

The Thermodynamics of Exhaust Gas Condensation

Nuria Garrido Gonzalez
Volkswagen AG

Roland Baar
Technische Universität Berlin

Jens Drucekhammer and Christoph Kaepfner
Volkswagen AG

ABSTRACT

Water vapor is, aside from carbon dioxide, the major fossil fuel combustion by-product. Depending on its concentration in the exhaust gas mixture as well as on the exhaust gas pressure, its condensation temperature can be derived. For typical gasoline engine stoichiometric operating conditions, the water vapor dew point lies at about 53 °C. The exhaust gas mixture does however contain some pollutants coming from the fuel, engine oil, and charge air, which can react with the water vapor and affect the condensation process. For instance, sulfur trioxide present in the exhaust, reacts with water vapor forming sulfuric acid. This acid builds a binary system with water vapor, which presents a dew point often above 100 °C.

Exhaust composition after leaving the combustion chamber strongly depends on fuel type, engine concept and operation point. Furthermore, the exhaust undergoes several chemical after treatments. The transformation of pollutants in these components drastically affects the composition of the possible exhaust condensate, which can for instance shift its pH-value from acidic to alkaline.

Detailed analysis of these condensable exhaust components and understanding of condensate composition becomes of increasing importance with the growing relevance of exhaust gas recirculation (EGR) cooling and when thinking of exhaust gas as a potential water source. In spite of this, the complexity of the exhaust condensation process is, especially with regard to gasoline engines, a field of relatively low focus up until now. The goal of this study is to present a theoretical analysis of the thermodynamics of gasoline engine exhaust condensation including an experimental data based validation. Through investigation of the influence of the air/fuel ratio, pollutant concentrations, and temperature conditions, an improved understanding of the condensation process is gained.

CITATION: Garrido Gonzalez, N., Baar, R., Drucekhammer, J., and Kaepfner, C., "The Thermodynamics of Exhaust Gas Condensation," *SAE Int. J. Engines* 10(4):2017, doi:10.4271/2017-01-9281.

INTRODUCTION

Gasoline exhaust gas is typically treated by a three way catalyst. The catalyst controls hydrocarbons, carbon monoxide and nitrogen oxides emissions in order to meet the required specifications. One of the secondary reactions taking place in the three way catalyst (TWC) is the production of ammonia coming from the hydrogen, formed via water-shift and steam reforming reactions between CO, HC and H₂O, [1]. Experimental data, [2], [3] showed how this ammonia affects the exhaust gas condensate's pH-value, which is neutral to alkaline, 7 - 9. It produces a large effect when compared to typical condensates coming from diesel or gasoline engines without a three way catalyst, which are rather acidic, 2.5 - 4, [2], [3], [4], [5].

Condensate, originated from diesel exhaust gas condensation, has been the scope of several studies due to the integration of EGR systems. This recirculation diminishes NO_x emissions by reducing

the achieved temperature in the combustion chamber based on the inert gas increase. One of the first studies was [6], where a model for describing the sulfuric acid condensation was developed. Both the low pressure (LP) EGR and high pressure (HP) EGR can be susceptible to condensation. Low pressure EGR systems deliver a part of the exhaust gas to the charge air upstream from the compressor. When the gas is mixed with the cold charge air, the mixed gas can exceed the saturation state and condensation occurs. This effect was studied in [4], where it was shown that operation points with high EGR rates and moderately high lambdas (less dilute) are the most susceptible to produce condensation. This study was complemented later, with the analysis of condensation in high pressure EGR systems, [5]. The use of improved low temperature coolers leads to condensation inside of them. Compared to LP EGR

exhaust gas, HP EGR gas normally contains more pollutants, in case LP EGR underwent any after treatment. However, condensates originated from both LP and HP systems present similar acidities.

The corrosivity associated with HP EGR systems was examined in [7]. A relevant difference was observed when measuring corrosion rates under condensing conditions with low (less than 15 ppm) and high (350 ppm) sulfur fuel. Low fuel engine operation conditions generated condensates with nitrate and sulfate concentrations between 5 - 110 mg/L and higher sulfur fuel condensates presented similar nitrates concentrations, but with higher sulfate levels of up to 100 - 1300 mg/L. The higher sulfate concentrations increased the corrosion rate of a mild steel probe significantly, from 0.4 mmpY to 4 mmpY.

In [8] it was measured, that acid condensates originated from diesel engines generally induce more corrosion than alkaline condensates generated from gasoline engines with a TWC.

Again in the framework of EGR coolers, the influence of condensation on fouling was investigated. Depending on the achieved temperature, three regimes can be defined [9]: I) above the acid-water dew point, II) between the sulfuric acid-water and pure water dew point, and III) below the pure water dew point. The second regime is responsible for sticky condensate, which favors fouling. Exposing this deposit layer to water condensation was found to be a successful method for removing it [10], especially in combination with the use of an oxidation catalyst, which stops the formation of hydrocarbon (HC) condensation layers, [11]. The HC condensation was studied in [12]; it showed that the mass flux rates for HC are several orders of magnitude lower than for water vapour, due to their very lower concentration in the exhaust gas (HC in ppm range against water in one to two digit % range).

The extraction of liquid water from the exhaust gas of a diesel engine was investigated in [13]. Cooling down to about 45 °C, up to 35 % water vapour coming from fuel combustion can be recovered, depending on engine speed and air/fuel ratio. It was also observed that lower exhaust gas velocities lead to higher condensation rates for the same cooling. However, the amount of recovered water strongly depended on the operation point, due to the extremely variable exhaust dilution coming from the fluctuating air/fuel ratio of a diesel engine.

Gasoline engines, with their nearly constant stoichiometric operation, produce a pretty uniform water vapor concentration of about 10 % weight, in the exhaust. The efficiency improvements associated with the use of a water injection in these engines are subject of ongoing research since the first investigations of Sir Ricardo, [14], with promising conclusions, [15], [16], [17]. This shows that further research on water recovery from gasoline exhaust, regarding achievable amount and quality, is of increasing importance.

The aim of this paper is to clarify when and how condensation of pure water and the several acid-water mixtures, present in a gasoline exhaust, occurs. It enables the prediction of the condensate composition when the exhaust component concentrations and collection temperature are known. This condensate collecting temperature represents a decisive factor on condensate

concentrations, because the pollutant dilution strongly depends on it. Experimental data based validation verifies the theoretically examined tendencies.

EXHAUST CONDENSATION

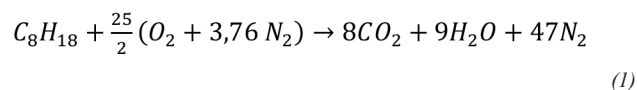
A gas is defined as a fluid that, for a given temperature and pressure range, could be regarded as non-condensable. A fluid that is capable of condensing under given temperature and pressure conditions is defined as vapour. For the following analysis of a gas-vapour mixture, the non-existence of any chemical association between the components is assumed. In addition to this, the behavior as an ideal gas is also assumed.

Air fuel mixtures as well as combustion exhausts are gas-vapour mixtures, thus these gas-vapour mixture systems are a topic of general significance when regarding combustion engines. The analysis of the thermodynamic behavior of these systems allows, among others, a prediction of the acid concentration of the first-condensing drops.

Regarding ideal gasoline combustions with pure oxygen, water vapour and carbon dioxide are the only reaction by-products obtained. In practice, air instead of pure oxygen comes into operation and gasoline contains a margined amount of pollutants. This leads to additional combustion by-products like nitrogen oxides, generated by the oxidation of nitrogen in the air; or sulfur oxides, resulting from the fuel sulfur. Some of these new by-products could react with the present water vapor and build acids, which do not always possess the same dew point as the water vapour in the gas mixture. The exhaust gas is then a mixture of non-condensable gases like nitrogen and carbon dioxide, with some condensable vapors like pure water vapor and some acid-water mixtures with different condensation temperature levels. In order to predict the possible condensate composition, it is essential to understand the condensation process in the presence of an inert gas.

Water Vapour

Gasoline engine exhaust gas contains a weight average value of 10 % water ratio. The main sources are hydrogen atoms as part of the hydrocarbons of the fuel and, in negligible amount, air moisture of aspired combustion air. To calculate the fuel induced water percentage, gasoline fuel can be approximated as Isooctane, one of its main components. Assuming the typical case of a stoichiometric combustion, [equation \(1\)](#) has to be executed using an air mass quantity corresponding with the required air mass for a complete combustion.



From this reaction it is derived that per kilogram of burned fuel, a mass of 1.4 kg water vapor is produced. This represents about 10 % weight ratio and 14 % in volume (or mol) water vapour in the exhaust gas stream, calculated with [equation \(2\)](#).

$$y_{H_2O} = \frac{\frac{w_{H_2O}}{M_{H_2O}}}{\frac{w_{H_2O}}{M_{H_2O}} + \frac{w_{N_2}}{M_{N_2}} + \frac{w_{CO_2}}{M_{CO_2}}} \quad (2)$$

According to these water concentration and exhaust pressure conditions of around 1 bar pressure, a water vapor partial pressure of about 0.14 bar is estimated with Dalton's law, [equation \(3\)](#).

$$p_{H_2O} = y_{H_2O} p_{exhaust} \quad (3)$$

A given water vapor pressure corresponds with a saturation temperature, [Figure 1](#). Thus the water dew point for gasoline exhaust gas at 53 °C can be derived. Below this temperature water vapour condenses. For this estimation, the fuel combustion by-products are assumed to be the only water source in the exhaust, neglecting the incoming air humidity or further water sources coming with EGR or possible water injection systems.

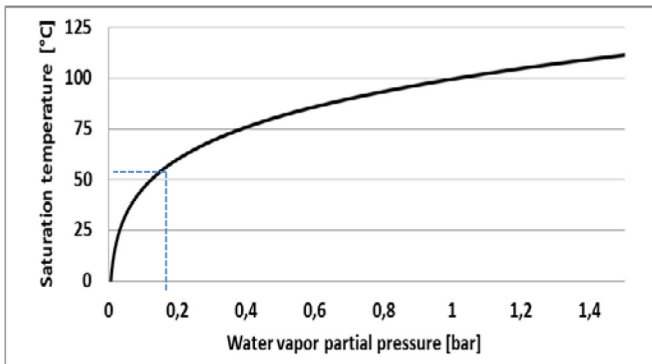
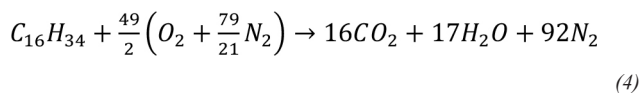


Figure 1. Vapour pressure curve for water.

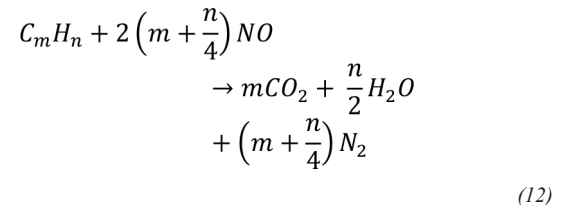
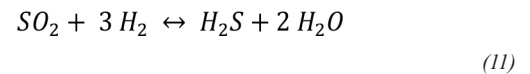
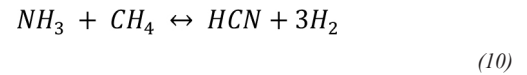
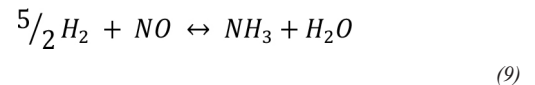
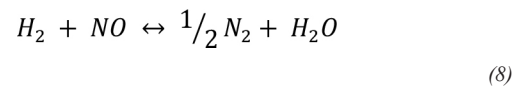
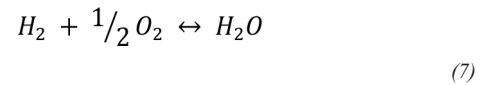
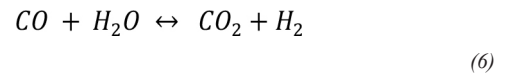
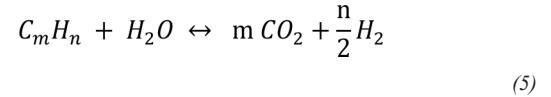
For diesel engines operating with -here untypical-stoichiometric combustion and approximating diesel fuel as hexadecane, [equation \(4\)](#), a nearly identical dew point of about 52 °C can, analog as for gasoline above explained, be derived. It is slightly lower than for isooctane due to the marginally lower hydrogen proportion contained in hexadecane.



Nevertheless, diesel engines predominantly operate at duty points with a significant air surplus (lean mixture). This factor results in a lower water concentration in the exhaust and thus a reduced dew point. The maximum possible dew point always corresponds with a stoichiometric combustion. Above $\lambda = 1$, a dilution effect occurs, resulting in a reduced dew point. In the case of high air excess, this could even lie below 20 °C, [3]. Below $\lambda = 1$, the dew point decreases only slightly due to the existence of unburned fuel in the exhaust gas.

Water takes an active role in the exhaust after treatment within the three way catalyst converter, especially under fuel rich conditions. It helps to reduce the CO and HC emissions by means of the steam reforming and water-gas shift reactions, [\(5\)](#), [\(6\)](#), respectively. The produced hydrogen

reacts with the NO, O_2 , or SO_2 again forming water vapour and other products, [18], [equations \(7\)](#), [\(8\)](#), [\(9\)](#), [\(10\)](#), and [\(11\)](#). Only the further oxidation of unburnt fuel can be seen here as a water source, [equation \(12\)](#). In this article, however, the whole fuel oxidation was taken into account assuming a complete and ideal combustion, reaction [\(1\)](#). Hence this contribution has already been considered.



Having calculated the dew point, the condensation starting temperature is known. Next, the quantity of condensate is to be determined. Below the dew point temperature, the exhaust gas is always in a water-saturated state, where the maximal possible water content can be calculated with the saturation pressure at each temperature, [equation \(13\)](#). As a simplification, it is assumed that the exhaust gas is an ideal gas mixture of water vapour, nitrogen and carbon dioxide, where the mass of already present water vapor can be determined with [equation \(2\)](#), since other mass contributions remain invariable. The condensed water results from the initial water vapor content less the water vapor content at the end temperature, [equation \(14\)](#).

$$p_{sat}(T) = y_{H_2O,max}(T) p_{exhaust} \quad (13)$$

$$\dot{m}_{cond} = \dot{m}_{exh_gas} * (w_{H_2O_initial} - w_{H_2O_T_end}) \quad (14)$$

This calculation enables the definition of a condensation rate as a fraction of condensed vapour related to the initial vapour content in the exhaust, [equation \(15\)](#).



Documents

Document Sharing Hub

$$K_{cond} = \frac{w_{H_2O_{initial}} - w_{H_2O_{T_{end}}}}{w_{H_2O_{initial}}} \quad (15)$$

The evolution of the condensation rate, shown in Figure 2, illustrates how the exhaust gas loses its water content when decreasing its temperature. The condensation rate is higher in the beginning, due to the higher temperature and its associated higher possible water content.

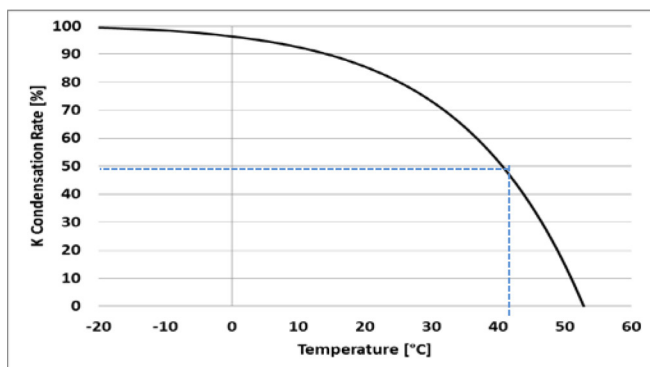


Figure 2. Condensation rate (water vapour from fuel) evolution with exhaust temperature.

Here, cooling the exhaust down to 40 °C results in the condensation of about 50 % of the exhaust water vapour. The quantity of condensate per cooled degree diminishes progressively, Figure 3. Further cooling below 20 °C would only condense some small water amounts more.

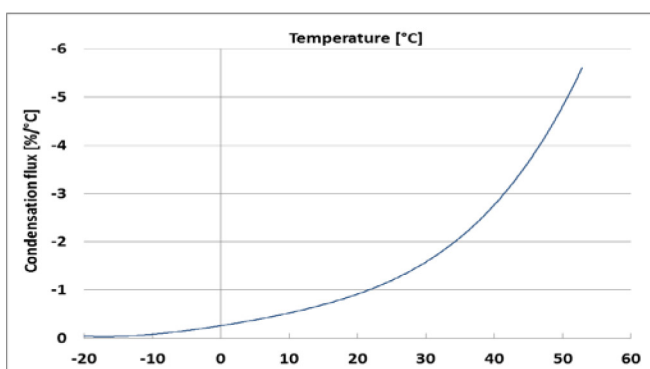


Figure 3. Condensation flux per cooled degree.

In the case of when an EGR-cooler reduces the temperature of 50 kg/h of exhaust gas down to only three degrees below the dew point, condensate amounts of up to 500 mL/h would be expected. Aside from the problem of the liquid presence, this condensation releases not negligible amounts of heat, which competes with the aimed cooling effect.

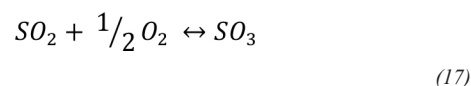
Sulfur Compounds

Within the European Union, the maximum sulfur content in gasoline as well as diesel fuel is limited to 10 ppm (EU VI). This arrangement should result in a reduced sulfur oxides level in the exhaust gas and thus in an improved durability of not only exhaust systems but intake systems too (mainly the intercooler), and in an enhanced efficiency of

the exhaust after treatment system. During the combustion, sulfur present in gasoline and diesel fuel is oxidized to sulfur dioxide. The exothermic reaction creating sulfur dioxide shows as follows:



When cooling down during the expansion stroke as well as later within the exhaust system, a small percentage of this sulfur dioxide does react with residual oxygen to sulfur trioxide.



It is worth to mention that diesel engines running under lean conditions present higher oxygen content in the exhaust gas than gasoline operating under stoichiometric, favoring the two above described reactions.

The equilibrium for SO_3 and SO_2 in a system with oxygen is dependent on temperature. Below 400°C the reaction equilibrium predicts close to 100% SO_3 . However, the very low reaction velocity does result in a shift of this equilibrium when regarding the transient situation within an automobile powertrain. Further parameters, like residual oxygen percentage or residence time within the exhaust, have effect on the sulfur trioxide creation [19]. A typical conversion ratio for diesel exhaust lies below 5% [20], [21]. This sulfur trioxide is so significant because, in presence of water, it reacts immediately to sulfuric acid, H_2SO_4 . Within the three way catalyst, sulfur dioxide also competes with the other exhaust pollutants for (for its oxidation required) oxygen. This reaction is undesired because it inhibits the three wanted reactions, while favoring the sulfuric acid formation.

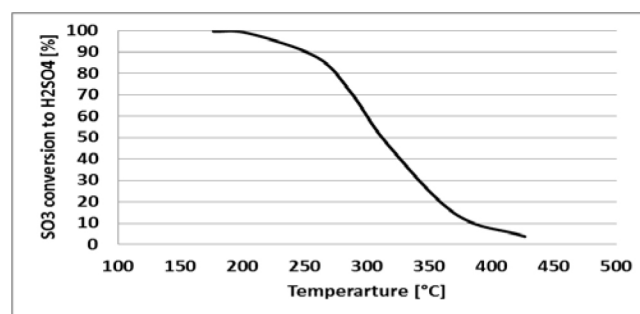
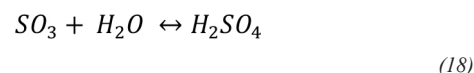


Figure 4. Conversion of SO_3 into H_2SO_4 and its temperature dependency.

For temperatures below 300 °C, the conversion rate of SO_3 into H_2SO_4 exceeds 60 %. Below 200°C, the conversion rate into sulfuric acid can be assumed as complete [22], Figure 4.

In the presence of further water vapor, a binary system is created. With help of ChemCAD [23] the vapor-liquid-equilibrium of an H_2SO_4 - H_2O mixture at its partial vapor pressure in the exhaust system and following the NRTL-model is created, Figure 5. The partial pressure of the mixture is approximately the same as the vapor partial pressure, assuming that the amount of sulfuric acid in