

GT2004-53704**CHEMICAL KINETIC MODELLING OF THE EVOLUTION OF GASEOUS AEROSOL PRECURSORS WITHIN A GAS TURBINE ENGINE**

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ABSTRACT

A sequence of kinetic models has been developed to simulate the chemical processes occurring throughout the hot section of a modern gas turbine engine. The work was performed as part of the EU funded PARTEMIS programme, which was designed to investigate the effect of both engine condition and fuel sulphur content on the production of gaseous aerosol precursors such as SO₃, H₂SO₄ and HONO. For the PARTEMIS programme, a Hot End Simulator (HES) was designed to recreate the thermodynamic profile through which the hot gases pass after leaving the combustor. Combustion rig tests were performed in which the concentrations of gaseous product species were measured at the exits of both the combustor and the HES. These measurements were used to validate the kinetic models.

The combustor was modelled by a sequence of five perfectly stirred reactors, using the Combustor Model Interface (CMI) developed at the University of Leeds. The CMI allows for the addition of dilution air at each stage of the combustor as well as re-circulation between each stage. The results at the combustor exit were then used as initial boundary conditions for the HES model, which followed the evolution of reacting gases through each of the pressure stages of the HES. This combination of the two models allowed the chemistry occurring throughout an engine, from combustor inlet to turbine exit, to be simulated.

The principal aim of this modelling programme was to determine the extent of conversion of the sulphur (IV) species, SO₂, to the sulphur (VI) species, SO₃ and H₂SO₄. The predicted level of this conversion at the exit of the HES was found to be in very good agreement with the experimentally measured values. These values were lower than had been previously determined by modelling studies and this was found to result from changes made to the thermodynamic properties of the key intermediate, HOSO₂, following recent experimental measurements. The results also showed that for these tests, the

predominant sulphur conversion process occurred within the combustor itself rather than the turbine or beyond.

INTRODUCTION

Sulphur compounds within aviation fuel are oxidised in the combustor of gas turbine engines to form sulphur dioxide, SO₂, together with small amounts of sulphur trioxide, SO₃. The SO₂ is further converted to SO₃ in the turbine section of the engine and beyond, as a result of oxidation processes driven principally by the OH radical. SO₃ reacts in turn with the water in the combustion products to form sulphuric acid, H₂SO₄. Similar oxidation processes are observed for the nitrogen oxides, predominantly by the reaction between NO and OH to produce HONO.

These oxidised species of sulphur and nitrogen are emitted at the engine exhaust and can lead to the formation of volatile aerosol particles. While there is some uncertainty concerning the effect of such aerosol emissions upon the atmosphere, they are believed to affect the radiation balance in the atmosphere both directly and by their role in the formation and enhancement of cirrus clouds [1]. The effect of cirrus clouds is currently thought to represent one of the largest potential contributors to radiative forcing from aviation, although there remains considerable uncertainty in the estimates of its contribution [2].

The extent to which sulphur (IV), SO₂, is converted in the engine to the sulphur (VI) aerosol precursors, SO₃ and H₂SO₄, can be represented by the conversion efficiency factor, ϵ , given by:

$$\epsilon = \frac{([\text{SO}_3] + [\text{H}_2\text{SO}_4])}{[\text{SO}_x]}$$

There have been many experimental studies of this conversion factor, and a number of computer models have been used to predict it. The results have shown a very wide distribution in the results obtained, with values of ϵ as high as 12 to 45 % [3] and 6 to 31 % [4] calculated from measurements

behind aircraft in flight or as low as 1.2 % [5] or 0.4% [6] from direct measurements of H₂SO₄ on the ground. A recent model calculated conversion factors of 1% at the combustor exit and ~ 10 % at engine exit [7], while earlier modeling studies of a JT9D-7A engine and a representative subsonic engine predicted $\epsilon \sim 3.8 \%$ [8] and up to 8.3 % respectively [9]. For both of these last two modeling studies, the efficiencies quoted represent sulphur conversion within the turbine section and nozzle only; no account is made of conversion within the combustor.

This paper presents a chemical kinetic modeling study of both the combustor and HES used during the EU funded PARTEMIS programme, with specific reference to the formation and evolution of the gaseous aerosol precursors: SO₂, SO₃, H₂SO₄ and HONO. The HES used during the experimental tests consisted of a series of heat exchangers, which were used to extract energy from the gas stream in order to recreate the thermodynamic profile through which the post combustion gases flow in a standard gas turbine engine. This allowed an extensive set of gas analysis measurements to be made, which were subsequently used to validate and test the kinetic models.

NOMENCLATURE

CMI	Combustor Model Interface
HES	Hot End Simulator
HP	High Pressure
IP	Intermediate Pressure
LIF	Laser Induced Fluorescence
LP	Low Pressure
PSR	Perfectly Stirred Reactor

MODEL PREPARATION

Combustor Model

The primary objective of this work was to create a chemical kinetic model to simulate the HES used in the PARTEMIS experimental test campaign [10]. In order to make this HES model as accurate as possible, however, it was important that the initial concentrations of each of the key combustion product species were clearly defined. Above all, it was apparent from previous work [8], that the production of the key species of interest, SO₃ and H₂SO₄, was highly dependant upon the mixing ratios of the oxidation radicals OH and O. While experimental measurements were made of OH at the exit of the HES during the PARTEMIS campaign, none were made at the combustor exit and it was also felt that using equilibrium calculations would not provide estimates of sufficiently high accuracy. For this reason, an additional kinetic model was developed to simulate the chemistry occurring within the test combustor. This was performed using the University of Leeds's Combustor Model Interface (CMI).

The CMI interface, based on the CHEMKIN PSR program [11], allows a sequence of perfectly stirred reactors to be used to represent different zones within a combustor. The PARTEMIS combustor was defined by a sequence of five PSRs, as shown in the representation of the combustor model given in Figure 1. The temperature and pressure of the fuel and air entering the first PSR were taken from the two operating

conditions of the combustor used in the experimental tests: Ordinary Cruise and Modern Cruise. These represent the cruise conditions of the actual model of combustor used in the tests, together with an updated condition designed to be more representative of modern engines.

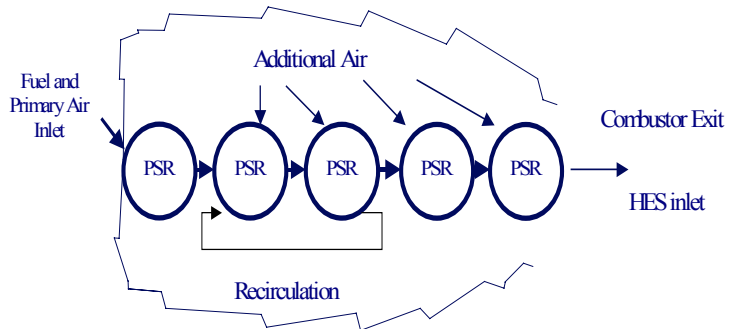


Figure 1 Schematic representation of combustor model

While the total amount of air entering the combustor was known from the experimental operating conditions, the amount entering each zone was not known with precision. This was calculated from the available information concerning the distribution of dilution air within the combustor. The inlet boundary conditions for each zone within the combustor were the outlet conditions from the previous zone together with an appropriate addition of dilution air. Although not used in this instance, the CMI is also capable of allowing for recirculation. Finally, the residence time within each zone was defined by the volume of the zone and the volumetric flow rate of the combustion gases passing through it.

Using the CMI model, the temperature and species concentration profiles were calculated at each zone of the combustor to produce ultimately a set of values at the exit of the final zone, corresponding to the combustor exit. These were validated against the measurements made during the experimental test campaign and used as inlet boundary conditions for the HES model described below. The chemical kinetic mechanism used within the combustor model was a previously developed kerosene scheme, updated to contain the same sulphur chemistry used in the subsequent HES model. As a result, the model could also be used to predict the concentrations of the key sulphur species, SO₂, SO₃ and H₂SO₄ within the combustor itself. It will be seen in subsequent sections, that this information was critical to understanding the chemical processes within the engine.

HES Model

The HES developed for the PARTEMIS experimental test programme consisted of an inlet duct, three pressure stages (HP, IP, LP) and an exit duct, all of which were recreated in the kinetic model. The model was produced using the program AURORA, which forms part of the CHEMKIN III software package [12]. The HES was considered to behave as a perfectly stirred reactor, in which the change in composition of the combustion products is predicted as a function of time as they

pass through its full length. For such a reactor, the change in gas composition is assumed to be controlled by the rates of chemical reaction rather than by those of physical mixing and the high levels of turbulent mixing in the combustor prior to the HES help to ensure the validity of this assumption. The principal advantage of assuming perfect mixing is that the resulting reduction in complexity is much less demanding in terms of computational time. As a result, it is possible to describe the chemistry of the gas mixture using a highly detailed reaction mechanism.

The reaction mechanism used in the HES model was developed by Hughes and Pilling as part of the PARTEMIS programme [13]. It is based on their own previous models for methane and nitrogen chemistry [14][15], with additional reactions evaluated and added to better describe the temperature and pressure regime encountered within the HES. The model also included an extended mechanism for the sulphur chemistry, which was again based on previous work [16]. The sulphur mechanism included reactions to describe the interaction between the key NO_x and SO_x species of interest in the current work. For this work, the sulphur mechanism was modified to incorporate revised rate coefficients from both recent theoretical calculations [17] and experimental measurements [18]. These will be seen to have a significant impact upon the sulphur conversion results obtained.

In order to model the HES, information was required about the physical properties within it at both power conditions used within the tests. These properties included the variation of pressure and temperature with distance down the HES, in addition to the residence times of the gases at each stage. These were based on a computational fluid dynamics (CFD) model of the HES, also performed as part of the PARTEMIS programme [19]. This CFD model was validated against the measured experimental data and provided profiles of temperature and pressure versus distance from the inlet to the HES. In order to apply these profiles to the HES model, they were converted to time-dependent profiles of temperature and pressure by applying the mean downstream velocity, calculated by CFD for each stage. The temperature and pressure profiles that were used in the HES model are given Figures 2 and 3 respectively.

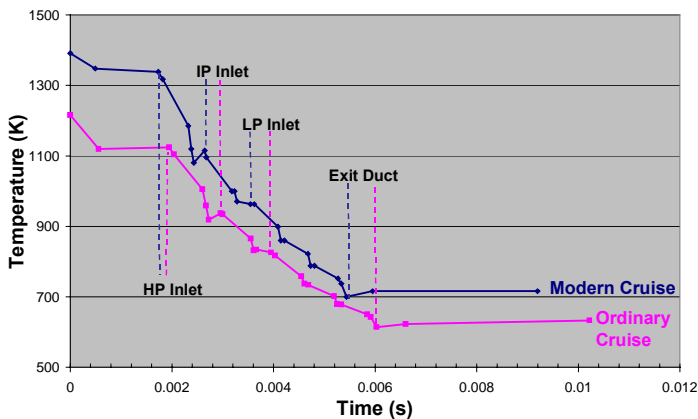


Figure 2 Temperature versus time profile in the HES model

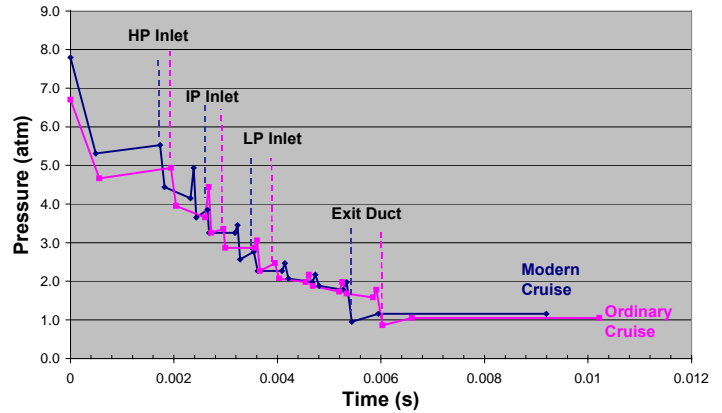


Figure 3 Pressure versus time profile in the HES model

COMBUSTOR MODEL RESULTS

The test measurements on the HES were performed at two operating conditions, Ordinary Cruise and Modern Cruise, and at three levels of fuel sulphur content, low (50 ppm) medium (400 ppm) and high (1300 ppm). There were, therefore, six possible combinations of operating condition and sulphur level, and the CMI combustor model was run for each of these in order to provide inlet boundary conditions for the HES model. The results for the medium sulphur level content at Ordinary Cruise and Modern Cruise conditions are shown in Table 1.

This table shows only the most important product species, but it is important to note that the concentration of all species were used to define the inlet boundary conditions of the HES model. The results are shown for one sulphur loading only because, with the exception of SO_2 , the concentration of each of the species shown is completely independent of the amount of sulphur in the fuel. Of the species in Table 1, the SO_2 values are the only ones that change and these scale exactly with the amount of sulphur in the fuel.

	Medium Sulphur	
	Modern Cruise	Cruise
O_2 (%)	15.4	15.6
H_2O (%)	4.4	4.3
CO_2 (%)	3.4	3.3
N_2 (%)	76.7	76.8
CO (ppm)	30	59
NO (ppm)	205	64
NO_2 (ppm)	5.6	4
SO_2 (ppm)	1.6	1.5
OH (ppm)	38	17
O (ppm)	1.5	0.9
Temp (K)	1391	1216
Press (atm)	7.8	6.7

Table 1 Combustor exit boundary conditions (medium sulphur loading)

In general, the results of the combustor model are in good agreement with the experimental measurements [10], especially at the Modern Cruise condition. The principal deviation between the experiments and the model was the temperature at the outlet of the combustor for the Ordinary Cruise condition, which was higher than the experimental measurement. It is possible that this over-prediction of temperature of the model at the Ordinary Cruise Condition will have led to a corresponding over-prediction of the concentration of the radical species OH and O. In turn, this will have affected the degree of oxidation of sulphur and nitrogen species.

In addition to providing an estimate of the boundary conditions at the inlet to the HES the other aim of the combustor model was to calculate the extent of sulphur conversion in the combustor, denoted by ϵ . Figure 4 shows the variation of this factor as the combustion gases pass through each of the five sequential zones representing the PARTEMIS combustor.

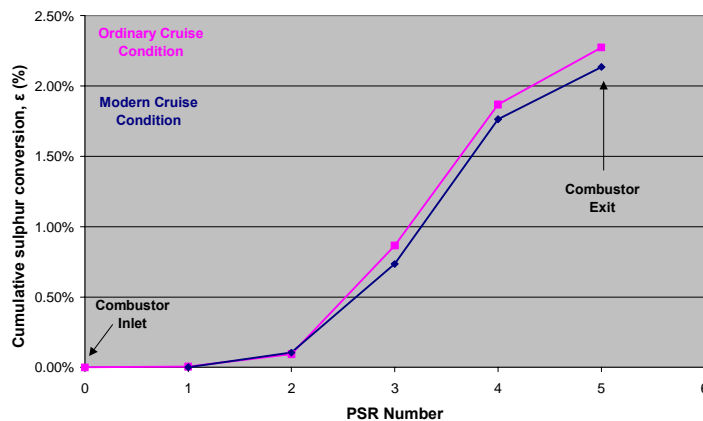


Figure 4 Conversion of S(IV) to S(VI) within combustor

These results show that the conversion of SO_2 to SO_3 and H_2SO_4 within the combustor does not differ substantially between the two conditions, with the value being only slightly higher for Ordinary Cruise, (2.2 %) than for Modern Cruise, (2.1%).

Sulphur conversion is dependent upon temperature and OH concentration, which are themselves interrelated. The reaction kinetics that lead to the formation of SO_3 from SO_2 are favoured by lower temperatures, but the concentration of OH tends to increase with temperature. There is therefore a trade-off that ultimately results in an intermediate temperature range within the combustor at which conversion to SO_3 is favoured. The marginally higher conversion observed for Ordinary Cruise is therefore a result of the lower temperatures of this condition.

The good agreement in temperature and bulk gas concentrations between the model and experiment provide a high degree of confidence in the combustor model at the Modern Cruise condition. This is less true at the Ordinary Cruise condition, however, since the temperature prediction of

the model will have a corresponding impact upon the validity of key species such as O and OH. Modelling a combustor is a very complex issue, because of the high degree of turbulent mixing and recirculation within it. The application of the Combustor Model Interface to the PARTEMIS combustor has proved an excellent first attempt at achieving this, but more work is needed in the future in order to improve the predictive capability of such a combustor model.

HOT END SIMULATOR MODEL RESULTS

The boundary conditions at the combustor exit calculated using the CMI model were used to provide initial mixing ratios for each species within the HES. Results were then obtained using the HES model for each combination of operating condition and sulphur level. Representative results are given, for medium sulphur loading, in Table 2. As for the combustor, repeating these calculations for the other fuel sulphur levels showed no change in any but the sulphur species. Also, there was no change in the efficiency of conversion, ϵ , from which it can be concluded that the degree of sulphur conversion is independent of the amount of sulphur in the fuel.

	Cruise Condition				
	Inlet to HES	HP sample point	IP sample point	LP sample point	Exit duct outlet
O2 (%)	15.6	15.6	15.6	15.6	15.6
H2O (%)	4.3	4.3	4.3	4.3	4.3
CO2 (%)	3.3	3.3	3.3	3.3	3.3
N2 (%)	76.8	76.8	76.8	76.8	76.8
CO (ppm)	57	48	48	48	48
NO (ppm)	63	60	59	59	59
NO2 (ppm)	5	7	8	8	8
SO2 (ppm)	1.5	1.5	1.5	1.5	1.5

	Modern Cruise Condition				
	Inlet to HES	HP sample point	IP sample point	LP sample point	Exit duct outlet
O2 (%)	15.4	15.4	15.4	15.4	15.4
H2O (%)	4.4	4.4	4.4	4.4	4.4
CO2 (%)	3.4	3.4	3.4	3.4	3.4
N2 (%)	76.8	76.8	76.8	76.8	76.8
CO (ppm)	30	17	15	15	15
NO (ppm)	205	206	203	198	198
NO2 (ppm)	6	5	7	10	10
SO2 (ppm)	1.6	1.6	1.6	1.6	1.6

Table 2 Change in bulk species concentrations through HES, (medium sulphur loading)

Table 2 shows that the bulk species undergo little modification in passing from the combustor to the HES exit. It is worth noting that there is no additional cooling air supplied to the HES, as there might be for an engine turbine, and so there is no external modification to the gas mixture. In addition, the conditions within the hot end simulator are too mild for significant combustion chemistry to continue. The only exceptions are CO, which demonstrates some additional oxidation in the early, high temperature stage of the HES, and the nitrogen oxides, which show conversion of NO to NO_2 as the reduction in temperature favours the dioxide

Of principal interest in the current work, however, are the changes to the aerosol precursor species and to the radical species that drive their oxidation. These changes can be seen graphically for the sulphur species, SO_2 , SO_3 and H_2SO_4 , and for the radicals O and OH in Figure 5 (Ordinary Cruise) and Figure 6 (Modern Cruise).

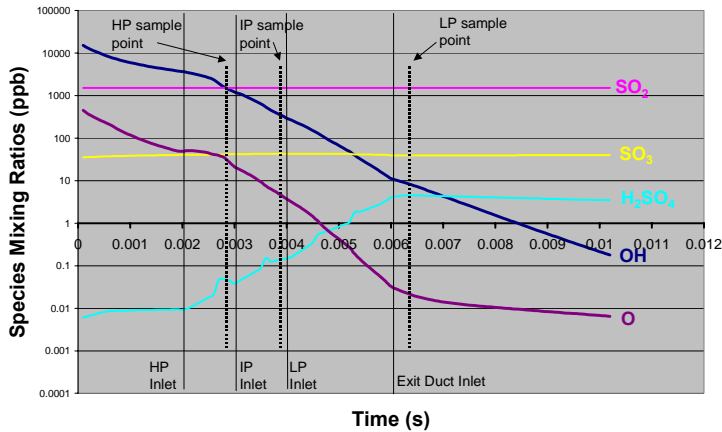


Figure 5 Mixing ratios v. time through HES. Ordinary Cruise, (medium sulphur loading).

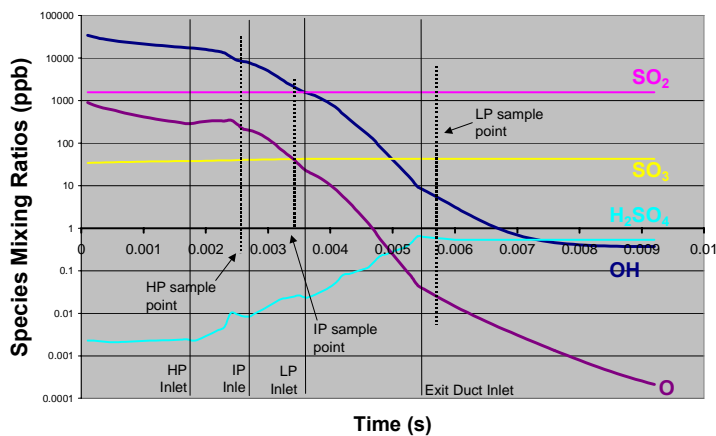


Figure 6 Mixing ratios v. time through HES. Modern Cruise, (medium sulphur loading).

Both graphs show a continuous decay in both O and OH through the HES, as these species contribute to the oxidation of CO, SO₂ and NO_x. The graphs also show the clear increase in sulphuric acid, which for both conditions occurs almost exclusively in the three pressure stages of the HES and not in the ducting before and after it.

The efficiency of conversion, ϵ , of SO₂ to SO₃ and H₂SO₄ has been plotted at all points from combustor exit to the exit of the HES, and typical results are shown in Figure 7 (Ordinary Cruise) and Figure 8 (Modern Cruise), for the medium sulphur condition. It can be seen that for both conditions, the rate of conversion is approximately the same throughout the early stages of the HES, up to the inlet of the LP stage. Thereafter it reduces rapidly such that by the time the gases leave the LP section of the HES, no further conversion is observed. Within the HES itself, the greater extent of conversion is observed at the Modern Cruise condition, for which $\epsilon = 0.61\%$, compared to the value of $\epsilon = 0.57\%$ at the Ordinary Cruise condition.

The results show that the sulphur conversion in the HES provides a relatively small contribution to the total conversion observed in the engine. The pink line in these figures represents

the total value of ϵ calculated including the production of S(VI) in the combustor. It is clear that the majority of the conversion has already occurred by the time that the gases leave the combustor. The values of efficiency, ϵ , at the combustor exit were calculated to be 2.1 % for Modern Cruise and 2.2 % for Ordinary Cruise, which represent 77 % and 79 % respectively of the total observed conversion. When the conversion within both the combustor and the HES are taken into account, the Ordinary Cruise condition shows marginally higher rates of conversion: $\epsilon = 2.79\%$ at Ordinary Cruise, compared with $\epsilon = 2.70\%$ at Modern Cruise.

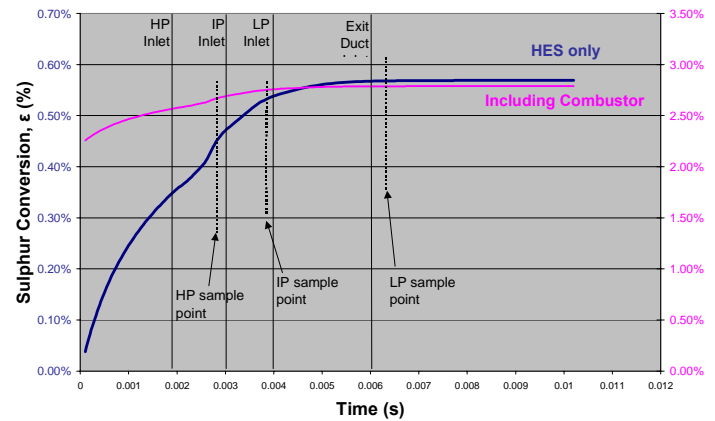


Figure 7 Conversion efficiency, ϵ , of S(IV) to S(VI), Ordinary Cruise, (medium sulphur loading)

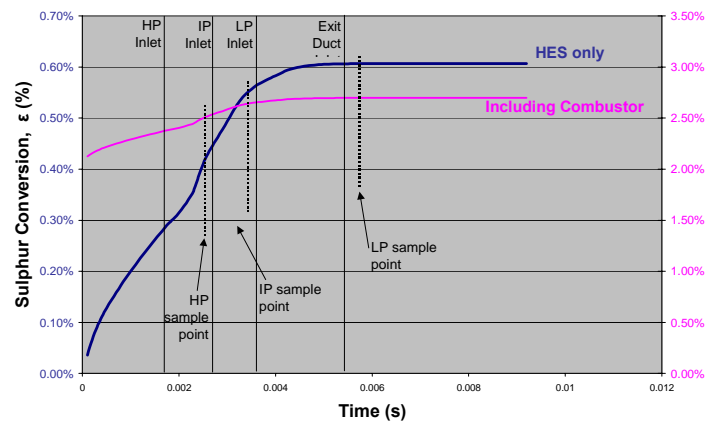


Figure 8 Conversion efficiency, ϵ , of S(IV) to S(VI), Modern Cruise, (medium sulphur loading)

The model was also used to calculate the production of HONO and HNO₃ species within the HES, with the results shown in Table 3. The first major increases in both species occur after the temperature has dropped significantly within the HP section of the HES. The concentrations of both species then continue to rise as the temperature drops further, until they reach their maximum values soon after the inlet to the LP section. This is the same position where the sulphur conversion reached its limit, and together these results suggest that this is

the point at which the radical concentrations become too low to drive further significant oxidation. Again, the results were found to be completely independent of fuel sulphur level.

	Cruise				
	Combustor exit	HP sample point	IP sample point	LP sample point	Exit duct outlet
HONO (ppb)	179	820	1302	1474	1470
HNO ₃ (ppb)	2	54	94	143	143
HONO/NOy (%)	0.26	1.2	1.9	2.1	2.1

	Modern Cruise				
	Combustor exit	HP sample point	IP sample point	LP sample point	Exit duct outlet
HONO (ppb)	104	1438	2521	3104	3023
HNO ₃ (ppb)	0.00	7	28	66	64
HONO/NOy	0.04	0.68	1.2	1.5	1.4

Table 3 Summary of calculations on HONO and HNO₃

DISCUSSION

Comparison with experimental results

In this section, comparison will be made between the model predictions and experimental measurements made of sulphur (VI) and OH radical concentrations during the PARTEMIS test campaigns. No experimental measurements were made of O atoms, HONO or HNO₃, so no such comparison can be made for these species.

Measurements of gaseous sulphur (VI) species were made by the Max Planck Institute for Nuclear Physics (MPI-K) using chemical ionisation mass spectrometry (CIMS) [19]. The results have been reported of measurements taken at the intermediate and low-pressure stages at both operating conditions. The measurements of S(VI) enabled the conversion factor, ϵ , to be calculated and these are compared against the model predictions in Figure 9.

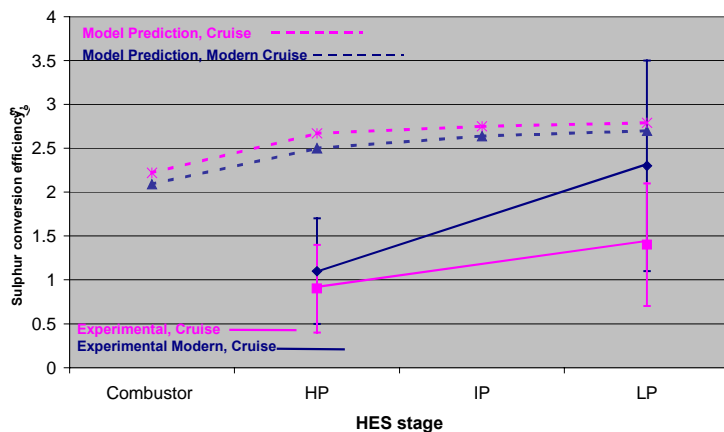


Figure 9 Comparison of calculated and experimental sulphur conversion, ϵ

The comparison shows that the prediction of total conversion at the end of the HES is close for both operating conditions, and is well within the experimental error for the Modern Cruise condition. The agreement is less good for the Ordinary Cruise condition, and is just outside the experimental error limits.

The other notable difference between the experimental and model results concerns the position at which the conversion

occurs. As has already been noted, the model calculations predict that all of the sulphur conversion will have occurred by the time that the gas enters the LP section of the HES. Indeed, the bulk of the conversion is calculated to occur before the gases leave the combustor. The experimental measurements, in contrast, suggest that the conversion occurs principally in the final, LP stage of the HES. Since the overall conversion is in good agreement, it would seem that either the combustor model is over-predicting the extent of conversion, or the experimental measurements are failing to account for all of the S(VI) in the early stages of the HES. The S(VI) species were reportedly prone to sample line losses and this could explain the low values measured during the experiment.

During the second experimental test campaign on the HES rig, Laser Induced Fluorescence (LIF) measurements were made at the HES exhaust in order to provide estimates of the concentration of OH radicals [21]. These experimental measurements are compared with the predictions of the HES model in Table 4. Optical access for the laser beam and fluorescence signal was available through small slits cut in the exit duct attached to the HES. The width of these slits limits the accuracy with which the sample position was known, which is reflected in the range of OH concentration predicted by the model. In each case, the higher value in predicted OH corresponds to the start of the slit, while the lower value corresponds to the downstream edge.

	Ordinary Cruise OH (ppb)	
	Experiment	Model
Medium Sulphur	0.76 ± 0.56	1.5 - 2.3
	Modern Cruise OH (ppb)	
	Experiment	Model
Medium Sulphur	0.66 ± 0.43	0.5 - 0.9
High Sulphur	0.67 ± 0.66	0.5 - 0.9

Table 4 Comparison of calculated and experimental [OH]

As with the sulphur conversion tests, the agreement between model and experiment is very good. This is especially true for the Modern Cruise condition, which again falls within the experimental error limits. It is also worth noting that the limited experimental results suggest that the value of OH concentration appears to be independent of sulphur content, a result that is consistent with the model predictions. At the Ordinary Cruise condition, the HES model over-predicts slightly the amount of OH at the exhaust. This over-prediction at Ordinary Cruise is consistent with the higher than experimental value of temperature, and therefore OH, calculated by the combustor model.

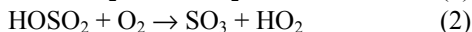
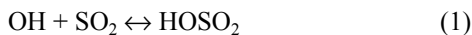
Comparison with previous results

The innovative use of the HES within the PARTEMIS programme has allowed a comparison to be made between a computer model and the experimental results for a simulated hot end of an engine. The results have shown an excellent agreement for the Modern Cruise condition and good agreement for the Ordinary Cruise condition. The unique nature of the

experiment makes it important that the current results be compared with previous results based on real engines. This is especially important since the mechanism used within the model has incorporated significant new experimental measurements.

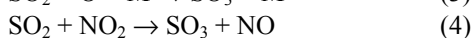
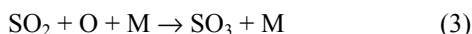
The pertinent comparison to be made is principally that of the conversion factor, ϵ , the ratio of S(VI) to S(IV). The values of sulphur conversion predicted by the current HES model are generally much lower than those calculated by earlier models describing real engines. In part, this will result from the differences in the temperature and pressure regime to which the gases are subjected in the combustor and turbine/HES section, but these are not sufficiently different to explain such wide variations in ϵ . The chemical kinetic mechanism used in the current model was therefore compared directly with the earlier study of the JT9D-7A by applying it to the identical boundary conditions used in that study [8]. A model was established using the current mechanism but with the temperature and pressure profiles and the combustor exit species utilised in the JT9D model.

Applying the current mechanism to the JT9D model results in a conversion factor, $\epsilon = 0.11\%$, which is very much lower than the previous calculation of 3.8% . Comparison of the two sets of results showed clearly that the predictions of OH and SO₂ profiles through the turbine were in good agreement, but that there were appreciable differences between the SO₃ and H₂SO₄ predictions. The reason for this is the significant changes made to the sulphur chemistry, following recent experimental and theoretical studies on the key sulphur conversion reactions, 1 and 2.



Recent experimental measurements of the rate of reaction 1 [18], and theoretical calculations of the heat of formation of the intermediate species, HOSO₂ [22] [23], both suggest that the overall conversion of SO₂ to SO₃ is much lower than previously thought. Analysis of the rates derived from these latest studies show that, at the key temperatures at which oxidation occurs, (~1000K), the reverse reaction rate, k_{-1} , is much faster than earlier measurements had suggested. As a result, there is much greater competition between the two reaction channels available to the intermediate species, HOSO₂. The decomposition channel, in which HOSO₂ reverts back to the reactants, is now much more important than previous models have suggested and at the temperatures found within the HES, this reaction dominates over the forward reaction to SO₃. It is for this reason that the rate of conversion of SO₂ to SO₃ and H₂SO₄ calculated by the current mechanism is much lower than that of all earlier models.

Despite this reduction in the rate of sulphur conversion by the reaction sequence involving HOSO₂, this path still dominates that of the alternative potential routes, reaction 3 and 4.



Rate of production analysis shows that at all positions within the HES, and for both conditions, by far the most important channel for SO₃ production is by reaction of SO₂ with OH. At higher operating temperatures, reaction 3 may become important but under the current conditions, the concentrations of O atoms are too low for this reaction to be of significance.

An important consequence of this increasing competition between the two reaction channels available to HOSO₂ is that the efficiency of sulphur conversion is now observed to be dependant upon the value used for the rate of the reaction between HOSO₂ and O₂. This is in contrast to the earlier results of Tremmel and Schumann [8], who found no such dependence upon this reaction. This result is especially important because the rate of this reaction is very poorly defined, especially at elevated temperatures. It is therefore recommended that this reaction be the subject of future study as it represents one of the greatest uncertainties in the calculation of sulphur conversion efficiency.

One further difference in the current results compared to some previous work concerns the position within the engine at which the sulphur conversion is seen to occur. The current combustor and HES models clearly show that sulphur conversion is predominantly complete as the gases leave the combustor exit, and only minimal additional conversion occurs within the turbine section. This is markedly different from the model predictions of Lukachko *et al.* [9], for which the bulk of the conversion occurs within the two turbine stages after the combustor exit. In spite of this apparent disagreement, the two sets of results can actually be seen to be broadly consistent by considering the dependence of the rate of conversion on temperature. This comparison can be seen in Figure 10, which shows the cumulative sulphur conversion as the temperature decreases through the engine. The results shown are for the Ordinary Cruise and Modern Cruise conditions of the current study, alongside the "Case 1" and "Case 2" results of Lukachko *et al.* [9].

The most immediate observation to be made from Figure 10 is the much higher conversion efficiencies calculated by Lukachko *et al.*. This is a result of the incorporation of revised rate coefficients in the current model, which inhibit conversion as discussed earlier in this section. Alongside this difference, however, it can be seen that at temperatures between 1600 K and 1000 K, all four conditions show a very similar rate of increase in conversion with temperature and of the four, only Case 1 of Lukachko *et al.* shows significant additional conversion below 1000 K. This good agreement, especially with Case 2, shows that the rate of sulphur conversion has a strong dependence upon temperature, irrespective of the position within the engine at which that temperature occurs. As a general rule, therefore, conversion will be more likely to occur in the combustor for lower rated engines, while for higher rated engines, it is more likely within the turbine.

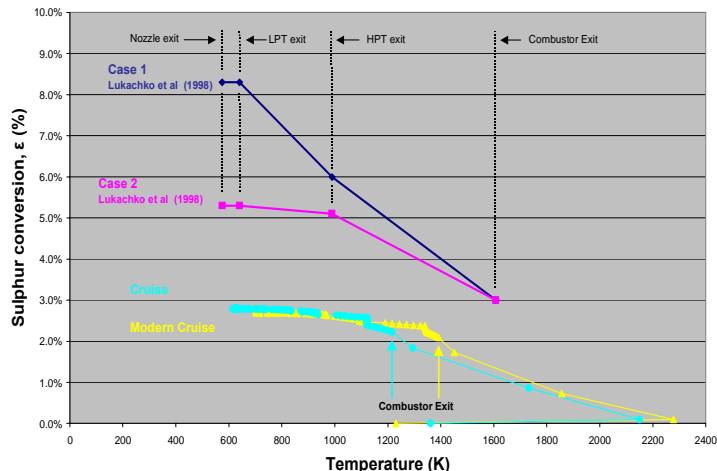


Figure 10 Cumulative sulphur conversion v temperature

The additional conversion below 1000 K for Case 1 of Lukachko *et al.* arises for two reasons. Firstly, the modifications to sulphur chemistry described above were such that for the current HES models at 1000K, the decomposition channel of the intermediate species HOSO_2 is much more important than the forward reaction to SO_3 and that conversion is therefore severely inhibited. In the earlier models, the two channels available to HOSO_2 are approximately equal, and it is therefore much more likely that conversion will occur. Of equal importance, however, is the concentration of the key OH radical, which reacts with SO_2 to produce HOSO_2 in the first instance. For the Ordinary Cruise, Modern Cruise and Case 2 conditions of the Lukachko model, by the time the engine reaches 1000K, the OH concentration has been depleted to such an extent that reaction with SO_2 is no longer significant. Case 1 of the Lukachko model, by contrast, still has significant amounts of OH, which allow conversion to continue up to the end of the LP turbine. The dependence of the chemistry upon OH emphasises the importance of further attempts to measure the concentration of this radical experimentally, including at the exit of a combustor.

The generally good agreement between the predictions of the HES and the experimental measurements provides a good basis for understanding the chemistry occurring within the post combustor region. It is clear that, consistent with previous studies, both the sulphur conversion efficiency and the production of HONO are governed by the chemistry of the OH radical. In the early stages of the HES, where the pressures and temperatures remain close to those found at combustor exit, rate of production analysis shows that the rate of change of OH is governed by the reaction with CO to form CO_2 . Once the temperature and pressure start to decrease further down the HES, the chemistry of OH is principally modified by the reaction with NO to form HONO. At all subsequent points within the HES, it is this reaction that dominates the OH chemistry. Ultimately, towards the exit of the HES there is insufficient OH to further oxidise either NO or SO_2 , and no

additional oxidation is observed. Moreover, this result suggests that in the exhaust plume of this engine, there would be very little additional conversion above that already observed at the engine exit. This is confirmed by plume modeling work also performed as part of the Partemis programme [24].

There is comparatively little loss of OH by reaction with SO_2 , simply because the concentration of NO is so much higher, even at the high sulphur Ordinary Cruise condition. As a result, the chemistry of nitrogen and sulphur oxides are effectively decoupled and there is no observable dependence of sulphur conversion on sulphur level. Conversely, the efficiency of sulphur conversion does depend on the concentration of OH radicals and it is correspondingly very important to ensure that this radical is predicted as accurately as possible.

CONCLUSION

A chemical kinetic model has been prepared which is able to simulate the gas phase chemistry occurring within the Hot End Simulator of the PARTEMIS programme. The model was developed using boundary conditions and a chemical mechanism obtained from other work packages within the project.

The results of the models were compared within the experimental measurements made during the PARTEMIS campaign and with previous studies on similar engine environments. Of particular interest were the oxidised sulphur species, SO_2 , SO_3 and H_2SO_4 , the nitrogen species, HONO and HNO_3 , and the radical species important in oxidation, OH and O. In general, agreement with experiment was very good, especially at the Modern Cruise condition. The predicted values of OH radical concentration and sulphur S(IV) to S(VI) conversion efficiency, ϵ , at the HES exit both matched experiment within the experimental error, at this condition. The agreement at the Ordinary Cruise condition was less good, but did not deviate too far from the experimental uncertainty limits. This deviation was believed to result from an over-prediction of the OH concentration at combustor exit by the CMI combustor model.

Overall, sulphur conversion efficiencies predicted by the current HES model were lower than previous models, as a result of recent experimental and theoretical studies of the key sulphur chemistry reactions. These result in a much slower rate of formation of SO_3 .

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