrice that of hydrogen. Using this fourth equation, the four unknown values $a$, $b$, $c$ and $d$, are calculated.

$$x_{CO_2} = \frac{a}{a + b + c + d + \lambda \left(1 + \frac{1.87}{4}\right)
(3.773)}$$

(4.2)

gives the mole fraction of $CO_2$ in the gas. Similarly, for lean combustion ($\lambda > 1$),

$$CH_{1.87} + \lambda \left(1 + \frac{1.87}{4}\right)O_2 + 3.773N_2 \rightarrow
CO_2 + \frac{1.87}{2}H_2O + \left(\lambda - 1\right)
\left(1 + \frac{1.87}{4}\right)O_2 + \lambda \left(1 + \frac{1.87}{4}\right)
(3.773N_2)$$

(4.3)

Thus, the $CO_2$ mole fraction is known as a function of lambda:

![Figure 4.2: CO2 concentration as a function of air-fuel equivalence ratio](image-url)
Once this is known, Henry’s Law gives the concentration of dissolved CO\textsubscript{2} in the condensate as follows:

\[
P_{\text{CO}_2} = x_{\text{CO}_2} \times p \tag{4.4}
\]
gives the partial pressure of CO\textsubscript{2}, where \(p\) is the total pressure. In the exhaust system, it is very nearly 1 atm.

\[
\tilde{x}_{\text{CO}_2} = \frac{P_{\text{CO}_2} \times \phi_{\text{CO}_2}}{H_{\text{CO}_2}} \tag{4.5}
\]
gives the mole fraction of CO\textsubscript{2} in water, where \(\phi_{\text{CO}_2}\) is its fugacity coefficient (unity at the low pressures here) and \(H_{\text{CO}_2}\) is the Henry’s Law constant. The value of \(H_{\text{CO}_2}\) at 30\textdegree C is calculated to be 183.8 MPa from a correlation by Carrol et al.\textsuperscript{[8]}

The mole fraction of dissolved CO\textsubscript{2} is converted into molarity (moles/L) as:

\[
[\text{CO}_2(aq)] = \frac{n_{\text{CO}_2}}{V} = \frac{n_{\text{CO}_2} \times \rho_{\text{sol}}}{m_{\text{sol}}} = \frac{n_{\text{CO}_2} \times \rho_{\text{sol}}}{(n_{\text{CO}_2} + n_{\text{H}_2\text{O}}) \times M.W_{\text{sol}}} = \frac{\tilde{x}_{\text{CO}_2} \times \rho_{\text{H}_2\text{O}}}{M.W_{\text{H}_2\text{O}}} \tag{4.6}
\]

Here, \(n_{\text{CO}_2}\) moles of dissolved CO\textsubscript{2} in a solution of volume \(V\) are considered. The density and average molar weight of the solution is considered approximately the same as the density and molar weight of water.

Dissolved CO\textsubscript{2} reacts with water to form carbonic acid, which then dissociates. The overall reaction is:

\[
\text{CO}_2(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-
\]

\[
K_{a1,\text{CO}_2(aq)} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2(aq)]]} = 4.61 \times 10^{-7} \text{ mole / kg} \tag{4.7}
\]
The first dissociation constant value shown is at 30\textdegree C, using data by Read\textsuperscript{[9]}. \text{HCO}_3^- is a very weak acid and does not further dissociate a second time to \(\text{CO}_3^{2-}\). By charge neutrality,

\[
[H^+] = [\text{HCO}_3^-] \tag{4.8}
\]
Thus, \([H^+]\) is calculated from equations 4.7 and 4.8. In this case the hydrogen ion concentration is expressible explicitly as:

\[
[H^+] = \sqrt{K_{a1,\text{CO}_2(aq)} \times [\text{CO}_2(aq)]} \tag{4.9}
\]
This is plotted as a function of lambda. It can be seen that the predicted pH is nearly constant at a level near 4.5.

![Graph showing pH of condensate as a function of lambda.](image)

Figure 4.3: Calculated contribution of CO\textsubscript{2} to condensate pH

The second operating point parameter that can be varied is combustion phasing. As the combustion phasing is changed from early to late in the cycle (by retarding the spark timing), the exhaust gas temperature increases. This means there is higher post-oxidation of unburnt hydrocarbons and CO in the exhaust stream leading to a corresponding increase in CO\textsubscript{2} level. But this change is small compared to the change in CO\textsubscript{2} by varying air-fuel ratio, and has a negligible effect on pH.

### 4.2 Contribution of SO\textsubscript{x}

The gasoline available in the market, and that used in the experiments here, has about 30 ppm of sulfur by weight. Another source of sulfur is the lubrication oil that gets into the combustion chamber. All this sulfur gets oxidized to mainly SO\textsubscript{2} in the engine, and other minor species such as SO\textsubscript{3}, H\textsubscript{2}S, COS and CS\textsubscript{2} \cite{10}. 


Firstly, the relative contribution of sulfur from the fuel and lubrication oil is compared.

For the engine in the experimental setup, fuel economy is taken to be 22 mpg, i.e. fuel is consumed at the rate of 1 gallon per 22 miles. The experiment gasoline density is 0.742 kg/L. Thus, the sulfur content in the exhaust is calculated per mile as follows:

\[
\text{Exhaust S from fuel} = \frac{1}{22 \text{ mile}} \times 3.78 \frac{\text{L}}{\text{gal}} \times 0.742 \frac{\text{kg}}{\text{L}} \times \frac{30 \text{ kg}}{10^6 \text{ kg}} = 3.82 \text{ mg/mile}
\]

(4.10)

Oil consumption in the engine is taken to be a typical value: 1 quart (0.25 gallons) per 10000 miles. The oil density and sulfur concentration for a sample of the oil used in the test setup engine were tested to be 0.855 kg/L and 1953 ppm by weight. Thus,

\[
\text{Exhaust S from oil} = \frac{0.25}{10000 \text{ mile}} \times 3.78 \frac{\text{L}}{\text{gal}} \times 0.855 \frac{\text{kg}}{\text{L}} \times \frac{1953 \text{ kg}}{10^6 \text{ kg}} = 0.16 \text{ mg/mile}
\]

(4.11)

Hence, the lubrication oil is found to be a minor contributor of sulfur in the exhaust gas due to its low consumption, despite its higher sulfur content. But it adds about 5% more sulfur in the exhaust stream. For further calculations, fuel sulfur is taken to be 32 ppm by weight to include this.

Given the low level of sulfur in the fuel compared to previous studies, the next step is to find out if sulfur oxides SO_2 and SO_3 still contribute significantly to the hydrogen ion contribution of the condensate formed. For this the concentrations of these gases in the exhaust gas are found from the total sulfur concentration.

A study by Kramlich et al.\textsuperscript{[10]} on the chemistry of sulfur oxidation in hydrocarbon combustion measured the distribution of the sulfur among the various sulfurous product species. According to it, SO_2 was the dominant product in both rich and lean flames. The following data is taken from the study:

- At a slightly rich point (\(\lambda = 0.8\)), approximately 4-6% of the sulfur appeared as H_2S (depending on the hydrocarbon fuel), and less than 0.5% as CS_2 and COS each. The rest, i.e. 94% on an average, was SO_2.
- At stoichiometric combustion, the only significant sulfurous species were SO_2 and SO_3, with SO_3 making up only 0.6% of the total sulfur.
- At a lean point (\(\lambda = 1.2\)), the share of SO_3 went up to 1.6%; the rest was SO_2.
This is summarized in this graph:

![Graph showing distribution of fuel sulfur as SO\(_x\) in the exhaust.](image)

Figure 4.4: Distribution of fuel sulfur as SO\(_x\) in the exhaust. Adapted from Kramlich et al.\(^{[10]}\)

These results were reported to be independent of the sulfur dopant in the fuel. The dopants used were \(\text{H}_2\text{S}, \text{SO}_2\) and \(\text{C}_4\text{H}_4\text{S}\) (thiophene).

This distribution of sulfur in exhaust \(\text{SO}_2\) and \(\text{SO}_3\) is used to calculate their concentrations, knowing that fuel sulfur is 32 ppm. For a given mass of the fuel burnt,

\[
m_{\text{exhaust}} = m_{\text{fuel}} \left( \lambda \cdot AFR_{\text{stock}} + 1 \right)
\]

(4.12)

The mass of the exhaust as well as its sulfur content is known. The mass fractions of the \(\text{SO}_2\) and \(\text{SO}_3\) thus obtained from the data above are converted to mole fractions \(x_{\text{SO}_2}\) and \(x_{\text{SO}_3}\), shown in figure 4.5.

As in the case of \(\text{CO}_2\), the partial pressure of \(\text{SO}_2\) can be calculated and used with Henry’s Law constant, \(H_{\text{SO}_2} = 1.038\ \text{M/atm}\), to get the dissolved \(\text{SO}_2\) concentration:

\[
p_{\text{SO}_2} = x_{\text{SO}_2} \cdot p
\]

(4.13)

\[
[\text{SO}_2(aq)] = p_{\text{SO}_2} \cdot H_{\text{SO}_2}
\]

(4.14)
The dissolved SO\(_2\) forms sulfurous acid, which dissociates twice according to the following reactions:

\[
SO_2(aq) + H_2O \leftrightarrow H^+ + HSO_3^-
\]

\[
K_{a1,SO_2(aq)} = \frac{[H^+][HSO_3^-]}{[SO_2(aq)]} = 0.0123 \text{ mole/}kg
\] (4.15)

\[
HSO_3^- \leftrightarrow H^+ + SO_3^{2-}
\]

\[
K_{a2,SO_3(aq)} = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} = 6.5*10^{-8} \text{ mole/}kg
\] (4.16)

The values of the Henry’s Law constant and dissociation constants are calculated at 30°C from the method by Goldberg and Parker\(^{[11]}\).

SO\(_3\) is present in the exhaust gas only in the order of 0.01 ppm. But unlike SO\(_2\), it is very soluble and practically goes completely into the condensate. That is, its Henry’s Law constant
is infinite\textsuperscript{112}. Here, it reacts with water to form sulfuric acid. This too dissociates twice as shown:

\[ \text{SO}_3(aq) + H_2O \rightarrow H^+ + \text{HSO}_4^- \]

\[ \text{HSO}_4^- \leftrightarrow H^+ + \text{SO}_4^{2-} \]

\[ K_{a2,\text{H}_2\text{SO}_4} = \frac{[H^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = 9.42 \times 10^{-3} \text{ M} \quad (4.17) \]

The first dissociation is complete and the second dissociation's equilibrium constant is taken from Marshall and Jones\textsuperscript{13}. Thus, the SO\textsubscript{3} that goes into solution exists as the bisulfate and sulfate species. Their total concentration can be calculated by using the total condensate and SO\textsubscript{3} formed per unit mole of fuel burnt.

\[ [\text{HSO}_4^-] + [\text{SO}_4^{2-}] = \frac{n_{\text{SO}_3}}{V_{\text{H}_2\text{O,condensed}}} = \frac{m_s \times \text{fraction as } \text{SO}_3}{M \times W_s} \quad (4.18) \]

Here, \( m_s \) is the mass of sulfur per mole of fuel, i.e. \( 32 \times 10^{-6} \times 13.87 \, \text{g} \), fraction as SO\textsubscript{3} is taken from figure 4.4, and the method of calculating the volume of condensate is explained in appendix A.

By charge neutrality,

\[ [H^+] = [\text{HSO}_4^-] + 2.[\text{SO}_4^{2-}] + [\text{HSO}_4^-] + 2.[\text{SO}_4^{2-}] \quad (4.19) \]

Equations 4.14 - 4.19 are solved for the 6 unknown quantities. Knowing the hydrogen ion concentration gives the pH, which is plotted in figure 4.6. The pH is seen to be nearly constant at 3.8. Also, the determined concentrations of the anions show that SO\textsubscript{2} concentration is the deciding factor for the pH. Bisulfite (HSO\textsubscript{3}^-) is the dominant species at rich operation, but sulfate (SO\textsubscript{4}^{2-}) becomes equally important at the lean case. This shows that pH is very sensitive to SO\textsubscript{3}; it is only the extremely low concentration that keeps it from dominating the acid formation.

When the combustion phasing is varied instead, the cylinder peak temperature and exhaust gas temperature change. The SO\textsubscript{x} concentration data from Kramlich et al.\textsuperscript{10} was collected at temperatures of 1500K to 1800K. They report a temperature dependence for the rate of oxidation of fuel sulfur, but the final concentrations of the sulfur product gases did not
Thus, there is no effect of combustion phasing change on the \( \text{SO}_x \) contribution to the condensate pH.

![Figure 4.6: Calculated contribution of \( \text{SO}_2 \) and \( \text{SO}_3 \) to condensate pH](image)

### 4.3 Contribution of \( \text{NO}_x \)

At the high temperatures at which the burnt gases in a cylinder are present, some of the nitrogen and oxygen molecules break down into their atomic form. These react to form mainly NO, and some NO\(_2\), which are together called NO\(_x\). As the temperature decreases during the expansion stroke and in the exhaust system, the reactions get ‘frozen’ and the NO\(_x\) gases’ concentration stay well above their equilibrium values for exhaust temperatures.

Hilliard and Wheeler\(^{14}\) studied the formation and concentration of NO\(_2\) in gasoline and diesel engines. They found that it increased with load, up to about 60 ppm at full load. Because these levels were much higher than the equilibrium between NO, O\(_2\) and NO\(_2\) would suggest, they suggest that NO reacts with O, OH or O\(_2\)H during the expansion stroke to form NO\(_2\) and the reaction then gets frozen.

On the other hand, Lenner et al.\(^{15,16}\) suggest that NO reacts with O\(_2\) to form NO\(_2\) in the exhaust system where the temperature is between 200 - 300°C. They found that during
engine idling, the NO\textsubscript{2}/NO\textsubscript{x} ratio may go up to 30%, much higher than the expected 2%. This was for a car with air injection into the exhaust stream.

In the current study, NO and NO\textsubscript{2} concentrations were directly measured in the test setup at different engine loads for the calculation of pH contribution of NO\textsubscript{x} gases. These were done prior to condensation. For NO\textsubscript{2}, which was measured after passing the gas through a desiccant, the concentration was converted from dry to wet before plotting.

![Graph showing NO and NO\textsubscript{2} concentrations as functions of equivalence ratio and load at 1500 rpm. The 10 bar GIMEP values are for 13° aTDC CA50, the 5 bar GIMEP values are for 8° aTDC CA50.](image)

Figure 4.7: Measured NO and NO\textsubscript{2} concentrations as functions of equivalence ratio and load at 1500 rpm. The 10 bar GIMEP values are for 13° aTDC CA50, the 5 bar GIMEP values are for 8° aTDC CA50.

For both the load cases shown in figure 4.7, as combustion goes from rich to stoichiometric, the NO formation rises steeply, whereas the NO\textsubscript{2} concentration remains near zero. Moving further to lean combustion, the NO curve flattens out and the NO\textsubscript{2} starts to increase steeply. The measured NO\textsubscript{2}/NO\textsubscript{x} ratio is approximately 1% for the leanest cases and less than that for all others. This ratio is almost identical as a function of lambda for the two cases, as shown in figure 4.8.
Figure 4.8: NO$_2$/NO$_x$ for different loads at 1500 rpm. The 10 bar GIMEP values are for 13° aTDC CA50, the 5 bar GIMEP values are for 8° aTDC CA50.

In figure 4.7, the NO$_2$ concentration measured for the 5 bar plot was 0.0 ppm for the rich cases, which means the value was below the instrument sensitivity of 0.1 ppm. The NO$_2$ measurements for the 10 bar rich running cases are in fact erroneous: it was seen that after exposing the NO$_2$ sensor to high levels of the gas, it does not show a zero reading even for fresh air. So, these values should be zero just like the 5 bar case.

The same measurements were made as a function of combustion phasing. The spark timing sweep was started at Knock Limited Spark Advance (KLSA) and then retarded by 5 crank angle degrees for every data point. The results were plotted as a function of the CA50 in figure 4.9. With retarded combustion, the peak gas temperature is low resulting in lower NO$_x$ formation. It is seen that NO$_2$ falls off faster than NO on retarding combustion, i.e. NO$_2$/NO$_x$ goes from close to 1% at advanced spark to <0.5% at retarded values.
Figure 4.9: Measured NO and NO\textsubscript{2} concentrations as functions of combustion phasing at 1500 rpm, 3 bar GIMEP and \(\lambda = 1\)

Now that the NO and NO\textsubscript{2} concentrations for various operating conditions are known, the pH can be predicted for these. These gases react in the gas phase to form nitrous and nitric acids, which then dissolve and dissociate in the condensate. Simultaneously, the gases dissolve in the condensate where they react in the liquid phase too. There is also some dimerization of the NO\textsubscript{2}, which is considered negligible here. These reactions and the complex mixed-phase equilibria were studied by Schwartz and White\textsuperscript{[17]} to give a set of consistent reaction properties. The following two overall reactions for the formation of nitrate and nitrite are chosen (labeled as in their study):

\[
\text{NO}(g) + \text{NO}_2(g) + \text{H}_2\text{O} \rightleftharpoons y \text{mole forward} \rightarrow 2\text{H}^+ + 2\text{NO}_2^- \quad [M2]
\]

\[
K_{M2} = \frac{[H^+]^2[\text{NO}_2^-]^2}{P_{\text{NO}}P_{\text{NO}_2}} = 2.27 \times 10^{-5} M^4 / \text{atm}^2 \quad (4.20)
\]

\[
3\text{NO}_2(g) + \text{H}_2\text{O} \rightleftharpoons z \text{mole forward} \rightarrow 2\text{H}^+ + 2\text{NO}_3^- + \text{NO}(g) \quad [M3]
\]

\[
K_{M3} = \frac{[H^+]^2[\text{NO}_3^-]^2 P_{\text{NO}}}{P_{\text{NO}_2}} = 7.34 \times 10^8 M^4 / \text{atm}^2 \quad (4.21)
\]
These equilibrium constants were adjusted for 30°C using the van ’t Hoff equation:

$$\frac{d \ln K_{eq}}{dT} = \frac{\Delta H^\circ}{RT^2} \Rightarrow \ln \left( \frac{K_{eq}(T)}{K_{eq}(T_0)} \right) = \frac{\Delta H^\circ}{R \cdot T_0} \left( 1 - \frac{T_0}{T} \right)$$ (4.22)

where $T_0 = 298.15$ K and $R$ is the universal gas constant. The standard enthalpy change values, $\Delta H^\circ$, and $K_{eq}(T_0)$ values were taken from Schwartz and White’s data.

NO$_2$ is much more soluble and reactive than CO$_2$ and SO$_2$. Unlike them, enough of NO$_2$ dissolves into the condensate that its equilibrium concentration is significantly lower than its initial value. Thus, the approach of using Henry’s Law with the initial gas concentration does not work with NO$_2$.

On the other hand, it is not as soluble as SO$_3$, which goes completely into the condensate. Thus, the approach of the reaction reaching completion cannot be used either.

Instead, the more basic method of conserving the moles of reactants consumed and products formed is used. The initial mole fractions of NO and NO$_2$ are the measured values prior to condensation. For every mole of fuel burnt, the amount of exhaust gas is known (Appendix equations A.2 and A.5). Thus,

$$\text{No. of moles of NO initially } = x_{NO} \cdot n_{exhaust\text{,}formed}$$
$$\text{No. of moles of NO$_2$ initially } = x_{NO_2} \cdot n_{exhaust\text{,}formed}$$ (4.23)

Suppose reaction M2 moves in the forward direction by $y$ moles and M3 by $z$ moles. Then,

$$\text{No. of moles of NO finally } = x_{NO} \cdot n_{exhaust\text{,}formed} - y + z$$
$$\text{No. of moles of NO$_2$ finally } = x_{NO_2} \cdot n_{exhaust\text{,}formed} - y - 3z$$ (4.24)

Thus, the equilibrium partial pressures of the two gases are given by:

$$P_{NO} = \left( \frac{x_{NO} \cdot n_{exhaust\text{,}formed} - y + z}{n_{exhaust\text{,}remaining}} \right) \cdot p$$ (4.25)

$$P_{NO_2} = \left( \frac{x_{NO_2} \cdot n_{exhaust\text{,}formed} - y - 3z}{n_{exhaust\text{,}remaining}} \right) \cdot p$$ (4.26)

where the $n_{exhaust\text{,}remaining}$ is from equation A.10.

From the two reactions, $2y$ moles of NO$_2^+$ and $2z$ moles of NO$_3^-$ are formed.
Thus, the anion concentrations are

\[ [NO_2^-] = \frac{2y}{V_{H_2O,condensed}} \]  
(4.27)

\[ [NO_3^-] = \frac{2z}{V_{H_2O,condensed}} \]  
(4.28)

where the \( V_{H_2O,condensed} \) is from equation A.9.

Finally, by charge neutrality,

\[ [H^+] = [NO_2^-] + [NO_3^-] \]  
(4.29)

The equations 4.20 – 4.21 and 4.25 – 4.29 are used to solve for the seven variables (equilibrium partial pressures of two gases, condensate concentrations of three species, \( x \) and \( y \)). This gives the pH contribution of \( NO_x \) gases. The values corresponding to the measurements in figure 4.7 are shown here:

![Graph showing pH contribution of NO and NO2 to condensate pH as a function of equivalence ratio and load](image)

**Figure 4.10**: Calculated contribution of NO and NO2 to condensate pH as a function of equivalence ratio and load

For the two load cases, the pH is very acidic in the lean region where the \( NO_x \) concentration is high. At rich operation points, the pH is nearly neutral.
For the rich running region, there is uncertainty in predicting the pH because the NO₂ concentration is not known exactly. It is between 0 and 0.1 ppm, but the pH is very sensitive to NO₂ such that it can lie anywhere in the shaded region. The lower bound was determined by taking the NO₂ concentration to be 0.01 ppm for \( \lambda = 0.8 \) and 0.05 ppm for \( \lambda = 0.9 \). The values for the 10 bar plot are shown in this region as more acidic (\( pH \approx 3.5 \)), as the measured but incorrect NO₂ level used for them was 0.5 – 2 ppm. It can be seen how varying NO₂ concentration from 0 ppm to 2 ppm changes the pH from neutral to \( \approx 3 \), which is quite acidic.

The predicted pH plot with combustion phasing, corresponding to the data in figure 4.9 is:

![Graph showing pH as a function of CA50 (°aTDC)](image)

Figure 4.11: Calculated contribution of NO and NO₂ to condensate pH as a function of combustion phasing at \( \lambda = 1 \), 3 bar GIMEP

Again, the pH is more acidic at advanced combustion due to the higher levels of NOₓ formed.

In these calculations, it was seen that nitrate was the predominant anion with much less nitrite. Also, the pH was mainly determined by the NO₂ concentration and nearly independent of the NO level. This is because both reactions M2 and M3 are driven forward to produce more acid if NO₂ levels rise, but an increase in NO concentration drives one reaction forward and the other backward.
4.4 Combined Equilibrium pH from All Gases

The hydrogen ion contributions of each of the gases can be combined by including all the anions in the charge neutrality equation.

\[
[H^+] = [HCO_3^-] + [HSO_4^-] + [SO_3^{2-}] + [HSO_3^-] + [SO_4^{2-}] + [NO_2^-] + [NO_3^-]
\] (4.30)

These concentrations are calculated by the simultaneous solution of all three sets of equations from the three previous sections, while replacing the individual charge balance equations in them by equation 4.30. This gives the combined total pH trend.

Figure 4.12: Calculated condensate pH at equilibrium due to all gases at 5 bar GIMEP, 8°aTDC CA50 as a function of equivalence ratio.

The individual contributions of the gases towards the formation of hydrogen ions are shown in figure 4.13 a. (The vertical scale in this graph is reversed compared to figure 4.12). It is evident that at rich operating points, the pH is determined by SO₃. Here, the SO₂/SO₃ fraction is low anyway, so SO₂ concentration determines pH. From stoichiometric to lean operating points, NOₓ is the major contributor to pH. NO and NO₂ react together to form acidic condensate, but the pH is much more sensitive to NO₂ concentrations.
Figure 4.13: a. Contribution of dissolving gases to form hydrogen ions in condensate, and
b. Anion composition of the condensate, as functions of equivalence ratio
Areas higher up on the graph are more significant since the vertical axis is on log scale.
Figure 4.13 b shows the individual anion concentrations which add up to equal the hydrogen ions' charge (as in equation 4.30) in decreasing order from top to bottom. Nitrate ions are the highest, except at rich conditions. Sulfur appears as bisulfite at rich conditions and sulfate and bisulfate at lean conditions.

The effect of combustion phasing at stoichimetric operation on the calculated combined pH is shown below.

![Graph showing pH at equilibrium as a function of combustion phasing](image)

Figure 4.14: Calculated condensate pH at equilibrium due to all gases at 3 bar GIMEP, $\lambda = 1$ as a function of combustion phasing.

Since the deciding factor for pH at stoichimetric operation is NO$_x$, this curve follows the predicted pH due to NO$_x$ only (from figure 4.11) very closely. It is very slightly more acidic than the values there, taking into account the smaller contributions from SO$_x$ and CO$_2$. At advanced CA50 points, where the NO$_x$ is at the highest, there is no difference between the two curves. The NO$_x$ levels have a relatively lower influence at retarded combustion cases, but the difference between the two plots is still just 0.1 pH point here. This decreasing influence is shown in the condensate composition graphs of figure 4.15.
Figure 4.15: a. Contribution of dissolving gases to form hydrogen ions in condensate, and b. Anion composition of the condensate, as functions of combustion phasing. Areas higher up on the graph are more significant since the vertical axis is on log scale.
The plots of figure 4.13 and 4.15 show that the contribution of SO\textsubscript{x} and CO\textsubscript{2} vary with both lambda and CA50 point, unlike the case where their influence was calculated separately. This is because the ions interact and shift the equilibrium point. For example, because hydrogen ion concentrations are higher than that predicted in section 4.1 (where only CO\textsubscript{2} dissolves), the bicarbonate ion concentration decreases well below the level seen there. This verifies the observation shown by Hunter\textsuperscript{[1]} and discussed in section 1.2.
Chapter 5: Experimental pH Results

Now, the experimentally measured condensate pH values are compared with the predicted ones after a discussion of the preliminary experiments.

Initially, some of the pre-catalyst condensate samples had their anion concentrations measured by ion chromatography. It was found that the pH would be higher than that predicted by these measured anion concentrations using charge neutrality (same as the method described in section 1.2; the points in this experiment would not lie close to the measured pH = predicted pH line). Possibly this was because the copper in the tubing would dissolve in the condensate to release hydrogen gas. The cations balancing the anions would thus be copper, not hydrogen.

As mentioned in the section on experimental setup, the pH measurements became fairly repeatable after all the tubing and fittings were changed so that they were corrosion resistant and did not alter the chemistry of the condensates. For repeated experiments (same operating point), the measured pH would generally vary by less than 0.3. This also corrected the earlier problem and now, the pH would match that predicted from anion measurements.

Preliminary experiments were run with both pre- and post-catalyst exhaust gas extraction to qualitatively check pH values. The post-catalyst condensates were close to neutral. They were basic (pH = 9) at rich operation due to the formation of NH$_3$ in the catalyst. At lean operation, they were very slightly acidic (pH between 6 and 7), because the catalyst cannot efficiently reduce NO to NH$_3$ in the presence of excess oxygen. After this was done, the experiments focused on pre-catalyst condensates only.

5.1 Lambda Sweeps

The majority of experiments formed part of lambda sweeps at fixed speed (1500 rpm for all cases), fixed load, and constant CA50. Going from rich to lean, the throttle was adjusted to keep the GIMEP constant and the spark timing was advanced to maintain the same CA50.

The measured values for the 5 bar GIMEP case are plotted with the predicted values from chapter 4 in figure 5.1. Predicted pH due to NO$_x$ only (from section 4.3) and due to all gases combined (from section 4.4) are both shown.
Figure 5.1: Measured and calculated condensate pH as a function of equivalence ratio. pH and NOx measurements for corresponding calculations were taken at 1500 rpm, 5 bar GIMEP, 8° aTDC CA50.

The measured pH is very slightly acidic for rich operation and becomes progressively more acidic for leaner points. It is higher than the predicted pH by about 1 (which is a difference in hydrogen ion concentration by a factor of 10), but follows the same general trend. In the richest case, it is significantly different from the pH curve due to all gases and is closer to the curve due to NOx only.

It indicates that equilibrium is not reached between the exhaust flow and condensate. This is a possibility if the water vapor in the exhaust gas condenses at a significantly faster rate than the gases dissolve into the condensate. Referring to figure 4.1, this means that the assumption of physical equilibrium between gases in the exhaust and in the dissolved state is not true. The gas and condensate were experimentally seen to be at thermal equilibrium; and because the condensate sits for a long time while collecting (for 10 minutes or more), the dissolved species must be in chemical equilibrium. It is the short residence time of the gas flowing through the condenser and flask that physical equilibrium may not be attained.
The fact that the plot is further away from the combined equilibrium value at rich cases, where \( \text{SO}_2 \) dominates the pH by formation of bisulfite, indicates that \( \text{SO}_2 \) is slower in dissolving into the condensate than other gases.

Figure 5.2 has measured pH results for various loads. They follow the same trend, but the spread is smaller at stoichiometric to lean conditions than at rich conditions. There was a variability of up to 0.3 in the pH when repeating experiments; and the pH spread at lean running is relatively within that range. Thus, the pH at these regions is nearly constant with load.

![Figure 5.2: Measured condensate pH as a function of equivalence ratio and load at 1500 rpm. The 10 bar GIMEP values are for 13° aTDC CA50, the 3 bar and 5 bar GIMEP values are for 8° aTDC CA50.](image)

There are two differences between the different load cases that cause a change in pH. Firstly, exhaust flow rate through the condenser increases with load, resulting in shorter residence times. Second, \( \text{NO}_x \) concentrations also rise with load. So, in the rich cases, where \( \text{NO}_x \) does not play a determining role, the pH at high load is less acidic since it is further away from equilibrium. For the stoichiometric and lean cases, where \( \text{NO}_x \) levels determine pH, the
increased NO\textsubscript{x} concentration competes with short residence time such that the pH is similar across different loads.

To check the effect of NO\textsubscript{2} on the condensate pH independently, extra NO\textsubscript{2} was introduced into the exhaust sampling tubing upstream of the condenser. This was from a bottle with a mixture of 50 ppm NO\textsubscript{2} in balance nitrogen. The flow rates of the gases were not measured, but the sampled exhaust stream’s flow rate was approximately the same as that of the NO\textsubscript{2} containing mixture being introduced in it. It was done for two points, one rich and one lean, shown in this plot:

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.3.png}
\caption{Measured condensate pH at 1500 rpm and 5 bar GIMEP. Comparison of cases with only exhaust and with extra NO\textsubscript{2} mixed with exhaust.}
\end{figure}

The NO\textsubscript{2} concentration in the exhaust was 13 ppm for the \( \lambda = 1.2 \) point and its condensate pH was 3.26. With 50 ppm NO\textsubscript{2} being added, the total NO\textsubscript{2} for the mixed gas should be \(~30\) ppm. This should cause the pH to drop by about 0.4. The actual pH dropped by 0.5 to 2.76 with the extra NO\textsubscript{2}, showing the pH’s sensitivity to NO\textsubscript{2}.
For the $\lambda = 0.8$ point, the measured NO$_2$ was 0.0 ppm, with a corresponding pH of 6.26. After mixing with the 50 ppm NO$_2$, its concentration should be ~25ppm. This should have caused the pH to drop significantly to 2-3, similar to the values seen at the leanest cases. However, the pH remained high, dropping only to 5.86. This result could not be explained.

### 5.2 Spark Sweeps

Combustion phasing was varied by changing the spark timing 5 crank angle degrees at a time. Starting at knock limited spark advance (KLSA), it was retarded till combustion became unsteady. The experiments were run at fixed speed (1500 rpm for all cases), fixed load (the throttle was adjusted to maintain it), and $\lambda = 1$.

Figure 5.4 shows the measured values along with calculated ones from chapter 4.

![Graph showing pH and NO$_x$ as a function of CA50](image)

Figure 5.4: Measured and calculated condensate pH as a function of combustion phasing.

pH and NO$_x$ measurements for corresponding calculations were taken at 1500 rpm, 3 bar GIMEP, $\lambda = 1$.

Measured pH was seen to be constant at approximately 3.5 across the full range of combustion phasing. At the KLSA point, the NO$_x$ level is high and the predicted pH is very low. Here, the measured and calculated pH differ significantly. The predicted pH matches the
calculated pH at the most retarded combustion phasing. At Maximum Brake Torque (MBT) timing, which is around 8° aTDC, the difference between the two pH values is less than 1.

If the gas and condensate are not in equilibrium as shown with the lambda sweeps, the measured pH should have been less acidic than the predicted value throughout the range by a similar amount. It could not be explained why the pH remained constant despite the wide variation in NOx concentration across the plot.
Chapter 6: Summary and Conclusions

In this study, properties of the condensate formed from pre-catalyst exhaust, namely pH and anion concentrations, were characterized with changing air-fuel ratios and combustion phasing. For the theoretical prediction, physical and chemical equilibrium was assumed between the exhaust gas passing through the condenser and the condensate formed from it.

Measurements found the pH to be higher than calculated values for most running conditions, indicating that equilibrium was not reached. It is thought that the physical equilibrium assumption is the one that does not hold true. The mass transport process may limit the gases from dissolving into the film of condensed water at the same rate as the condensate is being formed. The short residence time in the condenser may not allow all gases to form acid quickly enough. The summary for each of the studied gas is given below:

- CO₂ is present in exhaust gas at a high concentration, which does not change much with operating conditions. Nevertheless, its solubility is relatively low at such partial pressures and the acid it forms is a weak acid. Its corresponding anion bicarbonate has a very low concentration in the condensate and does not contribute to the acidity.

- SO₂ derived from the burning of fuel sulfur is present at about 2 ppm in the exhaust, which does not vary widely with operating conditions. Theoretically, the bisulfite anion it forms has the highest condensate concentration for rich operation and decides the pH at equilibrium. However, its dissolution into water may be slow, which prevents the condensate from getting as acidic as predicted.

- SO₃ is present mainly at lean operating conditions. It is highly soluble and goes completely into the condensate, where it forms significant amounts of both bisulfate and sulfate since sulfuric acid is very strong. The low sulfur fuel used limited its concentration in the exhaust to below 0.03 ppm, which prevented it from causing the condensate to be very acidic. However, the condensate pH is very sensitive to SO₃, and even a small increase in its concentration would make it the major contributor. This is significant for countries where the gasoline/diesel have higher sulfur levels.

- NO concentration varies significantly under different operating conditions. Its solubility is low and it cannot form acidic condensate on its own, as it needs to be oxidized first. The equilibrium pH is not very sensitive directly to its level.

- NO₂ is the oxidized form of NO which is present when NO and oxygen concentrations are high in the exhaust, i.e. lean combustion. (NO₂ concentration is
approximately 1% of the NO concentration, making the latter indirectly important.) It disproportionates to nitrite and nitrate, of which the latter dominates and determines the equilibrium pH at lean conditions. However, measurements showed that the actual nitrate concentration can is about an order of magnitude smaller than the calculated equilibrium value at MBT spark timings. But this is fairly constant for such combustion phasing at lean points and thus, NO₂ determines the trend of the pH.

The predicted values thus provide a bound on the actual pH, i.e. the condensate is always less acidic than predicted.

6.1 Applicability to Real Conditions

All experiments were carried out at steady state, and took about 15 minutes to collect the samples. The condensate took less than 5 minutes to build up after which it was enough to flow down the condenser’s walls. In a real EGR cooler, the rate of condensation would be lower because the engine coolant circulating through it is at 80 – 100°C. However during cold start conditions, if EGR is used, condensate will form rapidly in the first few minutes as shown in the experiments.

The engine operating conditions will vary as a vehicle is driven. However, in a three-way catalyst equipped engine, the air-fuel ratio is kept stoichiometric on average. The closed loop oscillations between rich and lean running were present in this study also. For such a running condition, the measured pH did not vary much with load or combustion phasing, and remained close to 3.5 – 4. This is the acidity a properly running engine EGR cooler will encounter.

An engine concept by Alger and Mangold[18] aims to reform gasoline in one of the engine cylinders by running it rich; and routing all the exhaust from that cylinder into the intake manifold as EGR. It has an EGR cooler in the loop but no catalyst. The EGR cooler would not face very corrosive conditions in this case due to the gases coming from rich combustion. Thus, condensation in pre-catalyst EGR coolers does not pose a problem in applications like these.

The theoretical pH values obtained in this study, which act as bounds to the actual pH may also be useful while designing and selecting the material for EGR cooler channel walls.
Bibliography


Appendix A: Calculation of Volume of Condensate

The calculations here are made on a per mole of fuel burnt basis. The chemical equations of gasoline combustion (as in section 4.1) for the rich and lean cases are:

For rich combustion,

\[
CH_{1.87} + \lambda \left(1 + \frac{1.87}{4}\right) (O_2 + 3.773N_2) \rightarrow aCO_2 + bH_2O + cCO + dH_2 + \lambda \left(1 + \frac{1.87}{4}\right) (3.773N_2)
\]

\[n_{H_2O,formed} = b\]  \hspace{1cm} (A.1)

\[n_{exhaust,formed} = a + b + c + d + \lambda \left(1 + \frac{1.87}{4}\right) (3.773)\]  \hspace{1cm} (A.2)

An empirical relationship for engines running at slightly rich conditions (\(\lambda = 0.8 - 1\)) has to be used, along with balance of C, H and O molecules to calculate a, b, c and d.

\[c \approx 3d\]  \hspace{1cm} (A.3)

For lean combustion,

\[
CH_{1.87} + \lambda \left(1 + \frac{1.87}{4}\right) (O_2 + 3.773N_2) \rightarrow CO_2 + \frac{1.87}{2} H_2O + (\lambda - 1)(1 + \frac{1.87}{4})O_2 + \lambda \left(1 + \frac{1.87}{4}\right) (3.773N_2)
\]

\[n_{H_2O,formed} = \frac{1.87}{2}\]  \hspace{1cm} (A.4)

\[n_{exhaust,formed} = 1 + \frac{1.87}{2} + (\lambda - 1)(1 + \frac{1.87}{4}) + \lambda \left(1 + \frac{1.87}{4}\right) (3.773)\]  \hspace{1cm} (A.5)

Using these equations for both cases,

\[m_{dryexhaust} = n_{dryexhaust} \times MW_{dryexhaust} = (n_{exhaust,formed} - n_{H_2O,formed}) \times MW_{dryexhaust}\]  \hspace{1cm} (A.6)

Here, an average molar weight of 30.43 g/mol has been used across the lambda range for the dry exhaust.

At atmospheric pressure, saturated air at 30°C contains 0.027 g moisture / g dry air. This moisture remains in the exhaust and does not condensate. Thus the moisture remaining in the exhaust after passing through the condenser is:

\[m_{H_2O,remaining} = m_{dryexhaust} \times 0.027 g \text{ moisture / g dryair}\]  \hspace{1cm} (A.7)
The volume of the condensate formed is then given as:

\[ n_{H_2O,\text{condensed}} = n_{H_2O,\text{formed}} - \frac{m_{H_2O,\text{remaining}}}{M_{\text{water}}} \]  

(A.8)

\[ V_{H_2O,\text{condensed}} = n_{H_2O,\text{condensed}} \times \frac{M_{\text{water}}}{\rho_{\text{water}}} \]  

(A.9)

Also, the number of moles remaining in the exhaust after this volume has condensed is:

\[ n_{\text{exhaust,remaining}} = n_{\text{exhaust,formed}} - n_{H_2O,\text{condensed}} \]  

(A.10)

It is important to take into account that not all of the water vapor condenses, since a significant fraction remains behind in the exhaust. At 30°C, about a third remains behind, while this fraction increases with temperature (i.e. less condensate is formed at higher temperatures).

Also, it is important to consider the water and total exhaust moles formed per mole of fuel burnt as a function of lambda (as done in equations 4.18 – 4.21), since there is about a 15% difference in the volume of condensate formed in the stoichiometric and rich cases.
Appendix B: Fuel Test Reports

The fuel used for running the engine for all the tests in this study was Haltermann HF0437 fuel, which is an EPA Tier II Emission Certification gasoline. The test specifications of several batches of fuel used are provided here.
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APPROVED BY: Hunter V. Davies
**PRODUCT INFORMATION**

**PRODUCT:** HQ0437

**PRODUCT CODE:** EPA TIER II EEE

**Batch No.:** DJ1221LT10

**Tank No.:** 105

**Date:** 10/15/2015

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**APPROVED BY**
## Product Information

**Telephone:** (800) 969-2542  
**FAX:** (281) 457-1469

**PRODUCT:** EPA TIER II EEEE  
**PRODUCT CODE:** FEDERAL REGISTER HF0437

**Batch No.:** EA1921LT20  
**Tank No.:** 105  
**Date:** 1/21/2016

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<tr>
<th>TEST</th>
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<th>UNITS</th>
<th>HALTERMANN Specs</th>
<th>RESULTS</th>
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**Recovery** vol % Report 97.1

**Residue** vol % Report 1.1

**Loss** vol % Report 1.8

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<tr>
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**APPROVED:**

[Signature]

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