

A parametric study on the sulfur species distribution within the cylinder of diesel engines

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Abstract

In emerging markets diesel fuel may contain high sulfur contents. Thus, a parametric study is conducted to get an insight to the sulfur species distribution during engine combustion. The parametric study is embedded in an overview of the sulfur pathway in diesel engines.

In general, fuel sulfur is oxidized to sulfur oxides (SO, SO₂, SO₃). These sulfur oxides can either stay in the cylinder and interact with engine parts or cylinder liner oil film or leave the cylinder with the exhaust gas and interact with other components to form acid and aerosol, respectively. The parametric study showed that under lean combustion conditions with high exhaust recirculation rates no SO₃ is formed. Under substoichiometric condition no SO₃ formation occurs but H₂S is formed.

Introduction

Emerging markets often feature relatively low quality of fuels; especially diesel fuel may have high amounts of impurities. Sulfur is one of the most critical impurity. In general, organic fuel sulfur is oxidized to sulfur oxides, in combination with water these sulfur oxides may form acids and may cause corrosion within the whole combustion and exhaust gas system of engines. [1, 2, 3, 4]

In this work a parameter study with the focus on the sulfur species distribution within the cylinder space in the compression and expansion stroke of a diesel engine with and without exhaust gas recirculation (EGR) is conducted. The varied parameters are the EGR rate, the fuel to air ratio and the fuel sulfur content.

The parameter study is embedded in an overview of the sulfur pathway from the organic sulfur compounds in diesel fuels to the sulfur oxides in the exhaust gas. Therefore, a short classification of common organic sulfur species in diesel fuel is given and the principal conversion steps are explained. Based on the parameter study, the sulfur oxide distribution during ignition, combustion and the expansion stroke is analyzed in more detail. For that purpose, species concentration profiles and reaction path analysis are conducted.

The parameter study is realized with the chemical solver LOGESOFIT and tries to cover a wide range of operation conditions regardless of the practical applicability. Thus, fuel sulfur concentrations up to one mass percent, fuel to air ratios ranging from 1.5 to 0.2 and EGR rates from zero to 70 percent mass based are considered. The cylinder space is modeled with a 0D homogeneous charged compression ignition (HCCI) model.

Sulfur pathway – from diesel fuel to exhaust gas

Sulfur is found in various organic compounds in diesel fuel. Common aliphatic compounds are thioles, sulfides, disulfides and common heterocyclic compounds are thiophenes, benzothiophenes,

dibenzothiophenes and thianthrens [5]. According to [5] dibenzothiophenes are the main sulfur compounds in low sulfur diesel fuels. Table 1 shows the results of the 2D gas chromatography measurement conducted by [5] for three different fuel sulfur concentrations. Analysis show that mercaptane, sulfide, thiophene and benzothiophene concentrations decrease with decreasing fuel sulfur content.

Table 1. Fuel sulfur concentrations according to compound classes: mercaptanes, sulfides and thiophenes (MST), benzothiophenes (BT) and dibenzothiophenes (DBT). Source: [5]

compound class	fuel sulfur content		
	7000 ppm	1200 ppm	120 ppm
MST	1,099	19	0
BT	3,908	355	0
DBT	2,077	922	112
total	7,084	1,276	112

In general, organic sulfur compounds are oxidized to carbon oxides, water, sulfur dioxide and a small fraction sulfur trioxide. The sulfur trioxide fraction depends on the combustion conditions and the subsequent exhaust gas conditions. [2, 4, 6, 7]

According to [2] the type of organic sulfur compound has no influence on this oxidation step. After the cooling during expansion, the ratio between sulfur dioxide and sulfur trioxide is frozen. The gaseous sulfur oxides can either leave the cylinder with the exhaust gas or interact with the cylinder wall or the oil layer on the cylinder wall.

If the sulfur oxides leave the cylinder with the exhaust gas, water and sulfur trioxide may form sulfuric acid. In case of exhaust gas temperatures below 200 °C virtually all sulfur trioxide found as sulfuric acid. [7]

According to [8, 9] an elevated sulfuric acid concentration in the exhaust gas promotes the formation of aerosols because of its stickiness. Thus, the aerosol size distribution shifts towards bigger particle sizes. The

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increased aerosol concentration could also lead to a change in the fouling coat at the inside of the exhaust pipes and heat exchangers. Furthermore, condensate could leach sulfur oxides out of the fouling layer, form sulfuric acid and cause corrosion problems. [4, 5, 9, 10] An alternative pathway is the dissolution of sulfur oxides in condensates and a subsequent sulfuric acid formation [4]. In general, sulfuric acid significantly increases the danger of acid corrosion.

If the sulfur oxides stay within the cylinder, they may react with water vapor from the exhaust gas and condense at colder parts of the cylinder wall. In consequence of a distinct boundary layer during combustion and the gas cooling during expansion, the cylinder liner is usually significant colder than the flame temperature. Thus, the coldest part of the cylinder wall is located somewhere near the bottom dead center (BDC). There, the sulfuric acid may condense on the cylinder wall oil layer and may react with the neutralizing agents of the oil. According to [11], under certain circumstances, crystalline structures form during neutralization, which may promote abrasive wear of the cylinder wall. However, if the sulfuric acid is able to diffuse through the oil layer before it is neutralized, acid corrosion may occur directly at the cylinder wall. Moreover, due to high partial pressures of sulfur oxides during and after the combustion, sulfur oxides dissolve in the oil layer at the cylinder wall. There they may react with dissolved water and form sulfuric acid as well as sulfurous acid. During expansion unreacted sulfur oxides are released due to a reduced partial pressure. [3, 11, 12, 13]

If an exhaust gas recirculation (EGR) system is active, the amount of dissolved sulfur oxides in the oil layer could increase due to the presence of sulfur oxides during compression and increased sulfur oxides concentrations after the combustion [13]. Moreover, the sulfur oxides concentration rises in the exhaust gas stream due to the additional sulfur from the EGR.

In general, high fuel sulfur concentrations cause an increased deposit formation at the cylinder liner [14]. Additionally, they may cause significant abrasion at the zone below the top dead center (TDC) position of the upper most piston ring [3, 12, 13].

Mechanisms and simulation assumptions

The kinetic mechanisms for the parameter study were taken from literature. Since diesel fuel is a mixture of organic compounds with carbon atoms ranging from ten to 24, it is common to use surrogate fuels for diesel combustion modeling. In this work n-dodecane was chosen as surrogate fuel and the mechanism developed by [15] was employed for the modeling. The sulfur mechanism developed by [16] with the modifications suggested by [7] is employed for modeling sulfur oxides. Fuel sulfur is modeled as elemental sulfur (S). Moreover, the suggestions of [7] for the sulfuric acid formation and the NO formation were employed. This

includes a single gas phase reaction between sulfur trioxide and water for the sulfuric acid formation. The Arrhenius parameters for the sulfuric acid formation reaction from [17] and for the NO formation from the GRI3.0 [18] mechanism were employed.

The employed homogenous charged compression ignition (HCCI) engine model is part of the LOGESOFT chemical solver. It is a zero dimensional engine model, which assumes perfect mixture of fuel and air and, thus, homogenous combustion, with a compression induced ignition. For this parametric study adiabatic combustion is assumed and, therefore, no heat loss model is employed. As a result, the combustion temperatures and the NO concentrations in the study exceed the practical measured values.

The modeled engine is a 100 kW turbo charged diesel engine, the engine data can be seen in Table 2. The manifold pressure was assumed to be 1.7 bar absolute pressure, the manifold temperature was assumed to be 340 K and the engine speed was assumed to be 2000 rpms. The fuel sulfur concentrations range from 10 ppm-m to 1 mass percent and the EGR rates range from zero mass percent to 70 mass percent. In order to study the influence of lean and rich combustion, fuel-to-air ratios of 0.2 to 1.5 (excess air numbers of approximately 5 to 0.67) are examined.

Table 2. Engine data

Compression ratio	18
Bore	80 mm
Stroke	95 mm
Connection rod length	155 mm

Sulfur species concentration profiles

The comparison of the species concentration profiles from the simulation results revealed that the ratio between the sulfur trioxide and sulfur dioxide concentration depends on temperature, pressure, fuel-to-air ratio and the EGR rate.

Fig. 1 shows the sulfur oxides ratio, which is the ratio of sulfur trioxide and sulfur trioxide in sulfuric acid to sulfur dioxide, for a fuel sulfur concentration of 1,000 ppm and fuel-to-air ratios between 0.2 and 1.5 without EGR. After the TDC (0 degree crank angle), the sulfur oxides ratio is higher for lower fuel-to-air ratios, but that does not necessary mean that the exhaust gas concentrations are higher for lower fuel-to-air ratios. During or shortly after the ignition (25 degree crank angle before TDC to TDC), the peaks of the sulfur oxides ratio indicate sulfur trioxide formation for all fuel-to-air ratios. However, in case of fuel-to-air ratios higher than 0.66 there is virtually no sulfur trioxide left after the TDC. This may be explained by the higher combustion temperatures and the lack of oxygen due to the high fuel-to-air ratios. According to [19] the thermal dissociation of sulfur trioxide starts at around 1,200 K for atmospheric pressure and has a steep increase until about 1,400 K.

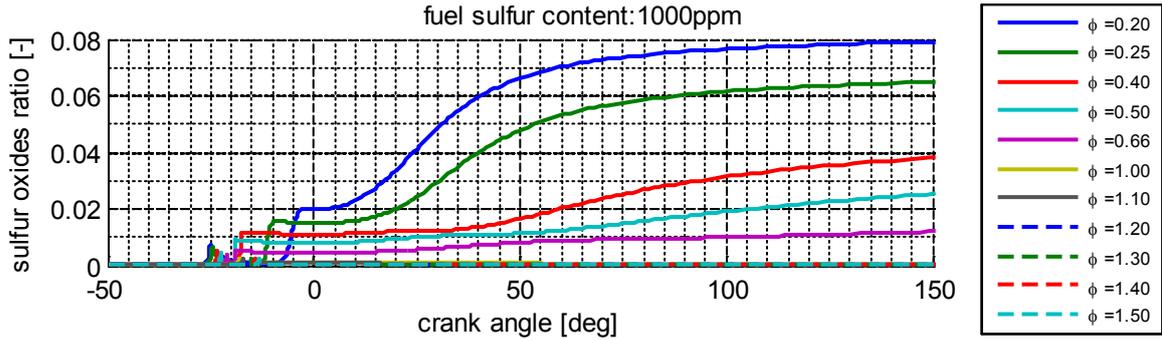


Fig. 1. Sulfur oxides ratios fuel-to-air ratios between 0.2 and 1.5 and a fuel sulfur content of 1,000 ppm-m.

Taking in to account the principle of Le Châtelier and the elevated combustion pressures the threshold of the thermal dissociation may shifts towards higher temperatures. Thus, the thermal sulfur trioxide dissociation has no significant effect on the sulfur trioxide concentration for lower fuel-to-air ratios, but for higher fuel-to-air ratios due to the higher combustion temperatures. In any case, missing excess oxygen

reduces the concentrations of oxygen containing radicals and, thus, is mainly responsible for the reduced oxidation of sulfur dioxide to sulfur trioxide [16].

In general, the sulfur oxides ratios of all investigated fuel sulfur contents have similar behavior, although the sulfur oxides ratios slightly decrease with increasing fuel sulfur content.

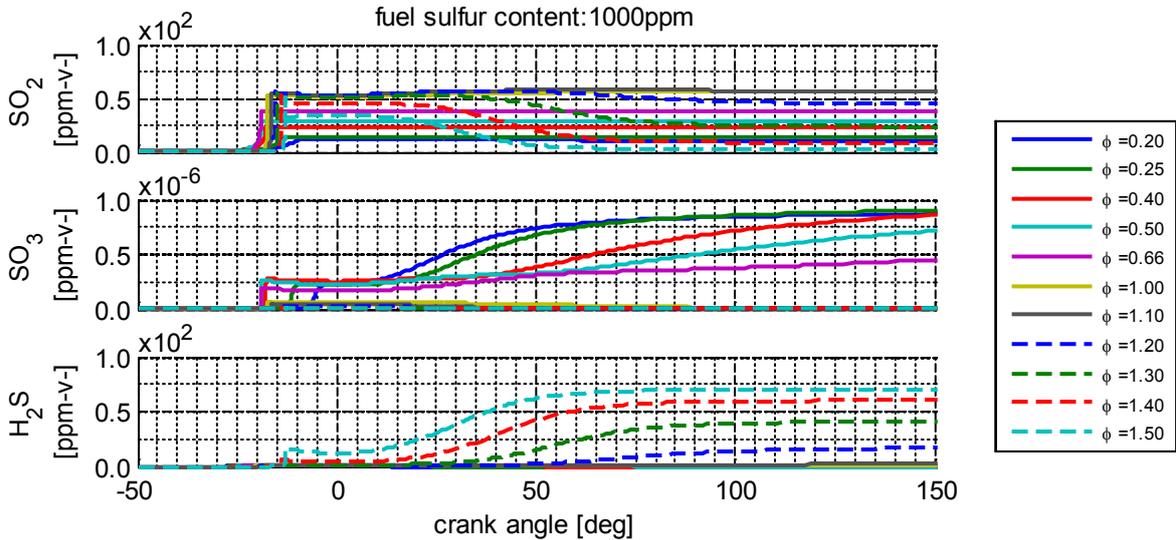


Fig. 2. Exhaust gas concentration profiles of sulfur dioxide (SO_2), sulfur trioxide (SO_3) (including sulfur trioxide from sulfuric acid) and hydrogen sulfide (H_2S) for fuel-to-air ratios between 0.2 to 1.5 and a fuel sulfur content of 1,000 ppm-m.

Fig. 2 shows the concentration profiles during combustion of sulfur dioxide, sulfur trioxide (including the sulfur trioxide in sulfuric acid), sulfuric acid and hydrogen sulfide for the conditions of Fig. 1. In any case, the sulfur dioxide concentration rapidly increases after the ignition start. The concentration magnitude increases for fuel-to-air ratios from 0.2 to 1.1 to around 50 ppm-v. In contrast, for fuel-to-air ratios above 1.1, the maximum sulfur dioxide concentrations decrease. Furthermore, the sulfur dioxide is decomposed starting at 50 degree crank angles after ignition. This effect is not observed for fuel-to-air ratios from 0.2 to 1.1. The decreasing sulfur dioxide concentrations may be explained by the reducing conditions during combustion caused by a lack of oxygen. As a result, as confirmed by the hydrogen sulfide concentration profile, sulfur dioxide is reduced to hydrogen sulfide.

The sulfur trioxide concentration profiles also suffer a dilution effect, but due to a high sulfur trioxide increase for fuel-to-air ratios below 0.66, the concentrations seem to suffer no dilution effect. In general, the sulfur trioxide concentrations reproduce the sulfur dioxide ratios: for fuel-to-air ratios below 0.66 the concentrations increase, whereas for the other cases virtually no sulfur trioxide forms. The different behavior may be explained by the excess or lack of oxygen during combustion and expansion, respectively.

As already mentioned, the hydrogen sulfide concentration profiles show that there is a significant hydrogen sulfide formation, due to the reducing combustion conditions, for fuel-to-air ratios above 1.1. Under oxidizing combustion conditions (fuel-to-air ratios below 1.0) there is no hydrogen sulfide formation.

Fig. 3 shows the results of the sulfur oxides ratios for a fuel sulfur content of 1,000 ppm, a fuel-to-air ratio

of 0.5 and EGR rates of 0, 10, 30 50 and 70 percent. In general, in case of 0.5 fuel-to-air ratio, the sulfur oxides ratio increases with increasing EGR rates. Higher EGR rates imply higher combustion air masses and, thus, higher combustion pressures. Furthermore, higher EGR rates cause lower combustion temperatures. As a consequence, following the principle of Le Châtelier more sulfur dioxide is oxidized to sulfur trioxide for

high EGR rates. It is also noticeable that, if exhaust gas is recycled, the sulfur oxides ratio during compression is almost as high as during expansion. Due to the low temperatures and the exhaust gas moisture content, significant amounts of sulfuric acid may exist before ignition. The sulfur oxides ratio shows that the sulfur trioxide is decomposed after ignition starts.

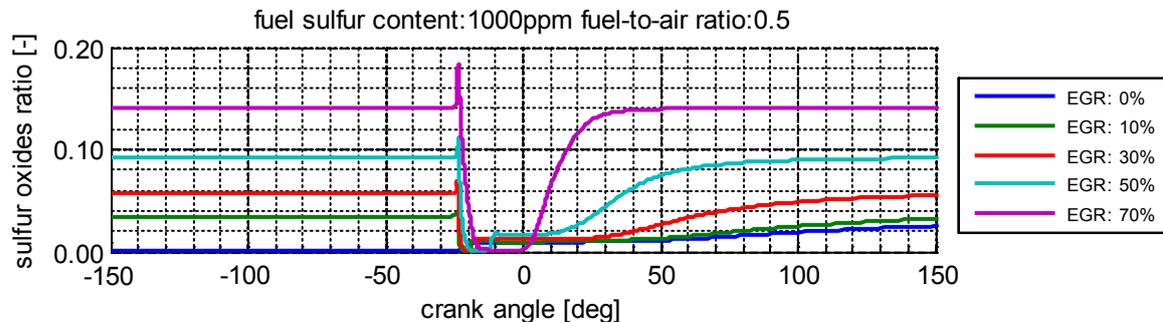


Fig. 3. Sulfur oxides ratios for exhaust gas recirculation (EGR) rates between 0 and 70 percent, a fuel-to-air ratio of 0.5 and a fuel sulfur content of 1,000 ppm-m.

No sulfur trioxide formation is observed in case of lean combustion and high EGR rates. If the combustion is lean enough there may be no sulfur trioxide formation even without EGR. This may be explained by the low combustion temperatures and the high exhaust gas dilution. Hence, the radical concentrations, which play an important role in the sulfur trioxide formation, are too low for significant sulfur trioxide formation [16].

In case of substoichiometric combustion, regardless of the EGR rate, no sulfur trioxide forms due to a lack of radicals containing oxygen. Furthermore, the hydrogen radical concentration is significantly higher in case of substoichiometric combustion compared to stoichiometric and overstoichiometric combustion conditions.

Fig. 4 shows the concentration profiles of sulfur dioxide, sulfur trioxide (including the sulfur trioxide from sulfuric acid) and hydrogen sulfide during combustion for the conditions of Fig. 3. Sulfur dioxide is present during compression, if exhaust gas is recirculated. Despite a significant dilution effect for high EGR rates, the sulfur dioxide exhaust gas concentrations increase with higher EGR rates. During and shortly after ignition, the sulfur dioxide concentrations increase compared to compression due to the fuel sulfur. However, starting at the TDC, the sulfur dioxide concentrations decrease and sulfur trioxide forms. This effect increases with higher EGR rates.

As already mentioned above, the increase of sulfur trioxide formation may result from the higher pressures and lower temperatures. Leaner combustion conditions, as already mentioned, result in low to no sulfur trioxide formation in case of higher EGR rates. In case of substoichiometric combustion, the sulfur dioxide concentration reduces immediately after formation. The final concentration in the exhaust gas depends on the EGR rate and fuel-to-air ratio. Sulfur trioxide is also present during compression as sulfuric acid, the

concentrations increase with the EGR rate despite the dilution effect caused by EGR. During ignition sulfur trioxide is decomposed, but formed again approximately 10 degree crank angles later. As during compression, the sulfur trioxide concentrations increase with EGR rate. In case of lean combustions, sulfur trioxide forms only for low EGR rates. In case of substoichiometric conditions, sulfur trioxide is only formed shortly after combustion, but decomposes immediately.

Hydrogen sulfide is not relevant for fuel-to-air ratios below 1.0, but for ratios above 1.0. In general, the hydrogen sulfide concentrations are lower during compression than during expansion. However, depending on the fuel sulfur concentration and EGR rates, significant hydrogen sulfate could be in the combustion air. The concentrations in the exhaust gas depend on the EGR rate and fuel-to-air ratio.

Reaction path analysis

In order to get insights in the reactions taking place during ignition, combustion and expansion reaction pathways are analyzed in more detail. Since the compression stroke is neglected, only the reaction pathways without EGR are considered. In order to get an insight to the processes under different conditions, fuel-to-air ratios of 0.5 and 1.3 are examined.

In case of a fuel-to-air ratio of 0.5, during ignition sulfur oxide is formed by elemental sulfur (S and S₂, each approximately 50 %). Subsequent, sulfur oxide reacts mainly to sulfur dioxide and small amounts hydroxidooxidosulfur (HOSO), which forms sulfur dioxide too. The formed sulfur dioxide is partly oxidized to sulfur trioxide, which subsequently is decomposed to hydroxysulfonyl radical (HOSO₂). In a further step, HOSO₂ radical decomposes to sulfur dioxide and closes a circle (subsequently called the sulfur trioxide cycle) where sulfur dioxide is oxidized to sulfur trioxide and reduced to sulfur dioxide again.

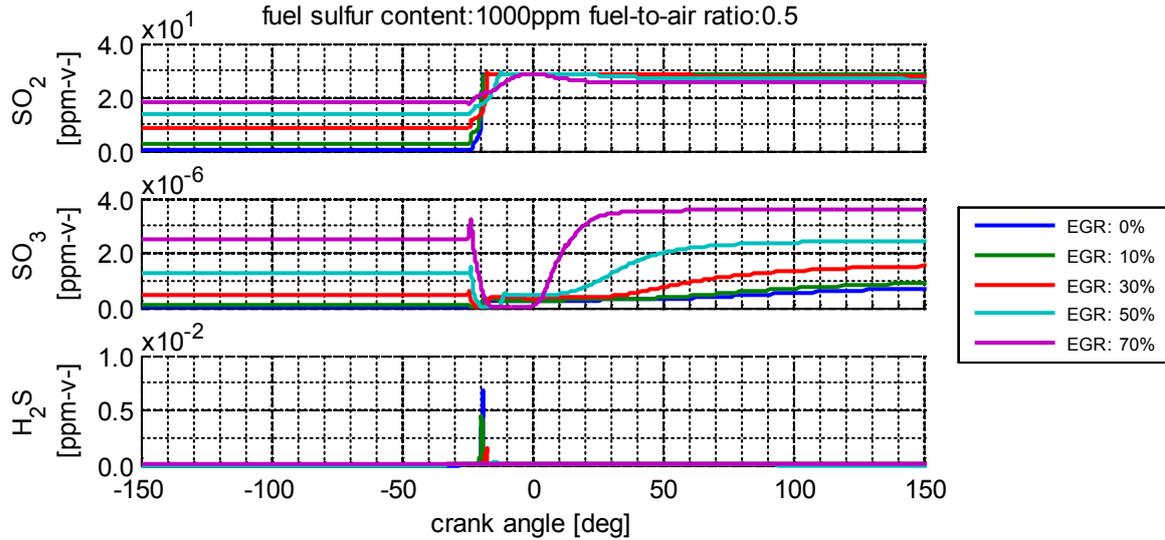


Fig. 4. Exhaust gas concentration profiles of sulfur dioxide (SO_2), sulfur trioxide (SO_3) (including sulfur trioxide from sulfuric acid) and hydrogen sulfide (H_2S) ratios for exhaust gas recirculation (EGR) rates between 0 and 70 percent, a fuel-to-air ratio of 0.5 and a fuel sulfur content of 1,000 ppm-m.

During combustion, this cycle is retained, but, in contrast to ignition, sulfur dioxide is reduced to sulfur oxide and not formed by sulfur oxide. Additionally, the share of produced sulfur dioxide by HOSO_2 is significant higher than during ignition. Sulfur oxide is exclusively consumed to produce HOSO , which subsequently forms sulfur dioxide, under combustion conditions. Furthermore, sulfur oxide is formed to an equal share by sulfur dioxide and elemental sulfur (S and S_2).

Similarly to combustion, the sulfur trioxide cycle retains during the expansion. The share of sulfur dioxide produced by HOSO_2 is increased compared to combustion conditions. In contrast, the share of sulfur dioxide reduced to sulfur oxide as well as the share of sulfur dioxide oxidized to sulfur trioxide remains similar. Contrary to combustion conditions, sulfur oxide is exclusively formed by sulfur dioxide, while it is consumed to HOSO like under combustion conditions.

radical. Sulfur dioxide is mainly (around 90 percent) formed by sulfur oxide and around 10 percent by HOSO . The sulfur trioxide cycle also exists, but a small amount of sulfur trioxide is consumed to form HOSO instead of HOSO_2 .

During combustion sulfur oxide is exclusively formed by S . Due to the lack of oxygen, the consumption of sulfur oxide differs significantly from the 0.5 fuel-to-air ratio case. Around half is consumed to SH and the other half is consumed to HSO . Sulfur dioxide is formed mainly by sulfur oxide and small amounts of HOSO_2 and HSO_2 . Subsequently, only a small amount of the sulfur dioxide is oxidized to sulfur trioxide, while the rest reacts to HSO and HOSO . The sulfur trioxide cycle is similar to the cycle during ignition.

During expansion no sulfur trioxide is formed. Although sulfur dioxide is only formed by sulfur oxide, the existing sulfur dioxide is mainly reduced to sulfur oxide and small amounts of HOSO and HSO . One third of the sulfur oxide is consumed to SH and the other two thirds to HSO . As under combustion conditions, sulfur oxide is formed by S only.

Fig. 5 summarizes the reaction paths for both fuel-to-air ratios, the black reaction paths occur in lean and rich combustion, whilst the blue and green reaction paths exclusively occur in lean or rich combustion respectively.

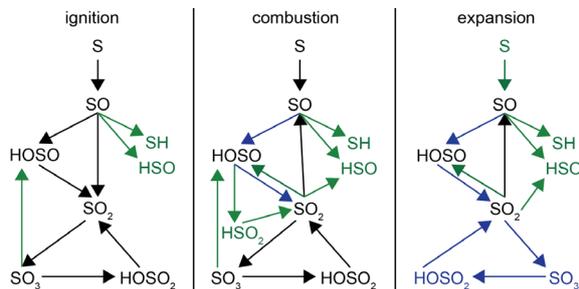


Fig. 5. Sulfur reaction pathways for ignition, combustion and expansion under fuel-lean (fuel-to-air ratio 0.5) and fuel-rich (fuel-to-air ratio 1.3) combustion conditions. Black paths occur in both fuel-lean and fuel-rich conditions; whereas blue paths occur in fuel-lean and green paths occur in fuel-rich only.

In case of a fuel-to-air ratio of 1.3, during ignition, sulfur oxide is also formed by elemental sulfur, but only around the half is subsequently oxidized to sulfur dioxide. The other half reacts to various radicals, including sulfanyl (HSO), HOSO and mercapto (SH)

Conclusion

An insight to the way of fuel sulfur through a diesel engine is given in this work. In general, fuel sulfur oxidizes to sulfur dioxide and a small amount to sulfur trioxide during combustion [7]. The sulfur dioxide and trioxide may interact with the oil layer on the cylinder line to produce corrosive compounds, like sulfuric acid (H_2SO_4), and may cause significant liner wear for high fuel sulfur contents [2, 3, 12]. Moreover, sulfur trioxide forms sulfuric acid and may cause high aerosol

concentrations in the exhaust gas and, thus, cause changes in the fouling characteristic in exhaust gas pipes or EGR coolers [10]. Additionally, sulfur oxides may react with condensate or condensate dissolves sulfur oxides from the fouling layer to form sulfuric or sulfurous acid (H_2SO_3) [8]. Additionally, sulfur trioxide and water vapor form sulfuric acid at temperatures below 600 °C [7].

The investigation of sulfur oxides concentration profiles for different fuel-to-air ratios without EGR showed that sulfur trioxide concentrations increase when the fuel-to-air ratios are decreased. Additionally, under reducing conditions (fuel-to-air ratios above 1) significant amounts of hydrogen sulfide may form.

The concentration profiles considering EGR rates showed that for low fuel-to-air ratios and high EGR rates no sulfur trioxide is formed. This is caused by low radical concentrations in the exhaust gas due to low combustion temperatures and dilution effects caused by EGR. Under typical combustion conditions, the sulfur trioxide increases when the EGR rate is increased. Furthermore, if sulfur trioxide is formed, significant sulfur trioxide and if temperatures are low sulfuric acid concentrations may arise during compression. In case of substoichiometric combustion conditions, no sulfur trioxide forms and, moreover, sulfur dioxide is decomposed during expansion. Furthermore, significant hydrogen sulfide amounts may arise due to the lack of oxygen.

The reaction pathways for fuel-to-air ratios of 0.5 and 1.3 have similarities for the formation of sulfur oxides. Especially, a reaction cycle forming sulfur trioxide from sulfur dioxide and the subsequent consumption of the sulfur trioxide to sulfur dioxide is found in both cases. In general, fuel sulfur is primarily oxidized to sulfur oxide and subsequently to sulfur dioxide and sulfur trioxide. Under rich combustion conditions, formation of oxygen free compounds or compounds with low oxygen contents is preferred, especially SH.

The results derived in this work are based on simplified models. The model assumes perfect mixing, which is not reached in a diesel engine.

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