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PRELIMINARY EVALUATION OF THE ROLE OF K_2S IN MHD HOT STREAM SEED RECOVERY

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THE ROLE OF K_2S IN MHD
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SUMMARY

Results are presented for recent analytical and experimental studies of the role of K_2S in MHD hot stream seed recovery. The existing thermodynamic data base was found to contain large uncertainties and to be nonexistent for vapor phase K_2S . Knudsen cell mass spectrometric experiments were undertaken to determine the vapor species in equilibrium with $K_2S(c)$. K atoms and S_2 molecules were found to be the major vapor phase species in vacuum, accounting for greater than 99% of the vapor phase. Combustion gas deposition studies using No. 2 diesel fuel were also undertaken and revealed that condensed phase K_2SO_3 may potentially be an important compound in the MHD stream at near-stoichiometric combustion.

INTRODUCTION

One of the concepts that has emerged for open-cycle MHD design is the use of the seed compound, potassium carbonate (K_2CO_3), to remove fuel-derived sulfur from the combustion stream by forming potassium sulfate (K_2SO_4). This process of sulfate formation is followed by some sort of hot stream seed recovery in which the K_2SO_4 is removed from the hot stream and reprocessed in an external chemical plant that not only yields the K_2CO_3 back again, but also converts the original fuel sulfur into an economically viable form such as elemental sulfur or sulfuric acid.

The best reprocessing scheme to employ on the K_2SO_4 is not clear at this time because there are deficiencies in the chemistry and thermodynamic data available on many compounds in the potassium-sulfur system. However, a common feature of nearly all K_2SO_4 seed reprocessing schemes is the intermediate formation (e.g., via solid carbon or gaseous reduction) of potassium sulfide (K_2S) which can be converted to K_2CO_3 and hydrogen sulfide gas (H_2S) (refs. 1 and 2). Hence, the idea of avoiding the formation of K_2SO_4 either in whole or in part by condensing K_2S directly from a slightly oxygen deficient stream is being considered. This would greatly reduce or possibly eliminate the capital cost and complexity associated with a reduction reactor. This concept was first advocated by W. D. Halstead of the Central Electricity Research Laboratories in England (ref. 3). In more recent years, the AVCO Everett Research Laboratory has advocated this approach first in their subcontractual effort to the General Electric Company's Phase II of the ECAS Study (ref. 4), and most recently in their ETF Conceptual Design Study (ref. 1).

This " K_2S seed reprocessing variation" would necessitate an initial combustion under reducing fuel-rich conditions which would open the possibility of K_2S formation instead of K_2SO_4 (ref. 3). The gaseous combustion products from this fuel-rich mixture would flow through the MHD channel. The K_2S would potentially be condensed from the stream, and a second combustion would then be carried out under air-rich, sulfur-free (ideally) conditions to complete the combustion process. NO_x formation is expected to be minimized in the first combustion because of the O_2 deficiency, and in the second combustion because of the lower temperatures and long residence times involved.

In Figure 1, the hot stream side arrangement of the AVCO ETF conceptual plant is shown for the heat recovery and seed recovery components. As the hot stream exits the diffuser of the MHD generator at 2292 K, it passes through the slag furnace for slag removal. Stream conditions are slightly reducing and remain such as the stream passes through the seed recovery furnace. Secondary air is injected after the seed recovery furnace at 1289 K to complete combustion. Hence, reducing conditions are established at the seed recovery furnace that potentially could lead to direct K_2S seed

recovery while oxidizing conditions are established in the air heater furnace, the economizers, and the electrostatic precipitator that could lead to K_2SO_4 seed recovery for any seed material being carried into these sections.

Calculations have shown that residence times and mixing for combustion species in the MHD stream are adequate for attainment of chemical equilibrium (ref. 4), except possibly for NO_x species, which do not concern us here. It is therefore logical to perform equilibrium calculations that predict which species will form, what their concentrations will be, and under what conditions they may be expected to condense from the stream. Such calculations can be made by use of the NASA Lewis Complex Chemical Equilibrium computer program (CEC) (ref. 5) for any fuel composition, fuel/oxidant ratio, and seed concentration. However, these calculations are meaningful only if adequate thermodynamic data are available. Unfortunately, the thermodynamic data available for $K_2S(s,l)^*$ (refs. 6 and 7), have a relatively large uncertainty. An extensive literature search showed that no data exist for $K_2S(g)$. Consequently, a precise and accurate evaluation of the "K₂S seed reprocessing variation" is impossible until such data are forthcoming. In fact, exact definition of the heat recovery and seed recovery component interfaces and operating conditions are impossible for a system such as the AVCO system described above. The situation regarding the data is similar for potassium sulfite (K_2SO_3) which, under fuel-rich combustion conditions, potentially could be produced in significant quantities along with K_2S . Again, the thermodynamic data for $K_2SO_3(s,l)$ are probably quite inaccurate (ref. 8) and no data exist for $K_2SO_3(g)$.

The considerations above have immediate impact on several problems, for which experimental and theoretical studies appear essential. These studies are:

1. Determination of the conditions necessary for condensing K_2S , K_2SO_4 , K_2SO_3 or K_2CO_3 from the combustion stream (e.g., fuel/oxidant ratio, temperature and sulfur and seed level). The resultant data would define the proper placement and operation of heat recovery and seed recovery components.

2. Assessment of the importance of K_2SO_3 as a seed recovery product from fuel-rich combustion.

3. Characterization of the condensed phases obtained from K_2CO_3 seeding and fuel-rich combustion. Possible condensed phases for the K-S-O-C system are KO_x , K_2SO_4 , K_2S , K_2S_x , K_2SO_3 and K_2CO_3 ; mixtures or solutions made up of these phases may also result.

4. Assessment of the containment problem. K_2S is known to be very reactive toward metals at high temperatures; K_2SO_3 is likely to be corrosive; and K_2SO_4 and K_2CO_3 are known to be highly corrosive.

*Throughout this paper (c) refers to condensed state, either solid (s) or liquid (l), (g) refers to gas.

5. Reclamation of K_2CO_3 from the condensed seed product.

Because such studies are scarce or nonexistent, systems evaluations consistently bog down. Accordingly, experimental efforts were begun, and top priority was given to K_2S . The data needed are common to other problems and the upstream occurrence of K_2S most directly addresses the idea of avoiding K_2SO_4 condensation. Therefore, work was begun to obtain data for the high temperature vaporization and condensation of K_2S , and to characterize the deposits from fuel-rich flames seeded with K_2CO_3 .

EXPERIMENTAL APPARATUS AND PROCEDURE

Mass Spectrometric Vaporization Experiments.- Knudsen cell mass spectrometric experiments (ref. 9) were undertaken to determine the vapor species in equilibrium with $K_2S(c)$. The Knudsen method is an equilibrium determination in which the gas phase sample is caused to effuse through a small orifice in the sample container (Knudsen cell). The rate at which a given species effuses from the cell determines the recorded intensity of that species as detected by the mass spectrometer. Intensity can be related to the equilibrium vapor pressure of the species above the condensed phase in the Knudsen cell. The present work was undertaken in the High Temperature Mass Spectrometry Laboratory at NASA Lewis, using a CEC Model 21-110 Mattauch-Herzog type double-focusing instrument (ref. 10).

The K_2S sample was obtained packed under N_2 from Alfa Division, Ventron Corporation, and was used without further purification. This material was labeled " K_2S_x , S > 12.8%." Two series of runs were performed with the mass spectrometer. For each, the sample bottle was opened and the Knudsen cell loaded in a N_2 dry box. The loaded Knudsen cell was transferred as quickly as possible to the mass spectrometer for pump down to the 10^{-6} torr range. Even with these precautions, hydrolysis with water from the air is expected to have occurred to some extent. This is inferred from the observed behavior of small quantities of $K_2S_x(c)$ deliberately exposed to air; immediate surface hydrolysis was noted as H_2S gas was given off. On prolonged exposure, such samples became tacky and eventually deliquesced.

Combustion Gas Deposition Experiments.- The objectives of flame deposition experiments using fuel-rich combustion and K_2CO_3 seeding were to test whether chemical equilibrium is reached in the exhaust stream and to determine what potassium-containing phases would deposit on a target collector immersed in the combustion product gas stream. An ideal experiment would have involved an actual coal-fired stream with about 4% S and provisions for mounting a cooled collector in the stream. Because no such facility was readily available, we used a Mach 0.3 burner rig at NASA Lewis (ref. 11). For these experiments, the burner rig was adapted to burn No. 2 diesel fuel and equipped to permit K_2CO_3 seeding as an atomized aqueous spray fed directly into the combustion chamber. A rotating target was located in the exhaust stream.

No. 2 diesel fuel was chosen because it typically has the highest sulfur content of the fuels that can be used on the burner rig which was available. Analysis of the fuel employed gave 0.197% S by weight. The concentrations of the seed substance, K_2CO_3 , was maintained at a low value of about 3 ppm in the initial experiments.

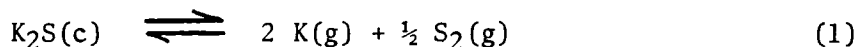
RESULTS AND DISCUSSION

Mass Spectrometric Vaporization Experiments.- Results from mass spectrometry are given in Table I. For the Series 1 experiment, the sample was heated in a molybdenum Knudsen cell for a total of 9 hours. After about 6 hours, the intensities of K^+ and S_2^+ were observed to be decreasing and the ratio K^+/S_2^+ increasing. The vacuum was broken for sample examination, and it was immediately obvious that the sample had reacted with the molybdenum cell though the melting point of the sample presumably had not been reached (m.p. K_2S is $948^\circ C$). A black reaction product covered the cell orifice. X-ray powder diffraction showed the reaction product to be $KMoS_2$ (JCPDS Card No. 18-1064).

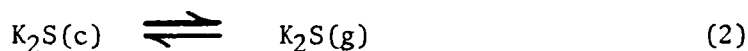
In the Series 2 experiment, the K_2S sample was loaded into an alumina liner in a tantalum cell. The objective in Series 2 was to measure the temperature dependence of K^+ , S_2^+ and K_2S^+ (while staying below the temperatures where the trouble had occurred previously), thereby establishing a $\ln P$ vs. $1/T$ or "second law" vapor pressure curve for $K_2S(c)$. Again, however, after several hours of heating, signals for K^+ and S_2^+ were observed to fall off (as in Series 1). On opening the system, no reaction was apparent between the K_2S and the alumina liner, but a white reaction product was present in the orifice of the tantalum cell so that the orifice was plugged. X-ray powder diffraction showed the product to be $KTaO_3$ (JCPDS Card No. 2-822), and it is hypothesized to be the result of products from a reaction between the cell and the sample. No $K_2S(c)$ sample was recovered from Series 2.

The mass spectrometric results summarized in Table I establish that the major species above $K_2S(c)$ are $K(g)$ and $S_2(g)$ with minor amounts of $K_2S(g)$. Caution should be applied in using the results in quantitative calculations, however, because the original sample is known to have contained greater than stoichiometric amounts of S. Furthermore, the extent of hydrolysis the sample experienced in being transferred into the mass spectrometer is not known. Measured intensities could not be converted to absolute partial pressures because no calibration was performed.

Vaporization and Condensation of $K_2S(c)$.- No previous reports of experimental studies on the vaporization behavior of $K_2S(c)$ were found in the literature. The present mass spectrometric experiments establish that the reaction



probably describes the major mode of vaporization in vacuum. Another possibility to be considered is that $K_2S(c)$ vaporizes to a molecule with the same stoichiometry as the condensed phase



Heywood and Womack (ref. 12) apparently assumed that reaction (2) represented the major mode of vaporization of $K_2S(c)$. However, the present mass spectrometric experiments establish that in vacuum, less than one percent of the vapor phase consists of K_2S molecules.

If one assumes that K_2S establishes equilibrium with its vapors according to reaction (1), calculations of the vapor pressures of $K(g)$ and $S_2(g)$ can be made. Equilibrium vapor pressures for reaction (1) may be calculated using Gibbs' free energy functions and enthalpies of formation for $K(g)$ and $S_2(g)$ (ref. 13) and for $K_2S(c)$ (ref. 7). However, uncertainties in the accuracy of the available thermodynamic data impose a problem. The most up-to-date summary of thermodynamic functions for $K_2S(c)$, superseding an earlier compilation by Mills (ref. 6), is given in the JANAF Tables (ref. 7). The heat of formation ($\Delta H_f^{\circ}, 298$) is an average value from the calorimetric work of Rengade and Costeanu (ref. 14) reported in 1914, and that of Letoffe et al (ref. 15) reported in 1974. An earlier value, reported by Sabatier (ref. 16) in 1881, was discounted. The estimated uncertainty in $\Delta H_f^{\circ}, 298$, is given as ± 3 kcal/mole (ref. 7). Heat capacity data for $K_2S(s)$ have been reported only once, by Dworkin and Bredig (ref. 17). The value for the standard entropy is based on estimates by Freeman (ref. 18), Voronin (ref. 19) and the JANAF group (ref. 7) and does not involve a direct experimental determination. Thermodynamic functions for $K_2S(l)$ are based on heat capacity measurements by Dworkin and Bredig (ref. 17) and have been extrapolated to cover a range of hundreds of degrees, even though the measurements only covered a range of 39 degrees. Thus, calculation of the vapor pressures over $K_2S(c)$ are uncertain to the degree that uncertainties exist in the data for this condensed phase.

Subject to the above reservations, equilibrium pressures for reaction (1) are listed in Table II and presented graphically in Figure 2. Because no thermodynamic data are available for $K_2S(g)$, a similar calculation cannot be carried out for reaction (2).

The equilibrium constant K_p for reaction (1) is given in terms of partial pressure by

$$K_p = P_{K(g)}^2 \cdot P_{S_2(g)}^{1/2} \quad (3)$$

If we assume that $K_2S(c)$ vaporizes congruently, and maintain the necessary element balance, then

$$P_{S_2(g)} = P_{K(g)} / 4 \quad (4)$$

Equation (4) can now be substituted into equation (3) to yield

$$K_p = 1/2 P_{K(g)}^{5/2} \quad (5)$$

The total pressure above $K_2S(c)$ is

$$P_T = P_{K(g)} + P_{S_2(g)} = 5/4 P_{K(g)} \quad (6)$$

Whenever $P_{S_2(g)}$ and $P_{K(g)}$ in a system attain values such that their combination according to equation (3) yields a numerical value equal to or greater than K_p , the condensation of $K_2S(c)$ may be expected to occur.

Alternatively, considering reaction (2), one sees that if the concentration (or partial pressure) of $K_2S(g)$ becomes equal to its saturated vapor pressure, then $K_2S(c)$ condensation would again be expected to occur. These situations are examples of the "pay off" available from a knowledge of saturated vapor pressures for MHD applications.

Heywood and Womack (ref. 3) employed a thermodynamic treatment to describe the deposition of $K_2S(c)$ from an MHD combustion gas stream. Some comments regarding their treatment and results are in order because we question the data and procedures presented in reference 3. We feel that their approach to the prediction of the formation of a condensed phase is a great oversimplification and misinterpretation of the problem because it does not take into account all of the possible interacting chemical equilibria simultaneously. Nonetheless, it is instructive to proceed through this example in order to elucidate the deficiencies. The starting point is Figure 9.9 on page 65 of reference 3, which is reproduced as Figure 3 in this report. The solid lines for K_2S , K_2CO_3 and K_2SO_4 represent the "concentrations" of the "major" potassium-containing species in an oil-fired MHD exhaust, with 1.0 atom percent potassium seeding, plotted against O_2 concentration. Because the authors of this figure probably did not have any data for the gaseous K_2CO_3 or K_2S molecules, and because no thermodynamic parameters are given or referred to, it is impossible to determine on what basis they calculated the so-called "pressures" (or "concentrations"). Nevertheless, the three molecules, K_2S , K_2CO_3 , and K_2SO_4 , are considered by the authors of reference 3 to be the major potassium-containing species at 1500 K. We have plotted the saturated vapor pressures of the K_2CO_3 (ref. 20) and K_2SO_4 (ref. 21) molecules for the purpose of examining condensation conditions relative to the MHD problem. Unfortunately, no value for the $K_2S(g)$ pressure is available. Because the predicted concentration of K_2SO_4 is greater than its vapor pressure for all stoichiometries to the left of about 0.6 volume percent O_2 deficient, $K_2SO_4(c)$ is expected to condense. $K_2CO_3(c)$ should not condense at 1500 K, and no conclusion can be made regarding $K_2S(c)$. Other than the uncertainties which have been mentioned, it is clear that the vapor species used by Heywood and Womack under reducing conditions is $K_2S(g)$ rather than $K(g)$ and $S_2(g)$. Just how much difference this discrepancy amounts to cannot be assessed without measured equilibrium vapor pressure data for $K_2S(g)$. In addition, other potassium-containing molecules, such as KOH , are expected to be important species in a combustion gas. These species are ignored in the treatment in

reference 3. A more comprehensive method for predicting deposition on the basis of thermodynamic data is given below.

Combustion Gas Deposition Experiments.- Several experiments were carried out with stainless steel or Waspalloy tubes at about 960 K as collectors. No definitive results regarding the chemical composition of the deposits could be ascertained from these experiments because the collection tubes sustained severe corrosive attack.

Significant results were obtained, however, in an experiment when an inert platinum collector was used. The fuel/air ratio was maintained at a value of 0.049 and the collector temperature at 816 K. A small amount of a yellow-white deposit was collected in the two-hour experiment. X-ray analysis of the "waxy" deposit yielded only two powder diffraction lines attributable to the deposit. The two lines were unidentifiable. A repeat of x-ray analysis three days later on the same sample gave an unmistakable pattern for $K_2SO_3 \cdot 2H_2O$ (JCPDS Card No. 1-895). Apparently the deposit had converted from an amorphous to a crystalline form. This preliminary result is particularly interesting because it indicates the possibility of having to cope with K_2SO_3 as a seed recovery product and because it was obtained under air-rich conditions.

Chemical Equilibrium Computer Program Calculation of Combustion Gas and Deposit Compositions.- The NASA Lewis Complex Chemical Equilibrium computer program (ref. 5) was used to calculate adiabatic flame temperatures, compositions of combustion gas at any temperature, composition of condensed pure phases (if any form), and thermodynamic dew points for condensation. References 22 and 23 give pertinent examples of these sorts of applications. To calculate the amount of deposit expected requires the use of additional sophisticated mass transport theory (see refs. 11 and 24) which is beyond the scope of the present work. Tables III to VI contain the results of equilibrium calculations for various burner rig conditions with the No. 2 diesel fuel which was employed in the experiments.

It should be pointed out again that reaction (1) is assumed for the vaporization of K_2S . No K_2S gas molecule is considered, and K_2SO_3 gas is also not considered in the program because no thermodynamic data exist for such a molecule, that is, if one exists at all. It is expected that even if data for $K_2S(g)$ and $K_2SO_3(g)$ were added into the calculations at a later time, the results would not be significantly different, because from our point of view, these are relatively minor vapor species. The largest uncertainties exist in the data for $K_2S(s,1)$, $K_2SO_4(g)$, and $K_2CO_3(g)$. An effort should be made to obtain improved data for these phases which might significantly affect the results of calculations.

Two sets of calculations were performed. The first set corresponds to the sulfur and K_2CO_3 seed levels used in the burner rig experiments. The calculated results presented in Tables III and IV are for various equivalence ratios representing oxidizing, stoichiometric and reducing combustion conditions. The results indicate that the condensate expected is $K_2SO_4(c)$ on the oxidizing side and $K_2CO_3(c)$ on the reducing side of stoichiometry. For the conditions considered herein, no $K_2S(c)$ or $K_2SO_3(c)$ condensates are predicted by the equilibrium calculations. On the reducing side of stoichiometry, most of the sulfur exists as $H_2S(g)$ at low temperatures while on the oxidizing side $SO_2(g)$ is predominant.

The second set of calculations are for a hypothetical burner rig case. For this case, the sulfur level was set at 4 weight percent in the fuel and 1 weight percent K_2CO_3 was added to the air. The results of the calculations are given in Tables V and VI. One significant observation is that $K_2S(c)$ is predicted to condense under certain conditions. $K_2S(c)$ appears under reducing conditions and at relatively high temperatures, i.e., 1300-1400 K for $\phi > 1.15$. The temperature for the onset of condensation of $K_2S(c)$ is found to be a sensitive function of the S- and K-seed level as well as the fuel/air ratio. At lower temperatures, $K_2CO_3(c)$ is predicted as the stable condensed phase. Again, most of the vapor phase sulfur exists as $H_2S(g)$. Experimental work with a combustion system of the compositions considered here should be undertaken to test the thermochemical predictions.

CONCLUSIONS

1. Knudsen cell mass spectrometry was used to show that $K_2S(s)$ vaporized, in vacuum, to give mainly K atoms and S_2 molecules.
2. The $K_2S(g)$ molecule exists, but is not a major component in the K-S system under the conditions investigated.
3. $K_2SO_3 \cdot 2H_2O$ was shown to be the deposit from a burner rig flame with a fuel/air weight ratio of 0.049. This was an unexpected and unexplainable result. Previous experiments with potassium-seeded flames have yielded K_2SO_4 deposits (ref. 25). However, sulfite species are indeed important in such systems as sodium/sulfur/oxygen and calcium/sulfur/oxygen.
4. Equilibrium calculations describing the burner rig runs (0.197 weight percent S in the fuel and 3 ppm K_2CO_3 in the air) predict that $K_2SO_4(c)$ should deposit under air-rich conditions, and that $K_2CO_3(c)$ should deposit under fuel-rich conditions. The calculations did not predict the formation of either $K_2S(c)$ or $K_2SO_3(c)$.
5. Equilibrium calculations for a hypothetical system with 4 weight percent S in the fuel and 1 weight percent K_2CO_3 in the air predict that $K_2SO_4(c)$, $K_2CO_3(c)$ and $K_2S(c)$ can form under specific conditions as a function of flame stoichiometry and temperature.
6. Sufficient data exist for $K_2S(c)$ so that pressures for $K(g)$ and $S_2(g)$ can be estimated for this system. However, the thermodynamic data in the literature for $K_2S(s,l)$ have large uncertainties associated with them. A complete and reliable determination of the mode of vaporization of K_2S should be carried out. The type of data desired includes a determination of whether $K_2S(c)$ vaporizes congruently or not, a precise determination of the composition of the vapor phase over $K_2S(c)$, vapor pressures and heat of vaporization for the gaseous species, and molecular structure parameters for $K_2S(g)$. The heat and entropy of formation of $K_2S(c)$ should be redetermined as well as heat capacities for the solid and liquid phases.

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TABLE I - KNUDSEN EFFUSION MASS SPECTROMETRIC
 DATA FOR K_2S VAPORIZATION AT 30 ELECTRON
 VOLTS IONIZING ENERGY

(a) Series 1, temperature = 1117 K

Species sought	m/e	Species found	Relative intensity*	Probable parent molecular species
K^+	39	K^+	100	K
S_2^+	64	S_2^+	22	S_2
K_2S^+ ($K_2O_2^+$)	110	K_2S^+	18	K_2S
$K_2S_2^+$	142	$K_2S_2^+$	0.015	K_2S_2
KS^+ (KO_2^+)	71	KS^+	0.023	K_2S
K_2O^+	94	K_2O^+	0.015	K_2O
KOH^+	56	None	0	----
KO^+	55	None	0	----

(b) Series 2, temperature dependence of $^{39}K^+$ and $^{64}S_2^+$

Point	Temperature, K	Relative intensity, K^+	Relative intensity, S_2^+
1	1007	50.6	29.0
2	1054	100.0	43.2
3	1066	96.3	33.3
4	1024	46.9	7.4
5	1022	29.6	5.9
6	1051	41.4	7.4
7	1082	51.2	11.1
8	1102	79.0	15.3
9	1070	48.1	4.7
10	1017	34.6	1.3
11	1102	82.7	5.4

* Maximum observed throughout series 1 relative to the maximum K^+ observed

Note K_2S^+ was not detectable in series 2. The temperatures were lower and the Knudsen cell orifice smaller than for series 1.

TABLE II - VALUES OF THE EQUILIBRIUM VAPOR
 PRESSURES OF K(g) AND S₂(g) OVER K₂S(c)
 CALCULATED FROM THERMODYNAMIC
 DATA IN THE LITERATURE

Temperature, K	P _{K(g)} , atm	P _{S₂(g)} , atm	P _{Total} , atm
1000	4.34 × 10 ⁻⁷	1.09 × 10 ⁻⁷	5.43 × 10 ⁻⁷
1100	7.9 × 10 ⁻⁶	1.45 × 10 ⁻⁶	7.24 × 10 ⁻⁶
1200	4.85 × 10 ⁻⁵	1.21 × 10 ⁻⁵	6.06 × 10 ⁻⁵
1300	2.76 × 10 ⁻⁴	6.90 × 10 ⁻⁵	3.45 × 10 ⁻⁴
1400	1.20 × 10 ⁻³	3.00 × 10 ⁻⁴	1.50 × 10 ⁻³
1500	4.24 × 10 ⁻³	1.06 × 10 ⁻³	5.30 × 10 ⁻³

TABLE III - CALCULATED COMBUSTION GAS COMPOSITIONS* FOR SEVERAL FLAME STOICHIOMETRIES

[Concentrations as mole fractions]

Species	c = 0.00 (oxidizing)			c = 1.00 (stoichiometric)			c = 1.10 (reducing)		
	Temperature, K								
	2176**	1500	900	2268**	1500	900	2270**	1500	900
K ₂ CO ₃ (g)	1.0 × 10 ⁻¹⁶	2.0 × 10 ⁻¹⁴	8.8 × 10 ⁻²⁴	4.3 × 10 ⁻¹⁷	1.9 × 10 ⁻¹⁴	6.2 × 10 ⁻¹⁹	2.5 × 10 ⁻¹⁷	1.2 × 10 ⁻¹⁴	9.9 × 10 ⁻¹²
K ₂ O(g)	1.0 × 10 ⁻¹⁷	4.3 × 10 ⁻¹⁹	-----	4.0 × 10 ⁻¹⁷	3.8 × 10 ⁻¹⁹	-----	2.6 × 10 ⁻¹⁷	2.8 × 10 ⁻¹⁹	-----
K ₂ SO ₄ (g)	3.1 × 10 ⁻¹⁶	8.2 × 10 ⁻¹⁰	2.1 × 10 ⁻¹⁰	3 × 10 ⁻¹⁷	4.1 × 10 ⁻¹¹	2.1 × 10 ⁻¹⁰	8.2 × 10 ⁻¹⁸	7.8 × 10 ⁻¹⁴	1.3 × 10 ⁻¹³
K(g)	2.4 × 10 ⁻⁷	2.4 × 10 ⁻⁹	7.8 × 10 ⁻²¹	9 × 10 ⁻⁷	1.0 × 10 ⁻⁸	7.3 × 10 ⁻¹⁶	5.1 × 10 ⁻⁷	1.6 × 10 ⁻⁷	8.0 × 10 ⁻¹⁰
KO(g)	1.9 × 10 ⁻⁹	6.1 × 10 ⁻¹¹	6.5 × 10 ⁻²²	4.4 × 10 ⁻⁹	1.6 × 10 ⁻¹¹	4.4 × 10 ⁻²²	2.1 × 10 ⁻⁹	7.5 × 10 ⁻¹³	6.6 × 10 ⁻²¹
KOH(g)	9 × 10 ⁻⁷	1.2 × 10 ⁻⁶	1.4 × 10 ⁻¹¹	7.7 × 10 ⁻⁷	1.2 × 10 ⁻⁶	8 × 10 ⁻¹¹	6.3 × 10 ⁻⁷	9.9 × 10 ⁻⁷	1.4 × 10 ⁻⁷
KH(g)	4 × 10 ⁻¹¹	6.4 × 10 ⁻¹⁵	-----	1.1 × 10 ⁻¹⁰	1.3 × 10 ⁻¹³	1.7 × 10 ⁻²²	2.4 × 10 ⁻¹⁰	7 × 10 ⁻¹¹	4.5 × 10 ⁻¹⁴
KCN(g)	2.9 × 10 ⁻¹⁶	2.0 × 10 ⁻²²	-----	3.6 × 10 ⁻¹⁵	3.6 × 10 ⁻¹⁹	-----	1 × 10 ⁻¹⁴	8 × 10 ⁻¹³	7.7 × 10 ⁻¹²
K ₂ (g)	1.3 × 10 ⁻¹⁶	5.1 × 10 ⁻²⁰	-----	2 × 10 ⁻¹⁶	9.1 × 10 ⁻¹⁹	-----	5 × 10 ⁻¹⁶	2.3 × 10 ⁻¹⁶	1.0 × 10 ⁻¹⁹
(KOH) ₂ (g)	8 × 10 ⁻¹⁶	6.9 × 10 ⁻¹⁴	1 × 10 ⁻²³	1.7 × 10 ⁻¹⁶	6.8 × 10 ⁻¹⁴	2.2 × 10 ⁻¹⁸	1.1 × 10 ⁻¹⁶	4.8 × 10 ⁻¹⁴	1 × 10 ⁻¹¹
H ₂ S(g)	2.1 × 10 ⁻¹¹	1 × 10 ⁻¹⁷	-----	1.5 × 10 ⁻¹⁰	4.8 × 10 ⁻¹³	1.3 × 10 ⁻¹³	9.6 × 10 ⁻⁹	1.7 × 10 ⁻⁵	1.2 × 10 ⁻⁴
H ₂ SO ₄ (g)	6.0 × 10 ⁻¹⁴	5.2 × 10 ⁻¹²	1.1 × 10 ⁻¹¹	2.7 × 10 ⁻¹⁴	1.2 × 10 ⁻¹³	1.2 × 10 ⁻¹²	1.1 × 10 ⁻¹⁴	8.0 × 10 ⁻¹⁶	9.8 × 10 ⁻²³
SO ₂ (g)	1.0 × 10 ⁻⁴	1.0 × 10 ⁻⁴	5.3 × 10 ⁻⁵	1.1 × 10 ⁻⁴	1.1 × 10 ⁻⁴	1.1 × 10 ⁻⁴	1.2 × 10 ⁻⁴	1.0 × 10 ⁻⁴	1.1 × 10 ⁻¹⁰
SO ₃ (g)	3.2 × 10 ⁻⁸	5.5 × 10 ⁻⁷	5.0 × 10 ⁻⁵	2.6 × 10 ⁻⁸	1 × 10 ⁻⁸	7.9 × 10 ⁻¹⁰	1.0 × 10 ⁻⁸	8.0 × 10 ⁻¹¹	2.9 × 10 ⁻²⁰
S ₂ (g)	4.3 × 10 ⁻¹⁵	6.8 × 10 ⁻²¹	-----	2.6 × 10 ⁻¹⁵	1.3 × 10 ⁻¹⁷	4.7 × 10 ⁻¹⁹	1.5 × 10 ⁻¹¹	1.5 × 10 ⁻⁷	9.9 × 10 ⁻¹¹
SO(g)	4.7 × 10 ⁻⁷	2.6 × 10 ⁻¹⁰	1.3 × 10 ⁻¹⁷	1.8 × 10 ⁻⁶	5.7 × 10 ⁻⁹	8 × 10 ⁻¹²	1 × 10 ⁻⁶	1.7 × 10 ⁻⁶	7.5 × 10 ⁻¹³
S(g)	6.1 × 10 ⁻¹⁰	1 × 10 ⁻¹⁶	-----	7 × 10 ⁻⁹	1.5 × 10 ⁻¹⁵	2.6 × 10 ⁻¹⁹	5.9 × 10 ⁻⁸	1.6 × 10 ⁻⁸	8 × 10 ⁻¹⁵
SH(g)	1.5 × 10 ⁻¹⁰	1.1 × 10 ⁻¹⁶	-----	2.5 × 10 ⁻⁹	2 × 10 ⁻¹¹	6.8 × 10 ⁻¹⁷	1.2 × 10 ⁻⁸	4.5 × 10 ⁻⁷	2.5 × 10 ⁻¹⁰
CO(g)	4.2 × 10 ⁻⁵	4.2 × 10 ⁻⁶	1.2 × 10 ⁻¹²	1.4 × 10 ⁻²	9.2 × 10 ⁻⁵	1.8 × 10 ⁻⁷	3.5 × 10 ⁻²	2.8 × 10 ⁻²	1 × 10 ⁻²
CO ₂ (g)	1.2 × 10 ⁻¹	1.2 × 10 ⁻¹	1.2 × 10 ⁻¹	1.2 × 10 ⁻¹	1.4 × 10 ⁻¹	1.4 × 10 ⁻¹	1.1 × 10 ⁻¹	1.2 × 10 ⁻¹	1.3 × 10 ⁻¹
H ₂ O(g)	1.2 × 10 ⁻¹	1.2 × 10 ⁻¹	1.2 × 10 ⁻¹	1 × 10 ⁻¹	1.3 × 10 ⁻¹	1.3 × 10 ⁻¹	1.3 × 10 ⁻¹	1.3 × 10 ⁻¹	1.2 × 10 ⁻¹
N ₂ (g)	7.2 × 10 ⁻¹	7 × 10 ⁻¹	7.3 × 10 ⁻¹	7.2 × 10 ⁻¹	7.2 × 10 ⁻¹	7.2 × 10 ⁻¹	7.0 × 10 ⁻¹	7.0 × 10 ⁻¹	7.0 × 10 ⁻¹
K ₂ S(c)	-----	-----	-----	-----	-----	-----	-----	-----	-----
K ₂ SO ₄ (c)	-----	-----	5.9 × 10 ⁻⁷	-----	-----	5.9 × 10 ⁻⁷	-----	-----	-----
K ₂ CO ₃ (c)	-----	-----	-----	-----	-----	-----	-----	-----	5.0 × 10 ⁻⁷

K- and/or S-containing species considered by the program are Gases - K₂CO₃, H₂SO₄, KCN, KOH, K₂O₂H₂, SH, S₂, K₂O, K₂SO₄, CS, K, SN, COS, S₂O, CS₂, KH, K₂C₂N₂, SO, S₈, H₂S, KO, S, SO₂, K₂, SO₃, Condensed phases - K₂S, K₂SO₃, K₂SO₄, KOH, K₂O₂, K₂CO₃, KCN, H₂SO₄, K, S, K₂O, K₂O₂

** Calculated adiabatic flame temperature

Input parameters

Fuel No. 2 Diesel, C₁ (H₁ 7421 \ 0 005 with 0.197 percent sulfur, 5 ppm K₂CO₃ in air, P = 1.0 atm

TABLE IV - CONDENSATE PREDICTED BY THE CEC
PROGRAM (REF 5) FOR COMBUSTION OF NO 2
DIESEL FUEL, CH_{1.7421}N_{0.005}, CONTAINING
0.197 PERCENT S AND THE AIR SEEDED
WITH 3 PPM K₂CO₃

ϕ^*	Condensate**	Dew point, K	Adiabatic flame temperature, K
0.4	K ₂ SO ₄	1150 - 1125	1244
0.5	K ₂ SO ₄	1150 - 1125	1462
0.6	K ₂ SO ₄	1150 - 1125	1666
0.7	K ₂ SO ₄	1150 - 1125	1856
0.8	K ₂ SO ₄	1150 - 1125	2030
0.9	K ₂ SO ₄	1150 - 1125	2176
0.95	K ₂ SO ₄	1150 - 1125	2231
0.99	K ₂ SO ₄	1150 - 1125	2262
1.0	K ₂ SO ₄	1125 - 1100	2268
1.01	K ₂ SO ₄	1025 - 1000	2273
	K ₂ CO ₃	800 - 750	
1.05	K ₂ CO ₃	975 - 950	2281
1.10	K ₂ CO ₃	975 - 950	2270
1.15	K ₂ CO ₃	975 - 950	2241
1.20	K ₂ CO ₃	975 - 950	2205

* ϕ = equivalence ratio

$\phi < 1$, oxidant-rich, $\phi = 1$, stoichiometric fuel/
oxidant weight ratio = 0.0691, $\phi > 1$, fuel-rich

** Condensed phases considered by the program in-
clude K₂S, K₂SO₃, K₂SO₄, KOH, KO₂, K₂CO₃,
KCN, K, S, H₂SO₄, K₂O, and K₂O₂

TABLE V - CALCULATED COMBUSTION GAS COMPOSITIONS* FOR SEVERAL FLAME STOICHIOMETRIES FOR

HYPOTHETICAL BURNER RIG FLAME

[Concentrations as mole fractions]

Species	$\phi = 0.90$ (oxidizing)			$\phi = 1.00$ (stoichiometric)			$\phi = 1.15$ (reducing)			
	Temperature, K									
	2139**	1500	900	2238**	1500	900	2201**	1500	1300	900
$K_2CO_3(g)$	1.5×10^{-9}	4.0×10^{-9}	5.5×10^{-24}	6.2×10^{-10}	9.9×10^{-8}	1.6×10^{-15}	3.3×10^{-10}	1.2×10^{-7}	1.2×10^{-6}	9.9×10^{-12}
$K_2O(g)$	4.1×10^{-10}	8.6×10^{-14}	-----	4.3×10^{-10}	2.0×10^{-12}	-----	1.9×10^{-10}	3.0×10^{-12}	2.1×10^{-13}	1.2×10^{-25}
$K_2SO_4(g)$	1.4×10^{-7}	6.8×10^{-4}	2.1×10^{-10}	1.2×10^{-8}	6.4×10^{-4}	2.1×10^{-10}	2.0×10^{-9}	7.9×10^{-6}	3.3×10^{-5}	8.2×10^{-13}
$K(g)$	7.0×10^{-4}	1.1×10^{-6}	6.2×10^{-21}	1.2×10^{-3}	5.1×10^{-5}	1.5×10^{-12}	1.8×10^{-3}	6.3×10^{-4}	2.6×10^{-4}	9.4×10^{-10}
$KO(g)$	1.5×10^{-5}	3.4×10^{-8}	5.1×10^{-22}	1.3×10^{-5}	1.6×10^{-8}	5.6×10^{-22}	3.4×10^{-6}	2.0×10^{-9}	4.1×10^{-11}	5.6×10^{-21}
$KOH(g)$	3.2×10^{-3}	5.3×10^{-4}	1.1×10^{-13}	2.7×10^{-3}	2.6×10^{-3}	1.9×10^{-9}	2.0×10^{-3}	3.2×10^{-3}	2.9×10^{-3}	1.4×10^{-7}
$KH(g)$	8.5×10^{-5}	2.9×10^{-12}	-----	3.1×10^{-7}	1.4×10^{-9}	1.3×10^{-17}	9.9×10^{-7}	1.7×10^{-7}	5.1×10^{-8}	6.0×10^{-14}
$KCN(g)$	5.8×10^{-11}	9.2×10^{-20}	-----	9.4×10^{-12}	4.5×10^{-14}	7.2×10^{-18}	2.8×10^{-10}	4.8×10^{-9}	1.2×10^{-8}	1.7×10^{-11}
$K_2(g)$	1.2×10^{-9}	1.0×10^{-14}	-----	3.2×10^{-9}	2.3×10^{-11}	3.5×10^{-25}	7.4×10^{-9}	3.6×10^{-9}	1.2×10^{-9}	1.4×10^{-19}
$(KOH)_2(g)$	5.4×10^{-9}	1.4×10^{-8}	1.9×10^{-23}	2.3×10^{-9}	3.4×10^{-7}	5.5×10^{-15}	1.5×10^{-9}	4.9×10^{-7}	4.5×10^{-6}	2.9×10^{-11}
$H_2S(g)$	2.6×10^{-10}	2.1×10^{-16}	-----	7.3×10^{-9}	8.8×10^{-10}	3.4×10^{-4}	1.0×10^{-6}	7.6×10^{-4}	1.9×10^{-3}	2.6×10^{-3}
$H_2SO_4(g)$	1.4×10^{-12}	2.1×10^{-11}	1.1×10^{-7}	6.0×10^{-13}	4.0×10^{-13}	4.6×10^{-16}	1.3×10^{-13}	1.3×10^{-14}	4.4×10^{-16}	3.0×10^{-22}
$SO_2(g)$	2.1×10^{-3}	4.1×10^{-4}	5.6×10^{-5}	2.5×10^{-3}	1.7×10^{-3}	7.2×10^{-5}	2.5×10^{-3}	1.5×10^{-3}	1.4×10^{-4}	2.7×10^{-9}
$SO_3(g)$	1.2×10^{-6}	2.3×10^{-6}	5.1×10^{-5}	5.6×10^{-7}	3.4×10^{-8}	3.1×10^{-13}	1.1×10^{-7}	7.7×10^{-10}	5.5×10^{-12}	1.9×10^{-19}
$SO_2(g)$	9.2×10^{-13}	1.2×10^{-21}	-----	8.1×10^{-11}	1.9×10^{-12}	1.2×10^{-6}	5.6×10^{-8}	1.5×10^{-4}	5.1×10^{-5}	3.0×10^{-8}
$SO(g)$	7.2×10^{-6}	1.1×10^{-9}	2.1×10^{-17}	3.1×10^{-5}	4.3×10^{-7}	3.8×10^{-9}	1.5×10^{-4}	3.6×10^{-5}	2.2×10^{-6}	5.9×10^{-12}
$S(g)$	7.2×10^{-9}	1.4×10^{-15}	-----	1.2×10^{-7}	5.6×10^{-11}	4.3×10^{-13}	2.5×10^{-6}	5.0×10^{-7}	2.5×10^{-8}	6.6×10^{-14}
$SH(g)$	1.8×10^{-9}	4.8×10^{-16}	-----	3.9×10^{-8}	2.0×10^{-10}	4.4×10^{-9}	2.1×10^{-6}	2.6×10^{-5}	8.1×10^{-6}	9.6×10^{-9}
$CO(g)$	3.2×10^{-3}	4.2×10^{-6}	1.2×10^{-12}	1.2×10^{-2}	4.6×10^{-4}	2.9×10^{-4}	4.7×10^{-2}	1.9×10^{-2}	3.3×10^{-2}	1.8×10^{-2}
$CO_2(g)$	1.2×10^{-1}	1.2×10^{-1}	1.2×10^{-1}	1.2×10^{-1}	1.3×10^{-1}	1.4×10^{-1}	1.0×10^{-1}	1.1×10^{-1}	1.2×10^{-1}	1.3×10^{-1}
$H_2O(g)$	1.2×10^{-1}	1.2×10^{-1}	1.2×10^{-1}	1.2×10^{-1}	1.3×10^{-1}	1.3×10^{-1}	1.3×10^{-1}	1.2×10^{-1}	1.2×10^{-1}	1.1×10^{-1}
$N_2(g)$	7.2×10^{-1}	7.3×10^{-1}	7.3×10^{-1}	7.1×10^{-1}	7.2×10^{-1}	7.2×10^{-1}	6.9×10^{-1}	6.9×10^{-1}	6.9×10^{-1}	7.0×10^{-1}
$K_2S(c)$	-----	-----	-----	-----	-----	-----	-----	-----	2.6×10^{-4}	-----
$K_2SO_4(c)$	-----	1.0×10^{-3}	2.0×10^{-3}	-----	-----	2.0×10^{-3}	-----	-----	2.6×10^{-5}	-----
$K_2CO_3(c)$	-----	-----	-----	-----	-----	-----	-----	-----	-----	1.9×10^{-3}

* K- and or S-containing species considered by the program are Gases - K_2CO_3 , H_2SO_4 , KCN , KOH , $K_2O_2H_2$, SH , S_2 , K_2O , K_2SO_4 , CS , K , SN , COS , S_2O , CS_2 , KH , $K_2C_2N_2$, SO , S_8 , H_2S , KO , S , SO_2 , K_2 , SO_3 , Condensed phases - K_2S , K_2SO_3 , K_2SO_4 , KOH , KO_2 , K_2CO_3 , KCN , H_2SO_4 , K , S , K_2O , K_2O_2

** Calculated adiabatic flame temperature

Inlet parameters

Fuel No 2 Diesel, $C_{10}H_{17.421}N_{0.005}$ with 4 weight percent sulfur, 1 weight percent K_2CO_3 in air, $P = 1.0$ atm

TABLE VI - CONDENSATE PREDICTED BY THE CEC
PROGRAM (REF 4) FOR COMBUSTION OF NO 2
DIESEL FUEL, CH_{1.7421}N_{0.005}, CONTAINING
4 WEIGHT PERCENT S AND THE AIR SEEDED
WITH 1 WEIGHT PERCENT K₂CO₃

ϕ^*	Condensate**	Dew point, K	Adiabatic flame temperature, K
0.4	K ₂ SO ₄	1600 - 1500	1215
	K ₂ CO ₃	1300 - 1250	
.5	K ₂ SO ₄	1600 - 1500	1430
	K ₂ CO ₃	1300 - 1250	
.6	K ₂ SO ₄	1600 - 1500	1628
	K ₂ CO ₃	1250 - 1200	
.7	K ₂ SO ₄	1600 - 1500	1809
	K ₂ CO ₃	1250 - 1200	
.8	K ₂ SO ₄	1600 - 1500	1986
	K ₂ CO ₃	1150 - 1125	
.9	K ₂ SO ₄	1600 - 1500	2139
.95	K ₂ SO ₄	1600 - 1500	2198
.99	K ₂ SO ₄	1600 - 1500	2232
1.0	K ₂ SO ₄	1500 - 1400	2238
1.01	K ₂ SO ₄	1500 - 1400	2242
	K ₂ CO ₃	800 - 750	
1.05	K ₂ SO ₄	1500 - 1400	2250
	K ₂ CO ₃	1075 - 1050	
1.10	H ₂ SO ₄	1400 - 1350	2234
	K ₂ CO ₃	1250 - 1200	
1.15	K ₂ S	1350 - 1300	2201
	K ₂ SO ₄	1350 - 1300	
	K ₂ CO ₃	1300 - 1250	
1.20	K ₂ S	1350 - 1300	2162
	K ₂ CO ₃	1250 - 1200	

* ϕ = equivalence ratio

$\phi < 1$, oxidant-rich, $\phi = 1$, stoichiometric fuel/
oxidant weight ratio = 0.0691, $\phi > 1$, fuel-rich

** Condensed phases considered by the program in-
clude K₂S, K₂SO₃, K₂SO₄, KOH, KO₂, K₂CO₃,
KCN, K, S, H₂SO₄, K₂O, and K₂O₂

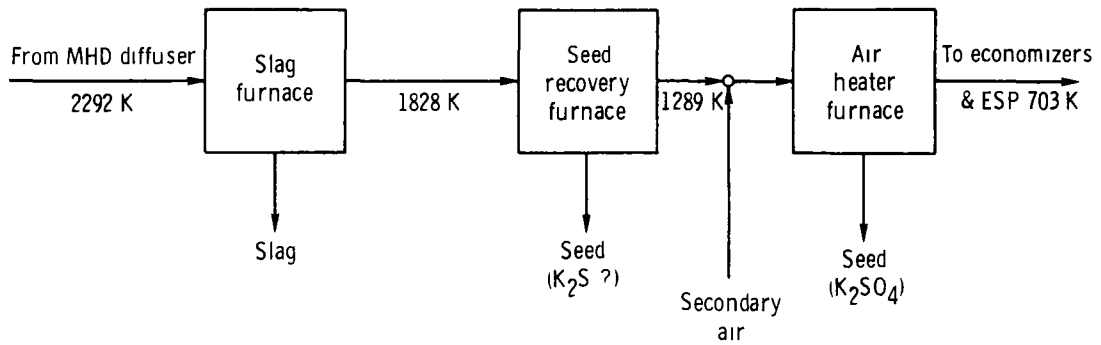


Figure 1 - Arrangement of heat recovery and seed recovery components in AVCO ETF conceptual design (ref 1)

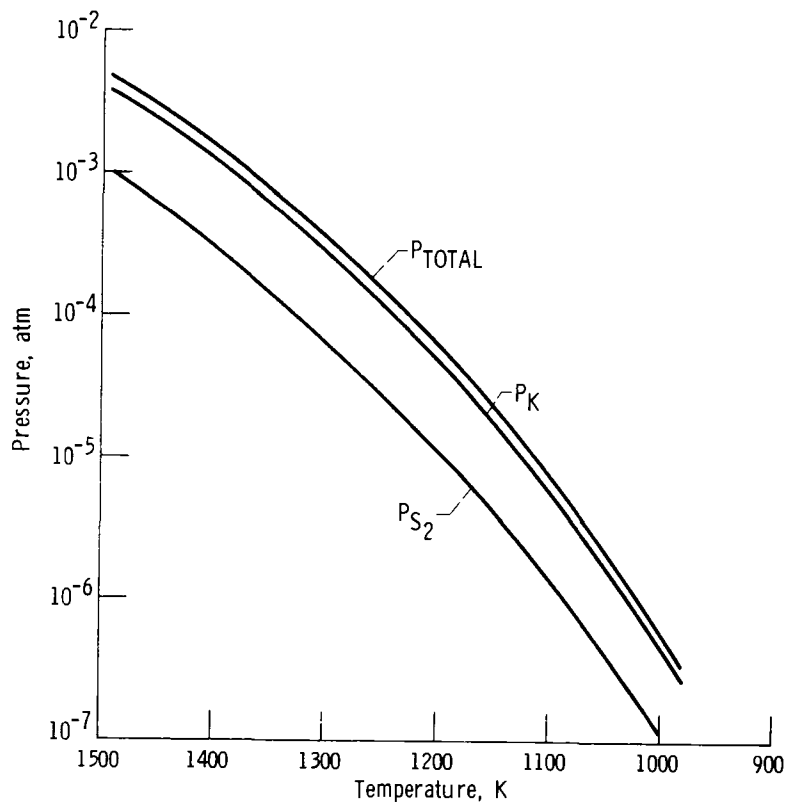


Figure 2. - Equilibrium vapor pressures for $K_2S(c)$, assuming the reaction $K_2S(c) \rightleftharpoons 2K(g) + 1/2 S_2(g)$

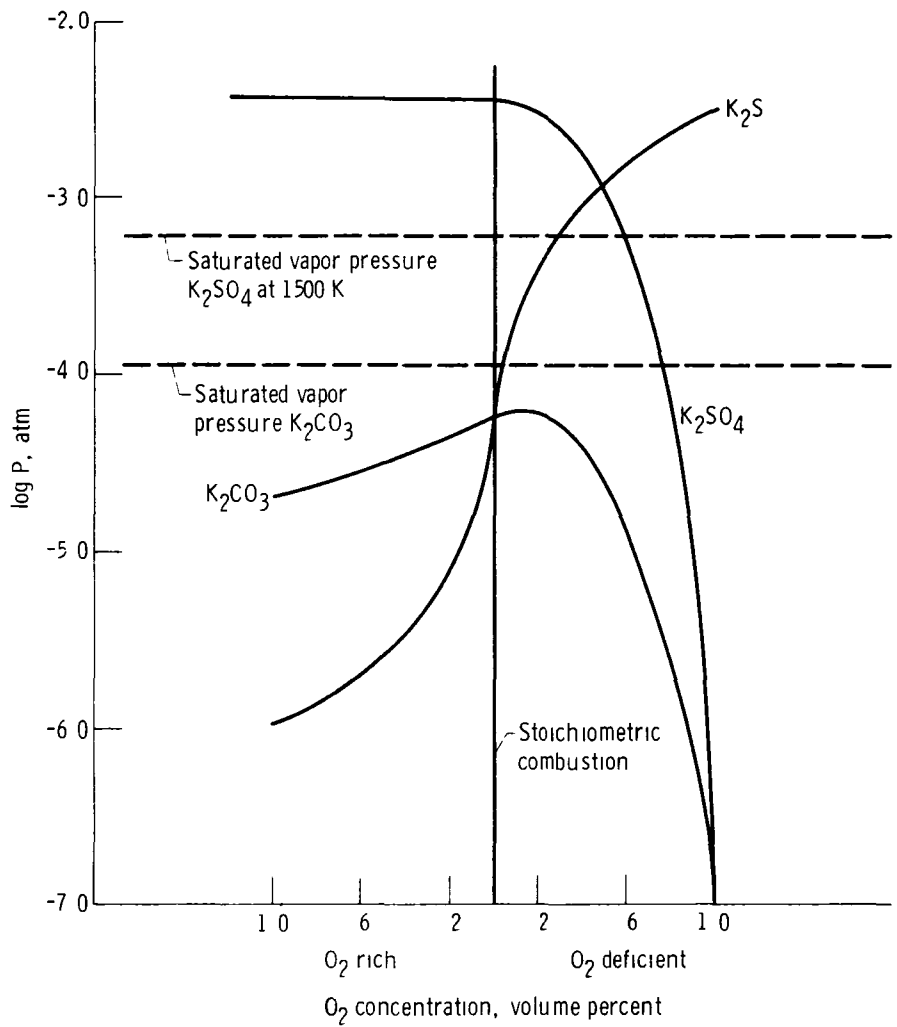


Figure 3 - Species pressures vs O₂ concentration. Solid lines from Heywood and Womack (ref. 3) for oil-fired MHD exhaust at 1500 K, 4% S, 1 atom % K seeding. The dashed lines are saturated vapor pressures at 1500 K. The solid lines represent the "pressure" of the K₂S, K₂CO₃, and K₂SO₄ molecules in the combustion gas.

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