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The importance of vanadium catalyzed oxidation of SO_2 to SO_3 in two-stroke marine Diesel engines

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Abstract

Low speed marine Diesel engines are mostly operated on heavy fuel oils, which have a high content of sulfur and ash including trace amounts of vanadium, nickel, and aluminum. In particular vanadium oxides could catalyze in-cylinder oxidation of SO_2 to SO_3, promoting formation of sulfuric acid and enhancing problems of corrosion. In the present work, the kinetics of the catalyzed oxidation was studied in a fixed bed reactor at atmospheric pressure. Vanadium oxide nanoparticles were synthesized by spray flame pyrolysis, i.e., by a mechanism similar to the one leading to formation of the catalytic species within the engine. Experiments with different particle compositions (vanadium/sodium ratio) and temperatures (300-800 ℃) show that both the temperature and the sodium content have a major impact on the oxidation rate. Kinetic

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parameters for the catalyzed reaction are determined and the proposed kinetic model fits well with the experimental data. The impact of the catalytic reaction is studied with a phenomenological 0D engine model where fuel oxidation and SO_x formation is modeled with a comprehensive gas phase reaction mechanism. Results indicate that the oxidation of SO_2 to SO_3 in the cylinder is dominated by gas phase reactions and that the vanadium catalyzed reaction is at most a very minor pathway.

Introduction

Compared to other ways of transport, maritime transport and shipping benefit from low CO_2 emissions, even though emissions of NO_x and SO_x may be a concern. Two-stroke marine Diesel engines used for low-speed vessels can operate on heavy fuel oils, which are the most economic option among fuels but typically contain large amounts of sulfur (2.5-3.5 wt%). During combustion, the sulfur is quickly oxidized to SO_2 with a small fraction oxidized further to SO_3. Presence of SO_3 may lead to formation of sulfuric acid (H_2SO_4), which can cause corrosion if the temperature locally drops below the sulfuric acid dew point (cold corrosion).[1,2] In order to improve the efficiency and future development of the engines, an understanding of the SO_3 formation mechanisms is required.

The formation of SO_3 in the cylinder of a large two-stroke marine Diesel engine burning heavy fuel oil was studied by Cordtz et al. with a phenomenological 0D model.[2] Oxidation of SO_2 to SO_3 can take place through a sequence of gas-phase reactions, which are reasonably well established.[3,4] However, fuel oil contains trace amounts of vanadium that cannot be easily removed from the oil. Particles emitted from two-stroke marine Diesel engines on modern container ships have been reported to belong to two size ranges: 5-8 and 30-100 nm,[5] particle measurements were done in the raw exhaust gases of the ship, and thus the ones in the stroke of the engine would correspond to the smaller size. The 5-8 nm nanoparticles, which dominate the total number of particles, are composed mainly of V, Ni, and S. Vana-

dium oxide (V_2O_5) is known to catalyze SO_2 oxidation[1] and thus may facilitate formation of SO_3 in the cylinder.

It has been reported that vanadium becomes more reactive when doped with alkali elements such as potassium, cesium or sodium.[1,6] Sodium is typically present in considerable quantities in the engine cylinder, originated partly from sea water contamination[7] and partly from the fuel oil. Reported mass ratios of V/Na in the engine exhaust are in fairly good agreement, with values of 7.9 in the exhaust gas ash particles of a large scale medium-speed Diesel engine[8] and 6.3 in the particulate matter from a large ship Diesel engine.[9] A report from the International Bunker Industry Association (IBIA) indicates that the V/Na ratio in the marine engine would be in the range 7-10 or higher, depending on the centrifuge system that removes water.

In this context, the objective of this work is to investigate the relative importance of homogeneous and heterogeneous (catalyzed by vanadium oxides) oxidation of SO_2 into SO_3 through experiments and kinetic modeling. Representative vanadium aerosols, produced by flame spray pyrolysis, are used in fixed bed reactor experiments to determine the rate of the catalytic reaction as a function of particle composition (V/Na ratio), SO_2 concentration, and temperature. The contribution of the catalyzed oxidation of SO_2 is then determined, based on computations with the phenomenological model of Cordtz et al.[2]

Experimental

The vanadium particles used in the present study are produced in a flame spray pyrolysis setup,[10,11] where oxide nanoparticles are formed by spraying a combustible solution of organometallic salts into a flame. The setup is described in detail by Høj et al.[12] In the flame, catalytically active oxide nanoparticles are produced by a mechanism similar to the

one leading to formation of the catalytic species within an engine.[13] The combustible solution is composed of organo-metallic precursors (vanadium (III) acetylacetonate and sodium 2-ethylhexanoate) at a total metal concentration of 0.125 M dissolved in methanol. The solution is fed at a rate of 3 mL min^{-1}, dispersed by a 5 NL min^{-1} flow of O_2 and ignited by an annular 1/3 mol/mol CH_4/O_2 flame.

The flame pyrolysis allows the vanadium aerosols to be formed under conditions that resemble those of an engine. The aerosol size range (11-21 nm) is similar to the values reported for marine Diesel engines (5-8 nm). The particle diameter d_p was calculated assuming spherical particles: $d_p = 6/(SSA\cdot\rho)$, where ρ is the density of the particles (taking into account the content and densities of V_2O_5 and Na_2O in the particles), and SSA is the specific surface area, determined by BET surface analysis. Table 1 summarizes these values. No agglomeration of particles is considered. The present experiments were conducted with V/Na mass ratios of 4, 7.9, and 15, in addition to reference experiments made with pure vanadium.

The kinetics of SO_2 oxidation over vanadium oxides is studied in a fixed bed reactor at atmospheric pressure. Details of the experimental setup and procedures can be found elsewhere.[14] The reactor is a fixed bed quartz reactor, with solids placed on a porous quartz plate in an isothermal zone. Reactant gases are introduced separately in the reactor and mixed just above the porous plate. The reactor is placed in a three-zone electrically heated oven, operated in the 300-800℃ temperature range. The reactor temperature is measured under inert conditions with a type K thermocouple. 0.25 grams of the synthesized aerosols are mixed with an equal amount of silica particles (150-200 μm) to form a fixed bed with good heat dispersion. At the higher temperatures, the vanadium-sodium compounds may melt (melting points are around 550-700℃) and the dispersion of the small synthesized particles with quartz particles can help to avoid a large pressure drop. A total flow rate of 157 mL min^{-1} (1 atm, 25℃) is used, with a composition of 1380 ppm of SO_2, 14% O_2 and 2.6%

H_2O, all diluted in N_2. The amount of oxygen is in large excess compared to the SO_2 to obtain pseudo-first order reaction conditions,[6,14] and representative of the exhaust gases of marine Diesel engines.[8]

The oxidation of SO_2 is exothermic, but due to the high dilution under the present experimental conditions the heat release can be neglected. Water vapor is present in significant amounts in the combustion products and may conceivably have an impact on the catalyzed reaction. For this reason, the stream including N_2 and O_2 was saturated with water vapor by passing the gas through an evaporator at room temperature. Upon dilution with N_2 to satisfy the flow rate needed in the analyzer ($\sim$1000 mL min^{-1}), the product gas from the reactor was led to a continuous UV-NGA2000 MLT4 analyzer (Rosemount Analytical) in order to quantify the SO_2 concentration.

Results and discussion

Vanadium catalyzed SO_2 oxidation

A series of experiments is conducted in the fixed-bed reactor for the different V/Na compositions (Table 1), varying the temperature and the SO_2 inlet concentration. Figure 1 shows results of the conversion of SO_2 as a function of aerosol composition and temperature.

Without catalyst (empty reactor) the SO_2 conversion is very limited, especially below 550℃; this is in line with results reported by Jørgensen et al.[14] Introduction of vanadium aerosols in the fixed bed leads to a significant oxidation of SO_2 above 350℃. Catalyst particles doped with sodium exhibit an even higher reactivity, with the maximum conversion increasing with the sodium content. The SO_2 conversion peaks at 550℃; above this temperature the conversion is limited since the reaction approaches chemical equilibrium. The importance of sodium in the catalyst is in agreement with findings from sulfuric acid pro-

duction where catalysts with a mass ratio of $V/Na = 0.75$ are used.[15]

The difference between thermal equilibrium and experimental data at higher temperatures may be attributed to experimental uncertainties. However, similar observations have been reported from sulfuric acid production, where SO_2 emissions from acid plants were slightly above equilibrium values.[16] It has been reported that commercial sulfuric acid catalysts suffer a sudden loss in activity at 420-450°C that is attributed to the precipitation of crystalline compounds of vanadium (V^{III} and V^{IV}).[15] This loss is a reversible process and the catalytic activity is regained upon heating the catalyst bed up to 500°C, showing a hysteresis behavior.

Figure 2 shows the influence of the SO_2 concentration. Below the temperature where the conversion peaks, a higher conversion is obtained with a lower concentration of SO_2. Above the peak temperature, the conversion is the same for the two SO_2 levels. It is not possible from the present work to determine a reaction order in SO_2, since the amount of data is limited and differences may be partly attributed to experimental uncertainties. Results from literature[17] suggest that the reaction is first order in SO_2.

Kinetic model

The experimental results (Figure 1) were used to establish the rate equation for the catalytic reaction. We assume the reaction to be first order in SO_2,[17]
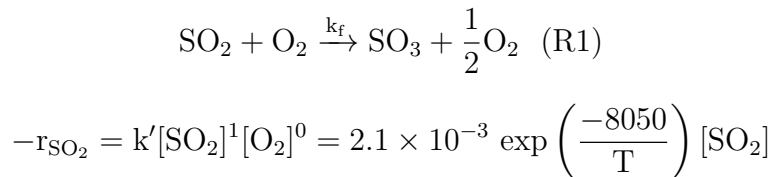
$$-r_{SO_2} = k \cdot P_{SO_2} \cdot (1 - \beta)$$

Here k is described by an Arrhenius expression with a pre-exponential factor A and an activation energy E_a. The rate is assumed to be independent of the oxygen concentration. As mentioned, O_2 is in large excess and it has been reported to be zero order in similar

experiments at 400℃ with vanadium catalysts.[6] The (1-β) term accounts for the decrease in the reaction rate as the reaction approaches equilibrium, with β related to the equilibrium constant K_e and the concentration of the molecules, $\beta = \frac{P_{SO_3}}{K_e \cdot P_{SO_2} \cdot P_{O_2}^{0.5}}$. If the concentrations of SO_2 and SO_3 reach the equilibrium values, β will be equal to 1 and the reaction rate will be zero.

Non-linear regression was made to determine the kinetic parameters A and E_a for each catalyst composition; the values obtained are listed in Table 2. A comparison between the experimental and calculated results for the particles with a V/Na ratio of 7.9 is shown in Figure 2. The measured activation energies are not directly comparable with values from literature because the present work constitutes the first study of the oxidation of SO_2 with flame-generated particles. Similar supported vanadium catalysts made by impregnation techniques have shown activation energies around 85 kJ mol^{-1},[6] approximately 25% higher compared to the values obtained in the present work. The difference is attributed to variations in morphology and catalyst support. Additionally, it can be seen in Figure 3 a comparisson of the turn over frequency of our catalysts (V/Na = 4 and 100% vanadium) and different composition of commercial vanadium catalyst shown in the work of Boghosian et al.[18].

The rate equation is used to evaluate the importance rate of vanadium-catalyzed SO_3 formation, compared to the rate of SO_3 formation by homogeneous oxidation, in a two-stroke Diesel engine. For the homogeneous oxidation rate, calculations were conducted with the detailed chemical kinetic model of Hindiyarti et al.,[4] using a 0D model described in the next section. The catalyzed reaction was introduced in the mechanism as a pseudo-first-order reaction,

$$SO_2 + O_2 \xrightarrow{k_f} SO_3 + \frac{1}{2}O_2 \quad (R1)$$

$$-r_{SO_2} = k'[SO_2]^1[O_2]^0 = 2.1 \times 10^{-3} \exp\left(\frac{-8050}{T}\right)[SO_2]$$

The rate constant k′ is based on the kinetic parameters for particles with V/Na ratio of 7.9 (see Table 2). This ratio corresponds to reported V/Na ratio in engines, as discussed above. To obtain the first-order rate constant, conditions representative of the cylinder were chosen, with the fuel consumption rate, exhaust flow, and fuel vanadium content (100 mg per kg fuel) drawn from literature.[9] Details of the calculations can be seen in the supplementary material.

Engine simulation

The phenomenological 0D model of Cordtz et al.[2] is adopted here to simulate a large two-stroke marine Diesel engine operating at a low power output at a speed of 80 revolutions per minute. A detailed gas phase reaction mechanism[4] is applied and integrated with MATLAB and CANTERA[19,20] to describe SO_x formation in the burned gas.

Figure 4 shows a sketch of a two-stroke Diesel engine cylinder. The piston position determines the volume of the trapped gas that is coupled to the angular position of the crank shaft (θ). The two-stroke cycle involves a compression stroke ($\theta < 0°$) and an expansion stroke ($\theta \geq 0°$). The position at $\theta = 0°$ is termed the piston top dead center (TDC). Close to TDC fuel is injected into the hot compressed fresh gas that consists mostly of air but includes residual gases, i.e., combustion products from the prior cycle. As the fuel burns (diffusion controlled combustion), thermal work/power is transferred to the rotating crank shaft. Late in the expansion stroke, the exhaust valve opens (EVO) and the cylinder gas products are replaced by fresh scavenging air at 30℃. The air is provided via scavenging ports in the bottom of the cylinder (not shown in the figure) and flows upward through the cylinder. The exhaust valve closes shortly after the crank shaft has passed the bottom dead center at $\theta = 180°$ where a new cycle begins.

In the 0D engine model, the burned fuel is separated in multiple, slightly lean and ho-

mogeneous gas zones. The computed mean temperature and the overall SO_3 concentration of the burned gas for a wide range of the pre-exponential factor of R1 are plotted in Figure 5. SO_3 is thermodynamically restricted at combustion temperatures but forms during the expansion stroke primarily through reactions of SO_2 with the radical pool.[2] Reaction R1 is comparably slow and the catalytic effect is negligible unless the pre-exponential factor is increased by three orders of magnitude.

The fraction of residual gases (in the fresh gas) is around 3% m/m. If the air and the residual gas are computationally separated during the cycle, the temperature of the residual gas (that holds SO_2 of the prior cycle) peaks above 2000 K during combustion, as illustrated in Figure 6. The temperature trace is determined from the cylinder pressure and the isentropic correlation,

$$\frac{T_{\theta+1}}{T_\theta} = \left(\frac{p_{\theta+1}}{p_\theta}\right) \quad (1)$$

Here, the mean cylinder gas temperature and species composition at EVO of the prior cycle are set as initial conditions. As indicated in Figure 6, SO_3 formation in the residual gas is thermodynamically restricted at the highest temperatures and the rate of R1 is too slow to contribute to SO_3 formation.

If the fresh charge air and the residual gas are fully mixed during the cycle, the mixture temperature peaks at $\sim$ 1000 K as shown in Figure 7. Below 1000 K, SO_3 is thermodynamically preferred over SO_2.[21] Still, R1 is too slow to form considerable amounts of SO_3, unless the pre-exponential factor is increased by three orders of magnitude.

Conclusions

The present work is the first study on the importance of catalytic species in the formation of sulfur oxides in engines. The SO_2 oxidation catalyzed by vanadium aerosols was studied in a

fixed bed reactor at atmospheric pressure. The aerosols were formed in a flame pyrolyzer and represent particles formed from combustion of heavy fuel oil in a marine two-stroke Diesel engine. The rate of the catalyzed reaction was determined in a fixed bed as a function of catalyst composition (V/Na ratio), temperature, and SO_2 concentration. Experiments showed that both the temperature and the sodium content had a major impact on the oxidation rate. Kinetic parameters for the catalyzed reaction were determined using a proposed kinetic model. To simulate fuel oxidation and SO_x formation inside a two-stroke marine Diesel engine a detailed gas phase reaction mechanism was combined with a step describing the catalyzed reaction and used with a phenomenological 0D model. Results indicate that the proposed catalytic vanadium reaction is slow compared to the gas phase reactions and it is unlikely that vanadium contributes significantly to SO_3 formation.

Acknowledgement

Supporting Information Available

Estimation of vanadium catalyzed oxidation rate constant for engine conditions.

This material is available free of charge via the Internet at `http://pubs.acs.org/`.

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Table 1: Catalyst particle properties

V/Na[a]	dp [nm]	SSA [m^2/g]
4	20.9	91.2
7.9	21.2	87.6
15	11.9	153.0
V 100%	11.5	155.1

a: on a mass basis.

Table 2: Kinetic parameters

V/Na[a]	Ea [kJ/mol]	A [mol/(s·g·bar)]
4	69.5	20.6
7.9	67.3	14.5
15	57.8	3.0
V 100%	47.9	0.2

a: on a mass basis.
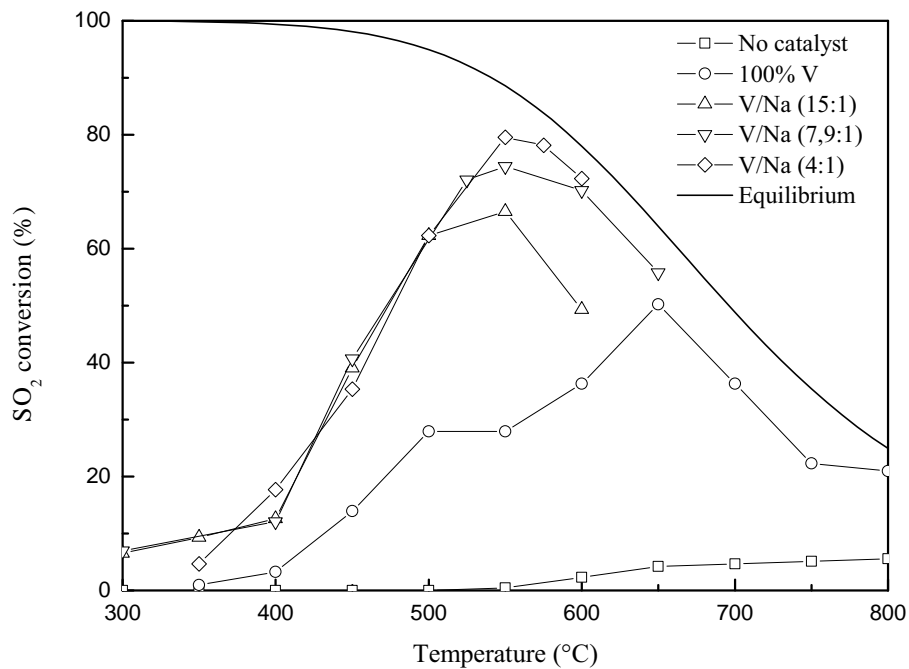
Figure 1: The effect of catalyst composition and temperature on the oxidation of SO_2 in the fixed-bed reactor. Results are shown for experiments with an empty reactor, with pure vanadium, and with particles with V/Na ratios in the range 4-15 (mass based). Flow rate: 157.4 mL min^{-1} (25℃, 1 atm); 1376 ppm SO_2, 14% O_2, 2.6% H_2O, balanced with N_2.
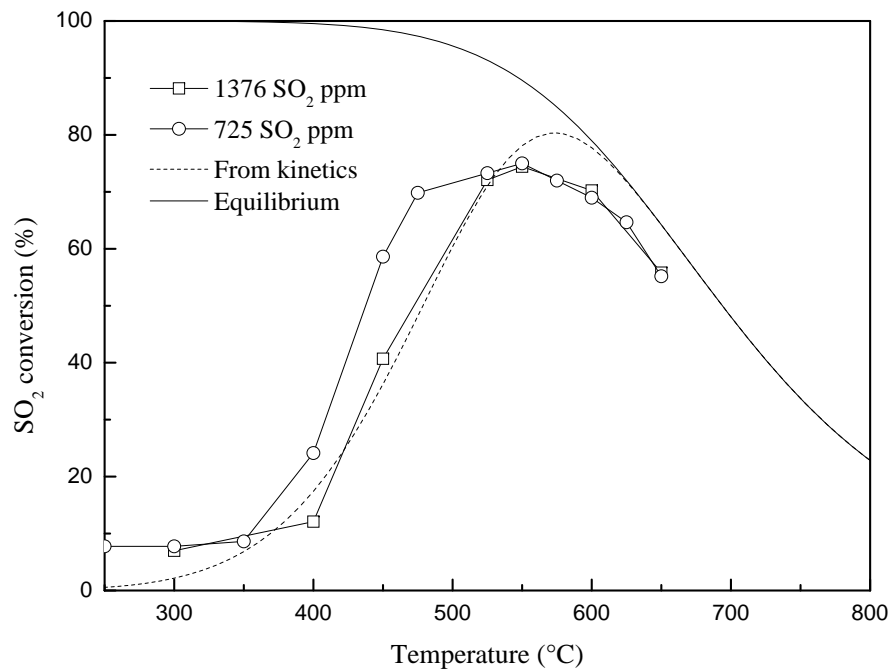
Figure 2: Conversion of SO_2 for two different initial concentrations of SO_2 and same catalyst (V/Na = 7.9). Comparison between experimental results and predictions with the kinetic model are also shown.
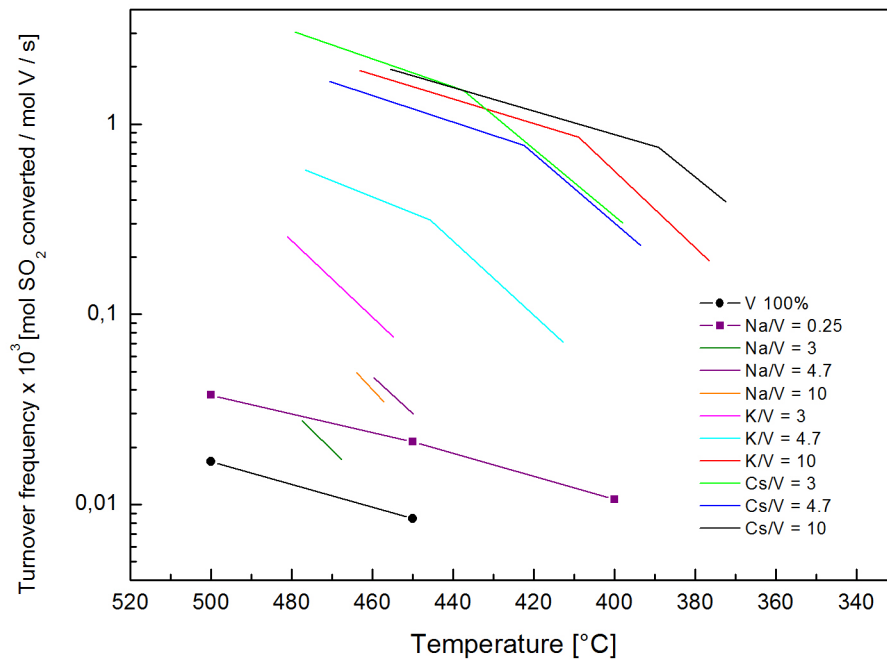
Figure 3: Turn over frequencies of different commercial catalysts (lines) and two of our catalysts (line+symbol). The mole rario of alkali to vanadium is indicated.
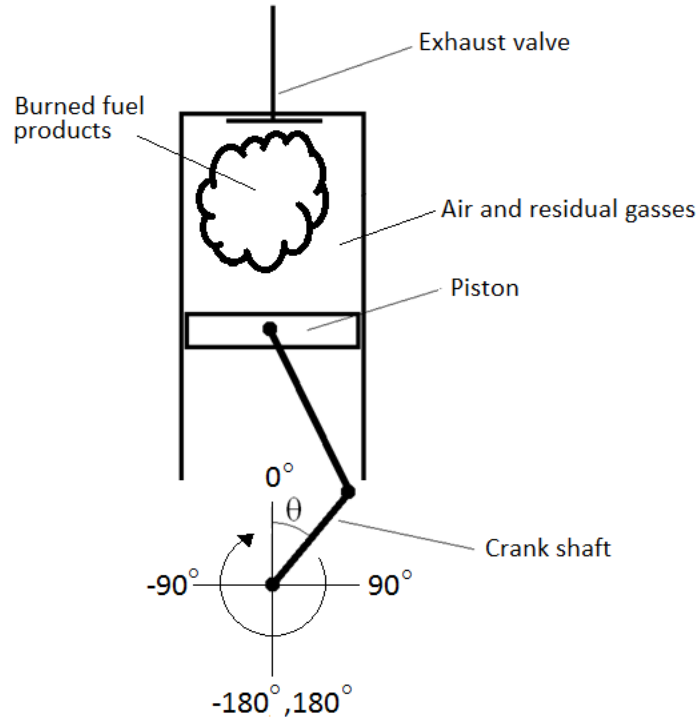
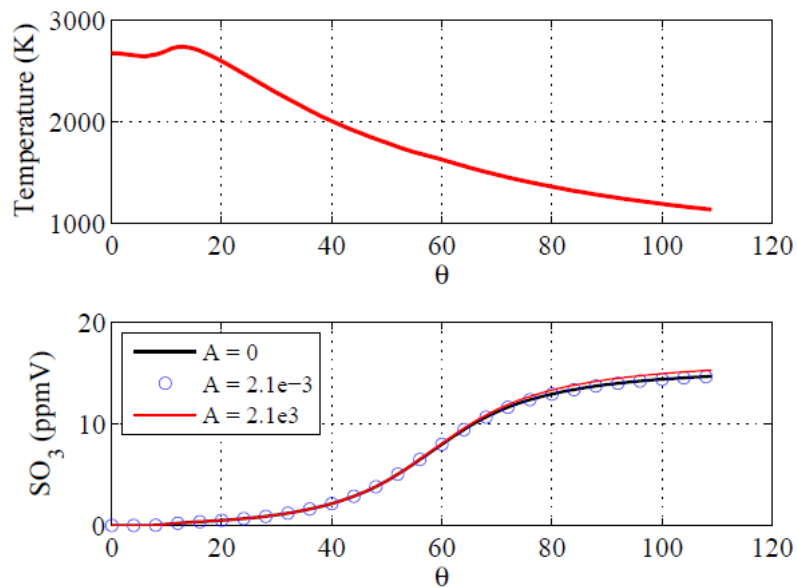Figure 4: Sketch of a two-stroke engine cylinder

Figure 5: Mean temperature and overall SO_3 concentration of the burned gas during combustion and expansion until the exhaust valve opens. The figure shows the effect of a factor 1000 change in the pre-exponential factor A for the catalytic vanadium reaction (R1).
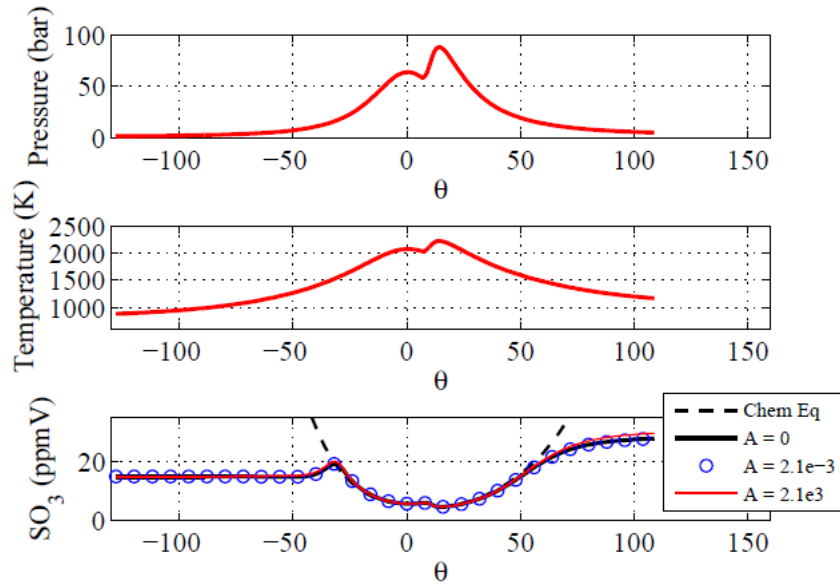
Figure 6: Cylinder gas pressure, residual gas temperature and catalytic SO_3 formation in the residual gas over the engine cycle. The figure shows the effect of a factor 1000 change in the pre-exponential factor A for the catalytic vanadium reaction (R1).
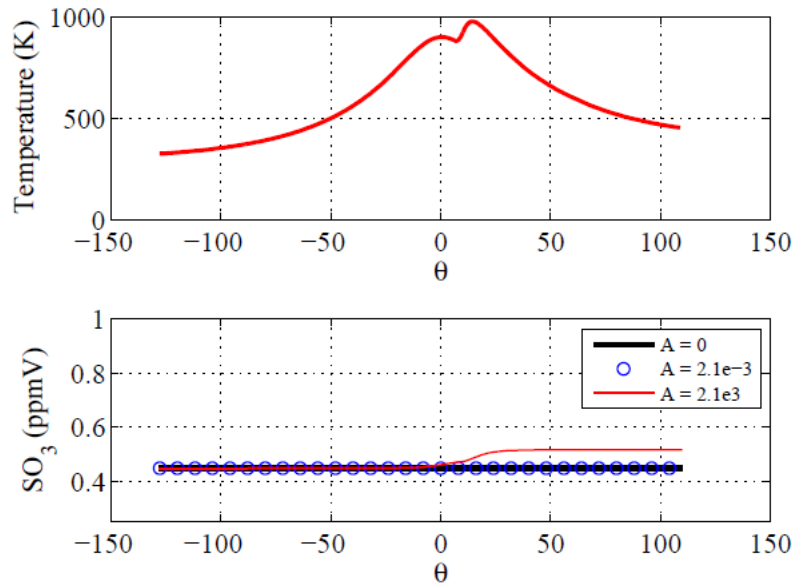

Figure 7: Fresh gas temperature and catalytic SO_3 formation in the fresh gas over the engine cycle. The figure shows the effect of a factor 1000 change in the pre-exponential factor A for the catalytic vanadium reaction (R1).

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